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**A "STATE-OF-THE-ART" REVIEW  
of HEALTH ASPECTS  
of WASTEWATER RECLAMATION  
for GROUNDWATER RECHARGE**

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STATE WATER CONTROL BOARD  
SAN FRANCISCO, CALIFORNIA

**November 1975**

**STATE OF CALIFORNIA**

**State Water Resources Control Board  
Department of Water Resources  
Department of Health**



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PREFACE

The state-of-the-art review was prepared for the Consulting Panel on Health Aspects of Wastewater Reclamation for Groundwater Recharge by participating state agencies and their consultants. The Consulting Panel was established by the State Water Resources Control Board and the Departments of Health and Water Resources to assist state agencies in developing research programs which would provide information needed for establishing criteria for groundwater recharge with reclaimed wastewater. The draft of this document was reviewed by the Consulting Panel members and their comments were incorporated.

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SUMMARY

SECTION I

STATEMENT OF THE PROBLEM

The planned augmentation of domestic water sources with reclaimed wastewater is being considered for several major population centers outside California. Within the state there are five planned groundwater basin augmentation facilities. The two major projects are at Whittier Narrows where reclaimed wastewater along with local and imported waters is spread on porous river beds to recharge a major groundwater basin and in Orange County at Fountain Valley where a major project will inject a mix of desalinated seawater (or other water) and reclaimed wastewater to provide a seawater intrusion barrier.

Future groundwater recharge projects in California have been identified which would introduce approximately 260,000 acre-feet of reclaimed wastewater into groundwater basins which are used for domestic water supply.

There are four water quality factors which are of particular significance in situations such as groundwater recharge which result in the augmentation of domestic water sources. These four are:

1. Microbiological
2. Total minerals
3. Mineral toxicants of the heavy metal type
4. Stable organic substances

There is a significant amount of knowledge and experience with the removal or destruction of biological pathogens in wastewater. There is much less information with regard to viruses. At present, viruses are difficult to monitor for--sampling and laboratory techniques have not been standardized--and there is limited information on the fate of virus in treatment processes and the environment.

Total minerals present problems with the potential for a gradual buildup of minerals to an intolerable level; however, means are available to control the situation. The net health effect of the mineral content of a water has not been thoroughly resolved.

Standards have been established for many heavy metal toxicants; however, the interactions between metals and organic material and the potential health effects of these complexes is not clearly understood. Antagonistic and synergistic effects of combinations of metals (e.g., zinc and cadmium) is an area that requires further documentation. There is a great need for information on the carcinogenicity of metals that may develop only after long-term exposure.

It is known that some organic materials are found in the most highly treated sewage effluents in milligram per liter quantities. These stable organics are of significance because of a combination of factors:

1. The composition of specific organic substances is not known.

2. The effect of treatment processes and passage through the soil on stable organic substances is unclear.
3. There is great uncertainty about the potential that these organics have to cause so-called chronic effects in man if ingested over a period of many years.

A number of responsible organizations have expressed the need for research into various aspects of water quality and treatment technology before reclaimed wastewater is used for domestic purposes.

There is an urgent need to identify the program of research needed to develop the information to reach decisions about conditions under which reclaimed wastewater can be used for groundwater recharge to augment domestic water sources.

SECTION II

WASTEWATER CONTAMINANTS AND THEIR EFFECT  
ON PUBLIC HEALTH

The state of knowledge on wastewater contaminants and their health effects was evaluated in order to determine areas in which information is lacking and research or study would be appropriate relative to the use of wastewater for groundwater recharge. Inasmuch as other tasks will cover effects of wastewater treatment on contaminants, effects of soil systems, analytical procedures and other factors, the evaluation is restricted to characteristics of the contaminants, their presence and significance in the water environment and their health effects.

Bacteria

There are many well defined bacterial, viral and parasitical agents of disease that can be associated with water and wastewater. The recent water-borne epidemic that occurred in this country involving significant numbers of people was caused by Salmonella typhimurium. Numerous other bacterial diseases have been transmitted by water but usually the incidence of resulting cases has been moderate and the incidents relatively limited. This situation speaks well for our modern water treatment practices since most reported episodes of disease have been the result of lack of treatment or obvious failure of the treatment-distribution system. These encouraging statistics do not preclude continued vigilance in monitoring for the presence of these organisms in our water supplies. If wastewater reuse is to be practiced, the strictest surveillance will most certainly be required.

Realistically, we cannot speak in terms of zero concentration of these organisms in water; thus, it is important to know as much about dose-response relationships as is possible. It would appear that significant numbers of bacteria, particularly the Salmonella, are required to produce disease in man as shown by the available dose-response data for humans. We are, therefore, allowed some tolerance in the numbers of these organisms that may be present in water to be recharged. Specific examination of waters for pathogenic bacteria is seldom done; however, the development of indicator organisms as indirect measurement of pathogenic bacteria and the experience gained through the use of such indicator organisms for over half a century, provides ample information on bacterial contaminants in waters, their sources, movement, survival and other factors which makes research on bacterial contaminants in groundwater recharge a subject of limited need.

#### Parasites

Adequate information is available on the characteristics of parasites and their role as waterborne disease agents. No detailed or extensive study has been done on the presence of human parasites in the water environment. Generally, the use of indicator bacteria is considered adequate to determine the quality of water with regard to parasites as well as bacterial pathogens. The general lack of disease through the water route associated with parasites tends to confirm this. Investigatory work into the presence or survival of parasites in wastewater or surface waters has not been considered essential and no concern has been expressed over parasites in groundwater. Size and other characteristics make their presence in groundwaters extremely unlikely.

Although definitive information on parasites in the water environment is lacking, there appears to be little evidence that parasites in water should be the subject of significant research with regard to the health effects of groundwater recharge with reclaimed water.

### Virus

In the cases of viruses, the tolerance for numbers of viruses present is most probably lower than for bacteria. Adequate dose-response data for viruses and human enteric disease does not exist. The consensus is that one tissue culture infectious dose-50% (TCID<sub>50</sub>) is enough to initiate infection in man, if not disease. Standards such as one viral plaque-forming unit (pfu) per 100 gallons have been suggested as the quality standard for finished drinking water. If such a standard as this is used, we are faced with the problem of being able to determine that such a standard is being met. Methods to detect small numbers of viruses in large volumes of water are presently being developed and evaluated.

Treatment systems designed to upgrade water quality prior to groundwater recharge must also be evaluated for their ability to remove infectious agents that may be present. The evaluation of bacterial removal in treatment systems is relatively straight-forward either by monitoring total numbers of bacteria or by monitoring the removal of fecal coliform bacteria. Virus monitoring is more difficult because the number of recognized viruses present is low relative to the number of bacteria, and thus some virus concentration method must be employed. Since all viruses that may be present cannot be isolated using a common detection method, it is urgent that some

representative indicator virus be selected as the target organism to use in measuring virus removal efficiency. Such an indicator should be commonly present in sewage throughout the year and should be as resistant to various treatment processes as is the agent of infectious hepatitis.

The preponderance of information on the presence of virus in the water environment has been developed in the last three decades. Water virology is in the developmental stage--new findings on types, presence and concentrations of virus in water continue to result from improvements in sampling and concentrating techniques and new laboratory procedures. Actual monitoring of surface waters, groundwaters and wastewaters has been extremely limited.

Information is needed on the presence and movement of virus in all portions of the water environment including percolating wastewater. Survival times in the water environment are needed.

Research into improved methods of concentration techniques and a broad program to optimize and standardize laboratory procedures is needed. There is little information on the health significance of low levels of virus in water.

#### Inorganic Chemicals

There are numerous inorganic chemicals found in water and wastewater. Such materials in water as arsenic, heavy metals, and nitrates are known to cause health problems. The permissible levels presently suggested for these constituents in drinking water appear to be adequate to protect the public health. Vigilance must be maintained for the presence of these compounds as

well as other inorganic chemical species which may arise due to the presence of industrial wastes in waters to be used in any recharge operation. Other water factors may affect the health of a population such as increased sodium, and changes in water hardness. Evidence exists that there is a negative correlation between certain forms of heart disease and infant mortality and water hardness. This latter phenomenon points out that one may have to consider the impact of relatively subtle changes in a community's water supply upon long-term health effects, such as forms of heart disease.

The health significances of inorganic constituents in water are reasonably well known and standards have been established based on chronic effects levels for heavy metals and other substances. The sources of such contaminants are known and the general concentration which may be present in the water environment are known. The movement of all inorganic contaminants in groundwater and percolating water is not well understood and is a suitable area for study.

#### Organic Chemicals

The presence of small amounts of organic material in treated reclaimed water is of great concern to health officials. The impact of long-term exposure of a population by ingestion of these compounds in drinking water is not clear. In terms of gross parameters (BOD, COD) the presence and levels of organic substances in domestic wastewater is well documented. To a much lesser degree, there is information on the presence of organics in surface waters and very limited data on organics in groundwaters. No standardized

procedure has been developed for a more refined classification of organic substances and only a few attempts have been made to identify the make-up of organics in water.

The identification of specific organic compounds has recently commenced with the development of analytical procedures and equipment to isolate and identify minute concentrations of specific compounds. A major problem is the myriad of compounds that are involved, and the difficulty of routine isolation and identification of these materials. More than 60 compounds have been isolated from water supplies originating from the Mississippi River, many of which can be shown to be toxic in concentrated form. A number of the halogenated compounds, principally chloroform, found in these finished waters may well arise from established chlorination procedures. These same kinds of compounds have been found in the waters of other countries. In the New Orleans area similar halogenated compounds have been found in the area of local residents using the water supply, which may suggest a bioaccumulation or biomagnification mechanism in humans.

Crude extracts of organic material (CCE and CAE), when concentrated, have been shown to be toxic to laboratory rodents and also demonstrate some carcinogenic activity when introduced parenterally. Unfortunately, there is scant data on the toxicity of most of the organic compounds involved, either in pure form or in mixtures such as CCE, when introduced into animals via the oral route.

At the present time there seems to be no reasonable way in which one can estimate chronic toxicity from acute toxicity data. Yet, one of the major problems in making judgments about the public health impact of reusing treated wastewater is predicting the long-term effect of exposure to low doses of potentially carcinogenic or mutagenic compounds in drinking water.

To date few intensive epidemiological studies have been conducted which examine the relationship between water quality and human disease, particularly cancer. The most well known are those dealing with the relationship between water hardness and death from cardiovascular heart disease. Limited studies in Holland and more recently in the state of Louisiana have indicated a correlation between cancer mortality rates and water source. In these instances the cancer mortality rates are usually higher among persons in communities who drink surface water as opposed to groundwater. The inference drawn from these studies is that since surface water is more apt to be contaminated with waste effluents and agricultural runoff the higher incidence of cancer deaths may well be due to the presence of carcinogens in these waters. No data is available which relates cancer morbidity with water quality. Carefully designed epidemiological studies dealing with these matters are essential to our estimation of the public health problem involved in wastewater reuse, including groundwater recharge.

Information is lacking on the chronic health effects of specific organic compounds in water, the health significance of different levels of gross parameters, the effects of groundwater travel on organics and their persistence in the water environment. All these subject areas require research or investigation.

### SECTION III

#### TREATMENT PROCESSES FOR WASTEWATER RECLAMATION FOR GROUNDWATER RECHARGE

The purpose of this section is to evaluate the capability of alternate processes for the purpose of treating municipal wastewater for recharge of domestic groundwater supplies.

##### Description of Wastewater Treatment Processes

Conventional secondary treatment plants, which have relied on biological treatment processes, are capable of removing essentially all soluble, biologically degradable organics found in municipal wastewaters. However, secondary effluent contains concentrations of viruses, bacteria, nitrogen, heavy metals, and refractory (biologically nondegradable) organics of concern in water reuse situations.

Advanced wastewater treatment (AWT) processes available to reduce the concentration of contaminants found in secondary effluent include chemical coagulation and sedimentation, filtration, carbon adsorption, biological and physical chemical nitrogen removal processes, disinfection, demineralization, chemical oxidation with ozone, and storage in effluent reservoirs.

Coagulation is accomplished by injecting aluminum salts, iron salts such as ferric chloride, or lime into the wastewater. The resulting floc is removed by gravity sedimentation. Filtration is achieved by passing wastewater through a granular bed typically 30" - 36" deep composed of relatively small particles (less than 1.5 mm in size). Activated carbon adsorption is

the most practical method available for removal of refractory organics. Wastewater is passed through beds of granular carbon made up of carbon particles about 0.8 mm in effective size. The spent carbon may be thermally regenerated and reused. Nitrogen may be removed by biological nitrification and denitrification; or by the physical-chemical processes of selective ion exchange, ammonia stripping, or breakpoint chlorination. Salt buildup in water reuse systems can be controlled when necessary by use of processes such as ion exchange, reverse osmosis, or electrodialysis. The AWT processes provide substantial reductions in bacteria and viruses but complete disinfection is dependent upon use of a disinfection process such as chlorination or ozonation. Storage of wastewater in open reservoirs can perform useful treatment functions by allowing natural purification processes to supplement the AWT processes.

#### Treatment Process Capabilities

Virus and Bacteria Removal - Virus and bacteria concentrations are reduced 95 to 99% by chemical coagulation and sedimentation. Use of high pH lime coagulation (pH of 11 or more) provides even further reductions due to the virucidal effects of high pH. When filtration is used in conjunction with chemical coagulation and filtration, overall removals of bacteria and virus typically exceed 99%. Filtration also removes particulate matter which could encapsulate virus and bacteria, protecting them from contact with any disinfectants added. Turbidities as low as 0.1 Jackson Turbidity Unit (JTU) are desirable to insure effective disinfection. Proper mixing of chlorine when injected is very important to disinfection and is an aspect not adequately addressed in many existing designs.

Generally, viruses are more resistant to disinfection than are the indicator coliform organisms. Combined forms of a chlorine resulting when ammonia is present are not as effective as disinfectants as free chlorine residuals. Disinfection is generally favored by pH values less than 7 and by increasing temperature. The removal of cysts is also favored by the same factors favoring removal of virus and bacteria. Ozone has been found to equal or exceed chlorine in its germicidal effects. The costs of ozonation are significantly higher than those of chlorination. Effluent storage in open reservoirs provides an opportunity for die-off of viruses and bacteria from hostile environmental factors.

An AWT plant can provide the following processes in series to insure complete disinfection prior to discharge into recharge system: Coagulation with alum or with lime at high pH, sedimentation, filtration, and disinfection with ozone and/or chlorine. Complete disinfection is dependent upon the proper operation of the coagulation, sedimentation, and filtration processes to produce minimum water turbidities to assure maximum contact between any remaining pathogens and the disinfectant added.

Heavy Metal Removal - Secondary treatment processes provide some reductions in heavy metals (40 - 50% for most metals) with the activated sludge process being more efficient than the trickling filter process. High pH lime coagulation forms insoluble hydroxides and carbonates from most metals and results in substantial removals of heavy metals. Alum coagulation removes certain heavy metals. Activated carbon adsorption, ion and exchange, and reverse osmosis also provide heavy metal removals. The data from several

ATW pilot plants and one full-scale AWT plant shown below indicate that current drinking water standards for heavy metals can be met when treating municipal wastewaters by the combined processes of lime coagulation, sedimentation, filtration and carbon adsorption.

Heavy Metal Removal by Lime Coagulation, Filtration, and Carbon Adsorption of Secondary Effluent:

|            | Drinking Water<br>Limit<br>mg/l | Concentration, mg/l as measured at |                           |                            |                  |
|------------|---------------------------------|------------------------------------|---------------------------|----------------------------|------------------|
|            |                                 | Colorado<br>Springs, Colo.         | Orange Co.,<br>California | South Tahoe,<br>California | Dallas,<br>Texas |
| Chromium   | 0.05                            | 0.022                              | 0.01 - 0.04               | 0.0005                     | 0.01 - 0.02      |
| Iron       | 0.3                             | 0.012                              | -                         | 0.0003                     | 0.08 - 0.15      |
| Manganese  | 0.05                            | 0.020                              | -                         | 0.002                      | 0.007 - 0.02     |
| Nickel     | None                            | 0.100                              | -                         | -                          | 0.05 - 0.10      |
| Copper     | 1.0                             | 0.024                              | 0.02 - 0.30               | 0.0116                     | 0.02 - 0.03      |
| Lead       | 0.05                            | 0.067                              | 0 - 0.04                  | -                          | 0.02 - 0.04      |
| Zinc       | 5.0                             | 0.012                              | 0.02 - 0.07               | 0.005                      | 0.02 - 0.07      |
| Magnesium  | None                            | 3.3                                | 2                         | -                          | -                |
| Cadmium    | 0.01                            | 0.000                              | 0 - 0.005                 | -                          | 0.002 - 0.004    |
| Mercury    | 0.005                           | 0.0                                | 0 - 0.006                 | -                          | 0.0002 - 0.0007  |
| Arsenic    | 0.05                            | 0.003                              | 0 - 0.03                  | 0.005                      | 0.003 - 0.005    |
| Molybdenum | None                            | 0.05                               | -                         | -                          | -                |
| Selenium   | 0.01                            | -                                  | 0 - 0.003                 | 0.0005                     | 0.0004 - 0.0005  |
| Silver     | 0.05                            | -                                  | 0 - 0.01                  | 0.000                      | -                |

Organic Removal - Secondary effluents contain refractory organics which are of concern in reuse applications. Upon chlorination, some of these organics are reported to form carcinogens. One study found that the humic substances in natural waters also formed haloforms during chlorination. Another study has identified 17 chlorine-containing organic compounds in a chlorinated secondary effluent. The limited available data on the character of organic compounds present in secondary effluents indicate that 40-50% of the organics are humic substances (humic acid, fulvic acid). About 70% have molecular weights of 500-50,000 according to one study. It has been found

that organics in municipal wastes with molecular weights less than 100 or more than 50,000 are the most difficult to remove by activated carbon adsorption.

The process of activated carbon adsorption is capable of removing substantial amounts of soluble refractory organics from municipal wastewaters. The effluent quality produced is dependent upon factors such as pH, temperature, the nature of the organics present, the degree of pretreatment, and the contact time in the carbon adsorption unit. The heterogeneous mixture of organics found in municipal wastewaters complicates the prediction of carbon effluent composition because the behavior of a given organic molecule is dependent on the other molecules present. The report presents data on the removal of specific compounds such as ABS (alkyl benzene sulfonate), triethanolamine, 2,4-DCP, 9N10, phenol, quinine, aldrin, endrin, ortho- and para-nitrochlorobenzenes, DDT, dieldrin, DDD, DDE, toxaphene, and PCB's (polychlorinated biphenyl) (see Tables 15-17 and related text). Most wastewater studies have not, however, determined specific organic constituents but rather report results as chemical oxygen demand (COD), total organic carbon (TOC), carbon chloroform extract (CCE), or carbon alcohol extract (CAE).

Although several data sources show only 2-3 mg/l of COD in municipal wastewater typically being resistant to removal by carbon adsorption, practical considerations appear to limit full-scale operations to producing a COD of 10-12 mg/l, TOC of 1-3 mg/l, and CCE of 0.01-0.02 mg/l. The reverse osmosis process has the capability to reduce the COD of carbon column effluent to less than 1 mg/l.

To put the COD value of 10-12 mg/l achievable with activated carbon in perspective the effluent spread for recharge for many years at Whittier Narrows has had an average COD of 30-40 mg/l. The Santa Ana River flow has a COD of 20-50 mg/l as it enters the percolation area of the Orange County groundwater basin. Treated Colorado River water is reported to have a COD of 11 mg/l. COD values of many raw water supplies used in the U. S. are substantially higher than 10 mg/l. However, where reuse is involved, there is a need to think less in terms of COD and TOC and more in terms of the specific organics present. Unfortunately, there are few data on the specific organic compounds which are likely to comprise the 10-12 mg/l COD escaping a carbon adsorption system. It is the questions about the nature of these organics, their possible health effects, and their stability in a groundwater recharge system which is the major uncertainty related to reuse of municipal wastewaters.

Other Elements of Concern - Other constituents of concern such as iron, manganese, nitrate, and cyanide are readily reduced by AWT processes to acceptable levels. Removal of TDS, if needed, can be accomplished but at a high cost.

#### Existing Project Performance

A project at Windhoek, S. Africa recycles reclaimed municipal wastewater directly to the municipal potable water distribution system (up to one-third of the total supply). Secondary effluent is reclaimed by chemical (lime) treatment, flotation, ammonia stripping, recarbonation, filtration, and granular carbon adsorption. No viruses have been found in the reclaimed

water. Reclaimed wastewater COD values of 10 mg/l and CCE of 0.13 mg/l have been produced. The reclaimed wastewater is mixed with treated surface water and groundwater before entering the distribution system. It is premature to judge the long-term effects of this direct recycling project but its initial reception by the public has been favorable.

A 7.5 mgd plant at South Lake Tahoe, California has demonstrated the capability to produce an odorless, colorless, very clear reclaimed water from secondary effluent having the following characteristics: COD = 10 mg/l; coliform bacteria = less than 2/100 ml; turbidity = 0.3 JTU; phosphorus = 0.1 mg/l. The Tahoe plant uses the AWT process of lime coagulation, ammonia stripping, filtration, carbon adsorption, and chlorination. No viruses or objectionable quantities of heavy metals have been found in the Tahoe effluent. The Tahoe effluent standards have been met continuously over the last 6.5 years. A 3 mgd (million gallons per day) plant at Colorado Springs using lime coagulation, filtration, and carbon adsorption also has no objectionable heavy metal concentration in its effluent and produces an effluent COD of 10 mg/l.

Two illustrative projects using secondary effluent for recharge are the Flushing Meadows project in Phoenix, Arizona and the Whittier Narrows project in Los Angeles County. The Flushing Meadows project goal is producing a water for unrestricted irrigation use. Where domestic reuse is the goal, some of the constituents found in the reclaimed water would be unacceptably high (although amenable to removal by AWT processes). In the Whittier Narrows

project, secondary effluent with an average COD of 30-40 mg/l constitutes about 29% of the water to be spread in water year 1973-1974 for groundwater recharge in the Montebello Forebay.

The Muskegon County Wastewater Management System was designed to treat liquid wastewater by biological treatment in aerated lagoons and subsequently store it for the winter season, and then spray irrigate on the crop farmland during the growing season. The land treatment "living filter" process is providing the advance treatment for the wastewater.

#### Pilot and Laboratory Studies

Several pilot studies also offer data of value. A pilot plant in Nassau Co., New York has been evaluated for the purpose of producing water for groundwater recharge, using alum coagulation, filtration, and carbon adsorption. An effluent COD of 13 mg/l was produced. A pilot plant at Pomona, California has evaluated carbon adsorption of secondary effluent (producing a COD of 10 mg/l, TOC of 3 mg/l, CCE of 0.026 mg/l) and reverse osmosis (producing a COD of 1 mg/l). The Orange County (Calif.) Water District evaluated several AWT processes in pilot studies for a 15 mgd recharge project. Using the same AWT processes as the Tahoe project, a water suitable for injection was produced. The full-scale project is in the startup phase at this time. The City of Los Angeles has conducted pilot tests at the Hyperion plant on carbon treatment of secondary effluent. As a result of these tests, a goal of a COD of 12 mg/l for effluent used for recharge has been adopted. A carbon adsorption plant followed by electro dialysis has been tested at Santee, California. The average carbon effluent COD of 13.1 mg/l was reduced to 8.8 mg/l by

electrodialysis. A pilot test of reverse osmosis was conducted at Hemet, California and produced a COD of 0.5-0.8 mg/l when carbon was used as pre-treatment. Dallas, Texas is currently conducting pilot tests of the AWT processing of lime coagulation, filtration, and carbon adsorption. Preliminary results indicate complete coliform and virus removal, acceptable heavy metal concentrations, and COD values of 2-12 mg/l. Other pilot studies at Lebanon, Ohio and Ontario, Canada are also discussed.

#### Overall Capability of Treatment Process Combinations

Due to variations in plant influent municipal wastewater composition from city to city, it is impossible to present predictions of effluent quality for various unit process combinations which would be universally applicable. However, based on the data presented in this report, it is possible to make some general predictions of typical quality. The following table summarizes two general approaches - one without chemical coagulation and one with chemical coagulation. Use of the coagulation process provides improved reliability as well as improved effluent quality. The table also includes very general costs to illustrate the relative costs for each increment of quality improvement.

Advanced waste treatment of municipal wastewater secondary effluent with the processes of lime coagulation, filtration, carbon adsorption, and disinfection is capable of producing the following water quality: COD = 10 mg/l or less; CCE = 0.02 mg/l; turbidity = 0.1 JTU;  $PO_4$  = 0.1 mg/l; coliform = 0; odorless; colorless; no detectable virus; and heavy metal concentrations

A. OVERALL PROCESS CAPABILITIES WITHOUT CHEMICAL COAGULATION

|                           | <u>BOD</u><br><u>mg/l</u> | <u>COD,</u><br><u>mg/l</u> | <u>Turbidity</u><br><u>JTU</u> | <u>PO<sub>4</sub>,</u><br><u>mg/l</u> | <u>N,</u><br><u>mg/l</u> | <u>TDS</u><br><u>mg/l</u> | <u>Coliform</u><br><u>Bacteria</u><br><u>MPN/100 ml</u> | <u>Approximate</u><br><u>Cost @ 10 mgd,</u><br><u>Cents/1,000 gals.*</u> |                |
|---------------------------|---------------------------|----------------------------|--------------------------------|---------------------------------------|--------------------------|---------------------------|---|--|----------------|
|                           |                           |                            |                                |                                       |                          |                           |   | <u>Per Process</u>   | <u>Cumula.</u> |
| Secondary Effluent        | 20-40                     | 30-80                      | 10-40                          | 20-30                                 | 15-30                    | 400-600                   | 1-3 x 10 <sup>6</sup>                                   | 20   | 20             |
| Carbon Adsorption         | 3-6                       | 10-12                      | 1-2                            | 20-30                                 | 18-28                    | 400-600                   | 1-3 x 10 <sup>6</sup>                                   | 14   | 34             |
| Disinfection              | 3-6                       | 10-12                      | 1-2                            | 20-30                                 | 18-28                    | 450-650                   | 2-100   | 1  | 35             |
| Demineralization<br>(R-0) | 1                         | 0.8-2                      | 1                              | 0.4                                   | 3-5                      | 100                       | 2   | 40   | 75             |

B. OVERALL PROCESS CAPABILITIES WITH CHEMICAL COAGULATION

|                                |       |         |       |       |       |         |                       |    |    |
|--------------------------------|-------|---------|-------|-------|-------|---------|-----------------------|----|----|
| Secondary Effluent             | 20-40 | 30-80   | 10-40 | 20-30 | 15-30 | 400-600 | 1-3 x 10 <sup>6</sup> | 20 | 20 |
| Chemical Coagulation<br>(lime) | 3-7   | 30-50   | 2-7   | 0.5-2 | 15-30 | 400-600 | 2000                  | 9  | 29 |
| Filtration                     | 1-2   | 25-45   | 0.1-1 | 0.1   | 15-30 | 400-600 | 50                    | 7  | 36 |
| Nitrogen Removal               | 1-2   | 25-45   | 0.1-1 | 0.1   | 1-3   | 400-600 | 50                    | 11 | 47 |
| Carbon Adsorption              | 0-1   | 3-10    | 0.1-1 | 0.1   | 1-3   | 400-600 | 50                    | 10 | 57 |
| Disinfection                   | 0     | 3-10    | 0.1   | 0.1   | 1-3   | 450-650 | 0                     | 1  | 58 |
| Demineralization<br>(R-0)      | 0     | 0.8-1.5 | 0.1   | 0.1   | 0.3-1 | 100     | 0                     | 40 | 98 |

\*Includes capital, operation, and maintenance costs.

less than drinking water standards. Reverse osmosis treatment of the AWT effluent described above can reduce the COD to less than 1 mg/l and provide control of TDS, (total dissolved solids).

#### Reliability Considerations

Treatment reliability is an important consideration. The State of California and EPA have published reports and requirements dealing with both design and operation aspects related to reliability. The State of Virginia requirements for reliability for an AWT plant discharging to a drinking water reservoir are discussed as an example of such considerations. The factors critical to the reliable operation of the South Lake Tahoe plant have been demonstrated to be a properly designed plant including ample operational flexibility, adequate operator training, motivation, staffing, and operational budgets. When these requirements are met, AWT processes can produce the effluent quality described earlier in a failsafe, reliable manner.

#### Need for Added Research

Research needs include: identification of organics resistant to removal by AWT processes; determination of the stability of these organics in recharge systems and any resulting health risks; a method for rapid detection of virus evaluation of techniques for removal of organics resistant to carbon adsorption; and techniques for rapid screening and quantification of residual metals.

SECTION IV

REMOVAL OF BIOLOGICAL AND CHEMICAL CONTAMINANTS  
BY SOIL SYSTEMS IN ASSOCIATION WITH GROUNDWATER  
RECHARGE BY SPREADING OR INJECTION OF TREATED  
MUNICIPAL WASTEWATER

Objectives and Scope

This section presents information obtained from pertinent literature dealing with the capabilities of soil systems to remove biological and chemical contaminants from municipal waste waters that have received secondary treatment, and identifies areas of uncertainty or lack of knowledge where additional or new research is urgently needed to evaluate the public health hazards of groundwater recharge using these treated wastewaters.

Types and Concentrations of Biological and Chemical Contaminants to be Expected in Treated Wastewaters

Biological and chemical contaminants in treated wastewaters depend mainly on the source of water and the types of wastes added during passage through municipal wastewater systems. Concentration of the contaminants vary widely depending upon the sources of wastewaters and the treatment processes used. Primary treatment removes less contaminants than secondary treatment. The various types of secondary treatment - trickling filters, activated sludge or oxidation ponds - remove contaminants to different degrees. If advanced, or tertiary, treatment is provided even greater amounts of contaminants are removed.

The concentrations of contaminants in the treated wastewater used for groundwater recharge have a great effect on the ability of soil systems to act as treatment vehicles as the treated wastewater passes through the soil mantle.

Biological Contaminants -- Biological contaminants in wastewater include bacteria, viruses, protozoa, and parasitic worms. Of these, only the pathogenic organisms are of concern to the health aspects of using treated wastewaters to recharge groundwater.

The following table gives an indication of the amount of some biological contaminants in secondary wastewater treatment plant effluents (before disinfection):

|                 |                                  |
|-----------------|----------------------------------|
| Coliforms       | $2.5 \times 10^6/100 \text{ ml}$ |
| Fecal coliforms | $4.5 \times 10^5/100 \text{ ml}$ |
| Viruses         | 0-430 PFU/100 ml                 |

Chemical Contaminants - Wastewaters contain both organic and inorganic contaminants in varying quantities. Normally, the rapidly biodegradable organic compounds are of less concern in recharging groundwaters than the more stable or slower biodegradable organic compounds. Some of the soluble inorganic chemical, including heavy metals, are reduced during secondary treatment by precipitation in, and adsorption on, sludges.

Organic Compounds - Organics are usually determined enmasse by their biochemical oxygen demand, chemical oxygen demand, and total organic carbon content. Because stable organics are present in secondary treated wastewater

in very low concentrations, their determination in the microgram per liter range requires costly, highly-refined instrumentation and specially trained analysts. While some attempts are made to determine specific compounds (pesticides, for example), many times only organic groupings and fractions are determined.

The following table presents ranges of concentrations of organic compounds (both biodegradable and stable) in secondary wastewater treatment plant effluents:

|             |             |
|-------------|-------------|
| BOD         | 10-80 mg/l  |
| Soluble BOD | 1-2 mg/l    |
| COD         | 30-200 mg/l |
| Soluble COD | 25-50 mg/l  |
| TOC         | 10-25 mg/l  |

Inorganic Compounds - Inorganic ions in treated wastewater include  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{=}$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , phosphate, and borate, some of which are nutrients; and the trace elements and heavy metal As, Ba, Bi, Cd, Cu, CN, Cr, F, Pb, Hg, Se, Ag, and Zn. However, unless the concentration of total minerals are excessive (greater than 1500 mg/l) and provided they are not predominately of one type such as Na or B, they are not of great concern in soil systems. The mechanics of removal of nitrogen ions and compounds and some of the trace elements and heavy metals by soil systems are of some concern.

Trace Elements and Heavy Metals - Trace element concentrations in secondary effluents vary considerably. Although there are many reports in the literature which give concentrations of trace elements in secondary effluents, most are for isolated instances and not sufficiently detailed and comprehensive to allow generalizations. Data derived for secondary effluents from 23 treatment plants in Michigan, and from 7 treatment plants in Southern California, are presented in the tabulation on page 36. The data show that median concentrations of those trace elements monitored meet existing standards for public drinking water supplies. The data available for trace element concentrations in secondary effluents point out that many, but certainly not all, effluents are suitable for use in groundwater recharge operations.

Nitrogen - Nitrogen may be present in treated wastewater as any or all of the following forms: nitrates, nitrites, ammonia or ammonium ion, and organic nitrogen. The form and concentration may vary as indicated by the following ranges found in activated sludge process effluents:

|                                |           |
|--------------------------------|-----------|
| Nitrates ( $\text{NO}_3^-$ -N) | 0-40 mg/l |
| Nitrites ( $\text{NO}_2^-$ -N) | 0-3 mg/l  |
| Ammonia ( $\text{NH}_3$ -N)    | 5-40 mg/l |
| Organic N                      | 2-15 mg/l |

| Element   | Range<br>-----mg/l----- | Median | No. with conc'ns.<br>which exceed<br>standards <sup>1/</sup> |
|---|-------------------------|--------|--|
| From 23 treatment plants in Michigan: <sup>2/</sup>           |                         |        |  |
| As  | <0.005 - 0.023          | <0.005 | 0  |
| Cd  | <0.01 - 0.15            | <0.01  | 1  |
| Cu  | 0.01 - 1.3              | 0.04   | 1  |
| Cr  | <0.01 - 1.2             | 0.03   | 7  |
| Pb  | <0.02 - 1.3             | 0.04   | 12   |
| Zn  | 0.03 - 1.2              | 0.19   | 0  |
| From 7 treatment plants in Southern California: <sup>3/</sup> |                         |        |  |
| Ba  | <0.05 - 0.13            | <0.05  | 0  |
| Cd  | <0.01 - 0.022           | 0.01   | 1  |
| Cu  | <0.01 - 0.05            | 0.02   | 0  |
| Cr  | <0.001 - 0.10           | 0.007  | 1  |
| Pb  | 0.-03- 0.35             | 0.02   | 1  |
| Zn  | 0.004- 0.35             | 0.05   | 0  |

<sup>1/</sup> Number of samples with concentrations which exceed those recommended for public drinking water supplies.

<sup>2/</sup> From Bradford, G. R., A. L. Page, L. V. Lund and W. Olmstead. See reference (2) for Section IV.

<sup>3/</sup> From Bookman-Edmonston Engineering, Inc. See reference (6) for Section IV.

Removal of Contaminants by Soil Systems

Soil systems have the capacity to remove biological and chemical contaminants in treated wastewater. The removal processes involved include filtration, adsorption, chemical and microbiological decomposition, ion-exchange, oxidation-reduction, complex formation, and precipitation.

General Soil Properties Related to Recharge - An ideal soil for groundwater recharge by land spreading and infiltration would have rapid rates of infiltration and transmission of water and at the same time provide soil surfaces and contact time for biochemical and microbiological reactions. Obviously, the ideal system does not exist because these two features of the system are mutually exclusive.

Rates of infiltration and transmission are dependent on pore size distribution in soils. Those soils with largest fractions of larger pores have the highest rates and those with the lowest fractions of large pores have the lowest rates. Generally, the pore size distribution is a function of texture, i.e., percentages of sand, silt, and clay with the percent of large pores decreasing with increase in contents of silt plus clay.

Biological Contaminants - The life cycle and the infection route are quite different for each species of disease causing organisms. When tertiary treatment of wastewater is obtained by groundwater recharge, the survival of pathogens in natural environments and their movement in soils are important.

Pathogenic microorganisms are found in abundance in wastewater influents. In properly treated wastewater, they are not expected to occur in high densities in the final effluent. The movement of pathogens in soils is governed not only by natural destruction processes of microorganism but also by soil and hydraulic parameters.

Although wastewater effluent has been returned to land for centuries, the recharging of groundwater was more or less incidental. Studies of planned groundwater recharge using treated wastewater accelerated in the early 1950's. Early studies using spreading basin infiltration methods indicated that coliform bacteria in unchlorinated secondary effluent can be reduced to meet the 1962 Public Health Drinking Water Standards after passing a rather short distance through soils.

The retention of bacteria in soils can be explained by their filtering action. Viruses are colloidal-sized particles usually small enough to pass through soil pores without resistance. While the relationship between soil characteristics and virus removal is not well established, soil with reasonable amounts of silt and clay remove virus within the first two feet. Many factors are expected to influence the effectiveness of soils in removing virus; but the most important are pH and the mineral concentration of the wastewater.

Chemical Contaminants - Chemical contaminants in treated wastewaters that are amenable to removal by soil systems during recharge of groundwaters include organic compounds, nitrogen, trace elements, and heavy metals. However, most soluble salts are not removed by soil systems.

The removal of chemical contaminants is more dependent upon the type and properties of the soils in the surface mantle than in the case for the removal of biologic contaminants. Adsorption and chemical reactions - complex formation, oxidation-reduction, and precipitation - depend not only on the biochemical properties of the soil but also on the physical structure necessary to provide the time needed for reaction and for chemical contaminant removal.

Organic Compounds - Toxic organic substances in wastewaters may originate from industrial and domestic wastes, accidental spillage, erosion from recently treated lands, and from natural processes. Carcinogenic compounds have been found in recent studies and are of concern.

Pesticides are considered a potential source of soluble toxic organic substances in waters. They are adsorbed by the soil clay, iron and aluminum oxides, and especially by organic colloids and are subject to microbial degradation. Soil studies, both field and laboratory, indicate that most pesticides remain in surface soils while a few may with time be found at depths of 30 to 60 cm.

Some carcinogenic compounds are not degraded in the activated sludge process during normal retention time because they normally decompose slowly. Many of these compounds could be toxic to microorganisms at 500 mg/l concentrations but may not be at 1 to 5 mg/l. Further, such compounds would probably be adsorbed near the surface during groundwater recharge by passage through the soil profile.

Nitrogen - The total system of the wastewater treatment plant and the soil system during groundwater recharge must be operated to remove the  $\text{NH}_4^+$  or convert it to nitrate ( $\text{NO}_3^-$ ). For removal of N, an ideal recharge system would provide an aerobic condition to convert  $\text{NH}_4^+$  to  $\text{NO}_3^-$  and an anaerobic condition to convert  $\text{NO}_3^-$  to nitrogen gas ( $\text{N}_2$ ), which escapes into the atmosphere. The usual secondary effluent, which has about equal concentrations of C and N, does not have sufficient C for denitrification of the  $\text{NO}_3^-$ . Because of this C deficiency other sources of C must be supplied if most of the  $\text{NO}_3^-$  that can be produced is to be denitrified.

With flooding periods up to two days, sufficient time usually is not available to develop anaerobic conditions and denitrification is small or non-existent. But, with longer flooding, anaerobic conditions develop that favor denitrification. In the operation of such a system the flooding period should be adjusted to not exceed the  $\text{NH}_4^+$  adsorption capacity of the soil nor to exceed the nitrification capacity of the soil during the drying period.

Experience has shown that in a cycle of a 10-day flooding period followed by a 10- to 20-day drying period, about 30% of the N was removed, presumably by denitrification. With this sequence of flooding and drying, a maximum of about 300 feet of treated wastewater can be applied per year.

Soluble Salts - During rapid recharge by spreading, decreases in soluble salts are highly unlikely. Also, with the exception of dissolution of carbonates and/or cation-exchange reactions associated with the acidification

that results from nitrification of  $\text{NH}_4^+$ , there is little possibility of TDS increases during groundwater recharge using secondary effluents.

Trace Elements and Heavy Metals - In groundwater recharge systems, chemical constituents in the water react with the soil to change the chemical composition of the water. The kind and extent of chemical reactions which may occur depend largely upon the amounts and kinds of colloidal clay and organic matter available to provide reactive surfaces for adsorptions and inactivation of these elements.

Methods of Spreading and Operation for Recharge and Their Impact on Contaminant Removal

Spreading of wastewater for groundwater recharge is accomplished by using basins or ponds, ditches or furrows, natural stream channels, or pits and shafts. The method used is dependent upon many factors including type of soils, depth to groundwater, area available for recharging, geographical location, quality and quantity of treated wastewater available, and to some degree the operator's specific preference.

For spreading of treated wastewaters to be effective in recharging the groundwater, the wetted surfaces of the soil must remain aerated and unclogged. Surface area should be such as to minimize evaporation while maximizing infiltration, the quality of the wastewater be such as to minimize the inhibition to infiltration, and operational procedures should maximize the quantity of actual groundwater recharge while optimizing the quality of the wastewater reaching the groundwater body through the removal of contaminants by soils and sediments.

The most common method of recharging groundwater in California is by impounding water in low leveed basins or ponds. The basins are usually constructed upon soils having good permeability. The shape and size of the basin are such that the wetted area to gross land area is maximized while permitting the best operational cycle to provide for flooding and resting.

#### Hydraulic Considerations in Removal of Contaminants

Hydraulic considerations in the removal of contaminants by soil systems relate primarily to the rate of flow through the soil. An ideal system would provide time for reaction in the soil while permitting large volumes to infiltrate. Graded sands with some gravels and silts are probably the most desirable followed by graded sands with reasonable permeabilities but with sufficiently long transit times to permit chemical reactions and adsorption to take place. The other principles in determining the optimum recharge area which apply to groundwater recharge using natural or fresh waters also apply to the use of treated wastewater.

To determine whether artificial groundwater recharge is physically possible in a basin or water management area, the following are necessary or desirable:

1. An efficient intake point or area.
2. Subsurface transmission to the point of pumping.
3. High storage capacity.
4. A point of high pumping capacity.

Organic constituents in soils are the most important contributors to the production of water-stable structure. The effect of dissolved inorganic constituents on the maintenance and magnitude of recharge intake rates is directly related to the chemical quality of the water to be spread. Soon after large-scale recharge begins, all but the most insoluble salts will be leached from the surface by the large volumes of water that pass through it.

While the surface soil may rapidly come to chemical equilibrium with the quality of the water recharged through it, it will never reach a physical equilibrium. Continued downward water flow through any soil provides internal transport of suspended as well as dissolved matter. The smaller particles are moved by the water until they become lodged or sieved out of the stream in restrictions between the large particles; which in turn trap even smaller particles.

#### Need for Additional Research

The need for additional research in the field of contaminant removal by soil systems includes:

1. Conduct and evaluation of statistical analysis of public health consequences of small quantities of bacteria and/or viruses present in recharged groundwater and the aquifer.
2. Identification of potentially toxic and odor causing substances resulting from microbial degradation in recharged aquifers.
3. Investigation of possible virus desorption and reactivation phenomena under field conditions.

4. Development or refinement of more specific methods for concentrating and determining quantities of known objectional organic compounds present in wastewater in an unaltered form.
5. Characterization, separation, and constituent determination of organic polymers in wastewaters based on various chemical and physical properties and on identification of the structural units.
6. Determination of whether certain molecular weight fractions of organic polymers will impart taste or odor to water.
7. Movement of soluble organic substances in groundwater aquifers recharged directly with both chlorinated and unchlorinated wastewaters, containing known and unknown soluble organic substances.
8. Development of a soil pretreatment system from which the effluent can be collected and spread in infiltration basins.
9. Adaptation of nitrogen removal techniques, developed for tile drainage effluents, to treated wastewater effluents as a means of pretreating these waters prior to land spreading.
10. Determination of the effectiveness of nitrogen removal during soil infiltration of nitrified reclaimed water.
11. Determination of the fate of nitrogen species during direct injection of treated wastewater into aquifers.
12. Critically evaluate the trace element load resulting from the use of treated wastewaters in groundwater recharge.
13. Evaluate relationships of chemical, mineralogical, and physical properties of soils to changes which occur in trace element concentration in treated wastewaters as they leach through soils.

14. Determination of the influence organo-metallic complexes in treated wastewater on the solubility and movement of trace elements through soils, the nature of these complexes, their stabilities and their reactions with representative types of soils.
15. Determination of the long-term (decades) effects of groundwater recharge using treated wastewaters.

SECTION V  
IDENTIFICATION AND MONITORING OF  
WASTEWATER CONSTITUENTS

Water quality monitoring is an essential tool in an effective water resources management program. It must establish baseline water quality data and provide information to direct water quality control processes and develop the relationships among causes and effects of water quality changes in the environment.

There are a variety of appropriate types of water quality monitoring programs that may be applied to surface and groundwater monitoring. The major ones include fixed station monitoring networks which provide well defined histories of the physical, chemical, and biological conditions of water; intensive surveys, that are a form of monitoring, useful in the determination of the status of non-conservative water quality characteristics; self-monitoring programs, which require the waste discharger to participate in the overall monitoring program; and indirect monitoring, which is designed to monitor the effects of pollution on the aquatic environment.

An effective monitoring program requires the development of a data management system. Such a system must process and store incoming data, evaluate the data and make necessary changes in the monitoring program in response to trends and changes in quality conditions.

Monitoring programs for groundwater recharge can be considered as monitoring for pollution from a point source. A typical program would involve the use of monitoring wells located downstream from the pollution source and near

use areas and the monitoring of existing water supply wells. Frequency of sampling will depend on the type of constituent to be monitored. Rapidly changing constituents would require more frequent surveillance while conservative materials require a less frequent sampling program. Important to the development of a groundwater monitoring program is knowledge of the movement of substances in the underground. Tracer studies can be conducted to determine information on groundwater movement.

There are two major groundwater recharge operations in the State, the Montebello Forebay recharge operation and the Orange County Water District's injection project (Water Factory 21). Both operations have established monitoring programs designed to monitor the quality of recharge waters as well as the groundwater under recharge.

Provision of timely accurate information regarding water quality is an essential part of any water resource management plan that envisions use of reclaimed wastewater. Such information can be generated in but a few California water laboratories. There is wide variation in staffing and instrumentation, but with proper coordination a monitoring approach using state of the art methods is possible.

For inorganic constituents, organized analytical approaches utilizing well tested and standardized methods are available. There is heavy dependence upon instrumentation with molecular and atomic absorption techniques representing state of the art for most California laboratories. A few laboratories utilize various sophisticated instrumental methods. Little of

the methodology or instrumentation produces real time information, but this capability does exist and could be exploited. Developmental efforts should be concentrated on development of integrated sampling/analysis systems designed to produce useful management information in a reasonable time frame.

For organic constituents organized analytical approaches are lacking, sampling methods generally predetermining the classes of compounds identified. Characterization of a waste on the basis of a specific compound is relatively easy, but usually very time consuming. A variety of instrumental methods are available for characterization of organic materials with infrared spectrometry and gas-liquid chromatography representing state of the art for water laboratories in California. Computer mediated gas-liquid chromatography/mass spectrometry appears to be the most promising approach to identification, but extreme cost has limited exploitation of the technic. Only a very few laboratories available to the discharger have this capability. Developmental efforts should be concentrated on general analytical schemes for all types of organic materials, on sampling methods, and on applications of the powerful instrumentation presently available.

For biological constituents the situation is much the same as for organics. Pursuit of a given entity is relatively easy but time consuming. Characterization of a waste in terms of the various biological factors which may be present requires a great deal of time and laboratory effort. The information developed may be of little value in the management process except as in indicator of trends.

California laboratories vary widely in ability to handle biological constituents with only a few research oriented organization capable of the type of analysis which might be considered necessary in a water quality monitoring plan.



SECTION I

STATEMENT OF THE PROBLEM

Prepared by:

Department of Health



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STATEMENT OF THE PROBLEMIncreased Discharges

The United States currently uses approximately 370 billion gallons of water per day for domestic, industrial, and irrigation activities, which is about 19 percent more than in 1965. The daily use is expected to reach 450 billion gallons in 1980, and may exceed 800 billion gallons by the year 2000.

Unplanned, indirect reuse of wastewater as a portion of domestic water supplies is commonly practiced (e.g. - sewage effluent discharges into rivers upstream from domestic water supplies). EPA has stated that approximately 50 percent of the population in the United States derives their water supply from surface sources that contain industrial wastes, untreated sewage, urban runoff, and effluents from a variety of sewage treatment plants. The percentage of sewage in surface waters is highly variable, and can be up to 18 percent under low flow conditions. For example, it has been estimated that the amount of wastewater in the Ohio River is as high as 17 percent during low flow conditions.

Both the quantities of wastewater produced and the demand for domestic water supplies will increase as the population of the United States increases. This will undoubtedly increase the pressures for reusing wastewater as a means for augmenting existing domestic sources, especially in water-short areas.

Increase in Planned Reuse

Planned wastewater reuse is not innovative in this country. Reclaimed wastewater is presently used for crop and landscape irrigation, industrial

uses, recreation and ornamental lakes, fire protection, and groundwater recharge. California alone has over 200 such projects.

Plans for reusing water for augmenting domestic water supplies are being developed in several parts of the country. Injection of wastewater is being planned at Long Island, New York to prevent saltwater intrusion and recharge the underground aquifers. Denver is currently reclaiming wastewater for industrial purposes and in the future proposes to reuse sewage treatment plant effluent for domestic water supply purposes.

California presently has five planned groundwater basin augmentation facilities in operation. The spreading of treated wastewater at Whittier Narrows began in 1962 with the recharge of approximately 11 MGD from the Whittier Narrows secondary treatment plant. In the past few years effluent from the San Jose Creek plant has contributed to the recharge water. A major project in the final testing stage is the Orange County Water District "Water Factory 21," where a 50 percent blend of desalinated seawater and reclaimed wastewater will be injected into a groundwater basin to provide a seawater intrusion barrier and recharge the groundwater basin. The other planned recharge facilities are relatively minor.

California policy is to encourage wastewater reuse where such uses do not present hazards to the public health. With greater public exposure, higher degrees of treatment are required, higher standards of performance are imposed, and the need for assured reliability becomes compelling. In California, regulations have been developed for the quality of reclaimed water for various uses, and include reliability requirements. These regulations, however, do not include standards for use of reclaimed wastewater for groundwater recharge projects, nor for more direct reuse of wastewater for domestic purposes.

In response to requirements of the Porter-Cologne Water Quality Act of 1970 and the Federal Water Pollution Control Act Amendments of 1972 (PL 92-500), water quality control plans are being developed for each of the 16 drainage basins of the State. A general goal is to achieve maximum use of fresh water through wastewater reclamation. Consequently, groundwater recharge operations have been proposed which would result in an augmentation of the underground domestic water supply with treated sewage effluent. In some of the Basin Water Quality Control Plans, immediate or near-term decisions must be made regarding the reclamation element. There are, of course, other cases where the reclamation element is in a latter stage of the plan, ten years or more in the future, and does not significantly affect earlier stages.

Standards for the reuse of wastewater for domestic purposes are not known to exist anywhere in the world. Along with the problems of effluent removal and performance reliability, a major obstacle lies in the uncertainty about the risks of chronic illness from long-term exposure to the stable organic material that may remain in the highly treated wastewater.

#### Development of Health Concerns

The contaminants in reclaimed water which are of health concern may be grossly classed as biological agents and chemical agents. The significance of biological agents of health concern, with the exception of virus, are known and measures are available to control these agents. Similarly, chemical constituents such as total minerals and heavy metals have acute health significance and these materials can be fairly effectively removed by treatment processes. However, the significance of other inorganic chemical agents and stable organic substances is largely uncertain. Specifically, there is very limited data on the identity of contaminants, the variability of these substances, and the health effects associated with their

consumption. This is particularly the case with regard to the chronic health effects which may be associated with long-term ingestion of low level concentrations of organic chemical substances.

Increasing attention has been given to the transmission of viral diseases through the water route. Waterborne outbreaks of infectious hepatitis have clearly been associated with the ingestion of sewage contaminated waters. Identification of virus in water and wastewater has been hampered by the limitations of sampling techniques, problems of concentration of samples, the complexity and high cost of laboratory procedures, and the limited number of facilities having the personnel and equipment necessary to perform the analytical service.

There is ample evidence that virus are more resistant than bacteria to the usual disinfection practices involving chlorination. This coupled with the many problems of virus monitoring, makes assurance of virus destruction or removal a difficult matter in wastewater treatment.

At the present time, almost 500,000 chemical products are in use which may find their way into wastewaters, and toxicological information is available on relatively few. Testing has essentially been directed at the acute and subacute effects of specific agents with the result that ability in this area has been described as "predicting the obvious and missing the unexpected." The episodes with mercury, polychlorinated biphenyls, cyclamates, nitritoltriacetate, diethylstilbesterol, and thalidomide, while not all involving the wastewater route, have demonstrated the seriousness and complex nature of the problem posed by chemical agents.

The principal problem associated with stable organics is the paucity of knowledge concerning the identity and significance of these substances remaining in treated wastewater. It is generally accepted that secondary

treatment employing a biological system can remove 65-90 percent of the organic material in a domestic wastewater. Advanced waste treatment processes result in added reduction of approximately 60-70 percent. Reclaimed water using advanced treatment processes would typically have an organic content of 10 mg/l as COD. Few studies have been undertaken in an attempt to identify all the organic components in raw and/or treated wastewater, and in describing the organic content of a reclaimed water, we are presently burdened with the use of gross parameters (e.g. - COD, BOD, TOC) that are of limited value and provide no real information regarding the constituents that make up the organic segment of a reclaimed water.

The lack of information, especially with regard to long-term exposure to trace quantities of organic substances, accentuates the need for research in this area. Toxicological evaluations and epidemiological studies are two possible approaches that can be undertaken to obtain information on health effects from long-term ingestion of reclaimed water.

Thorough toxicological study of even a single chemical agent is a lengthy and difficult task. Long-term irreversible toxic hazards can include such delayed effects as actions on fertility and reproduction, and teratogenic, mutagenic, and carcinogenic effects. Information on absorption, distribution, and elimination of the agent must be established as well as biotransformation factors. This information most generally does not exist for stable organic compounds that may be present in wastewater.

If the aforementioned proposed groundwater recharge projects are carried out in the absence of information on the long-term health effects of organics, and if data is later produced which indicates an adverse health effect, this could mean the virtual loss of the major groundwater basins as a source of domestic water and unprecedented catastrophe to California's domestic water supply resources.

Alternative Approaches to the Problem

It is important to this discussion to include reference to the range of options available to meet the problem. Because the concern expressed regarding recharge with reclaimed water relates to the health aspects of the water, the options should consider preservation for potable purposes water that can be of assured safety without depriving other users of suitable water that they require.

There are a number of options which deserve consideration. One involves the use of reclaimed water for intrabasin reclamation. Under this concept high quality water would be reserved for domestic purposes while reclaimed water would be employed for those uses involving a low degree of public health risk. The greatest potential for this approach appears to be with agricultural use and certain industrial uses.

This same approach could also be applied in the concept of dual water systems for domestic water use. Such systems involve the use of high quality water for potable purposes while employing reclaimed water in low risk situations (e.g., toilet flushing). This alternative has some historical precedent in both the United States (e.g., Colorado Springs) and in foreign countries (e.g., Singapore, Malaysia).

A third alternative could pursue the concept of interbasin reclamation particularly for agricultural use. The major element of this approach involves the collection and conveyance of large quantities of reclaimed water to water deficient areas for more productive agricultural use. This concept could be considered as analogous to the existing California State Water Project and would require the same philosophy concerning costs, subsidies, and the agriculturalists ability to pay.

The dedication of groundwater basins for special uses is an option to be considered. This option would set aside aquifers or entire basins for uses such as agricultural or industrial. Groundwaters would then be replenished with reclaimed water to prevent overdraft. These basins would also offer potential areas for studying the effects of recharge on groundwater quality.

#### WASTEWATER IN SURFACE AND GROUNDWATERS

A major position in support of reclaimed water uses involving augmentation of domestic water supply is that the public has been consuming such waters for decades through upstream sewage discharges, land disposal operations, and other such incidental reclamation practices without adverse health effects. Two elements need clarification or study in this position. On one point, the assumption that no adverse health effects have been associated with the incidental reclamation practices, there is little available information to support or refute this assumption. The other item and the one which this section addresses is the actual degree to which the public has been exposed to ingestion of water reclaimed from sewage.

California's groundwater basins contain a total of 250,000,000 acre-feet (81.7 billion gallons) of usable stored water and produce a maximum safe yield of 11,660,000 acre-feet per year (10.4 BGD).<sup>1</sup> (The safe yield is the annual pumpage which can be sustained without permanent change in groundwater level or which does not result in water quality degradation). This immense resource meets the needs of 48 percent of the total municipal and industrial demand of the State. Of the 1,050 large water systems in the State, 852 or 81 percent rely in part or exclusively on well supplies to meet domestic needs. In addition, most of the 3,000 small water systems as well as a large number of individual household wells rely on groundwater. It is estimated that

approximately one-half of the fresh water used in California comes from the underground.<sup>2</sup> However, since many domestic water systems use both surface and groundwater supplies, the total number of people exposed to groundwater probably amounts to about 80 percent of the State's population.

Sewage effluent is discharged to the underground from planned water reclamation operations, incidental recharge from wastes discharged to land, and from individual household septic tanks. In 1972 an estimated 19,400,000 people were served by community type sewage disposal systems, leaving over 2,000,000 people to be served by individual sewage disposal systems, with a total estimated sewage flow of 160,000 acre-feet per year (Ac-Ft/yr) (143.2 MGD). Table I-1 shows the 1972 volumes of sewage effluent discharged by community systems.<sup>3</sup>

The total volume of sewage disposed of to land from various sources was 538,000 Ac-Ft/yr (481.6 MGD) in 1972 including the effluent from individual septic tanks. This quantity represents approximately 20 percent of the total sewage flow. There are over 200 reclamation facilities that, with a few exceptions, are all essentially land disposal operations. At the present time there are only five planned groundwater recharge operations in California, which recharged an estimated 59,210 acre-feet (53 MGD) in 1972 (see Table I-2).

The following sections provide an indication of the amount of wastewater which reaches the surface waters and groundwaters of the State. The only intent of the sections is to provide the reader with a very general concept of present conditions.

#### Percent Sewage in Groundwater

It would be extremely difficult, if not impossible, to determine the percentage of wastewater in groundwaters throughout the State. Obviously,

Table I-1

VOLUMES OF SEWAGE EFFLUENT PRODUCED AND DISCHARGED  
IN 1972

|                            | VOLUME - AC-FT/YR | MGD     |
|----------------------------|-------------------|---------|
| Discharged to Saline Water | 1,708,000         | 1,529.1 |
| Discharged to Fresh Water  | 414,000           | 370.6   |
| Planned Reclamation        | 190,000           | 170.1   |
| Land Disposal*             | 188,000           | 168.3   |
| Total Sewage Produced      | 2,500,000         | 2,238.1 |

\*Does not include individual septic tank effluent discharges.

Table I-2

PLANNED GROUNDWATER RECHARGE FACILITIES IN OPERATION  
IN 1972

| NAME OF PLANT                   | WASTEWATER RECLAIMED |      |
|---------------------------------|----------------------|------|
|                                 | AC-FT/YR             | MGD  |
| San Jose Creek WRP*             | 34,350               | 30.8 |
| Whittier Narrows WRP*           | 17,540               | 15.7 |
| Camp Pendleton (Several Plants) | 4,120                | 3.7  |
| Palm Springs STP                | 1,460**              | 1.3  |
| Eastern MWD-Hemet               | 1,000                | 0.9  |
| Oceanside (3 Plants)            | 740                  | 0.7  |
| TOTAL                           | 59,200               | 53.1 |

\*The effluent from both of these plants is recharged into the Montebello Forebay.

\*\*Including Irrigation

there are wide differences both locally and from one basin to another. The lack of information on underground hydrology including flow and mixing patterns makes projections very tenuous. There is some data, however, available on a few individual groundwater basins.

The 1965 "Detergent Report"<sup>4</sup> identified wells which had been degraded with ABS (alkyl-benzene sulfonate) to the extent that they produced foaming water, i.e., contained an ABS concentration of at least 0.5 mg/l or 5 percent sewage. Foaming wells were reported in at least 20 different areas throughout the State; however, most of the affected wells were pumping from upper water-bearing strata and of these wells many were located in areas where large volumes of community sewage treatment plant effluents were percolating into the basins. Portions on the Mojave and Santa Ana River basins showed the highest degree of detergent pollution, containing up to 25 percent of sewage. In contrast, only traces of ABS, signifying one percent of sewage or less, were found in wells in an urban area of Sacramento County served by individual household septic tanks. The wells in that area all pumped from the upper strata.

#### Examples of Groundwater Pollution

As previously mentioned there are many instances of polluted groundwater throughout the State. The following case histories are examples of groundwater pollution resulting from a variety of different causes.

#### Nitrates - Delano

The Delano area, Kern County, is situated in the southernmost end of the San Joaquin Valley, an area of extensively irrigated agriculture. In the mid-1960's concern was expressed over the high levels of nitrates in the groundwater. Median concentrations of nitrate in some

wells ranged as high as 90 to 115 mg/l. In an effort to determine the source of nitrates, the California Department of Water Resources conducted a comprehensive study in the Delano area. Nitrates were found to have the highest concentrations in areas where the groundwater had risen markedly during recent years, where soils of high permeability required greater use of irrigation water, or where irrigation has been practiced for longer periods of time. Further, it was demonstrated that the source of excessive nitrate lies above the water table. Nitrate was transported into the groundwater by surface irrigation, or was eluted from the ground structures by rising water tables. The study concluded that domestic sewage could be excluded as being a major source of nitrate, and that the major source of nitrate pollution was the use of nitrogen fertilizers in the agricultural areas surrounding Delano.

#### Organics - Riverside

The City of Riverside is located along the Santa Ana River in Riverside County. The river has only intermittent natural flow and derives much of its actual flow from sewage discharges. The City has a series of six wells located adjacent to the river known as Flume wells. The wells, originally drilled for irrigation, were subsequently used for domestic purposes. In early 1973, water from these wells was found to have a very noticeable sewage odor. A study by the State Department of Health was undertaken to determine the quality of the groundwater and the cause of the odor problem. The results indicated that there were high concentrations of organic material in the groundwater. COD and TOC concentrations ranged from 7.4 to 9.9 mg/l and 8 to 9 mg/l, respectively, and MBAS was from 0.24 to 0.31 mg/l. The levels were much higher than those found in

water from other City wells farther away from the river and greater than would be expected to be present from natural sources.

An additional investigation was conducted by the Health Department to verify the earlier conclusions that sewage treatment plant effluent was percolating into the groundwater basin and causing the increase in organic material. Samples of well water were taken in the winter when the river flow was diluted by natural runoff and in the summer when the river was almost 100 percent sewage effluent. The results reinforced the original theory. They showed that the concentration of organic material increased significantly during the summer period. The COD alone had increased over 100 percent at each of the wells, ranging from 16.5 mg/l to 33.0 mg/l.

#### Arsenic - Inyo County

Inyo County is situated in the eastern Sierras along the California-Nevada border. In a number of areas in the county there are high levels of arsenic in the groundwater. Concentrations range from 0.02 to 0.08 mg/l in some areas to levels as high as 0.30 to 0.43 mg/l. Unlike the two previous examples, this problem has not been caused by man's activities but is the result of naturally occurring arsenic deposits with the groundwater basins.

#### Percent Sewage in Surface Waters

The total estimated volume of sewage discharged to fresh surface waters was 414,000 acre-feet (370.6 MGD) in 1972. When this is compared to the total mean annual runoff of 67,788,000 acre-feet (60.7 BGD),<sup>1</sup> the surface waters contain, on the average, 0.46 percent of sewage. This average itself is meaningless, because most of the domestic waters do not contain

sewage and some surface sources used for domestic water contain a larger percentage. The following are examples of surface waters which contain the higher percentages of wastewater:

|                                    | <u>Average</u> | <u>Maximum</u> |
|------------------------------------|----------------|----------------|
| Lower American River               | 0.9%           | 2.4%           |
| Russian River at Sonoma CWD Intake | <1.5%          | 11.0%          |
| Sacramento River at Hood           | 0.4%           | 0.7%           |

The maximum values have occurred only during the lowest flows and for a short period of time. In Southern California there are intermittent streams, such as the Santa Ana River, whose flow during the dry period is composed mostly of sewage effluent. These streams are not directly used for domestic water supply; however, they contribute to groundwater recharge.

Much of the surface water supplied to major metropolitan areas is essentially free from sewage discharges. Some can be considered "pristine" mountain water, such as the Mokelumne River source of the East Bay Municipal Utility District, Tuolumne River source of the San Francisco Water Department, and the Owens Valley source of the City of Los Angeles. In addition, the Colorado River water served to most of Southern California is relatively free from sewage.

It is estimated that approximately 5.5 percent of the State's population is presently ingesting ground or surface water containing a few percent originating from waste treatment. The great bulk of the population is consuming water which is either completely free from sewage or contains it in very low concentrations.

Recharge Projects

Water-short Southern California is the area where groundwater recharge with sewage effluent has had its most extensive application, and it is also where major recharge projects are being planned.

The construction of the Whittier Narrows Water Reclamation Plant has given impetus to many proposed reclamation schemes. Originally designed at 10 MGD, this activated sludge plant was completed in 1962 by the Los Angeles County Sanitation Districts for the purpose of demonstrating the feasibility of groundwater recharge with sewage effluent. The Sanitation Districts obtained a contract from the Central and West Basin Water Replenishment District to buy the reclaimed water. The first reclaimed water was discharged into the Rio Hondo River behind the Whittier Narrows Dam for delivery to the County Flood Control District's Rio Hondo spreading grounds. The San Gabriel River spreading grounds were an alternate point of discharge. These spreading grounds serve as water replenishment works for the aquifers of the Los Angeles Coastal plain which combine and reach ground level in the vicinity of Whittier Narrows.

Studies made by the California Institute of Technology on the site showed that dissolved solids and nitrate contents increased in the percolating water indicating the need for diluting the recharged effluent with fresh water. Enteric viruses and fecal coliform bacteria were not found in the percolate; however, non-fecal soil bacteria were found to proliferate in the underground below the spreading basin.

From 1962 to 1972 the operation involved recharge of 12,000-19,000 acre-feet of reclaimed water along with an average of 146,000 acre-feet of river water annually to a large groundwater basin and was the only major recharge operation in the area prior to 1972. However, there are plans to expand the

plant to 26 MGD capacity within the next 10-30 years as well as for construction of other reclamation plants in the area. A major recharge operation has already been added (San Jose Creek Water Renovation Plant) which markedly increases the amount of wastewater recharged.

The Los Angeles County Sanitation District's 37.5 MGD San Jose WRP was completed in 1972. The plant is located upstream from Whittier Narrows, and provides activated sludge and chlorination treatment to yield effluent for disposal or reuse. The Central and West Basin Water Replenishment District has contracted for all or a portion of the effluent for groundwater recharge in an unlined section of San Gabriel River or in the Rio Hondo spreading grounds. Whenever there is less than full utilization, either planned or because of rejection due to poor quality, the effluent will be discharged to the concrete-lined San Gabriel River Flood Control Channel. Due to the possible oxidation of nitrogenous compounds to nitrate in the underground, the total nitrogen content of the reclaimed water is termed the limiting factor by the Replenishment District in determining the maximum amount of sewage effluent which can be recharged in relation to recharge of local and imported fresh water. It has been determined, that in order to reduce the nitrogen content to safe levels, reclaimed water should not exceed 50 percent of the total water recharged. The amounts of reclaimed water and imported Colorado River water spread in the Montebello Forebay area since 1961 are as follows:

| <u>Time Period</u> | <u>Colorado River<br/>Water Ac-Ft</u> | <u>MG</u> | <u>Reclaimed<br/>Wastewater Ac-Ft</u> | <u>MG</u> |
|--------------------|---------------------------------------|-----------|---------------------------------------|-----------|
| 1961-1964          | 393,600                               | 128,600   | 26,841                                | 8,772     |
| 1964-1967          | 372,600                               | 121,800   | 45,807                                | 14,970    |
| 1967-1970          | 182,100                               | 59,500    | 49,310                                | 16,114    |
| 1970-1971          | 72,100                                | 23,600    | 19,500                                | 6,373     |
| 1971-1972          | 34,450                                | 11,300    | 17,500                                | 5,719     |
| 1972-1973          | 91,800                                | 30,000    | 21,800                                | 7,124     |
| 1973-1974          | 92,100                                | 30,100    | 21,300                                | 6,961     |

In the periods 1971-72, 1972-73, and 1973-74, reclaimed water constituted 23, 14, and 15 percent of the total water recharged. It is important to note that monitoring efforts in the recharge area have been limited in scope and principally directed at inorganic constituents. Recently, the Replenishment District has proposed an extensive program of monitoring. It involves sampling of all recharge water supplies, mixtures of recharge waters and wells within the groundwater basin. Constituents being monitored for include TDS, minerals, organic material (e.g., COD and BOD), trace constituents (e.g., heavy metals), chlorinated hydrocarbons, radioactivity, bacteria and virus.<sup>5</sup>

The construction of the San Jose Creek plant has drastically altered the groundwater recharge picture in the Los Angeles coastal plain by providing the potential for large volumes of available reclaimed water to the existing Whittier Narrows recharge. The combined production from the Whittier Narrows Reclamation Plant, plus the design capacity of the San Jose Plant, would be 60,000 acre-feet per year (53.7 MGD) of reclaimed water or 37.5 percent of the average 160,000 acre-feet per year (143 MGD) of total recharge to the Montebello Forebay. However, the actual recharge would be less than the total plant production by virtue of operational considerations which would prevent the full amount of reclaimed water from being utilized all of the time.

Expansion of the Whittier Narrows Plant by another 25 MGD capacity has been planned, but the Water Replenishment District does not intend to use any additional amounts of reclaimed water until data are available on the quality of the water produced in the basin.

In 1965, the Orange County Water District began a study of injecting treated sewage effluent into a water-bearing aquifer of the Santa Ana River

Basin. The purpose of the project was to study the feasibility of using tertiary treated sewage effluent in a hydraulic barrier system to prevent the encroachment of salt water into the aquifer. In 1971 the District presented a proposal which consists of a line of injection wells located four miles inland from the coast and a line of extraction wells located between the injection wells and the coast. Water for injection will be obtained from a 15 MGD water reclamation plant and blended with desalted seawater from a 15 MGD desalination plant prior to injection. The water reclamation plant will use secondary effluent from the Orange County Sanitation District's Treatment Plant No. 1 and provide tertiary treatment including lime coagulation, ammonia stripping, recarbonation, mixed media filtration, carbon adsorption, and breakpoint chlorination. Although this groundwater recharge project is ostensibly for the purpose of preventing salt water intrusion, recent estimates indicate that over 90 percent of the recharged water will move inland and augment the groundwaters which are presently extracted for domestic and other uses. Additional information on the two aforementioned operations can be found in Tasks IV and V.

Several other large-scale groundwater recharge projects are in the planning stage. For example, the Orange County Water District has proposed a groundwater recharge by surface spreading operation which would result in the recharging of over 10 MGD of sewage effluent into the Anaheim Forebay. One proposal in Los Angeles County entailed the recharging of treated sewage treatment plant effluent (secondary treatment followed by filtration and disinfection) to a spreading area near a City of Los Angeles' domestic water supply well field. Groundwater recharge projects are proposed in nearly every basin in California where adequate amounts of reclaimed water of suitable quality are available. These proposed projects could eventually cause

the groundwater basins to contain high concentrations of sewage effluent. A tabulation of proposed operations is given in Table I-3.

## POSITIONS AND POLICIES

### Introduction

The constantly increasing water demand in California necessitates that wastewater reclamation and reuse be considered as a part of a comprehensive water resources management program. The State Water Code directs that the State "undertake all possible steps to encourage development of water reclamation facilities so that reclaimed water may be made available to help meet the growing water requirements." Also Public Law 92-500, the Federal Water Pollution Control Act Amendments of 1972, encourages wastewater management which results in construction of facilities for wastewater reclamation.

The incidental augmentation of water resources used for domestic supply by wastewater has occurred in this country for many years where wastewater is discharged upstream from water supply intakes. Planned augmentation of domestic water sources is now being given a great deal of consideration. Programs have been proposed that would include the recharging of groundwater supplies, the augmentation of water supply reservoirs and the direct domestic reuse of treated wastewater.

In response to these activities, organizations have presented their positions, policies and guidelines on wastewater reuse. The following is a compilation of these statements:

Table I-3

## PROPOSED GROUNDWATER RECHARGE PROJECTS\*

| BASIN   | PROJECT OR AREA              | FLOW**<br>(Acre-Feet/Yr) |
|---------|------------------------------|--------------------------|
| 3       | Watsonville                  | 8,960                    |
|         | Paso Robles                  | 1,200                    |
|         | King City                    | 700                      |
|         | Pacific Grove Area           | 6,330                    |
| 4A      | Eastside                     | 1,300                    |
|         | Camarillo                    | 2,150                    |
| 4B      | Sepulveda                    | 24,640***                |
|         | San Jose Creek               | 47,040***                |
|         | Whittier Narrows             | 12,320***                |
|         | Las Virgenes                 | 448***                   |
| 5A      | Sacramento Metropolitan Area | 27,280                   |
|         | Redding                      | 6,210                    |
| 5B      | West Sacramento              | 3,810                    |
|         | Mokelumne River Area         | 2,170                    |
| 5C      | Modesto (Ceres)              | 12,640                   |
|         | Madera                       | 4,010                    |
|         | Oakdale                      | 1,450                    |
|         | El Nido (Gustine)            | 3,020                    |
| 5D      | Edison-Maricopa              | 220                      |
|         | Kern River Delta             | 2,180                    |
|         | Visalia-Hanford              | 8,470                    |
|         | Tulare                       | 3,960                    |
|         | Delano-Earlimart             | 3,030                    |
|         | Shafter-Wasco                | 2,230                    |
|         | Porterville                  | 2,130                    |
|         | Fresno                       | 34,220                   |
| 6A      | Suprise Valley               | -                        |
|         | Honey Lake                   | -                        |
| 6B      | Apple Valley-Desert Knolls   | -                        |
|         | Victor Valley                | 4,480                    |
|         | Barstow                      | 5,040                    |
| 7A & B  | Upper Coachella Valley       | 2,850                    |
| 8       | March AFB                    |                          |
|         | Perris Valley                | 25,112                   |
|         | Sun City                     |                          |
|         | San Jacinto-Hemet            |                          |
| TOTAL = |                              | 259,610                  |

\*The proposed projects are those identified in the Water Quality Control Plan Reports prepared for the California State Water Resources Control Board.

\*\*The flow figures are the average daily flows for 1973 at the existing treatment facility in order to provide a rough idea of the amount of recharge. No recharge flows were generally given in the Reports.

\*\*\*Year 2020 flows.

EPA POLICY STATEMENT ON WATER REUSE<sup>6</sup>

The demand for water is increasing both through population growth and changing life styles, while the supply of water from nature remains basically constant from year to year. This is not to imply that we are or will shortly be out of water, although water shortages are of great concern in some regions and indirect reuse has been common for generations. We must recognize the need to use and reuse wastewater. Therefore,

1. EPA supports and encourages the continued development and practice of successive wastewater reclamation, reuse, recycling and recharge as a major element in water resource management, providing the reclamation systems are designed and operated so as to avoid health hazards to the people or damage to the environment.
2. In particular, EPA recognizes and supports the potential for wastewater reuse in agriculture, industrial, municipal, recreational and groundwater recharge applications.
3. EPA does not currently support the direct interconnection of wastewater reclamation plants with municipal water treatment plants. The potable use of renovated wastewaters blended with other acceptable supplies in reservoirs may be employed once research and demonstration has shown that it can be done without hazard to health. EPA believes that other factors must also receive consideration, such as the ecological impact of various alternatives, quality of available sources, and economics.

4. EPA will continue to support reuse research and demonstration projects including procedures for the rapid identification and removal of viruses and organics, epidemiological and toxicological analyses of effects, advanced waste and drinking water treatment process design and operation, development of water quality requirements for various reuse opportunities, and cost-effectiveness studies.

U. S. ENVIRONMENTAL PROTECTION AGENCY  
BACKGROUND STATEMENT ON  
WATER REUSE

Background

While indirect and delayed reuse of water has many accepted applications, the direct application of measures to reuse wastewaters for constructive purposes presents both new opportunities and new problems. Direct reuse is currently being conducted in a number of places for specific purposes; in fact, California reported in 1969 over 200 non-potable reuse situations. Reuse is being applied for a number of purposes, including industrial use for cooling purposes, for groundwater recharge to prevent salt water intrusion in coastal areas; as a source for recreational waters; for irrigation and other agricultural uses, not involving direct contact with food surfaces; and for other uses. An appendix is included for definition of direct and indirect reuse and discussion of the differences related thereto.

The potential for water reuse, as a tool in broad water resources and water quality planning, is many times greater than current practice and should be routinely considered and developed to meet non-potable demands. As could be expected, activity with regard to reuse appears to be much intensified in water-short areas of the country, for instance in the arid West. The Water Resources Council (WRC) report, "The Nation's Water Resources, 1968" cites water shortage problems in 9 basins--Arkansas-White-Red; Texas-Gulf; Rio Grande; Upper Colorado; Souris-Red-Rainy; Missouri; Lower Colorado; Great Basin; and California--and pointedly shows that these problems will worsen by 2020 unless remedial measures are applied.

In addition to reuse of wastewaters, attention is being given to weather modification, desalination, water conservation, interbasin transfer, tapping

of the geothermal deep-water reservoirs and other approaches to conserve existing as well as tap new sources. Reuse should be considered in the light of water quality, environmental, ecological and economic aspects as well as the public health aspects; it should provide a vital link in meeting needs in water-short areas.

#### Reuse Application and Public Health Problems

Taking a national view of fresh water demands, it may be seen from the 1968 WRC report that for 2020, electric power (cooling water) will be first in demand (410 BGD); self-supplied industrial, second (210 BGD); irrigation, third (161 BGD); and municipal, fourth (74 BGD); with minor residue demands for livestock and rural domestic. Logically, one would expect that priorities for reuse would pattern after demand with electric power (cooling) first, industrial second, etc. Such a pattern of application would ideally suit health protection-water quality relationships since cooling and most industrial uses would present low health risks; irrigation for some crops would be potentially hazardous, but not for others; and municipal uses would offer the greatest human contact and the largest potential danger.

The problem may not be handled so simply on gross utilization terms since each call for water reuse will be situational, depending on geographic location, climate, public attitudes, the availability of wastewater sources and of potential water users, etc. One community may be non-conservative in utilizing its fresh waters and be willing to treat and recycle wastewaters in order to continue its easy-water practices while another community with a similar policy and an abundant supply of cheap water may be unwilling to treat and recycle wastewater just to conserve water for use by others--for instance for irrigation or municipal purposes elsewhere. In one case, a needy municipality may be in a position to utilize industrial wastewaters

and in another case a needy industry may be situated so as to use municipal wastewaters. In any event the technology is available for the treatment and reuse of many wastewaters for many purposes and such reuse should be broadly considered in the management of water resources.

Public health problems do occur and require attention as follows:

1. Industrial: The reuse of water by industry should be encouraged where it is technically and economically feasible. Quality needs for industrial uses vary so widely that it is not possible to generalize on this subject; however, except for food processing industries, they are usually lower than drinking water requirements.
2. Groundwater Recharge: Groundwater recharge can be used to raise or maintain the level of groundwater and/or to prevent the intrusion of salt water. For most recharge applications through spreading and percolation of reuse waters on the surface, quality requirements for health protection would be enhanced by natural filtering processes. However, percolation into a shallow basin used for drinking water supply should receive careful attention and the recharge of reuse water by subsurface injection should not be implemented without strict controls and a clear demonstration that such disposal will not harm present or potential subsurface water supplies or otherwise damage the environment.
3. Recreation: Indirect reuse of water for primary contact recreational purposes is clearly recognized in the section on recreational uses in Water Quality Criteria<sup>1</sup> by way of the recommended limits for fecal coliform organisms and the recommendation that sanitary surveys be conducted to determine the degree of threat of pathogens from specific sources.

3. (Continued) The hazards associated with direct contact recreation in waters receiving inadequately treated waste discharges are chiefly biological and are usually associated with the transmission of infectious diseases that may enter the body through the mouth or nasal passages or other portals such as the eyes, and certain areas of the skin. Numerous examples may be given of both direct and indirect use of treated wastewaters for recreational purposes and this appears to be a valid practice where health requirements can be met. However, much remains to be known about the health relationships of water quality and recreational use. For example, water high in nutrients may serve as a culture for pathogenic bacteria. Further research and epidemiological investigations into water quality and health relationships are urgently needed.
4. Irrigation: The reuse of waters for irrigation is and should be a satisfactory mode of reuse. Water quality requirements for crop protection relate primarily to salinity and toxic compounds. For irrigation of non-food or shelled-food crops, health considerations would be minimal but for irrigation of other food crops or of pasturage for food-animals, the hazards are significant unless the water is adequately treated. Much study and development of safeguards should precede this latter use.
5. Municipal: The concurrent use of the Nation's rivers and lakes for both water supply and waste disposal has been practiced for many years in many areas of the country. It is estimated that 50% of the Nation's population now derives their water supply from surface sources which have also received a variety of

5. (Continued) industrial wastes, untreated sewage, urban runoff and effluent from a variety of sewage treatment plants. Public health officials have relied upon time of travel or storage and treatment to protect the public against infectious diseases and toxic substances. Water quality standards and treatment requirements applicable to surface sources used for water supply have permitted the discharge of relatively high quantities of wastes. The continuing development of new advanced wastewater treatment technologies and implementation of new standards will necessitate a reappraisal of historical philosophies.

Indirect reuse for municipal public water supply is a fact of life; however, direct reuse is a new matter requiring careful research and investigation before introduction. Currently, there is insufficient data to support safety of direct interconnection of wastewater reclamation plants into municipal water supplies. However, the direct connection of municipal renovated water to supply industrial water needs is desirable and should be exploited where practical.

Health problems in a direct interconnection or in a recycling situation relate to viruses, bacterial build-up, chemical build-up, the possibility of accidental spills or sabotage and a record of questionable reliability in the operation of wastewater treatment plants. Viruses are difficult to identify and measure and are more resistant to disinfection than bacteria. Carbon columns and other possible advanced waste treatment elements may harbor bacteria or their metabolites and contribute to the development of unhealthful levels of bacteria in a recycling situation.

The direct introduction of chemicals from a waste-stream and their build-up through potable system-waste system recycling can present increased long-term chronic hazards, presently undefined. Accidental spills or sabotage present an acute threat which cannot be disregarded, as anyone can throw anything down the drain. Because of these, even if other objectionable problems were solved, some system of holding and dilution reservoirs may inevitable need to be provided between the reclamation plant and the potable water intake together with biological and chemical monitoring. With regard to the reliability of reclamation plant operation studies<sup>2</sup> in California have shown that 60% of wastewater treatment plants studied had some breakdown during the year. Observations of engineers and others confirm that reliability is a common problem in wastewater treatment plants; safeguards must be provided to prevent the introduction of non-treated or poorly treated wastes into a potable water system.

### Conclusions

1. The purposeful reuse of treated wastewaters has a large potential in helping to meet water supply needs. Expansion of reuse as a tool of water quality and water resources management should be encouraged as long as measures are taken to protect the public health.
2. We do not have the knowledge to support the direct interconnection of wastewater reclamation plants into municipal water supplies at this time. The potable use of renovated wastewaters blended with other acceptable supplies in reservoirs may be employed once research and demonstration has shown that all of the following conditions would be met:
  - a) protection from hazards to health,

- b) offers higher quality than available conventional sources,
  - c) results in less adverse ecological impact than conventional alternatives,
  - d) is tested and supplied using completely dependable chemical and biological control technology,
  - e) is more economical than conventional sources,
  - f) is approved by cognizant public health authorities.
3. An accelerated research and demonstration program is vitally needed to:

Develop basic information and remedial measures with respect to viruses, bacteria, chemical build-ups, toxicological aspects and other health problems. Develop criteria and standards to assure health protection in connection with reuse.

Upgrade the treatment process design and operation so as to assure continuously safe service to the public. Provide economic and other analyses to facilitate the planning and design of effective regional solutions to problems of water-shortage and water quality.

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1/ Water Quality Criteria, Report of the National Technical Advisory Committee to the Secretary of the Interior, April 1, 1968.

2/ Ongerth, H.J., Jopling, W.F., and Deaner, D.G. Fitness Needs for Wastewater Reclamation Plants, J. American Water Works Assn., Oct., 1971.

Appendix to EPA Statement: DEFINITIONS AND DISCUSSION OF DIFFERENCES  
FOR DIRECT AND INDIRECT REUSE

Definitions are derived from a report of the National Water Commission,  
"Wastewater Reuse," by Jerome Gavis, July 1971, as follows:

1. Direct Reuse: is the direct routing of treated wastewater effluents to the point of use.
2. Indirect Reuse: is the discharge of treated wastewater where it is subjected to natural purification processes and dilution before being withdrawn for use.

Differences in the two types of reuse that must be considered in any drinking water application are as follows:

1. Direct reuse is more vulnerable to sabotage, operational failure and the accidental spill of toxic or hazardous substances into the water-wastewater system. The provision of fail-safe equipment, processes and holding reservoirs may be necessary to meet this problem.
2. Direct reuse allows no margin for error in the destruction of pathogenic viruses, bacteria and other microorganisms.
3. Direct reuse could result in the buildup of trace substances to many times their usual concentration; depending on the degree of reuse and the efficiency of treatment, the concentration factor could run up to nine times.

Many of the factors influencing direct reuse may come into play for indirect reuse. If the time and dilution factors before indirect reuse are small, the impacts of dilution and natural purification may be minimal. Yet the question of what time and dilution factors are adequate cannot be answered

on the basis of today's knowledge. Research to acquire new basic knowledge and common sense in the application of today's limited knowledge is essential. Also, it is essential that each reuse situation be treated on an individual basis, taking into account all factors.

USE OF RECLAIMED WASTEWATERS AS A  
PUBLIC WATER SUPPLY SOURCE <sup>7</sup>

A Statement Adopted by the Board of Directors on June 18, 1971

The American Water Works Association recognizes that properly treated wastewaters constitute an increasingly important element of the total available water resources in many parts of the North American continent as well as elsewhere in the world.

Historically, wastewaters have been reused after discharge of the effluents to streams and into the ground. This practice has provided dilution, separation in time and space, and has allowed natural treatment phenomena to operate before reuse. In contrast to such indirect reuse, planned direct reuse is increasingly being made of reclaimed waters for wide varieties of beneficial uses such as industrial cooling, certain industrial processes, irrigation of specific crops, and recreational areas. Moreover, there is increasing use of reclaimed waters for planned ground water recharge.

The Association believes that the full potential of reclaimed water as a resource should be exploited as rapidly as scientific knowledge and technology will allow, to the maximum degree consistent with the overriding imperative of full protection of the health of the public and the assurance of wholesome and potable water supplied for domestic use. The Association encourages an increase in the use of reclaimed wastewaters for beneficial purposes, such as industrial cooling and processing, irrigation of crops, recreation, and, within the limits of historical practice, ground water recharge. Further, the Association commends efforts that are being made to upgrade wastewater treatment and to improve quality before discharge into sources of public water supplies.

The Association is of the opinion, however, that current scientific knowledge and technology in the field of wastewater treatment are not sufficiently advanced to permit direct use of treated wastewaters as a source of public water supply, and it notes with concern current proposals to increase significantly both indirect and direct use of treated wastewaters for such purposes. It urges, therefore, that immediate steps be taken, through intensive research and development, by the AWWA Research Foundation and the Water Hygiene Division of the Office of Water Programs in the Environmental Protection Agency to advance technological capability to reclaim wastewaters for all beneficial uses. Such research and development is considered to be of greater national need than that now being directed to desalinization. It should

1. Identify the full range of contaminants possibly present in treated wastewaters that might affect the safety of public health, the palatability of the water, and the range of concentrations
2. Determine the degree to which these contaminants are removed by various types and levels of treatment
3. Determine the long-range physiological effects of continued use of reclaimed wastewater, with various levels of treatment, as the partial or sole source of drinking water
4. Define the parameters, testing procedures, analytical methodology, allowable limits, and monitoring systems that should be employed with respect to the use of reclaimed wastewaters for public water supply purposes
5. Develop greater capability and reliability of treatment processes and equipment to produce reclaimed water of reasonably uniform quality in view of the extreme variability in the characteristics of untreated wastewaters

6. Improve the capabilities of operational personnel

The Association believes that the use of reclaimed wastewaters for public water supply purposes should be deferred until research and development demonstrate that such use will not be detrimental to the health of the public and will not adversely affect the wholesomeness and potability of water supplied for domestic use.

JOINT RESOLUTION OF THE AMERICAN WATER WORKS ASSOCIATION AND  
THE WATER POLLUTION CONTROL FEDERATION ON POTABLE REUSE OF WATER<sup>8</sup>

WHEREAS: Ever-greater amounts of treated wastewaters are being discharged to the waters of the nation and constitute an increasing proportion of many existing water supplies, and

WHEREAS: More and more proposals are being made to introduce reclaimed wastewaters directly into various elements of domestic water supply systems, and

WHEREAS: The sound management of our total available water resources must include consideration of the potential use of properly treated wastewaters as part of drinking water supplies, and

WHEREAS: There is insufficient scientific information about acute and long-term effects on man's health resulting from such uses of wastewaters, and

WHEREAS: Fail-safe technology to assure the removal of all potentially harmful substances from wastewaters is not available,

NOW THEREFORE BE IT RESOLVED: That the American Water Works Association and the Water Pollution Control Federation do hereby urge the Federal Government to support an immediate and sustained multidisciplinary national effort to provide the scientific knowledge and technology relative to the reuse of water for drinking purposes in order to assure the full protection of the public health.

AMERICAN PUBLIC HEALTH ASSOCIATION<sup>9</sup>  
POLICY STATEMENT

Reclaimed Wastewater as a Public Water Supply Source - 1972

The American Public Health Association joins the American Water Works Association in recommending increased research and development efforts by federal and state governments as well as professional associations, universities, and research institutions to assess the full potential of reclaimed water as a resource that should be exploited as rapidly as scientific knowledge and technology will allow. This should be done to the maximum degree consistent with the overriding imperative of full protection of the health of the public and the assurance of wholesome and potable water supplied for domestic use.

CONFERENCE OF STATE SANITARY ENGINEERS POLICY  
RECYCLING COMMUNITY WASTEWATER FOR DOMESTIC WATER SUPPLY<sup>10</sup>

In the light of a growing movement to recycle reclaimed community wastewaters for reuse as a source of domestic water supply, it is the position of the Conference of State Sanitary Engineers that in-depth studies of potential acute and chronic health effects of such practices on man are urgently needed in order to make health and engineering judgments concerning both current practices and future project proposals. In the absence of such scientific inquiry, projects which may result in significantly increased use of recycled wastewater for domestic purposes, are considered premature and ill advised.

WATER SANITATION SECTION  
CALIFORNIA STATE DEPARTMENT OF HEALTH<sup>11</sup>

POSITION ON BASIN PLAN PROPOSALS  
FOR  
RECLAIMED WATER USES INVOLVING INGESTION

September, 1973

WATER SANITATION SECTION  
CALIFORNIA STATE DEPARTMENT OF HEALTH

POSITION ON BASIN PLAN PROPOSALS  
FOR  
RECLAIMED WATER USES INVOLVING INGESTION

Introduction

The purpose of the position statement is to provide guidelines for Department of Health review and recommendations on basin plan reclamation components that involve augmentation of a domestic water supply. The Department of Health responsibility is to represent the best health interests of the State in this matter by assuring protection of the domestic water resource.

Three uses of reclaimed water are considered in the statement:

1. groundwater recharge by surface spreading,
2. direct injection into an aquifer suitable for use as a domestic water source, and
3. direct discharge of reclaimed water for supply augmentation into a domestic water system or storage facility.

Health risks from the use of renovated wastewater may arise from pathogenic organisms and toxic chemicals. The nature of the phenomenon associated with pathogens and heavy-metal toxicants are well enough understood to permit setting limits and creating treatment control systems. This is not the case, however, with regard to some organic constituents of wastewater. In particular, the ingestion of water reclaimed from sewage may produce long-term health effects associated with the stable organic materials which remain after treatment.

This is an area of unknowns -- unknowns involving the composition of the organic materials, the types of long-term effects, synergistic effects, metabolite formations, treatment effects, methods of detection and identification, and ultimately, the levels at which long-term health effects are exerted.

The urgent need for knowledge in this area has generated increased calls for answers by health authorities, the water industry, resource managers, and the scientific community. It now appears that the need for research is recognized and there should be action in the near future. As a suggestion of the time frame needed for research activity, it has been estimated that the interval needed before information can be generated through animal feeding experiments (one possible method of study) could range from six to ten years or longer depending on the results that are obtained. The health effects of concern are not immediate or acute. They are related to ingestion over an extended period, measured in years or decades, and may be serious but quite subtle.

In summary, stable organics pose a health question when reclaimed water is used to augment a domestic water supply. This question will not be answered for years, and years of exposure may be involved for the occurrence of adverse effects. It is in this setting that the position statement has been developed.

#### Uses Involving Ingestion

Three uses of reclaimed water have been identified which involve augmentation of a domestic water supply. These are ranked in ascending order of health significance for the reasons given.

1. Groundwater replenishment by surface spreading.

Health protection will depend on treatment, changes or removals which occur during percolation, dilution, and time.

There are presently four planned recharge systems in operation in California which replenish aquifers used for domestic supply. The largest and one which has operated for more than a decade is the Whittier Narrows recharge operation which involves the recharge of 12,000-18,000 acre-feet of reclaimed water and 160,000 acre-feet of natural surface water annually into a large groundwater basin. The degree of monitoring to determine effects on the organic quality of groundwater from the several planned operations to this time has not been significant.

2. Injection into a groundwater aquifer.

Health protection would depend upon treatment and time. There is little assurance that beneficial changes or removals will occur with horizontal movement through a saturated aquifer. Movement will most likely occur as a physical displacement of the natural groundwater with little mixing or dilution.

Most injection proposals thus far have been for the purpose of saline water repulsion. With mound and trough systems, there is opportunity for partial control of the movement of reclaimed water. The one proposal which has advanced to the construction stage (Orange County Water District) has a number of restrictive provisions and requirements applied to it including ". . . an alternate source of domestic water supply shall be provided any

user whose groundwater is found to be impaired by the injection program." Two other proposals for saline water repulsion are in the development stage in California.

3. Direct discharge into the domestic water system.

Health protection would depend on treatment and dilution. Except for extreme situations where the lack of water has been of greater health significance than that associated with use of water reclaimed from wastewater, no responsible authority has embarked on deliberate, direct augmentation by introducing water reclaimed from sewage into the water system. There are proposals for the future.

The Basin Plans

In the Water Quality Control Plans, it is expected that reclaimed water use involving ingestion may be categorized in the following manner:

1. The plan involves an immediate or near-term decision regarding the reclamation element. Funds are to be committed to near-term physical facilities based on the decision and, once the selection has been made, the options are pretty well closed off. This is essentially an immediate "go or no go" decision.
2. The plan involves an immediate or near-term decision regarding the reclamation element, however, there are reasonable options for other reclamation uses or for waste disposal employing the physical facilities. There will be some loss if the intended project is not completed in the proposed manner, however, regardless of eventual health findings the plan does not constitute an unalterable commitment to domestic supply augmentation.

3. The reclamation element is in a latter stage of the plan, 10 or more years in the future, and does not significantly affect earlier stages. A clear decision on health acceptability will be available prior to construction.

There are, of course, many other shadings, but the three categories should suffice for general direction within which reasonable judgment can be applied.

#### Position on Plans for Direct Discharge into a Water System

A plan which involves direct discharge into a domestic water supply system or storage unit for the near future (within the next decade) is not acceptable because of the uncertain health implications. The Department will recommend against the element of a basin plan which contains such a proposal.

Where a plan requiring a near-term decision involves options or alternatives for the use or disposal of the wastewater, the Department will reject the domestic water reuse alternative and consider the remaining options as the proposals for evaluation.

Direct discharge into a water system may be presented in a plan as a future option which may be appraised as additional information becomes available and future needs and attitudes are clearer.

#### Position on Plans for Injection for Groundwater Replenishment

The Department will recommend against injection for groundwater replenishment as a plan element which is to be implemented in the near future (within next

decade). Injection may be considered as a future option, contingent upon the availability of new supportive information and future needs.

Injection of reclaimed water for saline water repulsion and reclamation of saline aquifers is an acceptable use when accompanied by proper controls. Community domestic water supply may not be drawn from the immediate injection area and preferably, injection should be into the brackish water zone.

#### Position on Groundwater Recharge by Surface Spreading

Surface spreading appears to have the greatest potential for use of reclaimed water in the basin plans. It is expected that most groundwater recharge will be through this method since surface spreading involves the least cost and has the greatest history of practice.

Although this potential exists, it must be restated that there are no reclamation criteria for domestic use of reclaimed water, information relative to health effects from ingestion is uncertain and the interval involved before conclusive information is available may be considerable. It should also be emphasized that if new information indicates adverse effects are created with substantial recharge, closure of those basins involved would be required with regard to domestic use.

The application of limits on specific percentages of reclaimed water allowable in groundwater would be inappropriate because knowledge of health effects is lacking.

For near-term proposals, plans which involve the recharge of a substantial volume of reclaimed water into a small basin will be recommended against.

If information indicates uncertain or adverse effects are associated with recharge operations of this magnitude, the results would require a costly effort to reclaim the basin or might result in abandonment of the basin for domestic use. The serious implications of this situation, therefore, require the Department of Health to recommend against such a proposal.

Where recharge operations would constitute a small fraction of water in the underground, near-term proposals may be acceptable. Location relative to community wells will be considered as well as the domestic use of the basin waters. By limiting such proposals to operations involving only small percentages of reclaimed water in the groundwater, the corrective action, if required, may be without undue cost or loss of the basin as a domestic source. Near-term plans with available options to surface spreading are desired.

Surface spreading presented as a future option in a plan would be acceptable.

Reuse of Effluents: Methods of Wastewater Treatment and Health Safeguards,  
Report of World Health Organization Meeting of Experts.<sup>12</sup>

Considerations with regard to wastewater reuse for domestic purposes:

The World Health Organization Scientific Group on the Treatment and Disposal of Wastes called attention to the possible health problems inherent in the use of wastewater effluents for drinking. However efficiently designed and operated the treatment plant may be, there is always a risk of breakdown or human error; in addition, the long-term effects of trace chemicals that may remain in wastewater are as yet undetermined, and much has yet to be learned about the removal of microbiological pollutants, particularly viruses.

Summary and Recommendations: "Water reclamation and reuse may be the most practicable solution to water shortages, and they are likely to be forced on governments in certain areas with increasing urgency. They present no insuperable technical problems, although more knowledge will lead to economies and greater reliability. Reclamation is a practical solution to water scarcity in most conditions, provided that adequate precautions are taken in the design and operation of systems to protect the health of the individual and of the community."

Senate Bill 433

Safe Drinking Water Act

Title XIV                    Safety of Public Water Systems

Part E Section 1442 (a)<sup>13</sup>

"The Administrator shall conduct a comprehensive study of public water supplies and drinking water sources to determine the nature, extent, sources of and means of control of contamination by chemicals or other substances suspected of being carcinogenic . . . ."

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SECTION II  
WASTEWATER CONTAMINANTS AND  
THEIR EFFECT ON PUBLIC HEALTH

Prepared by:

Department of Health  
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## INTRODUCTION

The objective of this task is to compile information on the types and sources of biological and chemical contaminants found in municipal wastewaters which may affect public health or potability of the water, including information on the range of concentrations and the amount of unidentifiable organic material in wastewater. Included are estimates of the amount of wastewater in California surface and groundwaters and a compilation of information on the organic quality of selected waters.

## BIOLOGICAL CONTAMINANTS

Sanitary engineering and preventive medical practices have combined to reach a point where waterborne disease outbreaks of epidemic proportions have largely been eliminated. However, the potential for disease transmission through the water route has not been eliminated. With a few exceptions, the disease organisms of epidemic history are still present in today's sewage and the status of control is more one of severance of the transmission chain by good sanitary practices rather than total eradication of the disease agent. This concept has been more commonly referred to as the "multiple barrier" approach to practical reduction of the public health hazard due to pathogen exposure and reduction.

In attempting to evaluate the public health impact, it is imperative to consider the potential problem in terms of (a) the presence of infectious or toxic agents in a discharge stream; (b) the concentration of these agents (the dose) which may be expected to be present; (c) the response of a susceptible population to these agents (dose response); and (d) the probability and nature of human or animal contact with these materials.

The infectious agents of most importance are those whose origin is the intestinal discharge of man or animals. These can be broadly classified as bacterial, parasitical, and viral.

### Bacteria

Bacteria of the genus Salmonella contain a wide variety of species pathogenic for man and animals. These bacterial agents are transmitted from man to man by means of personal contact, contaminated food and contaminated water. There are three distinct forms of salmonellosis in man: enteric fevers, septicemias, and acute gastroenteritis. Typhoid fever caused by Salmonella typhosa is the most severe enteric fever form of salmonellosis, and man is the only host. At the turn of this century, typhoid fever death rates of more than 50 per 100,000 persons were not uncommon in cities of the United States. The death rate for the entire country in 1900 was 31.3 per 100,000 population; however, at present, death due to this disease is practically nonexistent. Over the last seventy years, the morbidity has also shown significant change; for example, the U.S. morbidity for typhoid fever in 1930 was 12.6 per 100,000 and in 1971 there were less than 0.2 isolations of S. typhosa per 100,000 population of which less than half were clinical cases.<sup>1</sup> The morbidity is getting so low that epidemiologists are beginning to speak in terms of eradication.<sup>2</sup> At this point in time in the United States, water is not a significant vehicle for the transmission of this disease; however, it should be pointed out that there recently has been an isolated outbreak of apparent waterborne typhoid fever among farm workers in Dade County, Florida, in which 213 cases occurred.<sup>3</sup>

The Salmonella septicemias are characterized by bacteremia and a high remittent fever usually without involvement of the gastrointestinal tract.

These are most commonly caused by S. choleraesuis and are relatively rare. S. choleraesuis has a predilection for swine and is not particularly common in human populations.

The third form of salmonellosis, acute gastroenteritis, is the form in which the Salmonella are most commonly encountered. In excess of 1500 serotypes have been identified and most, in contrast to S. typhosa, are not as host specific. The reported isolation rates for humans in the United States in 1972 were 12.5 per 100,000 and most health authorities agree is probably much lower than the actual total incidence.<sup>4</sup> An accurate assessment of the number of deaths attributed to Salmonella is not possible but of the recorded cases between 1962 and 1972 the case fatality rate was 0.43 percent, mostly among the very young and very old.

The most common nonhuman source of these organisms is food and overwhelmingly poultry products. Water, while an important source, contributes only a little more than two percent of the total (Table II-1). The most common form of Salmonella isolated from either human or nonhuman sources in the United States is S. typhimurium. Although the incidence of waterborne salmonellosis is very low, there are a number of occurrences, verified and suspected, in which large numbers of persons were infected by this route. One of the most documented is the outbreak in Riverside, California, in 1965, in which 18,000 people were infected with S. typhimurium.<sup>5</sup> The bacterium was isolated from 100 different stool specimens and from five samples of the drinking water. Although the source was not proven, there was evidence that contamination of the water supply was implicated. Thus, the potential for waterborne transmission remains a real one.

Bacteria of the genus Shigella produce an intestinal disease in man and higher apes known as bacillary dysentery. The disease spreads rapidly under conditions of overcrowding and improper sanitation. The mode of

Table II-1

SALMONELLA ISOLATIONS FROM NONHUMAN SOURCES  
 BY NUMBER PERCENTAGE. UNITED STATES, 1963-1967  
 (Adapted from Aserkoff et al.)<sup>2</sup>

| SOURCE        | NUMBER OF ISOLATES | PERCENT OF TOTAL |
|---------------|--------------------|------------------|
| Fowl          | 16,172             | 46.43            |
| Swine         | 2,791              | 8.01             |
| Cattle        | 2,306              | 6.62             |
| Other Animals | 2,474              | 7.10             |
| Eggs          | 2,117              | 6.08             |
| Dried Milk    | 846                | 2.43             |
| Other Foods   | 1,406              | 4.04             |
| Animal Feed   | 3,703              | 10.63            |
| Water         | 746                | 2.14             |
| Miscellaneous | 1,660              | 4.77             |
| Unknown       | 609                | 1.75             |
| TOTAL         | 34,830             | 100              |

transmission is primarily from person to person and through contaminated food. Generally, these organisms have been considered to be sensitive to the environmental conditions encountered in water and this route has not been considered to be too important but certainly should not be overlooked. Recently,<sup>6,7,8</sup> there have been three reports of waterborne outbreaks of shigellosis in small communities on the East and West coasts and in the Mid-West. All instances involved small, common, unchlorinated wells which were obviously contaminated with sewage. Shigella sonnei was isolated in all instances. The most recent outbreak involved 208 cases related to a contaminated well servicing a Stockport, Iowa, junior high school.

The isolation rate in the United States is approximately 15 per 1,000,000 population. Of the six species commonly pathogenic for man, S. sonnei and S. flexneri are most commonly isolated, the former 60.3 percent of the time and the latter 38.2 percent of the time from the various states.

Cholera is a serious disease of great historical--and current--interest. It is similar in many respects to typhoid fever but more rapid in onset, more virulent, and more often fatal. Death rates of 25 to 85 percent of the cases are commonly reported. The disease has been endemic in India for centuries and was unknown in the western world until 1817; at which time, an epidemic originating in India became pandemic. The United States was not spared; a number of epidemics occurred between 1826 and 1896 and were closely associated with the movement of European immigrants to this country. Until recently, except for occasional cases at seaports, there had been no cholera in the United States since the turn of the century.<sup>9</sup>

The etiologic agent of this disease is the small, curved, gram negative, motile, non-spore-forming rod, Vibrio cholerae. Man is the only known natural host and since a prolonged carrier state is uncommon, the disease must be maintained by an unbroken chain of mild inapparent infections. Infected water is the frequent mode of transmission.

Cholera is not now a problem in the western world. The most persistent endemic focus is in India and Bangla Desh. The most recent large epidemics outside of India were in Egypt in 1948, causing the loss of more than ten thousand lives. Interestingly, Egypt had been free of the disease since 1902. Since 1961, El Tor Cholera (a variety of V. cholerae) has continued to spread from Indonesia.<sup>10</sup> In 1970, it advanced into previously uninfected areas of the USSR, the Middle East, and Africa. As of January 15, 1971, the

State of Niger has reported the occurrence of the disease. In 1973, a number of cases were reported in Italy and the first case to occur in the U.S.A. since 1911 has been reported in Port Lavaca, Texas.<sup>11</sup> This latter case has been associated with a well contaminated by the leachate from a septic tank system.

Other bacteria considered to be of less importance in domestic wastewater would include the tubercle bacillus, Leptospira and "non-pathogenic" bacteria.

Mycobacterium tuberculosis<sup>12</sup> has been isolated from sewage, particularly where an institution treating tuberculosis patients is involved or where industries such as dairies and slaughterhouses handling tubercular animals may be expected to discharge their wastes. Human cases associated with wastewater usually involve swimmers in highly contaminated water who aspirate water into their lungs.

There have been a number of reports of swimmers contacting leptospirosis.<sup>13</sup> In these instances they have been swimming in ponds or slow moving streams in which cattle and swine have access. Forty cases were reported from Iowa in 1959 and 15 in 1964. Fifty cases were reported from New York in 1951. In all these instances, Leptospira pomona or L. grypotyphosa were involved. Most common species of leptospira are infectious for both man and animal and gain access to water via animal urine. There is one leptospira, L. biflexa, which is not pathogenic, but common to water. This latter form has a common generic antigen and could possibly be confused with the other pathogenic forms when isolations are made from water.

There are many reports of waterborne gastroenteritis of unknown etiology in which bacterial infections are suspected. It is important, therefore, to mention certain gram negative bacteria normally considered nonpathogenic as

potential sources for these disturbances. Both enteropathogenic Escherichia coli and certain strains of pseudomonas are often mentioned in the newborn.<sup>14</sup> Recently enterotoxigenic E. coli have been shown to be the etiology of traveler's diarrhea.<sup>158</sup> The well publicized gastrointestinal disease outbreak that occurred at Crater Lake National Park has been shown to be due to waterborne enterotoxigenic E. coli.<sup>159</sup>

There has been some speculation that coliforms exhibiting R factor resistance to antimicrobial agents are present in sewage and may be of public health significance.<sup>160</sup> The R factor is an extra-chromosomal nucleic acid element which can be transferred between individual bacteria of the same or different species and which confers drug resistance upon the recipient. Ingestion of coliforms containing the R factor may result in the transfer of this factor to the normal intestinal flora, thus creating a reservoir of resistance. This resistance may in turn be transferred to pathogens such as Salmonella typhosa (typhoid fever organism) which the host may encounter. That this phenomenon is operative is evidenced by the worldwide occurrence of R factor antibiotic resistant S. typhosa.<sup>161</sup>

From the preceding discussions, it would appear that at the present time in the United States the bacterial agents of most concern are the Salmonella sp. responsible for acute gastroenteritis and perhaps the suspected "nonpathogenic gram negatives." Until recently, cholera has not been present and the agents of tuberculosis and leptospirosis although important do not, from an epidemiological point of view, appear to be significant in municipal wastewater.

### Parasites

There are myriad diseases of protozoan and metazoan etiology which are transmitted from man to environment to man in fecal material and many

may be associated with water. An exhaustive list of these parasites would not be appropriate in this review and only the most important or potentially important organisms will be mentioned.

In the United States, perhaps the most serious parasitical disease to be associated with wastewater is amoebic dysentery. The etiology of this disease is Entamoeba histolytica, a protozoan which can infect the human colon causing erosion of the superficial mucous membranes. It may eventually invade the tissue with consequent ulceration. In certain severe cases, the parasite may metastasize to other body organs. The amoeba has the ability to form heavy walled cysts and transmission occurs when mature cysts are excreted with feces into water or food. Infection begins with the ingestion of cysts which germinate in the gut to become vegetative amoebae which multiply and may become invasive. The cysts are most important from an epidemiologic point of view because they are resistant to environmental forces. The vegetative forms do not survive outside the gut. The disease is worldwide and normally occurs as inapparent infections. The incidence of infection in the United States is not well established because of the frequent lack of clinical manifestations; it is most probably of considerable magnitude.

Giardiasis is an intestinal disease caused by protozoa of the genus Giardia and particularly G. lamblia. These protozoans grow in the human small intestine and frequently cause gastroenteritis. The disease is frequently seen to occur among tourists, particularly in Eastern Europe and the Mediterranean.<sup>162</sup> The source of infection may be contaminated drinking water. The disease is present in the United States and probably is frequently not recognized. A large water-associated outbreak occurred among skiers in Aspen, Colorado, in 1969.<sup>163</sup>

Human schistosomiasis is an important disease in many parts of the world, including South America, Africa and the Orient. Fortunately, this disease does not naturally occur in North America; however, "swimmers' itch" is a problem in many parts of the country. This is a schistosomiasis in which the primary hosts are water fowl. Man is accidentally infected by the cercariae and because he is not a natural host they cannot develop any further, resulting in local skin irritation and itching, which can be quite severe.

Other helminthic parasites which may be present in municipal wastewater could include the eggs of Ascaris lumbricoides (Giant round worm), whose host and reservoir is man, and various cestodes (tapeworms) Taenia sp. In this latter instance, cestode eggs would be transmitted to the intermediate host; swine or cattle and man would be infected by eating their meat. This is of the most importance when sewage sludge is spread in agricultural areas.

While referring to diseases caused by larger parasites, it seems appropriate to include reference to a condition in which naturally occurring soil amoeba have infected human swimmers causing over 50 deaths throughout the world including the United States. In these instances amoebas of the genus Naeglaria apparently have been aspirated by swimmers into their nasopharynx and such clinical conditions as meningoencephalitis, brain abscess and lung abscesses have resulted.<sup>15</sup>

### Viruses

Many types of human viruses are discharged in the feces of infected persons and are disseminated in the water environment from sewage and other sources of fecal pollution. Established laboratory criteria for measuring fecal pollution and monitoring treatment procedures for the removal of

pollutants are based on bacteriologic findings which do not provide a specific measure of the presence or extent of viral contamination. Overt instances of recognized waterborne viral disease transmission have been relatively uncommon. However, in recent years improved laboratory technology for recovery of viruses from water has resulted in a growing number of reports describing widespread occurrence of viruses in treated sewage effluents and surface waters. This has resulted in increased concern that such viral contamination may present a greater danger than heretofore recognized.

Once virus enters the water environment there are a number of potential modes of transmission to man, primarily through ingestion or bodily contact. This includes such activities as bathing, water contact sports, contact with crop or landscape irrigation waters, drinking from untreated or improperly treated water sources, and ingestion of shellfish. The potential for viral contamination has increased greatly with new trends in water use and with the growth in the volume of domestic wastes being discharged to natural water courses.

Viruses are obligate intracellular parasites able to multiply only within a host cell, where they are assembled as complex macromolecules utilizing the cell's biochemical system. Viruses occur in various shapes and range in size from 10-300 millimicrons in cross-section and are composed of a nucleic acid core surrounded by an outer coat of protein. Most plant or animal viruses are cylindrical or spherical in shape. Bacteriophages are viruses that infect bacteria as the host. No bacteriophage has been found capable of infecting a plant or animal.

Because small amounts of ingested virus may produce an infection but not disease, it is likely that small amounts of viruses could be present in

water and go undetected. In the case of infectious hepatitis, no host other than man has been found, making it extremely difficult to study the efficiency of treatment processes in removing or destroying the virus. Consequently, the viruses studied are usually poliovirus, coxsackie virus, and bacteriophages.

Viruses in the stool of infected persons commonly range from 1,000 to 100,000 infective units per gram of feces. The quantities of enteric viruses in water and sewage vary widely (enteric viruses are viruses that can multiply in the human intestinal wall and which are found in quantity in human feces and in sewage). It has been calculated<sup>16</sup> that the average enteric virus density in domestic sewage is probably about 500 virus units per 100 ml, and in polluted surface water not more than one virus unit per 100 ml. These quantities are very small in comparison to the quantities of coliforms. The coliform virus ratio is about 92,000:1 in sewage and about 50,000:1 in polluted surface water.<sup>17</sup> The human enteric viruses and the diseases associated with them are as follows:<sup>18,19</sup>

| <u>Virus Subgroup</u> | <u>No. of Types</u> | <u>Disease</u>   |
|-----------------------|---------------------|--|
| Poliovirus            | 3                   | paralytic poliomyelitis, aseptic meningitis                                  |
| Coxsackie virus       |                     |  |
| Group A               | 26                  | herpangina, aseptic meningitis, paralysis                                    |
| Group B               | 6                   | pleurodynia, aseptic meningitis, acute infantile myocarditis                 |
| Echovirus             | 34                  | aseptic meningitis, rash and fever, diarrheal disease, respiratory illnesses |
| Infectious hepatitis  | 1 (?)               | infectious hepatitis   |
| Reovirus              | 3                   | fever, respiratory infections, diarrhea                                      |
| Adenovirus            | 32                  | respiratory and eye infections   |

At present, infectious hepatitis (hepatitis A) is the enteric virus disease of most importance in wastewater and many outbreaks have been attributed

to contaminated water on the basis of epidemiologic evidence. Ten outbreaks have been documented in the United States,<sup>20</sup> most of which involved gross contamination of small supplies. It has been suggested that there may be many unrecognized infectious hepatitis epidemics.<sup>21</sup> Although it is a distinct possibility that some of these unrecognized outbreaks are waterborne, the water route still only accounts for less than one percent of the total outbreaks in the United States.

The only infectious hepatitis epidemic associated with a large metropolitan water supply was the celebrated New Delhi, India, incident in 1955-56.<sup>22</sup> In this instance a massive contamination of the water supply with sewage resulted in 30,000 to 70,000 cases of infectious hepatitis.

Recently, a report appeared which associates fourteen cases of infectious hepatitis among thirty individuals who were swimming in a North Carolina recreational lake of questionable sanitary quality.<sup>23</sup> This is the first time that such a definite case has been made for the potential of contracting this disease while swimming in sewage-polluted water.

A number of outbreaks of infectious hepatitis due to the ingestion of raw or steamed shellfish taken from sewage-polluted waters have been reported.<sup>21</sup> Although no outbreaks of shellfish-associated disease have been attributed to other members of the enteric virus group, several outbreaks of shellfish-associated "gastroenteritis" have been reported.<sup>24,25</sup>

The infectious agent responsible for infectious hepatitis has not yet been isolated; however, Feinstone, et al., have recently demonstrated the presence of virus-like particles in infected stools using immune electron microscopic techniques.<sup>26</sup> They have also been able to show that these particles are immunologically distinct from the observed Dana particles of serum hepatitis (hepatitis B).

The water route of transmission has been implicated in several outbreaks of poliomyelitis. Outbreaks in Edmonton, Alberta, Canada, and Huskerville, Nebraska, were attributed to contaminated water but the evidence is by no means conclusive.<sup>27,28</sup> Most authorities agree that in the developed countries poliomyelitis should be considered a disease in which water transmission is, at best, a rare occurrence. In underdeveloped countries where sanitation is poor, the transmission of poliomyelitis and other enteric viruses by water may be a common occurrence.

Three outbreaks of pharyngoconjunctivitis caused by adenovirus type 3 and one of type 7 have been attributed to contaminated swimming pools.<sup>29,30,31,32</sup> Isolation of the virus from the pool water was either unsuccessful or not attempted, and the water route of transmission was implicated only on the basis of epidemiologic evidence.

In 1974, five children showed symptoms of a disease with similar clinical characteristics. The disease was positively diagnosed as caused by coxsackie virus type A16.<sup>33</sup> In this instance, the infections were acquired while swimming in lake water that had relatively high fecal coliform counts and from which the specific virus was successfully isolated. This is one of the first instances in which a type A coxsackie virus has been shown to be transmitted to bathers.

No other enteric viruses have been specifically implicated as causative agents in documented outbreaks of waterborne viral disease. In this regard, it should be noted that a virus-like particle similar in appearance to the hepatitis A associated particle has been reported to be associated with an acute infectious nonbacterial gastroenteritis that occurred in Norwalk, Ohio.<sup>34</sup> This agent is immunologically distinct from the hepatitis associated particles. However, it should be pointed out that for many outbreaks of

gastroenteritis and diarrhea, no agent can be specifically incriminated. The cause of such outbreaks is often listed as "viral" in nature. For the years 1946 through 1960, 142 epidemics of waterborne gastroenteritis and diarrhea involving 18,790 cases were reported in the United States.<sup>35</sup> In terms of magnitude, gastroenteritis and diarrhea are the most important diseases transmitted by water. The possibility that enteric viruses are the causative agents of such episodes cannot be dismissed.

In addition to the possible role of waterborne viruses in epidemics, it has been suggested that even in well managed water supplies there is the possibility of low level transmission of viral infections resulting in sporadic clinical cases rather than explosive outbreaks.<sup>36</sup> The study of low level transmission or endemic occurrence of waterborne virus diseases has been virtually ignored for several reasons: (a) present virus detection methods are not sensitive enough to accurately detect low concentrations of viruses in large volumes of water; (b) enteric virus infections are often inapparent, thus making it difficult to establish the endemicity of such infections; (c) once introduced into a population, person-to-person contact would become a major mode of transmission of an enteric virus, thereby obscuring the role of water in its transmission.

#### Indicator Organisms

Sanitary scientists are extremely interested in the control of enteric diseases and would like to detect the presence of any of these agents in water and wastewater. None of these microbes are readily isolated from water, and, more importantly, they are not readily enumerated. Because of the difficulty in directly determining the presence of these microorganisms, the environmentalist must rely upon indicator microorganisms, those that can be readily detected and counted. Their presence is indicative of fecal

contamination and survival characteristics are similar to the disease-producing organisms you would expect to find.

The common means of ascertaining sanitary quality is to measure the number of coliform bacteria present in the water. The term coliform, designates a relatively large taxonomic group of bacteria which are commonly present in the gut of warm-blooded animals. These microorganisms are not usually considered to be pathogenic, but are believed to be indicative of the presence of fecal material. Since the direct measurement of enteric pathogens is difficult, health authorities rely on the more easily determined coliform indices to alert them to the presence of fecal material and, therefore, the potential presence of pathogenic microbes of enteric origin.

Unfortunately, the coliforms include a number of representatives which are ubiquitous in the general environment and are not necessarily associated with sewage or similar materials. These are commonly found in soil and on plants and during times of heavy runoff are flushed into local waters. These, of course, confuse the interpretations as to sanitary quality. A means of differentiating from nonfecal coliforms has been improved to a point where a routine test can be included in the standard measurement. This test is based upon the observed phenomenon that coliforms of fecal origin will grow at elevated temperatures.

At the present time, the measurement of fecal coliforms is a fairly reliable index of the presence of waste contaminated with potentially dangerous fecal material. When wastewater has been treated to one degree or another, the fecal coliform as well as the number of total coliforms will be reduced in proportion to the reduction of any bacterial pathogen which might be present. The reduction in coliform count is, therefore, indicative of the reduction of disease-producing bacteria. Unfortunately, this relationship does not necessarily hold for viruses, particularly when chlorination

is involved, as many viruses appear to be relatively more resistant than bacteria to such disinfection.

#### Dose-Response Considerations

From the previous sections it is clear that a variety of disease agents may find their way into water and wastewater. It is also certain that regardless of the degree of treatment, including disinfection and even sterilization, the complete removal of pathogenic organisms is a probability and not a certainty. Therefore, it must be assumed that a dose of infectious agent will be delivered to a susceptible host with some probability. The magnitude of the dose and the probability of its presence in a given volume of water becomes of paramount importance to the sanitarian. Ideally, standards should be developed on this basis.

Of all the parameters involved in evaluating the public health impact of various environmental activities, the dose of microorganisms required to cause disease (i.e., dose-response) in a given individual is the most difficult to determine. To be conservative, it could be assumed that one infectious agent (bacteria, virus, etc.,) is enough to cause disease; however, as might be expected, there is a great deal of variation in both the various agents and the susceptible hosts. One interesting example is the dose-response data recently published by Hornick et al.<sup>37</sup> in which the dose required to bring about human cases of typhoid fever is quite high. Table II-2 presents the results of their human volunteer study in which each subject was challenged with one dose of a given number of Salmonella typhosa. In further feeding experiments human volunteers were challenged with  $1 \times 10^7$  organisms of five different strains of typhoid bacilli which included Quarles, Zermatt, TYZU, O-901 and Ty2W, the latter two being non-Vi antigen strains. Fifty-one percent of those exposed to the Vi strains came down

Table II-2

RELATION OF DOSAGE OF *S. TYPHOSA* TO DISEASE  
(From Hornick et al)<sup>37</sup>

| NO. OF VIABLE<br><i>S. TYPHOSA</i> | TOTAL VOLUNTEERS<br>CHALLENGED | NO. WITH DISEASE |
|------------------------------------|--------------------------------|------------------|
| $10^9$                             | 42                             | 40 (95%)         |
| $10^8$                             | 9                              | 8 (89%)          |
| $10^7$                             | 32                             | 16 (50%)         |
| $10^5$                             | 116                            | 32 (28%)         |
| $10^3$                             | 14                             | 0 ( - )          |

with disease, while only 26 percent exposed to the non-Vi antigen strains were so affected. This further supported the dose response relationship shown in Table II-2 & also clearly demonstrated the increased virulence of those strains containing the Vi antigen. It was also noted that approximately 40 percent of all volunteers challenged developed infections but not clinical disease (10 showed a significant serological response, or positive blood culture or excreted *S. typhosa* in stools for more than five days) regardless of what the challenging strain was.

In earlier studies McCullough and Eisele<sup>38,39,40</sup> developed dose response data for a number of species and strains of salmonella isolated from spray-dried eggs. In this instance human volunteers were challenged orally with various numbers of the appropriate salmonella. The results of these studies are summarized in Table II-3. As with *S. typhosa* response data, it is evident that large doses of other species of *Salmonella* are also required to produce significant human response (disease). In all instances positive stool cultures or increased agglutinin titers were produced in various percentages of volunteers at much lower dose levels. The high level of resistance to

S. pullorum was attributed to the fact that most of the volunteers were immunized against S. typhosa which may well give cross protection against S. pullorum due to some common antigenicity.

Table II-3

DOSE OF VARIOUS SPECIES AND STRAINS OF  
SALMONELLA THAT CAUSED DISEASE IN HUMAN VOLUNTEERS  
(From McCullough and Eisele)<sup>38,39,40</sup>

| SALMONELLA<br>SPECIES/STRAIN | DOSE AT WHICH<br>50% OR MORE RESPOND* |
|------------------------------|---------------------------------------|
| <u>S. meleagridis I</u>      | 50,000,000                            |
| <u>S. meleagridis II</u>     | 41,000,000                            |
| <u>S. meleagridis III</u>    | >10,000,000                           |
| <u>S. anatum I</u>           | 860,000                               |
| <u>S. anatum II</u>          | 67,000,000                            |
| <u>S. anatum III</u>         | 4,700,000                             |
| <u>S. newport</u>            | 1,350,000                             |
| <u>S. derby</u>              | 15,000,000                            |
| <u>S. bareilly</u>           | 1,700,000                             |
| <u>S. pullorum I</u>         | >1,795,000,000                        |
| <u>S. pullorum II</u>        | >163,000,000                          |
| <u>S. pullorum III</u>       | >1,295,000,000                        |
| <u>S. pullorum IV</u>        | 1,280,000,000                         |

\*Develop clinical disease

These data emphasize the point that it often takes more than one infectious unit to produce disease and also demonstrates the existence of varying degrees of virulence between species and strains of pathogenic bacteria.

Unfortunately no dose response data have been found concerning S. typhimurium, the most common cause of salmonellosis in this country.

In the case of viruses, the consensus is that any dose capable of causing a tissue culture infection should be considered capable of causing infection in man. In this regard, it has been shown that as little as one tissue culture infective dose (TCID<sub>50</sub>)\* of polio is infective for susceptible infants.<sup>41</sup> It has been estimated that a TCID<sub>50</sub> of poliovirus may be equivalent to between 30 and 100 viral particles. The data available on human-virus dose response deal with infectivity. No data were found that quantify the dose required to produce clinical disease.

The relationship between indicator organisms and the dose of pathogenic microbes is most conservative. As regards bacterial agents, the coliforms have similar if not slightly greater survival capabilities when exposed to various treatments and procedures. Since there are more coliforms than pathogens in sewage, their reduction to low numbers would be indicative of the reduction of pathogenic bacteria to proportionately lower numbers. Kerr and Butterfield<sup>42</sup> estimated the relationship between coliform levels in wastewater and the number of typhoid bacilli present as a function of typhoid morbidity in the community. On the basis of their data, one would predict that at the present reported rate of Salmonella per 100,000 persons (approximately 12.0/100,000) in the United States, one would expect about 27.5 Salmonella per one million coliforms found in sewage while the number of S. typhosa would be far less than one per million coliforms.

Recently, Geldreich<sup>43</sup> related the number of fecal coliforms to isolations of Salmonella in surface waters. Salmonella isolations were made using the "swab" technique of Moore.<sup>44</sup> Table II-4 gives these relationships for fresh

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\*TCID is that dilution of virus suspension that produces infection in 50 percent of the tissue cultures inoculated.

water. It can be seen that when greater than 200 fecal coliforms per 100 ml are encountered, there is a marked increase in the isolation rate of Salmonella.

Table II-4

FECAL COLIFORM-SALMONELLA  
RELATIONSHIP IN FRESH WATER  
(From Geldreich)<sup>43</sup>

| FECAL COLIFORM PER 100 ML | TOTAL SAMPLES EXAMINED | PERCENT POSITIVE FOR SALMONELLA |
|---------------------------|------------------------|---------------------------------|
| 1-200                     | 29                     | 27.6                            |
| 201-2000                  | 27                     | 85.2                            |
| >2000                     | 54                     | 98.1                            |

They concluded that this provided good evidence of support for the National Technical Advisory Committee recommendation for bathing water standards of 200 or less fecal coliforms per 100 ml.

It can be said that coliforms are an acceptable indicator of the presence of fecal material that is apt to contain pathogenic bacteria and that present standards for water and wastewater are quite reasonable. As stated previously, their relationship to the presence of enteric viruses is at times questionable, particularly when evaluating disinfection procedures.

Mechalas et al.<sup>45</sup> in a report on recreational water quality integrated dose-response data and probability of contact with disease organisms via water. In this manner they were able to construct a curve relating numbers of organisms per volume of water with risk of contracting disease or infection. Their analysis for Salmonella is shown in Figure 1. In this instance

the dose-response information was gathered from the data of McCullough and Eisele (see Table II-3). Their assumption in making the risk analysis was that a swimmer imbibes 10 ml of water; thus, when relating this curve to drinking water the risk would be increased by one or two orders of magnitude. The relationship between coliform and fecal coliform levels and numbers of Salmonella were taken from the work of McCoy<sup>46</sup> and Strobel.<sup>47</sup> It should be noted that a comparison between these estimates of Salmonella to coliform and the estimate obtained using Kerr and Butterfield's relationship are in excellent agreement.

Extrapolating the curve in Figure II-1 to estimate the risk of drinking a liter of water that contains one coliform per 100 ml (approximate drinking water standard) one finds a risk of one in 10,000,000 of contracting salmonellosis when a liter of water is consumed. This would approximate the risk the public takes when drinking water of acceptable sanitary quality.

These authors (Mechalas et al.) also developed a similar association for virus infection; however, the validity of this relationship is questionable because of the nature of the virus dose-response data. The latter was gleaned from numerous sources of human virus dose-response results that dealt with a variety of viruses whose route of introduction was via the respiratory tract. For informational purposes these results are shown in Figure II-2.

This approach to estimating the relationship between pathogenic microorganisms and their indicator microorganisms should be encouraged and could become the basis for making rational standards relating water quality to human health.

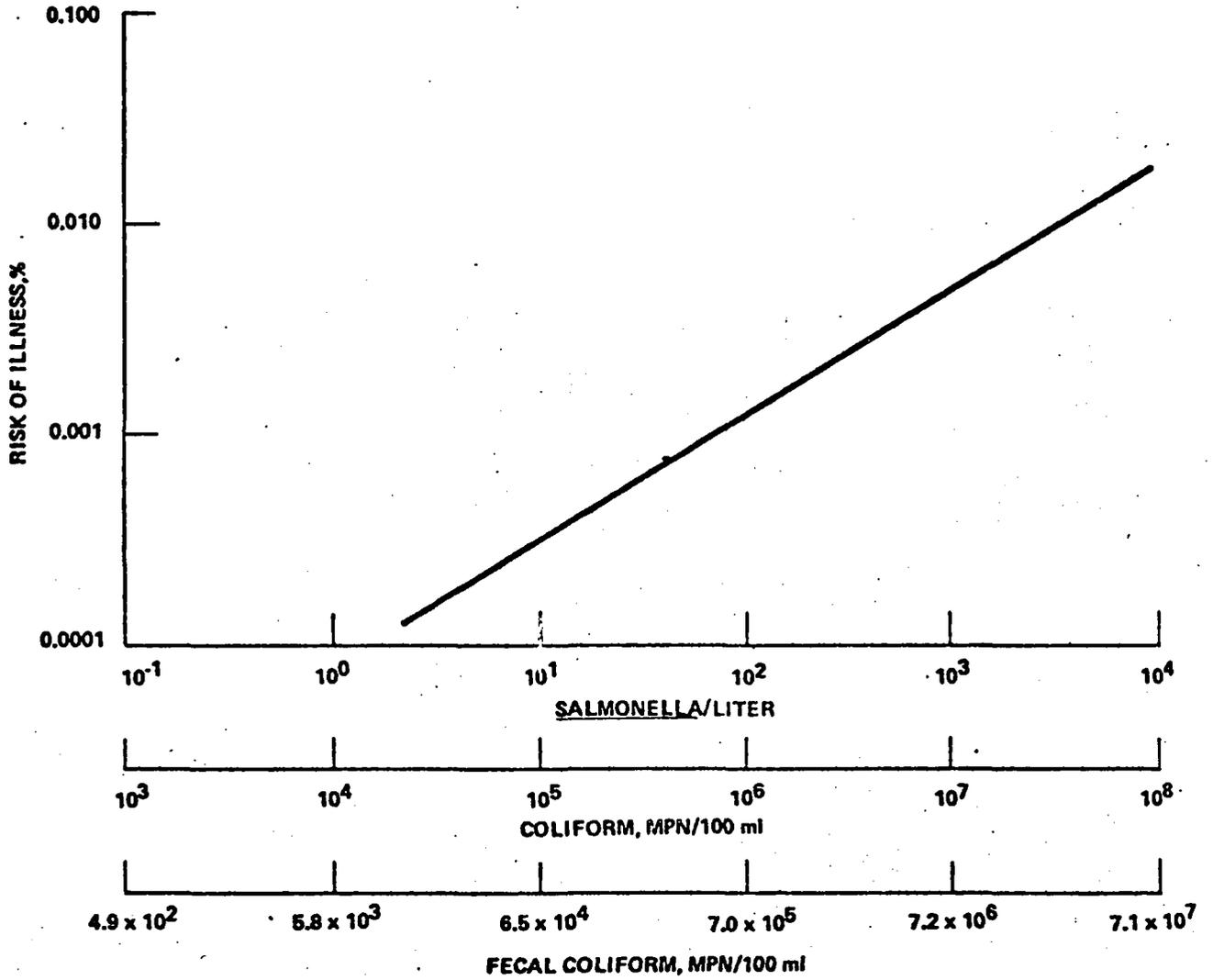


Figure II-1. RELATIONSHIP BETWEEN DISEASE RISK AND SALMONELLA, COLIFORMS, AND FECAL COLIFORMS. (After Mechalas, et al.)<sup>45</sup>

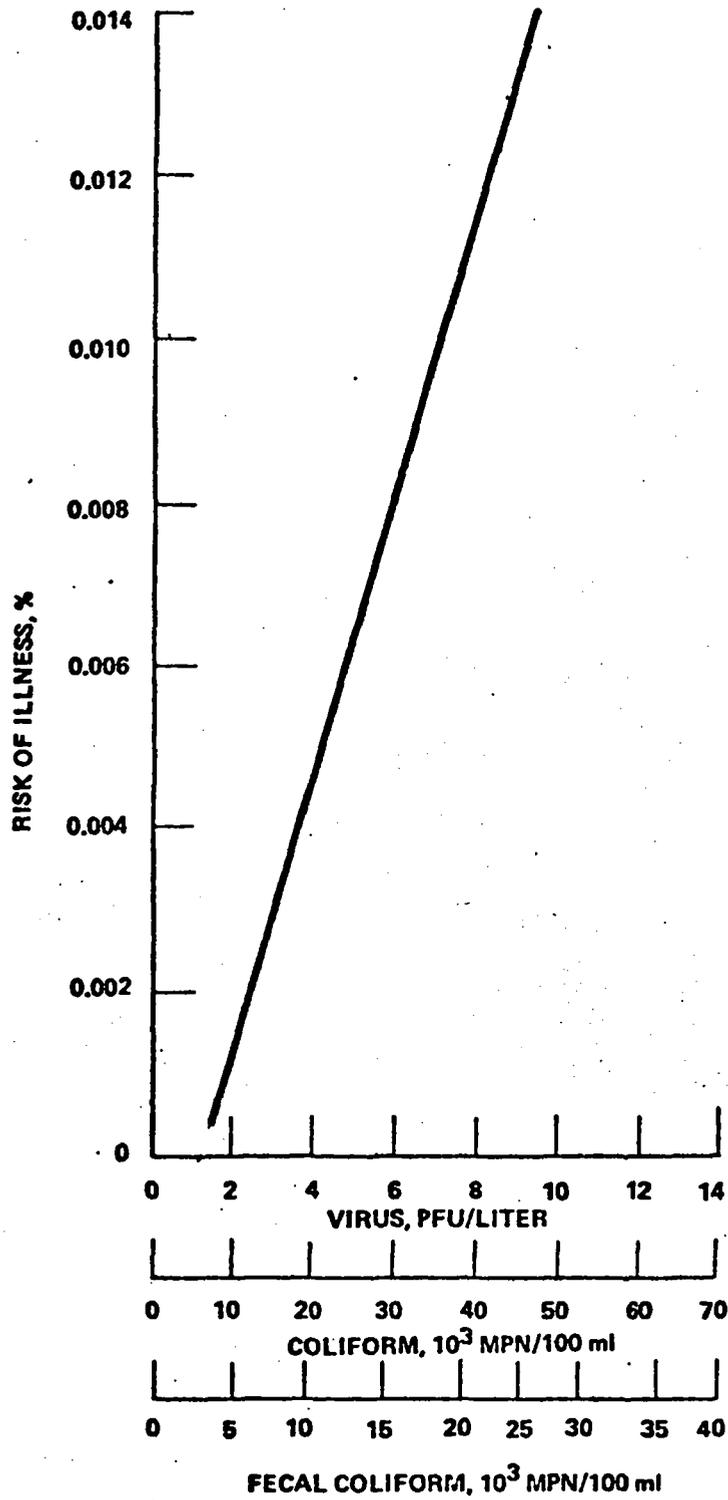


Figure II-2. RELATIONSHIP BETWEEN DISEASE RISK AND VIRUSES, COLIFORMS, AND FECAL COLIFORMS (After Mechelas, et al.)<sup>45</sup>

## CHEMICAL CONTAMINANTS

The chemical agents of health concern which may be present in reclaimed water include heavy metals, pesticides, and a wide variety of organic and inorganic chemicals. Substances may combine to create situations of greater health significance, products of decomposition may present new problems of contamination, and chemical and biological reactions may form more hazardous compounds. A reasonably clear understanding of the acute health significance of heavy metals and the more toxic chemical agents is available. Beyond this rather limited area, the full significance of chemical agents, including the great number of organic compounds which have appeared on the market as a result of technical advances since World War II, is largely uncertain. This is particularly the case with regard to the chronic health effects which may be associated with long-term exposure to low level concentrations of chemical substances.

At the present time, over 500,000 chemical products are in use which may find their way into wastewaters, and toxicological information is available on relatively few. Testing has essentially been directed at the acute and subacute effects of specific agents with the result that ability in this area has been described as "predicting the obvious and missing the unexpected." The episodes with mercury, polychlorinated biphenyls, cyclamates, nitrilotriacetate, diethylstilbestrol, and thalidomide while not all involving the wastewater route have demonstrated the serious and complex nature of the problem posed by chemical agents.

### Classification of Organics

#### Very Gross Classifications

The bulk of the data generated to date regarding the quantities of organic substances in water supply sources or domestic sewage is in

terms of gross parameters - biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and carbon chloroform extract (CCE) or carbon alcohol extract (CAE).

The BOD and COD tests do not lend themselves to the accurate measurement of small amounts of organic matter (i.e., less than 5 mg/l). Many synthetic chemicals are not readily biodegradable by common organisms, which limits the applicability of the BOD test. Also, dissolved oxygen (the measured parameter in the BOD test) will react with certain chemically oxidizable materials such as ferrous iron, sulfide, and sulfites.

The COD test fails to measure all organic compounds, either because of failure to oxidize them (e.g., does not give complete oxidation of saturated hydrocarbons), or because of loss of volatile material before it can be oxidized. In addition, it does not oxidize some common biodegradable compounds such as benzene, toluene, and pyridine, but does oxidize some biologically non-degradable organics such as phenols.

The TOC analysis essentially measures the oxidation of organic compounds to carbon dioxide by pyrolysis. This test is able to accurately determine smaller quantities of organic matter (1-125 mg/l) but has several drawbacks. As with the BOD and COD tests, it is non-specific and subject to interferences. In particular, the sample preparation technique of compensating for carbonates and carbon dioxide by acidification can cause a loss of volatile acids and the coagulation of suspended solids. Also, in many instances the sample may have to be prefiltered in order to prevent syringe clogging problems.

The carbon adsorption method (CCE-CAE) although classified as a gross determination, is more specific than the aforementioned analyses in that it differentiates between organic compounds that are soluble in either chloroform

or ethanol. This test determines the quantities of organic substances that are adsorbed onto activated carbon columns and subsequently extracted with the two solvents, chloroform and alcohol.

Some of the disadvantages of the carbon adsorption method are that waters high in inorganic substances yield CAE fractions having significant inorganic content, the carbon does not adsorb all of the organic matter present in the water (for example, recoveries range from 50-90 percent for known amounts of easily adsorbed materials) and total analysis takes at least 24 hours.

#### Major Groups

Many researchers have attempted to employ more definitive systems to determine the organic make-up of water and wastewater. They have combined standard sampling techniques with wet chemistry methods to characterize the organic materials in these waters.

A common approach has been the use of carbon adsorption columns to remove organic constituents from a water or wastewater. The removal of the adsorbed organics is effectuated by the application of solvent extraction techniques. The solvent most commonly used is chloroform although ethanol, acetone, and benzene are also employed. The extracted organics are subsequently classified according to group using solubility partition methods.<sup>48,49</sup> These groups usually include ether insolubles, water solubles, weak acids, strong acids, bases, and neutrals. The neutrals are further characterized into aliphatic, aromatic, and oxygenated subgroups using chromatographic techniques. The United States Public Health Service<sup>50</sup> utilized this system for a number of years when conducting quality surveys on selected rivers throughout the United States.

Some disadvantages to this method are the previously-mentioned shortcomings with the carbon adsorption sampling technique; namely, carbon does

not adsorb all organic materials, the organics adsorbed are not all effectively desorbed by the solvent employed and the time required for sampling and extraction is rather lengthy.

Somewhat different schemes have been used by other researchers<sup>51,52,53</sup> in the study of organics in wastewater. Grab and composite samples of wastewater are centrifuged to remove suspended solid material and concentrated by low temperature vacuum distillation. The distillate is subjected to a variety of tests that may include extraction with diethyl ether followed by solubility partitioning of the extract, fractionation to humic, fulvic, and humathomelanolic acid groups and analysis of distillate and fractions for groups such as anionic detergents, carbohydrates, tannins, proteins, fats (acids and esters), amino acids, amides, creatinine, amino sugars and muramic acid.

This procedure has the advantage of sampling for a wider spectrum of organic material than the carbon adsorption method. However, there is the potential loss of an unknown quantity of volatile constituents during distillation. There is also the problem that the organics present may not lend themselves to any of the classification groups. This has been the case in much of the work carried out to date.<sup>51,52</sup> This method is also time-consuming and cannot be conducted on a continuous basis.

#### Specific Compounds

The analysis of water and wastewater for organic compounds has recently been enhanced by the application of modern instrumentation and techniques. Although sample preparation still may be lengthy and exclusion of some constituent groups occurs, isolation and identification of individual compounds can be accomplished quite rapidly.

The most promising tool for organic identification is the gas chromatograph/mass spectrometer (GC/MS) couple system which has been used by a number

of researchers<sup>54-66</sup> in recent years. Computer data retrieval methods have also been applied to facilitate compound identification. Supplementing this system are a number of additional analytical methods that may be employed when further information is required for positive determinations. These include high pressure liquid chromatography with ultraviolet detectors, infra-red spectroscopy, and nuclear magnetic resonance.

The major disadvantage to the use of these modern instruments is the high cost involved to acquire such units and the need for highly qualified research personnel to operate them.

### Presence and Sources of Organics

#### Wastewater

The presence of organic materials in raw and treated domestic sewage is highly variable and dependent upon the source of the sewage and the degree of treatment which it receives. In terms of gross parameters, domestic sewage (i.e., wastewater derived from a community that may include residential dwellings, small businesses and associated light industries) generally has the following organic composition: Biochemical Oxygen Demand (BOD) 175 to 225 mg/l, Chemical Oxygen Demand (COD) 325 to 450 mg/l, and Total Organic Carbon (TOC) 100 to 130 mg/l.<sup>67</sup> The organic content of sewage after treatment is considerably less. The application of sedimentation and a biological system (conventional activated sludge) will reduce the BOD to 15-25 mg/l, COD to 40-70 mg/l and TOC to 15-25 mg/l.<sup>67</sup> Additional treatment (advanced waste treatment) such as chemical coagulation, sedimentation, multi-media filtration and carbon adsorption can produce an effluent with a BOD of 0.1-5.0 mg/l,<sup>68</sup> a COD of 3-25 mg/l,<sup>69</sup> and a TOC of 1-6 mg/l.<sup>69</sup>

Although the literature is replete with information on the organic content of raw and treated domestic sewage in the above cited terms, there

have been very few studies conducted to determine the nature and identity of the organic constituents present. Painter et al.<sup>51</sup> attempted to characterize the organic material in raw and treated sewage derived from a small English community of 6,000 people. The authors classified 75 percent of the organic material in the raw sewage, 79 percent in settled sewage and 29 percent in the sewage after aerobic treatment followed by settling. As shown in Table II-5, carbohydrates and fatty acids made up a large part of the organics in the raw and settled sewage while the soluble acids and anionic surface-active agents contributed the greatest amount to the identifiable organics in the treated sewage.

Bunch et al.<sup>52</sup> investigated the nature of the organic materials in secondary treated sewage effluents from five different sources. Table II-6 shows a summary of the constituent groups employed to classify the organics isolated as well as their concentrations. The ether extractables were further characterized according to solubility (Table II-7). Of the total soluble organic material present in the effluents expressed as COD, the authors identified only 35 percent.

Rebhum and Manka<sup>53</sup> examined the effluent from a trickling filter treating 80 percent domestic and 20 percent light industry sewage. They employed a classification scheme similar to Bunch et al.<sup>52</sup> and identified 50 to 60 percent of the total organic composition measured as COD. The remaining 40 to 50 percent of the organic content was classified as humic substances and these were separated into fulvic, humic, and humathomelanolic fractions. The contribution of each constituent group to the total composition of the soluble organics isolated is shown in Table II-8.

Recently, with the assistance of sophisticated analytical instrumentation and techniques, efforts have been made to identify individual stable

Table II-5

COMPOSITION OF STEVENAGE SEWAGE AND OF THE EFFLUENT OBTAINED ON TREATMENT  
IN A PERCOLATING FILTER

| Constituent                   | Sewage<br>(24-hr. composite sample) |                            |       | Effluent |                           |       | Removal<br>(%)                         |   |
|-------------------------------|-------------------------------------|----------------------------|-------|----------|---------------------------|-------|--|---|
|                               | (ppm)                               |                            |       |          |                           |       | by<br>biological<br>filtration<br>only | by<br>biological<br>filtration<br>followed by<br>settlement |
|                               | Whole                               | Settled<br>(BOD = 380 ppm) |       | Whole    | Settled<br>(BOD = 12 ppm) |       |  |   |
|                               |                                     | Soluble                    | Total |          | Soluble                   | Total |  |   |
| Fat - acid                    | 71.0                                | 0                          | 46.1  | 0.12     | 0                         | 0.04  | >99                                    | >99   |
| Fat - ester                   | 28.2                                | 0                          | 23.5  | 0.12     | 0                         | 0.02  | >99                                    | 99  |
| Protein                       | 31.0                                | 8.0                        | 21.5  | 2.99     | 0.25                      | 0.99  | 86                                     | 95  |
| Amino acids                   | 5.0                                 | 5.0                        | 5.0   | 0.06     | 0.06                      | 0.06  | 99                                     | 99  |
| Carbohydrates                 | 55.0                                | 40.0                       | 46.0  | 1.63     | 0.24                      | 0.57  | 96                                     | 99  |
| Soluble acids                 | 21.0                                | 17.0                       | 19.8  | 1.78     | 1.65                      | 1.69  | 91                                     | 91  |
| Amides                        | 1.5                                 | 0                          | 1.0   | --       | --                        | --    | --                                     | --  |
| Anionic surface-active-agents | 14.0                                | 11.0                       | 13.1  | 1.45     | 1.40                      | 1.41  | 89                                     | 89  |
| Creatinine                    | 3.5                                 | 3.5                        | 3.5   | --       | --                        | --    | --                                     | --  |
| Amino sugars                  | 1.8                                 | 0                          | 1.1   | 0.38     | 0                         | 0.07  | 65                                     | 94  |
| Muramic acid                  | 0.2                                 | 0                          | 0.1   | 0.05     | 0                         | 0.01  | 50                                     | 90  |
| Total - by analysis           | 311                                 | 106                        | 228   | 26.9     | 14.0                      | 16.5  | 88                                     | 93  |
| - by addition                 | 232                                 | 85                         | 181   | 8.6      | 3.6                       | 4.9   | --                                     | --  |
| Proportion identified (%)     | 75                                  | 80                         | 79    | 32       | 26                        | 29    | --                                     | --  |

Table II-6  
SUMMARY OF CONSTITUENTS

| CONSTITUENT   | SOURCE OF SAMPLE |          |         |          |                   |                   |                   |
|---|------------------|----------|---------|----------|-------------------|-------------------|-------------------|
|   | Dayton           | Richmond | Chicago | Hamilton | Loveland<br>No. 1 | Loveland<br>No. 2 | Loveland<br>No. 3 |
| Protein* (mg/l)   | 3.9              | 1.6      | 1.7     | 4.8      | 6.9               | 7.4               | 5.8               |
| Carbohydrates (mg/l)  | 2.4              | 2.0      | 1.3     | 1.1      | 2.2               | 1.5               | 0.8               |
| ABS (mg/l)  | 4.2              | 1.5      | 2.6     | 4.6      | 7.5               | 12.5              | 8.3               |
| Ether Extractable Material (mg/l)                             | 3.3              | 0.8      | 1.2     | 3.2      | 5.2               | 4.9               | 3.0               |
| Tannin and Lignin (mg/l)                                      | 0.94             | 0.51     | 0.52    | 0.93     | 0.82              | 1.70              | 1.40              |
| Sum of Constituents (mg/l)                                    | 14.74            | 6.41     | 7.32    | 11.63    | 22.62             | 28.00             | 19.30             |
| Ratio Constituents to Volatiles                               | 0.21             | 0.05     | 0.14    | 0.25     | 0.23              | 0.23              | 0.21              |
| Ratio to Volatiles to COD<br>(corrected for Cl <sup>-</sup> ) | 1.7              | 5.5      | 2.1     | 1.2      | 1.9               | 1.4               | 1.4               |
| Ratio COD (corrected for Cl <sup>-</sup> )<br>to constituents | 2.7              | 4.3      | 3.5     | 3.3      | 2.4               | 3.1               | 3.4               |

\*Non-dialyzable (N x 6.25)

Table II-7  
COMPOSITION OF ETHER EXTRACTABLES OF FINAL EFFLUENTS\*

| ORGANIC<br>CONSTITUENT | SOURCE OF SAMPLE |              |          |              |         |              |          |              |                   |              |                   |              |                   |              |
|------------------------|------------------|--------------|----------|--------------|---------|--------------|----------|--------------|-------------------|--------------|-------------------|--------------|-------------------|--------------|
|                        | Dayton           |              | Richmond |              | Chicago |              | Hamilton |              | Loveland<br>No. 1 |              | Loveland<br>No. 2 |              | Loveland<br>No. 3 |              |
|                        | mg/1             | Per-<br>cent | mg/1     | Per-<br>cent | mg/1    | Per-<br>cent | mg/1     | Per-<br>cent | mg/1              | Per-<br>cent | mg/1              | Per-<br>cent | mg/1              | Per-<br>cent |
| Strong Acids           | 1.79             | 54.9         | 0.54     | 66.3         | 0.79    | 66.4         | 1.93     | 61.3         | 2.29              | 44.3         | 2.70              | 55.6         | 1.55              | 51.3         |
| Weak Acids             | 0.18             | 5.5          | 0.07     | 8.4          | 0.09    | 7.6          | 0.28     | 8.9          | 0.49              | 9.5          | 0.39              | 8.0          | 0.23              | 7.6          |
| Bases                  | 0.08             | 2.5          | 0.01     | 1.2          | 0.04    | 3.3          | 0.07     | 2.2          | 0.09              | 1.7          | 0.18              | 3.7          | 0.06              | 2.0          |
| Amphoterics            | 0.16             | 4.9          | 0.02     | 2.4          | 0.09    | 7.6          | 0.13     | 4.1          | 0.39              | 7.6          | 0.36              | 7.4          | 0.13              | 4.3          |
| Neutrals               | 1.05             | 32.2         | 0.18     | 21.7         | 0.18    | 15.1         | 0.74     | 23.5         | 1.91              | 36.9         | 1.23              | 25.3         | 1.05              | 34.8         |
| TOTAL                  | 3.26             | 100.0        | 0.82     | 100.0        | 1.19    | 100.0        | 3.15     | 100.0        | 5.17              | 100.0        | 4.86              | 100.0        | 3.02              | 100.0        |

\*Based on total ether extractables from 20 liters.

Table II-8  
COMPOSITION OF SOLUBLE ORGANICS IN SECONDARY EFFLUENT AS PERCENT OF TOTAL COD

| CONSTITUENT           | SAMPLE 1 (3/26/69) |          |             | SAMPLE 2 (5/20/69) |          |             | SAMPLE 3 (7/24/69) |          |             |
|-----------------------|--------------------|----------|-------------|--------------------|----------|-------------|--------------------|----------|-------------|
|                       | Total              | Filtrate | Precipitate | Total              | Filtrate | Precipitate | Total              | Filtrate | Precipitate |
|                       | Effluent           |          |             | Effluent           |          |             | Effluent           |          |             |
| Ether Extractable     | 10.6               | 6.4      | 4.2         | 6.6                | 4.2      | 2.4         | 7.8                | 4.7      | 3.1         |
| Anionic Detergents    | 12.8               | 6.6      | 6.2         | 13.3               | 6.2      | 7.1         | 15.6               | 7.7      | 7.9         |
| Carbohydrates         | 10.9               | 8.1      | 2.8         | 12.7               | 8.1      | 4.6         | 11.0               | 8.3      | 2.7         |
| Tannins               | 1.5                | 0.9      | 0.6         | 1.4                | 0.7      | 0.7         | 2.2                | 1.0      | 1.2         |
| Proteins              | 21.0               | 16.9     | 4.1         | 22.0               | 16.8     | 5.2         | 24.1               | 17.3     | 6.8         |
| Fulvic Acid           | 22.5               | 19.2     | 3.3         | 18.8               | 15.4     | 3.4         | 25.8               | 20.4     | 5.4         |
| Humic Acid            | 10.4               | 2.9      | 7.5         | 11.0               | 1.7      | 9.3         | 11.9               | 2.9      | 9.0         |
| Humathomelanolic Acid | 7.4                | 0.9      | 6.5         | 9.5                | 1.0      | 8.5         | 7.5                | 1.3      | 6.2         |
| TOTAL                 | 97.1               | 61.9     | 35.2        | 95.3               | 54.1     | 41.2        | 105.9              | 63.6     | 42.3        |

organic compounds in sewage effluents. Katz et al.<sup>64</sup> examined primary and secondary sewage effluents from a municipal source in Oak Ridge, Tennessee. The authors were able to isolate seventy-seven constituents from the primary effluent. Each constituent was present at less than 100 ug/l. Thirty-eight constituents were obtained from the secondary effluent, with each at less than 20 ug/l. Thirteen compounds were positively identified in the primary effluent. Their identity and the concentrations of four of the compounds are indicated in Table II-9.

Jolley<sup>70</sup> studied the effects of chlorination on organic compounds in the secondary effluents from domestic sewage treatment plants. He found that over 50 chlorine-containing constituents were formed during the chlorination procedure. Seventeen of these were tentatively identified and quantified at the 0.5 to 4.3 micrograms per liter level (Table II-10). In addition, 32 stable organic constituents were identified, 23 in the primary effluents, ranging in concentration from 2 to 190 micrograms per liter, and 9 in the secondary effluents, ranging in concentration from 5 to 90 micrograms per liter.

Manka et al.<sup>65</sup> expanded their earlier study on secondary effluents to include identification of individual organic compounds. The authors examined the secondary effluents from two municipal treatment plants (trickling filter and stabilization pond) and an activated sludge plant receiving sewage from a residential area. They employed the same classification as previously documented to characterize the organic content of each effluent (Tables II-11, II-12, II-13, and II-14). The ether extractables were further examined and a number of compounds were identified (Table II-15).

Bellar and Lichtenberg<sup>66</sup> analyzed the effluent from a sewage treatment plant serving a municipal source with domestic and industrial wastewater. Seven compounds were identified and their concentrations determined (Table II-16).

Table II-9

COMPOUNDS IDENTIFIED IN PRIMARY SEWAGE EFFLUENT:  
 SAMPLE SEPARATED ON PREPARATIVE-SIZE ANION EXCHANGE SYSTEM

| COMPOUND  | CONCENTRATION (ug/l) |
|---|----------------------|
| Uracil  | 13                   |
| 5-Acetylamino-6-amino-3-methyluracil            | 30                   |
| N <sup>1</sup> -Methyl-2-pyridone-5-carboxamide | 10                   |
| Thymidine (tentative)                           |                      |
| Theobromine                                     |                      |
| 7-Methylxanthine                                |                      |
| 1,7-Dimethylxanthine                            |                      |
| 3-Methylxanthine                                |                      |
| 1-Methylxanthine                                | 17                   |
| Urocanic acid                                   |                      |
| 4-Hdroxyphenylacetic acid                       |                      |
| Caffeine  |                      |

Table II-10

CHLORO-ORGANIC COMPOUNDS FORMED DURING  
 CHLORINATION OF SECONDARY SEWAGE EFFLUENTS

| COMPOUND                       | CONCENTRATION<br>ug/l | COMPOUND                  | CONCENTRATION<br>ug/l |
|--------------------------------|-----------------------|---------------------------|-----------------------|
| 2-Chlorobenzoic acid           | 0.26                  | 2-Chlorophenol            | 1.70                  |
| 3-Chlorobenzoic acid           | 0.62                  | 3-Chlorophenol            | 0.51                  |
| 4-Chlorobenzoic acid           | 1.10                  | 4-Chlorophenol            | 0.69                  |
| 8-Chlorocaffeine               | 1.70                  | 4-Chlorophenylacetic acid | 0.38                  |
| 6-Chloroguanine                | 0.90                  | 4-Chloroesorcinol         | 1.20                  |
| 3-Chloro-4-Hydroxybenzoic acid | 1.30                  | 5-Chlorosalicylic acid    | 0.24                  |
| 4-Chloromandelic acid          | 1.10                  | 5-Chlorouracil            | 4.30                  |
| 4-Chloro-3-Methylphenol        | 1.50                  | 5-Chlorouridine           | 1.70                  |
|                                |                       | 8-Chloroxanthine          | 1.50                  |

Table II-11

COMPOSITION OF SOLUBLE ORGANICS IN SECONDARY EFFLUENTS  
AS PERCENT OF TOTAL COD

| SAMPLES OF SEC.<br>EFFLUENT AND ITS<br>COD AS MG O/L | CONSTITUENT, PERCENT |                    |                       |                           |                            |                |               |                             | Total |
|--|----------------------|--------------------|-----------------------|---------------------------|----------------------------|----------------|---------------|-----------------------------|-------|
|  | Proteins             | Carbo-<br>hydrates | Anionic<br>Detergents | Tannins<br>and<br>Lignins | Ether<br>Extract-<br>ables | Fulvic<br>Acid | Humic<br>Acid | Hymatho-<br>melanic<br>Acid |       |
| TF COD = 160   | 18.9                 | 7.1                | 19.6                  | 1.1                       | 13.4                       | 20.8           | 13.5          | 7.1                         | 101.5 |
| TF COD = 180.5                                       | 21.4                 | 5.4                | 14.1                  | 1.6                       | 15.6                       | 30.2           | 9.7           | 6.8                         | 104.8 |
| TF COD = 148.3                                       | 21.6                 | 6.7                | 13.3                  | 1.4                       | 10.8                       | 27.5           | 12.9          | 7.8                         | 99.9  |
| TF COD = 158.1                                       | 24.3                 | 6.0                | 15.6                  | 1.2                       | 15.6                       | 23.5           | 10.9          | 6.4                         | 102.9 |
| TF COD = 172.1                                       | 21.7                 | 4.2                | 20.5                  | 1.4                       | 11.7                       | 25.2           | 15.7          | 10.3                        | 107.3 |
| SP COD = 120.4                                       | 21.4                 | 8.0                | 11.2                  | 2.4                       | 10.3                       | 27.9           | 14.3          | 6.2                         | 101.7 |
| SP COD = 153.2                                       | 20.8                 | 7.5                | 13.1                  | 1.8                       | 13.2                       | 25.3           | 15.1          | 7.2                         | 107.0 |
| AS COD = 105.5                                       | 21.0                 | 5.1                | 15.6                  | 1.3                       | 16.5                       | 16.8           | 9.6           | 4.8                         | 90.7  |
| AS COD = 135.7                                       | 23.4                 | 5.1                | 15.3                  | 0.8                       | 16.7                       | 29.6           | 4.3           | 5.8                         | 101.0 |
| AS COD = 112.7                                       | 24.8                 | 4.6                | 15.9                  | 1.0                       | 19.9                       | 24.0           | 7.0           | 6.6                         | 103.8 |
| AS COD = 167.4                                       | 23.0                 | 3.6                | 17.2                  | 0.9                       | 12.2                       | 25.6           | 3.6           | 1.9                         | 98.0  |

Note: TF, trickling filter; SP, stabilization pond; AS, extended aeration activated sludge.

Table II-12  
 DISTRIBUTION OF ORGANIC GROUPINGS IN  
 SECONDARY EFFLUENTS--MEAN VALUES

| ORGANIC GROUPINGS<br>AND FRACTIONS | PERCENT OF TOTAL COD   |   |  |
|------------------------------------|--|---|--|
|                                    | Municipal<br>Wastewater;<br>High Rate<br>Trickling<br>Filter | Municipal<br>Wastewater;<br>Stabilization<br>Pond | Domestic<br>Wastewater;<br>Extended<br>Aeration<br>Activated<br>Sludge |
| Proteins                           | 21.6   | 21.1  | 23.1   |
| Carbohydrates                      | 5.9  | 7.8   | 4.6  |
| Tannins and Lignins                | 1.3  | 2.1   | 1.0  |
| Anionic Detergents                 | 16.6   | 12.2  | 16.0   |
| Ether Extractables                 | 13.4   | 11.9  | 16.3   |
| Fulvic Acid                        | 25.4   | 26.6  | 24.0   |
| Humic Acid                         | 12.5   | 14.7  | 6.1  |
| Hymathomelanic Acid                | 7.7  | 6.7   | 4.8  |

Table II-13

ACIDIC GROUPS OF HUMIC COMPOUNDS PRESENT  
IN SECONDARY EFFLUENTS

| HUMIC COMPOUND      | ACIDITY IN MEQ/G |          |                   |
|---------------------|------------------|----------|-------------------|
|                     | Total Acidity    | Carboxyl | Phenolic Hydroxyl |
| Fulvic Acid         | 12.3             | 9.2      | 3.1               |
| Humic Acid          | 8.3              | 8.3      | -                 |
| Hymathomelanic Acid | 8.7              | 8.7      | -                 |

Table II-14

MOLECULAR WEIGHT DISTRIBUTION OF HUMIC  
SUBSTANCES FROM SECONDARY EFFLUENTS

| MOLECULAR WEIGHT RANGE | PERCENT OF HUMIC COMPOUND PRESENT |            |                     |
|------------------------|-----------------------------------|------------|---------------------|
|                        | Fulvic Acid                       | Humic Acid | Hymathomelanic Acid |
| < 500                  | 27.5                              | 17.9       | 4.5                 |
| 500- 1,000             | 7.8                               | 6.2        | 12.2                |
| 1,000- 5,000           | 35.7                              | 29.4       | 48.0                |
| 5,000-10,000           | 15.3                              | 7.8        | 28.0                |
| 10,000-50,000          | 9.4                               | 36.7       | 7.5                 |
| > 50,000               | 4.3                               | 2.0        | 0                   |

Table II-15

## CHARACTERIZATION OF THE ETHER EXTRACTABLES

| FATTY ACIDS  | HYDROCARBONS   |
|--|--|
| Nonanoic Acid<br>$\text{CH}_3(\text{CH}_2)_7\text{COOH}$         | <b>n-Alkanes</b><br>$\text{C}_{17}\text{H}_{36} - \text{C}_{35}\text{H}_{72}$ (19 compounds) |
| Decanoic Acid<br>$\text{CH}_3(\text{CH}_2)_8\text{COOH}$         | Alkyl Benzenes<br>Isopropyl Benzene<br>Dodecyl Benzene                                       |
| Undecanoic Acid<br>$\text{CH}_3(\text{CH}_2)_9\text{COOH}$       | Higher Aromatics<br>Naphthalene  |
| Dodecanoic Acid<br>$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$    | Methylnaphthalene<br>Diphenyl<br>Diphenylmethane   |
| Tetradecanoic Acid<br>$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$ | Diethylphthalate<br>Phenol<br>Triethylphosphate  |
| Pentadecanoic Acid<br>$\text{CH}_3(\text{CH}_2)_{13}\text{COOH}$ |  |
| Palmitic Acid<br>$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$      |  |
| Stearic Acid<br>$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$       |  |

Table II-16

ORGANIC COMPOUNDS IDENTIFIED IN  
SEWAGE TREATMENT PLANT EFFLUENT

| COMPOUND                    | CONC.<br>ug/l |
|-----------------------------|---------------|
| Methylene Chloride          | 3.5           |
| Chloroform                  | 12.1          |
| 1,1,1-Trichloroethane       | 8.5           |
| 1,1,2-Trichloroethylene     | 9.8           |
| 1,1,2,2-Tetrachloroethylene | 4.2           |
| Dichlorobenzenes            | 6.3           |
| Trichlorobenzenes           | 56.9          |

### Surface Waters

Investigations on the presence of organics in surface waters and drinking water derived from surface sources have multiplied in recent years. A major reason for this increase has been the growing concern over the introduction of a large number of potentially toxic industrial and agricultural chemicals into water sources used for domestic purposes.

There is considerable data in terms of gross parameters and constituent groups (BOD, COD, TOC, CCE, solubility partitioning) on selected surface waters throughout the United States.<sup>71-75</sup> The information presented in Tables II-17 - II-23 and Figures II-3 - II-7 include surface waters of different quality as well as partially and completely treated drinking water from a variety of sources.

As in the examination of wastewater, efforts are being made to identify specific organic compounds through the application of modern analytical instrumentation and methodology.

Hites and Biemann<sup>55</sup> conducted studies on the Charles River Basin (Boston) to determine the presence of lipophilic organic compounds. The authors identified a large number (Table II-24) of aliphatic and aromatic compounds in the river. They concluded that the data suggest a multiplicity of sources ranging from indigenous biological materials to automobile exhaust condensate.

Gordon and Goodley<sup>54</sup> examined water and mud samples from the Lower Tennessee River for organic chemicals. Thirty-six organic compounds were identified (Table II-25) and an additional one hundred and fifty were partially characterized. The authors surmised that these materials were from industrial sources.

Table II-17

SOLUBILITY PARTITION OF  
ORGANIC REFRACTORIES FROM MISSOURI RIVER WATER

| SOLVENT<br>SEQUENCE                               | ETHER      | WATER    |        | AMPHO- | STRONG | WEAK  |          |
|---|------------|----------|--------|--------|--------|-------|----------|
|   | INSOLUBLES | SOLUBLES | AMINES | TERICS | ACIDS  | ACIDS | NEUTRALS |
| Percentage of Total Extract                       |            |          |        |        |        |       |          |
| Monitor Adsorption Unit Extracts                  |            |          |        |        |        |       |          |
| Chloroform  | 7.9        | 18.9     | 2.0    | 6.7    | 12.7   | 10.5  | 37.5     |
| Ethanol   | 99.0       | none     | none   | none   | none   | none  | none     |
| Benzene   | 51.8       | 29.0     | none   | none   | 1.3    | 7.2   | 10.0     |
| Basic Adsorption Unit Extracts                    |            |          |        |        |        |       |          |
| Chloroform  | 9.5        | 19.5     | 1.0    | 2.8    | 11.5   | 12.8  | 34.3     |
| Ethanol   | 99.0       | none     | none   | none   | none   | none  | none     |
| Acetone-1*  | 44.2       | 12.8     | none   | 4.4    | 12.4   | 1.5   | 14.8     |
| Benzene-2*  | 17.6       | 12.8     | none   | 12.0   | none   | 13.0  | 34.6     |
| Benzene-1   | 41.8       | 16.7     | none   | 3.4    | 12.8   | 7.0   | 10.4     |
| Acetone-2   | 92.8       | 0.5      | none   | 1.0    | 1.1    | none  | none     |
| Acidic Adsorption Unit Extracts                   |            |          |        |        |        |       |          |
| Chloroform  | 26.5       | 23.2     | 2.5    | 7.6    | 13.2   | 7.6   | 23.4     |
| Ethanol   | 100.0      | none     | none   | none   | none   | none  | none     |
| Acetone-1   | 68.0       | 12.5     | none   | 6.4    | 5.0    | 3.3   | 1.3      |
| Benzene-2   | 93.3       | none     | none   | none   | none   | 2.1   | 3.4      |
| Benzene-1   | 65.8       | 17.5     | none   | 2.6    | 5.1    | 2.2   | 1.9      |
| Acetone-2   | 62.7       | 9.7      | none   | 8.5    | 3.6    | 5.8   | 2.2      |
| Particulate Matter Extracts--Settleable Materials |            |          |        |        |        |       |          |
| Chloroform  | 13.5       | 1.8      | none   | none   | none   | 15.6  | 65.6     |
| Ethanol   | 27.6       | 4.5      | none   | none   | 10.0   | 36.3  | 10.6     |
| Particulate Matter Extracts--Backwash Materials   |            |          |        |        |        |       |          |
| Chloroform  | 11.5       | 2.3      | none   | none   | none   | 20.3  | 65.0     |
| Ethanol   | 25.2       | 4.8      | none   | none   | 9.8    | 37.5  | 13.2     |

\*Number 1 or 2 following acetone or benzene refers to the extraction sequence of these solvents following chloroform and ethanol.

Table II-18  
 CONCENTRATION AND COD VALUES OF  
 ORGANIC REFRACTORIES

| SOLVENT SEQUENCE                 | CONCENTRATION<br>ug/l | COD/MG<br>OF EXTRACT<br>mg |                         |             |
|----------------------------------|-----------------------|----------------------------|-------------------------|-------------|
| Monitor Adsorption Unit Extracts |                       |                            |                         |             |
| Chloroform                       | 58.3                  | 2.28                       |                         |             |
| Ethanol                          | 100.6                 | 1.35                       |                         |             |
| Benzene                          | 23.7                  | 1.53                       |                         |             |
| Basic Adsorption Unit Extracts   |                       |                            |                         |             |
| Chloroform                       | 81.2                  | 2.31                       |                         |             |
| Ethanol                          | 317.0                 | 1.14                       |                         |             |
| Acetone-1*                       | 105.0                 | 1.73                       |                         |             |
| Benzene-2                        | 84.0                  | 1.79                       |                         |             |
| Benzene-1                        | 184.0                 | 1.57                       |                         |             |
| Acetone-2                        | 35.0                  | 1.27                       |                         |             |
| Acidic Adsorption Unit Extracts  |                       |                            |                         |             |
| Chloroform                       | 67.5                  | 1.52                       |                         |             |
| Ethanol                          | 552.0                 | 1.10                       |                         |             |
| Acetone-1                        | 113.7                 | 1.56                       |                         |             |
| Benzene-2                        | 45.1                  | 1.25                       |                         |             |
| Benzene-1                        | 60.2                  | 1.55                       |                         |             |
| Acetone-2                        | 67.3                  | 1.53                       |                         |             |
| Particulate Matter Extracts      |                       |                            |                         |             |
|                                  | Backwash<br>Materials |                            | Settleable<br>Materials |             |
|                                  | Extract**<br>mg/g***  | COD<br>mg/l                | Extract**<br>mg/g***    | COD<br>mg/l |
| Chloroform                       | 0.42                  | 2.98                       | 0.31                    | 3.04        |
| Ethanol                          | 0.76                  | 1.81                       | 0.56                    | 1.83        |

\*Number 1 or 2 following acetone or benzene refers to the extraction sequence of these solvents following chloroform and ethanol.

\*\*Based on the quantity of particulate matter removed by the sedimentation and diatomite filtration processes.

\*\*\*Milligrams of extract per gram of particulate matter.

Table II-19

COLUMN CHROMATOGRAPHIC SEPARATION OF  
NEUTRAL ORGANIC REFRACTORIES

| SOLVENT<br>SEQUENCE                      | ALIPHATIC                      | AROMATIC | OXYGENATED |
|--|--------------------------------|----------|------------|
|  | Percentage of Neutral Fraction |          |            |
| Monitor Adsorption Unit                  |                                |          |            |
| Chloroform                               | 3.8                            | 6.7      | 86.3       |
| Benzene                                  | 2.3                            | 69.2     | 23.8       |
| Basic Adsorption Unit                    |                                |          |            |
| Chloroform                               | 3.2                            | 7.2      | 87.8       |
| Benzene-1*                               | 2.6                            | 66.8     | 27.5       |
| Benzene-2*                               | 1.8                            | 83.5     | 9.6        |
| Acetone-1                                | 3.6                            | 37.8     | 52.3       |
| Acidic Adsorption Unit                   |                                |          |            |
| Chloroform                               | 4.6                            | 56.3     | 33.4       |
| Particulate Matter--Settleable Materials |                                |          |            |
| Chloroform                               | none                           | 1.5      | 96.7       |
| Particulate Matter--Backwash Materials   |                                |          |            |
| Chloroform                               | none                           | 1.3      | 95.8       |

\*Number 1 or 2 following acetone or benzene refers to the extraction sequence of these solvents following chloroform and ethanol.

Table II-20

## ORGANICS - CARBON ADSORBABLE DETERMINATION ON VARIOUS WATERS

| LOCATION             | SOURCE               | DESCRIPTION OF WATER                 | SEASON | CCE-m |          |              | CAE-m |          |              |
|----------------------|----------------------|--------------------------------------|--------|-------|----------|--------------|-------|----------|--------------|
|                      |                      |                                      |        | n     | Avg mg/l | Min-Max mg/l | n     | Avg mg/l | Min-Max mg/l |
| Ohio                 | Well                 | Finished, after softening            | Winter | 2     | 0.1      | 0.1-0.1      | 2     | 0.4      | 0.3-0.4      |
| Ohio                 | Spring               | Stored in small open reservoir       | Autumn | 3     | 0.1      | 0.1-0.2      | 3     | 0.6      | 0.6-0.6      |
| Michigan             | Lake St. Clair       | Settled                              | Autumn | 10    | 0.3      | 0.2-0.4      | 10    | 1.2      | 0.8-1.6      |
| Michigan             | Lake St. Clair       | Settled                              | Winter | 3     | 0.3      | 0.3-0.3      | 2     | 1.5      | 1.5-1.5      |
| Ohio                 | Great Miami River    | Finished, Act. Carbon beds exhausted | Summer | 9     | 0.4      | 0.3-0.4      | 9     | 1.7      | 1.6-1.9      |
| Ohio                 | Great Miami River    | Finished, Act. Carbon beds exhausted | Autumn | 2     | 0.6      | 0.5-0.6      | 2     | 1.6      | 1.1-2.1      |
| Ohio                 | Ohio River           | Tap                                  | Autumn | 13    | 0.4      | 0.3-0.5      | 13    | 1.2      | 0.9-1.5      |
| Ohio                 | Ohio River           | Tap                                  | Winter | 8     | 0.5      | 0.4-0.5      | 8     | 1.8      | 1.4-2.0      |
| Massachusetts        | Merrimack River      | Finished, Act. Carbon beds exhausted | Summer | 5     | 0.8      | 0.8-0.9      | 5     | 2.8      | 2.3-3.5      |
| Massachusetts        | Merrimack River      | Finished, Act. Carbon beds exhausted | Autumn | 4     | 0.9      | 0.7-1.0      | 5     | 2.5      | 2.2-2.6      |
| Massachusetts        | Merrimack River      | Settled                              | Winter | 9     | 1.2      | 0.8-3.1      | 9     | 5.0      | 4.0-7.4      |
| West Virginia        | Kanawha River        | Settled                              | Spring | 3     | 0.5      | 0.5-0.5      | 2     | 4.5      | 4.1-4.9      |
| Pennsylvania         | Schuylkill River     | Finished                             | Winter | 1     | 0.7      | -            | 1     | 2.3      | -            |
| Pennsylvania         | Delaware River       | Finished                             | Winter | 1     | 0.5      | -            | 1     | 1.2      | -            |
| Maryland             | Liberty Reservoir    | Finished                             | Winter | 1     | 0.4      | -            | 1     | 1.2      | -            |
| Maryland             | Loch Raven Reservoir | Finished                             | Winter | 1     | 0.4      | -            | 1     | 2.6      | -            |
| District of Columbia | Potomac River        | Finished                             | Winter | 1     | 0.3      | -            | 1     | 1.5      | -            |
| Pennsylvania         | Allegheny River      | Finished                             | Winter | 1     | 0.3      | -            | 1     | 1.9      | -            |
| New Jersey           | Oradell Reservoir    | Finished                             | Spring | 1     | 0.7      | -            | 1     | 2.0      | -            |
| Minnesota            | Lake Superior        | Raw                                  | Summer | 2     | 0.2      | 0.2-0.2      | 2     | 0.8      | 0.7-0.8      |

Table II-21

SUPPLEMENTARY MINI-SAMPLER DATA TO THE EIGHTY  
SAMPLES LISTED IN TABLE 20

| LOCATION                   | SOURCE            | DESCRIPTION<br>OF WATER | SEASON | n  | AVERAGE       |               |
|----------------------------|-------------------|-------------------------|--------|----|---------------|---------------|
|                            |                   |                         |        |    | CCE-m<br>mg/l | CAE-m<br>mg/l |
| Lawrence, Massachusetts    |                   |                         |        |    |               |               |
| Lawrence                   | Merrimack River   | Settled                 | Spring | 12 | 0.6           | 3.8           |
| Lawrence                   | Merrimack River   | Settled                 | Summer | 4  | 0.7           | 5.0           |
| Connecticut State Survey   |                   |                         |        |    |               |               |
| Mystic                     | Dean's Mill Res.  | Finished                | Summer | 1  | 0.4           | 2.0           |
| Waterbury                  | Wigwam Res.       | Finished                | Summer | 1  | 0.4           | 1.8           |
| Waterbury                  | Morris Res.       | Finished                | Summer | 1  | 0.4           | 1.3           |
| New London                 | Lake Kanomoc      | Finished                | Summer | 1  | 0.6           | 1.0           |
| Groton                     | Poquonnoc Res.    | Finished                | Summer | 1  | 0.4           | 1.3           |
| Putnam                     | Little River      | Finished                | Summer | 1  | 0.4           | 1.2           |
| Rockville                  | Shinipsie Lake    | Finished                | Summer | 1  | 0.4           | 1.3           |
| Stafford                   | Surface           | Finished                | Summer | 1  | 0.5           | 1.2           |
| Winsted                    | Crystal Lake Res. | Finished                | Summer | 1  | 0.4           | 1.3           |
| Danbury                    | West Lake Res.    | Finished                | Summer | 1  | 0.6           | 2.0           |
| Danbury                    | Margery Res.      | Finished                | Fall   | 1  | 0.6           | 2.0           |
| ICWS Samples               |                   |                         |        |    |               |               |
| Richmond, Va.              | James River       | Finished                | Summer | 1  | 0.3           | 1.1           |
| Hartford, Ill.             | Ground Water      | Finished                | Summer | 1  | 0.4           | 1.4           |
| Peoria, Ill.               | Illinois River    | Finished                | Summer | 1  | 0.5           | 1.8           |
| Empire, La.                | Mississippi River | Finished                | Summer | 1  | 0.4           | 1.3           |
| Boothville-<br>Venice, La. | Mississippi River | Finished                | Summer | 1  | 0.6           | 2.2           |
| Birmingham, Ala.           | Cahaba River      | Finished                | Summer | 1  | 0.4           | 1.4           |
| Birmingham, Ala.           | Smith Res.        | Finished                | Summer | 1  | 0.3           | 0.7           |
| Birmingham, Ala.           | Inland Lake       | Finished                | Summer | 1  | 0.4           | 0.7           |
| Kansas City, Mo.           | Missouri River    | Finished                | Summer | 1  | 0.3           | 1.0           |
| Aztec, N.M.                | Animas River      | Finished                | Summer | 1  | 0.4           | 1.4           |
| Raton, N.M.                | Sugarite Creek    | Finished                | Fall   | 1  | 0.7           | 2.8           |
| Wichita, Kan.              | Ground Water      | Finished                | Fall   | 1  | 0.1           | 0.3           |

Table II-22

## Organic Analyses

## American and Sacramento River Water

| Station Number                        |     | 20   | 20   | 19   | <u>Sacto. R. @ Water Treatment Plant</u> |       |      |      |
|---------------------------------------|-----|------|------|------|--|-------|------|------|
| Date                                  |     | 9/62 | 8/63 | 9/64 | 9/62                                     | 12/62 | 5/62 | 4/63 |
| Total Extract                         | ppb | 209  | 353  | 281  | 236                                      | 192   | 189  | 111  |
| Chloroform                            | ppb | 109  | 95   | 105  | 82                                       | 67    | 60   | 42   |
| Extractables                          | %   | 52.1 | 27.0 | 37.6 | 34.7                                     | 34.7  | 31.8 | 37.5 |
| Alcohol                               | ppb | 100  | 258  | 176  | 154                                      | 125   | 129  | 69   |
| Extractables                          | %   | 47.9 | 73.0 | 62.4 | 65.3                                     | 65.3  | 68.2 | 62.5 |
| Breakdown of Chloroform Extractables: |     |      |      |      |  |       |      |      |
| Ether Soluble                         | ppb | 4    | 6    | 5    | 7  | 4     | 6    | 2    |
|                                       | %   | 3.6  | 6.1  | 5.0  | 8.6                                      | 6.4   | 10.3 | 5.6  |
| Water Soluble                         | ppb | 38   | 37   | 37   | 26                                       | 20    | 17   | 13   |
|                                       | %   | 34.5 | 38.6 | 35.6 | 32                                       | 29.6  | 27.6 | 31.7 |
| Amines                                | ppb | 1    | 1    | 2    | 1  | 1     | 1    | 1    |
|                                       | %   | 0.9  | 0.9  | 1.5  | 1.4                                      | 1.6   | 1.5  | 1.9  |
| Strong Acids                          | ppb | 11   | 7    | 11   | 8  | 6     | 5    | 3    |
|                                       | %   | 9.7  | 7.8  | 10.2 | 9.8                                      | 8.8   | 8.6  | 7.3  |
| Weak Acids                            | ppb | 8    | 9    | 9    | 8  | 7     | 6    | 4    |
|                                       | %   | 7.1  | 9.6  | 8.3  | 9.6                                      | 10.3  | 9.5  | 9.3  |
| Neutrals (see Breakdown)              | ppb | 16   | 17   | 26   | 16.1                                     | 17    | 11   | 9    |
|                                       | %   | 15.0 | 17.4 | 25.2 | 19.4                                     | 25.4  | 19.0 | 22.2 |
| Total                                 | ppb | 78   | 77   | 90   | 66                                       | 55    | 46   | 32   |
|                                       | %   | 70.8 | 80.4 | 85.8 | 80.8                                     | 82.1  | 76.5 | 78.0 |
| Loss                                  | ppb | 31   | 18   | 15   | 16                                       | 12    | 14   | 10   |
|                                       | %   | 29.2 | 19.6 | 14.2 | 19.2                                     | 17.9  | 23.5 | 22.0 |
| Breakdown of Neutrals                 |     |      |      |      |  |       |      |      |
| Aliphatics                            | ppb | 1    | 1    | 3    | 1  | 1     | 1    | 1    |
|                                       | %   | 3.2  | 4.0  | 10.8 | 8.4                                      | 5.7   | 6.8  | 7.7  |
| Aromatics                             | ppb | 1    | 0    | 0    | 1  | 1     | 0    | 0    |
|                                       | %   | 3.2  | 2.7  | 1.7  | 6.0                                      | 3.3   | 3.4  | 4.8  |
| Oxygenates                            | ppb | 13   | 15   | 20   | 12                                       | 12    | 9    | 8    |
|                                       | %   | 82.1 | 92.0 | 77.5 | 76.0                                     | 71.4  | 79.5 | 81.7 |
| Total                                 | ppb | 15   | 16   | 23   | 14                                       | 14    | 10   | 9    |
|                                       | %   | 88.5 | 98.7 | 90   | 90.4                                     | 80.4  | 89.7 | 94.2 |
| Loss                                  | ppb | 1    | 1    | 3    | 2  | 3     | 1    | 0    |
|                                       | %   | 11.5 | 1.3  | 10   | 9.6                                      | 19.6  | 10.3 | 5.8  |

River flows for the sampling periods were as follows:

| American River | Flow (cfs) | Sacramento River | Flow (cfs) |
|----------------|------------|------------------|------------|
| 9/62           | 2,654      | 9/62             | 12,110     |
| 8/63           | 3,530      | 12/62            | 15,690     |
| 9/64           | 3,383      | 4/63             | 61,630     |

Table II-23

GROUPS OF ORGANIC COMPOUNDS IN  
RHINE RIVER WATER

| GROUP             | PERCENTAGE PRESENT |
|-------------------|--------------------|
| Lignin Sulfonates | 20-25              |
| Sulfonic Acids    | 5-15               |
| Humic Acids       | 25-30              |
| Chloro-Organics   | 10                 |

Table II-24

ORGANIC COMPOUNDS FOUND IN THE  
CHARLES RIVER BASIN

| COMPOUNDS                           |                            |
|-------------------------------------|----------------------------|
| Alkanes $C_{15} - C_{31}$           | Pyrene                     |
| Naphthalene                         | Fluoranthene               |
| Alkyl Naphthalenes $C_1N - C_4N$    | Dibutyl Phthalate          |
| Anthracene or Phenanthracene<br>and | Di(2-ethylhexyl) Phthalate |
| Alkyl Derivatives $C_1AP - C_2AP$   |                            |

ORGANIC CONTENT OF SELECTED CALIFORNIA SURFACE WATERS

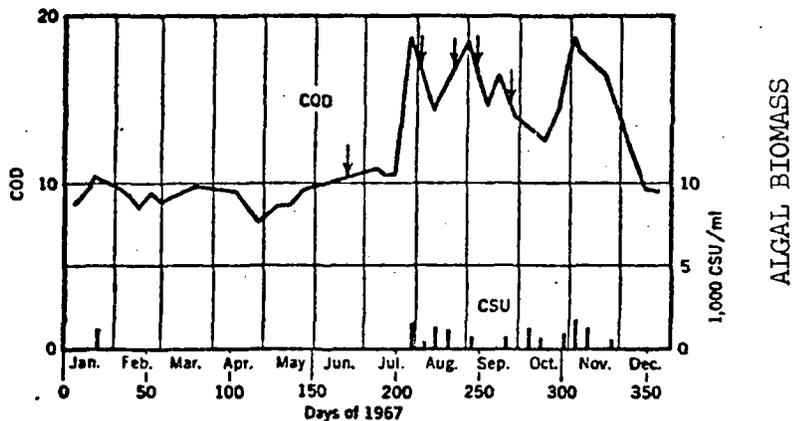


Fig. II-3. COD Values Obtained on Briones Reservoir

Values less than 250/ml are not plotted; vertical arrows indicate treatment with cooper sulfate. COD values were obtained on samples taken at a depth of 5 feet.

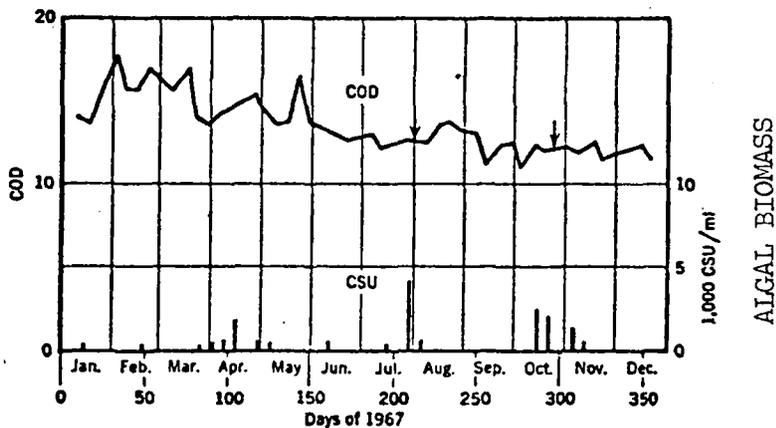


Fig. II-4. COD Values for Chabot Reservoir

Values less than 250/ml are not plotted; vertical arrows indicate treatment with cooper sulfate. COD values were obtained on samples taken at a depth of 5 feet.

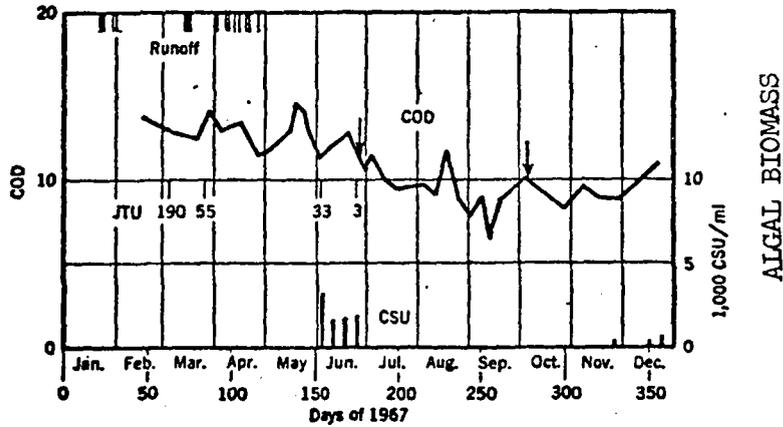


Fig. II-6. COD Values of San Pablo

Values less than 250/ml are not plotted. COD values were obtained on samples taken at a depth of 5 feet, and runoff of at least 50 mgd is indicated by vertical lines, as are selected turbidity values in Jackson Turbidity Units. Vertical arrows indicate treatment with copper sulfate.

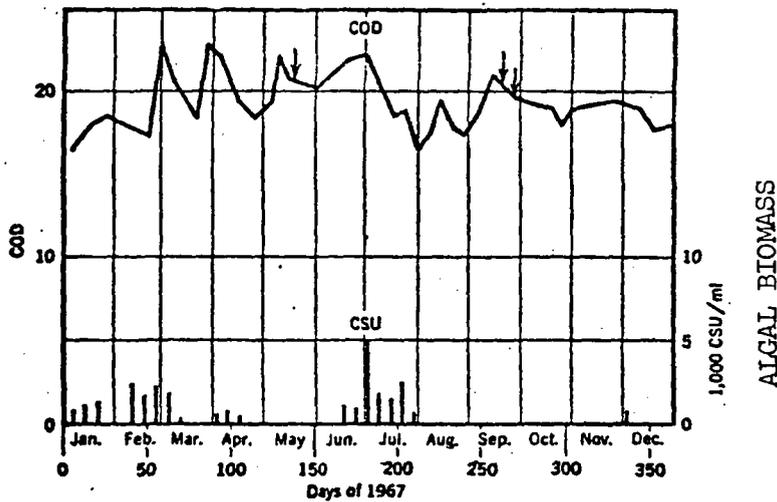


Fig. II-5. Lafayette Reservoir COD Values

Values less than 250/ml are not plotted; vertical arrows indicate treatment with copper sulfate. COD values were obtained on samples taken at a depth of 5 feet.

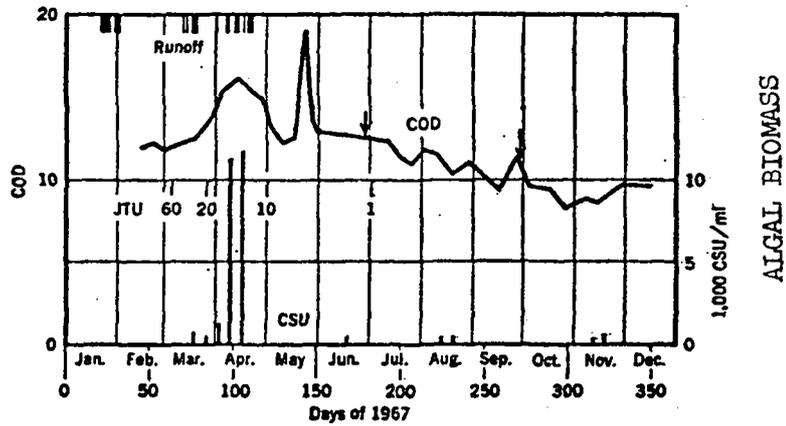


Fig. II-7. Upper San Leandro (USL) COD Values

Values less than 250/ml are not plotted. COD values were obtained on samples taken at a depth of 5 feet, and runoff of at least 50 mgd is indicated by vertical lines, as are selected turbidity values in Jackson Turbidity Units. Vertical arrows indicate treatment with copper sulfate.

Table II-25

ORGANIC COMPOUNDS IDENTIFIED TO DATE  
FROM LOWER TENNESSEE

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| C O M P O U N D S         |                                  |
|---------------------------|----------------------------------|
| Benzene                   | Fluorene                         |
| Toluene                   | 5-Chloro-2-Methylbenzofuran      |
| Styrene                   | 2-Methylbiphenyl                 |
| Xylene                    | Anthracene                       |
| Ethylbenzene              | Diphenylacetylene                |
| p-Cresol                  | 1,1-Diphenylethene               |
| Indene                    | 2-Methylantracene                |
| 3,4,4-Trimethyl-2-Hexene  | 4-Methyldiphenylacetylene        |
| Naphthalene               | Pyrene                           |
| 1-Methylnaphthalene       | Fluoranthene                     |
| Ethylene Dimethylacrylate | p-Nonylphenol                    |
| Methyl Indene (2 isomers) | 2,6-Di-Tert-Butyl-4-Methylphenol |
| Ethylstyrene              | Diallyl Adipate                  |
| Butylbenzene              | Ethyl o-Phthalate                |
| o-Methoxybenzoic Acid     | 1,2-Tetradecanediol              |
| Biphenyl                  | Dibutyl Phthalate                |
| Acenaphthene              | Hexachlorobenzene                |
| Allylbenzoate             | n-Octyl-o-Phthalate              |

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Pitt and Jolley<sup>63</sup> reported on work toward the characterization of organic materials in six natural water sources: Lake Marion, South Carolina; Fort Loudon Lake, Watts Bar Lake and Holston River, Tennessee; Walker Branch and Mississippi River. Eighteen compounds have been identified and their concentrations determined (Table II-26). Most of the compounds identified were defined as naturally-occurring organic constituents, although some such as ethylene glycol, diethylene glycol and p-cresol were attributed to industrial sources.

A number of studies have recently been conducted on drinking water from municipalities whose sources are subject to wastewater discharges of industrial and domestic origin. These included the works by Kleopfer and Fairless<sup>56</sup> on the drinking water of Evansville, Indiana, by Saunders et al.<sup>59</sup> and Scheiman et al.<sup>58</sup> on the District of Columbia's drinking water, by Rook<sup>61</sup> on the source for Rotterdam, Netherlands and the study conducted by the EPA<sup>62</sup> on the New Orleans area water supply. Tables II-27 - II-31 indicate the compounds identified in each work as well as quantitative data when given. In the study by Kleopfer and Fairless the probable source of one of the major organic contaminants, bis (2-chloroisopropyl)-ether, was determined to be an industrial outfall on the Ohio River located about 150 river miles upstream from the Evansville water intake.

#### Groundwater

There is little information on the identity of organic chemicals in groundwater. Most data is in terms of gross parameters and is limited in scope.

A study by the California State Department of Health<sup>76</sup> of the groundwater quality along the Santa Ana River in San Bernardino and Riverside Counties indicated that COD levels were less than 2 mg/l and CCE<sub>m</sub> between

Table II-26

MOLECULAR CONSTITUENTS IDENTIFIED IN NATURAL  
WATER SAMPLES

| CONSTITUENT                         | SAMPLE <sup>a</sup> | IDENTIFICATION<br>METHOD <sup>b</sup> | CONC. <sup>c</sup> ppb |
|-------------------------------------|---------------------|---------------------------------------|------------------------|
| p-Cresol                            | 3                   | AC,GC,MS                              | 7                      |
| Diethylene glycol                   | 5                   | AC,MS                                 | 1                      |
| Ethylene glycol                     | 5                   | AC,GC,MS                              | 20                     |
| Glycerine                           | 1,2,3,4,5           | AC,GC,MS                              | 1-20                   |
| Glycine                             | 1                   | AC,GC,MS                              | 2                      |
| Mannitol                            | 5                   | AC,GC,MS                              | 2                      |
| Methyl- $\alpha$ -D-glucopyranoside | 4                   | AC,GC,MS                              | 30                     |
| Methyl- $\beta$ -D-glucopyranoside  | 4                   | AC,GC,MS                              | 3                      |
| Sucrose                             | 1,5                 | AC,GC,MS                              | 2                      |
| Xylitol                             | 5                   | AC,GC,MS                              | 1                      |
| Urea                                | 1,2                 | AC,GC,MS                              | >4                     |
| Inositol                            | 1,2,3,4,5           | GC,MS                                 | 0.5-1                  |
| O-Methylinositol                    | 1,2,3,4,5           | GC,MS                                 | 0.3-10                 |
| Linoleic Acid                       | 1,5                 | MS                                    | 1                      |
| Oleic Acid                          | 1,5                 | MS                                    | 1                      |
| Palmitic Acid                       | 1,5                 | MS                                    | 0.4                    |
| Stearic Acid                        | 1                   | MS                                    | 0.5                    |
| 2,2'-Bipyridine                     | 4                   | MS                                    | 4                      |

<sup>a</sup>1 - Lake Marion, 2 - Fort Loudoun Lake, 3 - Holston River, 4 - Mississippi River, 5 - Watts Bar Lake, and 6 - Walker Branch.

<sup>b</sup>AC - anion exchange chromatography, CC - cation exchange chromatography, UV - ultraviolet spectrum, GC - gas chromatography, MS - mass spectroscopy.

<sup>c</sup>Concentrations are order-of-magnitude estimates based upon assuming linear FID response to carbon in the constituents.

Table II-27

ORGANIC COMPOUNDS FOUND IN MUNICIPAL  
WATER SUPPLY

| COMPOUND                               | EVIDENCE <sup>a</sup> |
|--|-----------------------|
| Bromodichloromethane                   | A                     |
| Toluene                                | A, B, C               |
| Chlorodibromomethane                   | A                     |
| Tetrachloroethylene                    | A, B, C               |
| Ethylbenzene <sup>b</sup>              | A, B, C               |
| Xylene <sup>b</sup>                    | A, B, C               |
| Styrene                                | A, B, C               |
| Bromoform                              | A, B, C               |
| Bis(2-chloroethyl)ether                | A, B, C               |
| Bis(2-chloroisopropyl)ether            | A, B, C, D            |
| Hexachloroethane                       | A, B                  |
| Hexachlorobenzene                      | A, B                  |
| Chlorohydroxybenzophenone <sup>c</sup> | A                     |

<sup>a</sup> A = interpretation of mass spectrum, B = comparison with mass spectrum of authentic sample, C = retention time match on two different glc columns, and D = comparison with ir spectrum of authentic sample.

<sup>b</sup> Analysis on a 1/1/10 Bentone 34, Silicone DC 430, Chromosorb W 60 80 mesh column indicated a mixture of xylene isomers and ethylbenzene.

<sup>c</sup> Substitution is on the same ring. This component was found in the acid fraction.

Table II-28

ORGANIC CONSTITUENTS IDENTIFIED  
IN DISTRICT OF COLUMBIA DRINKING WATER\*

| COMPOUND                    | CONC.<br>ppm | COMPOUND                 | CONC.<br>ppm |
|-----------------------------|--------------|--------------------------|--------------|
| Nonane                      | 0.01         | Trichloromethane**       | -            |
| Decane                      | 0.03         | Trichlorofluoromethane** | -            |
| Isodecane                   | 0.005        | Dichlorodifluoroethane** | -            |
| Benzene                     | 0.005        | Tetrachloroethane        | 0.01         |
| Toluene                     | 0.001        | Carbon Tetrachloride     | 0.005        |
| Dimethyl Benzene            | -            | Chlorobenzene            | 0.001        |
| C <sub>3</sub> - Benzenes** | -            | Dichlorobenzene          | 0.001        |
| Trimethyl Benzenes**        | -            | Trichlorobenzene         | 0.001        |
| C <sub>4</sub> - Benzenes** | -            | Octylchloride            | 0.001        |
| C <sub>5</sub> - Benzenes** | -            | Dichlorobromomethane**   | -            |
| Naphthalene                 | 0.001        | Butylbromide**           | -            |
| Dibutyl Phthalates          | -            | Bromoform Butanal        | 0.05         |
| Ethylamine                  | -            | Acetic Acid              | -            |
| Propyl Amine                | -            | Methyl Ethyl Ketone      | -            |
| Piperidine                  | -            | Propanol                 | 0.001        |
| Dichloromethane***          | -            | Pentanol                 | 0.001        |

\*Concentration Values are Estimated.

\*\*Calibrations were not made for these compounds

\*\*\*Detected in a CO<sub>2</sub> extract.

Table II-29

VOLATILE ORGANIC CONTAMINANTS  
IN WASHINGTON, D.C. DRINKING WATER

| <u>C O M P O U N D S</u>  |                          |
|---------------------------|--------------------------|
| 1. Carbon Dioxide         | 17. Aromatic Hydrocarbon |
| 2. Methylene Chloride     | 18. Aromatic Hydrocarbon |
| 3. Carbon Tetrachloride   | 19. Aromatic Hydrocarbon |
| 4. Benzene                | 20. x                    |
| 5. Chloroform             | 21. x                    |
| 6. Toluene                | 22. Aromatic Hydrocarbon |
| 7. Tetrachlorethylene     | 23. x                    |
| 8. Bromodichloromethane*  | 24. x                    |
| 9. o - Xylene             | 25. Bromoform*           |
| 10. m - Xylene            | 26. x                    |
| 11. p - Xylene            | 27. x                    |
| 12. Chlorobenzene         | 28. x                    |
| 13. x                     | 29. x                    |
| 14. Propyl Benzene        | 30. x                    |
| 15. Trimethyl Benzene     | 31. x                    |
| 16. Chlorodibromomethane* | 32. x                    |

x = unidentified compounds

\*These compounds have also been detected in municipal water processed from the Ohio River.

Table II-30

## HALOFORMS PRODUCED IN CHLORINATION OF STORED SURFACE WATERS

| 1973/1974 | AMMONIA<br>CONTENT<br>mg NH <sub>4</sub> /l | CHLORINE<br>DOSE<br>mg/l | pH DURING<br>REACTION | TEMP-<br>ERATURE<br>°C | INORGANIC<br>BROMIDE<br>ug/l | COLOR<br>mg Pt/l | CONCENTRATION OF HALOFORMS ug/l |                      |                     |                   |
|-----------|---|--------------------------|-----------------------|------------------------|------------------------------|------------------|---------------------------------|----------------------|---------------------|-------------------|
|           |   |                          |                       |                        |                              |                  | CHCl <sub>3</sub>               | CHCl <sub>2</sub> Br | CHClBr <sub>2</sub> | CHBr <sub>3</sub> |
| March 15  | 3.8   | 25                       | 7.8-7.4               | 4.5                    | 360                          | 25               | 54.0                            | 20.0                 | 13.3                | 2.0               |
| April 9   | 2.6   | 17                       | 8.3-7.3               | 7                      | 210                          | 27               | 16.5                            | 12.4                 | 9.7                 | 10.0              |
| May 10    | 0.08  | 4                        | 9.5-8.9               | 12                     | 150                          | 16               | 16.4                            | 4.2                  | 2.6                 | 1.1               |
| June 14   | 0.60  | 9                        | 9.1-8.6               | 17                     | 160                          | 16               | 44.1                            | 17.9                 | 8.0                 | 1.3               |
| July 12   | 0.18  | 6                        | 9.6-9.2               | 21                     | 150                          | 15               | 41.5                            | 7.3                  | 2.8                 | 2.8               |
| August 14 | 0.05  | 4                        | 9.6-9.3               | 20                     | 140                          | 14               | 52.0                            | 7.8                  | 2.8                 | 8.7               |
| Sept. 11  | 0.05  | 3                        | 9.4-9.1               | 19                     | 140                          | 10               | 20.3                            | 4.4                  | 1.7                 | 0.5               |
| Oct. 9    | 0.06  | 4                        | 8.7-8.2               | 15.5                   | 150                          | 10               | 11.9                            | 6.7                  | 5.2                 | 7.2               |
| Dec. 11   | 0.12  | 3                        | 9.1-8.7               | 6                      | 120                          | 7                | 6.0                             | 4.3                  | 3.0                 | -                 |
| Jan.      | 0.35  | 6.5                      | 8.8-8.7               | 4.5                    | 130                          | 9                | 9.5                             | 7.5                  | 4.6                 | 7.8               |
| Febr. 19  | 0.12  | 2                        | 8.9-8.6               | 6                      | 110                          | 6                | 10.0                            | 4.2                  | 3.6                 | 1.5               |

Table II-31  
 ORGANIC COMPOUND IDENTIFICATIONS  
 NEW ORLEANS AREA WATER SUPPLY STUDY

|          |   | Highest Measured Concentration<br>µg/l (ppb) |                              |                              |
|----------|---|--|------------------------------|------------------------------|
| Compound |   | Carrollton<br>Water Plant                    | Jefferson # 1<br>Water Plant | Jefferson # 2<br>Water Plant |
| 1        | Acetaldehyde  | D-VOA  | NE                           | NE                           |
| 2        | Acetone   | D-VOA  | NE                           | NE                           |
| 3        | Alkylbenzene-C <sub>2</sub> isomer  | 0.05   | ND                           | ND                           |
| 4        | Alkylbenzene-C <sub>2</sub> isomer  | 0.33   | ND                           | ND                           |
| 5        | Alkylbenzene-C <sub>2</sub> isomer  | 0.11   | 0.03                         | ND                           |
| 6        | Alkylbenzene-C <sub>3</sub> isomer  | 0.01   | ND                           | ND                           |
| 7        | Alkylbenzene-C <sub>3</sub> isomer  | 0.04   | 0.05                         | 0.02                         |
| 8        | Alkylbenzene-C <sub>3</sub> isomer  | 0.02   | ND                           | ND                           |
| 9        | Atrazine *<br>(2-chloro-4-ethylamino-<br>6-isopropylamino-<br>s-triazine) | 5.0  | 4.7                          | 5.1                          |
| 10       | Deethylatrazine<br>(2-chloro-4-amino-<br>6-isopropylamino-<br>s-triazine) | 0.51   | 0.27                         | 0.27                         |

Table II-31 (Cont.)

ORGANIC COMPOUND IDENTIFICATIONS  
NEW ORLEANS AREA WATER SUPPLY STUDY

|          |                                  | Highest Measured Concentration<br>µg/l (ppb) |                              |                              |
|----------|----------------------------------|--|------------------------------|------------------------------|
| Compound |                                  | Carrollton<br>Water Plant                    | Jefferson # 1<br>Water Plant | Jefferson # 2<br>Water Plant |
| 11       | Benzyl butyl phthalate*          | 0.64   | 0.81                         | 0.73                         |
| 12       | Bromodichloromethane             | D-VOA  | NE                           | NE                           |
| 13       | Bromoform *                      | 0.57   | ND                           | ND                           |
| 14       | Butanone                         | D-VOA  | NE                           | NE                           |
| 15       | Carbon disulfide                 | D-VOA  | NE                           | NE                           |
| 16       | Carbon tetrachloride             | D-VOA  | NE                           | NE                           |
| 17       | bis-2-Chloroethyl ether*         | 0.07   | 0.16                         | 0.12                         |
| 18       | Chloroform *,a                   | 133  | NE                           | NE                           |
| 19       | bis-2-Chloroisopropyl<br>ether * | 0.18   | 0.05                         | 0.03                         |
| 20       | n-Decane *                       | 0.04   | ND                           | ND                           |
| 21       | Decane-branched isomer           | 0.03   | ND                           | ND                           |

Table II-31 (Cont.)  
 ORGANIC COMPOUND IDENTIFICATIONS  
 NEW ORLEANS AREA WATER SUPPLY STUDY

|          |                                     | Highest Measured Concentration<br>ug/l (ppb) |                              |                              |
|----------|-------------------------------------|--|------------------------------|------------------------------|
| Compound |                                     | Carrollton<br>Water Plant                    | Jefferson # 1<br>Water Plant | Jefferson # 2<br>Water Plant |
| 22       | Dibromodichloroethane<br>isomer     | 0.33   | ND                           | 0.63                         |
| 23       | Dibromochloromethane *              | 1.1  | 0.30                         | 0.60                         |
| 24       | Dibutyl phthalate *                 | 0.10   | 0.16                         | 0.19                         |
| 25       | 2,6-Di-t-butyl-p-<br>benzoquinone * | 0.22   | 0.19                         | 0.23                         |
| 26       | Dichlorobenzene isomer              | 0.01   | D-RE                         | ND                           |
| 27       | 1,2-Dichloroethane <sup>a</sup>     | 8  | NE                           | NE                           |
| 28       | Dichloromethane                     | D-VOA  | NE                           | NE                           |
| 29       | Dieldrin **                         | 0.05   | 0.07                         | 0.05                         |
| 30       | Diethyl phthalate *                 | 0.03   | 0.03                         | 0.01                         |
| 31       | Di(2-ethylhexyl) phthalate *        | 0.10   | 0.31                         | 0.06                         |
| 32       | Dihexyl phthalate                   | 0.03   | ND                           | ND                           |

Table II-31 (Cont.)  
 ORGANIC COMPOUND IDENTIFICATIONS  
 NEW ORLEANS AREA WATER SUPPLY STUDY

| Compound   | Highest Measured Concentration<br>µg/l (ppb) |                              |                              |
|--|--|------------------------------|------------------------------|
|  | Carrollton<br>Water Plant                    | Jefferson # 1<br>Water Plant | Jefferson # 2<br>Water Plant |
| 33 Dihydrocarvone                                  | 0.14   | 0.06                         | 0.07                         |
| 34 Diisobutyl phthalate *                          | 0.59   | ND                           | ND                           |
| 35 Dimethyl phthalate                              | 0.27   | 0.13                         | 0.18                         |
| 36 Dioctyl adipate                                 | 0.10   | ND                           | ND                           |
| 37 Dipropyl phthalate *                            | 0.07   | 0.13                         | 0.14                         |
| 38 n-Dodecane *                                    | 0.01   | ND                           | ND                           |
| 39 Endrin **                                       | 0.004  | NYE                          | NYE                          |
| 40 Ethanol   | D-VOA  | NE                           | NE                           |
| 41 <u>o</u> -Ethyltoluene *                        | ND   | 0.04                         | 0.02                         |
| 42 <u>p</u> -Ethyltoluene *                        | 0.02   | 0.03                         | 0.03                         |
| 43 1, 2, 3, 4, 5, 7, 7-<br>Heptachloronorbornene * | 0.06   | 0.05                         | 0.05                         |

Table II-31 (Cont.)

ORGANIC COMPOUND IDENTIFICATIONS  
NEW ORLEANS AREA WATER SUPPLY STUDY

| Highest Measured Concentration<br>µg/l (ppb) |                           |                              |                              |
|--|---------------------------|------------------------------|------------------------------|
| Compound                                     | Carrollton<br>Water Plant | Jefferson # 1<br>Water Plant | Jefferson # 2<br>Water Plant |
| 44 Heptachloronorbornene<br>isomer           | 0.06                      | 0.04                         | 0.04                         |
| 45 Hexachloro-1,3-butadiene *                | 0.16                      | 0.27                         | 0.21                         |
| 46 Hexachloroethane *                        | 4.4                       | 0.19                         | 0.16                         |
| 47 Isophorone *                              | 1.5                       | 2.2                          | 2.9                          |
| 48 Limonene *                                | 0.03                      | ND                           | ND                           |
| 49 Methanol                                  | D-VOA                     | NE                           | NE                           |
| 50 Methylbenzoate                            | ND                        | D-RE                         | ND                           |
| 51 3-Methylbutanal                           | D-VOA                     | NE                           | NE                           |
| 52 2-Methylpropanal                          | D-VOA                     | NE                           | NE                           |
| 53 n-Nonane *                                | 0.03                      | ND                           | ND                           |
| 54 n-Pentadecane *                           | 0.02                      | ND                           | ND                           |

Table II-31 (Cont.)

ORGANIC COMPOUND IDENTIFICATIONS  
NEW ORLEANS AREA WATER SUPPLY STUDY

| Compound  | Highest Measured Concentration<br>ug/l (ppb) |                              |                              |
|---|--|------------------------------|------------------------------|
|   | Carrollton<br>Water Plant                    | Jefferson # 1<br>Water Plant | Jefferson # 2<br>Water Plant |
| 55 Tetrachloroethane<br>isomer                      | 0.11   | ND                           | ND                           |
| 56 Tetrachloroethylene                              | D  | 0.5                          | 0.41                         |
| 57 n-Tetradecane *                                  | 0.02   | ND                           | ND                           |
| 58 Toluene *  | 0.08   | 0.10                         | ND                           |
| 59 1,1,2-Trichloroethane *                          | 0.35   | 0.45                         | 0.41                         |
| 60 1,1,2-Trichloroethylene                          | D-VOA  | NE                           | NE                           |
| 61 n-Tridecane *                                    | 0.01   | ND                           | ND                           |
| 62 Trimethyl-trioxo-<br>hexahydrotriazine<br>isomer | 0.07   | ND                           | ND                           |
| 63 Triphenyl phosphate *                            | 0.12   | ND                           | ND                           |
| 64 n-Undecane *                                     | 0.02   | ND                           | ND                           |
| 65 Undecane-branched isomer                         | 0.04   | ND                           | ND                           |
| 66 Undecane-branched isomer                         | 0.06   | ND                           | ND                           |

Table II-31 (Cont.)

Symbols used in column headed Compound

- \* While all compounds listed in the table were identified by one or more methods, those marked with this symbol gained added confirmation by gas chromatography retention time match with an available standard of the compound.
- \*\* Compounds marked with this symbol gained further confirmation by gas chromatography retention time match with available standards on each of three different columns, polar and non-polar.
- a The quantitative values for these compounds were obtained on Volatile Organics Analysis by comparison with standards of known concentration at the Water Supply Research Laboratory. Compound 18 was detected but not quantified in Tetralin extracts of Carrollton water at Southeast Environmental Laboratory, but not in Tetralin extracts of Jefferson No. 1 or Jefferson No. 2. The latter laboratory did not detect compound 27.

Symbols used in columns headed Highest Concentration Measured.

- D-VOA These compounds were detected by Volatile Organics Analysis - Bellar Technique only. Quantitative values have not yet been obtained. This method was performed only on the Carrollton water at the Water Supply Research Laboratory.
- D-RE These compounds were detected only on XAD resin extracts in the specific water for which this symbol is used. Quantitative values were not obtained from the resin extracts. The compound may have been detected and quantified by another method in one or both of the other waters examined.
- D In the one instance where this symbol was used the compound was detected by both the Water Supply Research Laboratory and Southeast Environmental Research Laboratory but not quantified by either laboratory.
- NE This symbol means not examined. It is used exclusively for some compounds reported by the Water Supply Research Laboratory. This laboratory did not obtain samples of water from Jefferson No. 1 or Jefferson No. 2.

## Table II-31 (Cont.)

- ND This symbol means the compound was not detected in that specific water by any of the methods employed.
- NYE Compound 39 was confirmed in Carrollton water carbon chloroform extracts shortly before preparation of this report. Jefferson No. 1 and Jefferson No. 2 extracts have not yet been re-examined specifically for compound 39.

0.13 and 0.15 mg/l in wells above the City of San Bernardino sewage discharge. Wells downstream ranged from 4 to 8 mg/l COD nearest the river channel to 2 to 3 mg/l COD a mile from the river. TOC levels in this area were from 0 to 4 mg/l. Wells above the City of Riverside sewage discharge were also sampled. These wells were close to the river channel and showed COD values between 7.4 and 9.9 mg/l and CCE<sub>m</sub> ranging from 0.47 to 0.53 mg/l.

A similar study was conducted by the California State Department of Health on the groundwater in the Whittier Narrows area of Los Angeles County.<sup>77</sup> Samples from wells on the Montebello Forebay were tested for Carbon Chloroform Extract (CCE) and Chemical Oxygen Demand (COD). Results indicated that the CCE's ranged from 0.07 to 0.29 mg/l while the COD's were between 2.5 and 7.6 mg/l.

Grigoropoulos and Smith<sup>78</sup> examined natural groundwaters in Missouri for the presence of trace organic materials. Two wells, one a domestic water supply, and two springs were examined using carbon adsorption techniques. A variety of solvents were used to recover the organics (Table II-32). Solubility partitioning and column chromatography were employed to further separate the organic constituents (Tables II-33 and II-34).

The results appeared to indicate that the springs were supplied to a large part by surface waters particularly runoff from the immediate area and were subject to a considerable inflow of organic materials. The wells in comparison showed very little organic content.

Robinson et al.<sup>79</sup> studied Illinois groundwaters using carbon adsorption and solvent extraction to recover the organic matter. Groundwaters from four different communities were sampled and the results are shown in Tables II-35 and II-36. The authors concluded that the organic material in the groundwaters were sufficiently high to indicate further studies to evaluate the possible extent of the organic chemical pollution.

Table II-32

CONCENTRATION OF ORGANIC MICROPOLLUTANTS RECOVERED FROM  
MISSOURI SUBSURFACE WATERS

| LOCATION            | UNIT NO. | ORGANIC EXTRACTS, ug/1 |         |                 |                 |
|---------------------|----------|------------------------|---------|-----------------|-----------------|
|                     |          | Chloroform             | Ethanol | Acetone/Benzene | Benzene/Acetone |
| Spring Run<br>No. 1 | 1        | 30.4                   | 47.6    | 24.5/0.0        | 10.0/10.8       |
|                     | 2        | 10.8                   | 39.6    | 28.2/0.0        | 12.9/10.2       |
|                     | 3        | 2.5                    | 21.8    | 18.8/0.0        | 8.8/ 5.5        |
|                     | Total    | 43.7                   | 109.0   | 71.5/0.0        | 31.7/26.5       |
| Spring Run<br>No. 2 | 1        | 51.7                   | 76.4    | 4.0/0.8         | 2.0/ 1.6        |
|                     | 2        | 21.8                   | 73.3    | 9.9/1.0         | 6.8/17.4        |
|                     | 3        | 18.6                   | 45.8    | 15.8/5.6        | 2.6/14.5        |
|                     | Total    | 92.1                   | 195.5   | 29.7/7.4        | 11.4/33.5       |
| Well No. 1          | 1        | 4.8                    | 8.0     | 3.5/1.4         | 0.0/18.5        |
|                     | 2        | 0.0                    | 0.0     | 2.5/1.0         | 0.0/15.4        |
|                     | 3        | 0.0                    | 0.0     | 2.0/1.0         | 0.0/12.6        |
|                     | Total    | 4.8                    | 8.0     | 8.0/3.4         | 0.0/46.5        |
| Well No. 2          | 1        | 0.1                    | 2.1     | 0.2/0.1         | 1.2/ 1.4        |
|                     | 2        | 0.0                    | 0.0     | 0.2/0.2         | 1.1/ 1.2        |
|                     | 3        | 0.0                    | 0.0     | 0.2/0.1         | 1.1/ 1.1        |
|                     | Total    | 0.1                    | 2.1     | 0.6/0.4         | 3.4/ 3.7        |

Table II-33

SOLUBILITY PARTITIONING OF ORGANIC MICROPOLLUTANTS RECOVERED FROM  
MISSOURI SUBSURFACE WATERS

| EXTRACT          | FRACTION--PERCENT |                |            |              |       |              |          |                 |
|------------------|-------------------|----------------|------------|--------------|-------|--------------|----------|-----------------|
|                  | Ether Insolubles  | Water Solubles | Weak Acids | Strong Acids | Bases | Ampho-terics | Neutrals | Nonre-coverable |
| Spring Run No. 1 |                   |                |            |              |       |              |          |                 |
| Unit No. 1       |                   |                |            |              |       |              |          |                 |
| CCE              | 10.0              | 31.0           | 8.5        | 11.8         | 0.77  | 0.91         | 11.8     | 25.2            |
| CAE              | >99.0             | -              | -          | -            | -     | -            | -        | -               |
| Unit No. 2       |                   |                |            |              |       |              |          |                 |
| CCE              | 5.0               | 42.0           | 7.4        | 12.8         | 0.40  | 0.60         | 14.2     | 17.6            |
| Unit No. 3       |                   |                |            |              |       |              |          |                 |
| CCE              | 6.9               | 13.5           | 14.0       | 7.0          | 0     | 0            | 48.0     | 10.6            |
| CAE              | 44.0              | 33.0           | 2.5        | 9.5          | 0.20  | 0.20         | 3.1      | 7.5             |
| Spring Run No. 2 |                   |                |            |              |       |              |          |                 |
| Unit No. 1       |                   |                |            |              |       |              |          |                 |
| CCE              | 2.1               | 27.0           | 13.6       | 13.4         | 0.83  | 0.35         | 14.0     | 28.7            |
| CAE              | >99.0             | -              | -          | -            | -     | -            | -        | -               |
| Unit No. 2       |                   |                |            |              |       |              |          |                 |
| CCE              | 1.2               | 30.0           | 9.6        | 10.6         | 1.0   | 0.90         | 23.0     | 23.7            |
| Well No. 1       |                   |                |            |              |       |              |          |                 |
| Unit No. 1       |                   |                |            |              |       |              |          |                 |
| CCE              | 6.4               | 15.0           | 6.8        | 11.5         | 1.5   | 1.6          | 21.4     | 35.8            |
| CAE              | >99.0             | -              | -          | -            | -     | -            | -        | -               |
| CAcE-1*          | 1.6               | 5.0            | 8.3        | 5.0          | 0.60  | 0.50         | 71.0     | 8.0             |
| CBE-2*           | 0.0               | 0.6            | 2.2        | 0.6          | 0.50  | 0.20         | 83.5     | 12.4            |

\*The numbers 1 and 2 refer to the order at which acetone and benzene were used.

Table II-34

## COLUMN CHROMATOGRAPHIC SEPARATION OF NEUTRALS

| EXTRACT          | FRACTION--PERCENT |           |                         |                     |
|------------------|-------------------|-----------|-------------------------|---------------------|
|                  | Aliphatics        | Aromatics | Oxygenated<br>Materials | Nonre-<br>coverable |
| Spring Run No. 1 |                   |           |                         |                     |
| Unit No. 1       |                   |           |                         |                     |
| CCE              | 16.1              | 36.9      | 37.0                    | 10.0                |
| Unit No. 2       |                   |           |                         |                     |
| CCE              | 4.2               | 45.5      | 41.7                    | 8.6                 |
| Unit No. 3       |                   |           |                         |                     |
| CCE              | 50.8              | 5.0       | 25.4                    | 18.8                |
| CAE              | 16.2              | 0         | 56.7                    | 27.1                |
| Spring Run No. 2 |                   |           |                         |                     |
| Unit No. 1       |                   |           |                         |                     |
| CCE              | 22.0              | 24.5      | 50.5                    | 23.0                |
| Unit No. 2       |                   |           |                         |                     |
| CCE              | 6.8               | 21.0      | 44.3                    | 27.9                |
| Well No. 1       |                   |           |                         |                     |
| Unit No. 1       |                   |           |                         |                     |
| CCE              | 48.5              | 19.6      | 21.6                    | 10.3                |
| CAcE-1           | 0                 | 78.0      | 21.0                    | 1.0                 |
| CBE-2            | 5.0               | 56.2      | 25.4                    | 13.4                |

Table II-35

CONCENTRATION OF ORGANIC MATTER EXTRACTED FROM WELL WATERS

| TOWN IN ILLINOIS | EXP. NO. | TOTAL VOL. FILTERED gal. | SOLVENT USED              | FILTER A EXTRACT |      | FILTER B EXTRACT |        | FILTER C EXTRACT |      | TOTAL EXTRACT** mg/l |
|------------------|----------|--------------------------|---------------------------|------------------|------|------------------|--------|------------------|------|----------------------|
|                  |          |                          |                           | g                | mg/l | g                | mg/l   | g                | mg/l |                      |
| Oakwood          | 1        | 1,073                    | Chloroform                | 3.6              | 0.98 | 3.5              | 0.87   | 1.7              | 0.41 | 2.17                 |
|                  |          |                          | Water                     | 1.3              | 0.31 | 1.8              | 0.45   | 0.9              | 0.23 | 0.99                 |
|                  |          |                          | Ethanol                   | 1.2              | 0.30 | 2.1              | 0.52   | 1.3              | 0.32 | 1.14                 |
|                  |          |                          | Ethanol + NH <sub>3</sub> | 1.0              | 0.25 | 1.7              | 0.41   | 1.9              | 0.47 | 1.13                 |
|                  |          |                          | Ethanol + HCl             | 6.7              | 1.71 | 46               | 1.13   | 17.8             | 4.45 | 5.43                 |
| TOTAL            |          |                          |                           |                  |      |                  |        |                  |      |                      |
| Philo            | 2        | 950                      | Chloroform                | 0.2              | 0.06 | 0.3              | 0.07   |                  |      | 0.13                 |
|                  |          |                          | Water                     | 0.3              | 0.07 | 0.1              | 0.01   |                  |      | 0.08                 |
|                  |          |                          | Ethanol                   | 0.6              | 0.17 | 2.8              | 0.77   |                  |      | 0.94                 |
|                  |          |                          | Ethanol + NH <sub>3</sub> | 0.5              | 0.13 | 0.8              | 0.22   |                  |      | 0.35                 |
|                  |          |                          | Ethanol + HCl             | 2.4              | 0.68 | 0.4              | 0.12   |                  |      | 1.50                 |
| TOTAL            |          |                          |                           |                  |      |                  |        |                  |      |                      |
| Clinton          | 3        | 1,426                    | Chloroform                | 0.2              | 0.04 | Est              | 0.30** |                  |      | 0.34                 |
|                  |          |                          | Water                     | 0.0              | 0.00 | Est              | 0.68** |                  |      | 0.68**               |
|                  |          |                          | Ethanol                   | 0.7              | 0.12 | 10.2             | 1.88   |                  |      | 2.00                 |
|                  |          |                          | Ethanol + NH <sub>3</sub> | 1.6              | 0.29 | 2.3              | 0.42   |                  |      | 0.71                 |
|                  |          |                          | Ethanol + HCl             | 3.5              | 2.49 | 3.3              | 0.60   |                  |      | 3.75                 |
| TOTAL            |          |                          |                           |                  |      |                  |        |                  |      |                      |
| Atwood           | 4        | 1,293                    | Chloroform                | 0.4              | 0.09 | 1.2              | 0.25   |                  |      | 0.34                 |
|                  |          |                          | Water                     | 3.0              | 0.61 | 5.5              | 1.11   |                  |      | 1.72                 |
|                  |          |                          | Ethanol                   | 2.1              | 0.43 | 4.5              | 0.93   |                  |      | 1.36                 |
|                  |          |                          | Ethanol + NH <sub>3</sub> | 1.4              | 0.28 | 4.3              | 0.87   |                  |      | 1.15                 |
|                  |          |                          | Ethanol + HCl             | 5.7              | 1.16 | 2.0              | 0.41   |                  |      | 4.57                 |
| TOTAL            |          |                          |                           |                  |      |                  |        |                  |      |                      |
| Clinton          | 5        | 1,153                    | Chloroform                | 0.4              | 0.08 | 1.3              | 0.30   |                  |      | 0.55                 |
|                  |          |                          | Water                     | 0.0              | 0.00 | 3.0              | 0.68   |                  |      | 1.35                 |
|                  |          |                          | Ethanol                   | 2.6              | 0.59 | 7.5              | 1.72   |                  |      | 3.31                 |
|                  |          |                          | Ethanol + NH <sub>3</sub> | 2.0              | 0.46 | 4.6              | 1.05   |                  |      | 2.08                 |
|                  |          |                          | Ethanol + HCl             | 9.1              | 2.09 | 2.8              | 0.64   |                  |      | 7.29                 |
| TOTAL            |          |                          |                           |                  |      |                  |        |                  |      |                      |

\*Ethanol plus HCl extract not included.

\*\*Samples lost, values used are from Clinton Experiment 5.

Table II-36

CHEMICAL OXYGEN DEMAND OF ORGANIC EXTRACTS  
AND PURE COMPOUNDS

| TOWN IN<br>ILLINOIS | EXP. NO. | EXTRACT         | CHEMICAL OXYGEN DEMAND  |                          |
|---------------------|----------|-----------------|-------------------------|--------------------------|
|                     |          |                 | Measured<br>mg, mg Ext. | Theoretic<br>mg, mg Ext. |
| Oakwood             | 1        | Ethanol A       | 0.71                    |                          |
|                     |          | Ethanol B       | 2.08                    |                          |
| Philo               | 2        | Ethanol A       | 0.50                    |                          |
|                     |          | Ethanol B       | 0.12                    |                          |
|                     |          | Ammonia B       | 0.22                    |                          |
| Clinton             | 5        | Ethanol A       | 1.27                    |                          |
|                     |          | Ammonia A       | 1.39                    |                          |
|                     |          | Chloroform B    | 1.67                    |                          |
|                     |          | Water B         | 1.04                    |                          |
|                     |          | Ethanol B       | 1.23                    |                          |
| Pure Compounds      |          | D Tartaric Acid | 0.517                   | 0.533                    |
|                     |          | D Tartaric Acid | 0.539                   | 0.533                    |
|                     |          | Malonic Acid    | 0.680                   | 0.615                    |
|                     |          | Di, Malic Acid  | 0.714                   | 0.716                    |
|                     |          | Succinic Acid   | 0.928                   | 0.948                    |
|                     |          | Carbon          |                         | 2.66                     |

Burnham et al.<sup>57</sup> conducted a study on the groundwater supply of Ames, Iowa to identify and estimate organic contaminants causing taste and odor problems. The authors, employing solubility partitioning techniques, isolated 40 to 50 compounds from the neutral fraction. Sixteen compounds were identified and their concentrations, some individually and others collectively, were estimated. The source of these materials was believed to be coal tar residues buried in a pit hydraulically connected to the aquifer supplying the city water. The results are shown in Table II-37.

Appendix A contains a summary list of organic compounds identified in drinking waters in the United States.<sup>80</sup> Included are a list of the water supplies involved, classification according to chemical characteristics, a summary of acute toxicity and chronic toxicity information and information on the carcinogenicity and metabolic data of the organic compounds identified.

#### Health Effects

Very little is known concerning the public health impact of "trace" organics in water supplies. The list of compounds identified in water is growing larger with great rapidity, particularly with the development of newer and more sensitive analytical techniques. Most of the relevant published literature deals with the detection and measurement of organic material in water supplies. There is very little evidence presented which indicates a relationship between the presence of these compounds in drinking water and human disease. At this point in time, the diseases of most concern to the water quality managers are cancers that might possibly be produced as a result of long-term exposure to low concentrations of carcinogens.

The source of these compounds found in water is not thoroughly understood; however, their origin is certainly from natural, domestic, and industrial activities. In most cases the number of compounds present are

Table II-37  
 NEUTRAL COMPOUNDS IN A CONTAMINATED  
 AMES, IOWA, WELL

| NAME OF COMPONENT           | IDENTIFICATION | CONCENTRATION,<br>ppb | STD.<br>DEV. |
|-----------------------------|----------------|-----------------------|--------------|
| Acenaphthylene              | a, b, c        | 19.3                  | 1.4          |
| 1-Methylnaphthalene         | a, b, d        | 11.0                  | 0.6          |
| Methylindenes (two isomers) | e, f           | 18.8                  | 0.8          |
| Indene                      | a, b           | 18.0                  | 1.5          |
| Acenaphthene                | a, b           | 1.7                   | 0.2          |
| 2-2-Benzothiophene          | a, b           | 0.37                  | 0.11         |
| Isopropylbenzene            | a              |                       |              |
| Ethyl Benzene               | a              |                       |              |
| Naphthalene                 | a              |                       |              |
| 2,3-Dihydroindene           | e              |                       |              |
| Alkyl-2,3-dihydroindene     | e, f           | 15                    |              |
| Alkyl Benzenes              | e, f           |                       |              |
| Alkyl Benzothiophenes       | e, f           |                       |              |
| Alkyl Naphthalenes          | e, f           |                       |              |

<sup>a</sup> Identification was verified by comparison of retention time and mass spectrum with an authentic sample.

<sup>b</sup> Identification was verified by comparison of the ultraviolet spectrum with an authentic sample.

<sup>c</sup> Identification was verified by comparison of the proton magnetic spectrum with an authentic sample.

<sup>d</sup> Identification was verified by comparison of the infrared spectrum with an authentic sample.

<sup>e</sup> Identification based on mass spectral data alone.

<sup>f</sup> Knowledge of the exact positional isomer was not important for this work. This could be done by proton magnetic resonance if needed.

unknown and frequently when compounds have been identified their concentration is unknown. The USSR has developed maximum permissible concentrations for a large number of organic constituents<sup>81</sup> -- see Appendix B.

A gross measurement of organics in water is embodied in the carbon-chloroform extractables (CCE). The method is described in detail in Standard Methods<sup>82</sup> and consists of passing water through activated carbon and extracting the consequent absorbate with chloroform. Finally the solvent is evaporated and the organic residue weighed. At the present time it is suggested that organics-carbon absorbable should not exceed a CCE level of 0.7 mg/l in public water supply sources.<sup>83</sup> This level has been set because large values of CCE are aesthetically undesirable and because high levels may have adverse physiological effects.

Recently there have been two reports of the formation of organohalides when drinking water containing humic or other organic substances is chlorinated. Rook<sup>61</sup> measured the production of  $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$  and  $\text{CHBr}_3$  with chloroform ( $\text{CHCl}_3$ ) always the predominant species in chlorinated surface water in Holland. Bellar et al.<sup>60</sup> examined chlorinated waters in the Ohio, U.S.A., area and found very similar results. Again chloroform was the predominant organohalide species. The concentration of chloroform ranged from a high of 54 ug/l in Rook's study to 150 ug/l in the study of Bellar et al.

Andelman and Suess<sup>84</sup> extensively reviewed the literature pertaining to the presence of polynuclear aromatic hydrocarbons in water. These authors point out that these compounds appear to be ubiquitous, originating from both natural and from human activity. They were particularly interested in 3,4-benzpyrene because it is one of the most potent of the recognized carcinogens. Uncontaminated (fresh) groundwater contained polynuclear aromatic

hydrocarbon (PAH) concentrations from 0.001 to 0.010 ug/l. Carcinogenic PAH in groundwater has been as high as 0.0006 ug/l. Waste effluents have ranged from 87.5 to 0.5 ug/l for total PAH; 37.9 to 0.1 ug/l for carcinogenic PAH; and, 1.8 to 0.001 ug/l for benzpyrene.

It is readily apparent that a great number of organic compounds have been isolated from drinking water, particularly raw water downstream from pollution sources. Many of these compounds arouse the suspicion of the toxicologist as to their carcinogenic or other toxic potential.

The toxicological and epidemiological data concerning these compounds in water, thus far available, are relatively sparse and often inconclusive.

A number of investigators have looked at the carcinogenic nature of carbon chloroform and carbon alcohol extracts. In 1960 Hueper<sup>85</sup> experimented with absorbates on activated carbon obtained from the water of a river near the entrance of the discharge from a large coke oven plant. These absorbates were painted upon the skin of mice and no pathologic effects were noted. In 1963 Hueper and his colleagues<sup>86</sup> performed a more thorough study on the carcinogenic effects of carbon absorbates from both raw and finished supplies. In this instance the water came from Nitro, West Virginia, a short distance downstream from chemical and rubber manufacturing plants. One gram of each type of extract (CCE and CAE) was collected from both raw and finished water, and mice were exposed subcutaneously, cutaneously, and in one instance orally. In the first instance, the animals received from 2 to 4 mg every two weeks for 56 weeks. The cutaneous dose was one drop of extract every two weeks for 56 weeks, and the oral dose was 2 percent extract in the animals' chow for 3 months. A summary of results is shown in Table II-38. While these results are not overwhelmingly positive, they do tend to indicate the potential carcinogenicity of these extracts. No tumors occurred from

oral exposure. The tumors produced included one papilloma of the bladder, four spindle-cell sarcomas at the site of subcutaneous injection, and the rest included leukemia or lymphoma, and reticulum-cell sarcoma of the liver.

Table II-38

SUMMARY OF RESULTS OF INTRODUCING CCE AND CAE  
FROM RAW AND FINISHED WATER INTO MICE  
(From Hueper and Payne)<sup>86</sup>

| ROUTE OF EXPOSURE | NUMBER OF TUMORS PRODUCED/ANIMAL EXPOSED |            |                 |                 |
|-------------------|--|------------|-----------------|-----------------|
|                   | Water Source                             |            |                 |                 |
|                   | Raw<br>CCE                               | Raw<br>CAE | Finished<br>CCE | Finished<br>CAE |
| Subcutaneous      | 5/72                                     | 1/72       | 2/72            | 1/72            |
| Cutaneous         | 2/72                                     | 1/72       | 0/72            | 0/72            |
| Oral              | --*                                      | --         | 0/40            | --              |

\*No test.

The controls consisted of 40 nonexposed animals maintained during the time of testing. No tumors were observed among the 40 animals.

In 1967 Dunham et al.<sup>87</sup> collected carbon absorbates from finished New Orleans drinking water over a year's time. Both CCE and CAE were introduced subcutaneously into young mice. A total of 5 mg of either extract was introduced during the first 20 days after birth of the test animals. No tumors were induced during the time of the study; however, death rates of the animals varied considerably.

In 1973 Tardiff and Deinzer<sup>88</sup> reported letal dose-50 percent ( $LD_{50}$ ) data on CCE and CAE concentrates from the Kanawa River, West Virginia, and from Cincinnati tap water. The materials were introduced into mice via the interperitonel route. Using CCE from the Virginia area, a  $LD_{50}$  of 89 to

35 mg/Kg was observed. The difference between these values was shown to be due to the amount of chloroform present in the extract. Extracts containing 30 percent chloroform were more toxic. The increase in toxicity was equal to that produced by 30 percent chloroform itself. The second extract contained only 10 percent chloroform at which level the presence of chloroform had no significant effect. The LD<sub>50</sub> for the CAE obtained from this water was 84 mg/Kg. The CCE sample from Cincinnati tap water was 32 mg/Kg. These investigators also concentrated organics from tap water using reverse osmosis and extracting the concentrate with methylene-chloride and chloroform. These materials were shown to have a LD<sub>50</sub> of 65 to 290 mg/Kg. Based upon toxicity categories suggested by Gleason et al.<sup>89</sup> these extracts would be classified as being very toxic to extremely toxic. As these authors point out the interpretation of these data must be carefully considered, particularly when extrapolating the toxicity data gained from concentrated extracts to the toxicity at levels found in drinking water.

In light of determining the significance of these compounds in lower doses, the paper by Ottoboni and Greenberg<sup>90</sup> is interesting. These workers arranged an experiment in which the filter-sterilized effluent of an activated sludge plant was used as the sole source of drinking water for ten rats. Ten matched rats whose drinking water was from the local treated supply acted as control. During the course of the experiment, two male rats exposed to the effluent developed massive tumors which were unusual for the strain of animal used. Some physiological differences were also noticed between the two groups. Male rats exposed to the effluent gained more weight than the controls and exposed female rats developed significantly smaller adrenal glands. To date this work has not been corroborated.

The toxic effect of many of the individual compounds that have been identified in water has been reported in the literature. Of the sixty compounds identified from drinking water, Tardiff and Deinzer<sup>88</sup> classify one as nontoxic, 14 moderately toxic, 16 very toxic, two extremely toxic and 27 as unknown. Again it is impossible at this time to relate these toxicity classifications to the concentrations of these compounds found in water and treated wastewater.

Thorough epidemiologic studies on the impact of organic matter in water upon human health are rare. Most studies conducted relate this quality parameter to disease in an indirect way. As cited by Andelman and Suess,<sup>84</sup> Stocks in 1947<sup>91</sup> noted that four boroughs of London that were supplied with well water had lower cancer mortalities than those boroughs whose supply was from river water. The inference here is that river water receives more waste material, therefore causing the higher cancer death rates among those who drink its water. In Holland, studies<sup>92,93</sup> have shown that persons who drink water from a municipal system have lower cancer death rates than among those whose water is not delivered through such a system. The study also pointed out that the death rate from cancer was higher (606 per 100,000 population) among those persons whose municipal system derived water from a river than among those who derived their water from wells. In this latter instance the death rate was 568 per 100,000. In 1954, Wynne-Griffith and Davies<sup>94,95</sup> in England published two papers. The first suggested a relationship between cancer mortality and water supply. In the subsequent paper,<sup>95</sup> however, they indicated that when social factors and soil type were also considered, the involvement of the water factor became insignificant. These latter papers indicate the care that must be taken in all epidemiological studies to weigh all the "factors" involved before concluding as to the role of water supply in disease development.

Most recently statistical analyses were performed by Talbot and Harris<sup>96</sup> in which the correlation between cancer mortality and water supply source was determined among residents of the parishes of Louisiana. The statistical approach involved a multiple regression analysis in which the variables were: source of water (surface or ground), median family income, white population density per square mile, occupation (petroleum and coal industry, chemical industry and the mining industry), and the proportion of the white population living in rural communities. The cancer mortality rates were limited to white males. These correlations were made for all malignant neoplasms, urinary cancers, gastrointestinal cancers, cancer of the liver and for pulmonary cancers. In the case of water quality, it was assumed that the quality of river water is homogeneous throughout those areas of the state using the Mississippi River as a water source and that homogeneity also held true for the groundwater used throughout the state.

The following regression equation was developed for the mortality from all cancers per 100,000 white males (TCWM):

$$\text{TCWM} = 252.8 + 32.9(W) - 56.7(R) - 5.9(I) - 10.0(P) + 19.9(C) + 0.3(M)$$

$$(3.6)^* \quad (-4.6)^* \quad (-2.3)^* \quad (-.1)^* \quad (.4)^* \quad (.01)^*$$

in which (W) is the coefficient for water, (R) for ruralness, (I) for income, (P) employed in petrochemical industry, (C) employed in chemical industry, and (M) employed in mining. This analysis indicates a significant correlation between surface water and total cancer mortality in white males.

Significant correlations were also seen between mortality and urbanization and between mortality and income. Type of employment did not appear to have a significant effect on total cancer mortality in the selected group. From this equation the authors estimated that a parish that changed from 100 percent river water to groundwater would decrease its cancer death rates in white males by 33 per 100,000 population.

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\* = t values.

Surface water sources also correlated with specific types of cancer mortality rates, i.e., with urinary, lung and gastrointestinal cancers. Only lung cancer mortality rates correlated with water source when the occupational variables were removed; otherwise, no correlation was determined. Liver cancer did not correlate with any of the variables. A few analyses were made between these variables and cancer in white females. In this case, results were statistically insignificant. As stated by the authors the study was brief, the evidence fragmentary, but is highly suggestive. A good deal more careful statistical work will have to be done before any clear conclusions may be drawn.

In another recent investigation, Dowty et al.<sup>97</sup> determined the presence of various halogenated hydrocarbons both in New Orleans water and in the serum of residents of that area. Using a new elution method they isolated 13 halogenated hydrocarbons from New Orleans drinking water. From the pooled sera of eight people they were able to detect the presence of carbontetrachloride, tetrachloroethylene, plus three isomers of dichlorobenzene. The latter compound was not found in water. The true significance of these findings is not clear. It was suggested that if water is the source of these chemicals in plasma, then a biomagnification might be involved.

In another recent British paper, McConnell et al.<sup>164</sup> reported on the occurrence of chlorinated hydrocarbons in the environment, including chloroform, carbon tetrachloride, trichloroethane, trichloroethylene and perchloroethylene. They found the presence of small amounts (ug/Kg) of these compounds in many common food stuffs (dairy products, meat, oils and fats, beverages, fruits and vegetables). They also determined the levels of these compounds in various tissues of elderly humans and found these compounds to be present in concentrations similar to those found in foods. These investigators concluded that there was no evidence of biomagnification. This investigation also points to the potential ubiquity of these compounds.

A relationship between endemic goiter and water quality has been recognized for many years.<sup>165,166</sup> In 1973, Gaitan<sup>167</sup> conducted a thorough study of waterborne goitrogens in the Cauca Valley of Columbia, South America. The incidence of goiter among children in this area ranged from 25 to 52 percent. In this study it became readily apparent that water supply was an important factor. He was able to isolate three active anti-thyroidal compounds from groundwater taken from deep wells. These compounds were identified as low molecular weight (<220) sulfurated hydrocarbons. This author also noted that there was a ten-fold increase in cancer of the thyroid where endemic goiter exists in the Cauca Valley. The potential presence of low molecular weight goitrogenic compounds in reclaimed water should certainly be considered when evaluating the health effects of reclaimed water reuse.

An Ad Hoc Study Group to the Hazardous Materials Advisory Committee, Science Advisory Board, U.S. Environmental Protection Agency<sup>168</sup> has recently reported on the assessment of possible human health associated with consumption of drinking water contaminated with low concentrations of organic chemicals. The Study Group expressed concern that the chemicals which have been measured account for only a few percent of the total organic content of drinking water; thus, attempts to evaluate the health risk of contamination may be mistakenly directed toward identified, potentially toxic compounds while other groups of compounds perhaps of equal or greater toxicologic significance go undetected. The Study Group concluded:

"Based upon recent, reasonably extensive, water quality data for many U.S. water supplies and on extremely limited data from experimental carcinogenesis studies, there may be some cancer risk associated with consumption of chloroform in drinking water. The level

of risk, estimated from consideration of the worst case and for the expected cancer site for chloroform (the liver) might be extrapolated to account for up to 40% of the observed liver cancer incidence rate. A more reasonable assumption, based upon current water quality data which show much lower levels than the worst case in the majority of U.S. drinking water supplies, would place the risk of hepatic cancer much lower and possibly nil."

They also reported that although some other organic contaminants in drinking water have carcinogenic potential, the cancer risk to man was judged to be minor because of their low concentration and/or infrequent occurrences in drinking water.

#### Inorganic

Unlike the ill-defined organic constituents present in reclaimed water which pose serious health concerns, the inorganic constituents of health significance are, for the most part, well known. The 1962 U.S. Public Health Service Drinking Water Standards<sup>98</sup> include limits for heavy metals and other inorganic substances, some of which are listed below:

| <u>Substance</u> | <u>Rejection of Supply<br/>(mg/l)</u> | <u>Recommended Control Limits<br/>(mg/l)</u> |
|------------------|---------------------------------------|--|
| Arsenic          | 0.05                                  | 0.01   |
| Barium           | 1.0                                   | -  |
| Cadmium          | 0.01                                  | -  |
| Chloride         | -                                     | 250  |
| Chromium (+6)    | 0.05                                  | -  |
| Copper           | -                                     | 1.0  |
| Cyanide          | 0.2                                   | 0.01   |
| Iron             | -                                     | 0.3  |
| Lead             | 0.05                                  | -  |
| Manganese        | -                                     | 0.05   |
| Nitrate          | -                                     | 45   |
| Selenium         | 0.01                                  | -  |
| Silver           | 0.05                                  | -  |
| Sulfate          | -                                     | 250  |
| TDS              | -                                     | 500  |
| Zinc             | -                                     | 5  |

The quantities of inorganic constituents present in sewage effluents depend on several factors, but mainly on the type of waste (domestic or industrial) and the degree of treatment that the wastewater receives. Table II-39 presents the concentration of inorganics for secondary and tertiary treated effluents from a sewage treatment plant whose wastewater contains both domestic and industrial wastes<sup>99</sup> and for a tertiary effluent from the South Lake Tahoe Advanced Wastewater Treatment Plant,<sup>100</sup> which receives only domestic wastewater. The low concentrations of the measured inorganic constituents is due, in addition to the high degree of treatment, to the absence of industrial wastes in the wastewater.

#### Arsenic

Arsenic occurs ubiquitously in nature and can be both acutely and chronically toxic to man. The major sources of arsenic are from pesticide manufacturing or formulating plants. It is also added in small amounts to animal feed as a growth stimulant.<sup>83</sup> The action of arsenic as a growth stimulant is indirect in that it suppresses the growth of intestinal parasites competing with the animal for food. Kopp<sup>101</sup> reported that only 87 of 1,577 surface water samples collected from 130 sampling points in the United States had detectable concentrations of arsenic, ranging from 5 to 336 ug/l, with a mean level of 64 ug/l. The arsenic concentration in most drinking water in the United States is less than 0.1 mg/l.<sup>102</sup> There have not been any adverse health effects reported from the ingestion of drinking water containing arsenic concentrations of less than 0.1 mg/l.

Although arsenic has been suspected of being carcinogenic,<sup>83,101-103</sup> evidence from human experience and animal studies indicates that arsenic is not tumorigenic at the levels normally encountered in the environment.<sup>104,108</sup>

Table II-39

## INORGANIC CONTAMINANTS IN RAW AND TREATED SEWAGE

| Constituent    | CONCENTRATION (MG/L) |                     |                     |                      |
|----------------|----------------------|---------------------|---------------------|----------------------|
|                | Raw Sewage           | Secondary Effluent* | Tertiary Effluent** | Tertiary Effluent*** |
| Antimony       |                      | ---                 | ---                 | 0.00044              |
| Arsenic        |                      | 0.00-0.01           | 0.00-0.3            | 0.005                |
| Barium         |                      | 0.0-0.02            | 0.0 <1              | ---                  |
| Bicarbonate    |                      | 200-450             | 250                 | ---                  |
| Bromine        |                      | ---                 | ---                 | 0.065                |
| Cadmium        | 0.02-0.06            | 0.011-0.130         | 0.000-0.005         | ---                  |
| Calcium        |                      | 70-110              | 80                  | ---                  |
| Cesium         |                      | ---                 | ---                 | 0.000006             |
| Chloride       |                      | 300-350             | 300-350             | ---                  |
| Chromium (+6)  | 0.05-3.80            | 0.09-0.19           | 0.00-0.04           | 0.0005               |
| Cobalt         | 0.05                 | ---                 | ---                 | 0.00033              |
| Copper         | 0.1 -1.30            | 0.09-0.39           | 0.02-0.30           | 0.0116               |
| Iron           | 0.8 -3.90            | ---                 | ---                 | 0.0003               |
| Lead           | 0.2 -0.60            | 0.00-0.05           | 0.00-0.04           | ---                  |
| Manganese      | 0.1 -0.66            | ---                 | ---                 | 0.02                 |
| Magnesium      |                      | 20-45               | 2                   | ---                  |
| Mercury        | 0.0013-0.0680        | <0.001-0.003        | 0.000-0.006         | 0.0005               |
| Nitrate (as N) | 0 -2.10              | <1                  | <1                  | ---                  |
| Nitrite (as N) | 0.02- .230           | <1                  | <1                  | ---                  |
| Phosphate      | 3.6 -20.4            | 20-45               | <1                  | ---                  |
| Potassium      |                      | 20-35               | 20-35               | ---                  |
| Rabidium       |                      | ---                 | ---                 | 0.010                |
| Scandium       |                      | ---                 | ---                 | 0.00044              |
| Selenium       |                      | 0.00-0.009          | 0.00-0.003          | 0.0005               |
| Silver         | 0.05-0.60            | 0.00-0.01           | 0.00-0.01           | 0.0004               |
| Sodium         |                      | 240-260             | 240-260             | ---                  |
| Sulfate        |                      | 270-350             | 270-350             | ---                  |
| Zinc           | 0.16-0.84            | 0.09-2.08           | 0.02-0.07           | 0.005                |

\*Conventional Secondary Treatment - Trickling Filters.

\*\*Pilot Plant - Chemical Treatment, Sedimentation, Ammonia Stripping, Recarbonation, Mixed-Media Filtration, Activated Carbon Adsorption, and Chlorination.

\*\*\*South Lake Tahoe Advanced Wastewater Treatment Plant.

Epidemiological studies in Taiwan<sup>109</sup> have reported a correlation between the increased incidence of hyperkeratosis and skin cancer with consumption of water having arsenic levels greater than 0.3 mg/l. Children in Chile were noted to have dermatological manifestations of arsenicism; the arsenic concentration in their water supply was 0.8 mg/l.

Inorganic arsenic is absorbed easily from the gastrointestinal tract, the lungs, and to a lesser extent from the skin and becomes distributed throughout the body tissues and fluids. During chronic exposure arsenic accumulates mainly in bone, muscle, and skin and to a smaller degree in liver and kidneys. After cessation of continuous exposure, arsenic excretion may last up to 70 days.<sup>110</sup> It is excreted via urine, feces, sweat and the skin.

In man, subacute and chronic arsenic poisoning may be insidious and pernicious. The only symptoms present in mild chronic poisoning are fatigue and loss of energy. The symptoms observed in more severe cases include gastrointestinal catarrh, kidney degeneration, polyneuritis, tendency to edema, bone marrow injury, liver cirrhosis and exfoliate dermatitis.<sup>83</sup>

The total intake of arsenic from food averages approximately 900 ug/day.<sup>111</sup> At a concentration of 0.1 mg/l and an average intake of 2 liters of water per day, the intake from water would not exceed 200 ug/day, or approximately 18 percent of the total ingested arsenic.

#### Barium

The solubility product of barium sulfate indicates that 1.3 mg/l of sulfate ion limits the solubility of barium to 1.0 mg/l.<sup>83</sup> For the public water supplies of the 100 largest cities in the United States, the median barium concentration was 0.05 mg/l with a range of 0.01 to 0.058 mg/l.

For 1,577 samples of surface waters collected in 130 locations in the United States, the barium concentration in 1,568 samples ranged from 2 to 340 ug/l with a mean of 43 ug/l.<sup>101</sup>

Barium is a general muscle stimulant, especially of the heart muscle. Ingestion of barium can result in serious toxic effects on the heart, blood vessels, and nerves. The fatal dose for man is considered to be from 0.8 to 0.9 grams as the chloride (550 to 600 mg Ba). Barium is capable of causing nerve block and in small or moderate doses produces transient increase in blood pressure by vasoconstriction.<sup>83</sup>

Since food does not contain any substantial quantities of barium, it enters the body primarily through air and water. The amounts of barium that can be tolerated in drinking water have not been determined and there have not been any studies of the effects of long-term feeding of barium salts from which a standard might be developed. The barium limit presented in the 1962 Drinking Water Standards was based on the standard for barium in air.<sup>112,113</sup>

#### Cadmium

Cadmium is a contaminant of zinc ore and, consequently, sources of cadmium pollution in water are waste discharges from zinc smelting and refining and from processes using zinc ore for making galvanized steel. It is also used in agricultural chemicals and fertilizers. The possibility of seepage of cadmium into groundwater from electroplating plants was reported in 1954 when concentrations ranging from 0.01 to 3.2 mg/l were recorded.<sup>114</sup> Only 40 of 1,577 surface water samples collected at 130 sampling points in the U. S. showed detectable concentrations of cadmium, ranging from 1 to 20 ug/l with a mean of 9.5 ug/l. Six samples exceeded 10 ug/l.<sup>111</sup>

The toxic effects of cadmium are well documented. There is epidemiologic evidence that cadmium may be associated with renal arterial hypertension under certain conditions.<sup>115</sup>

The most recent example of direct toxicity from drinking water is the Itai-Itai disease observed in the Jintsu River region of Japan.<sup>116</sup> The source of cadmium was the wastewater discharge from a mine which produced zinc, lead, and cadmium. The disease is clinically characterized by bone-wasting. X-rays show a uniform decrease or radiopaque substance in bone. The disease appears to selectively affect middle-aged women and causes extreme pain. Similar bone-wasting pathology was produced in rats fed river water from the contaminated area. Effective antidotal therapy has not yet been developed. A severe endemic Itai-Itai disease syndrome has been associated with the ingestion of as little as 600 ug/day.

In one instance, symptoms of violent nausea were reported for 29 school children who had consumed fruit ice sticks containing cadmium concentrations of 13-15 mg/l.<sup>117</sup> This would be equivalent to 1.3 to 3.0 mg of cadmium ingested.

The ingestion of cadmium has not been positively associated with cardiovascular disease, particularly hypertension. Although conflicting evidence has been reported for man<sup>115,118</sup> and for animals,<sup>83</sup> it is notable that hypertension has not been associated with Itai-Itai disease. Because of the cumulative retention of cadmium by liver and kidney tissue, the Drinking Water Standards limit concentrations of cadmium to 10 ug/l so that the maximum daily intake of cadmium from water will not exceed 20 ug, which is approximately one-third of the amount of cadmium derived from food.

#### Chromium

Natural waters do not usually contain appreciable quantities of chromium. Chromium enters the water environment from plating wastes, blowdown from cooling towers or from circulating water in refrigeration equipment where it is used to control corrosion.<sup>83</sup> For 1,577 surface samples

collected at 130 sampling points in the United States, 386 samples showed concentrations ranging from 1 to 112 ug/l with a mean chromium concentration of 9.7 ug/l.<sup>101</sup>

The species toxic to man is the hexavalent chromium ion. Trivalent chromium salts do not appear to be toxic; however, the trivalent form is not likely to be present in waters of pH 5 or above, due to the low solubility of the hydrated oxide. At the present time, few studies have been undertaken to determine whether or not chromium is carcinogenic. In one case, a family of four individuals reportedly drank water containing hexavalent chromium as high as 0.45 mg/l for three years without having any known adverse health effects.<sup>119</sup>

No toxic responses were produced in rats who had ingested 0.45-25 mg/l in chromate and chromic ion form from their drinking water, but significant accumulation occurred abruptly in the tissues at concentrations above 5 mg/l.<sup>120</sup> In another study, 0.033 mg of chromium from potassium bichromate per kilogram of body weight in dogs enhanced the secretory and motor activity of the intestines.<sup>83</sup> Several studies have indicated that a chromium concentration of 0.05 mg/l with an average intake of 2 liters of water per day would avoid hazard to human health.

#### Cyanide

Many types of industrial wastes contain cyanide compounds. Cyanide-bearing wastes may derive from gas works, coke ovens, scrubbing of gases in steel plants, metal plating operations and chemical industries. The toxicity of cyanides varies widely with pH, temperature, and dissolved oxygen concentration. The pH is especially important, because the toxicity of some cyanide compounds changes many-fold over the range commonly found in surface waters.<sup>83</sup> The most toxic form is hydrogen cyanide (HCN) and is the predominant species of "free cyanide" at pH levels of natural waters as well as in unusually acid waters.

Cyanide in doses of 10 mg or less is easily converted to thiocyanate in the human body and in this form is much less toxic to man. Lethal toxic effects occur only when the detoxifying mechanism is overwhelmed. It would take a single dose of 50-60 mg to be fatal for man.<sup>121</sup>

The cyanide level in water can be reduced to below the recommended limit of 0.2 mg/l by chlorinating to produce a free chlorine residual. The acute oral toxicity of cyanogen chloride, which is the chlorination product of hydrogen cyanide, is approximately one-twentieth that of hydrogen cyanide.<sup>83</sup>

### Copper

The copper concentrations in surface and groundwaters are usually less than 1 mg/l. Copper is an essential and beneficial element in human metabolism, and a deficiency results in nutritional anemia in infants. Small quantities of copper are generally regarded as nontoxic, but large doses may produce emesis and prolonged oral administration may result in liver damage.<sup>83</sup>

In one large-scale surface water study, the copper concentration of 1,577 samples collected at 130 sampling stations ranged from less than 1 ug/l to 280 ug/l with a mean concentration of 15 ug/l.<sup>101</sup> The limit of 1 mg/l for drinking water is based on considerations of taste rather than hazards to health.

### Fluoride

Fluoride is a naturally occurring mineral contaminant which is a normal constituent of all diets and an essential nutrient.<sup>169</sup> Fluoride has potential beneficial effects but in excessive amounts in drinking water supplies produces objectionable dental fluorosis that increases as a continuum with increasing fluoride concentration above the recommended control limits. The mottling of teeth, widely observed in the middle and south-west

of North America, is the only harmful effect, however, resulting from fluoride found in drinking water in the United States.<sup>170-176</sup> The fluoride concentrations excessive for a given community depend on climatic conditions because the amount of water (and consequently the amount of fluoride) ingested by children is primarily influenced by air temperature.<sup>177-180</sup>

Other expected effects from excessively high intake levels are: (a) bone changes when water containing 8-20 mg fluoride per liter (8-20 mg/l) is consumed over a long period of time;<sup>181</sup> (b) crippling fluorosis when 20 or more mg of fluoride from all sources is consumed per day for 20 or more years;<sup>182</sup> (c) death when 2,250-4,500 mg of fluoride (5,000-10,000 mg sodium fluoride) is consumed in a single dose.<sup>181</sup>

#### Hardness

In 1960, Schroeder<sup>122,123</sup> in examining the 1949-1951 vital statistics found that the average annual age-adjusted death rate from cardiovascular disease in the U. S. varied from 290/100,000 in New Mexico to 511/100,000 in South Carolina. He compared these figures with data from the United States Geological Survey on the weighted average hardness in water for public consumption. He found a negative correlation between deaths from cardiovascular disease and hardness in the water supply. Since that time there have been a number of studies in various parts of the world that, for the most part, substantiate this relationship.<sup>124,127</sup>

The major cations in hard water are calcium and magnesium. Not surprisingly, several studies have been done on their possible role in human disease. Hankin et al.<sup>128</sup> concluded that water contributes about 7 percent of calcium, and 12 percent of magnesium, to the total human diet. These are modest but perhaps not inconsiderable amounts, enough to possibly affect the myocardial electrolyte balance or work load.<sup>129</sup> Schroeder et al.<sup>130</sup> found

that supplying rats from time of weaning with 200 ppm calcium in their drinking water, along with several dissolved trace elements, significantly reduced the levels of renal cadmium, copper, and zinc, and partly suppressed the incidence of hypertension in the females. Douglas and Langford<sup>131</sup> in an attempt to correlate calcium and hypertension, found that rats on a low calcium diet and saline water did develop higher blood pressure than controls. Yacowitz et al.<sup>132</sup> in studying human volunteers, found that increased calcium ingestion significantly lowered serum cholesterol and triglyceride values.

The other "hardness" element, magnesium, has long been considered to play a role in cardiovascular health. Two studies in 1967<sup>133,134</sup> demonstrated that serum cholesterol and serum magnesium were inversely related and that high levels of dietary magnesium could prevent the development of atherosclerotic lesions in the rat.

Goldsmith and Goldsmith<sup>135</sup> have reported that women taking birth control pills have lower levels of serum and urinary magnesium than ovulating women. Goldsmith and Baumberger<sup>136</sup> demonstrated this also for rats. Since women taking birth control pills allegedly have higher than normal rates of thromboembolic disease and since magnesium has been directly related to clotting time of blood, Goldsmith and Goldsmith speculate that magnesium could possibly be the factor in water which is related to human health.

A third hardness element, sodium, is discussed later in this document.

The primary relationship between water hardness and human disease appears to be an increased incidence of cardiovascular disease among people living in areas serviced with soft water. However, any review would be incomplete if the observed relationship between infant mortality and water hardness was not mentioned. A negative correlation between water hardness

and infant mortality was pointed out by Morris et al.<sup>124</sup> and Crawford et al.<sup>125</sup> More recently, Crawford et al.<sup>137</sup> reported a detailed study of these relationships as they occurred in England and Wales. These workers point out that it has been known for a long time that social conditions have a significant impact on infant mortality; however, when these factors are accounted for there appears a significant negative correlation between neonatal mortality and water hardness and with water calcium in particular. Still-birth rates did not appear to be significantly associated with water hardness. The authors were not able to explain the reason for the relationship between neonatal mortality and water hardness. They did not feel it was calcium per se because infants drink milk which has a good deal of calcium present. They suggested the more corrosive soft water might increase the lead content of drinking water in the low calcium areas but presented no evidence to support this notion.

As early as 1957, Penrose<sup>138</sup> suggested that anencephalus might be associated with the amount of calcium in water supplies. This was only a suggestion and Penrose did not elaborate further. In 1970 Fedrick<sup>139</sup> examined the relationship between anencephalus occurring among children born in certain areas of the United Kingdom and water hardness in those areas. A negative correlation was observed with total hardness, pH, calcium content, and a lesser correlation with sodium. In this report Fedrick also pointed out that a significantly higher incidence of death from spina bifida (a disease related to anencephalus) occurs in those states of the United States that have softer water (high incidence areas have average water hardness of  $88.6 \pm 11.2$  mg/l; low incidence areas have average water hardness of  $156 \pm 16.5$  mg/l). The reason for these correlations is unknown. In the study by Crawford et al.<sup>137</sup> dealing with infant mortality

and water hardness, the relationship between the incidence of anencephaly in perinatal deaths in England and Wales and water hardness was determined. Again, a negative correlation was observed; however, the correlation coefficients were considerably smaller than those seen between total infant mortality and water hardness. This would tend to corroborate the previous findings of Fedrick et al. Again, no adequate reason for this relationship was offered.

### Lead

Some of the principal sources of lead in the environment are agriculture, paint, smelters, metal salvage operations, and leaded gasoline. Lead is well known for its toxicity in both acute and chronic exposures. Acute lead toxicity is characterized by burning in the mouth, severe thirst, inflammation of the gastrointestinal tract accompanied by vomiting and diarrhea. Chronic toxicity produces anorexia, nausea, vomiting, severe abdominal pain, paralysis, mental confusion, visual disturbances, anemia, and convulsions.<sup>121</sup>

In one study involving several surface waters, 11.3 percent of the samples collected showed detectable concentrations of 0.002 to 0.140 mg/l with a mean of 0.023 mg/l.<sup>101</sup> Because the general population is exposed to dangerously high levels of lead through food and air, lead in water must be limited to low concentrations.

Lead intoxication is unlikely to occur at a long-time intake level of 0.6 mg of lead per day.<sup>83</sup> The normal intake from food is approximately 0.3 mg/day. Therefore, the recommended maximum level of 0.05 for public water sources would only add 0.1 mg/day, assuming a two liter daily consumption of water.

### Mercury

It has been estimated that in the United States in 1967, the amount of mercury wasted directly to surface waters was 639 tons.<sup>140</sup>

Gavis et al.<sup>141</sup> estimate that about 500,000 tons of mercury have been released from the lithosphere during this century as a result of human activities. Although the demand for mercury has been decreasing slightly the past few years, approximately 2,000 tons was consumed in the U. S. in 1971. Dissipative uses (infeasible to recycle) of mercury account for approximately 25 percent of this total. The dissipative uses of mercury include paints, agricultural seed dressings, catalysts, dental fillings, pharmaceuticals and fungicides. In addition to this, a great deal of the potentially recyclable mercury (batteries, switches, thermometers, fluorescent tubes, etc.) ended up in landfills, dumps, and incinerators, thus making its way to the environment.

A study by the U.S. Geological Survey in 1970 indicated that the mercury content of surface waters in the United States rarely exceeds 5.0 ug/l and is usually less than 1.0 ug/l.<sup>142</sup> However, rivers draining basins having worked or unworked mercury deposits may contain as much as 80 ug/l. In general, the mercury in these waters is associated with suspended particles and the mercury concentrations decrease markedly downstream from the deposit. Because of the tendency of mercury to adsorb readily on a variety of materials, stream sediments are likely to contain substantially higher mercury concentrations than the water itself.

The mercury content in groundwater is normally less than 0.1 ug/l. In areas containing cinnabar or other mercury-containing minerals, however, relatively high concentrations of mercury may be present.

Although not much data have been generated on the mercury concentrations in raw sewage, it appears that domestic sewage normally contains less than 5.0 ug/l and many of these wastes have mercury levels of less than 0.1 ug/l.<sup>143,144</sup> An extensive study of industrial waste discharges determined

that approximately 30 percent of the wastes had mercury concentrations greater than 10 ug/l.<sup>140</sup>

Inorganic mercury accumulates in the human body and concentrates most highly in the liver and kidney. Elimination from the brain, thyroid, and testis is slow, however, so that chronic exposure can result in mercury accumulation in these organs. Inorganic mercury compounds are excreted at a moderate rate (biological half-life is 30-60 days) as long as the dose given is not large enough to injure the excretory organs.

Mercury poisoning may be acute or chronic. Generally, mercurous salts are less soluble in the digestive tract than mercuric salts and are consequently less acutely toxic. For man the fatal oral dose of mercuric salts ranges from 20 to 30 mg.<sup>83</sup> Chronic poisoning from inorganic mercury compounds has most often been associated with industrial exposure, whereas that from the organic compounds has been the result of accidents or environmental contamination.

Acute mercury toxicity is characterized by severe nausea, vomiting, abdominal pain, bloody diarrhea, kidney damage, and death usually within ten days. Chronic exposure is characterized by inflammation of mouth and gums, swelling of salivary glands, excessive salivation, loosening of teeth, kidney damage, muscle tremors, spasms of extremities, personality changes, depression, irritability, and nervousness.<sup>121</sup> Certain antidotes have been found to be effective in treating cases of inorganic mercury poisoning. These antidotes, such as British-anti-lewisite and penicillamin, can prevent further deterioration but cannot cure neurological symptoms.<sup>145</sup>

#### Nitrate-Nitrite

Nitrates may find their way into surface and groundwaters from various sources, such as agricultural drainage, domestic sewage, and

leaching from naturally occurring nitrogenous formations. Serious and sometimes fatal poisonings in infants have occurred following ingestion of well waters shown to contain nitrate concentrations greater than 10 mg/l as nitrogen. This was first associated with a temporary blood disorder in infants called methemoglobinemia in 1945.<sup>146</sup> Since then, approximately 2,000 cases of this disease have been reported from private water supplies in North American and Europe, with a fatality rate of 7-8 percent.<sup>83</sup>

Shallow wells on farms and in rural communities often have high nitrate concentrations and increasing concentrations of nitrate in streams from farm tile drainage have been shown in regions of intense fertilization and farm crop production.<sup>147</sup>

The nitrate levels in many public water supplies in the United States are routinely higher than the standard of 10 mg/l; however, there has been only one reported case of methemoglobinemia associated with a public water supply.<sup>148</sup> Many small children have drunk water with nitrate-nitrogen concentrations greater than 10 mg/l without developing the disease.

Methemoglobinemia is largely confined to infants less than three months old, and is dependent upon the bacterial conversion of the relatively innocuous nitrate ion ( $\text{NO}_3$ ) to nitrite ( $\text{NO}_2$ ). When ingested the nitrates may be reduced to nitrite within the digestive tract of the infants. When absorbed from the digestive tract, the nitrites react with hemoglobin to form methemoglobin, a form of hemoglobin which is incapable of efficiently transporting oxygen to the tissues.<sup>149</sup> When large amounts of methemoglobin are present in infants, their skin and mucous membranes take on a dusky or bluish appearance and they may become acutely or, on rare occasions, fatally ill.

Older children and adults do not seem to be affected. The susceptibility of infants may be due to the stomach pH in infants, which is higher than

that of adults and can permit growth of bacteria that can reduce nitrate to nitrite, and infant gastrointestinal illness that may permit reduction of nitrate to nitrite to occur higher in the intestinal tract.<sup>150,151</sup>

Nitrites react with secondary amines to form carcinogenic nitrosamines. A no-effect level for nitrite toxicity has not been established. Nitrites have a more rapid and pronounced effect than nitrate. Concentrations in raw water are usually less than 1 mg/l as N and chlorination to a free chlorine residual converts nitrite to nitrate.<sup>83</sup>

On the basis of adverse physiological effects on infants and because the defined treatment process has no effect on the removal of nitrate, it is recommended by the Committee on Water Quality Criteria<sup>83</sup> that the nitrate-nitrogen concentration in public water supply sources not exceed 10 mg/l and the nitrite-nitrogen concentration in public water supply sources not exceed 1 mg/l.

#### Radiologic

Radioactivity in water systems may be broadly categorized as either naturally occurring or man-made. Of the naturally occurring radionuclides likely to be in water systems, radium-226 is of primary concern although other terrestrial alpha particle emitters and radium-228 also may be present. Radium is usually not present in significant amounts in surface waters but occurs in groundwater as a result of geological conditions.

Man-made radioactivity may enter water systems from a variety of sources. Past deposition of fallout material from nuclear weapons tests, particularly strontium-90 and tritium, is probably the most important source of contamination. The national use of radionuclides in medicine and industry and the utilization of nuclear power to supply energy needs may also lead to some radioactivity entering the aquatic environment.

For 25 years or more radiation protection limits have been based on the assumption that detrimental effects on health from radiation are proportional to the dose received. Estimates of the possible health effects from maximum contaminant levels of radioactivity in drinking water have been based on the assumption that there is no harmless dose from ionizing radiation and that the detrimental effects on health produced will be proportional to the dose equivalent delivered to a reference man drinking two liters of water per day.

As a result of geological conditions, radium concentrations in public water supply systems range from less than 0.1 pico Curies per liter to over 60 pico Curies per liter (pC/l).

Small quantities of radium are also present in many foods with the average daily intake being equal to or exceeding 1 pC/l. The U.S. Environmental Protection Agency has proposed a maximum contaminant level for radium in drinking water of 5 pC/l. Based on the Agency's analysis of a recent National Academy of Science study on radiation effects, the potential risk due to radium drinking water ingestion at 5 pC/l is estimated to be between 0.7 and 3 fatal cancers annually per million exposed persons.

The Agency has estimated that the total dose from man-made radioactivity in water supply systems is not likely to result in a total body or organ dose to any individual that exceeds 4 millirem per year and have proposed this number as a maximum contaminant level of beta particle and photon radioactivity from man-made radionuclides.

For man-made photon and beta particle radiation to the total body, the potential risk of fatal cancer from a dose equivalent rate of 4 millirem per year is about 0.4 to 2 cases per million exposed persons per year with risks from lower dose rates proportionally smaller. Additional health risks of genetic effects and non-fatal cancers are each estimated to be comparable

to that for cancer fatality. Partial body irradiation is common for ingested radionuclides since they may, like radium, be largely concentrated in a particular organ system. In such cases, the estimated risk per rem varies depending on the radio-sensitivity of the organs at risk. For example, the estimated number of thyroid cancers due to the thyroid gland receiving 4 millirem per year continuously range from about 0.2 to 0.5 per year per million exposed persons (averaged over all age groups). The fatality rate of thyroid cancers varies with age, from nearly zero for children and young adults to about 20 percent for persons well past middle age.<sup>183</sup>

### Selenium

Elemental selenium is highly insoluble and requires oxidation to selenite or selenate before appreciable quantities appear in water. The reaction may be catalyzed by certain soil bacteria and the ratio between selenium species is pH dependent. To date no systematic investigation of the forms of selenium in excessive concentrations in drinking water sources has been carried out.

Selenium toxicity is similar to that of arsenic and can cause death. Acute selenium toxicity is characterized by nervousness, vomiting, cough, dyspnea, convulsions, abdominal pain, diarrhea, hypotension and respiratory failure. Chronic exposure leads to marked pallor; red staining of fingers, teeth and hair; debility; depression; epistaxis; gastrointestinal disturbances; dermatitis; & irritation of the nose and throat.<sup>83</sup> Both acute and chronic exposure can cause odor on the breath similar to garlic.<sup>121</sup> There has only been one case of selenium toxicity from a water source, and it resulted from a three-month exposure to well water that had a selenium concentration of 9 mg/l.<sup>152</sup>

Silver

The solubility of silver in water ranges from 0.1 to 10 mg/l depending upon pH and chloride concentration.<sup>153</sup> In one study<sup>101</sup> less than ten percent of 1,577 samples collected from 130 sampling points in the U. S. had detectable concentrations (0.1 ug/l) and the maximum concentration in any sample was 38 ug/l.

Silver can cause a permanent gray discoloration of skin, eyes, and mucous membranes. The amounts of silver required to produce this condition (argyria, argyrosis) are not known, but any quantity of silver greater than one gram (from injected agarsphenamine) will cause argyria in an adult.<sup>83</sup>

Sodium

Sodium salts are ubiquitous in the water environment. They are highly soluble and their concentrations vary considerably in natural waters. Sodium compounds are introduced into the water environment with domestic and industrial sewage effluents and deicing salts. Groundwaters are often higher in sodium content than surface waters. The removal of sodium is costly and is not common in public water supply treatment.

The sodium content of the 100 largest public water supplies in the U. S. ranged from 1.1 to 177 mg/l with a median sodium content of 12 mg/l.<sup>154</sup> It should be noted that most of these were surface water supplies. For a healthy individual the sodium intake may average 6.0 g/day without adverse health effects.

Sodium has long been linked with hypertension<sup>155,156</sup> and physicians recommend restricted sodium intakes for persons suffering from hypertension, edema associated with congestive cardiac failure, and women with toxemias of pregnancy. The sodium intake for sources other than water recommended for very restricted diets is 500 mg/day. Diets for these individuals permit sodium concentrations of 20 mg/l in drinking water and water used for cooking.<sup>83</sup>

A retrospective study by Wolf and Esmond<sup>157</sup> indicated that increased deaths from heart disease may be related to increased sodium concentrations in drinking waters. Although this work was not definitive, it does lend support to the limiting of sodium in drinking waters.

#### Metal Carcinogens

The field of metal carcinogenesis is complicated. Although many elements are claimed to be carcinogens, there is adequate information for only a very few. Some of the metals which investigators have suggested may be potentially carcinogenic in drinking water under certain circumstances are arsenic, beryllium, cadmium, chromium, nickel, and selenium.

At present all these metals are being tested by EPA<sup>184</sup> for mutagenicity; those which show mutagenic effects may be subsequently tested for carcinogenicity. The available information indicates that pure metallic nickel and many of its compounds and metallic cadmium and some inorganic forms can be considered as causes of cancer.<sup>185</sup> Much more experimental work appears to be required to establish, without doubt, the carcinogenicity of the other metals listed. Some, such as arsenic, have been associated with the occurrence of cancer, however, their exact role as carcinogens has not been determined.

The relationship between metal ion content in urban drinking water and cancer mortality was studied by Granata et al.<sup>186</sup> within the 14 districts forming the Commune of Pesaro, Italy. The metals sampled for included iron, magnesium, aluminum, manganese, nickel, lead, copper, zinc, chromium, cadmium and tin. The results of the study indicated that a relationship between cancer mortality and drinking water metal ion content would appear to exist. The authors, however, cautioned that the very limited range of the work forbade the drawing of any clear conclusions.

Organo-Metallic Compounds

For most trace metals in water only a small fraction are found as the free metal ion; most of the metals exist in the form of hydroxo or other soluble complexes, or in association with colloidal organic or inorganic impurities suspended in the water. Many organic species are capable of complexing metals and altering their solubility and chemical reactivity. In waters containing appreciable concentrations of organic material, organo-metallic complexes are found; tannic acid and other products of vegetative decay have been shown to complex ferrous iron and interfere with Fe (II) oxidation and its subsequent removal from groundwater.<sup>187</sup>

The classic example of organo-metallic complex formation is the alkylation of metals particularly the methylation of heavy metals. The methylation of mercury is probably the most common example of this process. It is possible to predict, however, which other heavy metals can be transformed in the same way as mercury. For example, one can predict that tin, palladium, platinum, gold, and thallium will be methylated in the environment, but lead, cadmium, and zinc will not be methylated. This is because the latter alkylmetals are not stable in aqueous systems. Arsenic compounds also are reduced and methylated by anaerobic bacteria to give dimethylarsine and trimethylarsine as volatile products of extreme toxicity.<sup>188</sup>

Alkylated metals are of particular interest because of their strong potential as neuro toxins. Bioaccumulation of essential metals has been well studied, and it is clear that a variety of natural chelating agents have been evolved to selectively transport metals across cell membranes. For the toxic elements the principles for bioaccumulation are not well understood, but the synthesis and transport of metal alkyls seems to be the key to the problem of getting toxic elements into the cell. Most metal alkyls

are more soluble in organic solvents than in water and so they readily partition into the lipid regions of the cell. The nonpolarity of metal alkyls probably represents the basic property which allows these molecules to accumulate in the central nervous system of higher animals. Once the metal alkyl is present, solubility allows it to concentrate in areas where it can do the most damage.<sup>188</sup> It is clear that the ingestion of methylmercury-contaminated foods by humans leads to the synthesis of methylmercury chloride in the stomach, and that methylmercury chloride is very nonpolar so it is easily transported into the blood stream.<sup>189</sup> The distribution of methylmercury in animals is characteristically different from that of inorganic mercury, in that alkylmercury compounds have a tendency to partition into the lipids, or hydrophobic regions of the cell.<sup>190</sup> Post-mortem examinations of victims of the Minamata disaster revealed that extensive damage to the central nervous system had occurred. Widespread lysis of cell membranes, especially membranes of neuroglia and granule cells, occurred, according to the histological studies of Takeuchi.<sup>191,192</sup>

#### Assessment of Health Hazards at Low Effect Levels

The estimation of low effect levels of carcinogens and mutagens poses a difficult problem. For most biological effects it is assumed from experience that a threshold and a no-effect level exists. Threshold dose levels in mutagenesis have been questioned on the basis of studies of radiation-induced mutations and because mutations may even result from a change in only one base pair of DNA. A true no-effect level, however, cannot be observed experimentally. Any observed level has meaning only for a particular sample size.

The observation of "no-effect" for a test group may occur for one of two reasons: (1) The dosage level may indeed be below the theoretical

no-effect level; or (2) The number in the test group may have been inadequate to give a significantly high probability of detecting a biologically important change. Similarly, for a graded response, a small test group sample may fail to provide enough statistical precision to detect a change from baseline, whereas a larger sample may.

Although the lack of relevant biological data has made the estimation of risks from low-level carcinogen exposure difficult, the toxicologist must assess the risks associated with different levels of exposure. The first method of assessing the health hazards for carcinogens at very low levels of exposure was that proposed by Mantel and Bryan in 1961.<sup>193</sup> They took the position that the problem of determining what dose levels of an agent are safe, e.g., non-carcinogenic, cannot be resolved unless one first defines some level of permissible risk, no matter how small, rather than insisting on absolute safety. Furthermore, because of practical considerations and statistical variation, the determination of low-risk dose levels--for example, 1/100 million--cannot be made directly but only by extrapolation from observations at much higher levels. They describe a conservative approach for accomplishing this. In addition to an arbitrary definition of "virtual safety," it is necessary to define an arbitrarily high statistical assurance level and a rule for extrapolation by use of an arbitrarily shallow slope. They defined "virtual safety" as a probability of carcinogenicity of less than 1/100 million at a statistical assurance level of 99 percent and a conservative probit slope of 1 probit per 10-fold dose increase.

The choice of 1/100 million is arbitrary. The choice of a 99 percent statistical assurance level is, of course, also arbitrary, but it is obviously desirable for this level to be as high as possible. However, it may be that 90 percent would be adequate. The slope of a probit per 10-fold dose increase has been justified on the basis that the slope of the dose-response

curve near zero is bound to be less than the slope in the range of actual observation. The choice of 1 probit rather than 1 logit per 10-fold dose increase cannot be justified on the basis of available knowledge, but is an attempt to avoid being too conservative. Additional factors that are known to play a role in the determination of actual hazard are: (1) the probabilities that an individual will experience a given exposure; (2) the likelihood that the risk being studied will be overshadowed by some other competing risk and therefore will not have become fully operative; and, related to this, (3) the fact that the age of occurrence of cancer must also be considered when evaluating the hazard to health, especially as there is a long latent period for carcinogenesis, which usually gets longer as the exposure gets smaller.

Concern for this last factor is reflected in the approach to the assessment of health hazards of carcinogenesis at very low levels of exposure by Albert & Altshuler.<sup>194</sup> In their view, characterization of the carcinogenic response solely from the standpoint of incidence is not complete, since it ignores the age at which cancers occur. They point out that "the impact of cancer depends on the age of occurrence and is considerably less important in the very aged than in the young." In order to compare the dose-response relationships for cancer incidence with those for the age of occurrence of cancer and for the amount by which cancer shortens the life span, both in the exposed population as a whole and in the individuals who develop cancer, they developed a mathematical model. This is based on earlier work of Blum on the development of skin tumors in mice exposed to chronic ultraviolet irradiation, and on the work of Druckrey on a variety of chemical carcinogens and target tissues in rodents. They have extended the Druckrey formula and demonstrated its applicability to radiation cancer in mice exposed to

radium-226 and to the tumorigenic response to cigarette smoking in man. The basic relationship is that  $Dt^n = k$  where "k" is a constant and "n" is always greater than 1, "D" is the average dose and "t" is the time that elapses before the occurrence of tumors.

The problems that Albert & Altshuler are concerned with relate to shape of the dose-response curve with respect to both time of cancer occurrence and incidence of tumors at very low doses, the variations in the value of "n" for different compounds, and the fact that at high values of "n", for practical purposes, the time of occurrence is independent of dose. Much more quantitative data on incidence and on the time of occurrence of tumors are needed for proper evaluation of the Albert-Altshuler approach to calculation of carcinogenic risks at low dose levels. Certainly, the experimental designs needed for assessing the health hazards of carcinogens at low levels of exposure are quite different from those needed to determine whether or not a substance is a carcinogen. Such designs must emphasize what has been, for practical purposes, ignored in the past, namely, a provision for determining with greater accuracy the time at which tumors appear, so as to have a quantitative tumor-time-dose relationship.

A third method for assessing the health risk from exposure to chemical agents at low levels has been proposed by the Food and Drug Administration Advisory Committee on Protocols for Safety Evaluation.<sup>195</sup> They propose that a fairly conservative estimate of the risk can be made by employing the one-hit (one-particle) theory. This theory states that for low dosages, if an experimental dosage is divided by a factor f, then its upper confidence level of the risk is also divided by the factor f. Such an approach will often result in near-zero dosages for extremely small acceptable risks. For example, if zero deleterious responses were observed in 450 animals at a dose d, it can be stated with 99 percent confidence that the true response

rate is less than 1 percent (one out of 100). The predicted dose for risk of one out of 1,000,000 would then be  $10^{-4}$  d.

An alternate means of estimating low risk exposure levels involves extrapolation from parametric dose-response curves. Many different empirical mathematical models may be fitted to a set of experimental data.<sup>196</sup> The probit and logistic curves have been commonly used in biology, for example, and both curves may fit equally well in the region of experimental observations (2-98 percent response range) but give widely different estimates for extrapolated responses. For example, the probit curve will predict a dosage level approximately 140-times higher than the logistic curve for extrapolation to a dosage expected to elicit one response in 1,000,000 animals. In some instances<sup>197</sup> linear dose-response curves have been reported; often, however, these cover only a relatively limited response range.

Dose-response information is a valuable tool for assessing the safety of a chemical compound. Estimates of low effect levels are part of the information leading to the ultimate designation of safe and acceptable levels. The statistical problems of extrapolation from experimental dose levels to very low levels and the estimation of appropriate errors are particularly troublesome but can be handled if care is taken in the design and analysis of the experiments and the interpretation of results.

Without supporting experimental evidence, however, statistical analysis will never be capable of making the critical extrapolation from laboratory animals to man.<sup>198,199</sup>

#### Interactions Between Chemicals: Antagonism and Synergism

When attempting to determine the hazard to health from environmental chemicals, attention must be given to possible modifying effects, antagonism

and synergism, which may occur when combinations of these chemicals interact. In antagonism, the concurrent presence of a toxicant and non-toxicant in the body may result in a decrease in the toxicity of the toxicant. A common example of antagonism occurs in the treatment of pesticide poisoning, where the administration of a drug may decrease the toxic action of a pesticide by increasing the metabolism of the chemical into a less toxic compound.

In synergism, either between two toxicants or between a toxicant and a non-toxicant, the interaction in the body may produce a potentiating effect that is much greater than the sum of the separate effects of the toxicants.

Synergistic effects are of particular importance in the estimation of no-effect threshold levels for carcinogens and mutagens. At present there are few guidelines to assist in deciding which of the myriad of possible combinations of compounds should be tested for synergistic or enhancing interactions. As yet, no acceptable short-term tests for cocarcinogenesis have been developed although long-term tests can be modified since the effect is noted when the latency period is shortened.

It is known that precancerous changes associated with cocarcinogenesis are reversible. Therefore, their early recognition and attempts at their control in the environmental situation are of utmost concern.

Carcinogenesis and mutagenesis are dependent, in part, on overcoming normal protective mechanisms that rid the body of foreign materials. That these mechanisms can be impaired on exposure to various environmental toxicants has been well documented.

The process of enzyme induction, a mechanism which allows for ready elimination of foreign chemicals, is not always to the advantage of the organism. There are groups of compounds that either induce enzymatic activities in mammalian tissues which are likely subsequently to activate compounds to carcinogenic or mutagenic derivatives or inhibit enzymatic

activities which are capable of deactivating the carcinogenic or mutagenic potential of chemicals.

The process of DNA repair, which normally is quite efficient in excising altered nucleotide sequences, can be inhibited by certain chemicals. These have, so far, not been studied in detail, and it is likely that some environmental chemicals will be found to block repair enzymes.

Nutritional factors are important in carcinogenesis since they affect the outcome of tumor development in many ways. Considerable attention has been paid to the process of enzyme induction, which depends on adequate intake of protein, essential lipid components, members of the vitamin B family and vitamin E. However, when the requirements for enzyme induction are met, it cannot be predicted if a carcinogen requiring metabolic activation will be more or less potent since multiple enzymes may be involved.

Chemicals that cause enzyme induction may be dietary contaminants, for example, the frequently discussed chlorinated hydrocarbons (DDT) or prescription drugs (barbiturates). They are usually not present in high enough concentrations to make a significant contribution to enzyme induction.

When requirements for enzyme induction are not met, the results of exposure to a carcinogen may be unpredictable; the usual target tissue may not be affected but a different organ may respond by developing cancer.<sup>199,200</sup>

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APPENDIX A

ORGANIC COMPOUNDS IDENTIFIED IN DRINKING WATERS  
IN THE UNITED STATES

ORGANIC COMPOUNDS IDENTIFIED IN DRINKING WATER  
IN THE UNITED STATES  
(MARCH 15, 1975)

|     |                             |     |                              |
|-----|-----------------------------|-----|------------------------------|
| 1.  | acenaphthene                | 47. | chloromethyl ethyl ether     |
| 2.  | acenaphthylene              | 48. | m-chloronitrobenzene         |
| 3.  | acetaldehyde                | 49. | 1-chloropyropene             |
| 4.  | acetic acid                 | 50. | 3-chloropyridine             |
| 5.  | acetone                     | 51. | o-cresol                     |
| 6.  | acetophenone                | 52. | crotonaldehyde               |
| 7.  | acetylene dichloride        | 53. | cyanogen chloride            |
| 8.  | aldrin                      | 54. | cyclopheptanone              |
| 9.  | atrazine                    |     |                              |
| 10. | (deethyl) atrazine          | 55. | DDE                          |
|     |                             | 56. | DDT                          |
| 11. | barbital                    | 57. | decane                       |
| 12. | behenic acid, methyl ester  | 58. | dibromobenzene               |
| 13. | benzaldehyde                | 59. | dibromochloromethane         |
| 14. | benzene                     | 60. | dibromodichloroethane        |
| 15. | benzene sulfonic acid       | 61. | di-t-butyl-p-benzoquinone    |
| 16. | benzoic acid                | 62. | dibutyl phthalate            |
| 17. | benzopyrene                 | 63. | 1,3-dichlorobenzene          |
| 18. | benzothiazole               | 64. | 1,4-dichlorobenzene          |
| 19. | benzothiophene              | 65. | dichlorodifluoroethane       |
| 20. | benzyl butyl phthalate      | 66. | 1,2-dichloroethane           |
| 21. | bladex                      | 67. | 1,1-dichloro-2-hexanone      |
| 22. | borneol                     | 68. | 2,4-dichlorophenol           |
| 23. | bromobenzene                | 69. | dichloropropane              |
| 24. | bromochlorobenzene          | 70. | 1,3-dichloropropene          |
| 25. | bromodichloromethane        | 71. | dieldrin                     |
| 26. | bromoform                   | 72. | di-(2-ethylhexyl) adipate    |
| 27. | bromoform butanal           | 73. | diethyl benzene              |
| 28. | bromophenyl phenyl ether    | 74. | diethyl phthalate            |
| 29. | butyl benzene               | 75. | di (2-ethyl hexyl) phthalate |
| 30. | butyl bromide               | 76. | dihexyl phthalate            |
|     |                             | 77. | dihydrocarvone               |
| 31. | camphor                     | 78. | di-isobutyl carbinol         |
| 32. | ε-caprolactam               | 79. | di-isobutyl phthalate        |
| 33. | carbon dioxide              | 80. | 1,2-dimethoxy benzene        |
| 34. | carbon disulfide            | 81. | 1,3-dimethylnaphthalene      |
| 35. | carbon tetrachloride        | 82. | 2,4-dimethyl phenol          |
| 36. | chlordan(e)                 | 83. | dimethyl phthalate           |
| 37. | chlordene                   | 84. | dimethyl sulfoxide           |
| 38. | chlorobenzene               | 85. | 4,6-dinitro-2-aminophenol    |
| 39. | 1,2-bis-chloroethoxy ethane | 86. | 2,6-dinitrotoluene           |
| 40. | chloroethoxy ether          | 87. | dioctyl adipate              |
| 41. | bis-2-chloroethyl ether     | 88. | diphenylhydrazine            |
| 42. | 2-chloroethyl methyl ether  | 89. | dipropyl phthalate           |
| 43. | chloroform                  | 90. | docosane                     |
| 44. | chlorohydroxybenzophenone   | 91. | n-dodecane                   |
| 45. | bis-chloroisopropyl ether   |     |                              |
| 46. | chloromethyl ether          | 92. | elcosane                     |

93. endrin  
94. ethanol  
95. ethylamine  
96. ethyl benzene  
97. 2-ethyl-n-hexane  
98. cis-2-ethyl-4-methyl-1,3-dioxolane  
99. trans-2-ethyl-4-methyl-1,3-dioxolane  
100. o-ethyltoluene  
101. m-ethyltoluene  
102. p-ethyltoluene  
  
103. geosmin  
  
104. heptachlor  
105. heptachlor epoxide  
106. 1,2,3,4,5,7,7-heptachloronorbornene  
107. hexachlorobenzene  
108. hexachloro-1,3-butadiene  
109. hexachlorocyclohexane  
110. hexachloroethane  
111. hexachlorophene  
112. hexadecane  
113. 2-hydroxyadiponitrile  
  
114. indene  
115. isoborneol  
116. isodecane  
117. isophorone  
118. 1-isopropenyl-4-isopropylbenzene  
119. isopropyl benzene  
  
120. limonene  
  
121. p-menth-1-en-8-ol  
122. methane  
123. methanol  
124. 2-methoxy biphenyl  
125. o-methoxyphenol  
126. methyl benzoate  
127. methyl benzothiazole  
128. methyl biphenyl  
129. 3-methyl butanal  
130. methyl chloride  
131. methylene chloride  
132. methyl ethyl benzene  
133. methyl ethyl ketone  
134. 2-methyl-5-ethyl-pyridine  
135. methylindene  
136. methyl methacrylate  
137. methyl naphthalene  
138. methyl palmitate  
139. methyl phenyl carbinol  
140. 2-methylpropanal  
141. methyl stearate  
  
142. methyl tetracosanoate  
  
143. naphthalene  
144. nitroanisole  
145. nitrobenzene  
146. nonane  
  
147. octadecane  
148. octane  
149. octyl chloride  
  
150. pentachlorobiphenyl  
151. pentachlorophenol  
152. pentachlorophenyl methyl ether  
153. pentadecane  
154. pentane  
155. pentanol  
156. phenyl benzoate  
157. phthalic anhydride  
158. piperidene  
159. propanol  
160. propazine  
161. propylamine  
162. propylbenzene  
  
163. simazine  
  
164. 1,1,3,3-tetrachloroacetone  
165. tetrachlorobiphenyl  
166. 1,1,1,2-tetrachloroethane  
167. tetrachloroethylene  
168. tetradecane  
169. tetramethyl benzene  
170. thiomethylbenzothiazole  
171. toluene  
172. trichlorobenzene  
173. trichlorobiphenyl  
174. 1,1,2-trichloroethane  
175. 1,1,2-trichloroethylene  
176. trichlorofluoromethane  
177. 2,4,6-trichlorophenol  
178. n-tridecane  
179. trimethyl benzene  
180. 3,5,5-trimethyl-bicyclo  
(4,1,0) heptene-2-one  
181. trimethyl-trioxo-hexahydro-  
triazine isomer  
182. triphenyl phosphate  
  
183. n-undecane  
  
184. vinyl benzene  
  
185. o-xylene  
186. m-xylene  
187. p-xylene

WATER SUPPLIES FROM WHICH ORGANIC  
COMPOUNDS HAVE BEEN IDENTIFIED

| CITY                   | NO. OF COMPOUNDS |
|------------------------|------------------|
| Ames, Iowa             | 19               |
| Cincinnati, Ohio       | 28               |
| Evansville, Indiana    | 12               |
| Kansas City, Kansas    | 9                |
| New Orleans, Louisiana | 89*              |
| Washington, D. C.      | 27               |

\*Represents approximately 2% by weight of the total amount of organic compounds in the drinking water.

CLASSIFICATION OF CHEMICALS ACCORDING TO  
CHEMICAL CHARACTERISTICS

## I. Aliphatics

|                           |    |
|---------------------------|----|
| Halogenated - - - - -     | 33 |
| Non-Halogenated - - - - - | 38 |
| TOTAL - - - - -           | 71 |

## Aromatics

|                           |    |
|---------------------------|----|
| Halogenated - - - - -     | 23 |
| Non-Halogenated - - - - - | 68 |
| TOTAL - - - - -           | 91 |

Total Number of Compounds - - - - - 162

II. Total Halogenated - - - - - 56

Total Non-Halogenated - - - - - 106

Total Number of Compounds - - - - - 162

SUMMARY OF ACUTE TOXICITY OF ORGANIC  
COMPOUNDS IDENTIFIED IN DRINKING WATER

## A. Total List (162 compounds)

| <u>Category*</u> | <u>Description</u> | <u>Number</u> | <u>Percent</u> |
|------------------|--------------------|---------------|----------------|
| 6                | Super Toxic        | 1             | 1              |
| 5                | Extremely Toxic    | 6             | 3              |
| 4                | Very Toxic         | 41            | 25             |
| 3                | Moderately Toxic   | 51            | 32             |
| 2                | Slightly Toxic     | 10            | 6              |
| 1                | Non Toxic          | 2             | 1              |
| -                | Unknown            | 52            | 32             |
|                  | TOTAL              | 162           | 100            |

## B. New Orleans: '74 Study (66 compounds)

| <u>Category*</u> | <u>Description</u> | <u>Number</u> | <u>Percent</u> |
|------------------|--------------------|---------------|----------------|
| 6                | Super Toxic        | 1             | 1              |
| 5                | Extremely Toxic    | 2             | 3              |
| 4                | Very Toxic         | 15            | 23             |
| 3                | Moderately Toxic   | 17            | 26             |
| 2                | Slightly Toxic     | 3             | 5              |
| 1                | Non Toxic          | 0             | 0              |
| -                | Unknown            | 28            | 42             |
|                  | TOTAL              | 66            | 100            |

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\*Taken from Gleason, Gosselin, Hodge & Smith, Clinical Toxicology of Commercial Products, 1969.

COMPOUNDS IDENTIFIED AS ACUTELY "SUPER" TOXIC  
OR "EXTREMELY" TOXIC

| <u>Category</u> | <u>Description</u> | <u>Total List</u>  | <u>New Orleans - '74 Study</u> |
|-----------------|--------------------|--------------------|--------------------------------|
| 6               | Super Toxic        | Endrin             | Endrin                         |
| 5               | Extremely Toxic    | Acetaldehyde       | Acetaldehyde                   |
|                 |                    | Aldrin             | Dieldrin                       |
|                 |                    | Chloronitrobenzene |                                |
|                 |                    | Dieldrin           |                                |
|                 |                    | Nitrobenzene       |                                |
|                 |                    | Pentachlorophenol  |                                |

SUMMARY OF CHRONIC TOXICITY INFORMATION ON  
ORGANIC COMPOUNDS IDENTIFIED IN DRINKING WATER

|    |                                |               |                |
|----|--------------------------------|---------------|----------------|
| A. | <u>Total List</u>              | <u>Number</u> | <u>Percent</u> |
|    | Some Reported Data             | 58            | 36             |
|    | No Reported Data               | 104           | 64             |
|    | TOTAL                          | 162           | 100            |
| B. | <u>New Orleans - '74 Study</u> | <u>Number</u> | <u>Percent</u> |
|    | Some Reported Data             | 7             | 11             |
|    | No Reported Data               | 59            | 89             |
|    | TOTAL                          | 66            | 100            |

SUMMARY OF CARCINOGENICITY OF ORGANIC  
COMPOUNDS IDENTIFIED IN DRINKING WATER

## A. Total List

| <u>Category*</u> | <u>Description</u> | <u>Number</u> | <u>Percent</u> |
|------------------|--------------------|---------------|----------------|
| 1                | Positive           | 6             | 4              |
| 2                | Suspect            | 42            | 25             |
| 3                | Negative           | 6             | 4              |
| 4                | Unknown            | 108           | 67             |
|                  | TOTAL              | 162           | 100            |

## B. New Orleans - '74 Study

| <u>Category*</u> | <u>Description</u> | <u>Number</u> | <u>Percent</u> |
|------------------|--------------------|---------------|----------------|
| 1                | Positive           | 2             | 4              |
| 2                | Suspect            | 14            | 21             |
| 3                | Negative           | 3             | 5              |
| 4                | Unknown            | 47            | 70             |
|                  | TOTAL              | 66            | 100            |

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\*Taken from Kraybill, National Cancer Institute.

LIST OF COMPOUNDS DETERMINED TO BE  
"POSITIVE" CARCINOGENS

Aldrin  
Benzene  
Benzopyrene  
Carbon Tetrachloride\*  
DDT  
Dieldrin\*

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\*New Orleans - '74 Study

SUMMARY OF AVAILABLE METABOLIC DATA ON ORGANIC  
COMPOUNDS IDENTIFIED IN DRINKING WATER

|    |                                |               |                |
|----|--------------------------------|---------------|----------------|
| A. | <u>Total List</u>              | <u>Number</u> | <u>Percent</u> |
|    | Some Reported Data             | 84            | 52             |
|    | No Reported Data               | 78            | 48             |
|    | TOTAL                          | 162           | 100            |
| B. | <u>New Orleans - '74 Study</u> | <u>Number</u> | <u>Percent</u> |
|    | Some Reported Data             | 6             | 10             |
|    | No Reported Data               | 60            | 90             |
|    | TOTAL                          | 66            | 100            |

## ORGANICS IN NEW ORLEANS DRINKING WATER

CARCINOGENS

SUSPECT: Acetaldehyde  
Butanone  
Bis-2-chloroethyl ether  
Chloroform  
Bis-2-chloroisopropyl ether  
Dichlorobenzene ether  
N-dodecane  
O-ethyltoluene  
P-ethyltoluene  
Limonene  
N-nonene

POSITIVE: Carbon tetrachloride  
Dieldrin

NEGATIVE: Acetone  
Ethanol  
Methanol

POSSIBLE  
CONVERSION: Atrazine  
De-ethylatrazine  
Trimethyl-trioxo-hexahydro-triazine isomer

TERATOGENS

SUSPECTED: Dibutyl phthalate  
Diethyl phthalate  
Di(2-ethylhexyl)phthalate  
Dihexyl phthalate  
Diisobutyl phthalate  
Dimethyl phthalate

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ORGANICS IN NEW ORLEANS DRINKING WATER

Acute Toxicity Ratings

| 2   | 3  | 4   | 5                        | 6      |
|---|--|---|--------------------------|--------|
| Diisobutyl phthalate<br>Dihexyl phthalate<br>Dimethyl phthalate<br>Ethanol. | Acetone<br>Atrazine<br>Butanone<br>Chloroform<br>Bis-2-chloroiso-propyl ether<br>Dichlorobenzene<br>1,2-Dichloroethane<br>Dichloromethane<br>Diethylphthalate<br>Dihydroxycarvone<br>Isopharone<br>Limonene<br>Methanol<br>Methyl benzoate<br>2-Methylproponal<br>N-nonane<br>Tetrachloro-ethylene | Bromoform<br>Carbon Tetra-chloride<br>Bis-2-chloro-ethyl ether<br>Dibutyl phthalate<br>2,6-Di-t-butyl-p-benzoquinone<br>Di-(2-ethylhexyl) phthalate<br>O-ethyl toluene<br>P- ethyl toluene<br>Hexachloro-1,3-butadiene<br>Hexachloroethane<br>Tetrachloroethane<br>Toluene<br>1,1,2-Trichloro-ethane<br>1,1,2-Trichloro-ethylene<br>Triphenyl phosphate | Acetaldehyde<br>Dieldrin | Endrin |

APPENDIX B

MAXIMUM PERMISSIBLE CONCENTRATIONS OF HARMFUL SUBSTANCES  
IN DRINKING WATERS IN THE USSR

## WORLD HEALTH ORGANIZATION

## MINISTRY OF HEALTH OF THE USSR: MAXIMUM PERMISSIBLE CONCENTRATIONS OF HARMFUL SUBSTANCES IN THE WATER OF WATERCOURSES USED FOR HYGIENIC AND DOMESTIC PURPOSES

(Approved by D. Loranskij, Deputy Chief Sanitarian of the USSR, on 28 April 1970 No. 847-70)  
 These Standards were provided at the time of the WHO Expert Committee on Health Criteria for Water Supplies, held in Geneva from 30 March to 5 April 1971

| <u>Name of Ingredient</u>            | <u>Criterion of Harmfulness</u> | <u>Max. Permissible Conc., mg/liter</u> |
|--------------------------------------|---------------------------------|---|
| 1. Sodium adipate                    | Sanitary toxicological          | 1.0                                     |
| 2. Acrylic acid                      | "                               | 0.5                                     |
| 3. Anisol                            | "                               | 0.05                                    |
| 4. Aniline                           | "                               | 0.1                                     |
| 5. Acetone cyanhydrin                | "                               | 0.001                                   |
| 6. Acetophenone                      | "                               | 0.1                                     |
| 7. Benzene                           | "                               | 0.5                                     |
| 8. Beryllium (Be/II)                 | "                               | 0.0002                                  |
| 9. Vanadium (V - /V)                 | "                               | 0.1                                     |
| 10. Vinyl acetate                    | "                               | 0.2                                     |
| 11. Tungsten (Wo/VI)                 | "                               | 0.1                                     |
| 12. Hexamethylene diamine            | "                               | 0.01                                    |
| 13. Hexanate                         | "                               | 5.0                                     |
| 14. Hexachlorobenzene                | "                               | 0.05                                    |
| 15. Hexogen                          | "                               | 0.1                                     |
| 16. Hydrazine                        | "                               | 0.01                                    |
| 17. Isopropylbenzene hydroperoxide   | "                               | 0.5                                     |
| 18. Heptachlor                       | "                               | 0.05                                    |
| 19. Heptyl alcohol                   | "                               | 0.005                                   |
| 20. Dibutyl tin dilaurate            | "                               | 0.1                                     |
| 21. DDT                              | "                               | 0.1                                     |
| 22. Diisopropylamine                 | "                               | 0.5                                     |
| 23. <u>meta</u> - Diisopropylbenzene | "                               | 0.05                                    |
| 24. <u>para</u> - Diisopropylbenzene | "                               | 0.05                                    |
| 25. Dimethylamine .                  | "                               | 0.1                                     |
| 26. Dimethyldioxane                  | "                               | 0.005                                   |
| 27. Dimethyldithiocarbamate          | "                               | 0.5                                     |
| 28. Dimethylphenylcarbinol           | "                               | 0.05                                    |
| 29. Adipic acid dinitrile            | "                               | 0.1                                     |

(Appendix continued on next page)

|     | <u>Name of Ingredient</u>             | <u>Criterion of Harmfulness</u> | <u>Max. Permissible Conc., mg/liter</u> |
|-----|---------------------------------------|---------------------------------|---|
| 30. | 2,4 - Dinitrophenol                   | Sanitary toxicological          | 0.03                                    |
| 31. | Dibutyl tin chloride                  | "                               | 0.002                                   |
| 32. | 2,3 - Dichloro - 1,4 - naphthoquinone | "                               | 0.25                                    |
| 33. | Diethylamine                          | "                               | 2.0                                     |
| 34. | Diethyl tin caprylate                 | "                               | 0.01                                    |
| 35. | Diethyleneglycol                      | "                               | 1.0                                     |
| 36. | Diethyl maleate                       | "                               | 1.0                                     |
| 37. | Mercury ethide                        | "                               | 0.0001                                  |
| 38. | Isocrotonitrile                       | "                               | 0.1                                     |
| 39. | Isopropylamine                        | "                               | 2.0                                     |
| 40. | Crotonitrile                          | "                               | 0.1                                     |
| 41. | Cobalt (Co <sup>II</sup> )            | "                               | 1.0                                     |
| 42. | 2,5 - Lutidine                        | "                               | 0.05                                    |
| 43. | Methacrylamide                        | "                               | 0.1                                     |
| 44. | Methyl acetate                        | "                               | 0.1                                     |
| 45. | Methylol methacrylamide               | "                               | 0.1                                     |
| 46. | Molybdenum (Mo/VI)                    | "                               | 0.5                                     |
| 47. | Monomethylamine                       | "                               | 1.0                                     |
| 48. | Arsenic (As/III) <sup>a</sup>         | "                               | 0.05                                    |
| 49. | β - naphthol                          | "                               | 0.4                                     |
| 50. | Nitrates (as nitrogen)                | "                               | 10.0                                    |
| 51. | Acrylonitrile                         | "                               | 2.0                                     |
| 52. | <u>meta</u> - Nitrophenol             | "                               | 0.06                                    |
| 53. | <u>ortho</u> - Nitrophenol            | "                               | 0.06                                    |
| 54. | <u>para</u> - Nitrophenol             | "                               | 0.02                                    |
| 55. | Nitrochlorobenzene                    | "                               | 0.05                                    |
| 56. | Nitrocyclohexane                      | "                               | 0.1                                     |
| 57. | Nonyl alcohol                         | "                               | 0.01                                    |
| 58. | Paraphenylenediamine (ursol)          | "                               | 0.1                                     |
| 59. | Paraquinone dioxime                   | "                               | 0.1                                     |
| 60. | Pentamate                             | "                               | 2.5                                     |
| 61. | Ammonium perchlorate                  | "                               | 5.0                                     |
| 62. | Alpha-picoline                        | "                               | 0.05                                    |
| 63. | Pyridine                              | "                               | 0.2                                     |
| 64. | Polychloropinene                      | "                               | 0.2                                     |

<sup>a</sup>Exclusive of organic compounds.

(Appendix continued on next page)

| <u>Name of Ingredient</u>                      | <u>Criterion of Harmfulness</u> | <u>Max. Permissible Conc., mg/liter</u> |
|--|---------------------------------|---|
| 65. Thiocyanates                               | Sanitary toxicological          | 0.1                                     |
| 66. Mercury (Hg <sup>II</sup> ) <sup>a</sup>   | "                               | 0.005                                   |
| 67. Lead (Pb <sup>II</sup> )                   | "                               | 0.1                                     |
| 68. Selenium (SeO <sub>3</sub> <sup>II</sup> ) | "                               | 0.001                                   |
| 69. Strontium (stable)                         | "                               | 2.0                                     |
| 70. Antimony                                   | "                               | 0.05                                    |
| 71. Tellurium (Te <sup>II</sup> )              | "                               | 0.01                                    |
| 72. Tetrachlorobenzene                         | "                               | 0.01                                    |
| 73. Tetraethyl tin                             | "                               | 0.0002                                  |
| 74. Tetraethyl lead                            | "                               | Nil                                     |
| 75. Triethylamine                              | "                               | 2.0                                     |
| 76. Trifluorochloropropane                     | "                               | 0.1                                     |
| 77. Urotropin                                  | "                               | 0.5                                     |
| 78. Phenylhydrazine                            | "                               | 0.01                                    |
| 79. Ferrocyanides                              | "                               | 1.25                                    |
| 80. Formaldehyde                               | "                               | 0.5                                     |
| 81. Fluorine <sup>b</sup>                      | "                               | 1.5                                     |
| 82. Furan                                      | "                               | 0.2                                     |
| 83. <u>meta</u> - Chloraniline                 | "                               | 0.2                                     |
| 84. <u>para</u> - Chloraniline                 | "                               | 0.2                                     |
| 85. Chlorobenzene                              | "                               | 0.02                                    |
| 86. Cyanides <sup>c</sup>                      | "                               | 0.1                                     |
| 87. Cyclohexane                                | "                               | 0.1                                     |
| 88. Cyclohexene                                | "                               | 0.02                                    |
| 89. Cyclohexanol                               | "                               | 0.5                                     |
| 90. Cyclohexanone                              | "                               | 0.2                                     |
| 91. Cyclohexanone oxime                        | "                               | 1.0                                     |
| 92. Carbon tetrachloride                       | "                               | 0.3                                     |
| 93. Epichlorohydrin                            | "                               | 0.01                                    |
| 94. Ethylene glycol                            | "                               | 1.0                                     |
| 95. Ethyl mercuric chloride                    | "                               | 0.0001                                  |
| 96. Ammonia (on a nitrogen basis)              | General sanitary                | 2.0                                     |

<sup>a</sup>For inorganic compounds.

<sup>b</sup>In compound forms also.

<sup>c</sup>Simple and complex cyanides [except for cyanoferrates (?)] in terms of cyanogenes.

(Appendix continued on next page)

| <u>Name of Ingredient</u>                                      | <u>Criterion of Harmfulness</u> | <u>Max. Permissible Conc., mg/liter</u>  |
|--|---------------------------------|--|
| 97. Acetone  | General sanitary                | Within the limits calculated as permissible for content of organic substances in watercourses and on the basis of BOD and DO             |
| 98. Benzoic acid   | "                               |  |
| 99. Butyl acetate  | "                               | 0.1  |
| 100. Hexamethylene diamine adipate (nylon salt)                | "                               | 1.0  |
| 101. Dibutyl phthalate   | "                               | 0.2  |
| 102. Dimethyl formamide  | "                               | 10.0   |
| 103. Dinitrothiocyanobenzene                                   | "                               | 0.5  |
| 104. Dioctyl phthalate   | "                               | 1.0  |
| 105. Diphenylguanidine   | "                               | 1.0  |
| 106. Isobutyl alcohol  | "                               | 1.0  |
| 107. Cadmium (Cd <sup>II</sup> )                               | "                               | 0.01   |
| 108. Caprolactam   | "                               | 1.0  |
| 109. Butyric acid  | "                               | Within the limits calculated as permissible for content of organic substance in the water of watercourses and on the basis of BOD and DO |
| 110. Menthanol   | "                               |  |
| 111. Lactic acid   | "                               |  |
| 112. Formic acid   | "                               |  |
| 113. Copper (Cu <sup>II</sup> )                                | "                               | 0.1  |
| 114. Methyl pyrrolidone  | "                               | 0.5  |
| 115. Ethylene-glycol ethyl ether                               | "                               | 1.0  |
| 116. Nickel (Ni <sup>II</sup> )                                | "                               | 0.1  |
| 117. Norsulfazole  | "                               | 0.1  |
| 118. Propylene glycol  | "                               | Within the limits calculated as permissible for content of organic substances in the water of watercourses and on the basis of BOD & DO  |
| 119. Synthetic fatty acids (C <sub>5</sub> - C <sub>20</sub> ) | "                               |  |
| 120. Diphenyl guanidine hydrochloride                          | "                               | 1.0  |
| 121. Streptocide   | "                               | 0.5  |
| 122. Sulgin (sulfaguanidine)                                   | "                               | 0.01   |
| 123. Sulphides <sup>a</sup>                                    | "                               | Nil  |
| 124. Sulfadimezine (sulfadimidine)                             | "                               | 1.0  |
| 125. Terephthalic acid   | "                               | 0.1  |

<sup>a</sup>Taking into account the oxygen regime under winter conditions.

| <u>Name of Ingredient</u>                | <u>Criterion of Harmfulness</u> | <u>Max. Permissible Conc., mg/liter</u>   |
|--|---------------------------------|---|
| 126. Tetrahydrofuryl alcohol             | General sanitary                | 0.5   |
| 127. Titanium (Ti)                       | "                               | 0.1   |
| 128. Trinitrotoluene                     | "                               | 0.5   |
| 129. Sodium trichloracetate              | "                               | 5.0   |
| 130. Triethyleneglycol                   | "                               | Within the limits calculated as permissible for content of organic substances in the water of watercourses and on the basis of BOD & DO |
| 131. Acetic acid                         | "                               |   |
| 132. Phthalic acid                       | "                               | 0.5   |
| 133. Free chlorine <sup>a</sup>          | "                               | Nil   |
| 134. Zinc (Zn <sup>++</sup> )            | "                               | 1.0   |
| 135. Avadex                              | Organoleptic                    | 0.03  |
| 136. Aldrin                              | "                               | 0.002   |
| <u>Aliphatic amines</u>                  |                                 |   |
| 137. C <sub>7</sub> - C <sub>9</sub>     | "                               | 0.1   |
| 138. C <sub>10</sub> - C <sub>16</sub>   | "                               | 0.04  |
| 139. C <sub>16</sub> - C <sub>20</sub>   | "                               | 0.03  |
| 140. <u>ortho</u> - Aminophenol          | "                               | 0.01  |
| 141. <u>para</u> - Aminophenol           | "                               | 0.05  |
| 142. Acetaldehyde                        | "                               | 0.2   |
| 143. Acetophos                           | "                               | 0.03  |
| 144. Barium (Ba <sup>++</sup> )          | "                               | 4.0   |
| 145. Benzine                             | "                               | 0.1   |
| 146. Butyl acrylate                      | "                               | 0.015   |
| 147. Butyl benzene                       | "                               | 0.1   |
| 148. Butylene                            | "                               | 0.2   |
| 149. Butyl alcohol                       | "                               | 1.0   |
| 150. Sodium vinyl silicate<br>(GKZ - 12) | "                               | 2.0   |
| 151. Hexachlorocyclohexane               | "                               | 0.02  |
| 152. Hexachlorobutadiene                 | "                               | 0.01  |
| 153. Hexachlorobutane                    | "                               | 0.01  |
| 154. Hexachlorocyclopentadiene           | "                               | 0.001   |
| 155. Hexachloroethane                    | "                               | 0.01  |
| 156. hydroquinone                        | "                               | 0.2   |
| 157. Dalapon                             | "                               | 2.0   |

<sup>a</sup>Taking into account the chlorine demand of the water in watercourses.

|      | <u>Name of Ingredient</u>               | <u>Criterion of Harmfulness</u> | <u>Max. Permissible Conc., mg/liter</u> |
|------|---|---------------------------------|---|
| 158. | Dikotex                                 | Organoleptic                    | 0.25                                    |
| 159. | Dimethyldithiophosphoric acid           | "                               | 0.1                                     |
| 160. | Dichlorovinyl dimethyl phosphate (DDVP) | "                               | 1.0                                     |
| 161. | Dimethyl terephthalate                  | "                               | 1.5                                     |
| 162. | Diisobutylamine                         | "                               | 0.07                                    |
| 163. | Potassium diisopropylidithiophosphate   | "                               | 0.02                                    |
| 164. | Dinitrobenzene                          | "                               | 0.5                                     |
| 165. | Dinitronaphthalene                      | "                               | 1.0                                     |
| 166. | Dinitrochlorobenzene                    | "                               | 0.5                                     |
| 167. | Dipropylamine                           | "                               | 0.5                                     |
| 168. | Cresyl dithiophosphate                  | "                               | 0.001                                   |
| 169. | Diuron                                  | "                               | 1.0                                     |
| 170. | Diphenylpropane                         | "                               | 0.01                                    |
| 171. | 3,4 - Dichloraniline                    | "                               | 0.05                                    |
| 172. | 2,5 - Dichloraniline                    | "                               | 0.05                                    |
| 173. | <u>ortho</u> - Dichlorobenzene          | "                               | 0.002                                   |
| 174. | <u>para</u> - Dichlorobenzene           | "                               | 0.002                                   |
| 175. | Dichlorobutene                          | "                               | 0.05                                    |
| 176. | Dichlorohydrin                          | "                               | 1.0                                     |
| 177. | Dichloromethane                         | "                               | 7.5                                     |
| 178. | Dichlorophenol                          | "                               | 0.002                                   |
| 179. | Dichlorocyclohexane                     | "                               | 0.02                                    |
| 180. | Dichloroethane                          | "                               | 2.0                                     |
| 181. | Dicyanodiamide                          | "                               | 10.0                                    |
| 182. | Diethanolamine                          | "                               | 0.8                                     |
| 183. | Diethyl phosphorodithioic acid          | "                               | 0.2                                     |
| 184. | Potassium diethylphosphorodithiocate    | "                               | 0.5                                     |
| 185. | Ethyl ether                             | "                               | 0.3                                     |
| 186. | Iron (Fe <sup>++</sup> )                | "                               | 0.5                                     |
| 187. | Isobutylene                             | "                               | 0.5                                     |
| 188. | Isoprene                                | "                               | 0.005                                   |
| 189. | Isopropylphenyl carbamate               | "                               | 0.2                                     |
| 190. | Isopropyl N-(3-chlorophenyl) carbamate  | "                               | 1.0                                     |
| 191. | Carbide (a herbicide)                   | "                               | 0.03                                    |
| 192. | Carbofos (= malathion)                  | "                               | 0.05                                    |
| 193. | Kerosene                                | "                               | 0.1                                     |
| 194. | Butyl Xanthate                          | "                               | 0.001                                   |

(Appendix continued on next page)

| <u>Name of Ingredient</u>  | <u>Criterion of Harmfulness</u> | <u>Max. Permissible Conc., mg/liter</u> |
|--|---------------------------------|---|
| 195. Xylene  | Organoleptic                    | 0.05                                    |
| 196. Maleic acid   | "                               | 1.0                                     |
| 197. $\beta$ - Mercaptodiethylamine  | "                               | 0.1                                     |
| 198. Mercaptosfos (= Systox)   | "                               | 0.01                                    |
| 199. Metafos (- Methyl parathion)  | "                               | 0.02                                    |
| 200. Methyl acrylate   | "                               | 0.02                                    |
| 201. Methyl dithiocarbamate (carbathion)   | "                               | 0.02                                    |
| 202. Methylnitrofos  | "                               | 0.25                                    |
| 203. Sodium methylsiliconate (GKZ - 11)  | "                               | 2.0                                     |
| 204. Methylsystox  | "                               | 0.01                                    |
| 205. alpha - Methylstyrene   | "                               | 0.1                                     |
| 206. Methyl ethyl ketone   | "                               | 1.0                                     |
| 207. Monosodium salt of cyanuric acid  | "                               | 25.0                                    |
| 208. Monopropylamine   | "                               | 0.5                                     |
| 209. Monochlorohydrin  | "                               | 0.7                                     |
| 210. Monoethylamine  | "                               | 0.5                                     |
| 211. Monuron [= 1 - (p - Chlorophenyl) -3-3-dimethylurea]                          | "                               | 5.0                                     |
| 212. Sodium salt of dichlorophenoxyacetic acid (Na-2,4 - D)                        | "                               | 1.0                                     |
| 213. Naphthenic acids  | "                               | 0.3                                     |
| 214. alpha - Naphthol  | "                               | 0.1                                     |
| 215. High-sulphur petroleum  | "                               | 0.1                                     |
| 216. Other crude oil   | "                               | 0.3                                     |
| 217. <u>para</u> - Nitrophenylaminoethanol (oxyamine)                              | "                               | 0.5                                     |
| 218. <u>para</u> - Nitrophenylchloromethylcarbinol (carbinol)                      | "                               | 0.2                                     |
| 219. <u>para</u> - Nitrophenylacetylamin ethanol (oxyacetylamine)                  | "                               | 1.0                                     |
| 220. Nitroform   | "                               | 0.01                                    |
| 221. <u>O,O</u> - Dimethyl <u>S</u> - (2-ethylthioethyl) phosphorodithioate (M-81) | "                               | 0.001                                   |
| 222. Pentachlorobutane   | "                               | 0.02                                    |
| 223. Pentachlorophenol   | "                               | 0.3                                     |
| 224. Sodium pentachlorophenolate   | "                               | 5.0                                     |
| 225. Picric acid   | "                               | 0.5                                     |
| 226. Polymethylhydrosilicone (GKZ - 94m)   | "                               | 2.0                                     |
| 227. Polymethyldichlorophenylsilicone (HS-2-1)                                     | "                               | 10.0                                    |

(Appendix continued on next page)

|      | <u>Name of Ingredient</u>                      | <u>Criterion of Harmfulness</u> | <u>Max. Permissible Conc., mg/liter</u> |
|------|--|---------------------------------|---|
| 228. | Polyethylhydrosilicone (GKZ - 94)              | Organoleptic                    | 10.0                                    |
| 229. | Polyethyl silicone (lubricant)                 | "                               | 10.0                                    |
| 230. | Prometrine (a herbicide)                       | "                               | 3.0                                     |
| 231. | Propasine (a herbicide)                        | "                               | 1.0                                     |
| 232. | Propylbenzene                                  | "                               | 0.2                                     |
| 233. | Propylene                                      | "                               | 0.5                                     |
| 234. | Saponin  | "                               | 0.2                                     |
| 235. | Sevin  | "                               | 0.1                                     |
| 236. | Carbon bisulphide                              | "                               | 1.0                                     |
| 237. | Simazine (undissolved)                         | "                               | Nil                                     |
| 238. | 2-hydroxy derivative of simazine (undissolved) | "                               | Nil                                     |
| 239. | Turpentine                                     | "                               | 0.2                                     |
| 240. | Styrene  | "                               | 0.1                                     |
| 241. | Tetrahydroquinone                              | "                               | 0.05                                    |
| 242. | Tetranitromethane                              | "                               | 0.5                                     |
| 243. | Tetrachloroheptane                             | "                               | 0.0025                                  |
| 244. | Tetrachlorononane                              | "                               | 0.003                                   |
| 245. | Tetrachloropentane                             | "                               | 0.005                                   |
| 246. | Tetrachloropropane                             | "                               | 0.01                                    |
| 247. | Tetrachloroundecane                            | "                               | 0.007                                   |
| 248. | Tetrachloroethane                              | "                               | 0.2                                     |
| 249. | Thiophene                                      | "                               | 2.0                                     |
| 250. | Thiofos (= parathion)                          | "                               | 0.003                                   |
| 251. | Toluene  | "                               | 0.5                                     |
| 252. | Tributyl phosphate                             | "                               | 0.01                                    |
| 253. | Trichlorometafos - 3 (an insecticide)          | "                               | 0.4                                     |
| 254. | Triethanolamine                                | "                               | 1.4                                     |
| 255. | Trichloroethylene                              | "                               | 0.5                                     |
| 256. | Trichlorophenol                                | "                               | 0.0004                                  |
| 257. | Phenol <sup>a</sup> (carbolic acid)            | "                               | 0.001                                   |
| 258. | Phosbutyl                                      | "                               | 0.03                                    |
| 259. | Phosphamide (Roger)                            | "                               | 0.03                                    |
| 260. | Phthalophos                                    | "                               | 0.2                                     |
| 261. | Furfural                                       | "                               | 1.0                                     |
| 262. | Chloranil                                      | "                               | 0.01                                    |

<sup>a</sup>In the case of points where the water in watercourses is used as a source of supply for domestic and drinking purposes.

| <u>Name of Ingredient</u>                                       | <u>Criterion of Harmfulness</u> | <u>Max. Permissible Conc., mg/liter</u> |
|---|---------------------------------|---|
| 263. Sodium chlorate  | Organoleptic                    | 20.0                                    |
| 264. Chloronitrosocyclohexane                                   | "                               | 0.005                                   |
| 265. Chloroprene  | "                               | 0.1                                     |
| 266. Chlorophos (= Dipterex)                                    | "                               | 0.05                                    |
| 267. Chlorononanoic acid  | "                               | 0.3                                     |
| 268. Chloroundecanoic acid                                      | "                               | 0.1                                     |
| 269. Chloroheptanoic acid                                       | "                               | 0.05                                    |
| 270. Chlorendicoic anhydride (?)                                | "                               | 1.0                                     |
| 271. Chlorocyclohexane  | "                               | 0.05                                    |
| 272. Chromium (Cr/ <u>VI</u> )                                  | "                               | 0.1                                     |
| 273. Chromium (CR/III)  | "                               | 0.5                                     |
| 274. Celatox  | "                               | 0.5                                     |
| 275. Cyanuric acid  | "                               | 6.0                                     |
| 276. Ethyl acrylate   | "                               | 0.005                                   |
| 277. Ethylene   | "                               | 0.5                                     |
| 278. Ethyl benzene  | "                               | 0.01                                    |
| 279. Sodium ethylsiliconate (GKZ - 10)                          | "                               | 2.0                                     |
| 280. <u>p</u> -Chlorophenyl- <u>p</u> -chlorobenzene sulphonate | "                               | 0.2                                     |
| <u>Surface-active agents</u>                                    |                                 |   |
| 281. Alkyl benzenesulphonates                                   | "                               | 0.5                                     |
| 282. Alkyl sulphates  | "                               | 0.5                                     |
| 283. Alkyl sulphonates  | "                               | 0.5                                     |
| 284. Disodium salt of monoalkyl-sulfosuccinic acid              | "                               | 0.5                                     |
| <u>Flotation agents</u>   |                                 |   |
| 285. APN  | "                               | 0.05                                    |
| 286. OP - 7   | "                               | 0.4                                     |
| 287. OP - 10  | "                               | 1.5                                     |
| 288. OPS - B  | General sanitary                | 2.0                                     |
| 289. OPS - M  | Sanitary toxicological          | 0.5                                     |
| <u>Flocculating agents</u>                                      |                                 |   |
| 290. VA - 2 (polystyrene)                                       | "                               | 0.5                                     |
| 291. VA - 2 - T (polyvinyl toluene)                             | "                               | 0.5                                     |
| 292. VA - 102   | "                               | 2.0                                     |
| 293. VA - 212   | "                               | 2.0                                     |
| 294. Polyacrylamide   | "                               | 2.0                                     |

(Appendix continued on next page)

N.B. When the water in watercourses used for domestic supplies is polluted with a combination of substances with the same limiting index of harmfulness: organoleptic properties (smell, taste, colouring), effect on general sanitary conditions in the watercourse (on the processes of self-purification to eliminate organic pollution) or sanitary toxicological considerations, the maximum permissible concentrations given in the table for the individual substances should be adopted only subject to the following provisos:

1. In carrying out preventive sanitary inspection - the value of the maximum permissible concentration for each substance forming the combination should be reduced by as many times as the number of harmful substances with the same index of harmfulness which it is proposed to discharge with waste water or which are contained in the watercourse.
2. In carrying out routine sanitary inspection - the sum of the concentrations of all the substances expressed as a percentage of the corresponding maximum permissible concentrations for each substance separately should not exceed 100 percent.

The list of maximum permissible concentrations of harmful substances in the water of watercourses used for hygienic and domestic purposes (List No. 662/67 of 12 January 1967) is hereby superseded.



SECTION III

TREATMENT PROCESSES  
FOR WASTEWATER RECLAMATION  
FOR GROUNDWATER RECHARGE

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INTRODUCTION

The purpose of this section is to evaluate the capability of alternate processes for the purpose of treating municipal wastewater for recharge of domestic groundwater supplies. The scope specified for this section by the California State Water Resources Control Board is as follows:

Conduct an extensive literature and treatment plant performance survey to gather available information necessary for accomplishing the following tasks:

Task 1 - Identification of conventional and advanced wastewater treatment processes (or their combinations) with potential to provide an effluent suitable for groundwater recharge where domestic water supplies are involved.

Task 2 - Evaluation of the identified wastewater treatment processes:

- a. Capability for removal of chemical and biological contaminants found in municipal wastewaters which may affect public health or the potability of the water;  
and
- b. Reliability of processes for continuous production of effluent of minimum quality required.

Task 3 - Define information needed to: (1) complete the evaluation of identified treatment processes and (2) develop design and operation criteria for fail-safe operation of wastewater reclamation treatment plants.

DESCRIPTION OF WASTEWATER TREATMENT PROCESSES

Throughout this section, repeated references to the following classifications of sewage treatment processes will be made:

Primary treatment processes are those which act on the sewage in a mechanical or physical way to remove floating or settleable solids. Examples of such processes are: grit chambers, sedimentation basins, screens of various types, and sewage grinders. Primary settling usually removes about 35 percent of the raw sewage Biochemical Oxygen Demand (BOD) and 60 percent of the raw sewage suspended solids.

Secondary treatment processes utilize biological systems to remove dissolved or colloidal material contained in sewage. Examples of secondary treatment processes are: activated sludge units, biological filters (trickling filters), and waste stabilization ponds. Secondary treatment typically removes 85 to 90 percent of the raw sewage BOD and suspended solids but provides very little removal of phosphorus, nitrogen, nonbiodegradable organics and, even when coupled with a disinfection process, does not provide complete removal of virus and bacteria.

Advanced wastewater treatment (AWT) processes remove pollutants not normally removed by secondary or biological treatment processes such as phosphorus, nitrogen, organic materials contributing to color and odor which are not biologically removable, and the last traces of suspended solids. These processes are normally of a physical or chemical nature and

may be used downstream of a secondary process or in place of the secondary process. Examples of AWT processes are: chemical coagulation and sedimentation, filtration through sand or other types of filters, and contact with activated carbon. Demineralization processes may also be applied to municipal wastewaters for control of the Total Dissolved Solids (TDS) content.

It is the purpose of the remainder of this section to provide a description of alternate processes. The discussion does not compare design considerations but defines the processes which will later be discussed in terms of treatment capability.

#### Biological Processes

Biological processes have been principally used in the past for secondary treatment of wastewaters but are also capable, when designed for the purpose, of providing removal of nitrogen which is not normally removed in secondary treatment plants. Such processes include trickling filter processes and activated sludge processes. All biological processes are dependent upon bringing microorganisms into contact with the impurities in wastewater so that the microorganisms may remove these impurities. The trickling filter processes accomplish this by passing wastewater through a bed of large rocks or through a bed of synthetic plastic or wood packing. The microbial growth occurs on the surface of the rocks or packing in a "fixed film" with the wastewater passing over the stationary microbial population. In activated sludge processes, the organisms and the wastewater are mixed together in an aerated tank. A downstream settling step settles

out the microbes and recycles most of them to the aeration basin to maintain a high microbial population to insure efficient removals of the biodegradable organics.

Trickling filters have been a popular biologic treatment process for many years. Trickling filters, with their reservoir of attached biological growth on the surface of the filter media, provided a capability to tolerate shock loadings more dependably than did early day activated sludge systems. However, this advantage is accompanied by the disadvantage of poorer removals of soluble BOD than provided by activated sludge processes. Improvements in trickling filter design utilizing synthetic plastic and wood media rather than rock have led to improved economics and performance. However, the overall detention time in trickling filter systems is short and, as a result, a relatively large amount of soluble BOD is found in the effluent. Some of the compounds contributing to this soluble BOD, which may be 10-15 mg/l, are not readily removed in AWT processes. For example, if some sugars and alcohols found in sewage are not completely removed by the trickling filter process, they will not be removed by downstream treatment with activated carbon.

The activated sludge process is capable of removing essentially all of the soluble BOD found in raw sewage. In recent years, application of basic microbiology and biochemistry to the activated sludge process has led to some significant improvements in the stability of the process--a previous weakness. Because the process is still dependent upon the separation of the microbes from the wastewater by a gravity settling step, inevitable variations in the settling nature of the biological floc lead to variations in

the secondary effluent BOD and SS (suspended solids). However, even during periods when the floc settles poorly, the microbes continue to remove soluble BOD much more completely than the trickling filter process. In a plant where the secondary process is followed by the AWT process of chemical coagulation and settling, these variations in secondary effluent solids are not critical because the downstream AWT process will remove them.

An inherent limitation of biological processes is that they can remove only organic materials which are biologically degradable. These materials are normally measured by the Biochemical Oxygen Demand (BOD) test. Organic materials which are not biologically degradable are also present in wastewaters, and most of these can be included in the measure of organics by the Chemical Oxygen Demand (COD) test or the Total Organic Carbon (TOC) test. These materials (refractory organics) may contribute to the color and odor of secondary effluents and are of major concern in reuse situations where they raise uncertainties related to their long-term health effects in water supplies. If secondary effluent is not subjected to activated carbon treatment prior to groundwater recharge, then the only available system for removal of these refractory organics prior to reuse is removal in the soil. Removal of contaminants in soil systems is covered in a separate section. Biological processes are also susceptible to upset by certain toxic industrial wastes, shock loads, and temperature changes.

Advanced Wastewater Treatment ProcessesChemical Coagulation and Sedimentation:

Chemical coagulants (such as aluminum sulfate, ferric chloride or lime) are added to wastewaters for the primary purposes of removing suspended solids (turbidity) and phosphorus. As discussed later, related benefits include reductions in heavy metal concentrations and improved disinfection efficiency.

Chemical coagulants may be added to: (1) the primary clarifier influent; (2) the activated sludge aeration tank, (3) influent to secondary clarifier, or (4) a tertiary chemical clarifier. The first two of these potential points of coagulant addition are generally used when phosphorus removal is the overriding concern. The suspended solids content of the secondary effluent is generally not improved significantly when the coagulants are added to the primary clarifier or to the aeration tank. In those cases where secondary treatment does not provide adequate water quality for groundwater recharge, the coagulation process will be considered for its ability to remove suspended solids as well as phosphorus. Where the goal is to minimize suspended solids, a tertiary chemical clarification process is used.

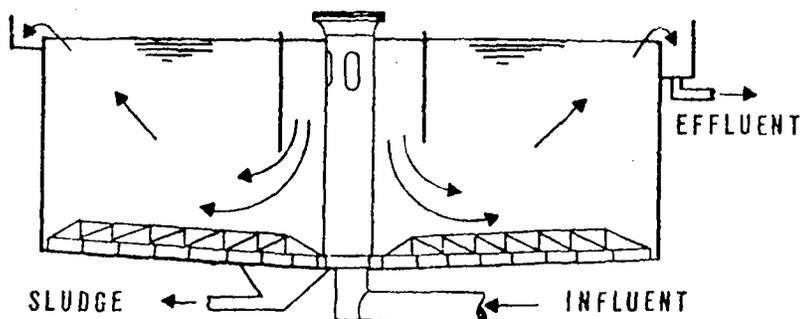
Chemical coagulation of secondary effluents in a separate tertiary step may be accomplished with lime, alum, polymers or iron salts. The separate, tertiary coagulation step has the advantage of providing a means of removal of suspended solids from the secondary effluent prior to the

potential downstream process of filtration and carbon adsorption. This feature not only improves the normal secondary effluent quality, but provides an important improvement in process reliability by providing a means to remove the excessive quantities of solids which may escape occasionally from the biological process and which would adversely affect filtration, adsorption or a recharge system. The coagulation-sedimentation process typically involves three separate operations: (1) the injection and rapid mixing of the coagulants which neutralize the predominantly negative charges on suspended matter, (2) gentle stirring to promote agglomeration of the coagulated particles into large, settleable floc, and (3) sedimentation in open basins 9-15 feet deep to provide gravity separation of the flocculated material from the wastewater. The settled material is continuously scraped to a sump in the sedimentation basin from which it is pumped to the sludge handling system. Figure III-1 illustrates some typical clarifier configuration.

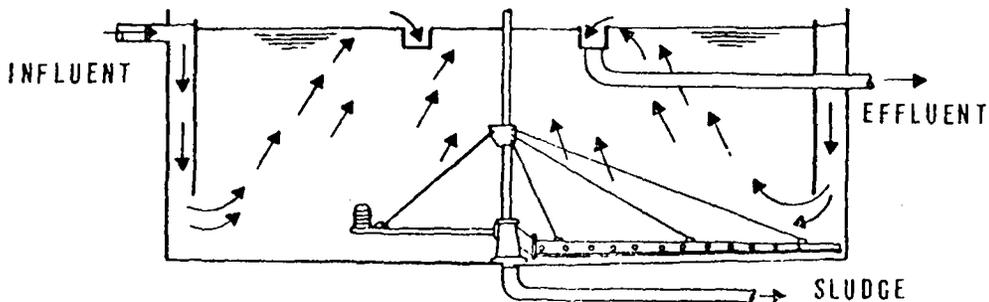
The quantity of chemical coagulant required to achieve good coagulation varies from wastewater to wastewater. Aluminum and iron salt requirements for good phosphorus removal are generally proportional to the phosphorus concentration, while lime requirements are largely determined by the alkalinity of the wastewater. Orthophosphate is converted to an insoluble form with calcium at pH values of about 9.5. As the pH increases above 9.5, precipitation of magnesium hydroxide begins and will be completed when the pH reaches 11. Magnesium hydroxide is a gelatinous precipitate which aids in the efficient removal of colloidal material. However, its gelatinous

FIGURE III-1

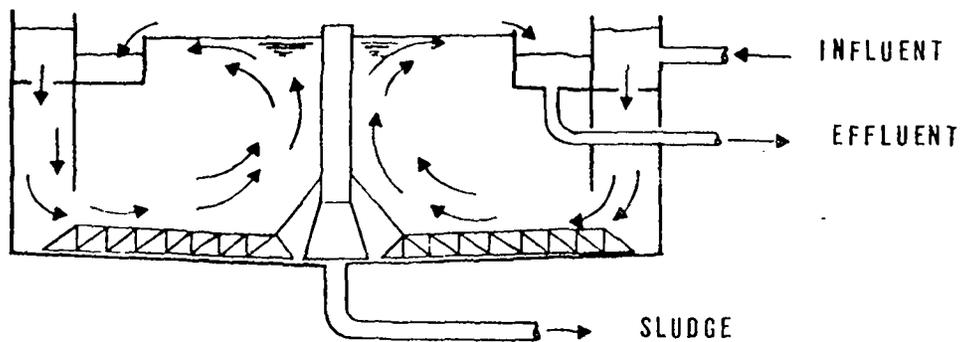
TYPICAL CLARIFIER CONFIGURATIONS



1a CIRCULAR CENTER-FEED CLARIFIER WITH A SCRAPER SLUDGE REMOVAL SYSTEM



1b CIRCULAR RIM-FEED, CENTER TAKE-OFF CLARIFIER WITH A HYDRAULIC SUCTION SLUDGE REMOVAL SYSTEM



1c CIRCULAR RIM-FEED, RIM TAKE-OFF CLARIFIER

nature may adversely affect sludge dewatering. Typical coagulant doses are: aluminum sulfate (alum) - 75-250 mg/l; ferric chloride - 45-90 mg/l; and lime - 200-400 mg/l.

Aluminum and iron salts have the disadvantage of adding significant quantities of dissolved solids (sulfates or chlorides) to the final effluent and of not being amenable to recovery and reuse, as may be done with lime by use of the recalcination process. Also, in some cases, the resulting sludges have proven to be more difficult to dewater than those resulting from lime treatment.

Tertiary-chemical coagulation has the advantage of being a simple, easily controlled process which serves to increase plant reliability by providing a means of leveling out variations in the solids content of the secondary effluent prior to any downstream processes. A bonus resulting from the use of tertiary high pH lime coagulation is the disinfecting action of high pH and the removal of certain heavy metals as discussed later in this report, and the preparation of the water for an ammonia-stripping process should this be desired.

#### Filtration:

The goal of filtration is the removal of particulate matter. For example, the effluent from the tertiary coagulation and sedimentation process will typically contain 3-5 mg/l suspended solids (SS) and 0.5-1 mg/l

phosphorus. Efficient filtration of chemical clarifier effluent can reduce SS to below detectable limits and phosphorus to 0.1 mg/l or less. Filtration of secondary effluents without chemical coagulation ("plain filtration") is also used. The results of plain filtration are dependent upon the biological flocculation achieved in the secondary process and are not as good as those achieved in conjunction with chemical coagulation.

Filtration of wastewater is most effectively achieved by passing the wastewater through a granular bed typically 30"-36" deep composed of relatively small particles (less than 1.5 mm in size). Filtration of wastewater is a difficult problem in many respects, however. The wastewater solids content may be variable and also may reach high levels if the processes upstream of the filtration process are not operated properly. The conventional rapid-sand filter used widely in water treatment has limited applicability in wastewater treatment because of its sensitivity to high suspended solids concentrations.

The sensitivity of a rapid sand filter to high suspended solids concentrations can be readily understood by examination of Figure III-2, which is a schematic cross-section of the media in a typical single media filter, such as a rapid sand filter. Wastewater is passed downward through the filter during its normal cycle of operation. Eventually, it becomes plugged with material removed from the wastewater and is then cleaned by reversing the flow. The suspended solids previously trapped by the media are washed from the bed, but the backwash rate is not so high as to lose the heavier filter media. In the terminal part of the backwashing procedure, the sand grades hydraulically with the finest media particles coming

to rest at the top of the bed. As a result of the presence of fines at the surface of the bed, most of the material removed by the filter is removed at or very near the surface of the bed and only a small part of the total voids in the bed are available to store particulates, and consequently headloss increases very rapidly.

One approach to increasing the effective filter depth is the use of a dual media bed using a discrete layer of coarse light-weight coal above a layer of heavier fine sand, as shown in Figure III-3. The effective filtration depth is extended, although it still does not include the full depth of the bed, as there is some fine to coarse stratification within each of the layers, as shown by the graph depicting grain size. Effective size of the sand in a typical dual filter is 0.4-0.5 mm.

Grain size is of major importance in determining how efficiently the filter removes suspended solids from activated sludge effluent. For example, investigators at Stanford<sup>1</sup> found that at a hydraulic loading rate of 5 gpm/sq. ft., a decrease in sand size from 1.1 mm to 0.5 mm increased the suspended solids removal from 10 percent to 40 percent.

It is apparent that the effluent should pass through as fine a filter material as is feasible. This presents a serious inconsistency in design of a dual media bed as shown in Figure III-3. It would be desirable to have the coal (specific gravity about 1.6) as coarse as is consistent with solids removal to prevent surface blinding, but have the sand (specific gravity about 2.6) as fine as possible to provide maximum solids removal. However, if the sand is too fine in relation to the coal, the sand will actually

rise above the top of the coal during the first backwash and remain there when the filter is returned to service. For example, if a 0.2 mm sand were placed below 1.0 mm coal, the materials would actually reverse during backwash with the sand becoming the upper layer and the coal the bottom layer. Although the sand has a higher specific gravity, its small diameter in this case would result in its rising above the coal. The only way to enable very fine sand to be used in the bottom filter layer would be the use of finer coal, which would defeat the purpose of a coarse upper filter layer since the fine coal would be susceptible to surface blinding.

The problem of keeping a very fine media at the bottom of the filter has been overcome by using a third, very heavy (specific gravity of about 4.2), very fine (0.15 mm) material (garnet) beneath the coal and sand. The garnet, sand and coal particles are sized so that some intermixing of these materials occurs and no discrete interface exists between the three materials. This eliminates the stratification illustrated for the dual media filter in Figure III-3. Also, a filter particle size gradation results which approximates the ideal of a uniform decrease in particle size with increasing filter depth as shown in Figure III-4. The resulting mixed-media filter may have a particle size gradation which decreases from about 1.5 mm at the top to about 0.25 mm at the bottom. This filter has a coarse upper layer to reduce sensitivity to surface blinding but forces the effluent to pass through a much finer media than either a sand or coal-sand bed does. The uniform decrease in particle size with the filter depth allows the entire filter depth to be utilized for floc removal and storage.

FIGURE III-2<sup>2</sup>

Cross-section through single-media bed such as conventional rapid sand filter.

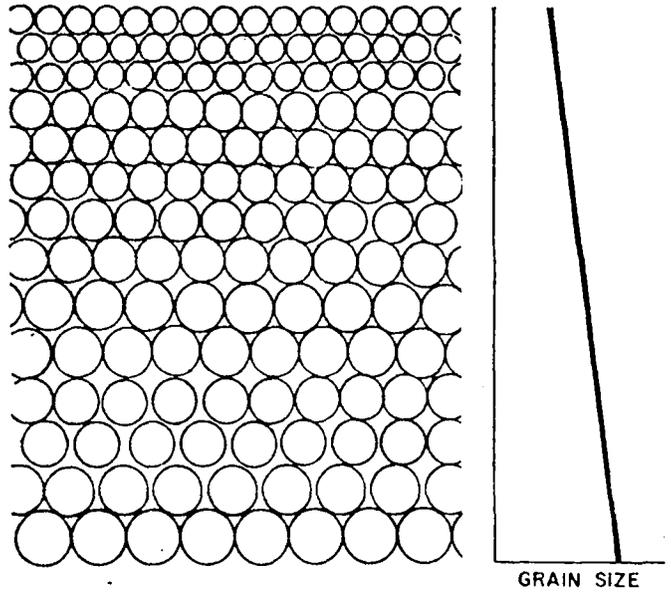


FIGURE III-3<sup>2</sup>

Cross-section through dual-media bed, coarse coal above fine sand.

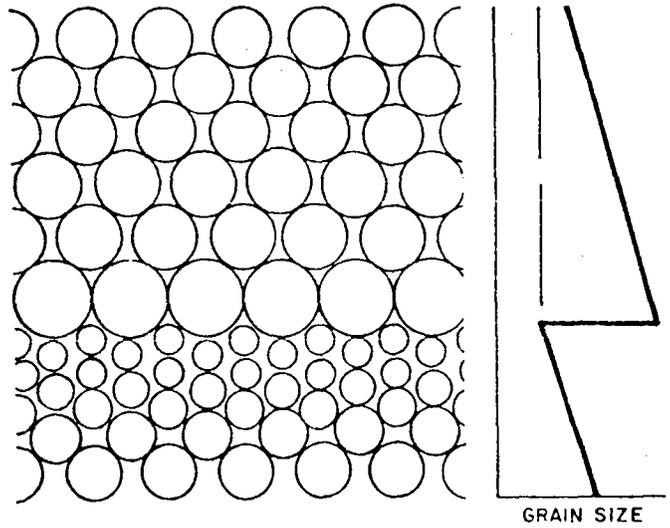
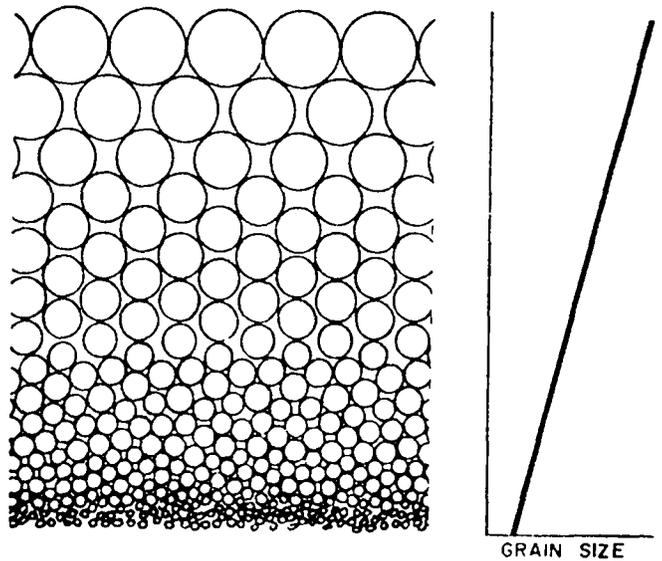


FIGURE III-4<sup>2</sup>

Cross-section through ideal filter uniformly graded from coarse to fine from top to bottom.



This latter filter media concept is referred to as "mixed-media" throughout this report. Unfortunately, the technical literature uses this term to describe a variety of filter media designs (including dual media), but its use in this report is specific to the use of three media sized for controlled intermixing.

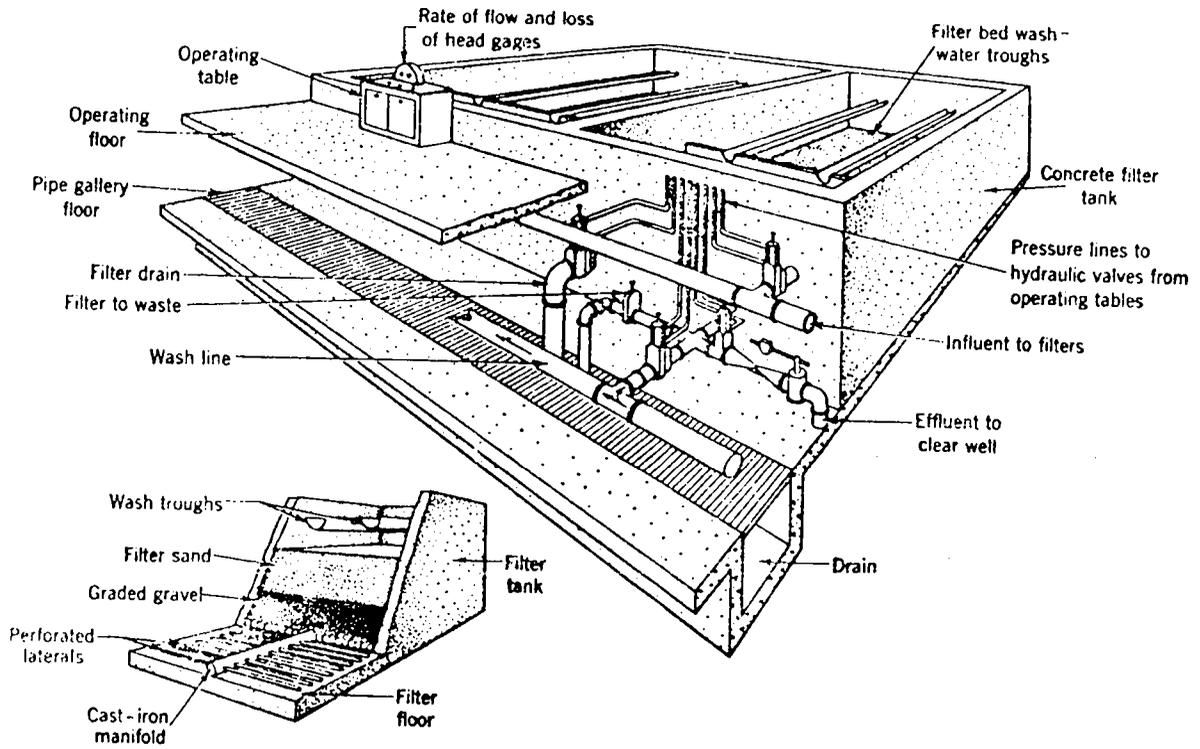
The use of mixed-media filters in water and tertiary waste treatment applications is a well established, successful practice. Filtration may be accomplished in open, concrete structures by gravity flow or in steel, pressure vessels. The operation and control of the process may be readily automated<sup>2,3</sup>. Figure III-5 illustrates a typical gravity filter structure.

#### Carbon Adsorption:

Coarse-to-fine filtration can also be provided in single-media, upward flow filters, but their use has been limited to date. There are a rather limited number of unit processes which are capable of removing refractory organic materials from wastewater, including reverse osmosis, freezing, chemical oxidation, adsorption on powdered carbon, and adsorption on granular carbon. The major problem associated with the use of powdered carbon is the recovery and reuse of carbon. Due to its very small size, the carbon is easily burned and lost in a thermal regeneration process. Powdered carbon was used in sugar refineries for many years, but its use was eventually discontinued in favor of the use of granular carbon, primarily due to inconsistent and generally poor recoveries of the finer carbon. Also, handling of the large quantities of powdered carbon required for wastewater

FIGURE III-5

TYPICAL GRAVITY FILTER



treatment presents some severe dust problems. The Federal Government is now sponsoring several research studies to develop attractive means of regenerating powdered carbon, but all of these potential techniques are far from proven processes.

Reverse osmosis, freezing and chemical oxidation are not yet developed to the point of being either practical or economical as the sole process for removing refractory organics. Adsorption on granular activated carbon is at this time the best candidate as the major process for removal of refractory organics<sup>4,5,6</sup>. The commercial availability of a high-activity, hard, dense granular activated carbon made from coal, plus the development of multiple hearth furnaces for on-site regeneration of this type of carbon make the cost of granular activated carbon for wastewater treatment practical. The fact that activated carbon has an extremely large surface area per unit weight (on the order of 1,000 m<sup>2</sup>/g) makes it an extremely efficient adsorptive material. The activation of carbon in its manufacture produces many pores within the particles, and it is the vast areas of the walls within these pores that accounts for most of the total surface area of the carbon. In water, activated carbon has a preference for large organic molecules and for substances which are nonpolar in nature. Many short-chained organic molecules (i.e., sugars, methanol) are not readily adsorbable. Preceding activated carbon treatment with conventional biological treatment will remove the biodegradable short-chained organics that are not readily adsorbable. Although some wastewater treatment systems are now relying solely on

carbon adsorption for removal of organics, the combination of biological processes and adsorption will minimize the organic content of the wastewater - a primary concern in domestic wastewater reuse.

Granular carbon used in wastewater treatment is typically about 0.8 mm effective size. Crushing of carbon particles to produce smaller particles enhances the rate of adsorption by exposing more entrances to the carbon pores. Because the carbon particle size primarily affects the rate of adsorption and not the total adsorptive capacity of the carbon, the difference in performance of columns containing different size carbons decreases as the contact time increases. Use of small carbon sizes also increases the head loss experienced when passing water through the column - another practical limitation on the size of carbon used.

The rate of adsorption of organics found in wastewater increases with decreasing pH of the water. Adsorption is very poor at pH values above 9.0.

The effect of turbidity or suspended solids in water applied to granular carbon on the efficiency and life of the carbon has not been determined precisely. However, any restriction of pore openings or buildup of ash or other materials within the pore openings due to the presence of suspended or colloidal materials may have an adverse effect upon the adsorptive capacity or service life of the carbon. These hazards can be minimized by applying water which has been pretreated to the highest practical clarity to the carbon.

Wastewater is passed through beds of granular carbon which may resemble pressure or gravity filters in configuration (Figure III-6) or they may be housed in deep (20-25 feet) columns (Figure III-7). Typical contact times (based on the column volume occupied by the carbon) are 20-40 minutes for domestic wastewaters.

Presently the best carbons for treatment of wastewater appear to be those made from select grades of coal. These carbons are hard and dense and can be conveyed in water slurry with no appreciable deterioration. The physical strength of the carbon must be great enough to withstand the repeated handling required during regeneration. Regeneration is accomplished by moving saturated carbon from the carbon contactor system to the regeneration system, typically in a water slurry.

The carbon is drained to remove moisture and regeneration is then accomplished by heating the carbon to 1650-1700<sup>o</sup>F in a low-oxygen environment (typically done in a multiple hearth furnace). This drives the organics off of the carbon while minimizing burning of the carbon itself. The off-gas from the regeneration furnace is then passed through an afterburner and scrubber to control air pollution. Carbon losses in regeneration (5 to 10 percent) are made up by adding virgin carbon.

#### Nitrogen Removal:

Nitrogen present in wastewaters used for recharge may lead to an undesirable buildup of nitrate-nitrogen in the groundwater supply. Nitrogen

FIGURE III-6 TYPICAL DOWNFLOW GRAVITY CARBON CONTACTOR 4

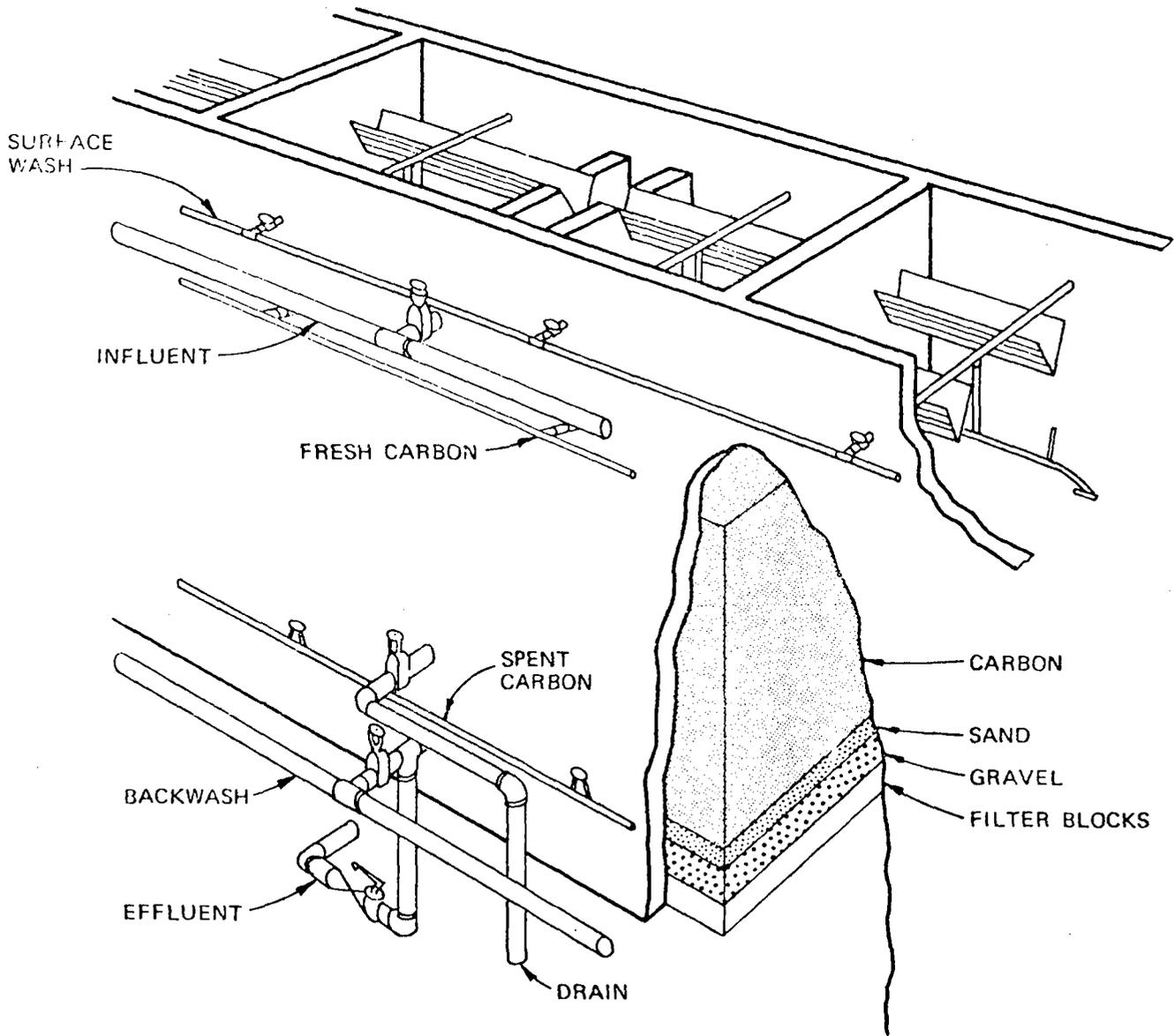
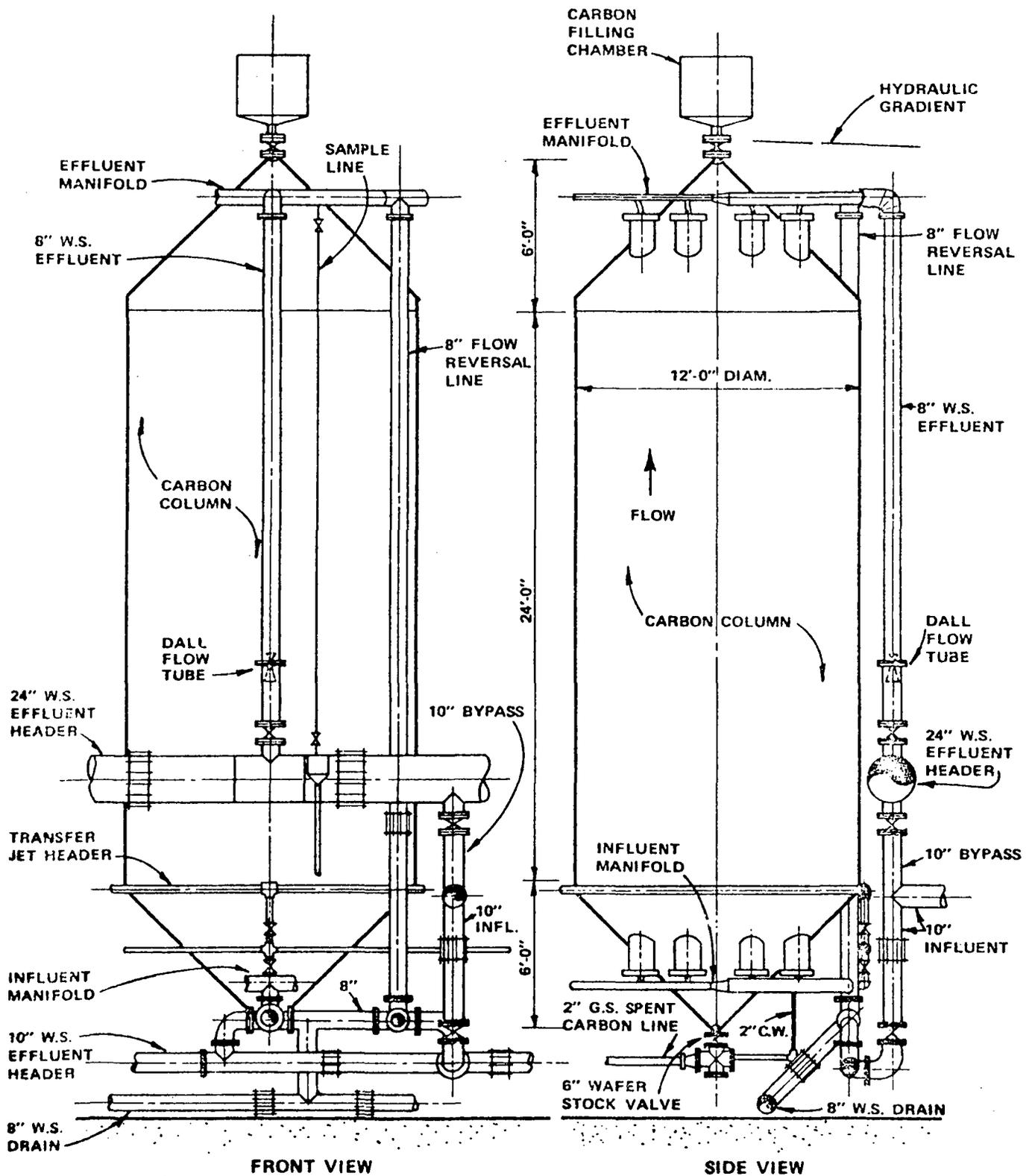


FIGURE III-7 UPFLOW COUNTERCURRENT CARBON COLUMN (Orange County, California)<sup>4</sup>



may be removed from wastewater by biological or by physical-chemical treatment processes.

Nitrogen can be present in water in several forms. Most of the nitrogen in raw wastewater is present as Organic-N and as ammonium ion ( $\text{NH}_4^+$ ) or as ammonia gas ( $\text{NH}_3$ ), the relative proportions of each being dependent on the pH of the water. At pH = 7 (neutral pH) virtually all of the ammonia-nitrogen is present as ammonium ion in true solution. At pH = 11 (alkaline or basic solution) almost all of the ammonia-nitrogen is present as dissolved ammonia gas ( $\text{NH}_3$ ) or is in a state similar to dissolved oxygen or free  $\text{CO}_2$ . Organic nitrogen in water is nitrogen which is present in organic molecules or compounds such as proteins or amino acids. Nitrate-nitrogen ( $\text{NO}_3^-$ ) is nitrogen which is present in water as an ion in true solution - a fully oxidized, relatively stable form. Nitrite-nitrogen ( $\text{NO}_2^-$ ) is a transitory, very unstable form of nitrogen in water. It is uninterruptedly being converted by biological action to either nitrate or ammonia-nitrogen.

Biological processes for removal of nitrogen have received a great deal of study and are being incorporated in several plants, including the 309 mgd Blue Plains Plant in Washington, D. C., now under construction. Several alternate systems have been studied. However, all are based on the same basic principles. The nitrogen compounds found in raw sewage may be converted to nitrates in a properly controlled biological process (the nitrification process). These nitrates may then be removed by subjecting the effluent from the nitrification process to treatment in the absence of oxygen. In essence, under these anaerobic conditions, the microbes utilize

the oxygen contained in the nitrate compounds and release the nitrogen as nitrogen gas. Since nearly 80 percent of the atmosphere consists of nitrogen, there is no air pollution associated with the release of nitrogen from the wastewater to the atmosphere. The process appeal is based on the simplicity of the equipment and structures involved and the fact that no liquid or solid waste byproducts are generated. Toxic industrial wastes, shock loads, and temperature changes may upset the process.

Figure III-8 summarizes the alternate approaches to biological nitrogen removal. The most reliable performance has been found to occur when the carbonaceous organic compounds are first oxidized in a high-rate activated sludge step with the resulting activated sludge settled and recycled to this step of the process. The nitrification step can then be accomplished in another activated sludge process or in a trickling-filter-like column of stones or synthetic media. The organisms which carry out the nitrifying step are very slow growing organisms and if they are lost from the process due to poor settling characteristics or for other reasons, process performance may suffer for many weeks until an adequate population of nitrifiers can be established again. Thus, the columnar operation for nitrification offers some advantage in that it provides greater assurance of retention of the nitrifying organisms.

The denitrification step can also be accomplished either in an anaerobic activated sludge system or in a columnar system. In order for this denitrification process to be practical, an oxygen-demand source must be added to the denitrification process so that the nitrates will be quickly reduced.

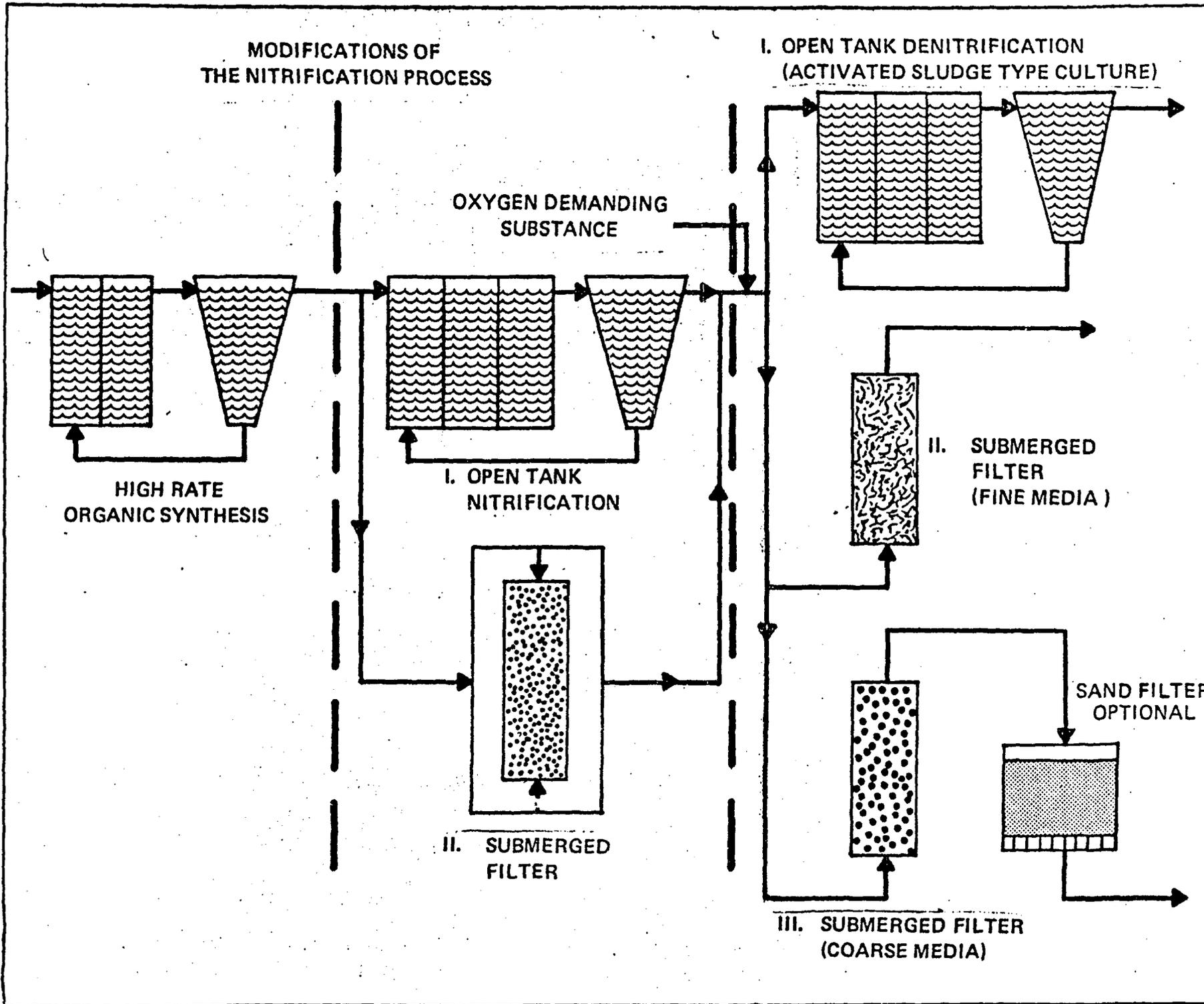


FIGURE III-8 ALTERNATES FOR BIOLOGICAL NITROGEN REMOVAL<sup>7</sup>

The most common method of supplying the needed oxygen demand is by the addition of methanol to the denitrification process.

If adequate nitrogen reduction is to be achieved, then nearly all of the incoming nitrogen must be biologically oxidized. Without prior oxidation, the denitrification step is totally ineffective. A review of the literature reveals that generally the efficiency of this approach has been 80 to 90 percent nitrogen removal when operating properly.

There are three physical-chemical techniques for nitrogen removal which are in use or are now being included in designs of full-scale wastewater treatment plants: (1) ammonia stripping; (2) breakpoint chlorination, and (3) selective ion exchange, or a combination of these processes.

The only process which has actually been used on a plant scale in wastewater treatment is the ammonia stripping process. This process has been in use for ammonia nitrogen at the South Lake Tahoe plant for about 6-1/2 years. Both the advantages and limitations of this process have been clearly demonstrated. The principle of the process is very simple. The ammonium ions in the secondary effluent can be converted to ammonia gas by raising the pH to high values. The gaseous ammonia can then be liberated by passing the high pH effluent through a stripping tower where the agitation of the water in the presence of a large air flow through the tower releases the ammonia (Figure III-9). The use of lime permits simultaneous coagulation for SS and phosphorus removal and upward adjustment of pH prior to the stripping process.

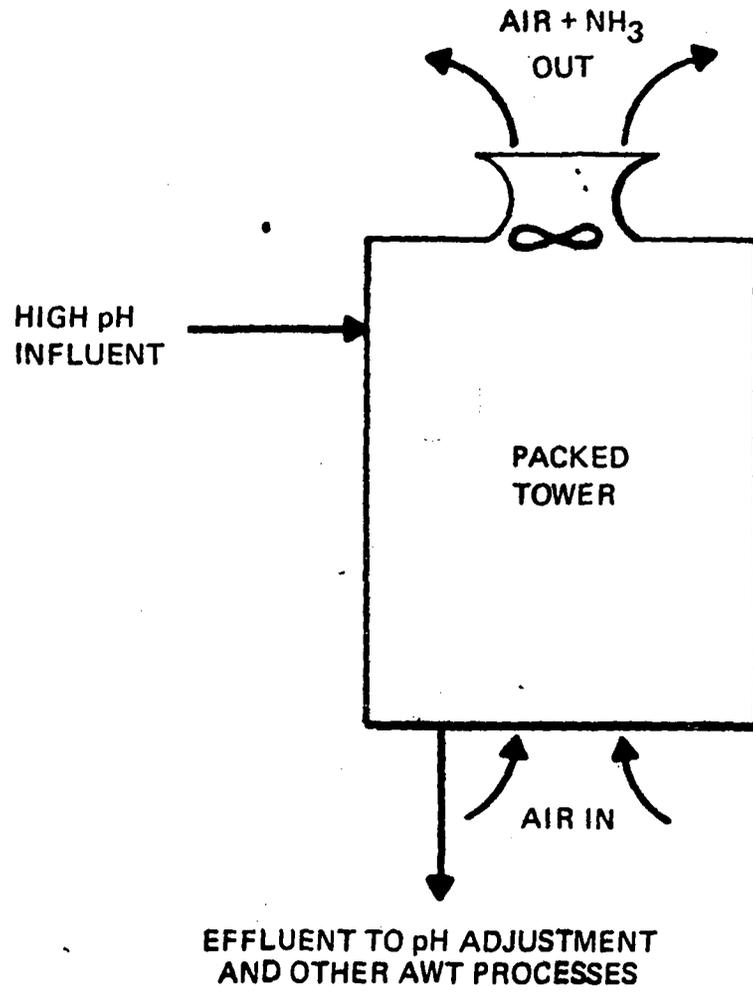


FIGURE III-9 AMMONIA STRIPPING PROCESS<sup>7</sup>

The ammonia stripping process then consists of (1) raising the pH of the water to values in the range of 10.8 to 11.5 generally with the lime used for phosphorus removal, (2) formation and reformation of water droplets in a stripping tower, and (3) providing air-water contact and droplet agitation by circulation of large quantities of air through the tower. The towers used for ammonia stripping closely resemble conventional cooling towers. The major process limitation is the effect of temperature on process efficiency. As the air temperature drops, the efficiency of the process also drops. For example, the stripping process removes about 95 percent of the ammonia in warm weather (20 degrees C air temperature) but only about 75 percent of the ammonia when the temperature falls to 10 degrees C. The process becomes inoperable due to freezing problems within the stripping tower when the air temperature falls very far below freezing. It is not practical to heat the large volumes of air required for the stripping process.

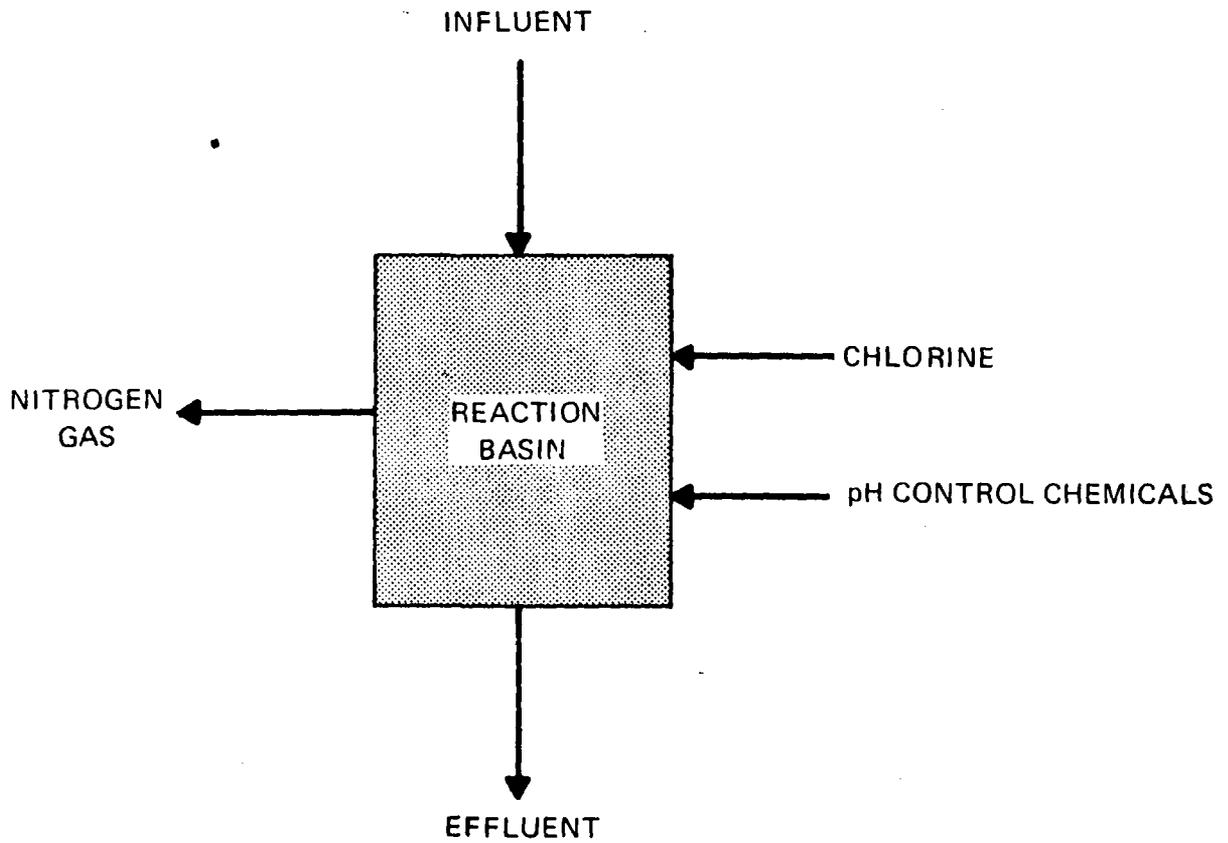
A major operating problem has been calcium carbonate scale deposition on the tower fill and structural members. However, in most cases, the scale which forms can be removed easily and economically if the tower is designed for convenient removal of this scale. An example of this is the 15 mgd tower now under construction at the Orange County California Water District plant where the tower packing has been designed to be readily removable for cleaning as a precaution against scaling problems. Under the right climatic conditions and with the proper precautions regarding scale prevention or removal, ammonia stripping is a practical, reliable method for nitrogen reduction.

The breakpoint chlorination process is based on the fact that when chlorine is added to wastewater containing ammonia nitrogen, ammonia reacts with the hypochlorous acid formed to produce chloramines. Further addition of chlorine to the breakpoint converts the chloramines to nitrogen gas. From 95 to 99 percent of the ammonia is converted to nitrogen gas with no significant amount of nitrous oxide formed. To achieve the conversion, about 10 mg/l of chlorine must be added per mg/l of ammonia-nitrogen in a wastewater subjected to tertiary treatment. This compares with a theoretical 7.6:1 ratio.

The use of chlorine produces an equivalent weight of hydrochloric acid which may depress the pH of the wastewater unless the natural alkalinity is adequate or a base such as sodium hydroxide is added (See Figure III-10). Another significant consideration is that a substantial increase in effluent chloride and Total Dissolved Solids (TDS) will result from the addition of such large quantities of chlorine. In addition to nitrogen removal ability, breakpoint chlorination also offers a high degree of assurance of complete disinfection of the wastewater as discussed later in this report.

The selective ion exchange process derives its name from the use of zeolites which are selective for ammonia relative to calcium, magnesium and sodium. The zeolite currently favored for this use is clinoptilolite, which occurs naturally in several extensive deposits in the western United States. The clinoptilolite is crushed and sieved to obtain a 20 by 50 mesh size (about the size of the sand in a rapid sand filter). Ammonia is removed by passing the wastewater through a bed of clinoptilolite at a rate of about

FIGURE III-10 BREAKPOINT CHLORINATION PROCESS <sup>7</sup>



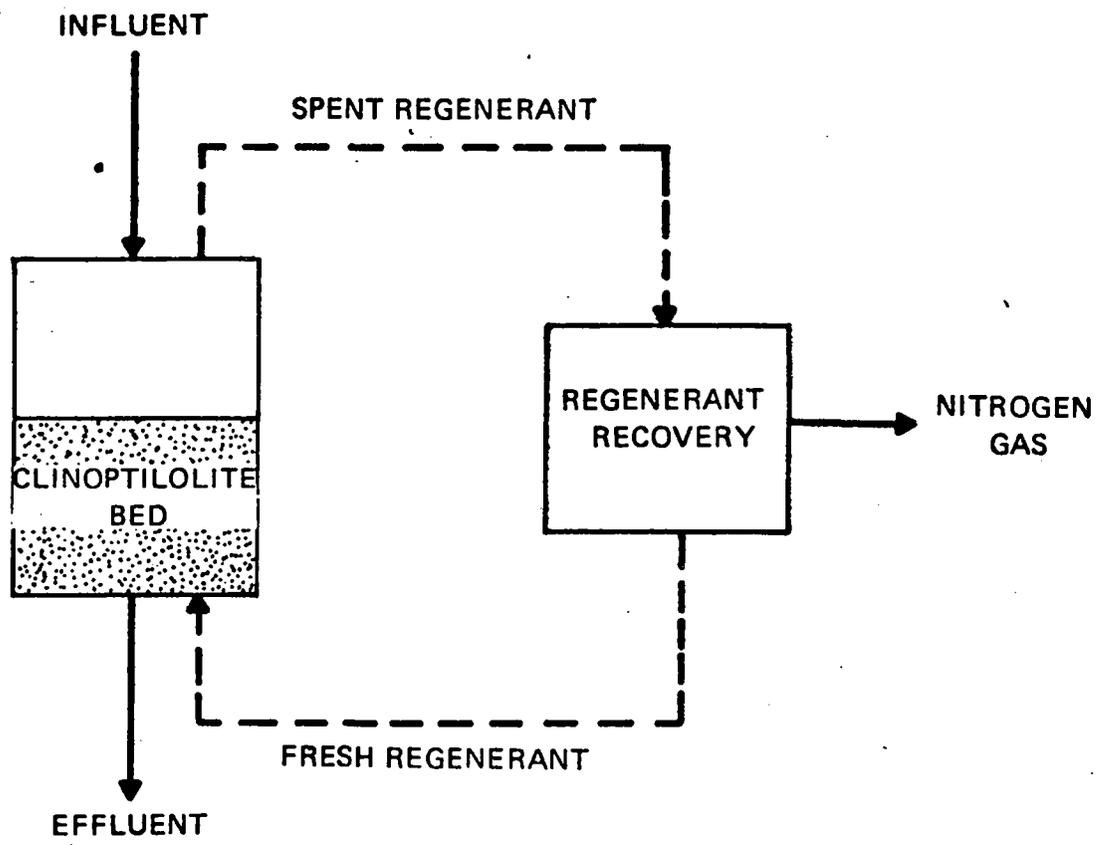
10 bed volumes per hour (Figure III-11). After about 200 bed volumes of normal strength municipal waste have passed through the bed, the capacity of the clinoptilolite has been used to the point that ammonia begins to leak through the bed. At this point, the clinoptilolite must be regenerated so that its capacity to remove ammonia is restored.

The resin is regenerated by passing concentrated salt solutions through the exchange bed when the ammonia concentration has reached the maximum desirable level. Following regeneration, the ammonia-laden spent regenerant volume is about five to six percent of the throughput treated prior to regeneration. Several techniques are available for removing the ammonia from the regenerant. Once the ammonia has been removed, the regenerant can be reused. Thus, there are no regenerant brines to dispose of - a major problem with conventional, non-selective exchange resins. Selective ion exchange has the advantages of removing the nitrogen without the addition of objectionable quantities of other materials and will perform well in cold weather and with wide variations in influent quality.

#### Demineralization Processes:

Salt buildup in water reuse systems can cause the water TDS to exceed the drinking water standard of 500 mg/l. Although no health problems result, TDS values greater than 500 mg/l may cause the water to be unattractive in its taste. The blending of reclaimed waters with makeup water will result in a decrease in TDS and the establishment of an equilibrium value which will depend upon the amount of makeup water used and the average TDS of both

FIGURE III-11 SELECTIVE ION EXCHANGE PROCESS<sup>7</sup>



waters. However, there may be circumstances where demineralization of the wastewater will be required to achieve a satisfactory salt balance in the reuse system. The capabilities of the desalting processes for removal of other contaminants is also of interest and is later discussed. There are three alternate approaches to desalting, which show promise for wastewaters: ion exchange, electrodialysis, and reverse osmosis<sup>8</sup>.

The ion exchange process has been used for many years in the treatment of industrial waters and in municipal softening plants. The equipment and operating procedures are well developed. However, the process has not been studied as extensively as other processes for wastewater desalting. Major pilot studies on the treatment of municipal wastewater have been conducted at Pomona, California; Santee, California; and Elgin, Illinois. The most effective system for treatment of wastewater is a three-unit system composed of weak acid, strong acid, and weak base resins in series. Resins can be contained in fixed bed or moving bed units. A typical fixed bed system is shown in Figure III-12. It is possible to easily reduce the dissolved solids in brackish water supplies and municipal wastewater to about 50 mg/l by ion exchange.

Advantages of the ion exchange process include: well developed and proven technology, large-scale equipment available which has a history of reliable operation, highly efficient removal of common inorganic salts and minimal problems with surface fouling with carbon treated municipal wastewater, and cost estimates are more reliable than for the membrane processes. Disadvantages include: direct relationship between operating costs and

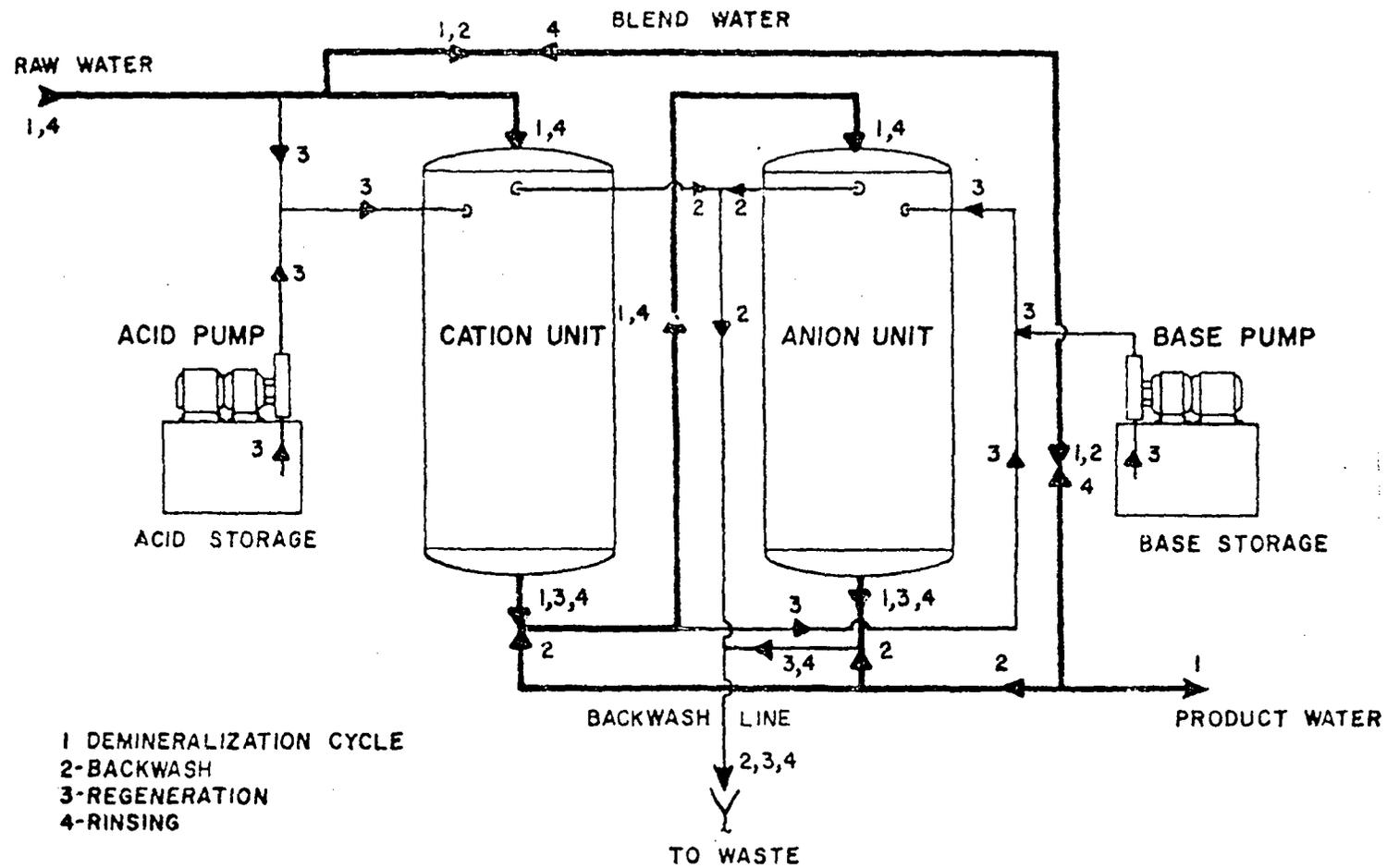


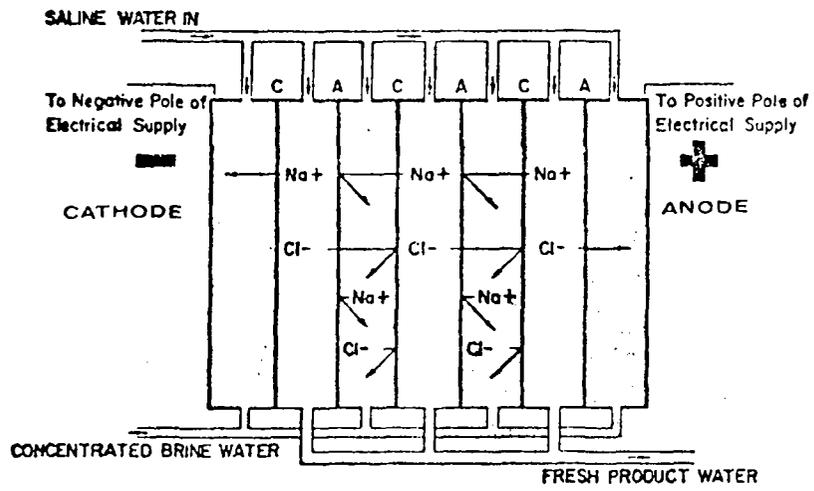
FIGURE III-12 TYPICAL ION EXCHANGE SYSTEM <sup>8</sup>

salts removed; therefore, as salt removal percentages increase, so do chemical operating costs, large amounts of chemicals are required, and wastes requiring disposal are regenerate chemicals which include strong acids and bases as well as the salts removed from the wastewater.

The only plant in the United States utilizing the ion exchange process for desalting a municipal water supply is a 500,000 gpd plant recently constructed in Burgettstown, Pennsylvania. This plant treats a potable water supply which has been contaminated by acid mine drainage.

The electrodialysis process is well developed and has been used for over ten years in the treatment of brackish water supplies. In the electrodialysis (ED) process, water flows between alternately placed cation-permeable (c) and anion-permeable (a) membranes as illustrated in Figure III-13. A direct electric current provides the motive force for the ion migrations through the membranes. Many alternating cation and anion membranes, each separated by a plastic spacer, are assembled into membrane stacks. Several hundred membranes and their separating spacers are usually assembled between a single set of electrodes to form a membrane stack. Passage of water between the membranes of a single stack, or stage, usually requires 10-20 seconds, during which time the entering minerals in the feed water are removed. The actual percentage removal that is achieved varies with water temperature, type and amounts of ions present, flow rate of the water, and stack design. Typical removals per stage range from 25-60 percent. Practical systems currently employ one to six stages.

FIGURE III-13 ELECTRODIALYSIS DEMINERALIZATION PROCESS <sup>8</sup>



Major pilot studies on the treatment of municipal wastewater have been conducted at Pomona, California; Santee, California; Orange County, California; and Lebanon, Ohio. The largest municipal water supply desalting plant in the United States (3 mgd), is currently under construction at the Foss Reservoir in Oklahoma and will utilize the electrodialysis process.

Treatment by activated carbon adsorption is a requirement for municipal wastewater to be desalted by electrodialysis to avoid fouling of the membranes. Power required for electrodialysis is about 0.2 to 0.4 kwh per 1,000 gallons for each 100 mg/l dissolved solids removed, plus 2 to 3 kwh per 1,000 gallons for pumping feed water and brine.

Advantages of the electrodialysis process include: well developed technology, including equipment and membranes, efficient removal of most inorganic constituents, and waste brine contains only salts removed plus a small amount of acid used for pH control. Disadvantages of the electrodialysis process include: salt removal is directly proportional to the amount of current used; therefore, as salt removal requirements increase, power consumption and operating costs also increase, low temperatures reduce removal efficiency, and organics must be removed by carbon adsorption to prevent excessive membrane fouling.

The reverse osmosis process is the newest of the salt removal processes. It has been intensively developed in the United States during the past 10 years by several large corporations.

A natural phenomenon known as osmosis occurs when solutions of two different concentrations are separated by a semi-permeable membrane. Water tends to pass through a semi-permeable membrane from the more dilute side to the more concentrated side, thus producing equal TDS concentrations on both sides of the membrane. The ideal osmotic membrane permits passage of water molecules but prevents passage of ions such as sodium and chloride. For example, if a solution of sodium chloride in water is separated from pure water by means of a semi-permeable membrane, water will pass through the membrane in both directions, but it will pass more rapidly in the direction of the salt solution. At equilibrium, the quantity of water passing in either direction is equal, and the pressure is defined as the osmotic pressure of the solution having that particular concentration of TDS. The magnitude of the osmotic pressure depends on the concentration of the salt solution which is related to the solution's vapor pressure and temperature. By exerting pressure on the salt solution, the osmosis process can be reversed. When the pressure on the salt solution is greater than the osmotic pressure, freshwater diffuses through the membrane in the opposite direction to normal osmotic flow - hence, the name for the process, reverse osmosis (RO).

Many materials have been studied for possible use as membranes for water and wastewater purification and related separation and concentration procedures. The most widely used membrane developed to date is a modified cellulose acetate film. Operating plants carry out the RO principle in

several different process designs and types of membrane configurations.

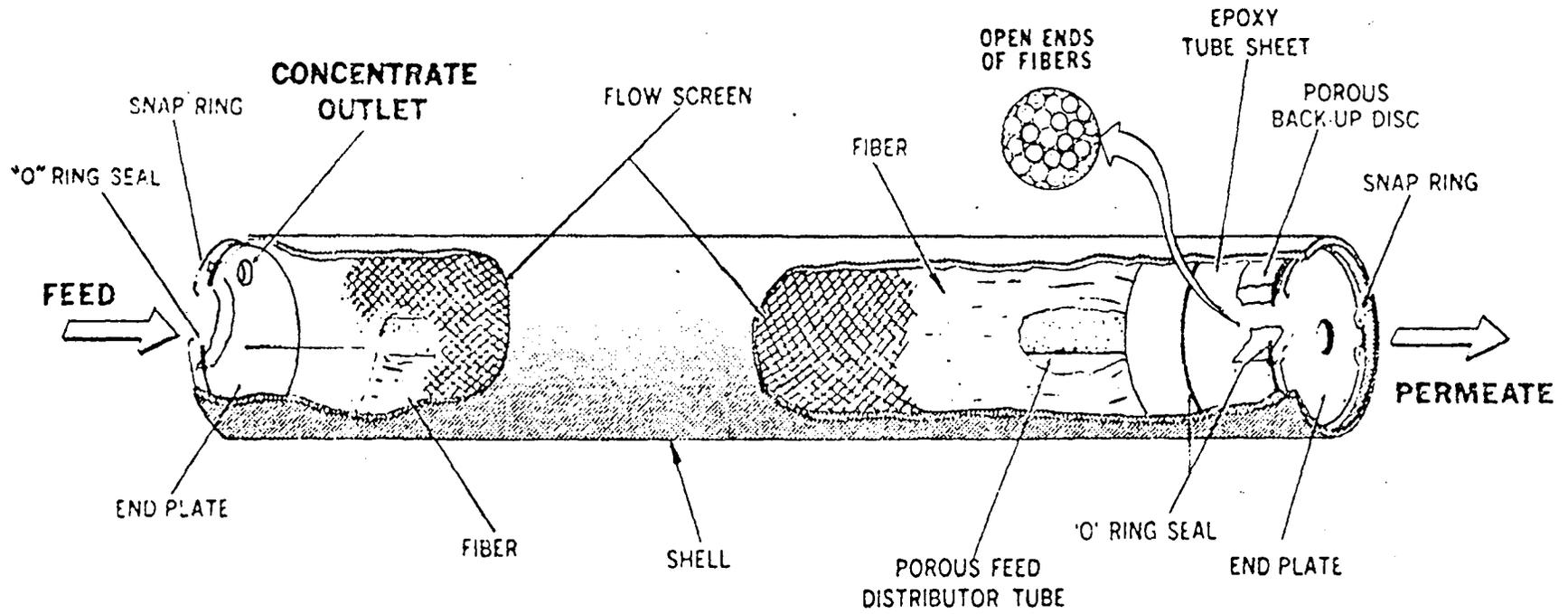
There are three types of membrane systems in commercial production:

1. Spiral wound
2. Hollow fine fiber
3. Tubular

A spiral wound membrane is supported on both sides of a backing material and sealed with a glue on three of the four edges of the laminate. The laminate is also sealed to a central tube which is drilled. The membrane surfaces are separated by a screen material which acts as a brine spacer. The entire package is then rolled into a spiral configuration and wrapped in a cylindrical form with tape as an outer wrap. Feed flow is parallel to the central tube while the permeate flow is through the membrane toward the central tube.

The hollow fiber type of membrane was developed initially by DuPont and Dow Chemical. The fine fibers are about the size of a human hair with an inside diameter of about .002 inches and an outside diameter of about .004 inches. In these very small diameters, fibers can withstand enormous pressures. In an operating process, the fibers are placed in a pressure vessel with one end sealed and the other end protruding outside of the vessel. The salt water is under pressure on the outside of the fibers and product water flows inside of the fiber to the open end. A module is illustrated in Figure III-14.

FIGURE III-14 HOLLOW FIBER RO MODULE AS MANUFACTURED BY DUPONT <sup>8</sup>



III-51

Tubular membrane processes operate on much the same principle as the hollow fine fiber except that the tubes are much larger, on the order of 0.5 in. ID. Typically, the membrane is supported by a network of polyester filaments. Composite metal and plastic fittings are attached to each end of the membrane tube and its polyester pressure support. The tubular membrane is enclosed by a plastic shroud to prevent damage to the membrane and provide a means for contamination-free product collection. Brackish water flows through the tube, product water is taken from the outside of the tubes and the concentrate remains inside.

Major pilot studies on the treatment of municipal wastewater have been conducted at Pomona, California; Hemet, California; and Lebanon, Ohio. The largest reverse osmosis plant in the world is in Kashima, Japan. The initial capacity of this plant was 800,000 gpd and it is currently being expanded to 1.4 mgd. The largest municipal water supply desalting plant in the United States utilizing the reverse osmosis process is in Florida. The capacity of this plant is 350,000 gpd and it is currently being expanded to 650,000 gpd. A 117,000 gpd reverse osmosis plant will be constructed near Yuma, Arizona to desalt irrigation return flows.

The principal problem in the treatment of municipal wastewater is membrane fouling which can greatly reduce the capacity of the units. However, fouling generally decreases with increasing degrees of wastewater pretreatment. Reverse osmosis membranes remove a high percentage of almost all inorganic ions, turbidity, organic material, bacteria and viruses. The dissolved solids in municipal water and wastewater can be easily reduced to

50-150 mg/l in one stage. Power requirements for commercially available reverse osmosis systems are about 6 to 8 kwh per 1,000 gallons of product water. This power requirement does not change appreciably over the range of dissolved solids generally present in municipal water supplies and wastewater.

Advantages of the reverse osmosis process include: removes a high percentage of organic material, turbidity, bacteria and viruses, as well as inorganic material, removal efficiencies and power consumption remain nearly stable over the range of dissolved solids present in most municipal wastewaters, and waste brine contains only salts removed plus a small amount of acid used for pH control. Disadvantages of the reverse osmosis process include: lack of operating experience, reduction in operating capacities due to membrane compaction and fouling, commercially available units are all relatively small modules; therefore, large-scale plants would be composed of many modules, and temperature should be 65<sup>o</sup> to 95<sup>o</sup>F and the pH controlled for efficient operation.

#### Disinfection Process

Even after AWT of secondary effluents, there is the likelihood that pathogenic bacteria and virus may persist. Thus, some disinfection process must be coupled with secondary and AWT processes to provide adequate disinfection. Chlorination is the process that is most commonly used for wastewater disinfection in the U. S. Although it is the process that most sanitary engineers associate with disinfection, other AWT processes in themselves provide disinfection as discussed later. In fact, complete wastewater disinfection is dependent upon optimizing the unit processes of

chemical coagulation, sedimentation and filtration (which in themselves provide substantial reductions in bacteria and viruses) to produce minimum water turbidities to assure the maximum contact between any remaining pathogens and the disinfectant<sup>3</sup>.

For purposes of disinfection of municipal supplies, chlorine is primarily used in two forms: as a gaseous element or as a solid or liquid chlorine-containing hypochlorite compound. Gaseous chlorine is generally considered the least costly form of chlorine that can be used in large facilities. Hypochlorite forms have been used primarily in small systems (less than 5,000 persons) or in large systems where safety concerns related to handling gaseous form outweigh economic concerns. Disinfection is achieved by injecting the chlorine into the wastewater (usually following all other treatment processes) and retaining the chlorinated water in a contact basin for 30-60 minutes before discharge. An important factor often given inadequate consideration in past designs is proper mixing of the chlorine with the wastewater when it is injected.

Although chlorine has proven to be an effective disinfectant, it does react with organic compounds found in wastewaters to form chlorinated hydrocarbons which are of concern from a health aspect in water reuse situations. A later part of this section deals with the efficiency of treatment processes in removing these compounds.

An alternate to chlorine (or other halogens such as iodine and bromine which have also been used for disinfection) which would eliminate the potentially undesirable side reactions of chlorine is the use of ozone as the

disinfectant. Ozone is one of the two most potent and effective germicides used in water treatment. Only free residual chlorine can approximate it in germicidal power. The use of ozone for disinfection of municipal drinking water actually antedates chlorination. Ozone is produced at its point of usage by passing dry air between two high potential electrodes to convert oxygen into ozone. Improvements in the technology of ozone production have bettered the reliability and economy of its generation. The advantages of using ozone are its high germicidal effectiveness, which is the greatest of all known substances, even against resistant organisms such as viruses and cysts, and the fact that upon decomposition, the only residual material is more dissolved oxygen. In addition, its potency is unaffected by pH or ammonia content. Ozone reactivity is affected by pH. Organics and ammonia exert an ozone demand. However, the use of ozone does have disadvantages. Because it must be produced electrically as it is needed and cannot be stored, it is difficult to adjust treatment to variations in load or to changes in raw water quality with regard to ozone demand. As a result, ozone historically has been found most useful for supplies with low or constant demand such as groundwater sources. Also, the cost of ozone is typically significantly higher than the cost of chlorine required to accomplish the same degree of disinfection. The use of ozone has been limited due to poor gas transfer facilities.

As with chlorine, the proper mixing of ozone with the wastewater upon injection is an important consideration. Also, the removal of turbidity prior to ozonation is important as it is with chlorination.

Both the chlorination and ozonation processes will be discussed in the subsequent part of this section.

#### Effluent Storage in Open Reservoirs

Although perhaps not typically thought of as a treatment process, storage of AWT effluent or intermediate processed water in open reservoirs itself can perform a useful treatment function. Some of the natural purification processes include: prolonged storage, sedimentation, exposure to sunlight, reaeration, biological action, and temperature. Water is not a natural environment for intestinal bacteria or viruses and they die off with time. Storage alone can result in a 99 percent removal of coliform organisms.

Natural processes, relative to plant treatment processes, are for the most part low-rate and slow-acting. They take place over a considerable time period and often over appreciable distances. Storage and separation in time and space between wastewater discharge and water reuse provides several advantages. It provides time for monitoring and testing of water quality before use and affords mixing and some compensation for variations in plant efficiency, for example. The combination of AWT and natural purification unquestionably provides a higher degree of treatment than either approach alone.

#### TREATMENT PROCESS CAPABILITIES

##### Virus and Bacteria Removal

###### Coagulation, Sedimentation, Filtration, Adsorption:

Conventional biological secondary processes do reduce the quantities of bacteria and viruses found in raw sewage. However, secondary effluents

still contain a significant number of pathogens. Although effluent chlorination is the process that is most commonly used to further reduce the pathogen population of secondary effluents, some of the AWT processes previously discussed also provide significant reductions, as well as to make the water more susceptible to action of disinfectants. The disinfecting capabilities of these other processes will be discussed before discussing the disinfecting processes such as chlorination and ozonation.

The chemical coagulation process used in conjunction with sedimentation (and also filtration in some cases) has been noted by several researchers<sup>9-19</sup> as providing high degrees of removal of viruses. For example, alum coagulation was found to remove 95 to 99 percent of coxsackie virus and ferric chloride coagulation was found to remove 92 to 94 percent of the same virus<sup>9</sup>. With both alum and ferric chloride, good virus removal was contingent upon good floc formation and the absence of interfering substances. The effectiveness of removal was not temperature-dependent with either coagulant. It has been determined that viruses were not inactivated by alum coagulation but could be partially recovered from the sludge. The presence of organic material was shown to decrease the amount of virus removed by alum or ferric chloride coagulation.

In a 20-month study of the removal of polio virus Type I from water, Robeck, Clarke and Dostal<sup>11</sup> observed that the polio virus organism is removed by flocculation and filtration with about the same efficiency as coliforms. They noted that if a low but well-mixed dose of alum was fed just ahead of the filters operated at 6 or 2 gpm/sf, more than 98 percent

of the viruses were removed by 16 inches of coarse coal on top of 8 inches of sand. If the alum dose was increased and conventional flocculators and settling were used, the removal was increased to over 99 percent. Floc breakthrough of the filter, sufficient to cause a turbidity of less than 0.5 units, was usually accompanied by virus breakthrough. Addition of a polyelectrolyte to the filter influent decreased virus in the effluent by increasing floc strength and floc retention in the filter.

The report of an AWWA committee on viruses in water<sup>13</sup> noted that viruses, because of their small size, more easily become enmeshed in a protective coating of turbidity-contributing matter than bacteria would. For most effective disinfection they concluded, turbidities should be kept below 1 Jackson Unit; indeed, they felt it would be best to keep the turbidity as low as 0.1 unit. With turbidities as low as 0.1 to 1, they concluded that a chlorine feed in water plants need be only enough to have a 1 mg/l free chlorine residual after 30 minutes contact time.

While the bulk of studies on virus removal using alum coagulation have been laboratory studies, Walton<sup>14</sup> reported a study of coliform bacteria removal in over 80 full-scale water treatment plants. He found that the removal of coliform bacteria by coagulation, sedimentation and filtration averaged about 98 percent for the several plants studied. The average coliform densities in filtered but unchlorinated waters ranged from 2.9 to 200 per 100 ml. Also, large-scale pilot studies conducted in Dallas, Texas<sup>10</sup> demonstrated that virus removals from secondary effluents by alum coagulation-sedimentation and coagulation-sedimentation-filtration processes are essentially the same as described in the water treatment literature

using smaller-scale processes. Removals of bacterial virus as high as 99.845 percent for coagulation-sedimentation and 99.985 percent for coagulation-sedimentation-filtration processes were observed using alum coagulation. Tests at a 300 gpm pilot plant in Orange County, California found no virus in 64 samples of alum coagulated, filtered and chlorinated secondary (trickling-filter) effluent<sup>87</sup>.

Lime coagulation has demonstrated the ability to effectively remove and inactivate viruses at high pH values. The mechanism of inactivation under alkaline conditions is probably caused by denaturation of the protein coat and by disruption of the virus. In some cases complete loss of structural integrity of the virus may occur under high pH conditions. The pH reached in lime coagulation is a critical factor in determining the degree of virus inactivation. Figure III-15 shows the marked difference in virus inactivation as the pH is increased from 10.1 to 10.8 and then to 11.1<sup>15</sup>. Figure III-16 illustrates the effects of pH on Escherichia coli and Salmonella typhosa.

The pilot plant at Dallas, Texas<sup>10</sup> also found that only a few gram-positive rods could survive high pH lime treatment (pH of 11.2-11.3 with contact times of 1.56-2.40 hours). The virucidal effect of the pH treatment is reflected by the fact that no viable poliovirus were recovered from the sludges resulting from the high pH treatment.

Activated carbon has the ability to adsorb, although not deactivate, virus from wastewater<sup>20</sup> - with maximum adsorption at near-neutral pH values. However, the significance of this ability in carbon treatment of wastewaters has yet to be demonstrated in the field.

FIGURE III-15<sup>15</sup>

Inactivation of Poliovirus 1 by high pH at 25°C in lime-treated (500 mg/l Ca (OH)<sub>2</sub>), sand-filtered secondary effluents.

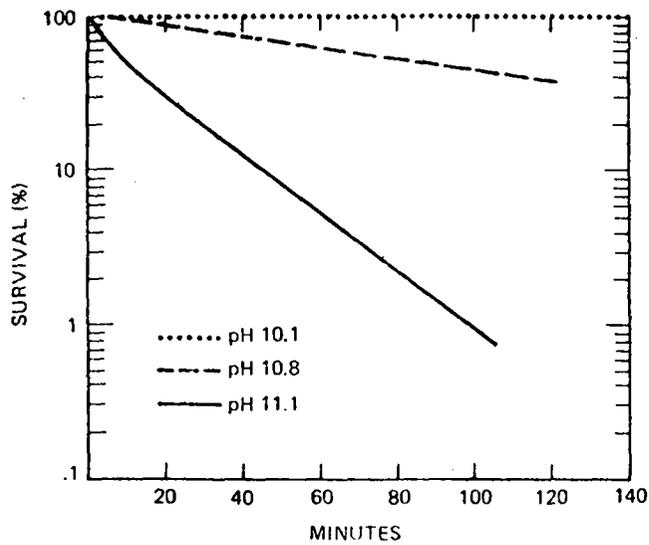
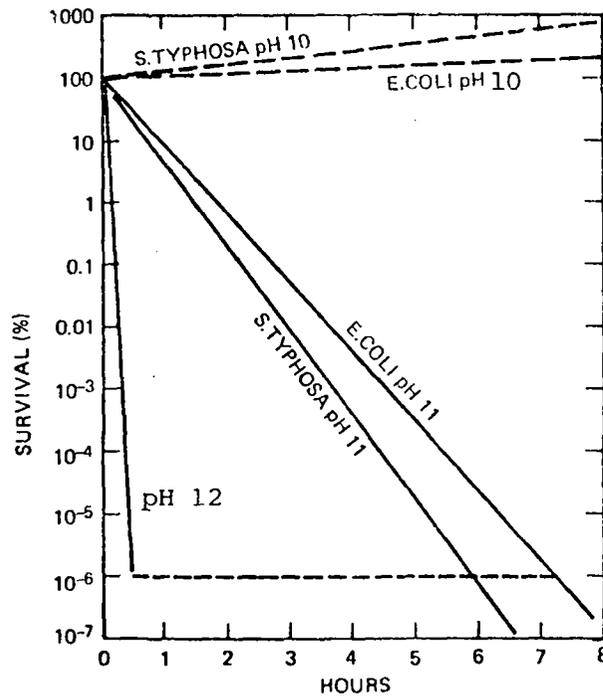


FIGURE III-16<sup>15</sup>

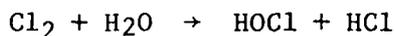
Survival of *E. coli* at pH 11 and 12 and *S. typhosa* at pH 10, 11, and 12 at 25°C.



Chlorination:

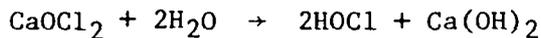
The destruction of pathogens by chlorination is dependent upon water temperature, pH, time of contact, degree of mixing, turbidity, presence of interfering substances, and concentration of chlorine available. Chloramines (which are formed if ammonia is present) are much less effective disinfectants than free chlorine. For example, in one study<sup>21</sup>, at normal pH values, approximately forty times more chloramine than free chlorine was required to produce a near 100 percent kill of E. coli in the same time period. For S. typhosa this ratio was about 25 to 1. To obtain a near 100 percent kill with the same amounts of residual chloramine as with free chlorine required approximately 100 times the contact period for chloramine.

When chlorine is dissolved in water at temperatures between 49°F and 212°F it reacts to form hypochlorous and hydrochloric acids:



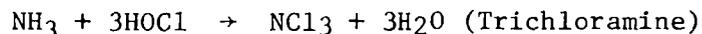
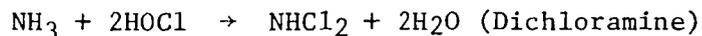
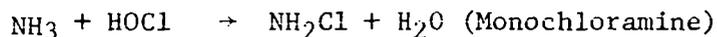
This reaction is essentially complete within a very few seconds. The hypochlorous acid ionizes or dissociates practically instantaneously into hydrogen and hypochlorite ions:  $\text{HOCl} \rightarrow \text{H}^+ + \text{OCl}^-$ . These reactions represent the basis for use of chlorine in most sanitary applications.

Hypochlorite chlorine forms also ionize in water and yield hypochlorite ion which establishes equilibrium with hydrogen ions:



Generally, the HOCl form has been considered to be a far more effective disinfectant than OCl<sup>-</sup>. Several investigators have reported that HOCl is 70-80 times as bactericidal as OCl<sup>-</sup> and that increasing the pH reduces germicidal efficiency because most of the free chlorine exists as the less microbicidal OCl<sup>-</sup> at the higher pH levels. However, one recent study<sup>22</sup> reported that one virus (polio-virus 1) was more rapidly inactivated at pH levels (pH = 10) where the free chlorine is in the form of OCl<sup>-</sup> rather than HOCl. This finding, contrary to the conclusions reached by many others which are presented in the next section, was undergoing evaluation on other animal viruses at the time of this writing.

The reactions of chlorine with ammonia in solution are of great significance in wastewater treatment. In the presence of ammonia, a complex of chloramines is obtained:



These chloramines have many different properties than HOCl and OCl<sup>-</sup> forms. They exist in various proportions depending on the relative rates of formation of monochloramine and dichloramine which change with the relative concentrations of chlorine and ammonia, as well as with pH and temperature. Above pH about 9, monochloramines exist almost exclusively; at pH about 6.5, monochloramines and dichloramines co-exist in approximately equal amounts; and below pH 6.5 dichloramines predominate, while trichloramines exist below pH about 4.5.

The point where all ammonia is converted to trichloramine or oxidized to free nitrogen is referred to as the breakpoint. Chlorination below this level is combined available residual chlorination; that above this level is free available residual chlorination.

Just as do free-available-chlorine forms differ in germicidal capacity, so do inorganic and organic chloramine combined-available-chlorine forms. Inorganic chloramines have a substantially lower oxidation-reduction potential and less germicidal capacity than HOCl; most organic chloramines have little or no germicidal capacity and are of concern primarily for the chlorine they consume that otherwise would be available for disinfection, and in the measurement and interpretation of residual chlorine.

Figure III-17 illustrates the relationship between chlorine concentration and the contact time required for 99 percent destruction of E. coli for three different forms of chlorine. Figure III-18 illustrates the relative resistance of three viruses and E. coli. While the polio and Coxsackie viruses are considerably more resistant than E. coli to HOCl, the adenovirus tested is apparently more sensitive. One-tenth ppm of chlorine as HOCl destroyed 99 percent of E. coli in about 99 seconds. The same quantity of the adenovirus tested was destroyed in about one-tenth of that time by the same amount of HOCl, but at this HOCl concentration the same amount of poliovirus required about 15 minutes more, and the Coxsackie virus required over 40 minutes.

Other researchers<sup>21</sup> conclude that with the exception of adenovirus 3, from 3 to 100 times more chlorine is required to kill the viruses than E. coli, Aerobacter aerogenes, Ebertella typhosa, or Shigella dysenteriae.

FIGURE III-17<sup>3</sup>

Relationship Between Concentration and Time for 99 Percent Destruction of E. coli by 3 Forms of Chlorine at 2-6°C

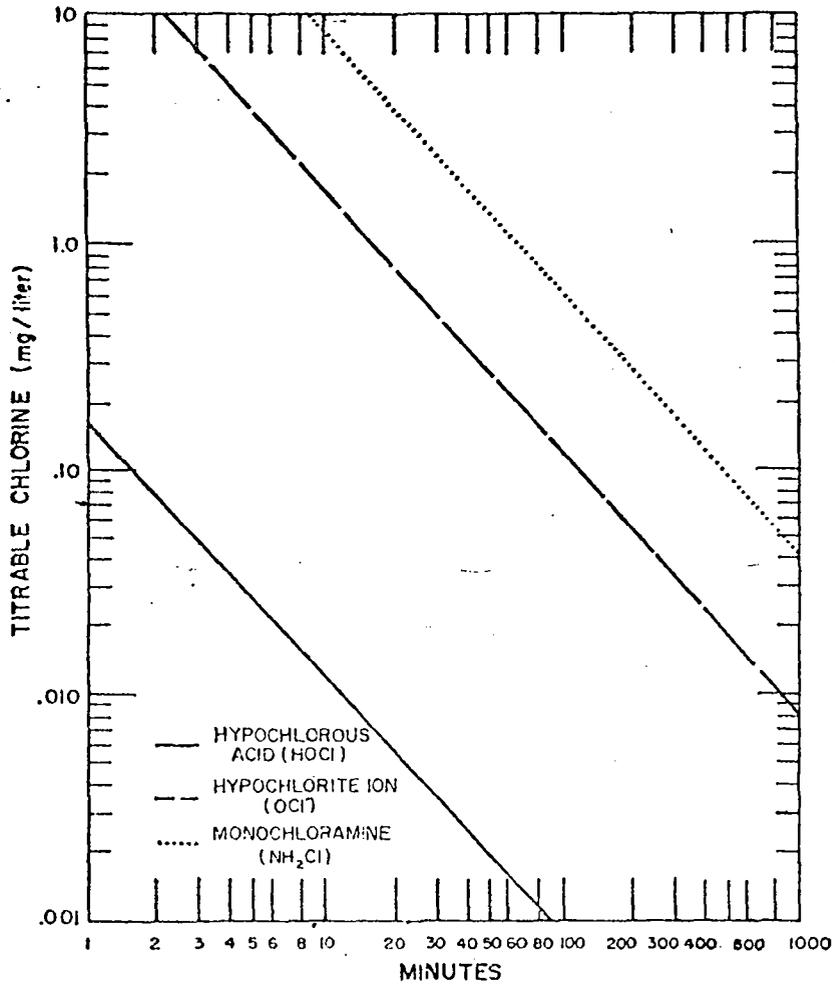
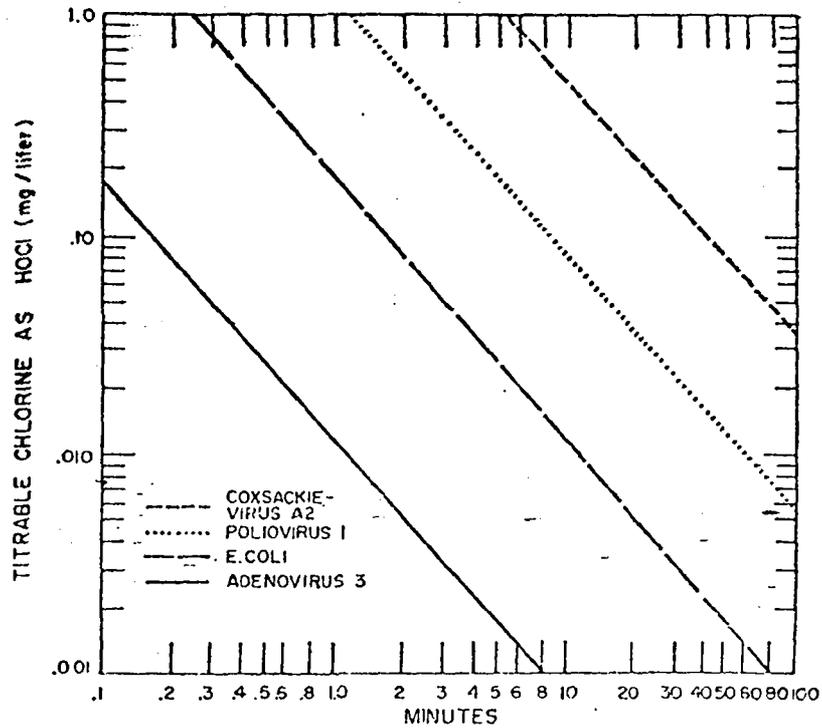


FIGURE III-18<sup>3</sup>

Relationship Between Concentration and Time for 99 Percent Destruction of E. coli and 3 Viruses by Hypochlorous Acid (HOCl) at 0-6°C



Both pH and temperature have a marked effect on the rate of virus kill by chlorine. Table III-1 summarizes data on virus inactivation rates at varying pH at 10°C in filtered secondary sewage effluent. The constants in Table III-1 were determined from experimental results using model f<sub>2</sub> virus which was seeded in filtered secondary sewage effluent buffered to the desired pH value. Chlorine solution was flash mixed at a dose of 30 mg/l and the time of persistence of any free chlorine as well as virus survival was determined<sup>23</sup>.

Since most sewage effluents are near natural pH, the 30 mg/l chlorine dose would result in less than 80 percent viral inactivation. However, by merely lowering the pH to 6.0, viral kill could be increased from 80 to 99.93 percent. The results dramatically show how the kill of virus may be enhanced, especially when hypochlorites are used for sewage disinfection by proper pH control. For four logs (99.99 percent) of viral inactivation, the flash mixing of the following dosages were required: 40 mg/l of chlorine solution (pH 6.3), 50 mg/l of hypochlorite solution (pH 7.4) and 25 mg/l hypochlorite in acidified sewage (pH 5.0).

Other studies show<sup>24</sup> that decreasing the pH from 7.0 to 6.0 reduced the required virus inactivation time by about 50 percent and that a rise in pH from 7.0 to 8.8 or 9.0 increased the inactivation period about six times. In the presence of low free chlorine residuals, the virus inactivation rate is markedly affected by variations of temperature and pH. In the destruction of viruses by chlorine, Clarke's work suggests that the temperature coefficient for a 10° change is in the range of 2 to 3, indicating that the inactivation time must be increased 2 to 3 times when the temperature is

TABLE III-1

VIRAL INACTIVATION RATE  
CONSTANTS AT VARYING pH  
OF SEWAGE AT 10°C  
(Reference 23)

| Sewage<br>pH | Flash mixing of 3 <sup>o</sup> mg/l chlorine                |                                    | Viral Kill<br>(percent) |
|--------------|---|------------------------------------|-------------------------|
|              | Viral Inactivation<br>Rate Constant<br>(min <sup>-1</sup> ) | Free Chlorine<br>Duration<br>(sec) |                         |
| 5.0          | 120.0   | 110.0                              | >99.9999                |
| 5.5          | 72.0  | 24.0                               | >99.9999                |
| 6.0          | 44.0  | 10.0                               | 99.93                   |
| 6.5          | 26.0  | 5.6                                | 92.0                    |
| 7.0          | 16.0  | 5.4                                | 76.0                    |
| 7.5          | 9.5   | 5.0                                | 55.0                    |
| 8.0          | 5.6   | 5.0                                | 40.0                    |
| 8.5          | 3.5   | 4.9                                | 25.0 <sup>a</sup>       |
| 9.0          | 2.0   | 4.8                                | 15.0 <sup>a</sup>       |
| 9.5          | 1.2   | 4.6                                | 10.0 <sup>a</sup>       |

<sup>a</sup>Essentially control survival.

lowered 10°C. Data also indicate that the chlorine concentration coefficient lies in the range of 0.7 to 0.9. This means that the inactivation time is reduced a little less than half when the free chlorine concentration is doubled. To increase virus kill, therefore, there is some advantage in increasing the contact time instead of raising the chlorine content.

The effects of chlorine on a mixture of cysts consisting predominantly of Entamoeba histolytica and Entamoeba coli has been reported<sup>26</sup>. The cysticidal efficiency was related to the residual concentration of halogen measured chemically after 10 minutes of contact time. It was concluded that the chemical species of free and combined halogens which prevail in low pH waters were superior cysticides when compared to forms which predominate in waters of high pH. The most rapid-acting cysticide was found to be the hypochlorous acid (HOCl) form of free available chlorine.

The AWWA Committee report on virus in water<sup>13</sup> concluded that "...in the prechlorination of raw water, any enteric virus so far studied would be destroyed by a free chlorine residual of about 1.0 ppm, provided this concentration could be maintained for about 30 minutes and that the virus was not embedded in particulate material. In postchlorination practices where relatively low chlorine residuals are usually maintained, and in water of about 20°C and pH values not more than 8.0-8.5, a free chlorine residual of 0.2-0.3 ppm would probably destroy in 30 minutes most viruses so far examined."

The Committee also states "...there is no doubt that water can be treated so that it is always free from infectious microorganisms - it will be biologically safe.

Adequate treatment means clarification (coagulation, sedimentation, and filtration) followed by effective disinfection. Effective disinfection can be carried out only on water free from suspended material." Turbidities should be less than 1 JU, or preferably less than 0.2 JU.

Ozonation:

Past research in the effectiveness of ozone as a germicide has been well summarized by Hann<sup>27</sup>. In general, ozone has been found to equal or exceed chlorine in its germicidal effects under a wide variety of circumstances. For example, ozone has been found to be many times more effective than chlorine in inactivating the virus of poliomyelitis. Under experimental conditions, an identical dilution of the same strain and pool of virus, when exposed to chlorine in residual amounts of 0.5-1.0 mg/l and to ozone in residual amounts of 0.05-0.45 mg/l was inactivated within 2 minutes by ozone, while 1-1/2 to 2 hours were required for inactivation by chlorine.

For many water reuse applications, it will be desirable to reduce coliform concentrations to less than 2.2/100 ml prior to recharge. Unfortunately, virtually none of the past research on wastewater disinfection by ozone has been oriented toward achieving a coliform concentration of less than 2.2/100 ml. Also, most of the work has been done with secondary effluents rather than AWT effluents. Table III-2 summarizes recent data from several sources. As noted by a supplier of ozone systems<sup>36</sup>: "These dosages are based on high quality effluent to meet disinfection standards of 200 fecal coliform per 100 ml. Since the specification in California is 2.3 total coliform per 100 ml and we have little experience on dosages to obtain this level, I would expect it to be in the range of 10-15 mg/l."

TABLE III-2

## REPORTED RESULTS - WASTEWATER DISINFECTION BY OZONE

| <u>Reference</u> | <u>Effluent Type</u>              | <u>Ozone Dose, mg/l</u> | <u>Contact Time, min.</u> | <u>Coliform MPN/100 ml</u> |
|------------------|-----------------------------------|-------------------------|---------------------------|----------------------------|
| 28,29            | Unox, Secondary                   | 15                      | 22                        | 500 Total<br>103 Fecal     |
| 12               | Unox, Secondary                   | 5                       | ?                         | 114 Fecal                  |
| 30               | Microstrained<br>Secondary        | 6.6                     | 8                         | 480 Total<br>100 Fecal     |
| 30               | Secondary                         | 15                      | 5-22                      | 774 Total<br>153 Fecal     |
| 30               | Unox, Secondary                   | 5                       | 1                         | 735 Total<br>114 Fecal     |
| 31               | Nitrified<br>Secondary            | 5                       | 1.6                       | 2200 Total<br><300 Fecal   |
| 31               | Filtered<br>Secondary             | 5                       | 1.6                       | 257 Total<br><30 Fecal     |
| 31               | AWT                               | 5                       | 1.6                       | < 30 Total<br>< 30 Fecal   |
| 31               | Secondary                         | 7.5                     | ?                         | 20 Total                   |
| 30               | Secondary                         | 5.4                     | ?                         | 0 Fecal                    |
| 30               | Secondary                         | 4.8                     | ?                         | 1.3 Fecal                  |
| 30               | Secondary                         | 4.2                     | ?                         | 5.7 Fecal                  |
| 30               | Secondary<br>Polishing Pond       | 5                       | ?                         | 120-530 Total<br>< 4 Fecal |
| 32               | Secondary                         | 50-60                   | 10                        | 33-1600 Total              |
| 32               | Secondary                         | 50-60                   | 30                        | 0-33 Total                 |
| 33               | Microstrained<br>Secondary        | 20                      | ?                         | 90 Total                   |
| 34               | Unox Sec. Effl,<br>Lime, Filtered | 20.6                    | 11.6                      | < 3 Total                  |

TABLE III-2  
(Continued)

| <u>Reference</u> | <u>Effluent Type</u>                        | <u>Ozone Dose, mg/l</u> | <u>Contact Time, min.</u> | <u>Coliform MPN/100 ml</u> |
|------------------|---|-------------------------|---------------------------|----------------------------|
| 34               | Three Stage<br>Biological<br>Lime, Filtered | 7                       | 8.1                       | 3 Total                    |
| 34               | Secondary<br>Lime, Coagulated               | 107                     | 12.5                      | 3 Total                    |
| 35               | Secondary                                   | 14                      | ?                         | 2 Total                    |

Measurements of virus kill<sup>37</sup> in secondary effluent found that seeded coliphage  $f_2$  was totally destroyed in five minutes in secondary effluent by 15 milligrams of applied ozone per liter. Another study<sup>38</sup> of virus found that only 0.006 percent of poliovirus in secondary effluent survived one minute of contact with an initial ozone concentration of 5.05 mg/l. It was found that a threshold value for initial ozone concentration of about 1 mg/l ozone had to be surpassed before extremely high (greater than 99.99 percent) virus kills resulted.

Ozone has also been reported to be several times faster than chlorine in its germicidal effects on Entamoeba histolytica. For most cases, an ozone residual of 0.1 ppm for five minutes is adequate to disinfect water low in organics and free of suspended material<sup>27</sup>. Organic material does exert a significant ozone demand; therefore, the ozone dosage required to achieve this residual will be dependent upon the degree of pretreatment. Although as effective or more so than chlorine, ozonation is significantly more costly<sup>39,40</sup>.

#### Effluent Storage:

The die-off rate of viruses in the aquatic environment is a complex phenomenon which is dependent upon many factors<sup>42</sup>. These rates vary with the type of virus as well as water temperature, nature of the water, and chemical characteristics of the water. Under otherwise identical conditions, virus survival is inversely related to temperature. Also, the die-off is directly related to the time the virus is in the water. Factors other than temperature and time have not been well defined. Studies have been made on virus survival in sewage stabilization ponds. Polio virus Type 3 was found

to be reduced by 99.99 percent in 96 hours in one case and by 99.9 percent in 72 hours in another. Still another study found a 99.5 percent reduction in polio virus Type 1 in 72 hours. Virus reductions of 99.9 percent were measured in detention times of 80-160 hours with polio virus Type 1 in another set of experiments. A review of the loss of infectivity of enteric viruses when suspended in various aquatic environments showed the time required for a 99.9 percent reduction at water temperatures of 15-16 degrees C varied from 7-56 days, but at temperatures of 20-25 degrees C, the time range was 2-28 days with most investigators reporting a 99.9 percent reduction in several types of enteric virus in 8 days or less.

System Requirements for Disinfection:

The disinfection of wastewater is dependent upon optimizing the unit processes of chemical coagulation, sedimentation, and filtration (which in themselves provide substantial reductions in bacteria and viruses) to produce minimum water turbidities to assure the maximum contact between any remaining pathogens and the disinfectant added. The interdependence of these unit processes to assure adequate disinfection is graphically illustrated by the reported results<sup>41</sup> of a study in which in 1945, at Philadelphia, Pa., members of Civilian Public Service Unit No. 140 served as experimental subjects in studies conducted by representatives of the University of Pennsylvania and the armed forces. These volunteers consumed water inoculated with known quantities of coliforms and infectious hepatitis virus. Some of this contaminated water was subjected to various water treatment processes. Hepatitis syndrome developed in one or more volunteers who consumed the water in each type of treatment except in those cases where adequate chlorination inactiv-

ated the virus. However, treatment other than chlorination reduced the incidence of infection by about 40 percent.

The report on this experiment concluded with the following:

"(a) Coagulation settling and filtration (diatomite filter) of contaminated water did not eliminate or inactivate infectious hepatitis virus..."

"(b) The application to such water (previously coagulated, settled and filtered) of sufficient chlorine to provide, after 30 minutes contact, total and free residual chlorine concentrations of 1.1 and 0.4 ppm, respectively, apparently was adequate to inactivate the hepatitis virus under the conditions of this experiment. However, the same 30-minute residual total chlorine concentration (1 part per million) in contaminated water that had not been pretreated by coagulation, settling and filtration, did not inactivate the infectious hepatitis virus."

The preceding discussion points to several factors that may be incorporated in the design of water reclamation facilities to alleviate potential problems with pathogenic bacteria in recharged groundwater supplies containing large quantities of wastewaters.

As discussed in another report, soil systems are also effective in removal of pathogenic bacteria, but maximizing the removal of pathogens prior to spreading or injection will provide an added factor of safety.

In AWT plant design utilizing effluent coagulation and filtration, provisions can be made so that a coagulant, alum, may be added continuously to the filter influent water as a filter aid following high lime treatment, so that maximum filterability is assured. At times, a polymer may also be applied at this point. Mixed-media filters which will be even more efficient than the coal-sand media tested by Robeck, et al.<sup>11</sup> in removing viruses, may be used. Several investigators have pointed out the close relationship between virus removal and turbidity reduction. The mixed-media filters at the South Lake Tahoe Plant (discussed later in detail) have under test produced water with turbidity as low as 0.02 JTU. Ordinarily they are operated to produce a turbidity of about 0.2 JTU. The excellent clarity obtainable with proper coagulation and filtration of the wastewater enhances chlorination efficiency so that viruses cannot escape chlorine contact by being encapsulated in particulate matter. Activated carbon treatment used for refractory organic removal removes chlorine (or ozone) demanding substances, further increasing the efficiency of disinfection.

The high pH of 11.0 when lime treatment of secondary effluent is used also benefits virus removal in addition to its bactericidal effects. As noted earlier, recent tests by EPA indicated that pH had little effect on virus at pH values of 10 or below. However, lime coagulation to raise the pH to 10.8-11.1 increased the rate of virus destruction rapidly. In addition to all of the above treatment considerations, AWT plant designs may also include breakpoint chlorination. The free chlorine residuals provided by this process are more effective disinfectants than the combined forms typically found in chlorinated wastewaters. Thus, even a higher degree of assurance of pathogen removal may be provided.

Subjecting the AWT effluent to storage in open reservoirs will provide another means of providing 99+ percent removal of any virus which might escape the AWT process. Although the combination of treatment processes discussed herein will provide a very high degree of assurance of complete removal of pathogenic bacteria and virus, the lack of an all-inclusive, reliable, rapid technique for virus detection and identification introduces some uncertainty. There is a need for improved virus detection techniques in light of the greater susceptibility of the coliform indicator organism to destruction by chlorination. In the interim, application of the established basis for minimizing the probability for viral survival (low turbidity, low pH, high free chlorine residual, adequate mixing, long contact times, effluent storage where practical) must be relied upon. The sections of this report dealing with plant-scale and pilot plant results present added information on the disinfecting capabilities of AWT processes.

#### Heavy Metal Removal

Concern for toxicity of heavy metals to human beings is reflected in the drinking water standards issued by the U. S. Public Health Service. A list of the standards for several heavy metals is given in Table III-3. It must be noted, however, that the standards are not only based on toxicity. For example, limits for Fe and Mn are prescribed because they are objectionable with respect to taste of the water and the color imparted to laundered goods washed in the water. In addition to these standards, it has been suggested<sup>43</sup> that a limit of 0.005 mg/l be set for mercury. The AWWA adopted water quality goals in 1968 which call for lower concentrations of some metals as follows: Iron - 0.05 mg/l; manganese - 0.01 mg/l; copper - 0.2 mg/l; zinc - 1.0 mg/l.

TABLE III-3

Heavy Metal Concentrations -  
U. S. Public Health Service  
Drinking Water Standards  
(1962 Revision)

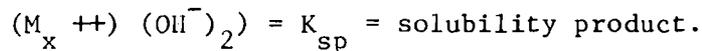
| <u>Substance</u>             | <u>Maximum Concentration<br/>in mg/l</u> |
|------------------------------|--|
| Arsenic (As)                 | 0.05                                     |
| Barium (Ba)                  | 1.0                                      |
| Cadmium (Cd)                 | 0.01                                     |
| Chromium (Cr <sup>+6</sup> ) | 0.05                                     |
| Copper (Cu)                  | 1.0                                      |
| Iron (Fe)                    | 0.3                                      |
| Lead (Pb)                    | 0.05                                     |
| Manganese (Mn)               | 0.05                                     |
| Selenium (Se)                | 0.01                                     |
| Silver (Ag)                  | 0.05                                     |
| Zinc (Zn)                    | 5.0                                      |

Biological Treatment:

The removal of heavy metals during primary and secondary treatment can proceed by two mechanisms<sup>44</sup>:

1. Precipitation of metal hydroxides, which are removed with the sludges;
2. Sorption of soluble trace metals by the sludges.

The precipitation of metal hydroxides is governed by the concentration of the metal ion in solution and the pH. Generally, as the pH increases, the solubility of the metal decreases. This relationship is expressed by the equation for the solubility product of a compound:



Some metals may resolubilize at high pH as anion hydroxide complexes.

As the concentration of the hydroxyl ion increases with increasing pH, the concentration of  $M_x^{++}$  must decrease for the solubility product to remain constant. The solubility products of several cationic heavy metal oxides and hydroxides are listed in Table III-4.

The precipitation of copper, chromium, nickel, and zinc by sewage has been reported by Jenkins, et al<sup>45</sup>. They found that within the range of concentrations of copper used, 0.5-100 ppm as Cu, the percentage precipitated increased with the concentration of copper and decreased with decreasing pH. At pH 3.0, the maximum precipitated was only 20 percent compared to 85 percent precipitated at pH 7-8. Soluble nickel salts were also precipitated by

TABLE III-4

Solubility Products of Cationic Heavy  
Metal Oxides or Hydroxides (55,56,57)

| <u>Compounds</u>                   | <u>K<sub>sp</sub></u>    |
|------------------------------------|--------------------------|
| Ag <sub>2</sub> O                  | 2 x 10 <sup>-8</sup>     |
| Au(OH) <sub>3</sub>                | 8.5 x 10 <sup>-45</sup>  |
| BaCO <sub>3</sub> *                | 1.6 x 10 <sup>-9</sup>   |
| BaSO <sub>4</sub> *                | 1 x 10 <sup>-10</sup>    |
| BiOOH                              | 3 x 10 <sup>-11</sup> ** |
| Cd(OH) <sub>2</sub>                | 2 x 10 <sup>-14</sup>    |
| Cr(OH) <sub>3</sub>                | 1 x 10 <sup>-30</sup>    |
| Cu(OH) <sub>2</sub>                | 3 x 10 <sup>-19</sup>    |
| Fe(OH) <sub>2</sub>                | 1.8 x 10 <sup>-15</sup>  |
| Fe(OH) <sub>3</sub>                | 6 x 10 <sup>-38</sup>    |
| HgO                                | 3 x 10 <sup>-26</sup>    |
| Mn(OH) <sub>2</sub>                | 2 x 10 <sup>-13</sup>    |
| Pb <sub>2</sub> O(OH) <sub>2</sub> | 1.6 x 10 <sup>-15</sup>  |
| SnO                                | 1 x 10 <sup>-61</sup>    |
| Ti(OH) <sub>3</sub>                | 1 x 10 <sup>-40</sup> ** |
| Zn                                 | 4.5 x 10 <sup>-17</sup>  |

\*Barium compounds that will form preferentially to the hydroxide in most waters.

\*\*Estimated value, not verified.

sewage. Average removals ranged between 50 and 60 percent and a reduction in pH produced little effect upon the removal of nickel.

Soluble salts of zinc were precipitated by sewage to the extent of 60 percent at 100 ppm as Zn, but increased to 80 percent at 10 ppm. The efficiency of precipitation was reduced to 50-60 percent at pH 5 and less than 20 percent at pH 3. The precipitation of chromium ( $\text{Cr}^{+6}$ ) was dependent on the period of contact to a much greater extent than the other metals. At low concentration, 50-70 percent was precipitated at the 0.5 ppm as Cr level in sewage for periods up to 24 hours, but instantaneous precipitation was less than 20 percent. It appears that the removal of chromate in sewage depends upon the reduction of hexavalent chromium to one trivalent form and subsequent precipitation of trivalent chromium.

Moore, et al.<sup>46</sup> conducted pilot plant studies to determine the effects of chromium on the activated sludge process and to determine the extent of its removal. Their results indicated that concentrations of hexavalent chromium up to 0.5 ppm were usually completely removed. For higher chromate feed concentrations, an increasing-but-variable amount of the chromium passed through the system.

McDermott, et al.<sup>47</sup> studied the effects of copper on three activated sludge pilot plants. Copper was added to two of the three plants, while the third served as a control. The effects of the copper were measured by differences in effluent quality. The activated sludge process averaged from 50 to 79 percent efficiency in removing copper over a range of feed concentrations from 0.4 to 25 ppm.

McDermott, et al.<sup>48,49</sup> also studied the removal of zinc and nickel in pilot-scale activated sludge plants. Their results show that 95 to 74 percent of the zinc was removed at feed concentrations of 2.5 and 20 ppm, respectively. Their results show the process was only about 30 percent efficient in removing nickel from wastewaters, because nickel is very soluble.

Barth, et al.<sup>50</sup> conducted pilot-scale studies on the effect of heavy metals on biological treatment processes and reported a material balance of the metals through an activated sludge process. They found the average efficiencies of the process for removing the metals were 44, 75, 28 and 89 percent for hexavalent chromium, copper, nickel and zinc, respectively. A survey of four municipal wastewater treatment plants was conducted by Barth, et al.<sup>51</sup> and the distribution of  $\text{Cr}^{+6}$ , copper, nickel and zinc through these plants indicated a satisfactory correlation with the pilot plant results.

Zemansky<sup>54</sup> evaluated ten full-scale wastewater plants for heavy metal removal. The average removals and influent concentrations are shown in Table III-5. The activated sludge process provided more efficient removals of heavy metals than did the trickling filter process.

#### Chemical Coagulation and Sedimentation:

As discussed earlier, the precipitation of metal hydroxides is governed by the concentration of the metal ion in solution and the pH. The logarithm for the sum of the concentration of free metal ions and the concentration of hydroxide complexes has been calculated<sup>52</sup> as a function of pH from values of

TABLE III-5

AVERAGE PERCENT REMOVAL OF HEAVY METALS BY  
WASTEWATER TREATMENT PLANTS<sup>(54)</sup>

| Metal                         | Average %<br>Pri Clar<br>Removal | Secondary Systems |                    | Highest Inf.<br>Concentration<br>Observed(mg/l) | Average Inf.<br>Concentration<br>Observed(mg/l) | % of Plants<br>W/Detectable<br>Concentration |
|-------------------------------|----------------------------------|-------------------|--------------------|---|---|--|
|                               |                                  | Average %<br>T/F* | Average %<br>A/S** |   |   |  |
| Analysis by X-ray Emission:   |                                  |                   |                    |   |   |  |
| Cd                            | 30                               | 5                 | 56                 | .015  | .004  | 60   |
| Cr                            | 36                               | 19                | 36                 | .359  | .103  | 100  |
| Cu                            | 40                               | 47                | 59                 | .903  | .164  | 100  |
| Fe                            | 57                               | 46                | 48                 | 2.763   | .992  | 100  |
| Pb                            | 54                               | 36                | 48                 | .163  | .074  | 100  |
| Mn                            | 27                               | 16                | 22                 | .388  | .097  | 100  |
| Mo                            | 22                               | 15                | 23                 | 1.326   | .201  | 100  |
| Ni                            | 25                               | 20                | 22                 | .311  | .134  | 100  |
| Ag                            | 46                               | 48                | 71                 | .014  | .006  | 60   |
| Zn                            | 50                               | 56                | 60                 | .972  | .248  | 100  |
| Analysis by AA/Wet Chemistry: |                                  |                   |                    |   |   |  |
| Cr                            | 48                               | 19                | 40                 | .25   | .14   | 80   |
| Cu                            | 38                               | 39                | 30                 | .92   | .29   | 100  |
| Fe                            | 50                               | 43                | 49                 | 4.78  | 1.84  | 100  |
| Mo                            | 6                                | 36                | 2                  | .230  | .143  | 70   |
| Zn                            | 43                               | 30                | 39                 | 1.16  | .41   | 100  |

\*T/F = Trickle filter and secondary clarifier.

\*\*A/S = Activated Sludge aeration system and secondary clarifier.

the solubility products and complex constants of the hydroxides taken from literature as shown in Figure III-19. The lines showing those areas where the content is greater than 1 mg/l are marked with heavier lines. The slope of the lines increases by one unit where the first hydroxide complex begins to dominate the contents of the free metal ions and with a further unit where the second complex begins to dominate the first.

If the rise in pH is brought about with NaOH, then the solubility of Cr (III) will rise again, when the pH value rises above that of approximately 8 and of Zn (II) when it rises above approximately 9.

The curves show that Pb (II), Cu (II) and Cr (III) are precipitated to the concentration of 1 mg/l at a pH value of about 7. Experimental results<sup>52</sup> concerning Zn (II), Cd (II) and Ni (II) were, however, much better than those shown in the diagram at pH 7 because the metals were co-precipitated with aluminum hydroxide.

Since many of the trace metals form insoluble hydroxides at pH 11, lime coagulation results in a reduction of these metal concentrations. It appears that it is possible to reduce some of the metal concentrations below that predicted by the solubility products. This may be due to adsorption of the metal ions by the chemical floc. On the other hand, when any of the metals exists in organic form, the concentration reduction during lime coagulation may be less than expected from solubility concentrations. Table III-6 summarizes the effects of lime coagulation on a number of heavy metals. Some of these data were collected on industrial metal wastes which have metal ion concentrations a great deal higher than occur in any municipal water treatment

TABLE III-6

REMOVAL OF HEAVY METALS BY LIME  
COAGULATION AND RECARBONATION

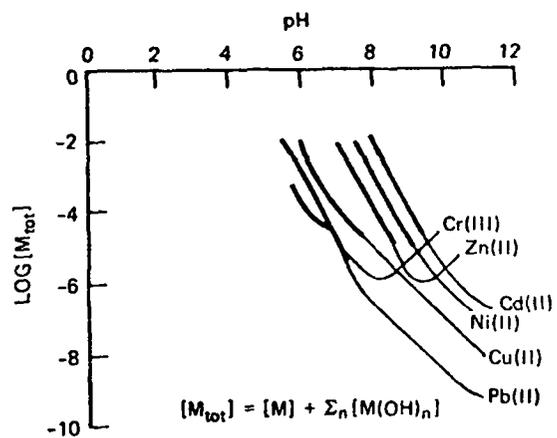
| Metal                    | Ref. | Concentration<br>Before Treatment<br>mg/l | Concentration<br>After Treatment<br>mg/l | Final<br>pH | % Removal |
|--------------------------|------|---|--|-------------|-----------|
| Antimony <sup>1</sup>    | 56   | -   | -  | 11          | 90        |
| Arsenic <sup>1</sup>     | 56   | -   | -  | 11          | <10       |
|                          | 52   | 23  | 23                                       | 9.5         | 0         |
| Barium <sup>1</sup>      | 56   | -   | 1.3 (sol) <sup>2</sup>                   | 11          |           |
| Bismuth <sup>1</sup>     | 56   | -   | .0002 (sol)                              | 11          |           |
| Cadmium                  | 58   | Trace                                     | -  | 11          | Abt. 50   |
|                          | 59   | 0.0137                                    | 0.00075                                  | > 11        | 94.5      |
| Chromium<br>(+6)         | 59   | 0.56                                      | 0.050                                    | > 11        | 11        |
| Chromium<br>(+3)         | 60   | 7,400                                     | 2.7                                      | 8.7         | 99.9+     |
|                          | 52   | 15  | 0.4                                      | 9.5         | 97        |
| Copper                   | 60   | 15,700                                    | 0.79                                     | 8.7         | 99.9+     |
|                          | 61   | 7   | 1  | 8           | 86        |
|                          | 61   | 7   | .05                                      | 9.5         | 93        |
|                          | 62   | 302                                       | Trace                                    | 9.1         | 99+       |
|                          | 52   | 15  | 0.6                                      | 9.5         | 97        |
| Gold <sup>1</sup>        | 56   | -   | < .001 (sol)                             | 11          | 90+       |
| Iron                     | 62   | 13  | 2.4                                      | 9.1         | 82        |
|                          | 63   | 17  | 0.1                                      | 10.8        | 99+       |
|                          | 63   | 2.0                                       | 1.2 <sup>3</sup>                         | 10.5        | 40        |
| Lead <sup>1</sup>        | 56   | -   | < .001 (sol) <sup>2</sup>                | 11          | 90+       |
|                          | 52   | 15  | 0.5                                      | 9.5         | 97        |
| Manganese                | 63   | 2.3                                       | < 0.1                                    | 10.8        | 96        |
|                          | 63   | 2.0                                       | 1.1 <sup>3</sup>                         | 10.5        | 45        |
|                          | 64   | 21.0                                      | 0.05                                     | 9.5         | 95        |
| Mercury <sup>1</sup>     | 56   | -   | Oxid: Soluble                            | -           | < 10      |
| Moleb-<br>denum          | 58   | Trace                                     | -  | 8.2         | Abt. 10   |
|                          | 52   | 11  | 9  | 9.5         | 18        |
| Nickel                   | 60   | 160                                       | 0.08                                     | 8.7         | 99.9+     |
|                          | 61   | 5   | 0.5                                      | 8           | 90        |
|                          | 61   | 5   | 0.5                                      | 9.5         | 90        |
|                          | 65   | 100                                       | 1.5                                      | 10.0        | 99        |
|                          | 52   | 16  | 1.4                                      | 9.5         | 91        |
| Selenium                 | 59   | 0.0123                                    | 0.0103                                   | > 11        | 16.2      |
| Silver                   | 59   | 0.0546                                    | 0.0164                                   | > 11        | 97        |
| Tellurium <sup>1,4</sup> | 56   | -   | (<0.001?)                                | 11          | (?90+)    |
| Titanium <sup>1,4</sup>  | 56   | -   | (<0.001?)                                | 11          | (?90+)    |
| Uranium <sup>5</sup>     | 56   | -   | ?  | -           | ?         |
| Zinc                     | 52   | 17  | 0.3                                      | 9.5         | 98        |
|                          | 56   | -   | .007 (sol)                               | 11          | 90+       |

- NOTES
1. The potential removal of these metals were estimated from solubility data.
  2. Barium and lead reductions and solubilities are based upon the carbonate.
  3. These data were from experiments using iron and manganese in the organic form.
  4. Titanium and Tellurium solubility and stability data made the potential red. est. unsure.
  5. Uranium forms complexes with carbonate ion. Quantitative data w/unavailable to allow determination of this effect.

FIGURE III-19

The Solubility of Pure Metal Hydroxides as a Function of pH.

(From reference 52 Heavy portions of lines show where concentrations are greater than 1 mg/l)



plant influent. These data were included due to the scarcity of metal reduction results from actual chemical coagulation of municipal wastewaters.

Alum coagulation will provide removal of some heavy metals at near neutral pH values. Table III-7 summarizes the removals noted by one observer<sup>52</sup>.

Results of tests made at 12 water treatment plants have also been reported<sup>53</sup> and are summarized in Table III-8. These results were obtained at near neutral pH values so do not reflect the added removals achieved at higher pH values.

#### Filtration:

After lime coagulation, filtration to remove residual particulate matter will provide additional removal of heavy metals. Table III-9 gives the results of sand filtration following lime coagulation.

#### Carbon Adsorption:

It has been found<sup>59</sup>, for several metal ions (see Table III-10), that activated carbon treatment of wastewaters results in a substantial reduction (over 96 percent for three of the four metal ions studied). The cause of this is not clearly identified, but it appears possible that organics may serve as coadsorbates linking the metal ions and the carbon. The above study did not include thermal regeneration of the carbon, so it is not known at this time what effect regeneration would have upon the capacity for adsorption of metal ions. Activated carbon has been used to remove unionized

TABLE III-7REMOVAL OF HEAVY METALS BY ALUM COAGULATION AT A pH OF 6.8-7.0 (52)

| <u>Metal</u>  | <u>Concentration Before Treatment, mg/l</u> | <u>Concentration After Treatment, mg/l</u> |
|---------------|---|--|
| Lead          | 17  | 1.3  |
| Copper        | 15  | 1.7  |
| Molybdenum    | 11  | 9.0  |
| Chromium (+6) | 3   | 2.3  |
| Chromium (+3) | 15  | 0.2  |
| Zinc          | 17  | 11.0                                       |
| Nickel        | 16  | 17.0                                       |

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TABLE III-8

AVERAGE PERCENT REMOVAL OF METALS BY WATER TREATMENT PLANTS(54)

| <u>Metal</u>                  | <u>Average<br/>Percent<br/>Clarifier<br/>Removal</u> | <u>Average<br/>Percent<br/>Filter<br/>Removal</u> | <u>Average<br/>Percent<br/>Plant<br/>Removal</u> | <u>Highest<br/>Influent<br/>Concentration<br/>Observed</u> | <u>Average<br/>Influent<br/>Concentration<br/>Observed</u> |
|-------------------------------|--|---|--|--|--|
| Analysis by X-ray Emmission:  |  |   |  |  |  |
| Cr                            | 35   | 15  | 31   | .084   | .022   |
| Cu                            | 26   | 37  | 49   | .160   | .030   |
| Fe                            | 51   | 49  | 65   | 1.704  | .381   |
| Pb                            | 27   | 29  | 32   | .042   | .012   |
| Mn                            | 30   | 55  | 65   | .963   | .128   |
| Mo                            | 8  | 12  | 15   | .296   | .109   |
| Ni                            | 40   | 41  | 54   | .020   | .005   |
| Zn                            | 36   | 37  | 48   | .538   | .078   |
| Analysis by AA/Wet Chemistry: |  |   |  |  |  |
| Cu                            | 50   | 39  | 55   | .32  | .06  |
| Fe                            | 51   | 60  | 81   | 1.77   | .41  |
| Mo                            | 8  | 8   | 11   | .419   | .233   |

TABLE III-9

HEAVY METAL REMOVAL BY FILTRATION FOLLOWING LIME COAGULATION

| <u>Metal</u>     | <u>Ref.</u> | <u>Concentration<br/>Before Filt.</u> | <u>Concentration<br/>After Treat.</u> | <u>pH</u> | <u>% Removal<br/>By Filt.</u> |
|------------------|-------------|---------------------------------------|---------------------------------------|-----------|-------------------------------|
| Cd               | 58          | Trace                                 |                                       | 8.1       | 95                            |
|                  | 59          | 0.00075 mg/l                          | 0.00070                               | 7.6       | 6.6                           |
| Cr <sup>+6</sup> | 59          | 0.0503                                | 0.049                                 | 7.6       | 2.6                           |
| Cr <sup>+3</sup> | 60          | 2.7                                   | 0.63                                  | 8.7       | 77                            |
| Cu               | 60          | 0.79                                  | 0.32                                  |           | 59.5                          |
|                  | 61          | -                                     | .5                                    | 9.5       |                               |
| Fe               | 63          |                                       | 0.1                                   | 10.8      |                               |
|                  | 63          |                                       | 1.2 Organic                           | 10.5      |                               |
| Mn               | 63          |                                       | 0.1                                   | 10.8      |                               |
|                  | 63          |                                       | 1.1 Organic                           | 10.5      |                               |
| Ni               | 60          | 0.08                                  | 0.1                                   | 8.7       |                               |
|                  | 61          |                                       | 0.5                                   | 9.5       |                               |
| Se               | 59          | .0103                                 | 0.00932                               | 11        | 9.5                           |
| Ag               | 59          | 0.00164                               | 0.00145                               | 11        | 11.6                          |
| Zn               | 60          | 0.97                                  | 0.23                                  | 8.7       | 76.3                          |
|                  | 61          |                                       | 2.5                                   | 9.5       |                               |

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TABLE III-10HEAVY METAL REMOVAL BY CARBON ADSORPTION<sup>(59)</sup>

| <u>Metal</u>     | <u>Ref.</u> | <u>pH Before<br/>Carbon</u> | <u>Concentration<br/>Before Carbon</u> | <u>Concentration<br/>After Carbon</u> | <u>% Removal</u> |
|------------------|-------------|-----------------------------|--|---------------------------------------|------------------|
| Cd               | 10          | 7.6                         | 0.00070                                | $9 \times 10^{-6}$                    | 98.7             |
| Cr <sup>+6</sup> | 10          | 7.6                         | 0.049                                  | 0.00171                               | 96.5             |
| Se               | 10          | 7.6                         | 0.00932                                | 0.00585                               | 37.2             |
| Ag               | 10          | 7.6                         | 0.00145                                | 0.000048                              | 96.7             |

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species such as arsenic and antimony from an acidic stream. The ability of carbon to reduce mercury to low levels has also been noted<sup>66</sup>. The capacity of the carbon for mercury was found to be greatly increased by lowering the pH to 4.

The range of removals of five metals by carbon treatment of municipal wastewaters has also been reported<sup>54</sup> as follows: chromium - 71-100 percent; copper - 25-38 percent; iron - 21-57 percent; molybdenum - 26-35 percent; zinc - 0-13 percent.

#### Reverse Osmosis:

The rejection of specific metals by the reverse osmosis process has been reported as follows<sup>116,117</sup>: cadmium - 66-98 percent; chromium - 82-98 percent; copper - 99 percent; iron - 94-99 percent; lead - 99+ percent; zinc - 97 percent; nickel - 98-99 percent; strontium - 99 percent; and silver - 96 percent.

#### Combined Processes:

The subsequent parts of this section which deal with pilot plant and plant scale results will present data on the overall efficiency of the combined processes of lime coagulation, filtration, and carbon adsorption of secondary effluent. The combined processes as evaluated at Colorado Springs, Dallas, Orange County (California), and South Lake Tahoe have shown the ability to produce effluent concentrations of heavy metals less than drinking water standards when treating municipal wastewaters (Table III-11 summarizes

**TABLE III-11**  
**EFFICIENCY OF THE COMBINED AWT PROCESSES**  
**FOR**  
**REMOVAL OF METALS**

Lime Coagulation, Filtration, and Carbon Adsorption of Secondary Effluent

|            | Drinking Water<br>Limit<br>mg/l | Concentration, mg/l as measured at |                           |                            |                  |
|------------|---------------------------------|------------------------------------|---------------------------|----------------------------|------------------|
|            |                                 | Colorado<br>Springs, Colo.         | Orange Co.,<br>California | South Tahoe,<br>California | Dallas,<br>Texas |
| Chromium   | 0.05                            | 0.022                              | 0.01 - 0.04               | 0.0005                     | 0.01 - 0.02      |
| Iron       | 0.3                             | 0.012                              | -                         | 0.0003                     | 0.08 - 0.15      |
| Manganese  | 0.05                            | 0.020                              | -                         | 0.002                      | 0.007 - 0.02     |
| Nickel     | None                            | 0.100                              | -                         | -                          | 0.05 - 0.10      |
| Copper     | 1.0                             | 0.024                              | 0.02 - 0.30               | 0.0116                     | 0.02 - 0.03      |
| Lead       | 0.05                            | 0.067                              | 0 - 0.04                  | -                          | 0.02 - 0.04      |
| Zinc       | 5.0                             | 0.012                              | 0.02 - 0.07               | 0.005                      | 0.02 - 0.07      |
| Magnesium  | None                            | 3.3                                | 2                         | -                          | -                |
| Cadmium -  | 0.01                            | 0.000                              | 0 - 0.005                 | -                          | 0.002 - 0.004    |
| Mercury    | 0.005                           | 0.0                                | 0 - 0.006                 | -                          | 0.0002 - 0.0007  |
| Arsenic    | 0.05                            | 0.003                              | 0 - 0.03                  | 0.005                      | 0.003 - 0.005    |
| Molybdenum | None                            | 0.05                               | -                         | -                          | -                |
| Selenium   | 0.01                            | -                                  | 0 - 0.003                 | 0.0005                     | 0.0004 - 0.0005  |
| Silver     | 0.05                            | -                                  | 0 - 0.01                  | 0.0004                     | -                |

Coagulation of Raw Sewage (Iron @ pH = 6.0; or low lime @ pH = 10.0; or high lime @ pH = 11.5); Filtration, and Carbon Adsorption<sup>(134)</sup>

Iron Coagulation

| <u>Σ % Removal</u> | <u>With New Carbon</u>   | <u>With Old Carbon</u>   |
|--------------------|--|--|
| 10 - 20            | Mn   |  |
| 20 - 30            |  | Mn   |
| 30 - 40            | Ni   |  |
| 90 - 95            |  | Zn   |
| 95 - 100           | Cr <sup>III</sup> , Pb, Zn, Cu<br>Cd, Ba, As, Cr <sup>VI</sup> | Cr <sup>III</sup> , Pb, Ni, Cu<br>Cd, Ba, As, Cr <sup>VI</sup> |

Low Lime Coagulation

| <u>Σ % Removal</u> | <u>With New Carbon</u>                                     | <u>With Old Carbon</u>                   |
|--------------------|--|--|
| 80 - 85            | As   | As, Cr <sup>VI</sup>                     |
| 85 - 90            | Zn   | Zn, Cu                                   |
| 90 - 95            | Mn   |  |
| 95 - 100           | Cr <sup>III</sup> , Pb, Ni, Cu<br>Cd, Ba, Cr <sup>VI</sup> | Cr <sup>III</sup> , Pb, Ni, Mn<br>Cd, Ba |

TABLE III-11  
(Continued)

| <u>Σ % Removal</u> | <u>High Lime Coagulation</u> |                            |
|--------------------|------------------------------|----------------------------|
|                    | <u>With New Carbon</u>       | <u>With Old Carbon</u>     |
| 75 - 80            |                              | Zn                         |
| 80 - 85            | Ba                           | As                         |
| 85 - 90            | Zn, As                       | Ba                         |
| 90 - 95            | Cu, Hg                       | Cu, Hg                     |
| 95 - 100           | Cr <sup>III</sup> , Pb, Ni   | Cr <sup>III</sup> , Pb, Ni |
|                    | Mn, Cd, Cr <sup>VI</sup>     | Mn, Cd, Cr <sup>VI</sup>   |

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these results). Table III-11 also contains data from coagulation (iron or lime), filtration, and adsorption of raw sewage<sup>134</sup>. Section IV covers the capacity of soil systems for removal of heavy metals.

#### Organic Removal

In the past, conventional secondary wastewater treatment processes have had as their objective the removal of 85-90 percent of the biodegradable organics found in raw municipal wastewaters primarily to prevent depletion of oxygen in the receiving waters. There was little, if any, concern over the removal of non-biodegradable (refractory) organics and certainly no provision for their removal in the design of the secondary plan. The refractory organics were recognized as potential sources of color and taste and odor problems in downstream water supplies. Generally the natural assimilation and dilution provided by the receiving stream was adequate to minimize these obvious problems for most of the year. If it was not, the downstream water treatment plant resorted to appropriate treatment practices to overcome the resulting aesthetic problems. In water reuse applications, these potential aesthetic problems become even more significant because of the decreased opportunity for natural stabilization to occur. Of even more concern, however, are the potential long-term health effects of the refractory organic materials found in a reclaimed wastewater which is totally acceptable from an aesthetic point (i.e., colorless and odorless). A recent study<sup>67</sup> concluded that there was a relationship between cancer mortality

among white males and drinking water obtained from the Mississippi River at New Orleans. The suggested cause was the formation of carcinogens by the chlorination of refractory organics found in the raw water supply. The New Orleans water treatment plant does not employ any process designed for refractory organic removal. An EPA study found 65 identifiable organics present in the treated New Orleans supply<sup>68</sup>. Some 32 organics have been identified<sup>69,70</sup> in the Washington, D. C. supply including aliphatic and aromatic hydrocarbons, chlorocarbons, bromine-containing compounds, alcohols, and ketones. Although the measured concentrations were low, very little is known<sup>71</sup> about the potential long-term health effects of these materials in drinking waters. Thus, there is ample reason to consider the capabilities of the available wastewater treatment processes for removal of refractory organics. Refractory, stable, or residual organics are organics which are not removed readily by natural means or by reclamation processes.

#### Biological Treatment With Chlorination:

A properly operating activated sludge plant will produce a secondary effluent with a soluble COD of 30-50 mg/l and a soluble BOD of 1-2 mg/l. It is the soluble COD fraction which is of greatest concern. Although another report in this series will present detailed information on the types and concentrations of contaminants in municipal wastewaters, it is appropriate to review briefly here the nature of the organics found in the effluent from secondary treatment processes since their removability in AWT processes is a function of their nature.

The organic composition of secondary effluents is only partially known. The most detailed accounting reveals partial characterization of about 30 percent of the total organic carbon<sup>74-77</sup>.

Using passage through a dialysis membrane as the criterion for molecular solubility, Bunch<sup>74</sup> determined that 60 percent by weight of the organic material in a secondary effluent (activated sludge) was soluble. The remaining 40 percent included two-thirds of the total nitrogen and was probably composed of large polymeric molecules resembling humic acids<sup>78</sup>.

The soluble organic compounds in secondary (trickling filter) effluent were characterized by Rebhun and Manka<sup>72,76</sup>. They first<sup>76</sup> determined that humic substances (humic, fulvic, and humathomelanolic acids) made up 40 to 50 percent by weight of the soluble organic constituents. The remainder included: ether extractable components, about 8.3 percent; anionic detergents, about 13.9 percent; carbohydrates, about 11.5 percent; protein, about 22.4 percent; and tannin, about 1.7 percent. A more extensive study<sup>72</sup> including activated sludge effluents has been reported and the results are summarized in Tables III-12 and III-13. These data show that the distribution of the main organic fractions is similar for the various biological treatment units studied. The authors<sup>72</sup> report the percent of humic acid and the total humic substances is smaller in the effluents from the pure residential area than in the effluents of municipal origin.

Using high-resolution chromatography, 38 UV-adsorbing constituents have been separated from a 500-fold concentrate of secondary effluent<sup>79</sup>. None were identified. Similarly<sup>80</sup>, 19 carbohydrates were separated from the

concentrate, and the 15 following sugars were identified: deoxyribose, sucrose, raffinose, cellobiose, maltose, rhamnose, lactose, ribose, mannose, fructose, arabinose, galactose, xylose, sorbose, and glucose.

As noted earlier, of particular concern is the fate of the refractory organics in the chlorination process. A recent study<sup>73</sup> found that chlorine-containing stable organic constituents are present after chlorination of effluents from domestic sanitary sewage treatment plants. Over 50 chlorine-containing constituents were separated from chlorinated secondary effluents. Seventeen of these chlorine-containing organic compounds were tentatively identified and quantified at the 0.5 to 4.3 ug/liter level. The tentatively identified compounds were the following: 2-chlorobenzoic acid, 3-chlorobenzoic acid, 4-chlorobenzoic acid, 8-chlorocaffeine, 6-chloroguanine, 3-chloro-4-hydroxybenzoic acid, 4-chloromandelic acid, 4-chloro-3-methylphenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 4-chlorophenylacetic acid, 4-chlororesorcinol, 5-chlorosalicylic acid, 5-chlorouracil, 5-chlorouridine, and 8-chloroxanthine.

The chlorination yield (the portion of the chlorine dose associated with chlorine-containing stable organic compounds at the end of the chlorination reaction period) was approximately 1.0 percent for secondary effluents which had been chlorinated with 3.2 mg/liter chlorine to a residual of 1 mg/liter for chlorination contact times of 15-45 minutes<sup>73</sup>. The chlorination yield was approximately constant with respect to chlorine dosage (in the range studied) but increased with increasing reaction time. Chlorination yields were approximately the same for both primary and secondary effluents.

TABLE III-12<sup>72</sup>

Distribution of Organic Groupings in Secondary Effluents - Mean Values

| Organic groupings and fractions | Percent of total COD                             |  |   |
|---------------------------------|--|--|---|
|                                 | Municipal wastewater; high rate trickling filter | Municipal wastewater; stabilization pond | Domestic wastewater; extended aeration activated sludge |
| Proteins                        | 21.6   | 21.1                                     | 23.1  |
| Carbohydrates                   | 5.9  | 7.8                                      | 4.6   |
| Tannins and lignins             | 1.3  | 2.1                                      | 1.0   |
| Anionic detergents              | 16.6   | 12.2                                     | 16.0  |
| Ether extractables              | 13.4   | 11.9                                     | 16.3  |
| Fulvic acid                     | 25.4   | 26.6                                     | 24.0  |
| Humic acid                      | 12.5   | 14.7                                     | 6.1   |
| Hymathomelanic acid             | 7.7  | 6.7                                      | 4.8   |

TABLE III-13<sup>72</sup>

Molecular Weight Distribution of Humic Substances From Secondary Effluents

| Molecular weight range | Percent of humic compound present |            |                     |
|------------------------|-----------------------------------|------------|---------------------|
|                        | Fulvic acid                       | Humic acid | Hymathomelanic acid |
| <500                   | 27.5                              | 17.9       | 4.5                 |
| 500-1000               | 7.8                               | 6.2        | 12.2                |
| 1000-5000              | 35.7                              | 29.4       | 48.0                |
| 5000-10,000            | 15.3                              | 7.8        | 28.0                |
| 10,000-50,000          | 9.4                               | 36.7       | 7.5                 |
| >50,000                | 4.3                               | 2.0        | 0                   |

Essentially the same effects were obtained by chlorination with either gas or hypochlorite solution.

In addition to the 17 chlorine-containing compounds that were identified, 32 stable organic constituents were identified and 23 of these were quantified at 2- to 190-ug/liter levels in the effluents from domestic sanitary primary sewage treatment plants<sup>73</sup>. Nine stable organic constituents were identified (see Table III-14), and eight of these were quantified at 5- to 90-ug/liter levels in the effluents from domestic sanitary secondary sewage treatment plants. None of these organic compounds had been previously reported by other investigators.

Other investigations<sup>81</sup> have also shown that haloforms are produced during chlorination of humic substances in natural waters. Specific compounds formed by chlorination of natural waters were chloroform ( $\text{CHCl}_3$ ),  $\text{CCl}_2$ ,  $\text{CHCl}$ ,  $\text{CHClBr}$ ,  $\text{CHBr}$ . Several of these are suspected carcinogens. Another study<sup>82</sup> found chloroform and other trihalogenated methanes in supplies originating from both surface water and groundwaters resulting from chlorination. Surface sources were found to have a higher concentration than groundwater sources. These latter two studies indicate that the presence of wastewaters in a water supply may increase the concentration of haloforms following chlorination but that natural humic substances present in surface and ground supplies are also a source of the compounds of concern. Where groundwater recharge with municipal wastewaters is practiced, special attention must be paid to the fate of the refractory organics found in secondary effluents.

TABLE III-14

IDENTIFICATIONS OF MOLECULAR CONSTITUENTS  
IN 1000-FOLD CONCENTRATIONS OF SECONDARY  
EFFLUENT<sup>(73)</sup>

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| <u>Compound</u>                       | <u>Concentration<br/>(ug/liter)</u> |
|---------------------------------------|-------------------------------------|
| Glycerine                             | 30                                  |
| Uracil                                | 30                                  |
| 5-Acetyloamino-6-amino-3-methyluracil | 80                                  |
| 1-Methylinosine                       | 20                                  |
| Inosine                               | 5                                   |
| 7-Methylxanthine                      | 6                                   |
| 1,7-Dimethylxanthine                  | Abt. 6                              |
| p-Cresol                              | 90                                  |

The AWT processes of coagulation, sedimentation, and filtration are capable of removing the particulate and small amounts of soluble COD from secondary effluent. However, the removal of most of the soluble COD must be accomplished by carbon adsorption, a membrane process such as reverse osmosis, ozonation, or in the soil system portion of the recharge system. The capabilities of the soil system are discussed in another section.

Carbon Adsorption:

The basic principles of adsorption are discussed in the literature<sup>2,3,4,5,83</sup> and there will be no attempt here to cover these basics in this report. The question of removals of specific organics from municipal wastewaters is a complex one. Even if data are available on the adsorption of a specific organic from a pure solution, the data are of limited value in predicting the removal of this compound from the heterogeneous mixture of organics found in municipal wastewaters because the behavior of a given organic molecule is dependent on other molecules present. Two different materials may mutually enhance the adsorption of each or they may interfere. One study found that the capacity of carbon is enhanced in the presence of several compounds as compared to that obtained in single-solute solutions<sup>84</sup>. Although the competitive effects of several compounds complicates the prediction of precise carbon effluent compositions, some general principles of adsorption may be stated.

The more a substance likes the solvent system - the more hydrophylic in the case of an aqueous solution - the less likely it is to move toward an interface to be adsorbed. Conversely, a hydrophobic - water disliking - substance will more likely be adsorbed from aqueous solution. A large number of organic contaminants, such as sulfonated alkylbenzenes, have a molecular structure comprised of both hydrophylic and hydrophobic groups. In this case, the hydrophobic part of the molecule tends to be active at the surface and undergo adsorption, whereas the hydrophylic part tends to stay in the solution phase if at all possible<sup>5</sup>.

For municipal wastewaters, a decrease in pH increases the extent of adsorption. Increasing temperature favors adsorption<sup>85</sup> in some cases, but lower temperatures are better in others<sup>83</sup>.

For groundwater recharge with municipal wastewaters, the primary questions of concern are:

- o How amenable to removal by carbon are specific organics known to be of concern which could potentially find their way into municipal wastewaters?
- o What overall concentrations of organic materials can be achieved by carbon treatment?
- o What are the specific compounds which are most probable to be present in carbon-treated wastewaters?

- o What are effects of chlorination or other disinfection processes on residual TOC?

The remainder of this section will discuss these major points of concern.

The literature<sup>5,84,85,88,89,90,123</sup> contains much information on removal of specific organic compounds, but unfortunately these studies have been made with single solutes or mixtures of solutes in pure water rather than in municipal wastewaters. These studies do indicate<sup>85</sup> that molecules having highly branched structures are removed much more slowly than those of identical molecular weight but with configurations that permit coiling and compactness which result in high rates of diffusion into the pores of the carbon. An illustrative example<sup>88</sup> of these studies using mixtures of refractory organics may be of interest. Mixtures of 4 and 8 solutes were subjected to carbon treatment in pilot columns. Table III-15 shows the composition of these mixtures. For the four-solute system, the influent concentration of organics was being reduced by the carbon treatment by 80 percent at the end of a 180-hour run. No significant quantities of ABS or 2,4-DCP were present in the effluent and the only material in the effluent in significant concentrations was TEA, 50 percent of which was passing through the columns. For the eight-solute mixture, the carbon was removing 90 percent of the influent organics at the end of a 100-hour run. Pure solute studies<sup>85</sup> showed that ortho- and para-nitrochlorobenzenes were adsorbed at much higher molar rates than alkylbenzenesulfonates and also higher than phenol. DDT was found<sup>85</sup> to be adsorbed at molar rates similar to that for 2-octylbenzenesulfonates.

TABLE III-15<sup>18</sup>

COMPOSITION OF MULTIPLE COMPONENT  
SOLUTIONS USED IN CARBON EVALUATION

Four Solute System

| <u>Solute</u>                        | <u>Influent Concentration (mg/l)</u> |
|--------------------------------------|--------------------------------------|
| ABS                                  | 24.5                                 |
| Triethanolamine (TEA)                | 15.5                                 |
| 2-4-dichlorophenol (2,4-DCP)         | 16.9                                 |
| Nonylphenoxypolyethoxyethanol (9N10) | 53.7                                 |

Eight Solute System

| <u>Solute</u>                          | <u>Influent Concentration (mg/l)</u> |
|--|--------------------------------------|
| Phenol                                 | 2.4                                  |
| Quinine                                | 9.3                                  |
| Dodecylsulfate                         | 7.2                                  |
| Sulfonated alkylbenzene                | 10.6                                 |
| 2-sec-butyl-4,6-dinitrophenol          | 6.0                                  |
| 2,4-dichlorophenoxyacetic acid         | 5.5                                  |
| Nonylphenoxypolyethoxyethanol          | 16.5                                 |
| Phenyl N,N'-dimethylphosphorodiamidate | 5.0                                  |

The ability of carbon to remove organics from water supplies has been reported in several articles<sup>91-98,123</sup>. An activated carbon column providing 14 minutes contact time reduced 6.3 ppb of endrin in lake water to 0.006-0.085 ppb<sup>91</sup>. Dieldrin (3.5 ppm) and lindane (8 ppm) have been reported to be removed by powdered carbon dosages of 35-40 ppm<sup>92</sup>. Table III-16 presents data collected in isotherm tests run on aldrin, dieldrin, endrin, DDD, DDE, DDT, toxaphene, and Arochlor 1242 and 1254<sup>123</sup>. The first seven are pesticides and the last two are mixtures of PCB's containing 42 percent and 54 percent chlorine by weight. The isotherm data were collected on solutions of the material added to distilled water. The capability of activated carbon for removal of these contaminants is well illustrated by these data.

Most wastewater treatment studies do not report specific organic constituents but rather report results in terms of COD, TOC, carbon chloroform extract (CCE), or carbon alcohol extract (CAE). Measurements of gross organic concentrations have well-known limitations. For example, the COD procedure fails to detect many straight-chain aliphatic and aromatic hydrocarbons, including pyridine, benzene, and others<sup>165</sup>. However, these measurements do give an indication of the total amount of organics present and make up the bulk of the available data. The drinking water standard for CCE has been 0.2 mg/l. However, an improved method for determining CCE has been developed and the standard is being revised to 0.7 mg/l<sup>99</sup>. The 0.7 mg/l standard is actually more stringent because of the increased sensitivity of the test. The previously published results discussed here, however, use the older CCE technique corresponding to the 0.2 mg/l limit. One of the most thoroughly reported cases is the application of granular carbon adsorption

TABLE III-16

REMOVAL OF SPECIFIC TOXIC MATERIALS BY CARBON ADSORPTION<sup>(123)</sup>

| CARBON<br>DOSAGE (mg/l) | RESIDUAL (ppb) |        |          |     |      |     |           |               |               |
|-------------------------|----------------|--------|----------|-----|------|-----|-----------|---------------|---------------|
|                         | ALDRIN         | ENDRIN | DIELDRIN | DDT | DDD  | DDE | TOXAPHENE | AROCHLOR 1242 | AROCHLOR 1254 |
| Control                 | 48             | 62     | 19       | 41  | 56   | 38  | 155       | 45            | 49            |
| 1.0                     | --             | --     | --       | 41  | --   | 34  | 147       | --            | --            |
| 2.0                     | 26             | 15     | 6.3      | --  | 6.9  | --  | 80        | 7.3           | 37            |
| 2.5                     | --             | --     | --       | 21  | --   | 29  | --        | --            | --            |
| 5.0                     | 15             | 3.4    | 2.4      | 3.7 | 3.7  | 12  | 31        | 1.6           | 17            |
| 10.0                    | 12             | 1.5    | 1.1      | --  | 2.2  | --  | 2.7       | 1.1           | 4.2           |
| 12.5                    | --             | --     | --       | <1  | --   | 3.3 | --        | --            | --            |
| 25.0                    | 6.3            | 0.56   | --       | --  | 0.45 | 1.1 | --        | --            | 1.6           |
| 50.0                    | 4.4            | 0.22   | --       | --  | 0.35 | 0.9 | --        | --            | 1.2           |

to Kanawha River water serving as the supply for Nitro, West Virginia<sup>93,94</sup>. Removals of specific organics contaminants from the highly polluted river water were determined for various carbon contact times in pilot studies. The results are shown in Table III-17. The performance of the plant-scale filters is shown in Figure III-20 in terms of CCE. Although the influent CCE frequently exceeded the standard of 200 ppb, the carbon treated water was typically less than 50 ppb. The carbon influent COD was 10-26 mg/l while the carbon effluent COD was 2-10 mg/l.

It has recently been reported that EPA is evaluating water treatment plants using activated carbon in their filters at Lawrence, Massachusetts and Davenport, Iowa which have installed granular carbon filters<sup>166</sup>. Preliminary results at the Lawrence plant showed that the carbon reduced the influent Threshold Odor Number from 8-9 to 3 or less for a period of 80-90 weeks. However, in only 16 weeks, the CCE removals reached zero. The CAE removals were found to be zero from the start. The EPA tests at Davenport will include similar measurements to determine if a similar pattern occurs.

The levels of organics which can be achieved by activated carbon treatment of secondary municipal wastewater effluents is affected by many variables such as the degree of pretreatment, the contact time in the carbon column, the frequency with which carbon is removed for regeneration, and the nature of the organics present. The subsequent portions of this report which discuss pilot and plant-scale results will present added information on this

TABLE III-17<sup>94</sup>

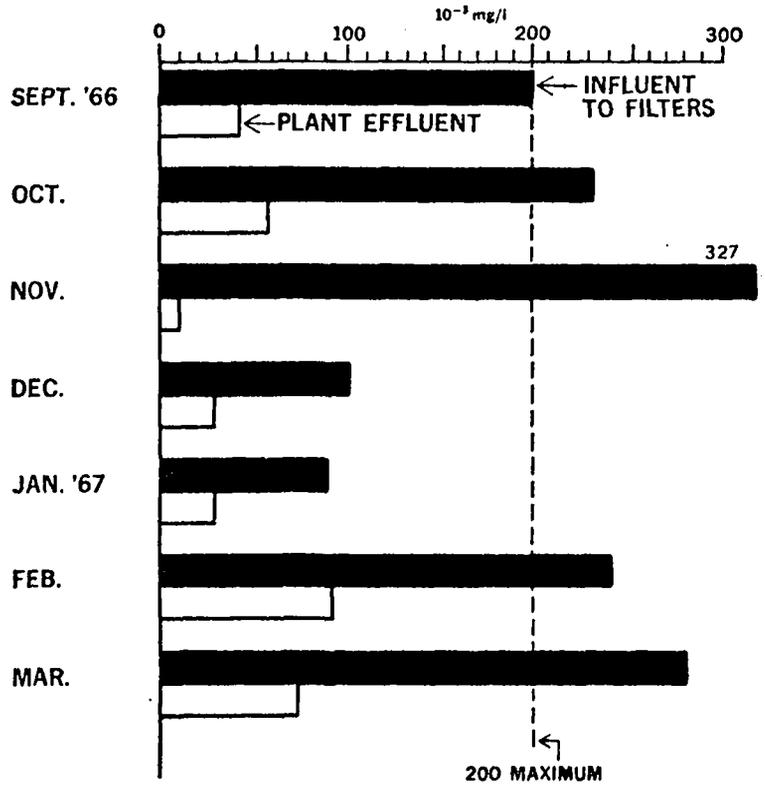
## INFLUENCE OF CONTACT TIME ON PASSAGE OF SPECIFIC CONTAMINANTS AT NITRO, W. VA.

| Contaminant                     | Contact Time — min |     |     |      |
|---------------------------------|--------------------|-----|-----|------|
|                                 | 1.9                | 3.8 | 5.6 | 7.5  |
|                                 | Depth — ft         |     |     |      |
|                                 | 5                  | 10  | 15  | 20   |
| Concentration — ppb             |                    |     |     |      |
| Ethylbenzene                    | 20                 | 18  | 15  | 5    |
| Bis (2-chloroethyl) ether       | 94                 | 44  | <D  | <D * |
| 2-Ethyl hexanol                 | 57                 | 20  | <D  | <D   |
| Bis (2-chloro-isopropyl ether   | 26                 | 10  | <D  | <D   |
| $\alpha$ -Methyl benzyl alcohol | 62                 | 13  | <D  | <D   |
| Acetophenone                    | 11                 | <D  | <D  | <D   |
| Isophorone                      | 12                 | 9   | <D  | <D   |
| <i>Total</i>                    | 285                | 114 | 15  | 5    |
| Threshold odor number (25°C)    | 32                 | 25  | 5   | 2    |

\*Less than detectable values.

FIGURE III-20<sup>94</sup>

Carbon-Chloroform Extract  
Data, Nitro, West Virginia,  
U.S.A.



point. One of the early studies<sup>86</sup> on carbon treatment found that provision of coagulation and filtration prior to adsorption provided a marked improvement in activated carbon effluent COD over that obtained with activated carbon treatment of secondary effluent. On the same wastewater, COD isotherms showed that COD values of 5 mg/l were achievable with coagulated and filtered secondary effluent while 20 mg/l was the best achieved with secondary effluent with no pretreatment. Pilot column tests at several locales<sup>104</sup> showed that effluent TOC values with chemical clarification and filtration as pretreatment were 0-1 mg/l while with filtration as the only pretreatment, TOC values were 2-5 mg/l. The Pomona pilot plant (discussed later in detail) has achieved COD values of less than 10 mg/l by carbon treatment of secondary effluent with no pretreatment<sup>100</sup>. The CCE of Pomona effluent has been 0.014-0.026 mg/l.

Middleton<sup>101</sup> has stated that COD values can be reduced to less than 3 mg/l with carbon treatment of a well-treated secondary effluent and that a TOC of less than 1 mg/l can be typically achieved at contact times of 15 minutes or more. He also reports achieving TOC values of 1.2 mg/l with powdered carbon treatment at Lebanon, Ohio. COD values of less than 3 mg/l have been produced in pilot tests and in the full-scale columns at Lake Tahoe<sup>102,103</sup>. The Dallas, Texas pilot plant (discussed in detail later) reports an average monthly COD of 1.7 mg/l for September 1974 from a tertiary system consisting of lime clarification, filtration, and carbon adsorption. However, a typical value of 12 mg/l is reported<sup>165</sup> for this pilot plant. Although these data indicate that there may only be about 2-3 mg/l of COD that is typically resistant to carbon adsorption, they do

not mean that it will be practical to continuously produce such a value. For example, analysis of the South Tahoe data from January–November 1974 indicates that only 7 percent of the measured COD values were less than 5 mg/l with 66 percent being less than 15 mg/l. In previous years, the COD has typically been 10 mg/l or less for 80 percent of the time with 20 percent of the values being between 10 and 22 mg/l<sup>2</sup>. The Windhoek, S. Africa plant (later discussed in detail) reports minimum COD values of 7.5 mg/l with values as high as 28 mg/l for carbon column effluent. One of the reasons that effluent COD values show variability is that it is not practical to have a carbon contactor continuously full of freshly regenerated carbon. Minimum values of COD (3 mg/l) are typically achieved with a column filled largely with fresh carbon. As the carbon becomes saturated, the effluent COD increases. When some of the spent carbon is replaced with regenerated carbon, the COD value drops. What is the level of COD associated with practical carbon column operation? The State of Virginia<sup>106,107</sup> has adopted a standard calling for a weekly average COD of 10 mg/l for indirect water reuse application. The Tahoe experience indicates that such an average value of COD of about 10 mg/l can be achieved with proper operation. The work at Hyperion with carbon treatment of secondary effluent (no pretreatment) has led to adoption of a COD standard of 12 mg/l with an average COD of 10.7 mg/l produced by carbon treatment of the secondary effluent from 1968-70 in pilot tests<sup>118</sup>. Thus, it appears that COD values of 10-12 mg/l are practical for activated carbon effluent.

Other reports will examine the capability of soil systems in detail. However, some comment should be made on the need for carbon treatment prior to recharge. Experience in the Orange County pilot injection program prior to use of activated carbon<sup>87,108</sup> showed levels of COD and MBAS moving through the injection aquifers in excess of that which would have been produced by activated carbon treatment. At least in this case, provision of activated carbon treatment will remove some organic materials which would not be removed in the soil system.

In order to put the COD value of 10-12 mg/l in perspective, the following observations may be made. In a survey made 15 years ago, the Columbia River at Pasco, Washington had a COD of 5-12 mg/l; the Snake River - 7-11 mg/l; Colorado River above Parker Dam - 20-28 mg/l; Ohio River at Evansville, Indiana - 15-43 mg/l; Mississippi River at Burlington, Iowa - 25-30 mg/l; Mississippi River at New Orleans - 8-32 mg/l; Missouri River at Kansas City - 15-104 mg/l<sup>110</sup>. In 1973-74, the Los Angeles Metropolitan Water District reports the treated water from the Colorado River at Lake Matthews had an average COD of 11 mg/l and from the California Aqueduct water (the Jensen Filtration Plant) had a COD of 6 mg/l. The effluent spread for recharge for many years at Whittier Narrows has had a COD of 30-40 mg/l. Analyses of the Santa Ana River flow for the past several years, as it enters the percolation area of the Orange County, California groundwater basin, indicates that the COD is almost always above 20 mg/l and has often been over 50 mg/l. Thus, it is possible with carbon adsorption to produce a COD lower than that used in the past for recharge in California and lower than that of many raw water supplies in the United States. However, as indicated by the

recent reports concerning New Orleans, concentrations of organics in some existing supplies may be high enough to cause adverse health effects and there is uncertainty about what level of organics is acceptable. As pointed out by the Dallas, Texas researchers<sup>99</sup>, where reuse is involved there is a definite need to think less in terms of BOD, COD, and TOC and more in terms of specific trace compounds. Unfortunately, there are few data on the specific organic compounds which are likely to comprise the 10-12 mg/l COD escaping an efficient carbon adsorption system. A recent study<sup>109</sup> reported that the major organic fraction adsorbed in activated carbon columns is a fulvic acid-like material with a molecular weight ranging from approximately 100-10,000. Both the low molecular weight fraction consisting of mostly polar organic compounds and the high molecular weight humic carbohydrate-like material, with a molecular weight above 50,000 were poorly adsorbed. The total COD passing the carbon column in these tests was 6 mg/l. EPA's Cincinnati Laboratory is currently sponsoring work by Gulf South Research which includes identification of organics in AWT effluents. Until these data are available, there will be little meaningful data available on the specific composition of the COD remaining after carbon treatment.

The uncertainty over the composition of the organics remaining after carbon treatment in turn introduces the major source of controversy related to reuse of municipal wastewaters. It is not universally agreed that trace organics need limit direct reuse in arid regions where such reuse is now a necessity due to lack of other water sources. The World Health Organization

has concluded<sup>111</sup>: "The currently available advanced wastewater treatment processes can remove nearly all the dissolved and suspended chemical contaminants in wastewater and can provide a high degree of protection against possible toxic contaminants. A polished effluent with only a very few milligrams per liter of total organic carbon and less than 0.2 mg/l of carbon chloroform extract can be produced from raw wastewater. Many rivers currently used as sources of water supply for millions of people do not even approach this quality." Also, in comparing the current wide-spread practice where polluted surface water serves as a water supply source to planned reuse, Israel's experts have noted<sup>112</sup>: "In fact, indirect, unplanned wastewater reuse of the former class may well be a greater risk than planned reuse which would include treatment processes better capable of coping with the organic pollutants found in wastewater."

#### Reverse Osmosis:

Although the desalting processes of ion exchange and electrodialysis are not very effective for removal of refractory organics, the reverse osmosis (RO) process provides very high removals of organics found in municipal wastewaters. Retention by RO membranes increases with increasing molecular weight and, at constant molecular weight, with increasing branching<sup>113</sup>. In the absence of experimental data, one cannot count on retention of compounds with molecular weights less than 100. Hydrocarbons have been reported to be much better retained than aromatic compounds. RO reduced the COD of secondary effluents from 39 mg/l to less than 1 mg/l at Pomona. The

COD of activated carbon effluent was reduced from 11.4 mg/l to 0.3-1.0 mg/l. Activated carbon effluent at Hemet, California was reduced from 7.6 mg/l to 0.5-0.8 mg/l by RO<sup>114</sup>. With chemical clarification and filtration as pre-treatment of the secondary effluent, the Hemet unit reduced the COD from 35.2 mg/l to 1.5-3.4 mg/l.

Although the reverse osmosis process offers a means of reducing the COD of carbon column effluents to extremely low levels, the process costs are high and the experience with the process has been limited to small plants (the largest plant in the world is an 0.8 mgd plant in Kashima, Japan).

#### Other Elements of Concern

##### Chloride, Sulfate, and Dissolved Solids:

These substances affect water quality with regard to its taste and its laxative properties. The taste threshold and laxative effects of various salts in water vary with individual sensitivity, the presence of other substances, and individual acclimatization to the use of a particular water. Therefore, the acceptable concentration is a range of values rather than a specific concentration for each salt. Various studies support reasonably well the Drinking Water Standards of 250 mg/l for chlorides and sulfates, and 500 mg/l for total solids. However, it is generally recognized that waters with concentrations of these salts exceeding the Standards are widely used without ill effect. People apparently become acclimated to the use of these high solids waters in a relatively short time. A more rational approach than the use of TDS as a controlling standard is the use of standards on individual ions as there may be health limits to some materials within TDS. Should

control of TDS prove necessary, demineralization technology as described earlier is available, although relatively high in cost. Blending of high TDS reclaimed wastewater with a low TDS source of water prior to recharge is also a means of TDS control being practiced.

Iron and Manganese:

Iron in water is not likely to have any toxicologic significance, but is otherwise objectionable at concentrations above 0.3 mg/l. It imparts a yellowish color (when oxidized) and a bitter or astringent taste to water, and appreciably affects the taste of beverages. Iron produces a brownish stain on laundered goods, plumbing fixtures, and buildings in lawn sprinkler range. It appears that the limiting of manganese in water for esthetic and economic reasons will preclude any possible physiologic effects from excessive intake. Manganese imparts a brownish or purplish color to water and laundered goods (when oxidized), and stains plumbing fixtures. It also impairs the taste of coffee and tea. Both iron and manganese are readily removed by oxidation and filtration of wastewater. The Tahoe effluent contains iron of 0.0003 mg/l and manganese of 0.002 mg/l.

Nitrate:

Ingestion of water containing nitrates in excess of 10 mg/l (as  $\text{NO}_3\text{-N}$ ) by infants may produce methemoglobinemia (blue baby condition). Also, breast-fed infants of mothers drinking such water may be poisoned. If the nitrate concentration is sufficiently high, both adults and animals can be poisoned, but this has not been reported to be a problem from drinking water. Even if the nitrogen is present in the reclaimed water in the form of ammonia,

there is the potential for oxidation to the nitrate form in the recharge system. Thus, control of the total nitrogen is necessary to insure control of the nitrate form. Either the biological or physical-chemical techniques described earlier in this report can readily produce effluents with less than 2 mg/l total nitrogen. Thus, nitrate considerations need not limit the utility of wastewaters for recharge. Nitrates can be removed from water by selective ion exchange.

Sodium:

One of the major dietary sources of sodium is water used for drinking and culinary purposes. If it is assumed that there is an average daily consumption of 2.5 liters of water in food and drink, it follows that when the water contains as much as 200 mg/l, the patient will receive 500 mg of sodium from water alone. While this sodium intake is not harmful to normal individuals, it must be considered for patients on a sodium-restricted diet. Waters high in sodium which are used for drinking and culinary purposes, could vitiate the results of sodium restriction in solid food intake and could be seriously detrimental to certain patients with cardiac, renal, or hepatic disease. Once the sodium content and fluid intake have been prescribed, the water supply available to the patient should receive careful consideration as a source of sodium independent of that from solid foods. In some instances, distilled, deionized, or low sodium surface waters may have to be substituted for drinking waters with a high sodium content in the dietary therapeutic regimen for these patients.

The presence of sodium in the concentrations found in a reclaimed municipal wastewater (about 60 mg/l is added in the domestic use of water) is not a threat to the health of the general population. However, it may be of concern for those on sodium-restricted diets. Processes selected for wastewater reclamation should use chemicals which minimize unnecessary addition of sodium during treatment. The demineralization process discussed earlier provides a means for removal of sodium but at a high cost. For example, the RO process has the capability of removing more than 90 percent of the sodium.

Cyanide:

Usually, 50 to 60 mg of cyanide in a single dose is fatal. However, in doses of 10 mg or less, cyanide is converted to thiocyanate in the body. Usually the lethal effects occur only when the detoxifying mechanism is overwhelmed. Chlorination under neutral or alkaline conditions of water cyanide will reduce cyanide below the maximum limit set forth in the 1975 IPS (EPA - Interim Primary Standards) of 0.2 mg/l.

Fluoride:

Optimum concentrations (0.7 to 1.2 mg/l) of fluoride in drinking water consumed during childhood will help prevent dental caries. Excessive concentrations (more than about 3.0 mg/l) can cause mottled enamel when consumed in water during the childhood years. Careful control of the fluoride content of the raw water is required and, as a result, the fluoride content of municipal wastewaters is also below the standard as no significant fluoride is added to wastewater during normal domestic use.

EXISTING PROJECT PERFORMANCEWindhoek, S. Africa

In this project, the subject of several published papers<sup>105,119-122</sup>, reclaimed water is taken directly from maturation (or holding) ponds to the public water system and comprises as much as one-third of the total municipal water supply. The secondary effluent is reclaimed for reuse by chemical (lime) treatment, flotation, ammonia stripping, recarbonation, filtration, foam fractionation, and granular carbon adsorption (see Figure III-21). Tables III-18 and III-19 summarize the results. The water supply sources consist of an impoundment reservoir (dam water in Table III-19), 36 wells (borehole water), and the reclaimed wastewater. The dam water is treated in a conventional plant while the borehole water is pumped directly to the distribution reservoirs. The reclaimed water is mixed with the purified dam water in the clearwell. The admixed streams are chlorinated to a free residual of 0.2 mg/l and then pumped to the service reservoir where they are mixed with the borehole water before final distribution. Although enteroviruses and reovirus entered the reclamation plant at levels as high as the TCID<sub>50</sub> (50 percent tissue culture infective dose) per liter, no virus could be recovered from the reclaimed wastewater<sup>122</sup>.

Table III-19 reflects the quality of blended water actually consumed for potable purposes (recirculated water after integration). The total dissolved solids (TDS) of the reclaimed water increases from  $\pm$  740 to 810 mg/l mainly as a result of chemical dosing. Due to changes in alkalinity and algal

FIGURE III-21

TERTIARY TREATMENT SCHEMATIC -  
WINDHOEK, SOUTH AFRICA

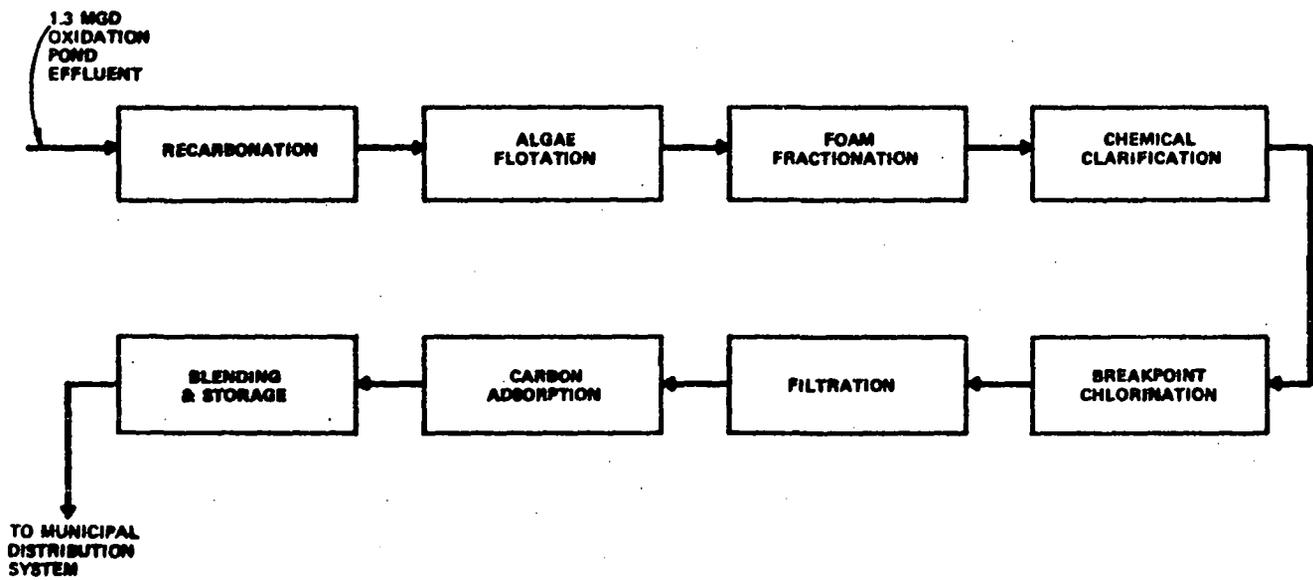


TABLE III-18<sup>121</sup>

WATER QUALITY AT VARIOUS STAGES OF  
TREATMENT AT WINDHOEK

| DETERMINATION                         | RAW WATER | PRIMARY FLOTATION | LIME, CHLORINE, AND SEDIMENTATION | SAND FILTRATION | ACTIVATED CARBON FILTRATION |
|---------------------------------------|-----------|-------------------|-----------------------------------|-----------------|-----------------------------|
| Total N (mg/l)                        | 35        | 32                | 15                                | 14              | 13                          |
| Organic N (mg/l)                      | 3.2       | 1.3               | 0.9                               | 0.7             | Nil                         |
| Ammonia N (mg/l)                      | 14.9      | 14.0              | 0.2                               | 0.3             | 0.1                         |
| Oxides of N (mg/l)                    | 17        | 17                | 14                                | 13              | 13                          |
| Phosphates, as PO <sub>4</sub> (mg/l) | 10        | Nil               | Nil                               | Nil             | Nil                         |
| ABS (mg/l)                            | 8         | 7                 | 4                                 | 4               | 0.7                         |
| BOD <sub>5</sub> (mg/l)               | 30        | 4                 | 1                                 | 1               | 0.3                         |
| Sulfate, as SO <sub>4</sub> (mg/l)    | 108       | 228               | 220                               | 220             | 220                         |
| pH                                    | 8.5       | 7.1               | 8.0                               | 8.0             | 8.0                         |

TABLE III-19

COMPOSITION OF WATERS FROM INDIVIDUAL AND COMBINED SOURCES  
AT WINDHOEK<sup>(105)</sup>

| Constituent                                | Treated Dam Water<br>A | Reclaimed Water<br>B | Borehole Water<br>C | Dam and reclaimed water mixed in ratio 1:1=(A+B) | Reticulated Water            |                               |
|--|------------------------|----------------------|---------------------|--|------------------------------|-------------------------------|
|  |                        |                      |                     |  | Before Integration<br>=(A+C) | After Integration<br>=(A+B+C) |
| Total dissolved Solids (TDS)               | 186                    | 740-810              | 498                 | 525-609  | 375                          | 475                           |
| Phosphate as PO <sub>4</sub>               | 0.1                    | 0.5-1.2              | 0.03                | 0.4  | 0.4                          | 0.6                           |
| Nitrate as N                               | 0.3                    | 18.0                 | 0.0                 | 9.0  | 0.9                          | 3.3                           |
| Synthetic detergents as Monoxol O.T. (ABS) | -                      | 0.05-0.40            | Nil                 | 0.10   | -                            | 0.1                           |
| Chemical oxygen demand as COD              | 18                     | 7.5-28               | 7.0                 | 7.5-34   | 8-12                         | 11.0-14.5                     |

density, the aluminum sulphate dosing requirements vary between 130-220 mg/l. Depending on the ratio of admixture of reclaimed water with purified raw water ( $\pm$  200 ppm), the TDS of the blended water is controlled well below 600 mg/l.

The COD of the maturation pond effluent is reduced by 70 percent up to the sand filter stage with a substantial further reduction by carbon adsorption. After optimum operation conditions were established, a final quality reclaimed water could be produced with COD less than 10 mg/l and ABS of less than 0.2 mg/l before blending with purified raw dam water. The CCE of the reclaimed water is about 0.13 mg/l. The level of organics present in the recycled water has not caused any customer complaints. In fact, the public complained of the "brackish" taste of the water during a temporary shut-down of the reclamation plant<sup>105</sup>. It is obviously premature to judge the long-term effects of this direct recycling project, but its initial reception by the public has been favorable.

Copious rains in early 1972 led to the temporary closing of operation of the Windhoek reclamation system because the impounded supplies could meet the demand. The process drawn in Figure III-22 has recently been modified to include ammonia stripping to replace the maturation ponds which provided unreliable removal of ammonia.

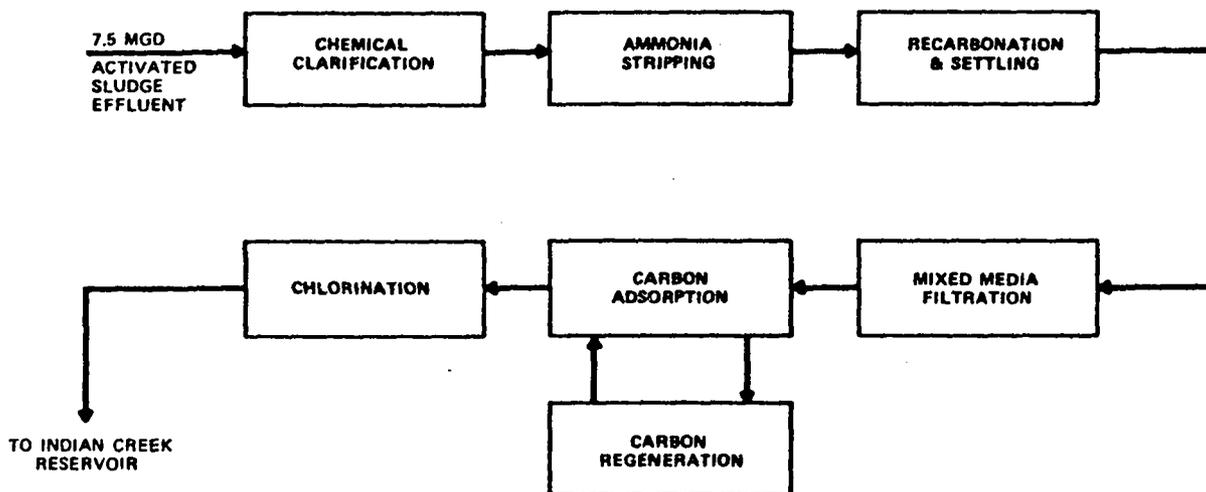
South Lake Tahoe, California

This 7.5 mgd project has been described in several publications<sup>2,124-131</sup>. A simplified schematic of the liquid treatment process is shown in Figure III-22.

Primary treatment takes place in two settling tanks of conventional design. Biological treatment is accomplished in aeration tanks of two different designs. One has plug-flow diffused air, and the other, mechanical aeration plus diffused air. The first step in the advanced waste treatment consists of the addition of lime, followed by flocculation and clarification of the water by settling. This treatment removes most of the phosphates present and raises the pH to a level high enough to convert ammonium ion to ammonia gas. The lime-treated water is then pumped to the nitrogen removal system where the ammonia is stripped from the wastewater as a gas. The stripping system effluent is stabilized by means of adding carbon dioxide gas in two stages of treatment. The first-stage recarbonation drops the pH to 9.3 for maximum calcium recovery. The second stage of recarbonation drops the pH to 7.0-8.5 as desired. Breakpoint chlorination is then applied to remove ammonia escaping from the upstream stripping process. The stabilized water then flows to two ballast ponds in series. The ponds provide storage for filter backwash water and equalize flows to the remainder of the plant. Water is pumped from the pond to the tertiary building where it passes first through mixed-media filters and then the carbon columns. When the filters

FIGURE III-22

TERTIARY TREATMENT SCHEMATIC -  
SOUTH LAKE TAHOE, CALIFORNIA



become plugged with material which has been removed from the wastewater, they are automatically taken off the line, backwashed, and restored to service. The waste backwash water is slowly returned for reprocessing in the plant. The filtered water flows under pressure to the carbon columns. There are 8 carbon columns containing about 22 tons of granular activated carbon which provide 17 minutes of carbon contact when operating under design flow rates.

Table III-20 summarizes typical water quality at various stages of treatment. Tables III-21 to III-24 present more detailed summaries of operational data.

The efficiency of the plant for bacterial removal is shown in Table III-21. Of the 1,053 samples examined in the last 35 months, 95.4 percent had coliform concentrations of less than 2.2/100 ml. The first eight months of 1974 produced 237 consecutive days of no detectable coliforms. Unfortunately, there are only limited data on virus in the Tahoe effluent. As shown in Table III-22, the available data show no detectable virus in the final effluent.

Extensive data on COD are available from the Tahoe plant. During a three-year study<sup>124</sup> from 1968 through 1970, the 80 percentile (i.e., the COD was less than this value 80 percent of the time) value for COD averaged 13.2 mg/l. The 50 percentile COD averaged 10 mg/l. During the year 1971, the COD averaged 9 mg/l<sup>124</sup> and 1972 - 9.5 mg/l (see Table III-23). The minimum COD values each month of 1972 were about 3 mg/l.

TABLE III-20<sup>4</sup>

TYPICAL WATER QUALITY AT VARIOUS STAGES OF TREATMENT AT SOUTH LAKE TAHOE

| QUALITY<br>PARAMETER     | RAW<br>WASTEWATER | EFFLUENT      |                |                       |        |        |                      |
|--------------------------|-------------------|---------------|----------------|-----------------------|--------|--------|----------------------|
|                          |                   | PRIMARY       | SECONDARY      | CHEMICAL<br>CLARIFIER | FILTER | CARBON | CHLORINATED<br>FINAL |
| BOD (mg/l)               | 140               | 100           | 30             |                       | 3      | 1      | 0.7                  |
| COD (mg/l)               | 280               | 220           | 70             |                       | 25     | 10     | 10                   |
| SS (mg/l)                | 230               | 100           | 26             | 10                    | 0      | 0      | 0                    |
| Turbidity (JTU)          | 250               | 150           | 15             | 10                    | 0.3    | 0.3    | 0.3                  |
| MBAS (mg/l)              | 7                 | 6             | 2.0            |                       | 0.5    | 0.10   | 0.10                 |
| Phosphorus (mg/l)        | 12                | 9             | 6              | 0.7                   | 0.10   | 0.10   | 0.10                 |
| Coliform<br>(MPN/100 ml) | 50<br>million     | 15<br>million | 2.5<br>million |                       | 50     | 50     | < 2.0                |

TABLE III-21<sup>103</sup>

SUMMARY OF BACTERIOLOGICAL TESTS AT SOUTH LAKE TAHOE, 1972 - PRESENT

| 1972        | Total<br>No. | Number of Samples<br>With Coliform MPN/100 ml of |     |     |     |    |    |     |
|-------------|--------------|--|-----|-----|-----|----|----|-----|
|             |              | Less Than<br>2.2                                 | 2.2 | 5.0 | 8.8 | 24 | 38 | >38 |
| January     | 31           | 25   | 3   | 1   | 1   | 0  | 0  | 1   |
| February    | 29           | 23   | 5   | 0   | 1   | 0  | 0  | 0   |
| March       | 30           | 22   | 6   | 1   | 0   | 0  | 1  | 0   |
| April       | 30           | 28   | 1   | 0   | 1   | 0  | 0  | 0   |
| May         | 31           | 31   | 0   | 0   | 0   | 0  | 0  | 0   |
| June        | 29           | 29   | 0   | 0   | 0   | 0  | 0  | 0   |
| July        | 31           | 29   | 0   | 0   | 2   | 0  | 0  | 0   |
| August      | 31           | 31   | 0   | 0   | 0   | 0  | 0  | 0   |
| September   | 30           | 30   | 0   | 0   | 0   | 0  | 0  | 0   |
| October     | 31           | 30   | 0   | 0   | 1   | 0  | 0  | 0   |
| November    | 30           | 25   | 0   | 0   | 2   | 1  | 2  | 0   |
| December    | 31           | 31   | 0   | 0   | 0   | 0  | 0  | 0   |
| <u>1973</u> |              |  |     |     |     |    |    |     |
| January     | 31           | 26   | 0   | 1   | 0   | 2  | 2  | 0   |
| February    | 28           | 28   | 0   | 0   | 0   | 0  | 0  | 0   |
| March       | 31           | 31   | 0   | 0   | 0   | 0  | 0  | 0   |
| April       | 30           | 30   | 0   | 0   | 0   | 0  | 0  | 0   |
| May         | 31           | 31   | 0   | 0   | 0   | 0  | 0  | 0   |
| June        | 30           | 30   | 0   | 0   | 0   | 0  | 0  | 0   |
| July        | 31           | 24   | 3   | 2   | 2   | 0  | 0  | 0   |
| August      | 31           | 31   | 0   | 0   | 0   | 0  | 0  | 0   |
| September   | 30           | 30   | 0   | 0   | 0   | 0  | 0  | 0   |
| October     | 31           | 31   | 0   | 0   | 0   | 0  | 0  | 0   |
| November    | 30           | 30   | 0   | 0   | 0   | 0  | 0  | 0   |
| December    | 27           | 26   | 0   | 0   | 1   | 0  | 0  | 0   |
| <u>1974</u> |              |  |     |     |     |    |    |     |
| January     | 26           | 26   | 0   | 0   | 0   | 0  | 0  | 0   |
| February    | 28           | 28   | 0   | 0   | 0   | 0  | 0  | 0   |
| March       | 31           | 31   | 0   | 0   | 0   | 0  | 0  | 0   |
| April       | 30           | 30   | 0   | 0   | 0   | 0  | 0  | 0   |
| May         | 31           | 31   | 0   | 0   | 0   | 0  | 0  | 0   |
| June        | 29           | 29   | 0   | 0   | 0   | 0  | 0  | 0   |
| July        | 31           | 31   | 0   | 0   | 0   | 0  | 0  | 0   |
| August      | 31           | 31   | 0   | 0   | 0   | 0  | 0  | 0   |
| September   | 30           | 28   | 0   | 0   | 2   | 0  | 0  | 0   |
| October     | 31           | 28   | 0   | 0   | 1   | 0  | 1  | 1   |
| November    | 30           | 30   | 0   | 0   | 0   | 0  | 0  | 0   |
| TOTALS      | 1053         | 1005   | 18  | 5   | 14  | 3  | 6  | 2   |
| %           |              | 95.4   | 1.7 |     |     |    |    |     |

TABLE III-22<sup>2</sup>

## VIRUS TESTS ON THE SOUTH LAKE TAHOE EFFLUENT

| <u>Date</u> | <u>Virus Recovered (PFU)<sup>1</sup></u> |                           |                            |                           |
|-------------|--|---------------------------|----------------------------|---------------------------|
|             | <u>Primary Effluent</u>                  | <u>Secondary Effluent</u> | <u>Column Effluent (U)</u> | <u>Final Effluent (C)</u> |
| May 29      | 3  | 0                         | 1                          | 0                         |
| June 5      | -  | -                         | 0                          | 0                         |
| June 12     | -  | -                         | 0                          | 0                         |
| Aug. 20     | 3  | 18                        | NRD <sup>3</sup>           | 0                         |
| Aug. 27     | -  | -                         | NRD                        | 0                         |
| Sept. 11    | -  | -                         | 0                          | 0                         |
| Sept. 18    | 179                                      | 14                        | 9                          | 0                         |
| Sept. 25    | NRD                                      | 430                       | 0                          | 0                         |
| Oct. 2      | 207                                      | 320                       | 0                          | 0                         |

<sup>1</sup>PFU = Plaque forming units

<sup>2</sup>P = primary; S = secondary; U = unchlorinated carbon column effluent;  
C = chlorinated carbon column effluent = final effluent

<sup>3</sup>NRD = no reliable data.

Tests performed by the FWPCA Laboratory in Cincinnati.

TABLE III-231972 COD VALUES AT SOUTH LAKE TAHOE<sup>(103)</sup>

|           | <u>COD, mg/l</u> |             |                |
|-----------|------------------|-------------|----------------|
|           | <u>Min.</u>      | <u>Max.</u> | <u>Average</u> |
| January   | 2.1              | 17.2        | 11.5           |
| February  | 3.3              | 13.1        | 9.8            |
| March     | 2.4              | 14.0        | 7.9            |
| April     | 2.6              | 20.1        | 8.3            |
| May       | 1.3              | 10.0        | 6.3            |
| June      | 2.2              | 11.3        | 5.5            |
| July      | 8.0              | 29.6        | 15.0           |
| August    | 4.5              | 28.7        | 12.0           |
| September | 5.4              | 19.5        | 10.1           |
| October   | 2.7              | 18.0        | 7.8            |
| November  | 3.4              | 17.5        | 11.3           |
| December  | 2.9              | 19.5        | 8.4            |

TABLE III-24<sup>3</sup>

## HEAVY METAL ANALYSIS OF SOUTH LAKE TAHOE EFFLUENT

| <i>Element</i>         | <i>Reclaimed<br/>Water</i> | <i>Maximum Allowable<br/>U.S.P.H.S.<br/>Drinking Water Standards<br/>Concentration in mg/l</i> |
|------------------------|----------------------------|--|
| Arsenic                | 0.005                      | 0.05   |
| Chromium <sup>+6</sup> | 0.0005                     | 0.05   |
| Copper                 | 0.0116                     | 1.0  |
| Iron                   | 0.0003                     | 0.3  |
| Manganese              | 0.002                      | 0.05   |
| Selenium               | 0.0005                     | 0.01   |
| Silver                 | 0.0004                     | 0.05   |
| Zinc                   | 0.005                      | 5.0  |
| Bromine                | 0.065                      |  |
| Uranium                | 0.0015                     |  |
| Cobalt                 | 0.00033                    |  |
| Cesium                 | 0.000006                   |  |
| Mercury                | 0.0005                     |  |
| Rubidium               | 0.010                      |  |
| Scandium               | 0.000001                   |  |
| Antimony               | 0.00044                    |  |

Table III-24 presents a heavy metal analysis made in 1971 by Battelle Northwest<sup>3</sup>.

The Tahoe plant also offers some insight into the reliability of the AWT processes. Because of state regulations which prohibit the discharge of any waste materials within the Tahoe basin, the AWT effluent is exported from the basin<sup>129</sup>. The AWT effluent is pumped over the surrounding mountains and has been used to create a recreational reservoir - Indian Creek Reservoir - outside of the Tahoe Basin. Table III-25 summarizes the effluent requirements for the Tahoe plant and performance data typical of the operation during the three-year EPA study<sup>2</sup>. There are no regulatory requirements for removal of phosphorus or nitrogen. However, phosphorus is being removed in order to restrict algal growths in Indian Creek Reservoir, which receives the reclaimed water. The ammonia concentration is being controlled to prevent ammonia toxicity to the trout in Indian Creek Reservoir. The Tahoe project has never failed to meet the regulatory requirements for exported water quality. One feature which has proven to provide valuable flexibility is an emergency storage pond of several days' detention. During prolonged power failures or severe mechanical failures, secondary effluent can be diverted to the emergency storage pond and later processed by the AWT plant for export. The storage pond has been used only five times in the last seven years. Of these five times, three have been for less than eight hours due to breaks in the export pipeline; one for less than eight hours due to a power outage; and one for three days due to spring-thaw flood waters entering a manhole through a removed cover which caused excessive flows (15 mgd). There have been no diversions due to process failures.

TABLE III-25

EFFLUENT REQUIREMENTS AT SOUTH TAHOE AND TYPICAL PERFORMANCE <sup>2</sup>

| Description                       | REQUIREMENTS<br>Lahontan R.W.Q.C.B.*  |         |     |     | Plant performance<br>(% of time)                           |      |      |
|-----------------------------------|---|---------|-----|-----|--|------|------|
|                                   | Alpine<br>Co.   | 50      | 80  | 100 | 50   | 80   | 100  |
| MBAS (mg/l), less than            | 0.5   | 0.3     | 0.5 | 1.0 | 0.19   | 0.35 | 0.35 |
| BOD (mg/l), less than             | 5   | 3       | 5   | 10  | 1.0  | 2.5  | 3.9  |
| COD (mg/l), less than             | 30  | 20      | 25  | 50  | 9  | 10   | 22   |
| Susp.S. (mg/l), less than         | 2   | 1       | 2   | 4   | 0  | 0    | 0    |
| Turbidity (JU), less than         | 5   | 3       | 5   | 10  | 0.4  | 0.5  | 1.3  |
| Phosphorus, (mg/l), less than     | no requirements   |         |     |     | 0.06   | 0.12 | 0.27 |
| pH (units)                        | 6.5-8.5   | 6.5-9.0 |     |     | 6.6-8.7  |      |      |
| Coliform, MPN/100 ml <sup>1</sup> | Adequately Median < 2.0<br>disinfected Max. no consecutive<br>sample > 23,2 |         |     |     | Median < 2.0<br>no. of consecutive<br>samples > 23,0, none |      |      |

<sup>1</sup>All 30 samples collected during November, 1969, were found to be free of coliform organisms.  
<sup>2</sup>Lahontan Regional Water Quality Control Board.

The only process in the Tahoe project which has proven to provide less-than-desired efficiency is the ammonia stripping process. Even though there are no regulatory agency requirements for ammonia removal, ammonia removal is desirable to minimize the possibility for ammonia toxicity to the trout in Indian Creek Reservoir. The original stripping tower built at Lake Tahoe was funded by EPA as a research project to evaluate the process on a plant scale. The packed tower was found to suffer cold weather limitations and from deposits of calcium carbonate scale on the tower packing. The scale deposits were not anticipated as they did not occur in pilot tests and no means were provided in the full-scale tower for removal of the deposits. The Tahoe plant has recently been modified to incorporate stripping ponds for ammonia removal<sup>132</sup> and breakpoint chlorination for removal of ammonia concentrations which escape the stripping process. Other process modifications have been developed<sup>133</sup> which will overcome the limitations noted in the experimental tower originally constructed at Tahoe by recycling the stripping tower off-gases after acid-scrubbing the ammonia from the off-gases.

#### Colorado Springs, Colorado

This AWT plant began operation in 1970 and provides lime coagulation, settling, dual media filtration, and carbon adsorption for 3 mgd of trickling filter effluent. The AWT effluent is reused for irrigation and power plant cooling. Table III-26 summarizes typical effluent quality data.

TABLE III-26

## EFFLUENT QUALITY AT COLORADO SPRINGS

|                 |             |
|-----------------|-------------|
| COD, mg/l       | 10          |
| Turbidity       | 2-6         |
| Color, Cu       | 5-10        |
| Cr, mg/l        | 0.01-0.02   |
| Fe, mg/l        | 0.01-0.05   |
| Mn, mg/l        | 0.017-0.020 |
| Ni, mg/l        | 0.05-0.10   |
| Cu, mg/l        | 0.02-0.05   |
| Pb, mg/l        | 0.004-0.07  |
| Zn, mg/l        | 0.01-0.02   |
| Cd, mg/l        | 0-0.0015    |
| Hg, mg/l        | 0           |
| As, mg/l        | 0.003       |
| CN, mg/l        | 0           |
| Mo, mg/l        | 0.05        |
| PCB & TCH, ug/l | 0.001-0.2   |
| TOC, mg/l       | 5           |
| MBAS, mg/l      | 0           |

Santa Clara Valley Water District (California)

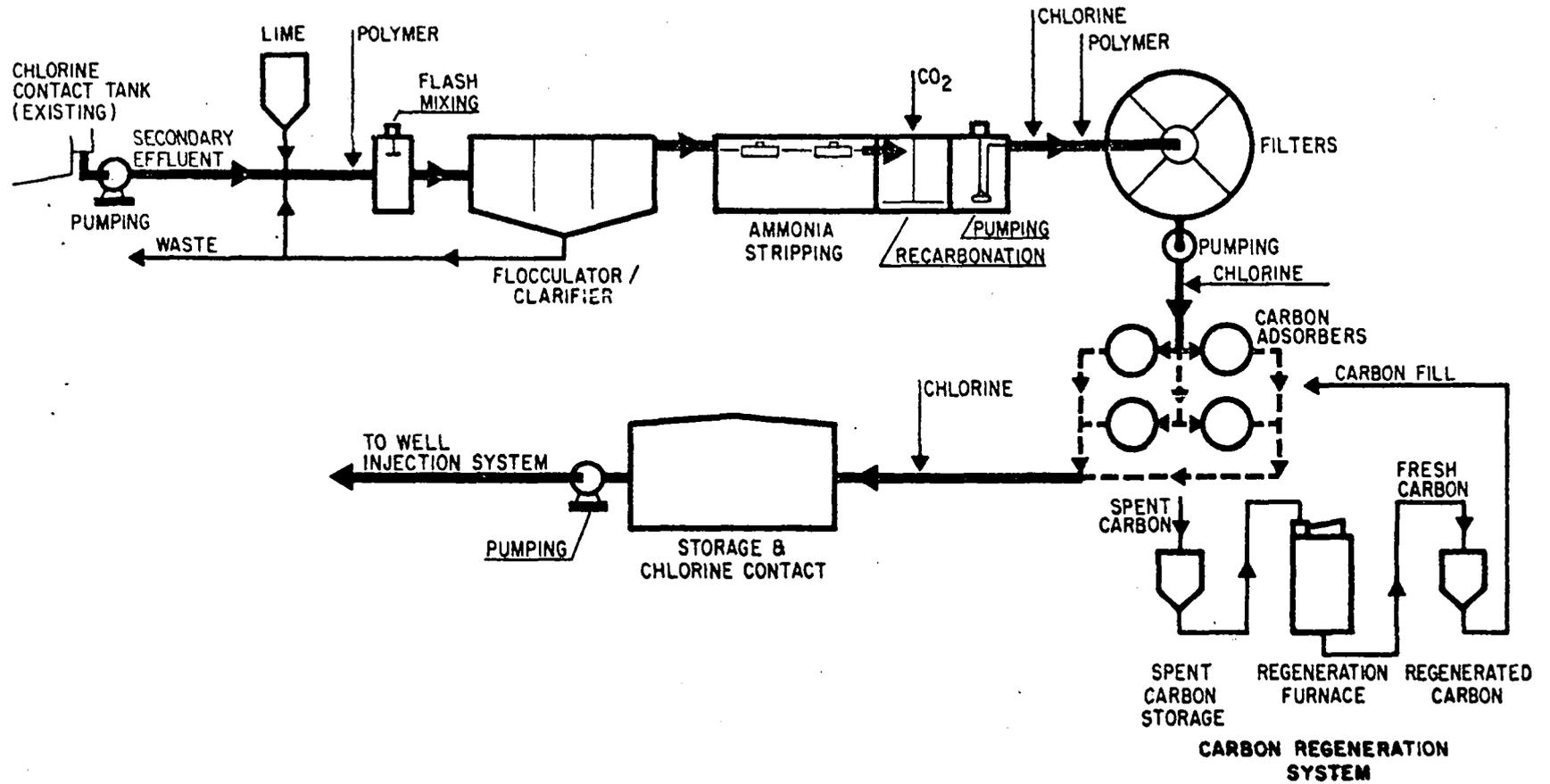
The Santa Clara Valley Water District is in the process of implementing a program of wastewater reclamation and groundwater recharge through injection wells<sup>135</sup>. The proposed project will treat 2.0 mgd of secondary effluent from the City of Palo Alto in an advanced treatment sequence shown in Figure III-23. The reclaimed wastewater will be injected through five wells in an area of the groundwater basin which is not used. The injected water will help control seawater intrusion and an extensive program is planned to monitor the injected water quality at various points in the groundwater basin.

Flushing Meadows (Phoenix, Arizona)

This project recharges the groundwater with secondary effluent<sup>138,139</sup>. The goal of the project is to obtain renovated water for unrestricted irrigation. Although not a project for municipal reuse, the project does offer an existing project based on recharge with secondary effluent. The recharge test site is located west of Phoenix within the flood plain of the Salt River. The two-acre site is divided into six basins that are 20 feet wide and 700 feet long. The soil is a sandy loam made up of 2-3 percent clay, 50 percent silt, and 47 percent sand. Infiltration rates of 1 foot per day or 300 feet per year are regularly achieved by flooding for 14 days and resting 10-20 days. During the two weeks of inundation (surcharge is about one foot), the infiltration rate drops from 2.5 feet per day to 1.5 feet per day with an average of 2 feet per day. During the summer, 10 days are sufficient for drying, reaeration, and biological oxidation which restore the infiltration capacity, but winter operation requires 20 days. The permeability of the

FIGURE III-23

BASIC PROCESS FLOW DIAGRAM  
Santa Clara, California



soil using well water is four feet per day. The groundwater table is at a depth of ten feet. A series of wells in the center of the riverbed are used to pump the infiltrated wastewater to prevent the renovated water from moving into aquifers outside the water reclamation system.

Quality parameters of the secondary effluent and the water pumped from the 30-foot deep East Center Well (ECW), mostly obtained in 1971, are shown in Table III-27. The water obtained from ECW is effluent that moved through about six feet of unsaturated soil to the water table, after which it traveled about 30 feet below the water table to the intake of the well. The underground detention time of ECW-water was about five to ten days, depending on the infiltration rate in the basins. Were domestic reuse the goal, some of the constituents found in the reclaimed water are unacceptably high.

#### Whittier Narrows, California

This is another example of recharge with secondary effluent. A report is currently in press which will provide an up-to-date summary of the experiences at Whittier Narrows. Unfortunately, this new report could not be obtained in time for inclusion in this document. However, data are available from an earlier study<sup>140</sup> which describes the water quality aspects of the project.

At the time of this report, the Whittier Narrows Water Reclamation Plant, constructed and operated by the Los Angeles County Sanitation Districts, had been discharging about 12 to 16 mgd of highly treated activated-sludge effluent since August 1962. The effluent is metered and turned over to the Los

TABLE III-27

WATER QUALITY DATA FROM RECHARGE WITH SECONDARY EFFLUENT AT PHOENIX, ARIZONA<sup>(139)</sup>

| Constituent                | Effluent                         | East Center Well |
|----------------------------|----------------------------------|------------------|
|                            | mg/l                             | mg/l             |
| BOD                        | 10-20                            | 0-1              |
| COD                        | 30-60                            | 10-20            |
| TOC                        | 10-25                            | 1-7              |
| Org.-N                     | 2-6                              | 0.3-0.7          |
| NO <sub>3</sub> -N         | 0-1                              | 0.1-50           |
| NO <sub>2</sub> -N         | 0-3                              | 0-1              |
| NH <sub>4</sub> -N         | 20-40                            | 5-20             |
| PO <sub>4</sub> -P         | 7-12                             | 4-8              |
| F                          | 3-5                              | 2-2.5            |
| B                          | 0.7-0.9                          | 0.7-0.9          |
| Cu                         | 0.1                              | 0.02             |
| Zn                         | 0.2                              | 0.1              |
| Cd                         | 0.008                            | 0.007            |
| Pb                         | 0.08                             | 0.07             |
| Total salts                | 1,000-1,200                      | 1,000-1,200      |
| pH                         | 7.7-8.1                          | 6.9-7.2          |
| Fecal coliforms per 100 ml | 10 <sup>5</sup> -10 <sup>6</sup> | 0-100            |

Angeles County Flood Control District (LACFCD) which conveys it in pipelines, open ditches, and river channels to the spreading basins of the Montebello Forebay along the Rio Hondo and San Gabriel River, where it is allowed to percolate into water-bearing strata. At the time (1966) of the report<sup>140</sup>, the reclaimed water constituted 11 percent of that spread with Colorado River water making up most of the rest of the water spread.

The secondary effluent spread did not meet drinking water standards for nitrogen, zinc, or TDS. It also probably failed to meet the organic standard (CCE), but this is uncertain since no CCE data were presented in the 1966 report. The COD of the effluent was measured and was found to be 30-66 mg/l which indicates that the CCE standard was probably exceeded by the effluent. The purpose of the earlier study was to determine the quality changes as the effluent moved through the soil. It was found that coliform concentrations increased in a few feet of vertical percolation. However, the fecal organisms were found to be very low in number. It was concluded that the increased number of coliforms resulted from growth of soil coliforms and that coliform concentrations would be reduced to acceptable levels by horizontal movement through the soil. Virus tests were inconclusive. Dilution with other water spread allowed the nitrate standards to be met in the groundwater.

The influent in two test basins was found to be reduced on the average from a COD of 31-38 mg/l to 9-19 mg/l by vertical percolation through the soil. However, both test basins exhibited a peculiar pattern of COD concentrations in the percolates below the four-foot level. At greater depths, the concentration of COD substances in the percolate was found to increase to

levels as high as 40 mg/l. It was found that the COD of the soil system was higher than the amount added by the recharge water and that this COD was, in fact, organic in nature. It was concluded that organic carbon was being synthesized in the soil system and that a portion of this organic carbon (probably in the form of bacterial bodies) was leached downward to appear in the percolates.

It was concluded from this study<sup>140</sup> that: "Insofar as the quality of groundwater at or below Whittier Narrows is concerned, there should be no fear that the present rate of spreading of effluent will have any marked or deleterious effect. Indeed, the output from the Whittier Narrows Plant could well be increased by a factor of two or three without concern. The concentration of nitrates in the blended groundwater will probably be the limiting factor on expansion of wastewater reclamation at this location."

Although the report reached the above favorable conclusion, an added factor of safety would unquestionably be introduced by use of the AWT processes described in this report rather than depending solely on secondary treatment of the wastewaters prior to spreading. For example, the bacteria of sewage origin could be eliminated prior to entry of the water into the recharge system. Also, the concentrations of COD could be reduced to 10 mg/l (the level achieved after percolation) before spreading, reducing the load of refractory organics in the soil system and providing more positive control of their fate. Nitrogen concentrations could also be reduced to drinking water standards before spreading.

Since the earlier report, the wastewater portion of water spread in the Montebello Forebay has increased. In addition to the output of the Whittier Narrows plant, effluent from the San Jose Creek Water Renovation Plant is also spread. It is reported<sup>141</sup> that reclaimed wastewater made up of 19.3 percent of the water spread in water year 1972-73 and it is estimated that it will make up 29.7 percent (32,700 AF reclaimed water, 77,300 acre-feet of Colorado River water) of the water spread in water year 1973-74. An experimental nitrification program is under way at the Whittier Narrows plant.

#### Muskegon County, Michigan - Land Treatment System

This system and its operation to date are the subject of a seminar manual entitled, "Land Treatment of Municipal Wastewater Effluents" which was prepared in 1975 for the U. S. EPA Technology Transfer Program by Dr. Y. A. Demirjian, Manager-Director for Muskegon County<sup>167</sup>. The material which follows has been extracted from this report.

#### "Summary

The Muskegon County Wastewater Management System was designed to treat liquid wastewater by biological treatment in aerated lagoons and subsequently store it for the winter season, and then spray irrigate on the crop farmland during the growing season. The land treatment 'living filter' process is providing the advance treatment for the wastewater.

"The design objectives for the Muskegon County Wastewater Treatment System are as follows:

1. The abatement of municipal and industrial wastewater discharge into the county's already polluted surface water.
2. Effectively renovating industrial and domestic wastewater into cleaner water before discharging into the surface water.
3. Reclaiming marginal non-productive land into productive agricultural land.
4. Stimulating county economical development by increased tourism and industrial expansion.
5. Creating a county-wide progressive and cooperative working atmosphere within the municipalities.

"The system is designed to be capable of treating 42 MGD of combined industrial and domestic liquid waste by 1992. The results and experience of the 1974 operation indicate that the system is effectively treating wastewater and renovating cleaner water. The surface water bodies are receiving a higher quality of treated water.

"During the 1974 corn growing season it was demonstrated that crops can be grown effectively in sandy soil conditions and under heavy application rates of treated liquid waste. The indications are that as the field and soil conditions improve, the crop yield will also improve substantially.

"By research and development, it has been found that the system is over-designed. It is capable of treating twice the amount of the present 28 MGP flow capacity wastewater. The research and development program has also demonstrated that the system can be operated much more economically by conserving energy.

"Systems of this magnitude and environmental significance require optimum consideration and critical management. Complete systems analysis is required as a management tool for maximum cost effectiveness versus treatment and utilization of nutrients by irrigation schedules compatible with crop requirements and land consideration.

"The 1974 operations demonstrated some temporary start-up problems. These problems were mainly the irrigation segment of the project. The following is a brief explanation and a list of the main problem areas:

1. Due to high water levels in the storage lagoons (one year of treated water), wind storms and ice cover damaged less than 10 percent of total dike area. The damages were repaired in the fall of 1974. This year there are no indications of major damages.
2. Breaks in irrigation pressure pipes. The reasons for these breaks are not certain yet and are under investigation. At the present time, all pressure pipes are under operational conditions.
3. Faults in the electrical cables caused 16 rigs to be inoperable toward the end of the 1974 irrigation season. Some faults are attributed to pin holes and the reasons for these failures are under investigation. The faulty cables are currently under repair.
4. Reduced organic and inorganic sulfur compounds emanating from the influent caused some nuisance to the surrounding area. Most of the odor from these reduced sulfur compounds has been eliminated. The intermittent emanation is under investigation currently and is expected to be resolved.

"The construction cost of the total system is \$42.1 million. The operational budget for 1975 is \$2,206,460.00, and the galonage fee for the users is \$170/MG. Included in this fee are

TABLE III-28<sup>167</sup>  
MUSKEGON COUNTY  
SUMMARY OF TREATMENT PERFORMANCE

| <u>Parameter</u>                 |       | <u>Influent</u> | <u>Discharge From</u> |               | <u>Storage Lagoon</u> |             | <u>Drain Tiles</u> | <u>Mosquito Creek</u> | <u>Black Creek</u> |
|----------------------------------|-------|-----------------|-----------------------|---------------|-----------------------|-------------|--------------------|-----------------------|--------------------|
|                                  |       |                 | <u>Cell 1</u>         | <u>Cell 2</u> | <u>East</u>           | <u>West</u> |                    |                       |                    |
| BOD                              | ppm   | 220             | 105                   | 65            | 20                    | 5           | 2.2                | 2                     | 2                  |
| DO                               | ppm   | 0               | 1                     | 2             | 3                     | 8.5         | 2-9                | 9.5                   | 1.6                |
| Temp.                            | °C    | 24              | 24                    | 20            | 1-26                  | 1-26        | -                  | 1-5                   | 12                 |
| pH                               |       | 7.5             | 7.5                   | 7.6           | 7.6                   | 8.2         | 7                  | 7.2                   | 6.8                |
| Sp COND                          | µmhos | 1300            | 1100                  | 1100          | 1200                  | 750         | 600                | 750                   | 800                |
| TS                               | ppm   | 1050            | 950                   | 1000          | 750                   | 550         | -                  | 375                   | 700                |
| TVS                              | ppm   | 500             | 400                   | 380           | 300                   | 200         | -                  | 160                   | 150                |
| SS                               | ppm   | 325             | 250                   | 250           | 20                    | 10          | -                  | 10                    | 30                 |
| COD                              | ppm   | 550             | 350                   | 325           | 140                   | 70          | -                  | 30                    | 25                 |
| TOC                              | ppm   | 140             | 75                    | 70            | 30                    | 20          | 5                  | 10                    | 10                 |
| NH <sub>4</sub> <sup>+</sup>     | ppm   | 9.0             | 6                     | 4             | 2.5                   | 0.2         | 0.40               | 0.45                  | 0.5                |
| NO <sub>3</sub> /NO <sub>2</sub> | ppm   | 0.0             | 0.07                  | 0.1           | 2.5                   | 0.8         | 2.8                | 1.9                   | 1.4                |
| PO <sub>4</sub> <sup>3-</sup>    | ppm   | 6.5             | 5                     | 5             | 5                     | 0.7         | 0.05               | 0.1                   | 0.05               |
| SO <sub>4</sub> <sup>2-</sup>    | ppm   | 85              | 100                   | 100           | 95                    | 70          | 150                | 80                    | 320                |
| Cl <sup>-</sup>                  | ppm   | 175             | 170                   | 170           | 160                   | 90          | 50                 | 60                    | 18                 |
| Na <sup>+</sup>                  | ppm   | 150             | 150                   | 150           | 145                   | 85          | 40                 | 40                    | 7                  |

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TABLE III-28 (Continued)

SUMMARY OF TREATMENT PERFORMANCE

| <u>Parameter</u>           | <u>Influent</u> | <u>Discharge From</u> |               | <u>Storage Lagoon</u> |                       | <u>Drain Tiles</u> | <u>Mosquito Creek</u>  | <u>Black Creek</u> |
|----------------------------|-----------------|-----------------------|---------------|-----------------------|-----------------------|--------------------|------------------------|--------------------|
|                            |                 | <u>Cell 1</u>         | <u>Cell 2</u> | <u>East</u>           | <u>West</u>           |                    |                        |                    |
| Ca                         | 70              | 70                    | 70            | 65                    | 60                    | 70                 | 60                     | 110                |
| Mg                         | 16              | 16                    | 16            | 16                    | 16                    | 25                 | 20                     | 40                 |
| K                          | 11              | 11                    | 11            | 11                    | 6                     | 2.8                | 5                      | 2.5                |
| Fe                         | 1.25            | 0.75                  | 0.75          | 1.0                   | 0.7                   | 4.0                | 0.08                   | 0.4                |
| Zn                         | 0.9             | 0.5                   | 0.5           | 0.25                  | 0.15                  | 0.06               | 0.1                    | 0.2                |
| Mn                         | 0.25            | 0.25                  | 0.25          | 0.25                  | 0.08                  | 0.15               | 0.08                   | 0.4                |
| Color Units                |                 |                       |               |                       | 100                   | 20-150             | 130                    |                    |
| Turbidity<br>Jackson Units |                 |                       |               |                       | 2.8                   | 0.1-50             | 4.5                    |                    |
| Total Coli (units/100 ml)  |                 |                       |               |                       | 0-1.3x10 <sup>5</sup> | 10-1000            | 40-1.5x10 <sup>4</sup> |                    |
| Fecal Coli (units/100 ml)  |                 |                       |               |                       | 0-2400                | 0-440              | 1-1500                 |                    |
| Fecal Strep (units/100 ml) |                 |                       |               |                       | 0-2300                | 2-700              | 7-5500                 |                    |

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operational and maintenance costs, amortization, depreciation, prior operational deficits, interest, and working capital requirements."

#### PILOT AND LABORATORY STUDIES

##### Nassau County, New York

Nassau County, New York, has evaluated treatment methods for its wastewater to provide a product water which is suitable for ground injection as a barrier to saltwater intrusion<sup>136,137</sup>. A pilot plant has been operated at 400 gpm. Effluent from high rate activated sludge is pumped into a 40-foot diameter by 14-foot deep clarifier where alum and polyelectrolyte are added. Sludge is recirculated into the coagulation zone to improve efficiency of floc formation. The treated wastewater then passes downward through a flocculation zone and upward through a clarification zone to orifice-type collectors. The clarified wastewater passes to two dual-media filters in parallel operated at 3.0 gpm/sf (gallons per minute per square foot). Each filter consists of a 36-inch bed of No. 1-1/2 anthracite (effective size of 0.90 mm) above a 12-inch layer of sand (effective size of 0.40 mm). Filter backwash includes air scour, surface wash and high and low-rate backwashing. The filter effluent passes through four granular carbon contactors operating in series to remove organics.

Typical operating results with about 200 mg/l alum are shown below:

|                    | <u>Influent</u> | <u>Effluent</u> |
|--------------------|-----------------|-----------------|
| Turbidity, JTU     | 20-25           | 0.2-1.5         |
| Color, Pt-Co Units | 20-40           | none            |
| COD, mg/l          | 78              | 13              |
| P, mg/l            | 9               | 0.1-1.0         |

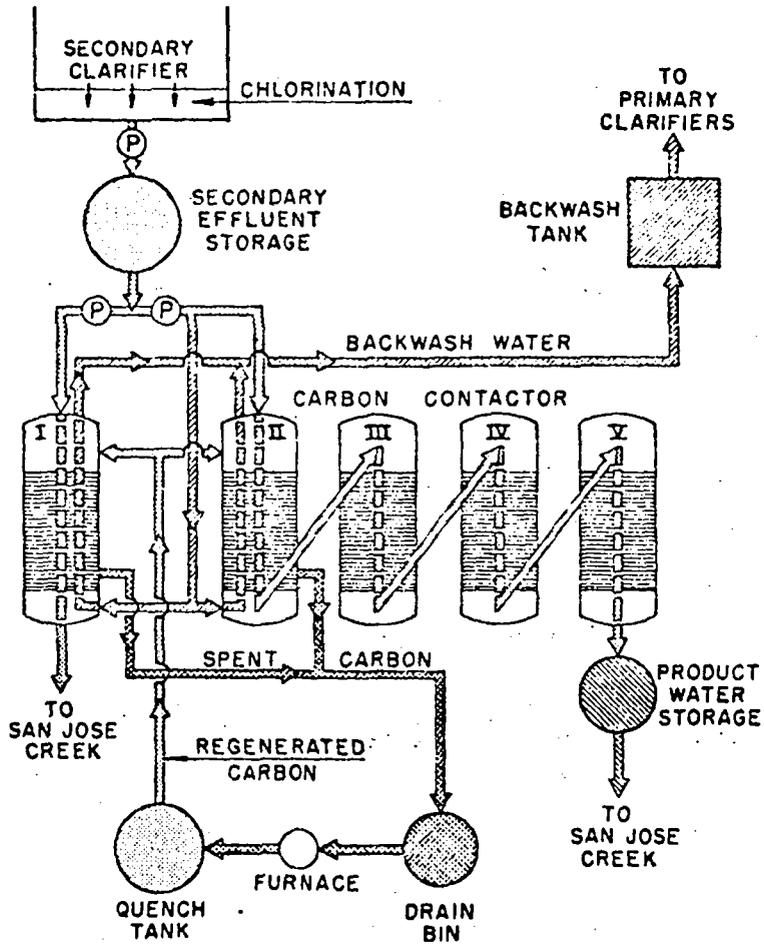
Pomona, California

A 0.3 mgd, four-stage, fixed bed granular activated carbon pilot plant treated unfiltered activated sludge effluent continuously at Pomona from June 1965 through July 1969<sup>100,142</sup>. The pilot plant components included five carbon vessels or contactors, influent and product water storage tanks, a carbon dewatering bin, a quench tank, and a regeneration furnace, all mounted on a concrete slab with related piping, pumps, and controls. A schematic flow diagram for the pilot plant is shown in Figure III-24. The activated sludge effluent was pumped directly to four downflow carbon contactors operated in series. The contactors were six feet in diameter, provided a total superficial contact time of 40 minutes at a flow rate of 200 gpm and hydraulic loading of 7 gpm/sq. ft.

Initially, chlorinated secondary effluent was used since it was more conveniently available from the activated sludge plant. However, during the course of the study, the plant was enlarged by the construction of a new parallel treatment plant and both chlorinated and unchlorinated secondary effluent from either the old or new treatment plants was used without any significant differences in operation of the carbon columns.

FIGURE III-24

POMONA PILOT PLANT SCHEMATIC FLOW DIAGRAM



Extensive operating data collected during four adsorption cycles, which required four years to complete, indicated that a high quality product water, characterized by an average dissolved COD of 8 mg/l was produced on a routine basis. This water contained, on the average, a concentration of carbon chloroform extract of 0.026 mg/l. The average quality of the pilot plant influent and effluent is summarized in Table III-29.

The following steady state conditions were achieved after the second thermal regeneration of the carbon:

1. Removal of 0.45 to 0.50 lbs. COD per lb. of carbon.
2. Required carbon dose of 350 lbs. per million gallons.
3. Removal of 71 percent of the dissolved COD.
4. Partially due to filtration, 46 percent of the total COD that was removed by the four columns was removed in the first stage.
5. About equal removals of dissolved organic matter, represented by dissolved COD, occurred in each stage.

Other processes which were tested to some extent at Pomona included: foam fractionation, nitrogen removal by microbial denitrification in the carbon units, ammonia stripping and demineralization by electro dialysis, reverse osmosis and ion exchange. The reverse osmosis process was more effective than electro dialysis or ion exchange for the removal of organic material.

TABLE III-29<sup>100</sup>

## AVERAGE WATER QUALITY POMONA PILOT PLANT

June 1965 to July 1969

| <u>PARAMETER</u>        |      | <u>INFLUENT</u> | <u>EFFLUENT</u> |
|-------------------------|------|-----------------|-----------------|
| SUSPENDED SOLIDS        | mg/l | 9               | 0.6             |
| COD                     | mg/l | 43              | 10              |
| DISSOLVED COD           | mg/l | 30              | 8               |
| TOC                     | mg/l | 12              | 3               |
| NITRATE as N            | mg/l | 8.1             | 6.6             |
| TURBIDITY (Jtu)         |      | 8.2             | 1.2             |
| COLOR (Platinum-Cobalt) |      | 28              | 3               |
| ODOR (Ton)              |      | 12              | 1               |
| CCE                     | mg/l | -               | 0.026           |
| BOD                     | mg/l | 3               | 1               |

Spiral wound and tubular reverse osmosis membrane modules were pilot tested at Pomona<sup>143,144</sup>. Two spiral wound units manufactured by Gulf, and tubular units manufactured by Havens and Universal Water were operated over a period of several months. The Gulf modules had capacities of 5,000 gpd and 12,000 gpd. The first tests at Pomona were with the spiral wound modules treating activated sludge secondary effluent. Based on these first tests, it was concluded that spiral wound modules could process secondary effluent with high organic and inorganic removals, but that some form of pretreatment (or additional treatment of the secondary effluent) was necessary to prevent excessive clogging from suspended solids.

The activated sludge effluent was then pretreated by granular carbon adsorption. Data for the 12,000 gpd Gulf unit, after 9,000 hours or approximately one year of operation, are summarized in Table III-30.

Initial tests with tubular membranes were with Havens modules consisting of seven 8-foot long 0.5-inch ID fiberglass tubes coated on the inside with a cellulose acetate membrane. The feed stream flows inside the tube and product water is collected from the outside of the tubes. The data from these tests is of general interest only as a guide to the performance of tubular modules since Havens does not now have a commercially available unit.

Tests with tubular configuration were continued at Pomona with a Universal Water Corporation unit that is currently commercially available. The system utilized a 0.5-inch plastic perforated tube, 50 inches long, with the cellulose acetate membranes on the inside. Universal Water now manufactures membranes which can be wound on the outside of tubes and the company

TABLE III-30<sup>143,144</sup>

TYPICAL WATER QUALITY  
 GULF 12,000 gpd RO UNIT  
POMONA, CALIFORNIA

| <u>Constituent</u> | <u>Concentration</u><br>(mg/l) |                 | <u>% Removal</u> |
|--------------------|--------------------------------|-----------------|------------------|
|                    | <u>Influent</u>                | <u>Effluent</u> |                  |
| COD                | 8.7                            | 1.0             | 88.5             |
| NH <sub>3</sub> -N | 10.1                           | 1.1             | 89.2             |
| NO <sub>3</sub> -N | 4.9                            | 2.4             | 51.0             |
| PO <sub>4</sub> -P | 10.9                           | 0.2             | 98.4             |
| TDS                | 750                            | 59              | 92.1             |

Notes

1. 12,000 gpd pilot plant
2. Influent is municipal wastewater treated by activated sludge system and granular carbon adsorption.
3. Averages based on 40 grab samples (June-September, 1969)
4. Average water recovery = 75%

has also developed a winding machine. Typical feed and product water quality for the Universal Water unit tests are shown in Table III-31.

Orange County Water District (California)

The Orange County Water District (OCWD) conducted an extensive applied research and development program in wastewater reclamation and groundwater recharge. The program began in July 1965 and progressed in three phases.

The first phase was concerned with the feasibility of treating trickling filter effluent for injection through wells into a confined aquifer system. During this phase, a study of treatment operations was conducted in both laboratory and pilot scale units. Treatment prior to injection into one single-casing gravel-packed well consisted of chemical clarification, filtration and chlorination. The progress of the first phase was reported by Hennessy, et al.<sup>145</sup>, and the findings of the first phase were reported in detail in a report to OCWD in 1967<sup>146</sup>.

The first phase was primarily concerned with treatment methods, and injection was not extensively studied. The primary objectives of phase two were to determine the long-term fate of injected reclaimed water, and evaluate the performance of a unique multi-casing injection well. During phase two, reclaimed water was injected through two multi-casing wells for about 10 months. The travel of the injected water was monitored by nine wells located 100 to 1,000 feet from the injection wells. The progress of this second phase of the work was reported by Wesner and Baier<sup>108</sup>, and the final report was published in October 1970<sup>147</sup>. It was the general conclusion of

TABLE III-31

FEED AND PRODUCT WATER QUALITY FOR UNIVERSAL  
WATER CORPORATION RO UNIT - POMONA, CALIFORNIA (143,144)

| Chemical Analysis  | No. of Tests | Feed |            | Product          |           | Brine             |             | Percent Rejection |
|--------------------|--------------|------|------------|------------------|-----------|-------------------|-------------|-------------------|
|                    |              | Ave. | Range      | Ave.             | Range     | Ave.              | Range       |                   |
| Total COD          | 10           | 9.4  | 7.2 - 12.7 | 0.3              | 0.0 - 1.0 | 14.6              | 11.1 - 19.0 | 96.8              |
| Dissolved COD      | 9            | 8.3  | 6.3 - 12.0 | ---              | ---       | 12.7              | 9.7 - 18.6  | ----              |
| NO <sub>3</sub> -N | 9            | 3.6  | 0.1 - 12.0 | 0.7              | 0.0 - 2.2 | 5.5 <sup>11</sup> | 0.1 - 19.0  | 80.6              |
| NH <sub>3</sub> -N | 10           | 11.7 | 2.5 - 18.1 | 0.7 <sup>1</sup> | 0.2 - 1.4 | 18.9              | 3.5 - 36.5  | 94.0              |
| PO <sub>4</sub> -P | 8            | 10.1 | 8.8 - 11.7 | 0.12             | 0.0 - 0.4 | 15.5              | 12.9 - 18.9 | 98.8              |
| TDS                | 10           | 6.9  | 540 - 711  | 39               | 20 - 72   | 1018              | 633 - 1859  | 93.7              |
| Ca                 | 4            | 39.6 |            | <1               |           | 55.4              |             | >97.5             |
| Mg                 | 3            | 24.5 |            | 2.0              |           | 39.3              |             | 91.8              |
| K                  | 4            | 12.1 |            | 0.8              |           | 17.9              |             | 93.4              |
| Na                 | 4            | 111  |            | 7.6              |           | 156               |             | 92.8              |
| SO <sub>4</sub>    | 3            | 227  |            | 0                |           | 383               |             | 100.0             |
| Cl                 | 3            | 85   |            | 8                |           | 153               |             | 90.6              |

- Notes: (1) All analyses run on grab samples.  
 (2) Feed samples taken after acidification with H<sub>2</sub>SO<sub>4</sub>; hence values of SO<sub>4</sub> shown in table include sulfate contributed by acid addition.  
 (3) All values shown are in mg/l.

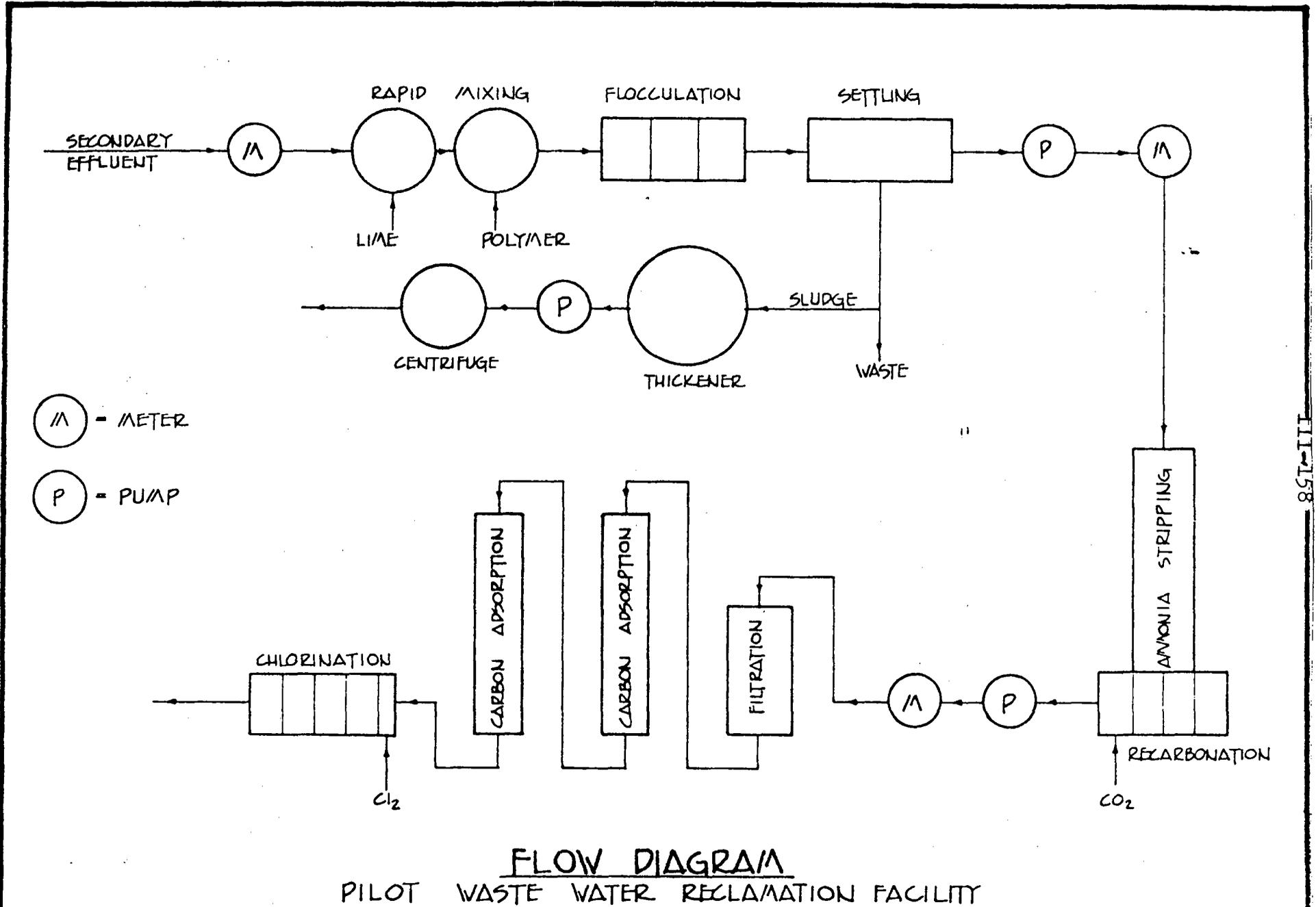
these phase two studies that additional treatment was required prior to injection because color and odor persisted in injected water even after 1,000 feet of underground travel.

Phase three consisted of additional pilot wastewater reclamation studies conducted from May 1970 to June 1971. The progress of the third phase was reported by Wesner and Culp<sup>148</sup> and a final report was issued in 1973<sup>149</sup>.

The treatment processes evaluated in the pilot study are shown on the flow diagram in Figure III-25:

1. Chemical clarification with lime and coagulant aids to remove phosphorus and to raise the pH. This process also reduced COD, turbidity, TDS, hardness and some trace elements;
2. Nitrogen removal by air stripping of ammonia;
3. Recarbonation in one-stage to lower the pH;
4. Mixed media filtration to remove suspended material;
5. Adsorption on beds of activated carbon to remove color and odor causing dissolved organic material;
6. Chlorination for disinfection and to oxidize residual ammonia;
7. Sludge treatment by thickening and centrifuging.

FIGURE III-25



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The capacity of the treatment units varied from 7,000 to 35,000 gpd, and most of these units were constructed especially for the pilot study. Sludge conditioning by thickening and centrifuging was evaluated in rented units. The individual pilot treatment units were operated for varying time periods and conditions.

Most of the laboratory analyses required during the pilot study were performed at OCWD's mobile laboratory, including most physical, chemical and bacteriological tests. All laboratory tests were done in accordance with the twelfth edition of "Standard Methods for the Examination of Water and Wastewater". Odor tests were conducted by a panel in the District's Board room. The California State Health Department assisted in the study by performing analyses for several trace constituents during part of the pilot work. Monthly composite samples of the pilot plant's influent and effluent were analyzed by the Health Department. Typical results of this pilot study are summarized in Table III-32.

#### Los Angeles, California

The City of Los Angeles Department of Water and Power operated a pilot plant from January 1968 through November 1970<sup>118,150</sup>. Activated sludge effluent from the Hyperion treatment plant was pumped directly to two carbon contactors. The contactors were operated in three different modes:

- o January 1968 to January 1970 - Two-stage downflow.
- o February 1970 - Two-stage upflow-downflow

TYPICAL WATER QUALITY OCWD PILOT WASTEWATER RECLAMATION PLANT  
INFLUENT AND EFFLUENT

| Constituent            | Concentration<br>(mg/l except odor and color) |         |          |         |
|------------------------|---|---------|----------|---------|
|                        | Influent                                      |         | Effluent |         |
| Calcium                | 70  | - 110   | 50       | - 80    |
| Magnesium              | 20  | - 45    | 1        | - 3     |
| Sodium                 | 240   | - 260   | 240      | - 260   |
| Potassium              | 20  | - 35    | 20       | - 35    |
| Bicarbonate            | 200   | - 450   | 150      | - 170   |
| Sulfate                | 270   | - 350   | 270      | - 350   |
| Chloride               | 300   | - 350   | 300      | - 350   |
| Phosphate              | 20  | - 25    | <1       |         |
| Nitrogen               |   |         |          |         |
| Organic                | 5   | - 15    | <1       |         |
| Ammonia                | 15  | - 30    | <2       |         |
| Nitrite                | <1  |         | <1       |         |
| Nitrate                | <1  |         | <1       |         |
| Total Dissolved Solids | 1200  | - 1400  | 1000     | - 1100  |
| Total Hardness         | 255   | - 460   | 130      | - 210   |
| Suspended Solids       | 30  | - 80    | <1       |         |
| BOD                    | 30  | - 80    | <2       |         |
| COD                    | 50  | - 200   | 10       | - 30    |
| MBAS                   | 3   | - 4     | 0.1      |         |
| Threshold Odor No.     | 50  | - 100   | <2       |         |
| Color, Units           | 30  | - 50    | <2       |         |
| Arsenic                | 0.00  | - 0.01  | 0.01     |         |
| Barium                 | <0.02   |         | <0.02    |         |
| Cadmium                | 0.01  | - 0.13  | 0.000    | - 0.005 |
| Chromium (hexavalent)  | 0.10  | - 0.20  | 0.00     | - 0.04  |
| Copper                 | 0.09  | - 0.39  | 0.02     | - 0.30  |
| Iron                   | -   |         | 0.05     | - 0.25  |
| Lead                   | 0.00  | - 0.05  | 0.00     | - 0.04  |
| Manganese              | -   |         | 0.05     | - 0.10  |
| Mercury                | <0.001  | - 0.003 | <0.001   | - 0.003 |
| Selenium               | 0.00  | - 0.09  | 0.000    | - 0.003 |
| Silver                 | 0.00  | - 0.01  | 0.00     | - 0.01  |
| Zinc                   | 0.07  | - 2.08  | 0.02     | - 0.07  |

- o April 1970 to November 1970 - Single-stage downflow.

The contactors were 24 inches in diameter and each contained 13.5 feet of granular activated carbon. The pilot studies included investigation of contact time, rate of filtration, adsorptive capacity and plant configuration. Some of the pilot study conclusions were:

- o Contact Time: Contact times of 12, 25 and 50 minutes were investigated. The use of a 50-minute contact time produced the best water with the longest comparative regeneration cycle. A general decreasing organic removal was correlated with a decreasing contact time.
- o Rate of Filtration: Various rates of filtration over the range of 2 to 8 gpm/sf were tested. The straining and head loss results for the various rates indicated that 8 x 30 mesh carbon should be used, two-stage provided better straining than single-stage, and the depth of carbon, 13.5 feet used in each bed, may be more important for straining than the rate of filtration.
- o Adsorptive Capacity: Three carbons were tested in the pilot plant for adsorptive capacity: Filtrasorb 400 (12 x 40 mesh), Filtrasorb 300 (8 x 30 mesh), and Nuchar WV-L (8 x 30 mesh). Under the test conditions, the carbon dosage requirements for Filtrasorbs 400 and 300 were approximately 380 pounds carbon per million gallons water treated, while the value for Nuchar WV-L was 590 pounds carbon per million gallons water treated (system changes may have been responsible for the greater dosage required with Nuchar WV-L).

- o Plant Configuration: Of the three types of plant configuration investigated (two-stage downflow, two-stage upflow-downflow, and single-stage downflow), two-stage downflow was believed to have several advantages. The two-stage downflow carbon efficiency was better than the single-stage, although the difference may have been the carbon and not the system. Also, two-stage was more reliable for operational consistency than either of the other systems, especially the two-stage upflow-downflow.

The average quality of the pilot plant influent and effluent is shown in Table III-33. These data indicate that about 64 percent of the COD in the activated sludge effluent was removed by activated carbon treatment. It should be noted that the Hyperion effluent is extremely high quality secondary effluent with suspended solids = 5.4 mg/l, BOD = 4.7 mg/l, and COD = 29.9 mg/l. In addition to organic removals, the activated carbon also effected good removals of several trace constituents: aluminum, boron, cadmium, chromium, iron, lead, lithium, selenium, silver, titanium, and strontium 90.

#### Santee, California

A 100,000 gpd activated carbon adsorption pilot plant followed by a 50,000 gpd electro dialysis pilot plant for demineralization of lime treated tertiary effluent was tested at Santee, California<sup>151</sup>. A flow diagram of the pilot plant is shown in Figure III-26. The three carbon contactors contained approximately 13,000 pounds of Darco activated carbon.

TABLE III-33<sup>118</sup>

## LOS ANGELES ACTIVATED CARBON PILOT PLANT

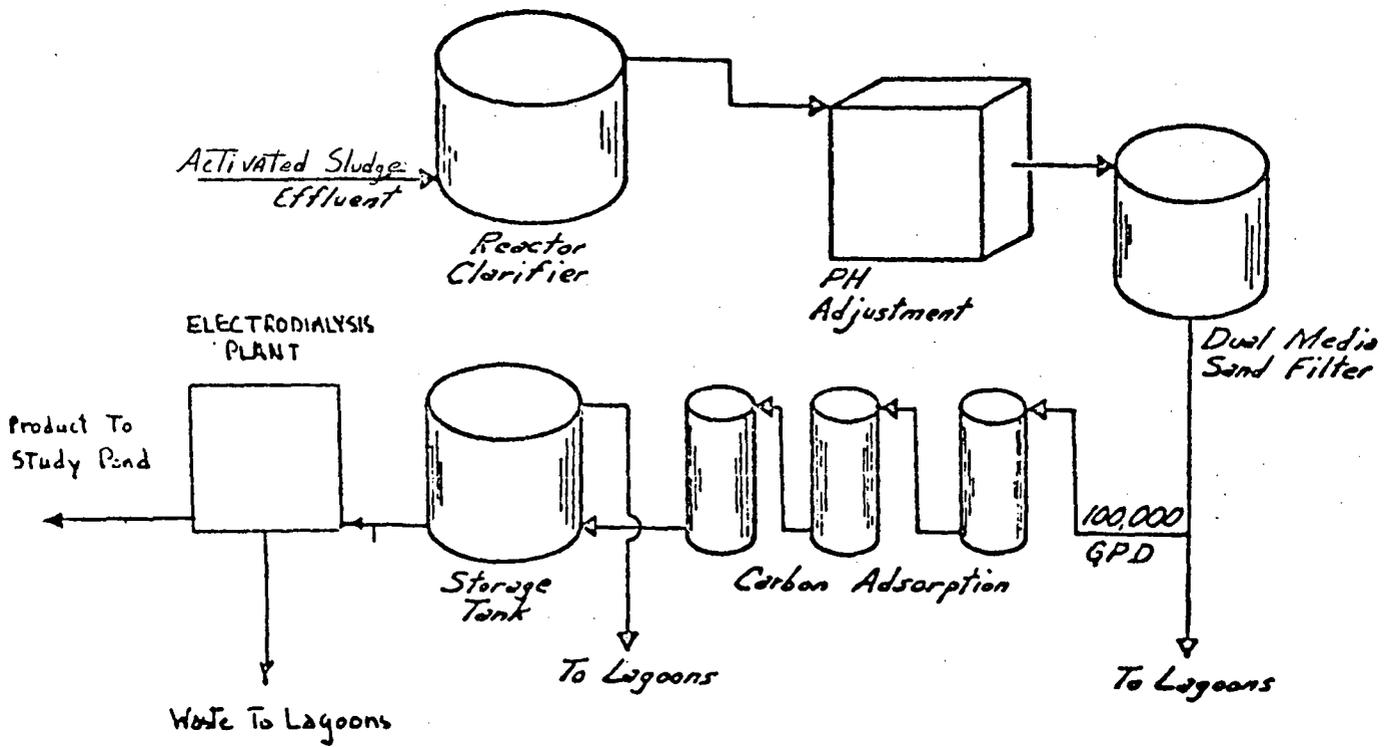
## AVERAGE WATER QUALITY

(all concentrations in mg/l except as noted)

| Constituent                                  | Secondary<br>Effluent<br>1968-1969 | Activated<br>Carbon<br>Effluent<br>1968-1970 |
|--|------------------------------------|--|
| Specific Conductance ( $\mu\text{mhos/cm}$ ) | 1450                               | 1440   |
| Total Dissolved Solids                       | 897                                | 839  |
| Suspended Solids                             | 5.6                                | 2.6  |
| Biochemical Oxygen Demand                    | 5.7                                | 2.4  |
| Turbidity (units)                            | 1.5                                | 0.8  |
| Chemical Oxygen Demand (COD)                 | 29.9                               | 10.7   |
| Dissolved COD                                | 24.6                               | 8.1  |
| Total Organic Carbon                         | ---                                | ---  |
| Dissolved Organic Carbon                     | ---                                | ---  |
| Color (color units)                          | 30                                 | < 5  |
| Nitrate as N                                 | 3.5                                | 3.0  |
| Nitrite as N                                 | 0.6                                | 0.5  |
| Ammonia as N                                 | 7.6                                | 7.1  |
| TKN as N                                     | 15.0                               | 9.3  |
| Dissolved Oxygen                             | 2.0                                | < 0.1  |
| Carbon Chloroform Extracts                   | 1.130                              | 0.027  |
| Detergents - MBAS                            | 0.15                               | < 0.02                                       |
| Total Hardness as $\text{CaCO}_3$            | 229                                | 229  |
| Alkalinity as $\text{CaCO}_3$                | 211                                | 215  |
| pH (pH scale)                                | ---                                | 7.5  |
| Odor (no units)                              | I-II                               | 0  |
| Temperature (C)                              | ---                                | 22.5   |
| Chloride                                     | 207                                | 207  |
| Cyanide                                      | .003                               | < 0.001                                      |
| Fluoride                                     | 1.0                                | 1.0  |
| Phenols                                      | < 0.001                            | ---  |
| Phosphate as P                               | 2.9                                | 2.9  |
| Silica                                       | 26                                 | 26   |
| Sulfate                                      | 207                                | 216  |
| Arsenic                                      | 0.02                               | 0.01   |
| Aluminum                                     | 0.16                               | 0.09   |
| Antimony                                     | ---                                | < 0.1  |
| Barium                                       | 0.18                               | 0.14   |
| Bismuth                                      | ---                                | < 0.01                                       |
| Boron  | 0.91                               | 0.03   |
| Cadmium                                      | 0.01                               | 0.004  |
| Calcium                                      | 55                                 | 55   |
| Chromium - Total                             | 0.08                               | 0.046  |
| Chromium - Hexavalent                        | < 0.01                             | < 0.01                                       |
| Copper                                       | 0.21                               | 0.21   |
| Callium                                      | ---                                | < 0.01                                       |
| Iron   | 0.02                               | < 0.01                                       |
| Lead   | 0.013                              | < 0.01                                       |
| Lithium                                      | 0.14                               | 0.075  |
| Magnesium                                    | 22                                 | 22   |
| Manganese                                    | < 0.05                             | < 0.04                                       |
| Mercury                                      | < 0.0001                           | < 0.0001                                     |
| Molybdenum                                   | 0.019                              | 0.017  |
| Nickel                                       | ---                                | 0.09   |
| Potassium                                    | 13                                 | 13   |
| Selenium                                     | 0.018                              | 0.005  |
| Silver                                       | 0.004                              | 0.002  |
| Sodium                                       | 219                                | 219  |
| Strontium                                    | 0.42                               | 0.40   |
| Tin  | ---                                | < 0.01                                       |
| Titanium                                     | 0.01                               | 0.006  |
| Tungsten                                     | ---                                | < 0.2  |
| Vanadium                                     | 0.03                               | 0.03   |
| Zinc   | 0.10                               | 0.12   |
| Zirconium                                    | 0.006                              | 0.004  |
| Radium 226 pCi/l                             | 0.17                               | 0.22   |
| Strontium                                    | 9.0                                | 3.8  |
| Gross Beta pCi/l                             | 22.3                               | 19.5   |
| Gross Alpha pCi/l                            | 2.3                                | 1.7  |

FIGURE III-26<sup>151</sup>

FLOW DIAGRAM  
SANTEE, CALIFORNIA



Following is a summary of the pilot test results:

1. The average total COD removal in the carbon columns was 57 percent with an average of 30.9 mg/l influent and an average of 13.4 mg/l effluent concentration. The average dissolved COD removal was 58 percent with an average of 26.9 mg/l influent and an average 11.4 mg/l effluent concentration.
2. The Darco virgin activated carbon treated 19.9 million gallons of tertiary effluent and removed 61.8 percent of the applied dissolved COD. The regenerated Darco carbon treated 15.3 million gallons of tertiary effluent and removed 53.8 percent of the applied dissolved COD.
3. The dissolved COD removal efficiency for the virgin carbon cycle was 0.401 pounds per pound of carbon, and 0.234 pounds per pound carbon for regenerated carbon. The 21.3 percent decrease in COD removal was primarily attributed to a 25 percent loss in activated carbon regeneration.
4. Difficulties in removing the exhausted carbon from the lead contactor dish-shaped vessel floor were responsible for 8 to 10 percent of the 25 percent carbon loss during regeneration.

The 50,000 gpd electrodialysis plant was operated from March 1970 through June 1971. The unit was a two-stage Ionics Mark III with 95 membrane pairs in each of the two stacks. Quality of the carbon contactor effluent and the electrodialysis effluent is summarized in Table III-34.

TABLE III-34<sup>151</sup>

## TYPICAL WATER QUALITY

## SANTEE PILOT PLANT

| Constituent                      | Concentration<br>(mg/l, except as noted) |         |                          |         | Electrodialysis<br>Average<br>Removal<br>(%) |
|----------------------------------|--|---------|--------------------------|---------|--|
|                                  | Carbon Contactor<br>Effluent             |         | Electrodialysis Effluent |         |  |
|                                  | Range                                    | Average | Range                    | Average |  |
| Chloride-Cl                      | 200 - 276                                | 243     | 44 - 127                 | 78      | 67.9   |
| Sulfate-SO <sub>4</sub>          | 300 - 490                                | 379     | 160 - 380                | 225     | 40.6   |
| Bicarbonate-HCO <sub>3</sub>     | 78 - 384                                 | 209     | 40 - 174                 | 103     | 50.7   |
| Nitrate-N                        | 0.02-22.5                                | 3.4     | 0.07 - 25.0              | 2.3     | 32.4   |
| Phosphate-P                      | 0.03- 3.53                               | 0.98    | 0.00 - 2.54              | 0.76    | 22.4   |
| Total Hardness-CaCO <sub>3</sub> | 140 - 430                                | 378     | 92 - 244                 | 146     | 61.4   |
| Calcium-Ca                       | 46 - 163                                 | 111     | 24 - 129                 | 38      | 65.8   |
| Magnesium-Mg                     | 0.0 - 43                                 | 24      | 1.5 - 22.4               | 12      | 50.0   |
| Potassium-K                      | 14 - 25                                  | 20      | 4 - 14                   | 11      | 45.0   |
| Sodium-Na                        | 196 - 255                                | 230     | 80 - 180                 | 124     | 46.1   |
| Ammonia-N                        | 0.03-14.1                                | 3.8     | 0.00 - 6.8               | 1.9     | 50.0   |
| Turbidity-JTU                    | 0.0 - 5.5                                | 1.2     | 0.1 - 2.5                | 1.1     | 8.3  |
| Color-Units                      | 5 - 20                                   | 7       | 5 - 15                   | 5.6     | 20.0   |
| Total COD                        | 0.0 -34.0                                | 15.3    | 0.0 - 21.8               | 10.4    | 32.0   |
| COD-filtrate                     | 0.0 -24.3                                | 13.1    | 0.0 - 14.7               | 8.8     | 32.8   |
| Iron-Fe                          | 0.0 - 0.25                               | 0.12    | 0.00 - 0.32              | 0.10    | 16.7   |
| TDS                              | 1000 - 1580                              | 1245    | 400 - 990                | 630     | 49.4   |

\* Influent - Municipal wastewater treated by activated sludge, chemical clarification, dual media filtration and granular activated carbon sorption.

Hemet, California

A pilot demonstration program on the use of reverse osmosis in reducing the concentrations of TDS and refractory substances present in secondary sewage effluent was conducted at Hemet, California from March 6, 1970, to June 25, 1971<sup>152</sup>. It was proposed that the reclaimed wastewater would be used for groundwater recharge in the Hemet area. Other objectives in the Hemet study were:

1. Determination of efficiencies and costs of pretreatment operations.
2. Comparison of the performance of a selected group of reverse osmosis units manufactured by major firms.

The nominal capacity of the pretreatment system was 150,000 gpd and consisted of: (1) Chemical clarification with alum in a sludge blanket-type clarifier, (2) filtration in pressure units with single media, 0.45-0.55 mm sand, (3) granular carbon adsorption with 8 by 12 mesh carbon, (4) diatomaceous earth filtration in a 30-inch diameter unit, and (5) chlorination with sodium hypochlorite. The sequence of unit operations could be by-passed and individual units could be taken out of service, but the sequence of treatment could not be changed.

There were six different reverse osmosis units tested:

1. Aerojet-General Corporation - Tubular-type unit with a design capacity of 8,000 gpd; tubes were 9/16 inches ID by 14 feet, 3

inches long. Start-up March 9, 1970, shutdown December 21, 1970, 2,031 hours of operation. Many tube failures and mechanical problems were experienced.

2. American Standard (ABCOR) - Design capacity 10,000 gpd at 90 percent TDS removal; tubular unit with 1/2-inch ID membrane on inside with turbulence promoters. Start-up June 3, 1970, shutdown June 25, 1971, 6,485 hours of operation. Numerous mechanical and membrane failures.
3. DuPont - Design capacity 10,000 gpd at 75 to 90 percent recovery. The B-5 modules were replaced by B-9 modules during the test program. B-5 modules - 15 inches diameter by 10.5 feet long. B-9 modules - 5.5 inches diameter by 47 inches long. The membranes fouled and required frequent and prolonged cleanings.
4. Gulf - Capacity 10,000 gpd at 60 percent recovery. Start-up March 9, 1970, shutdown June 25, 1971, 10,016 hours of operation. The membranes fouled and required flushing 100 times during the test period.
5. Raypak - Capacity 3,000 gpd at 50 percent recovery; tubular unit with 0.9-inch ID tubes. Start-up May 6, 1971, shutdown June 3, 1971; six weeks of operation. Product water recovery was less than 50 percent during the six-week test period.
6. Universal Water - Capacity 10,000 gpd. Tubular modules with 0.4-inch ID tubes; membrane on inside of tube. Start-up March 9, 1970,

shutdown June 25, 1971, 10,276 hours of operation (94.3 percent of available time). This unit gave reliable service and was less subject to fouling than several of the other units.

In early 1971, a staged reduction in the treatment of secondary effluent supplied to the reverse osmosis units began. First, carbon adsorption was eliminated, then chemical clarification and, finally, the units were supplied straight chlorinated secondary effluent.

First, the activated carbon treatment was removed and the reverse osmosis units were operated for about two months on chemically clarified, filtered and chlorinated secondary effluent. After this change, all units experienced an accelerated flux decline. Water quality data with and without activated carbon treatment are shown in Table III-35.

Next, the chemical clarification unit was taken out of operation and the reverse osmosis units were operated for about six weeks on filtered and chlorinated secondary effluent. Additional flux decreases were observed during this period. Average water quality data are shown in Table III-36.

The reverse osmosis units were then operated on chlorinated secondary effluent for about five weeks. The recovery in the DuPont and Gulf units decreased about 30 percent while the Universal Water unit decrease was about 14 percent. Membrane fouling was more severe in the Gulf and DuPont units than in the Universal Water tubular modules. Water quality data collected during this final part of the test program are shown in Table III-37.

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TABLE III-35<sup>152</sup>

TYPICAL WATER QUALITY - WITH & WITHOUT  
 ACTIVATED CARBON PRETREATMENT  
 REVERSE OSMOSIS PILOT PLANT  
 HEMET, CALIFORNIA

Activated Carbon Pretreatment

| Constituent                         | Feed<br>mg/l | Du Pont         |                | Gulf            |                | Universal<br>Water |                |
|-------------------------------------|--------------|-----------------|----------------|-----------------|----------------|--------------------|----------------|
|                                     |              | Product<br>mg/l | %<br>Rejection | Product<br>mg/l | %<br>Rejection | Product<br>mg/l    | %<br>Rejection |
| Total COD                           | 7.6          | 0.8             | 90             | 1.9             | 75             | 0.5                | 93             |
| Dissolved COD                       | 3.9          | 0.4             | 90             | 1.1             | 72             | 0.4                | 90             |
| TDS                                 | 726          | 100             | 86             | 95.1            | 87             | 45.0               | 94             |
| Nitrate-N                           | 5.2          | 0.6             | 88             | -               | -              | 2.6                | 50             |
| Total Phosphorus                    | 6.2          | 0.6             | 90             | 0.1             | 98             | 0.1                | 98             |
| Calcium                             | 69.5         | 4.5             | 93             | -               | -              | -                  | -              |
| Magnesium                           | 21.0         | 1.4             | 93             | -               | -              | -                  | -              |
| Turbidity, JTU                      | 0.35         | 0.2             | 43             | 0.2             | 54             | 0.7                | 51             |
| Hardness<br>(as CaCO <sub>3</sub> ) | 244          | 18.1            | 93             | 5.0             | 98             | 4.6                | 98             |

Without Activated Carbon Pretreatment

| Constituent                         | Feed<br>mg/l | Du Pont         |                | Gulf            |                | Universal<br>Water |                |
|-------------------------------------|--------------|-----------------|----------------|-----------------|----------------|--------------------|----------------|
|                                     |              | Product<br>mg/l | %<br>Rejection | Product<br>mg/l | %<br>Rejection | Product<br>mg/l    | %<br>Rejection |
| Total COD                           | 35.2         | 1.5             | 96             | 3.4             | 90             | 3.1                | 91             |
| Dissolved COD                       | 26.2         | 1.8             | 93             | 1.1             | 96             | 2.5                | 90             |
| TDS                                 | 718          | 103             | 86             | 52              | 93             | 25.1               | 96             |
| Nitrate-N                           | 9.7          | 1.6             | 83             | 3.8             | 61             | 1.7                | 82             |
| Total Phosphorus                    | 7.9          | 0.7             | 91             | 0.04            | 99             | 0.2                | 99             |
| Calcium                             | 63.9         | 5.2             | 92             | 0.4             | 99             | 0.5                | 99             |
| Magnesium                           | 16.4         | 1.6             | 90             | 0.3             | 98             | 0.3                | 98             |
| Turbidity, JTU                      | 3.0          | 0.4             | 87             | 0.2             | 93             | 0.2                | 93             |
| Hardness<br>(as CaCO <sub>3</sub> ) | 236          | 16.5            | 93             | 0.2             | 99             | 2.8                | 99             |

Feed water is activated sludge effluent treated by chemical clarification and filtration, with and without additional treatment by granular activated carbon.

TABLE III-36<sup>152</sup>

## TYPICAL WATER QUALITY - FILTERED SECONDARY EFFLUENT

## REVERSE OSMOSIS PILOT PLANT

## HEMET, CALIFORNIA

| Constituent                         | Feed<br>mg/l | Du Pont         |                | Gulf            |                | Universal<br>Water |                |
|-------------------------------------|--------------|-----------------|----------------|-----------------|----------------|--------------------|----------------|
|                                     |              | Product<br>mg/l | %<br>Rejection | Product<br>mg/l | %<br>Rejection | Product<br>mg/l    | %<br>Rejection |
| Total COD                           | 47.4         | 1.6             | 97             | 2.1             | 96             | 0.9                | 98             |
| Dissolved COD                       | 25.2         | 3.1             | 88             | 1.2             | 95             | 0                  | 100            |
| TDS                                 | 800          | 89              | 89             | 41              | 95             | 22                 | 97             |
| Nitrate N                           | 0.1          | -               | -              | -               | -              | -                  | -              |
| Total Phosphorus                    | 13.4         | 1.3             | 91             | 0.04            | 99             | 0.05               | 99             |
| Calcium                             | 61           | 3.4             | 94             | 0.3             | 99             | 0.4                | 99             |
| Magnesium                           | 16.4         | 1.5             | 91             | 0.3             | 98             | 0.4                | 97             |
| Turbidity, JTU                      | 2.1          | 0.4             | 80             | 0.5             | 80             | 0.6                | 67             |
| Hardness<br>(as CaCO <sub>3</sub> ) | 228          | 10.2            | 96             | 1.8             | 99             | 2.4                | 99             |

TABLE III-37<sup>152</sup>

TYPICAL WATER QUALITY - SECONDARY EFFLUENT  
 REVERSE OSMOSIS PILOT PLANT  
 HEMET, CALIFORNIA

| Constituent      | Feed<br>mg/l | Dupont          |                | Gulf            |                | Universal Water |                |
|------------------|--------------|-----------------|----------------|-----------------|----------------|-----------------|----------------|
|                  |              | Product<br>mg/l | %<br>Rejection | Product<br>mg/l | %<br>Rejection | Product<br>mg/l | %<br>Rejection |
| Total COD        | 60           | 5.5             | 91             | 4.8             | 92             | 2.1             | 97             |
| Dissolved COD    | 32           | 5.2             | 84             | 3.5             | 89             | 0.2             | 99             |
| TDS              | 731          | 198             | 73             | 80              | 91             | 29              | 96             |
| Nitrate N        | 4.1          | 3.4             | 17             | 1.4             | 66             | 0.6             | 85             |
| Ammonia N        | 13.6         | -               | -              | -               | -              | 0.1             | 99             |
| Organic N        | 3.9          | -               | -              | -               | -              | 0.1             | 97             |
| Sulfate          | 159          | 90              | 43             | 4               | 97             | 1               | 99             |
| Total Phosphorus | 11.7         | 3.0             | 74             | 0.3             | 97             | 3.5             | 70             |
| Calcium          | 65.5         | 9.3             | 86             | 0.6             | 99             | 0.4             | 99             |
| Magnesium        | 18.8         | 3.1             | 84             | 0.4             | 98             | 0.3             | 98             |
| Total Hardness   | 242          | 37              | 85             | 4               | 98             | 2               | 99             |
| Turbidity, JTU   | 10.0         | 0.8             | 92             | 0.4             | 96             | 0.4             | 96             |

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It was the general conclusion of this study that the percent recovery and percent rejection both declined with decreasing degrees of pretreatment and that the tubular units manufactured by Universal Water were best suited for treating poorer quality effluents.

Dallas, Texas

The City of Dallas, Texas, in conjunction with Texas A & M University and the Environmental Protection Agency, is conducting a pilot test program in wastewater reclamation. This is an ambitious program including testing for bacteria, virus, heavy metals and pesticides. It is probably the most comprehensive of any pilot work attempted to date. The project is still in progress and therefore many of the results have not been fully analyzed or widely reported. A general description of the study scope and objectives and preliminary results were reported by Graeser in 1971<sup>153</sup>. Some data from unpublished monthly reports by Dallas Water Utilities Department from July 1973 through September 1974 are reported herein.

Another project under way by the researchers in Dallas is an update of the information published in "Water Quality Criteria"<sup>154</sup>. The objectives of this study are to update the literature as it relates to public water supply, evaluate each constituent in terms of water reuse, and evaluate removal by conventional wastewater treatment and AWT technology and by conventional and specific water treatment technology. This project, originally scheduled for completion on June 30, 1974, has been extended.

The pilot plant is located adjacent to the Dallas White Rock Waste Treatment Plant, which has a design flow of 108 mgd and provides secondary treatment by trickling filters. Many different pilot treatment configurations have been tested. The treatment system which produced the best quality effluent, and for which the most data has been collected, is shown in Figure III-27 and consists of the following unit operations:

1. Activated sludge treatment in a completely mixed system.
2. Chemical clarification in a solids contact type unit with varying dosages and combinations of lime, alum, ferric chloride and polymers.
3. Recarbonation.
4. Mixed media filtration.
5. Carbon adsorption in two downflow contactors in series.

Average performance data for September 1974 are summarized in Table III-38, and removal efficiencies for the entire treatment system during September 1974 are shown in Table III-39. These data show the following effluent quality was achieved:

|                      |           |
|----------------------|-----------|
| Turbidity            | 0.7 units |
| COD                  | 1.7 mg/l  |
| Total Organic Carbon | 3.8 mg/l  |
| Total Nitrogen       | 6.8 mg/l  |
| Total Phosphorus     | 0.35 mg/l |

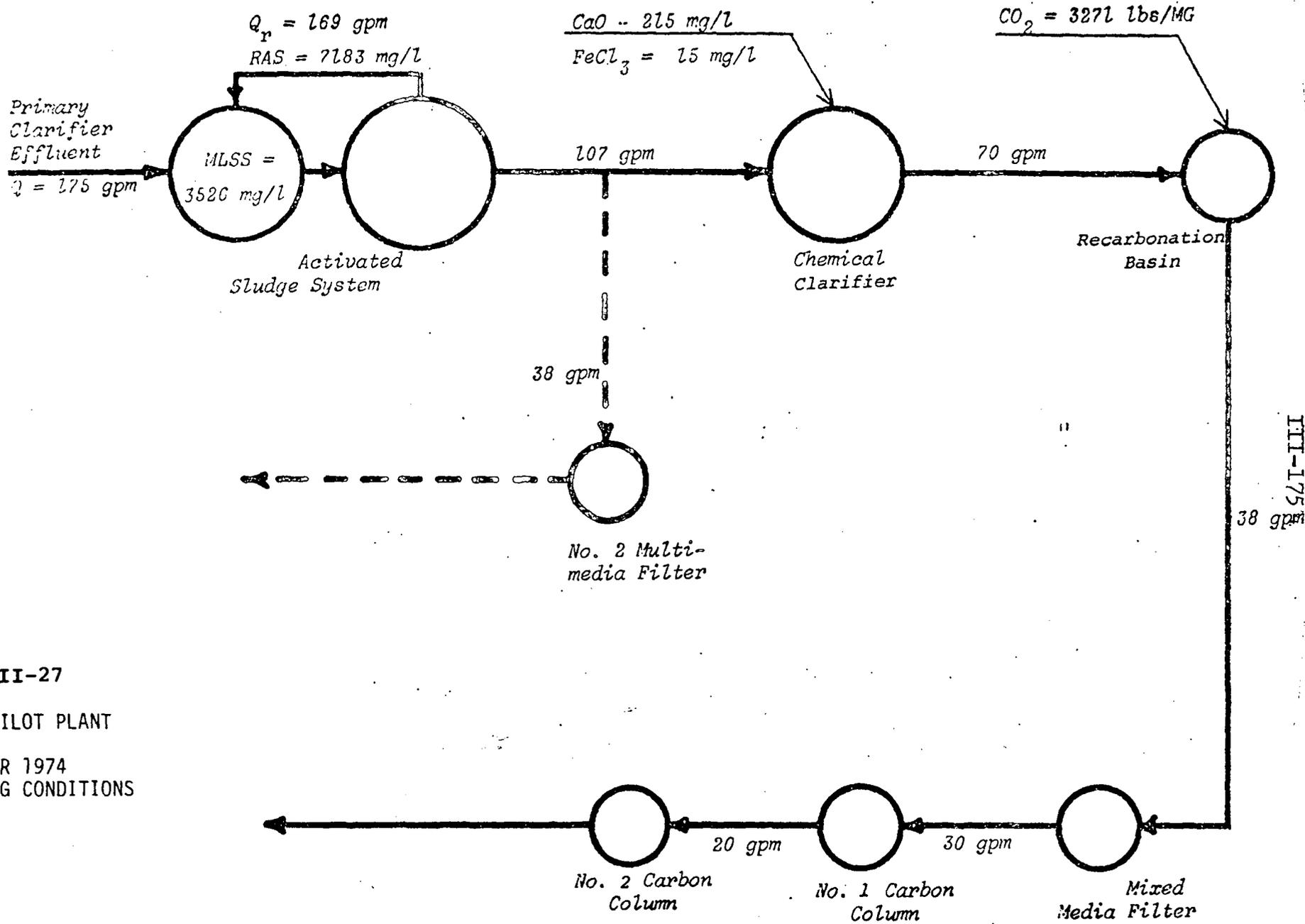


FIGURE III-27

DALLAS PILOT PLANT

SEPTEMBER 1974  
 OPERATING CONDITIONS

III-175  
38 gpm

TABLE III-38

PERFORMANCE SUMMARY

DALLAS PILOT PLANT

SEPTEMBER 1974

CONCENTRATION, mg/l except as noted

| <u>Parameter</u>                       | <u>Raw Wastewater</u> | <u>Primary Effluent</u> | <u>Activated Sludge Effluent</u> | <u>Chemical Clarifier Effluent</u> | <u>Recarbonation Basin Effluent</u> | <u>Filter Effluent</u> | <u>Carbon Columns No.1</u> | <u>Carbon Columns No.2</u> |
|--|-----------------------|-------------------------|----------------------------------|------------------------------------|-------------------------------------|------------------------|----------------------------|----------------------------|
| SS                                     | 231                   | 173                     | 25                               | 28                                 | 11                                  | ---                    | 2                          | 1.8                        |
| COD                                    | 442                   | 317                     | 49                               | 18.2                               | 18.1                                | 17.6                   | 4.6                        | 1.7                        |
| TOC (soluble)                          | ---                   | 39                      | 11                               | 8.6                                | 8.6                                 | 9                      | 5                          | 3.8                        |
| Total P                                | ---                   | 9.0                     | 6.6                              | 0.4                                | 0.4                                 | ---                    | 0.36                       | 0.35                       |
| NH <sub>3</sub> -N                     | 18.4                  | 17.9                    | 2.1                              | 1.9                                | 1.9                                 |                        | 1.4                        | 0.9                        |
| Org. N                                 | 18.3                  | 11.5                    | 4.8                              | 2.3                                | 2.2                                 |                        | 1.0                        | 0.5                        |
| NO <sub>2</sub> -N & NO <sub>3</sub> N | 0.5                   | 0.3                     | 6.1                              | 5.7                                | ---                                 |                        | 5.8                        | 5.4                        |
| Total N                                | 27.2                  | 29.7                    | 13.0                             | 9.9                                |                                     |                        | 8.2                        | 6.8                        |
| Color                                  | ---                   | ---                     |                                  |                                    |                                     |                        | 2                          | 0.6                        |
| Turbidity                              | ---                   |                         |                                  |                                    | 1.7                                 | 1.2                    | 1.9                        | 0.7                        |
| pH, units                              |                       | 7.1                     | 7.3                              | 11.1                               | 6.6                                 | 6.7                    |                            | 6.7                        |
| Temperature, °F                        |                       | 80                      |                                  |                                    |                                     |                        |                            | 80                         |
| Electrical Conductivity, umhos/cm      | 851                   |                         | 903                              |                                    |                                     |                        |                            | 792                        |
| Coliforms, colonies/100 ml             |                       | 36.6 x 10 <sup>5</sup>  | <1                               |                                    |                                     |                        |                            | 210                        |
| Fecal Coliforms, colonies/100 ml       |                       | 44.9 x 10 <sup>4</sup>  | <1                               |                                    |                                     |                        |                            | 6.7                        |

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TABLE III-39

## REMOVAL EFFICIENCY SUMMARY

DALLAS PILOT PLANT

September, 1974

| PARAMETER          | RAW<br>WASTEWATER<br>(mg/l) | AWT<br>EFFLUENT<br>(mg/l) | % REDUCTION |
|--------------------|-----------------------------|---------------------------|-------------|
| SS                 | 231                         | 1.8                       | 99.2        |
| COD                | 442                         | 1.74                      | 99.6        |
| TOC                | --                          | 3.8                       | --          |
| Total P            | --                          | 0.35                      | --          |
| NH <sub>3</sub> -N | 18.4                        | 0.89                      | 95.2        |
| Org. N             | 18.3                        | 0.52                      | 97.2        |
| NO <sub>2</sub> -N | --                          | 0.04                      | --          |
| NO <sub>3</sub> -N | 0.5                         | 5.36                      | --          |
| Total N            | 27.2                        | 6.81                      | 75.0        |
| Color              | --                          | 0.6                       | --          |
| Turbidity          | --                          | 0.67                      | --          |
| Alkalinity         | --                          | 162.5                     | --          |

The Dallas researchers found that the COD of the AWT process effluent was improved from about 35 mg/l to a typical value of 12 mg/l by utilization of more complete nitrification in the activated sludge portion of the process.

Most of the data on heavy metals and other trace constituents was collected during 1973. Average results through July 1973 and for November-December 1973 are shown in Table III-40. The concentrations of boron, calcium, mercury and sodium increased through the plant during November-December 1973. Calcium and sodium were added during chemical treatment; the boron and mercury data were considered anomalies.

A great amount of data was also collected on virus and pesticide removals. This test work is still in progress, but initial results with high lime treatment (pH > 11) indicated complete removal of polio I and F2 coliphage. A small, activated sludge unit (SBE #2) was operated in parallel and at a higher rate (lesser-nitrifying mode) than a large unit (SBE #1). Ammonia nitrogen in SBE #2 averaged 8.8 mg/l vs. 1.42 mg/l for SBE #1. The comparative pesticide removals of the two systems were:

| <u>Pesticide</u> | <u>Concentration, ppt</u> |               |               |
|------------------|---------------------------|---------------|---------------|
|                  | <u>Influent</u>           | <u>SBE #1</u> | <u>SBE #2</u> |
| Phosdrin         | 773                       | 466           | 573           |
| 2,4-D (ME)       | 253                       | 87            | 83            |
| 2,4-D (IPE)      | 633                       | 947           | 1000          |
| Diazinon         | 187                       | 147           | 173           |
| Aldrin           | 51                        | 37            | 40            |
| Dieldrin         | <u>14</u>                 | <u>21</u>     | <u>20</u>     |
|                  |                           | 1705          | 1889          |

TABLE III-40

## HEAVY METALS REMOVALS

## DALLAS PILOT PLANT

Average Concentration, mg/l except as noted

| Metal    | Through July 1973               |                              |                    | November-December, 1973         |                              |                    |
|----------|---------------------------------|------------------------------|--------------------|---------------------------------|------------------------------|--------------------|
|          | Activated<br>Sludge<br>Influent | Carbon<br>Column<br>Effluent | Percent<br>Removal | Activated<br>Sludge<br>Influent | Carbon<br>Column<br>Effluent | Percent<br>Removal |
| Al       | 0.51                            | 0.70                         | +37                | 0.92                            | 0.36                         | 60.9               |
| As, ug/l | 10                              | 5                            | 50                 | 23.5                            | 3.4                          | 85.5               |
| B        | 0.36                            | 0.34                         | 6                  | 0.34                            | 0.41                         | --                 |
| Ba       | 0.14                            | 0.06                         | 57                 | 0.12                            | 0.05                         | 58.3               |
| Ca       | 60                              | 69                           | +15                | 62.1                            | 84.0                         | --                 |
| Cd       | 0.012                           | 0.004                        | 67                 | 0.013                           | 0.002                        | 84.6               |
| Co       | 0.03                            | 0.02                         | 33                 | 0.055                           | 0.068                        | --                 |
| Cr       | 0.24                            | 0.02                         | 92                 | 0.177                           | 0.010                        | 94.4               |
| Cu       | 0.38                            | 0.03                         | 92                 | 0.129                           | 0.017                        | 86.8               |
| Fe       | 1.34                            | 0.08                         | 94                 | 1.07                            | 0.15                         | 86.0               |
| Hg, ug/l | 0.61                            | 0.25                         | 59                 | 0.54                            | 0.70                         | --                 |
| Mn       | 0.09                            | 0.02                         | 78                 | 0.084                           | 0.007                        | 91.7               |
| Na       | 91                              | 85                           | 7                  | 93.7                            | 104.8                        | --                 |
| Ni       | 0.11                            | 0.05                         | 55                 | 0.181                           | 0.097                        | 46.4               |
| Pb       | 0.13                            | 0.04                         | 69                 | 0.090                           | 0.023                        | 74.4               |
| Se, ug/l | 4.5                             | 0.54                         | 88                 | 14.2                            | 0.4                          | 97.2               |
| Sr       |                                 |                              |                    | 0.272                           | 0.233                        | 14.3               |
| V, ug/l  | 5.6                             | 6.1                          | + 9                | 4.6                             | 2.9                          | 37.0               |
| Zn       | 0.60                            | 0.07                         | 88                 | 0.221                           | 0.023                        | 89.6               |

The differences thus indicate that better organics removal accompanies a higher nitrification operation. (Sludge age for SBE #1 averaged 24 days, as compared to two days for SBE #2.)

The performance of the chemical clarifier using alum as a primary coagulant (data from May 1973) versus the high pH process (data from November 1973) shows the following:

| <u>Pesticide</u> | Concentration, ppt |            |           |            |
|------------------|--------------------|------------|-----------|------------|
|                  | Lime               |            | Alum      |            |
|                  | <u>In</u>          | <u>Out</u> | <u>In</u> | <u>Out</u> |
| Phosdrin         | 466                | 333        | 330       | 260        |
| 2,4-D (ME)       | 107                | 107        | 1200      | 1400       |
| 2,4-D (IPE)      | 946                | 950        | 500       | 600        |
| Diazinon         | 147                | 14         | 80        | No Data    |
| Aldrin           | 37                 | 37         | 20        | 16         |
| Dieldrin         | 21                 | 13         | 8         | 3          |

Lime effected good reductions on diazinon, some on phosdrin, none on the others.

Alum effected reductions on all but the 2,4-D's which show increases. Since these are single samples, results must be interpreted with caution.

The Dallas researchers offer these observations based on their work<sup>165</sup>:

"The final effluent in terms of traditional wastewater treatment analytical parameters is of very high quality, and with reference to current potable quality criteria is equal or superior to many municipal source water supplies. Furthermore, the quality fluctuations of this effluent are lower than many river waters;

hence, in terms of water supply, a well-operated reclamation plant has the potential to provide a very high quality product water...

"In making this statement, one should be aware that while the gross concentration of refractory organics (COD = 12 mg/liter) is within an acceptable range for typical source waters of the United States, these compounds have also withstood the rigors of a combination of treatments."

#### Lebanon, Ohio

Various treatment units have been tested at Lebanon including electro dialysis and reverse osmosis. The early pilot work at Lebanon was with electro dialysis<sup>155</sup> and a plate and frame reverse osmosis unit<sup>156</sup>. Subsequently, several commercially available reverse osmosis modules were tested at the Lebanon pilot plant, including tubular and hollow fiber configurations. The tubular assembly used was manufactured by Aerojet-General Corporation, and the study results have been reported<sup>157</sup>.

The pilot plant had a nominal capacity of 4,000 gpd and consisted of three modules with 32 tubes in each module. The tubes were 0.56 inches ID and 14 feet long. Four different types of municipal wastewater were treated: (1) lime clarified raw wastewater, (2) secondary effluent, (3) primary effluent, and (4) primary effluent with turbulence promoters in the module.

Membrane rejection performance for both inorganic and organic constituents was consistently good for all waste streams tested. TDS

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removals averaged 93 percent; total organic rejection averaged 94 percent for COD and 92 percent for TOC. Total COD in the feed water ranged from 66 to 90 mg/l; COD in the reverse osmosis product water was:

- o lime clarified raw wastewater, 8.4 mg/l
- o secondary effluent, 2.4 mg/l
- o primary effluent, 2.7 mg/l

#### Ontario, Canada

A 15,000 gpd pilot plant was operated by the Ontario Research Foundation and the results of 30-day test runs were reported<sup>115,158</sup>. The purpose of the study was to optimize a system suitable for installation in a multi-story apartment building to treat domestic sewage to drinking water quality.

The following unit operations were investigated:

- o biological treatment by aeration
- o bioflocculation
- o sedimentation
- o chemical clarification
- o dual media filtration
- o carbon adsorption
- o reverse osmosis demineralization
- o ozone disinfection
- o breakpoint chlorination

Table III-41 summarizes the results of 30 days continuous operation of the treatment system shown in Figure III-28. The combined biological-chemical treatment reportedly produced very consistent removal of organics, suspended solids, phosphates, color, odor, and turbidity. The system exhibited high operation stability throughout the entire 30 days of operation. The filter effluent maintained steady, low contaminant concentrations regardless of the daily variations in the influent TOC, COD, BOD concentrations in raw domestic sewage.

The results show that concentrations of TOC in the reverse osmosis effluent and carbon column effluent were the same. Distilled water, reverse osmosis effluent and carbon column effluent gave the same TOC readings on both instruments used in the analyses (TOC-Beckman, COD-Aqua Test).

Ontario drinking water was found to have a TOC of 3.5 mg/l compared to the value of less than 0.1 mg/l for reverse osmosis and carbon column effluent.

#### OVERALL CAPABILITY OF TREATMENT PROCESS COMBINATIONS

Due to variations in plant influent municipal wastewater composition from city to city, it is impossible to present predictions of effluent quality for various unit process combinations which would be universally applicable. However, based on the preceding portions of this report, it is possible to make some general predictions of typical quality. Table III-42 summarizes two general approaches. There are, of course, a great many possible combinations of processes which can be envisioned, but this table

FIGURE III-28<sup>158</sup>

FLOW DIAGRAM  
ONTARIO, CANADA PILOT PLANT

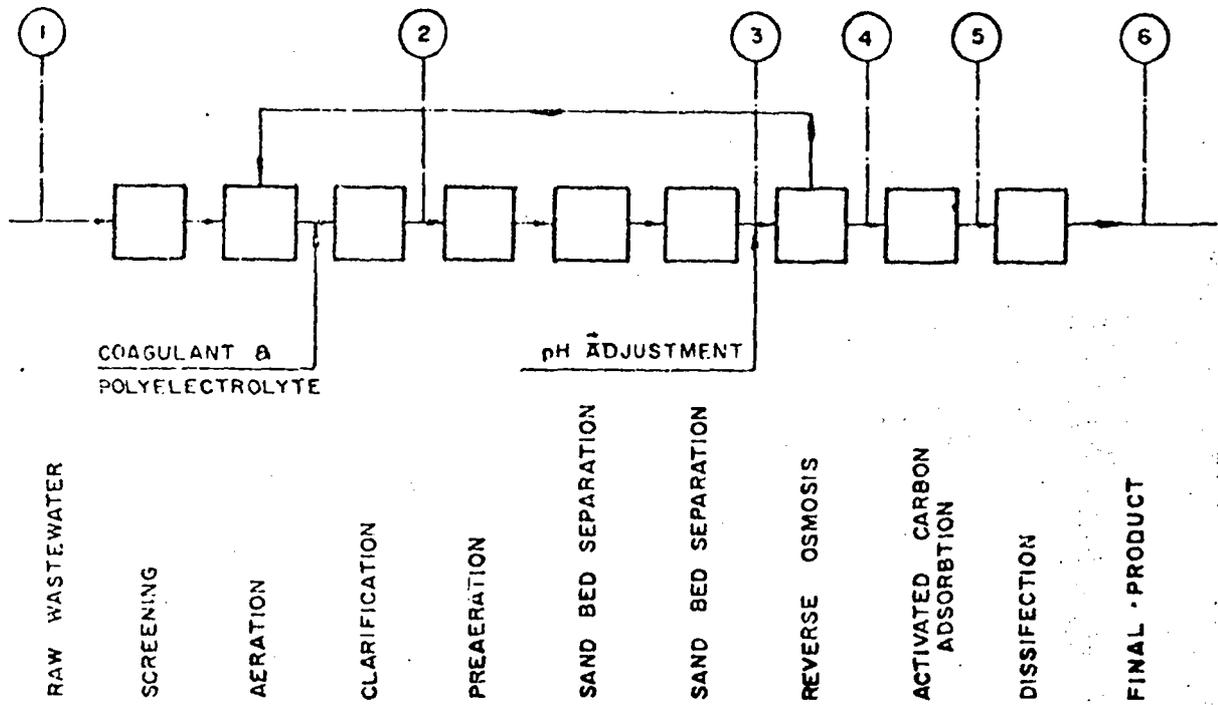


TABLE III-41<sup>158</sup>

TYPICAL WATER QUALITY  
ONTARIO, CANADA PILOT PLANT

| Quality Parameter                            | Raw Wastewater (1) | Secondary Effluent (2) | Separation Bed Effluent (3) | Rev. Osmosis Effluent (4) | Carbon Column Effluent (5) |
|--|--------------------|------------------------|-----------------------------|---------------------------|----------------------------|
| Total Organic Carbon (mg/l)                  | 110-165            | 14- 28                 | 4.5-7.5                     | <0.1                      | <0.1                       |
| Dissolved Org. Carbon (mg/l)                 | 34- 52             | 9- 17                  | 3.0-4.5                     | <0.1                      | <0.1                       |
| BOD (mg/l)                                   | 230-400            | 5- 14                  | App. 2.0-3.0                | <1.0                      | <1.0                       |
| PO <sub>4</sub> (as PO <sub>4</sub> ) (mg/l) | 9- 21              | 1.3-3.5                | 0.4-1.0                     | 0                         | 0                          |
| Total Nitrogen N (mg/l)                      | 27- 51             | 25- 37                 | 20- 35                      | App. 3.0-6.0              | App. 3.0-6.0               |
| Ammonia N (mg/l)                             | 17- 29             | 21- 29                 | 18- 29                      | 3.0-6.0                   | 3.0-6.0                    |
| NO <sub>2</sub> & NO <sub>3</sub> N (mg/l)   | 0                  | 0                      | 0                           | 0                         | 0                          |
| Suspended Solids (mg/l)                      | 148-268            | 13- 37                 | 3- 12                       | 0                         | 0                          |
| Dissolved Solids (mg/l)                      | 450-524            | 470-600                | 470-600                     | 20- 80                    | 20- 80                     |
| Turbidity Units (Jtu)                        | 74-110             | 5- 14                  | 1.5-4.0                     | 0.1-0.2                   | 0.1-0.2                    |
| Coliforms (MPN/100 ml)                       | App. 15,000,000    | App. 8,000,000         | App. 800,000                | App. 7,000                | App. 200                   |
| Disinfected (by ozone) (MPN/750 ml)          | —                  | —                      | —                           | —                         | Zero/750 ml                |

**TABLE III-42 - PROCESS CAPABILITIES**

**A. OVERALL PROCESS CAPABILITIES WITHOUT CHEMICAL COAGULATION**

|                           | <u>BOD</u><br>mg/l | <u>COD,</u><br>mg/l | <u>Turbidity</u><br>JTU | <u>PO<sub>4</sub>,</u><br>mg/l | <u>N,</u><br>mg/l | <u>TDS</u><br>mg/l | <u>Coliform</u><br><u>Bacteria</u><br>MPN/100 ml | <u>Approximate</u><br><u>Cost @ 10 mgd,</u><br><u>Cents/1,000 gals.*</u> |                |
|---------------------------|--------------------|---------------------|-------------------------|--------------------------------|-------------------|--------------------|--|--|----------------|
|                           |                    |                     |                         |                                |                   |                    |  | <u>Per Process</u>   | <u>Cumula.</u> |
| Secondary Effluent        | 20-40              | 30-80               | 10-40                   | 20-30                          | 15-30             | 400-600            | 1-3 x 10 <sup>6</sup>                            | 20   | 20             |
| Carbon Adsorption         | 3-6                | 10-12               | 1-2                     | 20-30                          | 18-28             | 400-600            | 1-3 x 10 <sup>6</sup>                            | 14   | 34             |
| Disinfection              | 3-6                | 10-12               | 1-2                     | 20-30                          | 18-28             | 450-650            | 2-100  | 1  | 35             |
| Demineralization<br>(R-0) | 1                  | 0.8-2               | 1                       | 0.4                            | 3-5               | 100                | 2  | 40   | 75             |

**B. OVERALL PROCESS CAPABILITIES WITH CHEMICAL COAGULATION**

|                                |       |         |       |       |       |         |                       |    |    |
|--------------------------------|-------|---------|-------|-------|-------|---------|-----------------------|----|----|
| Secondary Effluent             | 20-40 | 30-80   | 10-40 | 20-30 | 15-30 | 400-600 | 1-3 x 10 <sup>6</sup> | 20 | 20 |
| Chemical Coagulation<br>(lime) | 3-7   | 30-50   | 2-7   | 0.5-2 | 15-30 | 400-600 | 2000                  | 9  | 29 |
| Filtration                     | 1-2   | 25-45   | 0.1-1 | 0.1   | 15-30 | 400-600 | 50                    | 7  | 36 |
| Nitrogen Removal               | 1-2   | 25-45   | 0.1-1 | 0.1   | 1-3   | 400-600 | 50                    | 11 | 47 |
| Carbon Adsorption              | 0-1   | 3-10    | 0.1-1 | 0.1   | 1-3   | 400-600 | 50                    | 10 | 57 |
| Disinfection                   | 0     | 3-10    | 0.1   | 0.1   | 1-3   | 450-650 | 0                     | 1  | 58 |
| Demineralization<br>(R-0)      | 0     | 0.8-1.5 | 0.1   | 0.1   | 0.3-1 | 100     | 0                     | 40 | 98 |

\*Includes capital, operation, and maintenance costs. (EPA STP Construction Cost Index = 200)

illustrates the majority of those processes which are likely to be used in different approaches for groundwater recharge. The table also includes very general costs to illustrate the relative costs for each increment of quality improvement.

Table III-42-A presents a minimal system where secondary effluent is subjected directly to carbon adsorption. This system removes neither nitrogen nor phosphorus. As an optional step, demineralization could also be provided. Table III-42-B shows several other unit processes. Again, demineralization is shown as an optional step. As previously discussed, the overall flow sheet in Table III-42-B (without demineralization) should produce acceptable concentrations of heavy metals and viruses. Although not fully reflected by the data in the table, the effluent will have characteristics which are aesthetically pleasing - odorless, colorless, and very clear. Because of the higher turbidities associated with the approach in Table III-42-A, there is less assurance of complete virus removal prior to entry into the recharge system. Also, without the high pH coagulation, there will be lesser removals of heavy metals. However, as illustrated by the Hyperion pilot plant data, heavy metal standards in some cases may be met without reliance on high pH treatment. The values shown in Table III-42 and III-43 are based on the pilot and full-scale plant results discussed throughout the previous sections of this report. The reader should refer to the appropriate preceding section for added, detailed information. The greater reliability (see later section on reliability considerations) and level of treatment offered by the process in Table III-42-B is achieved at an incremental cost of 23 cents/1,000 gallons which is equivalent to a total

incremental cost of \$2.75/month/home (receipt of construction grants would reduce this increment to about \$1.40).

Figure III-29 and Table III-43 present an analysis made by Denver<sup>159</sup> for a combination of processes similar to that shown in Table III-42-B. The overall results are in good agreement with those projected in this report.

#### RELIABILITY CONSIDERATIONS

It is apparent that where domestic reuse through groundwater recharge is planned, that the reliability of the overall treatment and recharge system is very important. It is unfortunate but it is a fact that the operation of most municipal secondary wastewater plants in the past has not provided performance which reliably met design capabilities. The State of California has issued reports which deal with the reliability and suitability of wastewater reclamation systems<sup>160,161,162</sup>. Federal guidelines have also been published which deal with reliability considerations involved in wastewater treatment plant design<sup>163</sup>. Among the pertinent sections of the EPA guidelines are the following:

##### "Treatment Plant Reliability

- a. All water pollution control facilities should be planned and designed so as to provide for maximum reliability at all times.
- b. The facility should be capable of operating satisfactorily during power failures, flooding, peak loads,

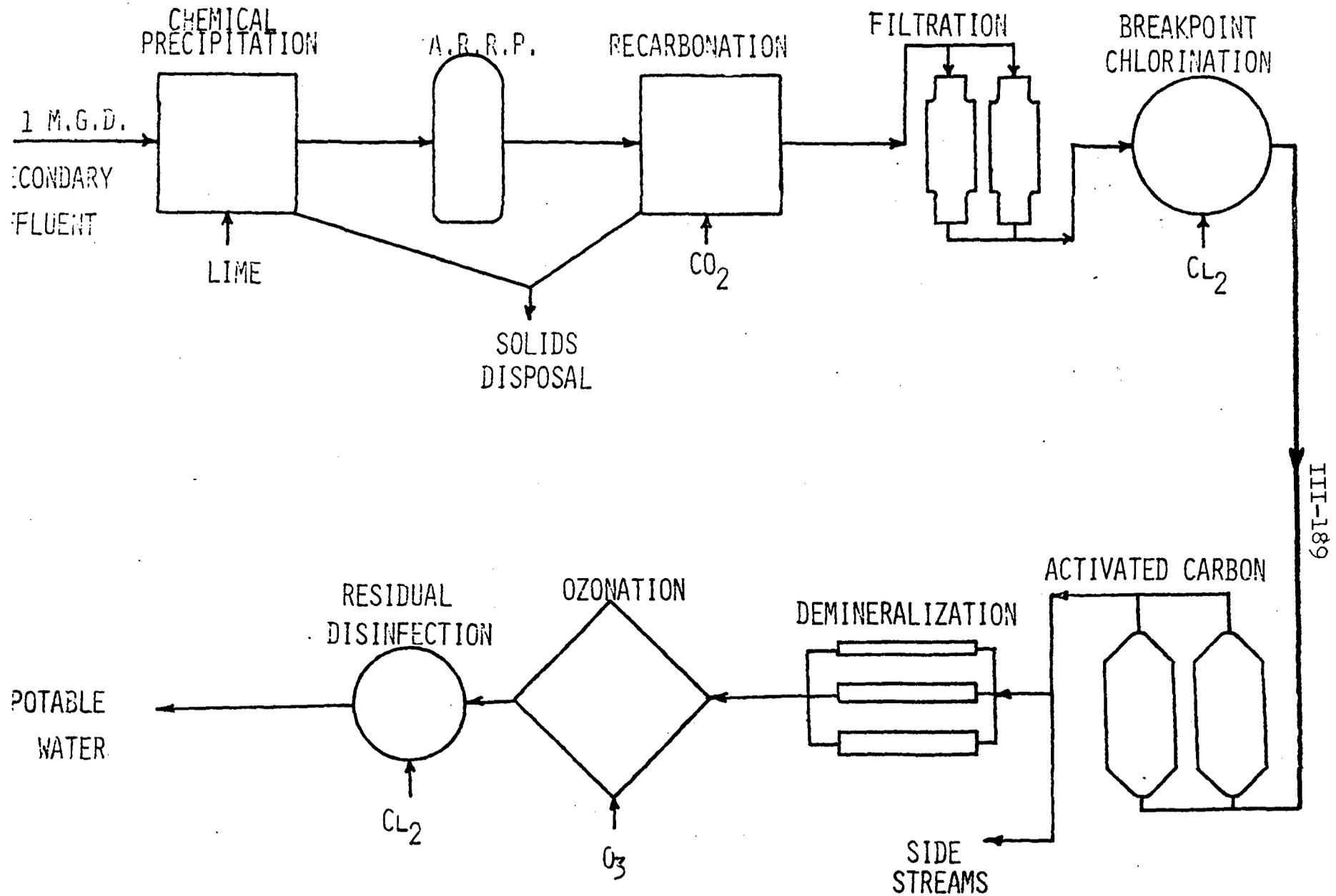


FIGURE III-29<sup>159</sup> A.W.T. PROCESS SCHEMATIC FOR DENVER WATER BOARD REUSE PROJECT

| PARAMETER        | CHEM. PRECIP. | A.R.R.P. | FILTR. | BRKPT. CL <sub>2</sub> | ACT. CARB. | DEMIN. | OZONE | RESID. CL <sub>2</sub> | EXPECTED PRODUCT QUALITY |
|------------------|---------------|----------|--------|------------------------|------------|--------|-------|------------------------|--------------------------|
| SUSPENDED SOLID. | 80            |          | 95     |                        | 50         | 99     |       |                        | 0.0                      |
| BACTERIA         | 90            | 10       | 90     | 100                    | 80         | 95     | 100   | 100                    | 0.0                      |
| VIRUS            | 90            | 10       | 50     | 100                    | 60         | 95     | 100   | 100                    | 0.0                      |
| PHOSPHATES       | 30            |          | 50     |                        | 50         | 80     |       |                        | < 0.05                   |
| AMMONIA          |               | 90       | 30     | 95                     | 30         | 80     |       |                        | < 0.1                    |
| TCC              | 70            | 10       | 10     | 80                     | 90         | 95     | 95    |                        | < 1                      |
| TDS              |               |          |        |                        |            | 90     |       |                        | < 50                     |
| HEAVY METALS     | 80            |          | 50     |                        | 50         | 90     |       |                        | < 0.01                   |

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TABLE III-43<sup>159</sup>

A.W.T. PROCESS EFFICIENCY AS PREDICTED BY DENVER WATER BOARD

equipment failure, and maintenance shutdowns. A minimum of primary treatment may be required where necessitated by the uses of the receiving waters.

- c. Such reliability can be obtained through the use of various design techniques which will result in a facility which is virtually 'failsafe'."

"Reliability

The treatment facility should be capable of satisfactory operation during emergencies, maintenance, shutdowns, and power failures. This type of reliability shall be achieved by consideration and appropriate inclusion of such design factors as:

- a. Duplicate sources of electric power.
- b. Stand-by power for essential plant elements.
- c. Multiple units and equipment.
- d. Holding tanks or basins to provide for emergency storage of overflow and adequate pump-back facilities.
- e. Flexibility of piping and pumping facilities to permit rerouting of flows under emergency conditions.
- f. Provision for emergency storage or disposal of sludge."

"Discharges to Shellfish, Potable, or Recreational Waters

"Discharges in close proximity to shellfishing beds, public water supply intakes, or contact recreation areas should be avoided. Where such discharges are unavoidable, special precautions must be taken. In addition to the items listed above, the following are recommended and may be required:

- a. Dual chlorination units.
- b. Automatic facilities to regulate and record chlorine residuals.
- c. Automatic alarm systems to give warning of high water, power failure, or equipment malfunction.
- d. Sand filters or polishing ponds following secondary treatment."

In summary, the Federal guidelines identify eight design provisions and four other significant factors which are related to reliability<sup>160</sup>:

Design Factors

Other Factors

Duplicate power sources  
 Stand-by power  
 Multiple units and equipment  
 Emergency storage  
 Piping and pumping flexibility

Engineering report  
 Qualified personnel  
 Effective monitoring program  
 Effective maintenance and process control program

Design Factors

Dual chlorination

Automatic residual control

Automatic alarms

The California criteria<sup>160</sup> contain explicit recommendations on these factors for reclamation systems; those which are related to recharge systems are summarized below:

Operation and Maintenance:

Full-time operator attendance

Required operator certification

Personnel training

Daily coliform analysis

Adequate operational records

Periodic (monthly or more frequently) reports to regulatory agency

Immediate notification of emergency conditions

Design:

Stand-by power source (gasoline generator or separate power system)

Emergency storage capacity of 20 days or longer

Alarms which effectively warn of treatment malfunctions

Automatically activated emergency control mechanisms

Stand-by treatment units to provide treatment when other units

are out of service

Multiple chemical feeders and reserve chemical supply  
Alarms for monitoring of and automatic controls for filters  
Rate-of-flow control on filters  
Continuous monitoring of filter effluent turbidity and filter  
head loss  
Stand-by chlorine cylinders  
Chlorine cylinder scales  
Manifold systems for chlorine cylinders  
Automatic chlorine cylinder changeover  
Stand-by chlorinators  
Multiple point chlorination  
Automatic control of chlorine dosage  
Automatic measuring and recording of chlorine residual

Reliability considerations were a major factor when the State of Virginia adopted a policy<sup>106</sup> concerning the design of wastewater treatment facilities which will discharge to a reservoir which serves as a raw drinking water supply for a downstream water treatment plant serving 500,000 people in the Washington, D. C. suburbs<sup>107,164</sup>. Major design factors specified in this policy are:

- o The initial backup capacity within the plant shall be 100 percent for the initial increments of the plant. If after the initial few years of operation, the plant's reliability has been satisfactorily demonstrated, additional treatment trains can be added up to a ratio of four treatment units to one stand-by train.

- o The design shall be such that expansions and maintenance of any unit can be accomplished without by-passing wastes or degrading treatment.
- o The mechanical and fluid system design shall be such that a single failure of a component or unit shall not interrupt plant operations which are required to meet the final effluent requirements (see Table III-44 for effluent standards).

There shall be two independent sources of outside power and one "on-site" power supply. Both the "off-site" and "on-site" electrical distributions shall be such that the failure of any given component (mechanical or electrical) in the distribution system shall not cause an interruption of electrical service to parts of the plant which are essential to meet the effluent requirements.

Specific design requirements for various elements of the plant include:

- o Retention basins to handle an unpredictable set of events which might temporarily overload the plant and to provide a margin of safety in event of operator error. The total required retention capacity can be provided at the treatment plant proper or on the interceptor system some distance away from the plant, depending on the availability of land. However, at least one-day capacity should be available at plant.

TABLE III-44

MINIMUM EFFLUENT QUALITY REQUIREMENTS\* FOR AWT PLANT ON THE OCCOQUAN RESERVOIR<sup>(106)</sup>

|   | BOD<br>Mg/L | COD<br>Mg/L | Suspended<br>Solids<br>Mg/L | Nitrogen<br>Mg/L | Phosphorus<br>Mg/L | MBAS<br>Mg/L | Turbidity<br>Jax Units | Coliform<br>Per 100 ML<br>Sample |
|---|-------------|-------------|-----------------------------|------------------|--------------------|--------------|------------------------|----------------------------------|
| Final Effluent<br>Requirements  | 1.0         | 10.0        | 0**                         | 1***             | 0.1                | 0.1          | 0.4                    | Less than<br>2                   |
| Typical Percent<br>Removals<br>(These are for<br>information only;<br>not requirements) | ~99.5%      | ~98.0%      | 100%                        | 97%              | ~99.5%             | ~99%         | ~100%                  | ~100%                            |

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\* As measured on a weekly average. Since these are minimum requirements, the normal average would be expected to be substantially better.

\*\* Unmeasurable.

\*\*\* When technology is available this requirement must be met with a reliable year-round nitrogen removal capability. Accordingly, in the detailed design of the initial plant, the designer should consider incorporating chemical means to achieve this lower limit, if EPA research work develops a proven, reliable all-weather unit. Until that time, the plant shall be designed such that its effluent contains not greater than 1 Mg/L of unoxidized nitrogen

- o Backup capacity of 100 percent for raw waste pumps.
- o Duplicate treatment facilities for primary and secondary treatment, flash mixing and flocculation, and chemical clarifiers, and chlorination. Adequate backup facilities for filtration and carbon columns.
- o A sampling basin to determine water quality before release. Effluent not meeting the required effluent quality is to be returned to the plant for reprocessing by the AWT processes.
- o Continuous operator attendance with at least five people per shift (initial plant capacity is 10.9 mgd).
- o Failure mode and effects analysis on mechanical and electrical systems.

As noted earlier, the South Tahoe plant (which does not provide the degree of design reliability required by the Occoquan policy) has an outstanding record of reliable operation. In the past 6-1/2 years, the quality of the effluent exported has never failed to meet the rigid effluent standards. Further discussion of the Tahoe experience as it affects plant reliability follows.

The success of any project will be in the hands of the operating staff. Although some experienced operators may be available, the number having experience with AWT processes will be very limited. An adequately financed and supervised on-the-job training program, carried out at the inception of

plant operations, is therefore essential. Experience in training operators for the South Tahoe AWT facility indicated that 33 two-hour sessions provided excellent results. Duplicate sessions were held, one from 7-9 a.m. and one from 4-6 p.m., to accommodate operators from all shifts. Operators were paid for time in class, a key point in indicating management's recognition of the importance of plant operation. The instructors, all of whom were also paid, were the district manager, consulting engineer staff members, construction contractors, and major equipment suppliers. The main text was a 200-plus page plant operations manual. Other course material included copies of the preliminary report, construction plans and specifications, shop drawings, all equipment descriptive material and instructions, and recent textbooks in the field. Laboratory training was achieved by assigning two to three operators to each instructor so each operator could actually perform all tests under close supervision. The results of this program were excellent.

One of the objectives at South Tahoe was to demonstrate that a wastewater plant could be operated as efficiently and as consistently as a power generation station or a water purification plant. Before the Tahoe plant was placed in service, many people were skeptical about the ability to keep a rather complex plant in continuous, uninterrupted operation and to produce consistently the high quality of water obtained in pilot plant tests of the process. The extensive, on-the-job training program was an important part of securing the desired goal. The Board of Directors, the district employees,

and the consulting engineer were all determined that the great effort and expenditures which had gone into conceiving, designing, financing, and constructing the plant would not be lost due to failure to properly operate or maintain the facilities. There is no doubt that this attitude and determination on the part of all parties directly involved with plant start-up and its day-to-day operation and maintenance were essential to the complete success of the project.

The South Tahoe plant has operated for the last six and one-half years continuously and without interruption, and the high quality standards set by the regulatory agencies for the finished water have been met continuously without exception. This has demonstrated the ability to operate AWT processes to their full potential. To do so does require adequate financing, the determination on the part of everyone involved in operation and maintenance, and the transfer of operating and technical knowledge from the plant designers to the operating personnel. At South Tahoe, the dedication of the operating and maintenance staff, the skills they have developed and demonstrated and the pride they have taken in setting a record of outstanding performance are a source of great satisfaction to all concerned with the project. This factor of dedication and motivation, which has been sadly absent in most municipal secondary plants, is the key to reliable plant operation.

Of course, reliability is also dependent upon a flexible plant design. Most of the mechanical design considerations required for plant reliability have been covered in the preceding paragraphs. A key process design consideration is providing several processes in series which can compensate for any malfunctions of the preceding processes. For example, a tertiary chemical clarifier offers the ability to remove any biological solids which escape the secondary process. This ability prevents the large solids carryovers which occur at times in most secondary plants from adversely affecting the downstream processes of filtration or adsorption. This design feature has been a key element in the reliable operation of the Tahoe plant. Thus, the process shown in Table III-42 offers a lower degree of reliability than that in Table III-43 because a solids carryover from the secondary process could cause the carbon column head loss to become so high as to cause a plant shutdown. Minor variations in soluble organic removal in the biological system may be compensated for by the operation of the carbon columns.

In summary, with proper design, operator training, staffing, and operational funding, AWT processes can be operated in a fail-safe, reliable manner.

#### NEED FOR ADDED RESEARCH

This report has described the AWT processes of proven reliability which are currently available to reduce pollutants to levels described in present drinking water standards. However, these standards were developed for relatively pure raw water supplies and not for applications of reuse involving

large quantities of wastewater. Thus, there are areas of uncertainty in which added research would be useful. Among these are:

- o Identification of the specific organics resistant to removal by AWT
- o Determination of the health significance of the trace organics remaining after AWT
- o A method of rapid detection of viruses

In terms of process research, it would be desirable to develop a lower cost nitrogen removal system than is currently available. Also, evaluation of techniques for removal of trace organics resistant to carbon adsorption is needed. Techniques for rapid screening and quantification of residual metals would also be useful.

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SECTION IV

REMOVAL OF BIOLOGICAL AND CHEMICAL CONTAMINANTS BY SOIL  
SYSTEMS IN ASSOCIATION WITH GROUND WATER RECHARGE BY SPREADING  
OR INJECTION OF TREATED MUNICIPAL WASTE WATER

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## INTRODUCTION

The application of treated waste waters to lands, either for disposal or for irrigation of crops, has been practiced in some parts of the world for centuries. However, deliberate surface spreading of treated waste waters for ground water recharge is relatively new. In all of these practices, the hope is that objectionable components in the treated waste waters will be removed by vegetation and/or soils and sediments before these waters mix with ground waters. Pathogenic organisms have been a potential hazard involved in the application of waste waters to land during the centuries that this practice has been used. More recently, as our industrial society has evolved, other health hazards have developed. Many types of organic compounds used as insecticides and herbicides or other biocides have been marketed. A large number of exotic chemicals and chemical mixtures have become part of our day-to-day life and are thus likely to get into municipal waste water systems. Heavy metals and trace elements are also of concern. Thus, even though the use of waste waters on lands is an old practice, some of the problems dealing with soils as removers of biological and chemical contaminants are relatively new. The combination of new problems with the relative new practice of deliberate ground water recharge with treated waste waters suggests a serious review of the capabilities of soils to provide waste water renovation.

### Objectives

The objectives of Section IV are 1) to compile information on the removal of selected biological and chemical contaminants by soil systems during ground water recharge by spreading and injection of treated municipal waste water, 2) to evaluate the magnitude and extent of problems posed by the presence of such undesirable materials in treated waste water to be used for ground water

recharge and how effective various soil systems are in removing them, and 3) to propose research needed to improve and to supply additional knowledge regarding soils and the soil mantle as waste water treatment systems during the process of ground water recharge.

### Scope

Although much experimental work has been done with regard to disposal of water to soils, major attention was directed toward getting the water into the ground and only very limited consideration has been given to the impact of such practice on the quality of existing supplies. Accordingly, this report presents a review of existing knowledge in this area and identifies areas of uncertainty or lack of knowledge.

This section was divided into two major parts -- the treatment afforded to waste water by soil systems during the recharge process; and the physical and hydrological aspects of ground water recharge. The first portion of the task was done under contract to the Department of Water Resources by Drs. Parker F. Pratt, Andrew C. Chang, James P. Martin and A. L. Page of the Department of Soil Science and Agricultural Engineering, University of California, Riverside. Dr. Pratt and his staff are all experts in the movement of conservative and nonconservative contaminants through the soil mantle. For this report, Dr. Pratt concerned himself with nitrogen, soluble salts, and general soil properties related to recharge. Dr. Chang's concern was pathogens; Dr. Martin reported on organics; and Dr. Page dealt with trace elements. The latter portion of the section was prepared by Charles F. Kleine of the Department of Water Resources.

The accomplishments reported herein are from a survey and review of the literature. In addition, a list of reports and technical papers which might be helpful was included.

TYPES AND CONCENTRATIONS OF BIOLOGICAL AND CHEMICAL CONTAMINANTS TO BE EXPECTED IN TREATED WASTE WATERS

Biological and chemical contaminants in treated waste water depend mainly on the source of water and the types of wastes added during passage through municipal waste water systems. Concentrations of the contaminants vary widely depending upon the sources of waste waters and the treatment processes used. Primary treatment removes less contaminants than secondary treatment. The various types of secondary treatment - trickling filters, activated sludge, or oxidation ponds - remove contaminants to different degrees. If advanced, or tertiary, treatment is provided, even greater amounts of contaminants are removed.

The concentrations of contaminants of the treated waste water used for ground water recharge will have a great effect on the ability of soil systems to act as treatment vehicles as the treated waste water passes through the soil mantle.

Biological Contaminants

Biological contaminants in waste water include bacteria, viruses, protozoa, and parasitic worms. Of these, only the pathogenic organisms are of concern to the health aspects of using treated waste waters to recharge ground water.

The following table gives an indication of biological contaminants in secondary waste water treatment plant effluents (before disinfection):

|                |                                  |
|----------------|----------------------------------|
| Coliforms      | $2.5 \times 10^6/100 \text{ ml}$ |
| Fecal coliform | $4.5 \times 10^5/100 \text{ ml}$ |
| Viruses        | 0-430 PFU/100 ml                 |

Chemical Contaminants

Waste waters contain both organic and inorganic contaminants in varying quantities. Normally the rapidly biodegradable organic compounds are of less concern in recharging ground waters than the more stable or slowly biodegradable organic compounds. Some of the soluble inorganic chemicals, including heavy metals, are reduced during secondary treatment by precipitation in, and adsorption on, sludges.

Organic Compounds - Organics are usually determined enmasse by their biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) content. Because stable organics are present in the effluent from secondary waste water treatment plants in very low concentrations, their determination in the microgram per liter range requires costly, highly-refined instrumentation and specially trained analysts. While some attempts are made to determine specific compounds (pesticides, for example), many times only organic groupings and fractions are determined.

The following table presents ranges of concentrations of organic compounds (both biodegradable and stable) in secondary effluents:

|             |             |
|-------------|-------------|
| BOD         | 10-80 mg/1  |
| Soluble BOD | 1-2 mg/1    |
| COD         | 30-200 mg/1 |
| Soluble COD | 25-50 mg/1  |
| TOC         | 10-25 mg/1  |

Inorganic Compounds - Inorganic ions in treated waste water include  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{=}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{=}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , phosphate and borate, some of which are nutrients; and the trace elements and heavy metal As, Ba, Bi, Cd, Cu, CN, Cr, F, Pb, Hg, Se, Ag, and Zn. However, unless the concentration of total minerals are excessive (greater than 1500 mg/1) and provided they are not predominately of one type such as Na or B, they are not of great concern in soil

systems. The removal of nitrogen ions and compounds and some of the trace elements and heavy metals by soil systems are of some concern.

Trace Elements and Heavy Metals - Trace element concentrations in secondary effluents vary considerably. Although there are many reports in the literature which give concentrations of trace elements in secondary effluents, most are for isolated instances and not sufficiently detailed and comprehensive to allow generalizations. Data derived for secondary effluents from 23 waste water treatment plants in Michigan, and from 7 treatment plants in Southern California, are presented in Table 1. The data show that median concentrations of those trace elements monitored meet existing standards for public drinking water supplies (Table 2) and for requirements for reclaimed waters to be used for ground water recharge established by the California Regional Water Quality Control Board, Los Angeles Region (Table 3). The data available show that in terms of trace element concentrations, many, but certainly not all, secondary effluents are suitable for use in ground water recharge operations.

Almost without exception, trace element concentrations decrease in relation to the extent to which waste waters are treated. To illustrate the extent to which trace element concentrations of waste water decrease in relation to treatment, the data in Table 4 show that secondary treatment has reduced concentrations of the trace elements monitored from 63 to 80%. Also suspended particles are reduced by 94%, demonstrating that high concentrations of trace elements in the primary effluents occur in association with suspended particles. The data also point out that the efficiency of the secondary treatment process, particularly as it affects the concentration of suspended particulates, will influence concentrations of trace elements in the secondary effluent.

TABLE 1  
TRACE ELEMENT CONCENTRATIONS IN SECONDARY WASTE  
WATER TREATMENT PLANT EFFLUENTS

| Element   | Range<br>-----mg/l----- | Median<br>----- | No. with conc'ns.<br>which exceed<br>standards |
|---|-------------------------|-----------------|--|
| From 23 treatment plants in Michigan <sup>(1)</sup> :           |                         |                 |  |
| As  | <0.005 - 0.023          | <0.005          | 0  |
| Cd  | <0.01 - 0.15            | <0.01           | 1  |
| Cu  | 0.01 - 1.3              | 0.04            | 1  |
| Cr  | <0.01 - 1.2             | 0.03            | 7  |
| Pb  | <0.02 - 1.3             | 0.04            | 12   |
| Hg  | <0.0002- 0.001          | 0.0002          | 0  |
| Zn  | 0.03 - 1.2              | 0.19            | 0  |
| From 7 treatment plants in Southern California <sup>(2)</sup> : |                         |                 |  |
| Ba  | <0.05 - 0.13            | <0.05           | 0  |
| Cd  | <0.01 - 0.022           | 0.01            | 1  |
| Cu  | <0.01 - 0.05            | 0.02            | 0  |
| Cr  | <0.001 - 0.10           | 0.007           | 1  |
| Pb  | 0.-03 - 0.35            | 0.02            | 1  |
| Zn  | 0.004 - 0.35            | 0.05            | 0  |

\*/ Number of samples with concentrations which exceed those recommended for public drinking water supplies. (5)

TABLE 2

RECOMMENDED UPPER LIMITS FOR CONCENTRATIONS OF TRACE  
ELEMENTS IN PUBLIC DRINKING WATER SUPPLIES

| Element          | U.S.<br>PHS (3) | Calif.<br>Dept<br>P.H. (4) | National<br>Academy<br>Sci. (5) |
|------------------|-----------------|----------------------------|---------------------------------|
|                  | -----mg/l-----  |                            |                                 |
| As               | 0.05            | 0.1                        | 0.1                             |
| Ba               | 1.0             | 1.0                        | 1.0                             |
| Cd               | 0.01            | 0.01                       | 0.01                            |
| Cu               | 1.0             | -                          | 1.0                             |
| CN               | 0.2             | 0.2                        | 0.2                             |
| Cr <sup>+6</sup> | 0.05            | -                          | -                               |
| Cr (Total)       | -               | 0.05                       | 0.05                            |
| F <sup>*/</sup>  | -               | 0.8 - 1.7                  | 1.4 - 2.4                       |
| Pb               | 0.05            | 0.05                       | 0.05                            |
| Hg               | -               | 0.005                      | 0.002                           |
| Se               | 0.01            | 0.01                       | 0.01                            |
| Ag               | 0.05            | -                          | -                               |
| Zn               | 5.0             | -                          | 5                               |

\*/ Recommended concentrations depend upon maximum air temperature. As air temperatures increase from 50°F to 80°F the upper limits for concentration decrease.

TABLE 3<sup>(6)</sup>

CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD, LOS ANGELES REGION  
 REQUIREMENTS FOR RECLAIMED WATER USED FOR GROUND WATER RECHARGE

| Element          | Pomona         |          | Whittier Narrows |          | San Jose |          |
|------------------|----------------|----------|------------------|----------|----------|----------|
|                  | Current        | Proposed | Current          | Proposed | Current  | Proposed |
|                  | -----mg/l----- |          |                  |          |          |          |
| As               | -              | 0.1      | 0.05             | 0.1      | 0.1      | 0.1      |
| Cd               | 0.01           | 0.01     | -                | 0.01     | 0.01     | 0.01     |
| Cu               | -              | 1.0      | 3.0              | 1.0      | -        | 1.0      |
| CN               | 0.2            | 0.2      | -                | 0.2      | 0.2      | 0.2      |
| Cr <sup>+6</sup> | 0.05           | 0.05     | 0.05             | 0.05     | 0.05     | 0.05     |
| Pb               | 0.05           | 0.05     | 0.10             | 0.05     | 0.05     | 0.05     |
| Hg               | -              | 0.005    | -                | 0.005    | -        | 0.005    |
| Se               | 0.01           | 0.01     | 0.05             | 0.01     | 0.01     | 0.01     |
| Ag               | 0.05           | -        | -                | -        | 0.05     | -        |
| Zn               | -              | 5        | 15               | 5        | -        | 5        |

TABLE 4<sup>(7)</sup>COMPARISON OF TRACE ELEMENT CONCENTRATIONS OF PRIMARY AND SECONDARY  
WASTE WATER TREATMENT PLANT EFFLUENTS

| Element                   | Primary<br>effluent | Secondary<br>effluent | Reduction |
|---------------------------|---------------------|-----------------------|-----------|
|                           | -----mg/l-----      |                       | %         |
| Cd                        | 0.028               | 0.010                 | 64        |
| Cr                        | 0.30                | 0.06                  | 80        |
| Cu                        | 0.13                | 0.04                  | 69        |
| Hg                        | 0.0005              | 0.00012               | 76        |
| Pb                        | 0.11                | 0.041                 | 63        |
| Zn                        | 0.43                | 0.10                  | 75        |
| <hr/>                     |                     |                       |           |
| Suspended<br>particulates | 0.118               | 0.007                 | 94        |

Data reproduced from the Annual Report on Results of Water Quality Monitoring, Water Year 1972-73<sup>(6)</sup> for reclaimed waters from the Whittier Narrows, San Jose Creek, and Pomona treatment plants are presented in Table 5. These data are for 24-hour composite samples collected monthly during 1972-73. The data show that during some months of the year concentrations of As, Cd, Cr, and Pb exceed those of drinking water standards (Table 2) and of the regional board's requirements for reclaimed water used for ground water recharge (Table 3). Also included in Table 5 for reference are trace element concentrations of imported waters from the Colorado River and the State Water Project. Concentrations of trace elements in the reclaimed waters frequently exceed those in the imported waters.

It is worthy to point out at this juncture that the California Regional Water Quality Control Board, Los Angeles Region Requirements for trace elements for reclaimed waters to be used for ground water recharge<sup>(6)</sup> correspond quite closely to recommended upper limits for concentrations of trace elements in public drinking water supplies<sup>(3)</sup>. Thus, if the requirements presented in Table 3 are strictly adhered to, even direct injection of these waters should not in most instances produce concentrations of trace elements which exceed the upper limits for public drinking waters.

Nitrogen - Nitrogen may be present in treated waste water as any or all of the following forms: nitrates, nitrites, ammonia or ammonium ion, and organic nitrogen. The constituent and magnitude may vary over a wide range as indicated by the following range found in activated sludge process effluents:

|                                |           |
|--------------------------------|-----------|
| Nitrates ( $\text{NO}_3^-$ -N) | 0-40 mg/1 |
| Nitrites ( $\text{NO}_2^-$ -N) | 0-3 mg/1  |
| Ammonia ( $\text{NH}_3$ -N)    | 5-40 mg/1 |
| Organic N                      | 2-15 mg/1 |

TABLE 5<sup>(6)</sup>COMPARISON OF TRACE ELEMENT CONCENTRATIONS OF  
IMPORTED WATER WITH RECLAIMED WATER

| Element       | Quality of Imported Water <sup>1/</sup> |               | Quality of Reclaimed Water <sup>2/</sup> |       |                |        |                |        |
|---------------|---|---------------|--|-------|----------------|--------|----------------|--------|
|               | Colorado River                          | State Project | Whittier Narrow                          |       | San Jose Creek |        | Pomona         |        |
|               | -----mg/l-----                          |               |  |       |                |        |                |        |
| As            | <0.01                                   | <0.01         | <0.01                                    | -0.03 | <0.01          | -0.02  | <0.01          | -0.03  |
| Cd            | <0.01                                   | <0.01         | <0.01                                    | -0.02 | <0.01          |        | <0.01          |        |
| Cu            | 0.01                                    | 0.01          | 0.06                                     | -0.24 | 0.01           | -0.04  | 0.03           | -0.17  |
| CN            | <0.006                                  | <0.006        | 0.02                                     | -0.16 | 0.02           | -0.06  | 0.01           | -0.07  |
| Cr<br>(Total) | <0.003                                  | <0.005        | 0.02                                     | -0.14 | 0.01           | -0.06  | 0.03           | -0.11  |
| Pb            | <0.01                                   | <0.01         | <0.01                                    | -0.08 | <0.01          | -0.06  | <0.01          | -0.04  |
| Hg            | <0.0001                                 | 0.0001        | <0.0001-0.0002                           |       | <0.0001-0.0002 |        | <0.0001-0.0006 |        |
| Se            | <0.01                                   | <0.01         | <0.01                                    | -0.01 | <0.01          |        | <0.01          |        |
| Ag            | <0.0004                                 | <0.0003       | <0.001                                   | -0.03 | <0.001         | -0.008 | <0.001         | -0.008 |
| Zn            | 0.02                                    | 0.03          | 0.16                                     | -0.38 | 0.07           | -0.11  | 0.05           | -0.12  |

<sup>1/</sup> One sample.<sup>2/</sup> Range of composite of monthly samples.

REMOVAL OF CONTAMINANTS BY SOIL SYSTEMS

Soil systems have the capacity to remove biological and chemical contaminants in treated waste water. The removal processes involved include filtration, adsorption, decomposition, ion-exchange, oxidation-reduction, chemical complex formation, chemical precipitation, and other chemical reactions.

General Soil Properties Related to Recharge

An ideal soil for ground water recharge by land spreading and infiltration would 1) have rapid rates of infiltration and transmission of water, 2) be underlain by sediments or soil materials that have no clay layers or other layers that restrict the movement of water to the desired aquifer, 3) have no expanding-contracting clays that create cracks when dried that would allow the reclaimed water to bypass the soil during the initial stages of a flooding period, 4) have sufficient clay contents to provide large capacities to adsorb trace elements and heavy metals and to provide surfaces on which microorganisms decompose organic constituents, and 5) have a supply of available C that would favor rapid denitrification during flooding periods, support an active microbial population to compete with pathogens, and favor rapid decomposition of introduced organics. In other words an ideal system would have rapid rates of infiltration and transmission of water and at the same time provide soil surfaces and contact time for chemical and microbiological reactions. Obviously, the ideal system does not exist because these two features of the system are mutually exclusive.

Rates of infiltration and transmission are dependent on pore size distribution in soils. Those soils with largest fractions of larger pores have the highest rates and those with the lowest fractions of large pores have the lowest rates. Generally, the pore size distribution is a function of texture,

i.e., percentages of sand, silt, and clay with the percent of large pores decreasing with increase in contents of silt plus clay. But, this correlation of pore size with texture is not highly useful because the arrangement of soil particles into aggregates and the stability of these aggregates also have effects on pore size distribution. That is, some clay soils have high rates of water transmission if they are highly aggregated, whereas some sandy loams have lower rates because of an absence of aggregates. However, irrespective of clay contents, soils with high infiltration and transmission rates in which the water passes mainly through large pores will provide a minimum of contact of contaminants with soil surfaces and a minimum of time for chemical and biological reactions and a minimum of treatment per distance of flow. Thus, some compromise might be needed between rates of application and degree of treatment. For example, in the Flushing Meadows project on the Salt River near Phoenix, Arizona the amount of N removed was a function of the application rate which defined the rate with which water was passed through the soil.

Sandy gravelly soils of stream beds such as found in recharge areas used for the Flushing Meadows project and the Montebello Forebay recharge operations have small clay contents, large fractions of larger pore spaces, and small contents of organic matter. Consequently large volumes of water can be recharged per unit area of flooded land, but treatment is minimal. For example, the adsorption of trace elements would be enhanced by using a soil with more clay and organic matter and a lower intake rate.

High infiltration rates used for ground water recharge have advantages of small effects of evaporation on the total dissolved solids content (TDS) of the infiltrated water and a small area devoted to the operation per unit volume of water used for recharge. Such recharge areas can be located in stream channels where flow to the desired aquifer is usually unobstructed and

where the natural flow of the stream can be used to dilute reclaimed waters. The mixing of these waters is perhaps most likely to take place in this stream channel situation. The main disadvantages of high infiltration rates is that dilution may be required to compensate for lack of treatment that could be obtained by a soil with lower intake rates.

While irrigation of cropland provides a maximum of treatment for trace elements and heavy metals, pathogens, and decomposition of organic materials, it is entirely unsuitable for recharging a ground water basin because of the large amount of water used during evapotranspiration with the resultant increase in soluble salts. Also, a productive agriculture does not necessarily produce an effluent that has sufficiently low concentrations of  $\text{NO}_3^-$ .

Some compromise between the two extreme situations, i.e., high infiltration rates with minimum treatment versus irrigation of croplands with its advantages and disadvantages, might be desirable. The preparation of a soil mix that might be incorporated into sandy gravelly river bed materials to reduce infiltration and transmission rates and provide better tertiary treatment of secondary effluents might be a desirable alternative to dilution with large volumes of high quality water. Another possibility is to install a soil treatment system from which the water could be recovered and put into high-rate infiltration spreading basins for recharge. Such a system could be operated so as to achieve maximum efficiency during the total N removal process by relying on the aerated soil of the spreading basins to remove organics remaining from the anaerobic N removal cycle. However, a soil treatment system that would precede land spreading would add costs to the recharge operation.

### Biological Contaminants

A major consideration of the fitness for reuse of reclaimed domestic waste water is the potential public has and that might be encountered. Pathogenic organisms of concern that may exist in waste water can be divided into four groups<sup>(8)</sup>. They are:

1. the viruses,
2. the bacteria,
3. the protozoa, and
4. the parasitic worms.

The life cycle and the infection route of each species of disease causing organisms are quite different. When waste water reclamation by ground water recharge is considered, the survival of pathogens in natural environments and in waste water treatment processes, and the movement of the pathogens in soils are important to the acceptance of renovated waste water for domestic consumption. While detailed examination of bacterial quality in reclaimed water is lacking and the migration of pathogens in hydraulically heavily loaded recharging areas is not fully understood, attempts are made here, through scanning of pertinent literature, to arrive at the rationale as to how existing ground water can be safeguarded from contamination during artificial recharge using reclaimed waste water.

Survival of Pathogens in Soils - Since soil is a natural habitat for microorganisms, the existence of potentially pathogenic organisms in soil is expected and well documented. For example, more than 20 pathogenic fungi have been isolated from soils<sup>(9)</sup>. Most, if not all, of these forms exist as common saprophytic fungi in soils or on plants and other organic debris and only occasionally do they infect humans. Organisms causing tetanus (Clostridium Tetani) and botulism (Clostridium botulinum) are common in soils. They do not infect healthy tissue but produce toxic proteins in human or animal wounds or in contaminated foods. These organisms are not likely to cause waterborne disease

outbreaks and are usually of little concern with respect to waste water disposal practices. A susceptible individual is more apt to become infected through direct contact with soil or by eating contaminated food than by drinking water.

The majority of pathogens prefer warm-blooded animals as their habitat and do not flourish in the soil environment. When introduced into soils, they do not compete well with the vast number and variety of normal soil inhabitants and are subject to attack by antagonistic soil species. The time involved for their ultimate destruction varies greatly with different species and environmental conditions. A compilation of pathogen survival data in the literature which was summarized by Burge <sup>(8)</sup> and Clark <sup>(10)</sup> is shown in Table 6. The most persistent pathogens in soils are probably ova, cysts, and spore-forming bacteria. Enteric viruses survival in soils has not been thoroughly studied. Due to their parasitic nature, viruses would not multiply and would not be expected to survive for a long period of time once they are outside of their host. However, they all may survive in soils long enough to cause public health concerns.

Survival of Pathogens in Waters - The same ecological factors which cause destruction of pathogens in soils are also active in reducing the numbers of pathogens in water. Unlike pathogens introduced into soils where their mobility is restricted, they can be carried by and dispersed in the water freely. Their impact on the health of the general public is far greater in water than in contaminated soils. Outbreaks of a waterborne disease usually involve many cases in a community.

The fecal discharge of man and domestic sewage are the major sources of pathogens that are carried in the water. The occurrence and density of pathogens in water contaminated by fecal matter are highly variable, reflecting

TABLE 6<sup>(8,10)</sup>

## SURVIVAL OF PATHOGENS IN SOILS

| Organism                           | Survival time  |
|------------------------------------|----------------|
| <u>Ascaris lumbricoides</u> ova    | 2.5 - 7 years  |
| <u>Endamoeba histolytica</u> cysts | 8 days         |
| Salmonella species                 | 6 hrs.-77 days |
| Coliform group organisms           | 133 - 147 days |
| Q-fever organisms                  | 148 days       |
| <u>Brucella abortus</u>            | 30 - 100 days  |
| Tuberculosis bacteria              | 6 months       |
| Enteroviruses                      | 12 days        |

prevalent diseases of the time and locale, the degree of waste water treatment, and dilution with the receiving water. Even though considerable amount of literature has been accumulated on the isolation of pathogenic organisms from water and waste water, there is very little quantitative data due to the rather cumbersome, time-consuming, and sometimes insensitive laboratory procedures involved. A more logical approach to the procedure of isolating pathogenic organisms is one which uses indicator microorganisms for routine monitoring but this also suffers the lack of quantitative correlation. The detection frequency of Salmonella in surface water sharply increased when fecal coliform densities exceed 200 MPN (most probably number) per 100 ml. In the ranges of over 2000 MPN of fecal coliform/100ml, Salmonella isolation occurred with almost 100% frequency<sup>(11)</sup>. While all domestic waste water is expected to contain indicator organisms (coliform group), viruses were detected in less than 25% of the waste water samples examined in the U.S., indicating a much lower density and less frequent occurrence of viruses in waste water<sup>(12)</sup>. The occurrence of viruses in waste water tends to be seasonal. Their isolation from waste water peaks in summer and fall with the exception of poliovirus whose occurrence is directly related to the oral administration of poliomyelitis vaccine. Studies have indicated virus survival in clean and grossly contaminated water appeared longer than in moderately polluted water. At 20°C, Coxsackie A2 virus survived for 41 days in sewage and only 6 days in the moderately polluted water of the Ohio River. Experimental results of researchers at the Robert A. Taft Sanitary Engineering Research Center, Cincinnati, Ohio<sup>(12)</sup> on the survival of viruses in water are summarized in Table 7. In general, viruses, with the exception of Coxsackie, would survive longer than microorganisms commonly used as water quality indicators.

TABLE 7<sup>(12)</sup>

AVERAGE TIME IN DAYS FOR 99.9% REDUCTION OF ORIGINAL  
TITER OF INDICATED MICROORGANISMS IN WATERS

| Microorganism       | Little Miami<br>River* (Ohio) |      |     | Ohio River*<br>(Ohio) |      |     | Sewage*<br>(Cincinnati) |      |     |
|---------------------|-------------------------------|------|-----|-----------------------|------|-----|-------------------------|------|-----|
|                     | 28°C                          | 20°C | 4°C | 28°C                  | 20°C | 4°C | 28°C                    | 20°C | 4°C |
| Poliovirus I        | 17                            | 20   | 27  | 11                    | 13   | 19  | 17                      | 23   | 110 |
| Echo 7              | 12                            | 16   | 26  | 5                     | 7    | 15  | 28                      | 41   | 130 |
| Echo 12             | 5                             | 12   | 33  | 3                     | 5    | 19  | 20                      | 32   | 60  |
| Coxsackie A9        | 8                             | 8    | 10  | 5                     | 8    | 20  | 6                       | 7    | 12  |
| <u>A. aerogenes</u> | 6                             | 8    | 15  | 15                    | 18   | 44  | 10                      | 21   | 56  |
| <u>E. coli</u>      | 6                             | 7    | 10  | 5                     | 5    | 11  | 12                      | 20   | 48  |
| <u>S. fecalis</u>   | 6                             | 8    | 17  | 18                    | 18   | 57  | 14                      | 26   | 48  |

\* Average coliform density

Little Miami River                      54/ml

Ohio River                                      197/ml

Sewage    20,800/ml

Movement of Biologic Contaminants During Ground Water Recharge - Bacteria and pathogenic microorganisms are found in abundance in waste water. In properly treated waste water, they are not expected to occur in high densities in the final effluent. If reclaimed water is to be used for recharging groundwater, the bacteria and pathogens remaining in the effluent will again be subject to adverse environmental conditions in soils. During recharging, a rather high hydraulic loading will move water through soil at a rapid rate. Therefore, the movement of bacteria and pathogens in soils is governed not only by natural destruction processes but also by soil and hydraulic parameters.

As particulate matter suspended in water, bacteria and pathogens do not move through a porous media as fast as water. Particles of larger sizes, such as ova and cysts, are expected to be retained on the ground surface by filtering. Bacteria and viruses are small enough to move through the pores of soils with the percolating water but due to adsorption phenomenon, they move at a slower pace compared to water. McGauhey, et al.<sup>(13)</sup>, summarized published literature on the traveling distance of coliform bacteria and pathogens in soils. Once they were introduced into soils, their movement varied from several hundred feet in less than a day to a rather short distance over a long period of time, depending on the texture of the soil. Case histories of bacterial contamination of ground water tended to suggest that channeling through cracks in soils and faulty construction of wells rather than seepage through the soil was the major cause.

Although waste water effluent has been returned to land for centuries, the recharging of ground water was more or less incidental. Study of carefully planned ground water recharging using treated waste water effluent began in the early 1950's. California has been a forerunner of the recharging experimentation. Early studies using spreading basin infiltration methods indicated that coliform

bacteria in unchlorinated secondary effluent can be reduced to meet Public Health Drinking Water Standards after passing a rather short distance through soils. During 2-1/2 years of continuous observation of waste water reclamation by land spreading in Lodi, California, it was found that MPN of coliform group organisms which, in secondary effluent, average  $1.8 \times 10^5/100$  ml was consistently reduced to less than one per 100 ml in 4-5 ft. of soil<sup>(14)</sup>. The average percolation rate was 0.58 ft. per day in rather coarse-textured Hanford sandy loam. In Los Angeles County, where studies were initiated in Whittier and Azusa, a depth of 3-7 ft. was required to achieve a similar result<sup>(15)</sup>. Occasional high coliform counts could all be traced to short-circuiting in non-uniform soils. When primary effluent with a much higher MPN coliform number was applied, the removal was less efficient, and greater depth of soil and lower water application rates were necessary to produce water of acceptable quality. Observations of bacteria removal in a silica (Ottawa sand) packed column produced similar results as in the soil. Thus, the retention of bacteria in soil could be explained by their filtering action. The formation of an organic-microbial slime layer at the water-soil interface increases the efficiency of the filtering action.

More recent studies of considerably larger scale waste water reclamation projects also substantiated findings of early investigation. Secondary effluents which surfaced after passing through 500 ft. of sand and alluvial fill were not found free of fecal coliforms. Bacteriological quality of the water, however, met public health standards for body contact recreation activities<sup>(16)</sup>. The Flushing Meadows project has been recharging ground water with rapid infiltration basins since 1967<sup>(17)</sup>. Data generated so far is favorable in terms of bacterial quality of renovated water and long-range operation problems. Bacteriological quality of secondary effluent at a magnitude of

$10^6/100$  ml (measured by membrane filter technique) was gradually reduced in a soil profile with 12 inches of sandy loam overlaid by sand and gravel. Most of the fecal coliforms were removed in the first two feet of the soil. However, fecal coliform densities from 10-100/100 ml (determined by membrane filter technique) have always been detected in monitoring wells located between recharge basins. The peak bacteria density always coincides with the arrival of each newly applied waste water on the dried spreading basins. Similar results were found by the Los Angeles County Flood Control District at Whittier Narrows recharging site<sup>(18)</sup>. Based on the experience and results of these full-scale, long-term waste water reclamation studies, it is fair to conclude that a small fraction of the fecal coliform bacteria may reach ground water reservoirs at high percolation rates. Their horizontal travel in the aquifer has not been found significant. Nearby wells drawing water from the same aquifers have no apparent incidence that may be linked to recharging<sup>(18)</sup>. However, the public health consequences of fecal coliforms in ground water requires further investigation.

Viruses are colloidal-sized particles usually small enough to pass through soil pores without resistance. Nevertheless, laboratory studies have indicated that soils, in general, are effective in immobilizing viruses<sup>(19,20)</sup>. The relationship of soil characteristics and virus removal was not established. In general, soil with reasonable amounts of silt and clay removed virus in less than 2 ft of soil. One Hawaiian soil found ineffective for virus removal was coarse-textured cinder ash. A water application rate as high as 10 inches/wk. made no apparent difference in their removal. The densities of the added virus in the water used in these laboratory studies were higher than would normally be expected in the secondary effluent.

Unlike bacteria, the outer layer of viruses is proteins which have a typical amphoteric behavior, Therefore, their removal from water percolating through soil is an adsorption phenomenon rather than a filtering action. Observations in controlled laboratory studies indicated their adsorption by clay particles can be represented by adsorption isotherms. Many factors are expected to influence the effectiveness of soil in removing virus:

1. pH - When the pH in soil solution is increased, a decreasing ionization of amino groups and increasing ionization of carboxyl groups of virus particles are expected. In this case, negatively charged virus particles and also negatively charged soil particles tend to repel each other resulting in decrease of total adsorption. At pH 7 or less, the adsorption of virus by soil was almost complete.

2. Ionic Strength - At the pH normally encountered in waste water, viruses are slightly negatively charged. Cations present in soil solution have a profound effect on neutralizing or reducing the repulsive potential of soil and virus particles. This leads to the formation of a soil-cation-virus bridge whereupon the virus is immobilized<sup>(21)</sup>.

At the same ionic strength, a divalent cation ( $\text{Ca}^{++}$ ) in solution is more effective than that of a monovalent ( $\text{Na}^+$ ) in solution in removing viruses from suspension. Aluminum ions ( $\text{Al}^{+++}$ ) are even more efficient. When waste water is used for recharging, there is sufficient hardness ( $\text{Ca}^{++} + \text{Mg}^{++}$ ) that ionic strength in percolating water should not limit the virus adsorption of soils. Other proteinaceous material in waste water may also compete with virus for potential adsorption sites, When the ionic strength of percolating water is significantly decreased, desorption of adsorbed virus may take place. In laboratory studies, when virus-adsorbed clay particles were washed with distilled water, essentially a complete desorption and reactivation took place<sup>(21)</sup>.

In field conditions, other mechanisms in soil systems may inactivate or destroy adsorbed viruses before they are subject to desorption.

Besides these two major factors, the clay content and organic matter in soil also demonstrated certain degrees of influence on adsorption. In general, soils of higher clay and/or organic matter are more effective. The only systematic field study of virus movement in the soil was conducted by Santee County Water District in 1963-64<sup>(16)</sup>. Water surfaced after 400 ft. of underground traveling was found consistently free of viruses. Grab samples from a monitoring well in the Whittier Narrows recharging area have not had any virus during the past three years<sup>(18)</sup>.

Removal During Ground Water Recharge by Direct Injection - When waste water is directly injected into the aquifer, large quantities of organic impurities and microorganisms are introduced into the ground water reservoir. Under a high hydraulic gradient, injected water is dispersed rapidly in the aquifer. Few results are available which analyze its impact on ground water quality conclusively. A few small-scale investigations resulted in some generalized speculations<sup>(22)</sup>. It is generally believed that organic suspended solids and bacteria trapped in soil pores form a biological sphere around the perforated zone. Coliform group organisms were detectable in surrounding monitoring wells 100 ft. from the injection point. Organic matter trapped in this zone is sufficient to support the continuing growth of microorganisms. However, it is not known at this time how rapid this microbial active zone would expand under continuous injection. Unless there is sufficient long-term data to substantiate the present findings, such a practice to increase water for domestic water consumption is not justified.

Chemical Contaminants

Chemical contaminants in treated waste waters amenable to removal by soil systems during recharge of ground waters include organic substances, nitrogen, soluble salts and trace elements and heavy metals.

The removal of chemical contaminants is more dependent upon the type and properties of the soils in the surface mantle than in the case for the removal of biologic contaminants. Adsorption and chemical reactions - complexing, oxidation-reduction, and precipitation - depend not only on the chemical properties of the soil but also on the physical structure necessary to provide the time needed for reaction. Soils which permit the most rapid passage of treated waste water may not provide the needed time for chemical contaminant removal. Therefore, it is desirable that the soils permit passage of the treated waste water while permitting the chemical and adsorptive properties of the soils to function optimally.

Organic Substances - The available evidence indicates that a relatively large variety of simple and soluble organic substances may be found at least in  $\mu\text{g}/\ell$  amounts in reclaimed and natural waters. These substances include both nontoxic and toxic substances and compounds that are synthesized by plants, animals, microorganisms or man. They enter the waters through natural processes, through domestic and industrial waste disposal operation, or are synthesized in the water by algae and numerous other organisms. One must be cautious in interpreting the results of chemical tests indicating the presence of many of the substances in waters as most methods of concentrating the organics in water are not ideal and many simple organic substances could be synthesized during the concentration process.

a. Soluble Organic Substances in Waters - The principles and phenomena responsible for the soluble organic substances in water are the same for both reclaimed and natural waters. Studies of the nature of the soluble organic materials in a variety of waters, therefore, are all pertinent to an understanding of the nature of these substances in reclaimed waters. The original source of most soluble organic substances in waters is the vast amount and variety of plant organic compounds synthesized through photosynthesis<sup>(23)</sup>. Small quantities of organic substances are synthesized by chemoautotrophic bacteria. Many of the plant organic constituents such as aliphatic, phenolic and amino acids, sugars, some proteins, a number of polysaccharides and others are water soluble. Some of these solubilized by rain or irrigation water move with the water into soil profiles or with runoff waters into sewage systems, streams and lakes. Animals feeding on plant products synthesize additional organic substances which may be solubilized in water.

Essentially all of the plant and animal organic substances both soluble and insoluble, are subject to microbial degradation. The decay processes occur on the soil, in the soil, in human and animal digestive systems, and in waters. The large numbers and variety of organisms involved synthesize a vast variety of new organic substances, many of which are soluble<sup>(24)</sup>. In reclaimed and other surface waters, algal growth is an important source of soluble and insoluble organic substances and an important carbon and energy source for growth of other organisms. Microscopic examination at Riverside of deposits which often form in sprinkler and drip irrigation lines have shown them to be masses of algal cells undergoing decomposition by bacteria and fungi.

The disposal of raw or reclaimed municipal and industrial waste waters into streams, lakes or percolation ponds is both a source of water soluble organics and a source of carbon and energy source for microorganisms. The carbon dioxide released from the decomposing organic materials may increase the growth of algae in surface waters<sup>(25)</sup>.

The kinds of soluble organic substances in waters may be subdivided into toxic and nontoxic compounds. Toxic compounds may be natural or synthesized by man. Examples of natural toxic organic compounds include nicotine, coumarins, aflatoxins, botulin, numerous phenolic substances, naphthalenic and anthracene derivatives, and many others. Man made toxic compounds include numerous pesticide and other industrial chemicals. The latter may get into waters through waste disposal into streams, lakes, and sewage systems; through runoff and erosion; from treated crop lands; and through accidental spills<sup>(26)</sup>.

The greater portion of the stable soluble organic matter in waters appears to be polymeric in nature and is similar to the stable soil humus polymers. As in soil, the polysaccharide or carbohydrate fraction may constitute up to 50% of the total. The polysaccharide fraction in waters percolating through soil is composed of polymers with relatively low molecular weights. The large molecules would be adsorbed by the soil particles and colloids. The polysaccharide portion as in soil is composed of numerous constituent sugar units<sup>(27,28,29)</sup>. The brown polymeric material appears to be similar to soil humic and fulvic acids. Studies with soil humus indicate that this fraction is a polymer of various phenolic, phenolic carboxylic acids, and other aromatic substances with linked peptides, amino sugar polymers, and other units<sup>(30,31,32,33,34)</sup>.

Almost any water-soluble organic compound excreted by plant roots, present in plant or animal wastes and residues, synthesized by microorganisms, or released during the microbial decomposition of organic residues could be

found in the soil solution, in natural waters, or in reclaimed water if one made the effort to identify them and concentrated sufficient water. The simple compounds which are readily degraded such as aliphatic and phenolic acids, amino acids, sugars, and many others are present because notwithstanding the fact that they are rapidly degraded by microorganisms they are continually being produced. It is also conceivable that very small quantities of biodegradable organic substances could exist in waters because the chance of contact between the organism and the susceptible molecules would be reduced. Adsorption of both the organism and the organic carbon source on colloidal surfaces would hasten utilization by the organisms. Stevenson<sup>(35)</sup>, in reviewing the literature on the presence of organic acids in soil solutions, found that acetic, formic, butyric, fumaric, propionic, valeric, succinic, lactic, p-hydroxybenzoic, vanillic, syringic, p-hydroxycinnamic, ferulic, benzoic, phenylacetic, protocatechuic, salicylic, and others have been identified. Quantities present range from a few  $\mu\text{g}/\text{l}$  to several  $\text{mg}/\text{l}$ . Quantities are highest in the presence of readily available organic residues and under waterlogged conditions. Numerous amino acids have also been noted in very small concentrations.

Phenolic substances are of special concern because they may impart a taste or odor to the water, especially after the water is chlorinated. They may get into the water from industrial wastes, they are released from plant phenolic substances and polymers during microbial decomposition processes, and they are synthesized by many microorganisms during decomposition of non-phenolic organic residues<sup>(31)</sup>.

A study in Colorado was made to compare the nature of the soluble organic material in a soil profile under a feedlot and under grassland with ground, well, and river waters<sup>(36)</sup>. It was concluded that the major portion of the soluble materials in all the waters were polymeric. The soluble organics

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under grassland were essentially the same as under the feedlot, although phenols were present in greater abundance in the manure and surface soil of the feedlots. About 13% of the soluble material in the soil profiles was carbohydrate (polysaccharides) and much of the remainder, based on IR spectra and reductive degradation procedures, appeared to be polymerized aromatic structures.

These observations suggest that the soluble organics under sewage or sewage effluent treated soils would also be the same as under feedlot manure or grassland. The soluble materials would, to a large extent, be dependent upon the organisms which decompose the plant, animal, or human organic wastes and which synthesize new organic substances.

At Riverside and in Imperial Valley<sup>(37,38)</sup>, studies were made to determine the nature and amount of soluble material percolating through the soil and into tile drainage lines in Imperial Valley. Total soluble carbon ranged from about 5 to 200 mg/l. It was highest in the surface soil and following the application of manure or other organic residues, it decreased with depth in the soil profile. The decrease with depth is related to degradation by soil organisms and to adsorption phenomena. The soil column could be viewed as a chromatographic column in which adsorption and desorption processes are operative. Adsorption could concentrate the organic material making it more available to the microorganisms which are also adsorbed or live on soil and colloidal surfaces. Simple phenolic and other acids were generally present in  $\mu\text{g/l}$  quantities. On the basis of C/N ratios, IR spectra, and analyses for carbohydrates the bulk of the water-soluble carbon was in the form of polysaccharides and soil humic-type polymers. The molecular weight of the material was generally 10,000 or less. Most of the higher molecular weight material (5,000 to 10,000) was polysaccharide. Including uronic acids the polysaccharide fraction accounted for 7 to 31% of the carbon. The higher values were noted after the addition of

fresh residues to the soils. These values are conservative as the anthrone method used gives low values. A study on the nature of the soluble organic nitrogen in ground waters in Oregon<sup>(39)</sup> showed that about 25% could be released as amino acid nitrogen upon 6 N HCl hydrolysis. This indicates a similarity to the stable nitrogen in soil humic and fulvic acid polymers.

Up to 50% of the carbon in soil solutions has been reported to be polysaccharide carbon<sup>(40,41)</sup>. Analyses of aqueous leachates collected in a lysimeter under a humic podzol soil disclosed that about 87% of the soluble organic material appeared to be a humic fulvic acid<sup>(42)</sup>. Lamer and Goerlitz<sup>(43)</sup> and Christman and Ghassemi<sup>(44)</sup> concluded that a large percentage of the brown colored material in natural waters was polymeric with aromatic constituents.

In studies of the nature of the soluble organic material in secondary effluents in Israel, from 40 to 50% of the soluble material was classified as humic<sup>(45)</sup>. Over 20% was designated as protein but this was probably stabilized by adsorption or linkage into the humic molecules<sup>(46)</sup>. If it were free protein it would be rapidly utilized by microorganisms. Carbohydrates which are also components of stable soil humus<sup>(28,31)</sup> constituted about 11%. The bulk of soluble organic material, therefore, appeared to consist of resistant polymeric substances similar to those in soil humus. The high COD to BOD ratio also supported these conclusions. The remainder of the soluble organic material consisted of about 9% ether soluble substances and 14% detergents.

b. Toxic Organic Substances in Waters - Toxic organic substances in waters may originate from industrial and domestic wastes, accidental spillage, erosion from recently treated lands, and from natural processes. Carcinogenic compounds have been reported in river water used for drinking purposes in Japan and Germany<sup>(47,48)</sup> and the buildup of pesticides in fish in river waters may have resulted in large scale kills<sup>(49)</sup>.

Pesticides are considered a potential source of soluble toxic organic substances in waters. Actually the behavior of and decomposition of pesticides in soils was studied long before environmental pollution became a popular phrase<sup>(50)</sup>. They are adsorbed by the soil clays, iron and aluminum oxides, and especially by organic colloids and are subject to microbial degradation<sup>(51,52)</sup>. Although vast numbers of organic pesticides have been used since early 1940, there is no evidence that pesticides moving with percolating waters have entered the groundwaters and caused injury to people utilizing these waters. Cases where wildlife has been injured have involved treatment of surfaces where wildlife normally lives or the contamination of surface waters through erosion from land, from discharge of chemical plant wastes into waters, or through accidental spills. Most erosion losses are of short duration and occur right after the pesticide has been applied<sup>(53)</sup>. The insecticide, DDT, has been singled out as an especially dangerous environmental pollutant because it is relatively resistant to decomposition and accumulates in the fats of wildlife and other organisms. At this time, use of DDT has been greatly restricted and its presence in surface waters is declining.

Soil studies, both field and laboratory, indicate that most pesticides remain in surface soils while a few may with time be found at depths of 30 to 60 cm<sup>(52)</sup>. The more mobile pesticides, such as TCA and dalapon, are usually subject to rapid microbial degradation. When the compound is both mobile and somewhat resistant to degradation it may penetrate to deeper soil depths. Picloram was reported to leach out of surface soils in 12 to 18 months and to reach the 45 to 51 inch depth in another soil in three months<sup>(52)</sup>. This chemical has not been registered for commercial use at this time.

Results of a study of reclaimed and well waters of the Central and West Basin Water Replenishment District in Downey, California<sup>(6)</sup>, showed that in

some samples the phenol content was 0.01 to 0.04  $\mu\text{g}/\text{l}$ . This was not considered a problem as no taste or odors were noted. Pesticide and chlorinated hydrocarbon estimations were all below the limits indicated in the 1962 U. S. Public Health Service drinking water standards and by the California Department of Health. A similar study was made of reclaimed waters at Whittier Narrows in southern California<sup>(54)</sup>. Most of the organic carbon and the organic nitrogen was removed by passage through two feet of soil in the test basin. After passage through about 8 to 10 feet of soil the water met all the requirements of the California Regional Water Quality Control Board, Los Angeles Region.

The techniques used in a study of the oxidation of numerous carcinogenic organic compounds in activated sludge involved oxygen uptake measurements in a Warburg respirometer over periods up to 144 hrs. Because most of the organic compounds tested, which were added at a concentration of 500 mg/l, showed little additional oxygen uptake over the controls with sludge only, it was concluded that most of these carcinogenic compounds would not be degraded in activated sludge during normal retention time<sup>(55)</sup>. It should be pointed out that many of these substances are aromatic including condensed ring aromatic substances which normally decompose slowly. They also include structures that are normally incorporated into aromatic humic polymers and thus may become part of the beneficial soil humus. Further many of these compounds could be toxic to microorganisms at 500 mg/l concentrations but may not be at 5 or 1 mg/l. Use of  $^{14}\text{C}$ -labeled compounds would be a good technique for studying decomposition at much lower or more normal concentrations. If such compounds were present in waste water effluents they would probably be adsorbed near the surface during groundwater recharge by passage through the soil profile. There they would be retained for the longer periods which may be required for their decomposition, detoxification, or linkage into humic polymers.

The bioresistant organic detergents previously used have been considered as important water pollutants<sup>(56)</sup>, because they have survived waste water treatments and entered natural waters. The present trend, however, which is to manufacture only biodegradable detergents, should solve this problem.

c. Removal During Ground Water Recharge-Percolation Versus Direct Injection - The same phenomena such as adsorption and decomposition involved in the removal of much of the soluble organic substances from water percolating through a soil profile would also be operative if the water were injected through a well directly into an aquifer. However, inasmuch as the aquifer layers may be quite sandy and devoid of organic colloids, the water soluble organics would probably move much further than they would through top soil. This would be especially true during the earlier stages of the injection and if the deposits were gravelly. With many substances such as most pesticides, the organic colloids are much more active than clay or soil particles in adsorbing the compounds. In addition, there would not be as great a number nor variety of microorganisms to decompose the organic materials as in top soil. With time an organic and microbial slime zone would develop near the water-aquifer interface which would tend to filter out the organic materials and allow decomposition of biodegradable substances. This developing slime layer could also reduce the efficiency of the water intake and in time it could become necessary to dry out the well or clean it out.

Reclamation of water by passing through the soil profile would probably prove to be more efficient in the adsorption and decomposition of soluble organic substances in the waters. It would also be easier to control the percolating procedures to prevent soil sealing which would occur under continued submergence. The spreading operations could be regulated to allow drying periods for each basin which would better maintain water penetration

rates. The alternate drying and percolation would also allow more time for the decomposition of toxic and other objectionable soluble organic substances.

Chlorination of reclaimed and other waters before injection into an aquifer would kill pathogenic organisms and delay or prevent the build up of an organic matter-microbial slime layer. Also, it could prevent the microbial destruction of undesirable soluble organic substances which could then move with the waters for great distances in sandy or gravelly deposits with low adsorptive capacity. It may be that water of good quality should be injected in a new or cleaned well until a bacterial slime zone has developed which would filter out and decompose objectionable soluble organic substances. Thereafter reclaimed water might be injected.

Nitrogen - The recommended maximum concentration of ammonium nitrogen ( $\text{NH}_4^+\text{-N}$ ) in drinking water is 0.5 mg/l<sup>(5)</sup>. Thus, the total system of the waste water treatment plant and the soil system during ground water recharge must be operated to remove the  $\text{NH}_4^+$  or convert it to nitrate ( $\text{NO}_3^-$ ). A combination of  $\text{NH}_4^+$  stripping to reduce the total N concentration to less than 10 mg/l and an aerobic surface recharge system that would insure conversion of the remaining  $\text{NH}_4^+$  and organic N to  $\text{NO}_3^-$  would produce a water that would meet the criteria for  $\text{NH}_4^+$  and the 10 mg/l U.S. Public Health Service standard for  $\text{NO}_3^-$ -N concentration in drinking water. Also, operation of the waste water treatment plant to produce a water containing  $\text{NO}_3^-$  rather than  $\text{NH}_4^+$  plus an anaerobic recharge system would produce a water with less than 10 mg  $\text{NO}_3^-$ -N/l.

Assuming that the costs of  $\text{NH}_4^+$  stripping from secondary effluents and that the operation of the waste water treatment plant to produce a nitrified effluent are too expensive for most ground water recharge systems, the following discussion will deal mainly with effluents that have 20 and 30 mg N/l, mostly in the  $\text{NH}_4^+$  form.

For removal of N an ideal recharge system would provide a cycle of aerobic and anaerobic conditions either in time or in depth in the soil profile. The aerobic condition is needed to convert  $\text{NH}_4^+$  to  $\text{NO}_3^-$  and the anaerobic condition is needed to convert  $\text{NO}_3^-$  to nitrogen gas ( $\text{N}_2$ ), which escapes into the atmosphere. Both processes are microbiological. The nitrification process requires oxygen whereas the denitrification process requires an oxygen deficiency and available C for an energy source for the microorganisms. Because anaerobic conditions favor the production of soluble organic compounds a second aerobic period in the cycle would be desirable. Alternate flooding and drying periods during land spreading provide a compromise between a need for nearly complete denitrification and a need to maintain low concentrations of organic substances.

Secondary effluents usually have a deficiency of available C for denitrification, which requires 1.3 grams of available C per gram of  $\text{NO}_3^-$ -N. The usual secondary effluent, which has about equal concentrations of C and N, does not have sufficient C for denitrification of the  $\text{NO}_3^-$  that can be produced even if all of the C is available and is used in this conversion. Because of this deficiency, other sources of C must be supplied if most of the  $\text{NO}_3^-$  that can be produced is to be denitrified.

a. The Flushing Meadows Project - This is an experimental project started in 1967 in the Salt River bed west of Phoenix, Arizona. The objective was to study various phases of the renovation of secondary effluent by ground water recharge with rapid infiltration basins. Many of the field and laboratory column studies have measured the effects of management on N conversions in the soil.

The effluent usually had 20 to 40 mg  $\text{NH}_4^+\text{-N}/1$ , up to 1 mg nitrite nitrogen ( $\text{NO}_2^-\text{-N}/1$ ), up to 3 mg  $\text{NO}_3^-\text{-N}/1$ , and 1 to 6 mg organic N/1<sup>(17)</sup>. In field operations, N transformations were affected by the length of flooding and drying periods. When short frequent flooding periods were used, for example 2 days flooding and 2 days drying, sufficient oxygen was available for complete conversion of N to  $\text{NO}_3^-$  so that the  $\text{NO}_3^-$  concentration of the percolating water was nearly the same as the concentration of total N in the input water. When long flooding periods were used, for example 2 to 3 weeks flooding and 2 weeks drying, the  $\text{NO}_3^-$  in the percolating water was near zero (<1 mg/1), except for a peak of high  $\text{NO}_3^-$  water that occurred soon after the start of each flooding cycle<sup>(17)</sup>.

With the short flooding periods not sufficient time was available to develop anaerobic conditions so that conversions proceeded to produce the  $\text{NO}_3^-$  form and denitrification was small or non-existent. But, with longer flooding, anaerobic conditions developed that prevented conversion of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  and favored denitrification, producing an effluent low in  $\text{NO}_3^-$  and with low  $\text{NH}_4^+$  concentrations. During flooding the  $\text{NH}_4^+$  accumulated in an adsorbed form on the surfaces of soil particles. When flooding ceased and oxygen entered the soil again the  $\text{NH}_4^+$  was converted to  $\text{NO}_3^-$  and was then leached at high concentrations when the next flooding period started. In the operation of such a system the flooding period should be adjusted to not exceed the  $\text{NH}_4^+$  adsorption capacity of the soil nor to exceed the nitrification capacity of the soil during the drying period. For the Flushing Meadows Project, flooding periods should be limited to 10 days to avoid more  $\text{NH}_4^+$  accumulation than can be nitrified during the drying period.

Bouwer et al.<sup>(17)</sup>, also reported that in a 10-day flooding period followed by a 10- to 20-day drying period removal of N was about 30%, presumably by denitrification. With this sequence of flooding and drying about 300 ft of water was applied per year.

Growing plants in the infiltration ponds increased the N loss to about two-thirds of the total N input. The effect of the plants resulted from increased denitrification, since the losses far exceeded the use of N by the plants.

Lance and Whisler<sup>(57)</sup>, in laboratory-column studies that gave data similar to those from the field study at Flushing Meadows, showed that net N removal averaged 30% when columns were flooded intermittently with secondary effluent which resulted in a total input of 280 ft/year. Nitrogen removal was increased to 80 to 90% in the soil columns by adding 150 mg soluble C/l in the form of glucose to the secondary effluent water. Removal of N was increased to 75 to 80% by collecting high-NO<sub>3</sub><sup>-</sup> water from the columns, mixing with the waste water, and recycling it through the columns. With this method net input was decreased to 215 ft/year. Removal of N was increased to 80% by reducing the intake rate from 280 ft/year to 132 ft/year or a decrease from 14 inches/day to 6 inches/day. Lance<sup>(58)</sup> reported a linear relationship between N removal and infiltration rate. Removal of N was above 80% at an infiltration rate of 6 inches/day and decreased to about 15% at a rate of 22 inches/day.

The research of this Flushing Meadows project on the sandy, gravelly soil of the Salt River bed has outlined in some detail the factors in the management of N in a ground water recharge project that should have relevance to ground water recharge in many if not all regions of California.

b. The Montebello Forebay - Research and experience in this area, which involves recharge with secondary effluents from the Pomona, Whittier Narrows, and San Jose water reclamation plants, have added to our knowledge of N conversions during ground water recharge. The sources of information used here are 1) McMichael and McKee<sup>(54)</sup>, 2) Bookman-Edmonston Engineering, Inc.<sup>(6)</sup>, and 3) Mitchell and Cooper<sup>(18)</sup>.

McMichael and McKee<sup>(54)</sup> reported data from test basins in the Whittier Narrows and the Rio Hondo spreading grounds. These basins, which were equipped to collect water at 2-, 4-, 6- and 8-ft depths, received treated waste waters using a short period of flooding and a longer period of drying on a daily basis. This cycle insured completely aerobic conditions. There was no dilution of the reclaimed water except by natural rainfall.

In the Whittier Narrows Test Basin the average  $\text{NO}_2^-$ -N and  $\text{NH}_4^+$  plus organic N were <0.2 and <1.0 mg/l respectively at the 8-ft depth indicating efficient conversion to the  $\text{NO}_3^-$  form. The total soluble N increased slightly as the water moved through 8 ft of soil, perhaps as a result of mineralization of organic N in the soil from the residual soil organic matter inherited from the pretest period when the area was cropped to alfalfa.

In the Rio Hondo test basin the N was also effectively converted to  $\text{NO}_3^-$  with about the same total N and  $\text{NO}_2^-$ -N concentrations at the 6- and 8-ft depths. Evidently the short daily flooding schedules are highly efficient in oxidizing N to the  $\text{NO}_3^-$  form.

In a report<sup>(6)</sup> dealing with Montebello Forebay area it was indicated that during the 1972-73 recharge year 173,449 acre-feet of water were recharged. Secondary effluent used for recharge was 29,949 acre-feet or about 17% of the total. The average N concentration of the recharge water was 4.2 mg/l whereas the secondary effluent averaged about 21 mg/l. The  $\text{NO}_3^-$ -N concentration of well waters in the area averaged about 2.5 mg/l with a maximum value of 6.1 mg/l.

Waters from wells adjacent to the Whittier Narrows spreading ground had  $\text{NO}_3^-$ -N concentrations less than the average total N of the input waters. The N removal during recharge could have been about 30% which is about the same removal as in the Flushing Meadows project when operated at high infiltration rates using 10-day flooding periods followed by 2-week drying periods.

Ground water recharge operations in the Montebello Forebay involve 1-week flooding and 2-week drying periods for control of midges<sup>(18)</sup>. The data from well waters and the flooding-drying schedule both suggest about 30% N removal. Data show that  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ , and organic N concentrations were, for practical purposes, essentially zero in well waters, indicating efficient conversion to the  $\text{NO}_3^-$  form with this flooding-drying cycle<sup>(6)</sup>.

Assuming a 30% removal of N, and secondary effluents containing 21 mg total N/l and dilution water with 2 mg total N/l, up to 50% secondary effluent could be used and still meet the U.S. Public Health Service standard for  $\text{NO}_3^-$ , without change in the present flooding-drying cycle. If appropriate management practices were initiated to increase N removal the proportion of reclaimed water could be increased.

c. The Lodi Experiment - Greenberg and Thomas<sup>(14)</sup> reported that various flooding and drying cycles, in recharge through a Hanford sandy loam, were effective in the conversion of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ . Ammonium was effectively converted to  $\text{NO}_3^-$  in the percolating water after percolation through several feet of soil. In some cases the  $\text{NO}_3^-$ -N concentration at the deeper depths was about equal to the  $\text{NH}_4^+$ -N concentration at the surface, but in other cases some losses of N were indicated.

d. Removal During Ground Water Recharge by Direct Injection - Injection into confined aquifers in the coastal area of Orange County is perhaps the most definitive experiment of its kind<sup>(22)</sup>. Chlorinated secondary effluent having a concentration of 13 mg  $\text{NH}_4^+$ -N/l was used. After 400 ft of travel  $\text{NH}_4^+$  disappeared but  $\text{NO}_2^-$  and  $\text{NO}_3^-$  did not increase. The  $\text{NH}_4^+$  could have been fixed by minerals in the aquifer or it could have been converted to  $\text{NO}_3^-$  which was lost by denitrification. If  $\text{NH}_4^+$  disappeared by fixation, which seems the more likely cause, continued injection would saturate the fixing capacity and  $\text{NH}_4^+$  would move out from the injection point in an ever widening circle.

Soluble Salts - When waters of low salt concentrations are infiltrated through soils the weathering of minerals occurs to produce soluble minerals. In poorly weathered soils of arid regions this weathering process is sufficiently rapid to insure about 250 mg TDS/l in the percolating waters<sup>(59)</sup>. Because of the increment in TDS added in one cycle of municipal use, most waters from secondary treatment plants have more than 250 mg TDS/l even if the TDS of the municipal supply is extremely low (<100 mg/l). Thus, with the exception of dissolution of carbonates and/or cation-exchange reactions associated with the acidification that results from nitrification of  $\text{NH}_4^+$ , there is little possibility of TDS increases during ground water recharge with secondary effluents. However, during the initial stages of recharge operations an increase in TDS can be expected if the soil materials and sediments have salts such as might be residual from irrigation agriculture or some geological processes. Also, because of the lack of a concentration effect as found in irrigation agriculture and because of the acidification from  $\text{NH}_4^+$  oxidation, the precipitation of  $\text{CaCO}_3$  is not likely to occur as the secondary effluent enters the soil.

The increase in TDS as a result of  $\text{NH}_4^+$  oxidation is variable. In the Flushing Meadows project the input and the percolating waters had 1000 to 1200 mg TDS/l with only a slightly higher value for the percolating water.<sup>(17)</sup> The pH of the input water was 7.6 to 8.1 whereas the percolating water had pH values near 7.0. Broadbent<sup>(60)</sup> found in column studies that the TDS concentration was 64 to 128 mg/l greater in the waste water effluents that had  $\text{NH}_4^+$ -N as compared to  $\text{NO}_3^-$ -N in the waste water influents. McMichael and McKee<sup>(54)</sup> found an increase of 380 mg TDS/l at the 8-ft depth in the Whittier Narrows test basin and an increase of 160 mg/l in the Rio Hondo test basin, using the residue at 103 C as a measure of TDS. At the Whittier Narrows test basin about 60% of the increase in TDS was volatile solids and at the Rio Hondo test basin about 40%

of the TDS was volatile solids as measured at 600 C. These volatile solids could have been partly the result of loss of  $\text{HCO}_3^-$  at this higher temperature.

More recent work with the Whittier Narrows test basin using a cycle of 7 days flooding and 14 days drying showed that the increase in TDS was 60 mg/l<sup>(18)</sup>. This increase was attributed to microbiological activity associated with N transformations.

Experience in Montebello Forebay with recharge with nitrified secondary effluents showed that when reclaimed water containing  $\text{NO}_3^-$  replaced water containing  $\text{NH}_4^+$  the TDS in the infiltrated water decreased gradually as a function of time<sup>(18)</sup>.

In an acidification reaction such as the conversion of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  the increase in TDS in a soil system can depend on how much of the acid generated reacts with soluble  $\text{HCO}_3^-$  in the water and how much reacts with soil solids. In the case of reaction with  $\text{HCO}_3^-$  the  $\text{NO}_3^-$  anion replaces the  $\text{HCO}_3^-$  anion with no increase in TDS whereas if the reaction is with  $\text{CaCO}_3$  in the soil an increase in TDS results. The increase in TDS obtained can be expected to be a result of increases in soluble Ca and Mg with proportionate increases in hardness.

For the Montebello Forebay area the average TDS of the recharge water in 1972-73 was 534 mg/l and well waters had 500 to 700 mg/l. However, two wells adjacent to the Whittier Narrows recharge area averaged 575 mg/l which would indicate an increase of 41 mg/l. In the same well the hardness averaged about 80 mg/l greater than the average for the recharge waters. The greater increase in hardness might be a result of a cation-exchange reaction in which Ca and Mg is exchanged with Na from the recharge water<sup>(6)</sup>.

In infiltration studies at Lodi, California, tendencies were found for K and Na to decrease and for Ca and Mg to increase in concentrations as the water percolated through a Hanford fine sandy loam soil<sup>(14)</sup>.

The use of secondary effluents for crop production should be considered a proper use of these waters. Quality criteria for irrigation waters should be applied to secondary effluents when they are considered for this use. But, because of the concentrating effect of irrigation agriculture it should not be considered as a method for ground water recharge.

If a water of low TDS (<100 mg/l) is used for the municipal supply and the secondary effluent has 300 mg/l, conventional irrigation agriculture would concentrate the TDS to somewhere in the range of about 800 to 1200 mg/l whereas rapid infiltration through sandy alluvium would most likely produce a water of 450 mg/l or less. In southern California the secondary effluent is more likely to have a TDS of 600 to 700 mg/l and the use of this water in conventional irrigation would produce an effluent of about 2000 mg TDS/l.

If secondary effluent is to be used for irrigation to produce food and fiber the production process should be first priority and the water managed to maximize crop production. If ground water recharge is the main objective, the qualitative and quantitative demands for reuse of the underground water can best be served in most cases by using infiltration basins.

However, if TDS in the ground water is not a problem because of high dilution with low TDS waters, such as found in humid regions, ground water recharge and irrigation might be compatible.

Trace Elements and Heavy Metals - Many ground water recharge systems involve the passage of reclaimed water through soil to the ground water basin. In the process, chemical constituents in the water react with the soil and the chemical composition of the water is changed. The kind and extent of chemical reactions which may occur depend largely upon the chemical properties of the soil.

The chemical properties of soil are governed mainly by the amount and kind of colloidal clay and organic matter. Waters passing through soils low in

organic matter with high percentages of sand-size particles have a much lower capacity to alter the composition of waters passing through them than do soils with high percentages of clay and organic matter. Reactions of constituents in waters with soils under conditions of saturated flow differ from those under conditions of unsaturated flow. In ground water recharge systems involving soils, therefore, the chemical composition of the percolate entering the ground water will depend not only upon the chemical composition of the water spread onto the soil, but also upon the chemical and physical properties of the soil.

In general, elements which occur in solution as anions or neutral molecules pass through soils more readily than do elements which occur as cations. The elements As, Se, and F in aerated soils in an inorganic form occur as anions or neutral molecules. Although there are exceptions which depend upon the chemistry of the system, Cd, Cu, Cr, Pb, Hg, Ag, and Zn most commonly occur in fresh waters and soil solutions in inorganic form as cations.

All of the trace elements for which water quality criteria have been established may occur as either soluble or insoluble organo-metallic complexes in fresh waters and soil solutions. The chemistry of the organo-metallic complexes in natural systems is extremely complex, and presently our knowledge of organic forms of the elements is not sufficiently well understood to generalize. Where concentrations of trace elements in soil solutions and waters are in excess of those predicted from inorganic solubility product considerations, the element is thought to occur in an organic form. Because adequate information on soluble and insoluble organic metal complexes in soils is not sufficient to generalize, the following discussion of the chemistry of those trace elements for which criteria for drinking waters have been established will stress inorganic forms. Typical concentrations which occur in other natural systems have been presented in recent reviews<sup>(61,62,63)</sup>.

a. Arsenic (As) - Arsenic is ubiquitous in nature. It occurs in igneous and sedimentary rocks at concentrations of 1 to 3 mg/kg and in soils at concentrations which normally range from 0.1 to 6.0 mg/kg. Normal concentrations reported for sea and fresh water are 0.003 and 0.0004 mg/l, respectively. Soil solutions from soils in regions where parent materials contain normal concentrations of As, and where there are no man-made sources of contamination have concentrations of As similar to those found in fresh waters.

In solution, As most commonly occurs in the trivalent state as  $\text{HAsO}_2$  and  $\text{AsO}_2^-$  or in the pentavalent state, depending upon pH, as  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ ,  $\text{AsO}_4^{3-}$ , or  $\text{AsO}_4^{=}$ . In the pH range of most water and soils, As occurs principally as the monovalent and divalent anion. Although the chemical reactions of As in soils are not completely understood, it is thought that they react with iron, aluminum and/or calcium to form insoluble compounds. Both alum and ferric sulfate at concentrations of 50 mg/l effectively removed 95 percent of the As from a solution containing 0.05 mg As/l at pH 7<sup>(64)</sup>. The iron arsenate is more soluble than its aluminum counterpart. In calcareous soils, the formulation of calcium arsenate is thought to limit the solubility of As. The calcium arsenates are more soluble than either the iron or aluminum arsenates. Generally, in natural soils the amounts of As in solution are below 0.01 mg/l. However, levels as high as a few mg/l have been reported in solutions from surface soils (0-15 cm) where arsenical agricultural chemicals have been applied to control diseases or weeds.

Where arsenicals have been used for many years in orchards to control diseases, movement of As to depths of 2 meters in the soil profile have been observed<sup>(65)</sup>. Generally, As mobility in soil is restricted but usually greater movement occurs in neutral and calcareous soils than in acid soils.

The concentration of As in a few secondary waste water treatment plant effluents has been observed to exceed the upper limit established for drinking

waters (Tables 1 and 5). If secondary effluents containing As at concentrations greater than those which occur in the soil solution are leached through soils, the soil will remove part of the As from the applied water. The extent to which its concentration is reduced will depend upon the chemical properties of the soil in question. Acid soils high in active iron and aluminum should reduce the concentration of As in the applied water to a greater extent than neutral or calcareous soils. Therefore, available information suggests that when the As concentration of waste water effluents exceed drinking water standards, percolation of the effluent through many, but not necessarily all, soils will reduce the concentration to an acceptable level.

b. Selenium (Se) - Selenium occurs in igneous rocks and sedimentary rocks at concentrations which usually range from 0.05 to 0.10 mg/kg. Reported concentrations for shales are slightly greater and commonly range from 0.1 to 1.0 mg/kg. In non-seleniferous regions normal concentrations of Se in soils are <0.1 to 0.5 mg/kg. Certain soils derived from parent materials high in Se may contain as much as 30 mg Se/kg<sup>(62)</sup>. Concentrations of Se in sea and fresh waters are normally 0,0001 mg/l and <0.01 mg/l, respectively. Surface and groundwaters in seleniferous regions are usually higher with concentrations as high as 0.5 mg/l<sup>(66)</sup>.

The chemistry of Se resembles somewhat the chemistry of S. In inorganic form Se occurs in solution as either selenate,  $\text{SeO}_4^{=}$  or selenite  $\text{SeO}_3^{=}$ . In acid soils, Se most probably reacts with iron oxides to form rather insoluble selenites. Most information available suggests that Se is more soluble in neutral and calcareous soils than in acid soils. Therefore, acid soils should exhibit a greater capacity to reduce concentrations of Se in applied waters than neutral or calcareous soils.

Although data on concentrations of Se in waste water effluents is quite limited, that which is available suggests that the Se concentrations of effluents

are below upper limits established for drinking waters. In situations where the concentration of Se in waste water effluents is greater than 0.01 mg/l, percolation through many soil types will reduce the concentration of the percolate to less than 0.01 mg/l.

c. Cadmium (Cd) and Zinc (Zn) - In inorganic form both Cd and Zn occur in solution as divalent cations,  $\text{Cd}^{+2}$  and  $\text{Zn}^{+2}$ , and depending upon the composition and concentration of the solution also as ion pairs. The ion pairs may be cationic, anionic, or neutral and have the general formula  $[\text{M}_a \text{X}_b]^{2a-by}$  where M represents the metal ion, X represents the anion, and y its valence. Ion pairs of Zn and Cd containing the anions  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{=}$ , and  $\text{SO}_4^{=}$  are known to occur in some solutions; however, their significance in natural and waste waters is presently not well understood.

Concentrations of Cd which occur in rocks are quite low and most commonly range from 0.03 to 0.2 mg/kg. In soils not subject to contamination from man's activities, concentrations of Cd commonly range from 0.03 to 0.08 mg/kg. Usual concentrations of Cd in fresh water and sea water are in the range of 0.0001 to 0.001 mg/l. In solutions extracted from non-contaminated soils, concentrations of cadmium ranges from <0.001 and 0.005 mg/l. However, in situations where cadmium salts or waste waters or sludges are added to soils, concentrations as high as a few mg/l have been observed<sup>(67)</sup>.

Factors which control the solubility of Cd in natural systems are not well understood. Most natural waters are undersaturated with respect to the solubility of those solid forms of Cd expected to occur. The available information suggests that the solubility of Cd in natural waters is controlled by adsorption reactions involving colloidal clays and amorphous oxides.

Cadmium in waters at concentrations of from 0.005 to 0.01 mg/l is apparently quite mobile in many soils. Data from the Flushing Meadows Project<sup>(17)</sup> showed that waters containing 0.007 mg Cd/l passed through soil to underground

wells with essentially no change in the concentration of Cd. At concentrations greater than 0.01 mg/l there is not sufficient published information to adequately evaluate the degree and extent to which Cd may move in soil profiles. Generally, it appears that the extent to which soils will reduce concentrations of Cd in applied waters depends upon the concentration in the applied water and the chemical properties of the soil.

The current upper limit for Cd in drinking waters is 0.01 mg/l. Data show that some secondary waste water treatment plant effluents contain Cd concentrations which exceed 0.01 mg/l. Presently, the available data on the extent to which soils will reduce the Cd concentration of effluents percolating through them is not sufficiently detailed to adequately evaluate the Cd concentration of the water reaching the ground water basin. Therefore, unless it is demonstrated that the soil in question has the capacity to reduce the concentration of Cd below 0.01 mg/l, it does not seem advisable to use waste water effluents containing concentrations of Cd greater than 0.01 mg/l in ground water recharge operations involving percolation through soil.

Rocks commonly contain between 20 and 100 mg Zn/kg. The average concentration for soils is 50 mg/kg. The normal concentration of Zn in sea water and fresh water is 0.01 mg/l and the range is usually from 0.01 to 0.05 mg/l, respectively. Soil solutions typically contain from 0.01 to 0.1 mgZn/l.

When salts or solution containing Zn are applied to soils, as long as the final pH of the system does not become excessively acid (<pH 4.5), the subsequent concentrations of Zn observed in the soil solution are below the upper limits recommended for reclaimed water used for ground water recharge and for public drinking water supplies. The attenuation of Zn in waters by soils is due to precipitation or coprecipitation of Zn and adsorption phenomenon involving colloidal clays, organic matter, and amorphous oxides. Most available information indicates that zinc concentration in secondary effluents will always

be considerably less than the upper limits prescribed by drinking water standards. When concentrations in excess of a few tenths of a mg/l are observed, contact with soils should result in some attenuation. Therefore, the probability that the use of secondary effluents in ground water recharge operations will produce concentrations of Zn in ground water in excess of established drinking water standards is remote.

d. Copper (Cu) - Copper concentrations in rocks in the surface of the earth's crust commonly range between 5 and 50 mg/kg. The average concentration in soils is 20 mg/kg and the range is from 2 to 100 mg/kg. Sea water contain on the average 0.003 mg Cu/l and fresh water 0.01 mg Cu/l. Soil solutions commonly contain from 0.01 to 0.1 mg Cu/l.

Copper occurs in aerated soils and solutions as a divalent cation and as ion pairs with compositions similar to those discussed for Cd and Zn. Under reducing conditions, the divalent cupric ions are reduced to the monovalent cuprous ions. In slightly acid, neutral, and calcareous soils, the solubility of inorganic forms of Cu does not exceed 1 mg/l due to the formation of basic cupric carbonate. Commonly, in soils, solubilities of Cu are less than those predicted from solubilities of the basic carbonate, and hence more insoluble compounds or adsorption reactions most probably control the solubility of Cu in soils.

As with Zn, when salts or solutions containing Cu are applied to soil and the final pH of the system is 4.5 or greater, the subsequent concentrations of inorganic Cu in the soil solution are below the upper limits established for drinking waters. Secondary effluents rarely if ever contain concentrations of Cu which exceed standards established for drinking waters or waters for use in ground water recharge. Consequently, the probability that the use of these effluents in ground water recharge operations will produce concentrations of Cu in excess of those established for drinking waters is quite remote.

e. Chromium (Cr) - Concentrations of Cr in most rocks (some basalts and serpentine rocks are exceptions) range between about 10 and 100 mg/kg. The concentrations of Cr in fresh and sea water are normally quite low and usually less than 0.0002 mg/l. The average concentration of Cr in soils is 100 mg/kg; however, soils derived from some basalts or serpentine rocks contain concentrations of Cr as high as 3000 mg/kg.

Chromium may occur in solution in inorganic form as the chromous ion  $\text{Cr}^{+2}$ , chromic ion  $\text{Cr}^{+3}$ , chromite ion  $\text{CrO}_3^{-3}$ , chromate ion  $\text{CrO}_4^{=}$ , and dichromate ion  $\text{Cr}_2\text{O}_7^{=}$ . The chromous ion,  $\text{Cr}^{+2}$ , is quite unstable and in natural systems is rapidly oxidized to the chromic ion,  $\text{Cr}^{+3}$ . Thus, only two oxidation states, +3 and +6, are normally found in nature. The oxidation potential for Cr is such that it is unlikely that trivalent Cr would be oxidized to hexavalent Cr in natural systems.

The chemistry of Cr in soils is not well understood. However, chromium added to soil as any of its salts is thought to revert in time to quite insoluble oxides. Concentrations of Cr (total) in soil solutions normally range from <0.001 to 0.02 mg/l. In secondary effluents from Michigan, concentrations of Cr as high as 1.2 mg/l are reported (Table 1). In southern California, the maximum concentration of Cr reported by Bradford et al.<sup>(2)</sup>, and Bookman-Edmonston Eng., Inc.<sup>(6)</sup> were 0.10 and 0.14 mg/l, respectively. These data show that Cr in secondary effluents may at times exceed the upper limits established for drinking waters. Present information is not sufficiently detailed to evaluate the extent to which Cr in solution at levels from 0.05 to 1.0 mg/l are reduced when these solutions leach through soils. However, available information suggests that many soils have the capacity to remove Cr from solution to the extent that the concentration leaching through soil is less than the upper limit of drinking

water standards. In ground water recharged using diluted secondary effluents in the Montebello Forebay show, in all cases, concentrations of Cr of 0.02 mg/l or less.

f. Lead (Pb) - Lead concentration of rocks and soils commonly range from 10 to 20 mg/kg. Normal concentrations in fresh and sea water range from traces to 0.01 mg/l. Near sources of lead ores concentrations from 0.01 to 1.0 mg/l have been observed.

Lead occurs in solution as divalent and tetravalent cations. The solubility of inorganic lead in natural waters is probably limited by the formation of sparingly soluble or insoluble compounds such as lead sulfate, lead carbonate, lead hydroxide, and possibly lead phosphate. Concentrations of Pb in soil solutions are normally less than 0.01 mg/l; however, higher values have been reported for soil solutions from soil near or derived from parent materials high in lead.

Since Pb has been and is used in domestic pipes and water storage facilities, drinking waters may be contaminated with lead from conveyance and transport systems. In domestic water supplies, Pb is thought to be more soluble in waters low in total dissolved solids.

When waters containing soluble Pb are added to or mixed with soil, the concentration of Pb in solution is usually reduced. The extent to which the concentration is reduced is related to the chemical properties of the soil. Presently, however, there is not sufficient data available to evaluate critically relationships between soil chemical properties and Pb solubilities in soils.

The concentrations of Pb in secondary effluent from Michigan ranged from <0.02 - 1.3 mg/l (Table 1). In California, Bradford's data<sup>(2)</sup> and those reported by Bookman-Edmonston Eng., Inc.<sup>(6)</sup> show concentration ranges for Pb in secondary effluents of <0.003 to 0.35 mg/l and <0.01 to 0.08 mg/l, respectively. Maximum values in each of the above reports exceed the upper limits established

for drinking waters, or 0.05 mg/l. Concentrations of Pb in ground waters recharged using diluted secondary effluents in the Whittier Narrows water reclamation project were all below the limits of drinking water standards<sup>(6)</sup>. In the Flushing Meadows Project<sup>(17)</sup>, however, secondary effluents containing 0.082 mg Pb/l leached through soil showed concentrations of 0.066 mg/l in the ground water which are in excess of drinking water standards. The soil at Flushing Meadows is a sand with a low adsorption capacity for many trace elements.

The data available show that when secondary effluents which contain Pb at concentrations greater than 0.05 mg/l are percolated through some soils, the water which reaches the ground water basin in some instances also has concentrations greater than 0.01 mg/l. The data indicate that effluents with Pb concentrations greater than 0.05 mg/l should not be used in ground water recharge operations involving soil percolation unless it is demonstrated that the soil in question has the capacity to reduce the Pb concentration of the percolate entering the ground water to levels below 0.05 mg/l.

g. Mercury (Hg) - The average concentration of Hg in rocks in the earth's crust and normal soils ranges from 0.03 to 0.4 mg/kg. In fresh and sea water average concentrations are 0.00008 and 0.00003 mg/l, respectively. Soil solutions usually have concentrations of Hg less than 0.0001 mg/l. Near Hg ore deposits or industrial sources of contamination concentrations of Hg may be somewhat greater. Levels as high as 0.0005 mg/l are reported.

In solution Hg occurs in inorganic form as a monovalent or divalent ion and as complex ions or ion pairs with compositions similar to those discussed for Cd and Zn. In sea water Hg occurs in inorganic form at least in part as a divalent mercuric tetrachloride anion,  $[\text{HgCl}_4]^{-2}$ . Elemental Hg is slightly soluble in water; its solubility is governed largely by redox potentials and ionic strength. In the presence of very small concentrations of chloride (0.005 mg/l), the solubility of Hg is generally less than 0.002 mg/l<sup>(68)</sup>.

In natural waters Hg may be converted chemically or biologically to the mono- and dimethyl forms of  $\text{Hg}^{+2}$ ,  $\text{CH}_3\text{Hg}^+$  and  $(\text{CH}_3)_2\text{Hg}$ , respectively.

The concentrations of Hg in soil solutions are governed by ionic adsorption by organic and inorganic materials and by the low solubilities of Hg as phosphate, carbonate, and sulfide. When solutions containing Hg are mixed with or added to soils, the resulting solubility of Hg in the soil solution is usually less than 0.001 mg/l. Mercury may be converted from inorganic and organic forms in soil to elemental Hg and be volatilized<sup>(69)</sup>.

The concentrations of Hg in secondary waste water treatment plant effluents is usually less than 0.001 mg/l (Tables 1 and 5) and, as such, less than the upper limit for public drinking water supplies. Data from studies in the Montebello Forebay<sup>(6)</sup> and Flushing Meadows<sup>(17)</sup> show concentrations of Hg less than 0.002 mg/l in ground waters beneath soils treated with secondary effluents. Thus, the information available suggests that ground water recharge operations involving secondary effluents will not result in Hg concentrations in the ground water in excess of drinking water standards.

h. Silver (Ag) - The typical concentration of Ag in igneous and sedimentary rocks is 0.07 mg/kg. Soils commonly contain 0.1 mg Ag/kg. Concentrations of Ag in fresh and sea waters are 0.00013 and 0.0003 mg/l, respectively. Soil solutions typically contain Ag at concentrations less than 0.001 mg/l.

Although the U. S. Public Health Service<sup>(3)</sup> set a limit of 0.05 mg Ag/l for drinking waters, a more recent study panel of the National Academy of Sciences, chose not to recommend a limit for Ag in drinking waters<sup>(5)</sup>. Their reason was that Ag is rarely detected in waters at concentrations greater than 0.001 mg/l.

Data on Ag concentrations in secondary effluents are not extensive, but those which are available usually show concentrations below the limit established by the U. S. Public Health Service. It seems quite unlikely that Ag would prove limiting in ground water recharge operations.

i. Fluoride (F) - Fluoride occurs in surface rocks in the earth's crust at concentrations which range from about 300 to 750 mg F/kg. Its concentration in soils averages about 200 mg/kg. Normal concentrations in fresh and sea water are 0.09 mg/l and 1.3 mg/l, respectively.

Because of adverse physiological effects, the national panel on Water Quality Criteria<sup>(5)</sup> recommended that the maximum level for F in public drinking waters not exceed a range, depending upon air temperature, of from 1.4 to 2.4 mg/l. There are essentially no data available on the concentration of F in secondary waste water treatment plant effluents; consequently, at this time, it is not possible to evaluate F in ground water recharge operations.

j. Cyanide (CN) - The maximum concentration of total CN considered safe for public drinking waters is 0.2 mg/l. At the pH values of most waters cyanide in inorganic form occurs mainly as molecular HCN<sup>(70)</sup>. As such, if it were to persist in soils, it would be expected to be quite mobile. However, CN in soils is degraded to more oxidized forms of carbon and nitrogen. Renn<sup>(71)</sup>, for example, observed 95 percent removal of CN from waste waters when they were passed through soil columns. Removal was more complete in soils rich in organic matter than in sands.

The maximum concentration of CN observed in those secondary effluents surveyed in the present report was 0.16 mg/l and below the upper limits established for drinking water. If effluents containing this concentration of CN were percolated through soils, the concentration should be further reduced. Therefore,

ground water recharge involving percolation through soil should yield CN levels of the percolating water entering the ground waters which are well below the limits recommended for drinking waters.

#### METHODS OF SPREADING AND OPERATION FOR RECHARGE AND THEIR IMPACT ON CONTAMINANT REMOVAL

Spreading of waste water for ground water recharge is accomplished by using basins or ponds, ditches and furrows, natural stream channels, or pits and shafts. The method used is dependent upon many factors including type of soils, depth to ground water, area available for recharging, geographical location, quality and quantity of treated waste water available, and to some degree the operator's specific preference.

In order for spreading of treated waste waters to be effective in recharging the ground water, the wetted surfaces of the soil must remain aerated and unclogged. Surface area should be such as to minimize evaporation while maximizing infiltration, the quality of the waste water be such so as to minimize the inhibition to infiltration, and operational procedures should maximize the quantity of actual ground water recharge while optimizing the quality of the waste water reaching the ground water body through the removal of contaminants by soil and sediments.

The description of the various types of recharge systems which follow is after work by Bianchi and Muchel<sup>(72)</sup>, which was performed under a cooperative contract with the State Department of Water Resources.

#### Basins or Ponds

The most common method of recharging ground water in California is by impounding water in low leveed basins or ponds. The levees, usually 1 to 3 feet high, follow the ground contour so the applied water can flow from one end to the other and from one basin to another. The basins are usually constructed

upon soils having rapid permeabilities. The shape and size of the basin are such that the wetted area to gross land area is maximized while permitting the best operational cycle to provide for flooding and rest. This cycle varies from 2 days flooding and 3 days rest to 2 to 3 weeks flooding and 10 days rest in summer and 20 days in winter. While the rest portion aids in the maintenance of an aerated soil condition, plowing or scarifying the top soils may also be required to prevent clogging.

Basins are the most efficient means of recharging ground water where large amounts of land are available and evaporation is minimal. In some areas the high cost of land may be offset by dual purpose use of the basins for recreational pursuits as well as ground water recharge, as is practiced at Camp Pendleton and Santee.

#### Ditches and Furrows

Ditches and furrows with relatively flat bottoms are used to transport waste water through the project permitting infiltration to the ground water through permeable soils. Ditches and furrows may be grouped into three basic classes - 1. contour where the ditches follow the ground contours, 2. tree shaped where the main ditches successively branch into smaller canals and ditches, and 3. lateral, where a series of small ditches extend laterally from the main ditch.

Ditches and furrows usually have a low ratio of wetted area to gross areas averaging about 10%. Also, operation procedures rely largely on the rest cycle, which amount to as much as two to three weeks following a like period of flooding, to rearate and otherwise unclog the soil. Since the ditches vary from one to six feet in width, physical means of unclogging the soil may require a revamping of the system and the making of new ditches.

The advantages of ditches and furrows over basins is that water can be spread on steeper lands, the ratio of perimeter to wetted area is greater, and

the same total recharge to ground water where infiltration is retarded by substrate less permeable than surface soils may be obtained with less surface area.

#### Natural Stream Channels

Natural stream channels can be used as recharge areas where the stream bed is wide as compared to the flow channel, where the summer flow is nil, or where the total flow is small. Stream bed or channels can be improved by constructing dikes or dams across the channel permitting the water to be spread over the total channel bottom as it flows downstream. This procedure also can provide some degree of dilution of the treated waste water with natural water. Caution has to be taken during flood periods not to aggravate flood problems and to prevent backing up the stream flow or diverting it out of its normal channel.

The advantages of using natural channels are 1) the channel is usually the most porous part of the area, and thus has high infiltration rates, 2) land costs are a minimum, and 3) operational costs relate only to inspection and maintenance of dikes and weirs.

#### Pits and Shafts

Pits and shafts, as used in ground water recharge, imply rather large depth-surface area as compared to basins, ditches, and stream channels. Pits and shafts may be abandoned excavations for sand and gravel, borrow pits, or excavations planned specifically for recharge. The latter is less desirable because of the cost and problem of removal of the excavated material.

The advantages of using pits and shafts for recharge, in addition to possible saving in capital costs associated with abandoned excavation or former borrow areas, is the large area exposed for infiltration per volume of recharge and because the larger depth permits more silting before rejuvenation is needed.

### Injection

Ground water may be recharged using injection wells which may be either abandoned wells or specifically designed wells. The use of ground water recharge by injection is practiced largely where land is limited in availability or by high costs. Injection wells are sometimes used when the surface soil has extremely low permeability or is highly alkaline. Wells permit the water to be injected into aquifers located below impermeable clay layers.

Wells are the least desirable method of ground water recharge largely because of problems of pore clogging, well silting, air entrainment, bacterial and algae growths, and deflocculation caused by reaction of high-sodium water with soil particles. However, chlorination and deaeration of the water supply and a comprehensive well maintenance program have permitted the successful operation of recharge wells to prevent sea water intrusion in the Manhattan-Redondo Beach area in Los Angeles County.

### HYDRAULIC CONSIDERATIONS IN REMOVAL OF CONTAMINANTS

Hydraulic characteristics to be applied in considering the removal of contaminants by a soil system relate primarily to the rate of flow through the soils, or the amount of time the treated waste water is subject to the removal mechanisms in soils. A soil with an extremely high permeability (large gravel and small boulders, for instance) will permit treated waste waters to pass through rapidly. This high permeability may not impede the removal of biologic and carbonaceous organic materials (because the soil system will act as a trickling filter) but the removal of soluble salts and organics may be impeded because the flow time through the soil may be less than the time needed for biochemical reaction or adsorption to be accomplished. Also, the large gravels and small boulders are more chemically inert than a soil containing some sand, clay, and

silt. On the other hand, silts provide for long transit time, are chemically active, and have large surface area. However, long transit times mean small quantities of infiltrate. Desirable characteristics require time for reaction while permitting large volumes to pass. Graded sands with some gravels and silts are probably the best. Next best probably would be graded sands with a high permeability, but with sufficient intransit time to permit biochemical reactions and adsorption to take place.

While the following discourse, based on Bianchi and Muckel,<sup>(72)</sup> pertains to ground water recharge using natural or fresh waters, the principles considered in determining the optimum recharge area (other than the rate of flow through soils as described above) also apply to the use of treated waste water.

#### Relation of Geology to Ground Water Recharge

In determining whether artificial ground water recharge is physically possible in a basin or water management area, an analysis of the geologic nature and structure of the area is necessary. The geologic environment affects the following four-step sequence necessary to make artificial recharge work well:

1. An efficient intake point or area.
2. Subsurface transmission to the point of discharge.
3. Subsurface storage at the point of discharge.
4. An efficient point of discharge.

This sequence is shown in Figure 1.

The flow of water is indicated by the arrows in the recharge sequence, while storage is merely the presence of a fillable void. Limitations in any one of the flow steps will control the rate of recharge.

Ground water occurs in permeable geologic formations known as aquifers. These formations have voids that permit appreciable water to move

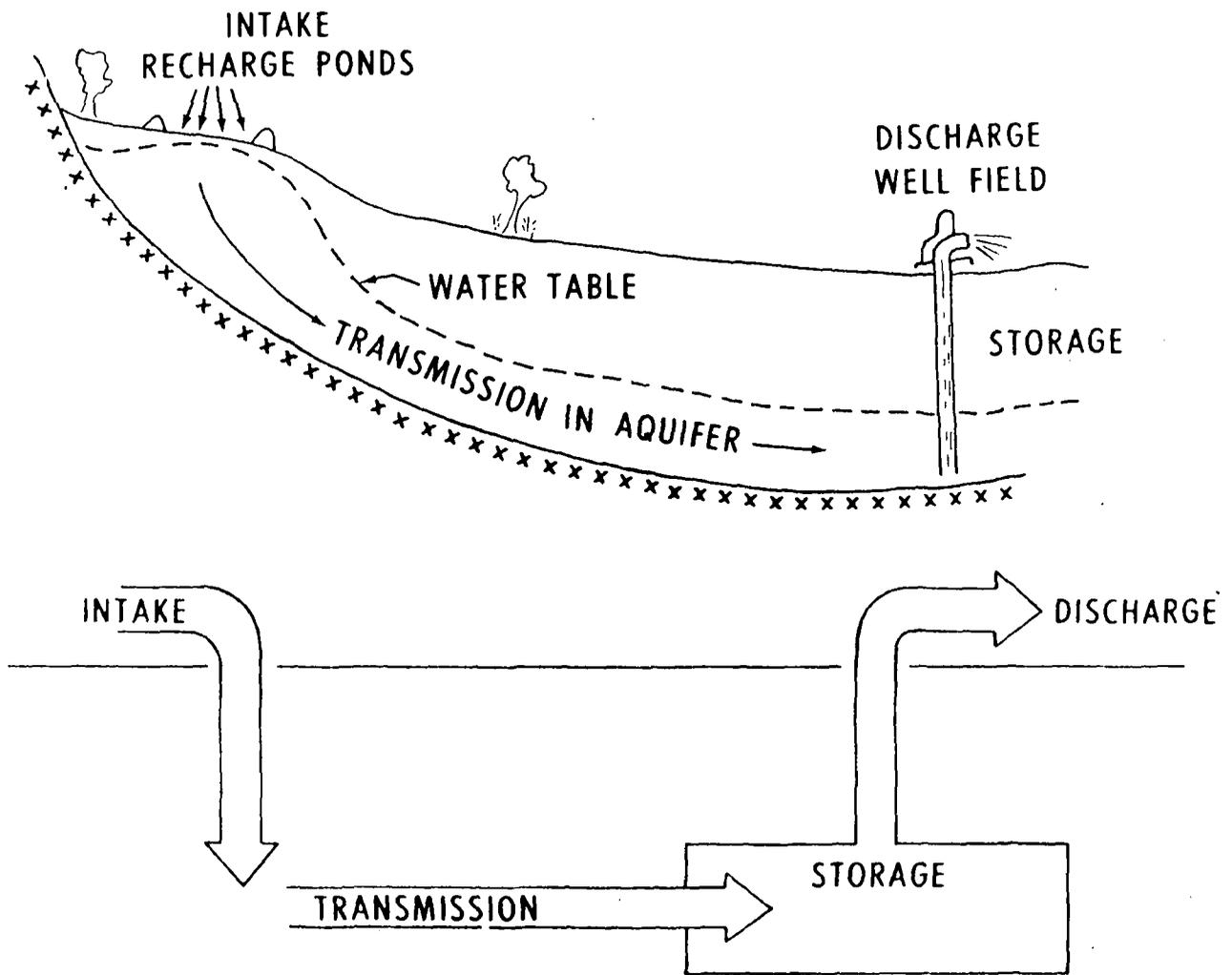


Figure 1. Sequence of Steps in Ground Water Recharge<sup>(72)</sup>.

through them under ordinary field conditions. As aquiclude is an impermeable formation that may contain water but is incapable of transmitting significant quantities of water. Clay is an example. An aquifuge is an impermeable formation that neither contains nor transmits water such as granite.

In most ground water basins, aquifers are of recent alluvial origin. The recharge capacity is controlled by the layering of the material, and is

directly related to the porous granular nature, and mode of deposition of the sediments at the surface and in the aquifers beneath the surface. It is through the surface soils and aquifers that the water must flow and in which it is stored. The larger pores of the coarser sand and gravel aquifer layers have a high hydraulic conductivity and therefore transmit ground water more readily. The smaller, more numerous pores of sandy aquifers will provide greatest volume for storage. Since silts and clays contain great amounts of small pores and little flow can occur in them (very low hydraulic conductivity), they act as confining layers and provide little storage. Thus a distinction can broadly be drawn between sediments that transmit water, those that store it, and those that impede flow almost entirely.

#### Alluvial Deposits

Nearly all the major ground water basins in the western United States are located in deposits of recent alluvium. That is, the surface soils and sub-surface aquifers were deposited in their present position when fresh water transported parent materials from adjacent mountain ranges. Such deposition occurred in recent geologic times,<sup>(73)</sup> and the pattern of placement has been altered only to a minor degree by other geologic forces such as faulting, glaciation, and volcanism. Although physical movement, other than subsidence, may have ceased, chemical changes continue primarily in the surface soil due to continual weathering, surface cultural practices, and vegetational processes.

Alluvium occurs as alluvial fans or in valley fill and flood plain deposits.

Alluvial Fans - As a stream discharges into a valley from a mountain canyon, it carries a load ranging from suspended fines to coarse rock materials. Sudden changes in stream velocity cause the selective deposition of these

materials, and forces the stream to shift its channels from one side to the other. The pattern assumed by these deposits is fan-shaped, with its apex at the canyon exit. A typical radial and cross-sectional view of such a fan is shown in Figure 2, where the idealized disposition of the sediments has been depicted by taking the extremes in grain size. The gravels, the most transmissive aquifers, were deposited during periods when streamflow was confined to the channels and velocities were swift. The clay or finest sized particles, which make up the aquiclude, were deposited in still or slowly moving water. During floodflows, great amounts of poorly sorted and mixed size material were provided as matrix for the above extremes. Because of their poor uniformity, these materials function poorly as aquifers.

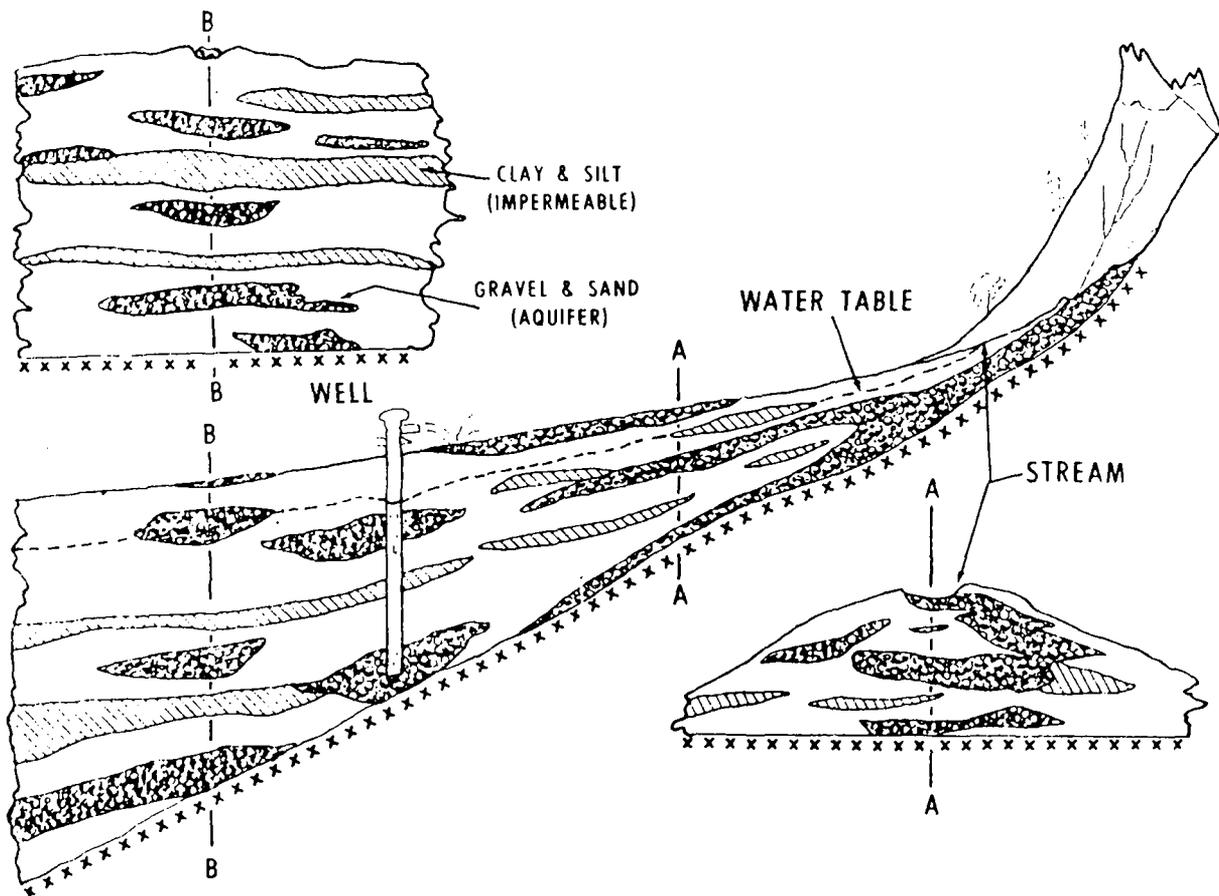


Figure 2. Cross-Sections of an Alluvial Fan<sup>(72)</sup>.

The stream's velocity is always highest in the narrow confines and steep slopes of mountain canyons. At the apex of the fan, the channel width is no longer confined, and as the stream is discharged onto the fan, its velocity decreases. The coarse gravels fall out first. The resultant flattening in slope further decreases the velocity, and as the stream flows down toward its flood plain, more sediment is dropped in a seemingly random pattern. Interconnection of gravel beds is more probable near the apex of the fan, while interconnection of clay lenses is more likely at the toe of the fan. This is illustrated in cross sections A and B in Figure 2.

These idealized pictures show where the distribution of surface soil textures and profiles best suited for ground water recharge on an alluvial fan can be expected. Regardless of the method of artificial recharge, the recharge intake rates should be highest on the coarsest, most uniform fan deposits. The chances of locating major layers of such deposits at the surface or in the profile is greatest near the apex of the alluvial fan where there is a natural water source for recharge to the fan's aquifers. Since the surface and subsurface profiles are dominated by finer textured sediments at the toe of the fan, there is limited surface intake or vertical flow into the aquifers.

Because of the abundance of coarse sediments and maximum interconnection between such deposits, it can be expected that the transmission of recharged water be most rapid at the apex. At the toe of the fan, on the other hand, the stream-channel deposits should be individually smaller in cross-section and finer in grain size, water-transmitting beds are more isolated, and the fan will be dominated by water-retarding lenses of fines, which may cut the coarser beds off from the rest of the aquifer network. However, because the total deposits are considerably deeper, and the aquifers are finer grained, more water is actually stored at the toe than at the apex of the fan.

Valley-Fill and Flood-Plain Deposits - The major valleys formed by drastic shifts in the earth's rock crust have been filled with sediments by deposition from peripheral streams. There is a significant break in slope between the fan deposits and the valley floor where the deposition characteristics of a rapidly moving water of a stream channel changes to a slow broad expansive movement of a meandering stream or the still water of a lake or marsh. When the water ends in a lake or marsh, fines can settle broadly across the relatively flat expanse of the valley floor. This valley-fill type of ground water system is generalized in Figure 3. If the lake changes in depth because the valley's discharge point changes, or subsidence of valley-fill occurs as overburden builds, the fine-textured layers resulting from the settling of fines can extend up on the fine-textured impermeable strata of the toe of the fan or interfan deposits. This creates a physical confining boundary transmitting pressures from the higher intake zones to lower lying aquifers in the valley-fill material. Drilling into these confined aquifers produces artesian wells - wells in which water rises naturally above the confining aquiclude. Because confined aquifers are under pressure, the water pumped from them does not necessarily come directly from storage next to the well but is transmitted from recharge areas on the fan and, to a small degree, is forced out by subsidence of the aquifer-aquiclude system. Thus, ground water recharge at the intake of the confined aquifer, if located, will be of no immediate consequence to a well that is far away. Surface recharge at the well may never reach the aquifer because of the aquiclude.

Shallower intervening layers of clay can also prevent vertical water movement and cause perched water tables to develop (Figure 4). Such shallow layers in the valley fill can cause poor soil drainage in areas subjected to incidental recharge resulting from irrigation developments, and make recharge by surface methods impractical.

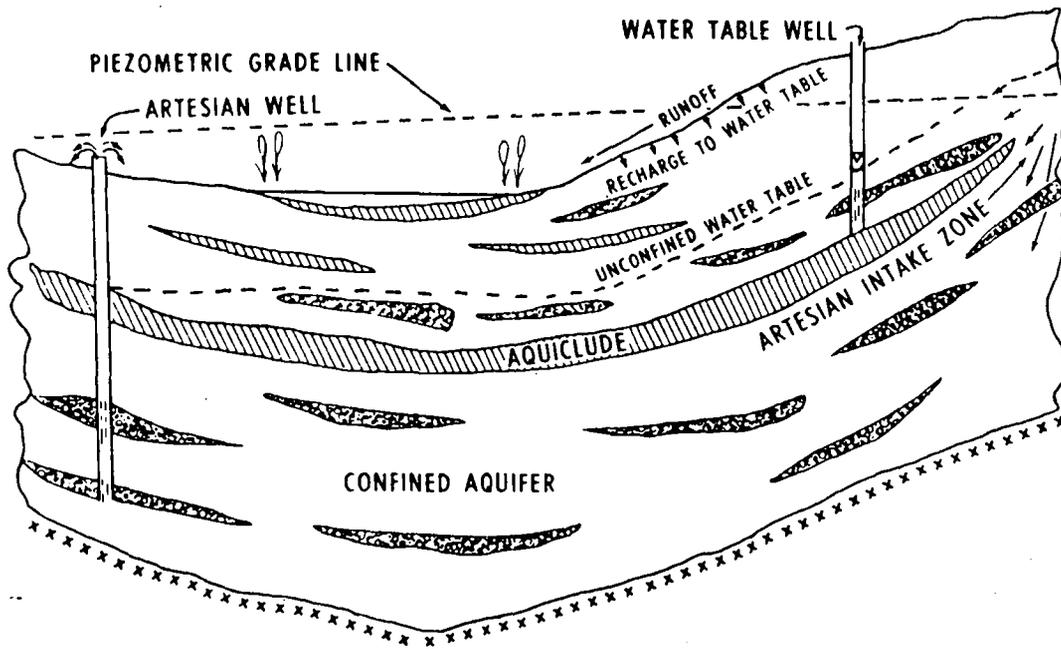


Figure 3. Cross-Section of a Valley Fill Formation (72).

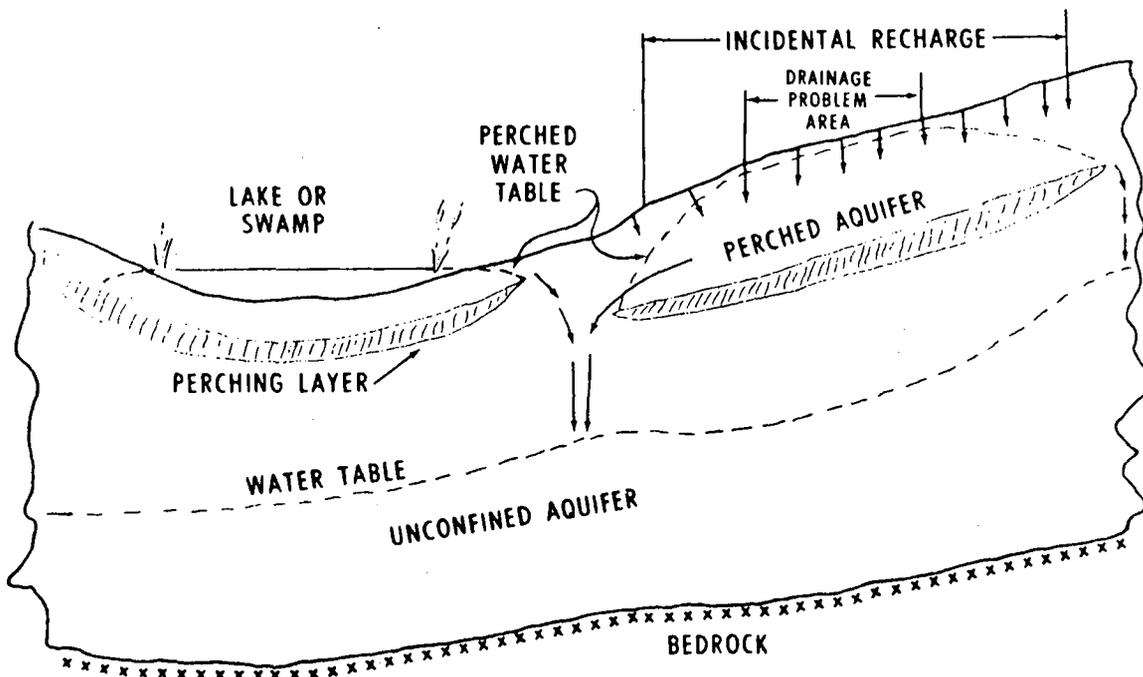


Figure 4. Cross-Section Showing Perched Water Tables (72).

There may be significant areas of interfan alluviation between major rivers. The sediments associated with flood water deposition of poorly sorted materials are mixed with the outwash of smaller drainages and seldom provide a proper recharge sequence because of the absence of well-graded aquifer layers and poor continuity.

#### Fractured and Porous Rock Systems

Other large bodies of water-bearing deposits are cemented sandstones, fractured limestone, and porous lava deposits. Water is stored and transmitted in the voids in otherwise nonporous rock. In volcanic rocks these voids are created by fracturing and venting of gases during cooling of the molten rock. In limestone and other more porous rocks, fractures are caused by shifts in the earth crust and the subsequent widening of these fissures due to water solution. The productivity of wells in these deposits varies within extreme limits, depending upon the amount of fracturing surrounding the wells. In relation to their total volume, the storage capacity of these materials is low, but water can be transmitted over long distances through interconnected fissures from large solution cavities. Therefore the storage and transmission parts of the recharge sequence can be met, but only on a selective basis. Intake rates depend on gaining access to the fissure network, which may be somewhat problematical.

#### Water Intake Rates

Most of the large-scale ground water recharge is accomplished by surface water-spreading methods. In water-spreading operations the intake step in the recharge sequence (Figure 1) is controlled by the flow of water through the first few inches or feet of soil just beneath the surface of the spreading area, basin, or pit. It is not practical to excavate, cultivate, or otherwise engineer in these surface sediments except in limited areas and to limited depths for the

purpose of developing the most efficient ground water recharge system. In a few cases excavation will allow direct recharge of a basin's ground water storage, but for the most part recharge water will have to travel through an unsaturated mantle of porous soil above the main body to storage.

This mantle or soil profile which may be a few inches thick if it lies on fractured bedrock, or tens of hundreds of feet thick if it is valley fill, is porous, unsaturated, and capable of transmitting water. The economic feasibility and engineering design of the recharge facilities and water conveyance systems are determined by the soil profile water-transmitting capacity and the area available. Recharge sites are sought which have sustained high intake rates, are close to a water source and are near to the eventual point of discharge within the ground water reservoir.

The field conditions and procedures for most efficient ground water recharge are to transmit as much water through the soil to the ground water body as quickly as possible considering the possible need for the soil system to provide treatment of the water being used for recharge purposes.

A soil profile to be evaluated for recharge should be classified as to:

1. The water-transmitting capacity of the soil.
2. Variations in this capacity with depth in the profile.
3. Expected changes in capacity in response to sediment load biological activity in the recharge water.
4. Expected changes in capacity due to the chemical constituents in the water.
5. Expected changes due to physical manipulations of the surface or subsurface.
6. Expected effects of chemical, physical, and vegetative treatments on the intake capacity, and on the water passing through the soil.

When water is spread over an unsaturated soil, the water intake rate will vary with the duration of flooding and periods of rest. This recharge cycle may be 2 days flooding, 2 days rest to 3 weeks flooding, 2 weeks rest. Control conditions for short-period entry (infiltration) are not the same as those over the long periods of recharge intake. The primary difference is the magnitude and source of the physical forces causing entry of water into the soil. During the first few minutes, the infiltration rate is determined by the very large gradient or driving force associated with the affinity of soil particle surfaces for water. As soon as the surfaces become wetted through a significant depth, the driving force is predominantly due to gravity. After gravity takes over, the changes in intake rate will be primarily associated with the water-transmitting properties of the first few inches of soil. The physical, chemical, and biological conditions that control the water-transmitting character (permeability or hydraulic conductivity) of this layer of soil over the period of recharge determine the recharge efficiency of the site.

#### Effect of Particle Size and Distribution

Soils are classified according to particle size distribution based on the percent of three size fractions—sand, silt, and clay. Table 8 indicates the range of diameters considered in the classification. This class description is called the texture of the soil. The name given to the soil - sand, silt, loam, clay loam, or clay - is determined by the proportion of each particle size in its composition.

TABLE 8<sup>(74)</sup>

U.S. DEPARTMENT OF AGRICULTURE SCALE FOR  
PARTICLE-SIZE ANALYSIS OF SOILS

[Soil Conservation Service Classification]

| Name of fraction      | Limiting mean effective diameter |        |      |     |
|-----------------------|----------------------------------|--------|------|-----|
| Fine gravel . . . . . | 1/2 inch                         | to     | 2    | mm. |
| Sand:                 |                                  |        |      |     |
| Very coarse. . . . .  | 2                                | mm. to | 1    | mm. |
| Coarse . . . . .      | 1                                | mm. to | 0.5  | mm. |
| Medium . . . . .      | 0.5                              | mm. to | .25  | mm. |
| Fine . . . . .        | .25                              | mm. to | .10  | mm. |
| Very fine . . . . .   | .10                              | mm. to | .05  | mm. |
| Silt. . . . .         | .05                              | mm. to | .002 | mm. |
| Clay. . . . .         | Less than                        |        | .002 | mm. |

Even though it is impossible to evaluate field soil permeabilities exactly from the soil texture, because field structure, particle aggregation, or even biological activity in the soil can override the influence of texture alone on permeability, texture is a starting point for classification of surface soil permeability in a ground water basin.

Since high rates of water intake are required for efficient ground water recharge, high surface soil permeability is a requirement in site selection. Generally high intake rates are associated with field soils that are single grained and contain a high fraction of the coarse grain sizes (sands and gravels). Any gradation in particle size will fill pore space with smaller particles that will impede water flow and decrease the permeability. The poorest permeability would exist when particles are so graded that successively smaller sized particles pack within the pores of the next size. The ideal recharge soil, one having relatively large particles of uniform size, can be approached in surface or

buried stream channels, dunes, and beach deposits. These areas can be of major significance in the ground water recharge, but usually are small in area. At most sites, surface soils will have been subjected to variations in sedimentation, to weathering, and to soil-forming processes that produce a broad distribution of particle sizes.

#### Effect of Pore Size Distribution

The transmission of water through the soil surface is affected by the particle size distribution and the continuity of the pores in the soil just as is true for aquifers. The larger and more continuous the pores in a unit volume of soil, the greater the permeability but the smaller the total porosity. A high recharge rate over an extended period of time depends on a high proportion of large pores that remain capable of transmitting water through a long recharge period. Many attempts have been made to relate permeability, recharge, and infiltration rates to the measured total porosity or to some power of the total porosity. Baver<sup>(75)</sup>, however, suggests an empirically determined porosity factor related to the volume of pore water. The apparent volume of noncapillary pores is measured by placing a given soil sample in a core on a porous plate and measuring the volume that is displaced as the suction (moisture tension) is increased incrementally from 0 to 300 cm.-H<sub>2</sub>O. The results are plotted and the first inflection point of the cumulative volumetric moisture release curve is taken as the moisture tension in the sample and volume moisture released from the noncapillary pores. The percolation rate is measured through these same samples and related to the porosity factor as shown in Table 9. The porosity factor assumes the percolation rate to be directly related to the volume of large pores and inversely proportional to the tension (expressed as the log of the tension in cm.-H<sub>2</sub>O) required to drain them.

TABLE 9<sup>(72)</sup>

## PERCOLATION AND NONCAPILLARY POROSITY OF VARIOUS SOILS

| Soil Type                | Moisture tension<br>at flex point<br>cm-H <sub>2</sub> O<br>A | Noncapillary<br>porosity at<br>flex point,<br>percent of<br>soil volume<br>B | Percolation<br>rate<br>cc./10 min. | Porosity<br>factor<br>B/log A |
|--------------------------|---|--|------------------------------------|-------------------------------|
| Genesee silt loam:       |   |  |                                    |                               |
| Sample 1.....            | 35.7  | 14.7   | 205                                | 9.5                           |
| Sample 3.....            | 31.6  | 13.0   | 137                                | 8.7                           |
| Cecil Clay:              |   |  |                                    |                               |
| Sample 1.....            | 44.7  | 12.0   | 127                                | 7.3                           |
| Sample 2.....            | 56.2  | 13.5   | 136                                | 7.7                           |
| Compressed.....          | 63.1  | 5.5  | 6                                  | 3.1                           |
| Davidson Clay:           |   |  |                                    |                               |
| A horizon.....           | 44.7  | 6.0  | 17                                 | 3.6                           |
| B horizon.....           | 44.7  | 8.0  | 28                                 | 4.8                           |
| B horizon, compressed    | 100.0   | 6.0  | 4                                  | 3.0                           |
| Chenango loam.....       |   |  |                                    |                               |
| Compressed.....          | 141.0   | 11.0   | 50                                 | 5.1                           |
|                          | 112.2   | 6.0  | 2                                  | 2.9                           |
| Iredell sandy clay loam: |   |  |                                    |                               |
| A-1 horizon.....         | 50.1  | 9.0  | 65                                 | 5.3                           |
| A-2 horizon.....         | 56.2  | 13.0   | 131                                | 7.4                           |
| B horizon.....           | 35.5  | 9.2  | 36                                 | 5.9                           |
| Paulding clay.....       | 39.8  | 11.5   | 93                                 | 7.2                           |
| Wooster silt loam...     | 398.0   | 10.0   | 10                                 | 3.8                           |
| Quartz sand:             |   |  |                                    |                               |
| (40 to 100 mesh)...      | 35.5  | 25.0   | 850                                | 16.1                          |
| (40 to 60 mesh)...       | 31.6  | 22.0   | 675                                | 14.7                          |
| (20 to 40 mesh)...       | 17.8  | 22.0   | 1216                               | 17.6                          |

### Soil Structure and Aggregation

Because of the random deposition and in-place weathering, most soils contain the entire range of particle sizes. They also contain organic constituents left by plant growth, inorganic salts brought in with irrigation water, or left by the evaporation from previous high water tables. Not all soil particles are inert. The larger the fraction of clay particles, the greater will be the surface area in a unit volume of soil. This surface area is capable of developing both attractive and repulsive forces toward other particles, depending upon the other chemical constituents present. The strength and direction of these forces control the spacing between the particles and, therefore, the soil's permeability to water. If the net effect is to draw the particles together in a combination that resists breakdown in the presence of water, the soil is said to have good water-stable aggregate structure. Field soils can have a high fraction of clay, yet transmit water readily because of this aggregate structure (Table 9).

On the other hand, soils with good particle size distribution can be nearly impermeable if the small particles are kept dispersed by mutually repulsive forces.

Organic constituents in soils are the most important contributors to the production of water-stable structure. The accumulation of biodegraded products of vegetation and roots in the soil pores, accompanied by the physical realignment of the individual particles by drying, tillage, or root growth, glues the particles together into aggregates, which may contain few large pores, but the pores between aggregates will be similar to those between single-grained particles of like size.

### Effect of Chemical Constituents

The effect of dissolved inorganic constituents on the maintenance and magnitude of recharge intake rates is directly related to the chemical quality of the water to be spread. Only soils with high initial intake rates

are used for recharge, but quite soon after large-scale recharge begins, all but the most insoluble salts will be leached from the surface by the large volumes of water that pass through it. The soil then will be in chemical equilibrium with the water being recharged.

Dispersion of the clay mineral fraction of a soil results from the formation of a zone of polarized water molecules around the individual clay particles. The thickness of this zone of hydration depends on the charge of the cations (+) that associate themselves with the negatively (-) charged surface of the clay. This association is called cation adsorption. The cations that predominate in natural waters, and absorbed on soil surfaces, are calcium ( $\text{Ca}^{++}$ ), magnesium ( $\text{Mg}^{++}$ ), sodium ( $\text{Na}^+$ ), and potassium ( $\text{K}^+$ ). Generally monovalent cations ( $\text{Na}^+$  and  $\text{K}^+$ ) disperse soils because of their high level of hydration, and divalent cations ( $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ ) flocculate, or weakly aggregate, because of their low hydration and the possibility of sharing their double charge between clay particles. The dispersion of a soil when recharged with a natural water containing all these ions depends on a weighted ratio of the cations called the Adjusted Sodium Adsorption Ratio, or Adj SAR, and since potassium ( $\text{K}^+$ ) is normally not present in large amounts,

$$\text{Adj SAR} = \frac{\text{Na}^+}{\sqrt{(\text{Ca}^{++} + \text{Mg}^{++})/2}} [1 + (8.4 - \text{pH}_c)]$$

where  $\text{Na}^+$ ,  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$  are concentrations in water in milliequivalents per liter and  $\text{pH}_c$  is a calculated value based on the chemistry of carbonic acid and calcium carbonate and on the  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ , and  $\text{HCO}_3^-$  concentrations in the water being used<sup>(76)</sup>. Preamability of the soil begins to become adversely affected when the adjusted SAR exceeds 6.0, and becomes a severe problem when it exceeds 9.0.

The bicarbonate and carbonate anions,  $\text{HCO}_3^-$  and  $\text{CO}_3^{=}$ , can also appreciably affect the chemical equilibrium by the precipitation of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  in the soil, thus increasing the relative amount of  $\text{Na}^+$ . This is particularly important under irrigation or in recharge, where frequent intermittent drying concentrates the soil solution at the soil surface. Normally where flooding is carried out over extended periods,  $\text{Ca}^{++}$  and  $\text{CO}_3^{=}$  concentrations will be in equilibrium with the water being spread.

Total electrolyte concentration can also affect the hydration of clays and, thus, intake rates. If the soil is not in equilibrium with the total salt concentration of the water, the intake will decrease as the soil solution concentration decreases. If poor-quality waters, high in dissolved salts, are recharged (as in waste water disposal), the high electrolyte concentration will decrease clay hydration and dispersion and intake rates will remain high even if the SAR is above 15. Subsequent spreading of low-concentration, low-SAR water can seal the area through dispersion after the leaching of the surface.

#### Effect of Clogging and Particle Realignment

While the surface soil may rapidly come to chemical equilibrium with the quality of the water recharged through it, it will never reach a physical equilibrium. Any individual soil particle is very slowly but continually subjected to forces that would reduce it to its lowest energy state. In other words, the only path is down.

Continued downward water flow through any soil provides internal transport of suspended as well as dissolved matter. Particle movement can result only in a progressive decrease in the size continuity and number of larger water-transmitting pores in a soil profile. The smaller particles are moved by the water until they become lodged or sieved out of the stream in restrictions between the larger particles; this in turn traps even smaller particles in succession.

There is a continuing supply of loose particles, even in well-aggregated soils. The most significant source is the suspended load of the recharge water itself. Suspended silts or clays can lodge on and in the surface of a sandy recharge area when flood waters are spread. This thin layer of fine particles effectively seals the soil surface.

Surface maintenance of the spreading basins breaks down the aggregates and releases the individual particles. Wetting and drying, freezing and thawing, and chemical weathering, all continuously subdivide the aggregates and soil particles. Provisions must be made for maintaining the open pore space in the soil of a recharge area if its capacity is to be maintained.

#### NEEDS FOR ADDITIONAL RESEARCH

While much is known about the behaviour of soil systems in removing contaminants from waste waters which have received at least secondary treatment, there still remains a large field of additional research that must be done before reclaimed waste water can be used for ground water recharge for indirect reuse for domestic purposes with complete assurance that no adverse effect to the public health will occur. The following discussion presents research needs that will lead to more complete knowledge of the removal of biological and chemical contaminants from secondary treatment plants effluents by soil systems. No attempt has been made to establish any priority relationship among the various proposals.

#### Biological Contaminants

The nature of bacterial and pathogenic contamination in public water supply is somewhat different from many other contaminants of water (i.e., trace elements and common minerals, etc.) whose removal by conventional water purification processes is rather ineffective. With proper monitoring and treatment (by disinfection), recharged ground water can always be ensured free of pathogens and safe for domestic consumption. In fact, many surface waters used as sources

of public water supplies have much higher frequency and magnitude of bacteria detection than has been found in recharged ground water. Unlike mineral constituents (such as TDS) in water, bacterial density will not increase with each cycle of use. Therefore, bacteria and pathogens in water are not likely to become a limiting factor of reusing recharged ground water.

However, the long-term public health effect of small quantities of microorganisms introduced into the aquifer is not fully understood. The lack of detailed information on microbial impact on the suitability of using recharged water for public water supply is due primarily to insensitive, inconsistent, and sometimes not quantitative detection techniques.

In viewing the recent advances in detection techniques (especially for virus), new research programs in the following areas are suggested:

- (1) Statistical analysis of public health consequences of small quantities of bacteria and/or viruses present in recharged ground water and the aquifer.
- (2) Identification of potentially toxic and odor causing substances resulted from microbial degradation in recharged aquifers.
- (3) Possible virus desorption and reactivation phenomena under field conditions.

#### Organic Substances

The methods of concentrating or collecting soluble organic substances in waters are not ideal. One cannot be sure how much of the substances found are actually present in the original water or are synthesized by microorganisms decomposing the organic substances during the concentrating or collecting procedure. Soluble organic substances can also be lost by precipitation during low temperature concentration. In the carbon filter adsorption procedure, some substances are not adsorbed and others are not released by the extraction procedures used.

The present evidence indicates that the bulk of the water soluble substances in waters consists of relatively low molecular weight polymeric substances. The constituent units of these polymers, as in soil humus, could be so numerous and diverse that nearly every molecule could be different from every other molecule. Characterization of these polymers, therefore, should be based on various chemical and physical properties and on identification of the structural units. They could be separated from the more simple organics and salts and into various molecular weight fractions by Biogel filtration. Constituent amino acids could be determined upon 6 N HCl hydrolysis and constituent sugar units of polysaccharides upon less drastic acid hydrolysis. Phenolic and other aromatic constituents could be determined following various oxidative and reductive degradation procedures. Other properties of the polymers could be studied by functional group and exchange acidity reactions.

Little information appears to be available on the movement of soluble-organic substances in waters injected directly into an aquifer. Tests in this area need to be made with both chlorinated and unchlorinated water at the beginning of the injection process compared with later periods after sufficient time has passed to allow the development of an organic-microbial slime zone near the area of injection. For these tests known organic substances could be added to the waste waters.

Therefore, the following suggested research studies in soluble organics could be of great value:

- (1) Development or refinement of more specific methods for concentrating and determining quantities of known objectionable soluble organic compounds which may be found in waste waters in an unaltered form.

- (2) Characterization, separation, and constituent determination of organic polymers in waste waters based on various chemical and physical properties and on identification of the structural units.
- (3) Determination of whether certain molecular weight fractions of organic polymers will impart taste or odor to water.
- (4) Movement of soluble organic substances in ground water aquifers recharged directly with chlorinated and unchlorinated waste water containing known and unknown organic substances.

### Nitrogen

Experience and experiments in ground water recharge suggest that land spreading of reclaimed waste waters containing total N greater than 20 mg/l, mostly in the  $\text{NH}_4^+$  form, should be diluted by at least an equal volume of water containing  $\text{NO}_3^-$ -N concentration of less than 2 mg/l. When water for dilution is not available and the secondary effluent meets all other standards for drinking water quality, some tertiary treatment to remove N before land spreading might be justified. The adaptation of N removal techniques developed for tile drainage effluents<sup>(77)</sup> to these secondary effluents is a possible means of pretreatment prior to land spreading.

The effectiveness of N removal during soil infiltration of nitrified reclaimed water is uncertain. If N removal is effective when  $\text{NO}_3^-$  is the dominant form of N in the input water, the increased costs of producing the nitrified water can be compared with the increased costs of tertiary treatment to remove N from effluents that have  $\text{NH}_4^+$  as the dominant form.

An understanding of the fate of N species during direct injection of reclaimed waters into aquifers is needed before this method of recharge is accepted. Knowledge of reactions of  $\text{NH}_4^+$  with silts and clays in the aquifer and

of microbiological transformation in the aquifer would help in making an evaluation of the desirability of direct injection for recharge in individual situations.

The following research studies involving nitrogen in treated waste water to be used for ground water recharge could produce much valuable needed knowledge on the ability of soil systems to act as further nitrogen contaminant removal processes:

- (1) Development of a soil pretreatment system from which the effluent could be collected and spread in infiltration basins.
- (2) Adaptation of nitrogen removal techniques developed for tile drainage effluents to secondary waste water treatment plant effluents as a means of pretreatment prior to land spreading.
- (3) Determination of the effectiveness of nitrogen removal during soil infiltration of nitrified waste water.
- (4) Determination of nitrogen species during direct injection of treated waste water into aquifers.

#### Soluble Salts

The problem of soluble salts in the use of reclaimed waste water for ground water recharge can be solved best by securing a water of low TDS for the municipal supply and by modifying municipal uses to decrease the soluble salt increment. Desalination research projects of the University of California Water Resources Center and in other places in the U.S.A. and in foreign lands are pertinent to the problem of removing salts from treated municipal waste waters. But, increased research in desalination as it might be applied to treated waste waters for ground water recharge does not seem appropriate.

Our knowledge of the reactions of soluble salts with soils and soil materials is fairly well known. Of course more research into details of these

reactions during recharge using flooding and drying cycles could be academically interesting but would probably not be of value in the planning and operation of a recharge system. Also, more research dealing with the effect of N conversions on TDS would not seem to be appropriate. Normal monitoring of recharge operations of various kinds will provide a suitable practical answer for this relationship.

Therefore, since little, other than for academic and curiosity value, research into soil systems as related to treating soluble inorganic salts does not appear to be needed to understand their effect using treated waste water to recharge ground water.

#### Trace Elements and Heavy Metals

Available data show rather wide variation in concentration of trace elements which occur in samples of secondary waste water treatment plant effluents collected at different times over an extended period. To critically evaluate the trace element load resulting from the use of secondary effluents in ground water recharge it is essential to know the mean concentration of the total volume of treated waste water used. Although data show that excessive concentrations of certain trace elements occur periodically in secondary effluents, their source or cause are not presently known. However, monitoring programs could be designed to obtain more complete detailed data on trace element concentrations of effluents. Also, to implement corrective measures, surveys of the waste water sources could disclose the causes of variation which occur in trace element concentrations of secondary effluents.

There is practically no information available to evaluate relationships of soil chemical, mineralogical, and physical properties to changes which occur in trace element concentrations of treated waste waters as they leach through soils. Since treated waste water used for ground water recharge involving percolation will pass through many soil types, including sands and

gravels, it is necessary to elucidate the factors that control the solubility of trace elements in each representative soil type.

Information suggests that organo-metallic complexes may form in secondary waste water treatment plant effluents. Since these complexes will influence the solubility and movement of trace elements through soil, the nature of these complexes, their stabilities, and reactions with representative types of soils need to be known.

Most of the information available on ground water recharge involving percolation through soils is based upon short term studies. It is expected that ground water recharge projects will entail the use of soils above ground water basins for rather long periods of time. Since waters percolating through soils tend to require long periods of time to equilibrate with soil, long term (decades) consequences of ground water recharge utilizing soil percolation need be determined.

Suggested research studies needed to assess the effect of trace elements and heavy metals on the use of treated water to recharge ground water basins include the following:

- (1) The critical evaluation of the trace element load resulting from the use of treated waste waters in ground water recharge.
- (2) Evaluation at relationships of chemical, mineralogical, and physical properties of soils to changes which occur in trace element concentrations of treated waste waters as they leach through soils.
- (3) Determination of the influence organo-metallic complexes in treated waste water will have on solubility and movement of trace elements through soils, the nature of these complexes, their stabilities, and their reactions with representative types of soils.
- (4) Determination of long-term (decades) effects of ground water recharge using treated waste water.

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SECTION V

IDENTIFICATION AND MONITORING OF WASTEWATER CONSTITUENTS

Prepared by:

Department of Health



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WATER QUALITY MONITORING

Water quality monitoring has been defined<sup>1</sup> as "planned, periodic measurement or recording of the physical, chemical and biological conditions of the aquatic environment..."

It is an essential tool in an effective water resources management program and (1) provides the information to direct water quality control processes, (2) establishes water quality and environmental baseline and trends and, (3) develops the relationships among causes and effects of water quality changes in the environment.

The development of an effective monitoring program must consider a number of factors which are related to the types of constituents or water quality characteristics which are of concern, the type of water (surface water, groundwater, wastewater, etc.) and the available sampling and analytical techniques. A monitoring activity, for example, which is directed at the detection of accidental spills of oily wastes to a surface water would involve a completely different program than one directed at determining the trends in mineral quality of waters in a major groundwater basin. The following is a discussion of the major types of water quality monitoring programs and their principal uses.

Fixed Station Monitoring Networks

The fixed monitoring network is a system of selected stations which will provide well defined histories of the physical, chemical, and

biological conditions of waters. As generally employed, it is not responsive to rapid fluctuations in water quality and is more useful in identifying gradual and ponderous changes in quality. A considerable effort must go into the selection of the network stations to assure that representative water quality information will be obtained and that the stations will provide the information on water quality influences that is needed. A proper selection of sampling stations might well necessitate a significant study effort involving a complete sanitary survey of the area to identify all activities which may have an effect on water quality and an intensive sampling program to determine water quality characteristics with some accuracy. For a surface water network, the following typical locations have been recommended for a fixed station monitoring network.

Fixed Station Network - Station Selection\*

| <u>Location</u>                                      | <u>Purpose</u>                              |
|--|---|
| 1. Site of most pronounced water quality degradation | Effectiveness of pollution control measures |
| 2. Major inputs and outlets to lakes and estuaries   | Nutrient inputs and releases                |
| 3. Critical locations in lakes and estuaries         | Eutrophication problems and control needs   |
| 4. Upstream and downstream from major discharges     | Effectiveness of pollution control measures |
| 5. Upstream and downstream from major land-use areas | Non-point sources of pollution              |

\*Summarized from: "Model State Water Monitoring Program"  
Environmental Protection Agency, June 1975

Fixed Station Network - Station Selection (continued)

| <u>Location</u>                             | <u>Purpose</u>                                 |
|---|--|
| 6. At confluence of major tributaries       | Impacts of tributaries on quality              |
| 7. Representative sites in main-stem rivers | Baseline quality and trends                    |
| 8. Major use areas                          | Health protection and quality characterization |

Fixed station monitoring networks is the basic monitoring approach used for surface and groundwaters by the California State Department of Water Resources. The overall objectives of the program are to "measure and make known the base-level quality of ground, surface and wastewater resources of the State, and to note changes in base-level quality of these water resources as they may be affected naturally or by man's activity."<sup>2</sup> The program is principally directed at monthly sampling and analysis of mineral constituents of water which are the constituents least susceptible to diurnal effects and short-term changes. Consequently, single once-per-month samples over a sufficient period may adequately identify the long-term trends or changes in these conservative constituents.

Analyses for certain heavy metals and other elements (arsenic, cadmium, chromium, barium, copper, iron, lead, mercury, and others) are carried out at less frequent intervals (semiannually) unless a problem situation has been found to exist with an element.

Although fixed-station monitoring network programs have been used to gather information on such water quality characteristics as bacteriological quality, dissolved oxygen, temperature and nutrients, these types of quality characteristics are better defined by intensive sampling programs.

A fixed-station monitoring network is more difficult to develop for a groundwater system than one for a surface water system. It must consider:

1. Sources of pollution or influences on groundwater quality.
2. The physical, chemical and biological characteristics of the pollutants.
3. Changes in water quality characteristics in horizontal and vertical movement through the soil.
4. The quality characteristics of the groundwaters.
5. The pattern and rate of movement of groundwater.
6. Hydrologic characteristics of the area.
7. The present and intended use of the groundwater.

The cause-effect of sources of groundwater pollution on groundwater quality is not as direct or demonstrable a relation as for surface water because of the above factors. Percolating pollutants may either ride above or sink below the natural groundwaters and may either physically displace the groundwater in an area or form a plume which moves downflow with the groundwater movement.

Instead of tailoring the sampling station and sample collection to the specific needs of the situation as may generally be done in surface water monitoring, the groundwater sampling network may have to depend principally upon existing wells. It is essential to have thorough and accurate information on the underground formation, location and extent of well perforations and the principal aquifers supplying the well.

#### Intensive Surveys

Intensive surveys are a form of monitoring which are useful in the determination of the status of non-conservative water quality characteristics such as bacteriological quality. The program involves the collection of a large number of samples in a short period of time from a large number of sampling stations in a specified study area. The principal example of an intensive survey is the sanitary survey which is directed at shellfish growing areas, water contact sports areas or sources of domestic water supply. The sampling must be accompanied by a thorough examination of all possible influences on water quality in the study area. The development of a large amount of data over a short period will provide the statistically sound basis for evaluation of results of data with inherent wide fluctuations such as coliform bacteria data. The intensive study will also provide useful information on diurnal fluctuations in water quality such as pH, temperature and dissolved oxygen variations.

The principal use of intensive monitoring is with surface waters, however, intensive groundwater monitoring has been employed to

determine the extent or movement of degraded water in a groundwater basin. At Barstow, intensive groundwater studies at several year intervals, using parameters which reflected the effects of a pollution source, were able to trace the extent and movement of degraded water.

#### Self-monitoring Programs

Self-monitoring programs require the waste discharger to participate in the overall monitoring program of a water system. Under such programs, the regulatory agency establishes limits on pollutants or pollutant effects that can be present in an effluent and/or the receiving waters. These discharge requirements must be met by the discharger and he is required to conduct a program of routine monitoring and to submit reports to the agency to ensure compliance with the requirements. This form of policing action permits the agency to keep a continuous record of the quantity of pollutants entering the water system, and the effectiveness of treatment being applied by the discharger. Through this procedure the regulatory agency can, in many cases, isolate the source of degradation of a water system. This is particularly true with the acute degradation of surface water systems which may result in conditions such as fish kills or aesthetically poor drinking water (e.g., taste and odor).

Self-monitoring by dischargers is extremely important for groundwater systems. Because of the problems with locating and following pollutants through the underground, degradation can be widespread before the problem becomes known. In severe cases this could cause irreparable damage to a groundwater basin rendering it unusable.

Through an intensive self-monitoring program, information on pollutant discharges can be made available before serious degradation is allowed to occur.

#### Remote Sensing

Remote sensing as a monitoring device involves the use of photographic methods as a means of locating and following pollutant movement. The most common examples include aerial photography using infrared imagery and the ERTS satellite program. Remote sensing, however, is limited in application to surface water systems only.

#### Indirect Monitoring

Indirect monitoring is designed to monitor the effects of pollution on the aquatic environment. An effective indirect monitoring program requires accurate baseline data on environmental conditions such as species diversification (types and population of organisms), and ambient water quality. The monitoring program should not be restricted to effects on macroorganisms (e.g., fish, reptiles, etc.) but should also include microorganisms as well. As with remote sensing, this form of monitoring is limited to use on surface water systems.

#### Data Management System

The information generated by an effective monitoring program would require the development of a data management system. Such a system would have to be flexible and adaptive and must assemble, schedule,

and supervise the processing of all data produced under the monitoring program. An essential element to an effective system is a data center which functions not only as the repository of information but which can operate as an effective data control and preparation center. The center should contain a complete inventory of all environmental sampling programs of separate agencies but it is not essential that all data be recorded or retained.

For data required for the essential environmental monitoring program a hard data storage system is needed, and the data must be prepared in the forms needed by the users and the evaluation unit.

An essential component of the data management system is effective and timely evaluation. The evaluation may be solely qualitative where the presence or absence of a specific concentration of a harmful substance is to be noted. However, in order to determine changes or trends, control charts, trend lines or the like must be employed.

The use of such trend charts for predicting or detecting undesirable changes is based on assumptions that (1) there may be natural changes or fluctuations in quality and (2) the range of such changes will lie within predictable limits unless there are changes in external influences. It should be noted that several years of record may be needed to establish baseline conditions, however, after the baseline quality and its normal fluctuation has been established, the maintenance of such control charts will provide immediate interpretation of the significance of new data. Through the use of warning limits based

on statistical analysis of normal data spread.

Continued evaluation of the monitoring program itself should be part of the data management system. Important to this evaluation is the relevance of the monitoring sites and water quality parameters which will reflect the existing situation. Periodic reconnaissance surveys should be undertaken as a means for developing this information.

Modification of the use of a water under surveillance will be important in the evaluation process. Changes (e.g., agricultural to domestic) which will create a higher degree of health risk, require an intensification of the monitoring program. Monitoring sites and water quality parameters must be chosen to reflect this use and immediately incorporated into the overall program. It is also important that background data be developed to establish the baseline prior to the higher use.

#### MONITORING PROGRAMS FOR GROUNDWATER RECHARGE

Groundwater recharge projects may be considered to be point sources of groundwater pollution. Consequently the monitoring considerations associated with pollution from point sources is covered here.

##### Point Source Pollution Monitoring

The effect of point sources of pollution can be determined by means of monitoring wells which are located downstream from the potential pollution source. Such monitoring could be applied to solid waste disposal sites, oil field brine pits, oxidation ponds or other land

disposal operations and the like. The extent of the monitoring program will depend on the type and size of the pollution source and the need for protection of the groundwater basin. The location of monitoring sites in the typical order of importance would be:

1. Downstream from pollution source.

Wells in proximity to the pollution source would provide information on adverse effects before significant widespread degradation could occur.

2. Near downstream use areas.

Monitoring wells further downstream from the pollution source would provide information on any trends in quality near points of use which might be due to the pollution source.

3. Water supply wells.

Monitoring of wells actually in use would provide similar information without benefit of providing any time for correction prior to arrival of the pollution effect at wells in use. Cost considerations may require use of existing wells.

4. Percolate monitoring.

The monitoring of percolating water from a potential pollution source may be a more important aspect of a monitoring program than some of those given above; however, there are several drawbacks. The percolate monitoring may be

difficult to achieve, changes may occur in percolate quality below the sampling point, and the effects of dilution, dispersion and quality changes in horizontal travel may make the interpretation of the significance of the results uncertain.

Beyond this, groundwater monitoring could be extended to include the determination of the spread, movement and change in distance and time of pollutants and groundwater flow patterns.

#### Frequency

The frequency of monitoring would depend on the type of potential pollution and the distance from the source. Sampling for changes in a conservative constituent such as chloride in a well which is distant from a pollution source would require only annual or perhaps seasonal (quarterly) samples.

Rapidly changing constituents might require weekly sampling at a nearby well. Typical frequencies would be:

|                           |   |                       |
|---------------------------|---|-----------------------|
| Pollutant quality         | - | daily or weekly       |
| Near pollution source     | - | monthly               |
| Far from pollution source | - | semiannually          |
| Monitoring for trends     | - | quarterly or annually |

#### Tracer Studies

Study of the movement of substance in the groundwater

may be valuable in laying out an effective monitoring program. It will provide information on the direction and rate of travel of groundwater and the dispersion and dilution of a pollutant. Substances used for tracer studies include salt, sugar, dyes and radioisotopes.

#### Geologic Conditions

It is essential to have information on underground conditions such as the location and extent of aquifers and impermeable strata, faults and other impediments to groundwater movement, areas of direct hydraulic communication with the surface, groundwater surfacing, and narrowing areas in order to define the appropriate location and details of monitoring wells. General information is available for most areas from past studies and specific information can be obtained from well logs.

#### Specific Groundwater Monitoring Programs

At the two major groundwater recharge operations in the State, the Montebello Forebay recharge operation and the Orange County Water District's injection project (Water Factory 21), programs have been established to monitor the quality of waters recharged to the respective groundwater basins as well as the groundwater under recharge. The following is a summary of these monitoring programs:

##### Montebello Forebay

A program has been established for the Central and West Basin Water Replenishment District to monitor the individual recharge water supplies, mixtures of the individual recharge waters and the

groundwater within the forebay as well as basinwide. The following is a summary of the monitoring program including constituents being sampled, sampling frequency and location and agencies responsible for performing the work.

**TABLE 1**  
**CATEGORIES OF CONSTITUENTS**  
**FOR WHICH ANALYSES ARE TO BE MADE**

| Category                       | : Constituents Included   |
|--------------------------------|---|
| <b>Total Dissolved Solids</b>  | <b>Total Dissolved Solids<sup>(a)</sup></b><br><b>Electrical Conductivity</b>   |
| <b>Major Minerals</b>          | <b>Calcium</b><br><b>Magnesium</b><br><b>Sodium</b><br><b>Potassium</b><br><b>Carbonate</b><br><b>Bicarbonate</b><br><b>Sulfate</b><br><b>Chloride</b><br><b>Hardness</b><br><b>Phosphate<sup>(b)</sup></b><br><b>Hydroxide<sup>(b)</sup></b><br><b>Alkalinity<sup>(b)</sup></b><br><b>Fluoride</b><br><b>Silica<sup>(b)</sup></b><br><b>pH</b> |
| <b>Nitrogen</b>                | <b>Nitrate<sup>(c)</sup></b><br><b>Nitrite</b><br><b>Ammonia Nitrogen</b><br><b>Organic Nitrogen</b>  |
| <b>Oxidants and Reductants</b> | <b>Chemical Oxygen Demand</b><br><b>Biological Oxygen Demand</b><br><b>Dissolved Oxygen<sup>(d)</sup></b><br><b>Chlorine Residual<sup>(d)</sup></b>   |

**TABLE 1 (Cont'd)**  
**CATEGORIES OF CONSTITUENTS**  
**FOR WHICH ANALYSES ARE TO BE MADE**

| Category                                | Constituents Included   |
|---|---|
| <b>Iron and Manganese</b>               | Iron<br>Manganese   |
| <b>Trace Constituents<sup>(e)</sup></b> | Arsenic<br>Boron<br>Cadmium<br>Copper<br>Cyanide<br>Chromium (Hexavalent)<br>Chromium (Total)<br>Lead<br><br>Lithium<br>Mercury<br>Nickel<br>Selenium<br>Silver<br>Zinc<br>MBAS (Detergent)<br>Chlorinated Hydrocarbons<br>Phenol |
| <b>Radioactivity</b>                    | Radium 220<br>Strontium 90<br>Gross Beta Activity   |
| <b>Bacteria</b>                         | Coliform Organisms  |
| <b>Virus</b>                            | Total Virus   |

TABLE 1 (Continued)  
 CATEGORIES OF CONSTITUENTS  
 FOR WHICH ANALYSES ARE TO BE MADE

| Category   | : | Constituents Included                     |
|--|---|---|
| Physical Properties<br>(Laboratory)                            |   | Taste (f)<br>Odor (f)<br>Color            |
| Physical Properties<br>(Field Observation<br>Non-quantitative) |   | Odor<br>Color<br>Temperature<br>Turbidity |

- (a) By sum of constituents, including all bicarbonates, or by evaporation at 103°C.
- (b) Desirable but not mandatory that this constituent be obtained.
- (c) May be included in major minerals.
- (d) May be excluded if obvious this constituent not present.
- (e) Other constituents may be added as future developments dictate.
- (f) Single observer quantitative determination of threshold numbers.

TABLE 2  
SAMPLING LOCATIONS<sup>(a)</sup>

| Program   | Sampling Location   |
|---|---|
| Reclaimed water                                     | Whittier Narrows Water Reclamation Plant Effluent<br>San Jose Creek Water Renovation Plant Effluent<br>Pomona Water Renovation Plant Effluent   |
| Imported water                                      | Colorado River Water <sup>(b)</sup><br>State Water <sup>(b)</sup>   |
| Storm Flow  | San Gabriel River (Sta. F261C-R above San Jose Creek and/or Sta. F263B-R at Beverly Boulevard)<br>Rio Hondo above Whittier Narrows (Sta. F64-R) |
| Rising water  | Mission Creek at Whittier Narrows, (Sta. F83-R)<br>San Gabriel River at Beverly Boulevard (Sta. F263B-R) <sup>(c)</sup>                         |
| Mixture in Stream Channels                          | San Jose Creek (Sta. F312-R)<br>Rio Hondo above Whittier Narrows (Sta. F64-R)   |
| Mixture at Spreading Grounds                        | San Gabriel River Spreading Grounds<br>Rio Hondo Spreading Grounds  |
| Montebello Forebay Ground Water (Intensive Program) | 16 Wells (See Plate 1) <sup>(d)</sup>   |
| Basinwide Ground Water                              | 193 Wells (See Plate 1) <sup>(e)</sup>  |

- (a) Excludes detailed monitoring program of reclaimed water and ground water which will be undertaken in connection with proposed demonstration project for reclamation of Hyperion wastewater and injection into West Coast Basin Barrier.
- (b) Appropriate sampling points representative of Colorado River water as received by Replenishment District. Possible present sampling points are Jensen Treatment Plant for State water and Diemer Treatment Plant for Colorado River water (raw water samples where appropriate).
- (c) In order to determine quality of rising water in San Gabriel River, allowance may be required for wastewaters contained in flow in San Jose Creek.
- (d) Includes Well No. 1590M, which also will be used for virus and bacteria sampling.
- (e) Excluding intensively monitored wells in Montebello Forebay.

**TABLE 3**  
**SUMMARY OF MONITORING PROGRAM**

| Constituents                | Sampling Frequency <sup>(a)</sup> |                |                  |                             |                 |                   |                              |           |
|-----------------------------|-----------------------------------|----------------|------------------|-----------------------------|-----------------|-------------------|------------------------------|-----------|
|                             | Individual Supplies               |                |                  |                             | Mixtures        |                   | Ground Water                 |           |
|                             | Reclaimed Water                   | Imported Water | Storm Flow       | Rising Water <sup>(g)</sup> | Stream Channels | Spreading Grounds | Montebello Forebay Intensive | Basinwide |
| TDS                         | D <sup>(b)</sup>                  | SA             | M <sup>(e)</sup> | SA                          | M               | M                 | Q                            | A         |
| Major Minerals              | M                                 | SA             | M <sup>(e)</sup> | SA                          | M               | M                 | Q                            | A         |
| Nitrogen                    | D <sup>(c)</sup>                  | SA             | M <sup>(e)</sup> | SA                          | M               | M                 | Q                            | -         |
| Oxidants and Reductants     | M                                 | SA             | M <sup>(e)</sup> | SA                          | M               | M                 | Q                            | -         |
| Iron and Manganese          | M                                 | SA             | M <sup>(e)</sup> | SA                          | M               | M                 | Q                            | -         |
| Trace Constituents          | M <sup>(d)</sup>                  | SA             | A <sup>(f)</sup> | -                           | -               | A                 | A                            | -         |
| Radioactivity               | A                                 | SA             | A <sup>(f)</sup> | -                           | -               | A                 | A                            | -         |
| Bacteria                    | M                                 | -              | M <sup>(e)</sup> | -                           | M               | M                 | M <sup>(h)</sup>             | -         |
| Virus                       | M                                 | -              | -                | -                           | -               | -                 | M <sup>(h)</sup>             | -         |
| Physical Properties (Lab)   | -                                 | -              | -                | -                           | -               | -                 | Q                            | -         |
| Physical Properties (Field) | M                                 | SA             | M <sup>(e)</sup> | SA                          | M               | M                 | Q                            | A         |

(a) D = Daily; W = Weekly; M = Monthly; Q = Quarterly; SA = Semi-Annually; A = Annually

(b) Conductivity to be determined daily. Total dissolved solids to be determined weekly.

(c) Nitrate, nitrite and ammonia to be determined daily. Organic nitrogen to be determined monthly.

(d) Analysis for heavy metals to be made on composite made up from daily samples.

(e) Monthly samples during winter months should be taken on days of high flow, where possible. Samples should be taken at times when storm runoff accounts for nearly all of flow. During summer months of low flow, or when there is significant water in stream from other sources, monthly samples of storm flow may be discontinued.

(f) Should be sampled at times of relatively high flow.

(g) To be sampled at times when rising water accounts for essentially all of flow.

(h) On Well No. 1590M only.

**TABLE 4**  
**RESPONSIBLE AGENCIES FOR SAMPLING PROGRAM**

| Constituents                | Agency Responsible for Sample Collection <sup>(a)(b)</sup> |          |                    |              |          |                    |                    |           |
|-----------------------------|--|----------|--------------------|--------------|----------|--------------------|--------------------|-----------|
|                             | Individual Supplies  |          |                    |              | Mixtures |                    | Ground Water       |           |
|                             | Reclaimed  | Imported |                    |              | Stream   | Spreading          | Montebello         |           |
|                             | Water  | Water    | Storm Flow         | Rising Water | Channels | Grounds            | Intensive          | Basinwide |
| TDS                         | CSD  | MWD      | FCD                | FCD          | FCD      | FCD                | FCD                | FCD & DWR |
| Major Minerals              | CSD  | MWD      | FCD                | FCD          | FCD      | FCD                | FCD                | FCD & DWR |
| Nitrogen                    | CSD  | MWD      | FCD                | FCD          | FCD      | FCD                | FCD                | -         |
| Oxidants and Reductants     | CSD  | MWD      | FCD                | FCD          | FCD      | FCD                | FCD                | -         |
| Iron and Manganese          | CSD  | MWD      | FCD                | FCD          | FCD      | FCD                | FCD                | -         |
| Trace Constituents          | CSD  | MWD      | FCD <sup>(c)</sup> | -            | -        | FCD <sup>(c)</sup> | FCD <sup>(c)</sup> | -         |
| Radioactivity               | CSD  | MWD      | FCD <sup>(d)</sup> | -            | -        | FCD <sup>(d)</sup> | FCD <sup>(d)</sup> | -         |
| Bacteria                    | CSD  | -        | FCD                | -            | FCD      | FCD                | FCD                | -         |
| Virus                       | CSD  | -        | -                  | -            | -        | -                  | FCD <sup>(e)</sup> | -         |
| Physical Properties (Lab)   | -  | -        | -                  | -            | -        | -                  | FCD <sup>(c)</sup> | -         |
| Physical Properties (Field) | CSD  | MWD      | FCD                | FCD          | FCD      | FCD                | FCD                | FCD & DWR |

(a) Indicated agency also responsible for analysis, except as noted by footnote.

(b) CSD = County Sanitation Districts; FCD = Flood Control District; WRD = Central and West Basin Water Replenishment District; MWD = Metropolitan Water District; DWR = Department of Water Resources.

(c) Analysis by County Sanitation Districts laboratory, at Replenishment District cost.

(d) Analysis by commercial laboratory at Replenishment District cost.

(e) Analysis by Los Angeles County Health Department.

Whittier Narrows

The California Regional Water Quality Control Board, Los Angeles Region, has also established waste discharge requirements for the Whittier Narrows Water Reclamation Plant which supplies a large percentage of the reclaimed wastewater spread at Montebello Forebay. The requirements include effluent limitations, monitoring, sampling, analysis, and reporting provisions and receiving water analysis requirements. The following are the pertinent portions of those requirements.

## TABLE 5

## EFFLUENT LIMITATIONS

Order  
County Sanitation Districts of Los Angeles County  
(Whittier Narrows Water Reclamation Plant)

CA 0 0 5 3 7 1 6

The Board has notified the discharger and interested agencies and persons of its intent to prescribe waste discharge requirements for this discharge and has provided them with an opportunity to submit their written views and recommendations.

The Board in a public hearing heard and considered all comments pertaining to the discharge and to the tentative requirements.

This Order shall serve as a National Pollutant Discharge Elimination System permit pursuant to Section 402 of the Federal Water Pollution Control Act, or amendments thereto, and shall take effect at the end of ten days from the date of its adoption, provided the Regional Administrator, EPA, has no objections.

TABLE 5. Effluent Limitations (Continued)

IT IS HEREBY ORDERED, that County Sanitation Districts of Los Angeles County, in order to meet the provisions of the Federal Water Pollution Control Act and regulations and guidelines adopted thereunder, shall comply with the following:

## A. Effluent Limitations

1. Wastes discharged shall be limited to treated municipal wastewater, as proposed.
2. The discharge of an effluent in excess of the following limits is prohibited:

| <u>Parameter</u>      | <u>Units</u> | <u>30-Day<br/>average</u> | <u>7-Day<br/>average</u> | <u>Daily<br/>maximum</u> |
|-----------------------|--------------|---------------------------|--------------------------|--------------------------|
| BOD <sub>5</sub> 20°C | lbs/day      | 4,880                     | 7,320                    | 7,320                    |
|                       | mg/l         | 20                        | 30                       | --                       |
| Suspended solids      | lbs/day      | 3,660                     | 9,750                    | 9,750                    |
|                       | mg/l         | 15                        | 40                       | --                       |
| Fecal coliform        | MPN/100 ml   | 200                       | 400                      | --                       |

(For BOD and suspended solids, the arithmetic average shall be used; for fecal coliform, the geometric mean shall be used).

| <u>Parameter</u>       | <u>Units</u> | <u>Average</u> | <u>Maximum</u> |
|------------------------|--------------|----------------|----------------|
| Oil and grease         | lbs/day      | 2,440          | 3,660          |
|                        | mg/l         | 10             | 15             |
| Settleable solids      | ml/l         | 0.1            | 0.2            |
| Turbidity              | TU           | ---            | 10             |
| Total dissolved solids | lbs/day      | ---            | 183,000        |
|                        | mg/l         | ---            | 750            |
| Chloride               | lbs/day      | ---            | 42,700         |
|                        | mg/l         | ---            | 175            |
| Sulfate                | lbs/day      | ---            | 61,000         |
|                        | mg/l         | ---            | 250            |
| Boron                  | lbs/day      | ---            | 366            |
|                        | mg/l         | ---            | 1.5            |

TABLE 5. Effluent Limitations (Continued)

3. The discharge of an effluent in excess of the following limits after August 1, 1978, is prohibited; provided, however, if it can be conclusively demonstrated by any discharger to ocean water tributaries that the treatment process required by Water Code Section 13379 (a and b) plus source control, will not result in complete compliance with the following limits by August 1, 1978, the State Board may allow additional time for compliance not to exceed July 1, 1985:

| <u>Constituent</u>                          | <u>Units</u>   | <u>Average</u> | <u>Maximum</u> |
|---|----------------|----------------|----------------|
| Arsenic                                     | mg/l           | 0.01           | 0.02           |
| Cadmium                                     | mg/l           | ----           | 0.01           |
| Total chromium                              | mg/l           | 0.005          | 0.01           |
| Copper                                      | mg/l           | 0.2            | 0.3            |
| Lead  | mg/l           | ----           | 0.05           |
| Mercury                                     | mg/l           | 0.001          | 0.002          |
| Nickel                                      | mg/l           | 0.1            | 0.2            |
| Silver                                      | mg/l           | 0.02           | 0.04           |
| Zinc  | mg/l           | 0.3            | 0.5            |
| Cyanide                                     | mg/l           | 0.1            | 0.2            |
| Selenium                                    | mg/l           | ----           | 0.01           |
| Phenolic compounds                          | mg/l           | 0.5            | 1.0            |
| Total nitrogen                              | mg/l           | 30             | 40             |
| Total identifiable chlorinated hydrocarbons | mg/l           | 0.002          | 0.004          |
| Toxicity concentration                      | toxicity units | 1.5            | 2.0            |
| Fluoride                                    | mg/l           | ----           | 1.5            |

4. The daily discharge rate listed in item 2 above shall be obtained from the following calculation for any calendar day:

$$\text{Daily discharge rate (lbs/day)} = \frac{8.34}{N} \sum_{1}^{N} Q_i C_i$$

in which N is the number of samples analyzed in any calendar day.  $Q_i$  and  $C_i$  are the flow rate (MGD) and the constituent concentration (mg/l) respectively, which are associated with each of the N grab samples which may be taken in any calendar day. If a composite sample is taken,  $C_i$  is the concentration measured in the composite sample, and  $Q_i$  is the average flow rate occurring during the period over which samples are composited.

TABLE 5. Effluent Limitations (Continued)

5. The 7-day and 30-day average discharge rates listed in item 2 above shall be the arithmetic average of all the values of daily discharge rate calculated using the results of analyses of all samples collected during any 7 and 30 consecutive calendar day periods, respectively. If fewer than four samples are collected and analyzed during any 30 consecutive calendar day period, compliance with the 30-day average discharge rate limitation shall not be determined. If fewer than three samples are collected and analyzed during any 7 consecutive calendar day period, compliance with the 7-day average discharge rate limitation shall not be determined.
6. The Maximum Allowable Daily Mass Emission Rate for each constituent listed in Item 3 above shall be calculated from the total waste flow occurring each specific day and the maximum concentration specified in waste discharge requirements. The mass emission rate of the discharge during any 24-hour period shall not exceed the Maximum Allowable Daily Mass Emission Rate.
7. The Maximum Allowable Monthly Mass Emission Rate for each constituent listed in Item 3 above shall be calculated from the total waste flow occurring in each specific month and the average concentration specified in waste discharge requirements. The mass emission rate of the discharge during any monthly period shall not exceed the Maximum Allowable Daily Mass Emission Rate.
8. The 30-day average effluent concentration shall not exceed more than 15 percent of the 30-day average influent concentration of BOD and suspended solids.
9. The pH of wastes discharged shall at all times be within the range 6.5 to 9.0.
10. Wastes discharged to watercourses shall at all times be adequately disinfected. For the purpose of this requirement, the wastes shall be considered adequately disinfected if the median most probable number of coliform organisms at some point in the treatment process does not exceed 2.2 per 100 milliliters. The median value shall be determined from samples taken on seven sampling days each week, at least one sample per sampling day, collected at a time when wastewater flow and characteristics are most demanding on the treatment facilities and disinfection procedures. Wastes discharged to watercourses shall have received treatment equivalent to that of a filtered wastewater. A filtered wastewater means an oxidized wastewater in which the finely divided suspended

TABLE 5. Effluent Limitations (Continued)

matter has been agglomerated by the addition of a suitable chemical or by an equally effective method and has passed through a filter media, such as sand or diatomaceous earth, so that the final turbidity does not exceed ten (10) Turbidity Units. (Sections 8032 and 8033, California Administrative Code, Title 17).

For the purposes of this requirement, carbon filtration may be accepted if in the judgment of the Executive Officer it can be demonstrated to produce an equivalent quality wastewater.

Nothing herein shall be construed to prevent the use of any alternative treatment process(es) provided that they can be demonstrated to the satisfaction of the Executive Officer to achieve compliance with the effluent limitations and requirements.

Compliance with this requirement (No. 10) shall be according to the following time schedule.

| <u>Procedure</u>                                       | <u>Latest completion date</u>                                       |
|--|---|
| Project report   | November 30, 1974   |
| State and EPA review of project report                 | March 31, 1975  |
| Design   | 5 months after approval of project report                           |
| State and EPA review of plans and specifications       | 2 months after completion of design                                 |
| Approval of project by District 15 Board of Directors* | 1 month after State and EPA approval of plans and specifications    |
| Advertise and receive bids*                            | 1 month after approval of project by District 15 Board of Directors |
| State and EPA approval of bids                         | 1 month after receipt of bids                                       |
| Award contract*  | 1 month after approval of bids                                      |
| Construction progress report*                          | 6 months after approval of bids                                     |
| Construction completion*                               | 12 months after award of contract                                   |
| Startup*   | 2 months after completion of construction                           |

- \* A report shall be submitted to this Board not later than 15 days following the scheduled completion date of each of these items. If the procedure has not been completed as scheduled, the report shall discuss the reason(s) therefor, show a firm completion date, and indicate whether all subsequent portions of the schedule will be met.

TABLE 5. Effluent Limitations (Continued)

11. The temperature of the wastes discharged shall not exceed 100°F.
12. Radioactivity in the effluent shall not exceed the limits specified in Title 17, Section 5, Subchapter 4, Group 3, Article 3, Section 30269 of the California Administrative Code.

**B. General Requirements**

1. Standby of emergency power facilities and/or storage capacity or other means shall be provided so that in the event of plant upset or outage due to power failure or other cause, discharge of raw or inadequately treated sewage does not occur.
2. The discharge of wastes to flood control channels or watercourses shall not result in problems due to breeding of mosquitoes, gnats, midges or other pests.
3. Neither the discharge nor any treatment of waste shall cause pollution or nuisance.
4. This discharge shall not cause a violation of any applicable water quality standard for receiving waters adopted by the Regional Board or the State Water Resources Control Board as required by the Federal Water Pollution Control Act and regulations adopted thereunder. If more stringent applicable water quality standards are promulgated or approved pursuant to Section 303 of the Federal Water Pollution Control Act, or amendments thereto, the Board will revise and modify this Order in accordance with such more stringent standards.
5. The wastes discharged shall not contain phenols, mercaptans, or other substances in concentrations which would impart odors, color, foaming, or other objectionable characteristics to receiving waters.
6. The wastes discharged shall not cause receiving waters to contain any substance in concentrations toxic to human, animal, plant, or fish life.
7. The wastes discharged shall not cause the appearance of grease, oil, or oily slick, persistent foam, discoloration, sludge banks, or other visible matter of waste origin in Rio Hondo Flood Control Channel or San Gabriel River at or downstream of any of the points of discharge.

TABLE 5. Effluent Limitations (Continued)

8. Odors of sewage origin shall not be perceivable beyond the limits of the treatment plant.
9. Wastes discharged shall not damage flood control structures or facilities.
10. The discharge of wastes to watercourses or flood control channels shall not result in residual chlorine in concentrations greater than 0.1 mg/l at the point(s) of transition from a lined structure to an unlined structure. Compliance with this requirement shall be according to the time schedule in A10, above.
11. Suitable storage and/or bypass facilities shall be provided to prevent continued discharge to any unlined areas of effluent which after treatment does not meet all of the foregoing requirements.

#### C. Provisions

1. This Order includes the attached "Standard Provisions".
2. This Order includes items 1, 2, 4, 5, and 6 of the attached "Reporting Requirements".
3. This Order includes the attached "General Monitoring and Reporting Provisions".
4. This Order expires on August 1, 1978, and County Sanitation Districts of Los Angeles County must file a Report of Waste Discharge in accordance with Title 23, California Administrative Code, not later than 180 days in advance of such date as application for issuance of new waste discharge requirements.
5. A copy of these waste discharge specifications shall be maintained at the discharge facility so as to be available at all times to operating personnel.
6. In the event of any change in name, ownership, or control of these waste disposal facilities, the discharger shall notify this Board of such change and shall notify the succeeding owner or operator of the existence of this order by letter, copy of which shall be forwarded to the Board.
7. Any discharge of wastes to navigable waterways or tributaries thereto at any point(s) other than specifically described in this permit is prohibited, and constitutes a violation of the permit.

TABLE 5. Effluent Limitations (Continued)

8. The discharger shall file a technical report with this Board not later than 30 days after receipt of this permit, relative to the operation and maintenance program for this waste disposal facility. The information to be contained in that report shall include, as a minimum, the following:
  - a. The name and address of the person or company responsible for operation and maintenance of the facility.
  - b. Type of maintenance (preventive or corrective).
  - c. Frequency of maintenance, if preventive.
9. Discharger shall file on or before January 1, 1978, a report comparing the quality of the discharge to the effluent quality requirements contained in effluent limitations A-3, A-6, and A-7 of this Order. The report shall contain a description of the treatment process and the efficiencies of each unit with regard to the removal of the parameters listed in effluent limitation A-2. The report shall outline the source control and pretreatment measures instituted by the discharger to achieve compliance with the effluent limitations contained in A-3, A-6, and A-7.

If the discharge does not comply with any effluent limitations in A-3, A-6, or A-7, the discharger shall discuss the reason for such noncompliance and outline steps which may be taken to achieve compliance with the effluent limitations and provide an estimate of the cost to achieve full compliance.
10. The report of waste discharge was incomplete in that it did not contain all the required information on industrial discharges to the municipal system. All missing information must be provided within one year from the adoption of this order. The Board may revise or modify this order at any time, as necessary, based upon subsequently submitted information regarding industrial discharges.
11. The discharger shall ensure compliance with any existing or future pretreatment standard promulgated by EPA under Section 307 of the FWPCA or amendments thereto, for any discharge to the municipal system.

I, Raymond M. Hertel, Executive Officer, do hereby certify that the foregoing is a full, true, and correct copy of an Order adopted by the California Regional Water Quality Control Board, Los Angeles Region, on May 20, 1974.

  
RAYMOND M. HERTEL, Executive Officer

TABLE 5. Effluent Limitations (Continued)

## CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD

## LOS ANGELES REGION

## GENERAL MONITORING AND REPORTING PROVISIONS

## GENERAL PROVISIONS FOR SAMPLING AND ANALYSIS

Unless otherwise noted, all sampling, sample preservation, and analyses shall be conducted in accordance with the current edition of "Standard Methods for the Examination of Water and Wastewater" or as approved by the Executive Officer.

All analyses shall be performed in a laboratory approved by the Executive Officer.

Effluent samples shall be taken downstream of any addition to the treatment works and prior to mixing with the receiving waters.

The discharger shall calibrate and perform maintenance procedures on all monitoring instruments and equipment to insure accuracy of measurements, or shall insure that both activities will be conducted.

A grab sample is defined as an individual sample collected in fewer than 15 minutes.

A composite sample is defined as a combination of no fewer than eight individual samples obtained over the specified sampling period. The volume of each individual sample is proportional to the discharge flow rate at the time of sampling. The sampling period shall equal the discharge period, or 24 hours, whichever period is shorter.

## GENERAL PROVISIONS FOR REPORTING

For every item where the requirements are not met, the discharger shall submit a statement of the actions undertaken or proposed which will bring the discharge into full compliance with requirements at the earliest time and submit a timetable for correction.

By January 30 of each year, the discharger shall submit an annual report to the Board. The report shall contain both tabular and graphical summaries of the monitoring data obtained during the previous year. In addition, the discharger shall discuss the compliance record and the corrective actions taken or planned which may be needed to bring the discharge into full compliance with the waste discharge requirements.

The discharger shall maintain all sampling and analytical results, including strip charts; date, exact place, and time of sampling; date analyses were performed; analyst's name; analytical techniques used; and results of all analyses. Such records shall be retained for a minimum of three years. This period of retention shall be extended during the course of any unresolved litigation regarding this discharge or when requested by the Board.

TABLE 5. Effluent Limitations (Continued)

Monitoring reports shall be signed by:

- a. In the case of corporations, by a principal executive officer at least of the level of vice-president or his duly authorized representative, if such representative is responsible for the overall operation of the facility from which discharge originates;
- b. In the case of a partnership, by a general partner;
- c. In the case of a sole proprietorship, by the proprietor;
- d. In the case of municipal, state or other public facility, by either a principal executive officer, ranking elected official, or other duly authorized employee.

The discharger shall mail a copy of each monitoring report to:

Regional Administrator  
Environmental Protection Agency  
Region IX  
100 California Street  
San Francisco, CA 94111

Each report shall contain the following completed declaration:

"I declare under penalty of perjury that the foregoing is true and correct.

Executed on the \_\_\_\_\_ day of \_\_\_\_\_ at \_\_\_\_\_.

\_\_\_\_\_  
(Signature)

\_\_\_\_\_  
(Title)"

TABLE 5. Effluent Limitations (Continued)

## CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD

## LOS ANGELES REGION

## STANDARD PROVISIONS

1. The requirements prescribed herein do not authorize the commission of any act causing injury to the property of another, nor protect the discharger from his liabilities under federal, state, or local laws, nor guarantee the discharger a capacity right in the receiving waters.
2. The discharge of any radiological, chemical, or biological warfare agent or high level radiological waste is prohibited.
3. The discharger shall require any industrial user of the treatment works to comply with applicable service charges and toxic and pretreatment standards promulgated in accordance with Sections 204(b), 307, and 308 of the Federal Water Pollution Control Act or amendments thereto. The discharger shall require each individual user to submit periodic notice (over intervals not to exceed nine months) of progress toward compliance with applicable toxic and pretreatment standards developed pursuant to the Federal Water Pollution Control Act or amendments thereto. The discharger shall forward a copy of such notice to the Board and the Regional Administrator.
4. The discharger shall permit the Regional Board:
  - (a) Entry upon premises in which an effluent source is located or in which any required records are kept;
  - (b) Access to copy any records required to be kept under terms and conditions of this Order;
  - (c) Inspection of monitoring equipment or records, and
  - (d) Sampling of any discharge.
5. All discharges authorized by this Order shall be consistent with the terms and conditions of this Order. The discharge of any pollutant more frequently than or at a level in excess of that identified and authorized by this Order shall constitute a violation of the terms and conditions of this Order.

TABLE 5. Effluent Limitations (Continued)

6. The discharger shall maintain in good working order and operate as efficiently as possible any facility or control system installed by the discharger to achieve compliance with the waste discharge requirements.
7. Collected screenings, sludges, and other solids removed from liquid wastes shall be disposed of at a legal point of disposal, and in accordance with the provisions of Division 7.5 of the California Water Code. For the purpose of this requirement, a legal point of disposal is defined as one for which waste discharge requirements have been prescribed by a regional water quality control board and which is in full compliance therewith.
8. After notice and opportunity for a hearing, this Order may be terminated or modified for cause, including, but not limited to:
  - (a) Violation of any term or condition contained in this Order;
  - (b) Obtaining this Order by misrepresentation, or failure to disclose all relevant facts;
  - (c) A change in any condition that requires either a temporary or permanent reduction or elimination of the authorized discharge.
9. If a toxic effluent standard or prohibition (including any schedule of compliance specified in such effluent standard or prohibition) is established under Section 307(a) of the Federal Water Pollution Control Act, or amendments thereto, for a toxic pollutant which is present in the discharge authorized herein and such standard or prohibition is more stringent than any limitation upon such pollutant in this Order, the Board will revise or modify this Order in accordance with such toxic effluent standard or prohibition and so notify the discharger.
10. There shall be no discharge of harmful quantities of oil or hazardous substances, as specified by regulation adopted pursuant to Section 311 of the Federal Water Pollution Control Act, or amendments thereto.
11. In the event the discharger is unable to comply with any of the conditions of this Order due to:
  - (a) breakdown of waste treatment equipment;
  - (b) accidents caused by human error or negligence; or
  - (c) other causes such as acts of nature,

the discharger shall notify the Executive Officer by telephone as soon as he or his agents have knowledge of the incident and confirm this notification in writing within two weeks of the telephone notification. The written notification shall include pertinent information explaining reasons for the non-compliance and shall indicate what steps were taken to correct the problem and the dates thereof, and what steps are being taken to prevent the problem from recurring.

TABLE 5. Effluent Limitations (Continued)

CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD  
LOS ANGELES REGION

## REPORTING REQUIREMENTS

1. The discharger shall file with the Board technical reports on self-monitoring work performed according to the detailed specifications contained in any Monitoring and Reporting Programs as directed by the Executive Officer.
2. The discharger shall file a written report with the Board within 90 days after the average dry-weather waste flow for any month equals or exceeds 75 percent of the design capacity of his waste treatment and/or disposal facilities. The discharger's senior administrative officer shall sign a letter which transmits that report and certifies that the policy-making body is adequately informed about it. The report shall include:

Average daily flow for the month, the date on which the instantaneous peak flow occurred, the rate of that peak flow, and the total flow for that day.

The discharger's best estimate of when the average daily dry-weather flow rate will equal or exceed the design capacity of his facilities.

The discharger's intended schedule for studies, design, and other steps needed to provide additional capacity for his waste treatment and/or disposal facilities before the waste flow rate equals the capacity of present units. (Reference: Sections 13260, 13267(b), and 13268, California Water Code.)

3. The discharger shall notify the Board not later than 120 days in advance of implementation of any plans to alter production capacity of the product line of the manufacturing, producing or processing facility by more than ten percent. Such notification shall include estimates of proposed production rate, the type of process, and projected effects on effluent quality. Notification shall include submittal of a new report of waste discharge and appropriate filing fee.
4. The discharger shall notify the Board of (a) new introduction into such works of pollutants from a source which would be a new source as defined in Section 306 of the Federal Water Pollution Control Act, or amendments thereto, if such source were discharging pollutants to the waters of the United States, (b) new introductions of pollutants into such works from a source which would be subject to Section 301 of the Federal Water Pollution Control Act, or amendments thereto, if it were discharging such pollutants to the waters of the United States, (c) a substantial change in the volume or character of pollutants being introduced into

TABLE 5. Effluent Limitations (Continued)

such works by a source introducing pollutants into such works at the time the waste discharge requirements were adopted. Notice shall include a description of the quantity and quality of pollutants and the impact of such change on the quantity and quality of effluent from such publicly owned treatment works. A substantial change in volume is considered an increase of ten percent in the mean dry-weather flow rate. The discharger shall forward a copy of such notice directly to the Regional Administrator.

5. The discharger shall file with the Board a report on waste discharge at least 120 days before making any material change or proposed change in the character, location or volume of the discharge.
6. This Board requires the discharger to file with the Board, within 90 days after the effective date of this Order, a technical report on his preventive (fail-safe) and contingency (cleanup) plans for controlling accidental discharges, and for minimizing the effect of such events. The technical report should:

Identify the possible sources of accidental loss, untreated waste bypass, and contaminated drainage. Loading and storage areas, power outage, waste treatment unit outage, and failure of process equipment, tanks and pipes should be considered.

Evaluate the effectiveness of present facilities and procedures and state when they became operational.

Describe facilities and procedures needed for effective preventive and contingency plans.

Predict the effectiveness of the proposed facilities and procedures and provide an implementation schedule containing interim and final dates when they will be constructed, implemented, or operational. (Reference: Sections 13267(b) and 13268, California Water Code.)

This Board, after review of the technical report, may establish conditions which it deems necessary to control accidental discharges and to minimize the effects of such events. Such conditions may be incorporated as part of this Order, upon notice to the discharger.

7. The discharger shall submit to the Board, by January 30 of each year, an annual summary of the quantities of all chemicals, listed by both trade and chemical names, which are used for cooling and/or boiler water treatment and which are discharged.
8. The discharger shall submit to the Board, together with the first monitoring report required by this permit, a list of all chemicals and proprietary additives which could affect this waste discharge, including quantities of each. Any subsequent changes in types and/or quantities shall be reported promptly.

TABLE 5. Effluent Limitations (Continued)

MONITORING AND REPORTING PROGRAM NO. 2848  
 FOR  
 COUNTY SANITATION DISTRICTS OF LOS ANGELES COUNTY  
 (Whittier Narrows Water Reclamation Plant - District No. 15)  
 CA 0053716

Effluent Monitoring

(Discharge Serial Nos. 001; 002; 003; 004)

A sampling station shall be established for each point of discharge and shall be located where representative samples of the effluent can be obtained. The following shall constitute the effluent monitoring program:

| <u>Parameter</u>                            | <u>Units</u>   | <u>Type of Sample</u> | <u>Minimum Frequency of Analysis</u> |
|---|----------------|-----------------------|--------------------------------------|
| Flow  | mgd            | continuous            | ---                                  |
| BOD <sub>5</sub> 20°C                       | mg/l           | 24-hr. composite      | daily                                |
| Suspended Solids                            | mg/l           | 24-hr. composite      | daily                                |
| Coliform group                              | MPN/100ml      | grab                  | daily                                |
| Fecal coliform                              | MPN/100ml      | grab                  | daily                                |
| pH  | pH units       | grab                  | daily                                |
| Oil and grease <u>1/</u>                    | mg/l           | grab                  | daily                                |
| Settleable solids                           | ml/l           | 24-hr. composite      | daily                                |
| Turbidity <u>2/</u>                         | TU             | continuous            | ---                                  |
| Arsenic                                     | mg/l           | 24-hr. composite      | monthly                              |
| Cadmium                                     | mg/l           | 24-hr. composite      | monthly                              |
| Chromium                                    | mg/l           | 24-hr. composite      | monthly                              |
| Copper                                      | mg/l           | 24-hr. composite      | monthly                              |
| Lead  | mg/l           | 24-hr. composite      | monthly                              |
| Mercury <u>3/</u>                           | mg/l           | 24-hr. composite      | monthly                              |
| Nickel                                      | mg/l           | 24-hr. composite      | monthly                              |
| Silver                                      | mg/l           | 24-hr. composite      | monthly                              |
| Zinc  | mg/l           | 24-hr. composite      | monthly                              |
| Cyanide                                     | mg/l           | 24-hr. composite      | monthly                              |
| Selenium                                    | mg/l           | 24-hr. composite      | monthly                              |
| Phenolic compounds                          | mg/l           | 24-hr. composite      | monthly                              |
| Total chlorine residual                     | mg/l           | continuous            | ---                                  |
| Total identifiable chlorinated hydrocarbons | mg/l           | 24-hr. composite      | monthly                              |
| Toxicity concentration                      | Toxicity units | 24-hr. composite      | monthly                              |

TABLE 5. Effluent Limitations (Continued)

| <u>Parameter</u>                                       | <u>Units</u> | <u>Type of Sample</u> | <u>Minimum Frequency of Analysis</u> |
|--|--------------|-----------------------|--------------------------------------|
| Radioactivity  | PCi/l        | 24-hr. composite      | quarterly                            |
| Polychlorinated biphenyls                              | mg/l         | 24-hr. composite      | monthly                              |
| Total dissolved solids <u>5/</u>                       | mg/l         | 24-hr. composite      | weekly                               |
| Chloride   | mg/l         | 24-hr. composite      | weekly                               |
| Sulfate  | mg/l         | 24-hr. composite      | weekly                               |
| Total nitrogen   | mg/l         | 24-hr. composite      | weekly                               |
| Detergents (as methylene blue-active substances, MBAS) | mg/l         | 24-hr. composite      | weekly                               |
| Boron <u>6/</u>  | mg/l         | 24-hr. composite      | monthly                              |
| Fluoride <u>7/</u>                                     | mg/l         | 24-hr. composite      | monthly                              |
| <u>Influent Monitoring</u>                             |              |                       |                                      |
| BOD <sub>5</sub> 20°C                                  | mg/l         | 24-hr. composite      | daily                                |
| Suspended solids                                       | mg/l         | 24-hr. composite      | daily                                |

1/ By the trichlorotrifluoroethane extraction method

2/ By means of a turbidimeter

3/ By flameless atomic absorption

4/ By the iodometric method, with the end-point determined either amperometrically or visually

5/ By glass fiber filtration with evaporation at 180°C - Reference: Methods for Chemical Analysis of Water and Wastes, 1971, Environmental Protection Agency ("EPA Methods"), p. 275

6/ By the curcumin method

7/ By distillation and SPADNS method

TABLE 5. Effluent Limitations (Continued)

Receiving Water Analyses and Observations

Receiving water stations shall be established at the following locations:

| <u>Station No.</u> | <u>Description</u>   |
|--------------------|--|
| R-A                | San Gabriel River just below San Gabriel River Spreading Grounds       |
| R-B                | Zone 1 Ditch   |
| R-C                | Discharge point to test basin  |
| R-D                | Rio Hondo Flood Control Channel just below Rio Hondo Spreading Grounds |

| <u>Observation for</u>         | <u>Station No.</u> | <u>Minimum Frequency</u> |  |
|--------------------------------|--------------------|--------------------------|--|
| Odor of water                  | R-A, R-B, R-C, R-D | weekly                   |  |
| Color of water                 | R-A, R-B, R-C, R-D | weekly                   |  |
| Sludge banks or deposits       | R-A, R-B, R-C, R-D | weekly                   |  |
| Oil, grease, or slicks         | R-A, R-B, R-C, R-D | weekly                   |  |
| Foam                           | R-A, R-B, R-C, R-D | weekly                   |  |
| Visible solids of waste origin | R-A, R-B, R-C, R-D | weekly                   |  |

| <u>Parameter</u>  | <u>Units</u> | <u>Station No.</u> | <u>Type of Sample</u> | <u>Minimum Frequency of Analysis</u> |
|-------------------|--------------|--------------------|-----------------------|--------------------------------------|
| Residual chlorine | mg/l         | R-A, R-B, R-C, R-D | grab                  | weekly                               |

Monitoring reports shall be submitted to the Board for each month by the first day of the second following month, beginning not later than August 1, 1974.

Bacteriological samples shall be obtained at some point in the treatment process at a time when wastewater flow and characteristics are most demanding on the treatment facilities and disinfection procedures.

Effluent samples may be obtained at a single station provided that station is representative of the effluent quality at all discharge points.

Ordered by

*Raymond M. Herte*

MAY 20 1974

Date

Orange County Water District

A program for monitoring at the Orange County Water District's injection project has been developed in response to the requirements placed on the treatment plant effluent and the injection water by the California Regional Water Quality Control Board, Santa Ana Region. The following is a list of those requirements, the sampling program for the injection water, and the requirements set by the State Board of Public Health.

TABLE 6

EFFLUENT REQUIREMENTSMicrobiological

|          |   |                   |   |
|----------|---|-------------------|---|
| Bacteria | - | 1 coliform/100 ml | Monthly mean<br>(membrane filter<br>method) |
|----------|---|-------------------|---|

|       |   |      |
|-------|---|------|
| Virus | - | Zero |
|-------|---|------|

Physical

|           |   |       |
|-----------|---|-------|
| Turbidity | - | 1 JTU |
|-----------|---|-------|

|       |   |   |
|-------|---|---|
| Color | - | 5 |
|-------|---|---|

|                          |   |   |
|--------------------------|---|---|
| Threshold<br>Odor Number | - | 3 |
|--------------------------|---|---|

|                            |   |          |
|----------------------------|---|----------|
| Foaming Agents -<br>(MBAS) | - | 0.5 mg/l |
|----------------------------|---|----------|

TABLE 6. Effluent Requirements (Continued)

Chemical

|           |                 |  |                          |                        |
|-----------|-----------------|--|--------------------------|------------------------|
|           |                 | Polynuclear Aromatic Hydrocarbons - 0.2 ug/l |                          |                        |
| Organic   | CCE             | -  | 0.7 mg/l (mini-sampler)  |                        |
|           | Pesticides      | -  | varies; total 0.412 mg/l |                        |
|           | +<br>Herbicides | -  |                          |                        |
|           | Phenol          | -  | 0.001                    |                        |
| Inorganic | Ammonia (N)     | -  | 0.5                      |                        |
|           | Arsenic         | -  | 0.1                      |                        |
|           | Barium          | -  | 1                        |                        |
|           | Cadmium         | -  | 0.01                     |                        |
|           | Chloride        | -  | 250                      | <u>Radioactivity</u>   |
|           | Chromium        | -  | 0.05                     |                        |
|           | Copper          | -  | 1                        | Gross Beta - 1000 pc/l |
|           | Cyanide         | -  | 0.2                      | Radium 226 - 3         |
|           | Fluoride        | -  | 1.2                      | Strontium 90 - 10      |
|           | Iron            | -  | 0.3                      |                        |
|           | Lead            | -  | 0.05                     |                        |
|           | Manganese       | -  | 0.05                     |                        |
|           | Mercury         | -  | 0.002                    |                        |
|           | Nitrate (N)     | -  | 10                       |                        |
|           | Selenium        | -  | 0.01                     |                        |
|           | Silver          | -  | 0.05                     |                        |
|           | Sodium          | -  | ?                        |                        |
| Sulfate   | -               | 250  |                          |                        |
| Zinc      | -               | 5  |                          |                        |
| TDS       | -               | 500  |                          |                        |

TABLE 7

## REGULATORY AGENCY REQUIREMENTS FOR INJECTION WATER

| CONSTITUENT                              | MAXIMUM CONCENTRATION<br>(mg/l) |
|--|---------------------------------|
| Ammonium                                 | 1.0                             |
| Sodium                                   | 110.0                           |
| Total hardness (CaCO <sub>3</sub> )      | 220.0                           |
| Sulfate                                  | 125.0                           |
| Chloride                                 | 120.0                           |
| Total nitrogen (N)                       | 10.0                            |
| Fluoride                                 | 0.8                             |
| Boron                                    | 0.5                             |
| MBAS                                     | 0.5                             |
| Hexavalent chromium                      | 0.05                            |
| Cadmium                                  | 0.01                            |
| Selenium                                 | 0.01                            |
| Phenol                                   | 0.001                           |
| Copper                                   | 1.0                             |
| Lead                                     | 0.05                            |
| Mercury                                  | 0.005                           |
| Arsenic                                  | 0.05                            |
| Iron                                     | 0.3                             |
| Manganese                                | 0.05                            |
| Barium                                   | 1.0                             |
| Silver                                   | 0.05                            |
| Cyanide                                  | 0.02                            |
| Electrical conductivity                  | 900 umhos/cm                    |
| pH                                       | 6.5 - 8.0                       |
| Taste                                    | None N                          |
| Odor                                     | None                            |
| Foam                                     | None                            |
| Color                                    | None                            |
| Filter effluent turbidity                | 1.0 JTU                         |
| Carbon adsorption column<br>effluent COD | 30 mg/l                         |
| Chlorine contact basin<br>effluent       | Free chlorine residual          |

TABLE 8

## MONITORING AND REPORTING PROGRAM

California Regional Water Quality Control Board  
Santa Ana Region

Monitoring and Reporting Program No. 71-27  
for  
Orange County Water District  
Waste Water Reclamation and Sea Water Barrier Project

1. A continuous recording electrical conductivity device shall be installed to measure all injection water.
2. All injection water samples shall be collected from the injection stream in the following manner, frequency, and parameters to be analyzed for:

| <u>Parameter</u>        | <u>Type of Sample</u> | <u>Analysis Frequency</u> |
|-------------------------|-----------------------|---------------------------|
| Ammonium                | 24-hour composite     | Weekly                    |
| Sodium                  | " "                   | "                         |
| Total Hardness          | " "                   | "                         |
| Sulfate                 | " "                   | "                         |
| Chloride                | " "                   | "                         |
| Fluoride                | " "                   | "                         |
| Boron                   | " "                   | "                         |
| MBAS                    | " "                   | "                         |
| Hexavalent Chromium     | " "                   | "                         |
| Cadmium                 | " "                   | "                         |
| Selenium                | " "                   | "                         |
| Phenol                  | Grab                  | "                         |
| Copper                  | 24-hour composite     | Monthly                   |
| Lead                    | " "                   | "                         |
| Mercury                 | " "                   | "                         |
| Arsenic                 | " "                   | "                         |
| Barium                  | " "                   | "                         |
| Silver                  | " "                   | "                         |
| Iron                    | " "                   | Weekly                    |
| Manganese               | " "                   | "                         |
| Cyanide                 | " "                   | "                         |
| pH                      | Grab                  | Daily                     |
| Total Kjeldahl Nitrogen | 24-hour composite     | Weekly                    |

TABLE 8. Monitoring and Reporting Program (Continued)

3. Samples shall be collected from the Talbert, Alpha, and Beta Zones of Well M-20 on the following frequency and analyzed for the parameters specified:

| <u>Parameter</u>        | <u>Type of Sample</u> | <u>Analysis Frequency</u> |
|-------------------------|-----------------------|---------------------------|
| Electrical Conductivity | Grab                  | Weekly                    |
| Chloride                | "                     | "                         |
| Total Hardness          | "                     | "                         |
| Odor                    | "                     | "                         |
| Taste                   | "                     | "                         |
| Color                   | "                     | "                         |

4. A suitable radioactive concentration measuring system shall be provided. This system should be of the continuous type.

BEFORE THE STATE BOARD OF PUBLIC HEALTH

STATE OF CALIFORNIA

In the Matter of:

ORANGE COUNTY WATER DISTRICT  
 PROPOSED WASTEWATER RECLAMATION  
 PROJECT

On April 7, 1971, the State Department of Public Health conducted a public hearing to consider an application of the Orange County Water District in regard to the proposed injection of reclaimed wastewater mixed with desalinated seawater into water-bearing aquifers in the Santa Ana Gap of Orange County. These aquifers are used as a source of domestic water supply.

The hearing was held under authority of Section 4458 of the California Health and Safety Code and Sections 13540 and 13541 of the California Water Code.

The hearing was conducted by Hamlet C. Pulley, M.D., Assistant Director of Public Health, with the assistance of Mr. Paul C. Ward, Assistant Chief; Mr. Arthur W. Reinhardt, Supervising Sanitary Engineer; Mr. William J. MacPherson, Senior Sanitary Engineer; all of the Bureau of Sanitary Engineering; and Dr. Alice Ottoboni, Public Health Toxicologist.

TABLE 8. Monitoring and Reporting Program (Continued)

The letter of February 18, 1971, from the Orange County Water District requesting approval of the State Board of Public Health for the construction of a 15 mgd wastewater treatment plant and the injection of the treated wastewater into water-bearing aquifers and the accompanying Engineering Report - Proposed Waste Water Reclamation and Sea Water Barrier Facilities, February, 1971, were accepted in evidence. The past progress reports of the Orange County Water District pilot plant and injection studies were also accepted in evidence.

Mr. Langdon W. Owen, Secretary-Manager of the Orange County Water District, testified concerning the District's overall needs and concepts of the proposed project. The Coastal Sea Water Barrier Project includes a row of extraction wells paralleling the coast across the "Santa Ana Gap", a row of injection wells inland from the extraction wells, the reclamation project for the treatment of sewage effluent and a desalination plant.

Mr. G. M. Wesner, Assistant District Engineer, Orange County Water District, gave a detailed presentation on the technical aspects of the treatment processes, facilities and controls, and the water quality parameters to be maintained for the injection water.

Mr. Robert A. Webber, Chief of Industrial and Permit Division of the County Sanitation Districts of Orange County, presented testimony as to the Sanitation Districts' progress in controlling industrial wastes in the sewerage system and the progress in segregation of poorer quality flow in the incoming sewer trunk lines. The latter would enable the Districts to bypass the more highly industrialized wastes around Treatment Plant No. 1, which provides the source water to be processed.

No testimony was offered in opposition to the Orange County Water District's proposal.

At the conclusion of the hearing additional data from the Orange County Water District and the County Sanitation Districts were requested and were received by letter dated April 14, 1971.

#### History, 1965 to Date

Prior to the present proposal the groundwater recharge and sea-water barrier project has gone through several developmental phases. The initial phase started when on March 29, 1965, the Orange County Water District presented to the State Department of Public Health a proposal to inject treated sewage effluent into a water-bearing aquifer known as the Talbert Aquifer. Trickling filter effluent from Treatment Plant No. 1, County Sanitation Districts of Orange County, was to be given treatment by coagulation, sedimentation, rapid sand filtration and chlorination prior to injection. This initial proposal also included the construction of four observation or

TABLE 8. Monitoring and Reporting Program (Continued)

monitoring wells. The purpose of the proposal was to study the feasibility of using tertiary treated sewage effluent in a hydraulic barrier system to prevent the encroachment of salt water into the aquifer. With additional information submitted by letter dated April 28, 1965, the State Board of Public Health, after a public hearing on May 7, 1965, found that the recharge as proposed by the Orange County Water District would not impair the quality of the water in the receiving aquifer as a source of water supply for domestic purposes. The finding was limited to the injection of 1,000 acre-feet and until June 1, 1966.

Because of technical problems encountered in the injection of both fresh and reclaimed water into the Talbert Aquifer, the Orange County Water District, on February 26, 1966, requested the State Board of Public Health to consider an extension of time and modification in the pilot injection study to inject reclaimed water into deeper underlying water-bearing aquifers, designated as Alpha and Beta. The modifications also included the drilling of two additional observation wells at distances of 40 and 100 feet from the injection well which allowed the sampling of the Alpha and Beta aquifers from each well. Following public hearing on March 22, 1966, the State Board of Public Health amended its findings to include the requested modifications and extended the time to June 1, 1967.

A report<sup>1/</sup>, dated December 1967, on the initial and modified study noted that prior to injection, the tertiary treatment processes removed virtually all of the phosphorus and suspended matter, but soluble organic and nitrogenous material remained. The injection water also contained over 1000 mg/l total dissolved solids. However, the studies were successful in describing the effectiveness and cost of the tertiary treatment processes. The studies were not designed for, nor did they yield information relative to the long-term effect on reclaimed water as it moves greater distances from the point of injection.

Consequently, by letter of March 4, 1968, the Water District proposed an expanded injection demonstration program whose objectives are described in part as follows:

1. Determine the long-term fate of reclaimed water following injection, including chemical, bacteriological and hydraulic processes in its transmission through the underground strata.
2. Demonstrate the acceptability or lack of acceptability, from the standpoint of potability (taste, odor, etc.), public health and safety, of a treated reclaimed water injected under conditions as proposed for the full-scale barrier.

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<sup>1/</sup>Report on Pilot Wastewater Reclamation and Injection Study for Orange County Water District, by the consulting engineering firms of James M. Montgomery and Toups Engineering, Inc., Dec. 1967.

TABLE 8. Monitoring and Reporting Program (Continued)

The project was to use three multiple-cased injection wells and thirteen multiple-point observation wells. The wells were perforated in the Talbert, Alpha, Beta and Lambda aquifers (listed in order of depth, the Lambda aquifer being deepest). This made it possible to inject reclaimed water, deep well water or blends of the two into each aquifer simultaneously and to extract from each aquifer as desired. The State Board of Public Health accepted the proposed modifications on March 26, 1968.

As in the prior study, effluent from the trickling filter was given tertiary treatment consisting of coagulation, sedimentation, filtration and chlorination. The reclaimed water was injected into the aquifers from March 4, 1969 to December 22, 1969. Reclaimed water only was injected into the Lambda aquifer, and a mixture of 50 percent reclaimed water and 50 percent deep well water was injected into the Beta aquifer. Deep well water only was injected into the Talbert and Alpha aquifers. At the termination of the injection operations, the Lambda aquifer was essentially saturated with injected water for more than 550 feet south of the injection wells; the Beta aquifer was saturated for more than 100 feet.

The findings were reported in detail in the Water District's report<sup>2/</sup> of October 1969. The report indicated that human intestinal viruses were never found in any of the injection water samples or in the 13 multiple casing observation wells located at distances up to 1,000 feet from the injection wells. However, it was stated that the sampling was not extensive for virus determination.

The residual organics were the major problems encountered. The threshold odor of the reclaimed water was relatively high and the odor was not significantly reduced or altered by travel through the aquifer. The report concluded that the odor-causing dissolved organic material and dissolved inorganic substances present in the tertiary treated injection water made it undesirable for a barrier supply. To overcome these undesirable characteristics the report recognized that additional treatment prior to injection was needed.

Commencing in May 1970, the Orange County Water District constructed and operated a second tertiary treatment pilot plant to explore means for removing the undesirable characteristics. The pilot process consisted of clarification with lime and various coagulant aids, ammonia stripping, recarbonation, filtration, carbon adsorption and chlorination. However, there was no injection into the aquifers of reclaimed water from the enhanced treatment facilities. The pilot plant produced a reclaimed wastewater low in organic material, free of odor.

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<sup>2/</sup>Wesner, G. M., Final Report on Injection Demonstration Program, 1969 (OCWD).

TABLE 8. Monitoring and Reporting Program (Continued)

Utilizing the data obtained from the pilot plant studies the District prepared a report<sup>3/</sup> dated February 1971, which summarizes the District's past and present activities in wastewater reclamation. The report also describes the facilities required to supply reclaimed wastewater for the proposed full scale injection barrier. As described earlier the hearing of April 7, 1971, was held and the Hearing Officer's decision is based on report data and testimony presented at the hearing together with supplemental information submitted on April 14, 1971.

#### Proposed Reclamation Project

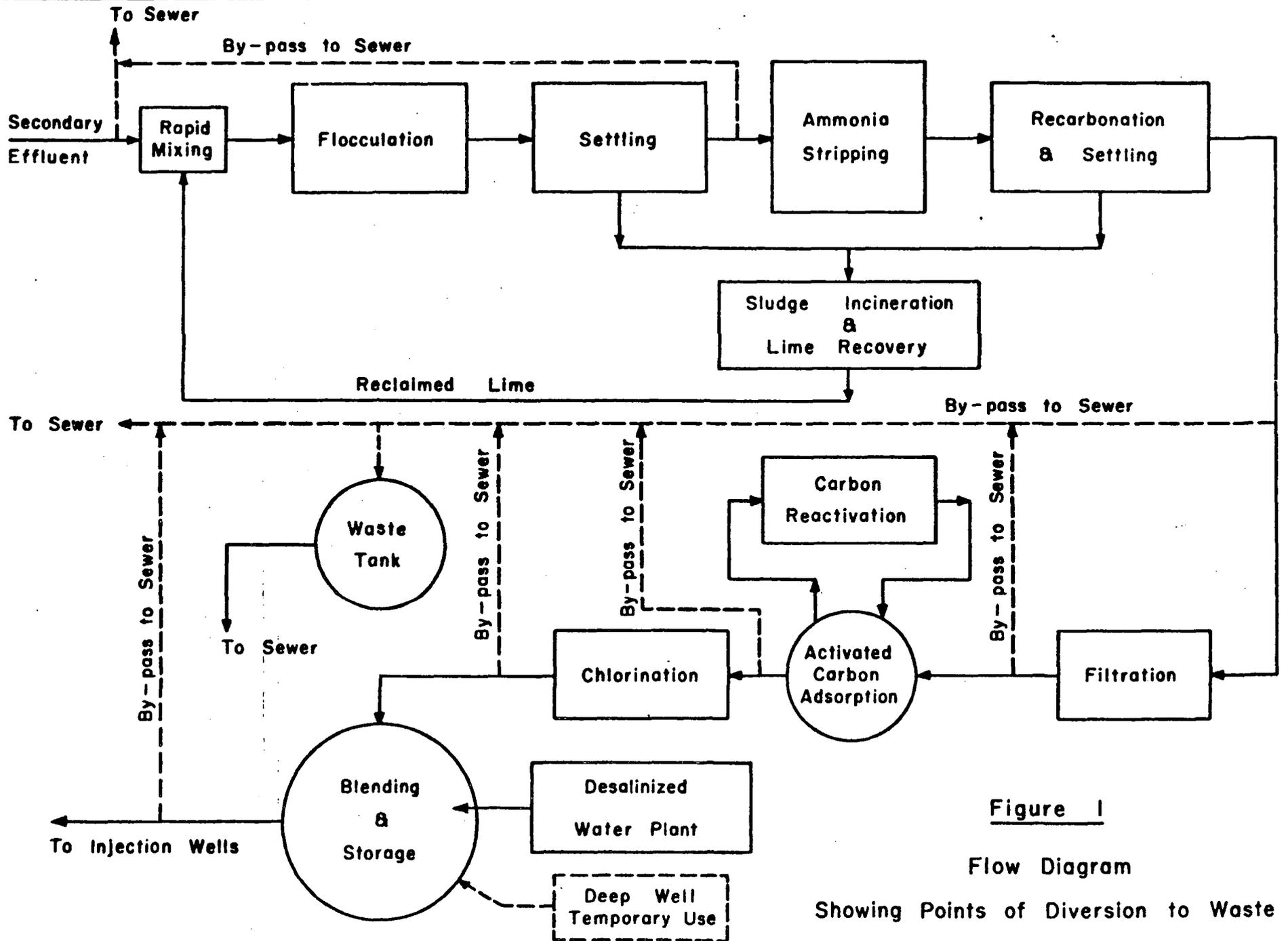
The proposed barrier will consist of a line of injection wells located four miles inland from the coast and a line of extraction wells (already constructed and in operation), located between the injection wells and the ocean. Three injection wells have been constructed to date and 19 additional injection wells are proposed. The Water District reports that 30,000 acre-feet per year or 26.7 million gallons per day will be required for the full-scale salt water barrier. The wastewater reclamation project will supply 15 million gallons per day. The remaining water needs for dilution and blending will be obtained from desalted seawater or from well water produced from a deep aquifer which is not subject to salt water intrusion, during any period of shutdown of the desalinization plant. The deep well is located on the site of the proposed reclamation plant.

The proposed water reclamation plant will utilize trickling filter effluent from the Orange County Sanitation District's (OCSD) Treatment Plant No. 1. In an effort at reducing the total mineral content of the sewage, the OCSD is in the process of segregating the trunk sewers that are carrying a heavy industrial waste load and to bypass these wastes around Treatment Plant No. 1. The bypass system is scheduled to go into operation in early 1973. The Orange County Water District expects that this will effect a 10 to 15 percent reduction in the total dissolved solids.

The proposed water reclamation facilities are based on the operation of the Water District's latest pilot plant studies. Lime coagulation will be used for clarification and phosphate removal, followed by ammonia stripping, recarbonation, mixed media filtration, carbon adsorption and breakpoint chlorination. (See Figure 1.)

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<sup>3/</sup>Engineering Report - Proposed Waste Water Reclamation and Sea Water Barrier Facilities, Feb., 1971 (OCWD).



64-A

**Figure 1**  
**Flow Diagram**  
 Showing Points of Diversion to Waste  
 SDPH 1971

TABLE 8. Monitoring and Reporting Program (Continued)

The nitrogenous material in the secondary effluent is in the form of organic nitrogen and ammonia. The ammonia will be removed in the ammonia stripping towers after elevating the pH to 11. Carbon dioxide will be injected in the stripping towers' effluent to stabilize the water with relationship to calcium carbonate. The two stage recarbonation and settling will further reduce the hardness and the total dissolved solids. Odor and color causing dissolved organic matter will be removed by the activated carbon adsorption process. Chlorine will be applied to destroy any remaining pathogens and to oxidize any residual ammonia.

The District expects that the proposed treatment will produce a reclaimed water prior to recharge and upon withdrawal from the ground will be: (a) odorless and colorless; (b) free of bacteria and virus; (c) meet the U.S. Public Health Service mandatory drinking water standards; and (d) be very low in suspended material, nitrogen and phosphorous.

The proposed treatment plant will be constructed on a portion of a 20-acre site owned by OCWD at the southeast corner of Ward Street and Ellis Avenue in the City of Fountain Valley.

The plant will require a highly qualified operation and maintenance staff of about 14 persons including one superintendent, eight operators, one chemist, and four maintenance men.

#### Safeguards

1. The County Sanitation Districts of Orange County, in addition to regulating industrial waste discharges into the sewerage system by ordinance, currently have under consideration materials of known toxicity for industrial discharge limitations which would improve the quality of water received at the reclamation plant. In addition, the combination of treatment processes proposed for the reclamation plant will minimize the possibility of toxic material reaching the point of injection.
2. The County Sanitation Districts are instituting a program of segregating inferior chemical quality wastewaters in the trunk sewers tributary to Treatment Plant No. 1.
3. The reclamation plant operation will be managed so that when any one treatment unit fails to function properly the flow will be diverted ultimately to an ocean outfall from any one of a number of check points, including one at the final blending tank prior to injection.
4. Bacteriological, chemical and physical monitoring programs will be designed and maintained to ensure adequate quality of the injection water.

TABLE 8. Monitoring and Reporting Program

5. Instrumentation and controls will be maintained over plant operations with regard to water quality, equipment failure, chemical feeders, power supply, etc. including:
  - a. Chemical and physical quality recording analyzers to guard against overloading of units and to detect malfunction.
  - b. Alarm system over treatment processes and equipment.
  - c. Chlorine residual analyzer and alarm system.
  - d. Two operators on duty at all times to monitor instrumentation and operate the plant.
6. Although no restrictions are presently proposed to control water withdrawal in the barrier vicinity, the District has the authority to establish restrictions and to supply those water users with other water.
7. Nine observation wells, located at intervals on both sides of the injection line, will be maintained to monitor the water quality in the aquifers.
8. Past operating data indicate adequate removal of viruses and bacteria to ensure safety from infectious disease.

#### Decision of Hearing Officer

After review of the plan presented in the "Engineering Report - Proposed Waste Water Reclamation and Sea Water Barrier Facilities" February 1971, the evidence presented at the April 7, 1971 hearing, and supplementary material dated April 14, 1971, the Hearing Officer recommends that the State Board of Public Health find that the Orange County Water District's proposed recharge will not impair the quality of water in the receiving aquifers as a source of domestic water supply.

It is further recommended that this finding be subject to the following conditions:

1. That the operation of the unit processes in the reclamation facility will be such that the return of any processed wastewater will be made to the waste sewer any time that any one of the following occurs:

TABLE 8. Monitoring and Reporting Program (Continued)

- a. The filter effluent exceeds 1.0 Turbidity Units.
  - b. The carbon adsorption column effluent exceeds 30 mg/l Chemical Oxygen Demand.
  - c. The effluent from the chlorine contact basin does not contain free chlorine residual.
  - d. It is known that the physical, bacterial, and toxic chemical limits of the Public Health Service Drinking Water Standards are not being met.
2. That in addition to the proposed monitoring instruments, a Total Organic Carbon analyzer with continuous recording be installed to monitor the carbon adsorption column effluent. Total Organic Carbon concentration will be used for control after a relationship with Chemical Oxygen Demand has been determined.
  3. That the reclaimed wastewater shall be blended at least 50 percent with desalinated seawater (or with deep well water during periods of shutdown of the desalinization plant) prior to recharge.
  4. That any change in the proposed daily sampling schedule for the wastewater reclamation plant be submitted to the State Department of Public Health for approval and that changes in the sampling schedule will be made if requested by the State Department of Public Health.
  5. That the Orange County Water District shall institute a virus monitoring program that is acceptable to the State Department of Public Health.
  6. That no recharge of groundwater shall be made until after it has been determined during the initial operation phases of the reclamation plant that the plant and its controls will perform effectively and reliably.
  7. That an alternate source of domestic water supply shall be provided any user whose groundwater is found to be impaired by the injection program.

TABLE 8. Monitoring and Reporting Program (Continued)

8. That the Orange County Water District shall retain a Consultant Sanitary Engineer who is a Diplomate of the American Academy of Environmental Engineers. The Consultant will make periodic in-depth review of the reclamation and recharge projects and report his observations together with any recommendations to the Orange County Water District and State Department of Public Health. The reports shall be made every three months unless the State Department of Public Health deems that reports may be made less frequently.

The above recommendations of the Hearing Officer are contingent upon a favorable determination by a panel of medical experts convened prior to full-scale injection. It is further recommended that the panel be reconvened annually by the State Department of Public Health to review the injection program and make recommendations.

\* \* \* \* \*

I hereby certify that the foregoing constitutes my recommendations in the above-entitled matter as a result of the hearing held before me on April 7, 1971, at the City Hall, Fountain Valley, California, and I hereby recommend its adoption as the decision of the Board of Public Health of the State of California.

DATED: May 18, 1971

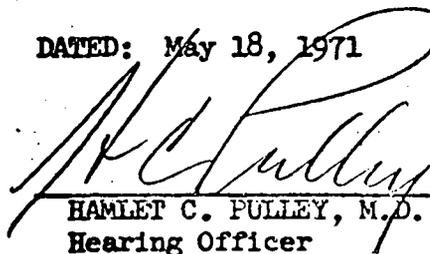
  
\_\_\_\_\_  
HAMLET C. PULLEY, M.D.  
Hearing Officer

TABLE 8. Monitoring and Reporting Program (Continued)

**BEFORE THE STATE BOARD OF PUBLIC HEALTH**

WHEREAS, the State Board of Public Health has considered carefully the proposed decision and recommendations of Hamlet C. Pulley, M.D. sitting on behalf of the Board of Public Health as Hearing Officer in the matter of:

**ORANGE COUNTY WATER DISTRICT - PROPOSED  
WASTE WATER RECLAMATION PROJECT**

IT IS THEREFORE RESOLVED that the decision and recommendations of the Hearing Officer in the above matter are hereby adopted by the State Board of Public Health as its decision.

The Orange County Water District is also proposing to conduct a two year monitoring and reliability study in cooperation with the U.S. Environmental Protection Agency. A number of analyses for chemical and microbiological constituents including virus would be performed. A description of the analytical procedures and reliability program is given below:

Procedures for all chemical and bacteriological analyses will be done in accordance with the recommended and approved procedure as detailed by current edition of "Standard Methods for the Examination of Water and Wastewater." All viral analyses will be done by the Orange County Health Department utilizing the carborundum Aquella virus concentrator.

Procedures for analysis of organics in water are rapidly evolving so that procedures which may appear best for routine monitoring at the present time may become rapidly outmoded. Nevertheless, it is important to select some procedures which will not vary over the evaluation period so that variations in plant performance can be detected. In addition, it is important to take advantage of new developments and also seek compounds which are likely to have health significance. Therefore, some portion of the analytical program must be permitted to evolve as the project proceeds. It is proposed that all procedures be standardized for the entire evaluation period except the detailed characterization procedures (DC) which will be allowed to evolve to take advantage of new information. The tentative procedures to be used for each analysis are outlined below. Before finalizing a particular analytical technique, however, it will be necessary for the chemist on the project to survey the literature and seek advice from the various analytical laboratories conducting organic analyses in order to insure that the best procedures are being used.

#### 1. General Organic Characterization

a. Volatile Organic Analysis (VOA) - The procedure described by Bellar and Lichtenberg in EPA-670/4-74-009, The Determination of Volatile Organic Compounds at the ug/l Level in Water by Gas Chromatography, (November 1974) will be used. In general, volatile organics will be stripped from a sample and concentrated on a porous polymer trap for gas chromatographic analysis with a flame ionization or electron capture detector. Initially, identity of peaks will be verified by a gas chromatograph-mass spectrometer (GC/MS) system. Routine analyses will be conducted with the gas chromatograph (GC) alone after that, unless new peaks appear which need identification, or for occasional verification.

b. Solvent Extractable Analysis (SEA) - Procedures similar to those developed by W. E. Loy and D. W. Brown, EPA Southeast Environmental Research Laboratory, Athens, Georgia, will be used to determine the identity and concentration of non-volatile low molecular weight compounds. The procedure essentially employs three separate extractions from about 1 liter of sample. First, the sample is extracted with hexane at a neutral pH. Next, it is extracted under acid conditions with a mixture of ethyl ether and methylene chloride. Finally, an extraction under basic conditions with methylene chloride is conducted. The extracts will be injected into a GC system for routine analyses, and into a GC/MS system for identification of components on some infrequent basis as needed. These procedures can be modified to obtain larger quantities of certain materials, and some exploration of procedures will need to be made in order to determine the best to use for routine monitoring.

c. Detailed Characterization - This analysis will be done less frequently on samples because of the large amount of time likely to be involved. The procedures will be directed toward determining the characteristics of the higher molecular weight materials which are not easily volatilized in a GC system. Procedures are expected to be along the lines of those being pursued by Thomas A. Pressley, EPA, Blue Plains Treatment Plant, Washington, D.C. The approach will be to conduct column chromatography with a selected group of solvents in order to determine general functional groups and overall organic characteristics. Samples of about 20 liter size will be first concentrated by vacuum distillation at reduced temperature in order to minimize changes in molecular configuration. The exact procedures will evolve after discussions with researchers in this area and consultation with EPA representatives. The objective of this series of analyses is to obtain a comparison between these more complex materials being evolved from reclaimed wastewaters and similar materials found present in the usual surface and groundwaters presently being used as sources of drinking water. In order to do this, adaptation will be necessary to some of the techniques presently being used for more detailed analysis of selected water supplies by the Water Research Group at the EPA, Cincinnati Laboratory. In addition, compounds which are known to have health significance will be sought. Guidance in this phase will be obtained through consultation with EPA representatives and with Dr. Joshua Lederberg, Chairman, Department of Genetics, Stanford University. This analytical task, thus, will combine the use of a routine procedure for detailed chemical characterization with an exploratory aspect to seek the presence of compounds of health significance.

2. Polynuclear Aromatic Hydrocarbons (PAH)- The procedure suggested by the World Health Organization in its European Standards for Drinking Water, 2nd ed. (1970) will be used. It consists of an evaluation of the concentration of 6 PAH compounds, namely: 3,4-benzfluoranthene, 1,12-benzfluoranthene, 3,4-benzpyrene, fluorethene, 1,12-benzperylene, and indeno (1,2,3-cd) pyrene.
3. Pesticides - The procedure to be followed is that outlined for organochlorine pesticides in Methods for Organic Pesticides in Water and Wastewater, Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio (1971). An electron capture detector will be used. Compounds will initially be identified using GC/MS system, but the GC alone will be used otherwise for routine analyses. Among the various pesticides which can be identified by this procedure are BHC, lindane, heptachlor aldrin, chlordane, dieldrin, endrin, DDT, DDD, DDE and methoxychlor.
4. Trichlorobenzene (TCB) - TCB will be determined as one of the volatile components under the TOA method of analysis already described.
5. Radioactivity - The procedure outlined in Standard Methods for the Examination of Water and Wastewater, 13th ed., American Public Health Association, will be used for measuring the gross alpha and beta activity of samples.

#### E. Sample Collection

Samples will be collected, prepared for shipment on ice if needed, transported to the Orange County Airport, and shipped by air freight to San Jose, California by OCWD personnel. The samples will be transported from San Jose to the Stanford Water Quality Control Laboratory by Stanford personnel. Only that portion of the sample collection and transportation costs from the San Jose Airport to Stanford are covered by the budget under this proposal.

OCWD will be responsible for following good procedures in sample collection, treatment and preservation as mutually agreed upon by OCWD and Stanford personnel. In general, 24-hour composite samples will be collected under refrigeration during the 24-hour period prior to air shipment to Stanford. Collection times will be determined to a degree by airline schedules so that samples can reach Stanford during the working day during which sample collection is completed. This should not be difficult since combined air and ground travel time from Water Factory 21 to Stanford is less than two hours.

The samples for VOA must be grab sampled (because volatile components would be lost by the usual 24-hour composite method of sampling) using techniques to minimize the loss of volatile components. The samples will immediately be placed in a purging device and volatile organics will be gas stripped onto an adsorbant packed trap by OCWD personnel. The trap will then be packaged for shipment by air freight to Stanford. The traps will be prepared for sample collection at Stanford and returned to OCWD at periodic intervals. Thus, OCWD will be responsible for collection with the trap and not for trap conditioning.

During days of the month when 24-hour grab samples are required, Stanford personnel will assist at Water Factory 21 in sample collection. This will help relieve the sample collection load on OCWD for that period and will also afford an opportunity for Stanford personnel to review progress and sampling techniques with OCWD.

#### Reliability Program:

The plant must be maintained in continuous operation at design conditions (7.5 or 15 mgd) during the task period. Contingency plans must be prepared and implemented when needed to keep the system operating to meet the required effluent standards. The production of water approaching potable quality at all times is the major objective of this task as well as being consistent with the major objective of the District to produce a usable product water which meets regulatory requirements and can be utilized for groundwater recharge. At various frequencies as shown in Figure 3, task schedule samples will be taken at 2 hour intervals for a seven (7) day period, Monday through Sunday, to evaluate the plant influent and effluent variability. The analyses to be performed on these samples are indicated in Table 9.

Sufficient personnel to provide continuous plant operation are required. The necessary records to determine operating problems and corrective actions, and costs should be maintained and summarized to fully document, how and at what cost, continuous reliable operation was attained.

The following is the proposed monitoring program for the study including the sampling and analytical schedule.

TABLE 9

PROPOSED SAMPLING AND ANALYTICAL SCHEDULE

| LOCATION ON FIGURE 2 -      | 1   | 2  | 3  | 4 | 5  | 6   | 7   | 8   | 9 | 10 | 2-hour Influent & Eff. Variability Samples |
|-----------------------------|-----|----|----|---|----|-----|-----|-----|---|----|--|
| PARAMETER:                  |     |    |    |   |    |     |     |     |   |    |  |
| Coliform-T                  |     |    |    |   |    |     |     | DC  |   |    |  |
| Coliform-F                  |     |    |    |   |    |     |     | DC  |   |    |  |
| Total Count                 |     |    |    |   |    |     |     | DC  |   |    |  |
| Animal Virus                | 2M  | 2M |    |   |    |     |     | 1W  |   |    |  |
| Salomonella                 |     |    |    |   |    |     |     | 1W  |   |    |  |
| Pseudemecna arugenesa       |     |    |    |   |    |     |     | 1W  |   |    |  |
| Pseudemonads                |     |    |    |   |    |     |     | 1W  |   |    |  |
| Dissolved Oxygen            |     |    |    |   |    |     |     | DG  |   |    |  |
| Calcium                     | DC  |    |    |   |    |     |     | DC  |   |    |  |
| Magnesium                   | DC  |    |    |   |    |     |     | DC  |   |    |  |
| Potassium                   |     |    |    |   |    |     |     | DC  |   |    |  |
| Chlorides                   |     |    |    |   |    |     |     | DC  |   |    |  |
| Sulfates                    |     |    |    |   |    |     |     | DC  |   |    |  |
| Alkalinity                  | DC  |    |    |   |    |     |     | DC  |   |    |  |
| CaCO <sub>3</sub> Stability |     |    |    |   |    |     |     | DC  |   |    |  |
| Sodium                      |     |    |    |   |    |     |     | DC  |   |    |  |
| Hardness                    |     |    |    |   |    |     |     | DC  |   |    |  |
| TDS                         | DC  |    |    |   |    | DC  | DC  | DC  |   |    |  |
| Nitrate                     |     |    |    |   |    |     |     | DC  |   |    |  |
| Nitrite                     |     |    |    |   |    |     |     | DC  |   |    |  |
| Ammonia                     | DG  |    | DG |   |    |     |     | DG  |   |    |  |
| TKN                         | DG  |    | DG |   |    |     |     | DG  |   |    | X  |
| Phosphorus Total            | DC  |    |    |   |    |     |     | DC  |   |    |  |
| Trace Elements (1)          | 1WW |    |    |   |    | 1WW | 1WW | 1WW |   |    |  |
| COD                         | DC  |    |    |   | DC | DC  |     | DC  |   |    |  |
| TOC                         |     |    |    |   | DC | DC  |     | DC  |   |    | X  |
| CCE                         |     |    |    |   |    |     |     | 1W  |   |    |  |
| CAE                         |     |    |    |   |    |     |     | 1W  |   |    |  |

LOCATION  
ON FIGURE 2 -

| Parameter:                           | 1                                     | 2  | 3 | 4  | 5                         | 6  | 7                         | 8                                     | 9 | 10 | 2 hr. Influent & Effluent Variability Samples |
|--------------------------------------|---------------------------------------|----|---|----|---------------------------|----|---------------------------|---------------------------------------|---|----|---|
| Chlorine Demand                      |                                       |    |   |    |                           |    |                           | 1W                                    |   |    |   |
| Chlorine Residual                    |                                       |    |   |    |                           |    |                           | CC                                    |   |    |   |
| Cyanids                              |                                       |    |   |    |                           |    |                           | 1W                                    |   |    |   |
| Phenols                              |                                       |    |   |    |                           |    |                           | 1W                                    |   |    |   |
| Organic Identity (2)                 | { 1-2/w+1 Diurnal/m<br>2-1m<br>3-1/3m |    |   |    | { 1-1/m<br>2-1m<br>3-1/3m |    | { 1-1/m<br>2-1m<br>3-1/3m | { 1-2/w+1 Diurnal/m<br>2-2w<br>3-1/3m |   |    |   |
| Pesticide (3)                        | 1m                                    |    |   |    |                           |    |                           | 1W                                    |   |    |   |
| Turbidity                            | CC                                    | CC |   | DC | CC                        |    |                           | DC                                    |   |    | X   |
| Odor                                 |                                       |    |   |    |                           |    |                           | 1W                                    |   |    |   |
| Color                                |                                       |    |   |    | DC                        | DC |                           | DC                                    |   |    |   |
| Suspend solids                       | DC                                    |    |   | DC | DC                        |    |                           | DC                                    |   |    |   |
| Vol. Sus. Solids                     |                                       |    |   |    |                           |    |                           | DC                                    |   |    |   |
| Vol. Solids                          |                                       |    |   |    |                           |    |                           | DC                                    |   |    |   |
| Total Solids                         |                                       |    |   |    |                           |    |                           | DC                                    |   |    |   |
| Temperature                          |                                       |    |   |    |                           |    |                           | DG                                    |   |    |   |
| pH                                   | CC                                    | CC |   |    |                           |    |                           | CC                                    |   |    |   |
| Conductivity                         | CC                                    | CC |   |    |                           |    |                           | CC                                    |   |    |   |
| MBAS                                 | 1W                                    |    |   |    |                           |    |                           | 2W                                    |   |    |   |
| UV                                   |                                       |    |   |    | 2W                        | 2W |                           | 2W                                    |   |    | X   |
| Radioactivity (4)                    |                                       |    |   |    |                           |    |                           | 1W                                    |   |    |   |
| Polycyclic Aromatic hydrocarbons (5) | 1M                                    |    |   |    | 1M                        | 1M |                           | 1W                                    |   |    |   |
| Trichlorobenzene                     | 1M                                    |    |   |    | 1M                        | 1M |                           | 1W                                    |   |    |   |

(1) Trace elements include: arsenic, chromium manganese, zinc, barium, copper, mercury, boron, fluorid selenium, cadium, lead, silver, iron

(2) Organic Identification: 1 - Volatile Organic Analysis; 2 - Solvent Extractable Analysis; 3 - Detailed Characterization

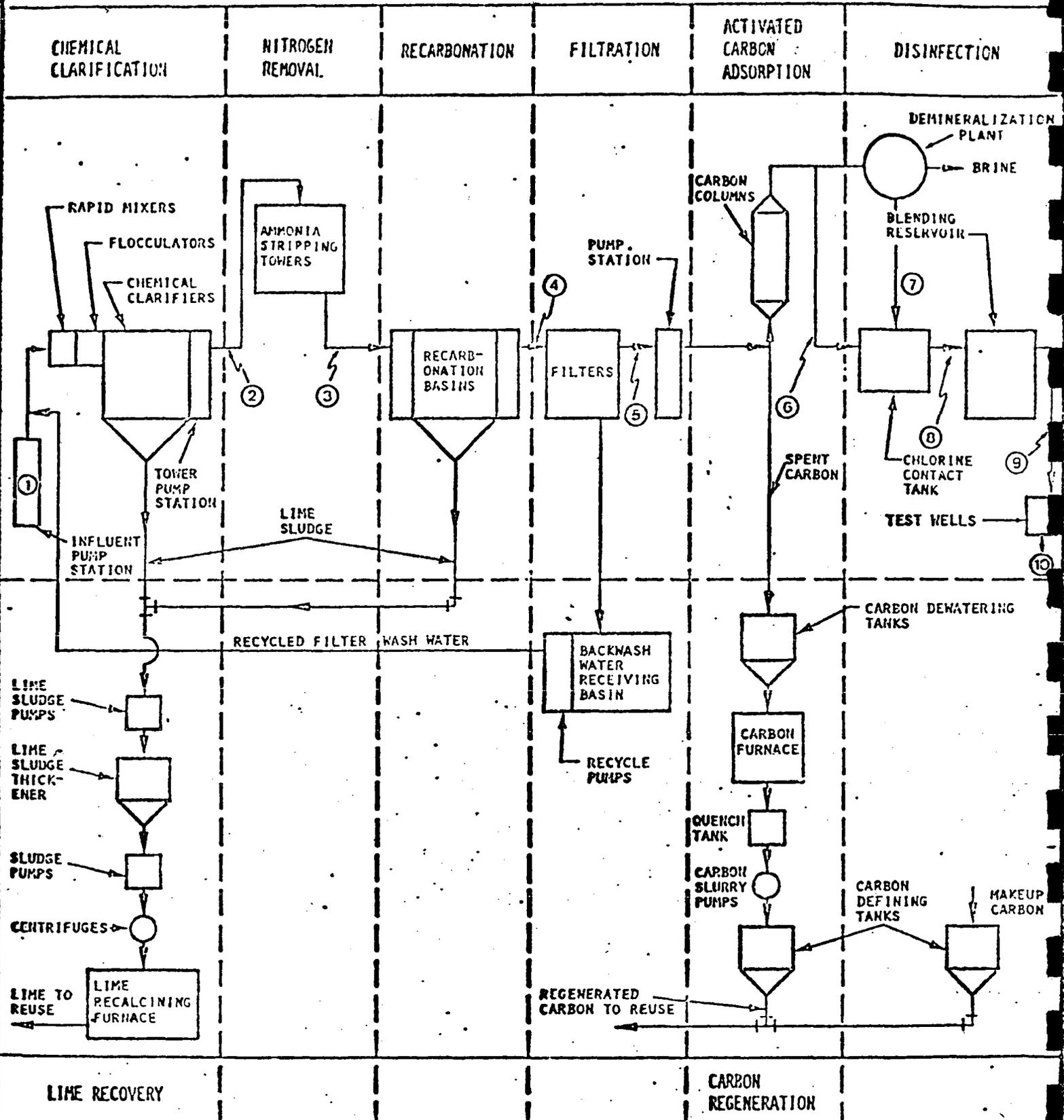
(3) Pesticides include: Aldrin, DDT, BHC, lindane, heptachlor, chlordane, dieldrin, endrin, DDD, DDE and methoxychlor.

(4) Radioactivity includes: gross alpha, gross beta, ...

(5) Polycyclic aromatic hydrocarbons include: fluoranthene, 3,4-benzofluoranthene, 1,2,3,4-tetrafluoranthene, 1,2,3,4,6-pentafluoranthene, 1,2,3,4,6,7-hexafluoranthene, 1,2,3,4,6,7,8-heptafluoranthene, 1,2,3,4,6,7,8,9-octafluoranthene, 1,2,3,4,6,7,8,9,10-nonafluoranthene, 1,2,3,4,6,7,8,9,10,11-decafluoranthene, 1,2,3,4,6,7,8,9,10,11,12-dodecafluoranthene

SAMPLING FREQUENCY

- 1 Diurnal/m - Diurnal evaluation  
once per month of 8 grab samples taken at 3-hour intervals
- 2/W- twice per week grab
- 1/m - once per month grab
- DC - Daily composite
- DG - Daily grab
- 1m - once per month on 24-hr. comp.
- 1W - once per week on 24-hr. comp.
- 2W - twice per week on 24-hr. comp.
- CC - continuous control
- 1/3M - once per 3 months on 24-hr. comp.
- 1WW - once per week on weekly comp.



°SAMPLE LOCATIONS SHOWN BY CIRCLED NUMBER, e.g. ①

SOLIDS HANDLING

FIGURE 2  
SCHEMATIC DIAGRAM OF WATER FACTORY 21  
PROCESSES AND SAMPLING LOCATIONS



IDENTIFICATION OF WASTEWATER CONSTITUENTS

Among the considerations going into the development of a water quality monitoring strategy must be an assessment of the analytical capabilities available. Typically these will vary among dischargers with the size or complexity of the process. A number of large dischargers, particularly those in the metropolitan areas of California, have developed fairly strong laboratories as an adjunct to process control and these may form the basis for one approach to water quality monitoring. Smaller dischargers generally display minimal laboratory capability and depend upon commercial laboratories for the more complicated analyses. Among the independent laboratories this same spectrum of capabilities is seen.

For more than twenty years the Department of Health has maintained a Water Laboratory Approval program for the purpose of assuring the adequacy of water quality data generated by public and private laboratories. With financial assistance from the State Water Resources Control Board during the past two years, this program has been intensified and information is now available on some 400 laboratories throughout the State. Among these laboratories are a few, perhaps 24, that could be considered as adequate for the most sophisticated of monitoring schemes. The bulk of the laboratories have more limited capabilities, but many could be utilized by good coordination of efforts. There are, of course, a few whose capabilities are so limited that they could not be considered for any but the most rudimentary monitoring schemes.

Inorganic Constituents

At present, molecular and atomic absorption spectroscopic methods represent the state of the art in inorganic analysis for most small to medium-sized laboratories. These technics are generally adequate for potable water samples down to the levels expressed in the first drafts of the new drinking water standards and are also cited for use in National Pollutant Discharge Elimination System permit monitoring programs. The molecular absorbance technics, in general, require more time in sample preparation and color development than do the atomic absorption approaches and are also less sensitive in general. They are the most practical methods when the factor to be measured is of a complex structure, but, in addition, lend themselves to automation of the analytic process. These automated methods may prove useful for monitoring where sample load can be maintained at a high level. The design concept comes from the clinical laboratory, or has seen its fullest utilization there, and has only in the past few years been applied to water quality chemistry. Most systems are justified on the need to estimate the concentration of a few factors in large numbers of samples. The heart of an automated system is the sample distribution system which is connected to a single channel or multiple channel analyzer. The use of such instruments can result in major improvements in test precision, but they are not without their faults. Samples must be delivered to the instrument and must be in the proper sequence on the sample distribution plate. With most systems a good deal of analyst time is spent in setup

and if problems occur during an analytic sequence the entire sequence must be repeated following troubleshooting procedures. Some instruments have been set up with fail safe and alarm systems to halt operation and alert the analyst should a value for an interspersed standard solution exceed the limits set for it. Such systems are rare, however, and generally in use in large clinical laboratories where the sample load makes them practical.

Atomic absorption methods have been used most effectively in estimation of trace element concentrations. Because of the sensitivity and the speed with which samples can be prepared and analyzed it has become a most useful tool. Atomic absorption spectroscopy may be used for normal and trace level analysis simply by alternation of the excitation method, flame for the more normal levels and one of the nonflame techniques for the trace levels. Lead, for example, may be measured to a level of 500 micrograms per liter ( $\mu\text{g}/\text{l}$ ) in water using a conventional flame method, but to a level of  $<1 \mu\text{g}/\text{l}$  using a heated graphite atomizer (HGA) for excitation. Certain elements can be measured effectively only by use of a flameless technic, as in the case with mercury. As a monitoring tool atomic absorption suffers several major faults. At present, there are no automatic means available to adjust for variations in concentration of the element to be measured and multielement capability is not yet out of the developmental stages. Thus, a series of samples containing an element at levels requiring both flame and flameless techniques or a single sample with several elements of interest requires the intervention of an analyst for change in mode, generally a time consuming

operation. For example, in the State Health Department Laboratories the examination of 15-20 wastewater samples for trace levels of 10 elements requires a minimum of 5 working days. High cost mediates against the use of several instruments in all but the best equipped laboratories.

Also to be found with increasing frequency in larger laboratories are instruments designed to measure fluorescence. In comparison to molecular absorption, molecular fluorescence allows for detection at much lower levels<sup>3</sup> and should be as easily applied in a continuous analysis scheme as the absorption methods. That these methods are not widely used may relate to the difficulty in eliminating interference from naturally fluorescing compounds in water.<sup>4</sup> Once this background is accounted for, fluorescent methods represent a fast, sensitive means for the estimation of many elements and compounds. Levels of detection vary widely, but many are in the range achievable by atomic absorption. This is an area where methods development should prove quite fruitful, since adequate instrumentation is commercially available.

Not as far along in development, but certainly an intriguing approach to low level measurement of metals is atomic fluorescence. Like its counterpart, molecular fluorescence, this technic depends upon quantitation of emitted radiation at a wave length different from that of the incident light. The method offers extremely low levels of detectability for certain elements, that for mercury in water has been reported to be in the sub-nanogram range.<sup>5</sup> Its most appealing feature lies in the possibilities for automation, for this technic could overcome the major

fault of commercially available atomic absorption, inability to function in a multielement mode. Ease of conversion of atomic absorption instrumentation to the fluorescence mode also makes fluorescence spectroscopy attractive where extremely low levels must be dealt with and budget restrictions preclude separate instruments. However, the method cannot be applied over a wide concentration range. Again, this is an area with the potential for great return on the research investment dollar.

Various forms of x-ray fluorescence spectroscopy are now being used in university and large research laboratories with varying claims being made for efficacy. In particular, energy-dispersive x-ray fluorescence spectrometers have been hailed as the answer to the simultaneous multi-element analysis problem. The solid state detectors used in these instruments have, in many cases, overcome the former inability of the instruments to distinguish between two elements of adjacent atomic number.<sup>6</sup> However, even the best of the energy-dispersive instruments cannot distinguish between neighbors in all cases, and this means the addition of computer capabilities to put the spectral data in usable form. Improvements in the wave length-dispersive technic in the past few years have made it more competitive with the energy methods in terms of sensitivity and amenability to automation. The varying claims for sensitivity emphasize that much more developmental and applications work must be done with these instruments before they can be employed with confidence in water quality analysis. Limited experience with laboratories in California indicates a tendency to ignore the necessity for a

highly skilled analyst, placing too much reliance upon the instrument, and a tendency to be over optimistic in stating detection limits.

Among the other spectroscopic technics available for the quantification of inorganics are spark source mass spectrometry, inductively coupled plasma emission spectroscopy and neutron flux activation analysis and in the developmental stage are atomic absorption and atomic emission technics using image tubes. All provide rapid, multi-element analysis once the sample is presented to the instrument. However, capital outlay is enormous and a high calibre analyst is required, driving the cost per sample to an extremely high level. Per sample costs using activation analysis can be reduced to a reasonable figure provided sample load is maintained at a high level. The need for a heavy sample load, the problems inherent in providing and maintaining an activation facility, and the inability to provide real time data mediate against activation analysis as a real life solution to water quality analysis problems. Plasma emission instruments are only now becoming available to the ordinary analyst leaving the very expensive but extremely effective spark source mass spectrometer as the only real possibility here. Combining multielement capabilities and detection limits at least a hundredfold better than atomic absorption this technic shows great promise but it is extremely expensive and can handle only low volume work because of sample preparation requirements. Attractive as these methods seem, they will only be a realistic approach for the large, well staffed laboratory, but could be of real value if properly coordinated in a large scale monitoring plan.

Interest in electrochemical methods for inorganic analysis arises from improvements that have been made in voltametric analysis and the large number of ion-selective electrodes now becoming available. Anodic stripping voltametry, in essence a reversal of the dropping mercury electrode approach to polarography, offers an extremely powerful tool for metals analysis in the parts per billion range.<sup>7</sup> Pulse polarography, in which the entire sweep is made in the lifetime of a single drop, has also been reported to have high sensitivity.<sup>8</sup> The instrumentation is priced within reach of most mid-sized laboratories and does represent a step toward multielement analysis, but requirements for sample pretreatment to remove interfering compounds and release all metal ions to a free state and to maintain the complex instrument mean that a highly skilled analyst must be available. This approach still suffers from a complexity which will limit its use to the most sophisticated of laboratories.

Ion selective electrodes, on the other hand, would appear to be ideally suited to the needs of the small water quality laboratory. The activity in solution of a specific ion is measured in much the same way that hydrogen ion activity is determined in pH measurements. However, the electrodes are really not as selective as one would hope and many possibilities for interference exist. These can be overcome with operator skill and familiarity with the character of the samples. Electrodes have a great potential for continuous monitoring, and many are in use in flow-through systems; for example, fluoride ion activity electrodes

are used in many water treatment plants where adjustment of the fluoride ion concentration is part of the treatment process. Experience in California laboratories indicates that a great deal of down time and maintenance may be expected from even the best of the systems, but it is expected that this approach will continue to be popular among analysts in laboratories with limited budgets. The higher rated facilities in California tend to employ professional chemists in their laboratories and equipment is generally far superior to that found in the other facilities. It is not at all uncommon to find state of the art instrumentation among the larger dischargers. Many medium-sized laboratories now are capable of flame mode atomic absorption spectrometry, with most of the larger facilities using the more sensitive graphite furnace (HGA) approach for atomization. This is also true of the independent or commercial laboratories, many of whom in addition have moved toward automation where it is available and sample load makes it economically attractive. There are several commercial laboratories presently providing analyses by x-ray fluorescence technics and by neutron activation analysis. Other multielement capabilities are generally found only in university or large research laboratories.

There are, then, a number of satisfactory approaches to analysis of inorganics, most of which depend upon instrumentation amenable to a scheme of simultaneous or sequential multielement analysis or the rapid analysis for a single factor in a large number of samples. It is generally in sampling that problems arise although a few manufacturers

offer instruments for the simultaneous analysis of a dozen factors and these have, in some cases, been connected to flow-controlled sampling devices to provide almost real time, on line data on water quality. In these cases, the water quality laboratory -- or a part of it -- has actually been moved to the sampling site. This approach, providing a large amount of data on a limited number of parameters for a single site, will certainly find use in certain monitoring situations. Such fixed station approaches, however, become quite costly as stations are added. When samples can be collected from many points and delivered to a central laboratory, efficient use of expensive instrumentation becomes possible. Well equipped water quality laboratories in California are capable of examining large numbers of samples for metals, the common ions, and trace elements in a reasonably prompt manner and at very low concentrations. At present we estimate that perhaps two dozen laboratories have these capabilities.

The ability to monitor water quality factors in real time is almost nonexistent. Only a few factors may be successfully measured in a time frame that allows immediate access to and use of the information. Most depend on an electrochemical approach and this may account for the extravagant claims made when ion selective electrodes were first introduced. Those factors which can presently be measured with confidence, on a routine basis, and in real time include chloride ion, conductivity, dissolved oxygen, oxidation-reduction potential, pH, temperature, and turbidity.

If immediate response to changes in water quality is a requisite for a monitoring program -- and no case has yet been made -- then this list of parameters is indicative of the shortcomings of our analytic capabilities. No factors of real health significance can be monitored in real time, but given the ion levels of inorganic pollutants one can expect in a well treated effluent and the considerable dilution effects following application, real time analysis may be relegated to a lower level of priority. Only in the case of massive spills or process breakdowns would problems arise and these may well be signalled in other fashions.

Identification and measurement of the inorganic constituents of wastewater can be accomplished by a variety of well tested methods. These have been compiled in such publications as Standard Methods for the Examination of Water and Wastewater,<sup>9</sup> Manual of Methods for Chemical Analysis of Water and Wastes,<sup>10</sup> Official Methods of Analysis of the Association of Official Analytical Chemists,<sup>11</sup> and Annual Book of American Society for Testing and Materials Standards.<sup>12</sup> These publications provide choices of methods to suit the needs of the analyst and provide background information necessary to proper use of the chosen method. Dischargers under National Pollutant Discharge Elimination System permit are required to use methods specified by the Environmental Protection Agency in Title 40, CFR, part 136.<sup>13</sup> In general, the methods cited are from the publications listed above.

In terms of inorganic constituents of wastewaters prospects for establishing adequate monitoring programs are good and should become

even better as instrumentation being developed becomes commercially available. Well developed and standardized methodology is currently in use and the level of proficiency in the larger independent and public laboratories is adequate for the more common determinations. Experience for the Monterey Basin Pilot Monitoring Project indicates that laboratory costs will be quite high, a factor which must be considered in the design of a monitoring program.

#### Organic Constituents

The situation in relation to identification, quantification and monitoring of organic compounds is much more serious. Even when dealing with pure compounds characterization and quantification are often difficult, time consuming and quite expensive. The wastewater matrix makes the task even more formidable and possible only in the most advanced laboratories. Presently, in California, not more than a dozen available laboratories are capable of providing trustworthy data on the organic constituents of wastewaters.

The major stumbling block is that no overall scheme for identification of the various types of organic compounds is at hand. A good deal of the problem revolves around methods of sampling, methods which often define the classes of compounds which may then be identified. A logical approach to characterization of the materials in a water sample must be developed. There have been attempts to face the problem utilizing fairly simple measurements of organics load. The organics-carbon adsorbable (O-CA) represent those organic materials which can be removed from a water

sample by passage over activated carbon, and are expressed by a simple weight statement. In reality a sampling method it provides a starting point in that the organics adsorbed on the carbon can be eluted on a selective basis for further study and characterization. It has seen limited use in studies of sewage effluents because of fouling and clogging problems and would be of little value in a monitoring program.

Neither this method nor the demand analyses commonly used to describe the kinetics of the treatment process can give us any real information on treatment refractory organics, and other more involved procedures have of necessity been used in the relatively few studies which have been completed. Additionally, most studies have concentrated on one or several readily identified compounds or classes of organic materials. Thus, reasonably detailed information is available regarding the organochlorine, organophosphate, and carbamate pesticides, their isolation from water samples and ultimate identification. The same is true for such classes of compounds as polychlorinated biphenyls (PCBs), phenolic compounds, and some of the plasticizers.

However, relatively few state of the art studies have been carried out in attempts to characterize stable organics in effluents because the methodology for collection, isolation and identification is quite complex and the instrumentation very costly. In addition to charcoal, various resins have been used to collect and concentrate organic material for further study, each adsorbent resulting in a different product mix for analysis. Liquid-liquid extraction has long been used, but also

suffers in that choice of solvent determines, at the outset, just what will be extracted. Inert gases can be used to strip volatile organics from solution, with subsequent trapping by liquid oxygen or nitrogen freeze-out.<sup>14</sup> The use of liquid oxygen or nitrogen obviously ties this method to a laboratory and thus, some investigators have sought to devise other trapping methods. Ambient temperature trapping for a variety of materials familiar to the gas chromatographer, followed by introduction of the trapped organics to a gas liquid chromatograph has lately been introduced.<sup>15</sup> Since no single column packing material is adequate to the task of trapping the wide range of compounds one might expect to find in an effluent some analysts have used layered trapping columns. Successful trapping of compounds of wide molecular weight range have been reported by analysts using this technic. Use of methods such as these should allow sampling at points remote from a central laboratory with the obvious attendant economic advantages.

Sampling, however, is but the first of the problems encountered with organics. The very high cost of the sophisticated instrumentation necessary for separation and identification of these compounds places them out of the reach of most laboratories. About all that will be available to most small to mid-sized laboratories will be a simple infrared spectrometer or gas-liquid chromatograph. Infrared spectrometry represents an excellent tool for characterization and quantification of well separated materials, but complex mixtures are less well handled even when the more expensive instruments are available. A considerable library of infrared spectra is available from commercial sources and computer mediated

identification of spectra is possible where cost is not a problem.

The gas-liquid chromatograph has been one of the most important tools added to the laboratory in recent years, and for most laboratories in California, along with atomic absorption spectroscopy, represents the state of the art in instrumentation. Essentially an instrument for detecting the separation of active groups in a complex mixture after passage through a separating column the gas-liquid chromatograph does not truly provide for identification, although quantification is possible. Choice of column packing material, temperature program, and detectors all affect the chromatogram, and even when several different columns indicate the presence of a particular group the cautious analyst will claim only about a ninety percent chance of being correct. The formation of derivatives may be used to further strengthen the original chromatographic information.

The applications of mass spectrometry technics to gas-liquid chromatograph-separated materials has resulted in an extremely powerful tool for identification of organic compounds. The extreme cost of this equipment and the necessity for highly qualified personnel to man it has limited this type of instrument to relatively few water quality laboratories. The recent work on organics in the New Orleans area water supply was done using combinations of all the sampling and identification methods mentioned above and involved three National Environmental Research Laboratories and one Regional Surveillance and Analysis Laboratory of the Environmental Protection Agency in addition to a university and private

research institute laboratory.<sup>16</sup>

Approaches to collection and identification of organics presently under development include the use of reverse osmosis for sampling and concentration and the decomposition of organics in a helium plasma followed by atomic emission spectroscopy,<sup>17</sup> gas chromatography after isolation and concentration by ion and ligand exchange,<sup>18</sup> Raman spectroscopy,<sup>19</sup> and infrared photometry measuring absorbance in the OH and CH bands by total attenuated reflectance.<sup>20</sup> These methods are far beyond the capabilities of all but a few research laboratories and presently cannot be considered as serious alternatives for the identification of organics on a routine basis.

Among dischargers in California there are only a very few laboratories with the qualified personnel and necessary equipment to carry out even the most rudimentary program of organics identification and quantitation. Larger commercial laboratories are more likely to have these capabilities, but preliminary surveys by the State Health Department's Water Laboratory Approval Group indicate wide variations between claimed expertise and actual performance.

Complete identification of organics in a given wastewater does not yet appear feasible but the most promising approach seems to be application of gas chromatography/mass spectrometry systems coupled to a computer for final identification. Time required for analysis and cost of such systems may remove them from consideration for routine monitoring schemes.

More important than considerations of possible instrumentation are the needs for logical analytical approaches. This need has been recognized and clearly stated by the Panel on Public Water Supplies in a report to the National Academies of Science and Engineering:

"Comprehensive analytical schemes for the isolation and identification of all classes of organic materials in aquatic environments must be developed. Specific objectives should be development of sampling procedures for dissolved and particulate organics, chromatographic and other separation procedures, and advanced instrumental techniques for specific compound identification. Current knowledge in this area should be integrated to produce a comprehensive handbook for scientists interested in analyzing water samples.

"Systematic studies of the origins of various classifications of organic compounds that occur in water and determinations of the concentrations, fate and persistence of these compounds in the aquatic environment are needed. ..."<sup>21</sup>

#### Biological Constituents

Time represents a major problem in the isolation and identification of biological contaminants to be expected in a reclaimed water. Methods are available but the information developed may be days or weeks in coming and will thus be of value only in the detection of long term trends.

Only examination for total numbers of organisms or for the common indicator organisms can be done quickly. The standard plate count may be completed in twenty-four hours but is of little real value in evaluating the condition of an effluent because the medium used does not permit the growth of the full spectrum of organisms present.

Estimation of the density of coliform organisms requires up to four days (through the confirmed test) when carried out by multiple fermentation methods but has a long history of use as an indicator of the efficacy of the treatment and disinfection process. Use of membrane filter methods can cut this time to eighteen to twenty-four hours and several research groups are working on methods requiring even less time -- as little as seven hours. Membrane filter methods do exhibit certain problems when applied to effluents of less than the highest degree of treatment. These problems can be overcome, but greater analyst skill and knowledge is necessary and, often, times comparable to tube methods are required.

Rapid biomass determinations have recently become possible through the use of instruments designed to measure adenosine triphosphate levels by means of the luciferin-luciferase reaction. These luminescence biometers have been used in a number of studies of natural and polluted waters, but, obviously, no identification is possible and levels of detection are higher than required for reclaimed waters. Analyst capability is of importance in these applications, especially in the preparation of reagents, thus removing applicability for most small laboratories.

Methods for the isolation and identification of specific organisms, particularly pathogens, have long been called for by those who feel that the use of indicator organisms does not provide a satisfactory margin for safety. Since the bulk of the pathogens in sewage originate in the gut it is natural that the enteric pathogens have been the organisms most widely sought. In the past few years a number of systems for the identification of enterics have become commercially available, but all suffer the shortcomings associated with time and with the need for enhanced capability of personnel. There is little question that, in the hands of a competent analyst, these methods provide information relating to enteric organisms quickly and without the logistical problems encountered using older methods. Even with these methods, however, quickly is measured in terms of days after primary isolation, and quantification is lacking. Methods for quantification of specific genera of enterics are in the process of development, with most of the effort being directed toward the salmonellae. These methods are quite important and deserve support for further refinement and development.

Until rapid, simple methods for isolation and quantification of specific pathogenic organisms becomes a reality we must be satisfied with the use of indicator organisms to assess the biological state of an effluent. Because of their long history of adequate use it is important to concentrate on these groups, developing more rapid and precise methods for their estimation.

Current developments in estimating viral densities in water are primarily related to sampling and concentration prior to isolation and identification. A number of methods are now available which allow for the concentration of small numbers of virus particles from large volumes of water. These vary from filtration through different types of filters, such as membranes or alginate, with the virus particles adsorbing to the filter material, adsorption to polyelectrolytes, adsorption in a two-phase aqueous polymer system, to adsorption on gauze pads. Each of these systems suffers from one or more drawbacks, ranging from low and variable recovery to requirements for enormous sample volumes. Clogging of filters, even when handling relatively clean waters, and inhibitory effects on some viruses are also problems which have been encountered. Use of these methods in a routine sampling/monitoring program has not, as yet, been completely evaluated. They are still restricted to the laboratory setting.

Even given an adequate method of sampling and concentration, applicable in all situations, there are still many technical problems to be overcome in identification and quantification. Most work on the collection methods has been done using one or a few readily identifiable virus strains. Since one need not expect this luxury in the real world, the analyst must be prepared to handle the large number of serotypes to be found among the enteroviruses. This implies the development and maintenance of a large number of host systems for propagation and a supply of specific immune sera for identification of the various

serotypes. Since there are at least one hundred enteric virus serotypes, only very large, well equipped laboratories with highly trained personnel will ever be able to handle such problems on any basis which even comes close to an adequate schedule for monitoring viruses in reclaimed water. Evaluation of and improvement upon these technics is a necessary first step to the development of a rational monitoring system and must be supported in laboratories where expertise is available and recognized. Much of the data, to date, comes from laboratories with limited resources and the question of the wide range of viral agents present in sewage has not been addressed.

Analytic capabilities vary widely among laboratories available to California dischargers. Most approved laboratories have capabilities for only indicator organisms and total count. Only the Public Health Laboratories and a few of the clinical laboratories have the ability to identify specific microorganisms and only a few laboratories have any real capabilities in virus isolation and identification. The latter are, for the most part, research oriented and thus not really available for monitoring.

Identification and enumeration of biological contaminants of wastewater will remain time consuming and difficult, requiring highly skilled personnel and well equipped laboratories. We shall be forced to depend upon the use of indicator organisms to estimate the sanitary quality of a waste in any reasonable time frame.

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