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SCIENTIFIC SERIES

# 43 (c2)

# Water Quality Criteria for Great Lakes Waters to be Used as Municipal and Industrial Water Supplies

D. H. Matheson



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# **Water Quality Criteria for Great Lakes Waters to be Used as Municipal and Industrial Water Supplies**

**D. H. Matheson**

Prepared under contract for the Lakes Research Division, Canada  
Centre for Inland Waters.

**SCIENTIFIC SERIES NO. 43**  
*(Résumé en français)*

**INLAND WATERS DIRECTORATE,  
CANADA CENTRE FOR INLAND WATERS,  
BURLINGTON, ONTARIO, 1975.**

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Information Canada  
Ottawa, 1975

Cat. No.: En 36-502/43

CONTRACT # KL327-4-8069  
THORN PRESS LIMITED

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## Summary

This report is to provide a frame of reference based on the practical problems and research needs of the industry concerned with the treatment and disposal of wastewater and the provision of suitably treated water for municipal and industrial water supplies. It concentrates on the physical situation of the Great Lakes and inter-connecting waterways, where the problems encountered are in many ways very different from those associated with other water sources. The importance of these large bodies of water, as sources of supplies for large and increasing populations and as receiving waters for disposal of treated wastewaters, is paramount. The need for the restoration and preservation of the lakes is the stated objective of the Agreement on Great Lakes Water Quality between the governments of the United States and Canada.

The history of the development of water quality standards is traced from the earliest regulations, which were concerned only with the quality of drinking water on public carriers to prevent the spread of communicable disease, through the phase which involved the adoption of these Standards by health departments for general municipal supplies, and finally to the shifting of responsibility and interest from strictly the disease-health aspects to the whole problem of environmental protection, which includes the management of water resources for public and industrial water supplies, as well as many beneficial uses.

Criteria applied to raw waters to be used as sources of public water supply differ considerably from criteria applied to finished waters. The capabilities of modern water treatment methods are considered in a brief description of conventional and supplementary treatment processes. The factors that affect the quality of raw waters are mentioned, including those caused by treated municipal and industrial wastes, agricultural and urban runoff, dredging and spoil disposal and finally the movement of polluted water from point sources to the vicinity of water intakes and the importance of proper siting of the intakes.

Water quality criteria for waters to be used for industrial supplies receive minimal attention in this report. In general, the requirements for the major portion of water

used by industry are well met by a conventionally treated municipal supply and for many of the requirements, even untreated Great Lakes water is more than adequate. For the relatively small amount of water required to be of quality superior to that of public supplies, industry is prepared to supply the required treatment itself; its demands would be unreasonable if applied to a public supply, and in-plant treatment gives the industry direct control at its own responsibility.

Consumer demands for municipal water supplies of high quality require the introduction of standards for parameters concerned with the aesthetic quality; the importance of these standards is an entirely different matter. In many cases, it is an economic decision whether such standards are achieved. Is the customer willing to pay for the extra cost entailed? This, however, is not always the only factor involved. It is now well known that water treated to have the greatest possible clarity, that is, the optimum aesthetic quality, is definitely a safer water from the sanitary point of view. A public water supply that is aesthetically undesirable because of color, turbidity or odor may drive consumers to the use of water from other sources more attractive in appearance, but having much less strict control of the sanitary qualities. The growing use of bottled waters in many cities shows in very concrete terms the importance of acceptable aesthetic parameters.

Criteria for a selected list of specific substances are discussed. Attention is directed particularly to the question of organic matter of various forms in water: organic matter from natural sources, from treated sewage, and many new "exotic" organics produced by the increasing organic chemical industry, which ultimately find their way into the environment and occasionally into the source waters used for public water supply.

Research needs include every facet of the water supply-and-use cycle: the effectiveness of waste treatment processes, the effects of substances in the treated wastes on the environment and particularly on intake water quality, and finally the effectiveness and efficiency of standard and advanced water purification processes.

## Résumé

Ce rapport est le fruit des efforts déployés pour donner une structure de référence fondée sur les problèmes pratiques et les besoins de recherche de l'industrie qui s'intéresse au traitement et à l'élimination des eaux résiduaires et à l'approvisionnement en eau traitée convenablement pour les stocks d'eau municipaux et industriels. Il traite de plus de la situation physique des Grands lacs et des voies navigables qui les relient où les problèmes décelés varient grandement de ceux liés aux autres sources d'eau. L'importance de ces grandes nappes d'eau à titre de sources d'approvisionnement des grandes populations toujours croissantes et d'eaux réceptrices pour l'élimination des eaux résiduaires traitées est capitale, et la remise en état ainsi que la conservation des lacs est le premier objectif de l'Entente sur la qualité de l'eau des Grands lacs, survenue entre les gouvernements des États-Unis et du Canada.

L'historique de la création des normes sur la qualité de l'eau est retracé depuis les premiers règlements, qui portaient uniquement sur la qualité de l'eau potable dans les systèmes publics pour empêcher la propagation des maladies transmissibles, jusqu'à l'adoption de ces normes par les ministères de Santé pour les stocks municipaux en général et finalement au transfert de responsabilité et d'intérêt, du point de vue strictement des maladies et de la santé jusqu'au problème d'ensemble de la protection environnementale, qui comprend la gestion des ressources en eau à des fins salutaires et celle des stocks d'eau publics et industriels.

Les critères à appliquer aux eaux brutes qui serviront de sources d'approvisionnement public en eau diffèrent considérablement de ceux à appliquer aux eaux traitées. Il faut tenir compte des possibilités des méthodes modernes de traitement des eaux et à cette fin, on donne une brève description des modes de traitement conventionnel et additionnel. Les facteurs qui touchent la qualité des eaux brutes sont étudiés, y compris ceux qui sont causés par les déchets industriels et municipaux traités, les écoulements agricoles et urbains, le dragage et le rejet des déchets et finalement le mouvement des eaux polluées à partir des sources ponctuelles jusqu'à proximité des prises d'eau ainsi que l'importance de l'emplacement approprié des dernières.

Peu d'attention est prêtée dans le présent rapport aux critères de la qualité des eaux d'approvisionnement industriel. En règle générale, les exigences concernant la principale partie de l'eau employée par les entreprises industrielles sont très bien respectées grâce à un approvisionnement municipal en eau traitée de façon conventionnelle et à ce titre, même les eaux non traitées des Grands lacs seraient plus que convenables. En ce qui concerne la petite quantité d'eau dont la qualité doit être supérieure à celle des stocks publics, l'industrie est prête à donner elle-même le traitement requis, non seulement parce que cette demande ne serait pas raisonnable si elle était appliquée à l'approvisionnement public, mais aussi parce que le traitement en usine permet à l'entreprise d'exercer un contrôle direct à ses propres risques.

La demande des consommateurs en stocks d'eau municipaux de première qualité nécessite la présentation de normes pour les paramètres concernant la qualité esthétique. L'importance des normes est tout autre chose. Dans bon nombre de cas, ce n'est qu'une question d'économie pour savoir si elles doivent être appliquées (le consommateur est-il prêt à payer les frais supplémentaires engagés?). Toutefois, il arrive parfois que d'autres facteurs sont impliqués, étant donné qu'on sait maintenant que l'eau traitée pour être plus claire, c'est-à-dire pour atteindre la qualité esthétique optimale, est certainement plus sûre sur le plan sanitaire. Un approvisionnement public en eau qui n'est pas esthétiquement souhaitable à cause de la couleur, de la turbidité ou de l'odeur peut pousser les consommateurs à se servir de l'eau d'une autre source, plus attrayante en apparence, mais moins contrôlée pour ses qualités sanitaires. L'utilisation croissante d'eaux embouteillées dans beaucoup de villes montre de façon concrète l'importance des paramètres esthétiques acceptables.

Les critères concernant la liste choisie des substances précises sont étudiés. Une attention particulière est prêtée à ce stade-ci à la question des matières organiques présentes dans l'eau sous diverses formes; on en a trouvées quelques-unes dans les sources naturelles, d'autres dans les eaux d'égouts traitées et beaucoup de matières "exotiques", produites par l'industrie toujours croissante des produits

chimiques, qu'on avait déversées, d'une manière ou d'une autre, dans l'environnement et aussi dans les eaux de sources servant à approvisionner le public en eau.

La recherche doit porter sur de nombreux domaines et inclure toutes les facettes du cycle de l'approvision-

nement et de l'utilisation de l'eau, du point de vue de l'efficacité des méthodes de traitement des déchets et des effets des substances contenues dans les déchets traités sur l'environnement et surtout sur la qualité de l'eau d'entrée, ainsi que sur l'efficacité des méthodes standard et avancées de purification des eaux.



## Introduction

The purpose of this report is to review existing water quality criteria, to consider the history of the development of these standards and their justification, and to comment on suitable standards and future trends. The identification of research needs is emphasized so that the Lakes Research Division can maintain a program of relevant research in the practical matters of public and industrial water supply.

The suitability of the Great Lakes waters as the raw water supply for municipal and industrial purposes is considered primarily. These purposes require quality standards quite different from those for other beneficial uses, such as agricultural and recreational needs and standards for the preservation of aquatic life. For the latter purpose, as an example, the criteria for many constituents may be much more restrictive because of the great sensitivity of aquatic organisms which remain their lifetime in this one environment. The ubiquitous chlorinated hydrocarbons have toxicity levels to fish that are several orders of magnitude lower than those significant to man. Observed damage to these organisms may therefore act as a distant, early warning signal with a large built-in factor of safety.

Substances that may accumulate in organisms by concentration *via* the food chain produce far-reaching effects on organisms including man. The levels at which the toxic substance occurs in the water phase itself, however, may have little significance to man, when the effects of standard water treatment and the relatively small daily intakes of drinking water are considered in perspective.

In assessing raw water quality in this report, the subsequent use of normal water purification processes is assumed. Although there are a few municipal water supplies using unfiltered Great Lakes waters, they are located in areas of good water quality and are subjected to chlorination as the minimum essential sanitary precaution. With the current demands for high quality consumer goods in all areas, there is no exception in the field of potable water supply. Quality water to the user has freedom from almost any taste and odor, and freedom from visible particles as well as safety from health hazards. Unfiltered lake waters, except those from the most pristine sources, are not acceptable. The water industry prides itself in setting goals for finished water quality that exceed substantially the minimum legal requirements of current Standards.

Therefore it is reasonable to assume that the quality requirements for raw waters will be subjected to the standard water treatment which includes chlorination, coagulation and filtration.

Consideration of raw water quality requirements can be directed toward three classes of substances:

- 1) substances which have known or suspected deleterious effects on the consumer, but which are not substantially affected by water treatment. The allowable concentration of these substances in the raw water will therefore be the same as those permitted in finished water. Substances having deleterious effects on the consumer can be classified further into those that have immediate and demonstrable toxic effects at the level in which they occur, and those whose effects are sub-clinical and result only from very long-term exposures. The first group has received more attention; now the latter group is becoming the subject of concern. Although outstanding improvements in health care and disease control have been made, there is no evidence of a marked increase in population longevity in the United States in the last few decades. This may indicate that the controlling factor now is the long-term, sub-clinical chronic effects of unknown substances affecting the population as a whole,
- 2) substances which interfere with normal purification plant operations and which thereby cause increased costs or result in a poorer quality product. This group includes the diatoms that interfere with filtration; various algae and other organisms that produce taste and odor; colloidal materials, possibly organic, that interfere with coagulation; and organic compounds and ammonia that interfere with chlorination, and
- 3) substances that affect the aesthetic quality of the finished water producing objectionable taste and odors, discoloration and staining of fixtures and utensils.

The information upon which this report is based has been derived from the literature and from personal conferences with many individuals who are involved directly in the theoretical and practical problems of the water supply industry. The opinions expressed, however, are those of the author.

## History of Development of Water Quality Standards

In England, as a result of the Industrial Revolution and the consequent development of areas of high population density near factories and complete lack of facilities to dispose of their wastes, gross pollution of streams was inevitable. Many of the rivers were overburdened by deposits of organic matter in the early 1800's. In 1859, the stench from the Thames River was so strong that "parliament sat with closed windows."

In the late 1800's, efforts to reduce the pollution load into streams led to the development of trickling filters for treating industrial and sanitary sewage. The development of slow sand filters for treating municipal water supplies began earlier than these efforts, and actually predated the demonstration by Pasteur of the germ theory of disease in the 1860's. The effectiveness of these filters in controlling the spread of disease was obvious. Consequently slow sand filters were widely employed. By 1852, the city of London required that all municipally supplied water be filtered. In America, the European practice was followed, and many slow sand filters were constructed in all the developing cities of the Atlantic seaboard. Some of these plants are still in use.

The concurrently developing science of bacteriology not only demonstrated the reason for the effectiveness of slow sand filtration, but it also allowed the quantitative evaluation of the performance of slow sand filtration emphasizing the limitations. By 1900, for example, although filtration reduced bacterial counts by orders of magnitude, the filtered water still contained appreciable and significant numbers of coliform bacteria.

About 1900 in Belgium, the development of water chlorination on a full-time plant-scale basis greatly improved the bacteriological quality of treated water and shifted the emphasis in water filtration from bacterial removal to improved clarification. Consequently the rapid development of mechanical filters occurred; relatively small filters operating at high rates, with chemical coagulation, could produce filtered water of good clarity. The poorer bacteriological quality of the effluent was improved by subsequent chlorination.

### UNITED STATES STANDARDS

In 1893, the involvement of the United States Public Health Service (USPHS) in water quality began with the Interstate Quarantine Act, the objective of which was to prevent the interstate spread of communicable disease. The first regulation, adopted in 1912, prohibited the use of a common drinking cup on interstate carriers.

In 1914, the first PHS Drinking Water Standards were applied to water supplies providing water to interstate carriers. These "Treasury Standards" published by the Secretary of the Treasury concerned only bacteriological quality, expressed as B. coli (now referred to as the "coliform group") as determined by the tube dilution technique and as total plate counts at 37° C. The Commission which developed the Standards, including well-known experts in the field of water treatment, limited the scope of the Standards to bacterial quality, as physical and chemical requirements could not be decided.

The 1925 Standards and later revisions are referred to as United States Public Health Service Drinking Water Standards. The Advisory Committee responsible for preparing the 1925 Standards considered a greater area of responsibility. They defined a "safe water" as one from which "the risk of infection is very small, compared with the ordinary hazards of life" — a concept which is still acceptable and rational, even in the complex environment of today.

In the 1925 Standards, bacteriological requirements were made more stringent. Mineral constituents (magnesium, sulphate, chloride and iron) were limited because of their physiological action at high concentrations; and lead, copper and zinc at specified levels were grounds for rejection of a supply. Of these elements, lead and copper were considered to be of chronic toxicological concern.

The 1942 revision of the Standards was prepared by a special Advisory Committee made up of "representatives of various federal organizations and scientific associations—and several members-at-large."

The bacteria limited were reduced further and were expressed as most probable numbers of coliform organisms. The limits of 1942 remained unchanged until the revision of 1962 when the membrane filter (MF) technique was recognized and substantially equivalent limits were expressed in MF counts.

Limitations on metals were extended. Maximum permissible concentrations of lead, arsenic, selenium and fluoride were established, and the use of salts of barium, chromates, heavy metal glucosides, and other physiologically deleterious materials were not allowed in water supply systems. Maximum concentrations that were not to be exceeded when more suitable supplies were available, were established for copper, iron and manganese, magnesium, zinc, chlorides, sulphates, phenolics, total dissolved substances and alkalinity.

The 1946 revision of the USPHS Standards was essentially the same as the 1942 Standards. Certain requirements, however, were re-phrased to make the Standards generally acceptable and applicable to all water supplies in the United States. A maximum permissible concentration for hexavalent chromium at 0.05 ppm was included.

In 1962, the extensive revision of the Standards reflected the effects on water quality of the development of advanced technology in many fields. To compose the revision, an Advisory Committee of the USPHS was assisted by a Technical Sub-committee and a Toxicological Task Force.

The major changes were

- 1) standards for radioactivity were added,
- 2) attention was directed to a wide range of chemical substances including an expanded list of potentially toxic elements, and
- 3) the rationale employed in determining limits was placed in an appendix.

The use of two types of limits continued. These are *mandatory limits* for substances having an adverse effect on health and which constitute grounds for rejection, and *desirable limits* above which the water may have undesirable or inconvenient properties.

In accordance with the recommendations of the Advisory Committee responsible for developing the 1962 Standards, the Public Health Service established a committee which continued to appraise water quality requirements. In 1969, this committee published "A Manual for Evaluating Public Water Supplies," which included limits for certain inorganic chemicals (boron, fluoride, nitrate plus nitrite and uranyl ion) and a list of 12

pesticides. These limits generally indicated levels at which no harmful or deleterious effects would result from ingestion for extended periods. In the case of four pesticides, even lower limits were suggested based on organoleptic properties.

## UNITED STATES WATER QUALITY GOALS

The American Water Works Association (AWWA) officially endorsed the USPHS Drinking Water Standards of 1962 as "the minimum standards which would be applicable to all water supplies." The AWWA proceeding immediately, formed a committee to develop "goals" for the water industry that would tend to raise the quality of water delivered to the consumer above the minimum levels required by the Standards.

In 1962, the group of four experts who had been working in this field published a progress report (Bean, 1962). In 1965, an augmented group of eleven was formed. It was instructed to prepare realistic quality goals substantially more exacting with respect to aesthetic qualities than the USPHS Standards, but still within the range that could be attained by the proper use of existing treatment processes. The report of this Task Group, "Quality Goals for Potable Water—a Statement of Policy," was adopted by the AWWA in 1968 and republished in 1972.

The committee accepted the Public Health Service criteria for the items which were particularly of health concern, deciding that these items had received sufficient attention and that adequate safety factors were incorporated in the limits. It therefore considered the non-toxic metals, aluminum, iron, manganese, copper and zinc and set objectives more exacting than the Standards. The limit for organic matter, expressed as carbon-chloroform extract, was reduced by a factor of five and an objective for carbon-alcohol extract was included. Radioactivity was considered to be extremely harmful, and the objective for gross beta activity was reduced to 100 pc/l from the Standard of 1000 pc/l.

## INTERNATIONAL STANDARDS

In 1958, the World Health Organization (WHO) published the first edition of "International Standards for Drinking Water," beginning the development of international standards. These Standards were adopted entirely or in part by a number of countries, as the basis for the formulation of their own national standards.

In 1961, the World Health Organization published "European Standards for Drinking Water." The justification

for issuing both International and European Standards is given in the preface as follows:

"International Standards for Drinking Water proposes minimal standards which are considered to be within the reach of all countries throughout the world at the present time. In view of the different economic and technological capacities of various countries, there will be some areas in which higher standards than those proposed for the world as a whole will be attained . . . and these areas should be encouraged to attain such higher standards. It is believed that Europe is such an area and that there is, therefore, nothing illogical in setting higher standards in Europe than internationally. One of the objectives in having standards at all is to stimulate improvement in water quality, and it is hoped . . . that improvements in economic and technological resources throughout the world will allow higher standards to be suggested in the future than those at present proposed for the whole world."

The second edition of the International Standards was issued in 1963, following the work of an Expert Committee drawn from all six WHO regions. Quality parameters were discussed under the headings of

- 1) compounds affecting potability (physical and chemical parameters affecting the aesthetic and convenience aspects),
- 2) compounds that affect health (fluoride and nitrates),
- 3) toxic substances,
- 4) pollution indicators (bacterial and chemical), and
- 5) radiological requirements.

Also for the first time, standards of quality for source waters were included (thus taking into account, to some extent at least, the effectiveness of water treatment processes).

In 1971, the third edition of the International Standards made some changes in limits (e.g., by raising the maximum for lead from 0.05 mg/l to 0.10 mg/l) and included polynuclear aromatic hydrocarbons as potentially hazardous waterborne contaminants. Little reference is made to the quality of raw waters (except for a paragraph on the choice of raw water sources). The discussion of the evidence considered by the committee in establishing limits for individual substances is considerably reduced from the previous edition and is available only in an unpublished WHO Report, WHO/CWS/71.2.

#### CANADIAN STANDARDS

In 1923, Canadian Standards for water quality commenced with an Order in Council which provided a Standard

of bacteriological quality for waters used for drinking and culinary purposes on vessels on the Great Lakes and inland waters.

In 1943, the use of the USPHS 1942 Drinking Water Standards was approved by the Department of National Health and Welfare, pending the development of Canadian Standards. In 1968, Canadian Standards developed by a joint committee of the Department and the Canadian Public Health Association were issued.

Canadian Standards were based on the most reasonable criteria and the best scientific information available. Three levels of quality were recognized — the objective, which would be the long-range goal, the acceptable level, and the maximum permissible limit. It was emphasized that the last level was the highest concentration that would be allowed for a short time and was not to be interpreted as the level at which degradation would be allowed to remain. No water should continuously contain any substance at the maximum level.

The values specified were determined from existing Standards and recently published information.

#### LATEST REVISION OF UNITED STATES STANDARDS

The current United States Standards are being reviewed and have not yet been issued. The following informal discussion is based on a presentation by G.G. Robeck, Director, Water Supply Research Laboratory, United States Environmental Protection Agency (USEPA), at the Water Quality Conference in February 1973, and the subsequent comment.

A substance included in standards should have a sufficiently widespread occurrence at levels high enough to be significant in health effects. Standards for nitrate should not be included since high concentrations in water are rare; only a small number of people (i.e., some infants) are affected by high nitrate and these may easily avoid unsuitable supplies. This statement is contrary to the opinion of many who would reduce the present Standards of 10 ppm  $\text{NO}_3\text{-N}$  on the basis of the effect on infants and possible effects in the suspected carcinogenicity of nitrosamines. Sodium was also mentioned as a substance for which standards were not appropriate, since it is rarely excessively high and few people need to restrict sodium intake.

The ability to identify and measure specific compounds is a factor to be considered in selecting substances to be limited in standards. This is applicable, particularly to organic substances which may not be identified as specific

compounds and for which the analytical methods are not well defined.

In evaluating toxic effects, the total intake from all sources must be considered, and in appropriate cases, a suitable portion of the allowable daily intake can be assigned to drinking water.

With respect to purely aesthetic parameters (color, odor, temperature) economic feasibility under the local circumstances is the controlling factor. Perhaps this type of parameter should be included in "goals" rather than "standards."

The following items were mentioned:

- 1) *detergents*: will remain at 0.5 mg/l expressed as methylene blue active substances (MBAS), disregarding any effect produced by the changeover to biodegradable detergents,
- 2) *odors*: a lower value than the present threshold odor number of 3 was discussed but not accepted. It is difficult to evaluate odors at low levels with the required precision,
- 3) *phenols*: the limit of 1 ppb was set to provide a margin of safety, since 6-10 ppb were required to produce odors on chlorination,
- 4) *mercury*: a limit of 2 ppb for alkyl-mercury, based on consideration of the levels in food and the analytical problems involved,
- 5) *NTA*: the inclusion of NTA was deferred, pending a policy decision on the use of NTA in detergents,
- 6) *PCB*: no action is to be taken at present, and
- 7) *organic carbon*: consideration was given to specifying a limit in terms of TOC; a limit was not

established, however, because of the cost and the lack of precision of the analysis. Standards will continue to be expressed as CCE. The addition of a standard for CAE was proposed also, but this has been deferred, since the extract has been found to contain varying amounts of inorganic matter. The determination of CCE is to be done with the new improved technique (the mini-sampler). The new standard proposed, 0.7 ppm, takes into account the increased recovery obtained with the new method and is actually about one-half of the previous standard since the recovery is six times greater.

### THE BRITISH ATTITUDE TO WATER QUALITY STANDARDS

In Britain the attitude toward water quality standards appears to be different from the North American approach (Martin, 1972). No actual standards are required by law; the sole requirement is that the water supply should be "wholesome," which the purveyor must be prepared to substantiate. The safety of a supply can be assumed if it meets WHO Standards, and as far as bacteriological quality is concerned, strict application of the criteria of "The Bacteriological Examination of Water Supplies" (Great Britain Department of Health and Social Security, 1969) is essential.

The absence of legal standards in Great Britain is said to allow a degree of flexibility in adapting to local situations and to permit continuous development as knowledge accumulates. When numerical standards are set, they must be arbitrary to some degree. If such detailed criteria are ultimately adopted, it is suggested that they might be in the form of a code of practice rather than as stringent standards with statutory authority which would have to be followed rigidly.

## Raw Water Quality

The Standards discussed are concerned primarily with water quality at the point of use, or at least at the point of delivery to a distribution system. They are justified, since the objective of the Standards is the protection of the health of the user.

It was not until 1968 that Standards for quality of the *raw source water* began to appear. These were set because of the need to develop water quality criteria for many beneficial water uses such as wildlife preservation, recreation and sources of public water supply.

Raw water criteria designed to protect the ecosystem may be much stricter than those required for water supplies, especially with respect to substances which are concentrated by chemical or biological reactions in organisms or sediments. In this form, they are not likely to pass through water treatment plants, and thus are not of great significance to the finished water quality. Nevertheless, the National Technical Advisory Committee of the United States Federal Water Pollution Control Administration recommended that all waters, except those immediately adjacent to waste outfalls, provide conditions suitable for the maintenance and production of fish.

Criteria developed for raw water quality must take into account the capabilities and limitations of water treatment technology to produce a finished water quality which meets the accepted criteria. The first such standards for raw waters appeared in 1968 in "Water Quality Criteria," a report of the National Technical Advisory Committee of the United States Federal Water Pollution Control Administration and in the Canadian Drinking Water Standards and Objectives. In 1970, the Ontario Water Resources Commission's (OWRC) "Guidelines and Criteria for Water Quality Management in Ontario" contained criteria for raw waters, as did the "Guidelines for Water Quality Objectives and Standards — a Preliminary Report," a technical bulletin of the Department of the Environment, published in Ottawa in 1972.

Criteria for raw waters to be used for public water supply differ from those for recreation or wildlife preservation in several respects. For example, the bacterial criteria designed to control the transmission of waterborne or water-associated disease in recreational uses are entirely different from criteria for raw waters to be treated by

stringent and highly controlled disinfection processes. Dissolved oxygen, which is of critical importance in aquatic life preservation, is of very minor importance in water supplies. Some trace organic substances, however, are of crucial importance at parts per billion levels in waters used for domestic purposes, but are of relatively slight importance for other uses.

There are many small water supply systems that are forced by economic factors to use available natural waters with a minimum of treatment. Such raw waters must therefore meet most of the drinking water standards without treatment, and for other parameters, such as coliform organisms, must be consistently at low enough levels to be treated in a satisfactory manner by minimal chlorination procedures.

### WATER PURIFICATION PROCESSES

To put raw water quality criteria in perspective the following discussion of water purification processes is included.

Presently there are few surface supplies that are acceptable for public use without a considerable degree of treatment because of the increasing pollution of surface waters by sanitary and particularly industrial wastes and because of the consumer's demand for high-quality water. Although the consumer may not be able to detect such undesirable characteristics as the presence of pathogenic organisms, viruses or toxic metals, he quickly detects deterioration in the aesthetic parameters of odor, color or turbidity.

In the relatively few water plants that are fortunate to have a source of water of acceptable quality in every respect except bacteriological parameters, the use of chlorination alone may enable the production of an output which is marginally acceptable under local circumstances. Such plants are generally small (where economic factors outweigh the aesthetic values of high-quality water), or they have an exceptionally well-protected source of supply which is free of industrial and sanitary pollution and is consistently low in turbidity and populations of nuisance organisms.

Although large-volume supplies obtained by pumping

through intakes are considered primarily here, many small-volume supplies exist which are obtained from wells sufficiently close to lakes or rivers, so that the water is substantially from those sources. In Canada, no large supplies are known which are derived from "bank filtration," where water must be taken from highly polluted rivers, as in Europe. The benefits resulting from this practice in Europe are documented, but little, if any information is available regarding small supplies in Canada. Improvements in turbidity and bacterial content might be assumed, but the latter is uncertain.

The usual form of water purification plant employs conventional "complete" treatment in a fairly standardized design. Such plants range in size from those with a capacity of much less than one million gallons per day to enormous installations which have daily outputs in the range of hundreds of millions of gallons serving major metropolitan areas.

In this conventional method, complete treatment includes three processes — coagulation and sedimentation, filtration, and chlorination.

Coagulation, which is usually done with aluminum sulphate, and the sedimentation which follows, prepare the water for filtration. In the case of waters of high turbidity or particulate-loading, coagulation produces a floc which settles readily and thus removes a substantial portion of the suspended solids before filtration. With low-turbidity raw waters, the floc may not settle readily but is in a form easily removable by filtration. Raw water constituents such as alkalinity and pH, colloidal turbidity, organic substances, planktonic organisms especially diatoms, and some, as yet undetermined, factors interfere with coagulation. In Chicago, the growth of *Stephanodiscus* in winter causes a precipitation of colloidal calcium carbonate in Lake Michigan water causing a serious coagulation problem. Coagulation can be improved in the treatment plant by adding artificial turbidity and by using coagulant aids including organic polymers (a number of these are approved for use in drinking water) and various silicate gels prepared on the site at the point of use.

Well-managed coagulation and filtration processes produce a filtered water product of low turbidity. The recommended limits in the USPHS 1962 Standards and the limit of 5 units in the WHO International Standards may be appropriate for unfiltered water, but such turbidity in filtered water indicates serious malfunction of the plant. Turbidity is now expressed in "units" without further definition (American Public Health Association, 1971). Filtration plants normally produce filtered water with a turbidity less than 0.5 units and the AWWA goal of less than 0.1 units can be achieved regularly. Finished water

of superior quality in many other respects is associated with low turbidity. This is so, particularly in relation to the bacterial quality, as measured by the number of coliforms which survive disinfection. Presumably better removal of viruses is also accomplished by good coagulation and filtration.

Advances in water treatment methods currently centre on improvements in coagulation and filtration. More concentration is on the study of the coagulation mechanism to effect as much removal of suspended solids as possible before filtration. The load on the filters is reduced and the use of higher filtration rates (up to 10 gallons per square foot per minute, as compared with the conventional 2-4 gallons per square foot per minute) is possible. Consequently a smaller plant size results. Also the design of filters is being improved by the use of two or more layers of different media of varying grain size and densities which can be washed in place and segregated again by virtue of differing specific gravities. The use of sensitive turbidity-indicating instruments on the effluent line of each filter signals the end of the effective filter run better than visual observation or loss-of-head measurements.

When the raw water is of good quality and low turbidity, direct filtration of water using alum coagulation, but no sedimentation, is practical. This process is used in several plants in Ontario and is being considered in connection with the renovation of the Toronto Island plant. The advantage over the standard plant is the reduced capital cost from the omission of the large settling tanks. In Great Lakes waters having turbidities generally in the range of 5-25 units, the use of 10 ppm alum will enable the production of a filtered water with turbidity less than 0.2 units. Higher turbidities in the raw water, up to 50-80 units, can be handled for short periods, but since all of the suspended solids are removed on the filters, the filter runs are very short and the amount of wash water required becomes a significant percentage of the filtered water output. In season, diatoms occurring in raw water of low turbidity cause serious problems by rapidly blocking the filters.

Even well-operated coagulation and filtration processes are not relied upon to produce water of satisfactory bacteriological quality. Chlorination is responsible entirely for this function; its use assures the provision of a product which regularly and consistently meets the most exacting standards.

Although chlorination is a simple process, it is practiced in varying ways. The simplest technique is the chlorination of the water for the destruction of surviving bacteria, after filtration has removed suspended organic and inorganic matter. The chlorine, however, is involved frequently in reaction with dissolved organic matter with the production of objectionable tastes and odors; since this

post-chlorination is the final step in water treatment, there is no opportunity to perform any additional corrective treatment.

The use of chlorination as the first treatment step (pre-chlorination) has advantages over post-chlorination, in permitting the use of higher dosages and much longer reaction times in the plant. Sufficiently high dosages can be used to destroy some organic compounds and ammonia, and the excess chlorine at the final stage can be removed by dechlorinating chemicals (usually sulphur dioxide) if necessary. Pre-chlorination has the further advantage of controlling biological growths in the whole treatment plant, and the high "free chlorine" residual maintained for a relatively long period has unexcelled bactericidal properties.

Chlorination with high dosages and subsequent dechlorination were formerly called "superchlorination" and had the advantage of completely oxidizing some organic substances (particularly phenols) by the high level of "free" chlorine (or hypochlorous acid). Ammonia, if present in water to be chlorinated, reacts with the chlorine producing chloramines with much lower oxidizing and disinfecting power. The term "superchlorination" is now replaced by "break-point" chlorination, since the first and essential reaction is the destruction of ammonia and then the addition of sufficient excess "free" chlorine to achieve the desired results. The destruction of one part of ammonia in actual practice requires about ten parts of chlorine.

The continuous monitoring of chlorine residuals in water is the most important single control test in water purification. Residuals must be maintained constantly at the prescribed level to ensure that no portion of the water passing through the plant escapes without adequate treatment. This is done conveniently by using modern amperometric instruments which may be set up to give a warning if a deficiency occurs. Although bacteriological tests are far too time-consuming for control purposes, they are required to demonstrate and confirm directly what chlorine residual meters indicate indirectly.

The present trend in water chlorination is to deliver to the distribution system a finished water carrying a "free chlorine" residual rather than the "combined residual" (resulting from the reaction of ammonia and chlorine) which is still widely used. Chloramines penetrate the distribution system more easily than free chlorine because of reduced chemical activity, but their bactericidal power is also much less. Introducing a water carrying a free chlorine residual into a distribution system which has had previously only combined residuals, involves some temporary problems in satisfying chlorine demand of coatings and deposits in the piping and the consequent production of

chemical odors. Once the system has reacted completely to the free chlorine, high residuals can be maintained without causing odor complaints.

Monitoring the bacteriological quality of water in the distribution system is important to detect malfunction of the disinfection process, aftergrowth of organisms that escaped disinfection, and re-infection from outside sources.

Ozone is used extensively in Europe for disinfection of drinking water, since it has good bactericidal properties and avoids the production of objectionable chlorinous odors resulting from the reaction of chlorine with organic substances. In North America, the use of ozone has not progressed in this field because of its greater cost and the excellent reputation for reliability that chlorination has. Also in England this seems to be so, since Martin (1972) says, "Chlorination had held its own from the beginning, and there would be strong disinclination to adopt any new method unless the absence of any harmful effect on the body could be assured." Ozone has a significant advantage over chlorine in having a much more rapid viricidal effect, as well as freedom from the production of odorous chlorination byproducts.

Other oxidants are also used in water treatment, chiefly for the destruction of organic matter in difficult cases of tastes and odors. These include chlorine dioxide (generated on the site by reaction of chlorine on sodium chlorite) and permanganate.

The use of activated carbon is an important additional treatment in water purification. A widely used practice is the addition of finely ground activated carbon to the water at some stage in the processes of treatment. The carbon absorbs a variety of organic substances, particularly those implicated in causing objectionable tastes and odors; the carbon having been used once is removed with other suspended solids by coagulation and filtration. Carbon dosages usually range from 10-50 ppm, but some difficult waters may require 100 ppm or more. The best point of application depends on the local situation and is determined by plant trials. Since phenol is more readily adsorbed than chlorinated phenol, when carbon is to be used to remove phenol, it is added before chlorination.

Granular activated carbon used in beds through which the water is passed, is an alternative method of using carbon. In one city, granular carbon was used to replace the filter sand, and functioned as the filter medium as well as being the absorbant for taste and odor bodies (Hansen, 1972). The carbon bed, 2 feet thick, was washed regularly as a sand filter would be, but there was no regeneration of the carbon which had an effective life, as determined by its ability to remove



taste and odor, of three years. In actual practice, carbon beds have been effective in removing odors and pesticides from water long after the capacity to remove organic matter expressed as chemical oxygen demand (COD) has been exhausted.

Carbon in powdered or granular form has potentialities for removing organics other than taste and odor substances, (e.g., pesticides). Recent work indicates that carbon is effective in reducing the levels of some toxic trace metals, by direct adsorption (Netzer and Norman, 1973) or in the chelated form with organic matter.

At the Fifteenth Water Quality Conference, "Organic Matter in Water Supplies," held on February 7-8, 1973, at the University of Illinois, it was suggested by some that activated carbon treatment ought to be standard practice in treating waters that are exposed to possible contamination by toxic materials. Routine carbon treatment would improve the aesthetic qualities of the finished water constantly, and moreover be available to remove trace toxicants when they occur.

#### FACTORS INFLUENCING INTAKE RAW WATER QUALITY

Since water intakes are located close to shore, the quality of the raw water is affected strongly by local sources of pollution — the discharge of rivers, the effluents from municipal sewage treatment plants and industrial waste discharges, the runoff from land and storm drainage from cities, and perhaps occasionally by harbor-dredging and channel-dredging when the spoil disposal is into open water or into shore areas behind dikes. The water quality is also affected by the degree of mixing and the dilution that occur. Wastes discharged into rivers at the bank tend to travel downstream in a narrow band at the edge with little cross-mixing. Water entering lakes tends to be confined to a narrow shore zone which may stretch for miles each way from the point of discharge (Csanady, 1970). Storms have important effects in altering circulation patterns and in re-suspending sediments. The temperature of the waste stream and the thermal structure of the lake determine if the effluent enters the epilimnion or the hypolimnion; and the elevation of the intake structure in relation to the thermocline determines from which stratum the raw water is drawn. Warm effluents may spread on the surface of colder water and pass over water intakes without affecting the raw water quality.

#### Sewage Treatment Effluents

Sewage treatment plant effluents, even from well-operated secondary plants meeting the current requirements of effluent standards, discharge large amounts of residual materials, in particular, relatively stable organics, to

the receiving water. A 100-million gallon per day plant, with an effluent BOD of 10 ppm, discharges 10,000 lb of oxygen demand per day which the resources of the receiving water must accommodate. In addition, the effluent will contain more stable organic matter, which in terms of COD, may be about 50 ppm. This material is not distinguishable from naturally occurring organics on the basis of present knowledge.

Since municipal sewers collect wastes from a variety of industries, some substances occur in sewage that have an industrial waste origin. The amount and variety of these substances depend on the city; cities having a primarily industrial base will contain more foreign materials than a typically commercial city. Some metals such as iron and manganese are removed almost completely in standard sewage treatment. Other metals, chromium, copper, nickel and zinc, which occur at levels up to a few parts per million, are removed to varying degrees, in the range of 25-90%. A high pH increases the percentage removal of these metals. These and several other elements of interest can be reduced to acceptable levels by the lime and aluminum treatment that might be used for phosphate removal. In the presence of chelating agents such as NTA, complexes of copper, nickel and lead are formed which are resistant to biodegradation and carry the metals through the treatment plant to the receiving water (Nilsson, 1971). Organic compounds of industrial origin are often not degradable by activated sludge organisms, but acclimatization may occur on regular exposure and substantial removals result.

Municipal bylaws regulate the discharge to sewers of substances that might damage the sewer system (strong acids or alkalies), be hazardous to workmen (substances with toxic, inflammable or explosive vapors) or have toxic effects on biological treatment processes (metals, cyanides).

#### Industrial Wastes

To surface waters industrial wastes contribute a wide range of substances; these vary from excessive amounts of suspended solids and BOD to quantities of trace metals that have toxic or other effects on the environment which may be of greater importance. Current environmental protection regulations imposed on industry are designed to limit such discharges by requiring adequate in-plant waste treatment before discharge to receiving waters. The efficiency of such treatment is usually based on monitoring such gross SS, BOD and COD that significant substances may not be detected until special attention is directed to them.

#### Urban Street Runoff

Runoff in the form of street drainage in urban areas usually flows directly to surface waters and, for short

periods of time during rains, is comparable in coliform counts, SS, BOD and organic matter to raw sewage (Anon., 1969; Burm, Krawczyk and Harlow, 1968). The lead content of urban street drainage is of interest. In a city using one million gallons of gasoline per day, the lead output into the air is about 4000 lb per day. A portion of this deposited on roofs and pavements is washed off by rains. Lead in a few samples of metro Toronto raw sewage ranged from 0.02-0.5 ppm (Anon., 1972).

#### Land Drainage

Drainage from land by creeks and sewers is important in affecting raw water quality because of the suspended solids, coliform content and the presence of agricultural biocides. This runoff has other indirect effects because of the input of nutrients and growth stimulators. Some streams provide a good environment for the growth of Actinomycetes, with the result that the stream water is contaminated with the very odorous and treatment-resistant metabolic products of this organism.

#### Dredging and Spoil Disposal

The effects of harbor-dredging and channel-dredging and spoil disposal on raw water quality is of current concern. The two most obvious effects, areas of increased turbidity and decreased dissolved oxygen, are of relatively minor concern in water treatment. Presumably spoil disposal would not be allowed in close proximity to water intakes. Knowledge of the settling characteristics of the spoil material and of water currents permits the estimation of the area to be affected. The seriousness of the effects should be gauged in relation to the increased turbidity normally caused by storms, bearing in mind that turbidity removal is one of the prime functions of a water treatment plant.

The most important aspect of reduced dissolved oxygen levels is the possible concurrence of odorous substances coming from the disturbed anoxic sediments. There is little reference in the literature to this effect.

Thus the most serious effect of dredging and spoil disposal is not on intake raw water quality where in most cases no important effect can be detected, but is on the lake environment in general — in the disturbance of the

habitat of bottom-dwelling organisms, the dissemination of oxygen-demanding substances which may cause local and transitory declines in dissolved oxygen, and on the recirculation of trace metals and organics which in nature would recycle very slowly.

#### Movement of Polluted Water

The movement of polluted streams after discharge to rivers or lakes is an important factor in determining what ranges of pollution are experienced at nearby intakes. This leads into the consideration of the proper siting of such intakes.

In rivers, a waste stream discharged at the bank flows downstream in a narrow ribbon close to the bank. Consequently wastes can be discharged into the Detroit River, and good quality raw water for public water supplies can be abstracted from midstream.

In lakes, the meandering of a discrete plume of polluted water emitted from a point source is an important factor in determining the rate of mixing which occurs. The passage of such a plume over a waterworks intake may cause sudden and spectacular changes in water quality. For example, the intermittent plume from Burlington Bay, passing over the Hamilton water intake, may cause an increase in ammonia concentration from the background level of uncontaminated lake water (about 0.02 ppm) to peaks reaching 1 ppm or more in a period of an hour or two.

The coastal entrainment phenomenon described by Csanady, resulting from the bi-stable nature of coastal currents, produces a buildup of pollutants in the near-shore waters in a narrow band extending to as much as 25 km either way from the source. Detailed knowledge of the extent, width and the persistence of this polluted band is important in the siting of water intakes, since the distance offshore is one of the few variables that can be considered.

The discharge of warm effluents into colder or stratified lakes results in the containment of pollutants in the upper and warmer strata. It has been observed at Hamilton, by sampling in the vicinity of the intakes, that the plume of high-ammonia water from Burlington Bay may pass over the intake without affecting the quality of the water samples being collected.

## Rationale Employed in Setting Water Quality Criteria

The rationale determining the initial decision of the United States to implement water quality standards and their subsequent evolution are outlined in Chapter 2. The U.S. Public Health Drinking Water Standards under federal law are presently applicable to only about 800 municipal water supplies that provide water to common carriers. These Standards, however, have been adopted, with perhaps minor modifications, by most state departments of health and are thus applicable indirectly to all public water supplies. Still there is some discussion whether parameters that do not relate directly to health can legally be included. Some of the legislation now pending in the U.S. Congress will give to the U.S. Environmental Protection Agency the legal right to set both health and aesthetic standards. According to Robeck (1973), if this type of legislation passes, the legal problem relating to non-health criteria can be avoided. The "grounds for rejection" limit for each substance was based on known health hazards to man and took into account the total environmental exposure. Thus there was a limit not to be exceeded, but at the same time, it was considered wise to set the desirable level at the lowest level that could be achieved in practice to minimize the total exposure as much as possible.

This still remains as the logical method of setting standards when sufficient data are available. If the long-term toxicity to man is known or can be inferred from data relating to other organisms, a portion of the allowable daily intake can be allotted to drinking water.

In actual practice, however, this is rarely the case. Theoretically, it is never possible to prove the safety of any substance, and the best that can be done is to consider the lowest concentration known to have a harmful effect on man and reduce it by a factor to give an adequate margin of safety. In many cases, knowledge in this area is so deficient that a large arbitrary element enters at this stage.

The "lowest practical level" standard is well illustrated in the example of mercury. The WHO limit of 0.001 mg/l is reasonable, as it allows the use of most natural waters, but it excludes supplies in which the natural levels have been substantially increased by industrial wastes. The use of "not detectable" levels is a convenient interim way of ensuring that the intake of a substance from water is as low as possible without saying "absent," which can never

be demonstrated. As more sensitive methods of analysis develop, the limit can be defined more exactly.

The necessity of setting definite numerical standards for toxic materials is obvious to administrators. Sometimes this must be done under conditions of urgency, for example, the setting of environmental standards for radioactivity. The sudden and rapid development of nuclear technology created the possibility of dangerous and widespread environmental pollution, which required the immediate establishment of numerical standards for administrative purposes.

Where knowledge of the effects of lifetime exposure to unnatural materials is unavailable (and this is the case with respect to many "new" pollutants presently being discovered), the tendency is to set, irrationally, very low and therefore presumably safe values. Obviously the lifetime effects of newly discovered materials cannot be known for a very long time, and can be inferred only very uncertainly from effects observed under extremely unrealistic conditions of dosage and exposure.

Examples of such materials for which it is difficult to set national standards are those reputed to have carcinogenic, teratogenic or mutagenic effects. The problem relates to the controversial Delaney Bill regarding food additives in the U.S. Federal Food, Drug and Cosmetic Act, which says that "no additive shall be deemed to be safe if it is found to induce cancer when ingested by man or animal. . ." The ban of cyclamates in foods resulted, and suspicion could conceivably arise concerning many natural products that contain substances with carcinogenic, teratogenic or mutagenic effects when tested under grossly unrealistic conditions of application.

The polynuclear aromatic hydrocarbons, currently of interest because of their carcinogenic properties, are examples of materials of this type which occur in water. They are found in nature, produced as the result of natural biological processes, and so occur at low levels in unpolluted waters. The demonstration of significant carcinogenicity toward man at these levels is substantially impossible, and the most stringent action that could logically be taken against this class of substance would be to allow no significant increase from man-made sources, above the

range found in uncontaminated waters.

The ill-defined mixture of organic compounds extracted and concentrated from water by various techniques constitutes a special problem in setting quality criteria. Certain fractions of the highly variable mixtures exhibit marked toxicity toward experimental organisms, but the specific substances responsible for the effect are unknown and probably constitute only a small portion of the total extract. Further, due to possible alterations in the chemical structures during the processes of concentration and extraction, it is uncertain that the toxic material found in the extract was present originally in the water sampled.

It is easily observed, however, that the quantity of some extracts (e.g., the carbon-chloroform extract, CCE) is low in obviously unpolluted waters and high in waters subjected to industrial chemical pollution. Limitations of the "best judgement" type are placed on the basis that such an extract represents an ill-defined mixture of unnatural chemicals largely of industrial origin.

The analytical values obtained for this type of material are highly dependent on the methods employed and require strict adherence to arbitrary details in technique. Using the high flow rate carbon-absorption method of the 12th edition of Standard Methods, the 1962 USPHS Standards include a recommended CCE limit of 200 ppb "as a safeguard against the intrusion of excessive amounts of potentially toxic material into water."

The pertinency of this limit can be gauged by the results of a survey of 969 community water supply systems of which 90% had CCE values of less than 200 ppb. In waters remote from human or industrial contamination, the CCE is usually below 50 ppb. In a survey extending over five years by the Ontario Ministry of the Environment, eight representative sample points on the Great Lakes system averaged less than 75 ppb for CCE (Diosady, 1973).

Material contribution to the CCE is not removed in standard water treatment practice unless activated carbon is employed. This use of activated carbon seems to be implied in "Quality Goals for Potable Water — a Statement of Policy" by the AWWA in 1968, where the objectives of less than 40 ppb for CCE and less than 100 ppb for CAE are given.

The high-flow and low-flow carbon absorption methods in the 13th edition of Standard Methods have several deficiencies, some of which are corrected by a newly introduced "mini" method (Buelow, Carswell and Symons, 1973), which has considerably improved recovery efficiencies. The revised U.S. Drinking Water Standards will

have a CCE limit of 700 ppb based on the new analytical method. This increased level reflects the 6-fold to 7-fold improvement in CCE recovery, and thus corresponds to the amount of 100 ppb when the older method was used.

To determine the rationale that influences water quality criteria, one may consider the "sane and realistic" advice of H. E. Stokinger, a veteran toxicologist in the U.S. Department of Health, Education and Welfare (Stokinger, 1971). In his concern that legal criteria should reflect what is known and not what is unknown, he proposed the following "commandments:"

- 1) Standards should be based on hard scientific data, and not on political feasibility, expedience or emotional reactions. When this is not possible at the moment and some guideline is required, it should be on a "best judgement" basis, derived by competent people, and it should be so labelled.
- 2) All standards and guidelines should be completely documented so that it may be quite evident on what basis (public health, environmental effects, etc.) that action is taken.
- 3) Standards should not be severe beyond what is actually necessary.
- 4) Levels proposed should be realistic and based on a dosage-response relationship (no effect, borderline effect and frank effect) modified by incorporating a safety factor.
- 5) Effects should be evaluated using appropriate means and realistic levels, and not by "any dose—any method of application."
- 6) Unrealistic and irrational extrapolation of local findings to a world-wide dimension should carefully be avoided.
- 7) Banning of specific substances should be avoided in general and emphasis placed on restricted use.

These points of good advice, which for environmentalists and maybe even for scientific researchers are difficult to follow, are nevertheless of fundamental importance in formulating legal standards. In the face of the increasing use of exotic chemicals which may escape into the environment in significant amounts, the vast amount of work which must be done is emphasized. The recent concept of requiring environmental impact studies before certain major undertakings are begun, should be extended to apply to the large-scale use of new chemicals which should be considered dangerous until adequate evidence is produced to prove their innocence.

## Criteria for Specific Parameters

In this Chapter, criteria for certain specific water quality parameters are discussed individually.

It may be noted that the limits given in existing standards have been derived from studies extending over many years and are the result of evaluations conducted by experts in many countries. Consequently, a degree of uniformity exists among the various standards.

In the case of some substances, the limits have been based on aesthetic considerations and thus more variation may be expected. In some cases, the levels of relatively harmless substances are restricted because their presence at any level indicates the presence of objectionable industrial wastes.

### MICROBIOLOGY

Since the prevention of waterborne disease is the first and supreme objective of water purification, microbiology is of prime importance.

In the nineteenth century, waterborne diseases, although not recognized as such, were rampant. As mentioned in Chapter 2, the introduction of slow sand filters, originally installed for clarification reasons, resulted in substantial reductions in mortality from these diseases.

The slow sand filters were effective in removing pathogenic bacteria because of the intense biological activity in and on the sandbed and the relatively long exposure to this, as a result of the low rate of filtration (about 0.04 gallons per square foot per minute, as compared with conventional rapid sand filtration rate of 2 - 4 gallons per square foot per minute). The practice of storing raw water for days or weeks before filtration contributed toward good bacterial removals. This practice continues to be favored in England and Europe where such storage provides marked improvements in the chemical and aesthetic properties of the water, as well as in the removal of bacteria.

Slow sand filtration had many disadvantages, including the large filter areas required to supply large

volumes of water, the great amount of labor required for maintenance and most importantly, severe limitations on the permissible bacterial loading in the applied water. About the beginning of this century, chlorine was introduced as a disinfectant of water and was so successful that reliance was soon placed on chlorination for providing safe water.

Rapid mechanical filters were soon developed, which with suitable pre-treatment (coagulation) could produce large volumes of water of high quality as far as clarity was concerned, and disinfection could be assured by subsequent chlorination. This combination has been developed over the years to such a degree that the transmission of the classical waterborne diseases by municipal water supplies no longer exists.

Attention is now directed, not so much to the acute waterborne diseases, but to the much less easily defined, long-term chronic effects of exposure to trace amounts of organic and inorganic substances. In the microbiological field, attention is focussed on the possibility of a drinking water vector in the transmission of viral diseases. In this latter field, it seems that, again, effective technology has been developed in advance of scientific knowledge. Present evidence seems to indicate that waters well treated by the best current practice are not implicated in the transmission of viral disease, but knowledge in this field is deficient — with respect to laboratory methods of enumerating virus particles in raw and treated waters, in demonstrating the sources, in evaluating the effectiveness of unit treatment processes in their removal and in estimating the infectivity of viruses at the levels that might occur in treated water.

The use of the coliform group of bacteria as indicators of sanitary pollution dates back to the isolation of "B. coli" by Escherich in 1884, which was followed a decade later by the development of a practical laboratory technique for their enumeration by Theobald Smith. In 1914, the United States Standards included a specification for B.coli in drinking water. By 1942, the term "B. coli" was replaced by the "coliform group," recognizing that a group of considerable size and variability was involved, rather than a distinct species.

Later, the widespread occurrence of the coliform group in a variety of environments encouraged efforts to

define a more specific indicator of pollution of fecal origin. This resulted in the definition of the "fecal coliform" group which has typical occurrence in the feces of man and warm-blooded animals.

The numerical expression of bacterial densities has changed from the Phelps index (the reciprocal of the smallest volume of sample having one recoverable organism) to the most probable number (MPN) which takes into account the probability of an organism being found in replicate portions of the sample in a range of dilutions. In 1962, the membrane filter (MF) technique was recognized in the U.S. Standards where it had been shown that comparable results from the MPN and MF techniques could be obtained under suitable conditions.

In evaluating water quality, it is important to take into consideration the adequacy of a sampling program and the frequency distribution of the coliform data. Expression of quality criteria, in such terms as "at least 90% of a specified number of consecutive samples taken in a 30-day period should not exceed a specified coliform density," covers this better than would arithmetic or geometric means and maximum values.

Criteria for the bacteriological quality of raw waters depend on the degree of treatment available. In 1900, experiments demonstrated that the best quality of water which could be produced by slow sand filtration of river water contained 66 coliform bacteria per 100 ml. By 1914, the first U.S. Standard required not more than two organisms per 100 ml; this improvement was made possible by the use of chlorination.

The degree of bacterial pollution that can be handled safely in modern plants is known from extensive experience and is conveniently summarized in the "Canadian Drinking Water Standards and Objectives" of 1968. For raw waters, in which 90% of the monthly samples contain less than 100 coliforms per 100 ml, chlorination only is acceptable. For waters exceeding this level but having less than 1000 coliforms per 100 ml, complete treatment is required, and above this to a maximum permissible level of 5000 per 100 ml, auxiliary treatment is required. Others have indicated that with prechlorination, water containing coliforms up to 20,000 per 100 ml can be handled satisfactorily in well-operated plants with good control and with continuous monitoring of chlorine residuals (Walton, 1956). It is evident that as the degree of pollution of raw water increases, more dependence is placed on the skill of the operators who must have plant capabilities to effect suitable treatment and technical means to monitor the raw water quality and the effectiveness of treatment.

All parameters used in connection with bacterial pollution must be related ultimately to the probable occurrence of actual pathogens in the water. Attention is therefore currently directed toward the study of organisms more closely connected with the human pathogens themselves. Isolation of single pathogens is difficult because of their extreme rarity in comparison with the indicator organisms, but *Salmonella*, as an example, can be isolated from relatively polluted waters. Fecal coliforms and fecal streptococci and the ratios of these to total coliforms are used to indicate probable sources of pollution (animal or human, recent or remote).

## VIRUSES

The significance of viruses in polluted and purified waters has not yet been completely resolved. This is a matter of possibly great importance, since it is known that a wide variety of viruses are excreted in feces; that present methods of sewage treatment do not produce virus-free effluents; that viruses may survive in surface waters for extended periods; and that removal by water purification processes is not assured. Nevertheless, in a report by the AWWA Committee on "Viruses in Water" (1969), it is indicated that well-treated municipal water supplies are rarely, if ever, implicated in the transmission of viral diseases. Even in the absence of marked outbreaks or epidemics, however, it is possible that the regular low-level transmission of viruses may be the source of ill-defined endemic disease. The infectious dose of viruses is very low, and although clinical illness occurs in only a small fraction of those who are infected, the sub-clinical infection should not be considered harmless.

Presently sewage treatment processes do not produce effluents free of viruses. The activated sludge process is superior to the trickling filters extensively used in Britain and perhaps could be improved by more complete removal of floc by filtration. The effectiveness of other treatment processes is unknown, but it is possible that tertiary treatment for phosphate removal using aluminum or iron flocculation and filtration could be highly effective.

Chlorination of activated sludge effluents to effect virus removal requires the maintenance of a free-chlorine residual which is difficult to do in an effluent containing much ammonia. Presently the activated sludge process is operated primarily to remove BOD and not necessarily to oxidize ammonia to nitrate. In the past, nitrification was used as a control parameter in the operation of the process. If the oxidation process was carried out to the complete nitrification of ammonia, chlorination of the effluent would be more effective.

Owing to the relatively greater susceptibility of bacteria to chlorine in combined form in comparison with viruses, the absence of coliforms in chlorinated sewage effluent does not indicate the absence of virus.

Viruses remain active in surface waters for long periods of time. The natural removal seems to be associated more with the microbiological activities in the water than with physical and chemical processes, since survival is longer in clean waters. Impoundment for two to three weeks of waters to be used for public water supplies, often done in Britain and Europe, has significant merits in making use of natural virus-removing processes.

In the processes employed in water purification, coagulation with metal coagulant is effective in producing substantial removals (Sproul, 1972). The mechanism suggested involves the formation of co-ordination complexes between the virus and the coagulant and the incorporation of the complex into the hydrated oxide precipitate. The virus is not inactivated but can be partially recovered, and consequently the filtration plant waste stream (settled sludge and filter wash water) contains the virus in a more concentrated form. This may be of some importance when aluminum is to be recovered from the waste stream or when filter wash water is recirculated. The use of organic coagulant aids with alum has given extremely variable results in virus removal.

Filters are effective in virus removal approximately in proportion to the floc removal. When the breakthrough of floc occurs, a breakthrough of virus occurs also. As a result, the filtration process appears highly variable in effectiveness. Slow sand filtration is remarkably effective in virus removal, but only after a suitably active zoogeal mat has developed.

Chemical water-softening is effective in removing virus only if precipitation of magnesium hydroxide occurs. Precipitation of calcium carbonate alone removes very little. Removal and inactivation occur where the pH is raised to high levels, i.e., to pH 11-12.

In water disinfection, a combined chlorine residual is ineffective and virtually useless as a viricidal agent. Free chlorine inactivates viruses at acceptable rates, although still much more slowly than it destroys bacteria. The time required for inactivation is affected by pH (longer at high pH), by the chlorine concentration and by temperature. Viruses exhibit marked differences in sensitivity to chlorine, between different viruses and between strains of a single virus. Ozone has markedly superior and more rapid viricidal properties than chlorine (Gomella, 1972).

Virus removal also takes place by absorption onto activated carbon. The virus is not inactivated, but may be recovered at least partially by elution. It has been shown that virus absorbed on carbon in treating secondary sewage effluents may be subsequently displaced by organic matter. The use of activated carbon in water treatment cannot be considered as a sterilizing process, but the virus removal that does occur is an added benefit.

The American Water Works Association's Committee on "Viruses in Water" concluded that there was no cause for panic or overreaction to the problem of viruses in water, but that a large field exists for research both in the laboratory and in epidemiological studies.

The report of this Committee and "Water Treatment and Examination" (Holden, 1970) provide excellent up-to-date reviews on this subject.

## MINERAL CONSTITUENTS

The parameters—total dissolved solids, pH, alkalinity, hardness, chloride and sulphate, cover a range of natural mineral constituents that affect the quality of water to be used for public water supplies only in a general way. Low TDS, pH, alkalinity and hardness describe a soft water with characteristic flat taste, good washing properties, and enhanced corrosivity and plumbo-solvency. Hard waters are characterized by a mineral taste, mildly laxative physiological properties and by a tendency to deposit scale and incrustations. The Great Lakes waters are at midscale in the most desirable range between the two extremes.

Chemicals used in water treatment, alum, chlorine gas and hydrofluosilicic acid have acid properties and tend to lower pH and alkalinity. The effects produced with the usual dosages are not great enough to require correction because of the considerable buffering capacity of Great Lakes waters. In some situations with higher dosages, a readjustment of the pH with lime may be required. (Alum dosages usually range from 5 - 30 ppm of "filter alum" which is a partly dehydrated aluminum sulphate containing 17%  $Al_2O_3$ . Chlorine dosages usually range from 0.5 - 3.0 ppm.)

Alkalinity, pH and hardness undergo natural seasonal changes in the lakes, as a result of the consumption of free and bound carbon dioxide by photosynthesis of algae. In extreme cases, pH may go as high as 10; this results in the precipitation of colloidal calcium carbonate which may redissolve as it settles into strata containing more carbon dioxide. This colloidal precipitate is reported to cause serious coagulation problems in Chicago (Vaughn, 1972).

Chloride and sulphate, at the ranges in which they occur in the Great Lakes, are of no significance in water quality. The long-term trend of increasing chloride concentrations in the lakes is of interest, chiefly in demonstrating the substantial effect that increasing populations and industrialization can have on large bodies of water.

## FLUORIDE

Fluoride occurs in natural waters, generally at low levels, from geochemical sources. In Lake Ontario, fluoride occurs at about 0.15 mg/l (CCIW cruise data, 1971) while in Lake Onondaga, which is high in chloride, the fluoride level is 4 mg/l (Moffa and Rand, 1970). In some areas fluoride occurs in groundwaters at concentrations from 2-10 mg/l and at these levels causes a pronounced mottling of the teeth of humans and animals. In the range of 2-5 mg/l, fluoride causes no demonstrable effects on the body except for the tooth mottling.

Fluorides are used extensively in some industries and can occur in their wastewater streams or, more importantly, in emissions to the air. The latter emissions occur significantly in the steel industry where fluoride is used in fluxes, in the manufacture of superphosphate where gaseous fluoride is released on acidification of phosphate rock, and in brick-making and tile-making where fluoride in the clays is released in the firing operation. Fluoride that is emitted to the air as a gas or an aerosol causes severe damage to sensitive plants in the area, and the deposition of particulates on grass and other vegetation causes injury to animals consuming this material. The contribution of aerosol emissions to the fluoride level in surface waters is probably quite small, since fluoride reaching the soil is fixed therein.

### Toxicity

The acute toxicity of single doses of fluoride to humans is not great; 250-500 mg are required to produce symptoms, and a lethal dose is in the order of 4 g.

The effects of the continuous use of high-fluoride water in producing fluorosis, characterized by the mottling of teeth, have been studied since the mid-1930's. Later the relationship between the prevalence of dental caries and fluoride deficiencies in drinking water was demonstrated. This was followed by long-term field studies of the effects of fluoride on the teeth of children living in areas of low and moderate fluoride levels. The experiments were centred on three areas (Grand Rapids, Michigan; Brantford, Ontario; Newburgh, New York). At the first two sites, comparisons were made in areas deficient in fluoride and in comparable areas where fluoride was near the optimum level, both naturally and produced artificially by the

addition of fluoride. The results reported in 1956 were decisive in demonstrating the benefits of an optimum fluoride level in drinking water during the period in youth when the permanent teeth are growing.

On the other hand, there is evidence that fluoride at or above the optimum level and up to 5 ppm does not cause any adverse effects; this opinion, of course, may be subject to change on further investigation.

There is copious literature on the controversy surrounding the artificial fluoridation of water which can only be alluded to here. Surprisingly, no such controversy seems to have occurred when the "mass medication" with iodine (in salt) commenced 25 years earlier.

The mechanisms by which fluoride exerts a beneficial effect on tooth structure (and the deleterious effects on other body processes as alleged by anti-fluoridationists) are beyond the scope of this review. It has been recently reported, however, that trace metals in drinking water complexed with natural or added fluoride contribute to the effectiveness of fluoride in preventing dental caries (Marier and Rose, 1971). This is of further interest to environmentalists, since fluoridation of water supplies may facilitate the carrying of trace metals through the wastewater treatment plant.

### Standards

The U.S. Standards of 1962 set mandatory limits on fluoride in drinking waters. The levels prescribed varied from 0.7-1.2 ppm F, depending on the local annual average air temperature. Since it is desirable to maintain a constant daily intake of fluoride, this adjustment was considered necessary because the drinking water consumed per day varies with the climate.

### Discussion

The chemicals used in fluoridation include sodium and calcium fluorides, hydrofluosilicic acid and its sodium and ammonium salts. The choice of the material to be used is dictated by economics and the ease and safety in handling. Hydrofluosilicic acid and its salts are byproducts recovered from the gases generated during the acidification of phosphate rock and thus carry a cost advantage. In many treatment plants the handling of liquids (hydrofluosilicic acid, 20-35% aqueous solution) is more convenient than the handling of dry solids. Special attention is given to feeding fluorides to water to preclude accidental over-dosing; this is required more to avoid adverse public reaction than because of any serious toxicity hazard that might result from an accidental over-dosing.



The subject of fluoridation is well reviewed by Maier (1963) in the "Manual of Water Fluoridation Practice." Environmental fluoride was reviewed by Marier and Rose in 1971. The American Water Works Association occasionally publishes updated reports on the "Status of Fluoridation in the United States and Canada," giving statistics on the number of treatment plants, the population served, and chemicals used.

## BROMINE

Bromine is considerably more abundant than iodine in nature. Since bromine can be recovered economically from several sources, it has a substantial industrial use and thus has become more widely dispersed in the environment. Its effects on the environment are unknown, but should be the subject of some interest because one of its compounds is proposed as a disinfectant of sewage effluents.

The oceans constitute the chief repository of the earth's bromine resources; the concentration is about 67 ppm. From the oceans, bromine is circulated on a world-wide scale by the atmospheric transport of ocean spray. The concentration of bromine in unpolluted marine air is about  $0.06 \mu\text{g}/\text{m}^3$ , and is largely in the gaseous form, probably resulting from the liberation of bromine from particulate bromides by the ultraviolet radiation in sunlight.

In the atmosphere of cities, the bromine concentration is increased further by the emission of particulate lead chlorobromide from automobile exhaust. The ratio of Br:Cl also increases. The ratio of particulate bromide to gaseous bromide increases to approximately 1:1, and the ratio of bromine to lead approaches that in ethyl fluid (Mills, 1973). The total bromine content of polluted city air is about  $0.25 \mu\text{g}/\text{m}^3$ .

In the Great Lakes, bromine occurs at a concentration averaging about 20 ppb, about ten times that of iodine (Winchester *et al*, 1967). The level found in all of the lakes except Lake Ontario appears to be compatible with its derivation from natural sources. In Lake Ontario the effect of pollution is possibly seen. The average bromine levels in the individual lakes are for Lake Superior and its tributaries, 13 ppb; Lake Michigan, 17 ppb; Lake Huron, 21 ppb; Lake Erie, 31 ppb; and Lake Ontario, 47 ppb. The unpolluted snow of Alaska averages 4 ppb (Woodward, 1963).

In commerce, bromine is obtained from certain mineral waters or saline deposits where the bromine concentration is 0.02-0.5%, and from the sea water which has a concentration of 60-70 ppm. Since 1950 most of the

bromine produced in United States has been made from ocean water.

The largest portion of the bromine produced is used in the manufacture of ethylene bromide, which is used as a scavenger of lead in the "ethyl fluid" of leaded gasoline. Lead and bromide are thus emitted as a fine aerosol to the atmosphere in equal atomic ratios, and the absolute quantities emitted per year are enormous.

The remainder of the bromine produced is used in manufacturing various chemicals, examples of which are methylene chlorobromide as a fire extinguisher and methyl bromide as a fumigant.

For a considerable time bromine has been used as a disinfectant for swimming pools when it is applied at dosages of 1-2 ppm as liquid bromine or generated from the reaction of chlorine on bromide. It has substantial advantages over chlorine, since the bromamine produced by reaction with ammonia has a good disinfecting power equal to that of free bromine.

The use of bromine (as bromine chloride, BrCl) for disinfecting sewage effluents is proposed and currently being investigated (Zellech, 1972). Although BrCl at dosages of 4-10 ppm treatment is more expensive than chlorination is at comparable dosages, it has the advantages of producing a more active bactericidal residual in the presence of ammonia and avoids the production of chloramines, which are now considered to be unduly toxic to fish (Mills).

If this process attained a widespread use, it would result in the injection of a large new input of bromide into the environment. For example, the treatment of a sewage effluent flow of 100 mgd at a dosage of 5 ppm BrCl would discharge over 3000 lb of bromine into the receiving waters daily. The bromine content of the effluent would be sixty times that of Lake Ontario water. The bromine would be predominantly in the form of bromide, with a small amount of organic bromine compounds. It is claimed that this effluent is non-toxic to fish and that the maximum possible intake by humans (assuming they drank treated effluent only) would be 30% of the normal daily dietary intake (American Public Health Association, 1971).

## IODINE

Iodine occurs in the oceans at a fairly uniform concentration of 60 ppb, and the oceans represent the main reservoir of iodine in the world. The ratio of I:Cl in marine air is some two orders of magnitude greater than in sea water, suggesting that iodine vapor is liberated from the

oceans by the effects of ultraviolet light. In contrast, the ratio of Br:Cl in the aerosol is the same as in sea water (Duce *et al*, 1963). Iodine circulates from the ocean surface to the atmosphere, is precipitated on the land and returns to the oceans in drainage. In the glaciated areas of the world, the iodine content of the soil is very low, and the only input of iodine to the surface waters is by way of precipitation. Rain falling in areas near the sea contains iodine in the order of 2-10 ppb, e.g., Hawaii (Duce *et al*, 1963), and the snows falling in areas remote from the sea, e.g., Alaska and Antarctica (Woodward, 1963), contain about 1 ppb.

In the Great Lakes basin, the level of iodine in Lake Superior and its tributaries is somewhat over 1 ppb and represents the integrated rainfall in the area. In Lake Huron, the mean iodine concentration is 1.33 ppb; in Lake Erie, 1.7 ppm; and in Lake Ontario, 2.9 ppb. This small increase downstream in the Great Lakes is considered to be not greater than what can be accounted for by evaporation (Winchester *et al*, 1967; Black, Lackey and Lackey, 1959).

#### Goiter

From the earliest times, goiter has been associated empirically with drinking water. The relationship between iodine and goiter was suspected as early as 1816, and the use of iodized salt was recommended before 1850 (Astwood, 1965). In 1917, Marine and Kimbal in Ohio administered iodine for simple goiter, and the success of this treatment led ultimately to the use of iodized salt in most countries. Iodized salt contains 50 ppm KI by weight.

The occurrence of simple goiter varies with the average daily intake of iodine. When the intake is very low, less than 10  $\mu\text{g}/\text{day}$ , goiter is general. In the range of intakes from 10-30  $\mu\text{g}$  goiter occurs in individuals otherwise predisposed to it. From 30-120  $\mu\text{g}/\text{day}$  factors influencing iodine excretion are effective, and at higher daily intake rates iodine-goiter develops. The consumption of 5 g/day of iodized salt provides about 100  $\mu\text{g}$  of iodine, which is midscale in the optimum range of dietary intakes. There is an interesting suggestion that certain salt-water fish that have apparently become well adapted to living in the fresh waters of the Great Lakes suffer from goitrous conditions because of the low level of iodine in their new environment (Winchester *et al*, 1967). This might have been a factor in the massive dying of alewife fish in Lake Michigan in 1967.

In technically undeveloped countries the use of iodized salt is not as prevalent, and endemic goiter still occurs in appropriate areas. In highly developed countries iodine intakes, in addition to those obtained in drinking water, come from the use of iodine compounds in foods

(iodate added to bread to improve its quality), in drugs which contain iodine, and in other chemicals "contaminating" foods (Tiffany, Winchester and Loucks, 1969).

External factors other than iodine deficiency may contribute to the incidence of goiter. Woodward in 1963 reviewed the relationship between water quality and goiter and concluded that goitrogenic substances in water might include unidentified heat-labile organic matter. Research in this area does not seem to have progressed since 1963, although it is known that specific substances in certain foods have goitrogenic properties.

The general and relatively unresisted use of iodized salt as a vehicle for "mass medication" is remarkable when compared with the furor created by the proposed fluoridation of drinking water. The addition of iodine (as iodide) to drinking water for goiter control was practiced in Rochester, N.Y., from 1923-33, but was discontinued because of the cost, because a better vehicle (salt) was available, and because an adverse reaction was experienced by sensitive individuals.

#### Iodine as a Disinfectant

Elemental iodine has been used as a disinfectant for swimming pools since its merits were described by Black, Lackey and Lackey in 1959. It appears to be an ideal disinfectant, as it has excellent bactericidal properties while being less reactive chemically than chlorine, which produces undesirable reaction products with ammonia and organic substances. Iodine does not produce iodo-amines with ammonia, and since it thus allows ammonia to accumulate, it provides a nutrient resource encouraging the growth of algae.

The use of iodine in disinfecting drinking water has been investigated and its advantages have been well presented in a recent paper (Black *et al*, 1968). Black *et al* in 1965 used iodine at dosages ranging from 1-5 ppm to disinfect the water supply to three institutions housing about 750 persons. The experiment lasted over 43 months during which time a variety of medical and physiological tests, including thyroid function, showed no evidence of deleterious effects on the consumers. This is despite the fact that at a dosage of 1 ppm, the per capita daily intake of iodine would exceed 1000  $\mu\text{g}$ . According to Kinman, Black and Thomas (1970), this treatment "continues to this day."

Black *et al* (1965) also reported the experimental iodination of the water supply for Gainesville, Florida, which was undertaken because this water system had at the time a potential to cause an outbreak of disease. The treatment was carried out by adding potassium iodide and

generating iodine by reaction with chloramine. The experiment was terminated after only 12 hours because of the production of an objectionable taste and odor. This presumably resulted from the reaction of the iodine with coatings and deposits in the mains, since odor production had not been anticipated from laboratory tests.

Iodine has a number of advantages over chlorine in the disinfection of drinking water and it may find some extensive application in small systems, for emergency uses, and in field use in portable plants where the ease and safety in handling are important factors. Any large-scale use of iodine is scarcely to be expected, not only because of the possible long-term effects of the resulting increased iodine intake, but because of the greatly increased cost and the relatively small world supply of the element. One purification plant treating 100 million gallons per day would consume a half-ton of iodine per day.

### DISSOLVED OXYGEN

Dissolved oxygen, *per se*, as a parameter is not significant in public water supplies. Deep well waters having zero dissolved oxygen are quite acceptable as drinking water. Absence of oxygen may have a small effect on taste in general, but this is only marginally detectable (Bruvold and Pangborn, 1970). Taste and odor and some other undesirable qualities associated with low dissolved oxygen are caused by other substances. Septic and sulphide odors are produced by the anaerobic decomposition of organic matter; and taste, color and precipitation of flocculent hydroxides are caused by elevated levels of iron and manganese.

At Cleveland, low dissolved oxygen occurs regularly in summer in the "dead water" of Lake Erie. DO is often below 1 ppm and goes down to 0.0 ppm, but causes no particular problem in two of the four treatment plants. At the Crown Plant, the serious problems that occurred were traced to a damaged intake structure, which caused water to be drawn from very near the lake bottom. This water was devoid of oxygen and high in iron, manganese and ammonia. The iron was considered to be organically bound; it did not precipitate on contact with air, and prechlorination produced a yellow color which persisted through the distribution system. Permanganate was used to oxidize the complex, and the iron was removed with the  $MnO_2$  precipitate from the permanganate (Schwartzwalder, 1973).

### AMMONIA

Ammonia is a relatively minor water pollutant as far as toxicity is concerned, but it has considerable importance as an indicator of pollution, both sanitary and industrial. It interferes with water chlorination to a significant degree.

### Source

In nature, ammonia is produced by the bacterial decomposition of organic matter in the soil and in water. In the soil, some of the ammonia produced escapes to the atmosphere and from there it is returned to land and water by rainfall. Rain always contains ammonia.

In sewage, ammonia occurs in much higher concentrations from the decomposition of proteinaceous matter and urea. In primary-treated sewage, the concentration is highest because decomposition processes are dominant. In secondary effluents, the concentration is lower because of losses occasioned by aeration and because of oxidation to nitrate. If activated sludge treatment is operated solely for BOD removal, aeration may not be continued to the nitrification stage and the possibly desirable effects of reduced ammonia discharge are lacking. Secondary effluents can be treated further for removal of inorganic nitrogen by denitrification using methanol, or for removal of ammonia, by reverse osmosis or ion exchange.

Certain industrial wastes, particularly coke-oven wastes, are large sources of ammonia. Recovery of ammonia as ammonium sulphate is practiced in this particular field, but the recovered material has little economic value in competition with the much purer synthetic product. In Burlington Bay, ammonia is very high (4 - 10 ppm) because of the large inputs from the industries and from municipal primary-treated sewage effluents. Outflows of Burlington Bay water to Lake Ontario produce abnormally high concentrations locally. In Lake Michigan near Chicago, high ammonia concentrations up to several tenths of a part per million occur in the lake in association with "petroleum refinery" odors of local industrial origin (Vaughn and Reed, 1972).

Some authorities believe that the concentration of ammonia in effluents discharged to receiving waters should be limited because of its nutrient properties toward algae and its toxic effects at high concentrations to fish. This toxicity is increased when the pH exceeds 8.0; in most waters the pH can be raised much higher than this by algae blooms. The toxicity to fish is also increased by reductions in dissolved oxygen.

### Occurrence in Water

At any time the concentration of ammonia in water is the balance between production (and other inputs) and consumption. The income is by way of decomposition of organic matter in solution and in sediments, from land runoff, from rainfall and from sanitary and industrial wastes. The mechanisms consuming ammonia are nutrient uptake by phytoplankton and bacterial nitrification and denitrification.

## Significance and Effects

Since in unpolluted waters ammonia concentrations are usually less than 0.10 ppm  $\text{NH}_3\text{-N}$ , higher values may indicate pollution from sanitary or industrial sources.

In water treatment, ammonia interferes with chlorination. Basically, if ammonia is present, chlorine will react with it first, producing mono-chloramine or di-chloramine, depending on pH and the ratio of chlorine to ammonia. Chloramines have bactericidal properties but slower chemical action than free chlorine (which in water is hypochlorite ion). Chloramines are much less active chemically and, in the past, were used extensively, being produced intentionally by adding ammonia to prevent the reaction of chlorine with phenols. The trend today, away from the use of chloramines, is the use of the greater oxidizing power and superior bactericidal and viricidal properties of free chlorine.

To destroy ammonia occurring in raw water, sufficient chlorine is added to oxidize it to  $\text{HCl}$  and  $\text{N}_2$ . In practice, this requires about 10 parts of chlorine to one part of ammonia-nitrogen. An intermediate product,  $\text{NCl}_3$ , occurs which has a strong chlorinous to geranium odor, which is accompanied by nose and eye irritation. This is a characteristic odor in water treatment plants using free chlorine residuals and is part of the odor in swimming pools where an attempt is made to maintain free chlorine in the pool.

The operating problem produced by ammonia in raw water involves the varying concentration of ammonia and the difficulty of adjusting chlorine dosages to follow rapid variations. Automatic controllers are available which are sensitive only to free chlorine residuals, and which can thus follow changes in ammonia fairly well.

At Hamilton, there is an extreme example of the ammonia problem. Burlington Bay water contains ammonia in amounts ranging from 4 - 10 ppm. Where this water is emitted to the lake as a plume, currents may carry the plume toward the intake, and ammonia in the raw water may change in a short time from the normal low values of 0.02 ppm to peaks usually ranging from 0.5-1.0 ppm.

## Standards

Most Standards, including the USPHS 1962 Standards, do not include a reference to ammonia. The WHO International Standards of 1963 include ammonia as an indicator of pollution if it exceeds 0.5 ppm. The OWRC Guidelines for public water supplies give 0.5 ppm as a

permissible level and 0.01 ppm as the desirable level. The lowest possible levels are obviously to be desired. At concentrations of 0.5 ppm and higher, problems associated with disinfection and taste and odor production become very serious.

## ARSENIC

Arsenic has acquired an unequalled notoriety as a poison over its long history. A single lethal dose may be as small as 5-50 mg  $\text{As}_2\text{O}_3$ . According to some authorities, it is excreted very slowly from the body, and thus may build up to chronic toxicity levels from very low daily intakes. Lisella, Long and Scott (1972) state that although arsenate is rapidly excreted and little if any can accumulate in the human body, trivalent arsenic as arsenite readily accumulates to significant levels.

The use of arsenicals in the world has steadily increased in this century. In 1966, the free-world production of arsenic trioxide was 55,000 tons, most of which went into insecticides (calcium and lead arsenates, sodium arsenite and copper acetoarsenite) and herbicides (sodium arsenite, disodium methyl arsenate, cacodylic acid and methyl arsenic acid). The use of arsenic in insecticides is decreasing in the United States, but its use as a herbicide and defoliant is increasing. Arsenic finds other industrial uses — in glass-making, felt-preservation, medicinals, additives to animal feeds, and as algicides and in aquatic weed control. In this latter application, its use in Ontario has not been permitted for many years.

Arsenic is considered to be a non-essential and non-beneficial element in the human body. It has a widespread occurrence in nature at low levels, but the concentrations found in the environment are increased by the extensive usage described. Therefore it occurs in foods in varying amounts. Early in this century, the tolerance for arsenic in certain foods was established in England, but the limit was raised in the United States and Canada to allow the use of apples and other fruits which contained higher arsenic levels from the use of insecticides. Presently the residual arsenic in fruits and vegetables is set at 3.5 ppm by the U.S. Food and Drug Administration. The arsenic content of American cigarettes ranged up to 42  $\mu\text{g}$  per cigarette when arsenical pesticides were used in tobacco-growing. When the use of these pesticides was discontinued, the level dropped to less than 12  $\mu\text{g}$ .

For a long time arsenic has been considered to be a carcinogenic agent (the arsenic-cancer myth of one writer), but McDermott, Kabler and Wolf (1971) say that "studies in this country (U.S.) have repeatedly failed to demonstrate any such effect."

Arsenic occurs at significant levels in many industrial wastes because of the widespread use of arsenicals in industry. In a five-year summary of trace metals in U.S. rivers and lakes (Kopp and Kroner, 1967), arsenic was found in less than 6% of the 1500 samples. The average of all samples examined was 0.067 mg/l, with the maximum of 0.33 mg/l in the Cuyahoga River at Cleveland. All the high samples came from industrially polluted streams.

In the reconnaissance survey of minor elements (Durum, Hem and Heidel, 1970), single samples from water at or near the waterworks intakes of major cities using Great Lakes water generally showed arsenic at levels below 10  $\mu\text{g/l}$  after filtration of the samples. One public water supply on Lake Michigan contained 10  $\mu\text{g}$  and the Buffalo supply contained 20  $\mu\text{g}$ . At sites where pollution from municipal and industrial wastes was expected (e.g., Detroit River below the city) only 10  $\mu\text{g/l}$  was found. On the nation-wide basis, arsenic was identified in as many samples from remote sites as from other sources.

Arsenic at levels up to 10  $\mu\text{g/l}$  appears to have little or no deleterious effect on lower forms of aquatic life. Fish, however, are injured by concentrations over 1 ppm or 2 ppm. McKee and Wolf (1963) suggest a limit of 1.0 ppm in water for the preservation of fish and aquatic life, while the OWRC Guidelines (1970) say that "an environmental level of 0.01 mg/l should not be exceeded under any circumstances."

Arsenic in drinking water was limited to a maximum permissible limit of 0.05 mg/l in the USPHS Drinking Water Standards of 1942 and 1946. In 1962, a recommended limit of 0.01 mg/l was included. Stokinger (1971) questions the need for such a low limit and suggests that 0.20 ppm would be more realistic. The WHO European Standards of 1961 set a tolerance limit as high as 0.20 mg/l, and the International Standards of 1963 have a tolerance limit of only 0.01 mg/l. The Canadian Standards of 1968 repeat without change the USPHS 1962 limits, and add as an "objective" an undetectable level. Arsenic in raw water is not reduced by conventional treatment.

The low limits set for arsenic in drinking water represent concern for this highly toxic and extensively used element and are influenced no doubt by its suspected, but undemonstrated, carcinogenic properties.

## CADMIUM

Cadmium is one of the most toxic metals whose importance in the environment has been identified and extensively studied only within the last twenty years.

Cadmium metal is recovered as a byproduct of zinc smelting; its high market price (\$4/lb) encourages its recovery. Nevertheless, commercial zinc metal contains about 1% cadmium as an impurity. The major industrial use of cadmium is in electroplating, since the coating deposited has advantages in appearance, corrosion resistance and adhesion. The metal is too easily attacked by weak acids that occur in foods to permit the use of cadmium-plated ware in food processing. Other industrial uses include pigments used in printing and dyeing fabrics, stabilizers in PVC plastics, alloys (solders and fusible alloys), batteries (nickel-cadmium) and a wide variety of smaller miscellaneous uses. Almost everything made by the industries using cadmium is discarded. As there is no recycling of cadmium, the potentiality of environmental contamination is great.

In 1969, the annual consumption of cadmium in the United States was 15,000,000 tons of which 6,000,000 tons went into electroplating and nearly 5,000,000 tons into pigment and plastic manufacturing.

Owing to the volatility of the oxide, a considerable amount of the metal entering the environment goes into the air as fumes and ultimately reaches the soil and water by precipitation, either dry or in rainfall. These emissions occur in scrap zinc recovery and incineration and recycling of scrap steel carrying zinc coatings. In 1968, it was estimated that nearly 4.6 million pounds of cadmium were emitted to the atmosphere in the United States (Anon., 1971).

### Occurrence in Water

Only traces of cadmium are found in natural waters. In the five-year summary of trace metals in rivers and lakes of the United States by Kopp and Kroner, cadmium was found in the soluble form in only 2.5% of 1500 samples. The metal, if present, is largely absorbed onto particulates because of the low solubility of the hydroxide and carbonate.

In a later report by Durum, Hem and Heidel, cadmium in the Great Lakes waters was below the detection limit (1 ppb) except for traces (1-3 ppb) at the Buffalo waterworks and in the Niagara River. In data produced in 1970 by CCIW, total and dissolved cadmium were below 1 ppb in the Lake Ontario samples. In the 1971 data for Lake Ontario, soluble cadmium averaged 0.15 ppb and ranged from 0-0.5 ppb. In the same year in Lake Erie the average for soluble cadmium was about 1.0 ppb; it was near 0.0 ppb in April, but averaged about 1.2 ppb in August. In a limited number of samples of raw water at Toronto (Anon., 1971-73), cadmium was reported at less

than 1 ppb. In the raw sewage at Toronto (Anon., 1972), cadmium was generally less than 10 ppb, but 30 ppb was reported in one sample.

Cadmium levels above 2 ppb or 3 ppb are attributed to industrial pollution. In the Cuyahoga River at Cleveland, values up to 120 ppb were found and 9 ppb was reported in the Maumee River at Toledo (Kopp and Kroner, 1967).

Cadmium can gain entrance to piped water supplies from contact with metal coated with zinc containing cadmium, from solder used on copper pipe and extraction from black polyethylene piping.

### Toxicity

Cadmium is a non-essential, non-beneficial element of high toxicity. It is present in normal plant and animal tissue to the extent of about 1 mg/kg. The daily human intake in food is quoted by McKee and Wolf as from 4-60  $\mu\text{g}$ , while Nilsson (1970) quotes two estimates which include the range 100-400  $\mu\text{g}$ . Most of the ingested metal is eliminated immediately in feces and only 2-3  $\mu\text{g}$  are absorbed per day. The average amount in the human body is about 30 mg, of which 10 mg is in the kidneys and 4 mg in the liver. Since at all levels of dietary intake down to 0.1 ppm cadmium accumulates in the body, the USPHS 1962 Standards set a limit of 0.01 ppm in drinking water.

The maximum allowable concentration (MAC) of cadmium in industrial atmospheres is set at 0.1 mg/m<sup>3</sup> in the United States, Japan and Sweden (Nilsson, 1970). This allows a much greater intake than that by way of diet, possibly as much as 100  $\mu\text{g}$  per 8-hour working day. This MAC protects only against acute effects, not long-exposure chronic effects.

In 1970, an extensive review of the toxicology of cadmium was made in Sweden (Nilsson, 1970). Cadmium affects many physiological processes and is suspect in cardiovascular diseases and possibly has carcinogenic and teratogenic implications. It is difficult to identify the effects of cadmium in the body, since all humans have accumulated a store of the metal in their tissues. Thus there is no adequate control material for comparative toxicological studies.

### Standards

Before 1950, the USSR had a maximum permissible limit of 0.10 ppm in water. The USPHS Standards of 1962 for the first time included a maximum limit of 0.01 ppm; the WHO European Standards of 1961 gave 0.05 ppm as the maximum and the International Standards of 1963 and

1971 gave 0.01 ppm. The Canadian Standards of 1968 quoted 0.01 ppm as the maximum level, less than this being acceptable, with the objective of a non-detectable level. The current Russian Standard is 0.01 ppm (USSR, 1970).

### Discussion

Although cadmium does not appear to present an immediate threat in public water supplies, especially in the Great Lakes sources, very little is known of the behavior of the element in the environment. Its high toxicity and widely diffused and growing industrial uses, however, necessitate more research. Information seems to be unavailable for cadmium in municipal sewage or concerning its behavior and removal in sewage treatment processes.

## CHROMIUM

### Source

Natural chromates are rare. If they are present in surface waters, industrial pollution is indicated. Chromates are stable in water under aerobic conditions, but are reduced by exposure to heat and reducing agents. Trivalent chromium is insoluble in neutral or alkaline waters.

Trivalent chromium is not used widely in industry and is not an important pollutant. Chromates and dichromates are used extensively in metal pickling and plating industries and in aluminum anodizing. Concentrated wastes from these sources contain from 600-10,000 mg Cr/l. The discharge of such wastes into sewers is usually prohibited by bylaws because of the toxicity of chromium at high concentrations to biological sewage treatment processes. Practical processes are available to reduce chromium emissions at the source by reduction of hexavalent chromium to trivalent state and subsequent precipitation.

Other sources of chromium in wastewaters are from leather treatment and from blow-down in cooling water systems (including large air-conditioning systems), where chromate is used as a corrosion inhibitor. Cooling tower blow-down water may contain 10-60 mg/l. The use of chromate as a corrosion inhibitor in road de-icing salt was promoted recently, but apparently was abandoned because of the lack of economic benefit.

Chromate occurs in raw sewage commonly at 1-3 mg/l level, accompanied not infrequently by slug discharges up to 50 mg/l. Except for the occurrence of short massive doses, chromium does not harm the operation of a biological plant. Low concentrations of chromate are reduced to the innocuous trivalent form. Experimental work and plant observations indicate good removal of

chromium when in sewage treatment plants the incoming heavy metals total less than 10 mg/l (Robert A. Taft Sanitary Engineering Center, 1965).

In the five-year summary of trace metals in rivers and lakes in the United States by Kopp and Kroner, chromium was found in more than half of the 91 samples examined with a mean value of 0.014 mg/l. The highest individual sample contained 0.110 mg/l and, unexpectedly, was from the St. Lawrence River at Massena. In 1971, 14 samples from public water supplies drawing water from the Great Lakes and connecting rivers contained hexavalent chromium below 0.002 mg/l (Durum, Hem and Heidel, 1970). The CCIW 1971 cruises on Lakes Erie and Ontario showed chromium levels at about 0.001 mg/l in spring and about 0.0005 mg/l in fall. There was no significant difference in chromium levels in points near cities as compared with those on the centre of the lake. Limited sampling of metro Toronto raw water shows the chromium to be less than 0.01 ppm.

#### Toxicity

It is thought generally that chromium is neither an essential nor beneficial element in human nutrition, but Mertz (1967) and Doisy *et al* (1967) showed that it is involved in glucose metabolism. Thus it could possibly be essential. Stokinger (1969) considers it a "beneficial element" which, among other things, counteracts the toxicity of lead.

Chromium, taken orally, is not highly toxic; it is completely and rapidly eliminated. Experimentally a dose of 225 mg Cr (in water at 10 mg Cr/l) was administered to a man with no ill-effects. Animal experiments indicate that continuous use of water containing as much as 5.0 mg/l is acceptable from the toxicological point of view (McKee and Wolf, 1963).

Natural foods contain small and varied amounts of chromium whose origin seems to be adventitious. A study of institutional diets indicated a daily intake of 0.2-1.2 mg for children. Inhaled chromate dust is known to be carcinogenic. There is no evidence, however, that on ingestion the same effect occurs.

Chromium shows toxicity to fish varying with species and several environmental factors. There is some indication that trivalent and hexavalent forms do not differ in toxicity. Some algae are said to be sensitive to concentrations well below 0.10 mg/l, and algae in general concentrate chromium 100-fold to 500-fold.

#### Standards

Existing Standards refer only to hexavalent chromium, apparently since trivalent chromium does not occur in drinking water because of the insolubility of the oxide. All the current Standards (USPHS, 1962, WHO European and International, and Canadian) specify a maximum allowable level of 0.05 mg/l. The Canadian Standards indicate that less than 0.05 mg/l is desirable and that the objective is below detectable levels.

#### Discussion

In view of the available toxicity data, it appears that factors other than toxicity dictate the low allowable levels in the current Standards. Probably the main reason is that the presence of any chromium in drinking water is indicative of undesirable pollution from industrial sources.

#### COBALT

Cobalt is an essential trace element with relatively low toxicity to man. Ingestion of 0.1-0.25 mg per day has shown no adverse effects and the desirable daily intake is quoted as about 7  $\mu$ g (Taylor, 1971). Maximum safe concentrations in drinking water cannot be determined from present information, and the metal is not included in any current Standards. Aquatic organisms tend to accumulate cobalt.

In 1969, the National Community Water Supply Study (McCabe *et al*, 1970) indicated that the average concentration of cobalt in drinking water in the United States was 2 ppb with values ranging from 0-19 ppb. In the 5-year study of trace metals by Kopp and Kroner, cobalt was rarely detected in the Great Lakes basin. Cobalt was found once at the then barely detectable level of 20 ppb in the Detroit raw water, and on two occasions, it occurred in the polluted Cuyahoga River at Cleveland at 20 ppb and 46 ppb.

In the reconnaissance of minor elements of 1970 (Durum, Hem and Heidel, 1970), cobalt was found in public water supplies derived from Lake Erie in concentrations ranging from less than 1-4 ppb and in similar situations in Lake Ontario from 5-6 ppb. Cobalt was not found in the Detroit River even in the areas examined that contained municipal and industrial pollution. In the Niagara River, however, cobalt occurred at the 5-6 ppb level.

In the CCIW data for 1971 (Chau *et al*, 1970), cobalt was below 0.1 ppb in Lake Ontario in March and near 1.5 ppb in November in the Niagara-Toronto-Hamilton area.

In the eastern region of the lake, it was less than 0.5 ppb. In Lake Erie cobalt was less than 0.1 ppb in April and about 1 ppb in August (Chawla and Chau, 1969).

### Standards

Cobalt is not included in any official Standards. The U.S. Bureau of Water Hygiene, considering substances not included in the USPHS 1962 Standards, suggests unofficially that cobalt should be absent from finished drinking water.

### Addendum

Cobalt in beer was determined to be the cause of a number of deaths among people having a high beer consumption in Quebec in 1965-66 (Canadian Medical Association, 1967). Cobalt sulphate was added to draft beer to improve the stability of the foam. The absence of foam was caused by traces of detergent remaining in washed glasses which were insufficiently rinsed.

The average heavy beer drinker would have a daily intake of about 4 mg cobalt sulphate, which is considerably less than what is considered to be the toxic dose. The toxicity of the metal was enhanced by the high level of alcohol intake.

Cobalt was used therapeutically for treating refractory anemias, but its effectiveness in raising the hemoglobin level was offset by its varied toxic side effects and it was concluded that "cobalt has no place in modern medicine" (Anon., 1967).

## COPPER

Copper is a metal that occurs commonly in natural waters, generally at concentrations less than 20 ppb. Higher concentrations can be interpreted as the result of man's activity.

In the 5-year summary of trace metals by Kopp and Kroner, copper was found in 74% of the samples; the average concentration was 15 ppb. In Lake Superior at Duluth, copper ranged from 3-6 ppb; in the St. Marys River at Sault Ste. Marie it was from 2 ppb to 28 ppb; in Lake Michigan at Milwaukee 2-34 ppb were found, and at Gary copper occurred only from 2 ppb to 7 ppb; in the St. Clair River it was 4-20 ppb and in the Detroit River 6-13 ppb.

The 1969 CCIW data indicated that total copper in Lake Erie averaged 15 ppb (Chawla and Chau, 1969) and in Lake Ontario dissolved copper averaged 6.4 ppb (Chau *et*

*al*, 1970). In the western region of the lake it averaged 14 ppb, while in the east it was only 3.3 ppb. The copper concentration seemed to be related to the iron concentration, and the higher levels of each in the western part of the lake were attributed to industrial activities. In the 1971 CCIW data, copper concentrations averaged about 4 ppb in both lakes.

### Source

The major source of copper concentrations much above the natural background levels is from industrial activities. The metal is used extensively in electroplating, as a catalyst in chemical manufacturing and in the removal of mercaptans in oil refining. Therefore copper occurs in municipal sewage in concentrations up to several parts per million. For example, in the industrial city of Grand Rapids, Michigan, it is found to range from 0.5-3.7 ppm. In experimental work on activated sludge, at the Robert A Taft Sanitary Engineering Center, it has been shown that copper in concentration up to 25 ppm reduces the biological activity only slightly when the sludge is acclimatized. Sludges of higher concentration have a severe effect, and the copper passes through the plant. Removal of copper at moderate levels is normally in the range of 50-80%.

Copper is extensively used in water supplies to control algal growths. If copper is not applied in a chelated form, it is rapidly precipitated in hard water. Where preservation of the aquatic environment is desirable, the limiting permissible concentration is about 20 ppb. Chau *et al* indicate that levels even lower than this control the production of chlorophyll in Lake Ontario.

### Toxicity

Copper is an essential and beneficial element in human diet. In the U.S. Public Health Service Drinking Water Standards (1962) the daily adult requirement is 2.0 mg; deficiency causes anemia in infants. Copper is not a cumulative poison, as lead and mercury are, and most of the ingested copper is not absorbed. It is used at quite high levels in animal diets (Robinson, Draper and Gelman, 1971); enough copper occurs in the feces from such animals to prevent proper decomposition.

The limiting factor in setting standards for copper in drinking water is not its toxicity, but the metallic taste which is noticeable at the 1-5 ppm levels. In some waters at these levels the staining of bathroom fixtures may occur.

### Standards

The United States Standards of 1925 limited copper



in drinking water to 0.2 ppm. In 1942, this limit was raised to 3.0 ppm, only a "recommended" level. The 1961 Standards reduced this to 1.0 ppm, based on taste considerations.

The WHO European Standards of 1961 recommended that water entering a distribution system should be below 0.05 ppm and allowed a limit of 3.0 ppm after 16 hours contact with copper piping. The WHO International Standards of 1963 allowed 1.5 ppm in raw water. In 1971, the highest desirable level in drinking water was set at 0.05 ppm with the maximum permissible amount at 1.5 ppm.

The Canadian Standards of 1968 for drinking water indicate that 1.0 ppm is acceptable, but the objective is less than 0.01 ppm. The OWRC Guidelines for raw water give a concentration of 1.0 ppm as permissible with the desirable condition being "virtually absent." Copper at these low levels is not reduced appreciably by normal water treatment.

#### Discussion

Since copper is an essential element in small amounts and is toxic only at concentrations well above those that would not be tolerated in drinking water for aesthetic reasons, it is not an element for much concern in Great Lakes drinking water supplies.

## CYANIDE

### Toxicity

Cyanides represent some of the most toxic materials handled in industry. A single lethal dose may be as low as 50-60 mg CN. In man, lower doses, for example, less than 10 mg, are handled easily and detoxified in the liver by conversion to thiocyanate. This reaction is rather slow, but there appears to be no limit to its capacity, as long as the system is not overloaded. McKee and Wolf indicate that the maximum safe daily intake from all sources including the normal environment, industrial exposure and foods, is 18 mg.

Fish and other aquatic life are more susceptible to cyanide poisoning and levels well under 1 mg/l are lethal. Toxicity in the aquatic environment varies with pH (less toxic under neutral or alkaline conditions), temperature, and dissolved oxygen. Some metals reduce the toxicity greatly by formation of complexes. For example, cyanide at 100 mg/l may be without toxic effect in the presence of nickel in neutral or alkaline conditions. If the pH is lowered, free cyanide is released and toxicity returns.

### Sources

The major sources of cyanides reaching the environment are the wastes from coke-oven byproducts plants and from metal-plating wastes. Practical commercial techniques are available for destroying cyanides in both wastes. The concentration of cyanide in the raw sewage of an industrial city may average about 1 mg/l, but momentary peaks may appear as high as 10-25 mg/l. Trickling filters, activated sludge and anaerobic sludge digestion processes can handle moderate levels of cyanide after acclimatization.

### Standards

Before 1950, no agency set standards for cyanides in drinking water. In 1951, the USSR set a Standard of 0.20 mg/l, and later several Standards were set in the United States at 0.10 mg/l and 0.15 mg/l. The WHO International Standards of 1958 set a desirable limit for drinking water at 0.01 mg/l and a maximum of 0.05 mg/l. The second edition of the International Standards in 1963 gave a limit of 0.01 mg/l for finished water and 0.20 mg/l for source water. The third edition in 1971 quoted a maximum of 0.05 mg/l. The Canadian Standards of 1968 indicated a maximum permissible level of 0.20 mg/l, an acceptable level of 0.01 mg/l with the objective to be "not detectable." The 1970 USSR Standard for cyanide is 0.10 ppm.

### Discussion

The low levels set by the current Standards seem to be influenced more by the toxic effects of cyanides on aquatic life rather than by undesirable effects on man. Chlorination, as practiced universally in water treatment, is capable of destroying low levels of cyanides. The third edition of the WHO International Standards indicates that the maximum daily intake of cyanide from all sources should be 0.05 mg/kg or about 3.5 mg per person. This is a conservative amount compared with the estimate of McKee and Wolf, who suggest 18 mg/day as the maximum safe intake. The daily intake of cyanide by way of drinking water containing the maximum allowable level of 0.05 mg/l would be negligibly small, in comparison with the 3.5 mg total intake.

Cyanide in surface waters is of industrial waste origin exclusively. Setting a low limit is desirable for it reduces the general level of exposure to industrial pollutants.

## IRON AND MANGANESE

Iron and manganese are considered together, since they frequently occur together in waters and their properties and effects in water are similar.

In oxygenated water, iron occurs at very low concentrations. Solubility data indicate a maximum concentration of 5 ppb and CCIW data on the Great Lakes show values in the order of 1 ppb (Chau *et al*, 1970). In anoxic groundwaters, iron in the ferrous form is much higher, but rarely above 10 ppm. In the presence of some types of organic matter, complexes are formed and the apparent solubility is increased. This formation is often referred to as organic iron without much knowledge of the actual form in which it exists. The organic matter can be oxidized by chlorine, ozone or permanganate and then the iron precipitates. In the hypolimnion of lakes, iron may be present in solution in the reduced form, but it rarely exceeds 0.2 ppm. In the interstitial water of organic muds, soluble iron may be as high as 1 ppm.

In raw waters, total iron may be present in concentrations much higher than those indicated by solubility; it is then present in colloidal form or deposited on particulate matter and is removed easily by filtration.

Manganese occurs in water in much lower concentration than iron does. Few groundwaters contain manganese in excess of 1 ppm. In oxygenated waters, the solubility is very low. In the CCIW data on the Great Lakes, manganese occurs at levels of less than 1 ppb in filtered samples (Chau *et al*, 1970).

The significance of iron and manganese in public water supplies is related more to aesthetic and convenience factors than to considerations of health or safety.

Iron is an important and essential dietary constituent but the nutritional requirement of 1-2 mg/day is small in comparison with normal dietary content (7-35 mg/day). Consequently the amount contained in drinking water is not significant. At a concentration of several parts per million, iron is detectable by an astringent, metallic taste and it affects tea by darkening the color.

Manganese is also an essential dietary constituent, but normal diets contain the element in excess of human requirements which appear to be 5 mg/day (Murthy, Rhea and Ceeler, 1971). The concentration required for detecting the metallic taste ranges from 0.5 ppm to over 100 ppm.

The limitations placed on iron and manganese in drinking water are based on aesthetic reasons and convenience. Both metals, if introduced into the distribution system in solution, may subsequently precipitate and cause complaints of turbidity, discoloration, staining of laundry and of plumbing fixtures. Both metals encourage the growth of iron and manganese bacteria in the distribution system. Since the energy available from oxidizing the -ous form to -ic is very small, large amounts of precipitated

hydroxides are formed from relatively small populations of the bacteria and, in extreme cases, result in the clogging of mains.

Most current Standards give a desirable limit for iron of 0.05 ppm and for manganese, 0.10 ppm, with maxima of 0.3 ppm and 0.5 ppm, respectively. Surface waters rarely require any special treatment for iron or manganese removal, the normal chlorination, coagulation and filtration sufficing.

Groundwaters containing small amounts of ferrous iron or manganese in solution may be stabilized to prevent subsequent precipitation by applying sodium hexameta-phosphate. About 5 mg of the salt is required per mg of metal to be stabilized, and it must be added before oxidation of the metal can take place.

## LEAD

Lead has long been known as a toxic element without redeeming beneficial features. Here the present situation regarding total lead exposure and the portion of that which can be attributed to water is discussed.

Man's exposure to lead comes from three main sources — food, air and water, and of these, food accounts for the largest portion. In the past, lead in food came mostly from utensils used in cooking and storing food and certain beverages. It is suggested that the decline and fall of ancient civilizations could be attributed to the effects of chronic lead poisoning on the governing classes which could afford to use pewter dishes. Now most of the lead in food comes from insecticide residues. This source is being reduced as much as possible because of the known toxicity of lead.

The occurrence of significant amounts of lead in air began in the 1920's with the introduction of tetraethyl lead into gasoline. This use has grown to such an extent that by 1970, the alkyl-lead industry (which uses 20,000 tons of lead per year in Canada) was the second largest user of lead, being exceeded only by lead storage battery manufacturing.

About 70% of the lead added to gasoline is emitted in the exhaust gases, and of this, about one-half is in the form of an aerosol. Ethylene dichloride and dibromide are added to gasoline to act as scavengers for lead to facilitate the removal of lead from the engine as lead bromochloride. This aerosol fraction has been circulated around the world and is apparent in the elevated lead levels in the polar ice caps. The total amount of lead emitted into the urban atmosphere is very large. In Los Angeles, which uses 7 million gallons of gasoline per day, the lead emission is 30,000 lb per day. The lead concentration in the air of

large cities ranges up to  $4 \mu\text{g}/\text{m}^3$ , and some cities have set limits for lead in air at  $5 \mu\text{g}/\text{m}^3$ . The lead inhaled in fume-size particles is absorbed by the body to a much greater extent than that in the coarser particles which are ingested.

Lead, therefore, occurs regularly as a contaminant in rainfall, the average concentration in United States being reported as 34 ppb (Lazrus, Lorange and Lodge, 1970). Shiomi found the annual average of lead in rain in Ontario was 20 ppb. In local situations, the amount of lead found in precipitation corresponds well with the local use of gasoline (Lazrus, Lorange and Lodge, 1970). Most of the lead in precipitation that falls on land does not reach the surface waters, as it is precipitated and adsorbed in the soil. Lead is especially high in snow removed from city streets because of the intimate contact of automobile exhausts and the accumulating snowfall. Disposal of this snow directly into surface waters in rivers or lakes is regarded unfavorably, although it is unlikely that the quantity of lead involved can have an appreciable effect on any large volume of water.

Lead occurs in natural waters in very low concentrations because of the low solubility of the hydroxide and carbonate. Concentrations of lead reported recently in unpolluted and polluted waters in the Great Lakes area are summarized in Table 1. The high maxima reported in the lakes near large cities may reflect the effect of local pollution, but these figures may be inaccurate where they are compared with the lake water at Toronto.

The lead pipe which is used in small sizes for water distribution in house plumbing does not contribute much lead to drinking water. With hard water, new lead pipe quickly acquires an insoluble protective coating which practically stops further corrosion. Soft water has greater

power to attack lead and may dissolve important amounts of the metal after some hours of contact. Plumbo-solvency is increased with decreasing hardness and by high levels of carbon dioxide and nitrates.

The use of lead for water distribution is practically obsolete, as copper pipe in the rigid or soft form has many advantages besides reducing lead exposure.

Lead is one of the most toxic metals found in the environment. It is of concern because of its widespread occurrence in nature coupled with the great increase in exposure owing to the emission of lead aerosols from automobiles.

The average daily intake of lead is 300-330  $\mu\text{g}$  Pb from food and beverages and the normal level of lead in blood ranges from 40-80  $\mu\text{g}/100$  ml. The blood level is higher in persons having a large exposure to lead aerosols (traffic police and people living near busy highways). Children living in slum urban areas are exposed to higher than normal lead intakes because of swallowing street dust and dirt and flakes of old high-lead paint in aged buildings.

#### Standards

Lead has been included in the U.S. Standards since 1925 where it was set at 0.1 ppm. In 1962, the limit was reduced to 0.05 ppm because of the cumulative effect resulting from long continued use of such water, and since it was economically possible to supply water at the lower level.

The WHO European Standards of 1961 allow 0.10 ppm in the supply and 0.30 ppm, after 16-hour contact with lead pipe, is permitted. The second edition of the International Standards limited lead to 0.05 ppm, but this limit was increased in the third edition of 1971 to

Table 1. Concentrations of Lead in Natural and Polluted Waters

Source	Maximum (ppb)	Average (ppb)	Reference
Lake Superior - Duluth intake	(2 samples)	7 & 20	(Kopp and Kroner, 1967)
Lake Michigan - Gary intake		34	
- Milwaukee intake	20		
St. Marys River - Sault Ste. Marie intake	12		
St. Clair River - Port Huron intake	28		
Detroit River - Detroit intake	53		
Lake Erie - CCIW lake cruises	4		
Lake Ontario - CCIW lake cruises	0.83		
Lake Ontario - metro Toronto raw and finished water	1		
Ottawa River - Carillon Dam to St. Lawrence River	190	70	
Cuyahoga River - Cleveland	88	47	(Anon., 1972)
Maumee River - Toledo	90	36	(Kopp and Kroner, 1967)
Sewage, raw - metro Toronto	range	10 - 840	(Kopp and Kroner, 1967)
Effluent - metro Toronto	range	10 - 170	(Anon., 1972)

0.10 ppm because "this level has been accepted in many countries and water has been consumed for many years without apparent ill effects. It is difficult to reach a lower level in countries where lead pipes are used."

The Canadian Standards state that the objective for lead should be below the detectable level; less than 0.05 ppm is acceptable and the maximum should be 0.05 ppm.

## MERCURY

Mercury, as an environmental pollutant, has been covered extensively in literature.

The publication of the 1962 U.S. Standards preceded the sudden rise in interest in mercury; no reference was made to it. In 1970, the Bureau of Water Hygiene of the USPHS prepared a statement on "Mercury in Water Supplies" (Anon., 1970) where a tentative standard of 5 ppb in drinking water was proposed. The rationale for such a low figure was given as "the danger to human health from either the acute or chronic ingestion of inorganic and organic mercurials." The same limit is in the Russian Standards (USSR, 1970) and is considered to include a "reasonable safety factor for the protection of human health in consideration of the degree of exposure, routes of entry, metabolic rate and excretion rate."

At laboratories in Chicago, over 1000 samples of Lake Michigan water (including open lake samples and samples from waterworks intakes and canals) all contained less than 0.1 ppb mercury (Vaughn and Reed, 1972). In 1971, a report on 273 water supplies (Turney, 1971) indicated that mercury occurred at less than 1 ppb in 96% of the samples and only one dubious result exceeded 5 ppb. In the raw water, samples from Toronto raw water (Anon., 1971-73) mercury was consistently below 1 ppb. A cursory examination of the CCIW cruise data shows mercury in Lake Ontario always well below 1 ppb.

In the sewage at Detroit's 800-million gallon per day plant, tested daily for several months, no mercury was found (Wolman, 1971). The Michigan Department of Public Health found traces of mercury (a few parts per billion) in the sewage of some smaller cities. The sewage in Toronto was reported to contain less than 1 ppb (Anon., 1972).

## NITRATE

High levels of nitrate in water have for a long time been associated with infant methemoglobinemia, a disease characterized by cyanosis. Since the disease, however, does not always occur when the water supply is high in nitrate, individual idiosyncrasies and hereditary (genetic

deficiency of methemoglobin reductase) and dietary (vitamin C deficiency) factors may be involved (McDermott, Kabler and Wolf, 1971). Infants are affected primarily because of their undeveloped metabolic enzyme systems, the greater reactivity of fetal hemoglobin and the relatively small blood volume relative to their fluid intake (Stokinger, 1969).

Nitrate was not included in any Standards before 1960. In 1961, the WHO European Standards recommended a limit of 50 ppm, and the 1962 USPHS Standards recommended a limit of 45 ppm. These limits are expressed in terms of "nitrate" as  $-\text{NO}_3$ . Later Standards, for example, the Canadian Standards of 1968, express nitrate as ppm N. Ten ppm nitrate expressed as N is the same as 45 ppm expressed as  $-\text{NO}_3$ .

Nitrate in unpolluted surface waters is always low. In the Great Lakes it is always less than 1 ppm. Shallow groundwaters receiving soil drainage are frequently high in nitrate, especially if the soil water contains well-oxidized septic tank effluent or barnyard drainage.

Municipal water supplies are well monitored for the nitrate content and present no hazard to consumers. Thus the elimination of nitrate requirements is proposed in the upcoming revision of the United States Standards; nitrate never occurs at significant levels, only a very small portion of the population is at risk, and it could be protected more effectively in ways other than by the limiting of nitrate concentration in public supplies (Robeck). Other opinions (Martin, 1972) concerning the significance of ingested nitrate differ. For example, in the discussion of the 3rd edition of the WHO International Standards (1971) concern is expressed over the possibility of the *in vivo* formation of carcinogenic nitrosamines. If this is shown to constitute a real hazard, reduction of the permissible level of nitrate in water might be considered, although the daily intake of nitrate by way of foods may exceed the amount by way of water (Martin, 1972).

## NICKEL

Nickel is a metal considered to be of no importance in the matter of water quality for drinking water purposes. In 1969, Stokinger referred to it as an environmental pollutant only to discourage its introduction into the atmosphere as a gasoline additive. The toxicity to man is very low and it occurs in water at very low levels. Nickel, however, is toxic to some plants and is limited in irrigation water to concentration in the 0.5-2.0 ppm range.

Nickel occurs in natural water generally in the low ppb ranges. In the extensive study of trace metals in U.S.

waters by Kopp and Kroner, nickel was found at detectable levels in only 16% of the samples where it ranged from 19-130 ppb. Of the six municipal intake samples from the Great Lakes, in three samples, nickel was not detectable, and in the balance it ranged from 2-28 ppb. In the CCIW cruise data from Lakes Erie and Ontario, nickel ranged from 2-4 ppb (Chau *et al*, 1970) (Chawla and Chau, 1969). In a few samples from the Toronto intakes, it was generally below 10 ppb, but there was one doubtful occurrence of 150 ppb at the Westerly Plant.

In industrially polluted rivers at Cleveland and Toledo, nickel ranged from 10-130 ppb. In the Toronto raw sewage supplies, it occurred at levels from 0.01-0.82 ppm. The sewage effluent ranged from 0.01-0.45 ppm.

### Standards

Most drinking water quality Standards (including USPHS 1962, Canadian 1968 and WHO International Standards) do not mention nickel. Limitations for agricultural use (irrigation) are set varying from 0.5-2.0 ppm. The latest information on Russian Standards (1970) includes a limit of 0.1 ppm for "general sanitary" reasons, a reduction from the 1.0 ppm of the previous Standards, as quoted by McKee and Wolf.

## ZINC

Zinc is an essential and beneficial element in human nutrition. Several body enzyme systems are dependent on zinc, and it appears to be essential in wound-healing processes. Zinc supplements are often used to remedy retardation in the growth of animals caused by a zinc deficiency. A similar zinc deficiency may occur in man. Zinc deficiency occurs in the soils of much of the United States and is considered to be the result of the widespread use of phosphate fertilizers.

The zinc content of the average human body is about 2 g. The daily intake is in the range of 10-15 mg.

Zinc occurs in trace amounts in most natural waters. Levels higher than this indicate a local source of the metal such as mineral deposits or industrial effluents. The occurrence of zinc in waters in the Great Lakes basin is summarized in Table 2.

In the industrially polluted Cuyahoga River at Cleveland, zinc was found to average 340 ppb with a maximum value of 1180 ppb.

Zinc occurs in municipal sewage in concentrations up to several parts per million. In Toronto (Anon., 1972) several analyses at four plants showed zinc in raw sewage at 0.10-2.2 ppm; in the treated effluents it ranged from 0.03-0.37 ppm. In experimental activated sludge plants when zinc was added in the range of 2-20 ppm, removals were from 70-95% (Argo and Culp, 1972).

### Standards

Since zinc has no detrimental health effects at the levels which may be found in water, standards are based on the undesirable aesthetic properties produced by excessive amounts. Turbidity or opalescence is produced by 30 ppm zinc, and a "greasy film" forms on boiling water containing 5 ppm. The astringent taste is noticed in the range of 2-4 ppm.

Standards generally limit zinc to 5 ppm on the aesthetic basis with concentrations less than 1 ppm being desirable.

## ASBESTOS

The detrimental effects of inhaled asbestos dust have been known for a long time, and now more attention than ever is being directed to them. The fibres are widely

Table 2. Occurrence of Zinc in Water

Source	Maximum (ppb)	Average (ppb)	Reference
Lake Superior - Duluth intake	17	9	(Kopp and Kroner, 1967)
- Sault Ste. Marie intake	406	41	(Kopp and Kroner, 1967)
Lake Michigan - Milwaukee intake	23	13	(Kopp and Kroner, 1967)
- Gary intake	55	25	(Kopp and Kroner, 1967)
St. Clair River - Port Huron intake	20	12	(Kopp and Kroner, 1967)
Detroit River - Detroit intake	69	24	(Kopp and Kroner, 1967)
Lake Erie - CCIW cruises	range	7 - 10	(Chawla and Chau, 1969)
Lake Ontario - CCIW cruises	range	5 - 12	(Chau <i>et al</i> , 1970)
- Toronto intakes	16	10	(Anon., 1971-73)
Ottawa River - Carillon Dam to St. Lawrence River	70	0	(Anon., 1972)

dispersed in the environment and are presently attracting attention as a water pollutant. Stokinger (1969) in a brief review of this matter indicates that polynuclear aromatic hydrocarbons and certain trace metals (Ni, Cr and Fe) are involved in the carcinogenicity of asbestos.

Asbestos fibres are identified by electron microscopy. They are presently found in beverages (beer, wine and soft drinks) and in raw and filtered waters at levels of hundreds and thousands of fibres per millilitre (Cunningham and Pontefract, 1971).

Little is known of the distribution of asbestos in water, the effects of water treatment, or the potential effects of the fibres. In the non-industrial environment, exposure results from the use of asbestos in brake linings, in fire-resistant paper, in cloth and board, and in cigar and cigarette paper. Stokinger considers that waterborne asbestos would provide a more continuous source of exposure.

## ORGANIC MATTER

The amount of soluble organic matter occurring in drinking water is one of the major concerns in setting water quality standards; it was the subject of the Fifteenth Water Quality Conference. Although soluble organic matter occurs in natural waters in appreciable concentrations, it is of relatively little significance from any point of view except the aesthetic, as it may affect the attractiveness of water because of the associated color or taste and odor. Natural organic matter affects the coagulation of water and introduces other treatment difficulties through the effects of chelation of iron.

Sewage treatment plants handling purely domestic wastes add substantial quantities of relatively stable organic matter to surface waters; wastes from the rapidly growing organic chemical manufacturing industries add a wide range of compounds never before encountered in the environment.

This complex mixture of trace organics of unknown composition and properties constitutes one of the most urgent and important problems in the fields of water pollution and purification. As one highly placed administrator in this field has said, the most significant aspect of the problem of organic matter in water "is how very little is really known about the sources, composition, identity of components and their effects in short and long-term exposure." Duce *et al* (1963) add in the same connection "nor is it known whether this ignorance is of any significance."

The larger portion of the organics occurring in water may be classified as metabolic products of algae, bacteria and other aquatic organisms and residues from the decomposition of dead organic matter in water and in soil. The naturally occurring organics are in this group, and man has probably adapted to this type of material through evolution. It is very unlikely that any deleterious effects of the ingestion of this type of matter in water could be demonstrated. Thus total organic matter is not a very significant parameter of water quality.

The effluents from biological sewage treatment plants concerned only with human wastes are essentially of similar nature. The large percentage reduction in BOD which a well-operated treatment plant should accomplish shows that the easily degradable substances in human wastes are removed, leaving a residue of stable organic bodies — the products of bacterial metabolism akin to those existing in nature. If rapid physical-chemical methods of sewage treatment should supersede the present biological methods, the "quality" of the organic matter in the effluent might be considerably different. Although the total reduction of organic matter might be equivalent to, or even better than that of biological processes, undegraded organic substances of distinctively human waste origin may pass through the process. There is evidence to suggest that man is not as well adapted to cope with direct recycling of his own metabolic waste products as he is to handling microbial byproducts.

The high molecular weight organics present in natural waters and those added from treated domestic sewage are indistinguishable. Most of the research on organic matter in water is concentrated on the low molecular weight fraction which amounts to only about 10% of the total. The remaining 90% is probably relatively harmless to man, and therefore not considered to be an important criterion of water quality. The presence of these materials in treated water becomes of some importance, however, in view of the increasing interest in the effects of the re-use of used water (many municipal raw water supplies, especially those on frequently used rivers, contain substantial percentages of used water). Preliminary, but indecisive, experiments give evidence of both good and bad effects attributable to these resistant residual substances in treated sewage (Ottoboni and Greenberg, 1970).

Within the last century chemical industries have contributed to surface waters an ever-increasing volume of "foreign" organic substances whose effects, realized and anticipated, far outweigh in importance those of the natural organic matter. Before 1930, natural aliphatics and the aromatics derived from coal dominated the industrial organic waste field. After 1930, petroleum became the main

base for organic chemical manufacturing and rapidly took over the field. In 1930, 2% of the organic chemical production was based on petroleum; in 1950, this had increased to 40% and by 1970 it was 88%. It is estimated that by 1985, 98% of organic production will be based on raw material of petroleum origin. As these percentages have increased, the total tonnages have also increased enormously.

At the same time the variety of organic chemicals and the volumes produced have multiplied exponentially. In the period since 1965, Chemical Abstracts has listed two million unique chemical substances. Currently about 60 million tons of organic chemicals are produced annually in the world, and by 1985, it is estimated that this production will have increased to 250 million tons. Of this production about one-half ultimately escapes into the environment in one form or another. Very few chemicals are "captive."

The disturbing aspect of the release of this much "foreign" material into the environment is that so little is known of the ultimate fate in nature of many of the substances involved and their properties in the environment in relation to organisms and even to man. Although many chemical products, such as certain plastics, are so resistant to degradation that they might be considered to be inert, others (even excluding those that were produced primarily for their toxicological properties) have toxicities toward man and lower organisms that are rated in the nanogram per gram basis.

As illustrations of the widespread nature of the occurrence of these synthetic organic chemicals in the environment, and particularly in water, the following items are cited. In the Rhine River, on which there are 50 water treatment plants serving 20 million people, the threshold odor number of the water has increased from 15 to 50, and at one sampling site, the total organic carbon is 65 ppm (multiply by 3 for an approximation of total organic matter). In the river water at Evansville, Indiana, unusually heavily polluted by industry, 40 compounds were found (as GC peaks) and 13 were identified. The Russians have published a list of 297 compounds which might be found in water, with maximum allowable concentrations which range from 2.5 ppm for cyanuric acid down to the parts per trillion level for ethyl-lead. In a report prepared by the A.D. Little Company for the EPA, 496 organics were reported occurring in drinking water. Of these, 66 were identified and some of these showed carcinogenic, teratogenic or mutagenic effects. Burnham *et al* (1973) identified nine industrial organic compounds in the water of the Delaware River at Philadelphia.

The study of organic matter in water is difficult because of the problems associated with the characteriza-

tion of such a complex mixture, the separation and identification of individual components and their measurement at such low concentrations. Measurements of the total organic content, as a whole or in the form of coarse fractions, are of limited significance. For example, a water may carry a total organic load of several parts per million, composed almost entirely of innocuous materials and the significant substance may be toxic at the ppb level.

This does not mean that the total organic content is insignificant and should be disregarded. Parameters that measure total organics can be determined with fairly simple equipment and at moderate costs and are valuable aids, especially in following changing pollution levels. Unfortunately continuous long-term measurements of organic matter by these simple techniques either in mass or in fractions are infrequently done; they are rarely a part of routine water treatment plant programs.

Currently these measurements of total organics may be done by several methods which include BOD, COD and TOC. The COD determination approximates the total organic matter, allowing for the fact that a few substances may escape oxidation because of their volatility or resistance to the relatively mild oxidation conditions. The BOD determination indicates the substances which are biologically degradable, and the TOC determination measures the total organic matter in terms of carbon. The first two determinations have the disadvantage that in most waters they must be used at the very lowest limit of their useful ranges. The TOC determination is of value in producing significant data at lower levels of concentration. A useful variation in TOC measurements is the separation into dissolved (DOC) and suspended (SOC) fractions. With some instrumental designs the determination of TOC on samples containing particulates is unsatisfactory.

The use of ultraviolet absorbance in monitoring organic matter in water has some interesting possibilities (Ogura and Hanya, 1967). As a contributor to the absorbance the relatively innocuous fraction of the total organic matter, because of its concentration, overshadows the effect of the more significant fractions. The technique, however, has useful capabilities in monitoring the efficiency of collection and separation of these more important fractions.

Concentration of organic matter before analyses offers (theoretically at least) several advantages in providing sufficient material to work with in analyses and for fractionation. Ideally, it is desirable to have a concentration method that permits the recovery of the organic matter in its original molecular form, with the same relative concentration of components and with a nearly quantitative recovery. It is not probable that a method could be devised

to meet all these requirements. Thus it is desirable to continue the investigation of available methods, understand their limitations and choose those which provide satisfactory recovery of particular components of interest. The alternative is to encourage the development of new methods of determining specific substances which have significant effects at very low levels. New methods already have been created for some substances, for example, the chemical determination of phenols and the chromatographic identification of pesticides.

Concentration methods currently in use include the following: adsorption on activated carbon with subsequent extraction by solvents, adsorption on macroporous resins, direct liquid-liquid extraction, reverse osmosis, fractional freezing and low temperature evaporation of water.

Adsorption of organics on activated carbon is a technique for which a considerable volume of historical data, dating back to 1952, is available. This method is likely to continue in use for some time in spite of the well-known limitations: some substances are not adsorbed; some are not removed by solvent extraction; the percentage recovery of total organics is poor; and the possibility of interaction among components while adsorbed on the carbon and during extraction may be significant. Some of the practical difficulties in its routine use which prevented its widespread application in waterworks have been overcome in the most recent modifications of the equipment (Carswell, Buelow and Symons, 1973) (Buelow, Carswell and Symons, 1973). These modifications include reduction of the long sampling period formerly required, the use of a small and more easily processed volume of activated carbon, and shorter exposure period to minimize the effects of biological growths in the carbon bed.

In any waterworks laboratory, the newly designed equipment is practical from the point of view of laboratory skills and time required; the collection of data on a more frequent schedule and from many more sources is made possible. The data, produced in the form of carbon-chloroform extract and carbon-alcohol extracts, are relevant especially with respect to pollutants of industrial origin. The amount of extracts produced is sufficient to permit some degree of characterization. The recovery of organic matter has been improved (about 6-fold for CCE, 20-fold for CAE) by increasing the contact time of the water on the carbon.

One of the most criticized deficiencies of the activated carbon method — the low efficiency of adsorption and desorption of organic matter, may be overcome, or at least explained. In 1972, Dr. Croll of the British Water Research Association reported that part of the material which resists desorption may be the humic acid fraction which is neither

adsorbed nor desorbed readily. The introduction of a highly basic macroporous resin column before the activated carbon column, removed a substantial amount of humic acid which was recoverable almost quantitatively and amounted to 40% of the total organic carbon. The activated carbon removed a further 30% of the organic carbon, and of this, three-quarters was recoverable.

Carbon adsorption is probably the least satisfactory method of concentrating organics if high percentage recoveries of unchanged material are the criteria. The relative simplicity of the method and the long history of its use, however, will keep it in active use for some time, especially since the upcoming revision of the U.S. Water Quality Standards will retain its use.

Liquid-liquid extraction of organics is preferred over carbon adsorption in Europe (WHO, 1961). To handle large volumes of water, expensive and complicated equipment is required; complete recoveries using one solvent system cannot be expected. The extent and selectivity in extraction can be controlled extensively by the choice of solvents and by adjusting the pH and inorganic salt concentration in the sample. Data, however, applicable to the recovery of the wide range of organics in water are not yet available. Loss of volatiles in the extraction and evaporation steps is probable, and the absence of artifacts is not assured.

Freeze concentration minimizes the possibility of biological, chemical and physical changes during analyses and almost assures the recovery of volatile materials without loss. An important drawback is the low concentration factor that can be achieved for many natural water systems containing inorganic ions.

#### Characterization of Organic Concentrates

The concentrated organics obtained by any of the methods described must be fractionated. The standard practice in the carbon adsorption technique is the serial extraction of the carbon by chloroform and alcohol, producing the carbon-chloroform extract (CCE) and the carbon-alcohol extract (CAE). The distinction between the two extracts is based largely on the polarity of the constituent compounds. Fractionating to this extent only is considered to have significance in the evaluation of water quality, although the severe limitations imposed by the technique must be respected. The prolonged exposure to high temperature during the extraction is likely to change the chemical identity of the materials involved, and therefore the toxicity of the extracts cannot definitely be related to the toxicity of the original materials in the water sampled. The CCE, however, is expected to include non-polar chemicals particularly of industrial origin, including pesticides, and some of the industrial chemicals known to



be present are found in the extract. The CAE fraction is considerably larger in quantity than the CCE. Natural organic materials that are usually polar are included in the CAE fraction, as are polar substances of industrial origin. Synthetic detergents appear in this fraction.

In general the CCE as a whole has a much higher toxicity than does the CAE, but some occurrences of highly toxic CAE were noted by Tardiff and Deinzer (1973). In another work, the separated CCE and CAE were of low toxicity even in levels considerably above those which occurred in water, but they were of high toxicity when recombined (Smith and Grigoropoulos, 1968).

Obviously CCE and CAE from different sources vary in composition and toxicity. The chloroform extract obtained from liquid-liquid extraction would not necessarily have the same composition as the CCE from the same source.

Concentrated extracts from any of these methods can be fractionated further. The scheme used in initial carbon adsorption work involves a separation into acid, basic and neutral fractions. Further separations by column chromatography, GC and TLC, show the number of individual substances present, and by using such advanced methods as GC-MS, some of these can be identified.

Identification of specific compounds in the organic materials mixture is considered to be of basic importance if the significance of organic matter is to be evaluated on a rational basis. In the meantime, toxicity tests on isolated (although perhaps as yet unidentified) compounds indicate areas of prime interest. For example, Tardiff and Deinzer reported isolating about 60 unique compounds (excluding pesticides) from drinking water; of these, one-half had very low toxicity. The toxicity of the other compounds ranged from moderate to very toxic, and two were rated as extremely toxic.

## ODOR IN WATER

### Problems Relating to Aesthetic Qualities

The presence of objectionable taste and odor is the most obvious failing in the endeavor to supply water of good aesthetic quality. Ideally, water should be free of all odor. Presently a slight chlorinous odor, however, is acceptable and is taken as evidence that the water has been adequately treated. Offensive foreign odors, whether from natural or industrial sources, are the cause of much consumer complaint and are rated as the "number one" aesthetic problem facing the industry. The water supplied

may be of the highest quality in every other respect and meet the strictest standards, but if the odor is offensive, the waterworks undertaking has failed conspicuously.

Evaluation of odor quality and its quantitative expression are difficult problems. Odor perception is a subjective reaction and wide variations occur among individuals in estimating both the intensity and the odor character. Odor evaluation is done by the use of panels which may consist of a large number of inexperienced observers supposedly representing the consumers, or of a few skilled persons, usually water treatment personnel who may have a built-in bias. Panels are affected by a number of factors which limit the reliability and reproducibility of results. These factors include varying personal sensitivity, fatigue of the olfactory senses, varying background-odor exposure, and the interaction of sample constituents. The efficiency of odor-testing panels can be improved by finer selection of members and possibly by conditioning to increase sensitivity to specific types of odors.

In routine water plant operation, odor testing usually devolves to one or two individuals or it is neglected entirely. Then reliance is directed toward consumer complaints. At the Fifteenth Water Quality Conference this neglect of odor monitoring was deplored, and it was recommended that a conscientiously performed odor-testing procedure should be used. In spite of its shortcomings, it is at present the only practical method for a treatment plant operator to detect abnormal occurrences of at least some trace organics in the water supply.

Odors in finished water are derived from two general sources: industrial wastes which cause medicinal, phenolic and chemical odors, and natural processes where the byproducts of the growth and death of algae and other aquatic organisms cause odors ranging from earthy and musty to the putrid odors of anaerobic decomposition.

Odors from substances in industrial wastes are associated with elevated values for CCE. Generally, if the CCE is less than 50 ppb, there is no odor problem. If it is greater than 200 ppb, the odor causes complaints which are continuous and universal and the water quality is judged as being quite unacceptable for community use. Between these two levels, there is a rough correlation between the odor intensity problem and the CCE (Ettinger, 1960).

Odors from natural sources are produced from substances which are the metabolic products of algae or other organisms such as the Actinomycetes or from the decomposition of dead organisms. Some algae, while living, have strong characteristic odors. These produce the most severe problems where blooms of the organism occur in

impounded waters. The Great Lakes, however, are not immune because of their great size. At Chicago, Dinobryon occurs periodically every year and has reached concentrations as high as 8000/ml to 12,000/ml (Vaughn, 1972). Its very strong odor is described as being fishy or resembling cod liver oil.

Odors described as earthy, musty and moldy are now attributed to Actinomycetes. Much work has been done on the odorous materials produced by these organisms, and from their pure cultures two specific and highly odorous metabolites (geosmin and mucidone) have been isolated (Silvey *et al*, 1950) (Romano and Safferman, 1963). As yet, these compounds have only been isolated from cultures and have not been recovered from natural waters. The separation and identification of these specific compounds are an important advancement in odor research and should permit more rational development of effective treatment processes.

The problem of musty, moldy odors in Chicago water has increased in the last few years (McMillan, Karshen and Willey, 1972); it is suspected that new sources of pollution entering Lake Michigan north of Chicago are responsible. The Actinomycetes organisms were enumerated by plate counts and found to be highest in summer. The numbers were highest near-shore and diminished only by about one-third at a distance of 10 miles offshore.

Water treatment processes, especially chlorination, may accentuate odors caused by the presence of organics in

water. The effects of chlorinating trace amounts of phenols with the production of the highly odorous chlorophenols are well known. The use of ammonia before chlorination, to produce chloramines rather than free chlorine, was practiced at length since chloramines do not react with phenol. Later, super-chlorination was preferred. High dosages of chlorine destroyed the phenol by breaking the benzene ring and avoided the serious disadvantage of the reduced bactericidal power of chloramines. Super-chlorination is now referred to as break-point chlorination, since the essential feature is the destruction of ammonia occurring in the raw water before a powerfully reactive residual of free chlorine can be produced.

Activated carbon, used for removing other odors, also adsorbs phenols. As chlorophenols are poorly adsorbed, it is essential if phenols are to be removed to contact them with the carbon before chlorine is introduced. The reaction of chlorine with phenol is not instantaneous. If only a short time for the contact of chlorine with the water containing phenol is provided in the treatment plant, the plant effluent may be free of the chlorophenol odor which will develop late in the distribution system.

Problems with phenols in water seem to have diminished in the last decade. This may be due partly to the better water treatments now generally used (break-point chlorination and activated carbon), but there also appears to be a reduction in phenol levels now found, which may be the result of improved methods of waste treatment.

## Research Needs

In this Chapter, research needs are discussed from the point of view of the more "practical" fields of wastewater disposal, water purification, and the general management of the environment related to these large-scale undertakings. Research of a more theoretical or academic nature in chemistry, physics and biology is undoubtedly the basic need, but the author does not feel particularly qualified to discuss this and so restricts this discussion to those matters having immediate and practical application.

In the field of sanitary engineering, the classic communicable disease problem is largely solved, but the study of the chronic effects of long-term exposure to micro-pollutants is just beginning. Detection of the subtle changes in human physiology indicating the approach to critical levels of inorganic and organic trace pollutants is an essential area for research.

### SCIENTIFIC DATA ON EFFECTS OF SPECIFIC COMPOUNDS

When the need to set definitive standards for pollutants arises, it is essential to have a firm base founded on concrete scientific data relating to identification, total environmental exposure, dosages and toxicological effects. Thus criteria based upon "probable" or "suspected" effects are avoided.

The need often arises, however, to set guidelines which may be based on different philosophies. For example, it is perhaps more desirable in the absence of documented scientific data to keep suspected foreign materials at as low a concentration in water as possible until evidence can be produced to demonstrate their harmlessness. To do this rationally, it is necessary to know the natural levels at which a particular substance occurs and something of its behavior in water, its half-life and its ultimate fate. Presumably man is adapted to the levels at which naturally occurring substances exist. If man's activities cause an increase above the natural level, it is important to know at what level they will become significant.

For several toxic trace metals, this has already been done to some extent, and for mercury, lead and cad-

mium, it is well done. For other toxic trace metals, the evidence supporting existing criteria is tenuous. In the cases of arsenic and chromium for example, the low mandatory limits exist in the face of evidence that long exposures to higher levels produced no observable effects.

### ORGANIC MATTER IN WATER

For organic substances in water, a scientific basis for quantitative criteria is barely touched, except possibly for the group of biocides which have been introduced into the environment specifically for their toxic properties.

Robeck suggests that the problems relating to organics in water presently rate higher in priority than do microbiological problems. More information is urgently needed on the methods of analysis (collection, concentration, separation, identification and quantitation) and on the sources and the evaluation of their effects.

The need for good methods of concentrating organics from the low levels at which they occur is required especially. The disadvantages of activated carbon as a concentrator is well publicized, which emphasizes the necessity of improvements. A solution might be the use of different adsorbing materials designed to incorporate selectivity toward specific groups of organics and the use of several selective adsorbants in a series of columns to provide initial fractionations.

Separations and identification of organics by means of gas chromatography followed by mass spectroscopy are the most advanced and the most promising method, but it is extremely expensive and limited in work load. Simpler methods are required which would produce the separation of significant substances, or at least, significant fractions and which would be usable in less well-equipped laboratories, even down to the level of those which could be provided in well-equipped water treatment plants. A major need is the development of a good practical indicator of organics that could be related to waterworks plant operation problems.

The interpretation of the significance of the effects of organics in water is important. It is known that some fractions separated from CCE exhibit marked toxicity when

the incompletely resolved mixtures are tested at high concentrations. Knowledge of the following is necessary: what specific substances are responsible for these effects; if the substance actually existed in the water sampled or was produced by reactions in the collecting, concentrating and isolation procedures; and what physiological effects are produced at realistic dosage levels.

## ODORS

The problem of taste and odor in water is one of the most difficult to handle because of the subjective nature of the response. Some means of judging odor on a chemical or instrumental, analytical basis is highly desirable. The characterization of odors to identify their sources (odors from living organisms, odors of decomposition and odors from industrial chemicals) would aid in providing effective treatment.

## INDUSTRIAL CLUES

The study of significant industrial organics in water might be pursued very profitably by attacking it from the opposite point of view — by compiling an inventory of all organic compounds which could conceivably occur in the water from their industrial uses. For those having potentially dangerous properties, further data on toxicity, persistence, and ultimate fate in the environment should be acquired. Of the hundreds of organics used in substantial quantities in industry, many would not be removed from wastewater by normal treatment processes, and might have combinations of properties making them undesirable in the environment. Examples of substances which might be important in this approach are the five known and five suspected carcinogens which are manufactured, used or handled by chemical companies and which are presently a matter of concern because of employee exposures (Anon., 1973).

All chemicals that are highly toxic and that are extensively used in industry and commerce should be included in this approach. In this connection, the Russians have compiled a list of nearly 300 industrial chemicals whose concentrations in water are limited for toxicological or organoleptic reasons (USSR, 1970).

## SEWAGE EFFLUENTS

The effluents from municipal sewage treatment plants, even after good secondary treatment, contain large amounts of relatively stable organic substances whose chemical, physical and biological properties are scarcely

known. Presently these substances cannot be distinguished from similar naturally occurring substances, but their presence in drinking water is the cause of great concern (Ottoboni and Greenberg, 1970), perhaps based more on suspicion than on knowledge. Many public water supplies unavoidably contain appreciable percentages of "used" water containing these substances and in the future, further substantial increases are likely to occur. Operators of sewage treatment plants who pride themselves on producing an effluent "of drinking water quality" are naive in suggesting that compliance with a few parameters of drinking water quality is sufficient.

The chlorination of secondary effluents is a common practice in North America, which is intended to destroy the remaining pathogens before the effluent is discharged to the receiving water. At the dosages employed (5-10 ppm), the "indicator" coliform organisms are eliminated and thereby many of the visible effects of the effluent on the receiving water are removed. Although this is a very general practice in North America, in England it is not favored (Taylor, 1966).

Sewage effluents contain ammonia at levels of 5-20 ppm, much in excess of those required to react with the chlorine added, and consequently, the residual produced is predominantly monochloramine. This has much less bactericidal activity than free chlorine (about 1/50 as much) and is almost without effect on viruses, cysts and worms. Owing to the high dosages which would be required, it is impractical to chlorinate effluents to yield free chlorine residuals.

Chloramines have recently been shown to be toxic to fish at extremely low levels (Mills), and chlorination of some compounds in industrial wastes produces toxic substances from non-toxic materials, e.g., cyanogen chloride from thiocyanate.

The amount of organics, including nitrogenous materials which react with chlorine, is quite considerable, as shown by the chlorine demand. Little knowledge, however, is available concerning the reaction products, especially those from higher molecular weight materials. The effect of chlorination on a few relatively simple organics of industrial origin in sewage effluents has been studied recently. Of the 14 chemicals studied, five reacted with chlorine under conditions that would be encountered in conventional effluent chlorination practice and produced a highly complex mixture of products, some of which were persistent and potentially could have deleterious effects in the environment (USEPA, 1972). In another report, a toxic substance was said to have been produced on chlorinating a waste containing methionine from flour milling waste (Long and Bell, 1972).

At Chicago, a strong musty taste was produced in the finished tap water from the reaction of chlorine with an unidentified, but odorless, organic material present in the wastes from a pharmaceutical plant (Vaughn, 1972). Presumably this odorous material would have been introduced into the lake water, as the parent substance had been in a sewage effluent receiving chlorination.

Other methods of disinfecting sewage effluents warrant study. Although the physical methods, including ultraviolet and nuclear radiation, need study, new methods which would most likely be practical would involve the use of different chemicals.

The use of bromine chloride (BrCl, a low-boiling liquid) to disinfect sewage is proposed by Zellech (1972). The advantages claimed include the superior bactericidal and viricidal properties of bromamines which are produced by reaction with ammonia. They are more reactive chemically than chloramines and therefore less persistent in the environment and less hazardous to higher aquatic life. It is claimed (Mills, 1973) that the resulting discharge of large amounts of bromine (as bromide) to the environment constitutes no hazard, although this has not been investigated thoroughly. A treatment plant discharging 100 million gallons per day of effluent treated with 5 ppm BrCl would discharge about 4000 lb of bromide ion per day at a concentration of nearly 4 ppm. Lake Ontario water contains about 0.05 ppm bromide.

## TOXICITY

The toxic effects of substances ingested at low dosages over very long periods of time can be determined only with great difficulty and probably only to a very limited extent if direct methods are employed. The most promising approach seems to be not to look for effects on an organism or even on an organ as these effects may never be identifiable, but to examine the effects on a cell or a cell reaction level. Interferences with the basic physiological reactions such as those associated with enzyme systems can be demonstrated. Mutagenicity might be detected by using cell cultures and concentrating on encouraging the growth of mutants rather than of unaffected cells.

## EPIDEMIOLOGY

In the past, epidemiology was an effective tool in identifying and demonstrating the effects of acute microbial contagious diseases having waterborne transmission, and in a different field, in studying the beneficial

effects of fluoride in water. It should continue to be an essential component in the overall study of the effects of presumably toxic materials at the concentrations found in water. Actually there can be little justification for restrictive standards or little confidence in the safety of liberal standards, unless epidemiological studies provide a definitive answer.

Environmental epidemiology is a tool that is exceedingly difficult to apply, and this is probably the reason why it was said, as late as 1971 by McDermott, Kabler and Wolf that the National Institutes of Health in the United States "frowned upon epidemiological studies in relation to water supply." In 1972 in England, Martin, however, said that "the new Division of the Department of Health would have a strong epidemiology section and had already under consideration, the epidemiology of lead, cadmium, mercury and nitrate pollution. Other trace elements and other substances would follow."

There are two major difficulties. It is very difficult to isolate the effects of one variable among the many variables acting on a population, especially when the suspected variable may have a relatively small effect. One possible approach might be to concentrate on the effects produced on a hypersensitive portion of the population, thus avoiding the diluting effect of including the larger resistant group. The second problem is to find an adequate control population not exposed to the critical factor. For example, among other substances of similar interest, mercury and cadmium are so ubiquitous that it is almost impossible to find a control population that is not exposed to low levels of these metals.

Infectious hepatitis is the only disease of viral origin for which transmission by drinking water is accepted by all, and then only rarely in the association with treated public water supplies. Many outbreaks of "gastroenteritis," however, occur and a relationship to well-treated water is possible. The epidemiological investigation of these would be difficult because of the low level of symptoms produced (sub-clinical), the consequent difficulty in acquiring data and the wide variety of potentially causative agents which might be suspected.

An example of the difficulties involved in epidemiological studies is found in the current investigations of the association observed between cardiovascular diseases and the hardness of water supplies. As early as 1960, an inverse relationship with a high degree of correlation was shown to exist between the water hardness in certain areas and coronary heart disease. Despite the large amount of work that has gone into this study, the particular constituent (present in hard water or absent in soft water) responsible for the relationship has not been identified.

Canada appears to be a promising area for epidemiological studies, since there are still large areas of the country where the population living under a wide variety of natural conditions is relatively free from stresses resulting from industrial pollution.

### **ADEQUACY OF CURRENT TREATMENT METHODS**

In the fields of water and sewage treatment, the effectiveness of current and advanced treatment methods is difficult to evaluate. This is well illustrated in the matter of viruses in water, where the best current practice is to employ a chlorination practice that removes as much bacteria as possible. Hopefully an adequate inactivation of the viruses will result also, although it is well known that the susceptibility of viruses to chlorination varies greatly.

Similarly, information on the removal of specific organics (with a few exceptions) is also vague, and dependence is placed on such gross parameters as TOC, COD or even BOD. Techniques which would facilitate the measurement of single compounds or significant fractions would be most valuable in monitoring the effectiveness of removal processes.

### **WASTEWATER TREATMENT TO REMOVE SPECIFIC PARAMETERS**

There is a need for improved methods of wastewater treatment directed toward the removal of specific substances or groups of substances. Treatment plants are generally operated to remove BOD; their effectiveness is gauged according to the performance of this function. Except where receiving waters have limited capacity to handle oxygen demands (and this would not apply to Great Lakes waters), the amount of organic matter represented by the BOD is very small when compared with the total expressed as COD; since it represents biodegradable matter, the significance is probably slight.

The development and use of supplementary treatments to remove additional amounts of organic matter warrant attention. For example, the application of powdered activated carbon to a secondary effluent followed by filtration can remove substantial amounts of dissolved organic matter and, at the same time, remove some of the trace metals chelated with the organic matter. The presence of added chelators, such as NTA and EDTA, and the natural chelating power of the residual sewage organics might not be as serious in transporting toxic metals if they could be removed in this way on carbon. Another interes-

ting possibility exists here since surplus activated sludge, which normally is wasted and requires additional disposal processes, might be pyrolyzed on site to produce carbon with an activity suitable for this application.

Supplementary treatment to remove toxic metals from sewage effluents needs investigation. In cities which are typically commercial centres, the concentrations of these metals in the effluents are always low (Anon., 1972), but in industrial cities substantial levels occur. In recent work, Netzer and Norman indicate that activated carbon has capabilities to adsorb these metals directly, that is, independent of organic matter, and thus would be applicable in treating wastes at their source.

In the management of a water resource to be used for public water supply a choice may sometimes be possible between the preservation of the source water in the best possible condition and the use of additional treatment in the water purification plant. If public water supply as the only beneficial use is to be considered, the choice could be determined easily on economic and technical bases. But this is not usually the case, and when interference with other legitimate uses is involved, the choice becomes a more arbitrary matter. Wolman (1971) has summed this up very well:

"The real difficulty in quick and easy solutions to problems generated in the environment rests forever in the fact that the issues are rarely, if ever, black or white. Their diagnosis and the ultimate solution to the degradation they may or may not create lies in a joint assessment of tangible and intangible benefits and costs. Such assessments are complex, time consuming, irritating and inevitably unsatisfactory to some."

Such a choice exists in making the decision whether certain constituents should be removed to a high degree in waste treatment plants or whether they should be permitted to enter the receiving water and reliance be placed on high efficiency treatment there. Minor improvements in raw water quality are not reflected in lower water treatment costs, and conversely, deterioration in raw water quality within certain ranges may not have a noticeable effect on costs associated with treatments that are required in any case.

To produce finished water of high quality from the aesthetic point of view, some supplementary treatments may soon be required very generally. An example of this is the use of activated carbon to remove naturally occurring odorous substances produced by Actinomycetes. The same treatment with possibly slightly increased dosages could be used to remove substantial quantities of the residual

organics in the raw water derived from sewage effluents. This could be a satisfactory and much more economical solution than that which would be required in a wastewater treatment plant, since it would be taking advantage of a large dilution factor and the natural purification processes in the receiving waters.

It has been suggested already by some that the

routine use of activated carbon in water treatment plants should be standard practice in view of the present concern attached to the presence of trace organics, particularly the pesticides. This steady use would not add substantially to the cost of water (considering the overall costs of supply, treatment and delivery), but would represent the employment of the best available practice to offset the, as yet undemonstrated, hazards of these materials.

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