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ENVIRONMENTAL STATUS OF THE LAKE MICHIGAN REGION

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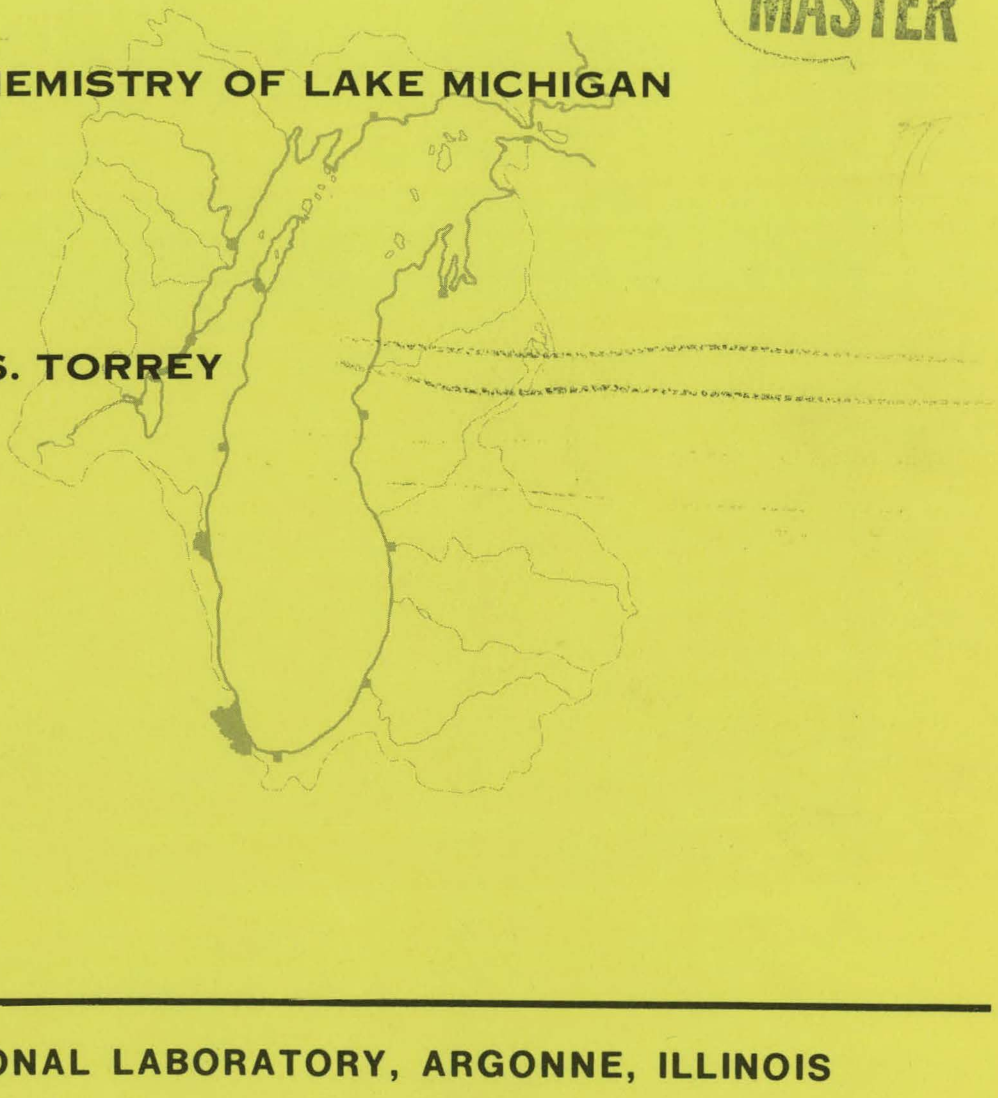

VOLUME 3. CHEMISTRY OF LAKE MICHIGAN

MARGUERITE S. TORREY

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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AND DEVELOPMENT ADMINISTRATION
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ENVIRONMENTAL STATUS OF THE LAKE MICHIGAN REGION

Volume 3. Chemistry of Lake Michigan

by

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May 1976

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PREFACE

Assessments of the environmental impacts of individual nuclear power plants sited on the shores of Lake Michigan have led to increased recognition of the need for regional considerations of the environmental impacts of various human activities, and a compendium of information on the environmental status of the region for use in assessing such impacts. In response to these needs, a report series describing the status of Lake Michigan and its watershed is in preparation. The series is entitled "Environmental Status of the Lake Michigan Region"; this report is part of that series.

The report series provides a reasonably comprehensive descriptive review and analysis of natural features and characteristics, as well as past, present, and proposed natural processes and human activities, that influence the environmental conditions of Lake Michigan, its watershed, and certain adjacent metropolitan areas. This series will constitute a regional reference document useful both to scientific investigators and to other persons involved in environmental protection, resource planning, and management. In these regards, the "Environmental Status of the Lake Michigan Region" will serve in part as an adjunct to reports of broader scope, such as the Great Lakes Basin Commission's Framework Study.

Other Volumes Published to Date in this Series

Vol. 2. *Physical Limnology of Lake Michigan. Part 1. Physical Characteristics of Lake Michigan and Its Responses to Applied Forces.* Clifford H. Mortimer. *Part 2. Diffusion and Dispersion.* Gabriel T. Csanady. 1975. 121 pp. NTIS-$5.45.

Vol. 7. *Earthquake History and Measurement with Application to the Lake Michigan Drainage Basin.* Richard B. Keener. 1974. 19 pp. NTIS-$4.00.

Vol. 9. *Soils of the Lake Michigan Drainage Basin--An Overview.* Forest Stearns, Francis D. Hole, and Jeffrey Klopatek. 1974. 22 pp. NTIS-$4.00.

Vol. 10. *Vegetation of the Lake Michigan Drainage Basin.* Forest Stearns and Nicholas Kobriger. 1975. 113 pp. NTIS-$5.45.

Vol. 15. *Mammals of the Lake Michigan Drainage Basin.* Charles A. Long. 1974. 109 pp. NTIS-$5.45.

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ENVIRONMENTAL STATUS OF THE LAKE MICHIGAN REGION

VOL. 3. CHEMISTRY OF LAKE MICHIGAN

by

Marguerite S. Torrey

Abstract

This report is a synoptic review of data collected over the past twenty years on the chemistry of Lake Michigan. Changes in water quality and sediment chemistry, attributable to cultural and natural influences, are considered in relation to interacting processes and factors controlling the distribution and concentration of chemical substances within the Lake. Temperature, light, and mixing processes are among the important natural influences that affect nutrient cycling, dispersal of pollutants, and fate of materials entering the Lake. Characterization of inshore-offshore and longitudinal differences in chemical concentrations and sediment chemistry for the main body of the Lake is supplemented by discussion of specific areas such as Green Bay and Grand Traverse Bay.

Residues, specific conductance, dissolved oxygen, major and trace nutrients, and contaminants are described in the following context: biological essentiality and/or toxicity, sources to the Lake, concentrations in the water column and sediments, chemical forms, seasonal variations and variation with depth.

A summary of existing water quality standards, statutes, and criteria applicable to Lake Michigan is appended.

INTRODUCTION

Lake Michigan constitutes an invaluable natural resource to the four states that border it and to the entire midwestern United States as well. A large volume of water of generally excellent quality lies within its shores. A number of demands are placed on this resource. For example, Lake Michigan provides an ample water supply for both domestic and industrial uses. Because of its great volume, the Lake is valuable for diluting waste effluents. Its waters are eminently suited for use as coolant in industrial processes. It represents a tremendous reservoir of irrigation water. Swimming and fishing in the Lake, as well as boating on its surface, are popular. Indeed, the

Lake is a great source of pleasure to people having diverse interests, whether for recreational activities or simply as a source of aesthetic enjoyment. And certainly not insignificantly, Lake Michigan serves as a component of an economical transportation system between the Atlantic Ocean and midcontinental North America.

Some of the demands on Lake Michigan conflict sharply with other uses of the Lake. For instance, excessive use of the inshore waters for municipal waste disposal ruins their value completely as a drinking water supply due to high concentrations of bacteria of fecal origin. Inadequately treated municipal wastes contain large quantities of nutrients that can stimulate the growth of undesirable aquatic organisms. These unwanted organisms may interfere with use of the inshore waters of the Lake as a water supply (taste- and odor-causing compounds synthesized by algae), for fishing (alteration in plant communities leading to enhancement of "trash" fish populations), and for aesthetic enjoyment (algal scums, windrows of dead plants along the shore).

A growing human population and expanding industrialization in the Basin are creating increasing demands on the Lake. To accommodate all these demands, present and future water users must strike a balance that optimizes as many uses as possible and at the same time minimizes or eliminates changes in water quality. Such a balance requires careful management, or even regulation, if certain uses are not to be totally excluded. But before such plans can be intelligently formulated, it is essential to consider the complex interrelationships among water chemistry, physical setting of Lake Michigan, physical processes within the Lake, organisms living in the Lake, and human impingement on the Lake.

Local geological variations create some of the differences in concentrations of chemicals carried to Lake Michigan by tributary streams; rivers draining the Canadian Shield area of Michigan's Upper Peninsula contribute lower levels of total dissolved solids than those lying in the glacial drift area of the southern portion of the Basin (*e.g.* see Wood, 1970). Winds from the south-to-west quadrant blow air pollutants from the Milwaukee-Chicago-Gary megalopolis out over the Lake, but winds from other directions may confine these wastes to shore or even drive them back over land. The north-to-south gradient in solar energy input affects the extent of photochemical reactions in the water. Distinctly different environments along the shoreline of Lake Michigan (rocky beaches, sandy shores, river mouths, municipalities, embayments) affect the rates of input and modes of dispersion of chemicals added to the Lake.

Physical processes within the Lake affect the fate of added pollutants. Wind-driven currents maintain distinct inshore-offshore water masses and tend to confine land-derived contaminants to the nearshore area. Because of the Lake's tremendous volume, centuries are required to remove a large fraction of conservative chemicals by simple dilution. The sun warms the surface waters of Lake Michigan more quickly than bottom waters, contributing to thermal stratification during summer. Stratification restricts physical mixing of warm surface waters with cold bottom waters and thus inhibits intermixing of the chemical constituents in the two water masses. In addition, these temperature differences lead to variations in rates of chemical and biochemical reactions between top and bottom waters.

As algae and other aquatic plants photosynthesize, they convert dissolved CO_2 into biomass and release O_2 to the water. Photosynthetic oxygen production supplies a portion of the O_2 needed for respiration by the biota and helps maintain oxidizing conditions in the water. Aquatic organisms return inorganic and organic chemicals to the water through excretion and upon their death. Microorganisms provide sorption sites for various kinds of chemicals and facilitate their removal to the sediments.

All lakes are naturally dynamic, exhibiting variations over periods as short as a day or nearly as long as a geologic epoch. Human influences, however, can accelerate or modify these natural processes, as witnessed in Lake Michigan. Alterations in concentrations of conservative chemical species noted over the past century (Beeton, 1965, 1969; Beeton and Edmondson, 1972) and recent changes in planktonic assemblages (Schelske and Stoermer, 1971, 1972) have been attributed to increased inputs of nutrients and conservative substances in waste effluents added to the Lake and its tributaries. But since lakes evolve in response to natural as well as culturally induced inputs, these are not the first changes to have occurred in Lake Michigan, nor will they be the last, even if every human being were suddenly and permanently removed from the Basin.

Surely it is desirable to minimize if not eliminate adverse cultural effects on Lake Michigan. Some information is available on the rates and amounts of chemicals added from point sources, partly from the National Pollution Discharge Elimination System effluent permit applications filed with the U. S. Environmental Protection Agency. However, the importance of contaminant additions from non-point sources has yet to be fully characterized. Information on synergistic or antagonistic interactions of chemicals within natural aquatic environments is scant. Our knowledge of the kinds and amounts of new chemical substances being introduced is minimal. A discussion of the DDT problem in the popular press led ultimately to restrictions on the use of this pesticide in the Lake Michigan Basin. Further, the removal or degradation behavior of some of the synthetic chemicals added to the Lake, such as organochlorine compounds, is insufficiently explored.

This report recognizes that Lake Michigan is not a homogeneous system. Instead, it represents a kaleidoscope of chemical, physical, and biological systems that interlock and overlap. Interrelationships among water chemistry, physical processes, and biota contribute to the heterogeneous nature of Lake Michigan and are a manifestation of its heterogeneous nature, as this report will elaborate. Although considerable amounts of information on Lake Michigan water chemistry have been recorded, and conservative substances, nutrients and potentially toxic substances have been investigated, our accumulated knowledge ultimately is site- and time-specific. Trace metal concentrations in the nearshore waters sampled around Chicago-Gary-Hammond will differ from those between Sturgeon Bay and Frankfort. Nutrient analyses of water from southern Green Bay will not be the same as those from the Straits of Mackinac; nor do these parameters remain constant with time, for they can vary over an annual cycle, from season to season, from day to day, or even from hour to hour. The use of lakewide averages to describe the chemical composition of Lake Michigan obscures and oversimplifies the sometimes dramatically different chemical environments found in this large body of water. But on the other hand, use of highly localized data may obscure evidence of regional effects, lakewide trends, or general characteristics. The influence of pollutants added at one place may not be visible for many miles, due to advection by currents in the Lake. Thus we must use an integrated approach to the chemistry of Lake Michigan, analogous to looking at the thread (local scale) woven into a fabric (regional scale) that is made into a garment (whole lake) in order to gain an idea of the overall value of the garment. Even here, the value of the integrated approach can best be appreciated in the context of the natural and human resources in the entire watershed.

This report summarizes chemical data collected over the past two decades in Lake Michigan and its two major embayments, Green Bay and Grand Traverse Bay. This account does not pretend to review exhaustively all chemical data ever collected in Lake Michigan. Nevertheless, it does attempt to include the most germane and thought-provoking work generally available. Concentrations of chemical substances in open water (> 16 km offshore) are discussed and compared with levels found in nearshore (< 16 km offshore) areas of Lake Michigan. Offshore values most nearly represent baseline concentrations, or water quality least affected by man, although even these values have probably changed somewhat in the past century or so. In contrast, inshore values have in many cases been appreciably altered by human activities. Concentrations of nutrients and toxicants in Lake Michigan are surveyed and compared with levels currently judged acceptable for the maintenance of human health and the propagation of desirable aquatic organisms. Where possible, sedimentary behavior of chemicals is considered. Major external factors modifying the chemistry of the Lake, such as erosion and weathering, municipal and industrial effluents, dry fallout and precipitation, and non-point surface and subsurface inputs, are considered. It is beyond the scope of this report to explore in detail the amounts of chemicals added by all point and non-point sources within the Lake Michigan Drainage Basin. This is not to say, however, that these topics are unimportant.

GENERAL COMMENTS ON FIELD PROCEDURES, SAMPLING TECHNIQUES, AND ANALYTICAL METHODS

Interpretation of chemical data from Lake Michigan requires some appreciation of how sampling locations are chosen, what sampling techniques are used, and which analytical methods are employed, since each of these influences the final results.

FIELD PROCEDURES

Collection of water samples in Lake Michigan depends largely on the weather, except when water samples are taken from a municipal water intake. Sample collection is less difficult in summer, when high seas and strong winds are infrequent. But in late fall, winter, and early spring, sampling can be hazardous. Ice-clogged harbors and strong winds prevent use of boats and ships during cold weather and explain the paucity of chemical data during these periods.

Logistics also affect the choice of sampling site. Inshore waters are safely accessible with a smaller boat, but offshore work requires a vessel sufficiently large to operate safely far from land. Personnel and materiel must be transported to the area where samples are to be collected; sampling far from home port requires provision of lodging and meals for participating scientists and crew. Seemingly there are always more people and organizations that would like to contract for use of a research vessel than there is time available during the sampling season. On occasion, commercial vessels (*e.g.* car ferries that crisscross Lake Michigan) willingly lend themselves to scientific endeavors if these efforts do not interfere with their main operations, but these ships of opportunity are not always available nor are they always able to cooperate. In fact, data collection in offshore areas of the Lake is often hindered or even prevented by the substantial problem of inaccessibility.

Both weather and logistical problems, therefore, have been factors in the accumulation of more chemical data from nearshore waters of Lake Michigan than offshore. Additionally, sampling has focused on inshore areas because the most obvious interactions of people with the Lake occur at the shoreline: municipalities and industries withdraw water from this area; sewage effluents are discharged here; tributaries empty into the Lake, and the effects of the soluble and suspended material brought in by the rivers are felt most acutely here; and harbors containing objectionable pollutants are located along the shore. Indeed, without concerned people to question the condition and quality of water along the shore, sampling and monitoring efforts are infrequent at best. These points are illustrated throughout this report by the fact that information from the southern half of Lake Michigan, around the population centers of Milwaukee, Chicago, Gary, and Hammond, is much more abundant than from the relatively unpopulated northern half.

For any particular region of Lake Michigan, the choice of site and selection of sampling depths contribute to the variability of data collected from that area. Robbins *et al.* (1972a) pointed out the importance of site selection in the nearshore area around Grand Haven. Onshore winds confine the Grand River plume to the shoreline, while offshore winds direct the plume out into Lake Michigan. Consequently, a fixed sampling site can exhibit considerable variation from one day to the next according to the location of the Grand River plume.

Choice of sampling depths also is a determinant in data variability. Both physical (*e.g.* temperature) and chemical (*e.g.* dissolved gases, nutrients) parameters can vary appreciably with depth during periods of stratification, so sampling depths must be specified when the chemistry of the Lake is described. Additionally, a distinction should be made between a sample of surface water and a sample that contains the surface film of water. In some fresh waters, particulate matter, nutrients and metals are concentrated in a surface film of < 1 mm thickness (Hatcher and Parker, 1974). A sample from the surface water may, therefore, differ greatly from a surface sample that includes this film.

SAMPLING TECHNIQUES

The choice of sampling techniques depends on the purposes for which samples are collected. For example, two general types of water collection devices have been used to sample surface and subsurface waters. When only major chemical constituents and nutrients are to be determined, water collection devices of no specified composition are usually adequate (*e.g.* Beeton and Moffett, 1964; U. S. Dep. Inter., 1968). However, if trace metal content or primary productivity is to be measured, then use of all-plastic or plastic-coated water collection devices minimizes sample contamination (*e.g.* Schelske and Callender, 1970; Wahlgren *et al.*, 1972b; Copeland and Ayers, 1972).

Studies of Lake Michigan sediments are characterized by two rather different objectives. If the purpose is to describe the surficial sediments qualitatively or semiquantitatively, then grab samples taken with nonquantitative devices such as Ekman, Petersen, Shipek, and Ponar grab samplers are adequate (*e.g.* Schelske and Roth, 1973; Shimp *et al.*, 1970). On the other hand, elucidation of the history of the Lake, as recorded in the sediments, is facilitated through the collection of bottom cores (Robbins *et al.*, 1972a; Robbins and Edgington, 1974; Shimp *et al.*, 1970, 1971). Analyses of fixed close-interval samples collected near the top of these sediment cores permit more precise delineation of recent changes (Robbins *et al.*, 1972a).

Procedures for handling samples also depend on the purpose for which samples were collected. In some instances water samples are filtered immediately, and the proportions of soluble and particulate matter are determined subsequently. Or, there may be no pretreatment before samples are set aside for storage. Choice of storage containers depends on the analyses to be run. Plastic storage vessels are frequently used to minimize sorptive removal of nutrients and trace metals by container walls. Glass containers, however, are preferred for storing certain pesticide samples.

Techniques for preserving the composition of a sample during storage vary. For example, poisons such as chloroform or mercuric chloride may be added to prevent biological alterations. Water samples are sometimes acidified to prevent precipitation of constituents during the time interval between sample collection and analysis, with the recognition that acidification leads to alterations of some chemical forms [*e.g.* $CO_3^{2-} + 2\ H^+ \rightarrow H_2O + CO_2 \uparrow$; $Fe(OH)_3 + 3\ H^+ \rightarrow Fe^{3+} + 3\ H_2O$]. Samples may be frozen till analysis to reduce chemical and biochemical changes, although this technique sometimes leads to falsely high or low measured concentrations (Burton *et al.*, 1970; Philbert, 1973; Schelske and Stoermer, 1972).

ANALYTICAL METHODS

After collection and storage, a sample may be subjected to any number of analytical techniques, each with its own inherent limitations of sensitivity, accuracy, and precision. These techniques may be as simple as weighing the residue remaining after a water sample is evaporated, or as sophisticated as neutron activation analysis, mass spectroscopy, and anodic stripping voltammetry.

It is difficult to be certain of the accuracy of a chemical determination in a water sample from Lake Michigan; to say that a measurement is accurate is to imply that the correct value of the parameter in question is already known. Yet it is this correct value that the measurement is intended to estimate. One can, however, discuss the reproducibility of a particular analysis, and if several different analytical methods yield the same result, then the question of the accuracy of chemical measurements can be addressed.

To interpret results of chemical analyses of Lake Michigan water, one should recognize the capabilities of the analytical techniques used. For example, colorimetry (a quantitative chemical analysis using a color comparison of samples and standards) is well suited for nitrate analysis, but useless for detection of pesticides. As another example, certain chemicals interfere in some analytical techniques. To illustrate, arsenate interferes with phosphate in the ascorbic acid method of determining phosphorus concentration; in sufficient quantities, arsenate produces an overestimate of the phosphate concentration. In other instances, an analytical technique, such as neutron activation analysis, can be ineffective under one set of conditions but appropriate under others. To illustrate, instrumental neutron activation analysis (Copeland and Ayers, 1972) is unsatisfactory for quantification of copper, whereas a simple chemical separation of the activated nuclides (Edgington and Lucas, 1971) renders neutron activation analysis practicable for the quantification of copper.

PHYSICAL PROPERTIES

BASIN MORPHOLOGY

Morphometric characteristics can be used to classify Lake Michigan into five areas: the southern basin, divide, northern basin, straits area, and Green Bay (Fig. 1). For description of water quality, however, the divide area is not usually considered a separate entity (U. S. Dep. Inter., 1967). For convenience, the straits area will usually be included with the northern basin in this volume.

The southern basin lies south of a line between Milwaukee and Grand Haven. In this basin the bottom has a gentle relief and maximum depth of 172 m (564 ft) (U. S. Dep. Inter., 1967).

The divide area, located between the northern and southern basins, is bounded by two approximately east-west trending ridges, and the topography within this area is more irregular than the southern basin. Two troughs in the divide area have depths exceeding 150 m (492 ft).

The northern basin is bounded by a line between Manitowoc and Manistee and another line from Frankfort to Manistique. Bottom topography of the northern basin is much more complex than the southern basin and the maximum Lake depth, 282 m (923 ft), is found here.

The straits area, including Grand Traverse Bay, has a very irregular bottom and its morphometry is more similar to that of northern Lake Huron than it is to the northern basin.

Green Bay is relatively shallow. The Door County peninsula shelters the south end of Green Bay from extreme wind action, but the north end is exposed to the same physical forces as the main portion of Lake Michigan.

Although an exact definition of "inshore" and "offshore" areas of Lake Michigan depends on the strength of wind mixing at any time and shoreline morphology, an arbitrary and convenient standard is used throughout this volume: inshore waters lie within 16 km (10 mi) of shore, while offshore waters are more than 16 km from shore.

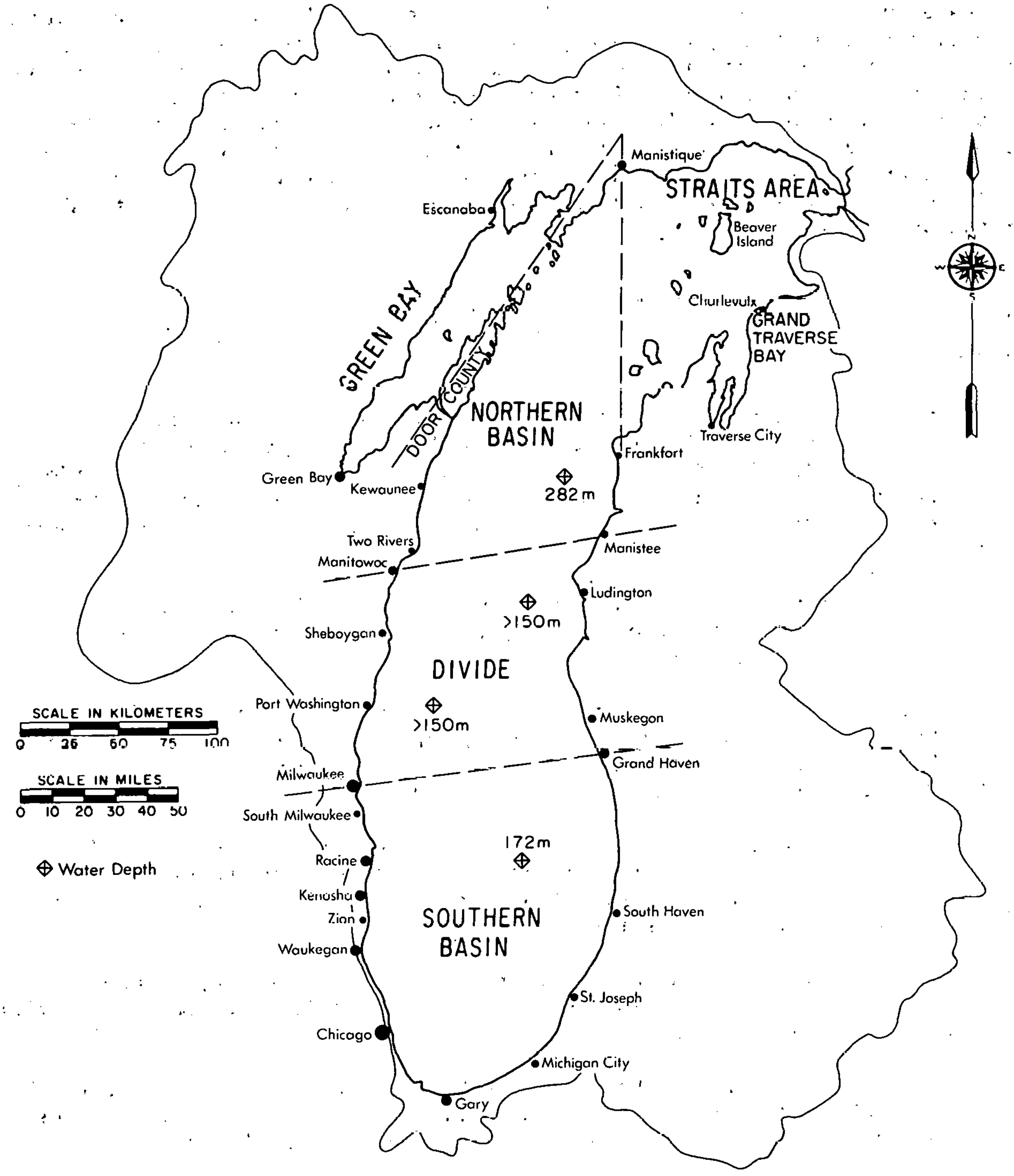


Fig. 1. Map of Lake Michigan with Five Area Classifications.

SEASONAL CYCLE OF TEMPERATURE

The following discussion is based, except where noted, on work by Mortimer (1975), Csanady (1975), and the U. S. Department of the Interior (1967).

Lake Michigan, like most deep lakes in the Temperate Zone, stratifies during summer and sometimes in winter (Fig. 2b, 2d). Typically, three strata are present during summer (Fig. 2b): a surface stratum (epilimnion); a middle stratum, where temperature and density change rapidly with depth (metalimnion or thermocline); and a bottom stratum (hypolimnion). That is, the water separates into layers having measurable temperature and density differences. Transitions from one stratum to another are pronounced.

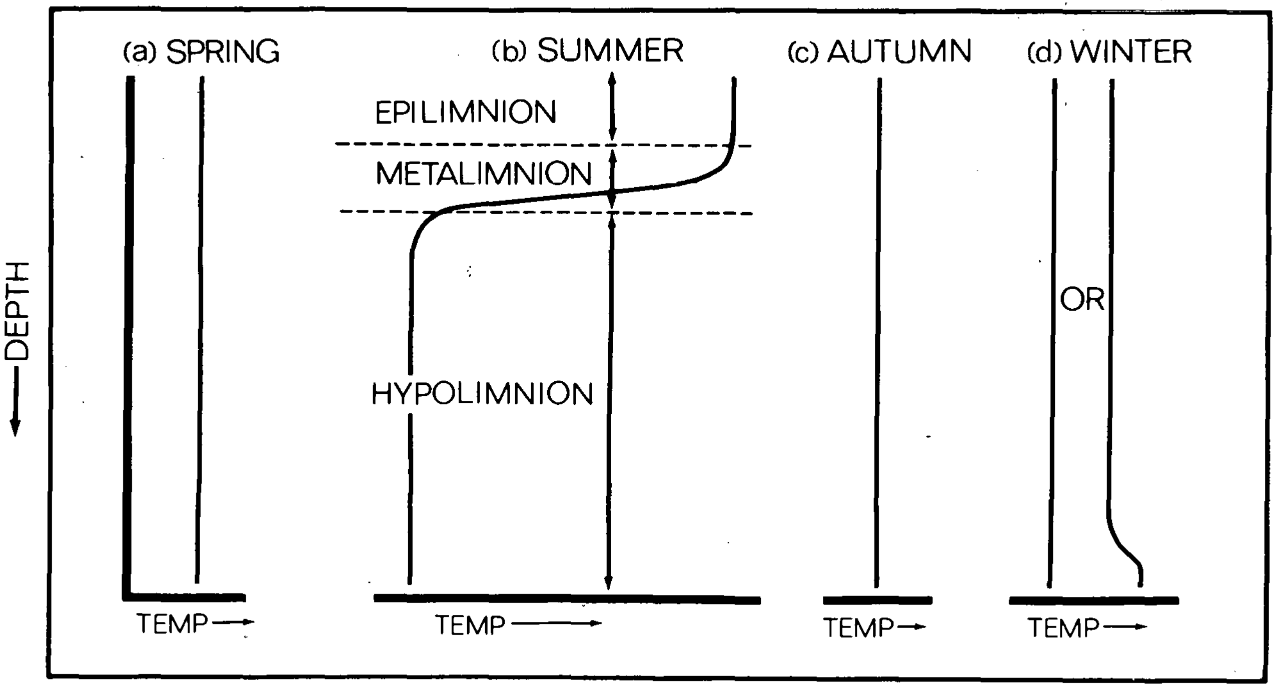


Fig. 2. Schematic Representation of Seasonal Thermal Regimes in Lake Michigan. Each panel represents the variation of temperature with depth.

Church (cited by Ayers, 1962) recorded an annual temperature cycle in Lake Michigan (Fig. 3). To understand the causes of alternate periods of mixing and stratification (Fig. 3), consider how the physical properties of the Lake change seasonally.

During fall, the water loses more heat than it gains from the sun, and therefore cools. Wind-induced turbulence in the epilimnion and convective mixing caused by heat loss through the surface lead to entrainment and erosion of the summer thermocline. By December the process of top-to-bottom mixing is complete (fall overturn). Vertical mixing has driven the thermocline to the bottom, and the water column is nearly isothermal in the range of 4-6°C.

Heat losses continue during January. Because of shallowness and smaller volume, the nearshore zones show these cooling effects more intensely than

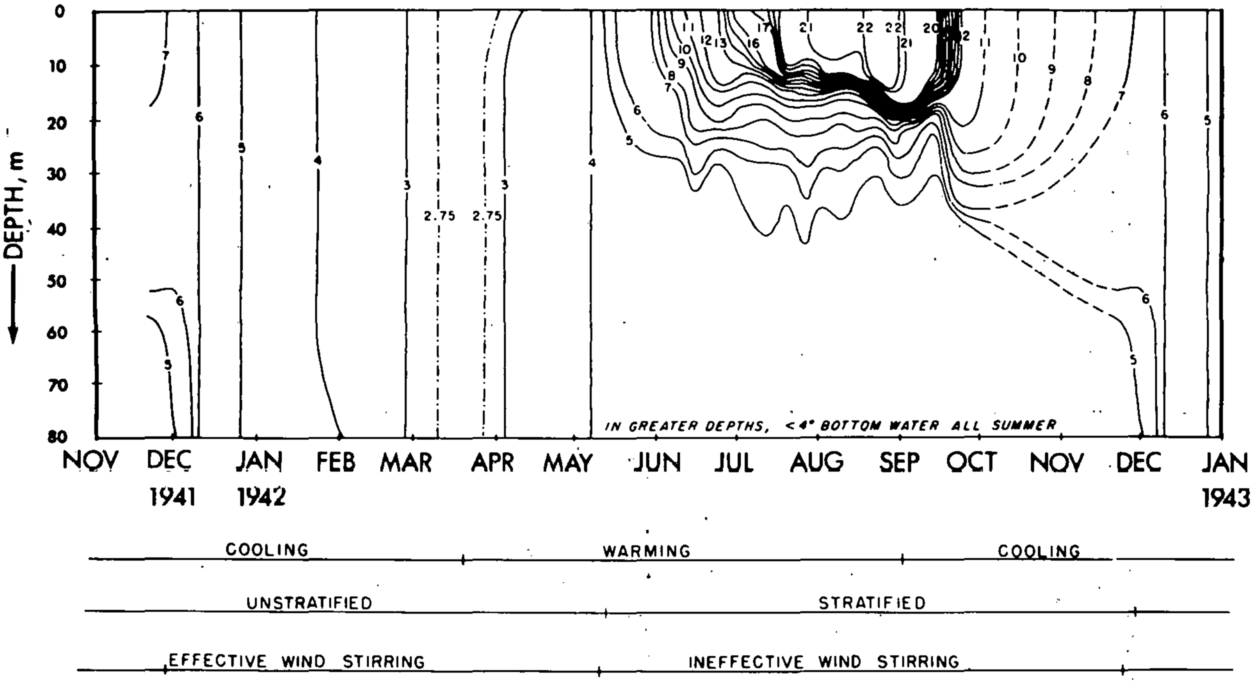
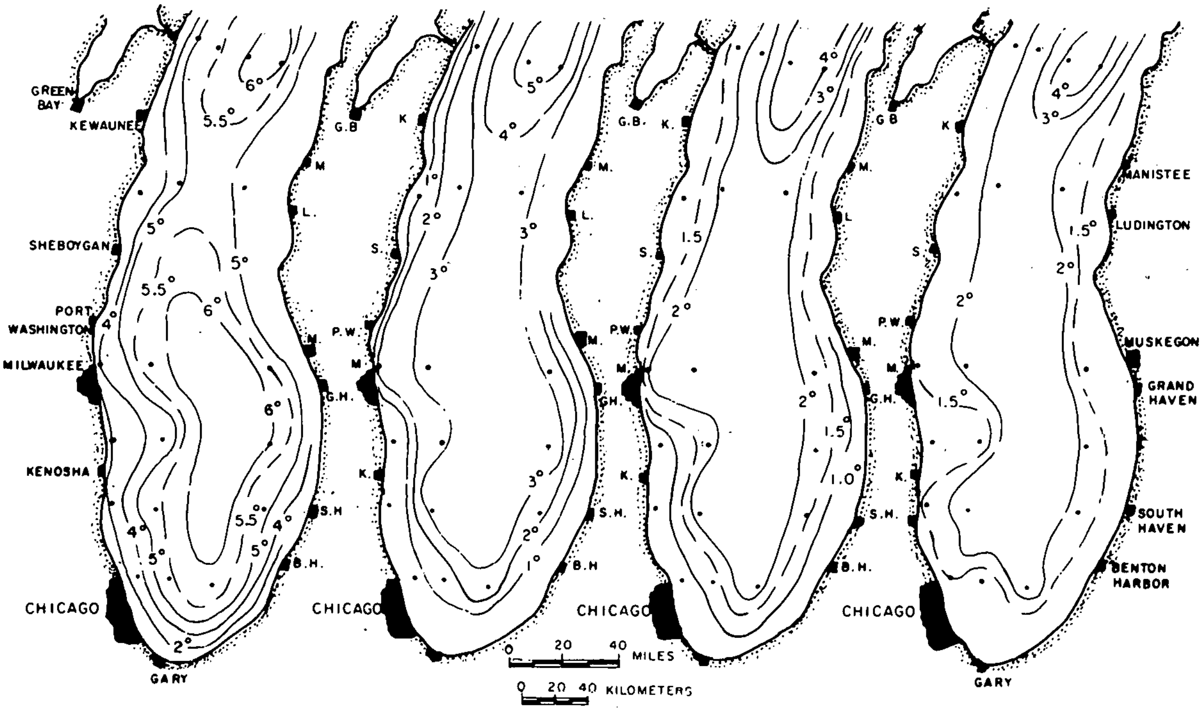


Fig. 3. Seasonal Changes of Temperature with Depth over an Annual Cycle at a Station 64.5 km (40 mi) off Milwaukee. Temperature, °C, is shown directly on the isothermal lines. Modified from Ayers (1962) (with permission, see credits).

deep waters. Horizontal temperature gradients are created and persist till spring. During January and February colder inshore waters may mix with warmer offshore waters, resulting in a winter thermal bar similar to the spring thermal bar (discussed below). With the progression of winter, inverse stratification is established in the northern basin and inshore areas where ice forms or drift ice accumulates (*i.e.* colder, less dense water lies over warmer denser water, Fig. 2d). By the end of March, the southern two-thirds of the Lake has cooled to less than 4°C (39.2°F) at 10 m (Fig. 4). The coldest water still hugs the shore.

During the lengthening days of spring, the shallowest inshore waters of Lake Michigan are the first to warm and the first to stratify, while offshore waters remain colder than 4°C and isothermal (Fig. 2a) until the end of April or later. In the course of this warming period, the remains of the coldest winter water, which was once closest to shore, can be found parallel to shore in a band, lying between the slightly warmer offshore waters and the rapidly warming shallow areas along the shore. As the heating rate accelerates during April and May, the distinction between the rapidly warming inshore waters and the colder waters farther from shore becomes more pronounced. Mixing occurs where the warmer inshore and colder water masses converge. The density of the mixture is greater than either of the two components because water is most dense at 3.96°C (Fig. 5); thus the mixture sinks. In this sinking zone (thermal bar), isotherms at or near 4°C are almost vertical (Fig. 6).



15-20 December 1963 15-20 January 1964 15-20 February 1964 15-20 March 1964

Fig. 4. Distribution of Temperature, °C, at 10 m Depth in the Southern Two-Thirds of Lake Michigan. Slightly modified from Mortimer (1975) (originally drawn from data in Noble and Michaelis, 1968).

Once the thermal bar is formed, it does not remain stationary. As spring warming continues to heat the inshore areas more rapidly than the deep waters, the bar moves away from shore. Rodgers (1966) reported an advance of as much as 0.8 km (0.5 mi) in 8-1/2 hr in Lake Ontario. As the bar moves into deeper water, an obvious boundary, often characterized by color differences, persists between the two water masses (Noble and Anderson, 1968). Because of stratification on the shoreward side of the bar (see Line A of inset, Fig. 6) and perhaps because nutrients carried by rivers and industrial and municipal sources are caught temporarily inside the bar, the burst of primary productivity

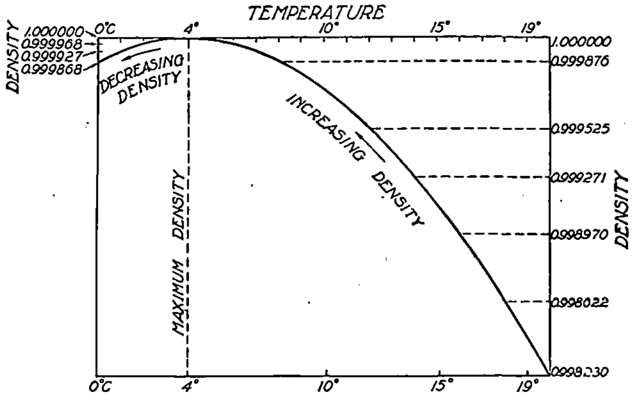


Fig. 5.

Density of Pure Water as a Function of Temperature (Welch, 1952) (with permission, see credits).

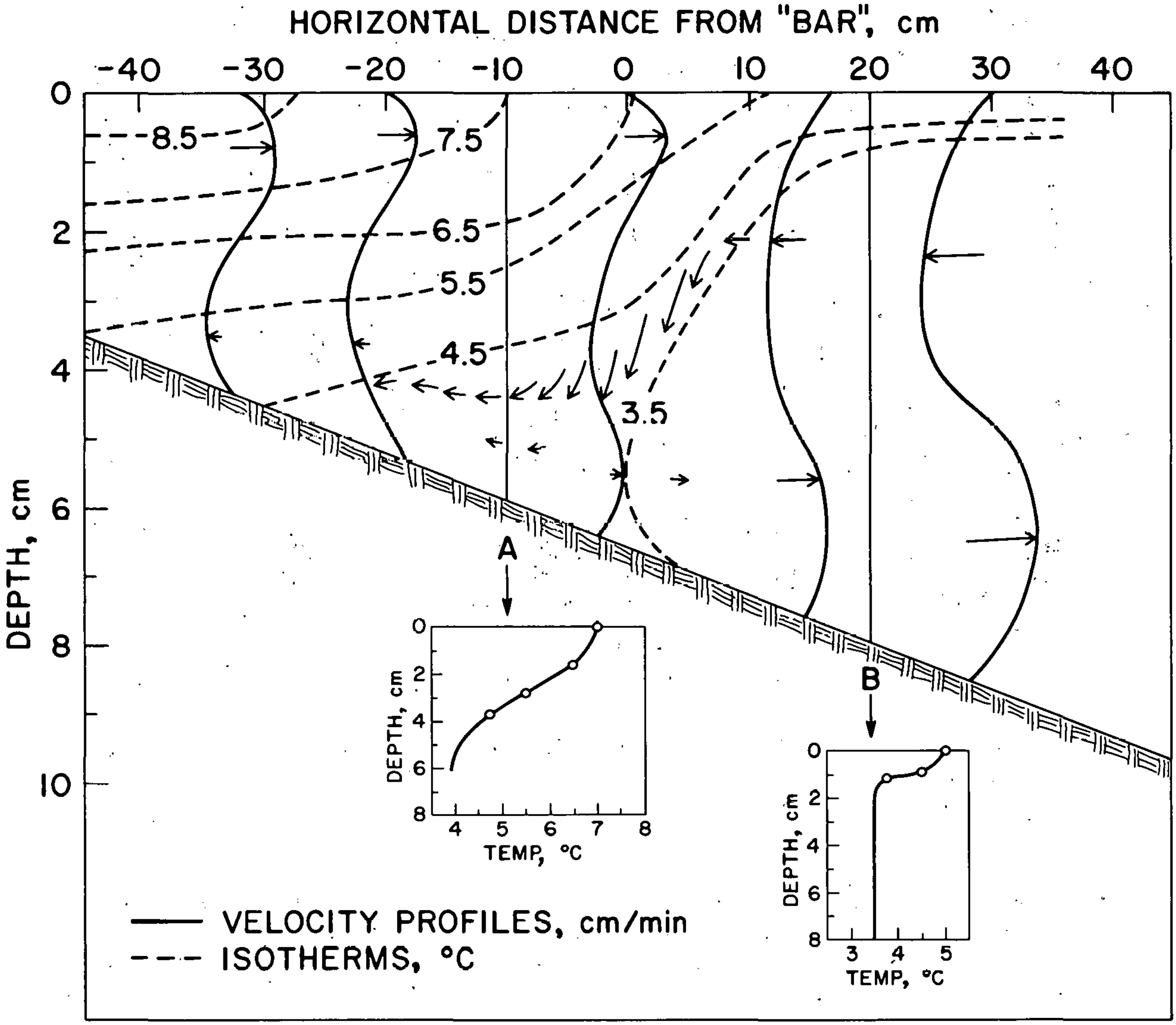


Fig. 6. Laboratory Model of a Spring Thermal Bar. Insets illustrate (A) stable inshore and (B) unstable offshore conditions. Modified from Elliott and Elliott (1969).

associated with spring warming starts earlier and achieves higher rates shoreward than in the colder, deeper, unstratified water on the lakeward side of the bar.

By late June, thermal stratification (Fig. 2b) is prevalent throughout Lake Michigan. The steep density gradient across the summer thermocline inhibits vertical mixing as long as the water gains more heat from the sun than it loses by back-radiation. But from mid-August onward, there is a net heat loss through the surface. Buoyancy-driven convection and increasing average wind stress associated with autumn push the thermocline downward, until the Lake is once again isothermal in late autumn (Fig. 2c).

LIGHT PENETRATION

Transparency

Light transmission through water is determined by its transparency, an important parameter in studies of photosynthesis, phototaxis, and photochemistry.

Light falling directly on the surface of Lake Michigan is both reflected and absorbed. The spectral composition of reflected light is essentially the same as incident light, but the spectrum of light penetrating the surface of the water is altered. Figure 7 shows the spectra of light transmitted to various depths in pure water. Note that the greatest transmission is in the blue-green region of the spectrum in pure water. Also, one sees that the

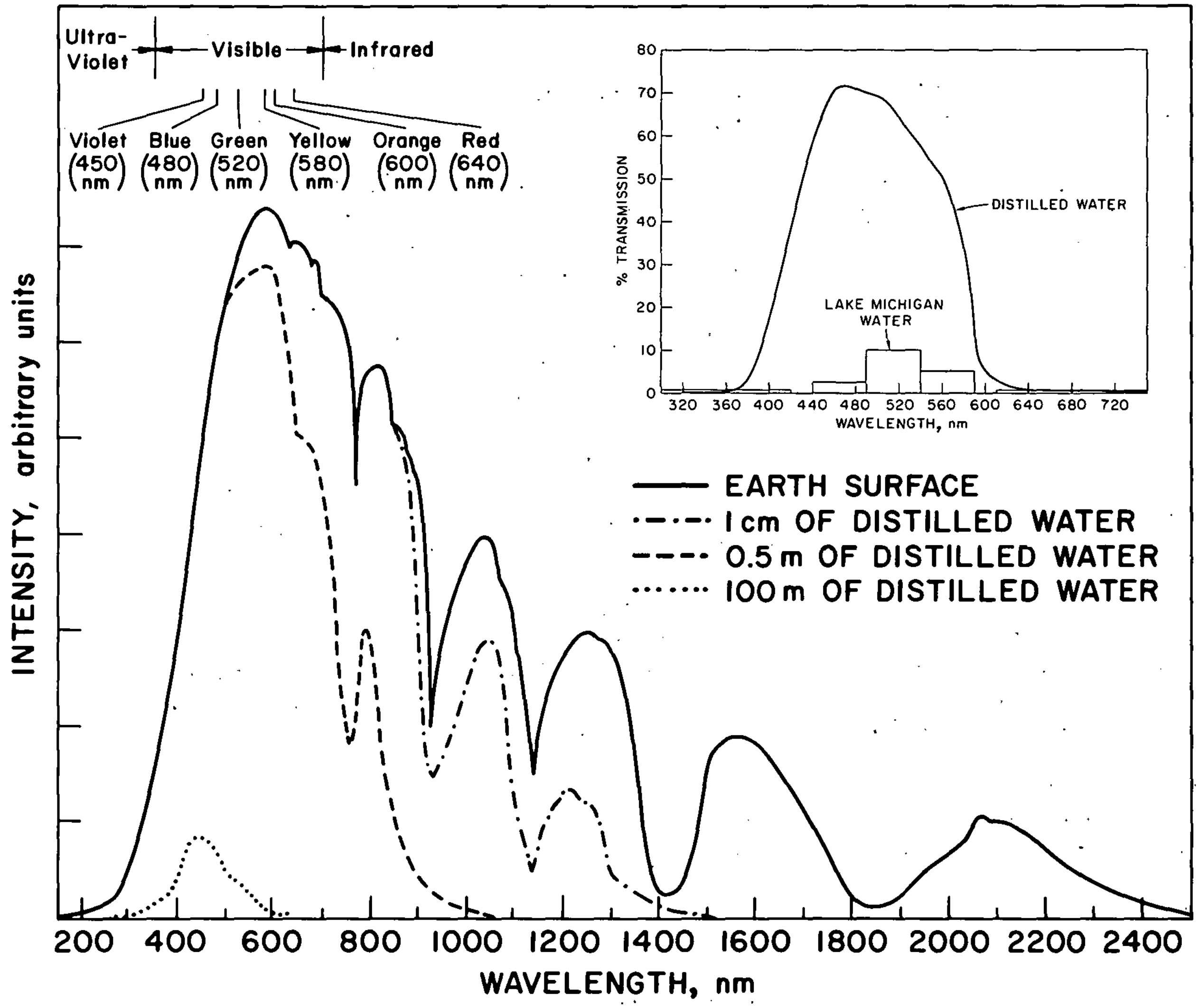


Fig. 7. Solar Energy Spectrum. Inset illustrates percent transmission of light in the visible region after passing through 10 m of distilled water (data from Sverdrup *et al.*, 1942) and through 10 m of water sampled off Sturgeon Bay, 8 May 1958 (data from Beeton, 1962).

attenuation depends on the wavelength(s) of the incident light and the depth to which the light has penetrated.*

The time of day, season, and atmospheric clarity contribute to the variations in intensity of light falling on the surface of Lake Michigan. Suspended and dissolved materials within the lake water induce variations in the depth of light penetration (transmission); the effects caused by suspended materials (turbidity) are the more important of the two (Pinsak, 1972). Increasing turbidity decreases transparency and shifts maximum color transmission from the blue-green region to longer wavelengths (red region), as shown in the inset of Figure 7. The inset shows a comparison of light transmission at 10 m in pure water and in water sampled near Sturgeon Bay (Beeton, 1962): the maximum transparency of the sample taken near Sturgeon Bay is shifted from the blue-green region (440-490 nm) to the green region (490-540 nm).

Turbidity

The effects of turbidity on transparency are determined by particle size, bottom sediment composition, shoreline proximity, depth, currents, depth of mixing during storm activity, flow variations in streams and attendant fluctuations in suspended solids loads, aerosol inputs, and plankton blooms. Storm activity, floating matter, and phytoplankton blooms produce the most pronounced short-term effects (Pinsak, 1972). Resuspension of fine sediment during spring and fall mixing reduces transparency, as recorded during June 1972 by Ladewski and Stoermer (1973). Increased tributary inflows from spring runoff also cause transient decreases in transparency. Longer-term reductions in transparency may be produced by the protracted presence of algal blooms and by continual inputs of non-settling suspended materials.

Several methods are commonly used to estimate transparency in natural waters. One of the simplest methods is to determine the depth at which one no longer can see a Secchi disc. This measurement of light penetration depends on the transparency of the water and light scattering due to turbidity.

Ayers *et al.* (1967) noted that turbidity, which they described as a milky-water color, in areas south of Frankfort, reduced Secchi disc visibility from the usual 6-14 m to 2-4 m during August 1966. Because the turbidity of the water generally decreased when acid was added, the authors concluded that one component of turbidity-causing substances was acid-soluble, whereas other

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**Expressed mathematically, the intensity of (monochromatic) light, I, at a given depth is described by Beer's law:*

$$I = I_o e^{-bc}$$

where I_o = *light intensity measured at the surface,*

e = *base of natural logarithms,*

b = *a proportionality constant, called the extinction coefficient, which depends on the absorbing medium and wavelength of light, and*

c = *the depth in the water column at which* I *is measured.*

components were not affected by acid. Subsequently, the cause of the milky color (turbidity) was identified as calcite ($CaCO_3$) (Schelske and Callender, 1970).

In examining previous records to discern whether reduced transparency in summer is a regular phenomenon, Ayers *et al.* (1967) assumed that any Secchi depth visibility of 5 m or less indicated that calcium carbonate probably was present. They concluded 1954 and 1966 were years in which calcite-causing turbidity was widespread and that it possibly occurred in 1960 and 1962. They also concluded that conditions leading to calcite precipitation had intensified from 1964 through 1966 at all stations in the sampling tracks (Chicago to Benton Harbor, Waukegan to South Haven, Racine to Holland, Sheboygan to Ludington, and Kewaunee to Frankfort) adopted for survey purposes by the University of Michigan Great Lakes Research Division.

The selection of 5 m as an indication of the presence of calcite places some restrictions on interpretation of the data. During late July 1969, Secchi depth visibility readings were recorded at 14 stations in southern Lake Michigan (Schelske and Callender, 1970). Four of the 14 Secchi readings were less than 5.0 m (3.5, 3.8, 4.1 and 4.8 m) and were taken in shallow areas (depth $\leq$ 21 m), where shoreline influences cannot be ignored. Furthermore, with one exception, carbon fixation rates at these four stations were the highest reported in this data set. These data suggest that suspended phytoplankton reduced the Secchi depth visibility. Data collected south of a line between Waukegan and South Haven in 1971 and 1972 support the hypothesis that phytoplankton populations influence Secchi depth visibility (Ladewski and Stoermer, 1973). Low offshore plankton concentrations were generally matched by high Secchi transparencies, while high phytoplankton counts inshore corresponded with low Secchi transparencies. In at least one instance low plankton concentrations did not correspond to high Secchi depth visibilities; in September milky waters at offshore stations reduced Secchi transparencies to 5 m or less, although algal cell counts were at their lowest seasonal level.

Schelske and Roth (1973) measured Secchi depths on 7 July 1970 at six stations located on a line passing east of the Manitou Islands from Frankfort to Beaver Island. All stations were within 16 km (10 mi) of land. The average Secchi depth visibility was 4.8 m, with a standard deviation of 0.6 m. The authors suggested that these findings indicated that transparency had decreased since the 1966 measurements of Ayers *et al.* (1967). However, it is difficult to draw conclusions from one day's data (*cf.* Schelske and Roth, 1973). Information on weather conditions is essential for assessing the effects on light transmission of preceding storms, high runoff, and high waves. Accordingly, data collected on the same day in the same vicinity near land are not evidence of lake-wide conditions.

The results of Secchi depth measurements depend on the transparency of water as well as scattering of light due to turbidity in the vertical distance between the disc and the observer. More recently, devices containing a photocell and a light source have been lowered into Lake Michigan to obtain a profile of transparency with depth. A relationship between Secchi depth transparencies and newer photocell determinations has not yet been derived theoretically. However, Pinsak (1972) presented a graph of empirical data (Fig. 8) showing that the relation between Secchi depth and photocell transparencies is nonlinear.

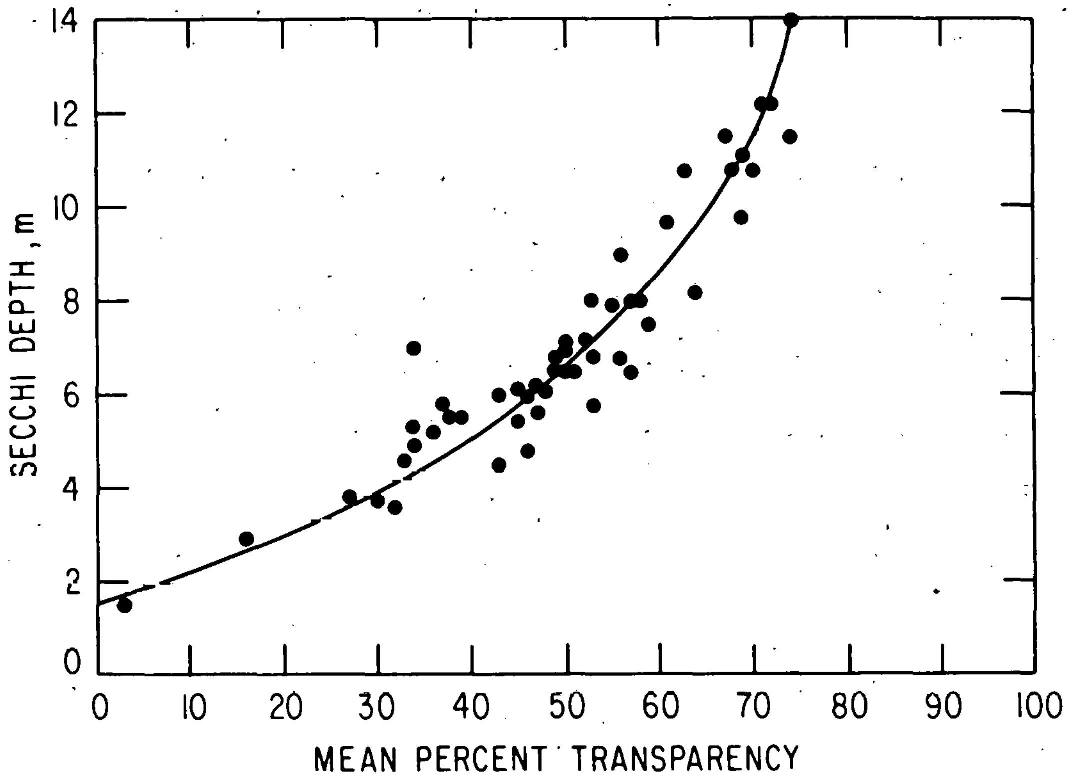

Fig. 8. Relationship Between Secchi Disc and Mean Percent Transparency in Lake Michigan, 23 May-8 June 1970. Redrawn from Pinsak (1972) (with permission, see credits).

Two other methods commonly used to determine a transparency profile avoid the need for an elaborate photocell and light source. These are measurement of turbidity with the Jackson Candle Turbidimeter [reported in units of Jackson Turbidity Units (JTU)] and the weight of suspended solids per unit volume of water (mg/l) (methods in APHA *et al.*, 1971). The data obtained by these two procedures are less sophisticated than those derived with a photocell, but they are useful in limnological studies. The two methods are compared in Tables 1 and 2 using data collected in southwestern Lake Michigan. These data show that turbidity 9.6 km (6 mi) from shore is characteristically less than nearer shore. This difference is not unusual because nearshore hydrodynamic processes increase the amount of light-scattering material suspended in the water. Table 1 indicates that at low turbidities measurements by a Jackson Candle Turbidimeter seem to be more sensitive than weighing suspended solids. Table 2 and possibly Table 1 suggest that suspended solids values are between one and two times greater than turbidity values. However, correlation of turbidity with weight concentration of suspended matter is impracticable, since the size, shape, and refractive index of the particulate materials are important optically but have little direct relationship to the concentration and specific gravity of suspended matter (APHA *et al.*, 1971).

Limitations on turbidity in public drinking water supplies (Appendix B, part 1) are based largely on aesthetic acceptability, although higher turbidities may interfere with disinfection, prevent maintenance of an effective disinfectant agent throughout the distribution system, and interfere with microbiological determinations (Environmental Protection Agency, 1975b).

Table 1. Average Values for Turbidity and Suspended Solids at Three Stations Located 9.6 km Offshore in Southwestern Lake Michigan (February 1970-April 1971)*

Date	*Turbidity, JTU*+	*Suspended Solids, mg/l*
22 Feb 1970	2	
6, 7 and 16 Mar 1970	4	
24 Apr 1970	2	4
18 May 1970	1	2
28 May 1970	1	2
16 Jun 1970	1	<1
30 Jun 1970	2	<1
13 Jul 1970	1	<1
28 Jul 1970	1	<1
5 Aug 1970	1	<1
22 Sep 1970	1	<1
13 Oct 1970	1	<1
11 Nov 1970	1	<1
9 Dec 1970	1	<1
11 Jan 1971	2	<1
8 Feb 1971	1	<1
24 Mar 1971	1	<1
26 Apr 1971	3	<1

**Data from Industrial Bio-Test, 1972b.*

+Jackson Turbidity Units.

Table 2. Average Values for Turbidity and Suspended Solids at Three Water Intakes Located Less than 3.2 km Offshore in Southwestern Lake Michigan (January 1970-April 1971)*

Date	*Turbidity, JTU*+	*Suspended Solids, mg/l*
12 Jan 1970	5	
28 Jan 1970	20	
13 Feb 1970	21	
26 Feb 1970	35	
16 Mar 1970	20	44
31 Mar 1970	18	23
15 Apr 1970	43	83
30 Apr 1970	14	41
27 May 1970	7	13
24 Jun 1970	10	29
30 Jul 1970	4	27
24 Aug 1970	2	2
9 Sep 1970	1	<1
1 Oct 1970	4	3
5 Nov 1970	7	13
10 Dec 1970	20	29
13 Jan 1971	19	26
11 Feb 1971	5	5
26 Mar 1971	21	35
27 Apr 1971	34	35

**Data from Industrial Bio-Test, 1972a.*

+Jackson Turbidity Units.

The National Academy of Sciences ... (1973) considered the effects of turbidity, measured as suspended solids, on the aquatic community (Appendix B, part 2). Excessive amounts of suspended matter reduce light penetration, clog gills of fish and mussels, and cover bottom habitats upon sedimentation. The Academy recommended that the combined effect of color and turbidity should not change the point at which oxygen production during photosynthesis equals oxygen consumption by respiration (compensation point) by more than 10% of the seasonal norm, and this change should not place more than 10% of the photosynthetic organisms below the compensation point.

Color

Absorption of light by substances dissolved in water contributes to the difference in transparency between distilled water (Fig. 7) and lake water. Substances which impart color to natural waters include naturally occurring metallic ions (especially iron and manganese), humus materials, peat, tannins, organic materials produced by plankton and macrophytes, and industrial wastes.

True color of a water sample is that color remaining in solution after suspended matter has been removed by centrifugation (filtration removes color as well as particulate matter and should not be used to remove suspended solids). Apparent color is caused by the presence of the dissolved and particulate material. In waters with low turbidity, *e.g.* Lake Michigan, apparent and true colors are substantially the same (McKee and Wolf, 1963).

Water color is generally quantified by comparing a lake sample with standard solutions of known color (see APHA *et al.*, 1971). In the United States the platinum-cobalt method is standard; the unit of measure is 1.0 mg Pt/l, present as the brownish-yellow chloroplatinate ion, $PtCl_6^{2-}$. Clear water has a color of zero, and darkest bog waters range up to 340 platinum units on a scale of 0-1000 (Hutchinson, 1957).

Industrial Bio-Test (1972a, 1972b, 1972c) recorded water color as part of their studies in southwestern Lake Michigan. Apparent color and true color were no higher than 5 dimensionless color units at three stations 9.6 km (6 mi) from shore (the dimensionless color units used by Industrial Bio-Test appear to be very similar to, if not the same as, standard platinum units). Of nearly 200 color determinations on samples collected monthly between February 1970 and April 1971, over 90% were $\leq$ 3 color units. Higher values were recorded in winter, while the lowest values were noted in June, July, and August. Color in nearshore waters varied more than in samples collected 9.6 km (6 mi) from shore, ranging from a minimum of < 1 to a maximum of 17 color units. Figure 9 illustrates the variation in apparent (January-December 1970) and true (January-April 1971) color measured at the Kenosha water treatment plant, the intake of the Waukegan Generating Station, and the North Chicago water treatment plant. As in the samples collected 9.6 km (6 mi) from shore, color was minimal in summer, while higher values were recorded in winter months. These higher values may be due to stirring of the bottom sediments by winter storms.

Appendix B, part 1, lists limitations on color in drinking water supplies applicable to the Lake Michigan Basin. These limits are based on aesthetic acceptability. With respect to the protection of freshwater aquatic life the recommendation was in combination with turbidity and is stated above.

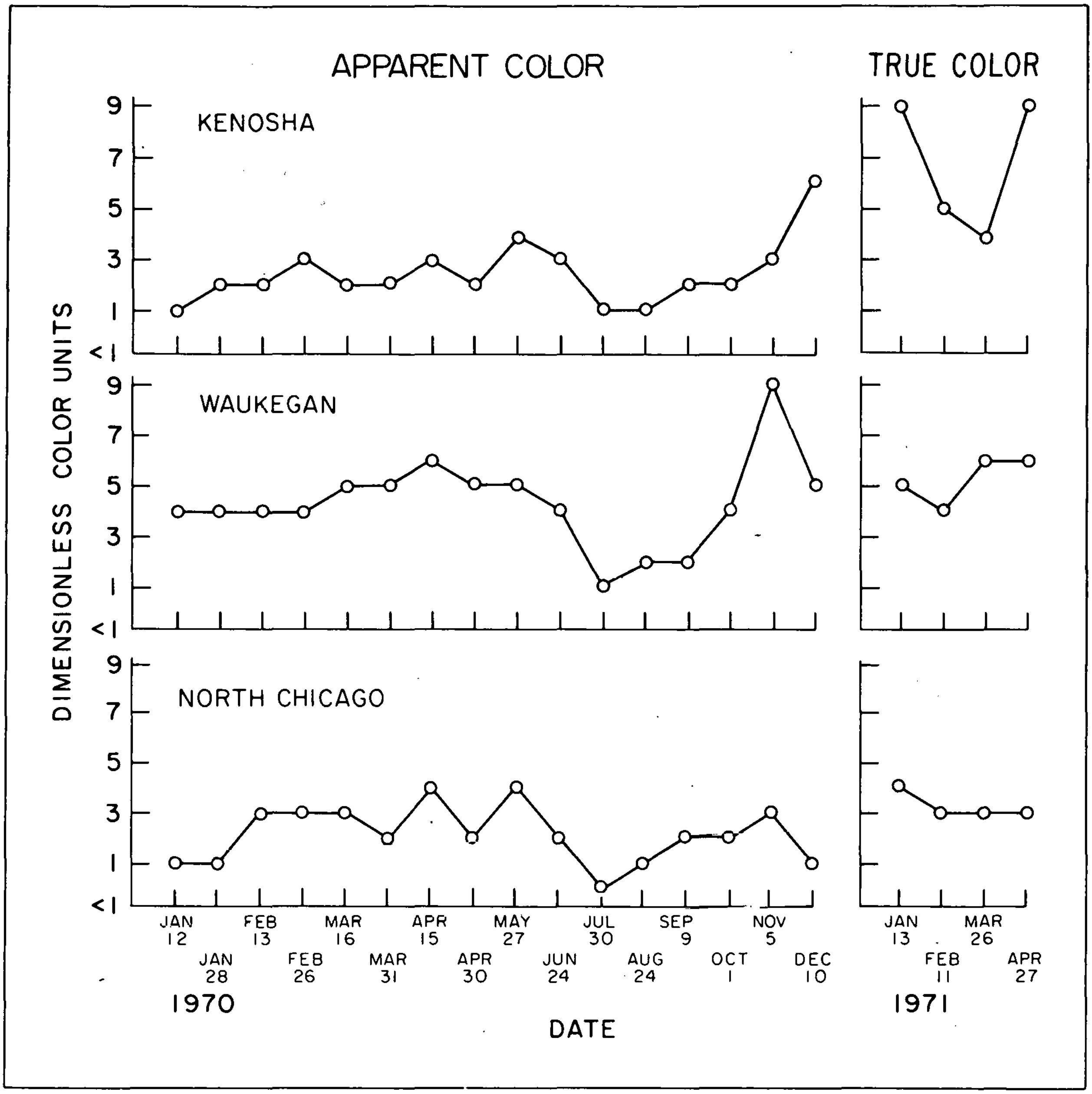

Fig. 9. Apparent and True Water Color at Three Inshore Stations. Samples collected at: Kenosha public water supply intake, 9.1 m (30 ft) deep, 1372 m (4500 ft) from shore; Waukegan Generating Station intake canal; North Chicago public water supply intakes, 9.1 m (30 ft) deep, 1981 m (6500 ft) from shore, and 5.5 m (18 ft) deep, 366 m (1200 ft) from shore. Data from Industrial Bio-Test (1972a).

WATER MOVEMENT

A pollutant added to Lake Michigan is dispersed by diffusion (molecular scale), mixing and dilution (larger scale), and movement by currents (larger scale still). Theoretical and experimental considerations of the effects of these processes in Lake Michigan are included in reports by the U. S. Department of the Interior (1967), Mortimer (1975), and Csanady (1975). This general discussion on diffusion, mixing, and currents, which is based on these three references, summarizes how these physical factors affect the dispersion of pollutants added to Lake Michigan.

Molecular Diffusion

Molecular diffusion is the molecular movement of one substance within another along a concentration gradient. Since molecular diffusion is probably the least important dispersal mechanism within Lake Michigan water, it will not be considered further.

Turbulent Mixing

Turbulent mixing (eddy diffusion) involves the random movement of a dissolved or suspended substance within water. Eddy diffusion also refers to this process, with no implication that the eddies of eddy diffusion have any regular structure. Eddy diffusion is distinct from molecular diffusion: the former involves motion of a water mass, while the latter describes the agitation of individual molecules. Wind is the principal mechanical force producing water movement in Lake Michigan. The wind transfers energy to water by (*i*) generating waves and the turbulence that accompanies particle movement in the waves, (*ii*) creating frictional drag, and (*iii*) wind-induced turbulence in breaking waves. Energy transferred from wind to water is ultimately dissipated as heat; however, the processes by which wind energy is converted to heat are complex and are associated with a large range of eddy sizes and frequencies.

Wind stress that produces waves (Fig. 10a) also gives rise to orbital particle motion (Fig. 10b) to depths at least half as great as the length of the wave (λ), and in some cases greater. This orbital motion allows mixing to proceed at and below the surface, although at greater depths the energy of mixing is damped entirely by the viscosity (resistance to flow in a liquid)

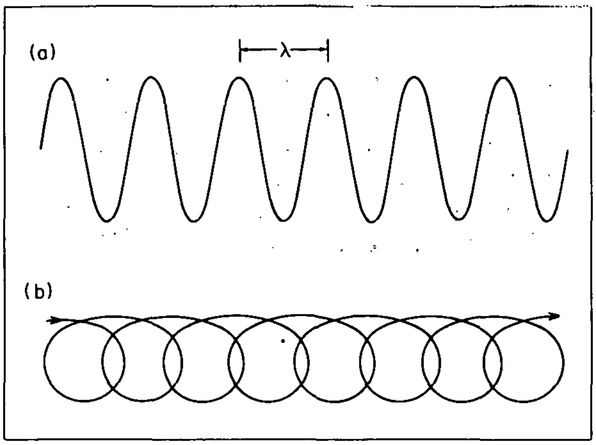

Fig. 10.

Wave Form and Water Movement. (a) Simple sine wave, wavelength λ, representing what an observer may see; (b) horizontal passage of water in a simple sine wave. Water moves orbitally with little forward motion but with some mixing.

of water. In stratified water the thermocline limits the depth of mixing; at a certain depth the energy of turbulence becomes insufficient to overcome the effect of stability created by stratification.

When the wind blows in the same direction for several hours, water piles up to form an upward slope at the downwind shore; this effect of wind stress is called set-up. Mixing occurs as the wind drags surface water by friction toward the leeward shore. Turbulent mixing is also accomplished as a portion of the piled-up water escapes in longshore currents due to gravity, or as undertow, by reverse flow.

Following wind reversal or cessation, the entire mass of piled-up water attempts to regain an equilibrium position by flowing from leeward to windward (Fig. 11a). The Lake is momentarily restored to its former level position; however, the current has not lost all the energy imparted to it by the wind and will continue to move, now piling up at the windward shore. This pile-up at the windward shore will in turn cause a new current in the direction that the wind was originally blowing. This oscillation, called a surface seiche, is familiar to anyone who has ever bumped a half-full cup of coffee and then watched the contents slosh back and forth, with gradually diminishing amplitude, until the surface is still once again. The period of time required for the surface of Lake Michigan to return to equilibrium depends on the density of the water, bottom topography, and the influence of the earth's rotation on the water. Until equilibrium is attained, the surface waters mix as the seiche moves back and forth.

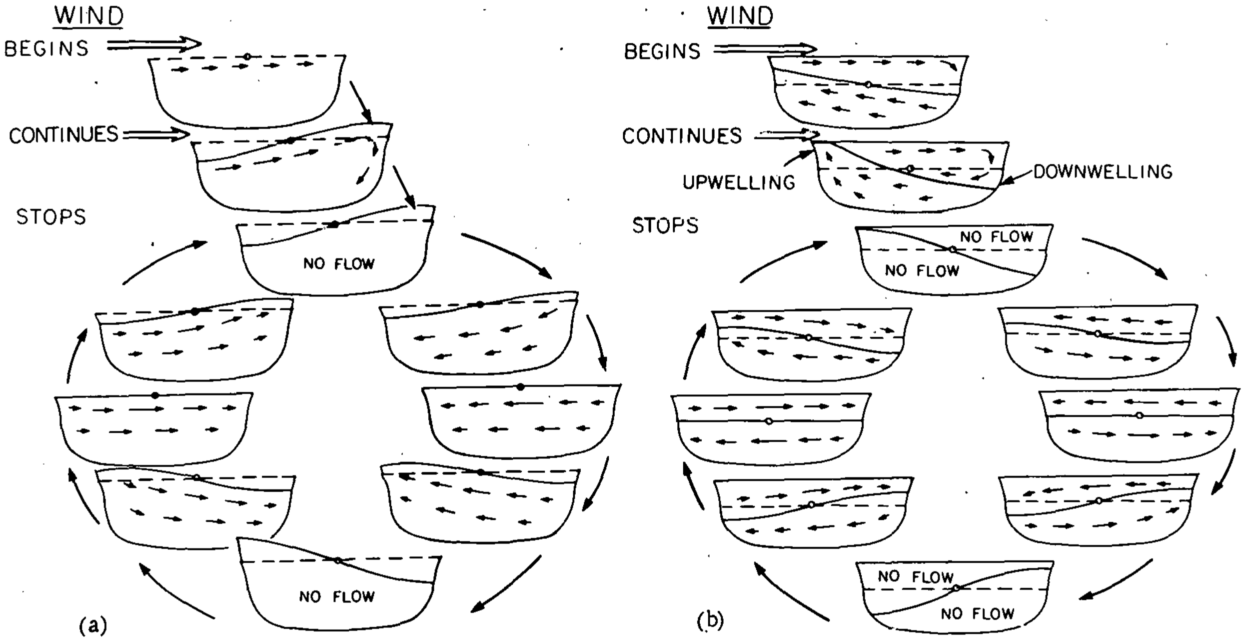

Fig. 11. Models of (a) a Surface Seiche in an Unstratified Lake and (b) an Internal Seiche in a Stratified Lake. The initial effect of the wind and one cycle of subsequent oscillation are shown. The dashed line represents the equilibrium position of the water surface in (a) and of the interface between the two layers in (b). From Mortimer (1975).

When Lake Michigan is stratified, a seiche occurs at the thermocline as well as at the surface. Evidence of this internal seiche is obtained by an integrated network of temperature measurements that reveal a tilting of the thermocline in the downwind direction (illustrated in the upper portion of Fig. 11b). If the water distance over which the wind has passed is great enough and if the wind is strong enough, then hypolimnetic water is lifted to the surface at the upwind side of the basin and the thermocline is lowered beneath equilibrium at the downwind side. These two events are termed upwelling and downwelling, respectively. Temporary upwelling allows addition of heat and oxygen to the hypolimnion and also facilitates the transfer of accumulated materials from the hypolimnion to the epilimnion. The latter process constitutes addition and mixing of bottom waters with top as long as the normal inhibitor of these exchanges, the thermocline, remains sufficiently tilted.

Mass Transport and Currents

Turbulent mixing results in changes of internal distribution within a water parcel but produces relatively little actual transport of the water parcel itself (*e.g.* Fig. 10b). Mass transport, or advection, is roughly opposite to turbulent mixing, for it refers to the overall movement of a parcel of water, with mixing along the edges. Since random turbulence and prevailing advection form a continuum, the distinction between the two actually is not clear-cut. In Lake Michigan, wind and pressure gradients are the major causes of advection.

General patterns of surface-water movement in Lake Michigan during summer and winter are summarized in Table 3. It should be emphasized that these are general patterns only. They are to some extent useless for day-to-day predictions, for they do not take into account the overriding effects of short-term fluctuations and the complexity that shoreline constraints impart to water movement. Inshore currents in Lake Michigan waters generally reflect wind direction (Table 3). Offshore surface currents, however, are dominated by internal seiches and forces resulting from the earth's rotation. In contrast to the surface water, counterclockwise movement of currents is general in both summer and winter at depths exceeding 60 m (Table 3). Although counterclockwise movement prevails in the deep waters of Lake Michigan, it is definitely not an invariant circulation pattern.

Inshore-Offshore Differences in Circulation

During summer, the break between inshore and offshore circulation occurs at or near the intersection of the thermocline with the Lake bottom. In midsummer this boundary will be near the 15- to 20-m contour, from 16 km (10 mi) to 3.2 km (2 mi) offshore, depending on weather conditions. Inshore of this boundary, the chief influences on circulation are wind and bottom topography. (Wind effects were discussed in the previous section.) Bottom topography inhibits inshore circulation by friction and by confinement. The resultant flow is predominantly parallel to shore, following the contours of the Lake bottom.

A pollutant discharged near shore tends to remain inshore because bottom topography and the results of wind stress combine to restrict offshore movement of water. The spring thermal bar, discussed in an earlier section,

Table 3. General Patterns of Current Movement in Surface Waters of Lake Michigan, Summer and Winter*

Season	*Wind*	*Basin*	*Location*	*Direction of Movement*
Winter	N-NW winds, frequently recorded Nov. through Mar. This wind direction occurs 25-30% of the year, principally in winter	Southern	Inshore	South
		Northern	Inshore	South
		Southern	Offshore	Clockwise gyre
		Northern	Offshore	Elongated clockwise gyre
Winter	S-SW winds, frequently recorded Jan. through Apr. on intermittent basis for a total of 20-25% of movement during a year	Southern	Inshore	North
		Northern	Inshore	North
		Southern	Offshore	Counterclockwise gyre
		Northern	Offshore	Elongated counterclockwise gyre
Summer	N-NE winds	Southern	Inshore	South
		Northern	Inshore	South
		Southern	Offshore	Counterclockwise gyre
		Northern	Offshore	Flows south along longitudinal axis of northern basin, splits in the divide area, part flowing east and part west. Each branch then flows north parallel to the east and west shores
Summer	S-SW winds	Southern	Inshore	North
		Northern	Inshore	North
		Southern	Offshore	Counterclockwise gyre
		Northern	Offshore	Flows south along longitudinal axis of northern basin, splits in the divide area, part flowing east and part west. Each branch then flows north parallel to the east and west shores.

**Summarized from the U. S. Department of the Interior, 1967.*

intensifies the difference between inshore and offshore circulation and thus exacerbates the adverse effects of pollutants discharged to the inshore zone in spring.

Fate of Added Pollutants

The following physical factors influence the dispersion of an effluent discharged to Lake Michigan: existing circulation pattern, winds, bottom topography, rotation of the earth, and density difference between effluent and lake water. The prevailing current regime determines the degree to which added pollutants are transported from the discharge area. For example, the gyre noted in offshore waters of the southern basin of Lake Michigan may allow pollutants to reach concentrations well above those that would be expected, due to limited dilution with the water mass contained in the northern basin.

Superposition of wind on existing currents, especially in inshore areas, can alter their direction within a few hours. Such conditions are frequently noted around Lake Michigan harbors, such as the Indiana Harbor Canal (Snow, 1974).

Topography may dictate whether a pollutant remains trapped in an area or moves on. Green Bay provides an excellent example of a cul-de-sac because of the Door County, Wisconsin, peninsula. Pollutants discharged at the southern end of Green Bay are contained within the area for an appreciable amount of time, allowing natural processes to remove some of the most noxious pollutants before they reach the main body of Lake Michigan (Fitzgerald *et al.*, 1975).

The density of an effluent can be quite important in determining the immediate fate of the pollutants contained therein. An effluent of low density may rise to the surface and be carried along by wind-induced currents, perhaps into shore. This situation frequently occurs in the Chicago-Gary-Hammond area, where warmer, less dense effluents discharged by industries and municipal sewage treatment plants are pushed into the vicinity of water intakes of Chicago, Hammond, Whiting, East Chicago, and Gary (U. S. Dep. Inter., 1967; Snow, 1974). To prepare water for public consumption, municipalities must use large amounts of absorbent carbon to remove taste- and odor-causing compounds, and must add high concentrations of chlorine to disinfect the water.

If discharged at or near the bottom, an effluent with the same density as the water to which it is added will not be well mixed vertically. Under some wind conditions, subsurface currents can carry this effluent with little mixing or dilution right back to shore, where it can produce unfavorable effects on beaches and water intakes.

A waste effluent more dense than Lake Michigan water will sink, and pollutants contained in this effluent may harm benthic organisms. Hoglund and Spigarelli (1972) reported a case of a sinking plume at Point Beach Nuclear Plant near Two Rivers, Wisconsin. In winter, when cooling water discharged from this installation is warmer and denser than the colder, lighter receiving water (*cf.* Fig. 5), this denser water sinks and follows the bottom slope outward in a sinking plume.

The consequences of these situations are intensified if they are preceded by a period of low wind and sluggish water currents, when effluent concentrations build up in the discharge point vicinity. After a period of increase, the concentrated effluents may then be moved en masse by the current.

Detention Time

By dividing the volume of Lake Michigan, *ca.* 4900 km^3, by its present outflow rate, 49 km^3/yr, Winchester (1969) calculated an emptying time* of 100 years. To arrive at this value, Winchester supposed that all inputs of water ceased, but that water continued to drain through the Straits of Mackinac at its current rate (for simplicity, outflow at Chicago and evaporative losses were not included).

This 100-year value for emptying time cannot be used to characterize the detention time of chemical additives in the Lake, for this computation excludes important physical processes. As an example, inputs of water to Lake Michigan cannot be cut off; these inputs are important (in diluting out certain additives) even as the Lake empties. The concepts of emptying time and continuous dilution must be combined in order to compute the detention time of chemical additives in the Lake. To visualize the consequences of having combined these concepts, let us imagine Lake Michigan as a one-gallon container of a solution of red dye. If we pour a gallon of pure water into

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**Termed the "theoretical detention time" in the original work.*

this container and let the excess fluid spill over, the fluid left in the container will be somewhat diluted; however, the solution will still be noticeably red. If more water is added, further dilution will occur and only after large quantities of water have been added will the solution in the one-gallon container no longer appear red. The same is true of conservative additives (those which are little affected by physical, chemical, or biochemical processes) in Lake Michigan.

Keeping in mind the concept exemplified by the gallon of dye, let us calculate the theoretical detention time of water, or of chemical additives, in Lake Michigan. We can do this by following the concentration of some conservative chemical additive, called X, already in the water. Since X is conservative, it is not affected by processes of evaporation, sedimentation, or chemical alteration. Because X behaves exactly as the mass of water, we can use X to trace the detention time of the water. For our calculation, we make three initial assumptions:

(*i*) Perfect mixing has resulted in equal concentration of X at every place in the Lake.

(*ii*) Since X is conservative, X is removed only by discharge, at the Straits of Mackinac and through the Chicago diversion.

(*iii*) Sum of inflow of all diluting water equals outflow of all water.

If all inputs of X are suddenly eliminated, then the concentration of X measured in the outflow at the Straits of Mackinac (or at Chicago) will depend on the amount of time elapsed since inputs of X ceased. To describe the dilution of X with time, we can use a logarithmic equation,* such as

$$-\frac{R_d}{V}t = \ln\frac{C}{C_o}\,, \tag{1}$$

or

$$\frac{C}{C_o} = e^{-(R_d/V)t}\,, \tag{2}$$

where t = time, yr,
C_o = initial concentration of X,
C = concentration of X at time t,
R_d = rate of discharge [Mortimer (1975) used values of 42.8 km^3/yr at the Straits of Mackinac and 2.9 km^3/yr at Chicago], and
V = volume of Lake Michigan [Mortimer (1975) used 4920 km^3].

The initial concentration of conservative additive X will be reduced to one-half ($C_o/2$) about 75 years after inputs stop (Fig. 12). It will be reduced to one-fourth the original concentration ($C_o/4$) in approximately 150 years. In 100 years the concentration of X will be diluted to about 0.396 C_o.

**Rainey (1967) made a similar calculation, but he used an outflow rate of 5 × 10^6 l/sec (= 158 km^3/yr). Equations 1 and 2 are derived in Appendix A.*

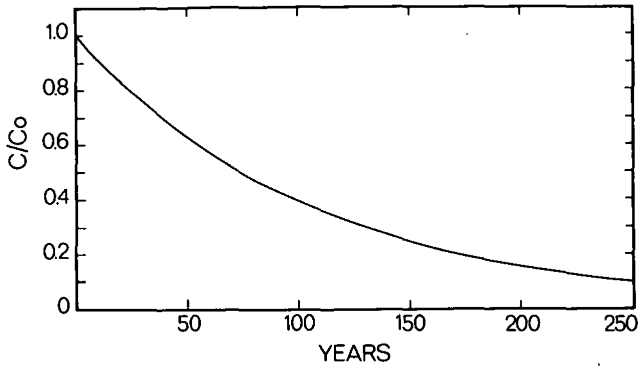

Fig. 12.

Theoretical Detention Time of Water or a Conservative Substance in Lake Michigan.

Our assumption of perfect mixing is not entirely justified. While all of Lake Michigan is probably mixed top-to-bottom at least once a year, and sometimes twice (U. S. Dep. Inter., 1967), we cannot consider it to be perfectly mixed over long periods of time. Thus, any prediction based on Equations 1 and 2 will be altered by the short-circuiting and tailing seen in every imperfectly mixed basin, and more sophisticated mathematics are needed to describe the detention time accurately. Nevertheless, the principle of discharge will remain the same: a pollutant is diluted out logarithmically, not arithmetically.

It is imperative to note that not all additives discharged to Lake Michigan are conservative. Detention times for non-conservative additives are shorter than for conservative additives, because sedimentation, evaporation, and chemical and biochemical reactions decrease the amount of *X* remaining in solution below that predicted in Equations 1 and 2.

Thus, the computation of 100 years as the theoretical detention time of water in Lake Michigan is inapplicable. This value represents only the arithmetic computation of the emptying time of the water; it does not correspond with the logarithmic manner in which water, and conservative additives, are diluted out. The logarithmic expression represented by Equations 1 and 2 is somewhat idealized, since Lake Michigan is not perfectly mixed at all times. However, the logarithmic calculation more nearly approximates the theoretical detention time of Lake Michigan water.

DYNAMIC FACTORS INFLUENCING LAKE CHEMISTRY

The chemistry of Lake Michigan is influenced by a number of factors that control the distribution and concentration of chemical substances in the aquatic environment. Some of these factors are related to features inherent in the soils of the watershed; others are closely related to meteorology, physical properties of water, lake morphometry, various factors influencing chemical reactions, communities of aquatic organisms, and cultural activities in the watershed.

Atmospheric gases (*e.g.* oxygen, nitrogen, and carbon dioxide) dissolve in rain and snow and are carried to the earth's surface along with particulate matter (*e.g.* dust) that was suspended in the air. Natural weathering processes lead to erosion and transport of dissolved and particulate matter from the watershed to the Lake. Microbial, plant, and animal communities modify the concentrations of substances in their environment by uptake, excretion, and decomposition. In turn, the dissolved and suspended substances found in water may affect the biota.

GEOLOGICAL FACTORS

The chemical compositions of the soils and geologic formations in the Lake Michigan Basin are an important influence on the composition of Lake Michigan water. Over long periods of time, chemical and mechanical weathering processes, as well as other geological forces, have broken down bedrock in the area, reshaping and reforming the Basin until today there are very few places where bedrock is exposed. Land surfaces are now covered largely by sedimentary deposits and soils derived from (*i*) weathering processes acting on bedrock and soils in the area and (*ii*) glacial deposits left behind after the retreat of the various glaciers that once covered the Great Lakes area (Hough, 1958). These sedimentary deposits and soils are continuously weathered and eroded, leading to the removal of dissolved and particulate substances (inorganic and organic) to the Lake *via* rivers, runoff, and groundwater. Minerals leached from the soil, as well as carried intact to the Lake, determine the background concentrations of many substances in Lake Michigan.

Weathering and erosional processes do not proceed at constant rates in the Basin, nor do the factors controlling these processes operate the same. Areas of greater rainfall may lose more mass per unit area to the Lake than a comparable drier area because water is a good agent of weathering (dissolution, hydration) and erosion (transport). Sections with greater relief (*e.g.* Michigan's Upper Peninsula) could lose material to the Lake more rapidly than the flatter areas found in most of the Basin. Well-drained areas, such as the southeastern part of the watershed, might be expected to lose more particulate matter to the Lake than areas with fewer drainage streams, for example, the southwestern part of the Lake Michigan Basin. Weathering is more rapid in areas subjected to freeze-thaw cycles than in areas where the temperature remains consistently below 0°C until the spring thaw. Vegetative cover also affects the amount of materials transported to the Lake; increased erosion from deforestation is a well-known phenomenon.

Because weathering and erosion do not occur at constant rates, the amount of substances added to Lake Michigan varies spatially and temporally. Temporal variations can be as short as a season or may represent changes in biogeochemical cycles over several thousands of years; spatial variations occur with changes in climatic cycles and the morphometry of the Basin.

METEOROLOGICAL FACTORS

Meteorological conditions can influence the physical limnology of Lake Michigan. Long-term climatic cycles may contribute to the cycles of high- and low-water variations throughout the Great Lakes. These variations affect shoreline erosion rates and organisms inhabiting the littoral zone. Wind conditions produce instances of seiching and upwelling (see Physical Properties section) and determine overall mixing processes in the Lake.

Seasonal variations in solar radiation input impose spatial and temporal distributions upon certain chemical compounds found in the Lake. For example, the spring thermal bar may inhibit inshore-offshore mixing for several weeks, thus temporarily modifying inshore concentrations of materials contributed by rivers and industrial and municipal sources (see Physical Properties section). Thermal stratification during summer can also lead to seasonal variations in chemical composition; for example, many atmospheric gases are less concentrated in surface water during summer than in winter because most gases are less soluble at higher temperatures (*cf.* Dissolved Oxygen and Carbon Dioxide sections).

MECHANICAL AND MOLECULAR PROPERTIES OF WATER

Decreases in the density of water above and below 3.96°C (Fig. 5) allow layers, caused by density differences, to form in the Lake during summer and sometimes in winter. These physical hindrances to vertical mixing are important to the biota, especially during the summer growing season, due to vertical segregation of nutrients and other substances.

Temperature differences that cause density differences also affect chemical processes. The solubility of many minerals is greater at higher temperatures ($CaCO_3$ is a notable exception to this generalization). Many reactions of chemical and biochemical importance occur more quickly at higher than lower temperatures.

The high dielectric constant of water largely accounts for the capacity of water to dissolve large quantities of ionic salts [*e.g.* NaCl, $CaCO_3$, $CaMg(CO_3)_2$, Na_2SO_4, and $CaSO_4$] and form ionic solutions. The formation of colloids in water also is related to its high dielectric constant (Hutchinson, 1957). The low solubility of certain organic compounds in Lake Michigan (*e.g.* organochlorine compounds) is attributable to the limited solubility of non-polar substances in high-dielectric, polar substances like water.

LAKE MORPHOMETRIC FACTORS

The morphometry of the Lake, like regional climatology, also influences spatial distributions of chemicals. Bays like Green Bay hinder mixing processes and allow concentrations of various chemicals to build up or decrease (Fitzgerald *et al.*, 1975). Basin morphometry may also contribute to differences in large-scale circulation patterns noted in the northern and southern basins (Table 3) and to north-south differences in chemical characteristics of Lake Michigan (see Bay Areas, Inshore-Offshore Differences, and Longitudinal Differences).

FACTORS AFFECTING CHEMICAL REACTIONS

Several types of chemical reactions in Lake Michigan affect the forms and concentrations in which biologically important compounds are found.

Dissolved oxygen, for example, oxidizes reduced ferrous iron to ferric iron. In the ferric form iron is a sparingly soluble solid, $Fe(OH)_3$, and is relatively unavailable for biological assimilation. There are certain sectors of the Lake where dissolved oxygen concentrations approach zero: southern Green Bay, Indiana Harbor, and bottom sediments more than about 5 cm deep. Under those conditions oxidized substances may be reduced [*e.g.* $Fe(OH)_3$ is converted to ferrous iron] and metabolic activities of anaerobic bacteria become more important. Nonmobile organisms requiring oxygen die or go into a resting state (*e.g.* spore formation by certain aerobic bacteria). Some motile organisms, such as fish, may be able to move to other areas having adequate dissolved oxygen concentrations.

Acid-base reactions are important in Lake Michigan, influencing the forms of major chemical constituents (see these sections: pH, Inorganic Carbon, Buffering, and Organic Carbon; Nitrogen; Phosphorus; Silicon; Calcium, Magnesium, and Hardness) and probably the forms of many of the minor ones as well. Acid-base reactions can also be involved in determining which chemicals remain in solution. As a single example, the precipitation of $CaCO_3$ in Lake Michigan is related to the amounts of acid and base present.

Sorption onto particulate matter is another factor affecting chemical reactions in Lake Michigan. In many instances sorptive removal of dissolved substances onto ferric and manganic hydroxides, organic matter, and clay-sized particles (Shimp *et al.*, 1970, 1971; Lineback and Gross, 1972; Leland *et al.*, 1973a, 1973b) is an important mechanism removing trace constituents (trace metals and organochlorine insecticides) from the water and concentrating them in a particulate form.

Complexation reactions, involving the close association of two or more chemical species in solution, variously serve (*i*) to keep certain trace constituents (*e.g.* iron) in solution, making them more readily available to plants and microorganisms, and (*ii*) to alter the toxicity of certain trace metals, *e.g.* copper (Stiff, 1971).

BIOLOGICAL MODIFICATION OF LAKE CHEMISTRY

Organisms in the Lake affect the forms and amounts of certain chemical compounds and nutrients found in the water and sediments (see these sections: Dissolved Oxygen; pH, Inorganic Carbon, Buffering, and Organic Carbon; Nitrogen; Phosphorus; and Silicon). Competition among the various organisms may regulate or even limit the availability of these nutrients, as discussed below in the sections on nitrogen, phosphorus, and silicon. Differences in spatial distributions of populations may be caused by or may lead to noticeable differences in nutrient concentrations (see section on Bay Areas, Inshore-Offshore Differences, and Longitudinal Differences).

Net photosynthesis determines the total amount of energy available to other trophic levels in Lake Michigan. During late spring and summer, photosynthesis is confined largely to surface waters because of the optimal combination there of warmer temperatures, adequate light, and the presence of nutrients. As a result of photosynthetic activities, dissolved nutrients may become depleted in summer surface waters (*cf.* Fig. 47) in favor of particulate forms of these nutrients. While there is a certain amount of decomposition and recycling of nutrients like phosphorus and silicon in surface waters, sedimentation of phytoplankton and other particulate matter from the epilimnion may lead to a progressive accumulation of certain nutrients in the hypolimnion (see Fig. 71) and sediments. Microbial degradation during and after sedimentation converts many compounds, for example, organic nitrogen, to a biologically available form like ammonia or nitrate. Limited mixing across the thermocline returns a small amount of the biologically important substances to the epilimnion; however, fairly homogeneous concentrations are achieved once again only after fall turnover. Return of some biologically important compounds to their former concentrations in surface water at fall turnover has a limited effect, over the short term, on the biota. Surface-water temperatures in fall, winter, and spring generally are lower than in summer and daylength is short so that differences in spatial distribution of chemicals attributable to biological activities are much less pronounced, if not absent, in winter than in summer. Only during the following spring are the effects of the previous fall mixing fully expressed.

INFLUENCE OF CULTURAL ACTIVITIES

Concentrations of total solids, chloride, sulfate, nitrate, albuminoid nitrogen, phosphorus, silica, lead, mercury, and certain organic contaminants in Lake Michigan have been affected by cultural activities in the watershed (see section on Changes in Water Quality and Sediment Chemistry). Major quantities of inorganic and organic substances, plus lesser quantities of trace metals and new synthetic organic compounds, are being added each year by ship and harbor discharges, urban and rural runoff, aerosol deposition, and municipal and industrial waste effluent discharges.

Increased inputs of nutrient substances like phosphorus may be increasing the rates of nutrient cycling in the Lake (see these sections: Nitrogen, Phosphorus, and Silicon). Increased inputs of trace metals (*e.g.* lead) and certain synthetic organic compounds like organochlorine compounds may adversely affect the biota of the Lake, either directly or through biological magnification.

RESIDUES

Total residue, or total solids, is that material remaining after a water sample has been evaporated and subsequently oven-dried at a defined temperature. At one time, substances in natural waters were classified either as dissolved, *i.e.* materials that would pass through a filter, or as suspended, *i.e.* materials that were retained by a filter. Not all analytical methods for residues produce the same results, and it is difficult to control the variables which cause the differences among methods. Because the results of the determination of dissolved and suspended substances depend on the procedures used to effect the separation, the terms filterable (passing through a filter) and nonfilterable residues are preferable (EPA, 1973). Use of the terms filterable and nonfilterable residues, therefore, acknowledges that dissolved and suspended solids are not precisely what was determined. By custom the term total dissolved solids (TDS) is frequently used although filterable residue is more accurate. Likewise, total suspended solids (TSS) is used in place of nonfilterable residue.

Results of a solids determination depend strongly on drying temperature. Residues dried at 103-105°C retain water of crystallization and some mechanically occluded water (APHA *et al.*, 1971); some bicarbonate is converted to carbonate, with a loss of CO_2 and water ($2\ HCO_3^- \rightarrow H_2O + CO_3^{2-} + CO_2 \uparrow$). Residues dried at 179-181°C lose almost all mechanically occluded water; some water of crystallization is retained; a portion of the organic matter is volatilized; bicarbonate is converted to carbonate, and carbonates may be partially converted to oxides; and some chloride and nitrate salts may volatilize. Values for filterable residues obtained by drying at 180°C generally are similar to those obtained by summing all of the individually determined mineral salts.

TOTAL DISSOLVED SOLIDS

Dissolved solids (filterable residue) in Lake Michigan consist mainly of calcium, magnesium, sodium, potassium, carbonates, bicarbonates, chlorides, sulfate, and some nitrates and phosphates. There are also traces of iron, manganese, and other substances. All matter dissolved in water changes the physical and chemical properties of the water and exerts osmotic pressure. Although individual substances may have physiological or toxic effects, the following discussion of the importance of dissolved solids is confined to effects attributable to total salt concentration, or osmotic pressure. The discussion does not consider the effects of salt constituents taken separately. Individual substances making up the TDS content are considered in subsequent sections of this volume.

People unaccustomed to water that tastes of minerals object to excessive concentrations of TDS in drinking water on the basis of taste (U. S. Public Health Service, 1962). In addition, if the sum total of magnesium plus sulfate content exceeds 1000 mg/l or the TDS content is above 2000 mg/l, then the water has a laxative effect on most persons. A similar effect is noted when livestock and poultry drink water with TDS concentrations above 1000 mg/l (National Academy of Sciences ..., 1973). Concentrations of TDS equivalent to or greater than 7000 mg/l as sodium chloride produce noticeable osmotic stress in adult fish (McKee and Wolf, 1963). This TDS concentration is higher than exists in most fresh waters of the United States (National Academy of Sciences ..., 1973); however, it is important to note that toxic effects of many individual dissolved substances are noted at concentrations much lower than those at which osmotic effects are apparent. High TDS levels are objectionable in industrial processes due to formation of boiler scale; acceleration of corrosion; and interference with clearness, color or taste in a number of finished products (McKee and Wolf, 1963).

Before urbanization and industrialization within the Basin, natural sources were the only supply of dissolved solids to Lake Michigan. Base flow of the tributaries contributes large quantities of dissolved salts (Waller and Allen, 1975). Overland flow also contributes dissolved material to the Lake, but it is of major importance only during periods of high surface runoff. Now, however, municipal and industrial waste effluents, agricultural runoff, and aerosol fallout are adding major quantities of dissolved solids over and above that brought in by natural sources. The amount of TDS discharged by the 117 major industrial polluters tabulated by Businessmen for the Public Interest (1972) is almost one-seventh of that carried into Lake Michigan by its tributaries (Ayers, 1970). Chemical manufacturing in the vicinity of Ludington and Manistee, Michigan, is said to have provided over two-thirds of the industrially based sources of dissolved solids (Businessmen for the Public Interest, 1972).

Because the TDS content is an important consideration in the acceptability of drinking water and the protection of aquatic life, monitoring programs frequently specify regular determinations of this parameter. Table 4 illustrates that nearly all the recent, readily available data on TDS content

Table 4. Total Dissolved Solids Content in Lake Michigan Water

Sample Description	Dates	Concentration, mg/l Average	 Range	Reference
Samples collected ~monthly from Peter Cooper Corp. intake, Oak Creek, ~0.75 km (2500 ft) offshore	1961	157	149-179	Wis. Comm. Water Pollut., 1965
	1962	162	150-179	
	1963	159	143-183	
	1964	153	147-162	
	1965	157	148-165	Wis. Dep. Nat. Resour., 1969
	1966	161	148-182	
	1967	163	152-175	
	1968	162	153-174	
	1969	181	153-370	Wis. Dep. Nat. Resour., 1973
	1970	180	145-370	
	1971	163	136-174	
	1972	174	155-183	
Whole Lake:	1962-63			USDOI, 1968
976 inshore samples		175	80-810	
417 offshore samples		155	100-240	
Samples (surface, 20 m, 1/4 and 3/4 the distance between 25 m and bottom) collected:				Powers and Ayers, 1967
9 offshore stations south of a line between Holland and Racine	Apr-Nov 1965	170		
	Mar-Jun 1966	154		
6 offshore stations south of a line between South Haven and Waukegan	Apr-Nov 1965	170		
	Mar-Jun 1966	156		
6 offshore stations--3 on a line between Holland and Racine and 3 on a line between Ludington and Sheboygan	Apr-Nov 1965	170		
	Mar-Jun 1966	155		
Samples collected in Indiana Harbor at east breakwall inner light:				Snow, 1974
3 samples	Dec 1965	220	210-225	
51 samples	Jan-Dec 1966	225	128-266	
42 samples	Jan-Dec 1967	228	164-274	
37 samples	Jan-Dec 1968	223	158-267	
25 samples	Jan-Jun 1969	247	200-323	
20 samples	Jan 1971-Jan 1973	209	170-270	
Samples collected at Chicago South Water Filtration Plant	1966	159		Vaughn and Reed, 1973
	1967	161		
	1968	162		
	1969	162		
	1970	166		
	1971	173		
Annual averages for samples collected at water filtration plants near Chicago:				
12 plants	1968	165	162-166	Ill. Sanit. Water Board, 1969
5 plants	1969	166	164-167	Ill. Sanit. Water Board, 1970
Samples collected ~weekly at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	Nov 1969-Sep 1970	155	135-169	USGS, 1972
	Oct 1970-Sep 1971	152	138-171	USGS, 1973
	Oct 1971-Sep 1972	150	140-162	USGS, 1974a
	Oct 1972-Jun 1973	155	143-183	USGS, 1974b
Monthly samples collected, surface to bottom, at 3 stations 9.6 km (6 mi) east of Zion	Feb 1970-Apr 1971	157	122-210	Industrial Bio-Test, 1972b
Monthly samples collected at intakes:	Mar 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		165	134-215	
Waukegan Generating Station		171	146-207	
North Chicago public water supply		158	138-186	

Table 4. (contd.)

Sample Description	Dates	Concentration, mg/l		Reference
		Average	Range	
Monthly samples collected at Lake County, Ill., public water intake	Jun 1970-Apr 1971, Jul 1972-Jun 1973	168	120-220	Howe, 1973
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		178[a]	151-224[a]	
Effluent plume		174[a]	148-215[a]	
South of plant, 4.8 km (3 mi)		169[a]	146-192[a]	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		178[a]	124-218[a]	
North of plant, 1.6 km (1 mi)		176[a]	109-236[a]	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		178[a]	153-189[a]	
South of plant, 1.6 km (1 mi)		180[a]	163-193[a]	

[a] *Monthly means taken from graphs.*

USDOI = U. S. Department of the Interior; USGS = U. S. Geological Survey.

in Lake Michigan waters have been collected in inshore waters, mostly from municipal and industrial water intakes. Furthermore, all data in Table 4 were collected in the southwestern quadrant of the Lake, with the exception of the determinations performed by the U. S. Department of the Interior (1968) and by Powers and Ayers (1967). Concentrations of TDS in the southwestern portion of the Lake are apparently increasing with time. This trend has been noted (Beeton, 1965, 1969; Beeton and Edmondson, 1972) and will be considered in more detail in a following section (Changes in Water Quality and Sediment Chemistry).

Figures 13 and 14 illustrate seasonal variations of TDS content in inshore waters. Within a fairly small area (Fig. 13), stations generally show the same trends. Data from more widely separated stations (Fig. 14), which are subject to more diverse influences, show that differences in stream influx, surface runoff, current movement, and effects of wave-generated turbulence contribute to site and time variations between the stations. The proximity of a station to municipal and industrial effluent discharge sites creates major station-to-station differences in TDS concentrations.

Although for this report there were no data readily available on the seasonal variations of TDS in offshore (> 16 km) areas, Industrial Bio-Test (1972b) sampled three stations 9.6 km (6 mi) east of Zion, Illinois, on a monthly schedule. Figure 15, based on these three stations, represents variations at sites farther from shore, but still within the influences of shore. TDS content at these stations averaged 157 mg/l over a one-year period, and was less variable than at inshore stations (Figs. 13 and 14). The sharp drop in concentration on 18 May 1970 at all three stations (Fig. 15) may be due to procedural error. Increases in March and April 1971 probably reflect effects of spring runoff, suggesting that the influence of inshore processes is measurable even at a distance of 9.6 km.

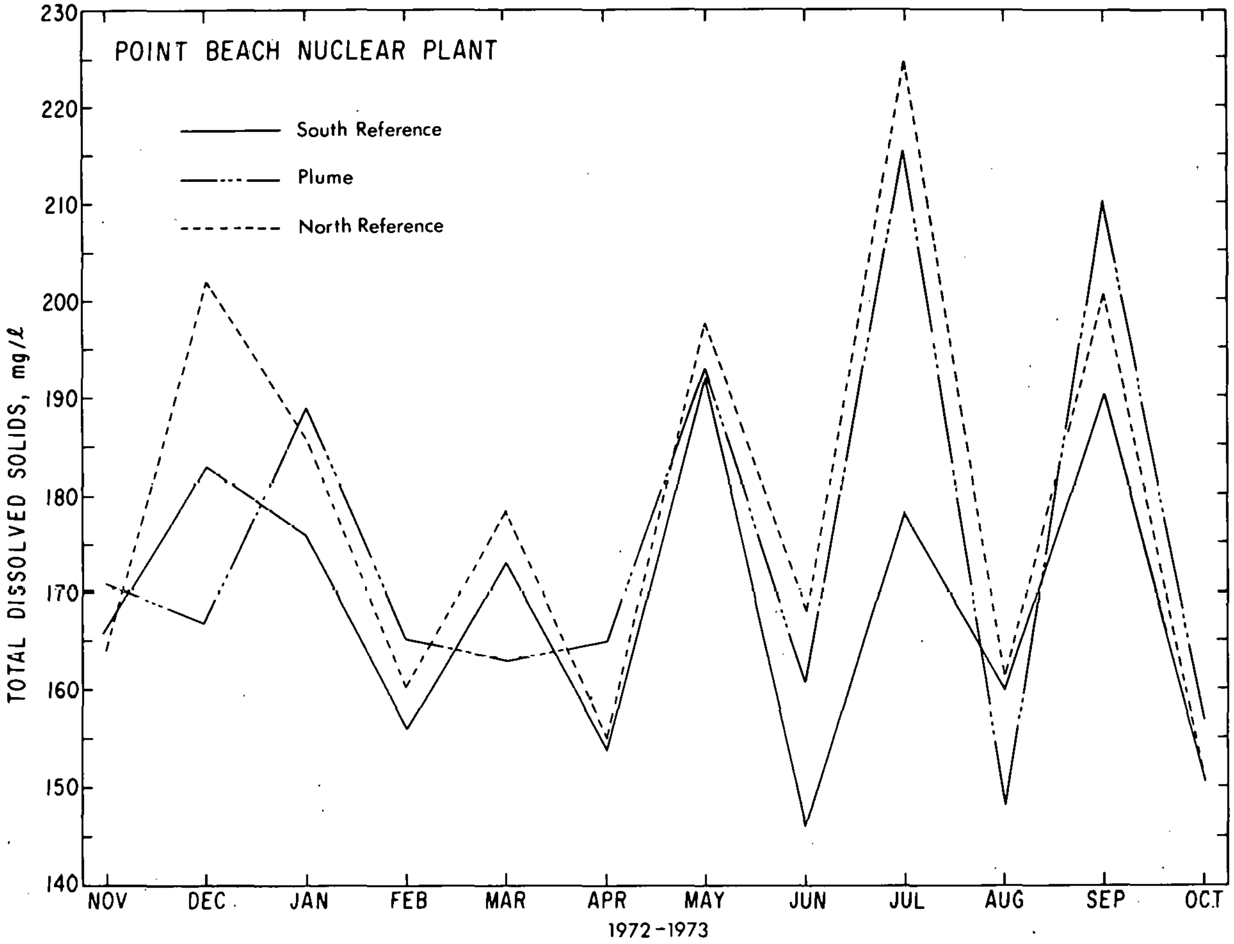

Fig. 13. Average Total Dissolved Solids at Point Beach Nuclear Plant near Two Rivers. See Table 4 for sample descriptions. Data from Limnetics (1974).

As stated above, most of the information on TDS content in Lake Michigan waters has been gathered during monitoring programs in compliance with various legal requirements. TDS levels in Lake Michigan (Table 4) are approaching the rigorous limit of 180 mg/l set by the Illinois Pollution Control Board (cited by Vaughn and Reed, 1973); this regulation encompasses the portion of Lake Michigan lying within Illinois boundaries. One-fourth of 250 samples taken in 1971 at Chicago's South Water Filtration Plant exceeded 180 mg TDS/l (Vaughn and Reed, 1973). It should be pointed out that all values in Table 4 are below the objective of 200 mg/l or less set for the International Great Lakes (U. S. Treaties, etc., 1972). Concentrations listed in Table 4 are well within the recommended limit of 500 mg/l for public drinking water supplies (U. S. Public Health Service, 1962).

TOTAL SUSPENDED SOLIDS

Suspended solids (nonfilterable residue) in natural waters have both inorganic and organic components. Erosion processes remove clay, silt- and sand-sized particles and organic detritus from the land surface and carry them to Lake Michigan and its tributaries. Within the Lake, particulate matter is

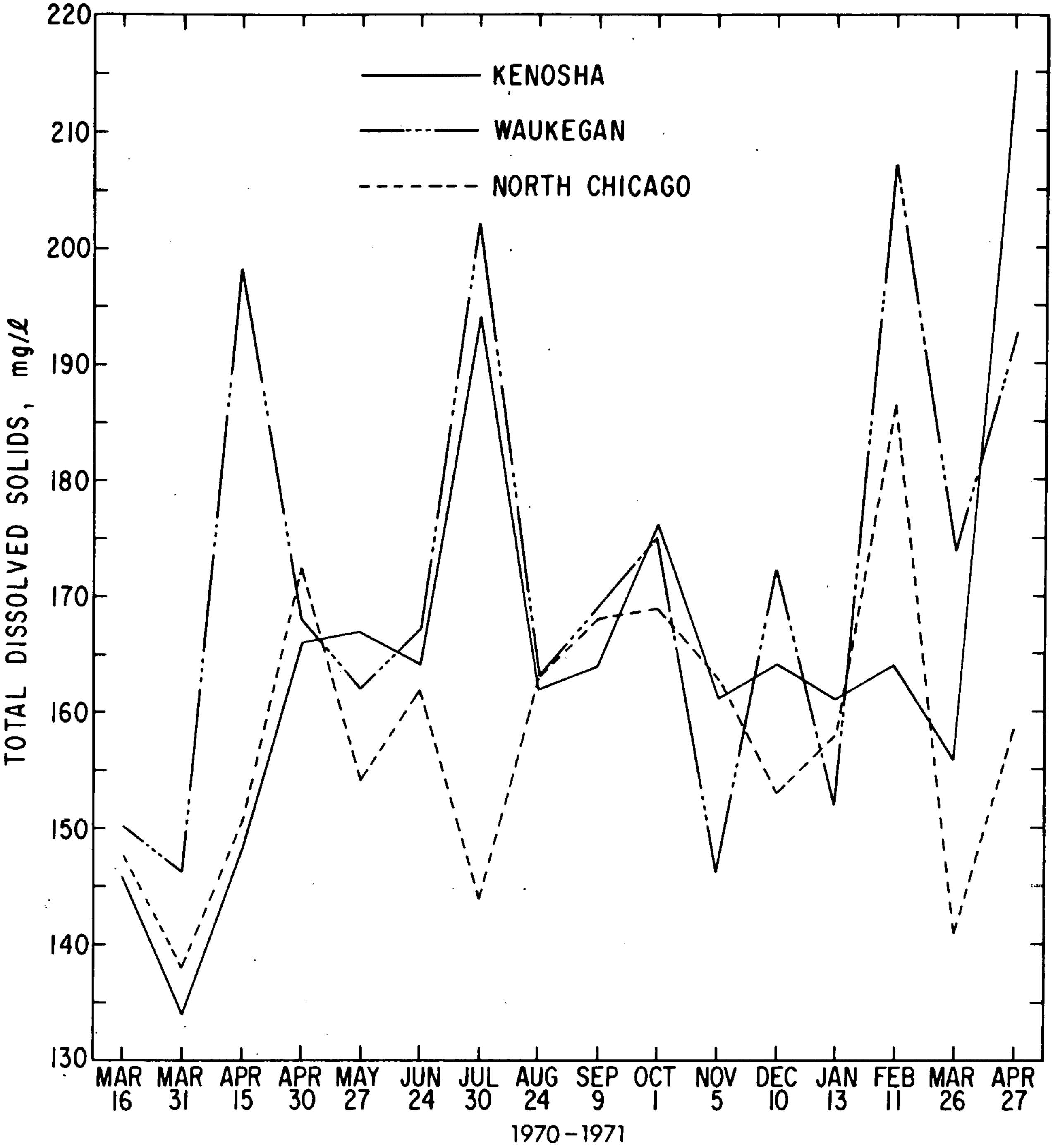

Fig. 14. Total Dissolved Solids at Intakes of Kenosha and North Chicago Water Treatment Plants and Waukegan Generating Station. Data from Industrial Bio-Test (1972a).

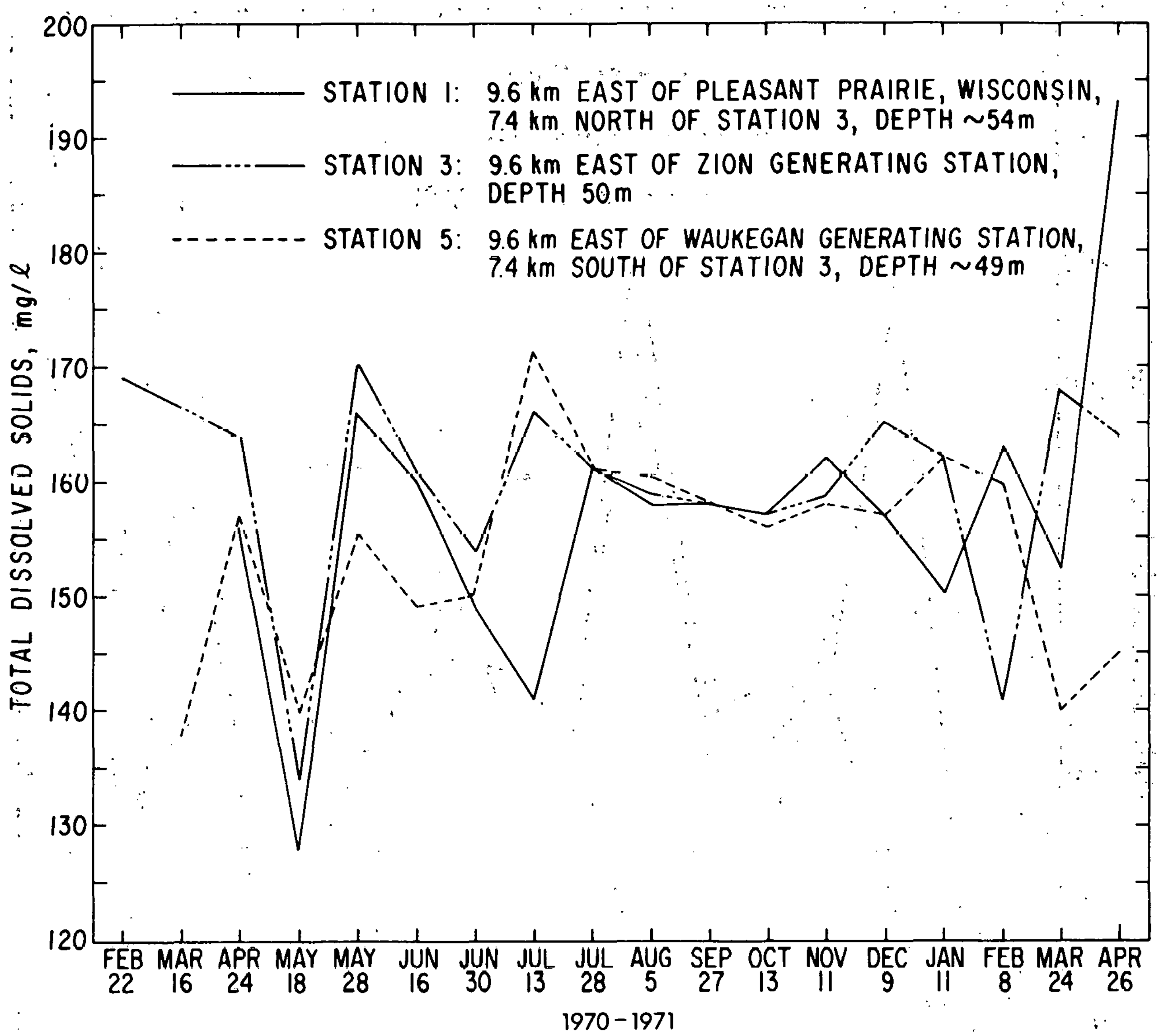

Fig. 15. Average Total Dissolved Solids at Three Stations East of Zion. During stratification, two samples were collected above and two below the thermocline. During periods of mixing, samples were collected at surface, middle, and bottom. Data from Industrial Bio-Test (1972b).

moved about by currents and is resuspended from the bottom by turbulent wave action. Solid matter also is formed within the Lake water (*e.g.* milky water caused by precipitation of $CaCO_3$). Phytoplankton (free-floating algae), zooplankton, and bacteria are part of the TSS and upon their death become part of the particulate organic matter.

Suspended solids are an important consideration in a drinking water supply, as they affect aesthetic acceptability. Many people switch to alternate sources of drinking water if the available water is turbid with suspended solids. Even without taking into account possible toxic effects of chemicals leached out by water from particulate matter, high suspended solids levels can be damaging to aquatic ecosystems because they reduce the depth of light penetration, clog gills of fish and mussels, and by sedimentation cover bottom habitats. Suspended solids content is critical for industries because particles can form incrustations on heat-exchange surfaces, cause imperfect dye transfer to textiles, reduce brightness of paper, or cause cloudiness in processed foods and beverages.

Natural erosional processes transfer suspended solids to any natural body of water; however, human activities alter and increase the suspended solids content of surface waters through increased erosion from deforested and cultivated land, by addition of mine tailings, and by increased wind transport of particulate matter from land to water. Municipal waste effluents add suspended solids to Lake Michigan; concentrations of suspended solids expected in effluents from activated sludge treatment range from 10 to 50 mg/l (EPA, 1975a). Certain industrial wastes contribute large quantities of suspended solids. The amount of TSS discharged by 117 major manufacturers (Businessmen for the Public Interest, 1972) is nearly one-fourth of that carried naturally into Lake Michigan by its tributaries (Ayers, 1970). Pulp and paper manufacturing plus metal-refining industries contributed over 95% of the industrially based sources of suspended solids (Businessmen for the Public Interest, 1972). Most of those solids are dumped into a relatively small area, such as Green Bay or the southwestern end of the Lake.

Because turbidity is easier to determine (see APHA *et al.*, 1971), it is monitored more frequently than suspended solids content. Few records of TSS content in Lake Michigan are available, and those data are confined to the southwestern portion of the Lake. Seasonal variations in TSS near Two Rivers (Fig. 16) and Kenosha, Waukegan, and North Chicago (Fig. 17) reflect the influence of inshore hydrodynamic processes. Concentrations are high during spring mixing (March and April) and fall mixing (November, December, and January) and are fairly low at other times. The flush of spring runoff also contributes to the high values in spring. With increasing distance from shore, the effects of wind-driven currents, turbulence, and tributary inflow are diminished. In monthly samples collected from February 1970 through April 1971, Industrial Bio-Test (1972b) found TSS concentrations above 1 mg/l in only one-fifth of the 170 samples collected at three stations 9.6 km (6 mi) east of Zion, Illinois. The highest value was only 10 mg/l, compared with the high shoreline value of 120 mg/l observed in the intake canal of the Waukegan Generating Station (Fig. 17).

Criteria and objectives pertaining to suspended solids for the protection of aquatic life are indicated in Appendix B, part 2.

SPECIFIC CONDUCTANCE

The ability of any substance to conduct an electrical current is termed its electrical conductance. The specific electrical conductance of water is defined as the conductance across a cube of water, 1 cm on a side; this value is usually expressed as micromhos per centimeter (μmhos/cm). Since the specific conductance of an aqueous solution increases about 2% per degree Centigrade, specific conductance data are usually reported at a standard temperature, often 25°C; all conductance data in this report are at 25°C unless stated otherwise.

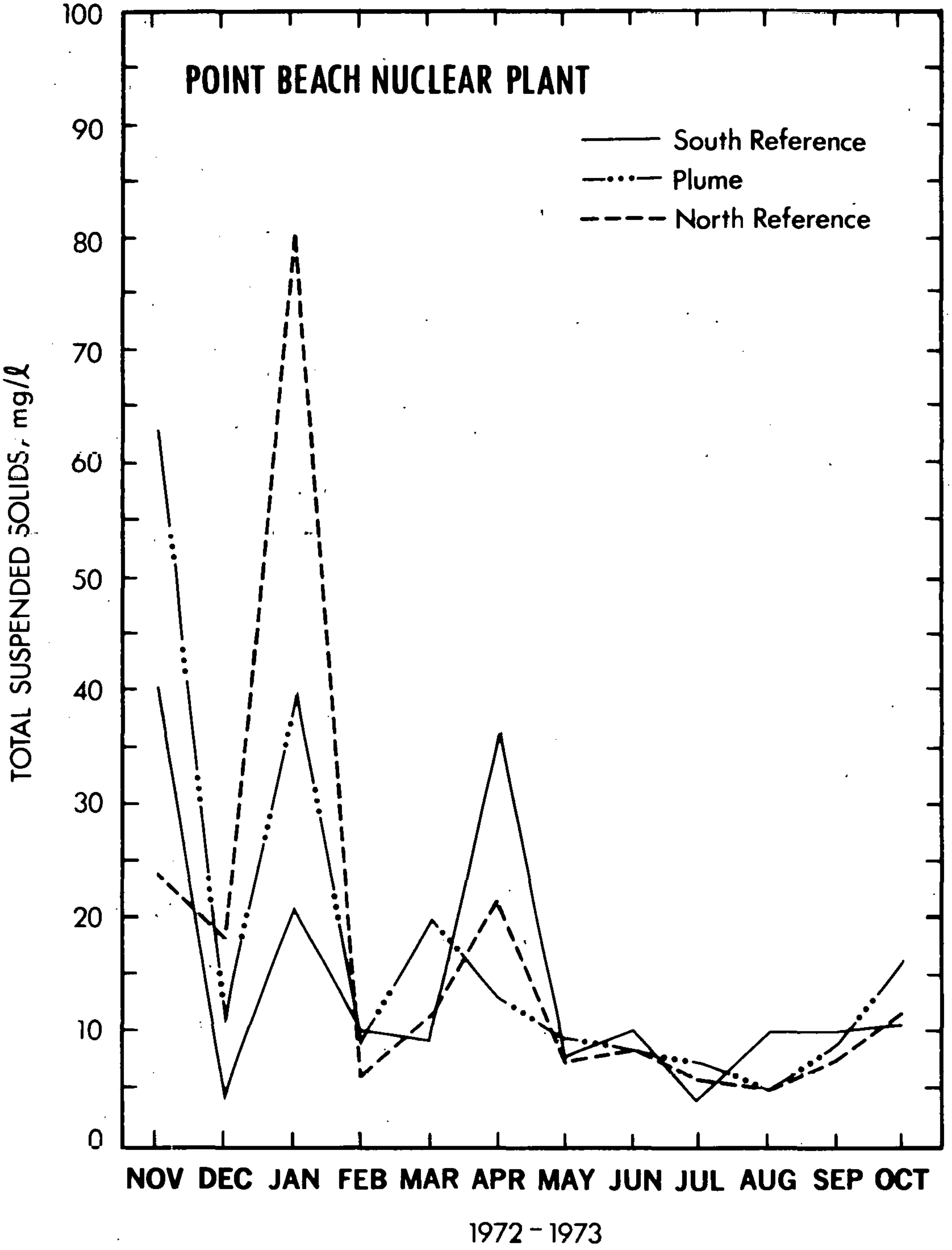

Fig. 16. Average Total Suspended Solids at Point Beach Nuclear Plant near Two Rivers. Sample descriptions are the same as in Figure 13. Modified from Limnetics (1974).

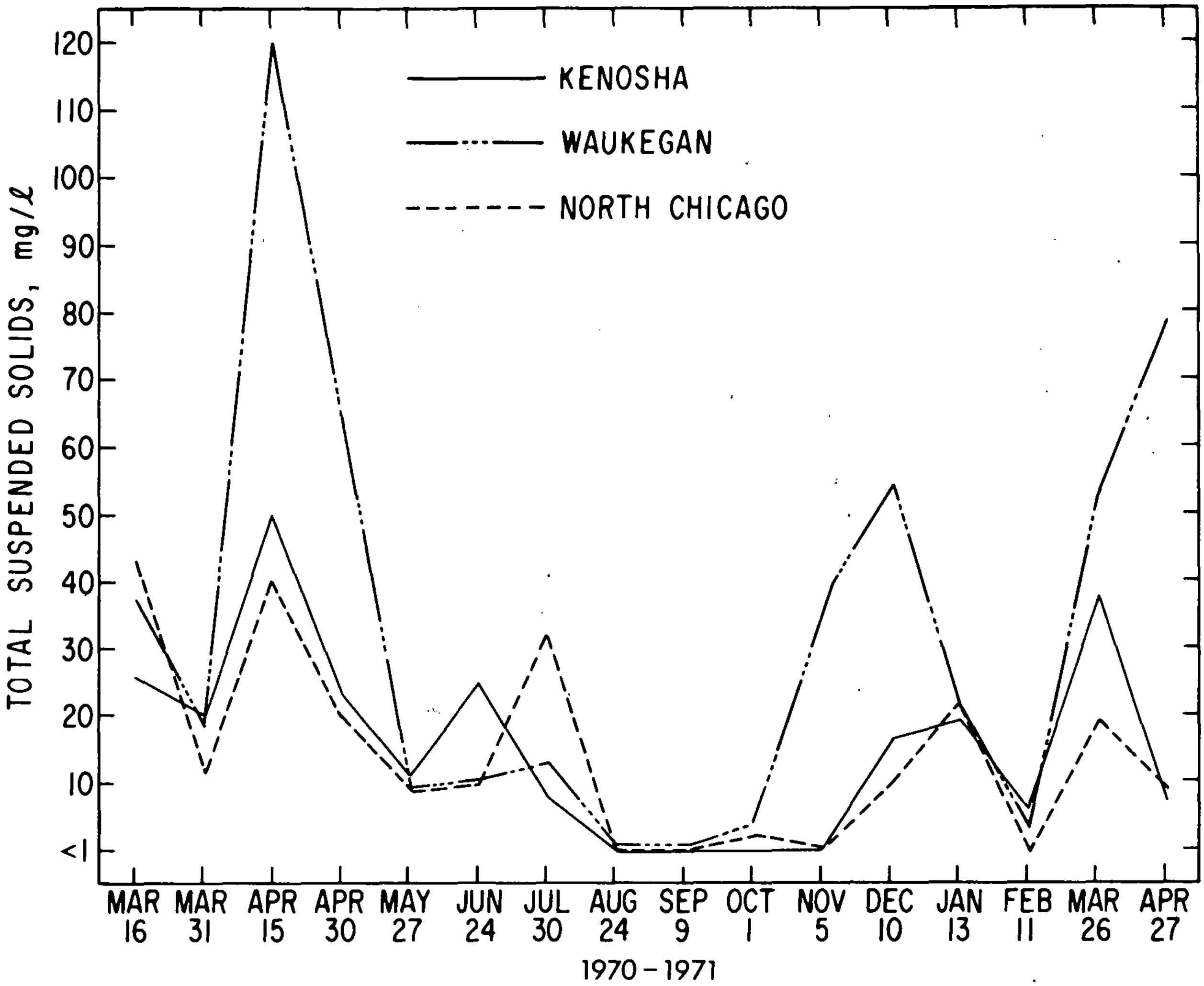

Fig. 17. Total Suspended Solids at Intakes of Kenosha and North Chicago Water Treatment Plants and Waukegan Generating Station. Data from Industrial Bio-Test (1972a).

Freshly distilled water has a negligible specific conductance. Natural waters like Lake Michigan, however, contain cations and anions formed by dissociation of inorganic and organic salts, and these ions make the water conductive. In a dilute solution containing only one salt (*e.g.* NaCl), specific conductance and TDS content are directly and linearly related. But Lake Michigan water contains more than one salt. Indeed, they can be thought of as a heterogeneous mixture of a number of dissociable substances, each with its own characteristic relationship between concentration and specific conductance. Examples of the variation of conductance with concentration for four common chemicals are illustrated in Figure 18. Thus, the ability of a natural water sample, containing a variety of cations and anions, to conduct electricity depends on the quantity and kinds of ions present, their relative charge, and their physicochemical properties. Because of these complexities, there is no exact relationship in natural waters between conductance and dissolved solids.

However, the equation

$$\text{Specific Conductance } (\mu\text{mhos/cm @ } 25°\text{C}) \times A = \text{Total Dissolved Solids (mg/l)} \qquad (3)$$

is often used to approximate the total dissolved solids (TDS) content; unless the water has an unusual composition (Hem, 1959), the factor A is generally between 0.55 and 0.75.* In the absence of an experimentally determined value for A, the factor 0.65 is most often employed. However, use of 0.65 for the coefficient A in Equation 3 is perhaps inappropriate for Lake Michigan. Raw data for specific conductance and TDS were collected by Industrial Bio-Test (1972a) at the Kenosha, Lake County, and North Chicago Water Filtration Plant intakes and the intake canal of the Waukegan Generating Station. These data were used to calculate A for inshore water of southwestern Lake Michigan; statistical analysis (least squares plot forced through the origin) produced a coefficient of 0.61. A similar computation for three stations 9.6 km (6 mi) east of Zion, Illinois (Industrial Bio-Test, 1972b), resulted in a coefficient of 0.60. If the analytical techniques of Industrial Bio-Test (1972a, 1972b) are adequate and unbiased, then use of the factor 0.65 to convert specific

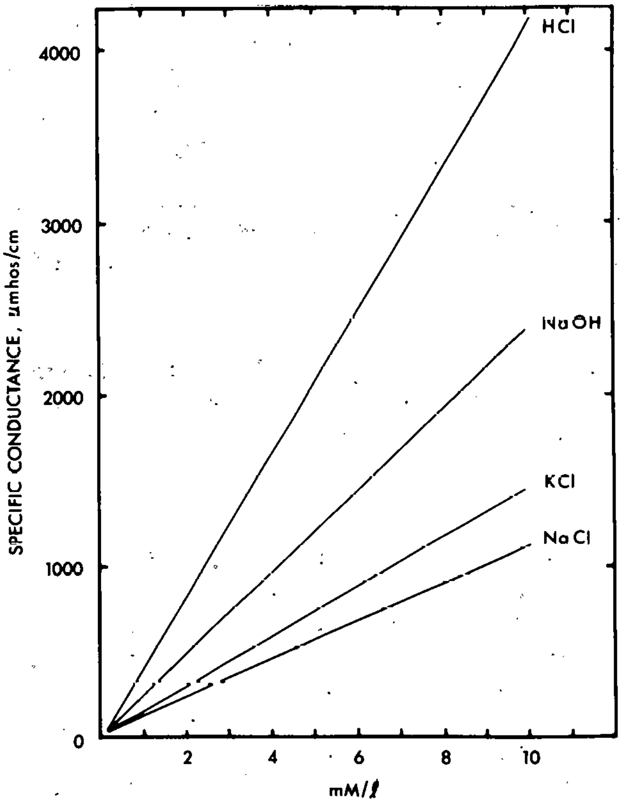

Fig. 18.

Variation of Specific Conductance with Different Concentrations of HCl, NaOH, KCl, and NaCl.

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*The derivation and meaning of the coefficient A in the equation relating specific conductance and total dissolved solids are discussed in greater detail in Hem (1959).

conductance data to TDS content may produce a slight overestimate for the southwestern portion of the Lake. Further information on this point is desirable for other areas of the Lake.

Specific conductance values by themselves have no relation to any chemical or biological property of Lake Michigan water. However, as estimators of TDS content, they have the same significance as TDS measurements. That is, excessively high values may indicate that use of the water as a drinking water supply is undesirable, that aquatic life may suffer osmotic shock, that irrigation may not be advisable, and that certain industrial processes may be adversely affected. Streams and rivers supporting good mixed fish populations generally have specific conductance values between 150 and 500 μmhos/cm (cited by McKee and Wolf, 1963).

Table 5 summarizes specific conductance determinations throughout Lake Michigan. Although Table 5 does not present any evidence of short-term variations in specific conductance, several studies have documented seasonal changes in this parameter. Limnetics (1974) sampled three inshore stations at the 3.7-, 5.5-, and 7.3-m (12-, 18-, and 24-ft) water-depth contours in the vicinity of Two Rivers, Wisconsin (Fig. 19). Each data point in Figure 19 represents the average of all samples taken at the surface, the middle, and the bottom at each station. Figure 19 shows that specific conductance is not constant over time at these inshore stations. The peak in conductance values in January is correlated with high turbidity values; perhaps wave action caused by winter storms stirred the bottom sediments sufficiently so that dissolved and suspended solids were transferred to the overlying waters. The secondary maximum in April most probably can be attributed to dissolved solids carried into Lake Michigan by spring runoff, and to wave action stirring up the sediments.

Although Beeton and Moffett (1964) did not collect samples in January, February, and March, their data provide evidence that specific conductance varies both seasonally and with depth. Figure 20 illustrates data collected in 1954 at a station 12.9 km (8 mi) west of Grand Haven. Specific conductance was highest at all depths during May. Conductance values then drifted downward until the end of October, when a slight upward trend was noted. The greatest range in conductance values (250-290 μmhos/cm) was recorded in samples collected at the surface during the period May to December; the smallest (258-273 μmhos/cm), at 70 m. During stratification (25 June-19 November), surface samples averaged 256 μmhos/cm, while bottom (70 m) waters averaged 261 μmhos/cm. A statistical test (t-test) shows that this difference is significant at the 95% confidence level. However, this statistical difference probably has neither chemical nor biological significance, since laboratory measurements of specific conductance are good only to ± 5% (Hem, 1959; APHA *et al.*, 1971); applying the factor of ± 5% to these averages shows considerable overlap (256 ± 13 μmhos/cm and 261 ± 13 μmhos/cm). Data recorded at three stations 9.6 km (6 mi) east of Zion, Illinois (Industrial Bio-Test, 1972b), also showed a statistical difference between surface (262 μmhos/cm) and bottom (265 μmhos/cm) waters, but again there is probably neither chemical nor biological significance in this difference.

Table 5 shows that inshore values of specific conductance tend to be higher than offshore values. One would expect such a trend, since municipal and industrial waste effluents are discharged near shore, tributaries carrying dissolved solids empty into the Lake at the shore, and groundwater bearing

Table 5. Specific Conductance Values at 25°C in Lake Michigan Water

Sample Description	Dates	*Specific Conductance* µmhos/cm* Average	Range	Reference
Samples collected, surface to bottom:				Beeton and Moffett, 1964
Southern basin and divide area				
387 inshore samples	May-Dec 1954	260	248-290	
427 offshore samples	May-Nov 1954	258	246-284	
Northern basin and divide area				
337 inshore samples	Mar-Nov 1955	256	218-304	
250 offshore samples	May-Nov 1955	256	244-262	
Southern basin				
3 inshore stations, 70 samples	Apr-Nov 1960	254	237-283	
1 offshore station, 13 samples	May, Jul-Sep 1960	252	241-260	
Northern basin				
5 inshore stations, 101 samples	May-Nov 1961	265	240-278	
2 offshore stations, 41 samples	May-Nov 1961	266	256-273	
Whole Lake:	1962-63			USDOI, 1968
2452 inshore samples		285	33-1130	
918 offshore samples		260	185-345	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City		280	215-500	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo		270	195-360	
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor		280	190-530	
On a line roughly between Sheboygan and Little Sable Point		220	225-350	
Samples collected:	1962-63			USDOI, 1968
Indiana Harbor, 24 samples		355	245-500	
Calumet Harbor, 30 samples		285	240-325	
Chicago Harbor, 10 samples		315	270-350	
Racine Harbor, 8 samples		305	230-335	
Samples collected:	Oct 1962, Jun 1963			USDOI, 1968
Milwaukee Harbor, 48 samples		393	245-585	
Adjacent to Milwaukee Harbor, 310 samples		310	220-485	
Samples collected:	22-28 Jul 1964			USDOI, 1968
Traverse Bay, 78 samples		305	300-315	
Adjacent to Traverse Bay, 29 samples		305	300-310	
Samples collected in Indiana Harbor at east breakwall inner light:				Snow, 1974
3 samples	Dec 1965	400	390-420	
51 samples	Jan-Dec 1966	372	310-470	
42 samples	Jan-Dec 1967	366	275-500	
37 samples	Jan-Dec 1968	340	300-420	
25 samples	Jan-Jun 1969	388	309-470	
20 samples	Jan 1971-Jan 1973	514	295-670	
Samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore:				
3 samples	Dec 1969; Jan, Sep 1970	247	225-276	USGS, 1972
10 samples	Nov 1970-Sep 1971	281	271-302	USGS, 1973
7 samples	Oct 1971-Sep 1972	269	265-272	USGS, 1974a
9 samples	Oct 1972-Jun 1973	274	264-302	USGS, 1974b
Monthly samples collected at intakes:	May 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		285	262-324	
Waukegan Generating Station		287	262-331	
North Chicago public water supply		275	255-286	

Table 5. (contd.)

		Specific Conductance µmhos/cm*		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Samples collected ∿monthly at 3 stations 9.6 km (6 mi) east of Zion:	May 1970-Apr 1971			Industrial Bio-Test, 1972b
Surface-water (1 m)		262	245-272	
Bottom-water (∿50 m)		265	252-277	
Monthly samples collected at Lake County, Ill., public water intake	Jun 1970-Jun 1973	277	234-322	Howe, 1973
Single surface-water sample collected at Mackinaw City dock	8 Jul 1970	261		Schelske and Roth, 1973
Samples collected at 8- to 21-day intervals (except 3 Feb-11 Mar) at a depth of 4 m:	Dec 1970-Oct 1971			Rousar, 1973
4.8 km (3.0 mi) east of Milwaukee		265	257-278	
Between Milwaukee and Ludington				
1/4 the distance		259	252-265	
1/2 the distance		259	251-266	
3/4 the distance		259	252-273	
4.8 km (3.0 mi) west of Ludington		262	252-276	
Samples collected (water depth 7.6 m) at a station east of Kewaunee Nuclear Plant:				Industrial Bio-Test, 1972d
Surface	25 May 1971	267	265-270	
Bottom	25 May 1971	267	265-268	
Surface	31 Aug 1971	262	260-263	
Bottom	31 Aug 1971	261	260-261	
Surface	16 Nov 1971	275	274-276	
Bottom	16 Nov 1971	274	273-275	
Samples collected <3.2 km (2 mi) offshore near Point Beach Nuclear Plant:				Weschler *et al.*, 1972
33 samples	Jun 1971	254[a]	250-260[a]	
28 samples	Jul 1971	260[a]	255-260[a]	
24 samples	Aug 1971	214[a]	200-230[a]	
27 samples	Sep 1971	260[a]	255-265[a]	
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun 1971-Apr 1972	289	268-328	Industrial Bio-Test, 1972c
Samples collected at 2 m and 15 m within the area bounded by lines connecting Milwaukee to Grand Haven and Sturgeon Bay to Frankfort:	8-14 Jul 1971			Rousar and Beeton, 1973
9 inshore stations		254		
8 offshore stations		259		
Monthly surface-water (2 m) samples collected near Milwaukee:	Oct-Dec 1971; Jan, Feb, Jun 1972			Beeton and Barker, 1974
8 stations <10 m deep		270	238-306	
4 stations 10-20 m deep		265	236-276	
5 stations 20-105 m deep		261	254-265	
Samples collected, surface and bottom, at 6 stations located every 0.8 km (0.5 mi) from 3.2-8 km (2-5 mi) east of Milwaukee Harbor	Mar 1972	270		Nienke, 1972
10 surface-water samples each collected at stations east of Milwaukee:	28 Nov 1972			Beeton and Barker, 1974
0.4 km (0.25 mi) east		272		
16 km (10 mi) east		260		

Table 5. (contd.)

		*Specific Conductance** *µmhos/cm*		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		281	250-353	
Effluent plume		279	250-342	
South of plant, 4.8 km (3 mi)		278	255-328	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		292	255-330	
North of plant, 1.6 km (1 mi)		299	268-335	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		319	275.0-352.5	
South of plant, 1.6 km (1 mi)		322	292.5-365.0	

**Where necessary, corrections to 25°C were made according to correction factors in APHA et al., 1971.*

[a] Unclear in the original work whether these values were determined at 25°C.

USDOI = U. S. Department of the Interior; USGS = U. S. Geological Survey.

dissolved solids probably enters near shore. At greater distances from shore additives become more dilute; therefore specific conductance values will be lower. Beeton and Barker (1974) confirmed these suppositions through synoptic studies conducted near Milwaukee in April and again in June 1972 (Figs. 21 and 22). Figure 21, based on the April study, shows that conductivity values fell in a narrow range (263-273 µmhos/cm) north of Milwaukee Harbor, and that the lowest values were observed farthest from shore. The highest value in the Lake (excluding data collected within the Milwaukee Harbor) occurred at the Harbor entrance. Conductivities were much higher south of the harbor than north, reflecting the alterations in water quality caused by discharge of industrial and municipal wastes into and south of the Harbor (Beeton and Barker, 1974).

The June synoptic study (Fig. 22) and April observations are similar in several respects. For example, the highest conductance values were found at the entrance to the Milwaukee Harbor. Also, the high-conductance water from the Harbor could be traced flowing south. North of the community of South Milwaukee, conductance values were highest at stations closest to shore. But in the June study, low-conductivity water (261-268 µmhos/cm) lay closest to shore south of South Milwaukee. Beeton and Barker (1974) found several distinct bands of high-conductivity water separated this low-conductivity inshore water from the low-conductivity water lying 6.4-8.0 km (4-5 mi) offshore.

Comparison of the two synoptic studies represented by Figures 21 and 22 suggests that conductance values closest to shore have the greatest variability with time. Shifting currents, variations in tributary input, and variable industrial and municipal waste discharge at the shore likely are responsible

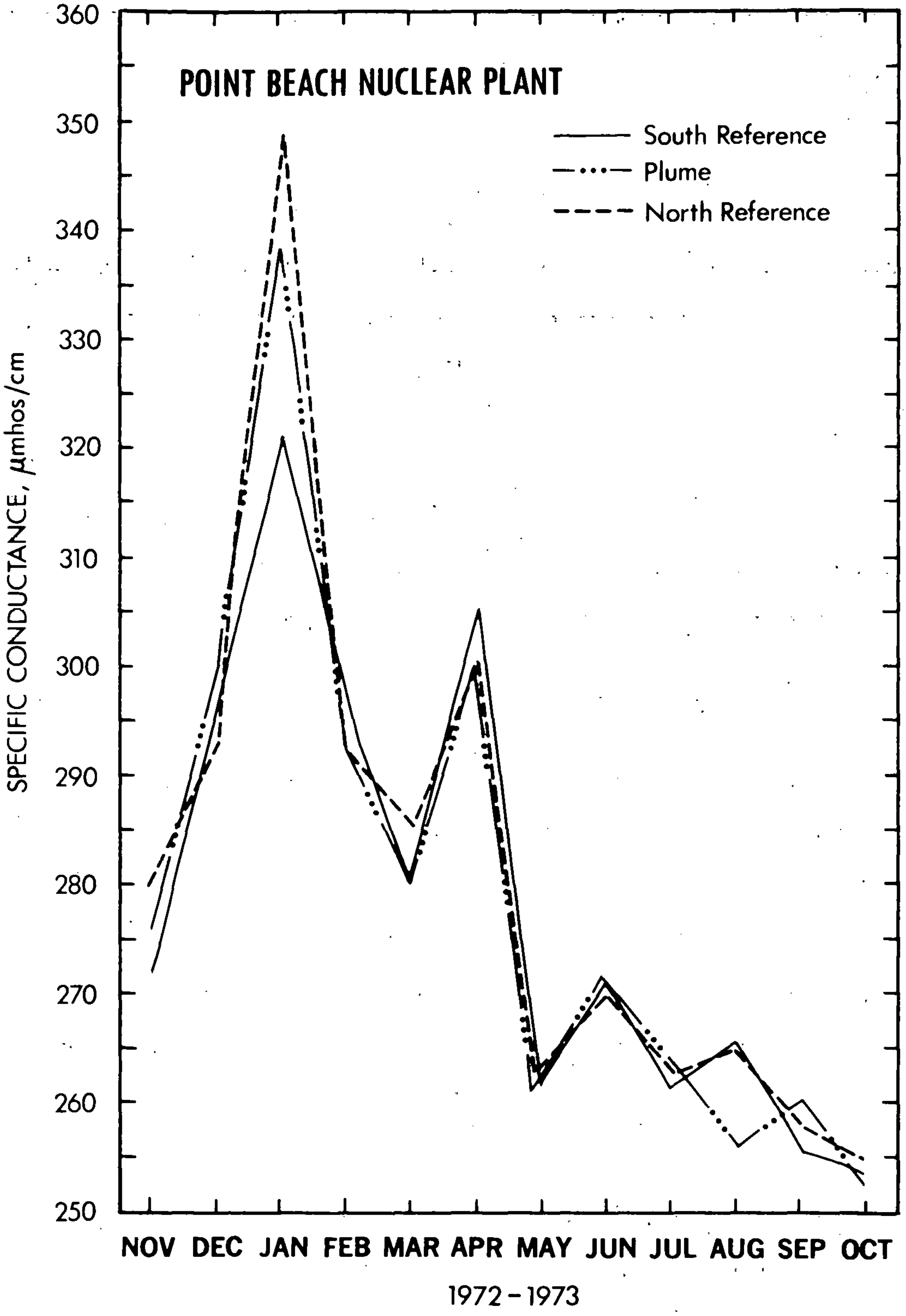

Fig. 19. Average Specific Conductance at Point Beach Nuclear Plant near Two Rivers. See Table 5 for sample descriptions. Modified from Limnetics (1974).

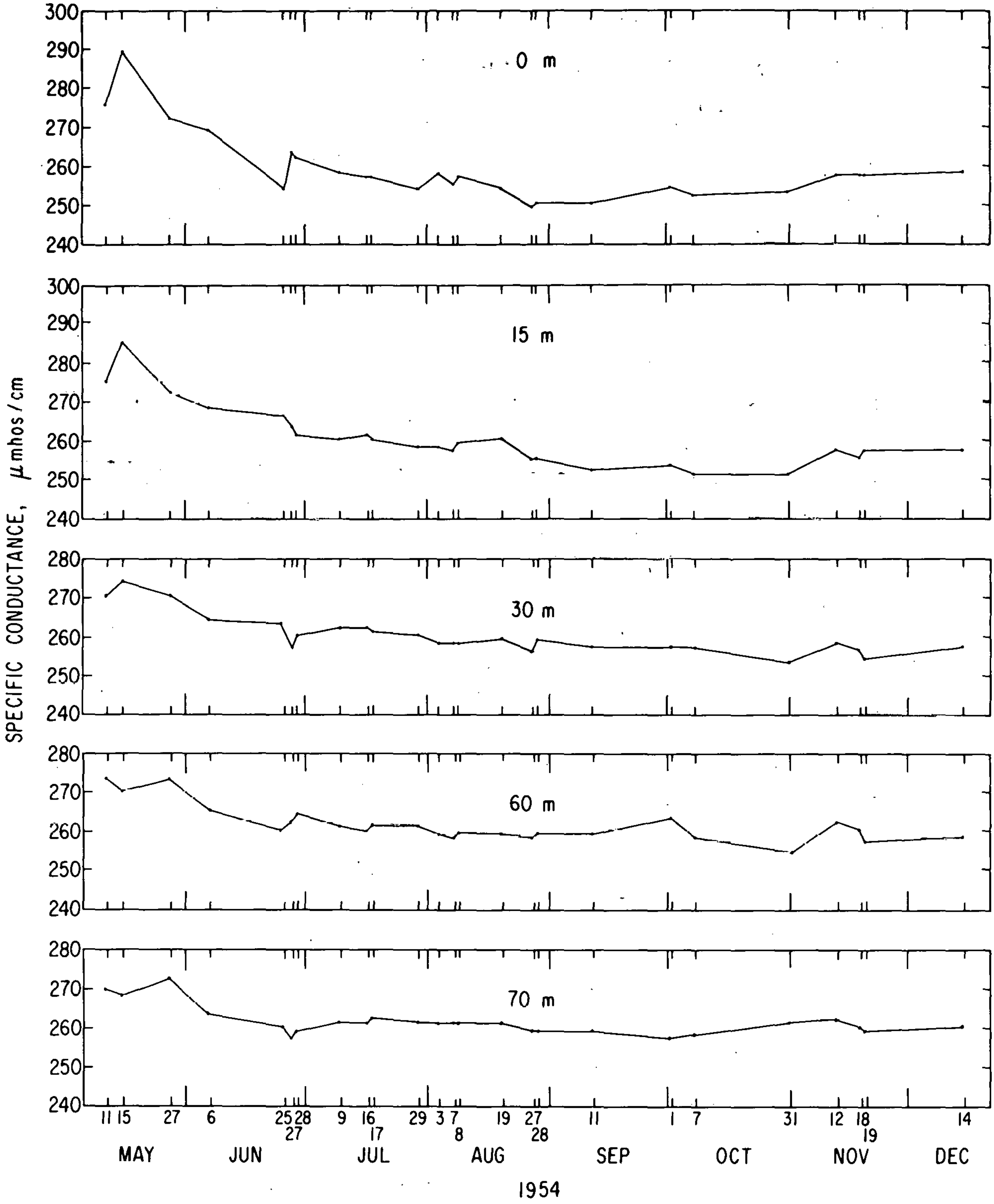

Fig. 20. Variation of Specific Conductance with Depth at a Station 12.9 km (8 mi) West of Grand Haven. Data from Beeton and Moffett (1964).

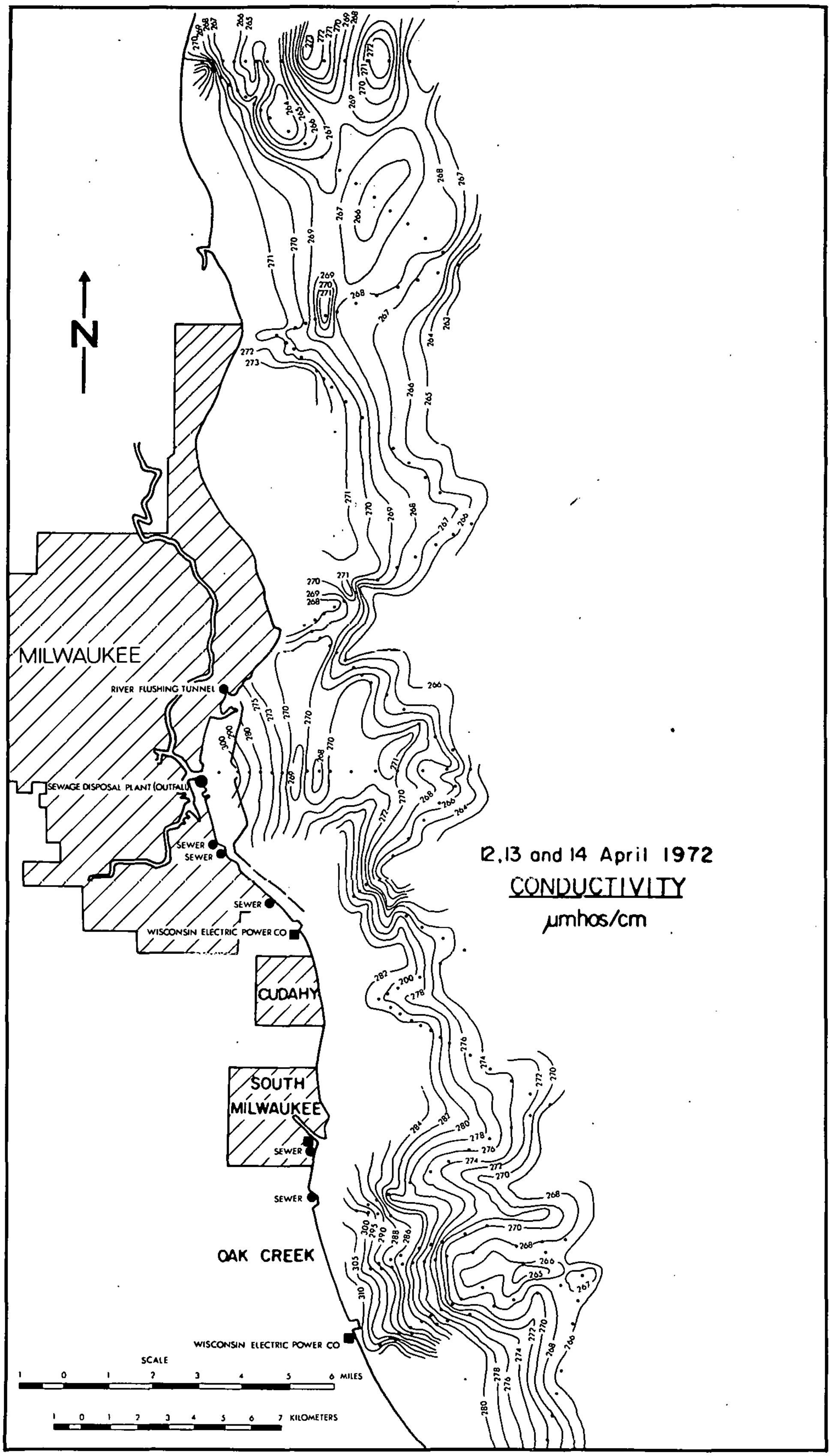

Fig. 21. Distribution of Specific Conductance near Milwaukee, 12-14 April 1972. Modified from Beeton and Barker (1974) (with permission, see credits).

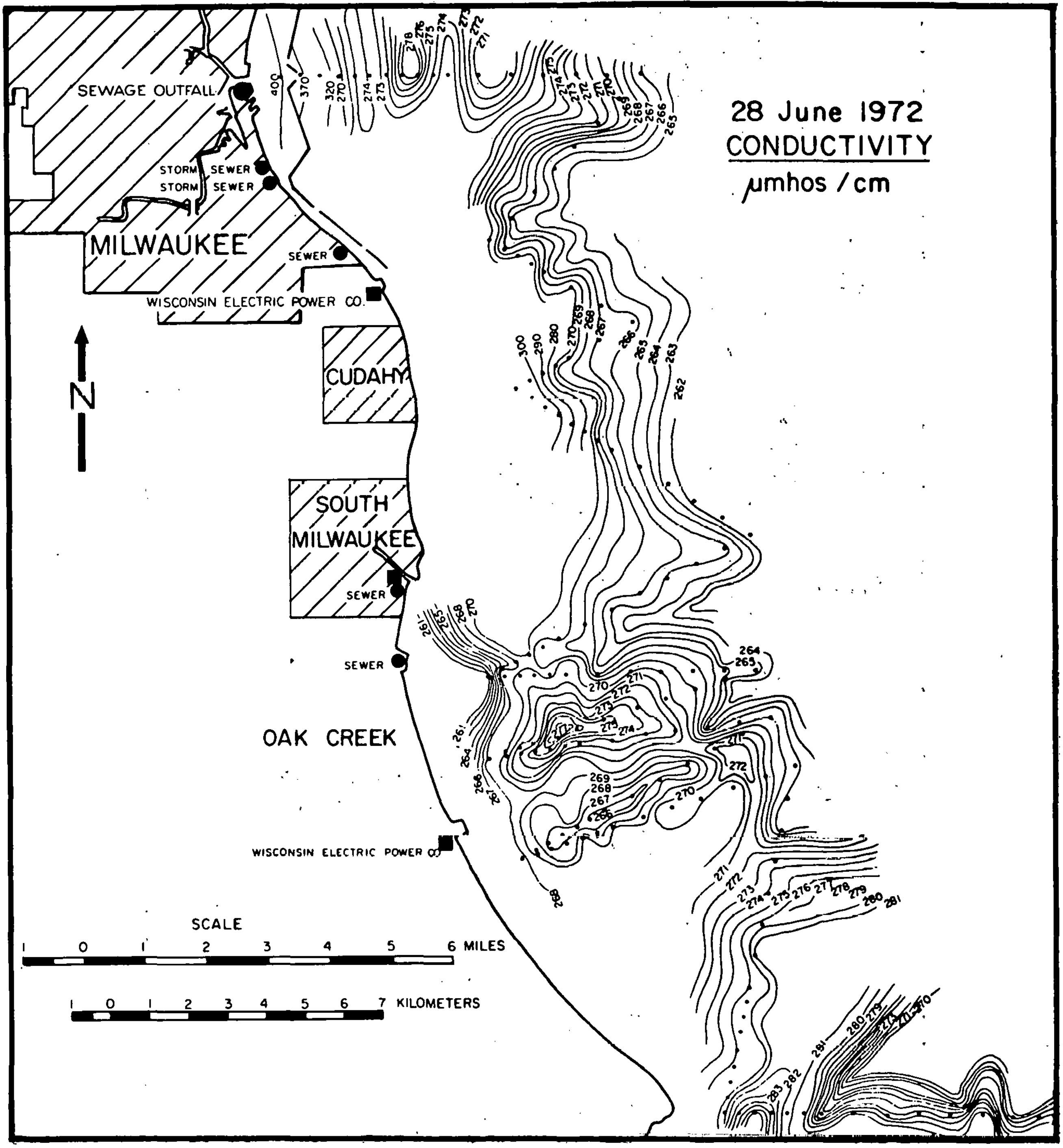

Fig. 22. Distribution of Specific Conductance near Milwaukee, 28 June 1972. Slightly modified from Beeton and Barker (1974) (with permission, see credits).

for the wide range of values recorded over time. Averages (Fig. 23a) do not show this variability so clearly as a plot of the standard deviations of these averages (Fig. 23b). In Figure 23b the greatest variability (*i.e.* largest standard deviation about the mean) occurs closest to shore in transects from shore to open water. Also, the closer the station is to Milwaukee, the greater the standard deviation (*e.g.* the progression from 27 to 14 to 10 μmhos/cm at the three stations closest to shore south of South Milwaukee).

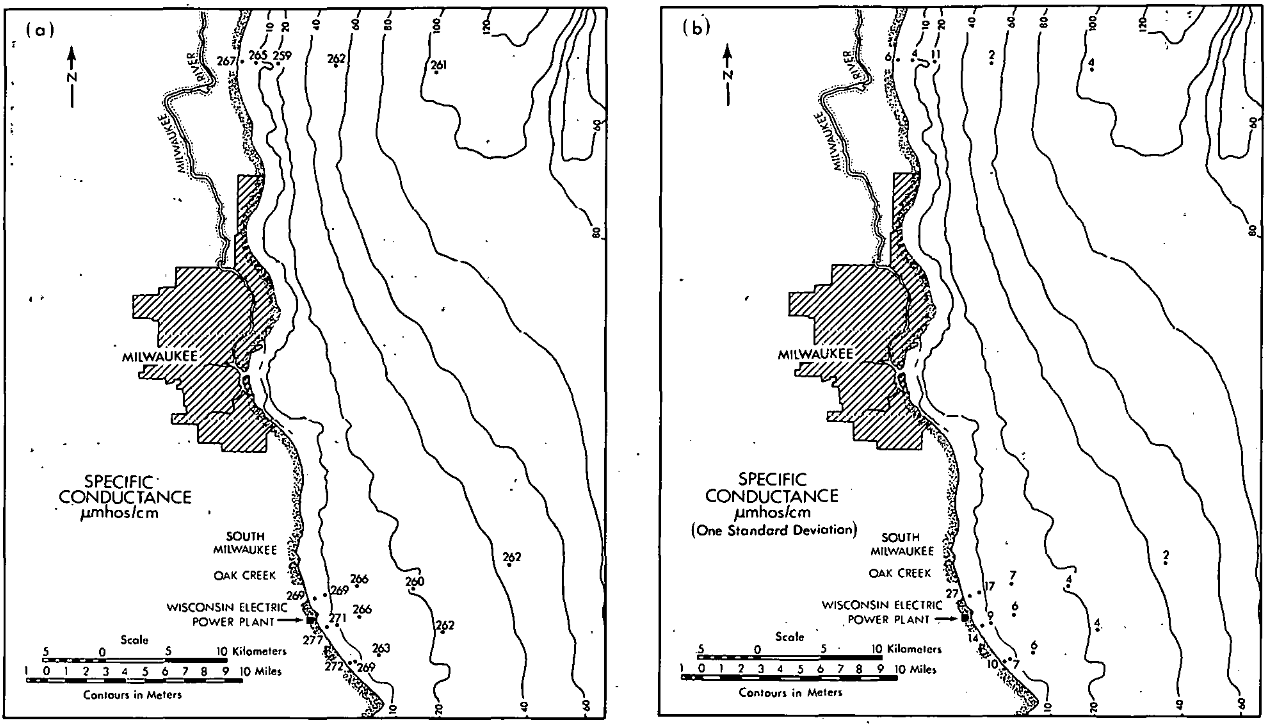

Fig. 23. Specific Conductance at 17 Stations near Milwaukee. (a) Specific conductance; (b) standard deviations. Values are averages for monthly samples collected October 1971-February 1972 and June 1972. Figure (modified) and data from Beeton and Barker (1974).

OXYGEN

The solubility of the O_2 molecule in water and the processes which alter the concentration of dissolved O_2 are vital to all organisms living in Lake Michigan.

PHYSICAL FACTORS INFLUENCING O_2 CONTENT

Temperature, Pressure, Atmospheric Composition

Oxygen gas is only moderately soluble in water (Fig. 24a), and the solubility decreases non-linearly with increasing temperature. The amount of oxygen dissolved in water in equilibrium with air depends on atmospheric pressure (Fig. 24b). Since atmospheric pressure varies inversely with elevation and Lake Michigan is above sea level (elev. 177 m, or 580 ft), 742.4 mm mercury

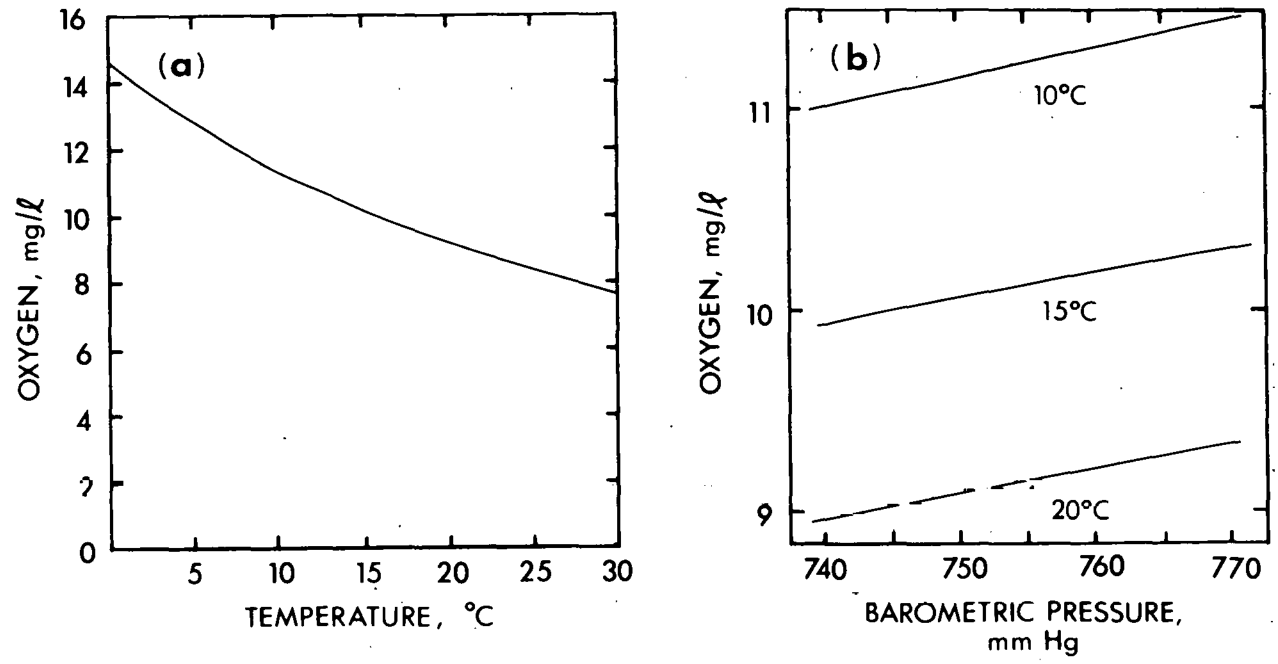

Fig. 24. Variation in Solubility of O_2 in Water with Temperature and Pressure. (a) Water-saturated air, 20.95% O_2 by volume, at a pressure of 760 mm Hg; (b) variation with increasing atmospheric pressure at three temperatures.

must be used in place of 760 mm mercury when computing oxygen saturation values. Short-term irregularities in air pressure can generally be ignored in computing O_2 solubility in water (Hutchinson, 1957). Since the oxygen content of dry air is essentially constant at 20.95% by volume (Hutchinson, 1957), this factor can be neglected under the temperature and elevation conditions of Lake Michigan (APHA *et al.*, 1971).

Gas Transfer

Three possible models for the transfer of O_2 into (or out of) water are: (*i*) molecular diffusion, (*ii*) molecular diffusion through two stagnant films of air and water at the air-water interface, and (*iii*) turbulence superimposed on the two-film model.

Molecular Diffusion

The rate of absorption of O_2 is infinite when air is first in contact with water containing no oxygen, then absorption decreases with time (Danckwerts, 1970). Hutchinson (1957) demonstrated the environmental significance of this decreasing rate of O_2 absorption by supposing a uniformly mixed lake, in equilibrium with normal air, containing 11.0 mg O_2/l. He hypothesized that this system was exposed to an atmosphere containing more than 20.95% O_2, so that the equilibrium concentration in water at the air-water interface increased to 12.6 mg O_2/l. With diffusion as the only means of O_2 transfer into water, the O_2 concentration would be 12.2 mg O_2/l at 3.1-cm depth after one month and only 11.4 mg/l at the 11.4-cm depth.

Two-Film Model

Since an undisturbed water surface is physically impossible in nature, other explanations for oxygen transfer to water must be found. The simplest theory is the two-film model (Fig. 25). This model postulates two stagnant films at the air-water interface; one is an air film and the other is a water film. Except for the air-water interface, the rest of the water and air are assumed to be thoroughly mixed (for greater theoretical detail see Danckwerts, 1970). In this model O_2 passes through the stagnant gas and water films by diffusion only. Once the gas has diffused through the stagnant films it is mixed by convection throughout the bulk of the water (or air). The rate of diffusion of O_2 within the liquid film controls the rate at which O_2 dissolves in water because: O_2 diffuses several orders of magnitude more slowly in water than air and O_2 is relatively insoluble in water (Liss, 1973).

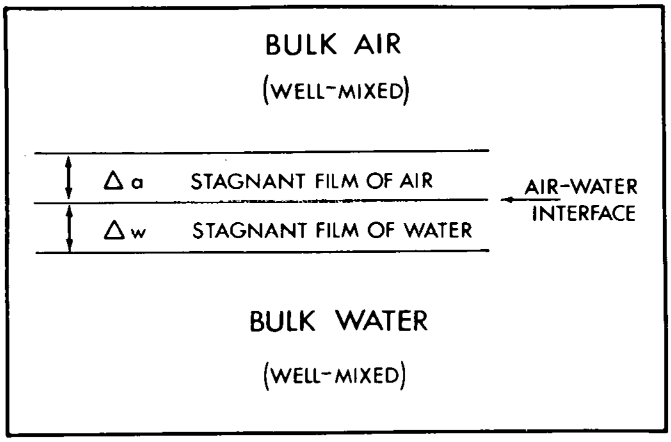

Fig. 25.

Model Describing the Transfer of Gases at the Air-Water Interface. The vertical arrows do not indicate the relative thickness of Δa and Δw.

Two-Film Model Plus Turbulence

Despite its usefulness in theoretical calculations, the concepts of stagnant air and water layers lack physical reality, for the water surface is almost always broken by turbulence. The most useful model includes turbulence as part of the theory describing gas transfer. Breaking the liquid surface from below increases the rate of O_2 transfer by 95% (Liss, 1973). Higher wind speeds create breaking waves and bubbles, which enhance the transport rate of atmospheric gases roughly in proportion to the square of the wind velocity (Kanwisher, 1963).

Effects of Organic Surface Layers

Organic surface layers reduce the rate of O_2 transfer into water (Liss, 1973), whether they originate from organic chemicals naturally present (Hatcher and Parker, 1974) or from chemicals derived from cultural activities (Downing and Truesdale, 1955). These thin surface layers, or slicks, on water damp wave action and turbulence that enhance gas transfer. Organic surface layers also reduce evaporation. Reduced evaporation lowers the gas transfer rate (Pardi, 1972, cited by Emerson *et al.*, 1973), because evaporative cooling stimulates convection near the surface. When the concentration of organic matter in the surface layer is high, *e.g.* in the case of an oil spill, the surface layer hinders O_2 transfer even further, for essentially a three-film system of air-organic matter-water is formed. This situation may be possible in places like the Calumet Harbor (*cf.* Snow, 1974).

Depth Profiles of O_2 Content

In spring, when Lake Michigan is thoroughly mixed, depth profiles of temperature, dissolved oxygen concentration, and dissolved oxygen saturation are uniform top-to-bottom (Fig. 26a). If all turbulence were to cease at the end of spring and the lake were warmed through the summer by radiation, then temperature would drop sharply with increasing depth (Fig. 26b). Surface waters would soon be supersaturated with O_2 relative to the increased temperature (Fig. 26b), because (*i*) oxygen solubility decreases with increasing temperature (Fig. 24) and (*ii*) molecular diffusion from water to the overlying air is too slow to affect supersaturation appreciably (Hutchinson, 1957). The situation in Lake Michigan is not this simple (see Seasonal Cycle of Temperature). Wind-generated turbulence allows warming of much more than a superficial thin film of lake water. The wind mixes the entire epilimnion, and oxygen is lost to the atmosphere as the temperature of the water increases. There is also limited mixing of warmer water containing less O_2 and colder water containing more O_2 at the thermocline. This produces water of intermediate temperature and O_2 content. The physical mixing process that leads to thermal stratification (Fig. 26c) results in a vertical distribution of dissolved O_2 (Fig. 26c) that is inversely related to the temperature profile.

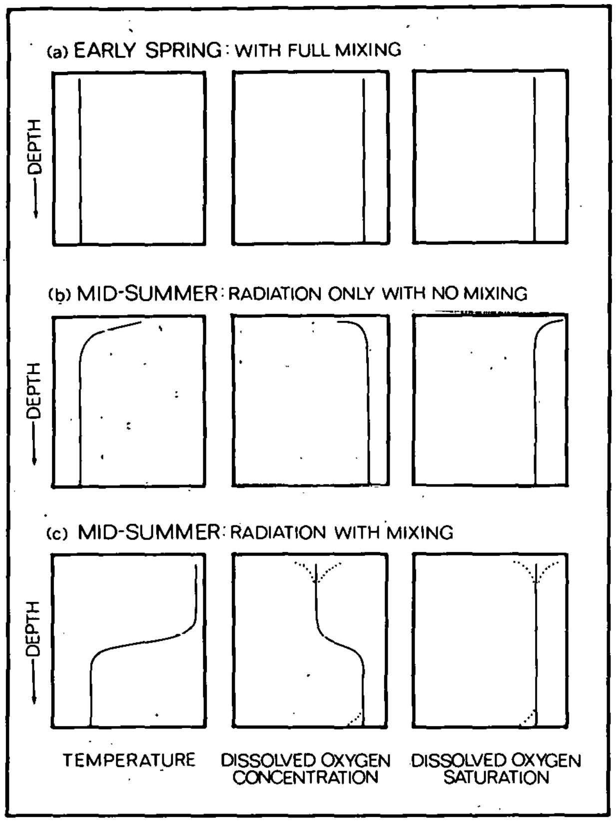

Fig. 26.

Schematic Showing the Effect of Mixing on Temperature and Oxygen Profiles with Depth. Dotted lines are explained in the section *In Situ* Processes Influencing O_2 Content.

IN SITU PROCESSES INFLUENCING O_2 CONTENT

Photosynthesis and Respiration

The solid lines in the second and third panels of Figure 26c were produced by purely physical processes and do not fully represent the situation in Lake Michigan. Biological processes change these profiles to those represented by the dotted lines in Figure 26c. Phytoplankton photosynthesis occurs primarily in the lighted surface water, and O_2 is a by-product,

$$x\ CO_2 + x\ H_2O \xrightarrow[\text{photosynthesizing organisms}]{\text{light}} C_xH_{2x}O_x + O_2\ . \qquad (4)$$

During daylight, marked supersaturation of dissolved oxygen may result wherever large populations of photosynthesizing plankton occur. Photosynthesizing plants in shallow warm water may form bubbles containing O_2.

Conversely, nighttime respiration by plants and animals,

$$C_xH_{2x}O_x + x\ O_2 \xrightarrow[\text{organisms}]{\text{respiring}} x\ CO_2 + x\ H_2O\ , \qquad (5)$$

may consume so much oxygen that undersaturation occurs. These two opposing processes, photosynthesis and respiration, occasionally produce an alternating cycle (diel variation) of higher and lower oxygen concentrations in the surface water. One published study of diel variation in dissolved oxygen content was conducted 13-14 July 1968 at two stations near Grand Haven (Manny and Hall, 1969). On those dates, the number of phytoplankton cells per unit volume of water was quite high. Percent saturation values of oxygen remained near 100% in the top 20 m (Fig. 27, left and right), ranging from 94% to 111%.

One should be aware of these daily variations when analyzing dissolved oxygen data from surface water. Data collected (U. S. Dep. Inter., 1968) in July 1962 south of Ludington and in July 1963 in northern areas of the Lake illustrate the problem. In the first 30 m, the same interval sampled in July 1968 by Manny and Hall (1969), the U. S. Department of the Interior (1968) found saturation ranged from 88% to 128% (Table 6). In the surface 10 m, the range in percent saturation was 98-119% (U. S. Dep. Inter., 1968). In their 24-hr study Manny and Hall (1969) found a range of 100-111% in the top 10 m. Clearly, the variation in saturation value over a daily cycle can be great enough to account for a significant portion of the variation (*e.g.* Table 6) that might otherwise be attributed to station-to-station variability.

Table 6. Dissolved Oxygen in Deep Water during July 1962 and 1963*

Sampling Depth, m	*Dissolved Oxygen Concentration, mg/l* *Minimum*	*Maximum*	*Percent Saturation* *Minimum*	*Maximum*
0- 5	8.6	12	98	115
6-10	9.4	14	103	119
11-30	9.0	15	88	128

**Data from U. S. Department of the Interior, 1968.*

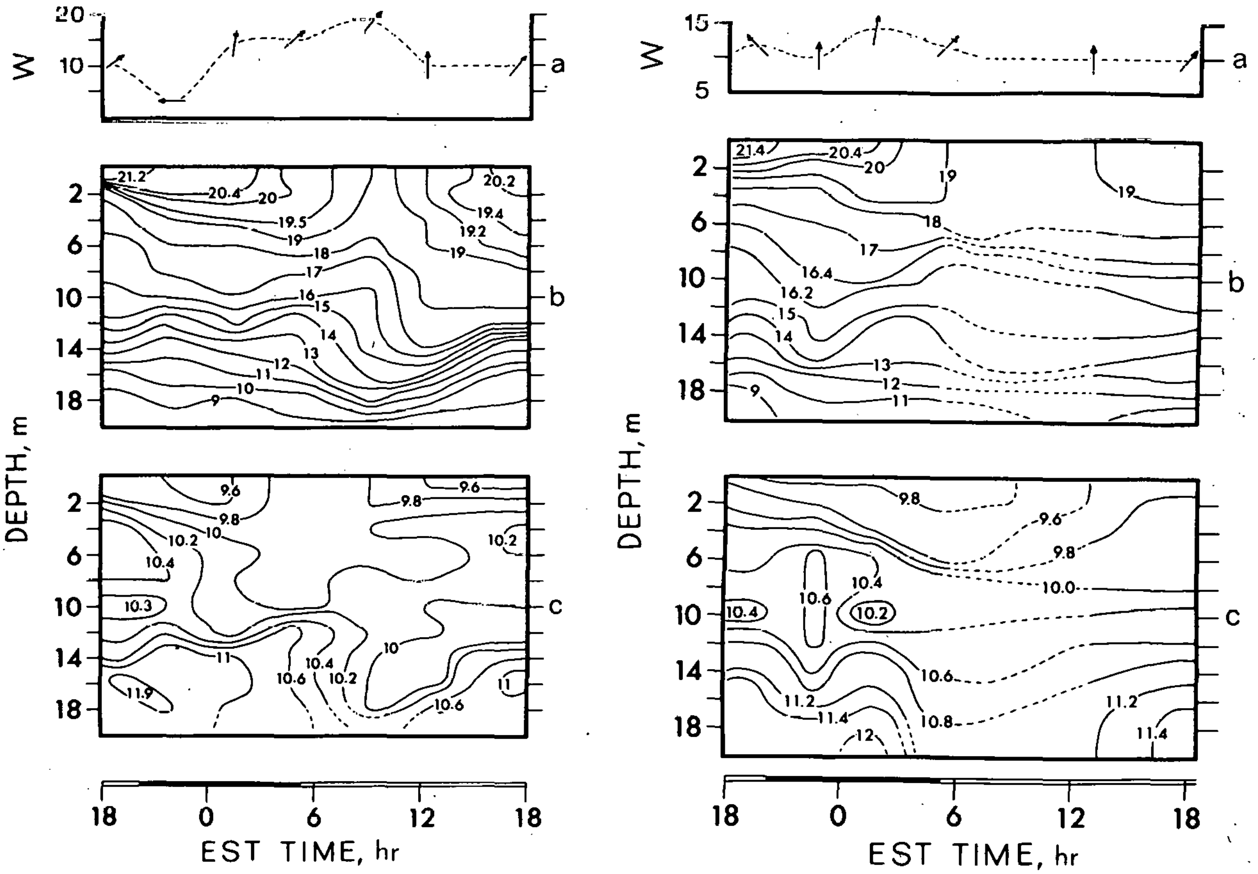

Fig. 27. Diurnal Variation in the Euphotic Zone Offshore from Grand Haven, 13-14 July 1968. Left: 4.8 km (3.0 mi) offshore in 30 m of water; Right: 8 km (5 mi) offshore in 61 m of water. (a) Wind velocity, W (knots), and direction (top of figure = north); (b) temperature (isotherms, °C); (c) dissolved O_2 (isopleths, mg/l). Dotted lines between 0600 and 1300 indicate probable changes had the 0900 samples been taken. Slightly modified from Manny and Hall (1969) (with permission, see credits).

Nonbiochemical Reactions

The nonbiochemical reaction of O_2 with dissolved inorganic and organic chemicals also causes reductions in dissolved oxygen concentrations. Examples of such reactions include the oxidation of ferrous iron to ferric,

$$4\ Fe^{2+} + 10\ H_2O + O_2 \longrightarrow 4\ Fe(OH)_3 + 8\ H^+ \ , \qquad (6)$$

and the conversion of reduced carbon species, such as methane, to oxidized forms,

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O \ . \qquad (7)$$

These nonbiochemical reactions are considered less important to the dynamics of dissolved oxygen in Lake Michigan water than the biochemical reactions; thus they are not considered further.

Oxygen-Demanding Materials

Classification

The types of chemicals which deplete dissolved oxygen concentrations can be categorized as follows: (*i*) carbonaceous organic matter used as a food source (Eq. 5); (*ii*) oxidizable nitrogenous matter (derived from organic nitrogen, ammonia, and nitrite) used for food by specialized organisms,

$$2\ NH_4^+ + 2\ OH^- + 3\ O_2 \xrightarrow{\text{bacteria}} 2\ H^+ + 2\ NO_2^- + 4\ H_2O \ , \qquad (8)$$

$$2\ NO_2^- + O_2 \xrightarrow{\text{bacteria}} 2\ NO_3^- \ ; \text{ and} \qquad (9)$$

(*iii*) reduced inorganic chemicals which react nonbiochemically with dissolved oxygen,

$$2\ Mn^{2+} + O_2 + 2\ H_2O \longrightarrow MnO_2\downarrow + 2\ H^+ \ . \qquad (10)$$

Numerous chemical analyses would be needed to characterize all the different constituents that react with O_2 and to determine their concentrations in natural water. Only after these analyses were completed could one accurately compute the total oxygen-consuming capacity of the water. Performance of all these analyses could not be done, even if the identity of all the chemical compounds in Lake water were known. Therefore, two tests are used routinely to estimate the concentrations of oxygen-demanding material in water: biochemical oxygen demand (BOD) and chemical oxygen demand (COD).

Biochemical Oxygen Demand

In brief, a BOD analysis measures the oxygen consumption (mg/l) under standardized conditions of container size, light, temperature, and incubation period (APHA *et al.*, 1971). BOD in a sample of raw or domestic sewage is due almost entirely to microbial oxidation of carbonaceous matter (Class *i*, mentioned in the preceding paragraph). A BOD determination on an effluent sample from a secondary sewage treatment facility may include considerable portions of oxidizable nitrogenous matter (Class *ii*) as well. In a standard BOD test, O_2 demand by Class *iii* compounds may not appear at all, although insertion of one additional step in the standard procedure allows their quantification.

Typically, BOD determinations are based on a standard incubation period of five days and expressed as BOD_5, mg/l. Not all organic compounds are easily oxidized by microbial action within this standard period, although they do exert their oxygen demand within the environment over longer periods. One sometimes sees reports of BOD_{21} or BOD_{100}, indicating the amount of O_2 consumption over 21 or 100 days. In this report, BOD is the general term, while BOD_5 refers to an actual determination of BOD over a five-day incubation (APHA *et al.*, 1971).

Intrinsically, BOD is not a pollutant and exercises no direct harm. However, BOD exerts an indirect effect by depressing dissolved oxygen concentrations to levels harmful to aquatic organisms. Sewage effluents contain significant quantities of oxidizable matter, thus BOD analyses are routinely done. BOD analyses are seldom performed on the open waters of relatively unpolluted bodies of water like Lake Michigan. With the exception of work done by Industrial Bio-Test (1972b) and the U. S. Department of the Interior (1968), all values in Table 7 were obtained less than 2 km (1.2 mi) from shore.

Several organizations have monitored BOD_5 on at least a monthly basis at selected locations along the west shore of Lake Michigan. At Two Rivers (Fig. 28a), Milwaukee (Fig. 28b), Oak Creek (Fig. 28c, d), and Lake County, Ill. (Fig. 28e), the BOD_5 tends to be highest from May to July or August and lowest from December to March. This trend may be related to the presence of larger quantities of biomass in summer than in winter, but this is conjectural. There seems to be a north-to-south gradient of increasing BOD_5 in Figure 28a-e. The cause of this trend, if it is real, must be speculative for the moment.

Natural sources contribute certain amounts of oxidizable matter to Lake Michigan. Streams and rivers are a source of organic matter which may lower the dissolved oxygen content. Photosynthesizing aquatic plants produce organic carbon compounds (Eq. 4). After the organisms die, these reduced organic compounds are oxidized and therefore represent a natural source of BOD.

More frequently, BOD is considered in relation to pollution. The average content of BOD_5 in effluents from secondary treatment of municipal waste water is 25 mg/l (Weinberger *et al.*, 1966). Certain industries, such as pulp and paper manufacture, are known for high BOD effluents. In a recent inventory (Businessmen for the Public Interest, 1972), pulp and paper manufacture account for approximately 88% of the BOD_5 in discharges by the 117 listed companies, and even this value was considered an underestimate. The value of 88% is even more impressive when one considers that over half of the total BOD in discharges

Table 7. Biochemical Oxygen Demand (BOD_5) in Lake Michigan Water

		Concentration O_2, mg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Samples collected in Green Bay:				Balch *et al.*, 1956
Between mouth of Fox River and Grassy Islands	Mid-Jun to Mid-Aug 1955		15.5-24.0	
Between Grassy Islands and a line between Long Tail Point and Point Sable	Summer 1955		4-26.5	
Along east shore near Point Sable	Late Jan, early Mar 1956		7.1-11.6	
Samples collected ∿monthly from Peter Cooper Corp. intake, Oak Creek, ∿0.75 km (2500 ft) offshore	May-Dec 1961	1.5	<0.5-2.3	Wis. Comm. Water Pollut., 1965
	1962	1.4	<0.5-2.2	
	1963	2.0	1.1-3.7	
	1964	1.7	1.0-2.7	
	1965	1.0	<0.5-1.7	Wis. Dep. Nat. Resour., 1969
	1966	1.0	<0.5-3.0	
	1967	1.2	<0.5-2.8	
	1968	2.2	<1.0-6.1	
	1969	1.8	<1.0-3.8	Wis. Dep. Nat. Resour., 1973
	1970	1.9	<1.0-3.7	
	1971	2.4	<1.0-6.0	
	1972	1.6	0.6-3.4	
730 inshore samples collected throughout Lake	1962-63	1.4	N.D.-8.6	USDOI, 1968
Samples collected:	1962-63			USDOI, 1968
Indiana Harbor, 12 samples		3.5	1.9-5.1	
Calumet Harbor, 15 samples		1.3	1.0-2.1	
Chicago Harbor, 4 samples		0.8	0.6-1.6	
Racine Harbor, 3 samples		0.7	0-2.1	
Samples collected:	Oct 1962, Jun 1963			USDOI, 1968
Milwaukee Harbor, 60 samples		3.4	1.5-8.1	
Adjacent to Milwaukee Harbor, 25 samples		2.5	0.3-6.7	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City		1.3	0.1-4.8	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo		1.2	0.3-7.4	
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor		1.6	0.4-7.7	
On a line roughly between Sheboygan and Little Sable Point		1.2	0.6-3.0	
6 samples collected in Traverse Bay	22-28 Jul 1964	1.2	0.6-1.7	USDOI, 1968
Samples collected in Indiana Harbor at east breakwall inner light:				Snow, 1974
3 samples	Dec 1965	3.1	2.9-3.4	
51 samples	Jan-Dec 1966	3.7	1.2-13	
42 samples	Jan-Dec 1967	4.5	1.3-8.8	
37 samples	Jan-Dec 1968	3.6	1.6-11	
25 samples	Jan-Jun 1969	4.7	2.8-9.1	
Samples collected ∿weekly at Milwaukee public water intake, 1.8 km (1.1 mi) offshore:				
47 samples	Nov 1969-Sep 1970	0.7	0.0-1.6	USGS, 1972
49 samples	Oct 1970-Sep 1971	0.6	0.1-1.5	USGS, 1973
43 samples	Oct 1971-Sep 1972	0.5	0.0-1.2	USGS, 1974a
35 samples	Oct 1972-Jun 1973	0.6	0.1-2.6	USGS, 1974b

Table 7. (contd.)

Sample Description	Dates	Concentration O_2, mg/l Average	Concentration O_2, mg/l Range	Reference
Monthly samples collected at intakes:	Jan 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		2	0.2-3.7	
Waukegan Generating Station		3	0.5-5.0	
North Chicago public water supply		2	0.6-3.5	
Monthly samples collected at 3 stations 9.6 km (6 mi) east of Zion:	May 1970-Apr 1971			Industrial Bio-Test, 1972b
Surface-water		1.4	0.2-3.5	
Bottom-water		1.2	0.2-3.0	
Monthly samples collected at Lake County, Ill., public water intake	Jun 1970-Jun 1973	2.2	0.4-6.2	Howe, 1973
Samples collected (water depth 7.6 m) at a station east of Kewaunee Nuclear Plant:				Industrial Bio-Test, 1972d
Surface	25 May 1971	2.5	1.2-4.6	
Bottom	25 May 1971	2.6	0.3-5.0	
Surface	31 Aug 1971	1.1	0.9-1.3	
Bottom	31 Aug 1971	1.0	0.9-1.2	
Surface	16 Nov 1971	2.3	2.0-2.6	
Bottom	16 Nov 1971	1.8	1.8-1.9	
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun 1971-Apr 1972	2.8	0.9-5.6	Industrial Bio-Test, 1972c
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		0.8	<0.5-1.6	
Effluent plume		0.8	<0.5-1.8	
South of plant, 4.8 km (3 mi)		0.7	<0.5-1.4	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		1.1	0.7-1.9	
North of plant, 1.6 km (1 mi)		1.3	0.6-7.4	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		1.33	0.25-2.70	
South of plant, 1.6 km (1 mi)		1.29	0.65-2.35	

USDOI = U. S. Department of the Interior; USGS = U. S. Geological Survey.

N.D. = not detected.

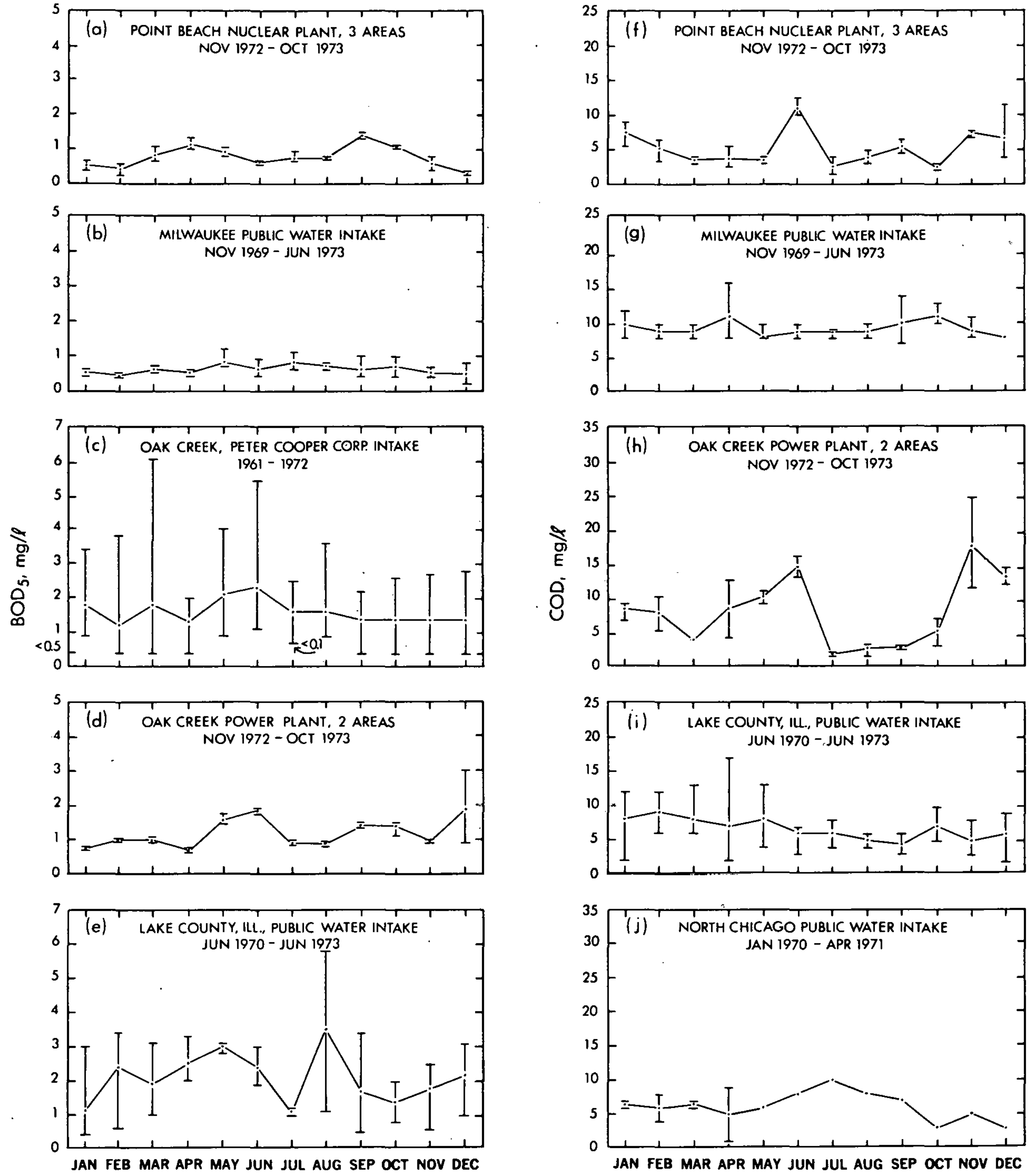

Fig. 28. Seasonal Variations in Average Biochemical Oxygen Demand (BOD_5) and Average Chemical Oxygen Demand (COD) along the Western Shore of Lake Michigan. Sources of BOD_5 data: (a,d) Limnetics, 1974; (b) U. S. Geological Survey, 1972, 1973, 1974a, 1974b; (c) Wisconsin Committee on Water Pollution, 1965, and Wisconsin Department of Natural Resources, 1969, 1973; (e) Howe, 1973--personal communication. Sources of COD data: (f,h) Limnetics, 1974; (g) U. S. Geological Survey, 1972, 1973, 1974a, 1974b; (i) Howe, 1973--personal communication; (j) Industrial Bio-Test, 1972a.

were attributed to effluents from pulp and paper mills located on the lower Fox River and around southern Green Bay (Businessmen for the Public Interest, 1972).

The BOD determination has shortcomings. First, it does not usually include the oxygen demand of reduced inorganic substances like ferrous iron. Second, the BOD test is highly sensitive to materials toxic to microorganisms. Third, five or more days are required before results are obtained. To mitigate these problems, a chemical oxygen demand determination may be made.

Chemical Oxygen Demand

COD is a measure of the oxygen equivalent of organic matter that can be oxidized by a strong chemical oxidant, such as a sulfuric acid-dichromate solution. The test is not sensitive to some compounds included in the BOD test, but it includes some biological compounds which are not usually a part of the BOD (APHA *et al.*, 1971). Reduced nitrogen species (ammonia and amino groups) are not detected in the determination of COD. For these reasons, there is no necessary correlation between the results of BOD and COD determinations.

COD determinations are made for the same reason as BOD measurements are made: to assess the potential effect of oxygen-demanding material. COD tests are seldom performed on samples of open waters from Lake Michigan (Table 8). With the exception of work done 9.6 km (6 mi) offshore by Industrial Bio-Test (1972b), all values in Table 8 were obtained less than 2 km (1.2 mi) from shore.

Several stations along the west shore of Lake Michigan have been monitored for COD on at least a monthly basis (Table 8). Unlike BOD (Fig. 28a-e), there is no obvious seasonal pattern of COD at Two Rivers (Fig. 28f), Milwaukee (Fig. 28g), Oak Creek (Fig. 28h), Lake County, Ill. (Fig. 28i), or North Chicago (Fig. 28j). There is no apparent trend in COD values from north-to-south, as there was for BOD. The increase in COD values between the Milwaukee water intake, located on the north side of Milwaukee, and the Oak Creek area, on Milwaukee's far south side, is notable. This increase is perhaps due to the effluent of the South Shore sewage treatment plant, located in Oak Creek, and to discharge flowing south from the Milwaukee Harbor. Similar trends were noted in synoptic studies of other water quality parameters conducted by Beeton and Barker (1974).

COD is frequently considered in relation to pollution. Certain industries are known for the content of COD in their effluents. Pulp and paper industries reportedly contributed 86% of the total COD discharged by 117 major industries (Businessmen for the Public Interest, 1972) and metal refineries discharged another 8.3%. These values are noteworthy, since much of the COD effluents are discharged to restricted areas.

DISSOLVED OXYGEN CONCENTRATIONS IN LAKE MICHIGAN

Comparison with Standards and Criteria

Dissolved oxygen at or near saturation levels is desirable in a drinking water supply because it helps precipitate undesirable substances like iron and manganese (*cf.* Eqs. 6 and 10), and allows for oxidation of taste- and odor-

Table 8. Chemical Oxygen Demand (COD) in Lake Michigan Water

		Concentration O_2, mg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Samples collected in Indiana Harbor at east breakwall inner light:				Snow, 1974
3 samples	Dec 1965	87	13-131	
51 samples	Jan-Dec 1966	16	4-72	
42 samples	Jan-Dec 1967	11	6-34	
37 samples	Jan-Dec 1968	22	1.5-220	
25 samples	Jan-Jun 1969	22	3-100	
20 samples	Jan 1971-Jan 1973	9.1	2-21	
Samples collected ∿weekly at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	Nov 1969-Sep 1970	9	7-11	USGS, 1972
	Oct 1970-Sep 1971	8	5-18	USGS, 1973
	Oct 1971-Sep 1972	10	6-20	USGS, 1974a
	Oct 1972-Jun 1973	11	5-40	USGS, 1974b
Monthly samples collected at intakes:	Jan 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		6	2-16	
Waukegan Generating Station		10	2-24	
North Chicago public water supply		2	0.6-4	
Monthly samples collected at 3 stations 9.6 km (6 mi) east of Zion:	May 1970-Apr 1971			Industrial Bio-Test, 1972b
Surface-water		6	2-22	
Bottom-water		6	<1-16	
Monthly samples collected at Lake County, Ill., public water intake	Jun 1970-Jun 1973	6.5	2.0-16	Howe, 1973
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers-- 3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		4.6	<2.0-19.0	
Effluent plume		5.6	<2.0-19.0	
South of plant, 4.8 km (3 mi)		5.6	<2.0-14.0	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee-- 2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		7.3	2.0-18.0	
North of plant, 1.6 km (1 mi)		9.8	2.0-26.0	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis-- 2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		11.4	1.9-19.2	
South of plant, 1.6 km (1 mi)		10.7	1.9-19.2	

USGS = U. S. Geological Survey.

causing organic chemicals (National Academy of Sciences ..., 1973). It also promotes growth of organisms which convert ammonia to nitrate (*cf.* Eqs. 8 and 9) and prevents anaerobic conditions that allow reduction of sulfate to H_2S. Dissolved oxygen levels at or near saturation indicate the probable absence of excess quantities of O_2-demanding substances. However, dissolved oxygen enhances corrosion of water treatment facilities, distribution systems, and household plumbing. Since these effects are not complementary, the U. S. Public Health Service (1962), the National Academy of Sciences ... (1973), and the Environmental Protection Agency (1975b) were not able to make recommendations on oxygen content for a drinking water supply (Appendix B, part 1).

The National Academy of Sciences ... (1973) based oxygen level recommendations on the most sensitive life stages of fish, usually the egg or larval stages (Appendix B, part 2). Thus, the criteria are based on O_2 minima, because harmful effects on fish and other organisms generally depend on extremes, not averages. In suggesting criteria, the Academy acknowledged that they had not included the fact that reduced O_2 levels increase the toxicity of some additives in effluents, such as ammonia, cyanides, zinc, copper, and creosols (McKee and Wolf, 1963). The National Academy of Sciences ... (1973) recommended levels of protection, summarized in Table 9, which can be achieved after social and economic factors are analyzed. If natural seasonal minima are taken as nearly the same as saturation values in Lake Michigan (harbors, southern Green Bay, and certain inshore areas near Milwaukee, Chicago, Gary, and Hammond are notable exceptions to this generalization), then one can calculate oxygen levels with temperature which will afford varying levels of protection to Lake Michigan fish (Table 10). These criteria are compared with oxygen levels found in Lake Michigan in Table 11. In the main portion of Lake Michigan, oxygen levels generally afford high to nearly maximum levels of protection for fish. It must be emphasized that data in Table 11 represent samples collected at single points in time. Ideally, one needs a continuous annual record for many locations in the Lake to assess the magnitudes of day-night fluctuations (*cf.* Fig. 27, left and right) and the effects of intermittent or continuous inputs of oxygen-demanding matter on the oxygen status of the water. One must consider as provisional the generalization that levels of protection with respect to oxygen are high to nearly maximal.

Table 9. Levels of Protection for Aquatic Organisms*

Level	*Meaning*
Nearly maximum	Nearly unimpaired productivity and unchanged quality of fishery.
High	Unlikely to cause significant change in ecosystem, nor major reduction of fish production. Some impairment is possible, but appreciable damage is not expected.
Moderate	Fisheries will probably persist, generally with no serious impairment, but with some decrease in production.
Low	Permits the persistence of large populations of tolerant species and allows most migrants to pass successfully. Much reduced production or elimination of sensitive species is likely.

**From National Academy of Sciences ..., 1973.*

Several areas of Lake Michigan are exceptions to the generalization that O_2 levels are high to nearly maximal. Dissolved oxygen levels in southern Green Bay (Epstein *et al.*, 1974) and the Indiana Harbor Canal (Snow, 1974) approach the lower detection limit at times due to high concentrations of O_2-demanding materials, but open water shows adequate dissolved oxygen content.

One can also compare Lake Michigan dissolved O_2 values with the minimum specific water quality objective (no less than 6.0 mg/l) for the International Great Lakes (U. S. Treaties, etc., 1972). Of all the values inspected for Lake Michigan (Table 11) only one was less than 6.0 mg/l, taken by Beeton and Moffett (1964) on 3 September 1955 in Lake Charlevoix, a restricted embayment.

Table 10. Recommended Minimum Concentrations of Dissolved Oxygen in Lake Michigan Water

Tempera-ture, °C	*Recommended Minimum Concentrations* for Various Levels of Protection, mg O_2/l*			
	Saturation Value (= Maximum Level)	*High*	*Moderate*	*Low*
0	14.3	9.4	6.7	4.8
2	13.5	9.3	6.8	4.9
4	12.8	9.1	6.8	4.9
6	12.2	9.1	6.8	4.9
8	11.6	8.8	6.7	4.8
10	11.0	8.6	6.7	4.8
12	10.5	8.4	6.6	4.7
14	10.2	8.3	6.5	4.7
16	9.8	8.1	6.4	4.6
18	9.3	7.9	6.3	4.6
20	9.0	7.7	6.2	4.5
22	8.6	7.5	6.0	4.4
24	8.3	7.3	5.9	4.4

**Computed from formulae in National Academy of Sciences ..., 1973.*

Table 11. Dissolved Oxygen Concentrations in Lake Michigan Water with Respect to Protection of Aquatic Life

			Samples		
Sample Description	*Dates*	*Level**	*Number*	*Percent*	*Reference*
Inshore and offshore stations, surface to bottom, southern basin and divide area	May-Dec 1954	Nearly maximum	270	54.0	Beeton and Moffett, 1964
		High	221	44.2	
		Moderate	9	1.8	
Inshore and offshore stations, surface to bottom, northern basin and divide area	Mar-Nov 1955	Nearly maximum	122	41.8	Beeton and Moffett, 1964
		High	168	57.6	
		Moderate	1	.3	
		Low	1	.3	
Inshore and offshore stations, surface to bottom, southern basin	Apr-Nov 1960	Nearly maximum	7	8.1	Beeton and Moffett, 1964
		High	42	48.8	
		Moderate	37	43.1	
Inshore and offshore stations, surface to bottom, northern basin	May-Nov 1961	Nearly maximum	14	9.9	Beeton and Moffett, 1964
		High	114	81.0	
		Moderate	13	9.1	
4 surface- and 10 bottom-water samples at ten offshore stations, northern and southern basins and divide area	Autumn 1966	Nearly maximum	4	28.6	Ayers *et al.*, 1967
		High	8	57.1	
		Moderate	2	14.3	
Monthly surface-water samples at 3 stations 9.6 km (6 mi) east of Zion	Mar 1970-Apr 1971	Nearly maximum	41	85.4	Industrial Bio-Test, 1972b
		High	7	14.6	
Monthly bottom-water samples at 3 stations 9.6 km (6 mi) east of Zion	Mar 1970-Apr 1971	Nearly maximum	19	50.0	Industrial Bio-Test, 1972b
		High	19	50.0	
Monthly samples, surface to bottom, at 10 stations within 4.8 km (3 mi) of Point Beach Nuclear Plant	Jun-Sep 1971	Nearly maximum	52	70.2	Weschler *et al.*, 1972
		High	22	29.8	

**The terms "nearly maximum," "high," "moderate," and "low" are defined in Table 9. Oxygen concentrations corresponding to these terms are presented in Table 10.*

Bottom-Water Values

Respiration occurs at all depths in Lake Michigan, but photosynthesis occurs only in the lighted surface waters. In some extremely unproductive lakes there is little respiratory consumption of oxygen below the thermocline because there is so little organic matter added to the lake or produced *in situ*. On the other hand, dissolved oxygen completely disappears below the thermocline in some extremely productive lakes because respiration processes utilize most of the available O_2 and because of stratification little mixing across the thermocline occurs to replace the O_2 consumed.

The U. S. Department of the Interior (1968) data for deep waters of Lake Michigan agreed in substance with Beeton (1969); the dissolved oxygen content of the Lake is near saturation at all depths throughout the year. In the surface 10 m, dissolved oxygen was never less than 89% saturated nor greater than 152% during spring, summer, and fall of 1962 and 1963 (U. S. Dep. Inter., 1968). Below 30 m, the lowest saturation value noted by the U. S. Department of the Interior was 73%.

Ayers *et al.* (1967) collected bottom-water samples for dissolved oxygen determinations at ten deep-water stations in early autumn of 1966 (Appendix C, part 1). These data were compared with data collected by Beeton and Moffett (1964) (Appendix C, part 2). Ayers *et al.* included all of the offshore stations reported by Beeton and Moffett plus selected inshore stations in their comparison. Statistical comparisons were not used by Ayers *et al.* (1967), but they reported a diminution in dissolved oxygen concentrations since the 1950's. Statistical comparison does not confirm the report that dissolved oxygen saturation decreased between 1954-55 and 1966. There is no difference between the two groups at the 95% confidence level. Statistical comparison of the offshore values [obtained more than 16 km (10 mi) from shore] shows no difference between dissolved oxygen saturation values in the bottom waters of offshore areas in 1954-55 and 1966.

Little work has been published since the work of Ayers *et al.* (1967), so it is not clear whether there has been a diminution in dissolved oxygen since the 1950's.

OXYGEN AND SEDIMENTS

Gravity and turbulent water movements are involved in carrying a great variety of inorganic and organic substances to the sediments. The quantity of organic matter reaching the bottom is related to the intensity of photosynthetic production or to organic pollution of the overlying water (Mortimer, 1971). This organic matter is continuously broken down by organisms in the water column. Benthic animals, fungi, and bacteria in the sediment decompose organic matter while fresh organic matter falls through the water onto the sediment surface. Aerobic organisms in the sediments require oxygen to degrade this organic matter. The rate at which O_2 enters through the sediment surface is governed by at least three factors: (*i*) biological oxygen demand arising from respiration and metabolic activities of benthic organisms, (*ii*) chemical oxygen demand arising from the accumulation of reduced inorganic chemical species such as ferrous iron, and (*iii*) diffusion which regulates transport of O_2 downward.

During periods of Lake mixing, oxygen is carried to the sediment surface by turbulent water movement. Oxygen passes into the sediment; the depth of penetration depends on the rate of supply to a unit area and the oxygen demand per unit volume of sediment.

During stratification the deep-water sediment-water system is cut off from the atmospheric source of O_2 by poor mixing across the thermocline. When this occurs, the rate of O_2 consumption at the surface of the sediment can be determined. Even with modern-day technology it is difficult, if not impossible, to determine the depth in the sediment at which oxygen disappears. Indirect methods are used to locate the presence or absence of O_2 in sediments (Mortimer, 1971). One indirect method measures the electrical potential by using a bright platinum electrode inserted into a sediment sample. The meaning of the measurement is unclear when strict chemical interpretation is attempted (Morris and Stumm, 1967). There are many oxidizable and reducible substances present, equilibrium may be attained slowly, and reactions at the electrode may not be reversible (for greater detail, see a physical chemistry text). Empirically, a positive potential is generally obtained when the system contains O_2 (or other oxidizing agents), whereas negative potentials are usually obtained in anaerobic systems.

Data from Callender (1969) suggested that electrode potentials in surficial sediments of Lake Michigan are high and positive (Fig. 29). Leland *et al.* (1973b) found a close correlation between stratigraphic relationships of the sediments of the southern basin (Lineback and Gross, 1972) and electrode potential measurements. Electrode potentials in the gray silt facies were much lower than those in the brown silt facies. This difference was attributed to the higher organic carbon content (*i.e.* COD) of the gray silts.

Green Bay presents an excellent illustration of the effects of oxygen-consuming material on measured electrode potentials in sediments. A great amount of oxygen-consuming material discharged by pulp and paper mills along the Fox River is carried out into the Bay. Regions of deoxygenation and recovery from deoxygenation have been identified in the water of the Bay (Epstein *et al.*, 1974). Data of Edgington and Callender (1970), showing an increase in electrode potential in surficial sediments with increasing distance from the mouth of the Fox River, also demonstrated the effects of deoxygenation near a large source of oxygen-demanding materials.

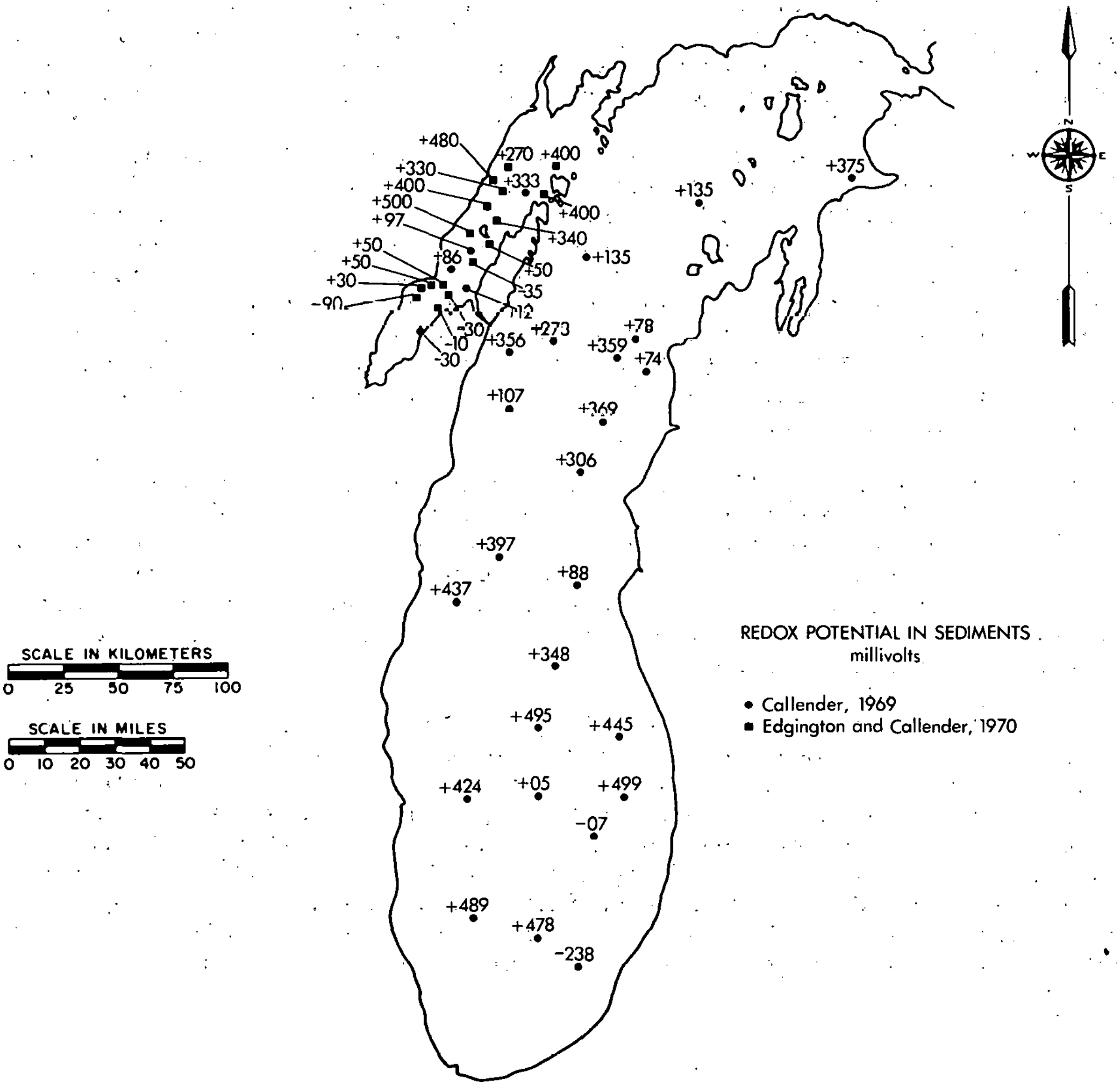

Fig. 29. Redox Potential in Lake Michigan Sediments. Data from Callender (1969) and Edgington and Callender (1970).

pH, INORGANIC CARBON, BUFFERING, AND ORGANIC CARBON

Rain absorbs small amounts of carbon dioxide, CO_2, from the air through gas transfer processes similar to those by which oxygen is transferred from air to water. CO_2 reacts with rainwater to form carbonic acid, H_2CO_3:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \ . \tag{11}$$

Carbonic acid may then dissociate in two steps. The first dissociation produces H^+ and HCO_3^- ions,

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \ . \tag{12}$$

The second step produces CO_3^{2-} and more hydrogen ions,

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \ . \tag{13}$$

These dissociations, leading to the release of H^+ ions to solution, demonstrate the acid character of aqueous CO_2.

Limestones, $CaCO_3$, and dolomites, $CaMg(CO_3)_2$, found throughout the Lake Michigan watershed, are readily dissolved by carbonic acid (Callender, 1969):

$$CaCO_3\ (s) + H_2CO_3 \rightleftharpoons Ca^{2+} + 2\ HCO_3^- \ , \tag{14}$$

and

$$CaMg\ (CO_3)_2 + 2\ H_2CO_3 \rightleftharpoons Ca^{2+} + Mg^{2+} + 4\ HCO_3^- \ . \tag{15}$$

The contribution of HCO_3^- to the Lake by tributaries is controlled by two factors:

(*i*) The amount of CO_2 in the water falling on the land and percolating through the soil.

(*ii*) The carbonate mineral content of the rocks and soils through and over which the CO_2-containing water has passed.

Equations 11-13 describe equilibrium processes. If the amount of one component in an equilibrium expression increases, then the others must change proportionately so that equilibrium is maintained. Consequently the concentration of H_2CO_3 depends on the amount of CO_2 in solution (Eq. 11). Likewise, the amount of $CaCO_3$ which can be dissolved by carbonic acid (Eq. 14) depends on the amount of H_2CO_3 present.

There must always be a certain surplus amount of free, unreacted CO_2 (aq) to maintain equilibrium in Equation 11 and, indirectly, equilibria in Equations 12-15. If this free CO_2 should somehow be lost, then it must be replaced by equilibrium processes (Eqs. 11-13).

The rate at which equilibrium is attained can be quite slow. This lag accounts for instances of extended periods of time when all conditions (temperature; pressure; concentrations of H_2CO_3, H^+, HCO_3^-, CO_3^{2-}, and Ca^{2+}) indicate that $CaCO_3$ should form, but no precipitate is detectable, *i.e.* supersaturation with respect to $CaCO_3$ (*cf.* Schelske and Callender, 1970).

Another reaction of HCO_3^- which needs to be introduced here is its reaction with water, resulting in the formation of H_2CO_3 and hydroxide ion,

$$HCO_3 + H_2O \rightleftharpoons H_2CO_3 + OH^- \ . \qquad (16)$$

There is a complex equilibrium system in Lake Michigan involving free CO_2, carbonic acid in combined (H_2CO_3) and dissociated (HCO_3^-, H^+, CO_3^{2-}) forms, Ca^{2+} and HCO_3^- from the dissolution of calcite and dolomite by H_2CO_3, and also OH^- ions from the hydrolysis of HCO_3^- (Eq. 16). Using methods such as those of Krauskopf (1967), one can calculate that Lake Michigan in equilibrium with atmospheric CO_2 and carbonate minerals (calcite and dolomite) should be weakly alkaline. We shall see this is true.

HYDROGEN ION CONCENTRATION, OR pH

The hydrogen ion concentration in aquatic environments may determine which organisms predominate, the availability of many nutrients, and the relative toxicity of certain trace constituents. Bicarbonate content has a major influence on hydrogen ion concentration in Lake Michigan (Eqs. 12, 13, and 16); the whole topic of hydrogen ion content is inextricably linked to carbonic acid, bicarbonate, and carbonate content.

Before discussing the hydrogen ion content in Lake Michigan, consider the simplest system, the hydrogen ion concentration of pure water. The dissociation of pure water is commonly written as

$$H_2O \rightleftharpoons H^+ + OH^- \ . \qquad (17)$$

Strictly speaking, Equation 17 is an oversimplification.* Since

$$(H^+)\ (OH^-) = K_w = 1 \times 10^{-14} \ , \qquad (18)$$

**Further detail is found, for example, in Hutchinson (1957), Stumm and Morgan (1970), or physical chemistry texts.*

the concentrations of H^+ and OH^- at neutrality are *ca.* 1×10^{-7} moles/l. In place of moles/l, hydrogen ion concentration is more frequently expressed as a pH value. The meaning of pH can be derived from rearranging Equation 18 to

$$(H^+) = \frac{K_w}{(OH^-)} \ . \tag{19}$$

Taking the logarithm of both sides of Equation 19 and multiplying by -1, we get

$$-\log (H^+) = -\log K_w + \log (OH^-) \ . \tag{20}$$

pH is defined as the negative logarithm of hydrogen ion activity.*. At neutrality $(H^+) = (OH^-) = 1 \times 10^{-7}$ moles/l, and pH = 7.00.

pH in Water

Hydrogen ion variations in Lake Michigan are much more complex than pure water. The pH of Lake Michigan water is determined by the H^+ ions generated by the dissociation of H_2CO_3 (Eq. 12) and OH^- ions arising from the hydrolysis of bicarbonate (Eq. 16). These chemical processes in turn are influenced by organisms living in the Lake. As CO_2 is removed from solution during photosynthesis, the reactions of Equations 11 and 12 shift to the left to replace lost CO_2. The pH increases as H^+ is used up to form H_2CO_3 (Eq. 12).

When intense photosynthetic activity removes virtually all CO_2, some phytoplankton are able to obtain CO_2 from HCO_3^-. This switch to an alternate carbon source leads eventually to the precipitation of $CaCO_3$ (Eqs. 11 and 14).

All organisms release CO_2 to the surrounding medium during respiration, leading to the formation of H_2CO_3, which dissociates to form HCO_3^- and H^+. In extremely productive lakes, there is a noticeable diel cycle of pH; pH is high during the day, when photosynthesis predominates, and low at night, when only respiration occurs. No noticeable diel cycle occurs in Lake Michigan.

Table 12 summarizes pH data collected in Lake Michigan water. Surface-water values generally lie between pH 8 and 9, and bottom-water values range between *ca.* 7.5 and 8.5. Since surface waters are warmer than bottom waters for much of the year, lower pH values in colder bottom waters might be due at least in part to enhanced solubility of CO_2 at lower temperatures (see Carbon Dioxide section below). Comparison of surface-water pH values in winter (Fig. 30) with summer values (Fig. 31) shows that winter values are 8.0-8.2, and summer values are 8.3-8.5. This seasonal difference might be at least partly attributable to variations in CO_2 solubility with temperature.

**In Lake Michigan water, the ionic strength is low enough (ca.* 4.4×10^{-3} *moles/l) that activities and concentrations are nearly identical. Thus the more familiar term concentration is used in this report, although activity is the more precise term.*

Table 12. pH Values in Lake Michigan Water

		pH Value		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Samples collected:				Beeton and Moffett, 1964
Southern basin and divide area				
6 inshore stations	May-Dec 1954			
Surface-water		8.3	8.0-8.5	
Bottom-water		8.0	7.4-8.4	
11 offshore stations	May-Nov 1954			
Surface-water		8.1	8.0-8.4	
Bottom-water		7.9	7.3-8.5	
Northern basin and divide area				
8 inshore stations	May-Nov 1955			
Surface-water		8.2	7.8-8.4	
Bottom-water		8.0	7.5-8.4	
4 offshore stations	May-Nov 1955			
Surface-water		8.2	7.9-8.4	
Bottom-water		7.9	7.6-8.3	
Southern basin				
3 inshore stations	Apr-Nov 1960			
Surface-water		8.3	8.0-8.4	
Bottom-water		8.0	7.4-8.4	
1 central station sampled 4 times	May-Sep 1960			
Surface-water		8.3	8.0-8.4	
Bottom-water		8.1	7.8-8.4	
Northern basin				
5 inshore stations	May-Nov 1961			
Surface-water		8.1	7.6-8.4	
Bottom-water		7.9	7.6-8.2	
2 offshore stations	May-Nov 1961			
Surface-water		8.2	7.8-8.2	
Bottom-water		7.9	7.6-8.2	
Samples collected ∿monthly from Peter Cooper Corp. intake, Oak Creek, ∿0.75 km (2500 ft) offshore	Jul-Dec 1961	7.8	7.7-8.3	Wis. Comm. Water Pollut., 1965
	Apr-Dec 1962	7.9	7.7-8.1	
	Jan-Dec 1963	8.2	7.8-8.7	
	Apr-Nov 1964	7.9	7.7-8.1	
	May-Dec 1965	7.9	7.7-8.5	Wis. Dep. Nat. Resour., 1969
	May-Oct 1966	7.8	7.6-7.9	
	Mar-Dec 1967	7.2	6.0-7.7	
	Apr-Dec 1968	7.7	7.7-7.8	
	May-Nov 1969	7.7	7.6-7.7	Wis. Dep. Nat. Resour., 1973
	Apr-Dec 1970	7.7[a]		
	May-Dec 1971	7.8	7.7-8.0	
	May-Aug 1972	7.8	7.7-7.8	
Single inshore samples collected along southwestern shore near:	1 May 1961			Ayers *et al.*, 1967
Dunne Crib		8.79		
Calumet Harbor entrance		8.50		
Hammond water plant intake		8.41		
Indiana Harbor ship canal entrance		7.50		
Whole Lake:	1962-63			USDOI, 1968
1040 offshore samples			7.5-8.9	
2113 inshore samples			6.4-9.3	
Samples collected:	1962-63			USDOI, 1968
Indiana Harbor, 26 samples			6.0-7.8	
Calumet Harbor, 24 samples			6.4-8.4	
Chicago Harbor, 11 samples			7.8-8.7	
Racine Harbor, 8 samples			7.9-8.3	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City		8.2	6.0-8.8	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo		8.3	7.4-9.3	

√

Table 12. (contd.)

		pH Value		
Sample Description	Dates	Average	Range	Reference
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor		8.3	7.8-8.8	
On a line roughly between Sheboygan and Little Sable Point		8.2	7.0-8.6	
Samples collected:	Oct 1962, Jun 1963			USDOI, 1968
Milwaukee Harbor, 38 samples			7.4-8.9	
Adjacent to Milwaukee Harbor, 84 samples			7.4-9.1	
Samples collected:	22-28 Jul 1964			USDOI, 1968
Traverse Bay, 78 samples			7.9-8.8	
Adjacent to Traverse Bay, 26 samples			7.9-8.5	
Samples collected in Indiana Harbor at east breakwall inner light:				Snow, 1974
3 samples	Dec 1965	6.8	6.7-6.9	
51 samples	Jan-Dec 1966		6.6-8.0	
42 samples	Jan-Dec 1967		6.0-8.0	
37 samples	Jan-Dec 1968	7.4	6.5-8.2	
25 samples	Jan-Jun 1969	7.4	7.0-8.5	
20 samples	Jan 1971-Jan 1973	7.4	6.8-7.8	
Samples collected at water filtration plants near Chicago:				
12 plants	1968			Ill. Sanit. Water Board, 1969
Annual median values			8.2-8.3	
Daily median values			7.8-8.6	
5 plants	1969			Ill. Sanit. Water Board, 1970
Annual median values			8.2-8.3	
Daily median values			8.0-8.5	
Samples collected:				Schelske and Callender, 1970
Southern basin	22-24 Jul 1969			
Surface-water, 9 inshore stations		8.6	8.5-8.7	
Bottom-water, 8 inshore stations		8.2	8.1-8.4	
Surface-water, 7 offshore stations		8.6	8.5-8.7	
Bottom-water, 7 offshore stations		8.2	8.1-8.6	
Northern basin	15-23 Aug 1969			
Surface-water, 6 offshore stations		8.6	8.45-8.65	
Bottom-water, 6 offshore stations		8.2	8.05-8.3	
Northern basin, including Traverse Bay	15-23 Aug 1969			
Surface-water, 15 inshore stations		8.6	8.5-8.65	
Bottom-water, 8 inshore stations		8.2	8.15-8.3	
Northern Green Bay, including Bays de Noc	15-23 Aug 1969			
Surface-water, 5 stations		8.5	8.45-8.55	
Northern Green Bay, including Big Bay de Noc	15-23 Aug 1969			
Bottom-water, 4 stations		8.1	8.05-8.15	
Southern Green Bay	15-23 Aug 1969			
Surface-water, 4 stations		8.6	8.45-8.75	
Bottom-water, 4 stations		7.7	7.6-7.85	
Weekly samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	Nov 1969-Sep 1970	8.2	8.0-8.6	USGS, 1972
	Oct 1970-Sep 1971	8.3	8.0-8.6	USGS, 1973
	Oct 1971-Sep 1972	8.3	7.9-8.6	USGS, 1974a
	Oct 1972-Jun 1973	8.3	8.2-8.4	USGS, 1974b
Samples collected ~monthly at intakes:	Jan 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		8.1	7.7-8.5	
Waukegan Generating Station		8.0	7.3-8.4	
North Chicago public water supply		8.1	7.8-8.4	

Table 12. (contd.)

Sample Description	Dates	pH Value		Reference
		Average	Range	
Samples collected ∿monthly at 3 stations 9.6 km (6 mi) east of Zion:	Apr 1970-Apr 1971			Industrial Bio-Test, 1972b
Surface-water		8.2	8.0-8.6	
Bottom-water		8.1	7.4-8.5	
Samples collected at 8- to 21-day intervals (except 3 Feb-11 Mar) at a depth of 4 m:	27 May 1970- 20 Oct 1971			Rousar, 1973
4.8 km (3.0 mi) east of Milwaukee		8.3	7.9-8.8	
Between Milwaukee and Ludington				
1/4 the distance		8.3	8.1-8.8	
1/2 the distance		8.3	8.1-9.0	
3/4 the distance		8.3	8.1-9.0	
4.8 km (3.0 mi) west of Ludington		8.4	8.1-9.0	
Monthly samples collected at Lake County, Ill., public water intake	Jun 1970-Jun 1973	8.1	7.7-8.3	Howe, 1973
Samples collected west of Grand Haven at a depth of 7 m:				Schelske *et al.*, 1971
Inshore station 1.2 km (0.75 mi) west, 10 samples	29 Jun-8 Sep 1970	8.56	8.35-8.81	
Inshore station 3.3 km (2.1 mi) west, 6 samples	16-26 Sep 1970	8.64	8.62-8.68	
Offshore station 6.7 km (4.2 mi) west, 8 samples	17 Jul-8 Sep 1970	8.64	8.57-8.78	
Samples collected at stations on a line passing east of Manitou Islands from Frankfort to Beaver Island:	7 Jul 1970			Schelske and Roth, 1970
6 stations, 19 surface-water samples		8.56	8.48-8.63	
4 stations, 5 bottom-water samples		8.30	8.00-8.44	
Single samples collected at public water intakes:	1971			Baumeister, 1972
Kenosha		8.1		
Milwaukee (5 intakes)		8.2	7.8-8.4	
Port Washington		7.6		
Racine		8.6		
Sheboygan		8.0		
Two Rivers		8.5		
Single samples collected (water depth 7.6 m) at a station east of Kewaunee Nuclear Plant:				Industrial Bio-Test, 1972d
Surface	25 May 1971	7.9		
Bottom	25 May 1971	8.1		
Surface	31 Aug 1971	8.4		
Bottom	31 Aug 1971	8.3		
Surface	16 Nov 1971	7.5		
Bottom	16 Nov 1971	7.4		
Samples collected ∿monthly, surface to bottom, near Point Beach Nuclear Plant:	Jun, Jul, Sep 1971			Weschler *et al.*, 1972
6 stations <0.37 km (1230 ft) from shore		8.5	8.2-8.6	
4 stations 1.1-2.7 km (3600-9000 ft) from shore		8.5	8.3-8.6	

Table 12. (contd.)

Sample Description	Dates	pH Value		Reference
		Average	Range	
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun 1971-Apr 1972	8.0	7.6-8.3	Industrial Bio-Test, 1972c
Samples collected every 0.4 km (0.25 mi) from 0.4-3.2 km (0.25-2.0 mi) and every 0.8 km (0.5 mi) from 3.2-8.0 km (2.0-5.0 mi) along a tangent east of Milwaukee Harbor:	Mar 1972			Nienke, 1972
Surface-water (1 m)		7.7	7.5-7.9	
Bottom-water		7.6	6.6-7.8	
Samples collected at 0.4 km (0.25 mi) and every 0.8 km (0.5 mi) from 0.8-8.0 km (0.5-5.0 mi) along a tangent east of Shorewood Beach, 8.0 km (5.0 mi) north of Milwaukee Harbor:	Mar 1972			Nienke, 1972
Surface-water (1 m)		7.8	7.7-7.9	
Bottom-water		7.8	7.7-7.9	
Surface-water samples collected at 9 shoreline stations between Milwaukee and Sheboygan	11 Apr 1972	7.8	7.6-7.9	Nienke, 1972
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		8.18	8.08-8.32	
Effluent plume		8.16	8.03-8.29	
South of plant, 4.8 km (3 mi)		8.15	7.77-8.30	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		8.13	8.00-8.30	
North of plant, 1.6 km (1 mi)		8.14	8.00-8.30	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		8.06	7.52-8.33	
South of plant, 1.6 km (1 mi)		8.11	7.70-8.38	

[a] *Same value for all samples.*

USDOI = U. S. Department of the Interior; USGS = U. S. Geological Survey.

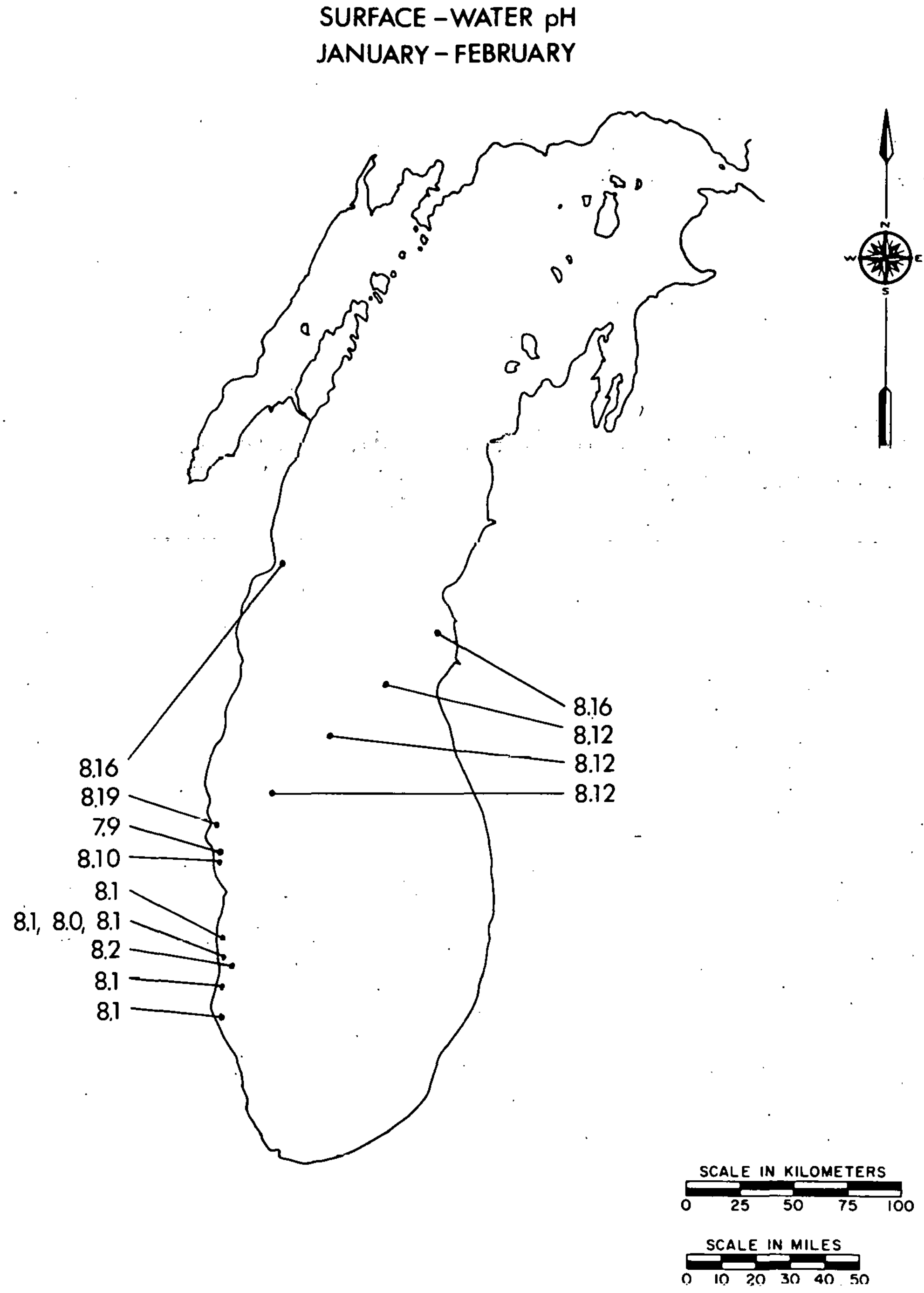

Fig. 30. Surface-Water pH Values in January-February over a Period of Ten Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 12.

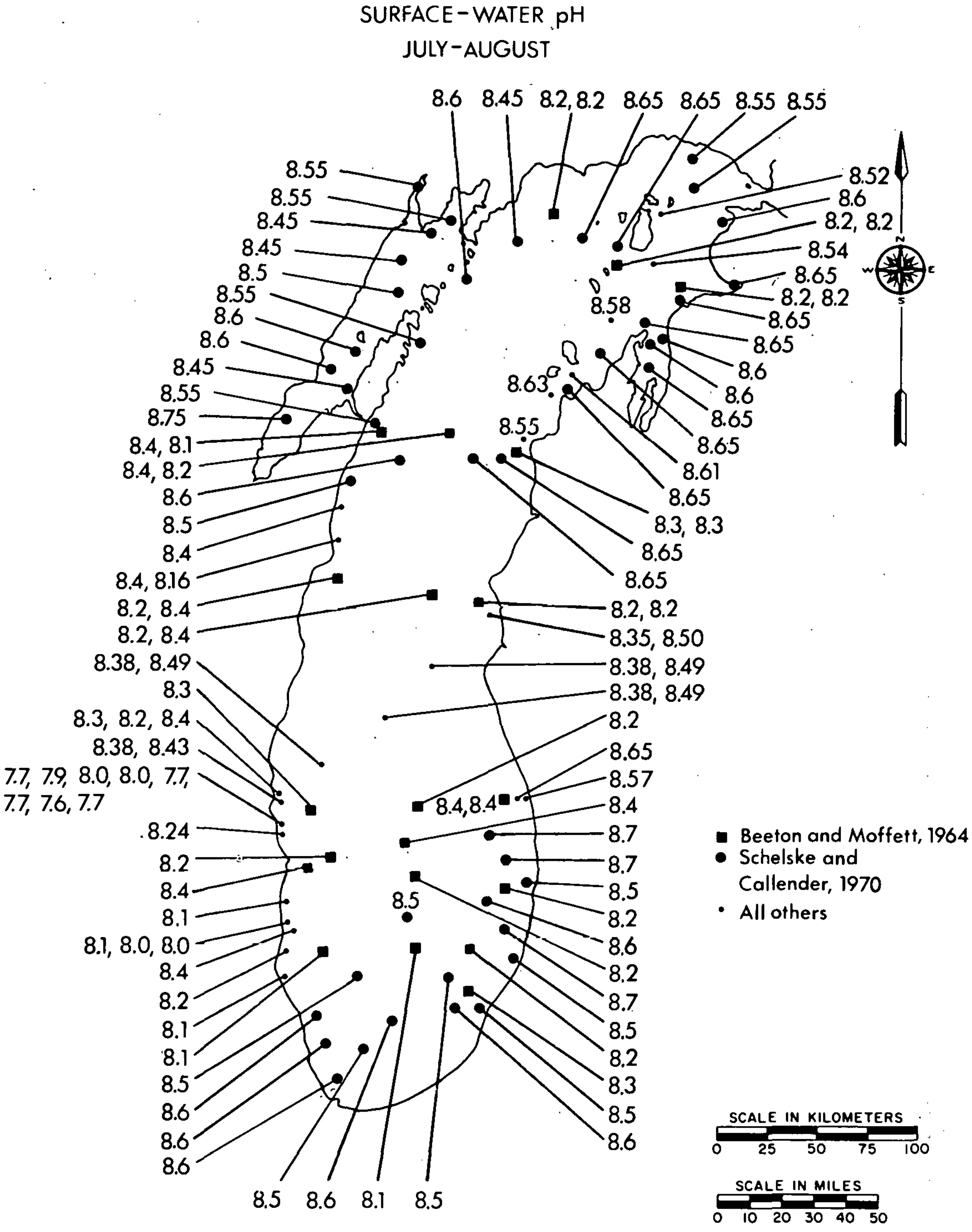

Fig. 31. Surface-Water pH Values in July-August over a Period of Twenty Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 12.

Simple gas solubility does not provide a complete explanation for variations in pH with season and depth. During summer, organisms photosynthesize in the surface water during daylight, removing CO_2 and raising the pH. At night, respiration returns much of this CO_2 to the water. However, there is usually slightly more photosynthesis than there is respiration; thus, there is a net removal of CO_2 from the water as organic matter. As long as net removal is greater than addition and net regeneration, pH values are higher in waters where photosynthesis takes place. Respiration may not occur at the same place in the water column as photosynthesis; that is, sinking phytoplankton release CO_2 at greater depths than where photosynthesis occurred. Thus pH values in surface waters are higher than in bottom waters (Table 12). The pH is higher in surface water during summer (Fig. 31) than in winter (Fig. 30), because of lower solubility of CO_2 and enhanced removal of CO_2 from warmer waters by photosynthesizing organisms.

During stratification, pH values are less in bottom waters than in surface waters; during periods of mixing, pH values in surface and bottom waters are nearly the same (Fig. 32; *cf.* Fig. 35). Greater solubility of CO_2 at lower temperatures as well as biochemical effects contribute to the differences during stratification. Organic matter added to or produced in the surface water settles out on the sediment surface. Microbial activities break down this organic matter while it settles out and after it reaches bottom, releasing CO_2. Respiration by organisms living in the bottom waters also produces CO_2.

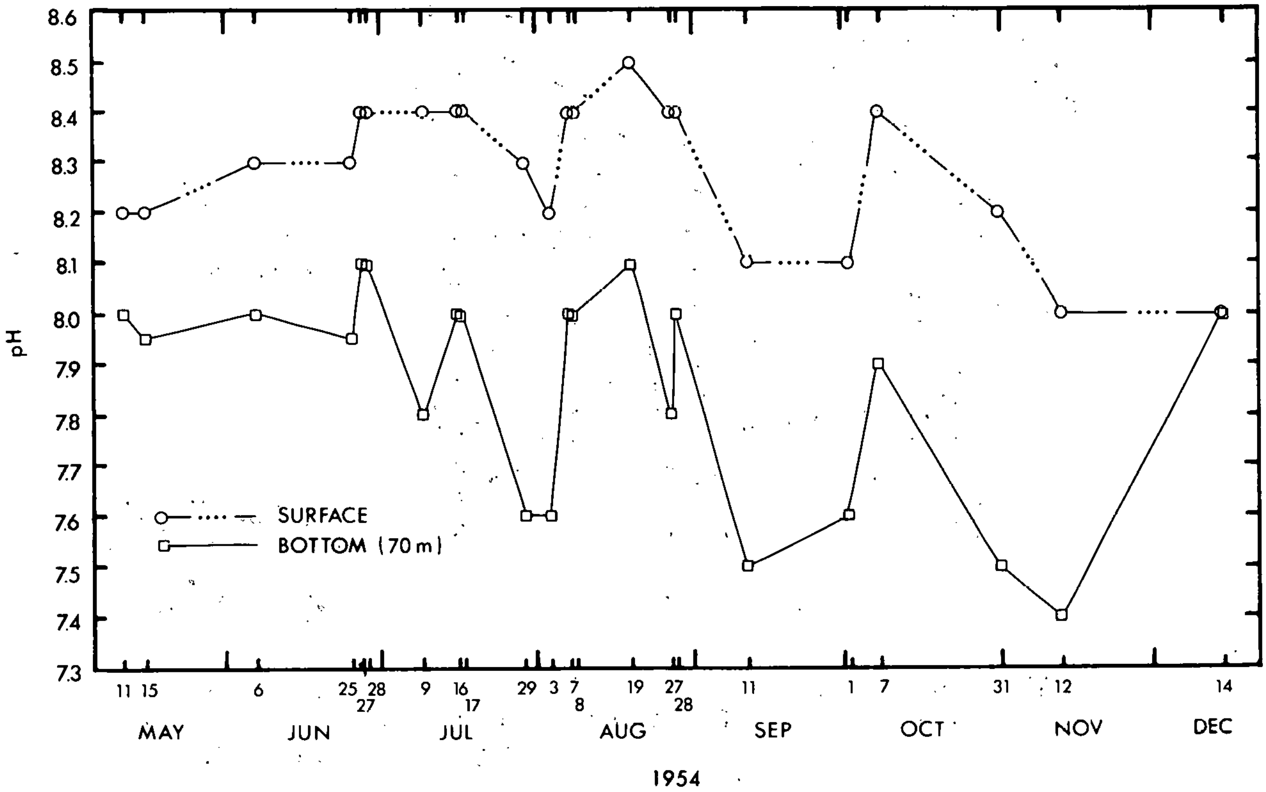

Fig. 32. Seasonal Variation of pH at a Station 12.9 km (8 mi) West of Grand Haven. Data from Beeton and Moffett (1964).

Since there is no net photosynthesis to remove CO_2 from these unlighted bottom waters, CO_2 builds up (see section on Carbon Dioxide below) and pH decreases. In late fall-early winter, mixing restores (nearly) homogeneous conditions top-to-bottom.

For the protection of freshwater organisms, the National Academy of Sciences ... (1973) made recommendations on pH values (Appendix B, part 2). These recommendations are based on attendant changes in toxicity of other compounds with pH, such as the alteration of hydrocyanic acid (HCN) to cyanide ion (CN^-), as well as other nonlethal effects. For example, the water flea *Daphnia magna* does not reproduce below pH 6.0. Alkaline conditions above pH 8.5 can reduce the fertility of many fish species. The availability and form of some important nutrients, *e.g.* NH_3 *vs.* NH_4^+ and Fe^{3+} *vs.* $Fe(OH)_3$, also may be affected by pH.

An International Agreement between the United States and Canada (U. S. Treaties, etc., 1972) concerning water quality of the international Great Lakes set a specific objective for pH of not less than 6.7 and not more than 8.5. Although this agreement is not applicable to Lake Michigan, Table 12 demonstrates that on occasion Lake Michigan water is not in compliance with this objective due to occasional high values in surface waters during summer and low values in harbors.

pH Values in Sediments

Callender (1969) measured pH values in Lake Michigan sediments during May-July 1968 (Fig. 33). In all cases, the pH was 7.8 or less in surficial sediments; these values are as low as or lower than those in bottom waters of the Lake (*cf.* Table 12). Decomposition of organic matter in the sediments with accompanying release of CO_2 and acid formation account for these observations.

Callender (1969) also measured pH with sediment depth in cores: the southern basin (1 core), Green Bay (2 cores), the northern basin (3 cores) and Little Traverse Bay (1 core). In the core from Little Traverse Bay, pH was constant to 75 cm. In the other six cores, pH decreased with sediment depth (Table 13). At the sediment surface, some of the CO_2 released during decomposition and respiration diffuses away or is carried away by turbulent mixing and mass transport. The latter two processes are absent in sediments at depth, so simple diffusion of CO_2 is extremely slow. A buildup of CO_2 and H^+ (decrease in pH) may occur with sediment depth.

Industrial Bio-Test (1972d) measured pH in sediment samples collected within 5.3 km (3.3 mi) of the Kewaunee Nuclear Power Plant (Table 14). It is not obvious whether the seasonal variation in average pH values shown by these data is real.

INORGANIC CARBON

Carbon Dioxide

Some knowledge of the processes by which CO_2 is added to and removed from Lake Michigan water is necessary to understand how organisms grow and interact in the Lake.

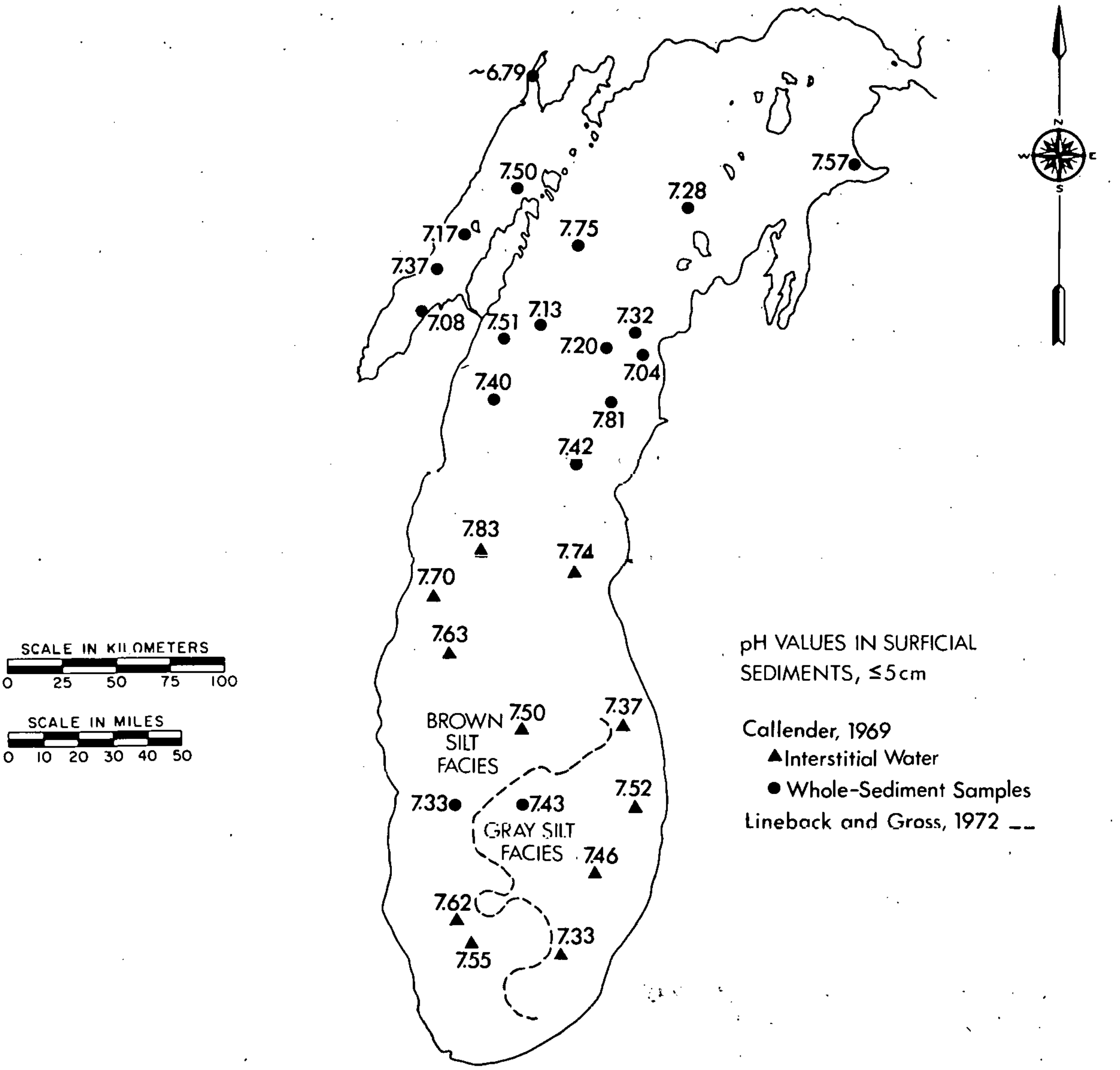

Fig. 33. pH Values in Surficial Sediments of Lake Michigan. Data collected May-July 1968 by Callender (1969). Boundary of brown and gray silt facies of the Waukegan member from Lineback and Gross (1972).

Carbon dioxide is about 30 times more soluble in water than is O_2 (Liss, 1973). Its solubility decreases nonlinearly with increasing temperature. Atmospheric pressure also affects the amount of CO_2 which dissolves. Since variations in atmospheric pressure are usually small and succeed each other rapidly, these short-term irregularities can be ignored in computing CO_2 solubility in water. Another factor influencing the solubility of CO_2 in water is its fraction in the overlying atmosphere. There is evidence (summarized by Skirrow, 1965) that the CO_2 content of the world's atmosphere is slowly increasing due to accelerating combustion of fossil fuels, but for the purposes of this report, the atmospheric content of CO_2 is 0.03% by volume.

Table 13. pH Variation in Sediment Cores of Lake Michigan*

Depth in Core, cm	pH Value Station S3-4	 Station C-5	 Station M1-12
0-5	7.75	7.43	7.37
22-27			6.73
30-35	7.30	7.23	
52-58			6.52
60-65	7.33	7.22	

*Station S3-4: In northern basin, 24 km (15 mi) east of Baileys Harbor in Door County (45°06', 86°46'); Station C-5: *ca.* halfway between Racine and Saugatuck (42°48', 86°59'); Station M1-12: slightly north of the Peshtigo River entrance into Green Bay (45°00', 87°34'). Data collected May-July 1968 by Callender, 1969.

Table 14. Seasonal Variation in Measured pH Values in Sediment Samples Collected near the Kewaunee Nuclear Power Plant*

Date	Number of Samples	pH Value Average	 Range
25 May 1971	6	8.4	6.8-9.4
31 August 1971	9	8.0	7.6-8.3
16 November 1971	9	7.5	7.2-7.6

*Data from Industrial Bio-Test, 1972d.

If pH values of 5 or less occurred in Lake Michigan, essentially all CO_2 would be present as CO_2 and H_2CO_3; there would be no HCO_3^- or CO_3^{2-} (Fig. 34). Under these pH conditions the factors controlling transfer of CO_2 into and out of the water resemble those controlling O_2 transfer. That is, CO_2 transfer can be described by a two-film model (Fig. 25) that also includes turbulence.

Above *ca.* pH 5, the exchange of CO_2 at the air-water interface is more complex than for O_2. Not only is there a concentration gradient for CO_2 molecules in solution, but there are also similar gradients for the HCO_3^- and CO_3^{2-} ions (Fig. 34). Under fairly calm conditions, this ionic gradient significantly enhances the exchange of CO_2 across the interface (Hoover and Berkshire, 1969; Liss, 1973).

In addition to transfer of CO_2 across the air-water interface, photosynthesis and respiration are important sinks and sources of CO_2 in Lake Michigan water. Groundwater too may contribute appreciable amounts of CO_2; rainwater percolating through the root zone in soil may easily pick up 1 to 5% CO_2, due to plant and microbial respiration (Hem, 1959). This additional CO_2 is carried in solution to the water table, where it is incorporated into the groundwater. Emergence of groundwater as tributary base flow or within the Lake itself adds CO_2 to the Lake.

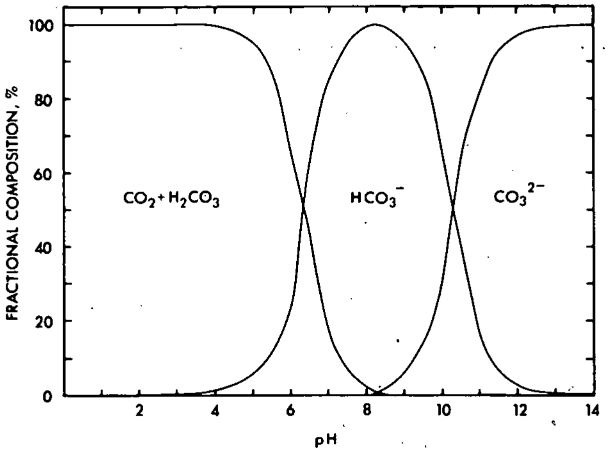

Fig. 34.
Variation in Fractional Composition of Inorganic Carbon Species with pH.

The U. S. Geological Survey (1974a, 1974b) has reported CO_2 concentrations in Lake Michigan waters. Their samples, collected October 1971-June 1973, from the intake of the Milwaukee public water supply, were taken at erratic intervals; thus it was not possible to see seasonal trends. The minimum concentration of CO_2 reported in these surface-water samples was 0.7 mg CO_2/l; the maximum was 2.6 mg CO_2/l.

Given sufficient information, total free CO_2 content can be computed without having to make an analysis for CO_2 concentration (APHA *et al.*, 1971). Data collected by Industrial Bio-Test (1972b) at a station 9.6 km (6 mi) east of the Waukegan Generating Station from May 1970 to April 1971 were used to compute CO_2 concentrations in southern Lake Michigan (Fig. 35). As temperatures

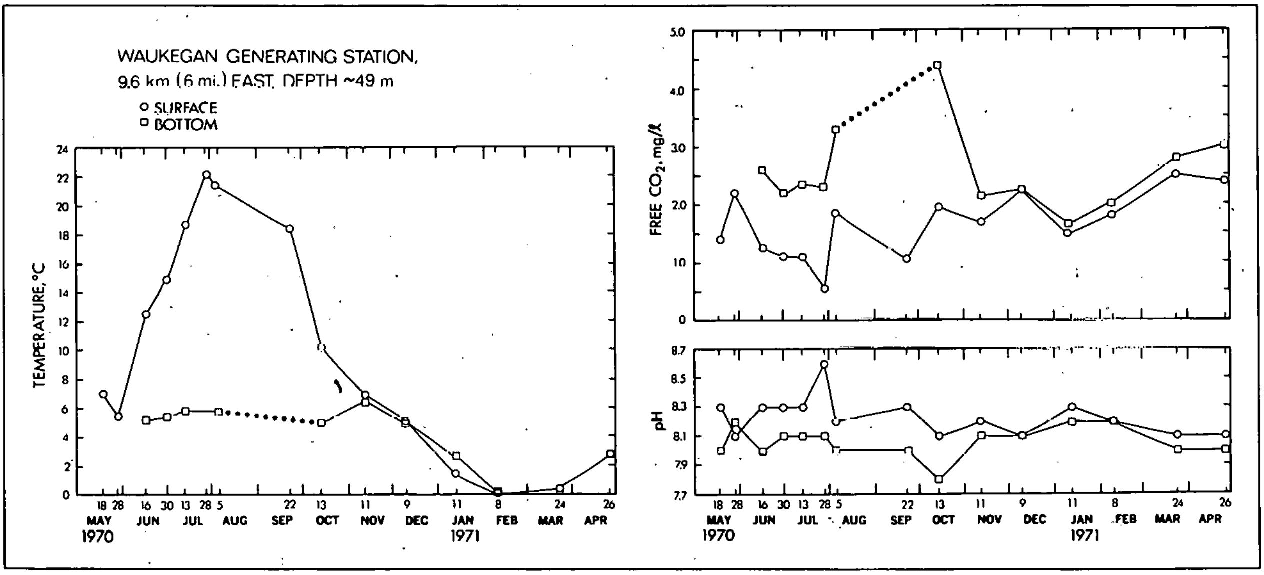

Fig. 35. Seasonal Variations of Temperature, Free CO_2, and pH at a Station East of Waukegan Generating Station. Dotted lines between 5 August and 13 October indicate probable values because the 22 September bottom-water sample was not measured for temperature and free CO_2. CO_2 content was computed according to APHA *et al.* (1971). Data from Industrial Bio-Test (1972b).

rose in the surface water in spring, CO_2 content fell from about 2.5 mg CO_2/l (26 April) to as low as 0.5 mg CO_2/l (28 July). CO_2 content in the surface water remained below that in bottom waters till stratification was completely broken down in November. Surface-water depletion of CO_2 is attributable to removal of CO_2 during photosynthesis as well as to its lower solubility at higher temperatures.

At the start of stratification, CO_2 content in the bottom water (Fig. 35) was about 2.5 mg CO_2/l. As summer progressed, CO_2 content rose in bottom water to 3.3 mg CO_2/l (5 August); just prior to the end of stratification, CO_2 content reached 4.4 mg CO_2/l (18 October). Accumulation of CO_2 in the bottom water is due to microbial degradation of organic matter that has settled into the bottom water and to respiration by organisms living there. Weiler (1974) found a similar depletion of CO_2 content in the surface water of Lake Ontario during summer, with an accompanying increase in the bottom water.

Carbonate, Bicarbonate, and Alkalinity

Carbonate and bicarbonate ion concentrations in Lake Michigan water are determined much less frequently than the related parameter, alkalinity.

Alkalinity of a water sample is a measure of the capacity of water to accept H^+ ions. Chemical species in natural waters which can accept H^+ ions include OH^-, CO_3^{2-}, HCO_3^-, ammonia ($NH_3 + H^+ \longrightarrow NH_4^+$), borates [$B(OH)_4^- + H^+ \longrightarrow B(OH)_3 + H_2O$], phosphates ($HPO_4^{2-} + H^+ \longrightarrow H_2PO_4^-$), and silicates [$SiO(OH)_3^- + H^+ \longrightarrow Si(OH)_4$]. In Lake Michigan, as in most fresh waters, only carbonate and bicarbonate are present in significant quantities. Alkalinity can be written

$$(Alk) = (HCO_3^-) + 2\ (CO_3^{2-}) + (OH^-) - (H^+)\ . \qquad (21)$$

The CO_3^{2-} is doubled since CO_3^{2-} can accept two protons. Alkalinity is determined by adding known amounts of strong acid to a sample to reach the pH of successive bicarbonate and carbonic acid end points. That is, acid is first added until all CO_3^{2-} has been converted to HCO_3^- at about pH 8.3 (Fig. 34). With addition of more acid, HCO_3^- is converted to H_2CO_3; this reaction is complete at pH 4.0-4.5 (Fig. 34). The amount of acid needed to convert carbonate to bicarbonate, added to the acid needed to convert bicarbonate initially present plus bicarbonate formed from carbonate (plus any acid needed to convert OH^- to H_2O) is a measure of the total alkalinity of the sample. By convention, total alkalinity is expressed as an equivalent weight of $CaCO_3$.

Alkalinity in Lake Michigan serves as a buffer (see discussion on Buffering below) and also acts as a reservoir of carbon for photosynthesis. This reservoir becomes important when photosynthesizing organisms remove CO_2 faster than CO_2 can move to the water from the air.

Weathering of rocks and soils in the watershed is the most important source of carbonate and bicarbonate to Lake Michigan. Bicarbonate is frequently discharged in industrial waste effluents, for bicarbonate salts are used in numerous industrial processes due to their high solubility. Bicarbonate, but not carbonate, is also found in sewage effluents. Weinberger *et al.* (1966)

reported an average increase of 100 mg HCO_3^-/l in effluent from secondary treatment of municipal waste water over tap water, or an increase in total alkalinity of 85 mg $CaCO_3$/l.

Total alkalinity data for Lake Michigan are tabulated in Table 15. Total alkalinity in the Lake is *ca.* 110 mg $CaCO_3$/l (Fig. 36). Spatial differences in alkalinity are not evident in Figure 36. There is no indication of changing alkalinity with depth (Table 15; *cf.* Beeton and Moffett, 1964; Industrial Bio-Test, 1972b; Schelske and Roth, 1973; Weschler *et al.*, 1972).

Although Rousar (1973) reported he found no seasonal variation in total alkalinity, there does seem to be a suggestion that total alkalinity decreases slightly as summer advances (Fig. 37). If this suggestion is real, then it may be attributable to precipitation of $CaCO_3$, *i.e.* the removal of carbonate alkalinity.

Only the U. S. Geological Survey (1972, 1973, 1974a, 1974b) has specifically reported carbonate alkalinity in Lake Michigan. Rousar (1973), Industrial Bio-Test (1972c), Ayers *et al.* (1967), Wisconsin Committee on Water Pollution (1965), and the Wisconsin Department of Natural Resources (1969) published data on phenolphthalein alkalinity in the Lake. Due to the small amount of phenolphthalein alkalinity in Lake Michigan water, one can assume that all phenolphthalein alkalinity is due to carbonate alkalinity (APHA *et al.*, 1971). Therefore, both phenolphthalein and carbonate alkalinity determinations are listed as carbonate alkalinities in Table 16. Carbonate alkalinity is present in low concentrations or absent from November through April (Rousar, 1973; Wis. Comm. Water Pollut., 1965; Wis. Dep. Nat. Resour., 1969; U. S. Geol. Surv., 1972, 1973, 1974a, 1974b) and reaches its highest levels in June, July, and August (Fig. 38). Photosynthetic activities in surface waters lead to the conversion of some bicarbonate ion to carbonate, accounting for the detection of carbonate alkalinity in the warmer summer months. There are no limits on alkalinity, carbonate, or bicarbonate content in public drinking water supplies (Appendix B, part 1). The National Academy of Sciences ... (1973) suggested that for the protection of aquatic life total alkalinity should not be allowed to drop more than 25% below the natural level. If a total alkalinity of 110 mg $CaCO_3$/l characterizes Lake Michigan (*cf.* Table 15), then total alkalinity should not be allowed to fall below 82 mg $CaCO_3$/l. Several values in Table 15 approach that limit.

Carbonates in Sediments

One of the major components of Lake Michigan sediments is carbonate, due to the formation of $CaCO_3$ within the Lake and to deposition of carbonates carried into the Lake from the surrounding watershed.

An extensive survey of carbonate content in Lake Michigan sediments was conducted May-July 1968 (Callender, 1969). Other data have been reported (Shimp *et al.*, 1970). Carbonate content of surficial ($\leq$ 5 cm) Lake Michigan sediments is illustrated in Figure 39. In the southern basin carbonate content averaged 5.53 weight percent (Table 17) in surficial sediments, about the same as the divide area and northern basin. Callender (1969) attributed lower carbonate content of surficial sediments in Green Bay to lower calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] contents.

Table 15. Total Alkalinity in Lake Michigan Water

Sample Description	Dates	Concentration as CaCO$_3$, mg/l		Reference
		Average	Range	
Samples collected:				Beeton and Moffett, 1964
Southern basin				
3 inshore stations	Apr-Nov 1960			
Surface-water		113	108-130	
Bottom-water		114	110-123	
1 central station sampled 4 times	May-Sep 1960			
Surface-water		112	109-117	
Bottom-water		113	112-115	
Northern basin				
5 inshore stations	May-Nov 1961			
Surface-water		111	105-117	
Bottom-water		111	105-115	
2 offshore stations	May-Nov 1961			
Surface-water		110	107-112	
Bottom-water		111	108-113	
Samples collected ∿monthly from Peter Cooper Corp. intake, Oak Creek, ∿0.75 km (2500 ft) offshore	May-Dec 1961	112	106-120	Wis. Comm. Water Pollut., 1965
	Feb-Dec 1962	110	84-120	
	Jan-Dec 1963	112	108-120	
	Jan-Dec 1964	106	68-112	
	Jan-Dec 1965	109	105-114	Wis. Dep. Nat. Resour., 1969
	Jan-Dec 1966	111	102-117	
	Jan-Dec 1967	105	102-108	
	Jan-Dec 1968	105	100-116	
	Jan-Dec 1969	105	100-110	Wis. Dep. Nat. Resour., 1973
	Jan-Dec 1970	108	92-114	
	Jan-Dec 1971	111	106-124	
	Feb-Dec 1972	110	102-116	
Whole Lake:	1962-63			USDOI, 1968
858 offshore samples		110	75-130	
2169 inshore samples		105	70-210	
Samples collected:	1962-63			USDOI, 1968
Indiana Harbor, 26 samples		110	100-125	
Calumet Harbor, 24 samples		110	95-135	
Chicago Harbor, 10 samples		100	70-120	
Racine Harbor, 10 samples		110	110-112	
Samples collected:	Oct 1962, Jun 1963			USDOI, 1968
Milwaukee Harbor, 37 samples		125	105-155	
Adjacent to Milwaukee Harbor, 82 samples		105	100-120	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City		105	90-133	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo		110	70-130	
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor		110	90-210	
On a line roughly between Sheboygan and Little Sable Point		110	90-170	
Samples collected:	22-28 Jul 1964			USDOI, 1968
Traverse Bay, 78 samples		115	110-130	
Adjacent to Traverse Bay, 29 samples		115	110-125	
Weekly samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	Nov 1969-Sep 1970	109	106-113	USGS, 1972
	Oct 1970-Sep 1971	108	105-114	USGS, 1973
	Oct 1971-Sep 1972	108	104-111	USGS, 1974a
	Oct 1972-Jun 1973	108	103-117	USGS, 1974b

Table 15. (contd.)

Sample Description	Dates	*Concentration as $CaCO_3$, mg/l* Average	Range	Reference
Samples collected ∿monthly at intakes:	Jan 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		113	104-132	
Waukegan Generating Station		113	104-130	
North Chicago public water supply		110	103-130	
Samples collected ∿monthly at 3 stations 9.6 km (6 mi) east of Zion:	Apr 1970-Apr 1971			Industrial Bio-Test, 1972b
Surface-water		106	100-115	
Bottom-water		106	102-112	
Samples collected at 8- to 21-day intervals (except 3 Feb-11 Mar) at a depth of 4 m:	27 May 1970-20 Oct 1971			Rousar, 1973
4.8 km (3.0 mi) east of Milwaukee		107	103-112	
Between Milwaukee and Ludington				
1/4 the distance		106	104-108	
1/2 the distance		106	102-108	
3/4 the distance		106	102-108	
4.8 km (3.0 mi) west of Ludington		107	103-122	
Monthly samples collected at Lake County, Ill., public water intake	Jun 1970-Jun 1973	110	96-123	Howe, 1973
Samples collected ∿monthly, surface to bottom, near Point Beach Nuclear Plant	Jul-Sep 1971			Weschler *et al.*, 1972
6 stations <0.37 km (1230 ft) from shore		111	108-114	
4 stations 1.1-2.7 km (3600-9000 ft) from shore		111	109-113	
19 samples collected, surface to bottom, at 6 stations on a line passing east of Manitou Islands from Frankfort to Beaver Island	7 Jul 1970	109	106-118	Schelske and Roth, 1973
Single samples collected at public water intakes	1971			Baumeister, 1972
Green Bay		110		
Kenosha		110		
Milwaukee (5 intakes)		114	106-118	
Port Washington		108		
Racine		116		
Sheboygan		112		
Two Rivers		112		
Samples collected (water depth 7.6 m) at a station east of Kewaunee Nuclear Plant:				Industrial Bio-Test, 1972d
Surface	25 May 1971	112	110-114	
Bottom	25 May 1971	109	108-110	
Surface	31 Aug 1971	98[a]		
Bottom	31 Aug 1971	100[a]		
Surface	16 Nov 1971	111[a]		
Bottom	16 Nov 1971	111[a]		
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun 1971-Apr 1972	107	97-139	Industrial Bio-Test, 1972c
Samples collected every 0.4 km (0.25 mi) from 0.4-3.2 km (0.25-2.0 mi) and every 0.8 km (0.5 mi) from 3.2-8.0 km (2.0-5.0 mi) along a tangent east of Milwaukee Harbor:	Mar 1972			Nienke, 1972
Surface-water (1 m)		110	108-112	
Bottom-water		110	66-141	

Table 15. (contd.)

Sample Description	Dates	Concentration as $CaCO_3$, mg/l		Reference
		Average	*Range*	
Samples collected at 0.4 km (0.25 mi) and every 0.8 km (0.5 mi) from 0.8-8.0 km (0.5-5.0 mi) along a tangent east of Shorewood Beach, 8.0 km (5.0 mi) north of Milwaukee Harbor:	Mar 1972			Nienke, 1972
Surface-water (1 m)		110	108-114	
Bottom-water		110	106-112	
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		99	87-136	
Effluent plume		98	86-124	
South of plant, 4.8 km (3 mi)		97	85-122	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		101	88-117	
North of plant, 1.6 km (1 mi)		102	89-120	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		110	91-124	
South of plant, 1.6 km (1 mi)		110	93-124	

[a] *Same value for all samples.*

USDOI = U. S. Department of the Interior; USGS = U. S. Geological Survey.

Looking more closely at Figure 39, one sees that carbonate content in the brown silt facies of the Waukegan member (Lineback and Gross, 1972) in the southern basin is lower [$\bar{x}$ = 5.46 weight percent, based on data from both Callender (1969) and Shimp *et al.* (1970)] than in the gray silt facies ($\bar{x}$ = 7.51 weight percent) along the eastern shore. This observation correlates well with the higher magnesium and calcium concentrations in sediments from the eastern portion than from the western part of the southern basin. In general, Callender (1969) found that calcium and magnesium contents correlated highly with carbonate (Table 18), suggesting that carbonate was present mostly in combination with calcium and magnesium.

In Table 17, the variation of carbonate content with sediment depth is summarized. In 21 of 39 cores collected by Callender (1969) and Shimp *et al.* (1970), carbonate content increased with sediment depth; in five cores, it remained the same, and in 13 cores carbonate content decreased with depth. Changes in carbonate content with depth can be rationalized in several ways:

(*i*) One may hypothesize that in recent years more carbonate is reaching the sediment than in the past, accounting for higher carbonate content at the sediment surface than at depth. Alternatively, less carbonate is reaching the sediment, accounting for lower carbonate content at the sediment surface than at depth.

(*ii*) One may hypothesize that the same absolute amount (mass/unit time) of carbonate is reaching the sediment, but the input of some other component

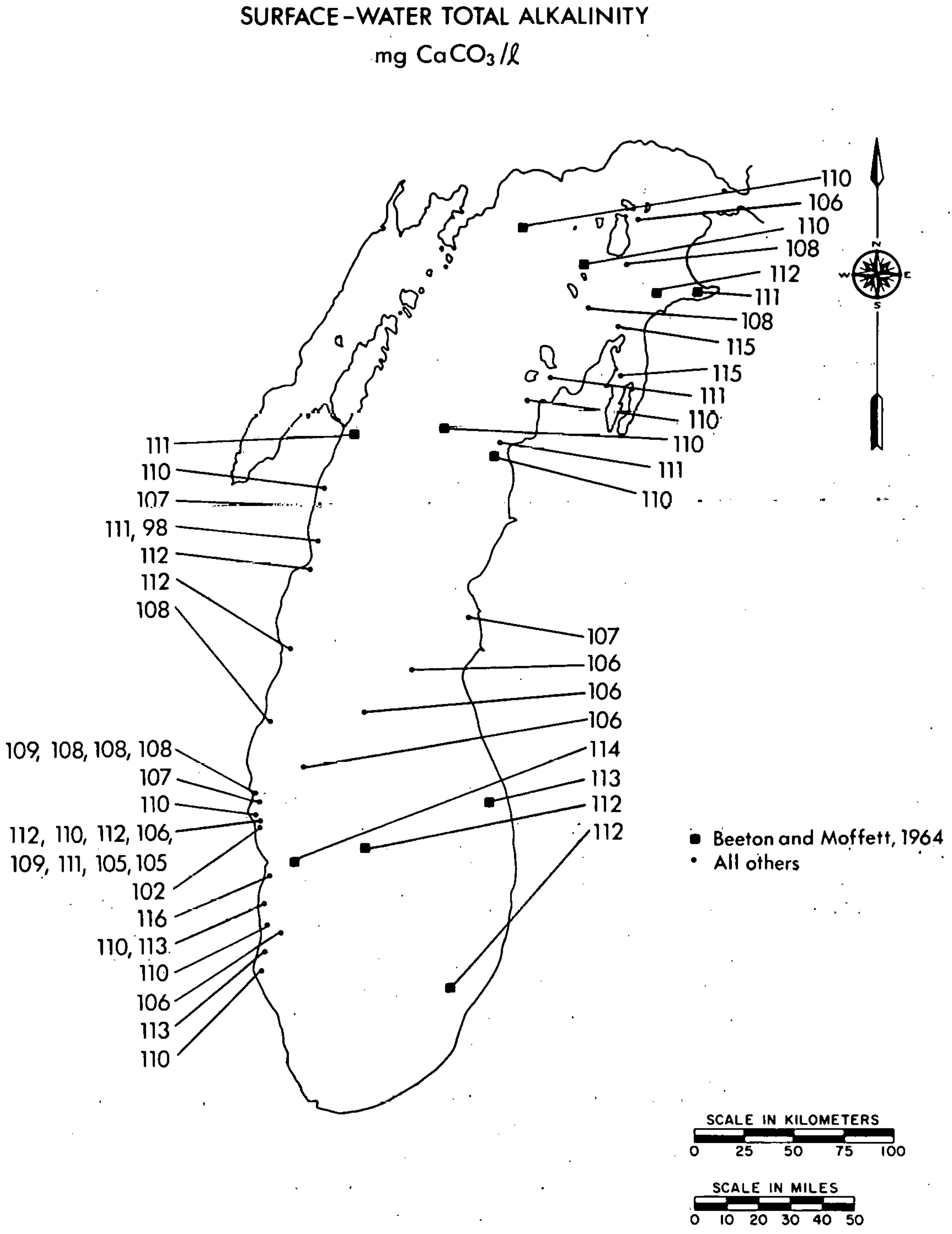

Fig. 36. Surface-Water Total Alkalinity Concentrations over a Period of Fifteen Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 15.

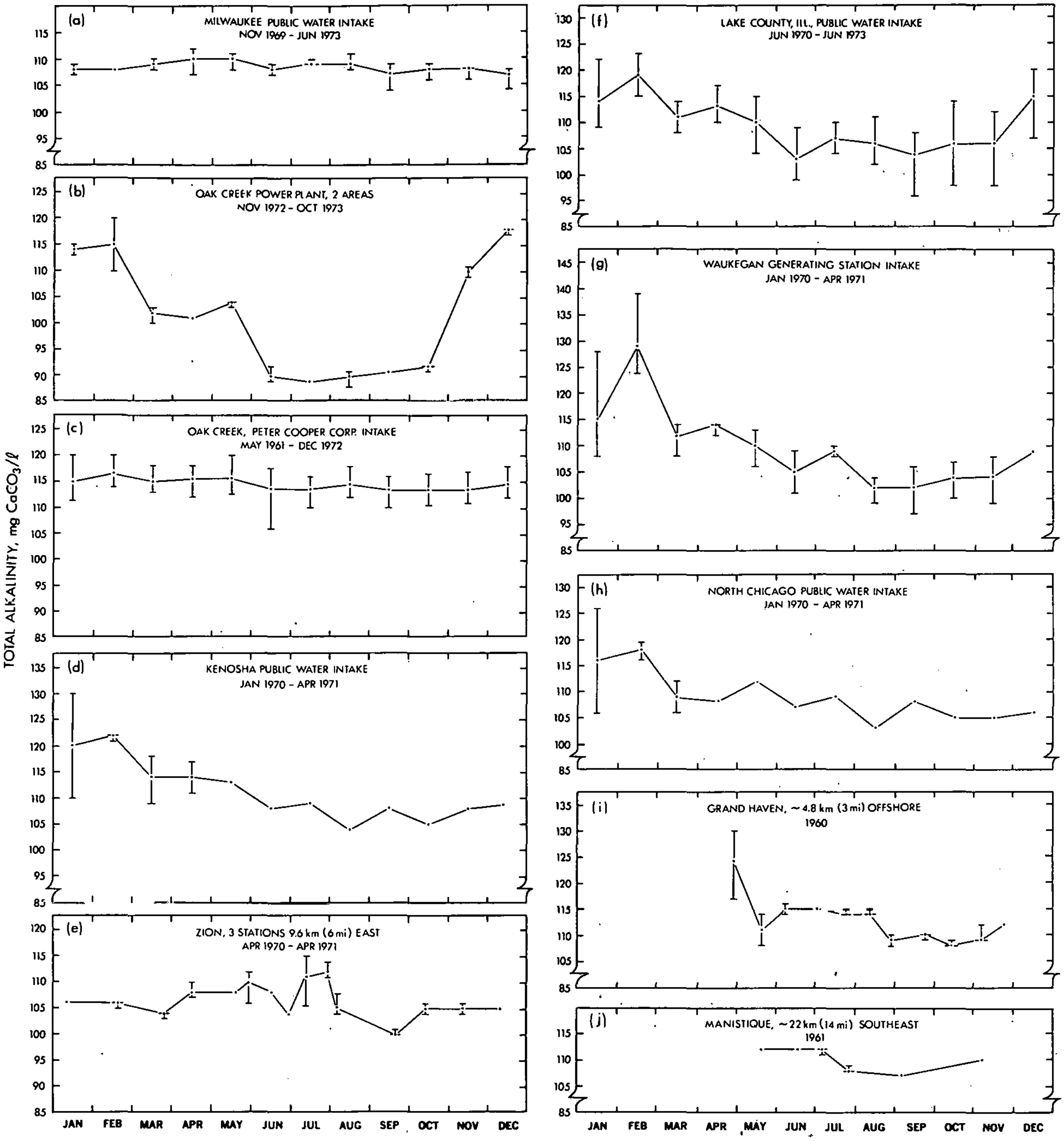

Fig. 37. Seasonal Variations of Average Total Alkalinity in Surface Waters of Lake Michigan. Sources of data: (a) U. S. Geological Survey, 1972, 1973, 1974a, 1974b; (b) Limnetics, 1974; (c) Wisconsin Committee on Water Pollution, 1965, and Wisconsin Department of Natural Resources, 1969, 1973; (d,h) Industrial Bio-Test, 1972a; (e) Industrial Bio-Test, 1972b; (f) Howe, 1973--personal communication; (g) Industrial Bio-Test, 1972a, 1972c; (i,j) Beeton and Moffett, 1964.

Table 16. Carbonate Alkalinity in Lake Michigan Water

Sample Description	Dates	Concentration as $CaCO_3$, mg/l: Average	Concentration as $CaCO_3$, mg/l: Range	Reference
Samples collected from raw water header at Chicago South Water Filtration Plant	24 Jan-16 May 1961		2.6-11.0^a	Ayers *et al.*, 1967
Samples collected from Peter Cooper Corp. intake, Oak Creek, ∿0.75 km (2500 ft) offshore				
Monthly	Mar-Dec 1961	1^a	0-3^a	Wis. Comm. Water Pollut., 1965
Monthly	Jan-Oct 1962	0^a	0-3^a	
Single	Oct 1963	2^a		
Single	Jul 1964	12^a		
Weekly	Jan-Dec 1965	$0^{a,b}$		Wis. Dep. Nat. Resour., 1969
Weekly	Jan-Dec 1966	$0^{a,b}$		
Weekly	Jan-Dec 1967	$0^{a,b}$		
∿Monthly	Jan-Dec 1968	1^a	0-6^a	
Samples collected ∿weekly from Milwaukee public water intake, 1.8 km (1.1 mi) offshore	May-Sep 1970	3	0-7	USGS, 1972
	Oct 1970-Sep 1971	1	0-8	USGS, 1973
	Oct 1971-Sep 1972	1	0-5	USGS, 1974a
	Oct 1972-Jun 1973	1	0-4	USGS, 1974b
Samples collected at 8- to 21-day intervals (except 3 Feb-11 Mar) at a depth of 4 m:	27 May 1970-20 Oct 1971			Rousar, 1973
4.8 km (3.0 mi) east of Milwaukee		2^a	0-9^a	
Between Milwaukee and Ludington				
1/4 the distance		2^a	0-9^a	
1/2 the distance		2^a	0-8^a	
3/4 the distance		2^a	0-6^a	
4.8 km (3.0 mi) west of Ludington		2^a	0-8^a	
Samples collected from Waukegan Generating Station intake canal, immediately inside the ice screen	24 May, 26 Jul, 25 Aug 1971	1^a	0-7^a	Industrial Bio-Test, 1972c

[a] *These data, originally reported as phenolphthalein alkalinity, are tabulated here as carbonate alkalinity since all phenolphthalein alkalinity in Lake Michigan is due to carbonate alkalinity (cf. APHA et al., 1971).*

[b] *Same value for all samples.*

USGS = U. S. Geological Survey.

is increasing, leading to the apparent dilution of carbonate content in the sediments. Alternatively, the input of some other component is decreasing, leading to the apparent enhancement of carbonate content in the sediments. For instance, Callender (1969) found carbonate content was lower in Green Bay (Table 17) than other Lake Michigan sediments, but organic carbon content was higher. If one assumes that Green Bay and Lake Michigan proper are both within the same geologic milieu, then organic carbon may be diluting the carbonate content of Green Bay sediments. Likewise, one may hypothesize that decomposition of organic matter and diffusion away of the degradation products (CO_2, NH_3, HPO_4^{2-}, etc.) may leave $CaCO_3$ more concentrated than it was prior to microbial breakdown of organic matter.

(*iii*) One may hypothesize that carbonate precipitates are being removed from the sediments. Release of CO_2 by degradation of organic matter may lead to dissolution of $CaCO_3$.

(*iv*) One may hypothesize that the assumption in (*ii*) of the same geologic milieu is in fact false. While the gray silt facies of the Waukegan member

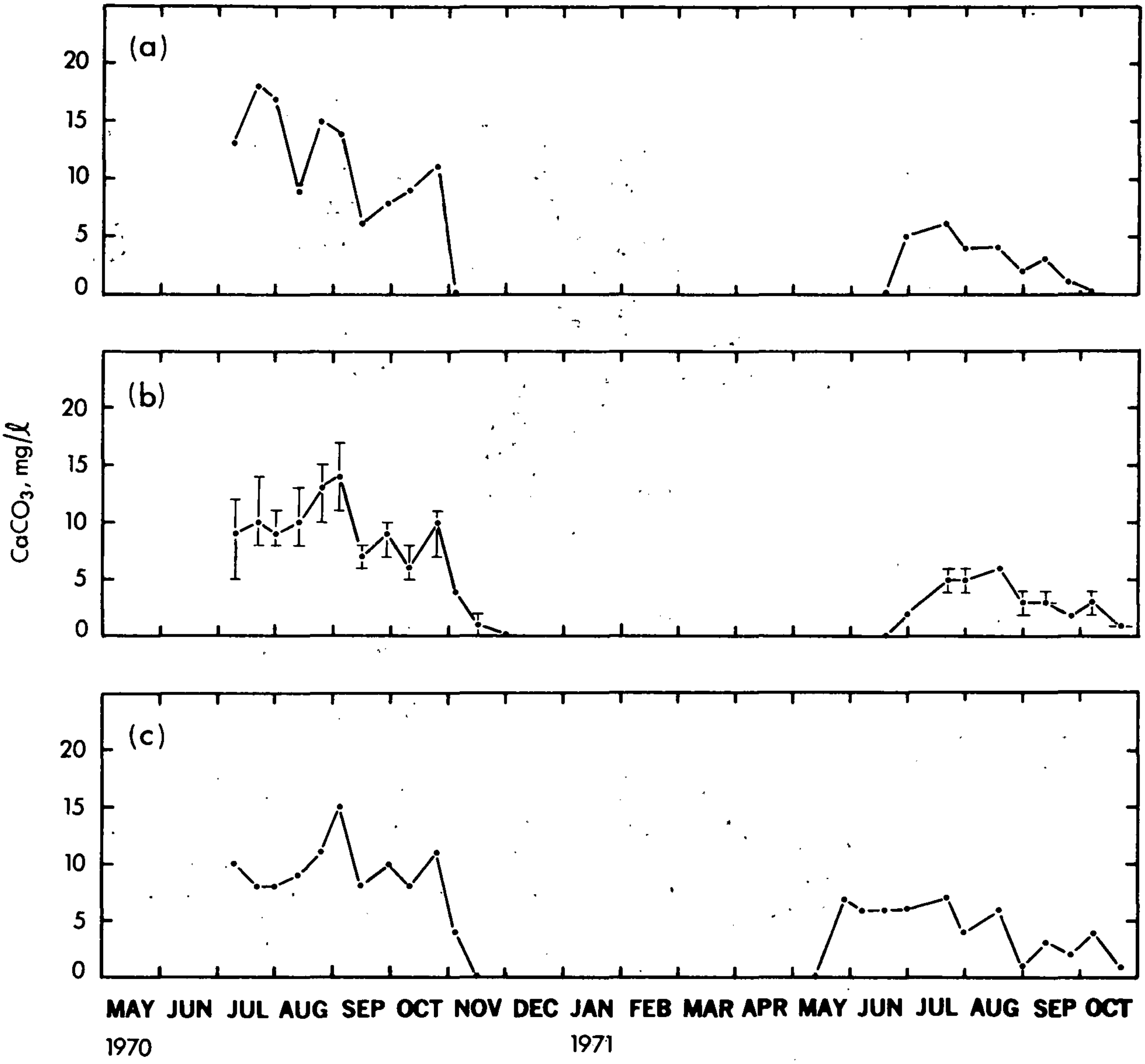

Fig. 38. Average Carbonate Alkalinity in Surface-Water (4 m) Samples at Five Stations during 1970-71. (a) Station 1: 4.8 km (3 mi) east of Milwaukee; (b) Stations 2, 3, 4: between Milwaukee and Ludington--1/4, 1/2, and 3/4 the distance, respectively; (c) Station 5: 4.8 km (3 mi) west of Ludington. Modified from Rousar (1973).

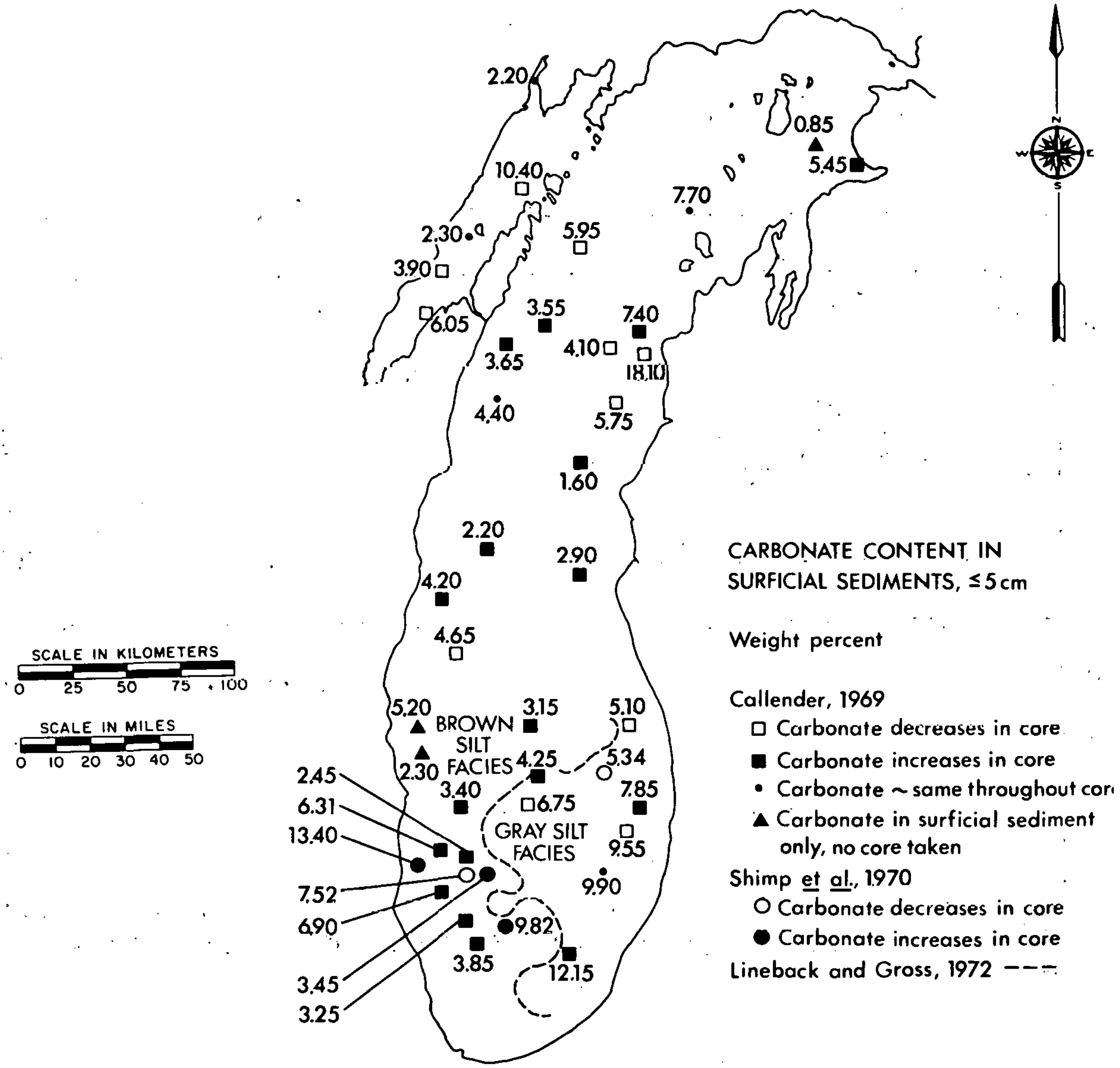

Fig. 39. Carbonate Content in Surficial Sediments of Lake Michigan. Callender (1969) collected samples May-July 1968. The plotted values represent surficial samples from the cores. Variation of values with depth in core is represented in the legend. Shimp *et al.* (1970) collected two grab and four core samples during the summer of 1969. The plotted values represent surficial sediment values. Variation of values with depth in core is represented in the legend. Boundary of brown and gray silt facies of the Waukegan member from Lineback and Gross (1972).

Table 17. Distribution of Carbonate Content in Lake Michigan Sediments*

	Weight Percent	
Location	*Surface Sediment*	*Sediment at Depth*
Southern basin	5.53	9.85
Divide area and northern basin	6.00	8.10
Green Bay	4.32	4.92

**Data from Callender, 1969.*

Table 18. Correlation between Several Components in Lake Michigan Sediments*

	Correlation Coefficients (r)	
	Ca *vs.* CO_3	Mg *vs.* CO_3
Southern basin	0.93	0.65
Divide area	0.98	0.81
Northern basin	0.98	0.66
Green Bay	0.96	0.97

**Data from Callender, 1969.*

(Lineback and Gross, 1972) is as much as 12.2 m (40 ft) thick along the eastern shore of the southern basin, it thins to less than 1.5 m (5 ft) in the central part of that basin. The brown silt facies of the Waukegan member, in the western part of the southern basin, is generally less than 30 cm (one foot) thick. Callender (1969) took seven cores in this western area. In each core he analyzed the 0-3 cm sediment interval. The next interval Callender examined in six of these seven cores was at *ca.* 30 cm, the depth at which the Waukegan member ends and the Lake Forest member begins (Lineback and Gross, 1972). Thus, indications from Callender's data that carbonate content increases from the surface to 30 cm in cores from the western portion of the southern basin must be examined in light of the stratigraphic descriptions developed by Lineback and Gross (1972). Callender (1969) was aware of this possibility, for he indicated,

> *"... the appreciable increase* [*with sediment depth*] *may be due to penetration of a higher-carbonate sediment (till or detrital carbonate) by the cores."*

Since no one pattern was found in all cores (carbonate content increased, decreased, or stayed the same with increasing sediment depth), it is probable that no one explanation can account for all the observed changes. Instead, combinations of two or more of the above hypotheses, as well as others not yet discovered, probably explain the behavior of carbonate in Lake Michigan sediments.

BUFFERING

One might consider it striking that pH is as invariant as it is in light of the wide diversity of environments in Lake Michigan: harbors, inshore waters, offshore waters, warm surface waters, cold bottom waters (*cf.* Table 12 and Figs. 30, 31, 32, and 35). In the laboratory, one can easily show that addition of a few drops of a strong acid, such as HCl, to a liter of Lake Michigan water causes a negligible change in pH, while addition of the same amount of acid to a liter of distilled water causes the pH to drop from 7 to 2-3. Figure 34 shows that a solution containing equal amounts of HCO_3^- and $(CO_2 + H_2CO_3)$ has a pH of 6.3. When strong acid is added to a solution containing equal amounts of $(CO_2 + H_2CO_3)$ and HCO_3^-, H^+ reacts with HCO_3^- to form H_2CO_3. This addition changes the ratio of $(CO_2 + H_2CO_3)$ to HCO_3^- in Equation 12, and the H^+ concentration also; but pH is not greatly affected unless the ratio changes by a large amount. For example, if enough strong acid is added to a sample of Lake Michigan water to change the ratio of H_2CO_3 to HCO_3^- from 1 to 2 (this can be accomplished by adding *ca.* 3 ml of 1 N HCl), then pH shifts from 6.3 to 6.0. If 3 ml of 1 N HCl is added to a liter of distilled water, then the resulting pH is about 2.5. Thus in the sample of Lake Michigan water the bicarbonate ion reacts with enough of the added H^+ to form H_2CO_3 so that the concentration of free H^+ is changed very little.

Similarly, if a strong base is added to a solution containing equal amounts of H_2CO_3 and HCO_3^-, hydroxide is removed (Eq. 16). Addition of base causes the ratio of (H_2CO_3) to (HCO_3^-) to decrease, and pH to increase; however, the effect is slight. Addition of 3 ml of 1.0 N NaOH to a sample of Lake Michigan water containing equal amounts of H_2CO_3 and HCO_3^- causes the pH to change from 6.3 to 6.6. The same amount of base added to a liter of distilled water would cause a shift to about pH 11.5.

Solutions which can absorb considerable amounts of strong acid or base without showing much change in pH are called well-buffered. Buffering action is not limited to HCO_3^- and H_2CO_3. A solution containing Ca^{2+} plus HCO_3^-, *e.g.* Lake Michigan water, in contact with solid $CaCO_3$ tends to maintain its pH:

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3- \ , \tag{22}$$

and

$$Ca^{2+} + HCO_3^- + OH^- \rightleftharpoons CaCO_3\ (s) + H_2O \ . \tag{23}$$

The controls on the ability of Lake Michigan water to resist changes in pH are CO_2 and $CaCO_3$ in the water column and sediments.

The carbonate-bicarbonate-carbon dioxide content controls the pH of Lake Michigan water within narrow limits. Well-buffered water is important to organisms living within the Lake. While some can undergo wide variations in pH successfully, many cannot tolerate excesses of H^+ or OH^- concentrations. There are occasions when the carbonate plus bicarbonate content of Lake Michigan water is insufficient to absorb added OH^-. Then both Ca^{2+} and HCO_3^- act together to reduce excess hydroxide by precitating $CaCO_3$. Supersaturation with respect to calcite (Schelske and Callender, 1970), and even incidents of milky water due to the formation of calcite (Ayers *et al.*, 1967; Schelske and Callender, 1970; Ladewski and Stoermer, 1973; *cf.* sections on Turbidity and Calcium) are evidence that the buffer system does work.

Precipitation of $CaCO_3$ has several implications for the biota of Lake Michigan. $CaCO_3$ precipitates only at higher pH values, values which may be inimical to organisms living in the Lake (*cf.* Table 13). Adsorption of organic substances onto particulate $CaCO_3$ (Wetzel, 1972; Otsuki and Wetzel, 1973) may cause at least some portion of these substances to be lost permanently to the sediments, reducing the amount of organic substances available for utilization by microorganisms in the water column.

ORGANIC CARBON

Total Organic Carbon

Total organic carbon (TOC) content is the sum of particulate and dissolved organic carbon. Particulate organic carbon (POC), which is composed of both living and nonliving particles, is grazed by fish and zooplankton and provides a substrate for attachment of microorganisms. Dissolved organic carbon (DOC) is a food source for bacteria and other organisms capable of assimilating preformed organic compounds. DOC may complex other nutrients, *e.g.* iron, increasing or decreasing their biological availability (Wetzel, 1972; Otsuki and Wetzel, 1973). Certain organic compounds, *e.g.* phenol, dissolved in water also may be toxic; specific compounds are discussed below in the section on Other Organic Substances. TOC content is also important due to the depletion of oxygen created by its oxidation (*cf.* Biochemical Oxygen Demand and Chemical Oxygen Demand).

Natural sources of organic carbon to Lake Michigan include land runoff, tributary inputs, and formation within the Lake by photosynthesis. Sewage effluents and industrial effluents, especially from the pulp and paper industries in the Basin, contribute major quantities of TOC to the Lake.

TOC content of Lake Michigan water has been measured along the western shore (Table 19). Average values of TOC are less than *ca.* 10 mg C/l, but the data on which these averages are based show considerable scatter.

Table 19. Total Organic Carbon Content of Lake Michigan Sediments*

	Weight Percent	
Location	*Surface Sediment*	*Sediment at Depth*
Southern basin	1.82	1.45
Divide area and northern basin	1.87	1.52
Green Bay	3.24	2.17

**Data from Callender, 1969.*

There is some indication that TOC content in inshore waters of the western portion of Lake Michigan varies seasonally. Values seem to be higher in spring and fall around Two Rivers (Fig. 40), Oak Creek (Limnetics, 1974), Kenosha (Industrial Bio-Test, 1972a), Lake County, Illinois (Howe, 1973--personal communication), Waukegan (Industrial Bio-Test, 1972a, 1972c), and North Chicago (Industrial Bio-Test, 1972a) and lower during winter and summer. This pattern may be due in part to resuspension of organic substances from the bottom sediments (see below) during spring and fall storms. Photosynthetic production of organic carbon may be involved.

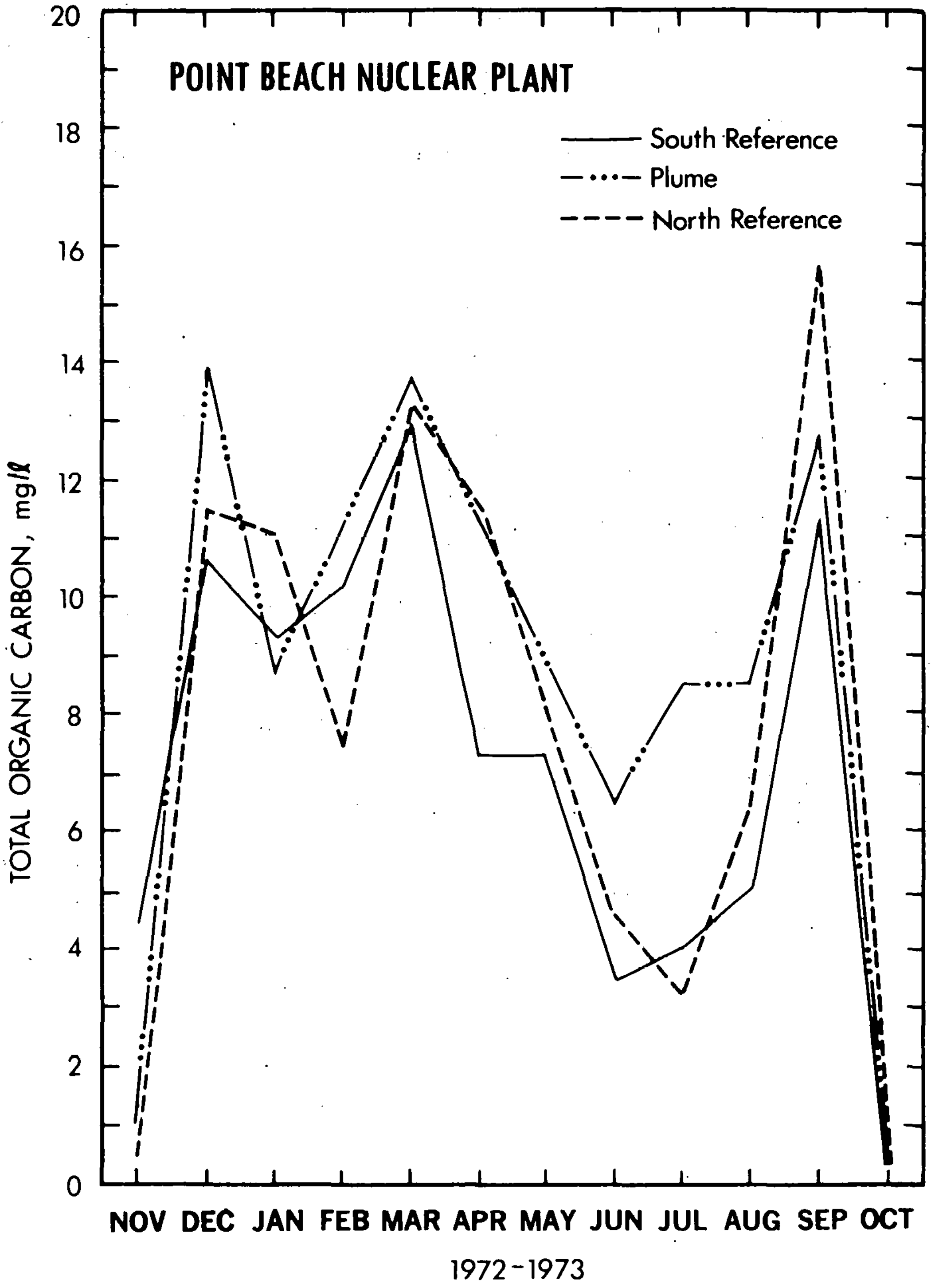

Fig. 40. Average Total Organic Carbon Content at Point Beach Nuclear Plant near Two Rivers. Sample descriptions are the same as in Figure 13. Modified from Limnetics (1974).

No attempt to analyze for the components of TOC, that is, DOC and POC, in Lake Michigan water has been reported.

Shimp *et al.* (1971) and Callender (1969) investigated the organic carbon content of Lake Michigan sediments (Figs. 41 and 42, respectively). Shimp *et al.* confined their sampling efforts to the southern basin, while Callender collected samples throughout the Lake, including Green Bay. Data from Callender are summarized in Table 19. Organic carbon content of sediments from the main portion of the Lake is notably lower than for Green Bay, which receives much organic material from the Fox River. Photosynthetic production of organic carbon is also higher in Green Bay (*cf.* Holland, 1969).

Callender attributed lower organic carbon concentrations in the main body of the Lake to the dilution by sand-sized material of bulk sediment organic carbon content. Sand was also said to obscure the decrease of organic carbon content with increasing sediment depth.

Although he did not specifically mention it, Callender's data showed that organic carbon content of sediments in the eastern portion of the southern basin is higher than in the western portion. These data agree with those of Shimp *et al.* (1971), who found organic carbon content was higher along the eastern shore in the gray silt facies of the Waukegan member (Lineback and Gross, 1972) than in the brown silt facies of the western area. The presence of these higher organic carbon concentrations in sediments from the eastern portion of the southern basin are mentioned many times in this report, for Lineback and Gross (1972) attribute the abundance of trace elements in the gray silt facies of the Waukegan member to the accumulation of organic particles, on which trace metals have sorbed.

Like Callender (1969), Shimp *et al.* (1971) found that organic carbon content was highest in the surficial sediment interval and decreased with depth. Similar observations have been made on cores from Lakes Ontario, Erie, and Huron (Kemp *et al.*, 1972). Callender (1969) proposed that organic carbon enrichment in surface sediments reflects increased organic productivity while the sediments were deposited. This enrichment of organic carbon may be related to the susceptibility of various organic carbon compounds to microbial degradation, *e.g.* sucrose *vs.* DDT. The decrease of organic carbon content in Lake Michigan with sediment depth to a nearly constant level may be due to degradation of less resistant material, leaving a residue of more resistant material to be buried by further sedimentation. Figure 43 (modified from Williams and Mayer, 1972) illustrates schematically how total organic carbon degrades and accumulates with time in a sediment core under conditions of absolutely uniform sedimentation. Instead of the more usual depth on the y-axis, time is used to avoid having to consider compaction with increasing extent of burial in a core. If depth is substituted for time in Figure 43, then the resulting profile of organic carbon content with depth resembles that in many of the cores taken by Shimp *et al.* (1971) and Callender (1969). Figure 43 (left) represents a sediment column of specified unit area such that 3% by weight of carbon [represented in Fig. 43 (right) by A_1A_1' $B_1'B_1$] accumulates at the top of the column in one year. Since we have assumed absolutely uniform sedimentation, the region of varying organic carbon content (represented by $A_0B_0C_0D_0E_0F_0$) moves upward in one year to $A_1'B_1'C_1'D_1'E_1'F_1'$. But the total net amount of organic carbon that is added during the year is represented by the area $F_1F_1'E_1'E_1$. Therefore, the area $E_1E_1'D_1'C_1'C_1D_1$ represents the amount of organic carbon that

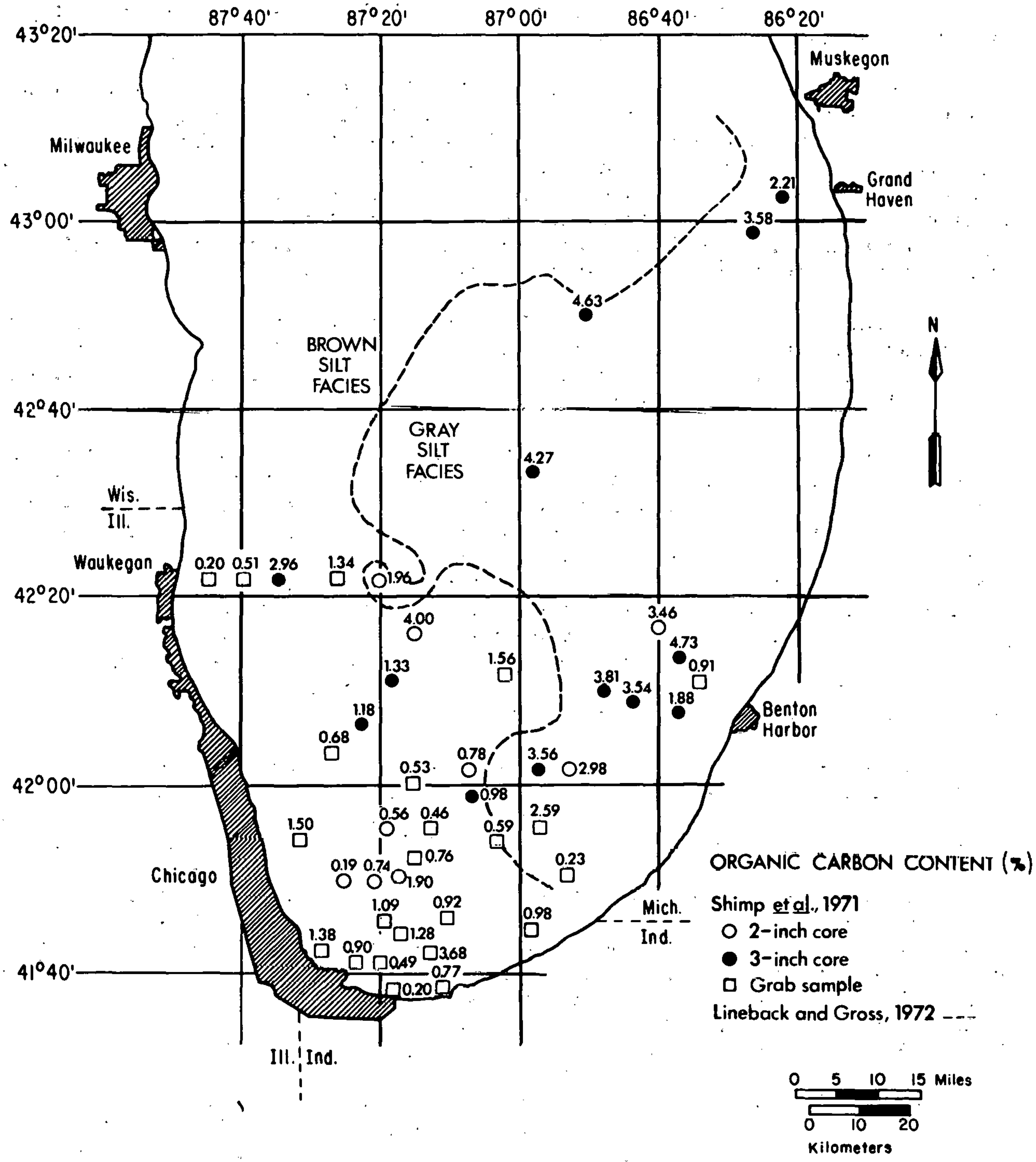

Fig. 41. Organic Carbon Content in the Most Recent Sediments of Southern Lake Michigan. Modified from Shimp *et al.* (1971). Boundary of brown and gray silt facies of the Waukegan member from Lineback and Gross (1972).

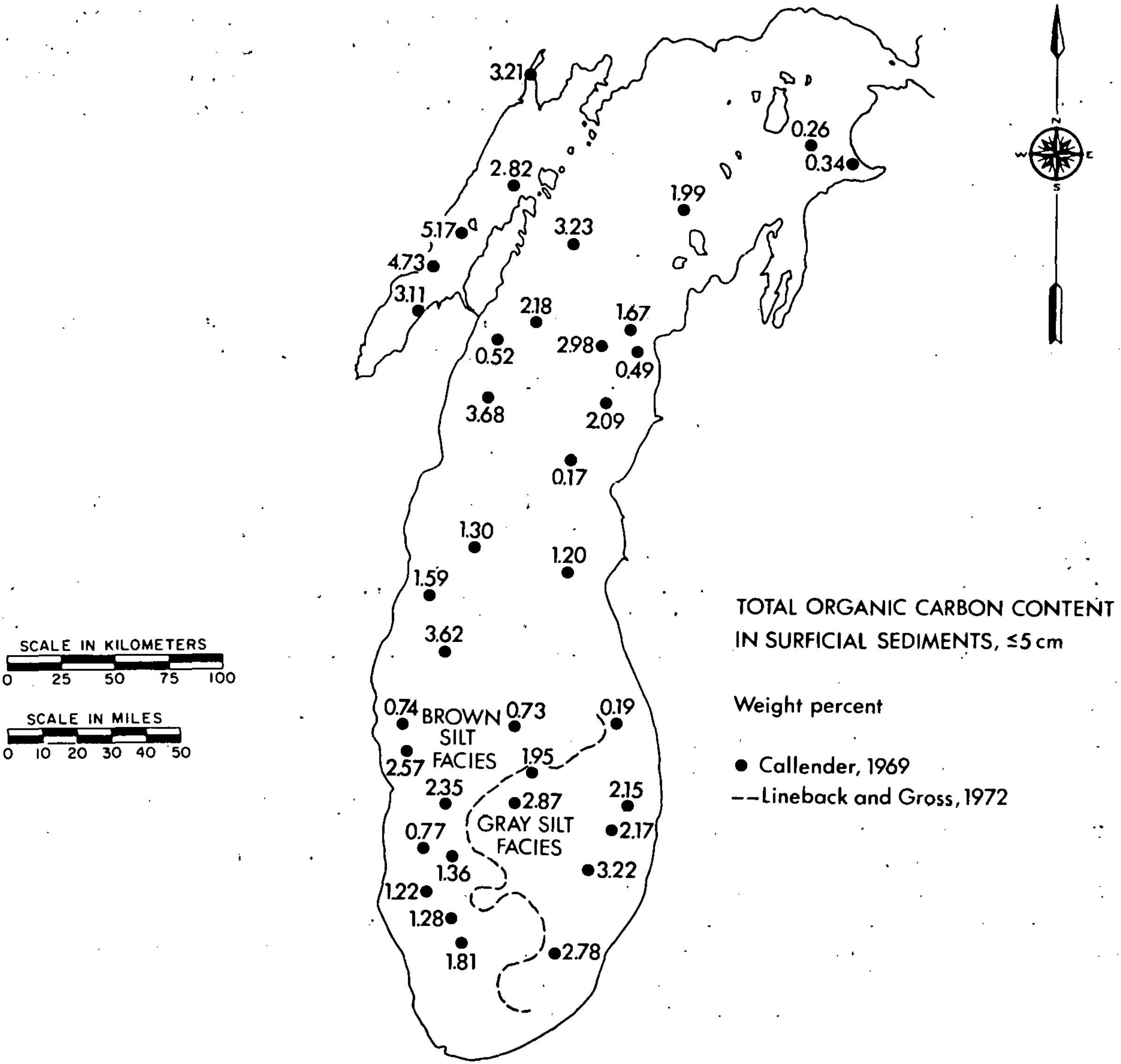

Fig. 42. Total Organic Carbon Content in Surficial Sediments of Lake Michigan. Samples collected May-July 1968 by Callender (1969). Boundary of brown and gray silt facies of the Waukegan member from Lineback and Gross (1972).

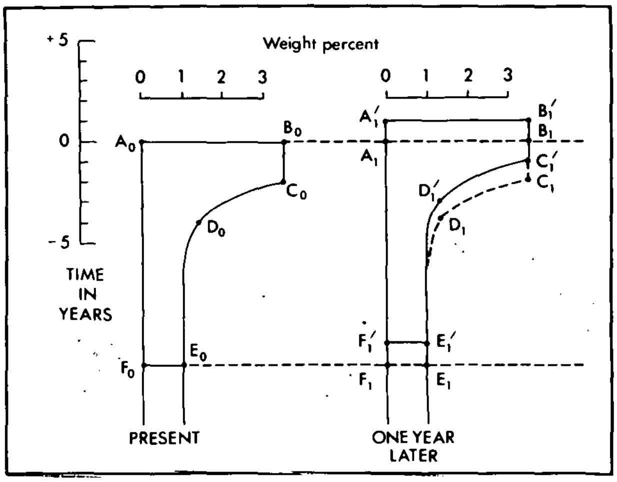

Fig. 43.

Organic Carbon Addition to and Degradation within an Idealized Sediment Column of Lake Michigan. Modified from Williams and Mayer (1972).

is degraded in the sediment column during the year. Thus, higher organic carbon concentrations at the sediment surface may be a natural phenomenon, due to less complete breakdown of recently deposited organic matter.

Total Organic Matter

Although no attempt to analyze for the components of TOC, *i.e.* DOC and POC, in Lake Michigan water has yet been reported, several papers have reported quantification of parameters that were called dissolved organic matter (DOM) and particulate organic matter (POM). Robertson and Powers (1965, 1967) and Robertson *et al.* (1971) determined POM by filtering water samples through preweighed filters having a mean pore size of 0.8 µm; particles down to the size of larger bacteria would be retained by such filters. These authors defined POM as the difference between the weight of dry particulate matter and the weight of the ash remaining after ignition of the dry particulate matter. POM determined in this fashion actually includes more than organic matter, for any particulate substance that volatilizes at 600°C appears as POM. Thus the determination of POM described by Robertson and Powers (1965, 1967) and Robertson *et al.* (1971) includes water of crystallization and occluded water of minerals or precipitates trapped on the filter and carbonate salts as well as particulate organic matter, both living and dead (APHA *et al.*, 1971). Nevertheless, in accordance with the reports discussed below, the term POM is used. It should be realized that all determinations of POM discussed here are overestimates of true values for POM content.

Robertson and Powers (1965) made determinations of POM to estimate the amount of biomass present in Lake Michigan at a particular time. They acknowledged that both detritus and phytoplankton would appear as POM, but they had no way to separate them. Samples were collected from April to November 1964 along five transects of the Lake, including Chicago to St. Joseph, Waukegan to South Haven, Racine to Holland, Sheboygan to Ludington, and Kewaunee to Frankfort. One chemistry station on each transect was midlake, and two others were about 16 km (10 mi) from each shore.

In 1964 the average weight of POM at the 15 stations sampled ranged from 0.70 to 1.24 mg/l above 25 m and from 0.49 to 1.02 mg/l below 25 m. There seemed to be no difference in POM content between northern and southern stations. Nearshore stations had somewhat more POM than midlake stations. They attributed this observation to enhanced biological productivity near shore due to influx of plant nutrients from the watershed. However, it is possible that inshore mixing processes may have stirred up organic matter and particulate $CaCO_3$ from the sediments into the overlying water. POM content was described as highest in April, and low and uniform from June through November. From April to June POM content was generally higher in bottom waters than surface waters, while from July through November the opposite was true.

In the summer of 1966 Robertson and Powers (1967) collected single samples at each of the three stations described above on the transect from Racine to Holland and also a station just north of Mackinaw City. Surface-water POM content at these four stations ranged from 1.05 to 1.18 mg/l; bottom-water POM content at the three southern stations ranged from 0.97-1.33 mg/l. The northern station was too shallow to permit collection of samples below 25 m.

Robertson *et al.* (1971) returned once again to the Racine-to-Holland transect. Based on monthly samples from May to October 1967, POM content averaged 0.89 mg/l (range 0.73-1.04 mg/l) in the top 25 m for the three stations taken together, while bottom-water samples averaged 0.81 mg/l (range 0.60-0.95 mg/l). These average values are comparable to those found in 1964 (Robertson and Powers, 1965) and lower than those in 1966 (Robertson and Powers, 1967). On the basis of these data, together with analyses of chlorophyll *a*, they concluded that detritus, expressed as POM, averages 0.5 mg/l. This value, subtracted from the total POM, indicated to Robertson *et al.* (1971) that living biomass made up 12 to 55% ($\bar{x}$ = 36%) of the POM. It is notable that the latter conclusion conflicts with the more widely accepted idea that living biomass constitutes perhaps 10% of the total organic matter at any time (*cf.* Parsons, 1963; Wetzel *et al.*, 1972).

Robertson and Powers (1967) also determined dissolved organic matter (DOM) by a dichromate oxidation; this determination therefore seems similar to a measurement of dissolved COD. DOM content in surface and bottom waters for four stations, each sampled once in the summer of 1966, is summarized in Table 20. Higher values in the upper waters were related to active photosynthesis, metabolism, and excretion by phytoplankton in the epilimnion.

Surface-water concentrations of DOM in Lake Superior ($\bar{x}$ = 2.62 mg/l) and Lake Huron ($\bar{x}$ = 2.71 mg/l) were lower than in Lake Michigan, but Lake Ontario values were higher ($\bar{x}$ = 6.01 mg/l) (Robertson and Powers, 1967). Concentrations of DOM in samples collected below 25 m were lowest in Lake Superior ($\bar{x}$ = 2.25 mg/l), intermediate in Lake Huron ($\bar{x}$ = 2.72 mg/l), and highest in Lake Michigan ($\bar{x}$ = 4.61 mg/l); bottom-water data for Lake Ontario were not reported.

Table 20. Dissolved Organic Matter in Lake Michigan Water*

	Average ± One Standard Deviation, mg/l	
Station	*0-25 m*	*25 m to Bottom*
16 km (10 mi) west of Holland	5.57 ± 0.79	4.77 ± 1.22
Halfway between Holland and Racine	5.02 ± 0.25	4.51 ± 0.70
16 km (10 mi) east of Racine	5.81 ± 0.97	4.55 ± 0.20
North of Mackinaw City	3.24 ± 0.29	- - - -

**Data from Robertson and Powers, 1967.*

NITROGEN

Several nitrogenous compounds are found in Lake Michigan. Interconversion of these nitrogenous compounds occurs primarily by biological metabolism. Figure 44 illustrates the role of oxidation and reduction in the nitrogen cycle. Reduced organic nitrogen is a constituent of proteins, peptides, amino acids, enzymes, nucleotides, and other biochemically important compounds. While plants and animals are living they excrete many nitrogenous compounds; additionally, upon their death, a variety of nitrogen-containing compounds are released. Microbial decomposition, or ammonification, of the reduced organic nitrogen compounds releases ammonia, NH_3, which can then be oxidized by specialized bacteria (*e.g. Nitrosomonas* and *Nitrobacter*) to form nitrate (NO_3^-) during nitrification. Green plants and microorganisms incorporate nitrate and subsequently reduce it to form organic nitrogen compounds. Two biochemical reactions may influence the amount of nitrogen gas (N_2) dissolved in a lake (Fig. 44); (*i*) nitrogen fixation (N_2 fixation) reduces the amount of N_2 by converting it to reduced organic nitrogen compounds, and (*ii*) denitrification increases the amount of N_2 by reducing nitrate to N_2.

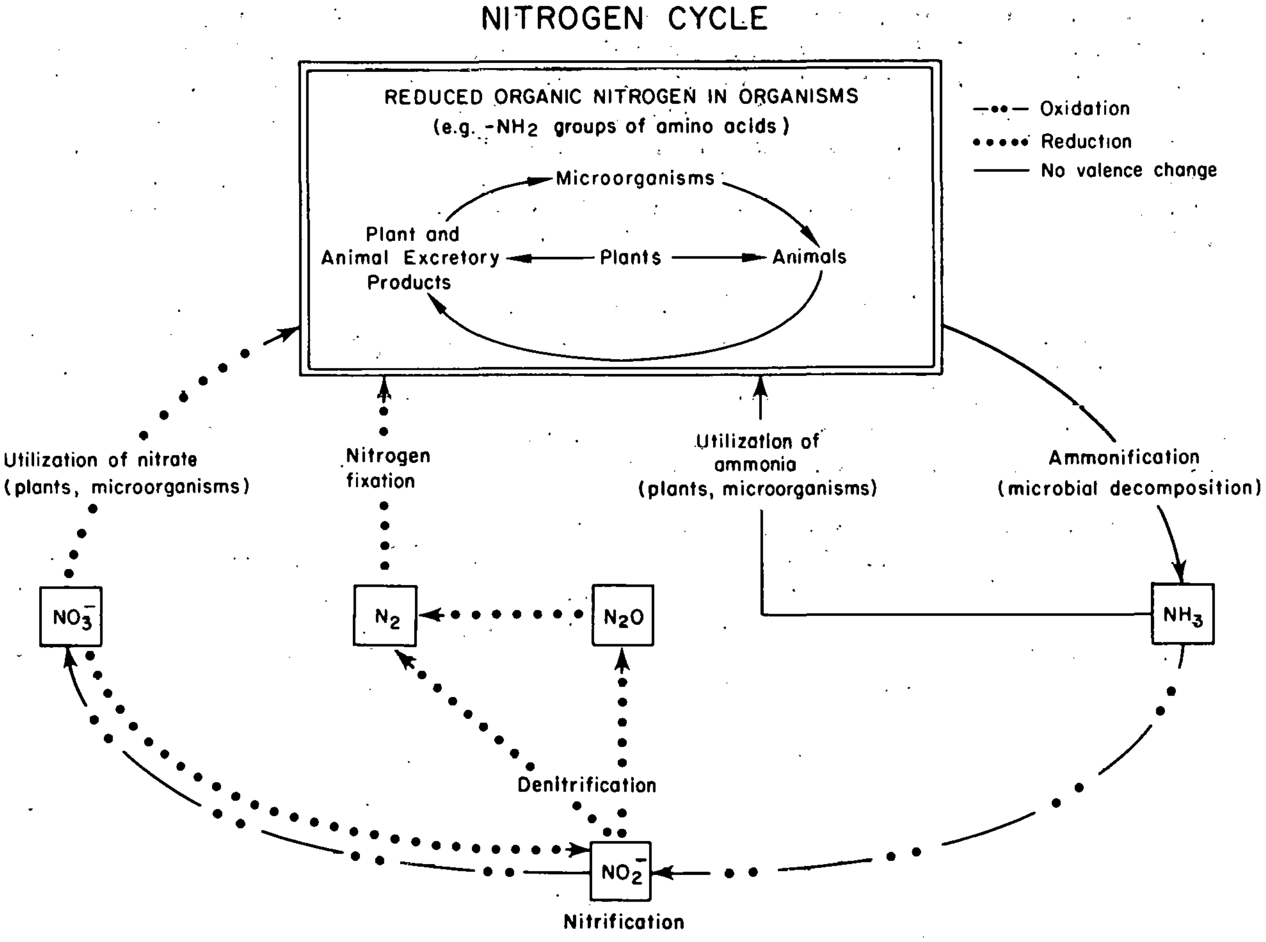

Fig. 44. Nitrogen Cycle.

The major chemical forms of nitrogen in Lake Michigan (N_2, ammonia, nitrite, nitrate, and organic nitrogen) are considered separately in this section. Nutritional properties (essentiality, toxicity), sources to the Lake, concentrations in the Lake, and the chemical behavior of each form are discussed.

NITROGEN GAS

The concentration of N_2 in any lake is determined chiefly by the quantity of atmospheric N_2 that dissolves at the surface of the lake and its tributaries. While seasonal changes in temperature alter the absolute amount of N_2 dissolved in natural waters, the relative amount is expected to remain at or very near saturation.

Supersaturation caused by biological processes could occur only if there were significant additions of N_2 to the water, as by denitrification (Fig. 44). Denitrification, which takes place only when O_2 is absent (Stanier *et al.*, 1970), probably does not occur in Lake Michigan except perhaps in localized areas where O_2 is sometimes exhausted, *e.g.* southern Green Bay or Calumet and Indiana Harbors.

Undersaturation of N_2 caused by biological processes would occur only if N_2 fixation removed N_2 from the water. Since the highest rate of N_2 fixation recorded in the main portion of Lake Michigan is 5.2 ng N_2 reduced/l/hr,* N_2 fixation does not appreciably alter the N_2 content from the saturation value of 17-20 mg N_2/l (depending on temperature).

Aside from N_2 saturation, N_2 fixation is important in Lake Michigan for another reason. N_2 fixation is considered one of several factors indicating eutrophication (*cf.* Stewart *et al.*, 1971), or the process of enrichment of a lake with nutrients. N_2 fixation has received increasing interest, not from its relation to the N_2 content of Lake Michigan, but rather for its utility as an indicator of trophic conditions in the Lake.

Before discussing N_2 fixation studies in Lake Michigan, let us consider what organisms perform this biochemical reaction. Bacteria probably fix insignificant quantities of N_2 in the main body of Lake Michigan since, with the exception of *Azotobacter*, all aquatic bacteria capable of fixing N_2 do so only when O_2 is absent. Some of the blue-green algae found in Lake Michigan, such as *Anabaena* and *Aphanizomenon*, can fix N_2 if they have heterocysts (Stewart, 1971), a specialized type of cell that allows the organism to reduce N_2 even in the presence of O_2. Heterocyst-containing blue-green algae are likely the major agents of N_2 fixation in Lake Michigan.

Some data suggest that N_2 fixation occurs consistently throughout the summer in the southern third of Green Bay (Mague and Burris, 1973; Vanderhoef *et al.*, 1972, 1974; Peterson and Burris, 1973-personal communication). In the northern basin, Mague and Burris (1973) detected N_2 fixation activity (expressed here as ng N_2 reduced/l/hr) in surface waters at two of six stations near the

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**Notation of rate function expressed as quantity y/unit volume or weight/unit time is employed for editorial convenience, but is meant to simulate the more accurate expression, quantity y/unit volume or weight time^{-1} (e.g. 5.2 ng N_2 reduced/l hr^{-1}).*

northeast shore in September 1970. The higher fixation rate in the two samples which exhibited N_2 fixation activity was equivalent to only 0.28 ng N_2 reduced/l/hr.

Peterson and Burris (1973--personal communication) found few instances of N_2 fixation activity south of a line from Milwaukee to Grand Haven, Michigan, during 12-20 June 1973. Appreciable activity (equivalent to 1.04-1.40 ng N_2 reduced/l/hr) occurred at only two stations, both midlake. In these cases, N_2 fixation activity at the surface was near zero, and maxima occurred at 10 and 15 m. During 7-13 August 1973, inshore samples around South Haven and just south of Benton Harbor demonstrated significant levels of N_2 fixation activity (0.71-1.06 ng N_2 reduced/l/hr). With the exception of one station 40 km (25 mi) east of Lake Forest, Illinois, the inshore and offshore stations had N_2 fixation activities less than 0.25 ng N_2 reduced/l/hr. *Anabaena* predominated at stations where N_2 fixation activities were high. During 7-10 September, N_2 fixation activity off South Haven was low (0.0-0.11 ng N_2 reduced/l/hr) while near Benton Harbor and Lake Forest it was moderate. In contrast with the August sampling, when activities in the extreme southern part of the Lake were quite low, inshore stations immediately north of Burns Ditch showed high N_2 fixation activities in September (5.2 ng N_2 reduced/l/hr). The algal bloom occurring near Burns Ditch was dominated by *Tabellaria* sp., which does not fix N_2, but *Anabaena* was also present. By 1-4 October 1973, N_2 fixation activity had dropped considerably throughout the southern part of the Lake, and diatoms, which cannot reduce N_2, were dominant at every station. The highest N_2 fixation activities in October, found around Evanston and Lake Forest, were only about 0.9 ng N_2 reduced/l/hr. Activities in the first four days of November were similar to those recorded in October. The highest N_2 fixation activities (0.28-0.56 ng N_2 reduced/l/hr) were measured at inshore stations near South Haven, near Lake Forest, just east of Evanston at a single station, and just north of Burns Ditch. Peterson and Burris (1973--personal communication) have recorded N_2 fixation activity in the Southern Basin during summer for the first time. With the exception of a single sample in June, all major instances of N_2 fixation activities were associated with inshore waters, where human inputs of nutrients are highest.

No measurements of N_2 content in water were made during N_2 fixation studies, since those studies were concerned with the total amount of N_2 converted to biomass rather than that remaining behind in solution. Limnetics (1974) studied N_2 content of water around the outfalls of cooling water from the Point Beach Power Plant near Two Rivers, Wisconsin. Total gas pressure (partial pressure N_2 plus partial pressure O_2) was occasionally above 110%, the upper limit suggested by the National Academy of Sciences ... (1973) for protection of salmonid fish from gas bubble disease. Areas in which total gas pressure exceeded 110% were seldom more than 250 m (800 ft) from the discharge points. The range of partial pressures of N_2 values found by Limnetics in their studies near the Point Beach outfalls was 70.1-100%, compared with the atmospheric partial pressure value of 78.1%.

AMMONIA

The most reduced inorganic form of nitrogen in water is ammonia, which in the present discussion includes NH_3, NH_4^+, and NH_4OH. Ammonia is present largely in the form of ammonium ion (NH_4^+) at the pH conditions found in Lake Michigan (Table 21).

Table 21. Percentage of Un-Ionized Ammonia at 20°C

pH	*Percentage*
7.0	0.6
7.5	1.8
8.0	5.3
8.5	15.1
9.0	36.0

Ammonia is the major nitrogenous end product of microbial decomposition of nitrogen-containing organic matter (Fig. 44). In addition to this natural internal source of ammonia, natural external sources add ammonia to Lake Michigan. Erosion of soil, which contains organic nitrogen compounds and NH_4^+ associated with clay minerals, carries particulate forms of nitrogen to receiving waters. Runoff from over-fertilized land is also a source of ammonia. Rain water may be an important source, for in the midwestern U. S. precipitation contains a notable concentration of ammonia (Junge, 1958; Kluesener, 1972). Dust fallout may also be an important source of ammonia-nitrogen to the Lake.

Large quantities of ammonia in a natural water may indicate sewage contamination. A municipal sewage treatment plant having both primary and secondary treatment units removes about 50% of the total influent nitrogen, and yet the average ammonia content in the secondary effluent is 15.5 mg NH_3-N/1 (Weinberger *et al.*, 1966). Paper mills in the Green Bay area (Epstein *et al.*, 1974) and metal refineries in East Chicago and Gary (Businessmen for the Public Interest, 1972) were reported to be large industrial sources of ammonia to Lake Michigan.

The form of nitrogen used in cellular biosynthesis is probably the most reduced form, ammonia. As the most readily assimilable form of nitrogen, ammonia is important to the biota in Lake Michigan.

Concentrations of ammonia reported for Lake Michigan over the past 15 years are surveyed in Table 22. Figure 45 depicts surface-water data, based on references in Table 22. Concentrations of ammonia are high in harbors (Indiana, Calumet, Milwaukee), extending out from the immediate vicinity of the harbors, and near the mouth of waste-laden tributaries (Green Bay). Risley and Fuller (1965) described a south-to-north gradient of decreasing ammonia concentration, although the U. S. Department of the Interior (1968) data used by Risley and Fuller may have been biased by sampling near river mouths and harbor entrances. Data from Lue-Hing (1973--unpublished) showed no clear evidence of any gradient in ammonia concentrations with distance from shore.

The surface-water ammonia content in most productive lakes is minimal during summer stratification due to biological utilization of ammonia, either as a nitrogen source for formation of reduced organic compounds or in nitrification (*cf.* Fig. 44). Such a seasonal cycle of ammonia may exist in the

Table 22. Ammonia Content in Lake Michigan Water

		Concentration NH_3-N, µg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Samples collected ∿weekly from Peter Cooper Corp. intake, Oak Creek, ∿0.75 km (2500 ft) offshore	1961	80	20-310	Wis. Comm. Water Pollut., 1965
	1962	80	10-310	
	1963	110	10-270	
	1964	100	20-430	
	1965	120	<10-550	Wis. Dep. Nat. Resour., 1969
	1966	90	<10-230	
	1967	100	20-390	
	1968	120	20-300	
	1969	150	20-<540	Wis. Dep. Nat. Resour., 1973
	1970	140	20-<500	
	1971	150	50-570	
	1972	140	10-670	
Whole Lake:	1962-63			USDOI, 1968
429 offshore samples		60	N.D.-300	
1751 inshore samples		130	N.D.-1400	
Samples collected:	1962-63			
Indiana Harbor, 49 samples		1400	100-2300	USDOI, 1968
Adjacent to Indiana Harbor, 462 samples		180	10-1400	Risley and Fuller, 1966
Samples collected:	1962-63			
Calumet Harbor, 53 samples		230	50-670	USDOI, 1968
Adjacent to Calumet Harbor, 51 samples		180	50-450	Risley and Fuller, 1966
Samples collected:	1962-63			USDOI, 1968
Chicago Harbor, 7 samples		70	20-160	
Racine Harbor, 7 samples		60	50-80	
Samples collected:	Oct 1962, Jun 1963			USDOI, 1968
Milwaukee Harbor, 35 samples		1100	280-2700	
Adjacent to Milwaukee Harbor, 74 samples		180	N.D.-1300	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City		160	10-1700	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo		110	0-1120	
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor		110	10-650	
On a line roughly between Sheboygan and Little Sable Point		70	10-200	
170 samples collected throughout Green Bay	26 Jun-17 Jul 1963	170	10-1200	USDOI, 1968
Samples collected:	22-28 Jul 1964			USDOI, 1968
Traverse Bay, 59 samples		50	10-420	
Adjacent to Traverse Bay, 27 samples		30	10-110	
Samples collected:	1965			Risley and Fuller, 1966
Indiana Harbor, 16 samples		1300	380-1900	
Calumet Harbor, 31 samples		510	100-1100	
Samples collected at water filtration plants:	1965-71			Snow, 1974
Chicago South		50	N.D.-330	
Hammond		120	10-590	
East Chicago		120	10-800	
Gary		60	10-500	

Table 22. (contd.)

		Concentration NH_3-N, µg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Samples collected in Indiana Harbor at east breakwall inner light:				Snow, 1974
3 samples	Dec 1965	1600	1500-1700	
51 samples	Jan-Dec 1966	1700	190-2800	
42 samples	Jan-Dec 1967	1700	340-4100	
6 samples	Jan-Dec 1968	1500	1100-2500	
6 samples	Jan-Jun 1969	2200	1100-2900	
20 samples	Jan 1971-Jan 1973	2800	600-27,000	
3 samples collected at Sturgeon Bay entry buoy	18 May-21 Oct 1966	40	20-50	Schraufnagel *et al.*, 1968
Samples collected at water filtration plants near Chicago:				
12 plants	1968			Ill. Sanit. Water Board, 1969
Average annual values			14-154	
Individual values			<14-2500	
5 plants	1969			Ill. Sanit. Water Board, 1970
Average annual values			20-100	
Individual values			0-500	
Weekly samples collected at Whiting water plant intake	1969	200	100-500	Snow, 1974
Samples collected:				Schelske and Callender, 1970
Southern basin	22-24 Jul 1969			
Surface-water, 7 offshore stations		10	2-19	
Bottom-water, 7 offshore stations		20	6-37	
Surface-water, 8 inshore stations		10	6-21	
Bottom-water, 8 inshore stations		30	5-50	
Northern basin	15-23 Aug 1969			
Surface-water, 6 offshore stations		10	6-20	
Bottom-water, 6 offshore stations		20	11-28	
Northern basin, including Traverse Bay	15-23 Aug 1969			
Surface-water, 15 inshore stations		20	1-34	
Bottom-water, 8 inshore stations		20	6-21	
Northern Green Bay, including Bays de Noc	15-23 Aug 1969			
5 surface-water samples		20	14-25	
Northern Green Bay, including Big Bay de Noc	15-23 Aug 1969			
4 bottom-water samples		20	15-38	
Monthly samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	Nov 1969-Sep 1970	20	0-50	USGS, 1972
	Oct 1970-Sep 1971	10	0-20	USGS, 1973
	Oct 1971-Sep 1972	40	0-110	USGS, 1974a
	Oct 1972-Jun 1973	42	0-120	USGS, 1974b
Monthly averages for samples collected offshore from northern Chicago:				Lue-Hing, 1973
6 stations 0.30 km (1000 ft) offshore	Jun-Nov 1970, May-Oct 1971	140	20-260	
7 stations 0.61-0.91 km (2000-3000 ft) offshore	Jun-Dec 1970, May-Oct 1971	100	20-160	
4 stations 1.37-1.83 km (4500-6000 ft) offshore	Jun-Dec 1970, May-Oct 1971	190	90-310	

Table 22. (contd.)

Sample Description	Dates	Concentration NH_3-N, µg/l		Reference
		Average	Range	
Samples collected at 6 stations on a line passing east of Manitou Islands from Frankfort to Beaver Island:	7 Jul 1970			Schelske and Roth, 1973
Surface-water, 12 samples		20	5-30	
Bottom-water, 4 samples		20	20-25	
Monthly averages for samples collected at a station 3.0 km (10,000 ft) offshore from Zion	Dec 1970, May-Oct 1971	150	100-300	Lue-Hing, 1973
Daily samples collected at Chicago South Water Filtration Plant:	1971			Vaughn and Reed, 1973
353 of 365 samples		<20[a]		
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		120		
Glendale (northern suburb of Milwaukee)		60		
Port Washington		30		
Sheboygan		40		
Two Rivers		50		
Monthly samples collected at Lake County, Ill., public water intake	Jan 1971-Jun 1973		10-120	Howe, 1973
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun 1971-Apr 1972	160	<30-890	Industrial Bio-Test, 1972c
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		12	<10-30	
Effluent plume		13	<10-50	
South of plant, 4.8 km (3 mi)		13	<10-40	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		19	<10-43	
North of plant, 1.6 km (1 mi)		26	<10-63	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov 1972; May, Oct 1973			
Effluent plume		13	5-15	
South of plant, 1.6 km (1 mi)		31	15-93	
Samples collected every 4 hr at Chicago 68th Street crib intake	6-15 Jun 1974	20	0-110	Schwab and Katz, 1975

[a] *Same value for all samples.*

N.D. = not detected.

USDOI = U. S. Department of the Interior; USGS = U. S. Geological Survey.

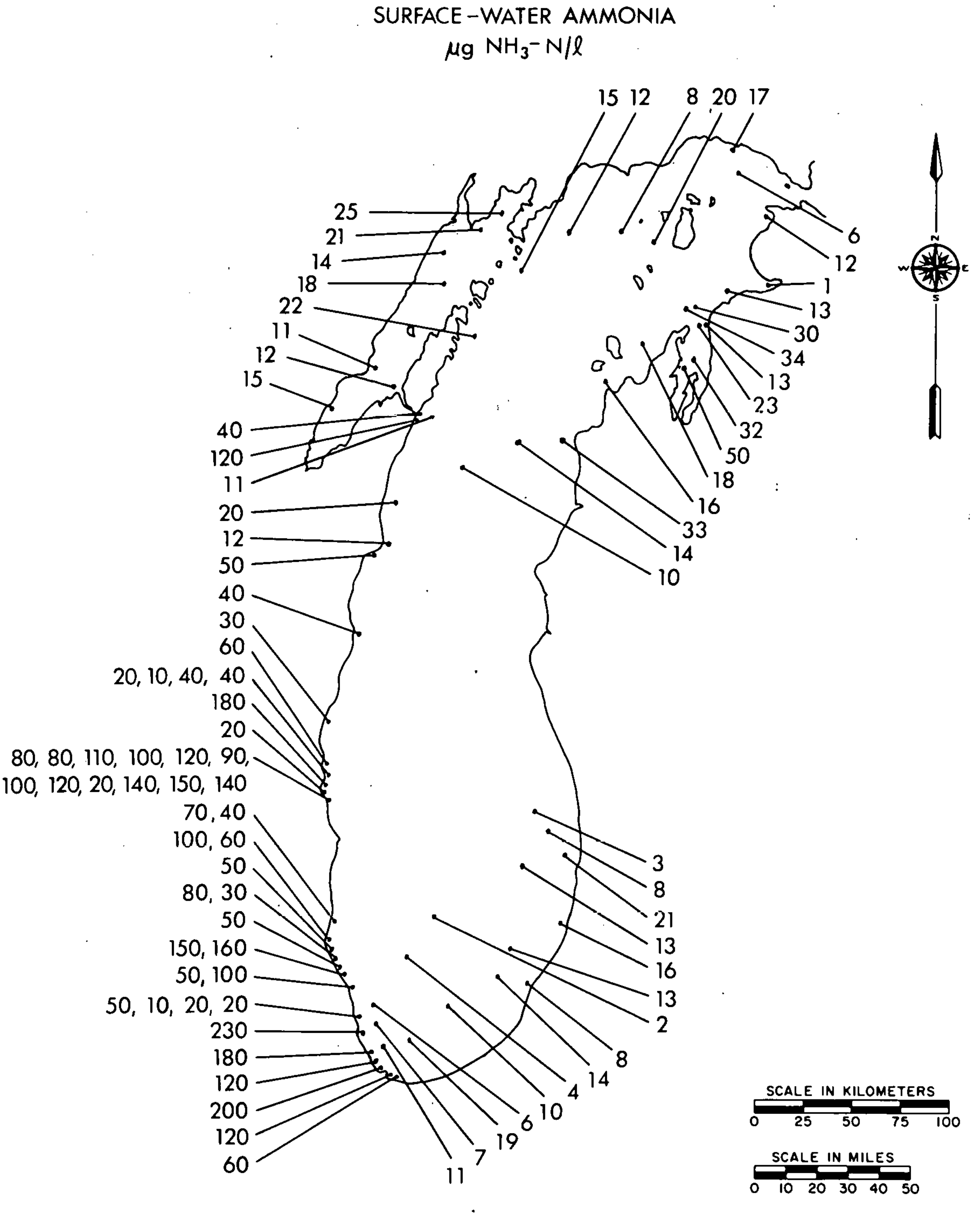


Fig. 45. Surface-Water Ammonia Concentrations over a Period of Fifteen Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 22.

inshore waters of Lake Michigan. Data collected weekly at the intake of the Peter Cooper Corporation, Oak Creek, Wisconsin, and plotted as monthly averages in Figure 46, showed lower concentrations of ammonia (*ca.* 100 µg NH_3-N/l) from April to October. Concentrations were higher from November through March. The same general pattern has been documented at the Lake County, Illinois, water supply intake (Howe, 1973--personal communication), in the vicinity of Two Rivers, Wisconsin (Limnetics, 1974), and at several water intakes in the southern Chicago-Gary-Hammond area. In the last case, seasonal patterns are not so clear because ammonia-laden water, carried by currents from the Indiana Harbor Canal (Snow, 1974) to these municipal water intakes, can cause temporary deviations from seasonal patterns. In contrast, data from the Milwaukee water intake (U. S. Geol. Surv., 1972, 1973, 1974a, 1974b) do not show obvious seasonal patterns of ammonia concentrations; however, the quality of data obtained from that location is poor. Thus patterns which may have been present are not obvious. Seasonal trends of ammonia content in offshore waters have not been documented.

If primary production in a lake is high during stratification, then ammonia may accumulate in the hypolimnion. Bodies of organisms which die in the surface water during the summer gradually settle into the hypolimnion. If

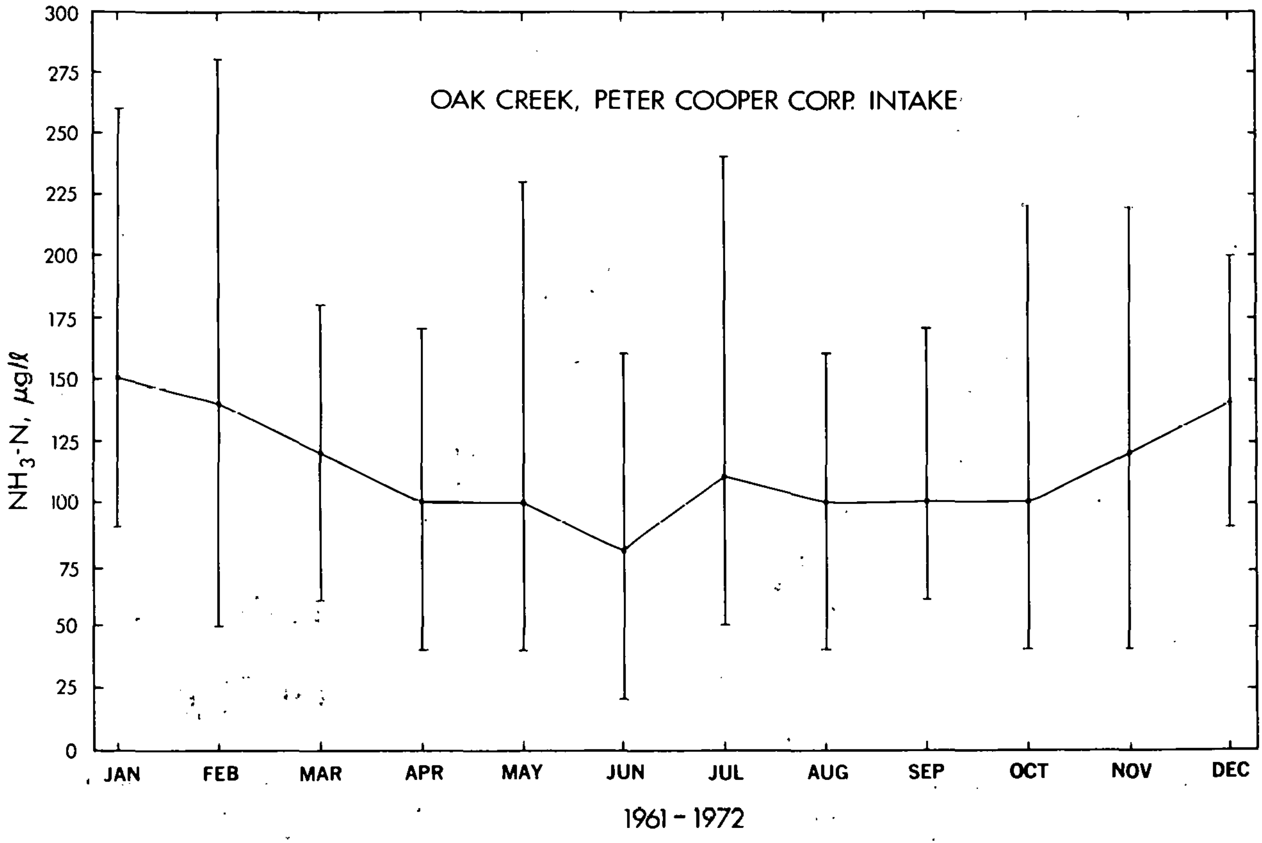


Fig. 46. Variation in Average Ammonia Concentrations at the Peter Cooper Corporation Intake, Oak Creek, 1961-1972. Bars represent range of monthly values over this 11-year period. Data from Wisconsin Committee on Water Pollution (1965) and Wisconsin Department of Natural Resources (1969, 1973).

O_2 is low or absent, ammonia released from the sediments contributes to the overall hypolimnetic increase in ammonia (*cf.* Mortimer, 1971); favorable conditions for sedimentary release of ammonia are found in certain areas of southern Green Bay, Calumet Harbor, and Indiana Harbor (Epstein *et al.*, 1974; Schraufnagel *et al.*, 1968; and Snow, 1974).

The relatively few annual data on ammonia in Lake Michigan do not suggest a highly productive lake; the bottom waters of the main portion of the Lake do not become anaerobic (*cf.* section on dissolved O_2). The data of Schelske and Roth (1973) indicate that one can assume a uniform distribution of ammonia with depth, since the error bars for one standard deviation overlap from the surface to 120 m (Fig. 47). Statistical comparison of data collected by Schelske and Callender (1970) shows no significant difference between surface- and bottom-water samples in either inshore or offshore waters of the northern basin in August 1969. This agrees with the data of Schelske and Roth (1973) which show no significant difference. In contrast, analysis of data on ammonia content in the water of the southern basin during July 1969 (Schelske and Callender, 1970) showed a statistically significant increase between surface- and bottom-waters both inshore and offshore.

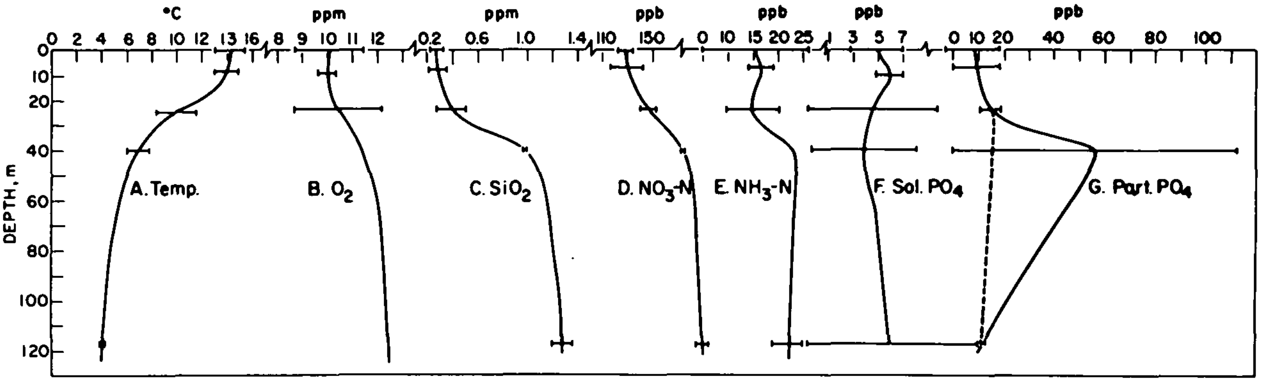


Fig. 47. Temperature, Dissolved Oxygen, Silica, Nitrate-Nitrogen, Ammonia-Nitrogen, Soluble Reactive Phosphate, and Particulate Phosphate at 6 Stations, 7 July 1970. Stations located on a line passing east of Manitou Islands from Frankfort, Mich., to Beaver Island. Curves depict means with error bars representing ± one standard deviation (Schelske and Roth, 1973) (with permission, see credits).

Drinking water standards for ammonia content are indicated in Appendix B, part 1. The criterion suggested by the National Academy of Sciences ... (1973) is based on the formation of chloramines (NH_2Cl, $NHCl_2$, and NCl_3) in the treatment process. Limitations on ammonia content for the protection of aquatic life are presented in Appendix B, part 2.

NITRITE

The presence of large quantities of nitrite ion (NO_2^-) is generally thought to indicate rapidly changing conditions, since it is present only as an intermediate form (Fig. 44) between NH_3 and NO_3^- (nitrification) or NO_3^- and N_2 (denitrification). In the presence of major quantities of other chemical forms of nitrogen, such as ammonia and nitrate, trace amounts of nitrite may indicate a contaminant source.

Nitrite ion may be used as a nitrogen source by plants, but the toxicity of nitrite to animals is more widely known. It is unclear to physiologists how nitrite combines with hemoglobin in the blood of human infants to cause the disease methemoglobinemia (blue baby).

There are relatively few sources of nitrite, as such, to Lake Michigan. Most of it is likely formed *in situ* from ammonia or reduced organic nitrogen compounds during nitrification. Groundwater may add nitrite to the Lake, and certain industries use nitrite as a corrosion inhibitor in their process water (APHA *et al.*, 1971). Effluents from the secondary treatment of municipal waste waters typically contain 300 μg NO_2^--N/l (Weinberger *et al.*, 1966).

Determinations of nitrite ion in inshore waters of the western part of Lake Michigan are detailed in Table 23 and Figure 48. All values are low, generally less than 6 μg NO_2^--N/l. The high values (10-15 μg NO_2^--N/l) around Milwaukee are noteworthy, and may reflect pollution in the inshore area.

Limnetics (1974) found a slight seasonal variability in NO_2^- content around Two Rivers; higher values occurred in October-December and again in July and August. At Oak Creek, high values were noted in May and again in September. Industrial Bio-Test (1972a) recorded high levels of nitrite in May and December 1971 at the Kenosha and North Chicago water intakes and at the Waukegan Generating Station.

A certain amount of the scatter in the nitrite data in Table 23 is attributable to the unavoidable errors encountered when trying to measure very small quantities of a substance near the detection limit of the experimental method. Some of the scatter is also attributable to purely physical factors. For example, Weschler *et al.* (1972) happened to sample around the Point Beach Power Plant during an episode of upwelling. In samples of water which had not been upwelled, nitrite was 1.0-1.5 μg NO_2^--N/l, while in upwelled water individual values were as much as 3 μg NO_2^--N/l (Fig. 49). This nitrite may represent the decomposition of organic nitrogen, which had sedimented into the bottom water (see Ammonia discussion), and subsequent oxidation to nitrite in the process of nitrification.

Limitations on nitrite content in public drinking water supplies are indicated in Appendix B, part 1.

NITRATE

Although abiotic reactions like the light-catalyzed oxidation of ammonia to nitrate (Joussot-Dubien and Kadiri, 1970) may have a certain small influence on the dynamics of nitrate in Lake Michigan, the biochemical process of production, consumption, and destruction (Fig. 44) are most likely the major forces controlling nitrate concentrations in the Lake. Bacteria (*e.g. Nitrosomonas*) oxidize ammonia to nitrite, and other bacteria (*e.g. Nitrobacter*) convert nitrite to nitrate in the process of nitrification. Denitrification, which removes nitrate as N_2 gas, will probably not occur in Lake Michigan except in areas where anaerobic conditions could allow a population of denitrifying bacteria to develop. Nitrate utilization by green plants and bacteria controls nitrate concentrations in the epilimnion.

Table 23. Nitrite Content in Lake Michigan Water

		Concentration NO_2^--N, µg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
3 samples collected at Sturgeon Bay entry buoy	18 May-21 Oct 1966	3	2-3	Schraufnagel *et al.*, 1968
5 samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	Dec 1969; Jan, May 1970	15	0-61	USGS, 1972
14 samples collected periodically at each intake:	Feb 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		6	1-16	
Waukegan Generating Station		6	3-11	
North Chicago public water supply		5	1-11	
Monthly samples collected at 3 stations 9.6 km (6 mi) east of Zion:	Feb 1970-Apr 1971			Industrial Bio-Test, 1972b
Surface-water		3	0.2-9	
Bottom-water		3	0.4-11	
Samples collected ∿monthly, surface to bottom, near Point Beach Nuclear Plant:	Jun-Sep 1971			Weschler *et al.*, 1972
6 stations <0.37 km (1230 ft) offshore		1.6	0.2-3.2	
4 stations 1.1-2.7 km (3600-9000 ft) offshore		1.5	0.2-2.8	
Samples collected from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Apr 1972	6.6	4.9-9.7	Industrial Bio-Test, 1972c
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		3	<2-12	
Effluent plume		4	<2-12	
South of plant, 4.8 km (3 mi)		3	<2-16	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		12	1-80	
North of plant, 1.6 km (1 mi)		11	1-80	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		8	3-10	
South of plant, 1.6 km (1 mi)		11	8-16	

USGS = U. S. Geological Survey.

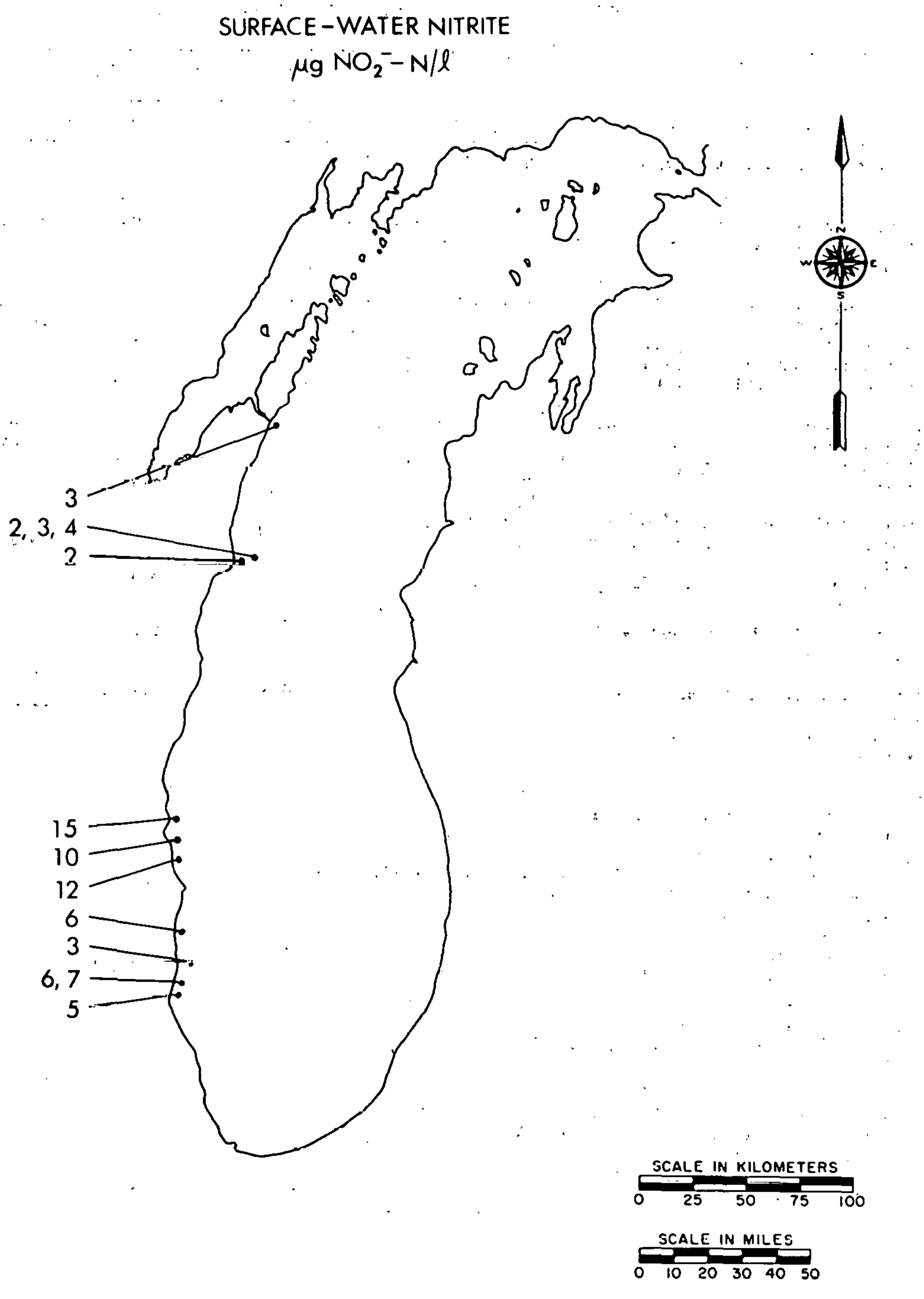


Fig. 48. Surface-Water Nitrite Concentrations over a Period of Ten Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 23.

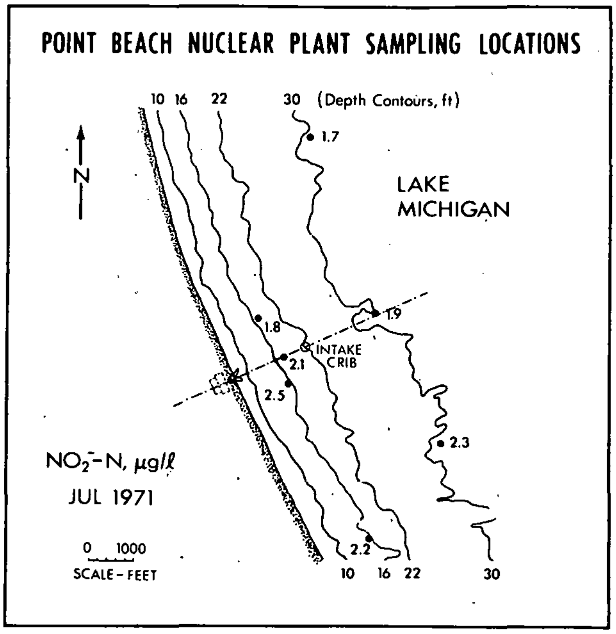


Fig. 49.

Nitrite Concentrations at Point Beach Nuclear Plant Showing Upwelled Water South of the Plant. Figure (modified) and data from Weschler *et al.* (1972).

Under certain conditions nitrate can be reduced to nitrite in the human intestine; therefore, nitrate concentrations in drinking water are a health concern.

There are few domestic, industrial, and agricultural sources of nitrate *per se* to Lake Michigan. As an end product of microbial decomposition of organic nitrogen compounds and subsequent nitrification, nitrate occurs in polluted waters subjected to fairly extensive oxidation. Thus nitrate in effluent from secondary sewage treatment, about 2.3 mg NO_3^--N/l (Weinberger *et al.*, 1966), results from oxidation of reduced forms of nitrogen during secondary treatment.

Nitrate is sometimes found in large quantities in groundwater, but the significance of this source to Lake Michigan is unknown. Rainwater is a source of nitrate (Junge, 1958), but the magnitude of this source is unknown.

Table 24 and Figures 50 and 51 summarize nitrate determinations in Lake Michigan. Since some analytical methods do not distinguish between nitrite and nitrate, some researchers report their data as $(NO_2^- + NO_3^-)$-N. This usage is noted where applicable in Table 24.

During summer active metabolism by phytoplankton removes nitrate from the water. Surface-water concentrations are about 150 µg NO_3^--N/l during July and August, whereas in January and February, when there is little biological activity, concentrations are about 250 µg NO_3^--N/l (*cf.* Figs. 50 and 51).

Biological controls on nitrate concentrations can be seen in vertical distributions (Fig. 47) as well as horizontal (Figs. 50 and 51). In July 1970 Schelske and Roth (1973) sampled six stations in the northern basin. The average surface-water concentration of 130 µg NO_3^--N/l rose to 180 µg NO_3^--N/l at 120 m. Similar increases with depth during summer stratification have been recorded at a number of stations in the northern and southern basins (Schelske and Callender, 1970), and at three stations 9.6 km (6 mi) east of Zion, Illinois

Table 24. Nitrate Content in Lake Michigan Water

Sample Description	*Dates*	*Concentration NO_3^--N, µg/l*		*Reference*
		Average	*Range*	
Samples collected ~weekly from Peter Cooper Corp. intake, Oak Creek, ~0.75 km (2500 ft) offshore	1961	240	0-760	Wis. Comm. Water Pollut., 1965
	1962	230	0-720	
	1963	210	40-500	
	1964	240	60-680	
	1965	280	10-880	Wis. Dep. Nat. Resour., 1969
	1966	250	40-780	
	1967	230	80-520	
	1968	230	20-800	
	1969	210	60-520	Wis. Dep. Nat. Resour., 1973
	1970	310	60-4000	
	1971	210	30-400	
	1972	180	10-490	
Whole Lake:	1962-63			USDOI, 1968
595 offshore samples		130	N.D.-650	
1654 inshore samples		140	N.D.-900	
Samples collected:	1962-63			USDOI, 1968
Indiana Harbor, 21 samples		160	10-840	
Calumet Harbor, 16 samples		120	10-350	
Chicago Harbor, 14 samples		100	50-110	
Samples collected:	Oct 1962, Jun 1963			USDOI, 1968
Milwaukee Harbor, 35 samples		150	40-240	
Adjacent to Milwaukee Harbor, 81 samples		140	30-900	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City		120	0-840	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo		90	10-380	
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor		100	10-290	
On a line roughly between Sheboygan and Little Sable Point		190	20-270	
Samples collected at surface, lower part of epilimnion, upper part of hypolimnion, and near bottom:				Powers and Ayers, 1967
41°51', 87°17'	Aug-Oct 1962	60	0-140	
42°01', 87°17'	Aug-Oct 1962	140	30-270	
42°17', 86°59'	Aug-Oct 1962	140	20-300	
42°34', 86°52'	Aug-Oct 1962	120	0-220	
41°51', 87°17'	Apr-Jun 1963	90	40-140	
42°01', 87°17'	Apr-Jun 1963	130	80-170	
42°17', 86°59'	Apr-Jun 1963	140	70-220	
42°34', 86°52'	Apr-Jun 1963	130	10-190	
149 samples collected throughout Green Bay	26 Jun-17 Jul 1963	80	N.D.-430	USDOI, 1968
Samples collected along lines from:	Apr-Nov 1964			Powers and Ayers, 1967
Chicago to Benton Harbor and Waukegan to South Haven		100	0-250	
Racine to Holland and Sheboygan to Ludington		70	0-360	
Samples collected:	22-28 Jul 1964			USDOI, 1968
Traverse Bay, 59 samples		160	60-400	
Adjacent to Traverse Bay, 29 samples		160	100-260	
Surface-water (2 m, 5 m, and 10 m) samples collected in northern basin:	1965			Holland, 1969 (from Allen, 1966?)
Inshore		105	97-114	
Offshore		112	103-123	

Table 24. (contd.)

		Concentration NO_3^--N, µg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Samples collected ∿biweekly at depths of 2 m, 5 m, and 10 m near:	Apr-Nov 1965			Allen, 1973
Ludington				
2 inshore stations		100[a]	12-175[a]	
2 offshore stations		110[a]	10-195[a]	
Sturgeon Bay				
2 inshore stations		110[a]	7-210[a]	
2 offshore stations		110[a]	8-187[a]	
Green Bay				
3 stations on a line from Little Sturgeon Bay to the southern edge of Door County		40[a]	0-98[a]	
Samples collected in Indiana Harbor at east breakwall inner light:				Snow, 1974
3 samples	Dec 1965	460[a]	300-600[a]	
51 samples	Jan-Dec 1966	450[a]	100-800[a]	
42 samples	Jan-Dec 1967	320[a]	90-650[a]	
6 samples	Jan-Dec 1968	450[a]	240-800[a]	
6 samples	Jan-Jun 1969	300[a]	100-400[a]	
3 samples collected at Sturgeon Bay entry buoy	18 May-21 Oct 1966	190	140-240	Schraufnagel *et al.*, 1968
Samples collected:				Schelske and Callender, 1970
Southern basin	22-24 Jul 1969			
Surface-water, 7 offshore stations		110	102-144	
Bottom-water, 7 offshore stations		220	184-273	
Surface-water, 8 inshore stations		100	67-111	
Bottom-water, 8 inshore stations		200	104-250	
Northern basin	15-23 Aug 1969			
Surface-water, 5 offshore stations		120	115-126	
Bottom-water, 6 offshore stations		210	119-240	
Northern basin, including Traverse Bay	15-23 Aug 1969			
Surface-water, 15 inshore stations		110	86-126	
Bottom-water, 8 inshore stations		220	196-249	
Northern Green Bay, excluding Bays de Noc	15-23 Aug 1969			
3 surface-water samples		80	74-92	
Northern Green Bay, including Bays de Noc	15-23 Aug 1969			
5 bottom-water samples		180	134-210	
Weekly samples (monthly Nov 1969-Mar 1971) collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	Nov 1969-Sep 1970	260	0-400	USGS, 1972
	Oct 1970-Sep 1971	230	90-410	USGS, 1973
	Oct 1971-Sep 1972	230	90-380	USGS, 1974a
	Oct 1972-Jun 1973	274	100-520	USGS, 1974b
Monthly samples collected at intakes:	Jan 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		210	60-390	
Waukegan Generating Station		220	60-390	
North Chicago public water supply		200	50-340	
Monthly samples collected at 3 stations 9.6 km (6 mi) east of Zion:	Feb 1970-Apr 1971			Industrial Bio-Test, 1972b
Surface-water		160	30-330	
Bottom-water		210	140-450	
Samples collected at a depth of 4 m at 5 stations (2 inshore, 3 offshore) along a line between Milwaukee and Ludington:	May, Jun, Aug, Oct, Nov 1970; Jan 1971			Holland and Beeton, 1972
Average values			170-180	
Individual values			100-290	
Samples collected at 8- to 21-day intervals (except 3 Feb-11 Mar) at a depth of 4 m:	27 May 1970-20 Oct 1971			Rousar, 1973
4.8 km (3.0 mi) east of Milwaukee		190	100-290	

Table 24. (contd.)

Sample Description	Dates	Concentration NO_3^--N, µg/l		Reference
		Average	Range	
Between Milwaukee and Ludington,				
1/4 the distance		190	100-280	
1/2 the distance		190	120-270	
3/4 the distance		190	120-270	
4.8 km (3.0 mi) west of Ludington		180	120-280	
Monthly averages for samples collected offshore from northern Chicago:				Lue-Hing, 1973
6 stations 0.30 km (1000 ft) offshore	Jun-Nov 1970, May-Oct 1971	210[a]	140-300[a]	
7 stations 0.61-0.91 km (2000-3000 ft) offshore	Jun-Dec 1970, May-Oct 1971	200[a]	100-280[a]	
4 stations 1.37-1.83 km (4500-6000 ft) offshore	Jun-Dec 1970, May-Oct 1971	240[a]	60-440[a]	
Monthly averages for samples collected at a station 3.0 km (10,000 ft) offshore from Zion	Dec 1970, May-Oct 1971	280[a]	150-520[a]	Lue-Hing, 1973
Monthly samples collected at Lake County, Ill., public water intake	Jun 1970-Jun 1973	240	60-840	Howe, 1973
Samples collected at 6 stations on a line passing east of Manitou Islands from Frankfort to Beaver Island:	7 Jul 1970			Schelske and Roth, 1973
Surface-water, 12 samples		140	117-156	
Bottom-water, 4 samples		180	174-193	
Samples collected (water depth 7.6 m) at a station east of Kewaunee Nuclear Plant:				Industrial Bio-Test, 1972d
Surface	25 May 1971	170[b]		
Bottom	25 May 1971	160[b]		
Surface	31 Aug 1971	200	190-210	
Bottom	31 Aug 1971	110	100-110	
Surface	16 Nov 1971	310	180-560	
Bottom	16 Nov 1971	300	230-430	
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun 1971-Apr 1972	380	80-2100	Industrial Bio-Test, 1972c
Monthly surface-water samples collected:	Oct 1971-Apr 1972 (except Mar)			Beeton and Barker, 1974
15 stations <8 km (5 mi) from shore, both north and south of Milwaukee		250	150-330	
2 stations ∿16 km (10 mi) from shore, one north and one south of Milwaukee		220	120-260	
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		200[a]		
Kenosha		300[a]		
Milwaukee (5 intakes)			<200-400[a]	
Port Washington		<200[a]		
Racine		500[a]		
Sheboygan		<200[a]		
Two Rivers		<200[a]		
10 surface-water samples each collected at stations east of Milwaukee:	28 Nov 1972			Beeton and Barker, 1974
0.4 km (0.25 mi) east		250		
16 km (10 mi) east		230		

Table 24. (contd.)

Sample Description	Dates	Concentration NO_3^--N, µg/l Average	Range	Reference
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		280	130-760	
Effluent plume		270	130-560	
South of plant, 4.8 km (3 mi)		270	140-720	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		320	230-550	
North of plant, 1.6 km (1 mi)		360	240-620	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		370	260-460	
South of plant, 1.6 km (1 mi)		390	300-510	

[a] *The sum of NO_2^--N plus NO_3^--N.*

[b] *Same value for all samples.*

N.D. = not detected.

USDOI = U. S. Department of the Interior; USGS = U. S. Geological Survey.

(Industrial Bio-Test, 1972b). Increases in nitrate concentrations with depth result from intense nitrate assimilation by the phytoplankton in the surface water during late spring and summer. Since there is little photosynthetic activity below the thermocline, there is relatively little conversion of nitrate in these bottom waters to the particulate organic nitrogen form. Indeed, NO_3^- in the bottom waters may even increase during summer stratification due to microbial decomposition and subsequent oxidation of nitrogen-containing organic detritus (*i.e.* settleable material consisting of the remains of organisms).

Although stratification generally reduces bottom waters containing higher concentrations of nitrate from mixing with nitrate-depleted surface waters, periodic upwelling carries these bottom waters to the surface. Schelske *et al.* (1971) observed surface-water nitrate concentrations increase from 10 to 180 µg NO_3^--N/l during a four-day period in July 1969 at a station 1.2 km west and 6.3 km south of Grand Haven. Upwelling, as evidenced by higher nitrate concentrations, was noted around the Point Beach Power Plant in July 1971 (Weschler *et al.*, 1972), and data from Industrial Bio-Test (1972b) also indicate upwelling on 13 July 1970 in the vicinity of Zion, Illinois.

Synoptic studies (Fig. 52a, b) by Beeton and Barker (1974) illustrate several points made above. Figure 52a shows Milwaukee Harbor was a notable source of nitrate to the nearshore area on 28 June 1972. Highest values were recorded at the Harbor entrance. These high values decreased due to dilution and perhaps biological uptake as well. Nitrate concentrations reached background levels as stations farther east of the Harbor were sampled. Around South Milwaukee, there are fewer cultural sources of nitrate, and in Figure 52a one sees nitrate concentrations increase to background levels offshore. This trend may be evidence of high nitrate uptake by macrophytes and phytoplankton

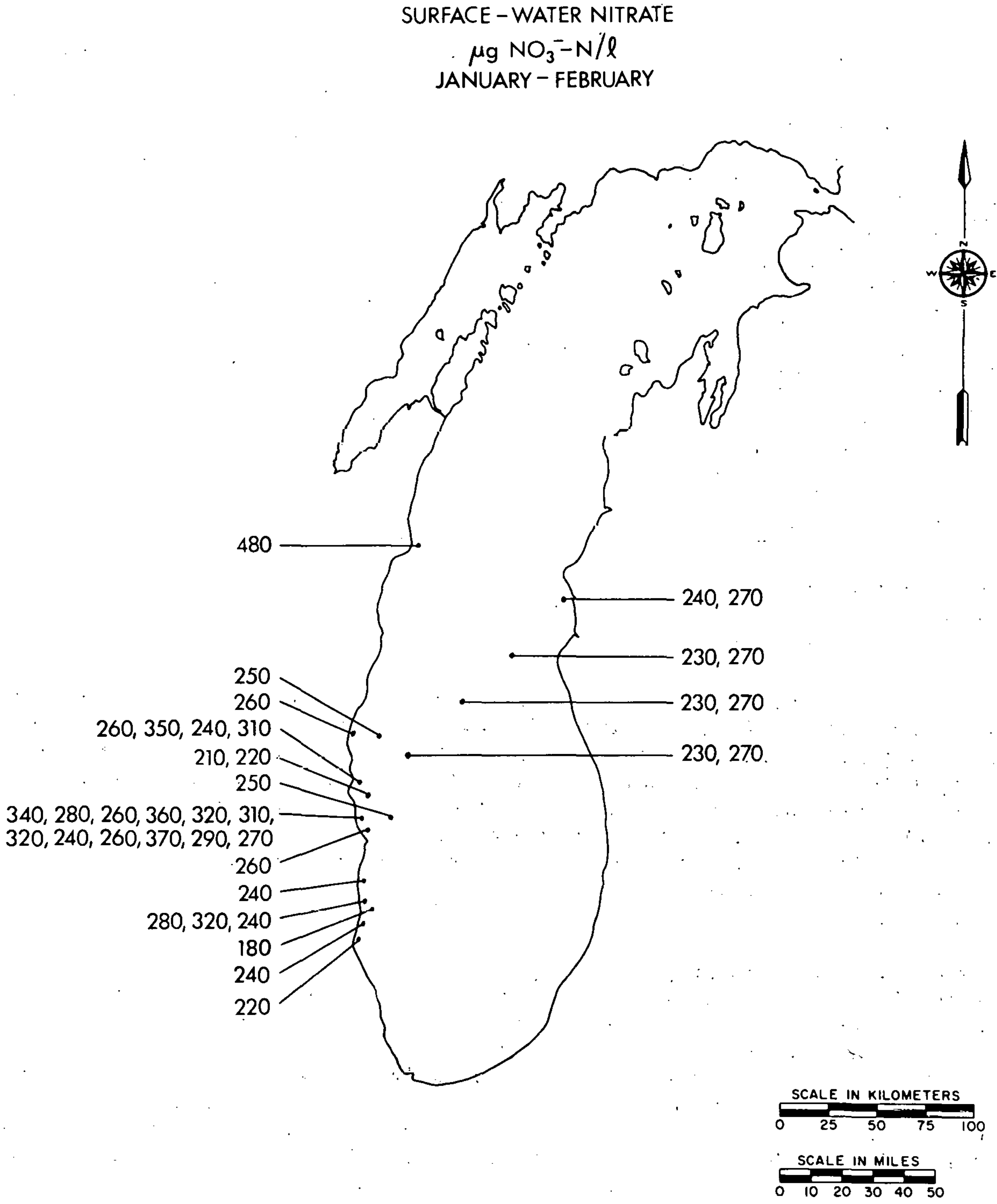


Fig. 50. Surface-Water Nitrate Concentrations in January-February over a Period of Fifteen Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 24.

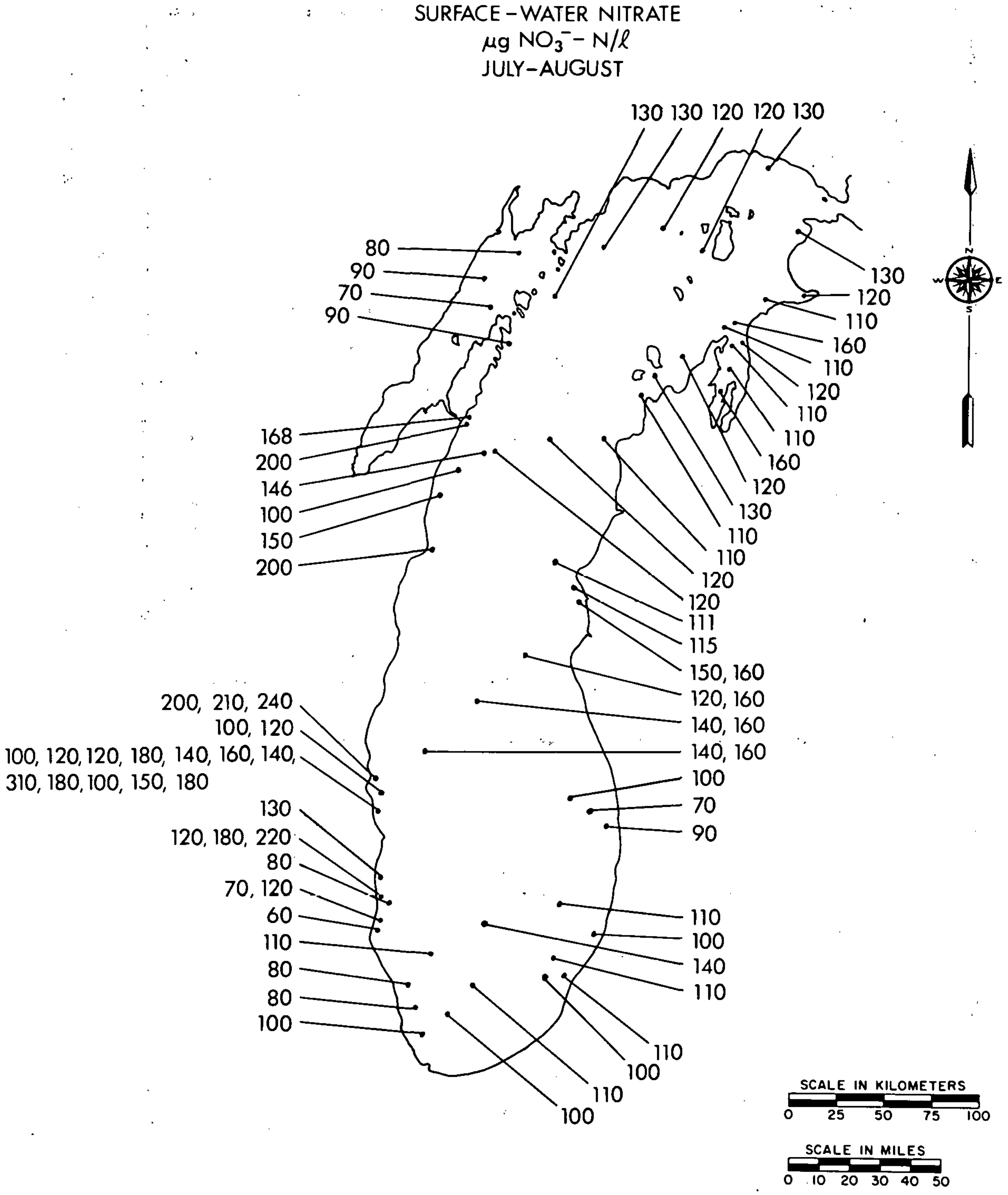


Fig. 51. Surface-Water Nitrate Concentrations in July-August over a Period of Fifteen Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 24.

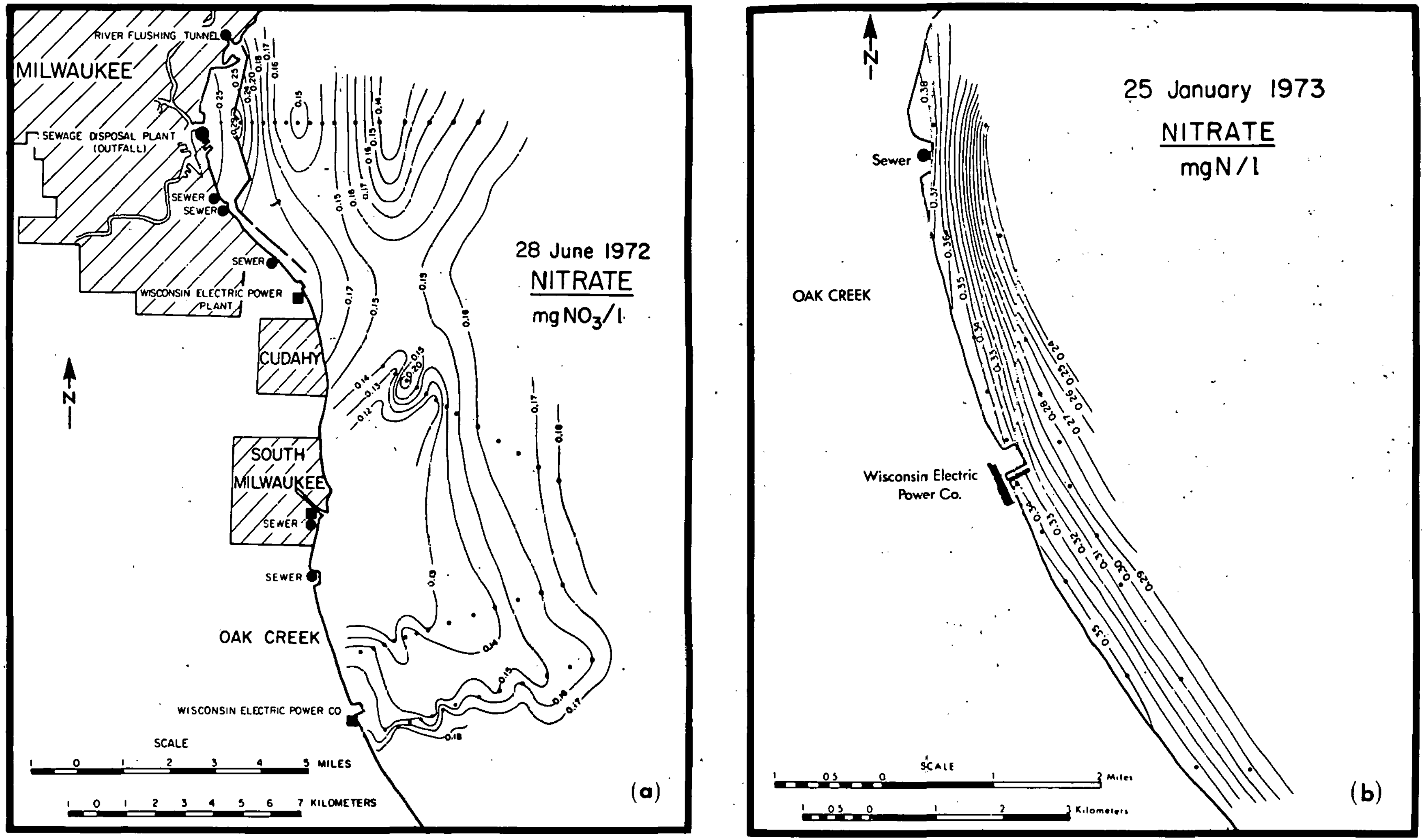


Fig. 52. Distribution of Surface-Water Nitrate Concentrations near Milwaukee. (a) 28 June 1972; (b) 25 January 1973. Modified from Beeton and Barker (1974) (with permission, see credits).

close to shore. In contrast, Figure 52b, based on data collected 25 January 1973, shows nitrate concentrations decline with distance from shore. This decrease may reflect dilution of nitrate sources in the shoreline area. Furthermore, absolute values for NO_3^--N were about twice as high in January as in June.

Standards, criteria, and objectives for nitrate content in public water supplies and in water to be managed for the protection of aquatic life are presented in Appendix B.

Biological implications of nitrate concentrations in Lake Michigan water are discussed in the section on Changes in Water Quality and Sediment Chemistry.

ORGANIC NITROGEN

The classical Kjeldahl determination measures organically bound nitrogen in the 3^- oxidation state (*e.g.* APHA *et al.*, 1971). Analysis of an unfiltered sample measures both particulate and soluble organic nitrogen, whereas analysis of a filtered sample determines only the soluble forms. The role of particulate organic nitrogen, represented by living and dead organisms, is much more clearly understood than is the role of dissolved organic nitrogen in the nitrogen cycle of a lake (Fig. 44).

If observations in seawater are analogous (Degens, 1970), then a certain amount of dissolved organic nitrogen is labile; that is, this portion is either readily assimilated or degraded by microbial decomposition. Another portion resists degradation (refractory) and little is known about it. Whether these comments are true for Lake Michigan is unknown, since only gross analyses of organic nitrogen content are available.

Dissolved organic nitrogen compounds may act as carbon or nitrogen sources for phytoplankton and zooplankton; there has been little or no research on dissolved organic nitrogen availability and utilization by plankton in Lake Michigan.

Dissolved organic nitrogen may form a nutrient source in at least one other manner. The action of rising bubbles can produce particles from dissolved organic compounds (Riley, 1963). Polypeptides may be important constituents of these particles, which could provide food for zooplankton.

Another proposed function of dissolved organic nitrogen compounds in aqueous systems is trace metal complexation. Compounds excreted by algae may complex or chelate substances in the growth medium (Fogg and Westlake, 1955), altering the solution chemistry of the metal, making it less toxic. Complexation may also be a means of maintaining higher concentrations of soluble nutrient elements, like iron, than would otherwise be possible. If the metals did not form complexes, they would likely react with oxygen and precipitate out as hydroxides or oxides.

There are several sources of organic nitrogen to Lake Michigan within the Lake. Some is synthesized from ammonia and nitrate by phytoplankton and bacteria; soon after death these organisms release their cell contents, including organic nitrogen, to the water. Even before death some phytoplankton are said to excrete, or exude, organic nitrogen compounds. Most studies of extracellular algal products have been made in laboratory systems; the significance of these nitrogenous exudates to Lake Michigan has yet to be evaluated. In the laboratory, Hellebust (1965) found that peptides and amino acids formed a considerable amount of the algal exudate.

Zooplankton release organic compounds to their environment by several mechanisms (Webb and Johannes, 1967), including: (*i*) simple diffusion, (*ii*) voiding of dissolved food residues, (*iii*) excretion. A variety of marine aquatic animals have been reported to release free amino acids (Johannes and Webb, 1970).

Sources of organic nitrogen external to Lake Michigan include tributaries, farm runoff, sewage and industrial waste effluents, and fallout of aerosols containing organic nitrogen.

Compared with ammonia and nitrate, there are relatively few determinations of organic nitrogen in Lake Michigan waters. Values observed within the past 15 years are summarized in Table 25. Organic nitrogen content is frequently high in harbors. Otherwise, average values for organic nitrogen content are relatively invariant at 200-300 μg N/l in Lake Michigan.

During July through November 1964, organic nitrogen content was low in inshore and offshore waters (Robertson and Powers, 1968). In contrast, organic nitrogen was low near Oak Creek, Wisconsin, only during August, September, and October (Wis. Comm. Water Pollut., 1965; Wis. Dep. Nat. Resour., 1969, 1973). Limnetics (1974) reported low organic nitrogen values near Oak Creek in March-April and July-August 1973. Near Two Rivers, Wisconsin, organic nitrogen content was lowest during June-October (Limnetics, 1974). At other places, such as the Milwaukee public water supply intake (U. S. Geol. Surv., 1972, 1973, 1974a, 1974b) and the Lake County, Illinois, public water supply intake (Howe, 1973--personal communication), data were so scattered that seasonal trends could not be discerned.

Robertson and Powers (1968) found that surface waters of inshore and offshore areas had about the same organic nitrogen concentrations as subsurface waters until July; after that, the surface concentrations were higher. Average concentrations were higher on the eastern side of the Lake than on the western. Robertson and Powers concluded that there is a lack of any large-scale difference in organic nitrogen content in the Lake.

There are no suggested limits or criteria for organic nitrogen concentrations in drinking water supplies or in lakes for aquatic life.

SEDIMENTS

Nitrogen-containing materials which reach the sediments of Lake Michigan are subject to the same kinds of reactions as they are in the overlying water, including decomposition, nitrification, denitrification, utilization, and N_2 fixation. In addition, NH_4^+ may be fixed irreversibly within the lattices of the clay minerals found in the sediments.

Table 25. Total Organic Nitrogen Content in Lake Michigan Water

		Concentration Organic N, μg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Samples collected ∿weekly from Peter Cooper Corp. intake, Oak Creek, ∿0.75 km (2500 ft) offshore	1961	250	80-<840	Wis. Comm. Water Pollut., 1965
	1962	320	80-840	
	1963	410	50-1920	
	1964	330	80-690	
	1965	320	<10-840	Wis. Dep. Nat. Resour., 1969
	1966	320	150-540	
	1967	320	160-910	
	1968	310	140-550	
	1969	400	170-870	Wis. Dep. Nat. Resour., 1973
	1970	330	150-790	
	1971	360	140-2080	
	1972	320	130-750	
Whole Lake:	1962-63			USDOI, 1968
313 offshore samples		190	N.D.-520	
529 inshore samples		210	10-700	
Samples collected:	1962-63			USDOI, 1968
Indiana Harbor, 2 samples		720	650-780	
Calumet Harbor, 2 samples		490	480-500	
Chicago Harbor, 6 samples		200	90-320	
Racine Harbor, 6 samples		290	170-360	
Samples collected:	Oct 1962, Jun 1963			USDOI, 1968
Milwaukee Harbor, 14 samples		370	300-670	
Adjacent to Milwaukee Harbor, 46 samples		270	10-580	
Monthly averages for samples collected inshore and offshore:	Apr-Nov 1964			Robertson and Powers, 1968
Surface-water (0-20 m) samples		118	80-273	
Bottom-water (>20 m) samples		117	61-341	
Samples collected in Indiana Harbor at east breakwall inner light:				Snow, 1974
3 samples	Dec 1965	400	200-500	
51 samples	Jan-Dec 1966	600	0-2700	
42 samples	Jan-Dec 1967	1200	0-6400	
6 samples	Jan-Dec 1968	400	200-600	
6 samples	Jan-Jun 1969	400	300-600	
3 samples collected at Sturgeon Bay entry buoy	18 May-21 Oct 1966	180	130-220	Schrautnagel *et al.*, 1968
Monthly samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	Nov 1969-Sep 1970	60	0-260	USGS, 1972
	Oct 1970-Sep 1971	50	0-210	USGS, 1973
	Oct 1971-Sep 1972	290	0-1100	USGS, 1974a
	Oct 1972-Jun 1973	170	40-320	USGS, 1974b
Monthly averages for samples collected offshore from northern Chicago:				Lue-Hing, 1973
6 stations 0.30 km (1000 ft) offshore	Jun-Nov 1970, May-Oct 1971	560	80-940	
7 stations 0.61-0.91 km (2000-3000 ft) offshore	Jun-Dec 1970, May-Oct 1971	420	210-630	
4 stations 1.37-1.83 km (4500-6000 ft) offshore	Jun-Dec 1970, May-Oct 1971	440	250-1120	
Monthly averages for samples collected at a station 3.0 km (10,000 ft) offshore from Zion	Dec 1970, May-Oct 1971	370	100-590	Lue-Hing, 1973
Samples collected ∿monthly at Lake County, Ill., public water intake	May 1972-Jun 1973		40-340	Howe, 1973

Table 25. (contd.)

		Concentration Organic N, μg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Stations at 3.7, 5.5 and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers-- 3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		220	90-450	
Effluent plume		220	150-350	
South of plant, 4.8 km (3 mi)		200	90-320	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee-- 2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		270	170-420	
North of plant, 1.6 km (1 mi)		280	130-430	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis-- 2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		280	90-450	
South of plant, 1.6 km (1 mi)		290	200-400	

N. D. = not detected.

USDOI = U. S. Department of the Interior; USGS = U. S. Geological Survey.

There have been few studies of nitrogen content in Lake Michigan sediments; but a brief review of data from Lake Ontario may help understand the nitrogen chemistry of Lake Michigan sediments.

Kemp and Mudrochova (1972) studied a sediment core taken near the deepest point in Lake Ontario. They found that the predominant form of inorganic nitrogen throughout the 10-m core was irreversibly fixed NH_4^+-N. Fixed ammonium content at the surface was less than at greater depths within the core. They presumed that much of this fixed ammonium was derived from land runoff; ammonia in soil is usually found only in the particulate form (as opposed to being dissolved in soil water), usually in association with clay minerals.

In the Lake Ontario sediment, NO_2^--N plus NO_3^--N concentrations were low throughout the core, except at the oxidized sediment-water interface, where a maximum of 28 μg NO_2^--N plus NO_3^--N/g dry weight sediment was found. Comparison of nitrate concentrations and electrode potentials (see Dissolved Oxygen section) with depth in the sediment showed that nitrification could occur only in the top 3 cm.

Exchangeable ammonium content (*i.e.* that which is either dissolved in interstitial water or else loosely held by particulate matter) increased with depth. Kemp and Mudrochova suggested that depletion of exchangeable ammonium at the surface was due to oxidation by nitrifying bacteria.

Organic nitrogen accounted for 94% of the total nitrogen at the surface of the Lake Ontario core examined by Kemp and Mudrochova. Organic nitrogen content decreased with depth in the core to about 10 cm. Then the content was relatively constant to the demarcation between post-glacial and glacial sediments. In the upper part of the core, fixed and exchangeable ammonium concentrations were mirror images of organic nitrogen content. This observation is explained by microbial decomposition, which is most intense in the first few centimeters, breaking down organic nitrogen and releasing ammonia. Below a certain depth in the core, organic nitrogen content changes little because only that organic nitrogen which is resistant to microbial degradation remains.

Callender (1969) measured total Kjeldahl nitrogen in sediment samples from Lake Michigan. This determination includes all of the organic nitrogen and an unknown amount of the exchangeable ammonium-nitrogen. It does not include fixed ammonium-, nitrite-, or nitrate-nitrogen. Surficial sediment concentrations of total Kjeldahl nitrogen are shown in Figure 53. In the

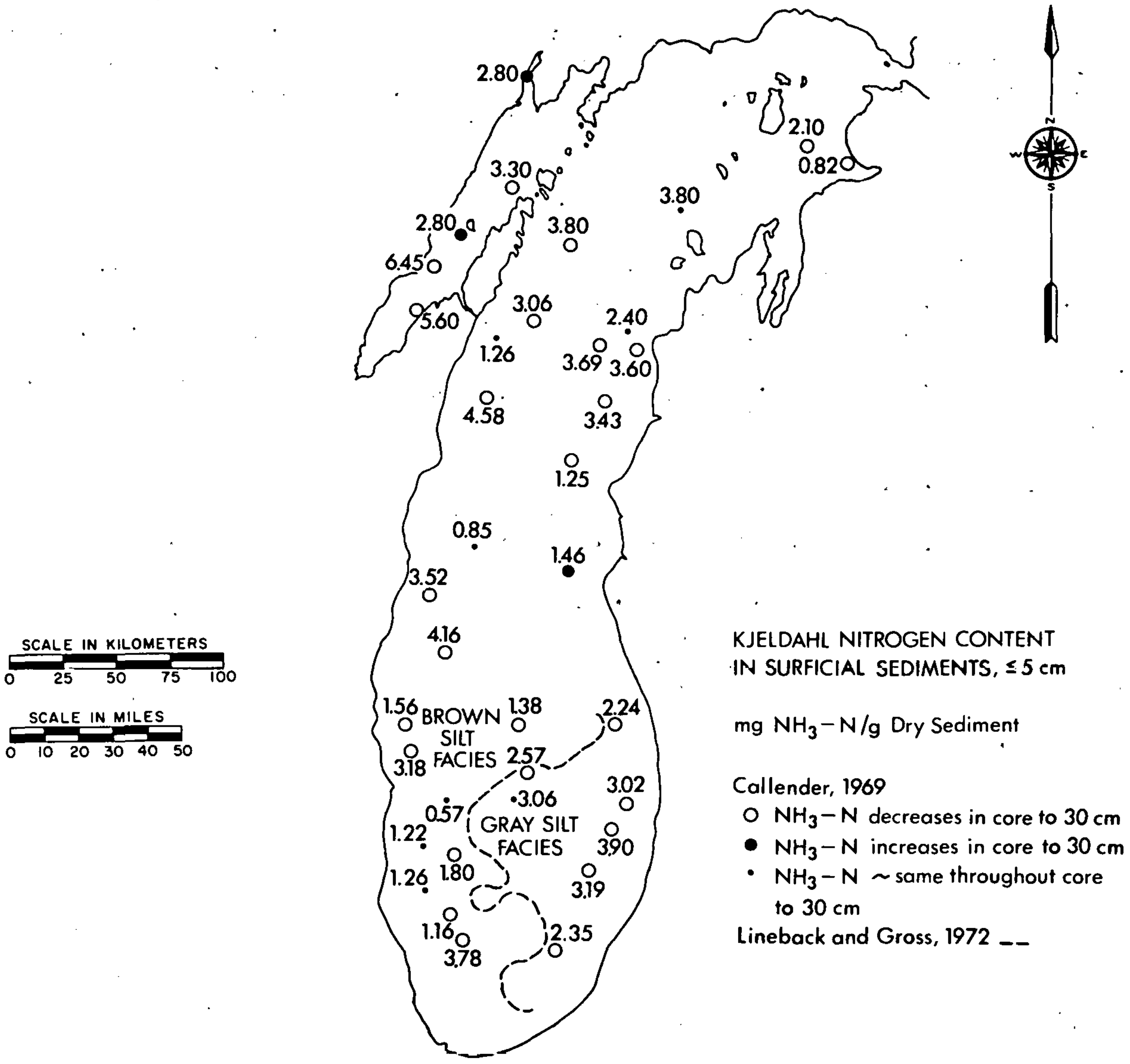


Fig. 53. Total Kjeldahl Nitrogen Content in Surficial Sediments of Lake Michigan. Samples were collected May-July 1968 by Callender (1969). The plotted values represent surficial samples from the cores. Variation of values with depth in core is represented in the legend. Boundary of brown and gray silt facies of the Waukegan member from Lineback and Gross (1972).

western portion of the southern basin, total Kjeldahl nitrogen concentrations are generally low (0.57-1.80 mg NH_3-N/g dry weight sediment) except for one station just east and somewhat south of Milwaukee. One can speculate that this set of low values is due to fewer rivers bearing reduced nitrogen compounds on the western side of the southern basin compared with the eastern side; there are no data presently available to verify or refute this speculation. The single high value in the southern basin along the western shore is near the entrance of the Milwaukee River. Figure 53 shows the high concentration of organic nitrogen of the surficial sediments of southern Green Bay.

Total Kjeldahl nitrogen content decreased between the surface and 30-35 cm in 21 of 33 cores (Callender, 1969). In eight cores there was no major change with depth, and in four (two in Green Bay, one in Little Traverse Bay, and one in the northern basin), Kjeldahl nitrogen increased between the surface and 30 cm. The pattern of decreasing Kjeldahl nitrogen with depth is likely due to the breakdown of organic nitrogen described by Kemp and Mudrochova (1972).

PHOSPHORUS

In contrast to the nitrogen cycle, phosphorus dynamics in Lake Michigan are not directly controlled by oxidation and reduction, for phosphorus exists almost exclusively in the 5+ oxidation state in the biosphere. Instead, both biochemical reactions; involving bacteria, plants and animals; and inorganic reactions act in concert to determine the dynamics of phosphorus in the Lake.

Discussion of phosphorus in Lake Michigan is organized in the following fashion: first, a brief discussion of phosphorus forms likely to be important in the Lake is presented in order to establish familiarity with terminology. Sources of phosphorus to the Lake are considered, followed by a discussion of potentially important reactions, both biochemical and inorganic, involving phosphorus. Problems of analyzing for phosphorus content in environmental systems like Lake Michigan, the measurement of phosphorus concentrations, and the significance of these measurements are discussed. Finally, characteristics of sedimentary phosphorus in Lake Michigan are reviewed.

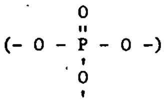
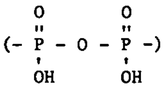
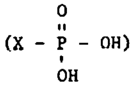
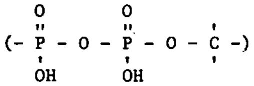
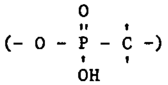
FORMS OF PHOSPHORUS

Dissolved forms of phosphorus which may be significant in Lake Michigan are indicated in Table 26. Inorganic orthophosphates, which are derived from orthophosphoric acid (H_3PO_4), are the simplest types of phosphorus in this table. Forms of orthophosphate found in Lake Michigan depend on pH. Figure 54 indicates that $H_2PO_4^-$ and HPO_4^{2-} predominate between pH 5 and 10.

Organic derivatives of orthophosphoric acid, such as phospholipids, sugar phosphates and phosphoramidates, are common in plants and animals. There is no direct evidence of the relative amounts of these compounds in natural waters, although Herbes *et al.* (1975) have presented preliminary evidence indicating that inositol phosphates may be an important component of the dissolved organic phosphorus fraction.

Condensed phosphates, containing -P-O-P- bonds, can be important. Inorganic condensed phosphates are still used extensively in synthetic detergents

Table 26. Dissolved Phosphorus Forms of Possible Significance in Lake Michigan

Name and Type of Bonding	*Representative Compounds or Series*
Orthophosphate  $(-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\mid}}{P}}-O-)$	$H_2PO_4^-$; HPO_4^{2-}; PO_4^{3-}; $CaH_2PO_4^+$
Inorganic Condensed Phosphates  $(-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\mid}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\mid}}{P}}-)$	
Pyrophosphate	$H_2P_2O_7^{2-}$; $HP_2O_7^{3-}$; $P_2O_7^{4-}$
Tripolyphosphate	$H_2P_3O_{10}^{3-}$; $HP_3O_{10}^{4-}$; $P_3O_{10}^{5-}$
Trimetaphosphate	$HP_3O_9^{2-}$; $P_3O_9^{3-}$
Organic Orthophosphates  $(X-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\mid}}{P}}-OH)$	
X = RO -- Sugar phosphates	Glucose-1-phosphate; adenosine monophosphate
Inositol phosphates	Inositol hexaphosphate
Phospholipids	Glycerophosphate; phosphatidic acids
X = RNH -- Phosphoramidates	Guanidinium phosphates
Organic Condensed Phosphates  $(-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\mid}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\mid}}{P}}-O-\overset{\mid}{\underset{\mid}{C}}-)$	Adenosine triphosphate
Organic Phosphonates  $(-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\mid}}{P}}-\overset{\mid}{\underset{\mid}{C}}-)$	Aminophosphonic acids

(see the following section on Sources). These phosphate compounds reach Lake Michigan through untreated or inadequately treated municipal waste effluents. Furthermore, several very important organic compounds contain condensed phosphate groups. A notable example is adenosine triphosphate, an agent for energy transfer in all living organisms.

Another form of organic phosphorus, containing -P-C- bonding, may exist in the aqueous environment, but knowledge of the occurrence of -P-C- compounds in fresh or marine waters is lacking. Aminophosphonic acids have been identified as a major component of the phospholipids of certain ciliates and mollusks (Quin, 1965), as well as in a planktonic amphipod and several species of phytoplankton (Kittredge *et al.*, 1969). Corner (1973) implied that only

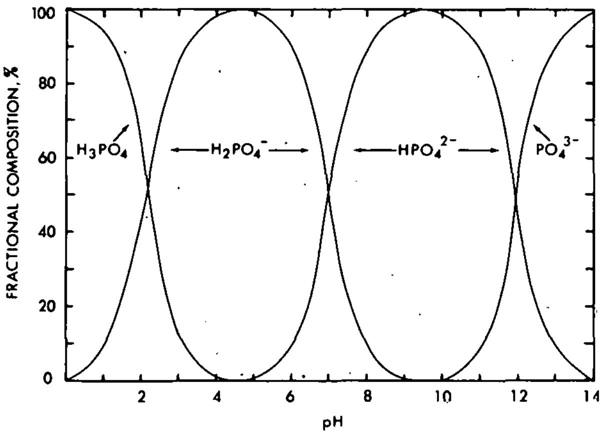


Fig. 54.

Variation in Fractional Composition of Orthophosphate Species with pH.

phytoplankton synthesize aminophosphonic acids. The -P-C- bond is very stable chemically, and compounds containing it may be metabolically inert.

Phosphorus is also found associated with particulate matter (Table 27). Phosphorus is a constituent of a number of minerals, such as apatite. It sorbs onto or into metal oxides and hydroxides, like iron, and associates with clay minerals. And, of course, it is found in all living matter and the remains of incompletely decomposed organisms.

Table 27. Particulate Phosphorus Forms of Possible Significance in Lake Michigan

Form	*Representative Compounds or Substances*
Soil and Rock Mineral Phases	
Hydroxyapatites	$Ca_{10}(OH)_2(PO_4)_6$
Fluorapatite	$Ca_{10}(F)_2(PO_4)_6$
Mixed Phases, Sorbed Species, etc.	
Phosphate associated with clay minerals	Kaolinite-phosphate
Phosphate associated with metal hydroxides or oxides	Iron oxides or hydroxides plus phosphates Manganese oxides or hydroxides plus phosphates Aluminum oxides or hydroxides plus phosphates
Collophane	Non-crystalline mixture of carbonate and fluorapatite, $\sim Ca_{10}(PO_4)_{6-x}(CO_3F)_x(F,OH)_2$, where $x \sim 1$
Organic phosphates associated with clay minerals	
Organic phosphates associated with metal hydroxides or oxides	
Suspended or Insoluble Organic Phosphorus	
Bacteria	
Phytoplankton	
Zooplankton	
Detritus	
Proteins	

SOURCES

Sources of phosphorus to Lake Michigan are many. Leaching and erosion of igneous rock, as well as sedimentary formations derived from igneous rock, supply apatite, fluorapatite and hydroxyapatite (Fisher, 1973) to Lake Michigan and its tributaries. Soil erosion adds both inorganic and organic phosphorus, especially from agricultural areas and around construction sites. Farming (*e.g.* dairying, animal feed lots, and excessive fertilizer application) and urban runoff can contribute large quantities of phosphorus.

Sewage effluents are especially important as phosphorus sources to Lake Michigan. The physiological level of phosphorus excretion for adult humans is about 1.5 g phosphorus per day (Fair *et al.*, 1968). However, since World War II, increasing use of detergent containing polyphosphate builders has caused the phosphorus content of sewage to rise appreciably above the physiological level. The most commonly used builders, pyrophosphates, tripolyphosphates and hexametaphosphates, are added to detergent formulations to soften hard water, complex discoloring heavy metals, disperse suspended particles, buffer the water, and increase the cleaning efficiency of the active ingredients by forming micelles (Devey and Harkness, 1973). These condensed phosphates subsequently appear in sewage, where they may constitute three to four times as much phosphorus as would be present were human excreta the only sources of phosphorus (Stumm and Morgan, 1962, cited by Vollenweider, 1968). Current levels may be above this estimate. Although recent restrictions (by the state of Indiana and the city of Chicago) on the use of detergents containing phosphate builders have reduced the size of this source somewhat (*e.g.* Indiana Stream Pollution Control Board, 1974), municipal sewage effluents are still a major source of phosphorus to the Lake. Primary plus secondary sewage treatment removes about 50% of the influent phosphorus, meaning that *ca.* 9 mg PO_4^{3-}-P/l are present in the waste effluent (Weinberger *et al.*, 1966).

Industrial waste effluents, notably pulp and paper manufacturers around Green Bay (Epstein *et al.*, 1974) and a few metal refineries in Indiana (Businessmen for the Public Interest, 1972) reportedly release major quantities of phosphorus to Lake Michigan.

Murphy and Cesarotti (1974--unpublished) recently suggested that rainfall is an important source of phosphorus to the Lake, as indicated by the data in Table 28. These authors did not examine the significance of dry fallout, but their estimate that as much as 36% of the phosphorus added to the southern part of the Lake comes in rain needs verification.

Table 28. Average Phosphorus Concentrations in Rainfall around Lake Michigan*

	Concentration, mg PO_4^{3-}-P/l	
Location	*Orthophosphate*	*Total Phosphorus*
Chicago	0.012	0.034
Beaver Island	0.007	0.017

**Data from Murphy and Cesarotti, 1974--unpublished.*

REACTIONS

Phosphorus can be present in a variety of forms in Lake Michigan (Tables 26 and 27). Transformations of phosphorus among the various forms are significant, considering that phosphorus was thought by Schelske and Stoermer (1972) and Thomas *et al.* (1972) to be an important element limiting primary productivity in Lake Michigan.

Two interlocking cycles in the Lake control phosphorus concentrations. One is dominated by biochemical reactions, the other by inorganic reactions. The two cycles will be considered separately for convenience, but they involve the same forms of phosphorus and similar reactions occur.

Biochemical Reactions

Although a number of researchers think phytoplankton use orthophosphate most readily for biosynthesis, most algae can synthesize intra- and/or extracellular phosphatases when the inorganic phosphate pool is depleted to enable them to utilize a wide range of condensed and organic compounds (Fig. 55) as ultimate phosphorus sources during periods of minimal orthophosphate content in the surrounding medium (Fogg, 1973). Presumably the phosphatases split off the phosphate group for subsequent intracellular incorporation (Kuenzler and Perras, 1965).

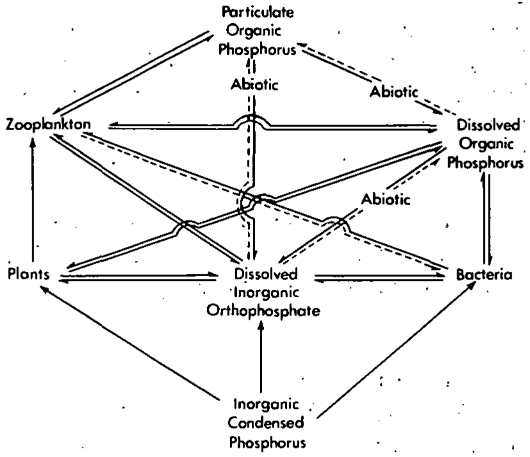


Fig. 55.

Biochemical Interactions Involving Phosphorus: —— Reactions known to occur in natural waters; --- Hypothetical reactions. Abiotic reactions are included for completeness.

During growth, algae can lose phosphorus as well as take it up. Phosphorus excretion by phytoplankton has usually been studied in the laboratory. Lean (1973) attempted to characterize a low apparent molecular weight organic phosphate compound, presumably excreted by microorganisms, in a eutrophic Ontario lake. After excretion, the material sorbed to colloids, from which orthophosphate was released. Lean's report was one of the first to claim excretion of organic phosphorus compounds by freshwater plankton, although the phenomenon has been known in marine systems for more than a decade (Antia *et al.*, 1963). If an alga dies before being eaten, then phosphate is returned to the water during autolysis of the cell. There are no data for Lake Michigan on rates of excretion or rates of release by phytoplankton during autolysis.

Marine zooplankton, typified by calanoid copepods, assimilate 60-80% or more of the phosphorus they consume (summarized in Corner, 1973). Unassimilated phosphorus is voided to the surrounding water, along with phosphorus which is excreted as a constituent of metabolic end products. The particulate and dissolved forms in which zooplankton release phosphorus are as important as the rates of release; both affect the significance of phosphate excretion to the phosphorus cycle in Lake Michigan. Peters and Lean (1973) found that freshwater zooplankton released about 90% orthophosphate in short-term experiments; by inference, about 10% was in another form or forms, such as organic phosphorus. During longer experiments, appreciable recycling of phosphorus between the animals and the water or the animals and the organisms living on the animals led to substantial underestimates of orthophosphate release. These data imply that soluble compounds released by zooplankton may constitute a significant fraction of the phosphorus required by phytoplankton and bacteria. There are no data on the rates of release of phosphorus by zooplankton in Lake Michigan.

Inorganic Reactions

Inorganic and biochemical reactions, and physical factors also, reduce phosphorus availability in the aquatic ecosystem. Precipitation, complexation, and sorption (Fig. 56) are among the inorganic chemical reactions in which phosphorus may be involved.

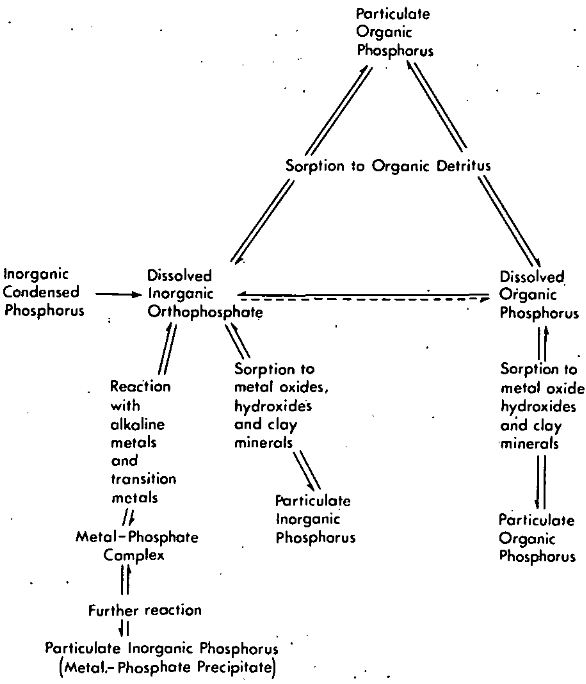


Fig. 56.

Inorganic Interactions Involving Phosphorus. ——— Reactions known to occur in natural waters; --- Hypothetical reactions.

Precipitation

Solubility product expressions for crystalline minerals and dissociation constants for acids found in natural waters allow one to calculate an equilibrium phosphate solubility under specified conditions (pH, metal ion concentrations, etc.). Hydroxyapatites, $Ca_{10}(OH)_2(PO_4)_6$, are the likely inorganic forms of solid phase phosphates in Lake Michigan. Unfortunately, computations based on pure substances like hydroxyapatite often cannot account for the total amount of phosphate observed in solution. Rates of precipitation and dissolution of apatite in a natural system appear too slow for hydroxyapatite to play a major role in controlling phosphorus concentrations in Lake Michigan water (sediments are considered below). Furthermore, phosphate anions enter solid oxides or hydroxides of iron and aluminum; these reactions cannot be described by simple solubility product expressions because they are not stoichiometric.

Complexation

Phosphate, pyrophosphate, tripolyphosphate, and higher polyphosphate anions are known to form complexes, chelates, and insoluble salts with a number of ions (Stumm and Morgan, 1970). The extent of complexation and chelation between various phosphorus forms and metal ions in natural waters depends on the relative concentrations of phosphorus and metal ions, the pH, and presence of other ligands (sulfate, carbonate, fluoride, organic species) in the water. Phosphate concentrations are generally low. Complex formation involving the major cations and various phosphate anions will have small effect on the metal ion distribution, but may have significant effects on the phosphate distribution. Complex formation may significantly affect the distribution of cations, phosphate ions, or both whenever concentrations of minor cations (*e.g.* Fe^{3+}, Mn^{2+}, Zn^{2+}, Cu^{2+} and others) are comparable to or lower than phosphate concentrations. The degree of complexation between phosphates and metal ions can influence solubilities of metal phosphates under environmental conditions, as well as rates of iron and manganese oxidation (Stumm and Morgan, 1970). No data on phosphorus complexation in Lake Michigan are available.

Sorption

Examples of sorption of phosphate to surfaces are well known and extensively discussed in texts such as Stumm and Morgan (1970). Phosphate anions are taken up from natural waters by clay minerals like kaolinite and montmorillonite, by freshly precipitated ferric and aluminum hydroxides, and by improperly chosen sampling bottles. Chemical bonding between phosphate groups and metal ions in a solid lattice is postulated to be the underlying principle for these various inorganic "sorption" phenomena. It is also likely that phosphate can sorb to organic compounds such as the organic aggregates present in sea water (Riley, 1963), as well as to seston (particulate matter suspended in water). Sorption may be an important factor controlling removal of orthophosphate to the sediments in Lake Michigan. Under the pH conditions of Lake Michigan, most iron oxides and hydroxides and many aluminum oxides plus hydroxides will have a net positive charge on their surfaces (Stumm and Morgan, 1970). Consequently, negatively charged phosphate species sorb onto these aluminum and iron species as well as other positively charged particles and are removed from solution by precipitation. Example of phosphorus removed by sorption to iron-containing compounds is found in the positive correlation of iron with phosphorus content in ferromanganese nodules from the sediments of northern Lake Michigan (Rossmann *et al.*, 1972; Torrey and Edgington, 1973b--unpublished).

ANALYSIS

Before presenting results of phosphorus analyses of Lake Michigan water, a short discussion of methods used to quantify phosphorus will be presented to clarify terminology and point out problems of interpretation.

Chemical Determinations

The quantification of phosphorus in water through colorimetric analysis depends ultimately on the conversion of all phosphorus-containing compounds into free orthophosphate, in which form phosphorus is measured. It is often assumed implicitly that analysis of a filtered, but otherwise untreated, sample determines free orthophosphate; that is, in a solution that has not been subjected to an oxidative acid digestion only free orthophosphate reacts with the color-forming reagents. Without solvent extraction, the limit of detection of this procedure is *ca.* 1 μg PO_4^{3-}-P/1 (Strickland and Parsons, 1968).

However, the ease of conversion of the various forms of phosphorus (*cf.* Tables 26 and 27) to free orthophosphate differs considerably, even for compounds having the same type of bonding. Because of the heterogeneity of phosphorus compounds in natural waters, analyses are based on arbitrary groups of compounds, having similar resistances to conversion to free orthophosphate, rather than on molecules having similar structures. A particular phosphorus compound could be included in several of these groups, depending on which analytical techniques were used to define the groups; that is, the groups are defined by the operations used to characterize them.

If experimental conditions inhibit hydrolysis of condensed phosphates and decomposition of labile compounds, then analysis of a filtered but chemically untreated sample in theory should yield the concentration of inorganic orthophosphate. It is convenient to designate this quantity as dissolved inorganic phosphate, although the term soluble reactive phosphate best acknowledges the empirical nature of the measurement (Strickland and Parsons, 1968). It is likewise convenient to refer to the remainder of the phosphorus in the sample as combined phosphorus.

At one time the major emphasis of phosphorus studies in natural waters was on determination of soluble reactive phosphate concentrations, due to the early discovery that inorganic orthophosphate is the principal form of phosphorus used in plant nutrition (Hooper, 1973). When it was realized that inorganic phosphorus compounds often comprise less than 10% of the total phosphorus in aquatic ecosystems (Hutchinson, 1957), the scope of phosphorus studies widened to include determination of total phosphorus concentrations, or phosphorus present after oxidative acid digestion of an unfiltered sample. The difference between total phosphorus and soluble reactive phosphate was usually termed organic phosphorus, until it was recognized that inorganic condensed phosphates, under those experimental conditions, could constitute an important portion of the "organic" phosphorus.

Thus the heterogeneity of phosphorus compounds in natural waters (*cf.* Tables 26 and 27) emphasizes the crudeness of trying to measure phosphorus compounds based on ease of conversion to free orthophosphate. The ability to place an unequivocal interpretation upon the data obtained by fractionation into many sub-groups may not warrant determination of more than total (including particulate) phosphorus, total soluble phosphorus, and soluble reactive phosphate (Jenkins, 1968). With the exception of work performed by the U. S. Department of the Interior (1968; also in Risley and Fuller, 1966), which reported total soluble phosphorus concentrations, measurements of phosphorus content in Lake Michigan have usually been reported as soluble reactive phosphate or total phosphorus.

Bioassay Determinations

Questions have been raised on the importance of various forms of phosphorus to aquatic primary producers. The Algal Assay Procedure (EPA, 1971) can be used to measure the amount of phosphorus available to organisms. In comparison studies, bioassay procedures and chemical analyses for dissolved inorganic phosphate have often yielded similar results. Agreement between bioassay and chemical procedures does not establish that the chemical procedure measures only orthophosphate. It does suggest, however, that the quality measured chemically bears a definite relationship to what is biologically available, an important ecological consideration. Fitzgerald *et al.* (1975) used the Algal Assay Procedure to compare chemically determined soluble reactive phosphate with biologically available phosphorus in Green Bay and concluded there was a direct linear relationship between the two. If soluble reactive phosphate concentrations had been negligible in comparison with concentrations of other forms, then the divergence between biologically available phosphorus and soluble reactive phosphate concentrations might have been appreciable.

SOLUBLE REACTIVE PHOSPHATE

Soluble reactive phosphate concentrations in the surface waters of Lake Michigan are generally near detection limits, except very close to shore (Figs. 57 and 58 and Table 29). Biological uptake is important in maintaining these low levels, since primary producers are considered to use dissolved inorganic phosphate most readily. Indeed, one may view soluble reactive phosphate content as that phosphorus which has not yet been taken up by a plant or bacterium.

In eutrophic lakes (Lake Michigan is not considered eutrophic) soluble reactive phosphate concentrations in surface waters have a pronounced seasonal variation. They are low in summer, when biological activity is high, and high in winter, when there is relatively little biological activity. Comparison of Figures 57 and 58 reveals no unequivocal proof of seasonal variation. Nor did Rousar (1973) find clear-cut evidence along a transect from Milwaukee to Ludington, although very low values were noted in August 1970 and September 1971. Concentrations at the Lake County, Illinois, public water supply intake (Howe, 1973--personal communication) tended to be lower in August and September and higher in December and February. Near Two Rivers, Wisconsin, soluble reactive phosphate concentrations were higher (0.005-0.022 mg PO_4^{3-}-P/l) from October to March and lower (0.002-0.003 mg PO_4^{3-}-P/l) from April to September (Limnetics, 1974). Around Oak Creek, at stations which probably were somewhat influenced by discharge of industrial and municipal wastes into the Milwaukee Harbor and directly to the Lake south of the Harbor (*cf.* Beeton and Barker, 1974), soluble reactive phosphate content was low (< 0.05 mg PO_4^{3-}-P/l) in April, June and July of 1973 and high from September through December. The influence of inshore mixing processes cannot be discounted in interpreting data collected at Two Rivers; Lake County, Illinois; and Oak Creek (see Total Phosphorus section below).

Another characteristic of eutrophic lakes is that soluble reactive phosphate content increases markedly below the thermocline, and that this increase intensifies over the period of stratification. Table 30 compares surface- and bottom-water concentrations of soluble reactive phosphate in the summer of 1969. In the majority of samples (16 of 30) there was no difference between surface- and bottom-water content. However, breaking the data down further, one sees that all bottom-water samples taken from less than 20 m showed no difference from surface-water samples; although temperature data were not given, these bottom-water samples were likely in the epilimnion, and thus should resemble surface-water samples. Offshore samples plus samples taken at depths exceeding 20 m were about equally divided, in both the northern and southern basins, between stations that had no difference with depth, and stations with increasing soluble reactive phosphate with depth. Five of six offshore stations in the northern basin showed increasing soluble reactive phosphate with depth; the maximum range between surface- and bottom-water samples was < 0.0005 to 0.0025 mg PO_4^{3-}-P/l.

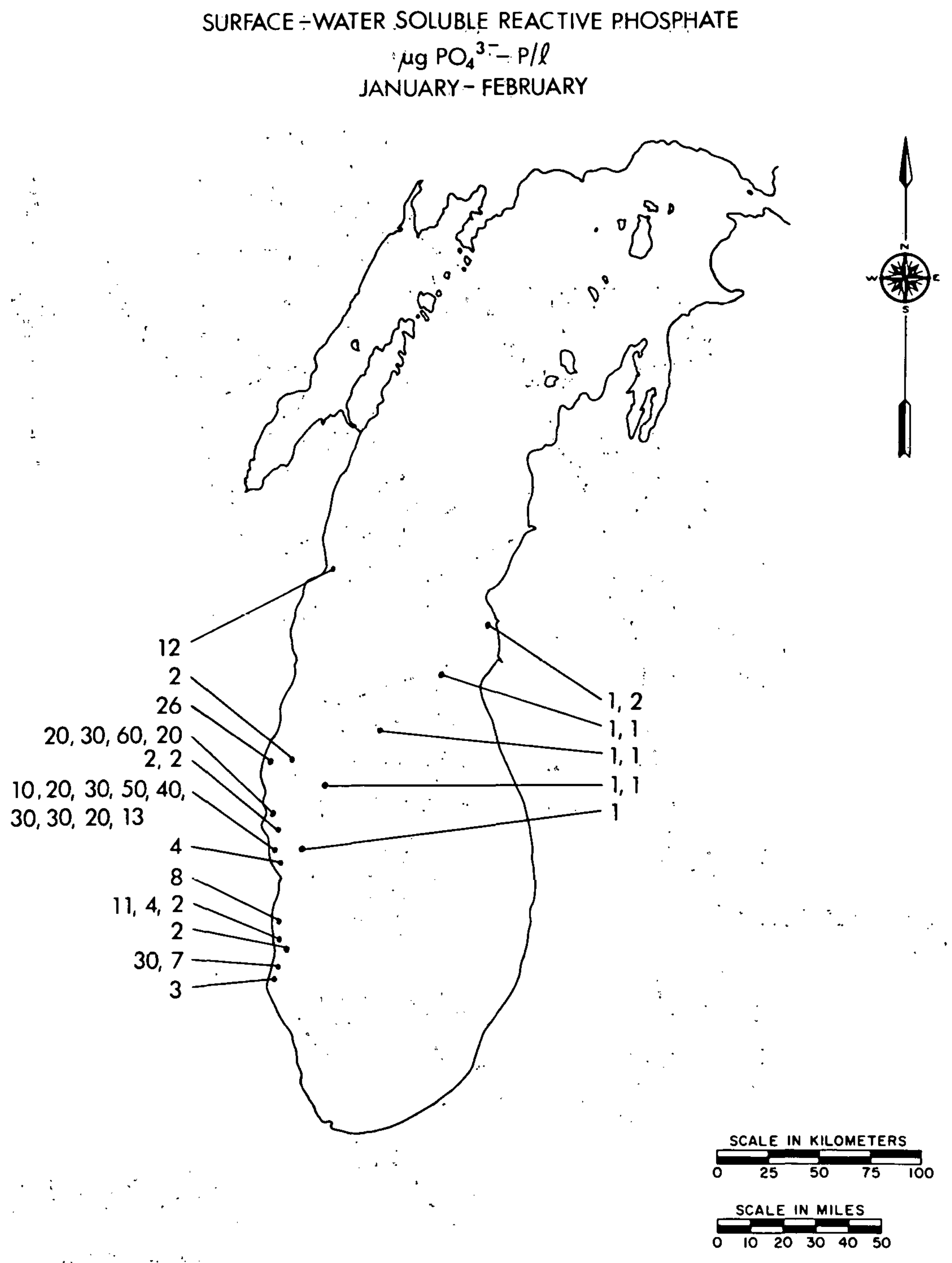


Fig. 57. Surface-Water Soluble Reactive Phosphate Concentrations in January-February over a Period of Fifteen Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 29.

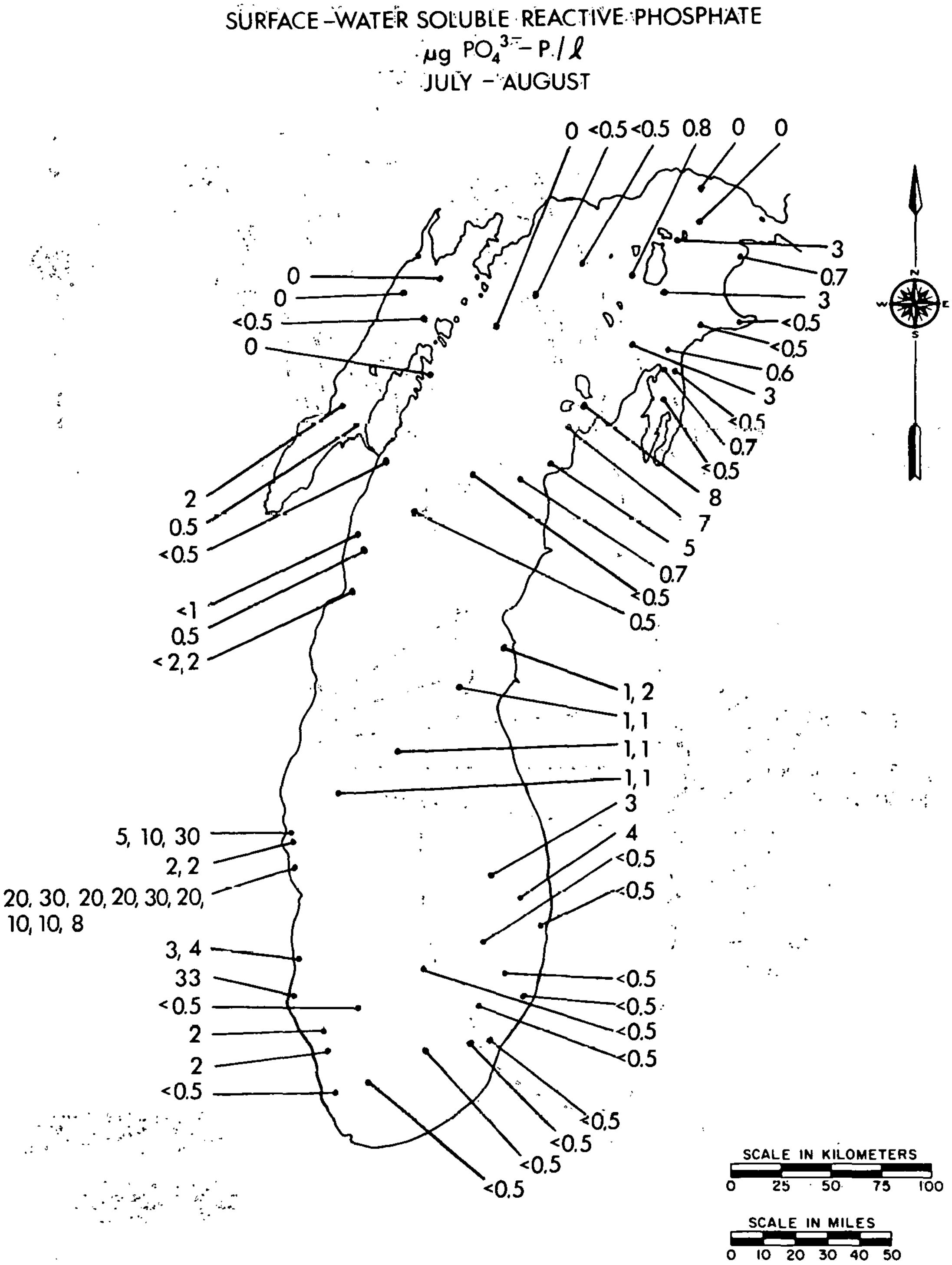


Fig. 58. Surface-Water Soluble Reactive Phosphate Concentrations in July-August over a Period of Fifteen Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 29.

Table 29. Soluble Reactive Phosphate Content in Lake Michigan Water

		Concentration $PO_4{}^{3-}$-P, µg/l		
Sample Description	Dates	Average	Range	Reference
Samples collected ∿weekly from Peter Cooper Corp. intake, Oak Creek, ∿0.75 km (2500 ft) offshore	1961	10	0-30	Wis. Comm. Water Pollut., 1965
	1962	30	10-50	
	1963	20	10-40	
	1964	30	<10-110	
	1965	30	<10-80	Wis. Dep. Nat. Resour., 1969
	1966	20	4-60	
	1967	20	2-60	
	1968	20	<10-<60	
Surface-water (2 m, 5 m, and 10 m) samples collected in northern basin:	1965			Holland, 1969 (from Allen, 1966?)
Inshore		3	2-4	
Offshore		3	2-3	
Samples collected in Indiana Harbor at east breakwall inner light:				Snow, 1974
3 samples	Dec 1965	36	33-59	
51 samples	Jan-Dec 1966	23	3-98	
42 samples	Jan-Dec 1967	96	6-3260	
6 samples	Jan-Dec 1968	24	6-55	
3 samples collected at the Sturgeon Bay entry buoy	18 May-21 Oct 1966	13	8-16	Schraufnagel *et al.*, 1968
Samples collected:	22-24 Jul 1969			Schelske and Callender, 1970
Southern basin				
Surface-water, 7 offshore stations			<0.5-3.1	
Bottom-water, 7 offshore stations			<0.5-7.1	
Surface-water, 9 inshore stations			<0.5-2.5	
Bottom-water, 9 inshore stations			<0.5-5.3	
Northern basin	15-23 Aug 1969			
Surface-water, 6 offshore stations			0-0.8	
Bottom-water, 6 offshore stations			<0.5-2.5	
Northern basin, including Traverse Bay	15-23 Aug 1969			
Surface-water, 15 inshore stations			<0.5-0.9	
Bottom-water, 8 inshore stations			<0.5-2.2	
Northern Green Bay, including the Bays de Noc	15-23 Aug 1969			
Surface-water samples			0-0.8	
Northern Green Bay, including Big Bay de Noc	15-23 Aug 1969			
Bottom-water samples			0-0.7	
Samples collected at a depth of 4 m at 5 stations [2 located 4.8 km (3.0 mi) from shore, 1 midlake, and 2 halfway between midlake and shore] along a line from Milwaukee to Ludington:	May, Jun, Aug, Oct, Nov 1970; Jan 1971			Holland and Beeton, 1972
Average values			1-2[a]	
Samples collected at 8- to 21-day intervals (except 3 Feb-11 Mar) at a depth of 4 m:	27 May 1970-20 Oct 1971			Rousar, 1973
A station 4.8 km (3.0 mi) east of Milwaukee		1.9	N.D.-10.8	
A station 4.8 km (3.0 mi) west of Ludington		1.1	N.D.-4.3	
3 offshore stations--midway and at quarter points between Milwaukee and Ludington				
Average values			1.0-1.2	
Individual values			N.D.-5.0	

Table 29. (contd.)

		Concentration PO_4^{3-}-P, µg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
16 samples collected, surface to bottom, at 6 stations on a line passing east of Manitou Islands from Frankfort to Beaver Island	7 Jul 1970	5.2	1.0-12.0	Schelske and Roth, 1973
Monthly samples collected at intakes:	Jan-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		6	3-10	
Waukegan Generating Station		31	1-59	
North Chicago public water supply		3	1-6	
Monthly samples collected at 3 stations 9.6 km (6 mi) east of Zion:	Jan-Apr 1971			Industrial Bio-Test, 1972b
Surface-water		2	<1-4	
Bottom-water		3	<1-10	
Monthly samples collected at Lake County, Ill., public water intake	Jan 1971-Jun 1973	4	2-9	Howe, 1973
Samples collected (water depth 7.6 m) at a station east of Kewaunee Nuclear Plant:				Industrial Bio-Test, 1972d
Surface	25 May 1971	1	<1-3	
Bottom	25 May 1971	<1[b,c]		
Surface	31 Aug 1971	<1	<1-1	
Bottom	31 Aug 1971	1	1-2	
Surface	16 Nov 1971	<1	<1-1	
Bottom	16 Nov 1971	<1	<1-2	
Monthly averages for samples collected at 10 stations <3 km (10,000 ft) from shore near Point Beach Nuclear Plant	Jun 1971 Jul-Sep 1971	5 <2		Weschler *et al.*, 1972
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun 1971-Apr 1972	39	2-280	Industrial Bio-Test, 1972c
Samples collected in or near Milwaukee Harbor:				Lin and Blum, 1973
<8 km (5 mi) north of main entrance outside breakwater, 3 samples	30 Sep 1971	3.5	2.7-4.8	
In Harbor, 3 samples	5 Oct 1971	81	52-135	
3.0 km (1.9 mi) east of main entrance, 1 sample	5 Oct 1971	4.5		
Surface-water samples collected monthly: 15 stations <8 km (5 mi) from shore, north and south of Milwaukee	Oct-Dec 1971; Jan, Feb, Apr, Jun 1972	2.7	0.5-16.5	Beeton and Barker, 1974
2 stations ∿16 km (10 mi) from shore, one north and one south of Milwaukee		1.5	0.8-2.7	
10 surface-water samples each collected at stations east of Milwaukee:	28 Nov 1972			Beeton and Barker, 1974
0.4 km (0.25 mi) east		4.8		
16 km (10 mi) east		1.6		
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers-- 3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		5	<5-20	
Effluent plume		6	<5-30	
South of plant, 4.8 km (3 mi)		5	<5-20	

Table 29. (contd.)

Sample Description	Dates	Concentration PO_4^{3-}-P, µg/l Average	 Range	Reference
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		14	3-30	
North of plant, 1.6 km (1 mi)		15	3-33	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations)	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		11	3.8-?2.5 [*sic*]	
South of plant, 1.6 km (1 mi)		17	2.5-42.5	

[a] *Nonparticulate phosphorus.*

[b] *Same value for all samples.*

[c] *Limit of detection.*

N.D = Not detected.

Table 30. Comparison of Soluble Reactive Phosphate Concentrations in Surface- and Bottom-Water Samples from 30 Stations*

Sample Location, Dates and Depths	Number of Stations Showing Increase between Surface and Bottom	 No Difference between Surface and Bottom	 Decrease between Surface and Bottom
Southern basin, 22-24 July 1969			
Inshore			
<20 m	0	5	0
>20 m	2	2	0
Offshore	3	3	1
Northern basin, including Traverse Bay, 15-23 August 1969			
Inshore			
<20 m	0	0	0
>20 m	2	5	1
Offshore	5	1	0

* *Summarized from data of Schelske and Callender, 1970.*

Since major sources of phosphorus to Lake Michigan are associated with cultural activities, one expects higher concentrations to be found near shore. Data from Beeton and Barker (1974) confirm this expectation (Fig. 59).

The National Academy of Sciences ... (1973) discussed phosphate in drinking water, but made no recommendation for limiting concentrations (Appendix B, part 1) because of complex interrelations among phosphate concentrations, biological productivity, and resulting odor and filtration problems. The specific objective for protection of aquatic life for the International Great Lakes, set by agreement between the United States of America and Canada (U. S. Treaties, etc., 1972), was that concentrations of phosphorus should be limited to prevent nuisance growths of algae, weeds, or slimes. No limiting concentration was set.

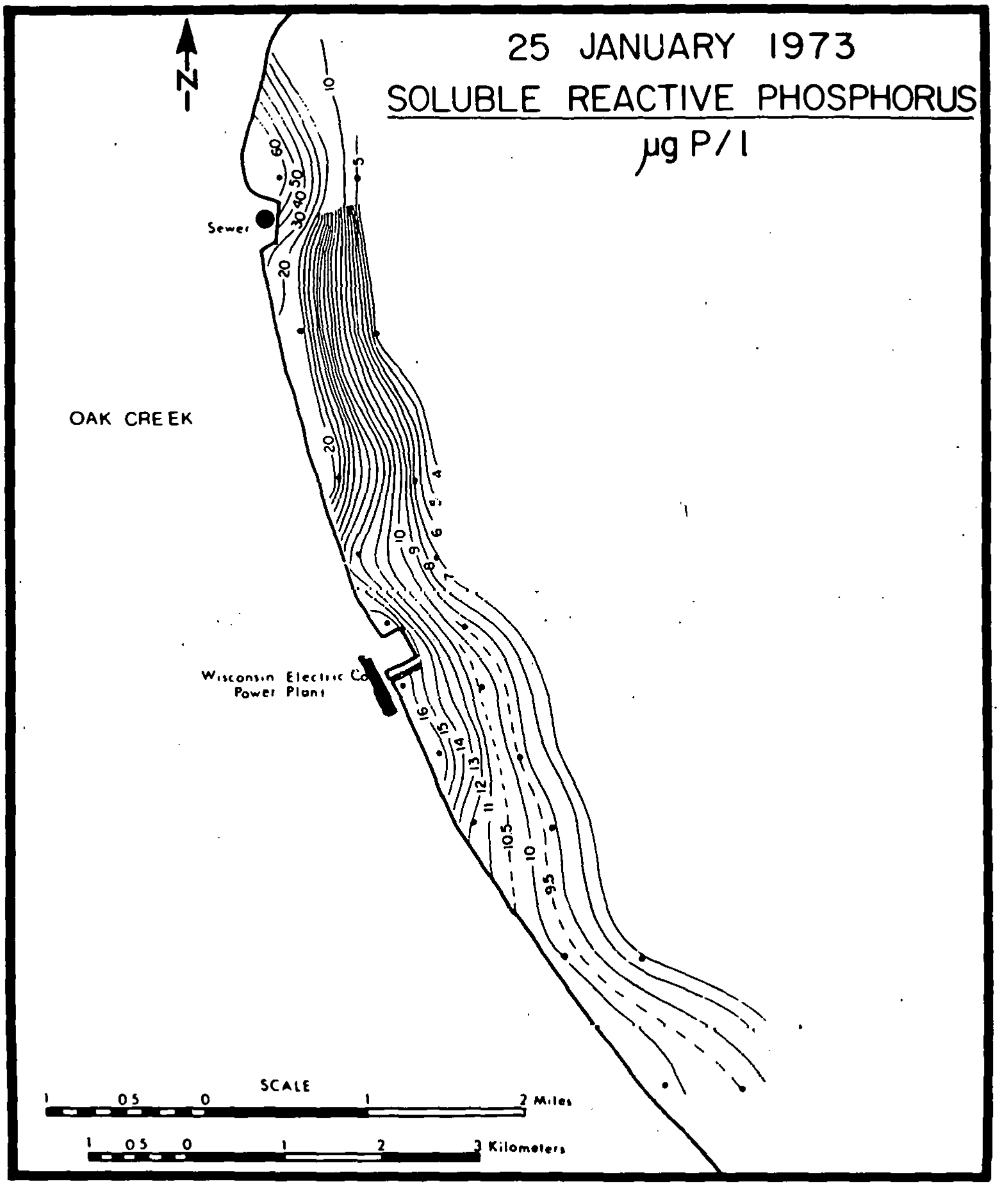


Fig. 59. Distribution of Soluble Reactive Phosphate near Milwaukee. Modified from Beeton and Barker (1974) (with permission, see credits).

TOTAL PHOSPHORUS

Determinations of total phosphorus in Lake Michigan over the past two decades are indicated in Table 31. At several of the inshore stations in Figures 60 and 61 there were notable seasonal variations in total phosphorus. At the Lake County public water supply intake, total phosphorus was low from June through September and highest in December (Howe, 1973--personal communication). Total phosphorus was low in August and September, and high in December and April at the Kenosha and North Chicago water intakes and in the intake canal of the Waukegan Generating Station (Industrial Bio-Test, 1972a). Total phosphorus peaked at 0.019 mg PO_4^{3-}-P/l in November and December at

SURFACE-WATER TOTAL PHOSPHORUS
$\mu g\ PO_4^{3-} - P/\ell$
JANUARY-FEBRUARY

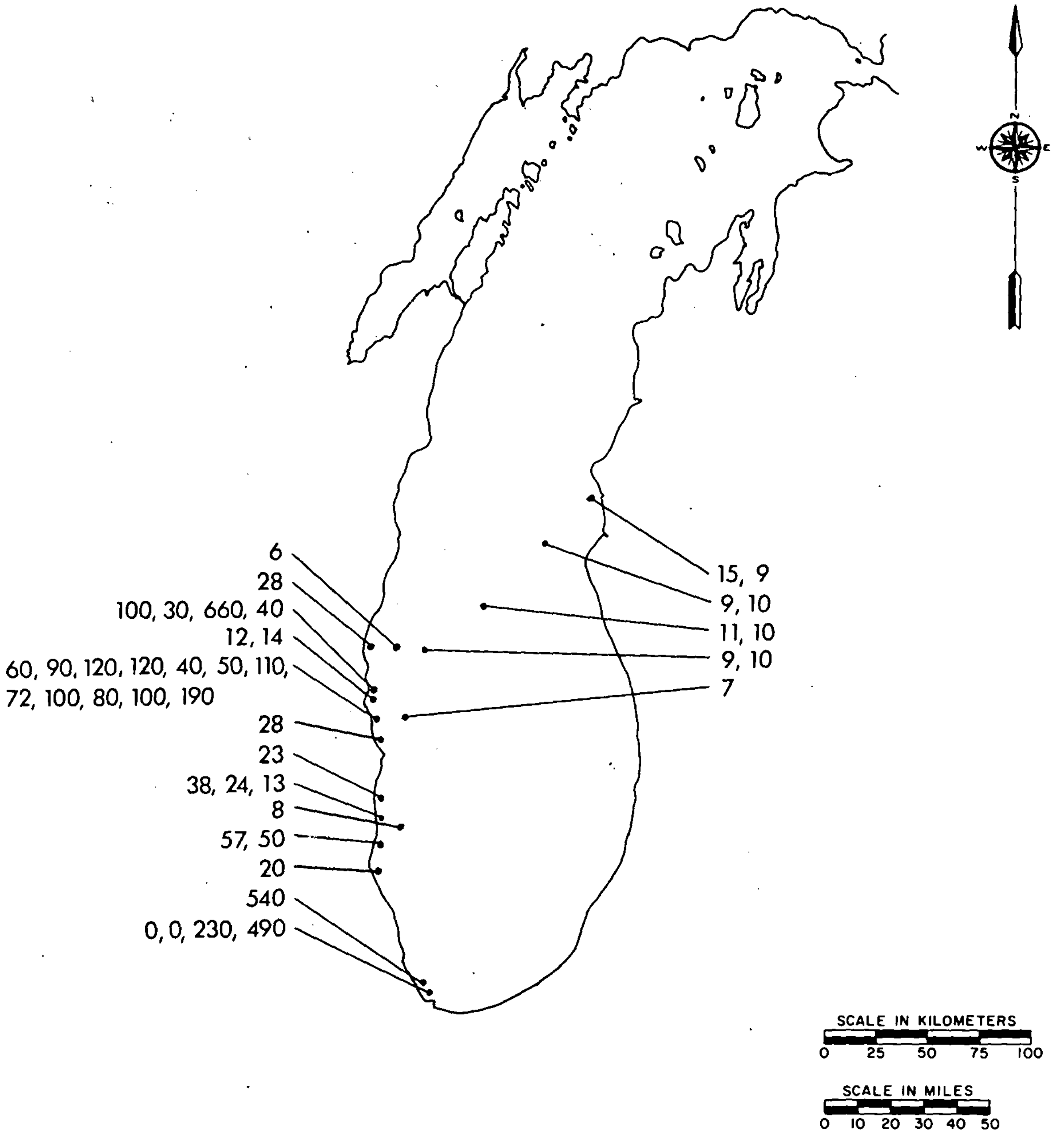


Fig. 60. Surface-Water Total Phosphorus Concentrations in January-February over a Period of Fifteen Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 31.

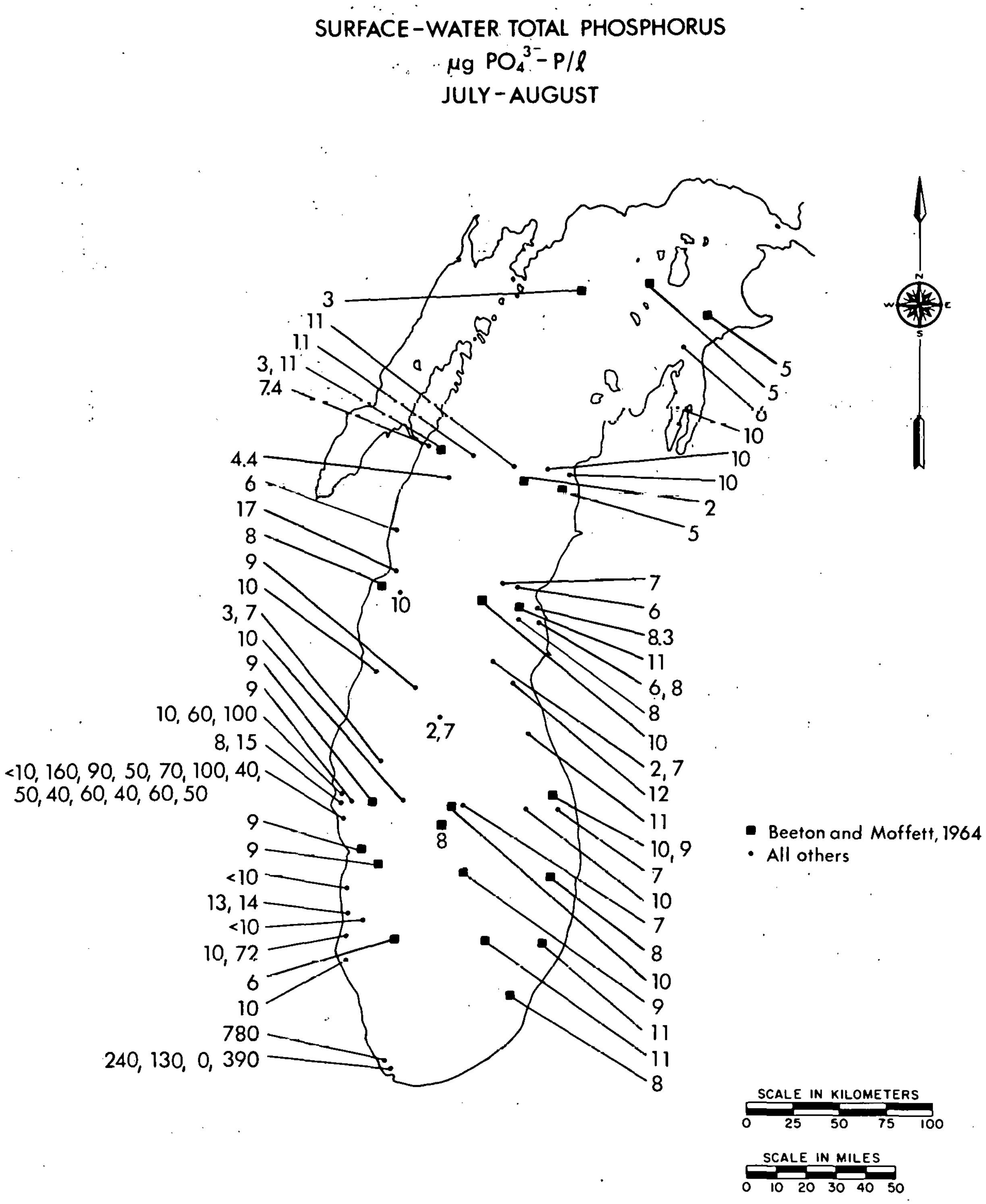


Fig. 61. Surface-Water Total Phosphorus Concentrations in July-August over a Period of Twenty Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 31.

Table 31. Total Phosphorus Content in Lake Michigan Water

Sample Description	Dates	Concentration PO_4^{3-}-P, µg/l Average	 Range	Reference
Samples collected (surface, ≤15 m; bottom, ≥30 m):				Beeton and Moffett, 1964
Southern basin and divide area				
Surface-water, offshore	9 May-12 Nov 1954	13.7	3.8-98.6	
Bottom-water, offshore	9 May-12 Nov 1954	14.0	4.2->100	
Surface-water, inshore	11 May-14 Dec 1954	11.1	2.9-28.0	
Bottom-water, inshore	11 May-14 Dec 1954	11.5	4.0-56.0	
5 samples collected, surface to bottom (73 m), at a station ∿12.9 km (8 mi) west of Grand Haven	9 Mar 1955	15	10.7-26.4	Beeton and Moffett, 1964
Samples collected (surface, ≤15 m; bottom, ≥30 m):				Beeton and Moffett, 1964
Southern basin				
3 inshore stations along east side	29 Apr-23 Nov 1960			
Surface-water		12	4-32	
Bottom-water		14	3-51	
1 central station sampled 4 times	27 May-26 Sep 1960			
Surface-water		13	6-32	
Bottom-water		19	8-40	
Northern basin				
2 offshore stations	19 May-5 Nov 1961			
Surface-water		5	1-11	
Bottom-water		6	1-11	
5 inshore stations	17 May-23 Nov 1961			
Surface-water		6	1-12	
Bottom-water		6	0-15	
Samples collected ∿monthly from Peter Cooper Corp. intake, Oak Creek, ∿0.75 km (2500 ft) offshore	1961	90	<10-160	Wis. Comm. Water Pollut., 1965
	1962	120	20-400	
	1963	80	60-100	
	1964	90	40-160	
	1965	90	40-160	Wis. Dep. Nat. Resour., 1969
	1966	80	30-140	
	1967	50	30-94	
	1968	70	20-160	
	1969	90	<20-320	Wis. Dep. Nat. Resour., 1973
	1970	110	30-420	
	1971	80	20-370	
	1972	80	20-500	
Whole Lake:	1962-63			USDOI, 1968
388 offshore samples		6[a]	N.D.-46[a]	
1382 inshore samples		13[a]	N.D.-163[a]	
Samples collected:	1962-63			
Indiana Harbor, 15 samples		16[a]	6-39[a]	USDOI, 1968
Adjacent to Indiana Harbor, 216 samples		10[a]	0-40[a]	Risley and Fuller, 1966
Samples collected:	1962-63			
Calumet Harbor, 15 samples		16[a]	3-46[a]	USDOI, 1968
Adjacent to Calumet Harbor, 15 samples		10[a]	0-30[a]	Risley and Fuller, 1966
Samples collected:	1962-63			USDOI, 1968
Chicago Harbor, 14 samples		13[a]	3-49[a]	
Racine Harbor, unspecified no. of samples		22[a]	3-33[a]	
Samples collected:	Oct 1962, Jun 1963			USDOI, 1968
Milwaukee Harbor, 36 samples		144[a]	N.D.-457[a]	
Adjacent to Milwaukee Harbor, 67 samples		23[a]	N.D.-228[a]	

Table 31. (contd.)

Sample Description	Dates	Concentration PO_4^{3-}-P, µg/l Average	Range	Reference
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City		20	0-190	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo		10	0-90	
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor		10	0-50	
On a line roughly between Sheboygan and Little Sable Point		10	0-30	
145 samples collected throughout Green Bay	26 Jun-17 Jul 1963	23[a]	3-196[a]	USDOI, 1968
Offshore samples collected, surface to bottom, at 3 stations [midlake and either end of a line ∿16 km (10 mi) from shore] along lines connecting:	Apr-Nov 1964			Powers and Ayers, 1967
Benton Harbor to Chicago and South Haven to Waukegan		5.4	0-47.7	
Holland to Racine and Ludington to Sheboygan		6.4	0-49.0	
Samples collected:	22-28 Jul 1964			USDOI, 1968
Traverse Bay, 59 samples		10[a]	3-59[a]	
Adjacent to Traverse Bay, 28 samples		6[a]	3-23[a]	
Samples collected:	1965			Risley and Fuller, 1966
Indiana Harbor, 17 samples		30[a]	10-60[a]	
Calumet Harbor, 31 samples		30[a]	10-90[a]	
Surface-water (2 m, 5 m, and 10 m) samples collected in northern basin:	1965			Holland, 1969 (from Allen, 1966?)
Inshore		8	6-10	
Offshore		6	6-7	
Samples collected in Indiana Harbor at east breakwall inner light:				Snow, 1974
3 samples	Dec 1965	62	26-120	
51 samples	Jan-Dec 1966	65	26-456	
42 samples	Jan-Dec 1967	244	33-8150	
37 samples	Jan-Dec 1968	136	25-491	
25 samples	Jan-Jun 1969	230	60-2190	
Samples collected ∿biweekly at depths of 2 m, 5 m, and 10 m near:	Apr-Nov 1965			Allen, 1973
Ludington				
2 inshore stations		9.3	4.5-16.3	
2 offshore stations		6.5	3.8-13.0	
Sturgeon Bay				
2 inshore stations		6.2	3.4-13.8	
2 offshore stations		6.0	2.9-8.6	
Green Bay				
3 stations on a line from Little Sturgeon Bay to the southern edge of Door County		33.7	13.0-61.5	
Samples collected at Chicago South Water Filtration Plant	1966	9		Vaughn and Reed, 1973
	1967	20		
	1968	26		
	1969	18		
	1970	22		
	1971	25		

Table 31. (contd.)

		Concentration PO_4^{3-}-P, µg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
3 samples collected at Sturgeon Bay entry buoy	18 May-21 Oct 1966	23	16-32	Schraufnagel *et al.*, 1968
Samples collected at Whiting water plant intake, 517 m (1696 ft) from shore	1967	180		Snow, 1974
	1968	90		
	1969	50		
	1970	590		
Daily samples collected at Chicago South Water Filtration Plant	1968	23[a]		Ill. Sanit. Water Board, 1969
Annual averages at water filtration plants near Chicago:				
11 plants	1968	99	62-176	Ill. Sanit. Water Board, 1969
5 plants	1969	97	26-235	Ill. Sanit. Water Board, 1970
Monthly samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	Nov 1969-Sep 1970	60	0-230	USGS, 1972
	Oct 1970-Sep 1971	150	0-1600	USGS, 1973
	Oct 1971-Sep 1972	110	20-660	USGS, 1974a
	Oct 1972-Jun 1973	73	30-200	USGS, 1974b
Samples collected at Hammond water plant intake	1970	950	320-3600	Snow, 1974
Samples collected at a depth of 4 m:	May, Jun, Aug, Oct, Nov 1970; Jan 1971			Holland and Beeton, 1972
2 inshore stations 4.8 km (3.0 mi) from shore				
Near Ludington		9		
Near Milwaukee		14		
3 offshore stations--midlake and halfway between midlake and Milwaukee or Ludington				
Average values			8-9	
Samples collected at 8- to 21-day intervals (except 3 Feb-11 Mar) at a depth of 4 m:	27 May 1970-20 Oct 1971			Rousar, 1973
A station 4.8 km (3.0 mi) east of Milwaukee		15.2	8.2-32.9	
A station 4.8 km (3.0 mi) west of Ludington		8.9	4.7-14.7	
3 offshore stations--midway and at quarter points between Milwaukee and Ludington				
Average values			8.0-8.9	
Individual values			2.4-20.2	
Monthly averages for samples collected offshore from northern Chicago:				Lue-Hing, 1973
6 stations 0.30 km (1000 ft) offshore	Jun-Nov 1970, May-Oct 1971	160	30-820	
7 stations 0.61-0.91 km (2000-3000 ft) offshore	Jun-Dec 1970, May-Oct 1971	40	10-60	
4 stations 1.37-1.83 km (4500-6000 ft) offshore	Jun-Dec 1970, May-Oct 1971	160	10-1110	
Monthly samples collected at intakes:	Aug 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		40	<10-110	
Waukegan Generating Station		70	<10-150	
North Chicago public water supply		20	<10-40	
Monthly samples collected at 3 stations 9.6 km (6 mi) east of Zion:	Aug 1970-Apr 1971			Industrial Bio-Test, 1972b
Surface-water		10	<10-30	
Bottom-water		10	0-30	

Table 31. (contd.)

		Concentration PO_4^{3-}-P, μg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Monthly samples collected at Lake County, Ill., public water intake	Sep 1970-Jun 1973	28	12-48	Howe, 1973
Monthly averages for samples collected at a station 3.0 km (10,000 ft) offshore from Zion	Dec 1970, May-Oct 1971	120	20-610	Lue-Hing, 1973
Samples collected (water depth 7.6 m) at a station east of Kewaunee Nuclear Plant:				Industrial Bio-Test, 1972d
Surface	25 May 1971	12	11-12	
Bottom	25 May 1971	13	12-14	
Surface	31 Aug 1971	5	4-6	
Bottom	31 Aug 1971	8	6-9	
Surface	16 Nov 1971	26	23-29	
Bottom	16 Nov 1971	23	20-26	
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun 1971-Apr 1972	35	11-550	Industrial Bio-Test, 1972c
Surface-water samples collected in northern basin and divide area:	8-14 Jul 1971			Rousar and Beeton, 1973
9 inshore stations		9.8	7.2-11.5	
8 offshore stations		9.4	7.0-11.2	
Samples collected in or near Milwaukee Harbor:				Lin and Blum, 1973
<8 km (5 mi) north of main entrance outside breakwater, 3 samples	30 Sep 1971	11	3-28	
In Harbor, 3 samples	5 Oct 1971	97	64-163	
3.0 km (1.9 mi) east of main entrance, 1 sample	5 Oct 1971	5		
Surface-water samples collected: 15 stations <8 km (5 mi) from shore, north and south of Milwaukee	Oct 1971-Jun 1972 (except Mar, May)	23.1	2.7-121	Beeton and Barker, 1974
2 stations ∿16 km (10 mi) from shore, one north and one south of Milwaukee		7.7	2.7-18.7	
10 surface-water samples each collected at stations east of Milwaukee:	28 Nov 1972			Beeton and Barker, 1974
0.4 km (0.25 mi) east		16.8		
16 km (10 mi) east		7.8		
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		86		
17 km (10.6 mi) offshore		5.5		
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		37	10-150	
Effluent plume		39	15-120	
South of plant, 4.8 km (3 mi)		34	5-75	

Table 31. (contd.)

Sample Description	Dates	Concentration PO_4^{3-}-P, µg/l Average	Range	Reference
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		70	20-120	
North of plant, 1.6 km (1 mi)		77	30-140	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		74	40-100	
South of plant, 1.6 km (1 mi)		82	50-110	

[a] *Total soluble phosphorus.*

N.D. = not detected.

USDOI = U. S. Department of the Interior; USGS = U. S. Geological Survey.

three stations 9.6 km (6 mi) east of Zion, Illinois, and was lowest in February, April and August (Industrial Bio-Test, 1972b). At inshore stations near Two Rivers, Wisconsin, total phosphorus was high in January and February, and low from May through October (Limnetics, 1974). At Oak Creek, Wisconsin, low values were recorded from June through August, and high ones from September through November (Limnetics, 1974). At 17 stations near Milwaukee, Beeton and Barker (1974) found total phosphorus concentrations were low in June and October and high in April. Allen (1973) found only slight seasonal (April-November 1965) variations in surface-water total phosphorus concentrations at stations inshore and offshore from Sturgeon Bay and offshore from Ludington. Inshore near Ludington, total phosphorus concentrations trended generally downward from May to October. In contrast, Rousar (1973) found no seasonal changes in total phosphorus content at five stations on a transect between Milwaukee and Ludington.

Seasonal changes at the inshore stations mentioned in the paragraph above may be due mainly to physical phenomena. Snow (1974) presented raw data for total phosphorus concentrations, turbidity and wind speed at the Chicago South Water Filtration Plant from 1 November through 31 December 1973. These data are plotted in Figure 62. High values for total phosphorus concentrations are paralleled by high turbidities, and low phosphorus content corresponds with low turbidity. Further, high turbidities correlate with high winds and the waves they generate. Thus much of the seasonal variation of total phosphorus concentrations at inshore stations may be due to wind stirring of the water and the sediments, and to large inputs of particulate phosphorus during spring runoff, rather than to any seasonal variation in inputs of phosphorus from domestic, municipal, and industrial waste effluents.

The only systematic study of variations of total phosphorus content with depth and time seems to have been conducted by Beeton and Moffett (1964). Figure 63 illustrates surface- and bottom-water (70 m) samples taken at one station about 12.8 km (8 mi) west of Grand Haven from 11 May to 14 December 1954. No distinct difference in trends between top and bottom is evident. There is cause to question the reliability of the data, considering large inexplicable jumps (25, 27, 28 June and 18, 19 November) which were not reflected in any of the other parameters these researchers measured that might

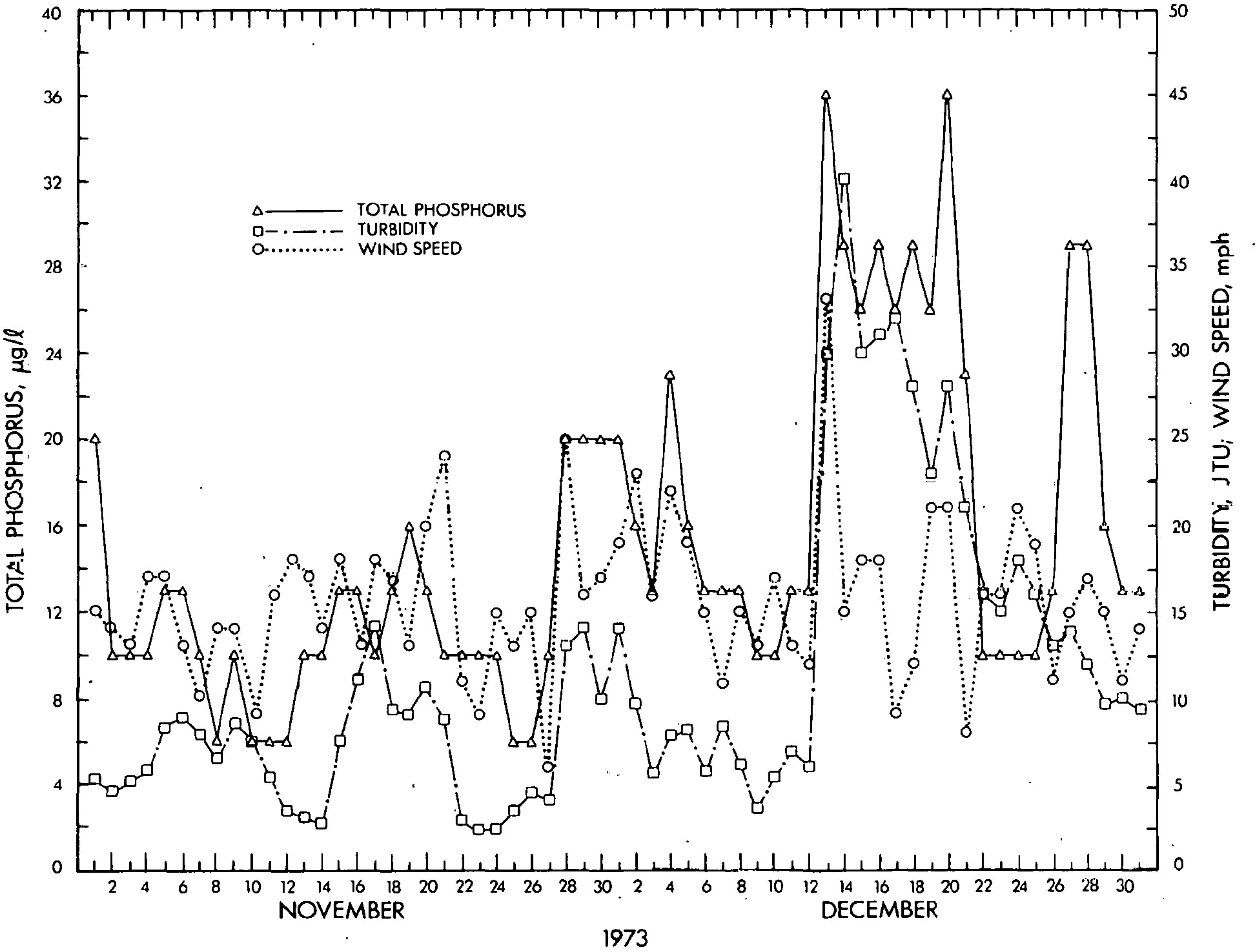


Fig. 62. Daily Variation of Total Phosphorus Content, Turbidity, and Wind Speed at Chicago South Water Filtration Plant. Data from Snow (1974).

indicate upwelling or downwelling (temperature, dissolved oxygen, pH, calcium, silica) or other sudden injections of chemicals (*e.g.* dissolved oxygen, pH, calcium, magnesium, sodium, specific conductance) to that area of the Lake. The behavior of total phosphorus concentrations with depth over an annual cycle remains unclear.

Since human activities provide major quantities of phosphorus to Lake Michigan, one expects higher concentrations to be found in harbors and near cities (Table 31). Data of Beeton and Barker (1974) demonstrate the dilution of high concentrations of phosphorus with increasing distance from the Milwaukee area (Fig. 64).

Strict standards for the protection of aquatic life (Appendix B, part 2) have been set by the Illinois Pollution Control Board (1974) and the Indiana Stream Pollution Control Board (1973). However, values in Table 31 indicate that Illinois standards are almost always exceeded and Indiana standards are frequently exceeded in the inshore water of the southwestern part of the Lake (*cf.* Snow, 1974).

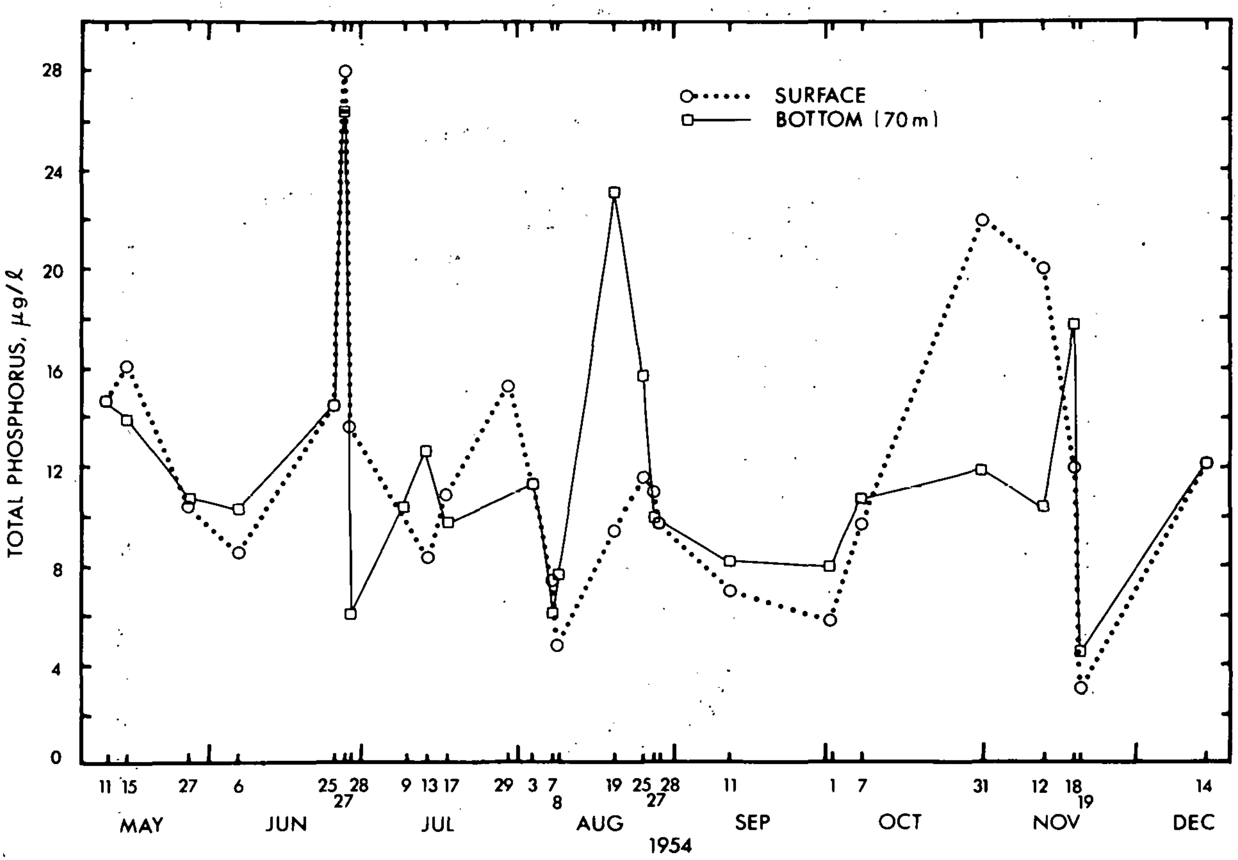


Fig. 63. Variation in Total Phosphorus Concentration at a Station 12.8 km (8 mi) West of Grand Haven. Data from Beeton and Moffett (1964).

CYCLING

Considering the amount of discussion presented above, it may seem contradictory to state that little is known about phosphorus in Lake Michigan water. Figures 55 and 56 illustrated paths which phosphorus can take in the Lake, from one organism to another and from one chemical form to another. Each of the arrows in those figures can be characterized by some kind of rate constant, which varies with temperature, from organism to organism, and from one chemical form to another (*e.g.* amorphous *vs.* crystalline). Knowledge of the values of these rate constants is lacking in some instances and inadequate in others.

Phosphorus reportedly limits primary productivity in Lake Michigan (Schelske and Stoermer, 1972; Thomas *et al.*, 1972). Yet we do not know to what extent phosphorus is limiting. The concentration of phosphorus is not nearly so important as the rate at which it is recycled into and out of biomass. As long as each organism has adequate phosphorus at crucial periods of its life (growth, reproduction), the concentration in the water at any given time is of less importance.

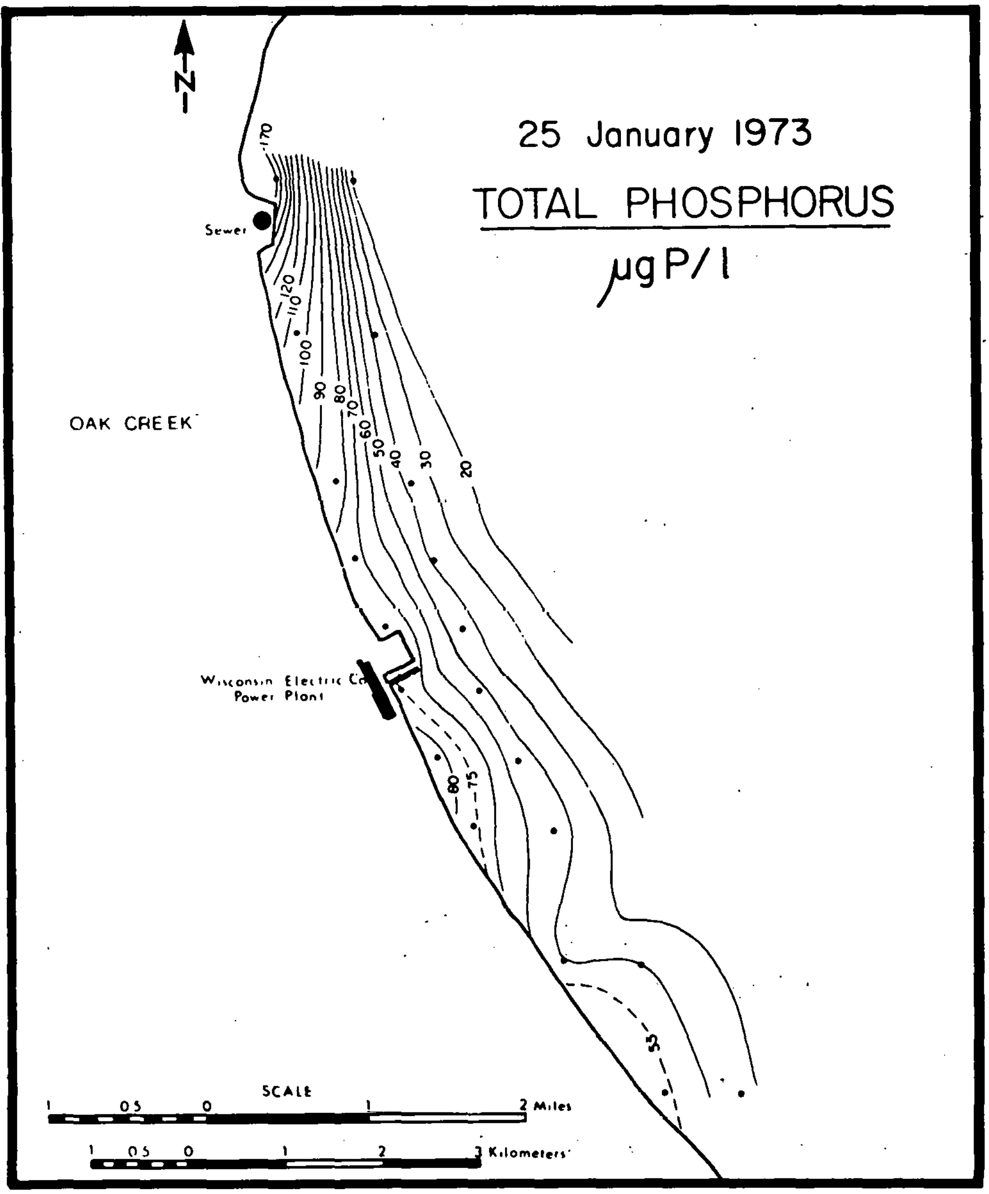


Fig. 64. Distribution of Total Phosphorus near Milwaukee. Modified from Beeton and Barker (1974) (with permission, see credits).

SEDIMENTS

Only the Illinois State Geological Survey (Schleicher and Kuhn, 1970; Shimp *et al.*, 1970) has investigated the phosphorus content of Lake Michigan sediments. Since the Survey reported total phosphorus only, a general description of phosphorus in Great Lakes sediments, based on work by Williams and Mayer (1972), will be presented prior to discussion of Lake Michigan data.

Phosphorus occurs in a number of chemical forms in lake sediments. Apatite and its various forms are the most common phosphate minerals in sedimentary environments. Their presence may be due to any or all of three factors: (*i*) runoff and erosion from the surrounding watershed, removing apatite to the lake; (*ii*) formation of apatite within the water (unlikely); and (*iii*) formation within the interstitial water of the sediment.

Organic phosphorus is a second important form of phosphorus in sediments. Organic phosphorus is derived from land runoff, remains of organisms that died in the lake, and sorption of dissolved organic phosphorus to particulates (*e.g.* clay minerals and metal hydroxides).

The third major form of phosphorus in Great Lakes sediments is orthophosphate, which is bound to non-crystalline materials that resemble amorphous iron oxides and hydroxides.

Except for the surficial sediment interval, Williams and Mayer (1972) found that total phosphorus content was relatively constant in the first two meters of a sediment core from central Lake Ontario. Total organic phosphorus decreased gradually with depth, until it became constant at a depth that corresponded roughly with the time of the last glacial ablation. In contrast, apatite-phosphorus increased with depth in the core. Total sorbed phosphorus, which is similar to if not the same as phosphorus associated with hydrated iron oxides, tended to decrease with increasing depth, but with less regularity than apatite-phosphorus.

The decline of organic phosphorus with depth in Lake Ontario sediments was attributed to processes that broke down organic molecules and released inorganic phosphate to interstitial water. Decreases of sorbed phosphorus with depth were thought to be caused by conversion of sorbed phosphorus to other compounds, probably with release of phosphate to interstitial water. With this increase of dissolved phosphorus in the interstitial waters, apatite could then form, resulting in a reduction in the concentration of dissolved interstitial phosphorus. These processes, plus diffusion of phosphorus within the interstitial water, contributed to the variations of phosphorus in solution in the interstitial water and the phosphorus associated with particulate matter.

No analyses reporting the forms in which phosphorus occurs in Lake Michigan sediments are available. Callender (1969) found that not all of the analyzed calcium in the sediments is combined in calcite or dolomite; and he has speculated that the excess calcium may be present in combination with phosphate as the X-ray amorphous mineral collophane (*cf.* Table 27).

Schleicher and Kuhn (1970) measured total phosphorus in sediment samples from Lake Michigan. All but two stations were located in the southern basin. Surficial sediment (< 5 cm) concentrations are plotted in Figure 65. In these surficial sediments total phosphorus content correlated fairly well with organic carbon content and iron concentrations. No trends with distance from shore, proximity to cities, or geologic formation were obvious.

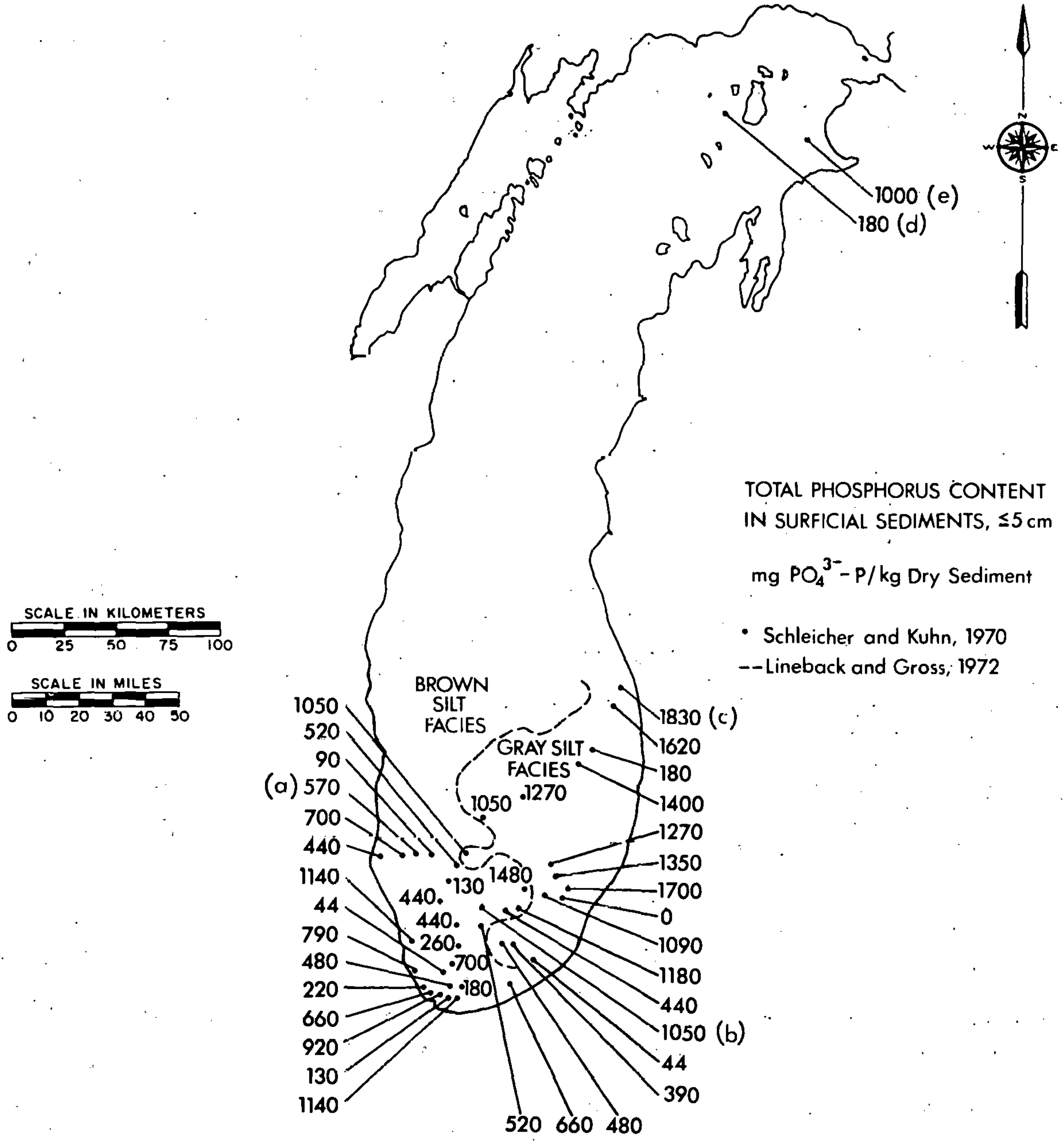


Fig. 65. Total Phosphorus Content in Surficial Sediments of Lake Michigan. Stations (a)-(e) are detailed in Figure 66. Data from Schleicher and Kuhn (1970). Boundary of brown and gray silt facies of the Waukegan member from Lineback and Gross (1972).

Schleicher and Kuhn also measured phosphorus content at various intervals in sediment cores. Data from five cores are plotted in Figure 66; locations of the cores are indicated in Figure 65 (a-e). In general, phosphorus content is higher in the surficial layer than at greater depths in the core. This observation cannot be attributed unequivocally to increased inputs of phosphorus. As Williams and Mayer (1972) noted,

> *"It is difficult to relate higher total P values at the top of [a] core to increased quantities of phosphorus . . . in the overlying waters in recent years. Diagenetic processes may account for variation in total P in a sediment column . . . ."*

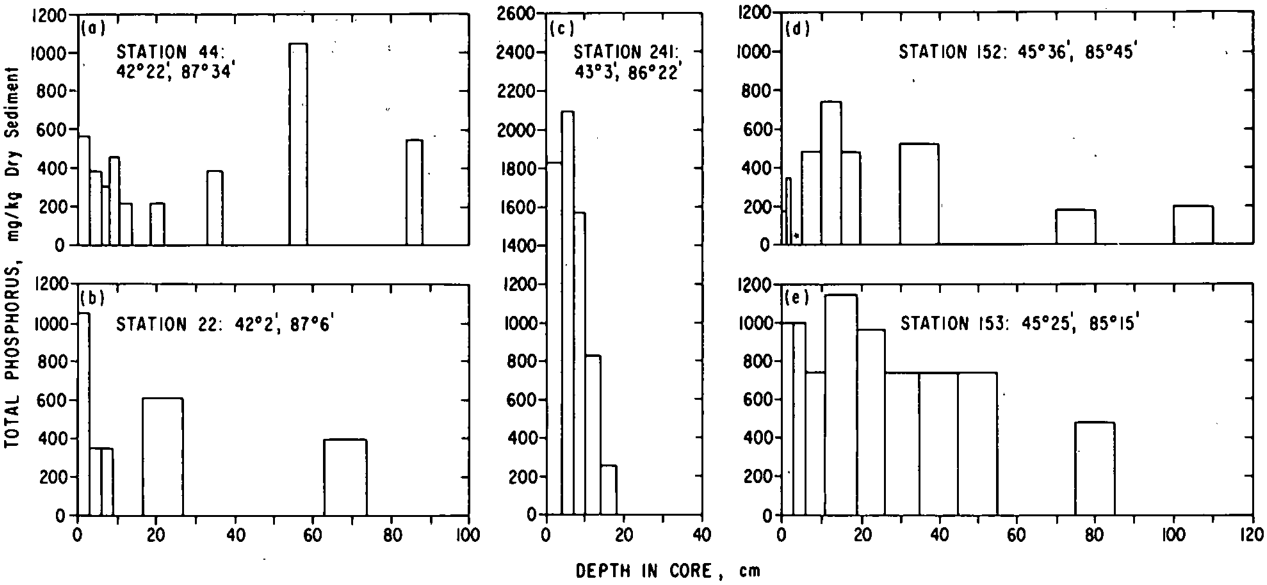


Fig. 66. Total Phosphorus Content in Five Sediment Cores from Southern Lake Michigan. Values converted from P_2O_5. (d) *2-5 cm = 0. Data from Schleicher and Kuhn (1970).

That is, normal aging processes (*i.e.* diagenesis) in the sediment naturally cause phosphorus concentrations to be higher at the surface. As discussed above, decomposition of organic phosphorus-containing compounds can release inorganic phosphate to the interstitial waters. Sorbed phosphorus may be released to the interstitial water when ferric hydroxides are reduced to ferrous ions under anoxic conditions (*cf.* Mortimer, 1971). Phosphorus released to interstitial water at depth within a sediment column can diffuse upward along the concentration gradient of decreasing phosphorus concentrations in the interstitial water. This interstitial phosphate can then be trapped at the sediment surface by the oxidizing conditions which convert ferrous iron to ferric hydroxides. These solid hydroxides then sorb phosphate. Without careful study, one cannot discern what portion of the enhanced phosphorus concentrations at the sediment surface is due to these natural reactions, and what portion is due to increased inputs resulting from human activities. Thus the sedimentary phosphorus profiles reported by Schleicher and Kuhn (1970) may be due entirely to natural processes.

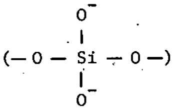
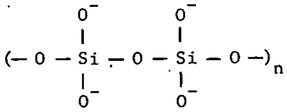
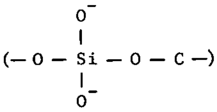
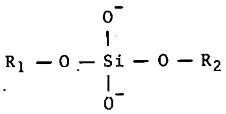
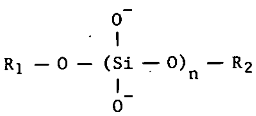
SILICON

The silicon requirement of certain freshwater organisms, including diatoms and siliceous sponges, is well known. In diatoms, silicon is a constituent of the frustules, or cell walls. Silicon is found in the spicules that make up the "skeleton" of a sponge.

FORMS OF SILICON

Dissolved forms of silicon which may be quantitatively important in Lake Michigan water are listed in Table 32. Inorganic orthosilicates, which are derived from orthosilicic acid (H_4SiO_4), are the simplest forms. The exact form of orthosilicate found in water is pH-dependent. Figure 67 illustrates that H_4SiO_4 would be the dominant form of orthosilicate in Lake Michigan; $H_3SiO_4^-$ constitutes only 10% of the total orthosilicate at pH 8.5, and 26% at pH 9.0. Standard methods (APHA *et al.*, 1971) for determining silicon in natural waters likely determine orthosilicate plus an unknown proportion of other chemical forms of silicon (*e.g.* silicon polymers).

Table 32. Dissolved Silicon Forms of Possible Significance in Lake Michigan

Name and Type of Bonding		*Representative Compounds or Series*
Orthosilicate	 $(-O-\overset{O^-}{\underset{O^-}{Si}}-O-)$	H_4SiO_4 (also written $SiO_2\cdot 2H_2O$); $H_3SiO_4^-$, $H_2SiO_4^{2-}$
Inorganic silicon polymers	 $(-O-\overset{O^-}{\underset{O^-}{Si}}-O-\overset{O^-}{\underset{O^-}{Si}}-O-)_n$	Polysilicic acids
Organic silicon polymers	 $(-O-\overset{O^-}{\underset{O^-}{Si}}-O-C-)$	Mucopolysaccharides (Schwarz, 1974)
	 $R_1-O-\overset{O^-}{\underset{O^-}{Si}}-O-R_2$	
	 $R_1-O-(\overset{O^-}{\underset{O^-}{Si}}-O)_n-R_2$	

R_1, R_2, etc. indicates an alkyl radical group.

Analyses for inorganic silicon polymers are seldom performed. Dissolved unreactive silicon in natural waters (Burton *et al.*, 1970; Philbert, 1973) is often assumed to be some inorganic (or perhaps organic) polymeric form of silicon, but little effort has been expended to investigate this question in freshwater systems.

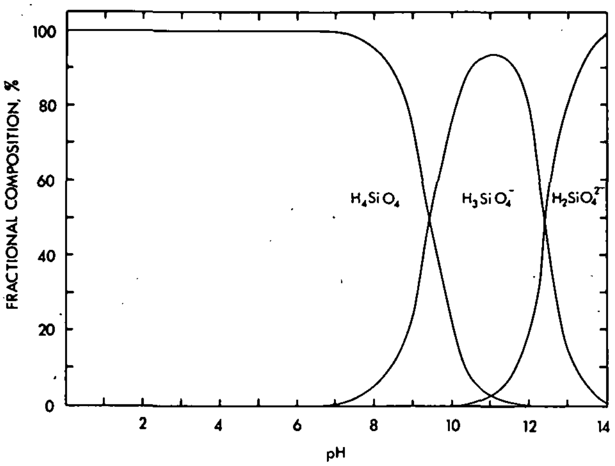


Fig. 67.

Variation in Fractional Composition of Orthosilicate Species with pH.

Table 33 lists particulate forms of silicon which may be quantitatively important in Lake Michigan. Soil and rock mineral phases, which are fairly well defined chemically, are present because of runoff from the surrounding watershed and perhaps by weathering reactions within the Lake itself. Mixed phases (*cf.* Table 33) may form within the Lake, or they may also be derived from the land. There are various origins of amorphous and colloidal silica. For example, diatoms deposit H_4SiO_4 (Lewin, 1962) in their frustules as amorphous silica. Dissolution of silicate minerals may lead subsequently to the formation of colloidal and/or amorphous silica (Krauskopf, 1967). Supersaturated solutions of silica result in the slow formation of colloidal silica,

Table 33. Particulate Silicon Forms of Possible Significance in Lake Michigan

Form	*Representative Compounds or Substances*
Colloidal Silica	Silica dispersed in particles of colloidal dimensions
Amorphous Silica	Any form of SiO_2 lacking crystal structure, variously written as H_4SiO_4, $(SiO_2)_n$, $SiO_2 \cdot nH_2O$, $(SiO_2 \cdot 2H_2O)_n$. *e.g.*, Diatom frustules, detritus resulting from the death of diatoms
Diatom Frustules	Amorphous silica
Soil and Rock Mineral Phases	
Clay minerals	
kaolinite	$\sim Al_4Si_4O_{10}(OH)_8$
chlorite	$\sim (Mg,Fe)_6(Si,Al)_8O_{20}(OH)_4 \cdot (Mg,Al)_6(OH)_{12}$
montmorillonite	$\sim Al_4Si_8O_{20}(OH)_4 \cdot nH_2O$
illite	$\sim K_{0-2}Al_4(Si_{8-6}Al_{0-2})O_{20}(OH)_4$
Quartz	Crystalline SiO_2
Feldspars	
potassium feldspar (orthoclase)	$KAlSi_3O_8$
albite	$NaAlSi_3O_8$
anorthite	$CaAl_2Si_2O_8$
Mixed Phases	
Metal ions sorbed to clay minerals	
Iron and aluminum oxides sorbed to amorphous silica	
Silicic acid sorbed to iron, manganese, and aluminum oxides/hydroxides	

but these particles are unstable for periods longer than a few days or weeks (Krauskopf, 1956). In Lake Michigan water supersaturation is not found, but it may occur in the interstitial water of the sediments.

SOURCES OF SILICON

Silicon is the second-most abundant element in the earth, exceeded only by oxygen (Krauskopf, 1967). Sources of silicon to Lake Michigan are largely natural and are derived for the most part from the hydrolysis of silicate minerals in the watershed. Upchurch (1972) estimated that annual stream loads of SiO_2 to Lake Michigan are about 21 × 10^7 kg (Table 34). Winchester and Nifong (1971) presented an estimate similar to that of Upchurch. A calculation by Klein (1975) was about 20 times higher than the first two estimates, but includes dissolved plus suspended silica.

Klein (1975) estimated that aerosol inputs (Table 34) of silicon to Lake Michigan are only 2% of soil inputs. Further field work may help resolve the quantitative importance of sources of silicon.

Table 34. Annual Inputs of Silica to Lake Michigan

Annual Input of SiO_2, 10^7 kg/yr	*Reference*
Stream Input	
9.4[a]	Winchester and Nifong, 1971
21[a]	Upchurch, 1972
493[b]	Klein, 1975
Aerosol Input	
1.3[c]	Winchester and Nifong, 1971
∼0	Upchurch, 1972
9.4	Klein, 1975

[a] *Dissolved SiO_2.*

[b] *Dissolved plus suspended SiO_2.*

[c] *Calculated by assuming that 10% of the 59,000 metric tons Si (= 126,000 metric tons SiO_2) emitted annually by burning of coal, coke, and fuel oil plus manufacture of iron, steel, and cement in the southwestern part of the Basin is transferred to Lake Michigan.*

At present, sewage effluents are likely not important sources of silica to Lake Michigan. From nationwide data, Weinberger *et al.* (1966) estimated an increase of 12 mg/l in SiO_2 content in effluent from secondary treatment of municipal waste water over tap water. If silicates supersede phosphates as builders in synthetic detergents, then the importance of sewage effluents as a source of silica to Lake Michigan would increase. A current source of soluble silicon is sodium silicofluoride (Na_2SiF_6), which is added prophylactically to fluoridate drinking water supplies.

INORGANIC REACTIONS OF SILICON

Dissolution

Amorphous silica is the most soluble form in which silica occurs naturally: at 25°C, a solution saturated with amorphous silica contains 100-140 mg of soluble SiO_2/l (Krauskopf, 1956). Amorphous silica dissolves slowly when compared with less soluble crystalline forms. These differences in rates permit lengthy periods of undersaturation in natural waters. Solubility of amorphous silica is little influenced by pH in the range 0-9; solubility is at least as great in acid as in dilute base. The relationship between the solubility of amorphous silica and temperature is roughly linear (Alexander *et al.*, 1954). Protective surface layers of metal silicates, formed by sorption/precipitation of metal ions to the surface, decrease the dissolution rate of amorphous silica appreciably (Lewin, 1961).

Silicate minerals are major sources of silica to Lake Michigan. Processes of hydrolysis are primarily responsible for chemical weathering of silicate minerals (Krauskopf, 1967) and release of orthosilicic acid,

$$\underset{\text{(forsterite)}}{Mg_2SiO_4} + 4\ H_2O \longrightarrow 2\ Mg^{2+} + 4\ OH^- + H_4SiO_4\ . \qquad (24)$$

Carbonic acid and other acids found naturally in water enhance the hydrolytic release of silica,

$$Mg_2SiO_4 + 4\ H_2CO_3 \longrightarrow 2\ Mg^{2+} + 4\ HCO_3^- + H_4SiO_4\ . \qquad (25)$$

Silicon-containing minerals are seldom as simple as forsterite. For silicate minerals containing several cations, the hydrolytic reaction is more complicated than Equation 24 indicates, because different cations go into solution at different rates. The implication of these different rates is that partially weathered silicate grains will be coated with an outer shell from which the more soluble cations have been removed. This shell of less soluble cations may serve to protect the interior of the grain from further chemical weathering, making the dissolution of most silicates a slow process.

Aluminum silicates like potassium feldspar hydrolyze during weathering to release silicic acid and, almost always, a clay mineral, *e.g.*

$$4\ \underset{\text{(K-feldspar)}}{KAlSi_3O_8} + 22\ H_2O \longrightarrow \underset{\text{(kaolinite)}}{Al_4Si_4O_{10}(OH)_8} + 8\ H_4SiO_4 + 4\ K^+ + 4\ OH^-\ . \qquad (26)$$

These clay minerals can then be hydrolyzed further to release more cations and more silicic acid. Ultimately, all the silica may be removed, and gibbsite [$Al(OH)_3$] may remain; however, these reactions are very slow at temperatures found in Lake Michigan.

Several reports (Mortimer, 1941, 1942; Hutchinson, 1957; Kato, 1969) have suggested that soluble reactive silica concentrations in lakes are related to the formation of iron, manganese, and aluminum oxides/hydroxides. Desorption of soluble orthosilicate from ferric hydroxides is favored by the absence of O_2, which in turn allows conversion of iron from the ferric to the much more soluble ferrous state. Conditions favorable for desorption of silica from preformed ferric hydroxides would be found in Lake Michigan only in areas where dissolved O_2 is depleted (*e.g.* lower Green Bay, Calumet and Indiana Harbors) and in sediments at depth (*cf.* Callender, 1969).

Precipitation

There are comparatively few strictly inorganic chemical reactions that could occur in Lake Michigan to remove dissolved silica from solution. Silica concentrations in Lake Michigan water are one to two orders of magnitude lower than saturation values (60-80 mg/l at 0-5°C; 100-140 mg/l at 25°C); thus supersaturation and resultant inorganic chemical precipitation of amorphous silica cannot occur.

Sorptive removal (polymerization) of H_4SiO_4 onto preformed amorphous silica carried in by tributaries is also unlikely, because dissolved silica in concentrations up to saturation values is stable indefinitely in the presence of amorphous silica. Nor would sorption of silica onto clay minerals be important. For example, dissolved silica concentrations must exceed 25 mg SiO_2/l before there is detectable sorptive removal of silica by kaolinite (Siever and Woodward, 1973).

The only inorganic reaction which might be important in removing dissolved SiO_2 from Lake Michigan water is the adsorptive removal of silica, from solutions containing as little as 0.5 mg SiO_2/l (Harder and Flehmig, 1970), by amorphous hydroxides of iron, aluminum, and manganese. This type of reaction is important only under aerobic conditions (*cf.* Mortimer, 1941, 1942; Hutchinson, 1957; Kato, 1969). Under anaerobic conditions, ferric hydroxides are reduced, and silica is released as ferrous iron goes into solution.

Biochemical Reactions of Silicon

Dissolution of Inorganic Silicates

The efficiency of lichens, mosses, ferns, bacteria, fungi, and green plants in the decomposition, degradation, and dissolution of terrigenous rock containing silicate minerals has long been recognized. Recent work indicates that bacteria in the aqueous environment may also be important in releasing SiO_2 to solution. *Proteus mirabilis* and thermophilic *Bacillus caldolyticus* released H_4SiO_4 from amorphous SiO_2 and from quartz (Lauwers and Heinen, 1974). Most of the silicate-dissolving bacteria isolated from brackish to fresh water by Purushothaman *et al.* (1974) were characterized as *Pseudomonas* spp. No work on the importance of bacteria with respect to dissolution of silicates in Lake Michigan has been reported.

Diatoms also can dissolve silicate-containing minerals. Hutchinson (1957) summarized a Russian study which followed the decomposition by diatoms of individual crystals of the clay mineral nacrite (similar to kaolinite) under the microscope. Observed changes noted included an increase of opacity in the crystal, then fracture along the cleavage plane of the crystal; ultimately, free alumina, Al_2O_3, was detected chemically. Hutchinson hypothesized that at least some of the silica released by the degradation of this mineral diffused into the medium.

Dissolution of Biochemically-Formed Silicates

Based on laboratory experiments conducted over several days with two marine diatoms, Paasche (1973b) postulated that frustules of living diatoms dissolve to some extent under conditions of very low soluble reactive silica concentrations, allowing continued growth.* However, Lewin (1961) said, "The amorphous silica structures in diatoms ... appear to be prevented from dissolving in their aqueous habitat while intact and associated with the living organisms." Yet her experiments with a freshwater diatom seemed to show that living diatoms suspended in solutions containing no silica at all release cellular silica to solution. An initial concentration of living diatom frustules of 100-150 mg SiO_2/l led to the dissolution in the dark of *ca.* 3 mg SiO_2/l in 15-20 days, and more than 4 mg/l in 50 days. On the other hand, Lewin did not show conclusively that the dissolved silica did not originate from dead cells; after 30 days in the dark suspensions were said to show "a high proportion of viable cells." The proportion of dead cells was not specified.

Every circumstance which kills diatoms (natural death, cell breakage, laboratory manipulations) results in increased rates of silica dissolution (Lewin, 1961) above those measured with live cells. Zooplankton ingestion, which causes diatom cell breakage (Ferrante *et al.*, 1975; Ferrante and Parker, 1976--in press) would also increase the rate of silica dissolution. Higher temperatures (range studied was 10-35°C) increase the rates of dissolution (Lewin, 1961). In laboratory experiments, higher pH values (range studied was pH 3-9) also enhance the dissolution of diatom frustules freed from organic matter; Lewin did not comment whether this situation is analogous to degradation by bacteria of organic slimes coating diatom frustules, followed by dissolution.

Certain metal ions, including Mn^{2+}, Al^{3+}, and Fe^{3+}, combine with the silica cell walls of diatoms to affect either their subsequent rates of dissolution or their final solubility. The metal ion concentrations Lewin (1961) used to study these effects were three to five orders of magnitude greater than those found in Lake Michigan. Nevertheless, she speculated that if growing diatom frustules are initially protected against solution by some biophysical or biochemical agent, then colloidal ferric and aluminum hydroxides could later passively sorb and accumulate on the frustule surfaces, stabilizing them against dissolution.

No information is available on possible dissolution of live diatom frustules in Lake Michigan water, nor has the possible significance of inorganic coatings on diatom frustules been investigated.

Removal from Solution

Soluble reactive silica concentrations in Lake Michigan water are controlled by diatoms (Schelske and Stoermer, 1971, 1972). No other chemical compound replaces silicon during diatom growth, and silicon is an absolute requirement for cell division (Lewin, 1962). Diatoms remove orthosilicic acid from solution and deposit it in their frustules in the form of silica gel (*i.e.* a form of hydrated amorphous silica represented as $SiO_2 \cdot nH_2O$).

**Azam et al. (1974) reported that a nonphotosynthetic marine diatom Nitzschia alba does not release significant quantities of intracellular silica to the surrounding medium within 60-minute experiments. The environmental importance of this observation awaits elucidation.*

By depositing dissolved silica in their frustules, diatoms can reduce soluble reactive silica concentrations to low or even undetectable levels in laboratory cultures (Lund, 1950; Jørgensen, 1953; Paasche, 1973a) and natural waters (Lund, 1969; Paasche, 1975). Low soluble reactive silica concentrations, however, do not indicate that the presence of viable diatom populations is impossible. At least two potentially complementary explanations can be proposed:

(*i*) Various diatom species have widely differing abilities to take up dissolved silica (*cf.* Guillard *et al.*, 1973; Paasche, 1973b, 1975). This observation is also implied in the hypothesis of Kilham (1971) that ambient silica concentrations may influence the sequence of seasonal succession of freshwater planktonic diatoms.

(*ii*) Growth rates may slow (Paasche, 1973a, 1975) under conditions of extremely low concentrations of dissolved silica, but growth continues even though there is seemingly no net removal of silica from solution. Paasche (1973b) hypothesized that sufficient silica for the formation of new frustules is obtained by limited dissolution of live cells. A consequence of continued growth under low silica concentrations is that diatoms form thin, weakly silicified walls instead of the thick walls formed under conditions of ample silica. This variability of the amount of silica in the cell wall may have an adaptive function. Thick walls offer rigidity and protection, but when silicate is in short supply diatoms form thin walls so that cell division can continue; this hypothesis has not yet been verified for diatoms in Lake Michigan.

TECHNIQUES OF SILICA ANALYSIS

Before considering the results of silica analyses of Lake Michigan water, a brief review of techniques used to quantify silica is needed to point out problems of interpretation created by these techniques.

Many of the early values for silica in natural waters were derived from the Diénert and Wandenbulcke (1923) method, in which a yellow color due to a silicomolybdate complex was generated by adding ammonium molybdate to the water acidified with H_2SO_4. Since the 1950's, this relatively insensitive method has been replaced by a procedure (*cf.* Krauskopf, 1956; Hutchinson, 1957) in which the yellow silicomolybdate complex is reduced to heteropoly blue by aminonaphthol-sulfuric acid (APHA *et al.*, 1971). The blue color is more intense than the yellow and thus provides greater sensitivity. If the sample was filtered, then the result is considered a measure of dissolved reactive silica; if the sample was not filtered, then the result indicates the amount of total reactive silica. Reports of research and monitoring studies have sometimes, perhaps inadvertently, omitted the word "reactive"; and thus have left the impression that dissolved silica and total silica were determined.

A major problem with both these analytical methods (silicomolybdate and heteropoly blue) is the question of what is actually measured. Silica concentrations are defined by the procedures used (*cf.* section on Phosphorus Analysis). These procedures assume that dissolved silica in fresh waters occurs predominantly in a reactive form and that little if any dissolved silica is present in an unreactive, highly polymerized form (Krauskopf, 1956). However, if there are appreciable quantities of soluble polymeric silica, then these polymers will pass through the filter but will not react under the experimental conditions specified in *Standard Methods* (APHA *et al.*, 1971). Use of the term "soluble reactive silica" rather than "dissolved silica" acknowledges that the results of the experimental determination of silica concentrations depend on the operations used in sample pretreatment.

Another problem in the determination of silica in natural waters, the chemical alteration in forms of silica during sample storage, has been appreciated only recently. Burton *et al.* (1970) examined the effect of sample freezing on measurable silica. They found that, immediately after filtered samples were thawed, river samples consistently had reactive silica concentrations only 10-20% of those measured before freezing. If the thawed samples were held at 25°C for about three hours, then the particulate matter in the freshly melted water decreased in size as reactive silica returned to its pre-freezing level. Philbert (1973) collected and filtered replicate samples of water from Lakes Ontario and Huron in 1971. He immediately analyzed one group for soluble reactive silica and then froze the remaining samples. After 3-28 days, the frozen samples were thawed and reanalyzed. Soluble reactive silica concentrations decreased by averages of 8-23% in thawed samples compared with duplicates run before freezing. Differences between analyses made before freezing and after freezing were significant at the 95% confidence level or better in five of six sets of samples. Additional samples collected in Lake Ontario in 1972-73 showed concentration decreases of 24-27% in analyses before and after freezing. In some instances, measured silica content rose to pre-freezing level if the thawed sample was allowed to stand three hours, suggesting partial resolution of precipitated silica, but the occurrence of this increase did not seem entirely predictable; in two of three data sets from Lake Ontario, samples allowed to stand three hours returned to raw-water levels, while the third exceeded the raw-water level. In all three data sets from Lake Huron, samples that were allowed to stand three hours after thawing showed lower soluble reactive silica concentrations than were measured prior to freezing.

Description of the silica cycle in Lake Michigan is hampered by the lack of determinations of total silica concentrations (analogous to the requirement for total phosphorus quantification in order to describe the phosphorus cycle). The lack of total silica data is understandable, since the analytical wet method does not lend itself to routine processing of numerous samples.

SOLUBLE REACTIVE SILICA

Soluble reactive silica determinations over the past two decades are presented in Table 35. Figures 68 and 69 depict surface-water (< 25 m) concentrations of soluble reactive silica in winter and summer, respectively.

During winter, when diatoms are less abundant (*e.g.* Holland and Beeton, 1972), surface-water soluble reactive silica concentrations have probably been about 1.0-1.6 mg SiO_2/1 over the past five years (Fig. 68). Most of the winter data have been collected from Milwaukee to North Chicago, and along the car ferry track between Milwaukee and Ludington. There are no data readily available for the extreme southern portion of the Lake, nor for most of the divide area and all of the northern basin.

More data are available for the summer period (Fig. 69). Beeton and Moffett (1964) collected samples throughout the Lake for silica analyses in 1954-1955; they resampled a number of their 1954-1955 stations during 1960-1961.

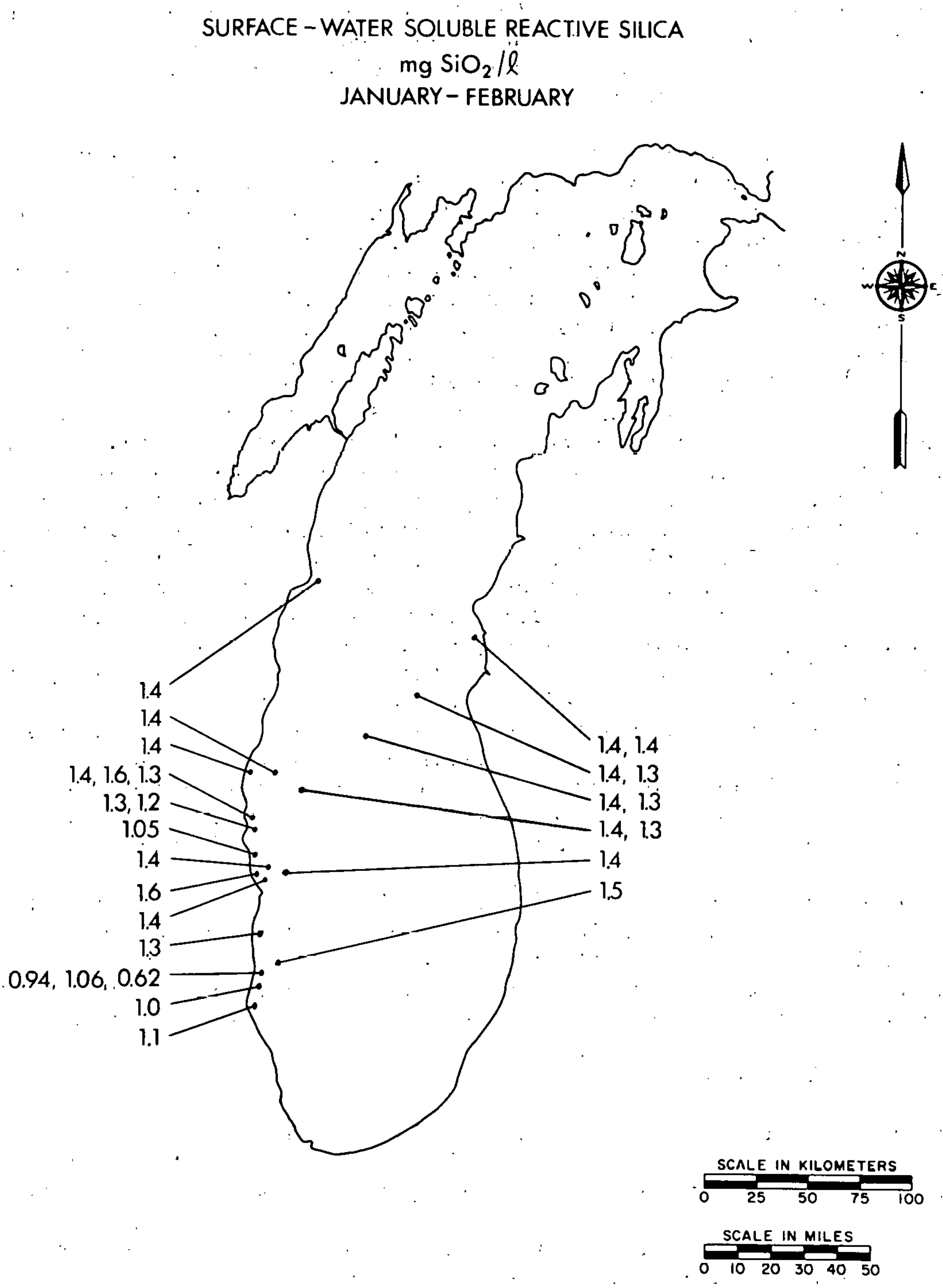


Fig. 68. Surface-Water Soluble Reactive Silica Concentrations in January-February over a Period of Five Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 35.

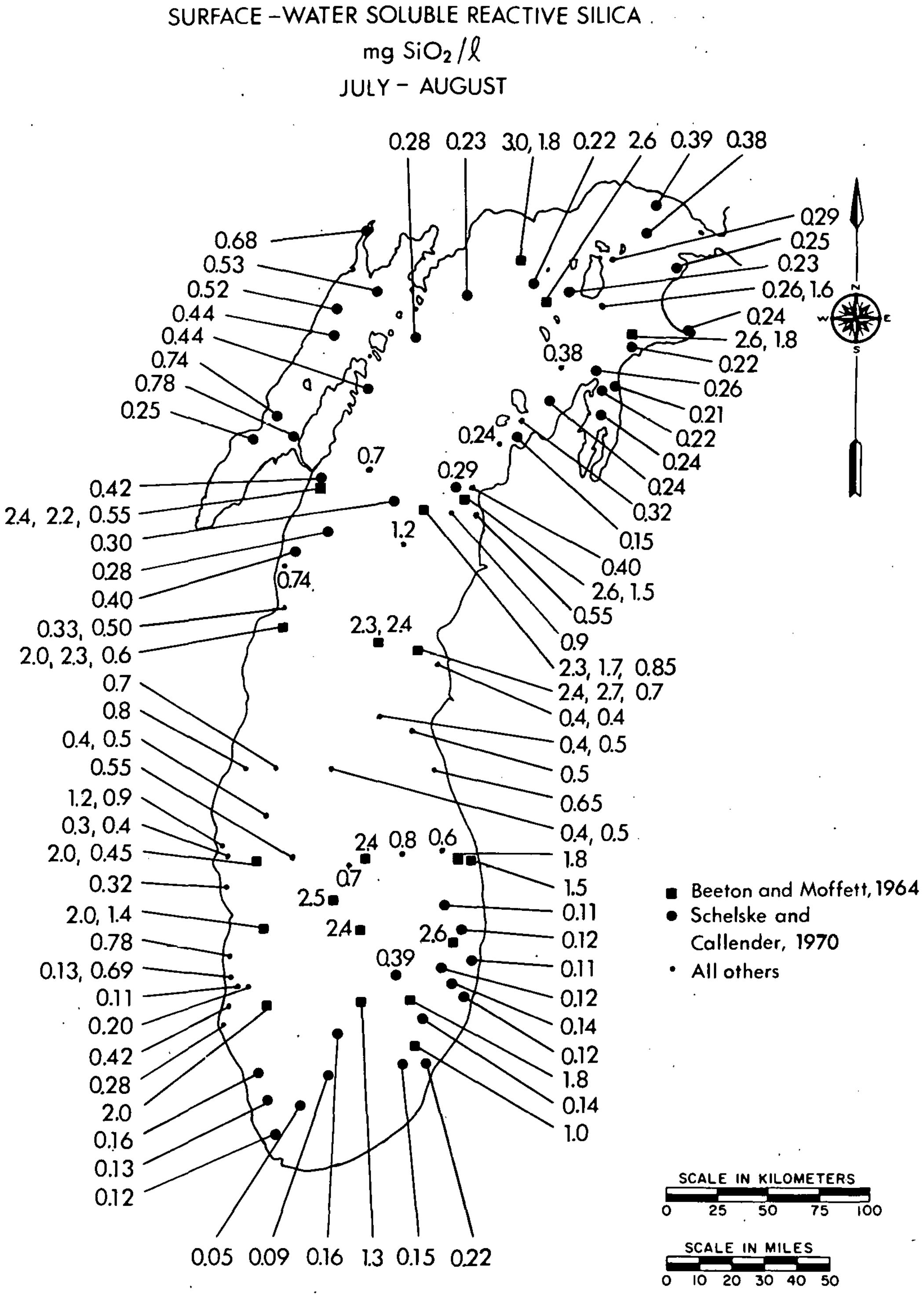


Fig. 69. Surface-Water Soluble Reactive Silica Concentrations in July-August over a Period of Twenty Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 35.

Table 35. Soluble Reactive Silica Content in Lake Michigan Water

Sample Description	Dates	Concentration SiO_2, mg/l Average	Concentration SiO_2, mg/l Range	Reference
Samples* collected at public water intakes:				Powers and Ayers, 1967
Chicago (6 intakes)	1954	1.7		
	1955	1.3		
	1956	1.6		
	1957	1.6		
	1958	1.9		
	1959	2.1		
	1960	1.9		
	1961	2.0		
	1962	2.1		
	1963	1.9		
	1964	2.5		
Milwaukee	1954	4.7		
	1955	4.0		
	1956	5.8		
	1957	4.0		
	1958	5.2		
	1959	3.9		
	1960	4.9		
	1961	3.1		
	1962	3.6		
	1963	3.4		
	1964	2.9		
Grand Rapids	1954	5.8		
	1955	5.2		
	1957 [*sic*]	4.1		
	1957 [*sic*]	8.1		
	1960	3.3		
	1961	3.5		
Samples collected:				Beeton and Moffett, 1964
Southern basin and divide area				
Inshore stations	May-Dec 1954			
Surface-water, 168 samples		2.5	0.7-5.4	
Bottom-water, 148 samples		3.4	2.0-5.3	
Offshore stations	May-Nov 1954			
Surface-water, 219 samples		2.4	1.1-4.1	
Bottom-water, 156 samples		3.3	1.8-6.5	
Northern basin and divide area				
Inshore stations	May-Nov 1955			
Surface-water, 238 samples		3.0	1.4-6.4	
Bottom-water, 103 samples		2.8	1.8-6.8	
Offshore stations	May-Nov 1955			
Surface-water, 195 samples		3.9	1.7-4.3	
Bottom-water, 72 samples		3.7	2.5-7.0	
Southern basin				
3 inshore stations	Apr-Nov 1960			
Surface-water		1.9	0.8-3.6	
Bottom-water		3.5	2.1-4.7	
1 offshore station	May-Sep 1960			
Surface-water		2.4	1.0-3.4	
Bottom-water		3.7	2.7-5.0	
Northern basin				
5 inshore stations	May-Nov 1961			
Surface-water		1.8	1.1-2.7	
Bottom-water		2.5	1.6-3.6	
2 offshore stations	May-Nov 1961			
Surface-water		1.8	1.1-2.8	
Bottom-water		2.6	2.0-3.4	
Whole Lake:	1962-63			USDOI, 1968
299 offshore samples		2.5	0.6-5.5	
645 inshore samples		1.7	0.4-4.4	

Table 35. (contd.)

		Concentration SiO_2, mg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Samples collected:	1962-63			USDOI, 1968
Indiana Harbor, 21 samples		2.5	1.6-3.8	
Calumet Harbor, 19 samples		1.6	1.0-3.0	
Chicago Harbor, 5 samples		1.2	0.75-2.0	
Racine Harbor, 7 samples		1.6	1.4-1.9	
Samples collected:	Oct 1962, Jun 1963			USDOI, 1968
Milwaukee Harbor, 23 samples		1.5	0.98-2.1	
Adjacent to Milwaukee Harbor, 46 samples		1.5	1.2-2.8	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City		1.7	0.4-3.7	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo		1.6	0.5-3.0	
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor		1.9	0.7-4.2	
On a line roughly between Sheboygan and Little Sable Point		2.9	1.8-5.1	
163 samples collected throughout Green Bay	26 Jun-17 Jul 1963	2.1	0.5-9.7	USDOI, 1968
Samples collected:	22-28 Jul 1964			USDOI, 1968
Traverse Bay, 51 samples		2.1	0.9-4.2	
Adjacent to Traverse Bay, 15 samples		1.4	0.9-2.1	
Samples collected:				Schelske and Callender, 1970
Southern basin	22-24 Jul 1969			
Surface-water, 9 inshore stations		0.14	0.11-0.22	
Bottom-water, 9 inshore stations		1.04	0.05-2.50	
Surface-water, 7 offshore stations		0.16	0.05-0.39	
Bottom-water, 7 offshore stations		1.51	0.96-2.23	
Northern basin	15-23 Aug 1969			
Surface-water, 6 offshore stations		0.27	0.22-0.38	
Bottom-water, 6 offshore stations		1.27	1.14-1.47	
Northern basin, including Traverse Bay	15-23 Aug 1969			
Surface-water, 15 inshore stations		0.28	0.15-0.44	
Bottom-water, 8 inshore stations		1.21	1.03-1.55	
Northern Green Bay, including Big Bay de Noc	15-23 Aug 1969			
Surface-water, 4 stations		0.52	0.34-0.68	
Northern Green Bay, including the Bays de Noc	15-23 Aug 1969			
Bottom-water, 4 stations		0.84	0.36-1.20	
4 samples (3 in Jan, 1 in May) collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	Jan, May 1970	1.2	0.7-1.4	USGS, 1972
Surface-water (5 m) samples collected at 12 stations in Grand Traverse Bay	18 May 1970	1.03	0.79-1.20	Stoermer *et al.*, 1972
Monthly samples collected at intakes:	May 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		1.1	0.27-2.1	
Waukegan Generating Station		0.94	0.15-2.0	
North Chicago public water supply		0.88	0.04-2.1	
Monthly samples collected at 3 stations 9.6 km (6 mi) east of Zion:	May 1970-Apr 1971			Industrial Bio-Test, 1972b
Surface-water		0.95	0.02-1.7	
Bottom-water		1.7	0.2-3.5	

Table 35. (contd.)

		Concentration SiO_2, mg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Monthly surface-water (4 m) samples collected:	May, Jun, Aug, Oct, Nov 1970; Jan 1971			Holland and Beeton, 1972
4.8 km (3.0 mi) east of Milwaukee		0.9	0.2-1.6	
Between Milwaukee and Ludington				
1/4 the distance		0.9	0.3-1.4	
1/2 the distance		1.0	0.5-1.4	
3/4 the distance		0.9	0.4-1.4	
4.8 km (3.0 mi) west of Ludington		0.6	0.3-1.3	
Samples collected at 8- to 21-day intervals (except 3 Feb-11 Mar) at a depth of 4 m:	27 May 1970-20 Oct 1971			Rousar, 1973
4.8 km (3.0 mi) east of Milwaukee		0.75	0.2-1.6	
Between Milwaukee and Ludington				
1/4 the distance		0.85	0.3-1.5	
1/2 the distance		0.87	0.3-1.5	
3/4 the distance		0.83	0.2-1.4	
4.8 km (3.0 mi) west of Ludington		0.71	0.3-1.4	
Samples collected in Grand Traverse Bay:	20 Jun 1970			Stoermer *et al.*, 1972
Surface-water (5 m), 12 stations		0.36	0.16-0.50	
Bottom-water (1 m above bottom), 11 stations		0.97	0.51-1.27	
Monthly averages for samples collected at stations offshore from northern Chicago:				Lue-Hing, 1973
6 stations 0.30 km (1000 ft) offshore	Jun-Nov 1970, May-Oct 1971	0.37	0.12-1.37	
7 stations 0.61-0.91 km (2000-3000 ft) offshore	Jun-Dec 1970, May-Oct 1971	0.62	0.06-1.32	
4 stations 1.37-1.83 km (4500-6000 ft) offshore	Jun-Dec 1970, May-Oct 1971	0.81	0.20-1.86	
Samples collected on a line passing east of Manitou Islands from Frankfort to Beaver Island:	7 Jul 1970			Schelske and Roth, 1973
13 surface-water samples, 6 stations		0.32	0.17-0.53	
4 bottom-water samples, 4 stations		1.14	0.98-1.34	
Monthly averages for samples collected at a station 3.0 km (10,000 ft) east of Zion	Dec 1970, May-Oct 1971	0.62	0.10-1.32	Lue-Hing, 1973
Samples collected ∿weekly at the Milwaukee public water intake, 1.8 km (1.1 mi) offshore	Mar-Sep 1971 Oct 1971-Sep 1972 Oct 1972-Jun 1973	1.1 1.3 1.1	0.7-1.8 0.3-2.2 0.5-2.3	USGS, 1973 USGS, 1974a USGS, 1974b
Samples collected ∿monthly, surface to bottom, near Point Beach Nuclear Plant:	Jun-Sep 1971			Weschler *et al.*, 1972
6 stations <0.37 km (1230 ft) from shore		0.34	0.18-0.62	
4 stations 1.1-2.7 km (3600-9000 ft) from shore		0.38	0.18-0.61	
Samples collected at 17 stations located between lines connecting Milwaukee to Grand Haven and Sturgeon Bay to Frankfort:	8-14 Jul 1971			Rousar and Beeton, 1973
Surface to bottom samples		1.0	0.4-1.9	
Epilimnetic samples		0.65	0.4-1.0	
Samples collected, surface to bottom, at 21 stations in southern Green Bay	12 Jul 1971	0.9	0.4-1.5	Rousar and Beeton, 1973

Table 35. (contd.)

Sample Description	*Dates*	*Concentration SiO_2, mg/l*		*Reference*
		Average	*Range*	
Samples collected (water depth 7.6 m) at a station east of Kewaunee Nuclear Plant:				Industrial Bio-Test, 1972d
Surface	31 Aug 1971	0.75	0.64-0.82	
Bottom	31 Aug 1971	0.74	0.71-0.76	
Surface	16 Nov 1971	1.4[a]		
Bottom	16 Nov 1971	1.4[a]		
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Oct 1971-Apr 1972	1.1	0.48-1.8	Industrial Bio-Test, 1972c
Monthly surface-water samples collected at stations between ∿0.4 km (0.25 mi) and ∿16 km (10 mi) from shore:	Oct-Dec 1971; Jan, Feb, Apr, Jun 1972			Beeton and Barker, 1974
5 stations on an east-west transect ∿9.6 km (6 mi) south of Grafton, Wis.		1.2	0.5-1.9	
12 stations east of Oak Creek		1.1	0.1-2.6	
10 surface-water samples each collected at stations east of Milwaukee:	28 Nov 1972			Beeton and Barker, 1974
0.4 km (0.25 mi) east		0.99		
16 km (10 mi) east		0.89		
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		1.28[b]		
17 km (10.6 mi) offshore		1.10[b]		
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		0.73	0.08-2.4	
Effluent plume		0.77	0.08-2.2	
South of plant, 4.8 km (3 mi)		0.78	0.12-1.7	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		0.67	0.10-1.2	
North of plant, 1.6 km (1 mi)		0.71	0.08-1.3	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		0.92	0.26-1.76	
South of plant, 1.6 km (1 mi)		0.88	0.24-1.58	

**Data plotted as mg Si/l, but the text suggests to this author that these data are mg SiO_2/l.*

[a] *Same value for all samples.*

[b] *Data converted from total soluble silica, μg/l, as originally reported.*

USDOI = U. S. Department of the Interior; USGS = U. S. Geological Survey.

Rousar and Beeton (1973) returned to many of these same stations in 1971. At first glance, comparison of data collected at these stations suggests that soluble reactive silica concentrations dropped dramatically over that period. However, one must reconsider this supposition in light of a comment made by Rousar and Beeton, referring to the work of Beeton and Moffett:

> ". . . *Their determinations were made on unfiltered samples stored for long*[*er*] *periods of time, and some silica may have been released from particulate matter.*"

Thus changes in soluble reactive silica concentrations over the past two decades may not be so dramatic as inspection of the raw data of Beeton and Moffett and of Rousar and Beeton might indicate, for storage procedures may have allowed changes in sample composition to occur.

Schelske and Callender (1970) reported notably low values for soluble reactive silica content in surface-water samples collected in the southern basin (22-24 July 1969) and the northern basin (15-23 August 1969). Sixteen surface-water (2 m) samples, taken both inshore and offshore in the southern basin, averaged 0.15 mg SiO_2/l; 21 surface-water samples, both inshore and offshore, in the northern basin, averaged 0.28 mg SiO_2/l. These low values may be real, or they may have resulted at least in part from problems created by the experimental techniques used (Burton *et al.*, 1970; Philbert, 1973). Schelske and Callender reported that samples were filtered, frozen in polyethylene bottles for several months, and thawed just prior to analysis.

Keeping in mind the problems of interpretation created by analytical methods, Figure 69 shows that summer concentrations of soluble reactive silica generally are much less than winter concentrations (Fig. 68). Schelske and Callender (1970) reported that surface-water concentrations were higher in the northern basin than the southern basin, but the data in Figure 69 are too variable to confirm this statement. During summer, silica content increases with distance from shore (Fig. 70b), unlike the winter pattern (Fig. 70a). Higher concentrations farther from shore are undoubtedly due to active removal of soluble reactive silica by planktonic and benthic diatoms in the inshore area; decreased diatom populations account for higher offshore concentrations.

Since at least 1954, researchers have consistently found that soluble reactive silica concentrations in the surface waters during summer are lower than those in the hypolimnion (*cf.* Fig. 47). A number of reports document the annual variation of soluble reactive silica content in surface water (*e.g.* U. S. Geol. Surv., 1972, 1973, 1974a, 1974b; Industrial Bio-Test, 1972a, 1972b; Holland and Beeton, 1972; Rousar, 1973; Beeton and Barker, 1974; Limnetics, 1974). Industrial Bio-Test (1972b) also collected data that show annual variations in bottom-water (*ca.* 50 m) concentrations at stations deep enough to stratify (Fig. 71). During January to March, surface- and bottom-water concentrations are similar at *ca.* 1.5 mg SiO_2/l. By April, as the water warms slightly and the days lengthen, diatom populations increase and soluble reactive silica concentrations start to decrease. Since the Lake is still well mixed, this decrease continues in both surface (*ca.* 1 m) and bottom (*ca.* 50 m) waters to the end of May. During June, however, temperature stratifications occurs; silica concentrations in the surface water remain at about the May levels through the rest of the summer, while bottom-water concentrations

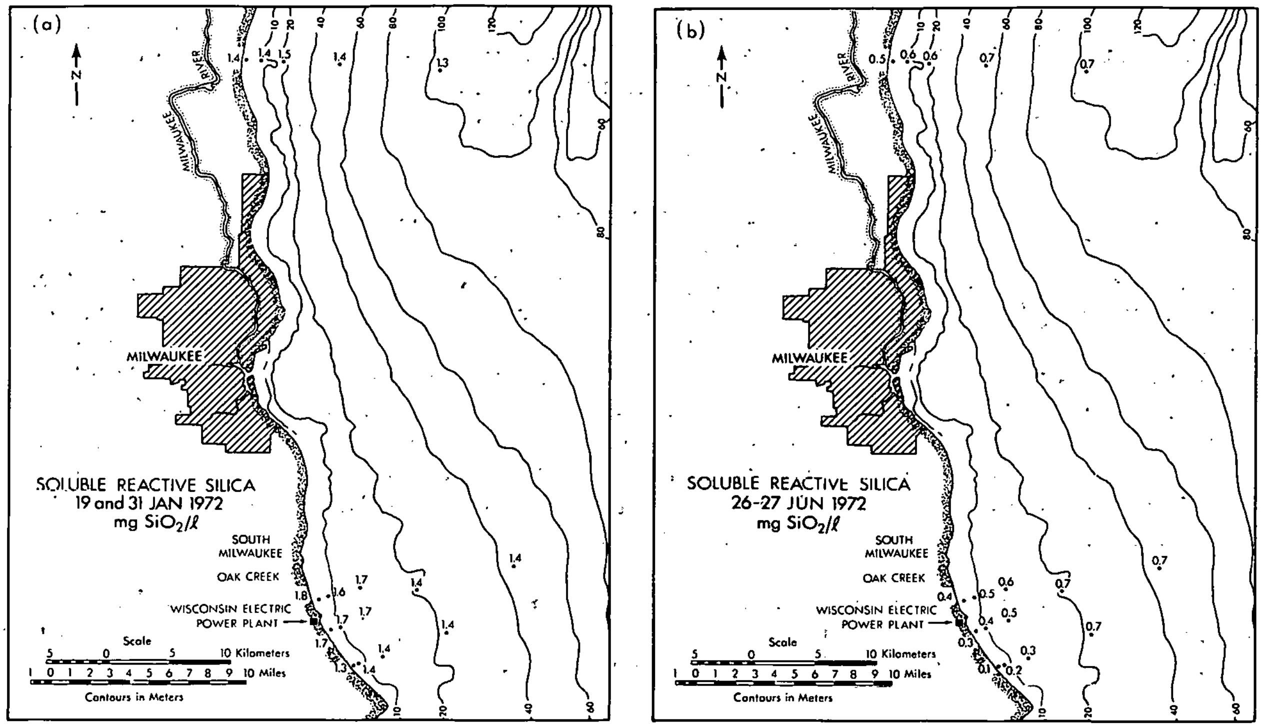


Fig. 70. Average Soluble Reactive Silica Concentrations at 17 Stations near Milwaukee, (a) January and (b) June 1972. Figure (modified) and data from Beeton and Barker (1974).

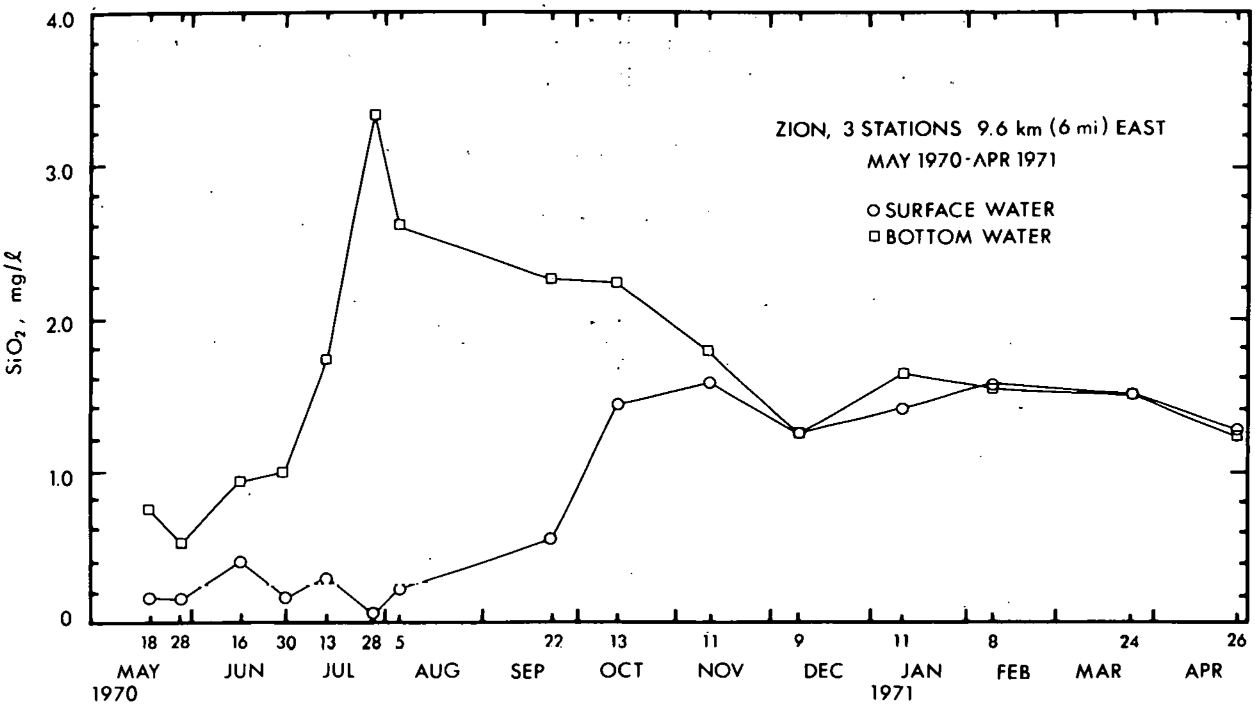


Fig. 71. Average Soluble Reactive Silica Concentrations at Three Stations East of Zion. Maximum depth at these stations ranged from 49-54 m (161-177 ft). Data from Industrial Bio-Test (1972b).

increase to the end of stratification. Part of this bottom-water increase may be attributable to dissolution of settling diatom frustules (see discussion on cycling below) and part may be due to diffusion of silica out of the sediments (see discussion of sediments below). When turnover is complete (December), surface- and bottom-water concentrations are once again similar.

Periodically, the higher concentrations of silica in stratified bottom water are injected into the surface water by upwelling. Schelske *et al.* (1971) reported that soluble reactive silica varied from 0.2 to 0.7 to 0.2 mg SiO_2/l in samples taken 21, 22, and 25 July 1969, respectively, at a station 1.2 km (0.75 mi) west of Grand Haven; this variation was attributed to upwelling of bottom water containing higher concentrations of silica. Weschler *et al.* (1972) also found increases in silica in upwelled water (0.53-0.59 mg SiO_2/l) compared with water which had not been upwelled (0.31-0.38 mg SiO_2/l) in samples collected near the Point Beach Nuclear Plant in July 1971. Upwelling may account for the high concentration of soluble reactive silica in bottom (*ca.* 50 m) water on 28 July 1970 in Fig. 71.

There are no statutory limitations on the silica content of drinking water. Nor have any limitations for the protection and maintenance of aquatic life been formulated by federal or state agencies concerned with Lake Michigan.

SILICA CONTENT IN SEDIMENTS

A number of different silica-containing forms (Table 36) have been identified in Lake Michigan sediments, including clay minerals (Shimp *et al.*, 1969; Callender, 1969), feldspars (Callender, 1969), and quartz. Callender (1969) attributed the higher average quartz and feldspar contents in surface sediments *vs.* sediments-at-depth in the divide area and northern basin to increased erosion in the watershed surrounding the Lake, allowing these minerals to be transferred intact to the Lake bottom.

Table 36. Mineralogical Data for Lake Michigan Sediments*

	Average Weight Percent					
	Southern Basin		*Divide Area and Northern Basin*		*Green Bay*	
Mineral	*Surface Sediment*	*Sediment at Depth*	*Surface Sediment*	*Sediment at Depth*	*Surface Sediment*	*Sediment at Depth*
Quartz	57	53	60	37	64	67
Feldspars	13	10	11	7	15	14
Chlorite[†]	7.7	8.6	7.1	7	5.2	7.7
Chlorite**	4.3	4	5.4	4.2	1.4	3
Total Clay Minerals	6	7	10	8	3	3

**Data from Callender, 1969.*

[†] *Calculated from chemical data.*

***Determined by X-ray analysis.*

The presence of amorphous silica is strongly implied by chemical data (Callender, 1969) and confirmed by the detection of diatom frustules in the sediments of Lake Michigan (Parker and Edgington, 1976--in press). In marine sediments, the amount of dissolved silica measured in interstitial water seems to depend on the amount of biogenic amorphous silica present, *e.g.* diatom frustules (Schink *et al.*, 1974; Fanning and Pilson, 1974; Hurd, 1973). Callender (1969) measured interstitial silica concentrations in Lake Michigan cores collected in summer 1968. In all cases, surficial concentrations of interstitial silica (Fig. 72) greatly exceeded concentrations in overlying water (*cf.* Table 35). Such a differential provides a driving force for the diffusional transfer of dissolved silica from the sediment to the overlying water (Fanning and Pilson, 1974; Hurd, 1973).

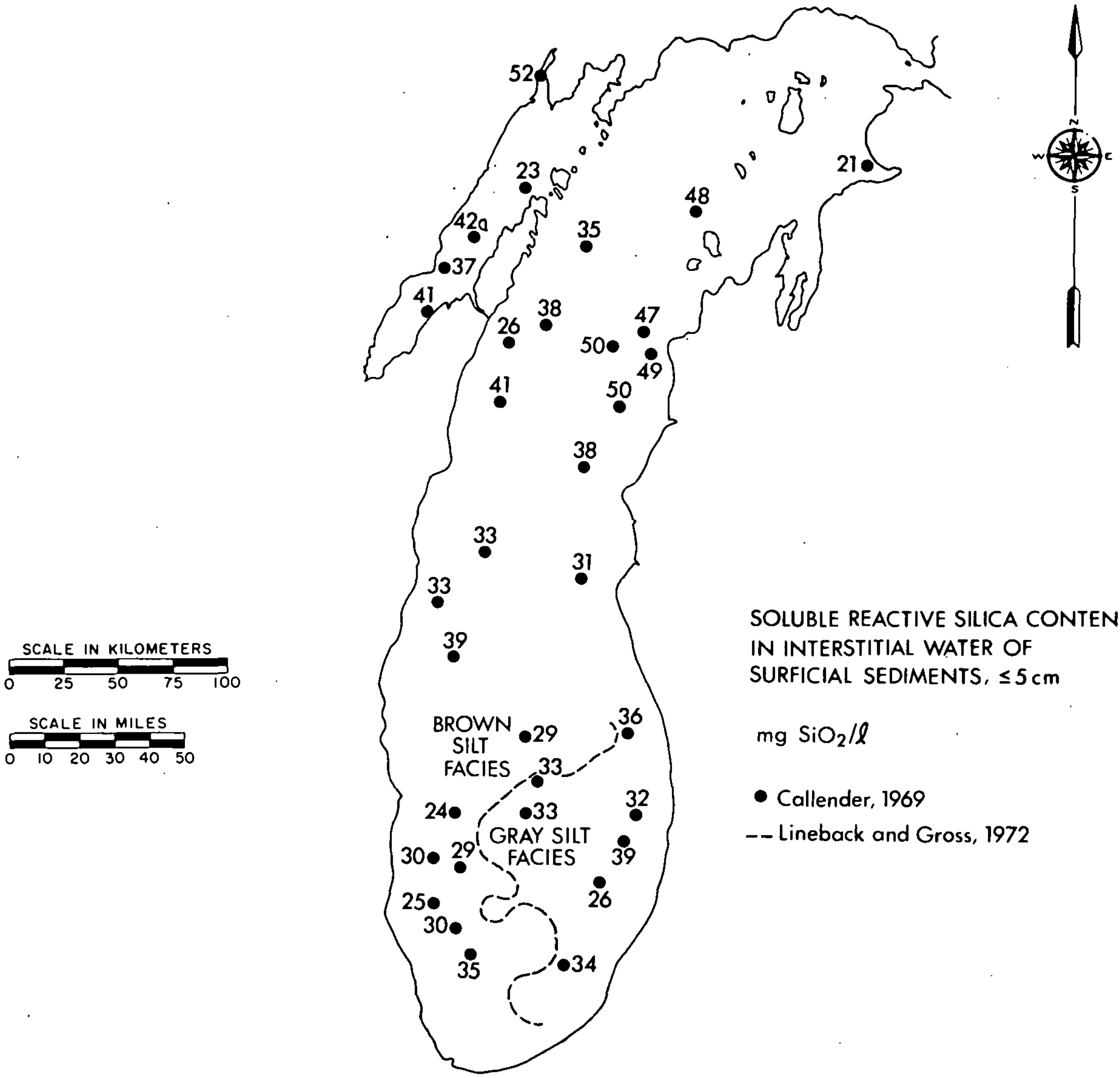


Fig. 72. Soluble Reactive Silica Concentrations in Interstitial Water of Surficial Sediments. Data from Callender (1969). Boundary of brown and gray silt facies of the Waukegan member from Lineback and Gross (1972).

Robbins *et al.* (1975b) also have measured soluble reactive silica concentrations in interstitial waters. They sectioned their core much more closely than Callender (1969) and obtained results shown in Figure 73. This pattern of increasing concentration with depth to a nearly constant value somewhere below the sediment surface is characteristic of diffusional transfer of silica from sediment to the overlying water (*cf.* Hurd, 1973; Fanning and Pilson, 1974).

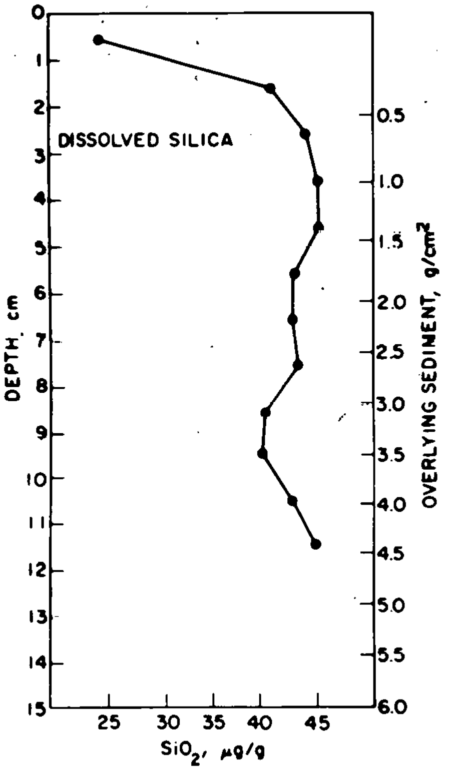


Fig. 73.

Distribution of Dissolved Silica in a Sediment Core from Southern Lake Michigan. Modified from Robbins *et al.* (1975b).

THE SILICA CYCLE

Present knowledge of the dynamics of the silica cycle (Fig. 74) in Lake Michigan is incomplete. Recent investigations (Ferrante *et al.*, 1975; Parker and Edgington, 1976--in press; Parker and Ferrante, 1975; Robbins *et al.*, 1975b; Ferrante and Parker, 1976--in press), however, have added to our understanding.

Natural sources such as land runoff provide most of the silica to Lake Michigan (Upchurch, 1972). Within the Lake, diatoms remove soluble reactive silica from solution (Schelske and Stoermer, 1971, 1972) as well as recycle it among themselves (*cf.* Paasche, 1973b). On the other hand, diatoms (Hutchinson, 1957) and bacteria (Lauwers and Heinen, 1974; Purushothaman *et al.*, 1974) also release silica to solution by solubilizing amorphous and crystalline forms of silica. Organisms within the water column, capable of degrading and dissolving silica-containing particles, are likely responsible for the estimate (Parker and Edgington, 1976--in press) that less than 5% of the annual diatom crop potentially available for settling reaches the sediment surface. Grazing of

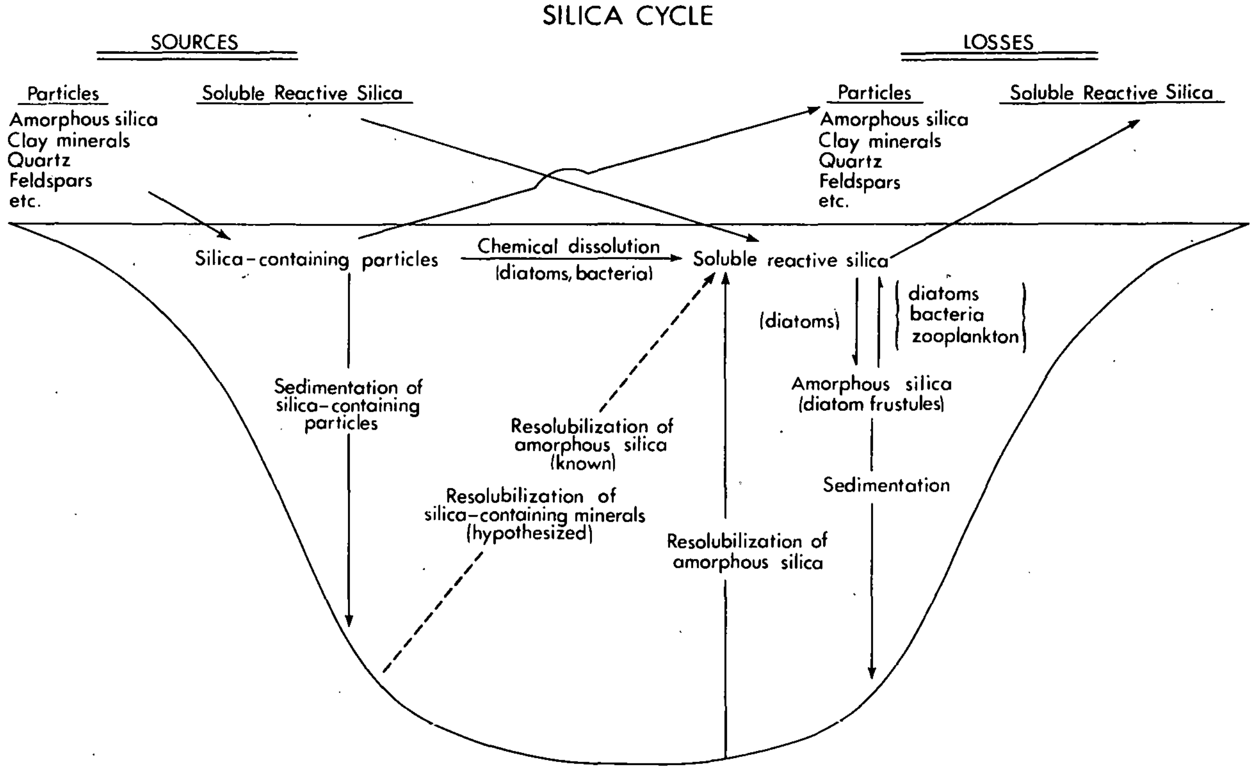


Fig. 74. Idealized Cycle of Silica in Lake Michigan.

diatoms by zooplankton enhances dissolution and recycling, for these animals fracture frustules while feeding (Ferrante *et al.*, 1975; Ferrante and Parker, 1976--in press). The rates of all these resolubilization reactions, about which little is known, in the photic zone are of more interest than the concentration data tabulated in Table 35. It is known that amorphous silica is solubilized within the sediment at appreciable rates (half life of frustule dissolution of 12-15 years) (Parker and Edgington, 1976--in press) and returned to the overlying water by diffusion and subsequent mixing (*cf.* Fanning and Pilson, 1974; Hurd, 1973).

Data are available on rates of soluble reactive silica input (Ayers, 1970); there is also an estimate of the importance of particulate silica loads (Table 34). Work of Parker and Edgington (1976--in press) provides preliminary evidence of rates of recycling from the sediments. Investigations of the types performed by Ferrante *et al.* (1975); Parker and Ferrante (1975), and Ferrante and Parker (1976--in press) may lead ultimately to estimates of recycling due to zooplankton interactions with diatoms. One of the largest gaps in understanding silica cycling in Lake Michigan is lack of information on rates of reactions involving silica and diatoms. Data from Paasche (1973b) suggest that marine diatoms can continue to grow uninterrupted even at low concentrations of soluble reactive silica, due to dissolution and reutilization of diatom frustules. Similar information from freshwater systems is unavailable.

MAJOR CATIONS

SODIUM

Sodium is an essential element for all animals and many plants. The sodium requirement for maximum growth rate of freshwater algae has been variously reported as 0.4 mg/l, 1.0 mg/l, and over 4.0 mg/l (summarized by Healey, 1973). Within plants and animals, sodium has electrochemical functions related to ion balance; it also activates several enzymes (Bowen, 1966). Certain blue-green algae need sodium to metabolize nitrate and N_2 (Allen and Arnon, 1955).

The sodium ion is also potentially harmful. Sodium content of food and water has long been recognized as a problem in the management of human diseases of the cardiovascular system (especially hypertension, atherosclerosis, and congestive heart failure), kidney and liver ailments, some complications of pregnancy, and several metabolic disorders (Terry, 1974). Of the disorders mentioned, hypertension requires the most severe restriction of sodium intake. A drinking water supply containing more than 20 mg/l of sodium (American Heart Association, 1957) will force persons on a strict low-sodium diet (500 mg/day) to purchase distilled water or else adjust their diets to allow for the excess sodium. At high concentrations (100 mg/l) sodium can be harmful to freshwater organisms (McKee and Wolf, 1963), but the toxicity of sodium salts to aquatic organisms is more often related to the anion of the salt than to sodium.

Natural sources of sodium to Lake Michigan include weathering and erosion of soils and rocks in the Basin. Based on average concentrations data (Bowen, 1966), igneous rocks contain more sodium than sedimentary rocks or soils. Exposed igneous rock is found only in the most northern part of the Lake Michigan Basin; the rest of the Basin consists of sedimentary rock and soils.

Sodium salts, which are commonly used in industry, are extremely soluble. That is, when these sodium salts (*e.g.* NaCl) dissolve in water, the ions dissociate completely, so that the resulting solution contains hydrated Na^+ and Cl^- ions in equal numbers. In addition to general industrial use of sodium salts, several industries along the eastern shore of Lake Michigan recover the sodium chloride brine underlying the western part of the state of Michigan and discharge the spent brine to the Lake. Sodium is also abundant in domestic wastes; Weinberger *et al.* (1966) reported that secondary-treatment municipal waste-water effluent contained 70 mg/l more sodium than did tap water. Conventional sewage treatment does not remove sodium; therefore, both domestic and industrial sewage effluents contribute sodium to the Lake. Many municipalities and government agencies in the Lake Michigan Basin use large quantities (*cf.* O'Connor and Mueller, 1970) of salt during winter for deicing their streets and highways. This road salt reaches Lake Michigan via storm and combined sewers.

Determinations of sodium concentrations in Lake Michigan are summarized in Table 37. Beeton and Moffett (1964) conducted an extensive survey during 1954-1955 and 1960-1961. These authors found 1954-1955 average sodium concentrations over the entire Lake to be 3.3 to 3.4 mg/l. In 1960-1961 the averages for samples taken in the northern and southern basins of the Lake

Table 37. Sodium Content in Lake Michigan Water

		Concentration Na, mg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Samples collected inshore and offshore, surface to bottom:				Beeton and Moffett, 1964
Southern basin and divide area, 759 samples	May-Dec 1954	3.4	3.2-4.6	
Northern basin and divide area, 610 samples	Mar-Nov 1955	3.3	2.4-4.3	
Southern basin, 83 samples	Apr-Nov 1960	3.7	3.0-4.6	
Northern basin, 141 samples	May-Nov 1961	3.6	2.4-5.5	
Whole Lake:	1962-63			USDOI, 1968
321 offshore samples		3.9	2.7-6.5	
400 inshore samples		4.0	1.8-7.5	
Samples collected:	1962-63			USDOI, 1968
Indiana Harbor, 21 samples		10	7.4-16	
Calumet Harbor, 20 samples		4.9	4.1-6.1	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City		4.3	1.8-15	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo		4.0	3.0-4.7	
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor		4.0	3.3-4.7	
On a line roughly between Sheboygan and Little Sable Point		3.8	2.8-5.3	
Samples collected:	22-28 Jul 1964			USDOI, 1968
Traverse Bay, 51 samples		3.9	2.8-4.8	
Adjacent to Traverse Bay, 15 samples		4.2	3.9-4.6	
Samples collected at public water distribution systems:	1964-65			Lawton and Busse, 1966
Cudahy		4.0	3.3-4.4	
Green Bay		4.2	3.9-4.4	
Kenosha		3.8	3.3-4.2	
Milwaukee		4.6	4.0-5.3	
North Shore Water Communities (Milwaukee suburbs)		4.4		
Oak Creek		12.7	10-15	
Port Washington		4.4	4.0-5.0	
Racine		4.2	2.6-4.8	
Sheboygan		5.2	5.0-5.5	
South Milwaukee		5.2	4.5-7.2	
Two Rivers		4.0	3.5-4.2	
Surface-water samples collected throughout the Lake at 20 stations sampled 3 times each	Aug 1969-Jun 1970	5.2	4.1-6.3	Copeland and Ayers, 1972
Samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore:				
4 samples	Dec 1969, Jun 1970	4.4	4.3-4.6	USGS, 1972
3 samples	Dec 1970, Jun 1971	5.1	4.6-6.0	USGS, 1973
3 samples	Dec 1971, Jun 1972	4.4	4.4-4.5	USGS, 1974a
Samples collected monthly at intakes:	Jan 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		5.6	4.3-8.1	
Waukegan Generating Station		6.3	4.4-10.0	
North Chicago public water supply		5.1	4.1-6.0	

Table 37. (contd.)

Sample Description	Dates	Concentration Na, mg/l Average	Concentration Na, mg/l Range	Reference
Samples collected throughout water column at 3 stations 9.6 km (6 mi) east of Zion	May-Oct 1970	4.6	4.1-5.0	Industrial Bio-Test, 1972b
Monthly samples collected at Lake County, Ill., public water intake	Jun 1970-Dec 1971, Sep 1972-Apr 1973	4.9	4.1-7.0	Howe, 1973
Single samples collected northwest of Grand River entrance, outside River plume	6 Oct 1970			Robbins *et al.*, 1972a
A station 1.0 km (0.62 mi) NW:				
Surface-water, soluble sodium		5.1		
Bottom-water, soluble sodium		6.0		
Surface-water, extractable particulate sodium		0.0401		
Bottom-water, extractable particulate sodium		0.0438		
A station 1.25 km (0.78 mi) NW:				
Bottom-water, soluble sodium		20.4^a		
Bottom-water, extractable particulate sodium		0.0553^a		
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		4.5		
Kenosha		5.5		
Milwaukee (5 intakes)		7.1	4.5-9.5	
Port Washington		4.5		
Racine		8.5		
Sheboygan		4.5		
Two Rivers		4.5		
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun 1971-Apr 1972	6.2	4.7-10.3	Industrial Bio-Test, 1972c
Samples (3 replicate analyses) collected off Grand Haven	13-14 Sep 1971			Edgington *et al.*, 1972b
16 km (10 mi) west at a depth of:				
10 m (BNWL)*		5.78		
10 m (VD)*		5.78		
45 m		6.27		
60 m		5.66		
8 km (5 mi) west at a depth of:				
40 m		5.71		
Surface- and bottom-water samples collected at 6 stations 3.2-8.0 km (2.0-5.0 mi) east of Milwaukee Harbor	Mar 1972	5.0^b		Nienke, 1972
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		4.1	3.8-5.0	
Effluent plume		4.1	4.0-5.0	
South of plant, 4.8 km (3 mi)		4.1	3.8-5.0	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		5.7	4.2-7.0	
North of plant, 1.6 km (1 mi)		6.1	4.2-8.5	

Table 37. (contd.)

Sample Description	Dates	Concentration Na, mg/l		Reference
		Average	Range	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		7.5	5.6-10.0	
South of plant, 1.6 km (1 mi)		8.0	6.0-9.5	

[a] *This author questions whether this sample was outside the River plume.*

[b] *Same value for all samples.*

**BNWL = noncontaminating Niskin water bottle; VD = Van Dorn water bottle.*

USDOI = U. S. Department of the Interior; USGS = U. S. Geological Survey.

were 3.6 to 3.7 mg/l. The Beeton-Moffett data showed no change in sodium concentration with season, nor was there evidence of depth variations. The only anomaly their data (not in Table 37) revealed was higher-than-average (6-7 mg/l) sodium concentrations in Lake Charlevoix, a restricted embayment of Lake Michigan; these higher values can be attributed to the close proximity of Charlevoix and Boyne City.

The U. S. Department of the Interior (1968) measured sodium in 1962-1963. The average value for 321 deep-water samples was 3.9 mg/l, while the 400 inshore samples averaged 4.0 mg/l.

Lawton and Busse (1966) conducted an extensive survey of municipal water distribution systems in Wisconsin in 1964-1965, including a number of systems which draw water from Lake Michigan. Average sodium content was less than 4.7 mg/l except at Oak Creek, South Milwaukee, and Sheboygan. The high values at Oak Creek and South Milwaukee were attributable to sodium discharges from the Milwaukee Harbor and Milwaukee's South Shore sewage treatment plant (*cf.* Beeton and Barker, 1974). Causes for high sodium values at Sheboygan were not described.

Copeland and Ayers (1972) visited 20 stations three times each from August 1969 to June 1970. These stations were located inshore and offshore throughout the Lake. The average sodium concentration at the 12 inshore stations [< 16 km (10 mi)] was 5.2 mg/l, the same as the average at the eight offshore stations. These averages obscure the fact that two stations located along the eastern shore, near Ludington and near Frankfort, were consistently higher than average. The high values near Ludington might be attributable to industrial brine discharges in Ludington; data presented by Copeland and Ayers (1972) neither confirm nor deny this speculation. There is no ready explanation for the high values near Frankfort, unless industrial or municipal sources influenced the concentrations measured at this inshore station. Copeland and Ayers (1972) also found high values (6.0-6.6 mg/l) at a deep-water station midway between Manistique and Charlevoix; no explanation was apparent for such high concentrations in open water.

Industrial Bio-Test (1972a) sampled the Kenosha Water Treatment Plant intake on at least a monthly basis from January 1970 through April 1971. The intake is located in 9.1 m (30 ft) of water 1372 m (4500 ft) from shore.

Figure 75 shows variations of sodium and chloride concentrations over this 16-month period. The changes with season are obvious; in winter, both sodium and chloride are high, while in summer they are low. Thus, one infers that NaCl is responsible for these changes. It is instructive to formulate Na:Cl ratios using these data. In the salt molecule, NaCl, sodium comprises 39.5% of the total mass; the Na:Cl ratio is 0.648. From January to August 1970, the Na:Cl ratios in Figure 75 are between 0.58 and 0.70, close enough to 0.648 that one can attribute virtually all of the sodium to the input of NaCl. From September 1970 to April 1971, the ratio decreased. This decrease is not related to use of $CaCl_2$ as an alternative deicer, for Kenosha has always used a negligible quantity of calcium chloride in any year (Holland, 1975--personal communication). Thus, some other as-yet-unidentified source boosted the chloride content without affecting the sodium concentration proportionately. Considering the proximity of the municipal water intake pipe to Kenosha, winter increase in sodium could easily be a result of the influence of the city, specifically, the use of NaCl for street deicing in winter.

Baumeister (1972) collected single grab samples from water intakes at Kenosha, Racine, Milwaukee, Port Washington, Sheboygan, Two Rivers, and Green Bay within the period of January to June 1971 (Baumeister, 1973--personal

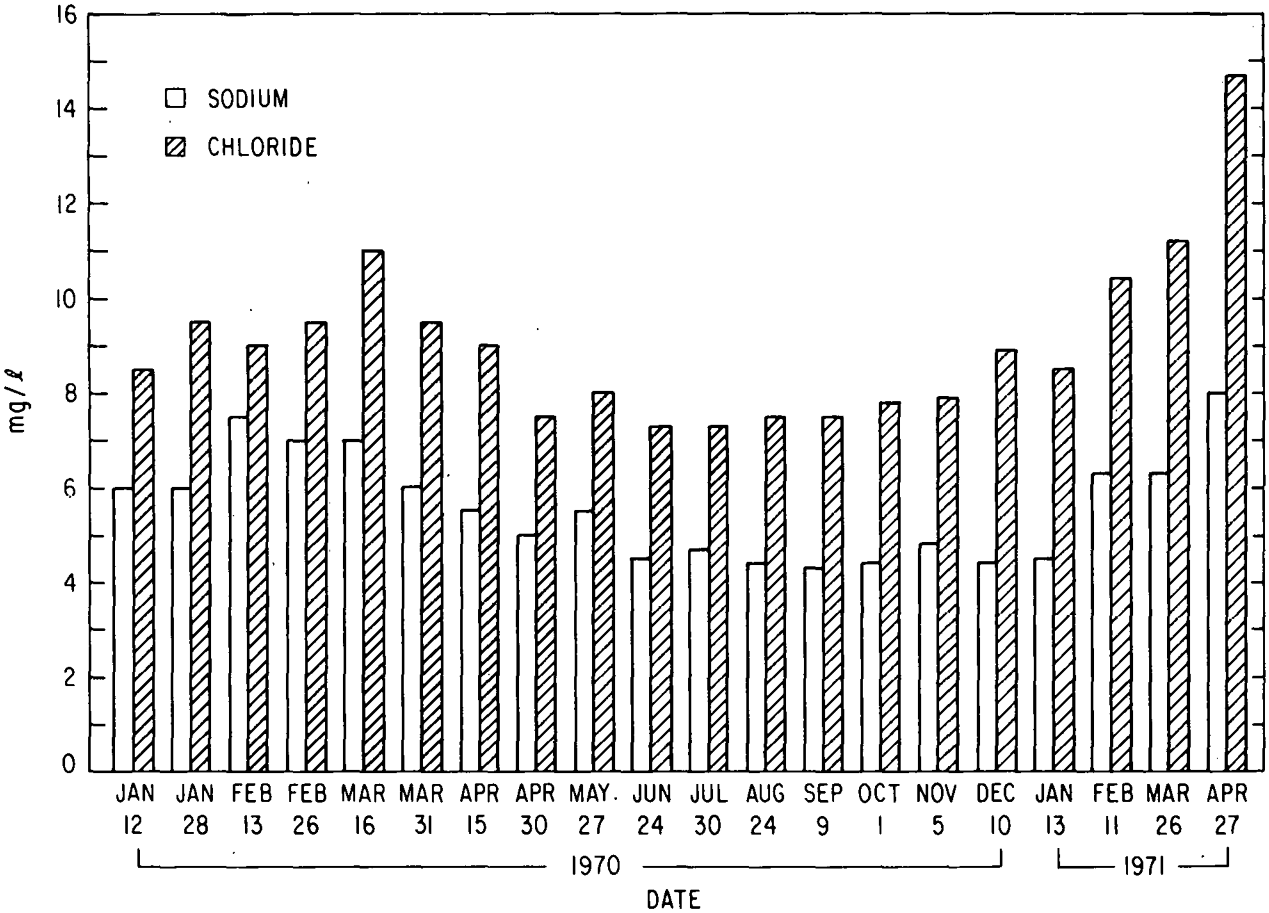


Fig. 75. Variation of Sodium and Chloride Concentrations at Kenosha Water Treatment Plant. Data from Industrial Bio-Test (1972a).

communication). Data for these intakes (Table 37) do not demonstrate widespread differences. Rather, these numbers probably represent conditions extremely close to shore, where human influence is most pronounced. While the locations of the intakes were not recorded, higher sodium concentrations, as recorded by Baumeister (1972), are likely correlated with the proximity of the intake to shore.

Figure 76 summarizes sodium concentration data over the past 15 years, as detailed in Table 37. One readily sees the higher concentration of sodium close to the western shore, from the area of the Lakeside Power Plant (on the south side of Milwaukee) to the Chicago area. Human influences likely are responsible for these high concentrations. One also notes that most of the sodium data have been collected inshore; knowledge of sodium content in the offshore waters is much less.

No recommendations for limitation of sodium in drinking water have been made by the U. S. Public Health Service (1962), the National Academy of Sciences ... (1973), or the EPA (1975b) (Appendix B, part 1). Nor have criteria been set for the protection of aquatic life (Appendix B, part 2).

Sodium has been determined with fair frequency in Lake Michigan sediments in conjunction with other studies of elemental composition. Data on sodium concentrations in surficial (≤ 5 cm) sediments are compiled in Figure 77. Sodium content is higher (5-6 mg/g dry weight) in the western area from Door County, Wisconsin, to Waukegan than in the rest of the Lake (≤ 4 mg/g dry weight). In addition, from Milwaukee south to the Waukegan area, higher sodium values are found in the surficial brown silt facies of the geologic unit termed the Waukegan member (Lineback and Gross, 1972). The sediment in the brown silt facies contains more clay than the gray silt facies along the eastern shore; this fact is probably at least one reason sodium is higher along the western shore, for sodium ion is frequently found associated with clay minerals (*cf*. Stumm and Morgan, 1970). In addition, the outcrop of Silurian rock, containing higher sodium, along the western shore of Lake Michigan, may contribute to the higher sodium values in sediments along the western shore.

Robbins and Edgington (1974) measured acid-extractable sodium (*ca*. total sodium) in nine shallow (20-cm) cores taken on a transect off Grand Haven (Fig. 78). There was little variation of sodium with depth in the cores, but sodium content increased with distance from shore; the authors speculated that the latter observation was due to an increase in clay content in sediments farther from shore.

In contrast, Callender (1969) and Shimp *et al.* (1970) occasionally found increases in sedimentary sodium content in southern Lake Michigan at depths exceeding 30 cm. These higher values were found at depths that correspond to the Winnetka member (Lineback *et al.*, 1970). Sodium content also increased markedly with depth in a core (Shimp *et al.*, 1970) which penetrated the Sheboygan member, the layer below the Winnetka member.

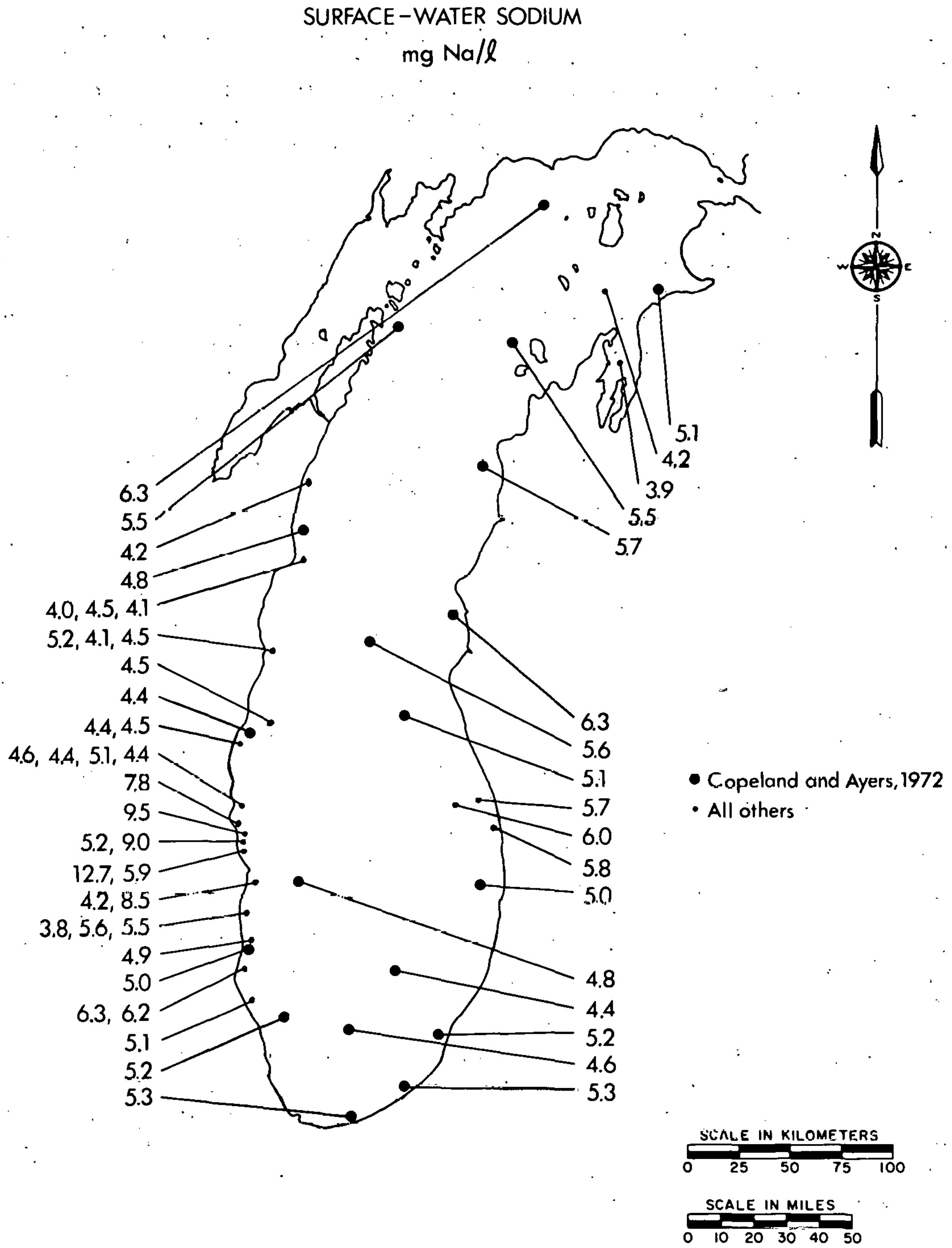


Fig. 76. Surface-Water Sodium Concentrations over a Period of Fifteen Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 37.

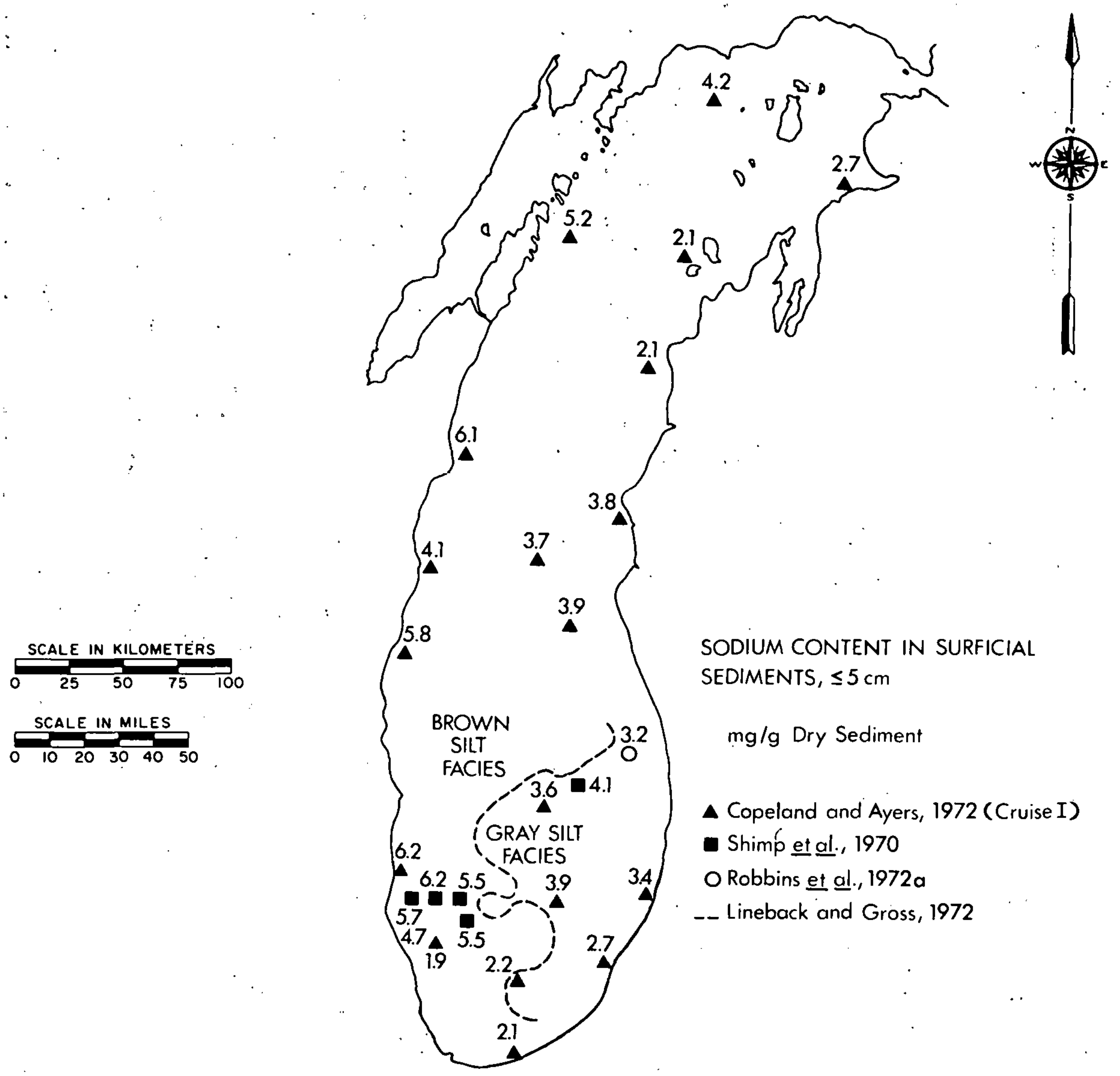


Fig. 77. Sodium Content in Surficial Sediments of Southern Lake Michigan. Data from Copeland and Ayers (1972), Shimp *et al.* (1970), and Robbins *et al.* (1972a). Boundary of brown and gray silt facies of the Waukegan member from Lineback and Gross (1972).

POTASSIUM

The ion, K^+, is a cofactor of a number of enzymes; potassium is required by all organisms (Bowen, 1966; Healey, 1973). It plays an important role in the active transport process within cytoplasm, where K^+ is many times enriched. If injected intravenously, potassium is moderately toxic to mammals (Bowen, 1966); otherwise, it is relatively harmless. Potassium is cathartic (1-2 g) to humans (McKee and Wolf, 1963). With the exception of one publication (a 1939 paper) which reported sticklebacks were killed by a ten-day exposure to 50 mg KNO_3/l (= 19.3 mg K/l), all the papers listed by Kemp *et al.* (1971)

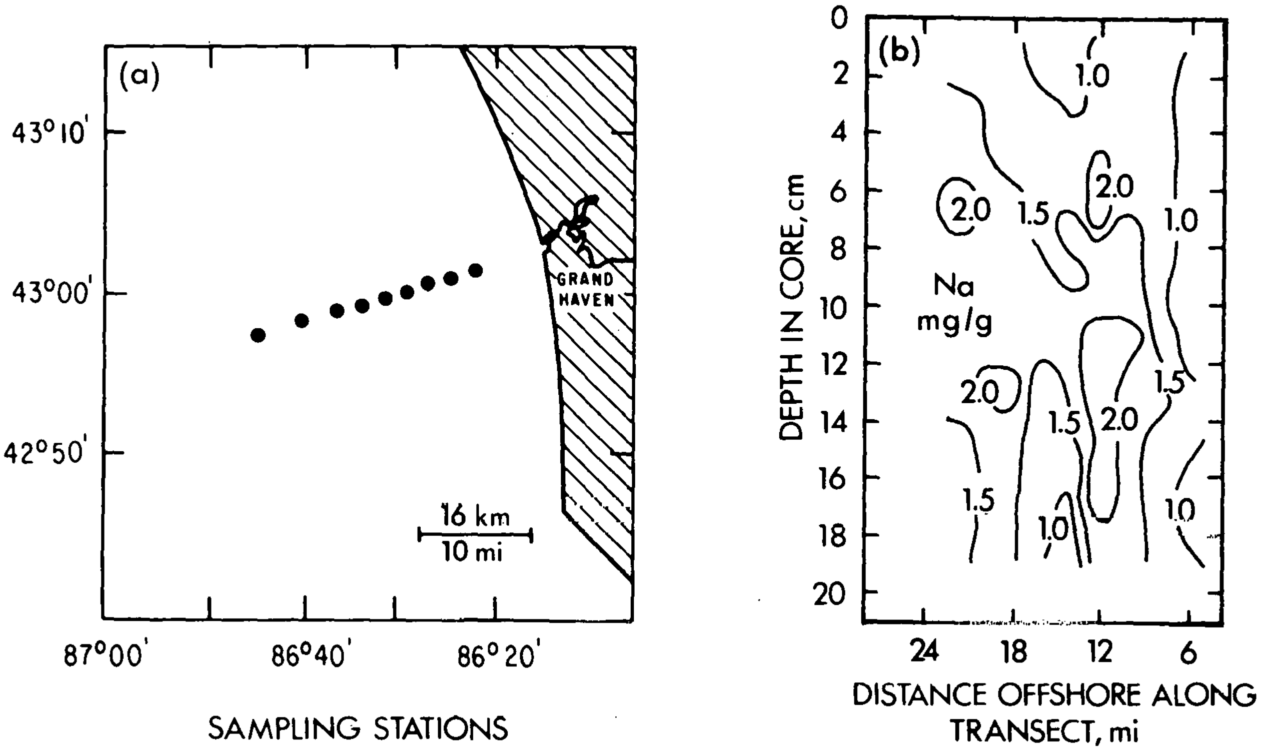


Fig. 78. Sodium Content in Cores Collected off Grand Haven, October 1971. (a) Location of sampling stations; (b) concentration of sodium (mg/g dry weight acid-soluble sediment). Modified from Robbins and Edgington (1974).

reported no toxicity of potassium to aquatic organisms at levels below 200 mg K/l with respect to KNO_3, KOH, K_2SO_4, or KCl.

Primary sources of potassium to Lake Michigan are possibly natural. Potassium averages 20.9 mg/g in igneous rock, 26.6 mg/g in shales, 10.7 mg/g in sandstones, and only 2.7 mg/g in limestones (Bowen, 1966). Sodium and potassium have a number of similar chemical characteristics (Hem, 1959). However, potassium recombines readily with other products of weathering, especially with clay minerals, while sodium remains in solution. This difference accounts for the higher potassium content in shales than in igneous rock. The low potassium content of limestones, prevalent in the Lake Michigan watershed, combined with the tendency of potassium not to stay in solution, probably determine the relatively low concentrations of potassium in the Lake.

Since sodium salts were reported to be less expensive than potassium salts (McKee and Wolf, 1963), sodium salts were more frequently used in industry. Potassium salts must be used, however, in potassium fertilizers and some varieties of glass. Other sources of potassium are: potassium chloride in brines from oil wells and other industrial wastes, and potassium ferri- and ferrocyanides used in electroplating and textile processing. On the average, potassium content increases 10 mg K/l from tap water to secondary effluent in municipal waste waters throughout the United States (Weinberger *et al.*, 1966).

Reports on potassium concentrations in Lake Michigan waters over the past 15 years are summarized in Table 38 and illustrated in Figure 79. Experimental methods did not always indicate if samples were filtered prior to analysis. Distinctions are made, where possible, between soluble and particulate potassium concentrations (Table 38). Robbins *et al.* (1972a) showed extractable particulate potassium concentrations, at stations outside the Grand River plume, were 1-3% of the dissolved potassium content. Within the plume, extractable particulate potassium was as much as 6% of the dissolved potassium value. It seems, under certain conditions in the nearshore area, that particulate potassium concentrations may contribute a measurable portion of the total potassium content.

There are no geographic trends evident in potassium concentrations in Table 38 or Figure 79. Concentrations reported by Copeland and Ayers (1972) are ≥ 50% higher than other values in Table 38. A positive error in their procedures may have caused this increase, *i.e.* according to APHA *et al.* (1971) soft-glass containers leach potassium; samples were filtered in a glass apparatus (Copeland and Ayers, 1972). Also, water samples were collected often only after several hours on station, increasing the potential for contamination.

Statistical analysis of data from 1960 and 1961 (Beeton and Moffett, 1964) reveals no significant difference in potassium concentrations with depth or with distance from shore, either in the southern basin or in the northern basin. The 20 stations sampled by Copeland and Ayers (1972) also show no inshore-offshore differences.

In inshore areas there is a slight variation in potassium concentrations with season (Fig. 80). The greatest ranges in concentration were recorded less than 710 m (2000 ft) from shore in the vicinity of the Point Beach Nuclear Plant and Oak Creek Power Plant, Wisconsin (Fig. 80a, b). The least variation occurred at the North Chicago Water Treatment Plant, which mixes water from intakes at 1981 m (6500 ft) and 366 m (1200 ft) from shore (Fig. 80f). Changes at stations near shore are likely caused by inshore hydrodynamic processes that increase potassium concentrations, such as tributary input and wave action stirring up interstitial water containing potassium. Seasonal variations have not been reported for offshore stations.

The U. S. Public Health Service (1962), the National Academy of Sciences ... (1973), and the Environmental Protection Agency (1975b) have not suggested limiting potassium in drinking water. Nor has the Academy made any comment on potassium concentrations with respect to aquatic life. According to a review by Kemp *et al.* (1971), potassium concentrations in Lake Michigan water are harmless to the organisms living there.

Only Copeland and Ayers (1972) and Shimp *et al.* (1970) have reported potassium analyses of bulk sediments. Considering the data of Copeland and Ayers, potassium content in surficial sediments of the southern basin (Fig. 81) seems to be slightly higher along the eastern shore in the gray silt facies of the Waukegan member, described by Lineback and Gross (1972). In contrast, sodium in bulk sediments was lower along the eastern shore of the southern basin (see Sodium section). Copeland and Ayers (1972) were unable to document trends in the divide area and the northern basin. Data reported by Shimp *et al.* (1970) do not agree with those of Copeland and Ayers. Perhaps this is due to sampling different environments or using different methods.

Table 38. Potassium Content in Lake Michigan Water

		Concentration K, mg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
76 samples collected, surface to bottom, at 3 inshore and 1 offshore stations in southern basin	Apr-Nov 1960	0.9	0.8-1.3	Beeton and Moffett, 1964
Inshore and offshore samples collected in northern basin:	May-Nov 1961			Beeton and Moffett, 1964
48 surface-water samples		1.1	0.7-1.6	
73 bottom-water samples		1.0	0.6-1.8	
Whole Lake:	1962-63			USDOI, 1968
325 offshore samples		1.1	0.4-2.0	
453 inshore samples		1.2	0.5-3.8	
Samples collected:	1962-63			USDOI, 1968
Indiana Harbor, 20 samples		2.6	1.8-3.8	
Calumet Harbor, 20 samples		1.6	1.1-2.0	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City		1.0	0.1-9.5	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo		0.9	0.6-1.3	
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor		1.1	0.4-1.4	
On a line roughly between Sheboygan and Little Sable Point		1.0	0.6-1.6	
Samples collected:	22-28 Jul 1964			USDOI, 1968
Traverse Bay, 51 samples		1.2	1.0-1.6	
Adjacent to Traverse Bay, 15 samples		1.2	1.0-1.3	
Surface-water samples collected throughout Lake at stations sampled 3 times each:	Aug 1969-Jun 1970			Copeland and Ayers, 1972
12 inshore stations		1.6[a]	0.6-2.0[a]	
8 offshore stations		1.7[a]	1.4-2.5[a]	
Samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore:				
4 samples	Dec 1969; Jan, Jun 1970	1.2	1.0-1.2	USGS, 1972
3 samples	Dec 1970, Jun 1971	1.2	1.1-1.3	USGS, 1973
3 samples	Dec 1971, Jun 1972	1.0	0.8-1.2	USGS, 1974a
Samples collected ~monthly at intakes:	Jan 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		1.1	0.9-1.6	
Waukegan Generating Station		1.3	1.0-2.6	
North Chicago public water supply		1.1	0.9-1.3	
Samples collected ~monthly, surface to bottom, at 3 stations 9.6 km (6 mi) east of Zion	Apr-Oct 1970	1.0	0.9-1.2	Industrial Bio-Test, 1972b
Monthly samples collected at Lake County, Ill., public water intake	Jun 1970-Apr 1971, Jul 1972-Jun 1973	1.3	0.9-2.2	Howe, 1973
Single samples collected northwest of Grand River entrance, outside River plume	6 Oct 1970			Robbins *et al.*, 1972a
A station 1.0 km (0.62 mi) NW:				
Surface-water, soluble potassium		1.5		

Table 38. (contd.)

Sample Description	Dates	Concentration K, mg/l		Reference
		Average	Range	
Bottom-water, soluble potassium		1.7		
Surface-water, extractable particulate potassium		0.022		
Bottom-water, extractable particulate potassium		0.018		
A station 1.25 km (0.78 mi) NW:				
Bottom-water, soluble potassium		3.1[b]		
Bottom-water, extractable particulate potassium		0.081[b]		
Samples (3 replicate analyses) collected off Grand Haven	13-14 Sep 1971			Edgington *et al.*, 1972b
16 km (10 mi) west at a depth of:				
10 m (BNWL)*		1.15		
10 m (VD)*		0.97		
45 m		1.03		
60 m		0.96		
8 km (5 mi) west at a depth of:				
40 m		1.01		
Single sample collected offshore from Grand Haven	Unspecified	≤3.0[a]		Wahlgren *et al.*, 1972b
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		1.5	1.0-3.0	
Effluent plume		1.3	1.0-2.0	
South of plant, 4.8 km (3 mi)		1.4	1.0-2.0	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		1.8	1.0-3.0	
North of plant, 1.6 km (1 mi)		2.1	1.2-3.0	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		1.89	1.40-2.00	
South of plant, 1.6 km (1 mi)		1.93	1.50-2.15	

[a] *Soluble potassium.*

[b] *This author questions whether this sample was outside the River plume.*

**BNWL = noncontaminating Niskin water bottle; VD = Van Dorn water bottle.*

USDOI = U. S. Department of the Interior; USGS = U. S. Geological Survey.

Callender (1969) investigated the potassium content of the interstitial water in a number of sediment cores. In surfical sediments of the gray silt facies (Lineback and Gross, 1972) of the southern basin, interstitial potassium content averaged 2.7 mg K/l (n = 7), while potassium was 2.8 mg K/l (n = 7) in the brown silt facies. In the divide area, the northern basin, and Green Bay, interstitial potassium concentrations in surficial sediments averaged 2.0 mg K/l. In all cases, interstitial potassium concentrations were higher than the overlying water (*ca.* 1 mg K/l, *cf.* Table 38). Within sediment cores, interstitial potassium concentrations did not change appreciably between the surface and a depth of 1 m.

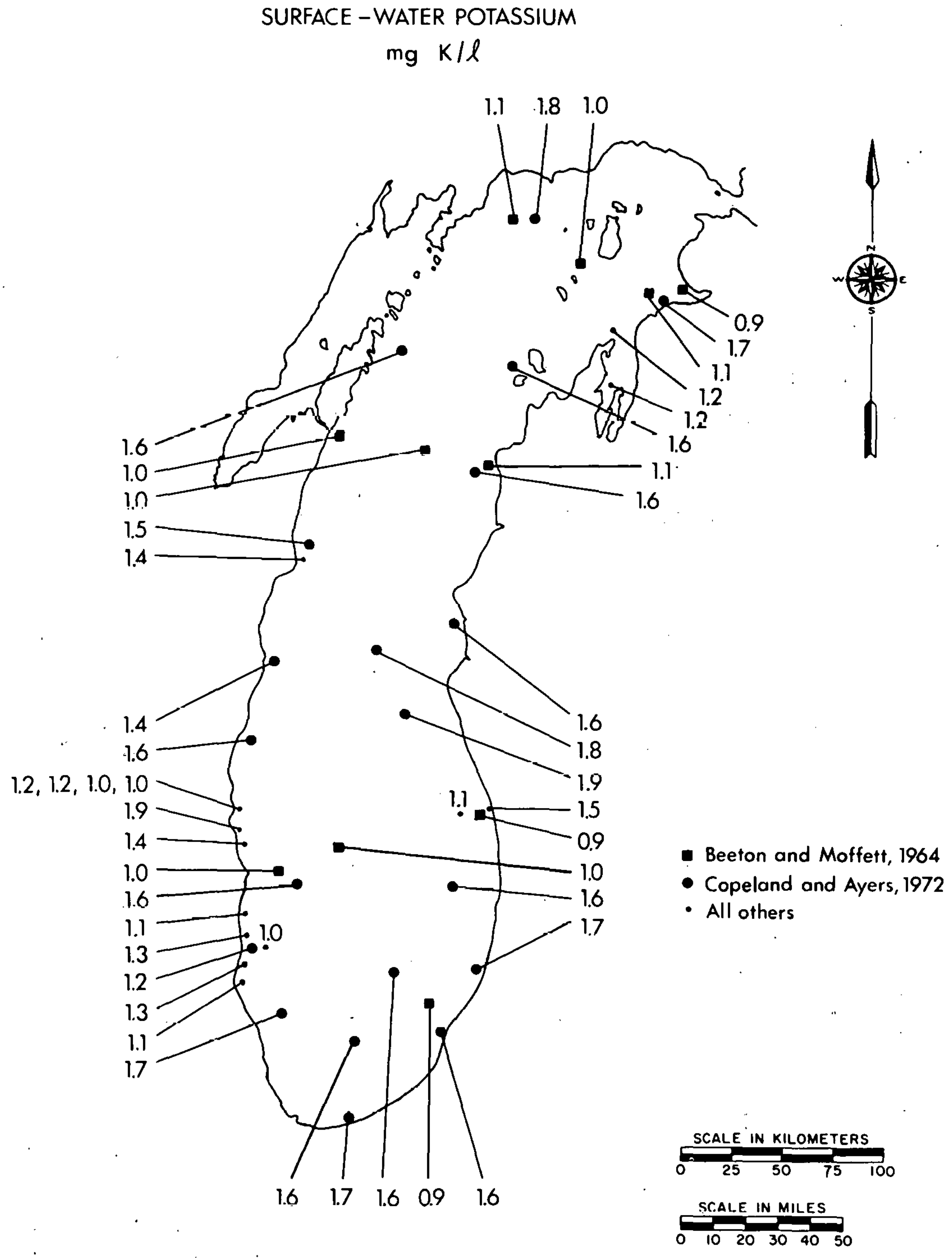


Fig. 79. Surface-Water Potassium Concentrations over a Period of Fifteen Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 38.

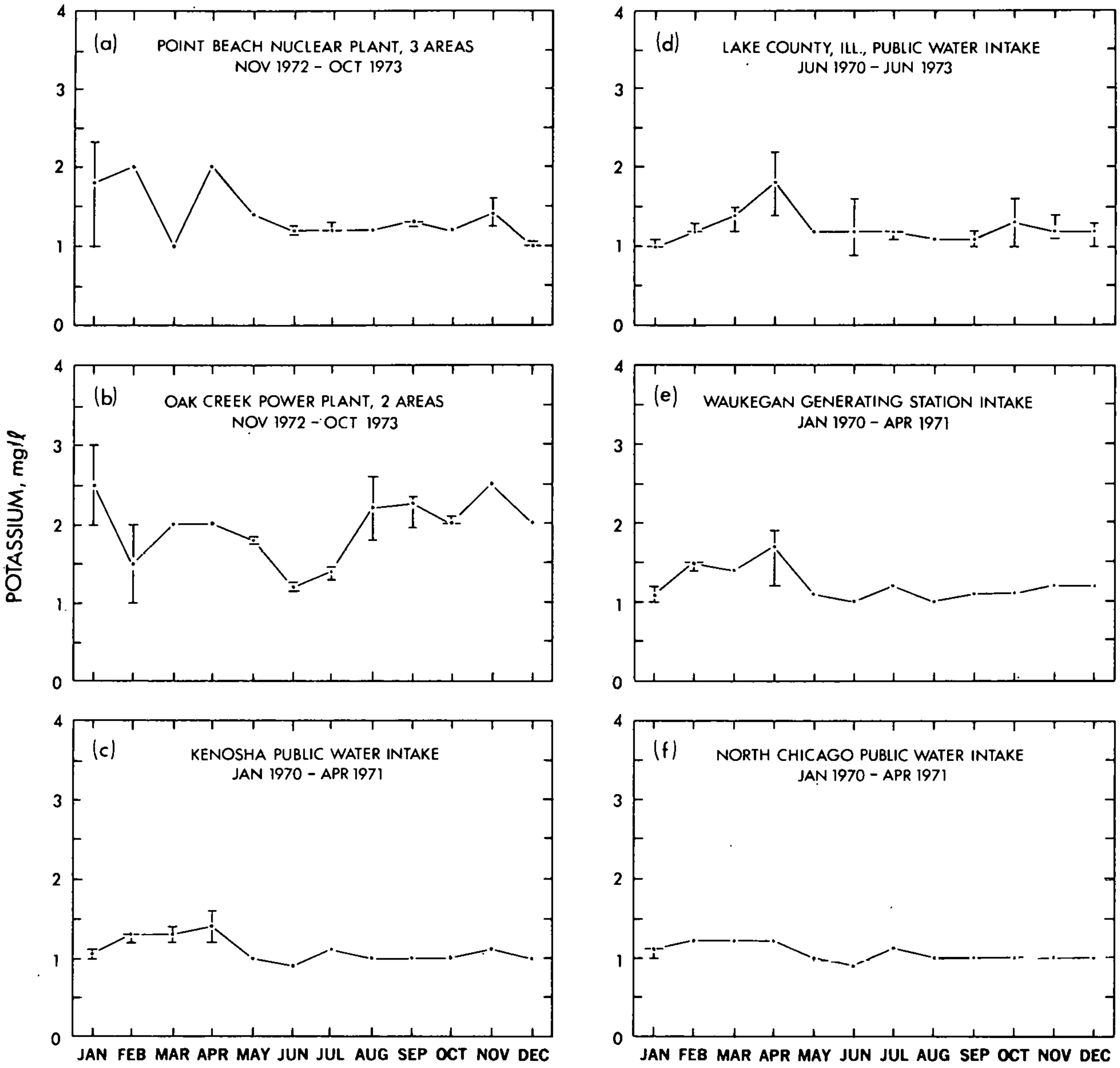


Fig. 80. Seasonal Variations in Average Potassium Concentrations Along the Western Shore of Lake Michigan. Distance from shore and depth, if given: (a) 710 m (2000 ft) from shore; (b) 710 m (2000 ft) from shore; (c) 1372 m (4500 ft) from shore, 9.1 m (30 ft) deep; (d) 823 m (2700 ft) from shore, 9.1 m (30 ft) deep; (e) intake canal; (f) mixed water from intakes 1981 m (6500 ft) and 366 m (1200 ft) from shore, 5.5 m (18 ft) and 9.1 m (30 ft) deep, respectively. Sources of data: (a,b) Limnetics, 1974; (c,e,f) Industrial Bio-Test, 1972a; (d) Howe, 1973--personal communication.

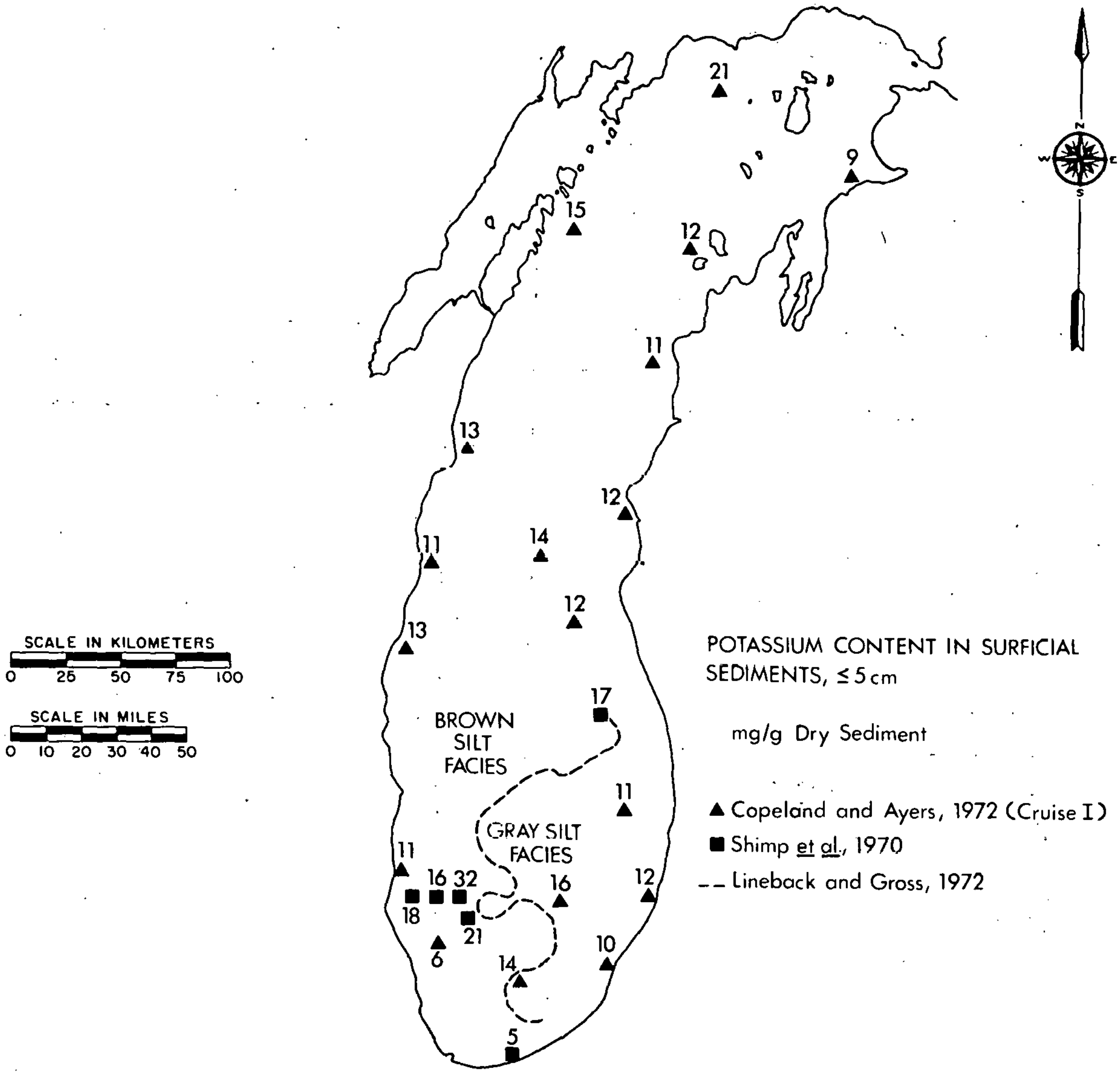


Fig. 81. Potassium Content in Surficial Sediments of Southern Lake Michigan. Data from Copeland and Ayers (1972) and Shimp *et al.* (1970). Boundary of brown and gray silt facies of the Waukegan member from Lineback and Gross (1972).

Robbins and Edgington (1974) treated sediment samples with acid and reported their results as mg potassium per gram sediment soluble in acid. Their experimental methods likely encompassed all interstitial potassium plus an unknown proportion of the potassium associated with feldspars, 7-15% of dry weight, and clays, 3-10% of dry weight (Callender, 1969). Acid-soluble potassium content was generally uniform (Robbins and Edgington, 1974) to 20 cm in nine cores taken off Grand Haven (Fig. 82). However, there was a notable increase in acid-soluble potassium content with distance from shore. They thought this was due to increased clay content in sediments farther from shore. No measurements of clay content in their samples were presented.

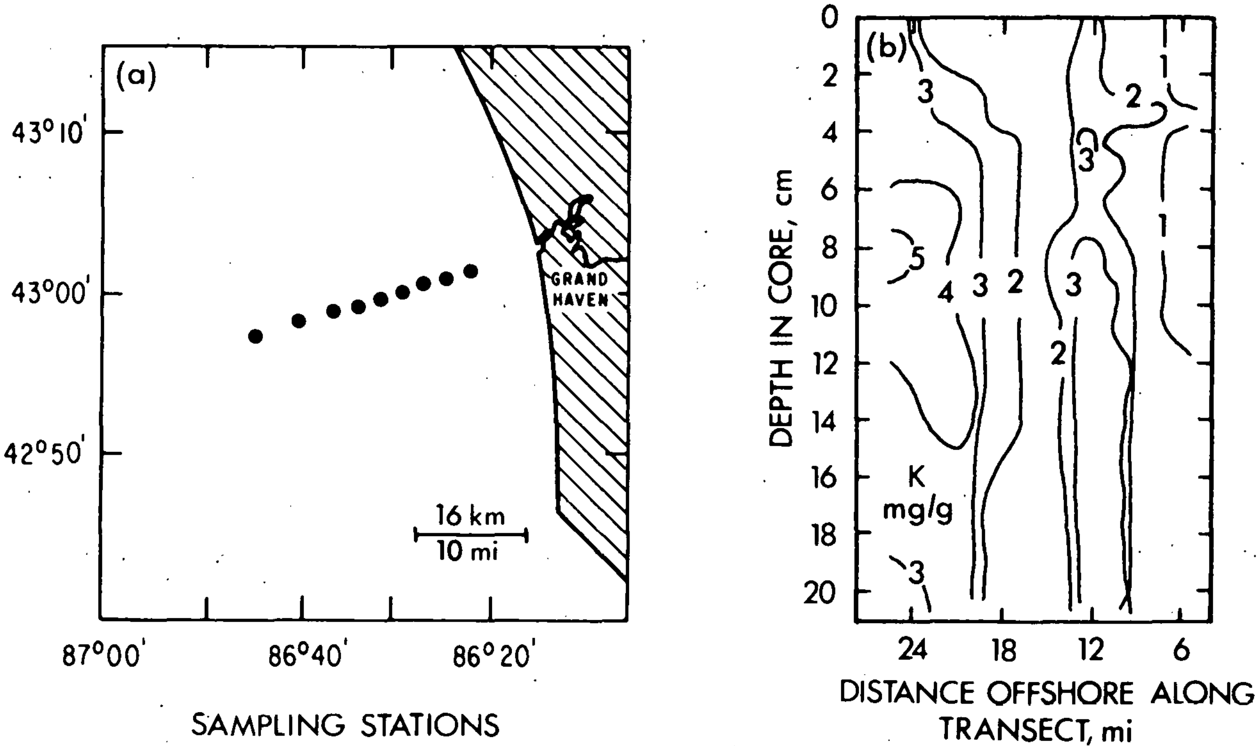


Fig. 82. Potassium Content in Cores Collected off Grand Haven, October 1971. (a) Location of sampling stations; (b) concentration of potassium (mg/g dry weight acid-soluble sediment). Modified from Robbins and Edgington (1974).

CALCIUM AND MAGNESIUM

The major components of water hardness are calcium and magnesium ions. Some researchers have reported hardness only, while others have analyzed specifically for calcium and magnesium. Calcium, magnesium, and hardness are considered individually here because of the nonuniformity in reporting these substances.

Calcium

Calcium helps maintain the structure of plant cells and is found in calcareous tissues, such as mollusk shells, and bones of vertebrates (Bowen, 1966). Within cells, calcium functions electrochemically, and it activates several enzymes, *e.g.* cholinesterase.

Optimal calcium concentrations for growth of freshwater blue-green algae have been reported from 0.25 to more than 10 mg Ca/l (Gerloff *et al.*, 1950, 1952; Kratz and Myers, 1955). Adult humans require 0.7-2.0 g Ca/day, an amount considerably larger than could be consumed even by drinking normal quantities of hard water (McKee and Wolf, 1963).

High concentrations of calcium are relatively harmless to all organisms. Indeed, calcium reduces the toxicity of many chemicals to fish and other aquatic animals, *e.g.* lead and zinc (McKee and Wolf, 1963). Calcium salts have not been reported to be lethal at concentrations less than 300 mg Ca/l.

Natural sources are important in maintaining the calcium content of Lake Michigan. Most of the watershed of the Lake is covered by extensive sedimentary carbonate deposits, containing both calcite, $CaCO_3$, and dolomite, $CaMg(CO_3)_2$. Calcium is also found in geologic formations containing apatite. Weathering and erosion leads to dissolution of these calcium-containing minerals:

$$CaCO_3 + H_2O \rightleftharpoons Ca^{2+} + OH^- + HCO_3^- \ , \tag{27}$$

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca^{2+} + 2\ HCO_3^- \ , \tag{28}$$

$$CaMg(CO_3)_2 \overset{H_2O}{\rightleftharpoons} Ca^{2+} + Mg^{2+} + 2\ CO_3^{2-} \ , \text{ and} \tag{29}$$

$$Ca_{10}(OH)_2(PO_4)_6 \overset{H_2O}{\rightleftharpoons} 10\ Ca^{2+} + 2\ OH^- + 6\ PO_4^{3-} \ . \tag{30}$$

These processes aid removal of particulate calcium to the Lake and its tributaries. Similar reactions occur in groundwater aquifers and result in movement of calcium-laden water into baseflow of tributaries and directly into the Lake.

Industrial and cultural activities also add calcium to the Lake. Calcium chloride, $CaCl_2$, enters the Lake via wastes from brewing (McKee and Wolf, 1963), surface runoff from roads treated with deicing agents, and wastes from bromine and salt works. Slaked lime, $Ca(OH)_2$, is added from tanneries, canneries, chemical and paint plants, glue manufacturing, and numerous other industrial processes. Gypsum, $CaSO_4$, is used in paper manufacture. Upchurch (1972) estimated that cultural factors contribute 12% of the calcium entering Lake Michigan; natural factors are responsible for the remaining 88%.

Measurements of calcium in Lake Michigan are surveyed in Tables 39 and 40 and depicted in Figure 83. In some publications it was not possible to determine whether samples were filtered prior to analysis. Where possible, distinctions are made between soluble and particulate calcium concentrations (Table 39). Considering the low particulate calcium concentrations found by Robbins *et al.* (1972a), one infers soluble calcium concentrations may approximate total calcium values (depending upon sample location and date).

No clear geographic trends in calcium content are evident, either north-to-south or east-to-west (Fig. 83). Powers and Ayers (1967) suggested that calcium levels are somewhat higher on the eastern side of the Lake, around Grand Haven, than in the Milwaukee and Chicago regions.

The most extensive study of calcium in Lake Michigan was conducted by Beeton and Moffett (1964), during 1954-1955 and 1960-1961 (Fig. 84). Sampling sites were primarily in the southern basin in 1954 and 1960, with fewer samples in the divide area. In 1955 and 1961, samples were mostly from the northern basin, with some from the divide area. In the southern basin, inshore surface-water concentrations were significantly less than bottom-water concentrations in 1954 and 1960 (Table 40). Inshore surface-water samples exceeded offshore values in 1954, but there was no difference in 1960. In the northern basin there were no differences in calcium concentrations with depth or with distance from shore in either 1955 or 1961.

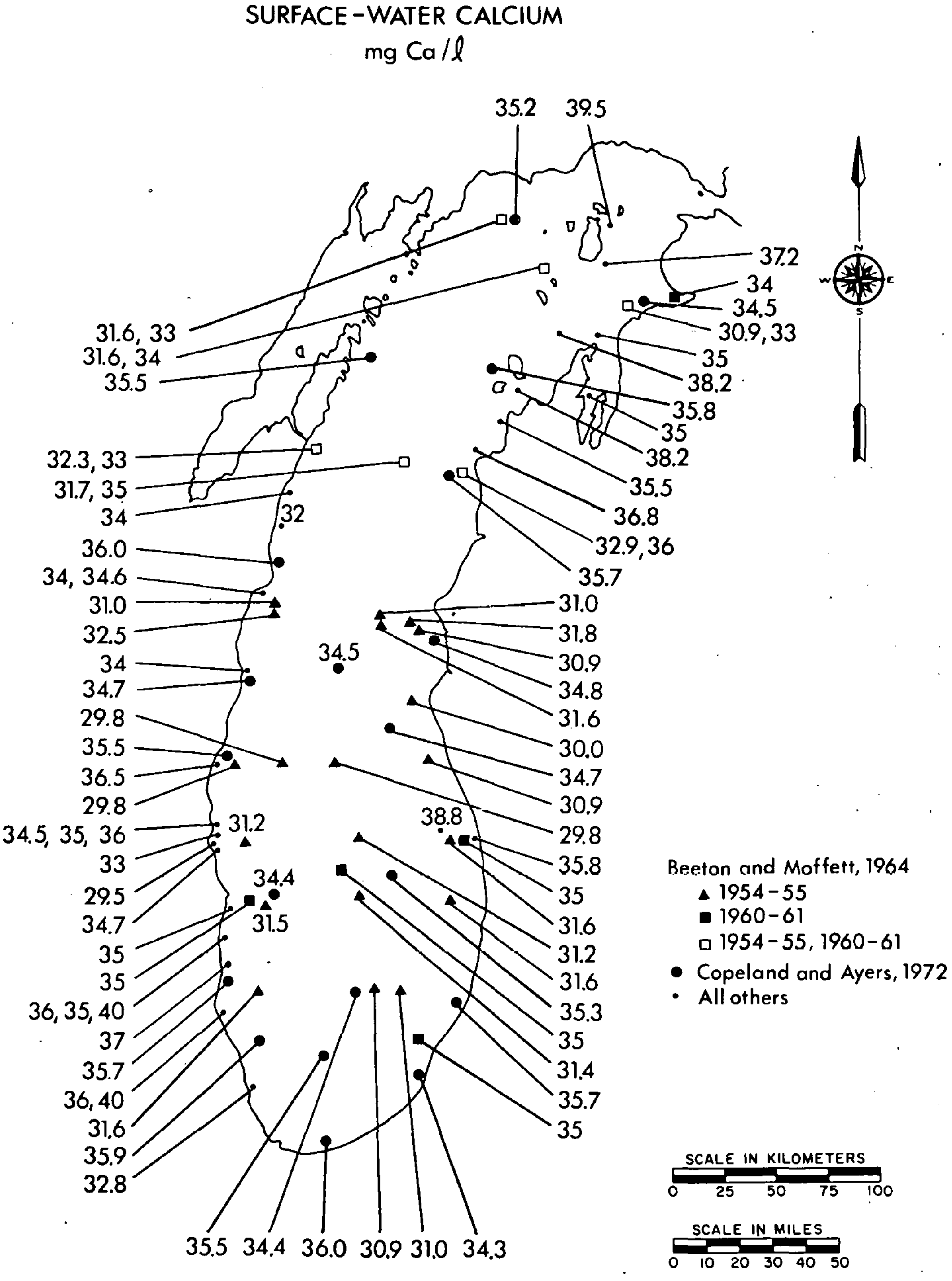


Fig. 83. Surface-Water Calcium Concentrations over a Period of Twenty Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 39.

Table 39. Calcium Content in Lake Michigan Water

Sample Description	Dates	Concentration Ca, mg/l Average	Range	Reference
Annual median values at public water intakes:				Powers and Ayers, 1967
Chicago (6 intakes)	1926-62	32.8	28.5-35.8	
Milwaukee	1939-62	34.5	33.0-35.2	
Grand Rapids	1941-61	35.8	31.9-37.1	
Whole Lake:	1962-63			USDOI, 1968
395 offshore samples		33	25-40	
616 inshore samples.		35	17-40	
Samples collected:	1962-63			USDOI, 1968
Indiana Harbor, 23 samples		40	37-43	
Calumet Harbor, 20 samples		35	34-37	
Chicago Harbor, 6 samples		32	31-33	
Racine Harbor, 7 samples		34	33-34	
Samples collected:	Oct 1962, Jun 1963			USDOI, 1968
Milwaukee Harbor, 23 samples		39	32-45	
Adjacent to Milwaukee Harbor, 46 samples		33	32-44	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City		34	31-40	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo		33	25-40	
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor		33	24-39	
On a line roughly between Sheboygan and Little Sable Point		33	30-36	
Samples collected:	22-28 Jul 1964			USDOI, 1968
Traverse Bay, 72 samples		35	26-43	
Adjacent to Traverse Bay, 29 samples		35	30-38	
Surface-water samples collected at stations throughout Lake, sampled 3 times each:	Aug 1969-Jun 1970			Copeland and Ayers, 1972
12 inshore stations		35.4[a]	34.3-36.0[a]	
8 offshore stations		35.0[a]	34.4-35.8[a]	
3 samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	15 Dec 1969; 5, 12 Jan 1970	35	34-35	USGS, 1972
17 samples collected, surface to bottom, at 6 stations on line passing east of Manitou Islands from Frankfort to Beaver Island	7 Jul 1970	37.4[a]	34.5-40.0[a]	Schelske and Roth, 1973
Monthly samples collected at intakes:	Sep 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		36	34-40	
Waukegan Generating Station		38	34-44	
North Chicago public water supply		36	31-39	
Monthly samples collected at Lake County, Ill., public water intake	Sep 1970-Jun 1973	37	33-51	Howe, 1973
Single samples collected northwest of Grand River entrance, outside River plume	6 Oct 1970			Robbins *et al.*, 1972a
A station 1.0 km (0.62 mi) NW:				
Surface-water, soluble calcium		35.4		

Table 39. (contd.)

Sample Description	Dates	Concentration Ca, mg/l		Reference
		Average	Range	
Bottom-water, soluble calcium		37.6		
Surface-water, extractable particulate calcium		0.022		
Bottom-water, extractable particulate calcium		0.018		
A station 1.25 km (0.78 mi) NW:				
Bottom-water, soluble calcium		61.6[b]		
Bottom-water, extractable particulate calcium		0.069[b]		
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		34		
Kenosha		35		
Milwaukee (5 intakes)		36	34-37	
Port Washington		36.5		
Racine		35		
Sheboygan		34		
Two Rivers		34		
Samples (3 replicate analyses) collected off Grand Haven	13-14 Sep 1971			Edgington *et al.*, 1972b
16 km (10 mi) west at a depth of:				
10 m (BNWL)*		40.4		
10 m (VD)*		37.1		
45 m		45.3		
60 m		44.7		
8 km (5 mi) west at a depth of:				
40 m		39.8		
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers—3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		34.7	30.0-39.0	
Effluent plume		34.7	30.0-38.0	
South of plant, 4.8 km (3 mi)		34.4	30.0-39.0	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee—2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		34.1	21.0-39.0	
North of plant, 1.6 km (1 mi)		35.3	22.0-40.0	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis—2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		29.5	15.0-39.5	
South of plant, 1.6 km (1 mi)		29.5	15.0-39.5	

[a] *Soluble calcium.*

[b] *This author questions whether this sample was outside the River plume.*

**BNWL = noncontaminating Niskin water bottle; VD = Van Dorn water bottle.*

USDOI = U. S. Department of the Interior; USGS = U. S. Geological Survey.

Table 40. Analysis of Raw Calcium Data Published by Beeton and Moffett (1964)

	Inshore, <16 km from shore Ca, mg/l ± one S.D.			*Offshore, >16 km from shore Ca, mg/l ± one S.D.*		
Year	*Number of Observations*	*Surface (≤15m)*	*Bottom (≥25m)*	*Number of Observations*	*Surface (≤15m)*	*Bottom (≥25m)*
1954	202	31.4±0.7		258	31.1±0.7	
	156		31.6±0.6	158		31.3±0.7
1955	235	31.8±2.2		194	31.8±2.0	
	104		32.0±1.9	73		32.1±2.1
1960	32	35±2		5	35±1	
	31		36±1	8		33±4
1961	34	33±3		14	34±3	
	65		34±3	25		34±3

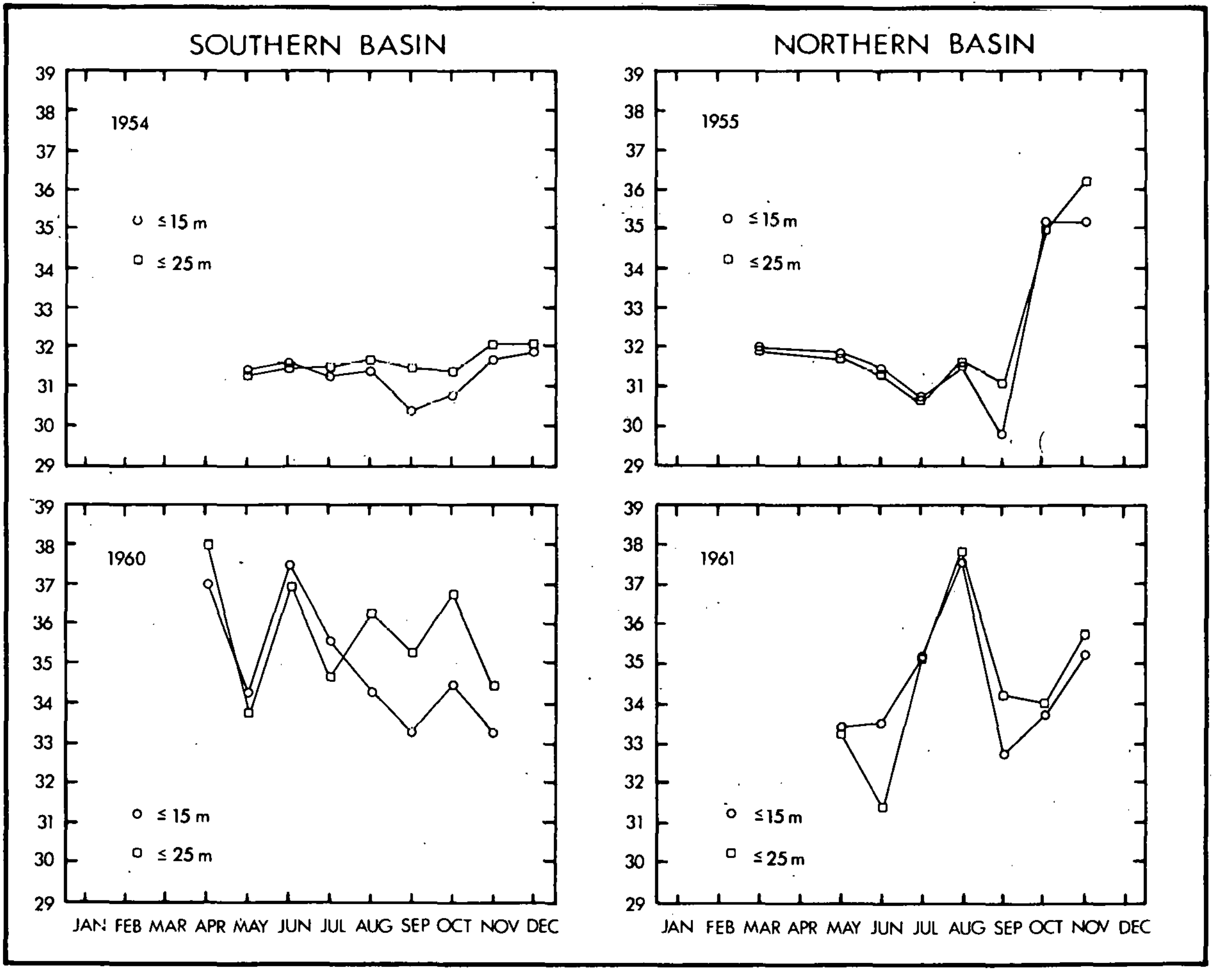


Fig. 84. Average Monthly Calcium Concentrations in Northern and Southern Basins during 1954 and 1960. Data from Beeton and Moffett (1964).

To explain some of the significant differences between surface- and bottom-water calcium concentrations, one must understand the chemical behavior of calcium in Lake Michigan. Concentrations of calcium are so large (30-40 mg/l) that biological uptake cannot alter the content of soluble calcium appreciably. Inorganic chemical reactions of calcium with carbonate and bicarbonate ions are likely to be directly responsible for changes in calcium concentrations (see section on pH, CO_2, Alkalinity, and the Carbonate System). However, for parts of the year these reactions may be influenced by photoplankton activities.

Unlike most inorganic salts, calcite is less soluble at higher temperatures than at lower temperatures. In addition to this effect, the solubility of $CaCO_3$ in natural water decreases at higher temperatures because CO_2 is less soluble in hot water than in cold water. If both calcium and carbonate are present in sufficient amounts, then total calcium concentrations will decrease in the surface water during summer, due to precipitation of $CaCO_3$. One would expect the calcium concentration to increase in the bottom water, since precipitated calcite would redissolve at the colder temperatures and higher CO_2 concentrations (Fig. 35) of the hypolimnion. Kramer (1967) estimated that, under conditions of constant atmospheric pressure and constant CO_2 content, the waters of the Great Lakes are supersaturated with calcite above 13°C and with dolomite above 14°C.

Any process that decreases the amount of CO_2 in solution is a cause for $CaCO_3$ precipitation. These reactions are involved:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \ , \tag{31}$$

$$H_2CO_3 + CaCO_3 \rightleftharpoons Ca^{2+} + 2\ HCO_3^- \ . \tag{32}$$

Lake Michigan surface waters are warmest in August and September (*cf*. Fig. 3), and CO_2 is least soluble then. Phytoplankton, which are most active in summer, may cause precipitation of $CaCO_3$ in the Lake indirectly, by removing CO_2 during photosynthesis.

Both changes in temperature and changes in CO_2 content can lead to conditions, *i.e.* saturation, that should permit precipitation of calcite and/or dolomite in the surface waters of Lake Michigan in summer. All surface-water samples taken by Schelske and Callender (1970) approached saturation (Table 41), and most were supersaturated. All bottom-water samples were undersaturated. Obviously, calcite should have been precipitating in those surface-water samples and lowering the levels of saturation to 100%. The interested reader can find further explanation of calcite supersaturation in geochemical texts.

Table 41. Ranges of Saturation Values with Respect to Calcite in Lake Michigan Water during Summer*

Date	*Location*	*Surface Water* %	*Bottom Water* %
July 1969	Southern basin	125 - 200	25 - 90
August 1969	Northern basin	95 - 175	10 - 50

**Summarized from Schelske and Callender, 1970.*

While supersaturation with calcite was well documented by Schelske and Callender (1970), this does not suggest that supersaturation is permanent. Incidents of milky water (see Turbidity section) represent isolated instances of reduction of supersaturation to simple saturation by precipitation of calcite. Conditions which allow precipitation of $CaCO_3$ in one part, but not other parts, of the Lake during summer are incompletely understood. Ayers *et al.* (1967) considered 1954 a "year of widespread occurrence of the milky-water condition." This is the only year in which calcium increased significantly (Table 40), both inshore and offshore, with depth. They also thought, "... milky water probably occurred in 1960 and 1962." Data from 1960 (Table 40) tend to support the supposition of $CaCO_3$ precipitation in the inshore area; no judgment can be made about offshore waters, for very few samples were taken.

Beeton and Moffett (1964) apparently changed analytical methods between September and October 1955 (note dramatic, parallel increases in both surface and bottom water in Fig. 84). The change in analytical methods obscured differences between surface and bottom water in late summer in the northern basin.

Figure 85 shows monthly variations in calcium concentrations at the Lake County, Illinois, public water supply intake, 823 m (2700 ft) from shore. Calcium concentrations are slightly higher from December to April (Fig. 85b) than during the rest of the year. This may be attributable to greater solubility of $CaCO_3$ at lower temperatures and to wave action during the winter stirring up the bottom sediments in the inshore area, releasing interstitial calcium. Support for this hypothesis is found in the correspondence of higher turbidity values with higher calcium concentrations in Figure 85. No offshore stations have yet been sampled year-around to see if there are pronounced seasonal changes in calcium content. Changes caused by mixing of the sediments would probably be negligible more than a few miles from shore, for only severe storms would have enough energy to affect the bottom appreciably.

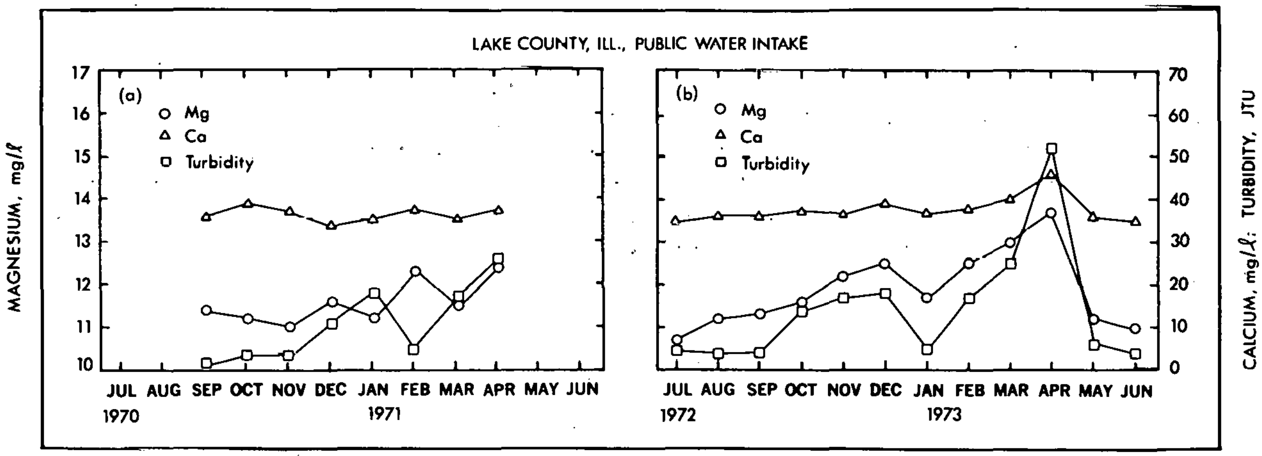


Fig. 85. Monthly Variations in Magnesium, Calcium, and Turbidity Concentrations at the Lake County, Ill., Public Water Intake. Data from Howe (1973--personal communication).

The U. S. Public Health Service (1962), the National Academy of Sciences (1973), and the Environmental Protection Agency (1975b) have set no limits on calcium concentrations in drinking water, nor has any limit been recommended for the protection of aquatic life (Appendix B).

Calcium content in sediments of Lake Michigan has been reported by Callender (1969), Shimp *et al.* (1970), Copeland and Ayers (1972), and Robbins and Edgington (1974). Figure 86 illustrates surficial sedimentary calcium concentrations throughout the Lake. Callender (1969) pointed out that surface sediments are higher in calcium in the southern basin than elsewhere in the Lake. The highest values are found in the eastern portion of the southern

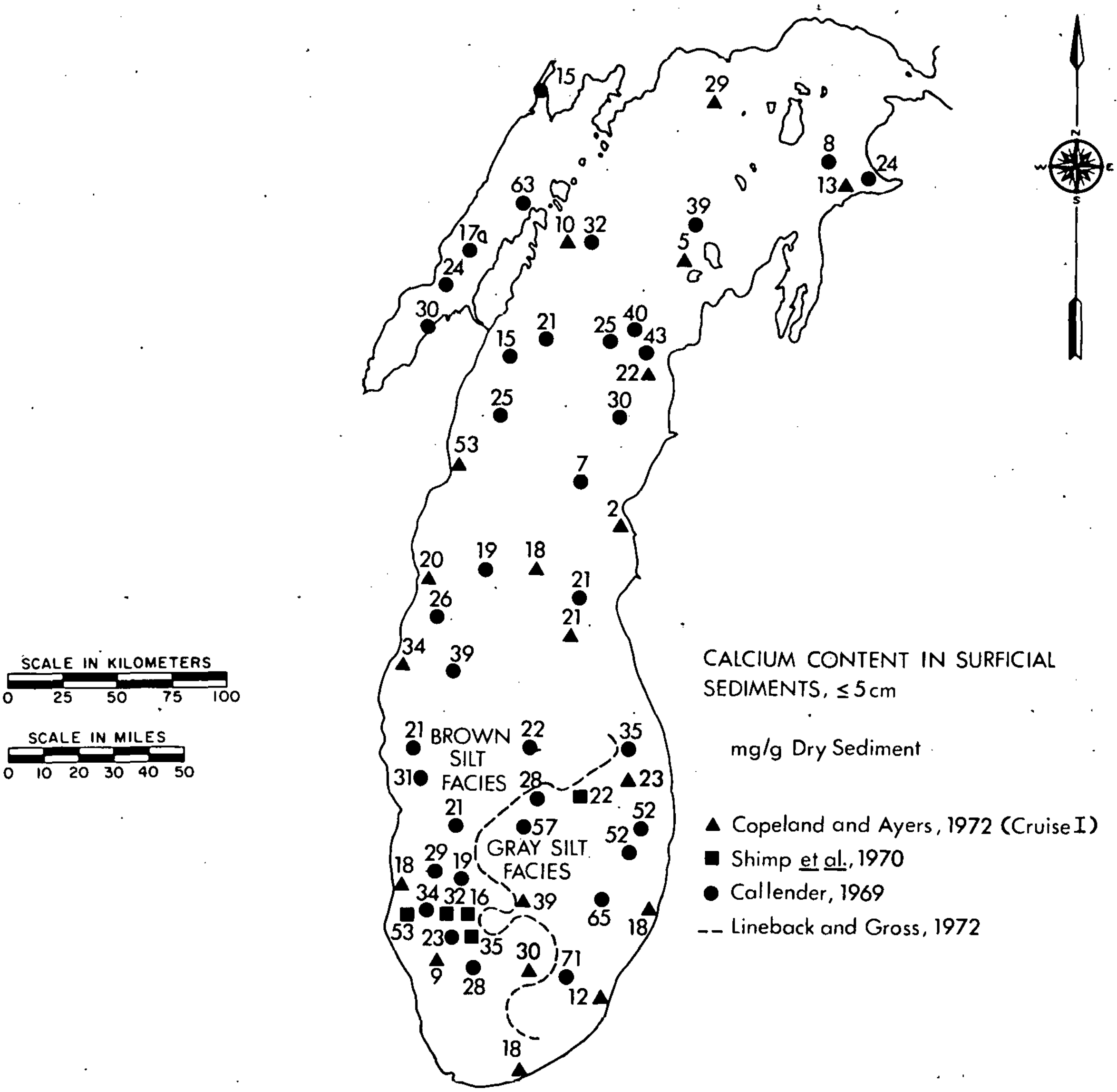


Fig. 86. Calcium Content in Surficial Sediments of Southern Lake Michigan. Data from Copeland and Ayers (1972), Shimp *et al.* (1970), and Callender (1969). Boundary of brown and gray silt facies of the Waukegan member from Lineback and Gross (1972).

basin, in the gray silt facies of the Waukegan member described by Lineback and Gross (1972). This observation agrees with the suggestion by Powers and Ayers (1967) that calcium concentrations in water along the eastern shore of the southern basin are higher than around Milwaukee and Chicago. Water concentration data (Fig. 83) did not confirm this suggestion.

In the divide area, surficial sediment content of calcium is lower than in the southern basin (Fig. 86), while concentrations in the northern basin are similar to those in the southwestern part of the Lake. Callender (1969) attributed lower calcium concentrations in Green Bay sediments to lower carbonate content (*cf.* Table 17).

Callender (1969) found that in cores collected throughout the Lake, surficial calcium content was significantly lower than at depth (up to 1 m). Three cores taken by Shimp *et al.* (1970), which penetrated to 1.2 m, also showed lower calcium content in surficial sediments. Since much of the sedimentary calcium was combined with carbonate, as calcite or dolomite, Callender (1969) attributed the increases at depth to penetration of a higher-carbonate sediment. He also estimated that 8% of the total surficial sediment consisted of calcite and dolomite, whereas calcite and dolomite content at depth was 16%. X-ray diffraction analysis did not identify the presence of any crystalline calcium-phosphate minerals, but the presence of a substantial amount of an amorphous calcium-phosphate combination at greater depths in the cores was inferred on the basis of chemical analyses.

The proportion of calcite to dolomite increases with depth in sediments from the divide area, the northern basin, and Green Bay. However, at all stations and depths (Callender, 1969) the dolomite/calcite ratio was > 1, reflecting the abundance of dolomite in the geologic formations that are the source of most of the sediments in the Lake.

Callender (1969) also measured the calcium concentration of interstitial water and found that values in all areas of the Lake were higher than the overlying lake water (*cf.* Tables 39 and 40 with Table 42). This difference was attributed to the instability of carbonate minerals after sedimentation. Interstitial calcium concentrations did not change appreciably with depth in the cores. Lake Michigan interstitial water was calculated to be in equilibrium with both calcite and dolomite.

Table 42. Distribution of Calcium in Interstitial Water of Lake Michigan Sediments*

	Concentration Ca, mg/l	
Location	*Surface Sediment*	*Sediment at Depth*
Southern basin	44.1	44.1
Divide area and northern basin	41.7	43.7
Green Bay	38.7	40.3

**Data from Callender, 1969.*

Robbins and Edgington (1974) measured acid-extractable calcium content at intervals in nine cores taken from 9.6 to 40 km (6-25 mi) offshore on a transect west of Grand Haven. Maximum concentrations were found close to shore (Fig. 87). Cores from inshore stations showed little variation to 20 cm, but offshore depth profiles were considered complex. Below 4 cm in the core, a decrease in calcium with distance from shore was thought to be due to greater inshore deposition either of biogenic calcareous material, or calcium-containing minerals washed off the watershed, or both. No explanation was given for the nearly constant value (140-160 mg/g dry weight acid-soluble sediment) in the upper 2 cm of these nine cores. Because Robbins and Edgington expressed their data on an acid-soluble basis, the influence of comparatively inert major sedimentary components, such as silica, was excluded. The differences between concentrations reported by Robbins and Edgington (1974) and by Callender (1969), Shimp *et al.* (1970), and Copeland and Ayers (1972) are due to differences in methodologies, and not necessarily to compositional differences between the stations.

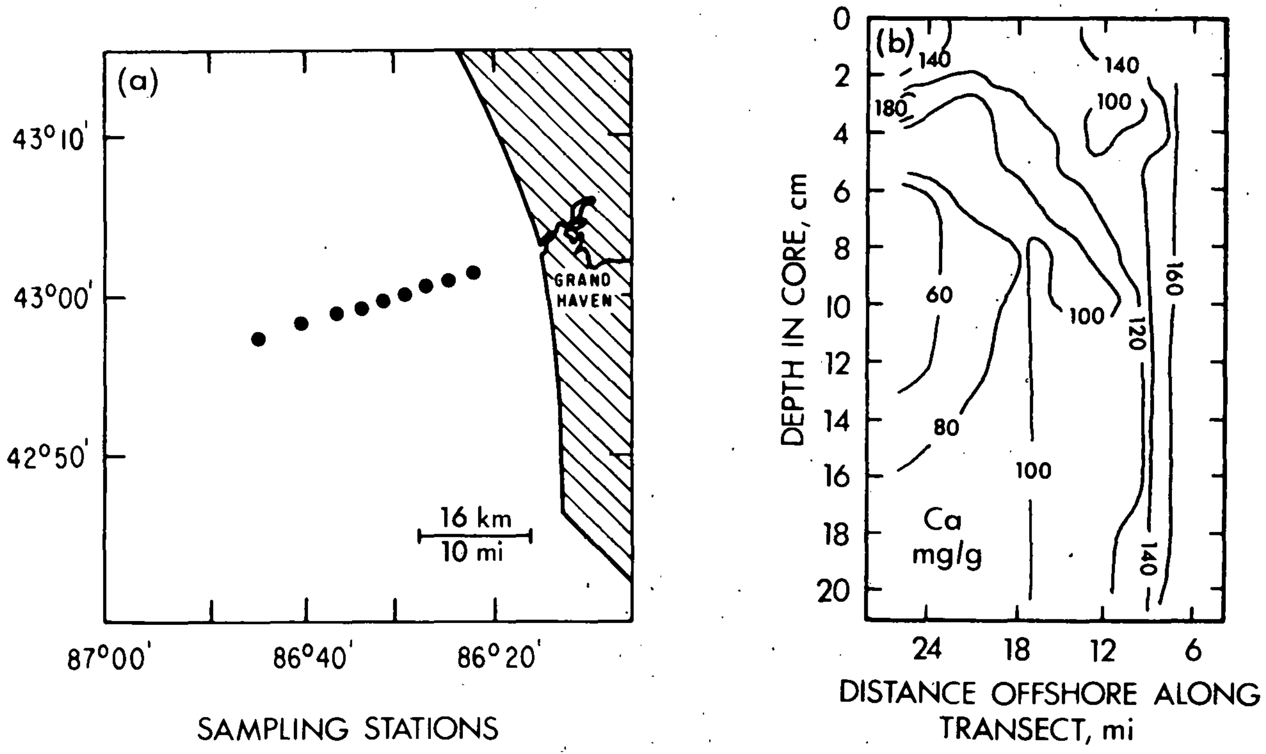


Fig. 87. Calcium Content in Cores Collected off Grand Haven, October 1971. (a) Location of sampling stations; (b) concentration of calcium (mg/g dry weight acid-soluble sediment). Modified from Robbins and Edgington (1974).

Magnesium

Magnesium is a constituent of all chlorophylls in plants and photosynthetic bacteria. On a subcellular basis, magnesium ions activate a number of enzymes, including phosphate transferases, decarboxylases, and acyl transferases; magnesium also has electrochemical functions (Bowen, 1966).

Optimal magnesium concentrations recommended for laboratory growth of freshwater blue-green algae vary from 0.1-3 mg Mg/l (Gerloff *et al.*, 1950, 1952) to 15-50 mg Mg/l (Kratz and Myers, 1955). Humans require an intake of about 0.7 g Mg/day (McKee and Wolf, 1963). Before toxic concentrations of magnesium are reached in water, the taste becomes unpleasant. Magnesium salts (*e.g.* epsom salts, $MgSO_4 \cdot 7H_2O$) have a laxative effect at concentrations exceeding *ca.* 100 mg Mg/l (U. S. Public Health Service, 1962), especially on those unaccustomed to drinking the water.

Natural sources are important in maintaining the magnesium content of Lake Michigan. Most of the watershed of the Lake is covered by extensive carbonate deposits containing dolomite. Weathering and erosion of these materials, as in Equations 27-30, cause dissolution of these deposits and aid removal of particulate forms of magnesium to the Lake and its tributaries. Similar reactions occur in groundwater, so magnesium is transferred into baseflow and directly into the Lake by groundwater.

There are also several industrial and domestic sources of magnesium. Magnesium chloride, $MgCl_2$, is used to manufacture chemicals, imitation leather, cements, fireproofing materials, and road coverings (McKee and Wolf, 1963). Magnesium sulfate, $MgSO_4$, is used in tanning, textile processing, fertilizers, explosives, and matches. Upchurch (1972) estimated that natural calcium sources were 7.3 times greater than cultural. Considering the similarities in chemical behavior of magnesium and calcium, natural sources of magnesium likely outweigh cultural sources greatly.

Magnesium determinations in Lake Michigan are summarized in Figure 88 and Table 43. In most reports, the description of experimental methods did not indicate whether samples were filtered prior to analysis. Where possible, soluble and particulate magnesium concentrations are indicated (Table 43). No clear geographic trends in magnesium concentrations are evident.

Beeton and Moffett (1964) conducted an extensive study of magnesium content in Lake Michigan water. Their work centered on the southern basin, except for 10 stations largely in the northern basin sampled in September 1955. The raw data of Beeton and Moffett for 1954 and 1960 are summarized and analyzed in Table 44. Analysis of the data of Beeton and Moffett reveals no inshore-offshore differences in surface-water magnesium concentrations. Analysis of surface-water data collected by Copeland and Ayers (1972) also shows no differences with distance from shore.

Figure 85 depicts monthly variations in magnesium concentrations at the Lake County, Illinois, public water supply intake, located at a depth of 9.1 m (30 ft) and a distance of 823 m (2700 ft) from shore. Concentrations tended to be higher from December to April and lower for the rest of the year. This increase may be due to wave action stirring up the bottom sediments in the

Table 43. Magnesium Content in Lake Michigan Water

Sample Description	*Dates*	*Concentration Mg, mg/l*		*Reference*
		Average	*Range*	
Annual median values at public water intakes:				Powers and Ayers, 1967
Chicago (6 intakes)	1926-62	10.7	9.5-11.9	
Milwaukee	1939-62	11.0	9.9-12.9	
Grand Rapids	1941-61	10.8	9.7-11.3	
Samples collected, surface to bottom, in southern basin and divide area:				Beeton and Moffett, 1964
360 inshore samples	May-Dec 1954	10.3	6.5-11.8	
415 offshore samples	May-Nov 1954	10.4	6.7-12.3	
106 samples collected inshore and offshore, surface to bottom, in northern basin and divide area	Sep 1955	11.7	10.1-12.8	Beeton and Moffett, 1964
Samples collected, surface to bottom, in southern basin:				Beeton and Moffett, 1964
63 inshore samples, 3 stations	Apr-Nov 1960	11.1	9.2-11.7	
13 samples, 1 central station	May-Sep 1960	10.8	9.6-11.6	
Whole Lake:	1962-63			USDOI, 1968
318 offshore samples		12	8-16	
898 inshore samples		12	7-14	
Samples collected:	1962-63			USDOI, 1968
Indiana Harbor, 21 samples		15	14-15	
Calumet Harbor, 14 samples		13	11-14	
Chicago Harbor, 6 samples		11	10-12	
Racine Harbor, 7 samples		11	10-12	
Samples collected:	Oct 1962, Jun 1963			USDOI, 1968
Milwaukee Harbor, 37 samples		15	11-19	
Adjacent to Milwaukee Harbor, 82 samples		10	8-19	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City		12	7-15	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo		11	8-15	
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor		11	9-14	
On a line roughly between Sheboygan and Little Sable Point		12	10-14	
Samples collected:	22-28 Jul 1964			USDOI, 1968
Traverse Bay, 51 samples		12	11-13	
Adjacent to Traverse Bay, 15 samples		12	12-13	
Surface-water samples collected throughout Lake at stations sampled 3 times each:	Aug 1969-Jun 1970			Copeland and Ayers, 1972
12 inshore stations		11.5[a]	10.6-12.0[a]	
8 offshore stations		11.5[a]	10.9-12.2[a]	
3 samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	15 Dec 1969; 5, 12 Jan 1970	10[a]	10-11[a]	USGS, 1972
Monthly samples collected at intakes:	Sep 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		11.9	11.0-13.5	
Waukegan Generating Station		12.8	11.4-16.1	
North Chicago public water supply		11.3	10.4-12.0	

Table 43. (contd.)

		Concentration Mg, mg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Monthly samples collected at Lake County, Ill., public water intake	Sep 1970-Apr 1971, Jul 1972-Jun 1973	11.8	10.6-13.7	Howe, 1973
Single samples collected northwest of Grand River entrance outside River plume	6 Oct 1970			Robbins *et al.*, 1972a
A station 1.0 km (0.62 mi) NW:				
Surface-water, soluble magnesium		11.2		
Bottom-water, soluble magnesium		11.7		
Surface-water, extractable particulate magnesium		0.035		
Bottom-water, extractable particulate magnesium		0.0163		
A station 1.25 km (0.78 mi) NW:				
Bottom-water, soluble magnesium		10.2[b]		
Bottom-water, extractable particulate magnesium		0.111[b]		
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		13		
Kenosha		12		
Milwaukee (5 intakes)		12	11-12	
Port Washington		10		
Racine		12		
Sheboygan		12		
Two Rivers		12		
Samples collected (water depth 7.6 m) at a station east of Kewaunee Nuclear Plant:				Industrial Bio-Test, 1972d
Surface	25 May 1971	11.0	10.9-11.0	
Bottom	25 May 1971	10.8	10.8-10.9	
Surface	31 Aug 1971	10.6	10.6-10.7	
Bottom	31 Aug 1971	11.0[c]		
Surface	16 Nov 1971	11.5	11.2-11.6	
Bottom	16 Nov 1971	11.5	11.3-11.6	
Samples (3 replicate analyses) collected off Grand Haven	13-14 Sep 1971			Edgington *et al.*, 1972b
16 km (10 mi) west at a depth of:				
10 m (BNWL)*		12.4		
10 m (VD)*		11.9		
45 m		13.8		
60 m		14.1		
8 km (5 mi) west at a depth of:				
40 m		12.4		
Single sample collected offshore from Grand Haven	Unspecified	≤9.0[a]		Wahlgren *et al.*, 1972b
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		11.5	10.0-14.0	
Effluent plume		11.4	10.0-13.0	
South of plant, 4.8 km (3 mi)		11.3	10.0-15.0	

Table 43. (contd.)

Sample Description	Dates	Concentration Mg, mg/l		Reference
		Average	Range	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		11.9	10.0-14.0	
North of plant, 1.6 km (1 mi)		12.4	10.0-14.0	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		12.8	12.0-14.0	
South of plant, 1.6 km (1 mi)		12.9	12.0-14.0	

[a] *Soluble magnesium.*

[b] *This author questions whether this sample was outside the River plume.*

[c] *Same value for all samples.*

**BNWL = noncontaminating Niskin water bottle; VD = Van Dorn water bottle.*

USDOI = U. S. Department of the Interior; USGS = U. S. Geological Survey.

inshore area. Correspondence of higher turbidity values with higher magnesium concentrations in Figure 85 supports this hypothesis. Seasonal variations of magnesium in offshore waters have not been documented.

The U. S. Public Health Service (1962), the National Academy of Sciences (1973), and the Environmental Protection Agency (1975b) have set no limits on magnesium concentrations in drinking water, nor has any limit been recommended for the protection of aquatic life (Appendix B).

Magnesium content in surficial (≤ 5 cm) sediments is illustrated in Figure 89. Callender (1969) stated the magnesium content of open Lake sediments is higher than Green Bay sediments. This suggestion is not confirmed by the data in Figure 89, perhaps due to analytical scatter among the data. In the southern basin, higher magnesium concentrations are found in the eastern portion, in the gray silt facies of the Waukegan member (Lineback and Gross, 1972).

Callender (1969) compared surficial sediment compositions with those deeper in the cores (up to 1 m). Magnesium content increased with sediment depth in all parts of the Lake. Increases with depth were less obvious in samples analyzed by Shimp *et al.* (1970). Since most of the magnesium is combined with carbonate, Callender (1969) attributed the increases to higher carbonate-containing sediment in the deeper cores. About 8% of the surface

Table 44. Analysis of Raw Magnesium Data Published by Beeton and Moffett (1964)

Year	Inshore, <16 km from shore Mg, mg/l ± one S.D.			Offshore, >16 km from shore Mg, mg/l ± one S.D.		
	Number of Observations	Surface (≤15m)	Bottom (≥25m)	Number of Observations	Surface (≤15m)	Bottom (≥25m)
1954	204	10.4±0.4		258	10.4±0.4	
	156		10.3±0.3	157		10.4±0.3
1960	32	11.2±0.4		5	11.0±0.8	
	31		11.1±0.3	8		10.8±0.5

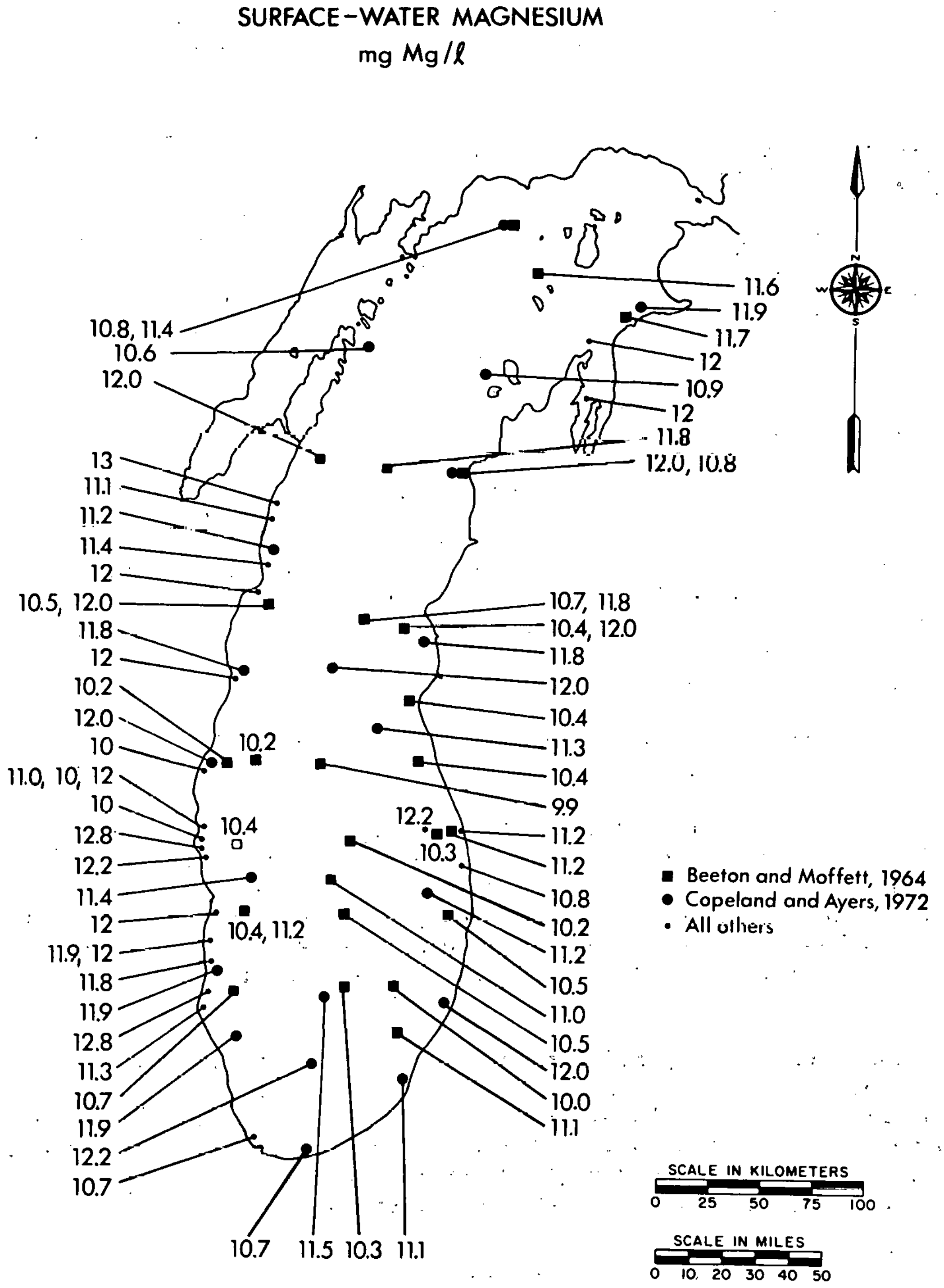


Fig. 88. Surface-Water Magnesium Concentrations during Twenty Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 43.

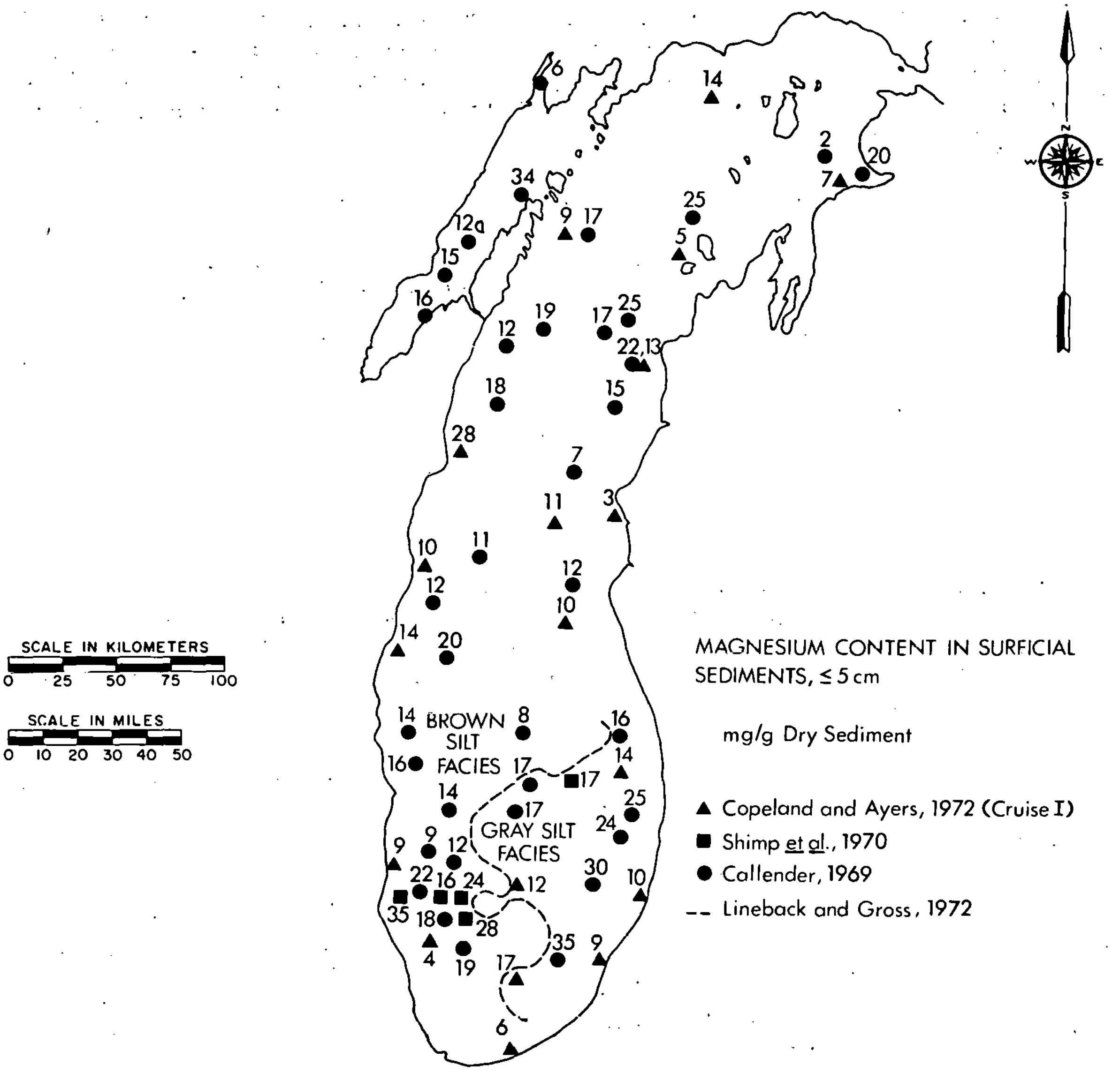


Fig. 89. Magnesium Content in Surficial Sediments of Southern Lake Michigan. Data from Copeland and Ayers (1972), Shimp *et al.* (1970), and Callender (1969). Boundary of brown and gray silt facies of the Waukegan member from Lineback and Gross (1972).

sediment was calculated to be calcite and dolomite, while the corresponding value at depth was 16%. About 0.9% of the sediment at the surface and at depth was the magnesium-containing clay mineral, chlorite.

In the divide area, northern basin, and Green Bay, the calcite:dolomite ratio increases with depth in the sediments. This ratio exceeded 1.0 at all stations and depths sampled by Callender (1969) and reflected the abundance of dolomite in the materials that are the main source of sediments in the Lake.

Callender (1969) also determined the magnesium content of interstitial water. Values in all areas of the Lake were higher than the overlying Lake water (compare data in Tables 43 and 45). Interstitial water was calculated to be in equilibrium with both calcite and dolomite and to approach equilibrium with respect to chlorite.

Table 45. Distribution of Magnesium in Interstitial Water of Lake Michigan Sediments*

Location	*Concentration Mg, mg/l* *Surface Sediment*	 *Sediment at Depth*
Southern basin	12.7	16.6
Divide area and northern basin	14.4	17.3
Green Bay	16.4	18.3

*Data from Callender, 1969.

Acid-extractable magnesium content varied little to 20 cm (Fig. 90) in cores taken near Grand Haven (Robbins and Edgington, 1974). Magnesium content decreased by a factor of nearly two between 9.6 and 40 km (6 and 25 mi) offshore; this decrease was attributed to greater inshore deposition of biological material containing magnesium, of magnesium-containing minerals, or both.

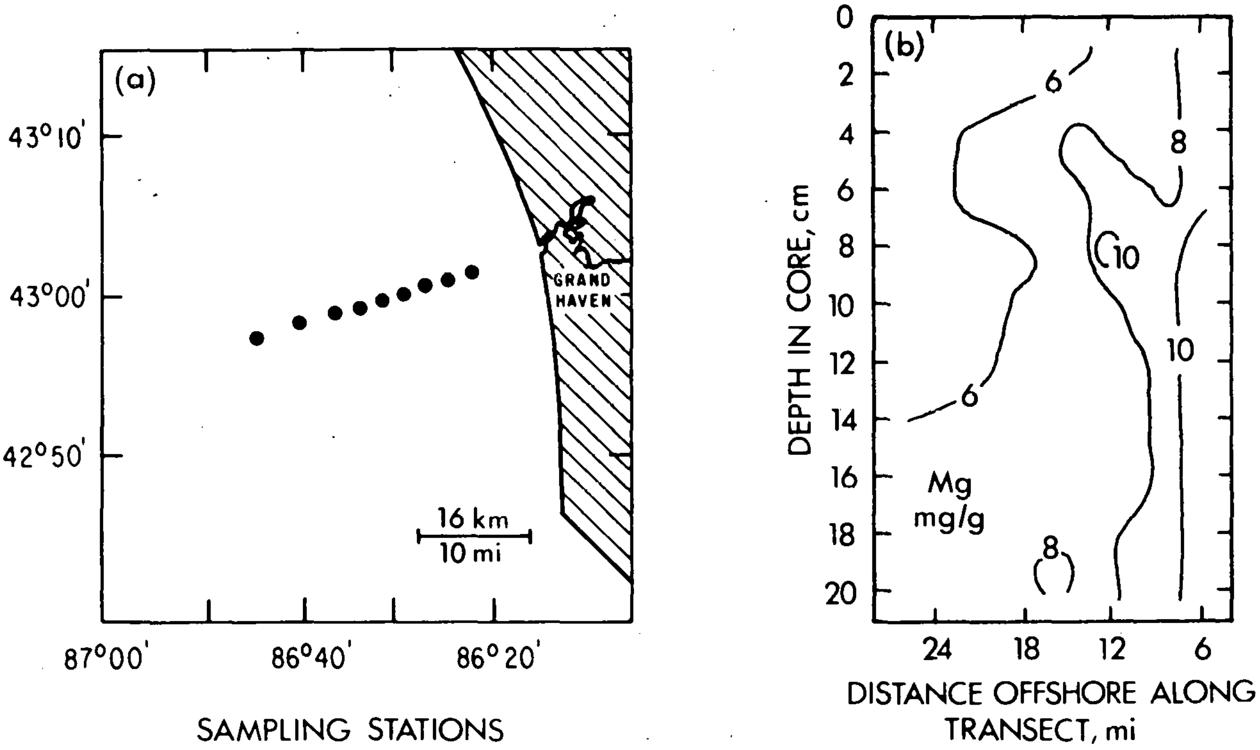


Fig. 90. Magnesium Content in Cores Collected off Grand Haven, October 1971. (a) Location of sampling stations; (b) concentration of magnesium (mg/g dry weight acid-soluble sediment). Modified from Robbins and Edgington (1974).

Total Hardness

Water hardness is an indication of the capacity of water to form an insoluble curd with soap, although standard methods for hardness (APHA *et al.*, 1971) are no longer based on soap titrations. Multivalent cations like calcium, magnesium, aluminum, iron, manganese, barium, strontium, and zinc precipitate soap. Since calcium and magnesium are usually the dominant cations, hardness is attributable principally to these two ions. By convention, hardness is expressed as an equivalent weight of $CaCO_3$ (*e.g.* 40 mg Ca/l or 24 mg Mg/l is equivalent to 100 mg $CaCO_3$/l).

Biological productivity and water hardness are usually directly related (National Academy of Sciences ..., 1973); however, hardness *per se* has no biological significance, since any effects that may be noted are due to the specific concentrations and combinations of elements present.

The major detrimental effects of hardness are economic (McKee and Wolf, 1963). Hardness exceeding 100 mg $CaCO_3$/l leads to excessive use of soap; and the calcium portion of hardness leads to incrustation of hot-water pipes, since $CaCO_3$ is less soluble at higher temperatures. Excessive hardness is undesirable in intermediate-to-high pressure boiler feedwater, due to scale formation (National Academy of Sciences ..., 1973). Scouring, rinsing, and dyeing operations in the textile industry are adversely affected by hardness, especially where soap curds may form. Hardness interferes with washing operations in paper manufacture. Excessive hardness in the processing water leads to an undesirable produce in the canning of certain fruits and vegetables, *e.g.* peas, beans and beets (McKee and Wolf, 1963).

Determinations of hardness are summarized in Table 46 and illustrated in Figure 91. Since the primary importance of hardness is economic, the fact that only inshore determinations of hardness are available is understandable. There is little variation in hardness along the western shore of the Lake, except for higher values immediately south of Milwaukee. The latter observation may be due to input of calcium- and magnesium-laden water from the Milwaukee River (U. S. Dep. Inter., 1968; Ayers, 1970; Robbins *et al.*, 1972b).

Figure 92 demonstrates variations in hardness with season and with distance from shore. The largest variations occur nearest to shore (Fig. 92a, b), with high values from December to April and low values from May to October or November. These observations may be related to wave action in the inshore areas (*cf.* Calcium and Magnesium sections). Farther from shore, hardness values are much less variable (Fig. 92c, d). The latter phenomenon shows the decreasing influence of inshore hydrodynamic processes with distance from land.

The U. S. Public Health Service (1962) and the Environmental Protection Agency (1975b) have set no limits on hardness in drinking water (Appendix B, part 1). The National Academy of Sciences ... (1973) discussed hardness with respect to aquatic life, but made no recommendation for limitation (Appendix B, part 2). The Academy suggested more emphasis should be placed on determination of concentrations of the specific ions that make up hardness.

Table 46. Total Hardness in Lake Michigan Water

		Concentration $CaCO_3$, mg/l		
Sample Description	Dates	Average	Range	Reference
Samples collected ∿monthly from Peter Cooper Corp. intake, Oak Creek, ∿0.75 km (2500 ft) offshore	1961	134	128-144	Wis. Comm. Water Pollut., 1965
	1962	135	122-144	
	1963	134	128-148	
	1964	133	108-150	
	1965	136	126-148	Wis. Dep. Nat. Resour., 1969
	1966	152 [*sic*]	128-290 [*sic*]	
	1967	135	128-144	
	1968	133	128-140	
	1969	136	132-144	Wis. Dep. Nat. Resour., 1973
	1970	132	128-140	
	1971	134	124-148	
	1972	138	127-148	
Weekly samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	Nov 1969-Sep 1970	131	128-138	USGS, 1972
	Oct 1970-Sep 1971	131	127-136	USGS, 1973
	Oct 1971-Sep 1972	132	128-136	USGS, 1974a
	Oct 1972-Jun 1973	135	128-150	USGS, 1974b
Monthly samples collected at intakes:	Jan 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		138	129-153	
Waukegan Generating Station		139	130-159	
North Chicago public water supply		136	129-146	
Samples collected ∿monthly at 3 stations 9.6 km (6 mi) east of Zion:	Apr 1970-Apr 1971			Industrial Bio-Test, 1972b
Surface-water		131	118-137	
Bottom-water		132	117-138	
Monthly samples collected at Lake County, Ill., public water intake	Jun 1970-Apr 1971, Jul 1972-Jun 1973	140	130-166	Howe, 1973
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		136		
Kenosha		136		
Milwaukee (5 intakes)		137	132-140	
Port Washington		132		
Racine		140		
Sheboygan		136		
Two Rivers		136		
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		136	126-185	
Effluent plume		136	120-175	
South of plant, 4.8 km (3 mi)		133	124-150	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		141	128-150	
North of plant, 1.6 km (1 mi)		144	130-160	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		149.1	141.5-153.5	
South of plant, 1.6 km (1 mi)		150.8	142.5-158.0	

USGS = U.S. Geological Survey.

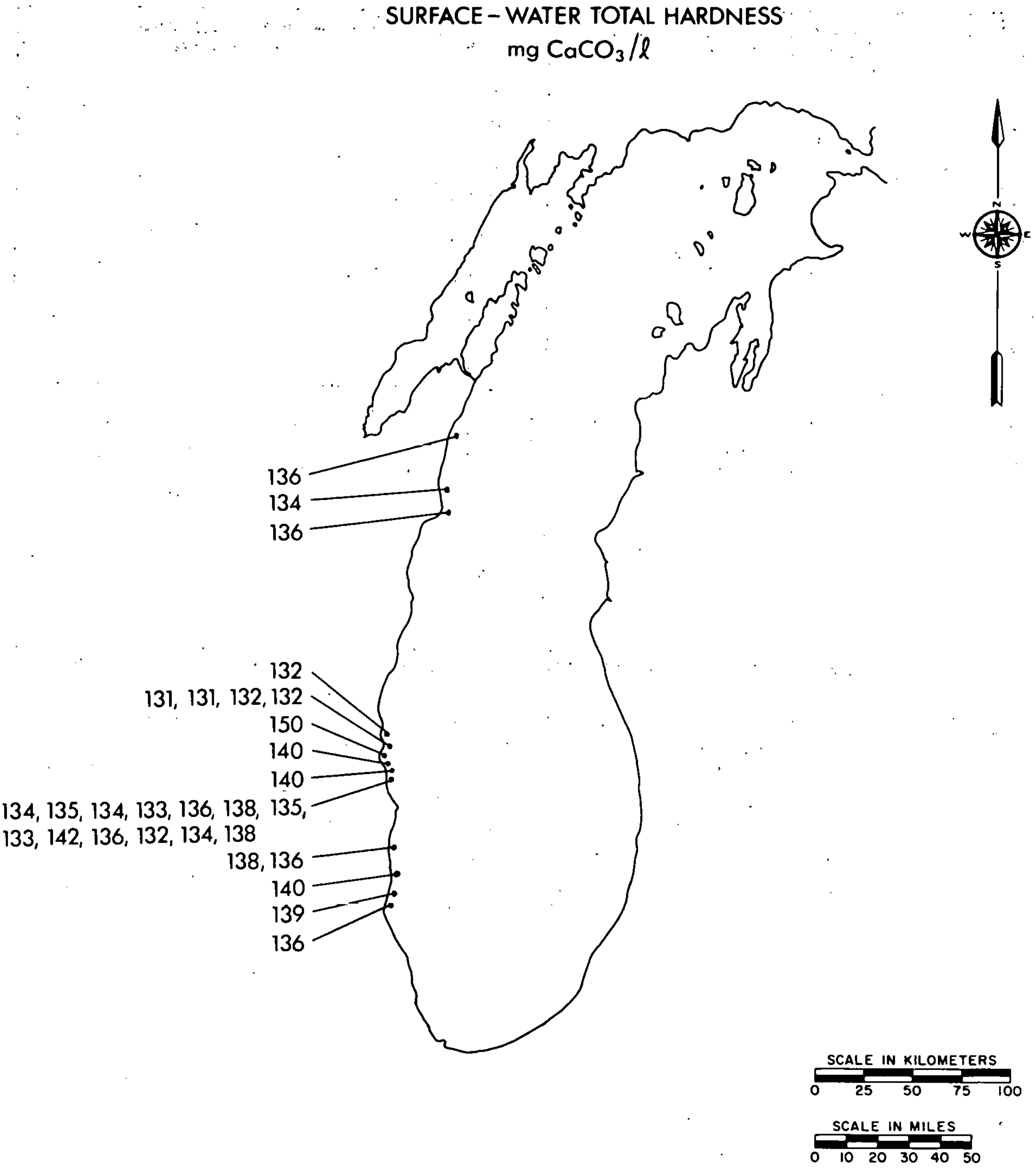


Fig. 91. Surface-Water Total Hardness over a Period of Fifteen Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 46.

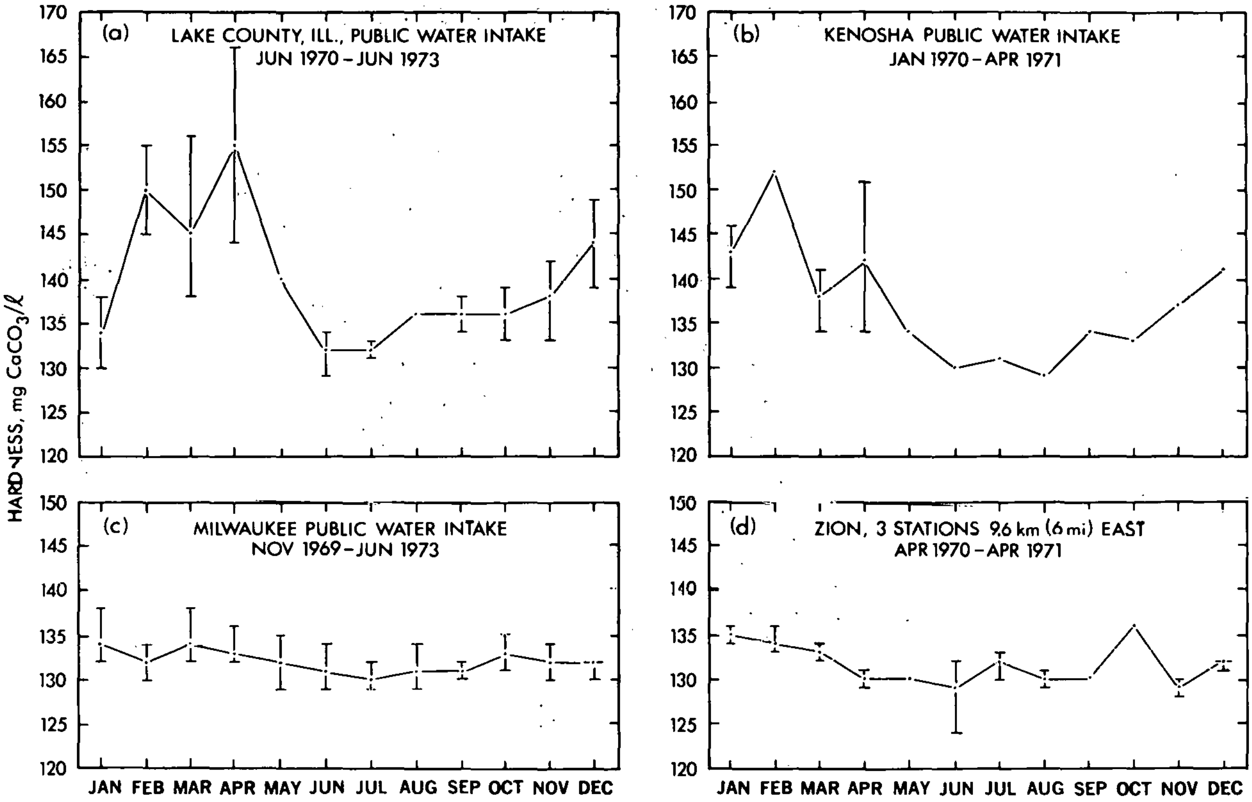


Fig. 92. Seasonal Variations of Average Surface-Water Hardness along the Western Shore of Lake Michigan. Distance from shore and depth: (a) 823 m (2700 ft) from shore, 9.1 m (30 ft) deep; (b) 1372 m (4500 ft) from shore, 9.1 m (30 ft) deep; (c) 2000 m (6565 ft) from shore, 20.4 m (67 ft) deep; (d) 9.6 km (6 mi) from shore, surface water. Sources of data: (a) Howe, 1973--personal communication; (b) Industrial Bio-Test, 1972a; (c) U. S. Geological Survey, 1972, 1973, 1974a, 1974b; (d) Industrial Bio-Test, 1972b.

MAJOR ANIONS
OTHER THAN CARBONATE AND BICARBONATE

CHLORIDE

Chloride ion is essential for angiosperms and mammals (Bowen, 1966). In both plants and animals chloride has electrochemical and catalytic functions; for example, chloride helps maintain charge balance in human blood, and it also acts catalytically in plants in the release of O_2 and the formation of adenosine triphosphate during noncyclic photophosphorylation (O'Kelley, 1968). Some research indicates that chloride is required by certain lower plants. For instance, Eyster *et al.* (1958) reported that photosynthetic growth of the green alga *Chlorella pyrenoidosa* was inadequate unless chloride was present.

Natural sources of chloride to Lake Michigan include weathering and erosion of rocks and soils in the Basin. Igneous rocks generally have lower chloride content than shales and limestones (Bowen, 1966). Soils average 100 mg chloride/kg, but concentrations are much higher in alkaline soils. The alkaline soils of the Lake Michigan watershed determine the background amount of chloride washed into the Lake. Tiffany *et al.* (1969) mentioned rainfall as a natural source of chloride; the chloride is derived ultimately from the salt constituents of sea spray.

Chloride-containing compounds, widely used in industrial processes and generally quite soluble, are one source of chlorides to the Lake. In addition, several industries recover brine underlying the western part of the state of Michigan, and the spent brine is discharged into the Lake.

Chloride is abundant in domestic wastes. Data in Fair *et al.* (1968) suggest that the average person excretes 7.0 g chloride per day. Taking into account kitchen wastes as well as commercial and small manufacturing sources, average sewage contains 40-80 mg chloride/l, depending on per capita water consumption (O'Connor and Mueller, 1970). Conventional sewage treatment does not remove chloride; therefore, sewage effluents, domestic and industrial, contribute chloride to the Lake.

Numerous municipalities and government agencies in the Basin use large quantities of chlorides during winter as deicers on their streets and highways. Sodium chloride is used much more extensively than calcium chloride, since the latter was reported to be about six times more expensive (Terry, 1974). These road salts reach Lake Michigan *via* storm and combined sewers.

Ownbey and Willeke (1965) and Upchurch (1972), using two different computational models, attempted to differentiate the annual load of chloride reaching Lake Michigan from natural and cultural sources. The former authors computed a total input of 54.3×10^7 kg chloride/yr. Of that total, 57% was due to industrial and municipal effluents; the remainder was due to land runoff. Two-thirds of the industrial chloride input was derived from brine discharge in the area between Muskegon and Manistee. Upchurch calculated that 81×10^7 kg chloride/yr enter Lake Michigan, and 73% was due to cultural influences. The discrepancy in the absolute amounts calculated by Ownbey and Willeke and by Upchurch must remain unexplained at the moment, for in both instances the mid-1960's was used as the base period for calculation. It is important to note that as of 1965, human activities were responsible for at least half to as much as three-fourths of the total chloride entering the Lake each year. There is no reason to think that this proportion will decrease appreciably as long as growth of population, industrial discharges, and use of road salt continues unchecked (*cf.* O'Connor and Mueller, 1970). Curtailment of the use of road salt might limit or reverse this upward trend.

Chloride data from Lake Michigan water are summarized in Table 47. Beeton and Moffett (1964) collected chloride samples during spring, summer, and fall. Average chloride concentrations during 1960 and 1961 were about 6 mg/l. During their study no seasonal or depth variations were noted, but inshore chloride concentrations were usually higher than offshore concentrations.

The U. S. Department of the Interior (1968) found an average chloride concentration of 6.5 mg/l in offshore waters in 1962-1963, based on 607 samples. The 1611 inshore samples averaged 7.1 mg/l. Their data were treated in several other papers published in the mid-1960's with greater elaboration than was available in the original report. Risley and Fuller (1965) classified the data by areas of the Lake in which samples were taken and found that chloride was highest (average 8.0 mg/l) in the area from Calumet Harbor to Michigan City and decreased northward. In the area around Sheboygan to Little Sable Point, Michigan, chloride was only 6.6 mg/l. The effects of rivers and harbors on chloride concentrations were also explored (Table 48) by collecting samples in these areas.

Copeland and Ayers (1972) visited twenty stations three times each during August 1969-June 1970. These stations were located throughout the Lake, both inshore and offshore. The average chloride concentration at the twelve inshore stations, 11.0 mg/l, was the same as the average at the eight offshore sites (and, incidentally, much higher than most of the other values in Table 47 except for those taken quite close to shore). However, much higher than average inshore chloride concentrations were found at two stations along the eastern shore, near Ludington and near Frankfort, and in the area between Kewaunee and Point Beach on the western shore. These high inshore values might be attributable to industrial or municipal effluents; however, the data (Copeland and Ayers, 1972) neither confirm nor deny this speculation by this author. Copeland and Ayers also found high values, 14.8-15.4 mg Cl/l, at a deep-water station midway between Manistique and Charlevoix; no explanation was apparent for such high concentrations in open water.

Figure 93 summarizes data from Table 47. The number of samples and length of record at inshore stations from Milwaukee south to Chicago-Gary-Hammond are noteworthy. Chloride concentrations in the southern portion of the Lake seem higher than those in the north, although regrettably most of the northern values were collected in the early 1960's while most of the southern values were obtained in the late 1960's-early 1970's; thus the data from the north and the south may not be comparable. The data from Copeland and Ayers (1972), shown in Figure 93, are noticeably higher than other values in a given area. It is not known whether this observation represents a real difference or some positive error in sampling techniques or experimental methods.

Industrial Bio-Test (1972a) sampled the Kenosha water treatment plant intake on at least a monthly basis from January 1970 through April 1971. The intake is located in 9.1 m (30 ft) of water, 1372 m (4500 ft) from shore. Figure 75 shows variations of chloride and sodium concentrations over this

Table 47. Chloride Content in Lake Michigan Water

Sample Description	*Dates*	*Concentration Cl^-, mg/l* *Average*	*Range*	*Reference*
Samples collected, surface to bottom, in southern basin:				Beeton and Moffett, 1964
3 inshore stations	29 Apr-23 Nov 1960	6.2	5.7-7.1	
1 central station sampled 4 times	27 May-26 Sep 1960	5.9	5.1-7.5	
Samples collected $\sim$weekly from Peter Cooper Corp. intake, Oak Creek, $\sim$0.75 km (2500 ft) offshore	1961	6.8	4.5-11.0	Wis. Comm. Water Pollut., 1965
	1962	7.6	5.0-17.5	
	1963	7.3	5-12	
	1964	7.2	5-12.5	
	1965	8.6	5-18	Wis. Dep. Nat. Resour., 1969
	1966	8.6	6-21	
	1967	9.1	7-15	
	1968	9.2	5-28	
	1969	10.1	5.5-21.5	Wis. Dep. Nat. Resour., 1973
	1970	9.3	7.0-15.0	
	1971	10.0	6.5-19.0	
	1972	12.5	1.0-95.0	
Samples collected, surface to bottom, in northern basin:				Beeton and Moffett, 1964
5 inshore stations	17 May-23 Nov 1961	6.2	5.6-16.4	
2 offshore stations sampled 5-6 times	19 May-9 Nov 1961	6.1	5.7-10.7	
Whole Lake:	1962-63			USDOI, 1968
607 offshore samples		6.5	3.3-11	
1611 inshore samples		7.1	1.5-94	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City		8.0	4.2-22	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo		6.6	4.4-8.2	
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor		7.3	5.3-18	
On a line roughly between Sheboygan and Little Sable Point		6.6	5.4-10	
Samples collected:	1962-63			
Indiana Harbor, 21 samples		16	10-22	USDOI, 1968
Adjacent to Indiana Harbor, 317 samples		7.1	4.2-12	Risley and Fuller, 1966
Samples collected:	1962-63			
Calumet Harbor, 21 samples		7.6	6.8-9.0	USDOI, 1968
Adjacent to Calumet Harbor, 20 samples		7.9	6.0-11	Risley and Fuller, 1966
Samples collected:	1962-63			USDOI, 1968
Chicago Harbor, 6 samples		7.1	6.6-7.9	
Racine Harbor, 7 samples		8.5	6.8-9.1	
Samples collected:	Oct 1962, Jun 1963			USDOI, 1968
Milwaukee Harbor, 31 samples		19	5.3-36	
Adjacent to Milwaukee Harbor, 81 samples		8.3	5.3-23	
143 samples collected throughout Green Bay	26 Jun-17 Jul 1963	7.0	1.5-18	USDOI, 1968
Samples collected:	22-28 Jul 1964			USDOI, 1968
Traverse Bay, 51 samples		7.2	5.5-13	

Table 47. (contd.)

		Concentration Cl^-, mg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Adjacent to Traverse Bay, 15 samples		6.7	6.0-7.5	
Samples collected in Indiana Harbor at east breakwall inner light:				Snow, 1974
51 samples	Jan-Dec 1966	21	9-33	
42 samples	Jan-Dec 1967	24	11-40	
6 samples	Jan-Dec 1968	23	15-39	
6 samples	Jan-Jun 1969	28	21-34	
20 samples	Jan 1971-Jan 1973	25.6	12-50	
Annual averages at Chicago South Water Filtration Plant	1966-70		7.2-7.7	Vaughn and Reed, 1973
Samples collected at water plant intakes:	1967-70			Snow, 1974
Hammond				
Annual averages			8-11	
Individual values			0-20	
East Chicago				
Annual averages			9-11	
Individual values			6-19	
Gary				
Annual averages			7-10	
Individual values			0-26	
Single samples collected at 2 shoreline stations, northwest of the Straits of Mackinac	9 Jul 1967	6.1	5.1-7.1	Tiffany *et al.*, 1969
9 samples collected between surface and 110 m at a station 9.6 km (6 mi) north of South Fox Island	19 Jul 1967	5.7	4.6-7.4	Tiffany *et al.*, 1969
4 samples collected between 5 m and 115 m at a station in middle of southern basin	22 May 1968	4.7	4.4-5.5	Tiffany *et al.*, 1969
Annual averages for samples collected at water filtration plants near Chicago:				
11 plants with intakes <2.5 km (8200 ft) from shore	1968	8.6	8.3-8.9	Ill. Sanit. Water Board, 1969
5 plants	1969	9.9	9.8-10	Ill. Sanit. Water Board, 1970
Surface-water samples collected throughout Lake at 20 stations sampled 3 times each	Aug 1969-Jun 1970	11.0[a]	9.1-14.5[a]	Copeland and Ayers, 1972
Weekly samples collected from Milwaukee public water intake, 1.8 km (1.1 mi) offshore	Nov 1969-Sep 1970	8.0	7.0-9.7	USGS, 1972
	Oct 1970-Sep 1971	8.0	7.2-11	USGS, 1973
	Oct 1971-Sep 1972	8.3	7.5-12	USGS, 1974a
	Oct 1972-Jun 1973	9.1	7.8-16	USGS, 1974b
Annual average, Metropolitan Sanitary District of Greater Chicago	1970	9.0		Lue-Hing, 1973
	1971	8.9		
Samples collected at Whiting water plant intake	1970	9	5-12	Snow, 1974
Monthly samples collected at intakes:	Jan 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		9.0	7.3-14.7	
Waukegan Generating Station		9.9	7.8-14.0	
North Chicago public water supply		8.2	7.0-10.6	
Monthly samples collected, surface to bottom, at 3 stations 9.6 km (6 mi) east of Zion	Apr 1970-Apr 1971	7.4	6.5-10.5	Industrial Bio-Test, 1972b
Monthly samples collected at Lake County, Ill., public water intake	Jun 1970-Apr 1972, Sep 1972-Jun 1973	8.4	6.5-12.0	Howe, 1973

Table 47. (contd.)

Sample Description	Dates	Concentration Cl^-, mg/l		Reference
		Average	Range	
16 samples collected, surface to bottom, at 6 stations on a line passing east of Manitou Islands from Frankfort to Beaver Island	7 Jul 1970	7.2	6.8-7.8	Schelske and Roth, 1973
Samples collected at Chicago South Water Filtration Plant	1971	9.1	8.4-10.2	Vaughn and Reed, 1973
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		8		
Kenosha		10		
Milwaukee (5 intakes)		13	8-17	
Port Washington		6.5		
Racine		16		
Sheboygan		8		
Two Rivers		7		
Samples collected (water depth 7.6 m) at a station east of Kewaunee Nuclear Plant:				Industrial Bio-Test, 1972d
Surface	25 May 1971	6.6	6.5-6.8	
Bottom	25 May 1971	6.8[b]		
Surface	31 Aug 1971	6.7	6.5-6.8	
Bottom	31 Aug 1971	6.8[b]		
Surface	16 Nov 1971	8.4	8.3-8.5	
Bottom	16 Nov 1971	8.5[b]		
Monthly averages for samples collected once a month over a 24-hr period at the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun 1971-Apr 1972	11.2	7.8-14.9	Industrial Bio-Test, 1972c
6 stations sampled at surface and bottom every 0.8 km (0.5 mi) from 3.2-8.0 km (2.0-5.0 mi) east of:	Mar 1972			Nienke, 1972
Shorewood, Wis.		7.6		
Milwaukee Harbor		7.3		
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		8	5.7-13.3	
Effluent plume		8	5.7-10.4	
South of plant, 4.8 km (3 mi)		8	5.7-11.4	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		9.9	8.1-14.2	
North of plant, 1.6 km (1 mi)		10.3	7.1-13.8	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		13	8.1-16.7	
South of plant, 1.6 km (1 mi)		13	10.4-16.2	

[a] *Total soluble chlorine.*

[b] *Same value for all samples.*

USDOI = U. S. Department of the Interior; USGS = U. S. Geological Survey.

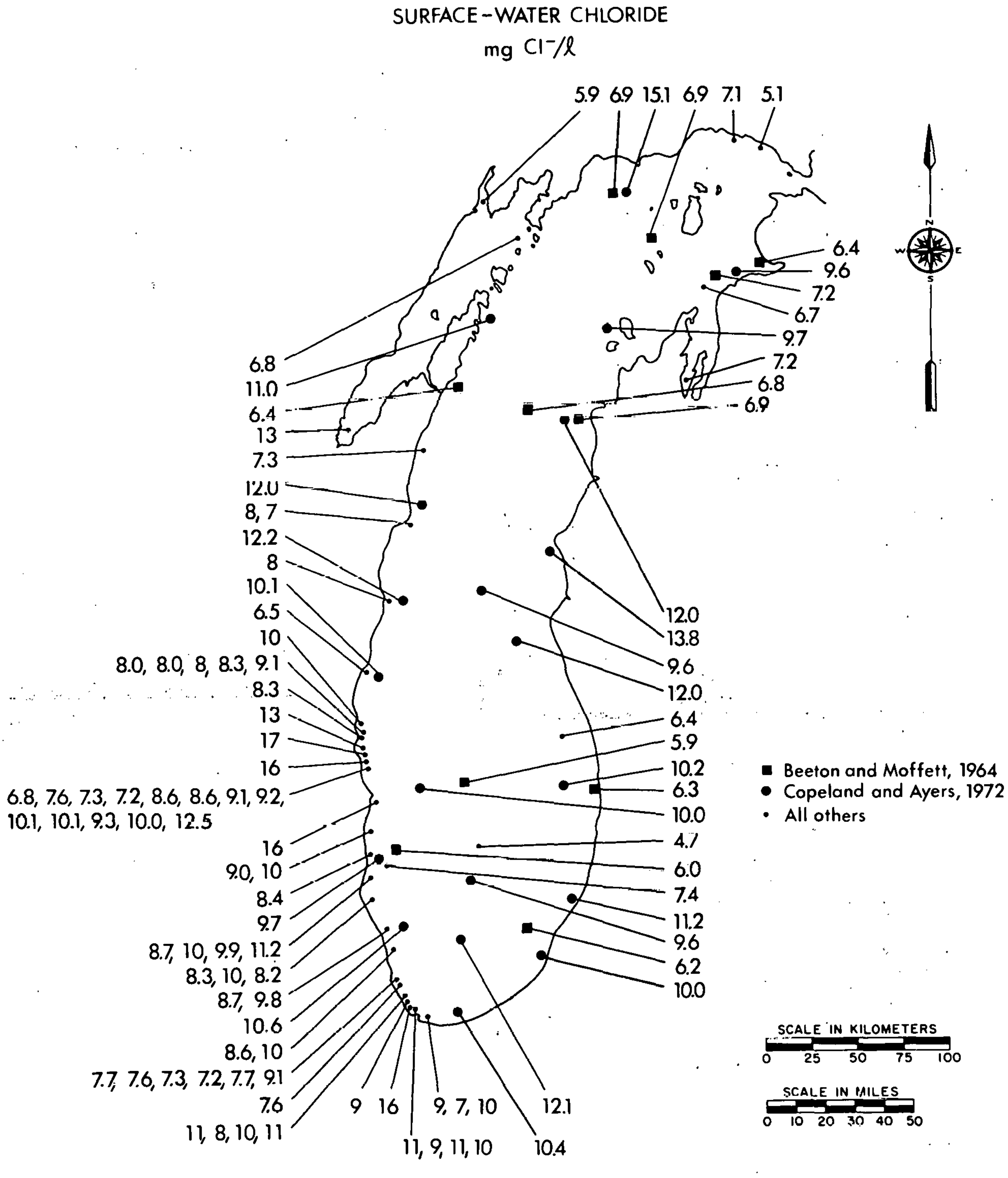


Fig. 93. Surface-Water Chloride Concentrations over a Period of Fifteen Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 47.

Table 48. Effect of Rivers and Harbors on Chloride Content

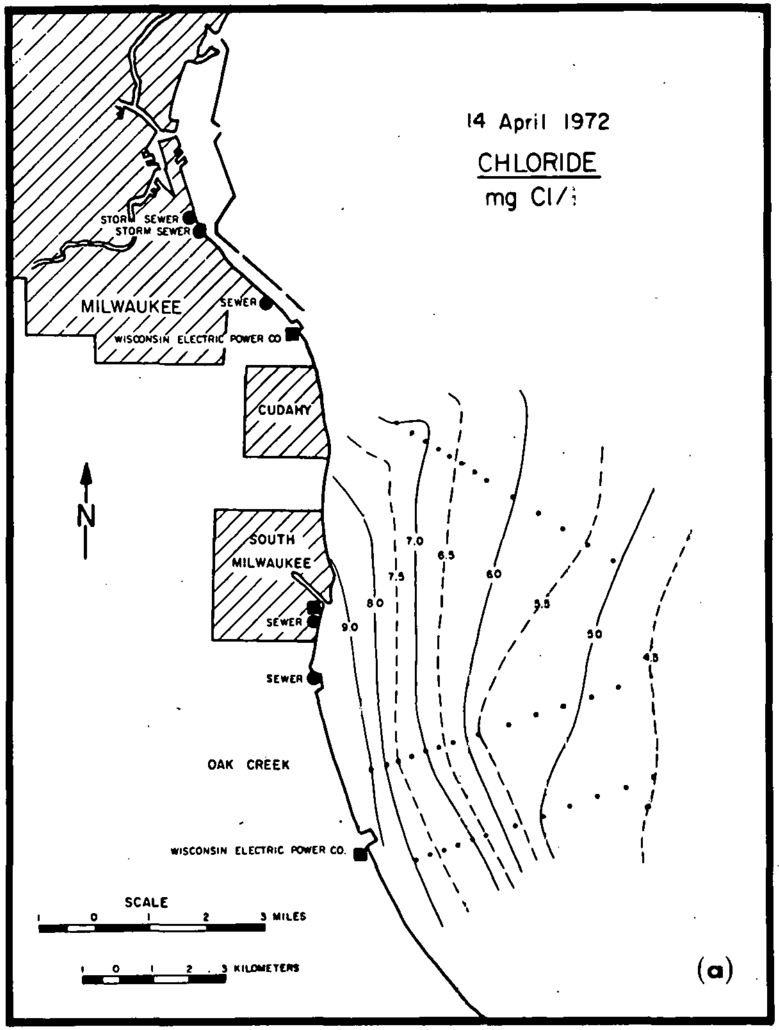
Sample Location	*Concentration Cl, mg/l*	*Reference*
Calumet Harbor	7.6	USDOI, 1968
Adjacent waters of Lake Michigan	7.9	Risley and Fuller, 1966
Indiana Harbor	16	USDOI, 1968
Adjacent waters of Lake Michigan	7.1	Risley and Fuller, 1966
Milwaukee Harbor	19	USDOI, 1968
Area adjacent to the Harbor	8.3	USDOI, 1968
Stations in the west arm of Traverse Bay clustered around the entrance of the Boardman River	7.2	USDOI, 1968
Area adjacent to Traverse Bay	6.7	USDOI, 1968
South of Oconto in Green Bay	13	USDOI, 1968
Rest of Green Bay	5.9-6.7	USDOI, 1968

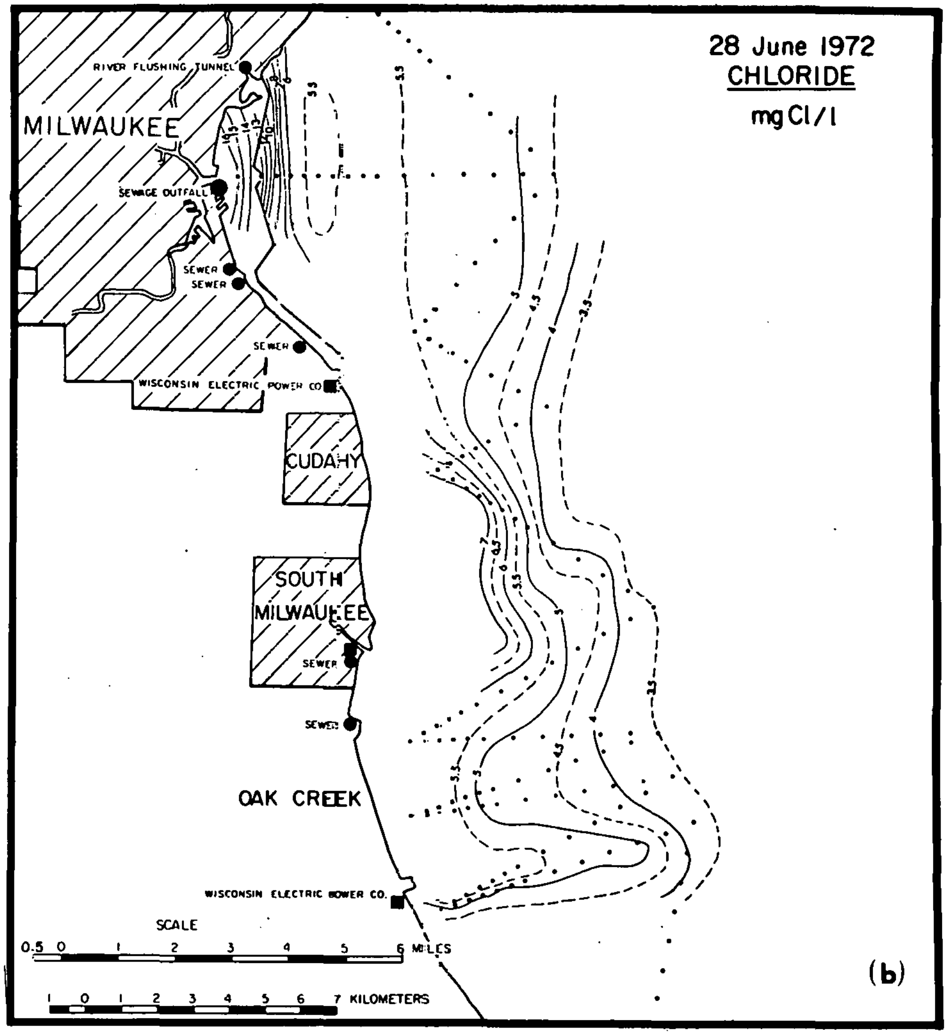
USDOI = U. S. Department of the Interior.

16-month period. Seasonal changes are obvious. In winter, both chloride and sodium are higher, while in summer they decrease. Although not all the chloride increase in winter can be attributed to NaCl (see Sodium section), a major portion must be due to sodium chloride influx. Considering the proximity of the intake pipe to the city of Kenosha, increases in chloride during winter could be attributed to the influence of the city, specifically, to the use of salt as a street deicer.

Similar increases in chloride concentration during winter have been noted at inshore stations all along the western shore, including the Milwaukee water intake (U. S. Geol. Surv., 1973, 1974a), the intake of the Lakeside Power Plant (Limnetics, 1974), the Peter Cooper Corporation at Oak Creek (Wis. Comm. Water Pollut., 1965; Wis. Dep. Nat. Resour., 1969), the intake of the Waukegan Generating Station (Industrial Bio-Test, 1972a), the North Chicago water intake (Industrial Bio-Test, 1972a), the Chicago South Water Filtration Plant (Vaughn and Reed, 1973), and perhaps the Lake County water intake (Howe, 1973--personal communication). However, In 1970, 1971, and 1972, the previously well-marked seasonal changes at Chicago's Southern plant disappeared for no apparent reason. There was no clear-cut seasonal variation in chloride content in the vicinity of Two Rivers, probably due to its relatively small urban population (20,000) needing street salting in comparison with the large population center that extends from Milwaukee to Chicago.

The variation of chloride concentrations with distance from shore was investigated in more detail by Beeton and Barker (1974). Figure 94 presents near-shore surveys made near Milwaukee, concentrating on the Oak Creek area. In all cases, one sees that chloride is highest close to shore and decreases with increasing distance. It may be seen that (*i*) chloride content is highest close to shore and decreases with increasing distance in all cases; (*ii*) high concentrations of chloride are present in Milwaukee Harbor (Fig. 94); (*iii*) there is a sometimes marked influence of a sewer outfall, located on the north side of Oak Creek (Fig. 94c, d); and (*iv*) there is evidence of the winter increase in chloride content due to human activities such as street salting (*cf.* Fig. 94c, d).


14 April 1972
CHLORIDE
mg Cl/l
STORM SEWER
STORM SEWER
SEWER
MILWAUKEE
WISCONSIN ELECTRIC POWER CO
CUDAHY
SOUTH MILWAUKEE
SEWER
SEWER
OAK CREEK
WISCONSIN ELECTRIC POWER CO.
N
9.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
SCALE
1 0 1 2 3 MILES
1 0 1 2 3 KILOMETERS
(a)


28 June 1972
CHLORIDE
mg Cl/l
RIVER FLUSHING TUNNEL
MILWAUKEE
SEWAGE OUTFALL
SEWER
SEWER
SEWER
WISCONSIN ELECTRIC POWER CO.
CUDAHY
SOUTH MILWAUKEE
SEWER
SEWER
OAK CREEK
WISCONSIN ELECTRIC POWER CO.
5.5
7
6.5
6
5.5
5
4.5
4
3.5
SCALE
0.5 0 1 2 3 4 5 6 MILES
1 0 1 2 3 4 5 6 7 KILOMETERS
(b)

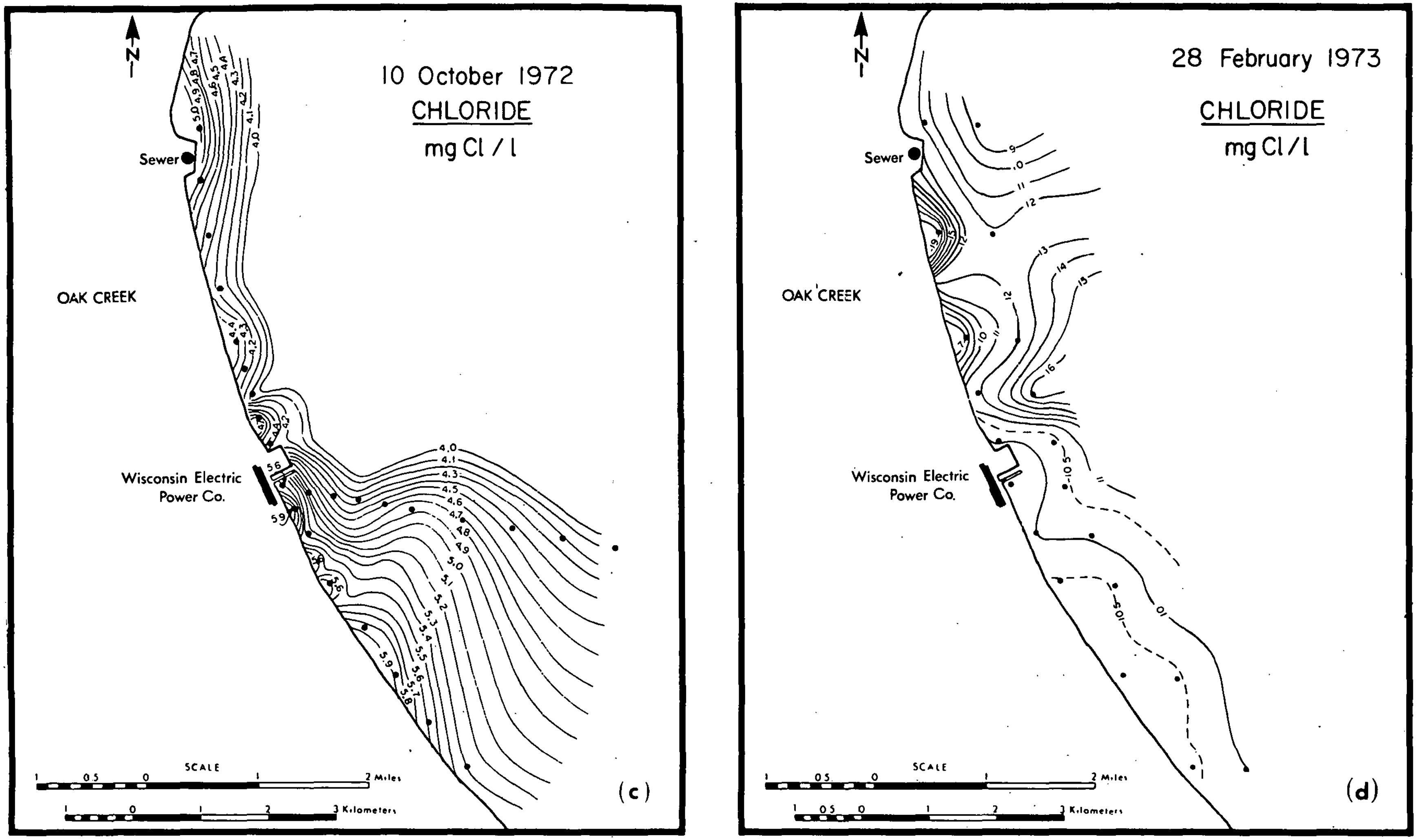


Fig. 94. Quarterly Near-Shore Surveys of Chloride Distribution near Milwaukee. (a) 14 April 1972; (b) 28 June 1972; (c) 10 October 1972; (d) 28 February 1973. Modified from Beeton and Barker (1974) (with permission, see credits).

Based on taste preference, not toxicity to humans, the U. S. Public Health Service (1962) recommended a limit of 250 mg Cl^-/l in drinking water. The National Academy of Sciences ... (1973) concurred with this recommendation (Appendix B, part 1). More recently the EPA (1975b) did not mention chloride concentrations in its Interim Primary Drinking Water Standards. A number of samples (Table 47) have exceeded the maximum limit of 12 mg Cl^-/l set in 1970 by the Illinois Pollution Control Board (1974). The Indiana Stream Pollution Control Board (1973) standards for chloride in the open water of Lake Michigan are often exceeded in the Indiana portion of the Lake (*cf*. Snow, 1974).

No specific recommendation on limitation of chloride concentrations for the protection of aquatic life have been made (Appendix B, part 2).

Chloride analyses on Lake Michigan sediments are performed infrequently. Callender (1969) collected sediments in 1968 and examined interstitial water for chloride content. Since chlorides are generally quite soluble, it is assumed that interstitial chloride content approximates total chloride. Figure 95 presents interstitial chloride concentrations (mg/l) in a number of surficial ($\leq$ 5 cm) sediment samples. Contours have been added to show more clearly the areas of low chloride content in the deep areas of the northern and southern basins and an area of high chloride content near Frankfort. Chloride concentrations seem to decrease with increasing distance from shore. It is not known if there is a major difference in chloride content between sediments along the eastern shore and the western shore.

Interstitial chloride content increases between surficial layers and sediments 30-40 cm beneath the surface (Callender, 1969). This occurs south of a line between Sturgeon Bay and Manistee. North of this line, the opposite situation is generally observed. Whether this latter observation is due to geologic phenomena, or to cultural influences on the northern part of the Lake (industrial brine discharge) is open to question.

SULFIDE AND SULFATE

The element sulfur is essential to all organisms. Sulfate, the most oxidized form of sulfur, is used by some organisms to form esters of polysaccharides, phenols, steriods, and other organic compounds (Schiff and Hodson, 1973). In addition, all organisms require reduced sulfur. Plants and many bacteria are able to reduce sulfate to the thiol level (R-SH) for assimilation into organic compounds such as the important amino acids cysteine and methionine; these organisms probably can also incorporate sulfide directly to form organic compounds containing reduced sulfur (Peck, 1970). Since animals, protozoans, certain bacteria and fungi, and viruses require all their reduced sulfur in preformed organic combination, they depend on plants and microorganisms to supply their sulfur needs (Bandurski, 1965).

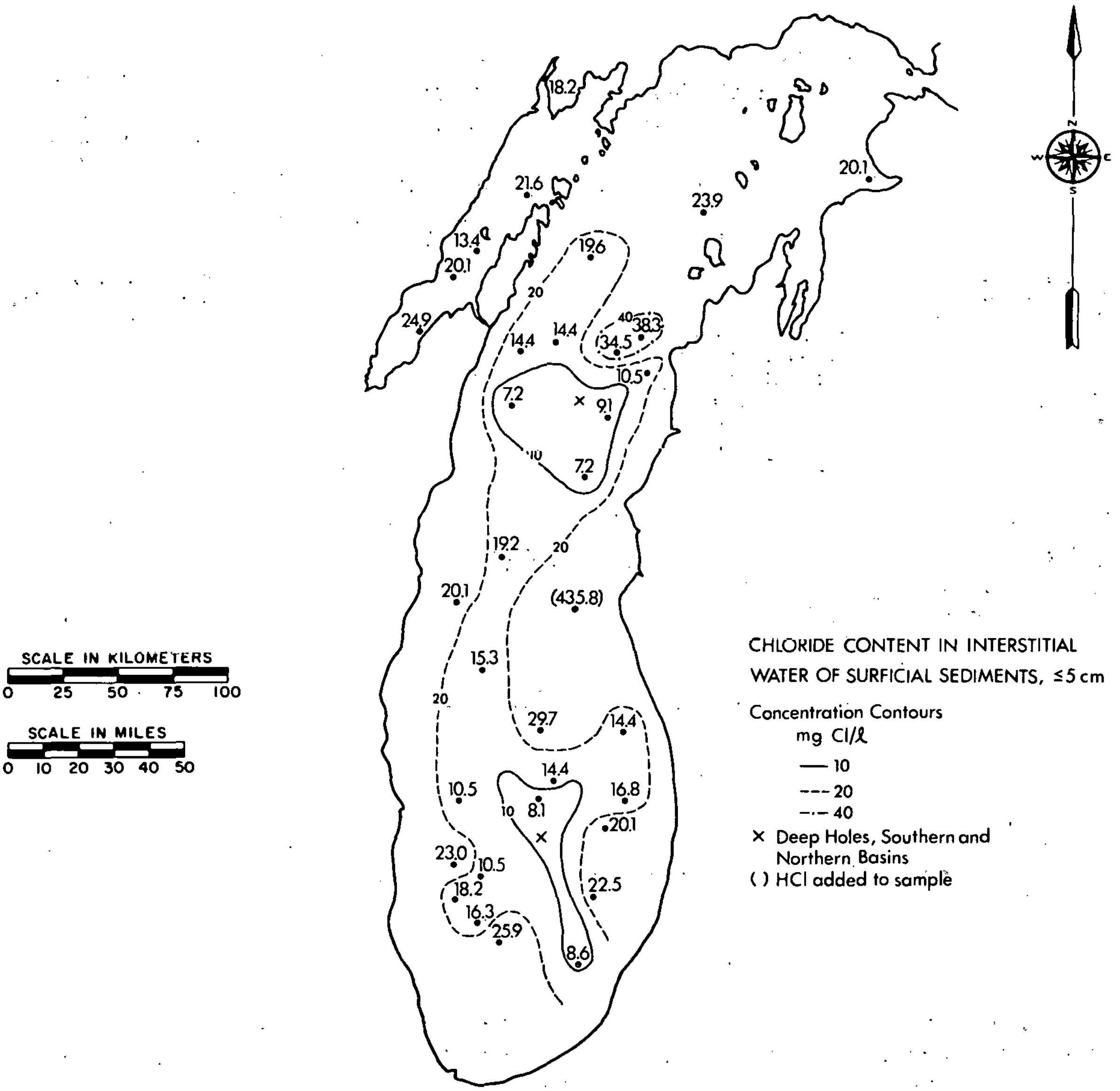


Fig. 95. Chloride Content in Interstitial Water of Surficial Sediments during 1968. Data from Callender (1969).

The sulfur cycle (Fig. 96) is similar in many respects to the nitrogen cycle (Fig. 44), notably in the importance of microorganisms and the role of oxidation and reduction. Specialized bacteria (such as *Desulfovibrio*, *Desulfotomaculum*, and several *Clostridium* spp.) reduce sulfate to H_2S (Stanier *et al.*, 1970); this reduction is analogous to denitrification. Most organisms, including animals and higher plants, are able to oxidize reduced sulfur compounds to sulfate. Only the colorless and photosynthetic bacteria use the energy released in this oxidation for their metabolic needs (Schiff and Hodson, 1973).

The two major forms of sulfur (potentially) present in Lake Michigan, sulfide and sulfate, are considered separately.

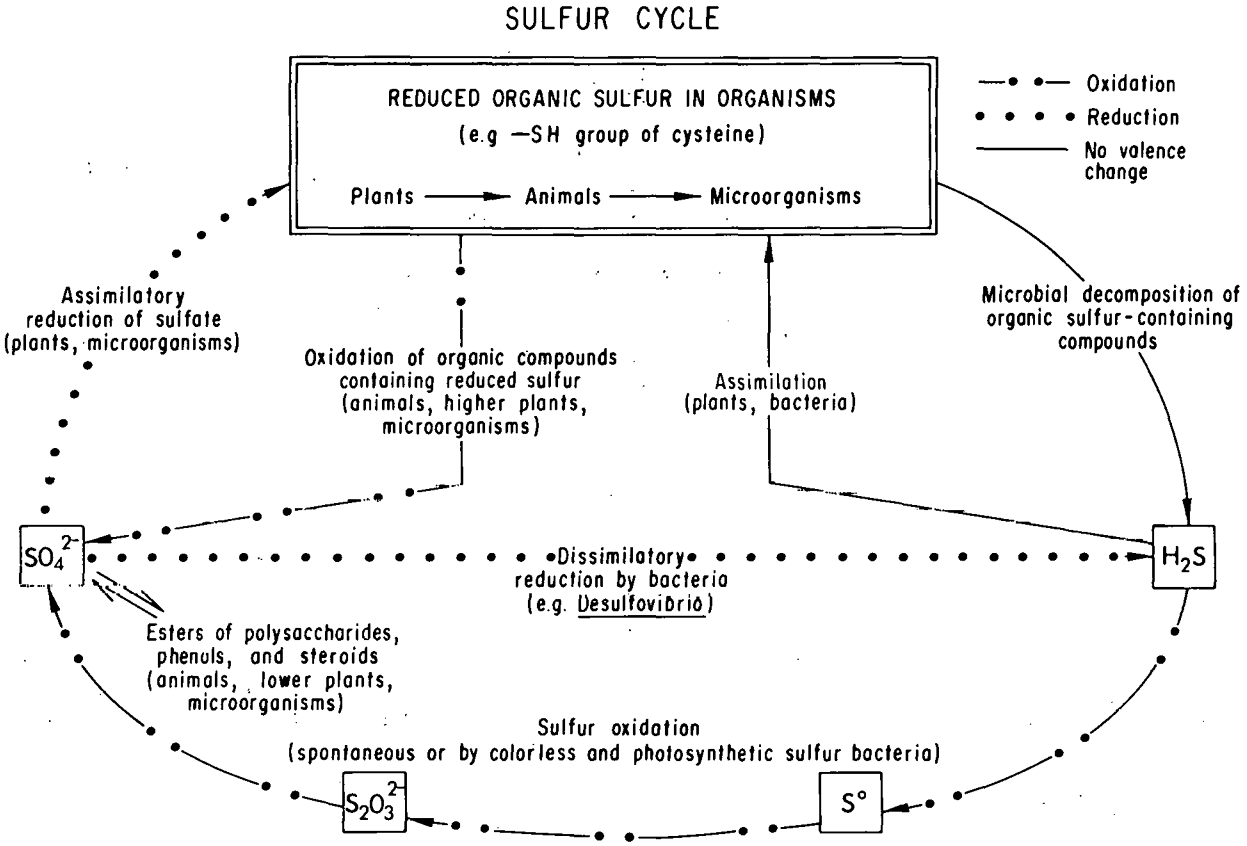


Fig. 96. Sulfur Cycle. Compiled from information in Stanier *et al.* (1970), Peck (1970), and Schiff and Hodson (1973).

Sulfide

The most reduced inorganic form of sulfur in water is sulfide, which in the present discussion includes H_2S, HS^-, and S^{2-}. Hydrogen sulfide, H_2S, is known for its rotten egg odor, and at higher concentrations, for its toxicity. The threshold concentration at which humans can detect H_2S is between 0.01 and 0.1 ng/l (Pomeroy and Cruse, 1969). The toxicity of sulfides is associated largely with undissociated H_2S; thus pH must be defined in estimating concentrations of sulfide that are harmful (Table 49). By taking into account variations in pH and temperature, the National Academy of Sciences ... (1973) concluded that concentrations of total sulfides ($H_2S + HS^- + S^{2-}$) below 0.002 mg/l should be safe for all aquatic organisms including fish. Above those concentrations, hatching of fish eggs is reduced, growth of juveniles is retarded, and survival of mature animals is reduced.

Natural processes of decomposition (*cf.* Fig. 96) supply sulfides to Lake Michigan. Sewage effluent that are in sufficiently oxidized may contain sulfides; industrial wastes from tanneries, pulp and paper mills (Kraft and soda pulp), textile mills, chemical plants, and gas-manufacturing works often contain sulfides (McKee and Wolf, 1963).

Sulfide content is not routinely measured in Lake Michigan water. Reduced sulfur oxidizes in the presence of O_2, and specialized bacteria also oxidize

Table 49. Percentage of Un-Ionized Hydrogen Sulfide at 20°C

pH	*Percentage*
6.5	76.0
7.0	50.0
7.5	24.0
8.0	9.1
8.5	3.1
9.0	1.0

reduced sulfur (Fig. 96). Thus one does not expect to find measurable concentrations of sulfide anywhere in Lake Michigan except in polluted harbors where O_2 is exhausted and perhaps in southern Green Bay after extended periods of ice cover. Sulfides are present in sediments in the absence of O_2 (*cf.* Mortimer, 1971; Kemp *et al.*, 1972), usually several centimeters below the sediment surface.

Sulfate

Sulfate, the most highly oxidized form of sulfur, is the most stable and prevalent form of sulfur in Lake Michigan water. The major inorganic form of sulfur used by animals is sulfate. However, only plants and microorganisms can reduce sulfate to form the important amino acids cysteine and methionine. Strict anaerobic bacteria such as *Desulfovibrio* reduce sulfate to H_2S; these organisms are quantitatively unimportant in Lake Michigan because they require anaerobic conditions. Data tabulated by Kemp *et al.* (1971) and McKee and Wolfe (1963) indicate sulfate concentrations are seldom high enough in fresh waters to threaten aquatic life.

There are many sources of sulfate to Lake Michigan. Weathering and erosion of sulfur-containing minerals and soils remove sulfur from the watershed to the Lake. Gypsum, $CaSO_4 \cdot 2H_2O$, is probably dissolved and transported to the Lake as Ca^{2+} and SO_4^{2-} ions. Sulfide minerals such as spahlerite, ZnS, are oxidized during weathering to mobilize sulfur as sulfate (Krauskopf, 1967). Groundwater in some areas of the Basin contains large quantities of sulfate (Waller and Allen, 1975). Although movement of groundwater directly into Lake Michigan is minimal, groundwater constitutes perhaps 60-70% of the total tributary inflow in areas of shallow unconsolidated sediment aquifers. Thus groundwater as base flow of influent streams is an important natural source of sulfate to the Lake.

Human activities contribute major quantities of sulfate to Lake Michigan. Sewage effluents from secondary treatment of municipal waste water averaged 30 mg SO_4^{2-}/1 more than the tap water supplied to the municipality (Weinberger *et al.*, 1966). Industrial activities add large quantities of sulfate to Lake Michigan. Businessmen for the Public Interest (1972) calculated that 47,000 kg (104,000 lb) of sulfate are discharged daily by petrochemical, chemical, metal refining, metal working and fabricating, and metal mining industries in the region. Unfortunately, waste discharges by pulp and paper manufacturers were not included in the computation. Kraft pulping operations resulted in the discharge of as much as 100 lb Na_2SO_4 per ton of pulp produced, or 34 kg sulfate/metric ton (68 lb sulfate/ton) of pulp (Nemerow, 1963). Sulfur makes up 9% of the total (dry) solids in the waste liquor from sulfite pulping operations. In semi-chemical pulping wastes sulfur content depends on the chemical(s) used.

Dry fallout and wet precipitation may be important sources of sulfate-containing soil and mineral particles to Lake Michigan. Sulfur is also discharged to the atmosphere in both particulate and gaseous forms by the burning of fossil fuels. Winchester and Nifong (1971) calculated that burning of coal, coke, and fuel oil around the southwestern shore of the Lake releases 680,000 metric tons of sulfur annually; an estimated 10% of this amount is transferred to the Lake, or almost one-third as much as the 180,000 metric tons of the estimated annual tributary input. Klein (1975) calculated that rainout and fallout contribute 134 times more sulfur to the Lake than soil erosion. Considering the discrepancies summarized in Table 50, it is readily apparent that the importance of dry and wet precipitation as a source of sulfur to the Lake is incompletely understood.

Ownbey and Willeke (1965) calculated that in the early 1960's municipal and industrial waste loads added 53% of the total sulfate entering Lake Michigan. They also estimated that reduction of sulfate input from man-related sources would have comparatively little effect on concentrations of sulfate in the Lake, since 47% of the total sulfate contribution was derived from natural sources.

Table 50. Precipitation as a Source of Sulfur to Lake Michigan

Component Measured or Estimated	*Dates*	*Place*	*Annual Input of S, metric tons*	*Reference*
Bulk precipitation*			510,000	Klein, 1975
Dry fallout plus gas transfer of gaseous and particulate sulfur emissions		Milwaukee, Chicago, and northwestern Indiana	68,000[a]	Winchester and Nifong, 1971
Wet precipitation, computed on an assumed concentration of 2 mg SO_4^{2-}/l (= 0.7 mg S/l)			29,000[b]	Ownbey and Willeke, 1965
Bulk precipitation, based on the weighted mean concentration of 7.9 mg SO_4^{2-}/l (= 2.6 mg S/l)		Area around Lake Ontario	114,000[b]	Shiomi and Kuntz, 1973
Wet precipitation, based on the mean concentration of 23.9 mg SO_4^{2-}/l (= 8.0 mg S/l)	1963-66	Midway Field (Chicago)	344,000[b]	Lodge *et al.*, 1968
Wet precipitation, based on the mean concentration of 12.1 mg SO_4^{2-}/l (= 4.0 mg S/l)	1963-66	O'Hare Field (Chicago)	174,000[b]	Lodge *et al.*, 1968
Wet precipitation, based on the mean concentration of 4.2 mg SO_4^{2-}/l (= 1.4 mg S/l)	1963-66	Sault Ste. Marie	60,000[b]	Lodge *et al.*, 1968

**Includes dry fallout and wet precipitation.*

[a] *Based on an estimate that 10% of the 680,000 metric tons of sulfur emitted is transferred to the Lake.*

[b] *Calculated by assuming that annual precipitation on the surface of Lake Michigan is 43.2 × 10^{12} l/yr (= 75 cm/yr).*

Table 51 outlines determinations of sulfate in Lake Michigan water during the past 20 years. Data from this table are illustrated in Figure 97. There are more sulfate data from the southern basin than from the divide area or northern basin. There are few samples from offshore areas compared with data acquired from municipal water intakes. Some of the data in Table 51 may be considered more reliable than others. Vaughn and Reed (1973) reported annual averages for sulfate concentrations at Chicago's South Water Filtration Plant raw header, and Snow (1974) plotted Environmental Protection Agency STORET data. Averages of these data are presented in Table 52. The values of Vaughn and Reed appear more reliable of these two reports.

Figure 97 demonstrates several points: (*i*) offshore sulfate concentrations in the southern basin are generally lower than inshore; (*ii*) in the southern basin, sulfate values are highest along the southern and western shores; (*iii*) sulfate concentrations in the northern basin are similar to offshore values in the southern basin, although the paucity of data makes this hypothesis provisional; and (*iv*) sulfate concentrations decrease with increasing distance from a cultural source, *e.g.* sulfate values decrease south of Milwaukee. This last point is shown in greater detail in Figure 98. North of Milwaukee, sulfate averages ranged from 18.5-19.3 mg/l, with the highest average value closest to shore. South of the city, in the vicinity of Oak Creek, sulfate averaged as much as 21.4 mg/l. The highest values again were closest to shore. At a given distance from shore sulfate concentrations were highest at stations closest to Milwaukee.

Seasonal variations of sulfate concentrations in offshore waters have not been studied. In inshore waters, patterns of variations in concentrations seem to be peculiar to each location (Fig. 99). Spring runoff may account for higher sulfate concentrations in March-April at Milwaukee, Oak Creek, Waukegan, and offshore from Zion, Illinois. Causes for high sulfate content in December are less obvious; stirring of bottom sediments by winter storms cannot account for high sulfate, since interstitial sulfate concentrations are the same as or lower than those found in the Lake (*cf.* Callender, 1969, Table 51). Perhaps higher values in winter are due to transfer to the Lake of sulfur compounds emitted by the burning of sulfur-containing fossil fuels.

None of the concentration data in Table 51 approaches the limit of 250 mg SO_4^{2-}/l, recommended for drinking water by the U. S. Public Health Service (1962) on the basis of taste (Appendix B, part 1). Illinois and Indiana have stricter standards for sulfate in the open water of Lake Michigan than the U. S. Public Health Service limits for drinking water. Data in Table 51 show that limits of these two states are exceeded frequently in a number of Lake Michigan harbors and in the inshore waters of the southwestern part of the Lake.

The National Academy of Sciences ... (1973) made no comment on sulfate concentrations for protection of aquatic life, but inspection of data tabulated by Kemp *et al.* (1971) and McKee and Wolf (1963) suggests that sulfate *per se* has little harmful effect on aquatic organisms (Appendix B, part 2).

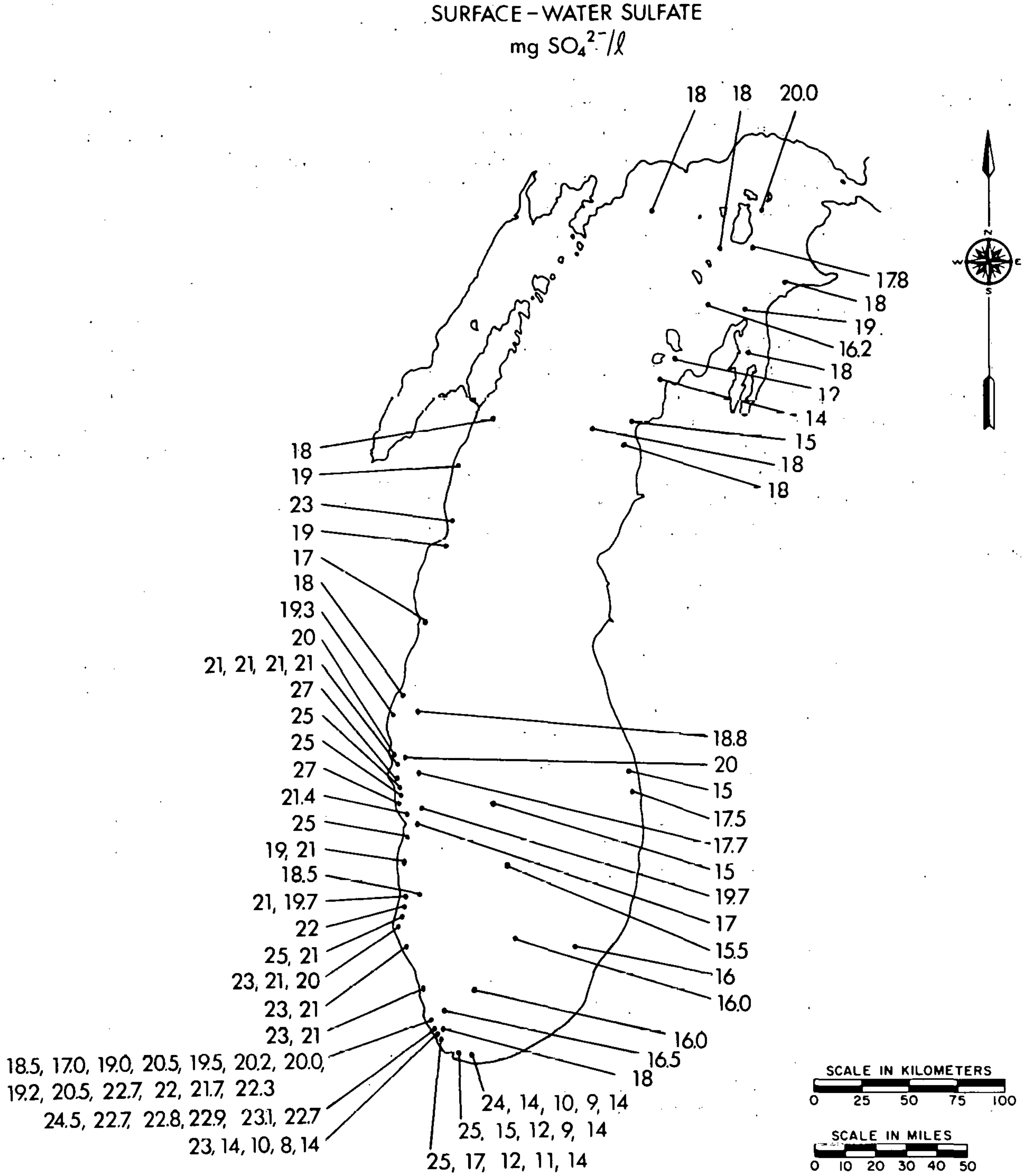


Fig. 97. Surface-Water Sulfate Concentrations over a Period of Twenty Years. Chronological order of multiple-value stations reads from left to right. All data are from references in Table 51.

Table 51. Sulfate Content in Lake Michigan Water

		Concentration SO_4^{2-}, mg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Daily samples collected at Chicago 68th Street water intake crib	1954	18.5		Snow, 1974
	1955	17.0		
	1956	19.0		
	1957	20.5		
	1958	19.5		
	1959	20.2		
	1960	20.0		
	1961	19.2		
	1962	20.5		
Samples collected, surface to bottom:				Beeton and Moffett, 1964
Southern basin				
3 inshore stations	Apr-Nov 1960	16	9-22	
1 central station sampled 4 times	May-Sep 1960	16	10-20	
Northern basin and divide area				
5 inshore stations	May-Nov 1961	18	16-26	
2 offshore stations	May-Nov 1961	18	16-30	
Samples collected in the vicinity of public water intakes:				Powers and Ayers, 1967
Grand Rapids	Jul 1961	17.5	15.0-20.0	
Chicago	Jul 1961	18.0	15.5-27.0	
Milwaukee	Aug 1961	20.0	18.0-29.0	
Samples collected at surface, lower part of epilimnion, upper part of epilimnion, upper part of hypolimnion, and near bottom:	Aug-Oct 1962			Powers and Ayers, 1967
41°51', 87°30'		16.5	15.5-18.5	
42°00', 87°17'		16.0	14.5-19.0	
42°17', 86°59'		16.0	14.5-18.0	
42°34', 86°52"		15.5	14.5-18.0	
Whole Lake:	1962-63			USDOI, 1968
561 offshore samples		20	12-30	
1547 inshore samples		20	10-76	
Samples collected:	1962-63			
Indiana Harbor, 21 samples		47	38-69	USDOI, 1968
Adjacent to Indiana Harbor, 317 samples		23	15-43	Risley and Fuller, 1966
Samples collected:	1962-63			
Calumet Harbor, 18 samples		24	22-25	USDOI, 1968
Adjacent to Calumet Harbor, 20 samples		23	20-29	Risley and Fuller, 1966
Samples collected:	1962-63			USDOI, 1968
Chicago Harbor, 6 samples		22	20-23	
Racine Harbor, 7 samples		22	18-24	
Samples collected:	Oct 1962, Jun 1963			USDOI, 1968
Milwaukee Harbor, 24 samples		29	16-43	
Adjacent to Milwaukee Harbor, 50 samples		22	16-53	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City		22	15-57	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo		20	12-28	
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor		22	12-40	
On a line roughly between Sheboygan and Little Sable Point		21	10-49	

Table 51. (contd.)

Sample Description	Dates	Concentration $SO_4{}^{2-}$, mg/l Average	Range	Reference
143 samples collected throughout Green Bay	17 Jul 1963	19	9.5-26	USDOI, 1968
Offshore samples collected, surface to bottom, at 3 stations [midlake and either end of line ∿16 km (10 mi) from shore] along lines connecting:	Apr-Nov 1964			Powers and Ayers, 1967
Benton Harbor to Chicago and South Haven to Waukegan		16.5	12.0-21.5	
Holland to Racine and Ludington to Sheboygan		16.0	12.5-22.5	
Samples collected:	22-28 Jul 1964			USDOI, 1968
Traverse Bay, 31 samples		18	12-22	
Adjacent to Traverse Bay, 15 samples		19	17-24	
Samples collected:	1965			Risley and Fuller, 1966
Indiana Harbor, 17 samples		55	32-68	
Calumet Harbor, 31 samples		24	17-37	
Samples collected in Indiana Harbor at east breakwall inner light:				Snow, 1974
3 samples	Dec 1965	64	56-68	
51 samples	Jan-Dec 1966	51	22-77	
42 samples	Jan-Dec 1967	43	11-70	
37 samples	Jan-Dec 1968	37	21-61	
25 samples	Jan-Jun 1969	32	15-48	
20 samples	Jan 1971-Jan 1973	39.2	31-58	
Samples collected at Chicago South Water Filtration Plant	1966	24.5		Vaughn and Reed, 1973
	1967	22.7		
	1968	22.8		
	1969	22.9		
	1970	23.1		
	1971	22.7		
Samples collected (variable sampling schedules) at water plant intakes:				Snow, 1974
Hammond	1967	25	19-55	
	1968	17	0-28	
	1969	12	3-26	
	1970	11	3-29	
	1971	14	11-19	
East Chicago	1967	25	18-35	
	1968	15	3-32	
	1969	12	3-24	
	1970	9	3-18	
	1971	14	9-20	
Gary	1967	24	17-32	
	1968	14	0-28	
	1969	10	4-18	
	1970	9	4-16	
	1971	14	11-18	
Chicago South	1967	23	17-30	
	1968	14	0-27	
	1969	10	3-22	
	1970	8	3-15	
	1971	14	8-17	
Annual averages for samples collected at water filtration plants near Chicago:				
12 plants	1968	23.5	23-25	Ill. Sanit. Water Board, 1969
5 plants	1969	21[a]		Ill. Sanit. Water Board, 1970

Table 51. (contd.)

		Concentration SO_4^{2-}, mg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Weekly samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	Nov 1969-Sep 1970	21	18-24	USGS, 1972
	Oct 1970-Sep 1971	21	19-24	USGS, 1973
	Oct 1971-Sep 1972	21	18-24	USGS, 1974a
	Oct 1972-Jun 1973	21	18-33	USGS, 1974b
Monthly averages for daily samples collected at Chicago 68th Street water intake crib	1969	22.7	22-25	Snow, 1974
	1970	22	21-23	
	1971	21.7	18.4-25	
	1972	22.3	19.2-27	
Annual average, Metropolitan Sanitary District of Greater Chicago	1970	21.7		Lue-Hing, 1973
	1971	22.2		
Samples collected ∿monthly at intakes:	Jan 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		19	11-26	
Waukegan Generating Station		22	14-35	
North Chicago public water supply		20	13-28	
Samples collected ∿monthly, surface and bottom, at 3 stations 9.6 km (6 mi) east of Zion	Apr 1970-Apr 1971	18.5	10-40	Industrial Bio-Test, 1972b
Samples collected ∿monthly at Lake County, Ill., public water intake	Jun 1970-Apr 1971	21	15-25	Howe, 1973
17 samples collected, surface to bottom, at 6 stations on a line passing east of Manitou Islands from Frankfort to Beaver Island	7 Jul 1970	15.5	11.0-21.5	Schelske and Roth, 1973
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		19		
Kenosha		21		
Milwaukee (5 intakes)		22	17-25	
Port Washington		18		
Racine		25		
Sheboygan		17		
Two Rivers		19		
Monthly surface-water samples collected at stations between ∿0.4 km (0.25 mi) and ∿16 km (10 mi) from shore:	Sep, Oct, Dec 1971; Jan, Feb, Apr, Jun 1972			Beeton and Barker, 1974
5 stations on an east-west transect ∿9.6 km (6 mi) south of Grafton, Wis.		18.8	15.5-21.0	
12 stations east of Oak Creek		20.1	16.5-28.5	
Monthly samples collected at Lake County, Ill., public water intake	Jul 1972-Jun 1973	19.7	14.5-24.1	Howe, 1973
10 surface-water samples each collected at stations east of Milwaukee:	28 Nov 1972			Beeton and Barker, 1974
0.4 km (0.25 mi) east		18.4		
16 km (10 mi) east		17.7		
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers-- 3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		23	19-28	
Effluent plume		23	18-26	
South of plant, 4.8 km (3 mi)		23	20-26	

Table 51. (contd.)

Sample Description	Dates	Concentration SO_4^{2-}, mg/l Average	 Range	Reference
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		27	21-31	
North of plant, 1.6 km (1 mi)		27	22-34	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		26.6	24.0-29.0	
South of plant, 1.6 km (1 mi)		27.1	25.0-28.5	

[a] *Same value for all samples.*

USDOI = U. S. Department of the Interior, USGS = U. S. Geological Survey.

Table 52. Variation in Sulfate Concentrations Reported for the Chicago South Water Filtration Plant

Year	Concentration SO_4^{2-}, mg/l Vaughn and Reed (1973)	 Snow (1974)
1966	24.5	-
1967	22.7	23
1968	22.8	14
1969	22.9	10
1970	23.1	8
1971	22.7	14

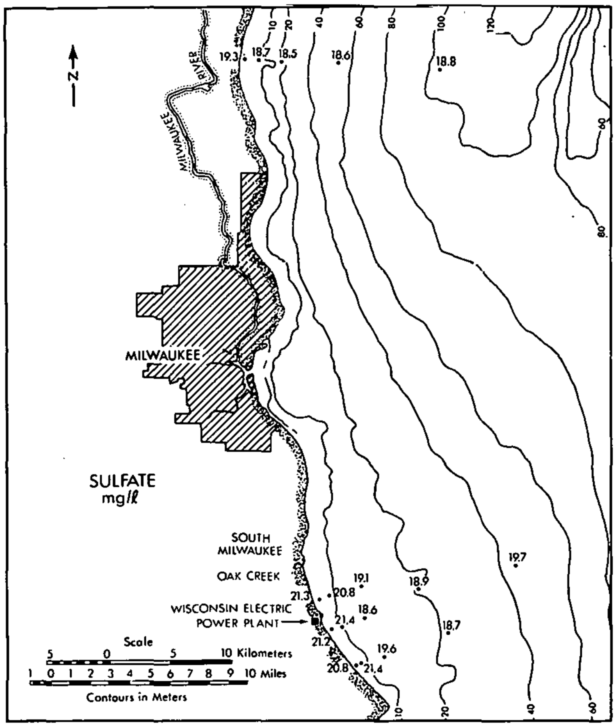


Fig. 98.

Average Sulfate Concentrations at 17 Stations near Milwaukee. Monthly samples collected September, October, December 1971, and January, February, April, June 1972. Figure (modified) and data from Beeton and Barker (1974).

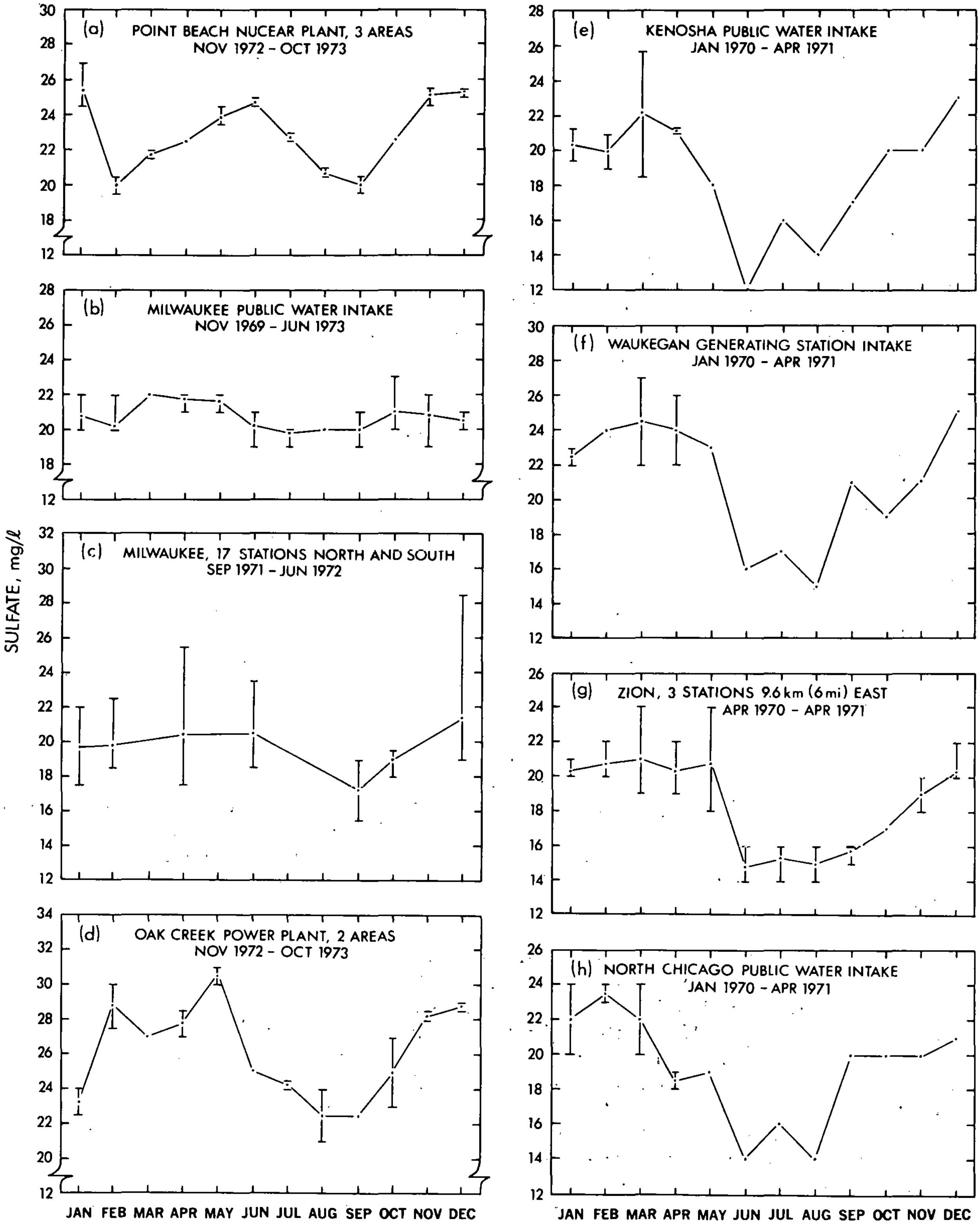


Fig. 99. Seasonal Variations in Average Sulfate Concentrations along the Western Shore of Lake Michigan. Sources of data: (a,d) Limnetics, 1974; (b) U. S. Geological Survey, 1972, 1973, 1974a, 1974b; (c) Beeton and Barker, 1974; (e,f,h) Industrial Bio-Test, 1972a; (g) Industrial Bio-Test, 1972b. See Table 51 for sample descriptions.

Sulfate is at present a conservative species in Lake Michigan. Chemical and biochemical reactions have little effect on the concentration of sulfate in the water; *e.g.* Klein (1975) calculated that only 0.8% of the sulfur entering Lake Michigan annually reaches the sediments. As long as the Lake continues as a well-aerated system, preventing the reduction of sulfate to sulfide in the absence of O_2, sulfate concentrations will continue to reflect sulfate influxes to the Lake.

There has been little interest in the sulfur content of Great Lakes sediments. Kemp *et al.* (1972) determined total sulfur in one core each from Lakes Ontario, Erie, and Huron. The Illinois State Geological Survey (Shimp *et al.*, 1970; Frye and Shimp, 1973) has reported total sulfur in sediment samples from four stations in southern Lake Michigan, while Callender (1969) measured sulfate concentrations in interstitial water from 29 cores throughout the Lake and Green Bay.

Despite the increases since 1830 in sulfate concentrations in the water of Lakes Ontario, Erie, and Huron, Kemp *et al.* (1972) found no increases in sulfur content near the surface of the cores they took in those lakes. Instead, they found that total sulfur correlated well with electrode potentials they measured in the sediments. The authors offered the following explanation for these observations: bacteria like *Desulfovibrio* reduce sulfate when the electrode potentionals drop below +100 mV. At negative potentials, sulfide precipitates as FeS. At higher electrode potentials, sulfide oxidizes to sulfur and then sulfate (*cf.* Fig. 96); sulfate is able to move upward through the interstitial water of the sediment to the overlying water. One would expect total sulfur content in the sediments to be enhanced above baseline values only in zones of negative electrode potentials.

Total sulfur content in two cores from the southern basin of Lake Michigan seemed to decrease in the first few centimeters (Fig. 100); in a third core, sulfur increased with depth; and in the fourth, too few data were available to establish any trend. Since electrode potentials were not presented by Shimp *et al.* (1970) or Frye and Shimp (1973), it is impossible to tell whether the explanation advanced by Kemp *et al.* (1972) is applicable to Lake Michigan sediments.

Callender (1969) determined interstitial sulfate in 54 of 104 samples from 29 cores of Lake Michigan. In 13 of 22 cores from the main portion of the Lake, he measured sulfate in the surficial sediment ($\leq$ 5 cm) interval; Callender considered 12 of these 13 values reliable, and the average of these 12 is 17.0 mg SO_4^{2-}/1. This concentration is similar to or lower than sulfate concentrations in the overlying water (*cf.* Table 51). There was no uniform variation in interstitial sulfate concentrations with sediment depth. All cores from the southern basin and divide area for which Callender presented sufficient detail showed decreasing interstitial sulfate concentrations with increasing depth; all but two cores (one off Frankfort, one in Little Traverse Bay) in the northern basin and Green Bay showed sulfate concentrations increasing with depth. Attempts to correlate interstitial sulfate concentrations with electrode potentials produce the plot presented in Figure 101.

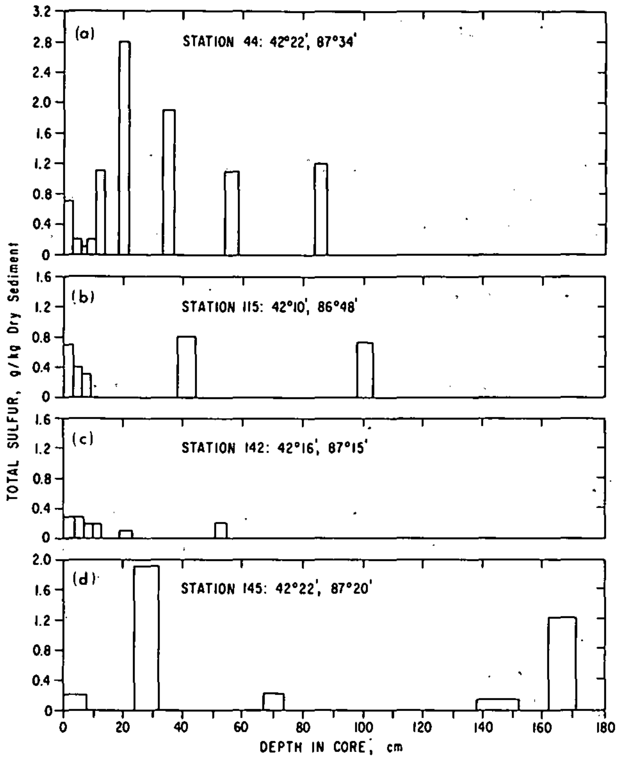
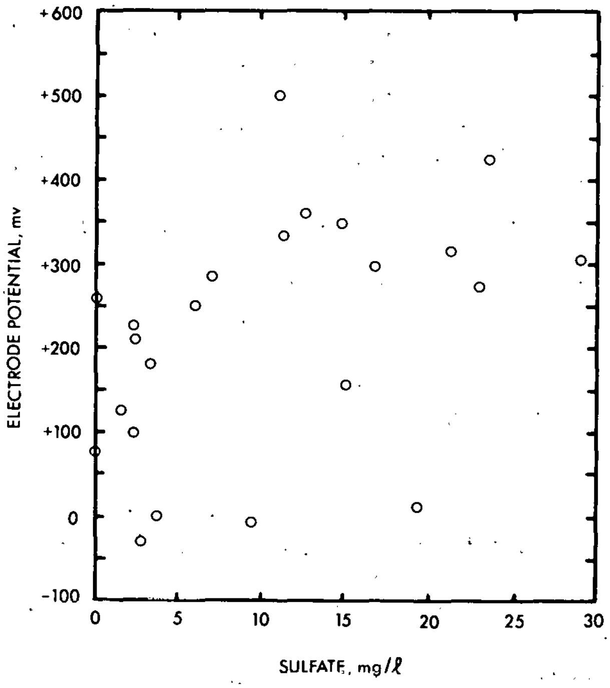


Fig. 100.

Total Sulfur Content in Four Sediment Cores from Southern Lake Michigan. Data for Stations 44, 142, and 145 from Shimp *et al.* (1970); data for Station 155 from Frye and Shimp (1973), with coordinates from Shimp *et al.* (1971).

Fig. 101.

Relationship between Sulfate Concentration and Electrode Potential in Lake Michigan Sediments. Data from Callender (1969).



OTHER INORGANIC CONSTITUENTS

ALUMINUM

There has been little evidence that aluminum is required by either plants or animals, although Bowen (1966) indicated it may activate the enzyme succinic dehydrogenase. Aluminum is not generally harmful to aquatic organisms at concentrations below 500 µg/l in hard water (National Academy of Sciences ..., 1973; McKee and Wolf, 1963). Turbidity and pH also affect the toxicity of aluminum.

Sources of aluminum to Lake Michigan are largely natural (Winchester and Nifong, 1971; Klein, 1975). Aluminum is the third-most abundant element in the earth's crust (Krauskopf, 1967), and it likely reaches the Lake in the forms of clay minerals and feldspars (Table 33), gibbsite [$Al(OH)_3$], mixed phases (for example, aluminum oxides sorbed to amorphous silica), the ion $Al(OH)_4^-$, aluminum hydroxide polymers, and perhaps aluminum complexed with organic matter.

Aluminum entering the Lake as a result of human activities is probably not a major source. Common industrial uses of aluminum salts include dye manufacture, tanning, fillings in paper manufacture, and as a mordant in printing fabrics (McKee and Wolf, 1963). Alum, or aluminum sulfate, is used in water treatment as a coagulant for colloidal and suspended solids.

Determinations of aluminum concentrations in Lake Michigan water are summarized in Table 53. The great variability of the values in this table is notable. Bowen (1966) suggested that 240 µg Al/l was typical for fresh water, but he did not specify whether this value represented soluble or total aluminum. Jones *et al.* (1974) indicated that at pH 7-8.5 aluminum concentrations in true solution should generally be less than 10 µg/l. Higher concentrations indicate the presence of particulate and/or colloidal aluminum species, for example, clay minerals. Even water filtered through a standard 0.45 µm pore size filter may contain appreciable amounts of fine-grained particles (Kennedy *et al.*, 1974). Although the values reported by Kopp and Kroner (1968) and Copeland and Ayers (1972) are low, they are probably overestimates of soluble aluminum, since 0.45 µm filters were used to separate soluble aluminum. The high values indicated by Limnetics (1974) are likely closer to total than soluble aluminum concentrations, since their analytical methods would lead to an appreciable dissolution of particulate aluminum, according to Kennedy *et al.* (1974).

Since aluminum is considered fairly nontoxic and it does not produce other undesirable conditions, no limitations have been set for aluminum in drinking water or for the protection of aquatic life.

Forms of aluminum in Lake Michigan water have not been identified. Some of the particulate forms no doubt include feldspars and clay minerals, for these have been found in the sediments (Callender, 1969). Kramer (1967) suggested that Great Lakes waters are stable (saturated) in winter with respect to gibbsite and in summer with respect to kaolinite, $Al_2Si_2O_5(OH)_4$. Kaolinite has been identified in Lake Michigan sediments (Shimp *et al.*, 1969, 1970), but gibbsite has not been found so far (Kramer, 1967). Gibbsite, $Al(OH)_4^-$, and polymerized aluminum hydroxides are known for their ability to sorb or coprecipitate other trace substances and remove them to the sediments (Stumm and Morgan, 1970).

Table 53. Aluminum Content in Lake Michigan Water

		Concentration Al, μg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Semiannual composites from monthly samples collected at public water intakes:	Oct 1962-Sep 1967			Kopp and Kroner, 1968
Milwaukee				
8 composites		N.D.		
2 composites		50[a]	28-71[a]	
Gary				
5 composites		N.D.		
4 composites		21[a]	3-58[a]	
Surface-water samples collected throughout Lake at 20 stations sampled 3 times each	Aug 1969-Jun 1970	27[a]	9.6-77[a]	Copeland and Ayers, 1972
Two samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	5, 12 Jan 1970	50	0-100	USGS, 1972
Monthly samples collected at Lake County, Ill., public water intake:	Jul 1972-Jun 1973			Howe, 1973
5 samples		<100		
7 samples		530	200-1600	
Single sample collected offshore from Grand Haven	Unspecified	≤10[a]		Wahlgren *et al.*, 1972b
Stations at 3.7, 5.5, and 7.3 m (12-18-, and 24-ft) water-depth coutours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		540	100-3000	
Effluent plume		700	100-6000	
South of plant, 4.8 km (3 mi)		490	100-3000	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		1400	300-3400	
North of plant, 1.6 km (1 mi)		1500	200-4000	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		890	200-2000	
South of plant, 1.6 km (1 mi)		1450	200-4000	

[a] *Total soluble aluminum.*

N.D. = not detected.

USGS = U. S. Geological Survey.

Aluminum content in Lake Michigan sediments in the form of aluminosilicates is indicated in Table 36. Callender (1969) attributed changes in mineral content with sediment depth to accelerated erosion in the Basin, resulting from cultural activities and deforestation. Copeland and Ayers (1972) collected 19 sediment samples throughout the Lake with a Ponar dredge and analyzed the top 3 cm for aluminum content. Their data indicate that aluminum is more concentrated at offshore stations ($\bar{x}$ = 5.12% bulk dry weight) than inshore ($\bar{x}$ = 3.60% bulk dry weight), but this difference is not significant ($P > 0.05$).

The Illinois State Geological Survey has reported aluminum content in sediments from southern Lake Michigan (Shimp *et al.*, 1970; Frye and Shimp, 1973; Leland *et al.*, 1973b). Leland *et al.* (1973b) indicated that average aluminum concentrations ($\bar{x}$ = 4.20 weight %) in surficial sediments were less than in samples collected between 15 and 100 cm in the cores ($\bar{x}$ = 5.05 weight %). The authors did not report whether this difference was statistically significant, nor did they speculate on the cause(s) of this increase with depth. At least one possibility for this difference might be the higher organic carbon content in these surficial sediments, leading to an apparent dilution of aluminum at the surface.

Leland *et al.* (1973b) also analyzed aluminum content in suspended matter, collected 1 m above the Lake bottom. The average value was 2.59 weight %, much less than the 4.20 weight % in the surficial sediments. This difference is probably due to the different methods by which surficial sediments and suspended matter were sampled.

ARSENIC

Arsenic is not known to be essential for plants or animals. However, organic arsenicals fed to poultry and pigs may exercise beneficial effects by killing internal parasites (Underwood, 1971).

The toxicity of large doses of this metalloid depends on its oxidation state. Arsenate, the 5+ form of arsenic, is 60 times less toxic to humans than arsenite, the 3+ form of arsenic. Arsenite exerts its toxic properties by reacting with sulfhydryl groups in amino acids; arsenate does not react with sulfhydryl groups (Webb, 1966). Data summarized by McKee and Wolf (1963) indicate that reduced forms of arsenic are much more toxic to fish and fish-food organisms than are oxidized forms. Fish-food organisms were reported susceptible to sodium arsenite at concentrations as low as 1.0 mg As/l. Penrose (1974) indicated he found no evidence in the scientific literature of bio-magnification of arsenic in either marine or freshwater food chains.

Humans are subject to both acute and chronic effects of arsenic toxicity. Arsenic at levels higher than 0.3 mg As/l in drinking water has been shown to cause hyperkertosis and skin cancer in Taiwanese citizens (Shen and Chen, 1965).

Weathering and erosion of rocks and soils contribute some arsenic to Lake Michigan. Igneous rocks average 1.8 mg As/kg; shales, 13 mg/kg; sandstones and limestones, 1 mg/kg; and soils, 6 mg/kg (Bowen, 1966). In undisturbed regions of the Pacific Ocean and Antarctica arsenic in rain ranged from 0.2-1.0 μg As/l (Kanamori and Sugawara, 1965). In populous areas arsenic content in rain is higher, due to industrial burning of arsenic-containing coal and smelting of sulfide ores contaminated by arsenic.

Industrial and municipal effluents provide major quantities of arsenic to Lake Michigan. Arsenic oxide is a by-product of the smelting of copper, lead, zinc and tin ores (McKee and Wolf, 1963). Elemental arsenic is used in semiconductors and in alloys to increase hardness and heat resistance; arsenic compounds are used in the manufacture of glass and textile dyes and in therapeutic drugs. The most important uses of arsenic are as a wood preservative and as a pesticide against insects, weeds, rodents, and fungi. Sodium arsenite is used to control aquatic weeds in recreational lakes; if properly applied (McKee and Wolf, 1963), it is effective against a wide range of submerged weeds and filamentous algae without undesirable side effects, such as fish kills.

Arsenic is also a major contaminant of phosphate fertilizers (Bowen, 1966) and detergents (Angino *et al.*, 1970), but Ferguson and Gavis (1972) considered these negligible compared with other sources of arsenic.

Winchester and Nifong (1971) did not think arsenic was a major constituent in aerosol pollution of Lake Michigan, but localized contamination in the vicinity of coal-burning plants might be important (Kanamori and Sugawara, 1965). Klein (1975) calculated that aerosols contribute 2.5 times more arsenic to the Lake than soil erosion.

Determinations of arsenic in Lake Michigan are summarized in Table 54 and may be compared with the median value of 0.4 μg As/l for fresh waters (summarized by Bowen, 1966). Many measurements have been made in inshore areas from which municipalities withdraw their drinking water supplies. Few samples have been taken offshore. Copeland and Ayers (1972) measured total soluble arsenic in surface-water samples. Average concentrations in offshore samples exceeded inshore values (1.10 *vs.* 0.98 μg As/l); and the range for offshore samples (0.75-1.5 μg As/l) was also higher than inshore samples (0.60-1.2 μg As/l). There is no immediate explanation for this difference.

Since the chemical characteristics of arsenate and phosphate are somewhat similar, utilization of arsenate by organisms may be responsible for the lower soluble arsenic concentrations in inshore areas, since there are larger numbers of organisms inshore.

Stations and sampling dates of Seydel (1972) resemble those of Copeland and Ayers (1972). The average offshore arsenic concentration she determined was the same as the inshore average, 1.7 μg As/l. Comparison of data in Seydel (1972) and Copeland and Ayers (1972) may be evidence that surface-water arsenic concentrations are the same inshore and offshore, and that the fraction present as soluble arsenic differs in inshore and offshore waters.

Industrial Bio-Test (1972b) collected samples at three stations 9.6 km (6 mi) east of Zion, Illinois, from 18 May-22 September 1970. Before stratification, samples were collected at the surface, in the middle of the water column, and at the bottom. During stratification, samples were taken at the surface, just above the thermocline, just below the thermocline, and at the bottom. After stratification arsenic concentrations in bottom waters tend to exceed those in surface waters (Fig. 102).

None of the experimental techniques used in the analyses summarized in Table 54 identifies the chemical form(s) of arsenic in Lake Michigan water. Equilibrium data in Ferguson and Gavis (1972) suggest that one expects inorganic arsenic to be present as arsenate in oxygenated waters above pH 7. However, equilibrium conditions may not exist. Arsenic may also be present in organic form. Braman and Foreback (1973) detected methylarsonic acid [$CH_3AsO(OH)_2$] and dimethyl arsinic acid [$(CH_3)_2AsO(OH)$] in freshwater samples in and around Tampa, Florida. Crecelius (1975) found dimethyl arsinic acid in the interstitial water of Lake Washington sediments. Implications of these findings are discussed by Wood (1974).

Table 54. Arsenic Content in Lake Michigan Water

		Concentration As, µg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Stations throughout Lake sampled 3 times each:	Aug 1969-Jun 1970			Copeland and Ayers, 1972
12 inshore stations		0.98[a]	0.17-1.9[a]	
8 offshore stations		1.10[a]	0.38-2.6[a]	
Monthly samples collected at intakes:	May 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply				
11 samples		1.6	0.7-3.7	
1 sample		N.D.		
Waukegan Generating Station				
11 samples		2.4	0.6-4.9	
1 sample		N.D.		
North Chicago public water supply				
12 samples		1.4	0.5-3.4	
3 stations 9.6 km (6 mi) east of Zion sampled 8 times:	18 May-22 Sep 1970			Industrial Bio-Test, 1972b
84 samples		1.8	0.5-7.3	
3 samples		N.D.		
Single samples collected from water intakes at Milwaukee, Chicago, Evanston, Gary, Whiting, and Agnew, Mich.	Oct 1970	≤10[a,b,c]		Durum *et al.*, 1971
Single samples collected from public water intakes at Green Bay, Kenosha, Milwaukee (5 intakes), Port Washington, Racine, Sheboygan, and Two Rivers	1971	<20[b]		Baumeister, 1972
Samples collected at:	Unspecified			Seydel, 1972
7 inshore stations		1.7	0.7-2.4	
1 inshore station		N.D.		
3 offshore stations		1.7	0.5-2.3	
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers-- 3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		1	<1-3	
Effluent plume		1	<1-4	
South of plant, 4.8 km (3 mi)		1	<1-4	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee-- 2 areas (Unspecified no. of observations):	Nov 1972-Oct 1973			
Effluent plume		1.1[d]	0.5-2.8[d]	
North of plant, 1.6 km (1 mi)		1.0[d]	0.5-2.7[d]	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis-- 2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		1.3	0.5-3.0	
South of plant, 1.6 km (1 mi)		1.4	0.5-2.5	

[a] *Total soluble arsenic.*

[b] *Same value for all samples.*

[c] *Limit of detection.*

[d] *Monthly means taken from graphs.*

N.D. = not detected.

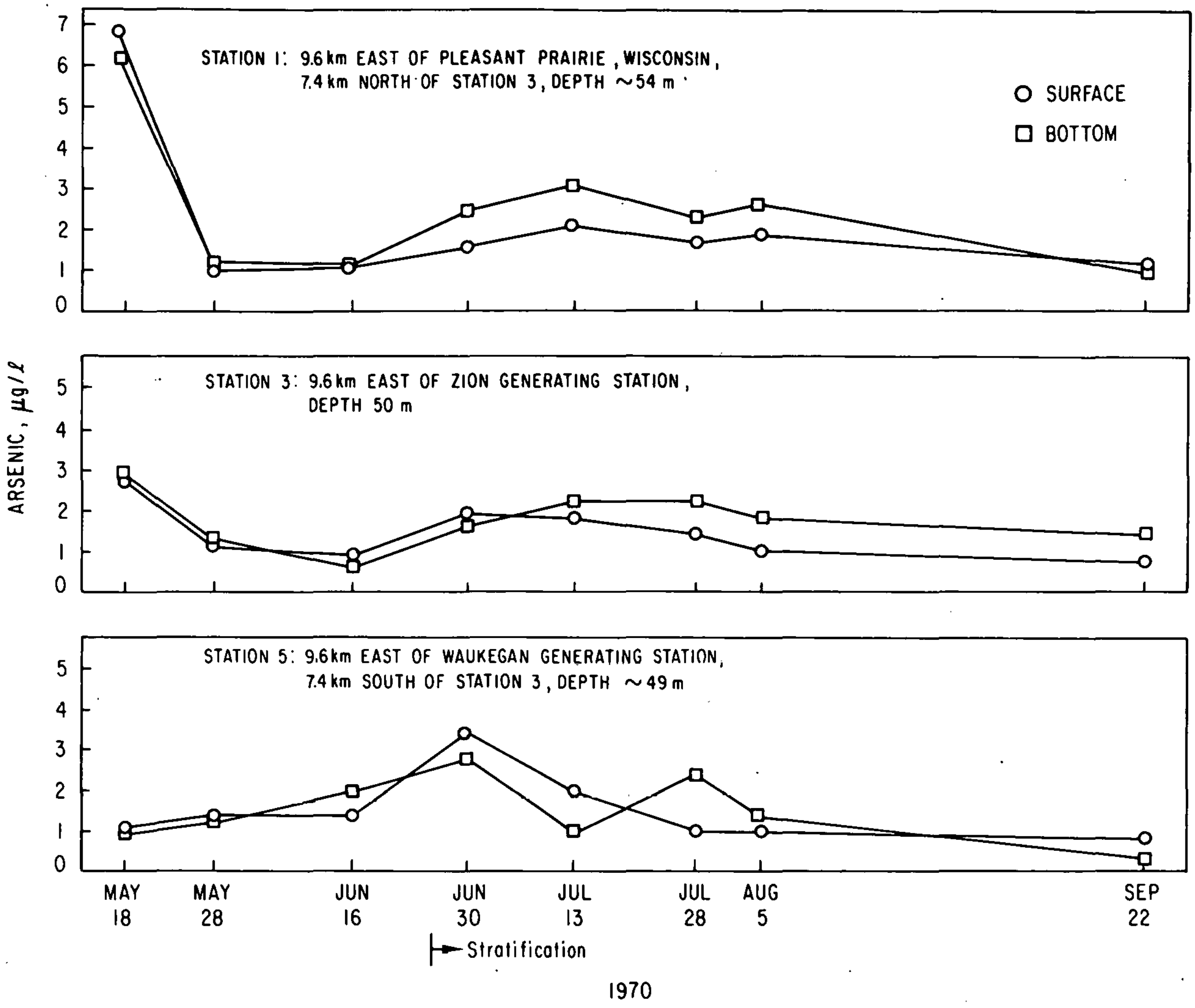


Fig. 102. Arsenic Concentrations at Three Stations East of Zion (Industrial Bio-Test, 1972b).

Standards and criteria for arsenic content in drinking water and for the maintenance of freshwater fish and aquatic life are summarized in Appendix B.

Arsenic content of sediments in the southern basin of Lake Michigan correlates with iron (Leland *et al.*, 1973b) and organic carbon (Leland *et al.*, 1973b; Ruch *et al.*, 1970) contents. Coprecipitation and sorption of arsenite and arsenate with ferric hydroxides are considered important mechanisms for removing arsenic from natural waters (Ferguson and Gavis, 1972; Crecelius, 1975). In oxygen-depleted waters or in sediments, reduction of ferric ions could cause arsenic to be released to solution.

Copeland and Ayers (1972) surveyed arsenic content in bulk sediments throughout the Lake. With the exception of one station (55 mg As/kg dry weight of bulk sediment) northeast of Chicago, arsenic content ranged from undetectable to 6 mg As/kg. Inshore-offshore trends were not evident.

Ruch *et al.* (1970) have looked in more detail at arsenic content in sediments of the southern basin. Arsenic is more concentrated in surficial sediments in the eastern portion of the southern basin ($\bar{x}$ = 19 mg As/kg sediment) than in the western portion ($\bar{x}$ = 7 mg As/kg sediment) (Lineback and Gross, 1972). Arsenic concentrations were found to decrease with depth in a sediment core (Ruch *et al.*, 1970); this observation was considered likely a result of human activities in the watershed. Leland *et al.* (1973b) attempted to determine whether deposition of arsenic-containing particles accounts for the surface accumulation of arsenic by measuring arsenic content in suspended particles collected one meter above the Lake bottom. Mean concentrations of arsenic in these suspended particles were reportedly 27 mg As/kg, or twice the average value for surficial sediments (14 mg As/kg sediment). No explanation was offered for the enrichment of arsenic in these suspended particles.

BARIUM

None of the toxicity data summarized by McKee and Wolf (1963), the National Academy of Sciences ... (1973), or Kemp *et al.* (1971) indicates that barium salts are harmful to aquatic organisms at concentrations below 10 mg/l. Dosages fatal to man are in the range of 500-600 mg (National Academy of Sciences ..., 1973).

Natural sources of barium to Lake Michigan are likely more important than cultural sources. Weathering and erosion of geologic formations in the Basin represent background values. Bowen (1966) reported that igneous rocks typically contain 425 mg Ba/kg; shales, 580 mg Ba/kg; sandstones, 50 mg Ba/kg; and limestones, 120 mg Ba/kg.

Barium chloride, barium acetate, barium nitrate, and various other barium salts are used industrially in: special alloys, mordants in dyeing, paint manufacture (McKee and Wolf, 1963), and lubricating oils and greases (Merck Index, 1968). Winchester and Nifong (1971) estimated that stream sources to Lake Michigan contribute 330 metric tons of barium per year; while aerosol fallout, mostly from combustion of coal and fuel oil in the Milwaukee-Chicago-Gary-Hammond area, adds 21 metric tons per year (assuming a 10% transfer efficiency). The stream source may be larger than Winchester and Nifong estimated, for their assumed stream concentration (10 µg/l) is lower than most of the tributary data presented by Robbins *et al.* (1972b).

The few data available on barium concentrations in Lake Michigan water are summarized in Table 55. Total soluble barium is apparently less than 50-75 µg/l. These low concentrations agree with the 54 µg Ba/l value presented by Bowen (1966) as typical of fresh water.

Limits of 1 mg Ba/l in drinking water have been suggested by a number of agencies (Appendix B, part 1) for the protection of human health. In the absence of experimental data that would establish a safe level for aquatic life, Illinois and Indiana (Appendix B, part 2) have applied the drinking water limit to Lake Michigan water.

Several mechanisms keep barium concentrations in Lake Michigan waters at low levels. Carbonate and sulfate salts of barium are both insoluble. If carbonate alone controlled barium, then it could be present at concentrations

Table 55. Barium Content in Lake Michigan Water

Sample Description	Dates	Concentration Ba, µg/l		Reference
		Average	*Range*	
Semiannual composites from monthly samples collected at public water intakes:	Oct 1962-Sep 1967			Kopp and Kroner, 1968
Milwaukee, 10 composites		18[a]	10-26[a]	
Gary, 9 composites		21[a]	14-41[a]	
Surface-water samples collected throughout Lake at 20 inshore and offshore stations sampled ∿3 times each	Aug 1969-Jun 1970	36[a]	11-76[a]	Copeland and Ayers, 1972
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		<500		
Kenosha		<500		
Milwaukee (5 intakes)		<500[b]		
Port Washington		<500		
Racine		<500		
Sheboygan		<500		
Two Rivers		<500		
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		16[a]		
17 km (10.6 mi) offshore		24[a]		

[a] *Total soluble barium.*

[b] *Same value for all samples.*

as high as 2 mg Ba^{2+}/l (assuming a total alkalinity of 110 mg $CaCO_3/l$). However, if one assumes sulfate is present at 20 mg/l in the Lake water (*cf.* Table 51), then soluble barium is limited to 72 µg/l.

Barium is also removed from solution by sorption and/or coprecipitation with manganese oxides and hydroxides (National Academy of Sciences ..., 1973). Edgington and Callender (1970) noticed high concentrations of barium (as much as 2.2 weight %, based on soluble material) in ferromanganese nodules collected in Green Bay and Little Traverse Bay. Subsequently, positive correlations were shown between barium and manganese concentrations in these nodules (Rossman *et al.*, 1972; Torrey and Edgington, 1973a). Sorptive processes may keep barium concentrations below the level predicted from $BaSO_4$ solubility.

Copeland and Ayers (1972) determined barium concentrations in bulk sediments of 19 grab samples collected throughout the Lake. The average value was 421 mg Ba/kg bulk dry sediment. Average offshore concentrations (497 mg Ba/kg) were slightly higher than inshore (406 mg Ba/kg), but this difference was not statistically significant.

BORON

Animals do not require boron (National Academy of Sciences ..., 1973). Boron is essential for higher plants (Dugger, 1973); it is involved with maintenance of membrane integrity, and regulation and utilization of sugars and starches. Concentrations of 0.05-0.1 mg B/l are safe and adequate for higher plants. About 0.5 mg B/l satisfies the boron requirements of diatoms (Lewin, 1966). Reports of boron requirements among other microorganisms are contradictory. Forsberg *et al.* (1967) found that growth rates of the blue-green alga *Microcystis* and the green alga *Ankistrodesmus* were stimulated by addition of boron, whereas the green alga *Scenedesmus* was inhibited. Gerloff (1968) found no response to boron addition by three species of green algae (*Chlorella pyrenoidosa*, *Draparnaldia plumosa*, and *Stigeoclonium tenue*), but yields of four blue-green algae (*Calothrix parietina*, *Nostoc muscorum*, *Anabaena cylindrica*, and *Microcystis aeruginosa*) increased in response to 0.27 mg B/l.

Boron in drinking water is seldom considered a hazard to humans (McKee and Wolf, 1963). Boron-sensitive higher plants are adversely affected by 0.5-1.0 mg B/l (Bingham, 1973). Boric acid [$B(OH)_3$] and sodium borate, or borax ($Na_2B_4O_7$), do not affect fish below concentrations of several grams per liter (National Academy of Sciences ..., 1973). The threshold concentration of sodium perborate ($NaBO_3$) that immobilized *Daphnia magna* in Lake Erie at 25°C was about 2.6 mg/l (McKee and Wolf, 1963).

At present, both natural and cultural sources of boron to Lake Michigan are likely important. Data collected in the United States showed an overall average of 30 mg B/kg of soil (Bingham, 1973). Soils derived from igneous and sedimentary rocks averaged 14 and 40 mg B/kg, respectively.

Boron as borax is used as a domestic and industrial cleaning agent, and sodium perborate bleaches are used increasingly to launder clothing made of synthetic fibers. Bingham (1973) indicated that waste discharges from several communities south of Los Angeles contained 0.75-1.50 mg B/l; the amount of boron contributed by households was estimated as 50%.

Elemental boron is used in metallurgy to harden other metals and as a shielding material in nuclear installations (McKee and Wolf, 1963). Boric acid can be used as a bactericide and fungicide, while both boric acid and boron salts are used to fireproof fabrics and manufacture glass. Brines discharged by salt and chemical companies in western Michigan may be a source of boron to the Lake considering the high boron content of sea water (Krauskopf, 1967).

Aerosol inputs of boron, derived from the Milwaukee-Chicago-Gary-Hammond area, are negligible compared with tributary contributions (Winchester and Nifong, 1971).

Table 56 summarizes boron determinations in Lake Michigan water. Average concentrations are about 0.1 mg B/l. For comparison, Bowen (1966) said typical values for fresh water are 0.013 mg B/l. It is not obvious why Lake Michigan boron concentrations are higher; perhaps Bowen's values represent only soluble reactive boron.

The chemical forms of boron in Lake Michigan are unknown. Soluble inorganic forms probably include boric acid, $B(OH)_3$, and borate ion, $B(OH)_4^-$, under the pH conditions of the Lake. By analogy with sea water, boron may also be present in a soluble form associated with organic compounds (Gast and Thompson, 1958). Particulate forms likely include boron in soil minerals, washed off the surrounding watershed, and boron adsorbed to the surfaces of soil particles (Bingham, 1973).

Table 56. Boron Content in Lake Michigan Water

Sample Description	Dates	Concentration B, µg/l		Reference
		Average	Range	
Semiannual composites from monthly samples collected at public water intakes:	Oct 1962-Sep 1967			Kopp and Kroner, 1968
Milwaukee, 10 composites		25[b]	13-49[b]	
Gary, 9 composites		29[b]	16-43[b]	
Monthly samples (semimonthly May-Jul) collected at 3 stations 9.6 km (6 mi) east of Zion:	May-Sep 1970			Industrial Bio-Test, 1972b
Surface-water		100	50-230	
Bottom-water		60	50-150	
Samples collected ∿monthly at Lake County, Ill., public water intake	Jun 1970-Apr 1971 Jul 1972-Jun 1973	90 50	7-140 30-80	Howe, 1973
Monthly samples collected at intakes:	Jun 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		100	60-200	
Waukegan Generating Station		110	40-170	
North Chicago public water supply		90	50-140	
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		<200		
Kenosha		200		
Milwaukee (5 intakes)		<200[a]		
Port Washington		<200		
Racine		<200		
Sheboygan		<200		
Two Rivers		<200		
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		130[b]		
17 km (10.6 mi) offshore		33[b]		
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		<100[a]		
Effluent plume		<100[a]		
South of plant, 4.8 km (3 mi)		<100[a]		
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		<100[a]		
North of plant, 1.6 km (1 mi)		<100[a]		
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		100[a]		
South of plant 1.6 km (1 mi)		110	100-200	

[a] *Same value for all samples.*

[b] *Total soluble boron.*

There are no limits on boron in drinking water. The state of Michigan has a limit of 1.0 mg B/1 for the protection of aquatic life (Appendix B, part 2).

Boron has been determined in sediments of the southern basin by the Illinois State Geological Survey (Shimp *et al.*, 1970, 1971; Lineback and Gross, 1972; Leland *et al.*, 1973b). There is no indication that boron is accumulating in these sediments. The median value in sediments less than one meter deep (Shimp *et al.*, 1971) was 43 mg B/kg bulk dry sediment. Boron concentrations in surficial sediment samples from the eastern part of the Waukegan member (Lineback and Gross, 1972) were higher ($\bar{x}$ = 44 mg/kg) than in the western part ($\bar{x}$ = 32 mg/kg). Shimp *et al.* (1971) did not calculate statistical relationships, but their data suggest that boron content is more closely related to the content of < 2 µm clay size particles than to organic carbon content.

BROMINE

Bromine has not been proved to be essential for any vital functions in higher plants or animals (Underwood, 1971), although there is recent evidence that bromine plays some sort of role in the detoxification of mercury, selenium, and cadmium in mammals (Anon., 1975). No requirement for bromine has been demonstrated for freshwater algae. While bromine (Br_2) is very toxic to organisms, bromide (Br^-) is relatively harmless (Bowen, 1966).

Both natural and cultural sources contribute bromine to Lake Michigan. Bromine reaches fresh water by way of rainfall (Tiffany *et al.*, 1969); reported concentrations of bromide in rain range from 4 to 700 µg/l (Warner and Bressan, 1973). The bromide in rain has its origin from the sea. Igneous and sedimentary rocks contain 1-6 mg Br/kg (Bowen, 1966), and soils worldwide average 5 mg Br/kg, the same as the average concentration of iodine.

Air pollutants are potentially a major source of bromine to Lake Michigan. Gasoline additives with tetraethyl lead also contain ethylene dichloride and ethylene dibromide. During combustion, these additives burn to the relatively volatile $PbClBr$. Of the bromine produced in the United States, 95% is used in ethyl fluid (Loucks and Winchester, 1969). Winchester and Nifong (1971) computed that the amount of bromine carried into Lake Michigan by its tributaries is about the same as that carried in atmospherically from the burning of gasoline. Klein (1975) computed that aerosol inputs of bromine were almost 100 times greater than those due to soil erosion.

Bromine is measured infrequently in Lake Michigan; available data are summarized in Table 57. Tiffany *et al.* (1969) and Copeland and Ayers (1972) used neutron activation to quantify total bromine, while Wahlgren *et al.* (1972b) used mass spectrometry. Neither analytical method distinguishes the chemical form of bromine, but by filtration Lake water samples can be partitioned into soluble and particulate portions. Tiffany *et al.* (1969) did not indicate if their samples were filtered, but Copeland and Ayers (1972) and Wahlgren *et al.* (1972b) determined total soluble bromine. Using the electrode potentials of Latimer (1952) to calculate equilibrium relationships, one sees that the stable form of bromine in oxygenated water at pH values similar to

Table 57. Bromine Content in Lake Michigan Water

Sample Description	*Dates*	*Concentration Br, μg/l* *Average*	 *Range*	*Reference*
Single samples collected at 2 shoreline stations northwest of the Straits of Mackinac	9 Jul 1967	14	13-14	Tiffany *et al.*, 1969
9 samples collected between surface and 110 m at a station 9.6 km (6 mi) north of South Fox Island	19 Jul 1967	19	16-21	Tiffany *et al.*, 1969
4 samples collected between 5 and 115 m at a station in middle of southern basin	22 May 1968	15	13-17	Tiffany *et al.*, 1969
20 stations throughout Lake sampled 3 times each	Aug 1969-Jun 1970	50[a]	20-84[a]	Copeland and Ayers, 1972
Single sample collected offshore from Grand Haven	Unspecified	≤25[a]		Wahlgren *et al.*, 1972b

[a] *Total soluble bromine.*

those in Lake Michigan is bromide (Br^-) rather than bromine (Br_2) or bromate (BrO_3^-). However, since there is no reason to think Lake Michigan is at equilibrium, the chemical forms in which bromine occurs remain unknown.

The concentration of bromine in Lake Michigan is perhaps near 20 μg/l (Table 57). Sea water, with 65 mg Br/l (Goldberg, 1965), is 3200 times more concentrated. Both iodine and bromine are considered conservative by Tiffany *et al.* (1969). The major source of both is rain.

Concentrations of bromine in sediments from the southern basin of Lake Michigan have been reported and discussed by Shimp *et al.* (1970, 1971), Lineback and Gross (1972), and Leland *et al.* (1973b). Shimp *et al.* (1970, 1971) reported that bromine content is highest in the most recently deposited sediments (Fig. 103). This observation was attributed to the introduction of materials to the Lake by cultural activity (*e.g.* burning of leaded fuels). Bromine content correlated well with organic carbon content both at the sediment surface ($r = 0.77$) and at depth ($r = 0.92$) within the cores. The greater average bromine concentration (69 mg/kg) in the gray silt facies along the eastern shore of the southern basin was attributed to the higher organic carbon content of those sediments (Lineback and Gross, 1972). For comparison, bromine content averaged 23 mg/kg in the brown silt facies along the western shore of the southern basin.

Determinations of bromine in suspended matter collected 1 m from the lake bottom were made to ascertain whether bromine associated with particles accounted for surface enrichment of bromine (Leland *et al.*, 1973b). Bromine averaged 10 mg/kg in 12 samples of suspended particles, while the mean bromine concentration in 20 surficial sediment samples was 62 mg/kg. Leland *et al.* (1973b) speculated that bromine may be held more tightly to particulate matter in the sediments than to particles in the water because hydrous iron oxides are able to sorb more bromide at the lower pH's of the sediments. The authors pointed out this explanation would be applicable only if hydrous iron oxides

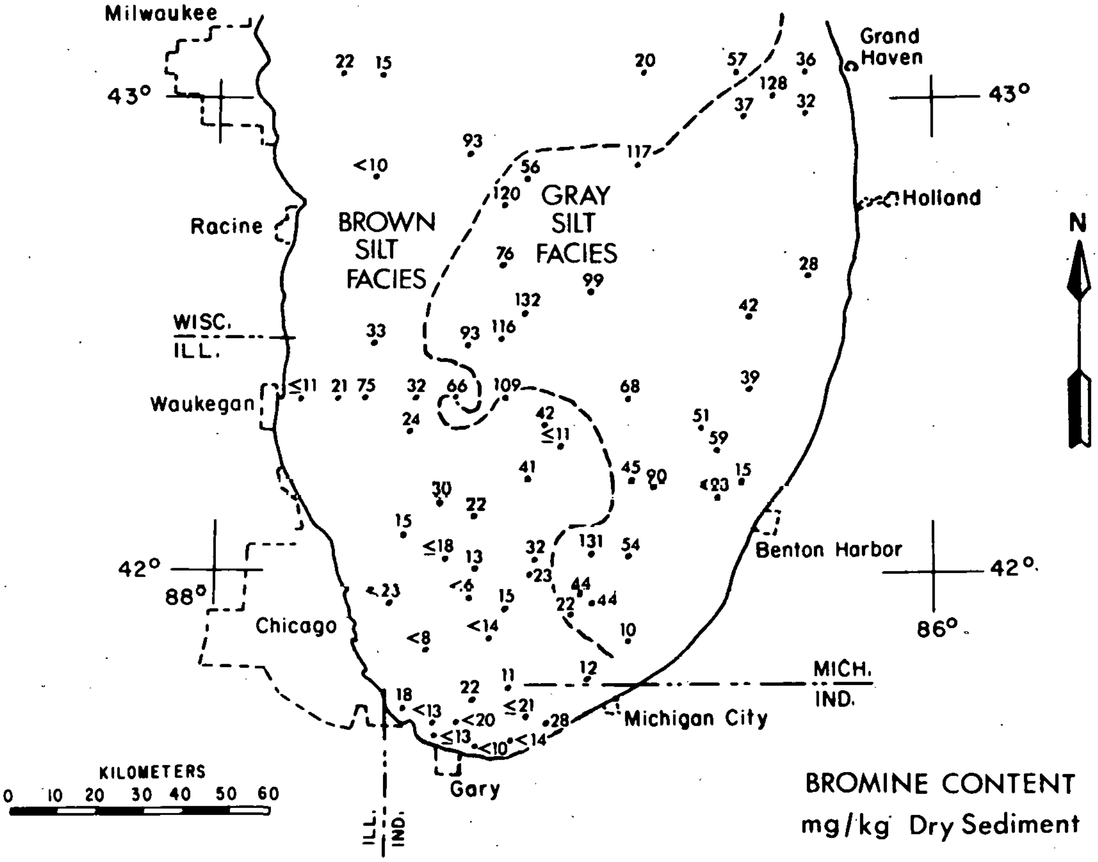


Fig. 103. Bromine Content in the Most Recent Sediments of Southern Lake Michigan. Modified from Leland *et al.* (1973b). Boundary of brown and gray silt facies of the Waukegan member from Lineback and Gross (1972).

are a dominant factor in removing bromine from the dissolved phase in Lake Michigan water. Based on 38 surficial sediment samples, bromine content was shown to be correlated with iron content (r = 0.65). Leland *et al.* (1973b) suggested that bromine enrichment in surficial sediments might also be due to specific incorporation of bromine by aquatic organisms; they discounted non-specific sorption of bromine to organic matter since the complexing capability of organic matter for anions like bromide is low.

CADMIUM

Cadmium has not been found essential for plant (Hemphill, 1972) or animal (Friberg *et al.*, 1971) metabolism. Cadmium is toxic to higher plants (Page *et al.*, 1972) at concentrations as low as 0.2 mg Cd/l. To date cadmium toxicity to higher plants has not been a problem except near mining and smelting operations. Inhalation of cadmium dust has generally been the means of toxicity in humans (Friberg *et al.*, 1971). One well-known exception to this generalization is that ingested cadmium is known to cause "itai-itai" (ouch-ouch) disease (Yamagata and Shigematsu, 1970). This malady was first identified in an area of Japan that received mine drainage containing large quantities of cadmium. Schroeder (1965) suggested cadmium is a cause of high blood pressure.

Aquatic organisms are especially sensitive to small concentrations of cadmium. Concentrations as low as 6.1 µg Cd^{2+}/l inhibit the growth of *Scenedesmus quadracauda*, a green alga (Klass *et al.*, 1974). In unpublished data cited by Gardiner (1974a) cadmium (5-10 µg/l) affected growth rates of fish. The cadmium level safe for coho salmon fry was 1 to 4 µg/l, and reproduction in *Daphnia magna* was reduced at a cadmium concentration of 0.5 µg/l (cited by the National Academy of Sciences ..., 1973).

Because the chemistry of cadmium and zinc are closely related, they occur together in nature. Weathering and subsequent erosion of rocks and soils carry cadmium into Lake Michigan, probably in a particulate or unreactive form (Hem, 1972). Igneous rocks and shales typically contain 0.2-0.3 mg Cd/kg, while sandstones and limestones average 35-50 µg Cd/kg (Bowen, 1966). Coal deposits contain about as much cadmium as shales and igneous rocks. Since cadmium is released to the atmosphere during combustion of fossil fuels, rainfall has been suspected as a source of cadmium to aquatic systems (Hem, 1972); however, the significance of precipitation as a cadmium source to Lake Michigan is unknown. Rattonetti (1974) found soluble cadmium concentrations in rain collected around St. Louis, Missouri, in the summer of 1972 ranged from 0.3 to 1.3 µg/l.

Industrial and domestic activities are a source of cadmium to Lake Michigan. Electroplating consumes about 50% of the cadmium used in the U. S. (Hem, 1972). Another 45% goes into pigments for paints, printing inks and plastics, and into stabilizers of polyvinyl chloride plastics. Fluorescent tubes, television tubes and certain kinds of batteries also require cadmium. Vehicular tire dust, resulting from impure zinc compounds used in vulcanization (Lagerwerff and Specht, 1970), as well as mine and smelter emissions (Friberg *et al.*, 1971) supply unknown quantities of cadmium to Lake Michigan. Cadmium is seldom determined in sewage effluents unless industries using zinc or synthesizing plastics have known discharges in the sewage system. Konrad and Kleinert (1974) recently surveyed sewage effluents from Kenosha, Racine, South Milwaukee, Milwaukee (Jones Island and South Shore plants), Sheboygan, Manitowoc, and Two Rivers. With the exception of Two Rivers (20 µg Cd/l), all of these plants had cadmium levels below the detection limit of 20 µg Cd/l.

Cadmium determinations (Table 58) are difficult, since many standard analytical techniques are insensitive to the low levels of cadmium present in Lake Michigan water. Effective methods include anodic stripping voltammetry (Matson *et al.*, 1969--unpublished), spark source mass spectroscopy (Wahlgren *et al.*, 1972a), and flameless atomic absorption (Limnetics, 1974).

Apparently the first effective quantifications of cadmium in Lake Michigan were carried out by Matson *et al.* (1969--unpublished). They found a labile cadmium concentration of *ca.* 0.1 µg Cd/l in eight samples taken over a depth profile of 110 m. Labile cadmium is a measure of at least some of the cadmium dissolved in the water, including soluble Cd^{2+} plus any cadmium complexes which dissociate easily under experimental conditions used in this method. Wahlgren *et al.* (1972a) measured total soluble cadmium in samples collected near Grand Haven and found 0.1 µg Cd/l. More recently, Limnetics (1974) measured total cadmium, including particulate matter, in inshore waters near Two Rivers, St. Francis (8 km south of Milwaukee), and Oak Creek (32 km south of Milwaukee), Wisconsin. At Two Rivers and Oak Creek the total cadmium concentration was 0.6-0.7 µg Cd/l. Cadmium averaged 1.7 µg/l at St. Francis;

Table 58. Cadmium Content in Lake Michigan Water

Sample Description	Dates	Concentration Cd, µg/l Average	 Range	Reference
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City, 63 samples		$<5^{a}$		
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo, 39 samples		$<5^{a}$		
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor, 26 samples		$<5^{a}$		
On a line roughly between Sheboygan and Little Sable Point, 8 samples		$<5^{a}$		
Samples collected:	1962-63			Risley and Fuller, 1966
Calumet Harbor, 7 samples		$<5^{a}$		
Indiana Harbor, 8 samples		$<5^{a}$		
Adjacent to Calumet and Indiana Harbors, 52 samples		$<5^{a}$		
61 offshore samples collected throughout Lake	1962-63	$<5^{a,b}$		USDOI, 1968
8 samples collected between 0 and 110 m at 43°10', 86°15' [*sic*]	Unspecified	0.1^{c}	0.05-0.15	Matson *et al.*, 1969
Single sample collected at 10 m near Waukegan	Unspecified	1.0^{d}		Allen *et al.*, 1970
180 unfiltered samples collected by FWQA at unidentified locations	Aug-Oct 1970	$<5^{a,b}$		Lake Mich. Enforcement Conf., 1972a
51 samples collected by Illinois EPA from water plants and open waters	Aug-Oct 1970	<1		Lake Mich. Enforcement Conf., 1972a
Single samples collected from water intakes at Milwaukee, Evanston, Chicago, Gary, Whiting, and Agnew, Mich.	Oct 1970	$<1^{a,b}$		Durum *et al.*, 1971
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		0.1^{e}		
17 km (10.6 mi) offshore		0.1^{e}		
Single samples collected at public water intakes at Green Bay, Kenosha, Milwaukee (5 intakes), Port Washington, Racine, Sheboygan, and Two Rivers	1971	$<10^{a}$		Baumeister, 1972
Monthly samples collected from intakes at Kenosha and North Chicago public water supplies and Waukegan Generating Station	Jan-Apr 1971	<1		Industrial Bio-Test, 1972a
Samples collected ~monthly at Lake County, Ill., public water supply intake:				Howe, 1973
12 samples	1971		<0.1-0.5	
5 samples	1972	$<0.1^{a}$		
6 samples	1972	0.3	0.1-0.7	
2 samples	Jan-Jun 1973	$<0.1^{a}$		
4 samples	Jan-Jun 1973	0.8	0.1-2.9	
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun 1971-Apr 1972		<0.1-1.1	Industrial Bio-Test, 1972c

Table 58. (contd.)

Sample Description	Dates	Concentration Cd, μg/l		Reference
		Average	Range	
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		0.6	<0.1-<10	
Effluent plume		0.7	<0.1-<10	
South of plant, 4.8 km (3 mi)		0.7	<0.1-10	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		0.6	<0.1-5	
North of plant, 1.6 km (1 mi)		0.6	<0.1-5	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		1.7	.05-10	
South of plant, 1.6 km (1 mi)		1.7	0.1-7.5	

[a] *Same value for all samples.*

[b] *Limit of detection.*

[c] *Labile cadmium.*

[d] *Free cadmium.*

[e] *Total soluble cadmium.*

USDOI = U. S. Department of the Interior.

the higher concentration at this station was attributed to mixing with water from Milwaukee Harbor. If the measurements made by Matson *et al.* (1969--unpublished), Wahlgren *et al.* (1972a), and Limnetics (1974) are representative, then the following inferences may be drawn: (*i*) labile cadmium, at *ca.* 0.1 μg Cd/l (Matson *et al.*, 1969--unpublished), constitutes a major portion of the total soluble cadmium, which was 0.1 μg/l (Wahlgren *et al.*, 1972a); and (*ii*) a major fraction of the total cadmium is contained in particulate matter, since the total cadmium concentration was 0.6 μg/l (Limnetics, 1974) and total soluble cadmium concentration was only 0.1 μg/l. Further study would determine whether these two speculations are true. Since most of the samples in Table 58 were taken in inshore areas, more offshore data should be collected.

The various chemical forms of cadmium in Lake Michigan have not been determined. In unpolluted waters with low concentrations of both cadmium and dissolved humic material, the predominant form is Cd^{2+} (Gardiner, 1974a). At higher levels of humic material, cadmium-humic-material complexes may become more prevalent.

In aerobic water the least soluble inorganic cadmium salt is cadmium carbonate (Hem, 1972), but the concentration of cadmium in Lake Michigan is well below the level allowed by the equilibrium dissolution/formation of solid $CdCO_3$. Occlusion within precipitating calcium carbonate and, more importantly, adsorption to humic materials contained within suspended solids and sediments (Gardiner, 1974a, 1974b) are likely to control the soluble cadmium level in Lake Michigan.

The U. S. Public Health Service (1962), the Environmental Protection Agency (1975b), and the National Academy of Sciences ... (1973) recommended a limit of no more than 0.011 mg Cd/l in public water supplies (Appendix B, part 1). Because of the lethal and sublethal effects of cadmium on aquatic life, the National Academy of Sciences ... (1973) recommended that cadmium should not exceed 0.03 mg/l in hard water (Appendix B, part 2).

Edgington *et al.* (1972a) and Shimp *et al.* (1970) reported cadmium content in four sediment cores from Green Bay and three cores from the western part of the southern basin, respectively. Cadmium concentrations were typically 1-5 mg Cd/kg sediment in cores collected in both southern and northern Green Bay. Only one of the Green Bay cores, taken from Little Bay du Noc, showed any evidence of surficial enrichment. There was no clear evidence of surficial cadmium enrichment in the three cores taken in the southern basin. Sediment cadmium concentrations reported for these southern cores were much higher than in Green Bay; typical values were 5-15 mg Cd/kg bulk dry sediment. It is not immediately obvious why cadmium concentrations in Green Bay and southern basin sediments are higher than in igneous rocks and shales (0.2-0.3 mg Cd/kg) and sandstones and limestones (35-50 μg/kg) (Bowen, 1966).

CHROMIUM

Interest in chromium has been directed largely to its toxic effects. Bowen (1966) reported that Cr (III) is moderately toxic to organisms, while Cr (VI) is highly toxic. Within the last decade, however, evidence suggests that chromium performs several essential functions in mammals (Mertz, 1969; Hambidge, 1971; Mertz and Roginski, 1971; Schroeder, 1973; and Mertz *et al.*, 1974).

Although plants absorb chromium from soils, no data have demonstrated that this element is essential for either microorganisms or higher plants (Underwood, 1971). Excess chromium in certain soils has been considered responsible for various disease conditions in plants.

Chromium is not especially abundant in geological formations. Bowen (1966) reported the following averages: igneous rock, 100 mg Cr/kg; shales, 90 mg/kg; sandstone, 35 mg/kg; limestone, 11 mg/kg; and coal, 60 mg/kg. Chromium in soils is typically 100 mg/kg, with higher concentrations in basalt and serpentine silts and soils. Chromium in rocks and soils is generally present as insoluble chromic oxide (Lisk, 1972). The maximum solubility of Cr (III) at pH 7 is only 50 μg/l (calculated from Pourbaix, 1963).

Since Cr (III) is the predominant form in soils and rocks and it is insoluble, Foster (1963) indicated these natural sources of chromium are unimportant in water. The chief source of chromium is industrial, especially Cr (VI) chromium salts. Leather tanning, electroplating, and aluminum anodizing industries utilize Cr (VI). Either Cr (III) or Cr (VI) may be employed in manufacturing paints, dyes, explosives, ceramics, and colored glass. Chromium is used as a corrosion inhibitor in cooling systems and is released to receiving waters during blowdown and leakage.

Winchester and Nifong (1971) estimated that natural (unpolluted) stream inputs of chromium to Lake Michigan were 33 metric tons annually; assuming a 10% transfer efficiency, 10 metric tons of the 100 metric tons of particulate chromium emitted annually by the burning of coal, coke and fuel oil in the Chicago-Milwaukee-northwest Indiana area are carried into Lake Michigan. Using different computation methods, Klein (1975) estimated that soil erosion (540 metric tons of chromium per year) is more important than aerosol deposition (210 metric tons per year) to Lake Michigan.

The efficiency of chromium removal by municipal sewage treatment plants is highly variable. In eight plants discharging effluents to Lake Michigan, Konrad and Kleinert (1974) found removal varied from 28% (South Milwaukee) to 95% (Milwaukee's Jones Island Plant). Chromium content in effluent from the Sheboygan Sewage Treatment Plant was 3.2 mg Cr/l, while the Kenosha Sewage Treatment Plant discharged effluent containing < 0.05 mg Cr/l. Most of the chromium was removed as Cr (III) in the settled activated sludge, even when the influent was Cr (VI) (Moore *et al.*, 1961). This observation implies that trivalent chromium is removed more effectively than hexavalent chromium.

Table 59 shows that data developed with analytical methods adequate for detecting the lower concentrations of chromium in Lake Michigan (*e.g.* atomic absorption spectroscopy, neutron activiation analysis) were available only recently. It seems probable that chromium concentrations in most areas of Lake Michigan are under 10 μg/l. According to Bowen (1966), the median freshwater concentration of chromium is 0.18 μg Cr/l, but it is not clear whether this value represents soluble or total chromium.

These concentrations are much below the U. S. Public Health Service (1962) drinking water standard of 50 μg/l as Cr (VI) and the newer recommendation by the National Academy of Sciences ... (1973) of 50 μg/l total chromium (Appendix B, part 1). The limit on chromium for maintenance of mixed aquatic populations is not exceeded (Appendix B, part 2).

The chemical forms of chromium in Lake Michigan are unknown. One cannot assume equilibrium of inorganic forms of chromium in Lake Michigan; however, if the Lake was at equilibrium, one would expect to find inorganic chromium as $Cr(OH_2)^+$, $CrO_4{}^{2-}$, or solid $Cr_2O_3 \cdot nH_2O$, depending on pH and dissolved oxygen concentration (based on data from Latimer, 1952; and Pourbaix, 1963). There are no data on possible organic chromium derivatives in the Lake.

Chromium determinations in Lake Michigan sediments have been reported by Copeland and Ayers (1972), Robbins *et al.* (1972a), Edgington *et al.* (1972a), Robbins and Edgington (1974), Shimp *et al.* (1970, 1971), Lineback and Gross (1972), and Leland *et al.* (1973b). Except for the grab samples collected by Copeland and Ayers (1972), results of the other six studies have demonstrated that there is a surficial enrichment of chromium in sediment cores from Green Bay and from the southern basin. Surficial accumulation of chromium was especially pronounced near Grand Haven, the mouth of the Grand River, and near Benton Harbor, where the St. Joseph River enters (Shimp *et al.*, 1971); concentrations were as high as 116 mg Cr/kg dry sediment, compared with background concentrations of about 50 mg Cr/kg dry sediment. Preliminary data (Robbins *et al.*, 1972a), based on one core collected about 13 km (8 mi) off Grand Haven, suggested that acid-soluble chromium was more enriched at the sediment surface than was total chromium.

Table 59. Chromium Content in Lake Michigan Water

		Concentration Cr, µg/l		
Sample Description	Dates	Average	Range	Reference
Semiannual composites from monthly samples collected at public water intakes:	Oct 1962-Sep 1967			Kopp and Kroner, 1968
Milwaukee				
8 composites		N.D.		
2 composites		3[a]	2-4[a]	
Gary				
6 composites		N.D.		
3 composites		10[a]	5-19[a]	
Whole Lake:	1962-63			USDOI, 1968
57 offshore samples		<5		
3 offshore samples		6	5-8	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City, 63 samples		<5[b]		
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo, 39 samples		<5[b]		
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor				
22 samples		<5[b]		
4 samples			5-8	
On a line roughly between Sheboygan and Little Sable Point, 8 samples		<5[b]		
Samples collected:	1962-63			Risley and Fuller, 1966
Calumet Harbor, 7 samples		<5[b]		
Indiana Harbor, 8 samples		<5[b]		
Adjacent to Calumet and Indiana Harbors, 39 samples		<5[b]		
Samples collected at 11 water intakes in Michigan	1967	<10[b]		Lake Mich. Enforcement Conf., 1972a
Stations throughout Lake sampled 3 times each:	Aug 1969-Jun 1970			Copeland and Ayers, 1972
12 inshore stations		1.6[a]	0.50-3.2[a]	
8 offshore stations		1.8[a]	0.78-4.0[a]	
Monthly samples collected at intakes:	May 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply				
4 samples		<1[b]		
8 samples		3	1-7	
Waukegan Generating Station				
1 sample		<1		
11 samples		4	1-14	
North Chicago public water supply				
1 sample		<1		
11 samples		2	1-4	
Samples collected monthly at 3 stations 9.6 km (6 mi) east of Zion:	May-Aug 1970			Industrial Bio-Test, 1972b
9 samples		<1[b]		
35 samples		2	1-6	
Monthly samples collected at Lake County, Ill., public water intake	Jun 1970-Sep 1971 Jul 1972-Feb 1973	2[c] 2[c]	<1-9[c] <1-4[c]	Howe, 1973
180 unfiltered samples collected by FWQA at unidentified locations	Aug-Oct 1970	<5[b]		Lake Mich. Enforcement Conf., 1972a

Table 59. (contd.)

Sample Description	*Dates*	*Concentration Cr, μg/l*		*Reference*
		Average	*Range*	
Single samples collected northwest of Grand River entrance, outside River plume	6 Oct 1970			Robbins *et al.*, 1972a
A station 1.0 km (0.62 mi) NW:				
Surface-water, soluble chromium		0.9		
Bottom-water, soluble chromium		1.6		
Surface-water, extractable particulate chromium		2.1		
Bottom-water, extractable particulate chromium		0.56		
A station 1.25 km (0.78 mi) NW:				
Bottom-water, soluble chromium		3.2		
Bottom-water, extractable particulate chromium		1.3		
Single samples collected at water intakes:				Durum *et al.*, 1971
Milwaukee	7 Oct 1970	1[d]		
Evanston	7 Oct 1970	1[d]		
Chicago	7 Oct 1970	1[d]		
Whiting	13 Oct 1970	<1[d]		
Gary	13 Oct 1970	1		
Agnew, Mich.	22 Oct 1970	<1[d]		
Single samples collected from public water intakes at Green Bay, Kenosha, Port Washington, Racine, Sheboygan, and Two Rivers	1971	<30[b]		Baumeister, 1972
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun-Sep 1971	2	<1-3	Industrial Bio-Test, 1972c
Samples collected (water depth 7.6 m) at a station east of Kewaunee Nuclear Plant:				Industrial Bio-Test, 1972d
Surface	31 Aug 1971	7	<1-19	
Bottom	31 Aug 1971	3	<1-9	
Surface	16 Nov 1971	1[b]		
Bottom	16 Nov 1971	1[b]		
Monthly samples collected at Lake County, Ill., public water intake	May-Jun 1972, Mar-Jun 1973	<1[b,d]		Howe, 1973
	Mar-Jun 1973	3[e]	2-4[e]	
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		8.3[a]		
17 km (10.6 mi) offshore		7.2[a]		
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		3	<5-<20	
Effluent plume		3	<5-<20	
South of plant, 4.8 km (3 mi)		3	<5-<20	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		6	<5-17	
North of plant, 1.6 km (1 mi)		8	<5-31	

Table 59. (contd.)

Sample Description	Dates	Concentration Cr, μg/l Average	Concentration Cr, μg/l Range	Reference
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis—2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		5.9	2.5-10	
South of plant, 1.6 km (1 mi)		7.1	2.5-10	

[a] *Total soluble chromium.*

[b] *Same value for all samples.*

[c] *Total chromium.*

[d] *Hexavalent chromium.*

[e] *Trivalent chromium.*

USDOI = U. S. Department of the Interior.

Chromium content of sediments from the southern basin showed strong statistical correlations with organic carbon content both at the surface and at depth within a core (Shimp *et al.*, 1971), and good correlations with iron oxide content. The greater average chromium concentration (75 mg/kg dry sediment) in surface samples from the gray silt facies of the Waukegan member than in the brown silt facies (40 mg/kg dry sediment) was related to the higher organic carbon content of the gray silt facies (Lineback and Gross, 1972).

Robbins and Edgington (1974) found that the acid-extractable chromium content of sediments increased with distance from shore, along a transect off Grand Haven, to a maximum at 19.3-29.0 km (12-18 mi) from shore and then fell somewhat to 40 km (25 mi). The tendency for higher concentrations at intermediate distances along the transect was noted both in surficial sediments and in the deeper portions of the sediment. The authors hypothesized these variations may have been related to local variations in sedimentation rate, but data on sedimentation rates were not available to verify this supposition.

COBALT

Cobalt is essential for optimal growth and reproduction in many plants and animals. Cobalt porphyrin cyanocobalamin, or vitamin B_{12}, is used by organisms in biochemical enzyme systems. Many bacteria are able to synthesize B_{12} when cobalt is present; however, other organisms requiring this vitamin must obtain it preformed (Bowen, 1966). Selected algal species, including diatoms, blue-green algae, and green algae, require cobalt, or vitamin B_{12}; Healey (1973) suggested a widespread requirement for vitamin B_{12} can be assumed. Provasoli (1958) showed that the concentrations of vitamin B_{12} required varied from 0.1 to 5 ng/l.

Free-living bacteria (Nicholas *et al.*, 1964), blue-green algae (Johnson *et al.*, 1966), and nodulated higher plants (Kliewer and Evans, 1963; Bond, 1967) that are capable of nitrogen fixation require cobalt. Otherwise, there is no evidence that cobalt is essential to non-nodulated higher plants (*cf.* Hemphill, 1972).

Vitamin B_{12} participates in two important types of biochemical reactions in both plants and animals: (*i*) isomerization of dicarboxylic acids, and (*ii*) conversion of vicinal dihydroxyl compounds to the deoxy, monohydroxyl grouping (Conn and Stumpf, 1966).

In one unconfirmed study Goryunova and Maksudov (1971) found that cobalt was toxic to certain nitrogen-fixing blue-green algae at concentrations exceeding 50 µg Co/l. Data summarized by McKee and Wolf (1963) and Kemp *et al.* (1971) indicate that cobalt is harmful to plants and animals at concentrations exceeding 1 mg Co/l.

Igneous rocks (25 mg Co/kg) and shales (10 mg/kg) have higher cobalt concentrations than sandstones (0.3 mg/kg) and limestones (0.1 mg/kg) (Bowen, 1966). These rocks, together with soils (8 mg/kg), provide the natural sources of cobalt to Lake Michigan during weathering and erosion.

Municipal and industrial effluents also add cobalt to Lake Michigan. Cobalt and its salts are used in alloys, china and glass pigments, galvanoplating, binders in the tungsten-carbide tool industry, and animal feed supplements (McKee and Wolf, 1963). Winchester and Nifong (1971) estimated that aerosol fallout from the burning of fuel oil and coal in the Lake Michigan Basin provides a significant source of cobalt to the Lake, but Klein (1975) calculated that soil mobilization is the major source of cobalt to Lake Michigan, not aerosol deposition. Vitamin B_{12} content is high in municipal sewage sludge (Provasoli, 1969) and probably in treated effluents.

Cobalt is rarely measured in Lake Michigan (Table 60). Durum *et al.* (1971) and Copeland and Ayers (1972) both determined that soluble cobalt is present at 1 µg Co/l or less. For comparison, Bowen (1966) said that fresh water typically contains 0.9 µg Co/l. Analyses in Table 60 did not discern the chemical form in which cobalt was present. Data from Garrels and Christ (1965) suggest the major stable forms of inorganic cobalt in oxygenated water between pH 6 and 10 are Co^{2+} and solid cobaltous carbonate. The fraction of the total cobalt in Lake Michigan water which is present in organic form, such as vitamin B_{12}, is unknown.

Table 60. Total Soluble Cobalt Content in Lake Michigan Water

		Concentration Co, µg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Stations throughout Lake sampled 3 times each:	Aug 1969-Jun 1970			Copeland and Ayers, 1972
12 inshore stations		0.20	0.033-0.57	
8 offshore stations		0.17	0.061-0.55	
Single samples collected at water intakes:				Durum *et al.*, 1971
Evanston and Chicago	7 Oct 1970	1		
Milwaukee	7 Oct 1970	<1		
Whiting and Gary	13 Oct 1970	<1		
Agnew, Mich.	22 Oct 1970	<1		

There are no suggested limits on cobalt in drinking water or in aquatic systems managed for the maintenance of aquatic life. The National Academy of Sciences ... (1973) suggested that cobalt in water consumed by livestock should be limited to 1.0 mg/l.

Cobalt content of Lake Michigan sediments has been determined by Edgington *et al.* (1972a), Robbins *et al.* (1972a), Copeland and Ayers (1972), and Shimp *et al.* (1970, 1971). Further discussion of cobalt concentration data from the southern basin has been offered by Lineback and Gross (1972) and Leland *et al.* (1973b). Two cores from shallower areas in Green Bay showed more evidence of surficial cobalt accumulation than did cores from two deep areas (Edgington *et al.*, 1972a). In the southern basin, however, average cobalt content in surface-sediment samples (13 mg/kg dry sediment) was similar to samples collected between 15 and 100 cm deep in the cores (14 mg/kg dry sediment) (Leland *et al.*, 1973b; Lineback and Gross, 1972; Robbins *et al.*, 1972a). Lineback and Gross (1972) found that average cobalt concentrations in surficial sediments of the gray silt facies of the eastern part of the southern basin (Waukegan member) were higher than in the brown silt facies of the western part of the southern basin (13 mg/kg dry sediment *vs.* 10 mg/kg dry sediment). They attributed this difference to greater deposition of cobalt with the organic and clay-sized particles that are especially abundant in the gray silt facies of the Waukegan member.

COPPER

All organisms require minute quantities of copper (Bowen, 1966). This trace element is a constituent of several metalloenzymes, most of which participate in oxidation. Copper is also found in other proteins including respiratory pigments in the blood of many invertebrates such as annelids, arthropods, and mollusks.

Free cupric ion at higher concentrations is quite toxic to plants. This toxic property has been used to control nuisance algal blooms. The concentration of copper (as copper sulfate) required to control phytoplankton ranges from 0.05-0.10 mg/l for susceptible organisms, to 12 mg/l for more resistant species (McKee and Wolf, 1963). The toxicity of copper to algae depends on temperature and alkalinity: temperatures below 15°C enhance the toxicity; and higher alkalinities, which precipitate free copper ions, lower toxicity.

Deleterious effects of free copper on fish and fish-food organisms depend on pH, temperature, water hardness, exposure period, and species (McKee and Wolf, 1963). Fathead minnows reproduced with no adverse effects in hard water, *i.e.* 200 mg/l as $CaCO_3$, containing < 33 μg Cu/l (Mount, 1968) and in soft water, *i.e.* 30 mg/l as $CaCO_3$, with < 18 μg Cu/l (Mount and Stephen, 1969). Copper levels harmless to fish are similar to concentrations safe for zooplankton like *Daphnia magna* (National Academy of Sciences ..., 1973). Humic substances complex copper (Stiff, 1971), and as a constituent of an organic complex, copper may be less toxic to fish than simple Cu^{2+}. Copper is only moderately toxic to humans (Bowen, 1966). Drinking water would become unpalatable before copper concentrations reached toxic levels (McKee and Wolf, 1963).

Igneous rocks and shales contain similar amounts of copper, 45-55 mg Cu/kg (Bowen, 1966). Sandstones and limestones are an order of magnitude lower, or 4-5 mg/kg. Soils are intermediate, at 20 mg/kg. Runoff and erosional processes transfer cupric salts from the watershed to Lake Michigan, quite likely in crystalline particles (*cf*. Gibbs, 1973).

Major cultural inputs of copper to aquatic systems usually include industrial effluents, corrosion of copper-containing tubes and pipes, and residues from treatment of water to control algal nuisances.

Depending on the industrial wastes within a sewerage system, municipal sewage effluents may constitute a measurable source of copper pollution to Lake Michigan. Konrad and Kleinert (1974) surveyed a number of primary and secondary sewage treatment plants in Wisconsin in 1972. Copper concentrations in treated effluents ranged from < 50 μg/l at Kenosha, Jones Island (Milwaukee), and South Milwaukee, to 360 μg/l at Milwaukee's South Shore treatment plant. This difference in values (Jones Island *vs*. Milwaukee's South Shore) suggests that secondary treatment can remove appreciable portions of copper. Copper values in the effluent of a tertiary treatment plant were reported as 11.6 μg/l (Tanner *et al*., 1972).

Aerosol deposition by dry fallout and precipitation is a source of copper to Lake Michigan. At 32 U. S. rain-gauge stations operated from September 1966 to January 1967, soluble copper averaged 21 μg/l (Lazrus *et al*., 1970). This mean was biased upward by very high copper concentrations recorded at Midway and O'Hare Airports. Such high concentrations in precipitation are probably not typical of the entire Basin (*cf*. Jonasson, 1973). Winchester and Nifong (1971) estimated that aerosol fallout from the burning of coal and from the iron and steel industries in the Chicago-Gary-Hammond area is a major source of copper to Lake Michigan. Klein (1975) computed aerosol input contributed 2300 metric tons of copper per year to Lake Michigan and soil erosion added 110 metric tons; however, Klein thought the estimate of aerosol input had been biased upward unduly by poor choice of sampling location and/or improper choice of sampling equipment.

A number of determinations of copper in Lake Michigan water have been made in the last decade (Table 61), but agreement is poor. Improper sample preservation, sample contamination, and improper analytical methods may account for several of the markedly higher values in Table 61. Contamination may be the reason for the high concentrations noted by Industrial Bio-Test (1972a) at the Kenosha water intake and by Baumeister (1972) at the Kenosha, Racine, Milwaukee, Port Washington, Sheboygan, and Two Rivers water intakes. From the remaining values in Table 61, one can tentatively conclude that copper in the Lake is *ca*. 5-10 μg/l, except in near-shore areas, where concentrations may be greater. For comparison, Bowen (1966) said fresh waters typically contain 10 μg Cu/l. The surface-water and bottom-water samples taken by Robbins *et al*. (1972a) showed a measurable difference, but it is not clear whether this is a widespread phenomenon in the Lake. The two values presented by Wahlgren *et al*. (1972a) suggest an inshore-offshore difference in copper concentrations, but data are too limited to say this with certainty. Limnetics (1974) data revealed no clear-cut evidence of seasonal variations in inshore copper concentrations.

Table 61. Copper Content in Lake Michigan Water

Sample Description	Dates	Concentration Cu, µg/l		Reference
		Average	Range	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City				
61 samples		<5[a]		
2 samples		5[a]		
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo				
38 samples		<5[a]		
1 sample		9		
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor				
25 samples		<5[a]		
1 sample		12[a]		
On a line roughly between Sheboygan and Little Sable Point, 8 samples		<5[a]		
Samples collected:	1962-63			Risley and Fuller, 1966
Calumet Harbor, 7 samples		<5[a]		
Indiana Harbor, 8 samples		<5[a]		
Adjacent to Calumet and Indiana Harbors, 52 samples		<5[a]		
Whole Lake:	1962-63			USDOI, 1968
58 offshore samples		<5[a,b]		
3 offshore samples		10	7-12	
Semiannual composites from monthly samples collected at public water intakes:	Oct 1962-Sep 1967			Kopp and Kroner, 1968
Milwaukee				
9 composites		13[c]	2-34[c]	
1 composite		N.D.		
Gary				
8 composites		4[c]	2-7[c]	
1 composite		N.D.		
Samples collected at 11 public water intakes in Michigan	1967	<100[a,b]		Lake Mich. Enforcement Conf., 1972a
Samples collected between 0 and 110 m at 43°10', 86°15' [*sic*]:	Unspecified			Matson *et al.*, 1969
Labile Cu, 8 samples		0.01[a]		
Total acid-exchangeable Cu, 10 samples		0.29	0.16-0.4	
Single samples collected at 10 m near:	Unspecified			Allen *et al.*, 1970
Waukegan				
Free Cu		0.8		
Acid-exchangeable Cu		19		
Ludington				
Acid-exchangeable Cu		0.4		
Stations throughout Lake sampled ∿3 times each:	Aug 1969-Jun 1970			Copeland and Ayers, 1972
12 inshore stations				
11 samples		11[c]	7-18[c]	
22 samples		N.D.		
8 offshore stations				
5 samples		16[c]	15-17[c]	
15 samples		N.D.		

Table 61. (contd.)

Sample Description	Dates	Concentration Cu, μg/l		Reference
		Average	*Range*	
180 unfiltered samples collected by FWQA at unidentified locations	Aug-Oct 1970	$<5^{a,b}$		Lake Mich. Enforcement Conf., 1972a
Monthly samples collected at intakes:	Aug 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply			46-118	
Waukegan Generating Station		14	1-35	
North Chicago public water supply			<1-2	
Monthly samples collected at Lake County, Ill., public water intake	Sep 1970-Apr 1971, Oct 1971-Jun 1973	3.5	0.8-9.3	Howe, 1973
Single samples collected northwest of Grand River entrance, outside River plume	6 Oct 1970			Robbins *et al.*, 1972a
A station 1.0 km (0.62 mi) NW:				
Surface-water, soluble copper		2.3		
Bottom-water, soluble copper		3.4		
Surface-water, extractable particulate copper		1.3		
Bottom-water, extractable particulate copper		0.55		
A station 1.25 km (0.78 mi) NW:				
Bottom-water, soluble copper		3.5		
Bottom-water, extractable particulate copper		2.8		
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		<30		
Kenosha		60		
Milwaukee (5 intakes)			<20-40	
Port Washington		<30		
Racine		50		
Sheboygan		<20		
Two Rivers		30		
Samples (3 replicate anaylses) collected off Grand Haven	13-14 Sep 1971			Edgington *et al.*, 1972b
16 km (10 mi) west at a depth of:				
10 m (BNWL)*		2.01		
10 m (VD)*		1.24		
45 m		1.34		
60 m		1.54		
8 km (5 mi) west at a depth of:				
40 m		1.36		
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Oct 1971-Apr 1972	20	7.2-71	Industrial Bio-Test, 1972c
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		4.9^{c}		
17 km (10.6 mi) offshore		9.3^{c}		
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		3	<5-10	
Effluent plume		4	<5-10	
South of plant, 4.8 km (3 mi)		3	<5-10	

Table 61. (cont'd.)

Sample Description	*Dates*	*Concentration Cu, µg/l*		*Reference*
		Average	*Range*	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		6	<5-10	
North of plant, 1.6 km (1 mi)		3	<5-10	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar May, Oct 1973			
Effluent plume		4.7	2.5-10	
South of plant, 1.6 km (1 mi)		5.5	2.5-12.5	

[a] *Same value for all samples.*

[b] *Limit of detection.*

[c] *Total soluble copper.*

[*] *BNWL = noncontaminating Niskin water bottle; VD = Van Dorn water bottle.*

N.D. = not detected.

USDOI = U. S. Department of the Interior.

The limit of 1.0 mg Cu/l in drinking water (U. S. Public Health Service, 1962; National Academy of Sciences ..., 1973) is based on palatability rather than toxic aspects (Appendix B, part 1). Ten micrograms Cu/l is safe for fish and zooplankton in the hard water (*ca.* 140 mg/l as $CaCO_3$) of Lake Michigan (Appendix B, part 2).

From a consideration of inorganic chemistry, the mineral malachite, $Cu_2(OH)_2CO_3$, controls the amount of copper in solution below pH 8, and tenorite, CuO, controls above pH 8 (Garrels and Christ, 1965) under conditions similar to those in Lake Michigan. The solubility of these copper salts decreases with increasing pH, and at pH 8 one would predict a total dissolved copper concentration of 3-6 µg/l. Soluble forms of copper would include Cu^{2+} and the soluble complexes $CuOH^+$, $Cu(CO_3)_2^{2-}$, and $CuCO_3$ in the pH 6-10 range. However, the behavior of copper in Lake Michigan water cannot be understood entirely on the basis of inorganic chemistry, for both inorganic and organic species are present, in particulate as well as dissolved forms.

Using anodic stripping voltammetry (ASV), Matson *et al.* (1969--unpublished) and Allen *et al.* (1970) attempted to differentiate various forms of copper in Lake Michigan water. Labile copper, as defined by Matson *et al.* (1969--unpublished), consists of Cu^{2+} plus copper ion complexes [*e.g.* $CuOH^+$, $CuCO_3$, and $Cu(CO_3)_2^{2-}$]. Labile copper was uniform at 0.01 µg/l from the surface to 110 m at a station described as being at 43°10', 86°15' [*sic*]. At this same station Matson *et al.* also determined total acid-exchangeable copper, or copper which is released from a complex by exchange with acid,

$$CuL + 2\ H^+ \longrightarrow H_2L + Cu^{2+}, \qquad (33)$$

where CuL is a metal-organic ligand complex. Concentrations of acid-exchangeable copper in the surface 40 m were roughly 0.2 µg Cu/l, while at both 90 and 110 m the value was 0.4 µg/l. Matson *et al.* considered these acid-exchangeable copper concentrations to be low. The authors could not detect copper in particulate matter analyzed separately from labile and acid-exchangeable copper.

In the vicinity of Waukegan, Allen *et al.* (1970) found free copper to be 0.8 μg/l, while acid-exchangeable copper was 19 μg/l. In this instance, free was used in the same sense that Matson *et al.* (1969--unpublished) used labile. Although Allen *et al.* (1970) did not determine total copper, one can draw at least one inference from their data. The amount of acid-exchangeable copper associated with what is presumed to be organic materials greatly exceeds the amount of free or labile copper.

Simple precipitation of tenorite or malachite does not account for the removal of copper to the sediments, for Lake Michigan is a heterogeneous system. Hydrous iron and manganese oxides, known for their high sorptive capacity, likely influence copper concentrations in natural waters (Jenne, 1968). Particulate algal material, whether alive or dead, intact or broken, can sorb significant portions of dissolved copper (Ferguson and Bubela, 1974) and carry the sorbed metal downward.

Within the sediments themselves, Jenne (1968) stated that hydrous iron and manganese oxides would dictate the behavior of copper except in two cases: (*i*) in sediments containing high amounts of organic matter, and (*ii*) in sediments where pH or oxidation-reduction conditions are such that hydrous oxides and occluded copper undergo partial dissolution. Except for the southern half of Green Bay, the surficial sediments of Lake Michigan are not high in organic matter (Callender, 1969; Shimp *et al.*, 1971); organic carbon is typically less than 3% by weight. However, the conditions which would allow partial dissolution of copper in sediments were met in at least some of the cores described by Callender (1969) and Leland *et al.* (1973b).

Edgington *et al.* (1972a), Robbins and Edgington (1974), Robbins *et al.* (1972a), Copeland and Ayers (1972), Leland *et al.* (1973b), and Shimp *et al.* (1970, 1971) have reported determinations of copper in Lake Michigan sediments. Their data show that copper is highest in the uppermost sediment interval and decreases with core depth. Shimp *et al.* (1971) suggested that elevated copper concentrations in surficial sediments in the southern basin (Fig. 104) were attributable partly to cultural activities. It is also possible that copper enrichment in surficial sediments results from natural processes. Cline and Upchurch (1973) showed that in initially homogeneous cores copper content increased at the surface even as it decreased in the lower part of the cores. They suggested that copper was transported upward through the interstitial water by bubble interfaces, ion diffusion, and dewatering. They also suggested that copper reprecipitated when it reached the biologically active portion of the sediment, *i.e.* the surface 5-10 cm.

Statistical analysis of the relation of copper to organic carbon content of sediments from the southern basin showed a good correlation in the uppermost sediments (Shimp *et al.*, 1971). At greater depths within a core, correlations with < 2 μm clay-size particles, iron, and manganese increased.

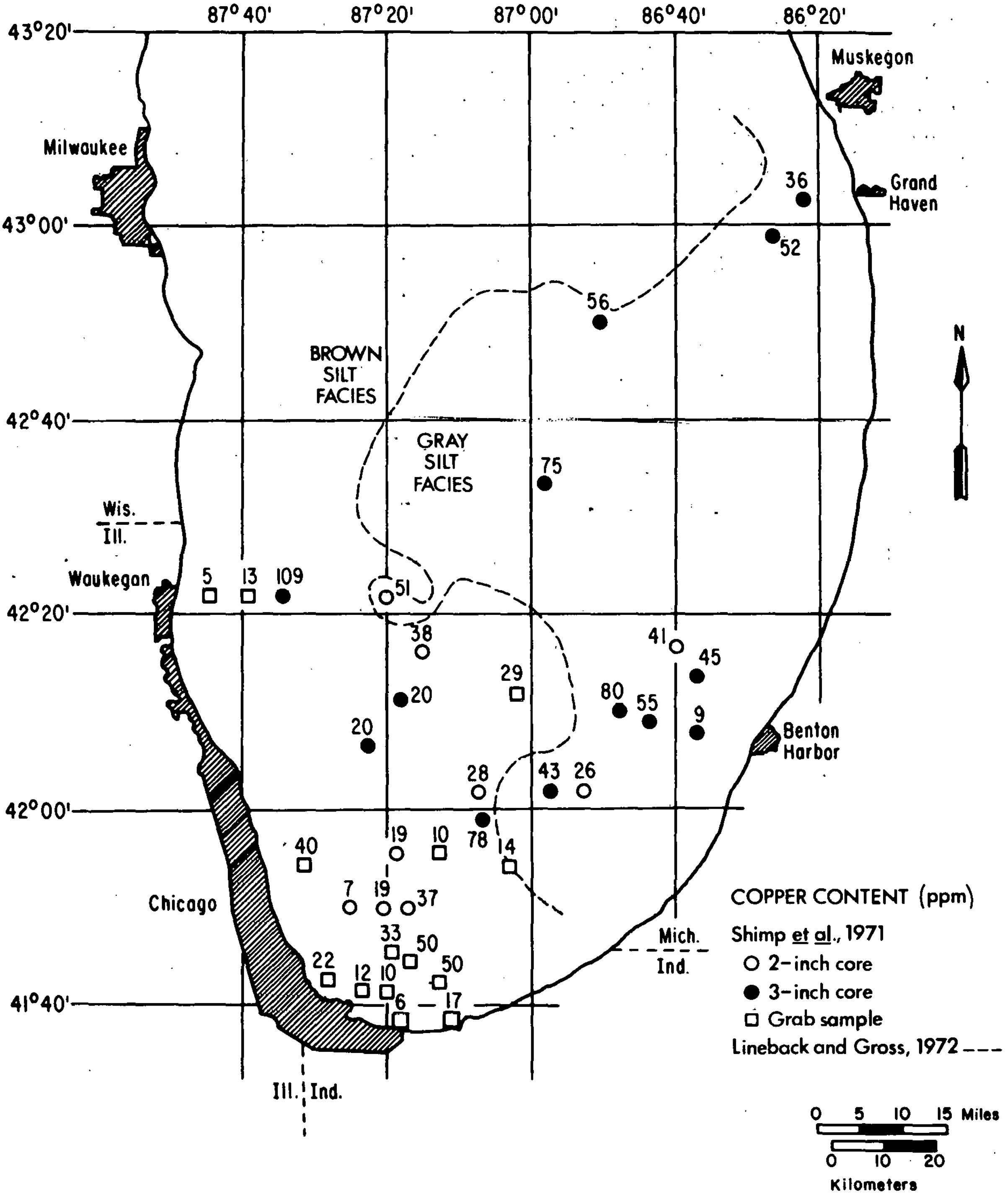


Fig. 104. Copper Content in the Most Recent Sediments of Southern Lake Michigan. Modified from Shimp *et al.* (1971). Boundary of brown and gray silt facies of the Waukegan member from Lineback and Gross (1972).

FLUORINE

Formerly, fluoride was not considered essential for the survival of microorganisms, plants or animals (Underwood, 1971); however, the ability of fluoride to confer maximal resistance to human dental caries, assist in maintenance of a normal skeleton, and reduce the incidence of osteoporosis in the mature adult population is now recognized. More recently, Schwarz (1974) placed fluoride in the list of essential elements and listed several metabolic functions for fluoride. These functions include growth stimulation in tissue culture and activation of (*i*) citrulline synthesis, (*ii*) enzymatic decomposition of nitromethane, and (*iii*) the enzyme adenyl cyclase. Schwarz also suggested that organic forms of fluorine may be more important in maintaining the health of an organism than fluoride ion.

In adult humans concentrations of fluoride greater than 3-4 mg/l in drinking water can cause mottling of the teeth; lower concentrations produce mottled tooth enamel in children (McKee and Wolf, 1963). Still higher concentrations lead to increased density of the bones and other conditions that interfere with the use of bones and joints.

Since the margin between beneficial and toxic intakes of fluoride is small, the U. S. Public Health Service (1962) set mandatory limits (Table 62) for fluoride in drinking water supplies. The National Academy of Sciences ... (1973) has recently reconsidered these limits, and their suggestions are also incorporated into Table 62. The new EPA (1975b) Interim Primary Drinking Water Standards present the same limits suggested by the National Academy of Sciences (Appendix B, Part 1).

The amount of water ingested by children, the most sensitive members of the population to fluoride, is primarily influenced by air temperature. At higher temperatures, more water is consumed, and consequently, the amount of fluoride consumed increases also. Therefore, as average daily air temperature increases, allowable fluoride decreases, as described in Table 62.

Higher concentrations of fluoride in natural surface water occur infrequently, but they may occur at harmful levels in groundwaters (McKee and Wolf, 1963); fluoride concentrations in groundwater reaching Lake Michigan are not

Table 62. Fluoride Concentrations Allowable in Drinking Water

	Upper Limit, mg fluoride/l		
Annual Average of Maximum Daily Air Temperatures	*U: S. Public Health Service Drinking Water Stds. 1962*	*EPA Int. Prim. Drinking Water Stds. 1975*	*NAS-NAE Water Quality Criteria 1972**
50.053.7°F (10.0-12.0°C)	1.7	2.4	2.4
53.8-58.3°F (12.1-14.6°C)	1.5	2.2	2.2
58.4-63.8°F (14.7-17.6°C)	1.3	2.0	2.0
63.9-70.6°F (17.7-21.4°C)	1.2	1.8	1.8
70.7-79.2°F (21.5-26.2°C)	1.0	1.6	1.6
79.3-90.5°F (26.3-32.5°C)	0.8	1.4	1.4

**Air temperatures (°F) are 50-54, 55-58, 59-64, 65-71, 72-79, 80-91, respectively.*

References: U. S. Public Health Service, 1962; Environmental Protection Agency (U. S.), 1975b; National Academy of Sciences-National Academy of Engineering Committee on Water Quality Criteria, 1973.

well known. Other sources of fluoride to surface waters are both natural and domestic. One natural source is erosion of rock and soil. Fluoride averages 625 mg/kg in igneous rocks, 740 mg/kg in shales, 270 mg/kg in sandstones, and 330 mg/kg in limestones (Bowen, 1966). Soils world-wide average 200 mg fluoride/kg, where the ions are fixed in many clay minerals and in fluorapatite, $Ca_{10}F_2(PO_4)_6$. Reported concentrations of fluoride in rain range from 0.001 to 1.0 mg fluoride/l (Warner and Bressan, 1973).

McKee and Wolf (1963) reported that fluorides are seldom found in even trace amounts in industrial wastes unless there has been spillage. However, society adds fluoride to Lake Michigan whenever the sewage effluent from fluoridated drinking water supplies enters Lake Michigan. Fluoride is not removed by conventional sewage treatment.

Fluoride concentrations in Lake Michigan have been determined only in inshore waters (Table 63). In these shallow areas, fluoride is probably 0.1-0.2 mg/l, similar to the world-wide freshwater average of 0.1 mg/l (Bowen, 1966). These levels are lower than the recommended control limits of fluoride for drinking water supplies (U. S. Public Health Service, 1962; EPA, 1975b). The fluoride concentrations in Lake Michigan water are harmless to humans. Some municipalities may augment the fluoride content of drinking water drawn from Lake Michigan as a prophylactic measure.

The chemical processes controlling the behavior of fluoride are not known; they are probably quite similar to that of chlorine.

Fluoride content in Lake Michigan sediments has not been determined. One might expect to find fluoride in fluorapatite and clay minerals like biotite or muscovite in addition to fluoride dissolved in interstitial water.

IODINE

In vertebrates, iodine is essential for proper thyroid function. Dietary deficiency of iodine can lead to the development of goiter. High incidence of goiter was associated with < about 5 μg I/1 in drinking water in two populous areas of Europe (summarized by Underwood, 1971). Endemic goiter is present in much of the Great Lakes region (Goldschmidt, 1954).

Iodine is required for or stimulatory to the growth of some, but not all, red and brown algae (Healey, 1973). The precise role of iodine in the metabolism of these plants is unknown. No requirement by green and blue-green algae for iodine has been demonstrated (Winchester, 1970).

Natural sources contribute virtually all of the iodine to Lake Michigan. The soils of the Great Lakes Basin, and other recently glaciated regions, are deficient in iodine, since they have not yet recovered from the glacial removal of soils rich in iodine (Tiffany *et al.*, 1969). Iodine levels in glaciated soils increase as the result of sea spray carried inland and incorporated in rainfall (Winchester, 1970). Since the last glacial incursion 10,000-15,000 years ago, the concentration of iodine in Lake Michigan probably has achieved steady state, near that of the rain input, if there are no other sources or sinks of iodine to the Lake (Tiffany *et al.*, 1969). Reported concentrations of iodide in rain vary from 0.2 to 10 μg/l (Warner and Bressan, 1973).

Table 63. Fluoride Content in Lake Michigan Water

Sample Description	Dates	Concentration F, mg/l		Reference
		Average	*Range*	
Annual averages at water filtration plants near Chicago:				
12 plants	1968		0.1-0.2	Ill. Sanit. Water Board, 1969
5 plants	1969	0.1	0.1-0.4	Ill. Sanit. Water Board, 1970
Single samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	Dec 1969; Jan, Jun 1970	0.2	0.1-0.2	USGS, 1972
	Dec 1970, Apr 1971	0.2	0.1-0.2	USGS, 1973
Samples collected ∿monthly at intakes:	Jan 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		0.18	0.02-0.43	
Waukegan Generating Station		0.20	0.05-0.4	
North Chicago public water supply		0.16	0.06-0.36	
Samples collected ∿monthly, surface to bottom, at 3 stations 9.6 km (6 mi) east of Zion	Apr 1970-Apr 1971	0.14	0.04-0.29	Industrial Bio-Test, 1972b
Monthly samples collected at Lake County, Ill., public water intake	Jun 1970-Apr 1971, Apr 1972-Jun 1973	0.12	0.065-0.3	Howe, 1973
Weekly samples collected at Milwaukee public water intake, 1.8 km (1.1 mi) offshore	May-Sep 1971	0.2	0.2-0.4	USGS, 1973
	Oct 1971-Sep 1972	0.2	0.1-0.2	USGS, 1974a
	Oct 1972-Jun 1973	0.2	0.1-0.4	USGS, 1974b
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		0.20		
Kenosha		0.20		
Milwaukee (5 intakes)		0.23	0.20-0.25	
Port Washington		0.20		
Racine		0.25		
Sheboygan		0.20		
Two Rivers		0.20		
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		0.15		
17 km (10.6 mi) offshore		0.091		
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24- ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		<0.1		
Effluent plume		<0.1		
South of plant, 4.8 km (3 mi)		<0.1		
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		0.1		
North of plant, 1.6 km (1 mi)		0.1		
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		0.10		
South of plant, 1.6 km (1 mi)		0.10		

USGS = U. S. Geological Survey.

Iodine and iodide are unlikely to occur in significant quantities in polluted waters because they are used infrequently and sparingly in industry, for example, in medicines, germicides, and analytical chemistry (McKee and Wolf, 1963).

Iodine is seldom measured in Lake Michigan. Available data are summarized in Table 64. Copeland and Ayers (1972) analyzed filtered water samples by neutron activation to determine total soluble iodine. Tiffany *et al.* (1969) also used neutron activation, but they did not state whether samples were filtered before analysis. Wahlgren *et al.* (1972a) measured total soluble iodine by mass spectrometry. Neither neutron activation nor mass spectrometry distinguishes the chemical form(s) of iodine in the sample.

Freshwater vertebrates require iodide, the most reduced form of iodine. However, Winchester (1970) pointed out that in oxygenated water the thermodynamically stable form of iodine is iodate, IO_3^-,

$$2\,I^- \longrightarrow I_2 \xrightarrow{3\,O_2} 2\,IO_3^- \,, \qquad (34)$$

This reaction proceeds to the right and at equilibrium, in the presence of oxygen, all iodine is present as iodate. Marine systems are not at equilibrium, for marine vertebrates and marine red and brown algae recycle iodine between I_2 and I^-. In freshwater systems, blue-green and green algae probably do not play a role in recycling iodine; thus the molar ratio of iodide to iodate may be much lower in Lake Michigan than in the oceans. Lake Michigan

Table 64. Iodine Content in Lake Michigan Water

		Concentration I, µg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Single samples collected at 2 shoreline stations northwest of Straits of Mackinac	9 Jul 1967	0.7[a]		Tiffany *et al.*, 1969
9 samples collected between surface and 110 m at a station 9.6 km (6 mi) north of South Fox Island	19 Jul 1967	0.9	0.7-1.0	Tiffany *et al.*, 1969
4 samples collected between 5 m and 115 m at a station in middle of southern basin	22 May 1968	1.1	0.9-1.4	Tiffany *et al.*, 1969
20 stations throughout Lake sampled ∿3 times each:	Aug 1969-Jun 1970			Copeland and Ayers, 1972
25 samples		1.1[b]	0.39-3.5[b]	
29 samples		N.D.		
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		7.8[b]		
17 km (10.6 mi) offshore		2.7[b]		

[a] *Same value for all samples.*

[b] *Total soluble iodine.*

N.D. = not detected.

waters contain 1-2 μg total soluble iodine/l (Table 64), and sea water contains 60 μg/l (Goldberg, 1965). However, comparison of total soluble iodine concentrations does not indicate the amount of iodine available to the biota; an appreciable portion of the total soluble iodine in Lake Michigan water may be present as iodate. The presence of organically bound iodine stable to remineralization (Truesdale, 1975) may reduce even further the amount of iodine available to vertebrates in the Lake.

Not all fish found in Lake Michigan are well-adapted to the low available iodine concentrations. A large proportion of spawning rainbow trout, collected mostly in the tributary Black River of the Upper Peninsula of Michigan, showed hyperplasia (an abnormal increase in size) of the thyroid due to hypofunctioning of the gland (Robertson and Chaney, 1953). Coho salmon, which are native to the North Pacific, also develop hyperplasia of the thyroid when they grow and mature in Lake Michigan (Drongowski, 1972) and Lake Erie (Black and Simpson, 1974). Smith (1968) postulated that the alewife, a marine fish which has successfully invaded Lake Michigan, has not adapted well to the low available iodine content in the Lake. Consequently, Smith suggested that thyroid disorders may have been a contributing factor to the massive die-off of alewives in the Lake during 1967.

Iodide and iodate ion concentrations might be expected to be conservative, like chloride. However, coprecipitation of iodide ions with metallic hydrated oxides (Sugawara *et al.*, 1958), such as iron and aluminum oxides, might tend to remove iodide to the sediments.

Instrumental neutron activation analysis, used by Copeland and Ayers (1972), was too insensitive to quantify iodine in Lake Michigan sediments; one would expect iodine to be present at concentrations of 1-2 mg/kg, similar to the iodine content of shales, sandstones, and limestones (Bowen, 1966).

IRON

Iron functions catalytically in the metabolism of all organisms. It is a key constituent of many metalloenzymes involved in oxidation and reduction (*e.g.* nitrogenase, ferredoxin, catalase, peroxidase), respiratory pigments (*e.g.* hemoglobins, some cytochromes), and other biological molecules whose functions are not yet clearly understood (Bowen, 1966). Optimum iron concentrations for growth of algae have been variously reported as 0.03-0.6 mg iron/l (Gerloff *et al.*, 1950, 1952) to 0.9 mg iron/l (Kratz and Myers, 1955). Iron is considered slightly toxic to aquatic organisms at concentrations exceeding *ca.* 20 mg iron/l (*cf.* Kemp *et al.*, 1971).

Weathering and erosion of rocks and soils in the Lake Michigan watershed contribute major quantities of iron to the Lake. It is likely that most of this iron reaches the Lake in a particulate form; as crystalline minerals, as precipitated or coprecipitated coatings on solids, or incorporated into biological materials (*cf.* Gibbs, 1973). In some areas of the Lake Michigan Basin, iron content is normally high in groundwater (Waller and Allen, 1975).

Rainwater *per se* is not a major source of iron to the Lake. Lazrus *et al.* (1970) reported that iron content in wet precipitation collected at Chicago's Midway Field averaged 10 μg/l, and at O'Hare Field, 50 μg/l. However, bulk

Table 65. Iron Content in Lake Michigan Water

Sample Description	Dates	Concentration Fe, μg/l Average	Concentration Fe, μg/l Range	Reference
Semiannual composites from monthly samples collected at public water intakes:	Oct 1962-Sep 1967			Kopp and Kroner, 1968
Milwaukee				
4 composites		N.D.		
6 composites		20^{a}	7-37^{a}	
Gary				
5 composites		N.D.		
4 composites		49^{a}	4-114^{a}	
Samples collected in Indiana Harbor at east breakwall inner light:				Snow, 1974
3 samples	Dec 1965	2200	1500-3100	
51 samples	Jan-Dec 1966	3400	1100-15,000	
42 samples	Jan-Dec 1967	2800	760-7700	
37 samples	Jan-Dec 1968	2100	830-9000	
25 samples	Jan-Jun 1969	2300	940-7800	
37 samples	Jan-Dec 1968	130^{a}	0-380^{a}	
25 samples	Jan-Jun 1969	170^{a}	60-450^{a}	
Samples collected at water filtration plants near Chicago:				
12 plants sampled ∿16 times each	1968			Ill. Sanit. Water Board, 1969
Annual averages		360^{a}	200-730^{a}	
5 plants	1969			Ill. Sanit. Water Board, 1970
Annual averages		90^{a}	70-120^{a}	
Individual values			0-700^{a}	
Surface-water samples collected throughout Lake at 20 stations sampled 3 times each	Aug 1969-Jun 1970	19^{a}	12-31^{a}	Copeland and Ayers, 1972
Monthly samples collected at intakes:	Aug 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		210	9-460	
Waukegan Generating Station		420	15-930	
North Chicago public water supply		170	7-490	
Monthly samples collected at Lake County, Ill., public water intake	Sep 1970-Apr 1971 Oct 1971-Jun 1973	260 420	9-450 4-1500	Howe, 1973
Single samples collected northwest of Grand River entrance, outside River plume	6 Oct 1970			Robbins *et al.*, 1972a
A station 1.0 km (0.62 mi) NW:				
Surface-water, soluble iron		14.7		
Bottom-water, soluble iron		31.4		
Surface-water, extractable particulate iron		43		
Bottom-water, extractable particulate iron		19		
A station 1.25 km (0.78 mi) NW:				
Bottom-water, soluble iron		7.3		
Bottom-water, extractable particulate iron		25		
Daily samples collected at Chicago South Water Filtration Plant	1971	<300^{a}		Vaughn and Reed, 1973
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		60		
Kenosha		180		
Milwaukee (5 intakes)		250	60-560	
Port Washington		500		
Racine		40		
Sheboygan		260		
Two Rivers		540		

Table 65. (contd.)

Sample Description	Dates	Concentration Fe, µg/l		Reference
		Average	Range	
Samples collected (water depth 7.6 m) at a station east of Kewaunee Nuclear Plant:				Industrial Bio-Test, 1972d
Surface	31 Aug 1971	10	6-13	
Bottom	31 Aug 1971	120[b]		
Surface	16 Nov 1971	240	220-280	
Bottom	16 Nov 1971	260	250-270	
Samples (3 replicate analyses) collected off Grand Haven	13-14 Sep 1971			Edgington *et al.*, 1972b
16 km (10 mi) west at a depth of:				
10 m (VD)*		7.63		
45 m		7.23		
60 m		9.96		
8 km (5 mi) west at a depth of:				
40 m		8.77		
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Oct 1971-Apr 1972	980	45-2900	Industrial Bio-Test, 1972c
Single sample collected offshore from Grand Haven	Unspecified	≤25		Wahlgren *et al.*, 1972b
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		290	100-1400	
Effluent plume		290	50-1000	
South of plant, 4.8 km (3 mi)		240	<50-1000	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		850	100-2200	
North of plant, 1.6 km (1 mi)		940	200-2600	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		400	200-750	
South of plant, 1.6 km (1 mi)		580	200-1350	
Samples collected in Indiana Harbor at east breakwall inner light	14 Nov 1973	670		Snow, 1974
	19 Nov 1973	480		
	7 Dec 1973	980		

[a] *Total soluble iron.*

[b] *Same value for all samples.*

**VD = Van Dorn water bottle.*

precipitation (wet plus dry fallout) may be important. Winchester and Nifong (1971) pointed out that burning of coal and coke and production of iron and steel in the Milwaukee-to-Hammond region release major quantities of iron to the air. Klein (1975) calculated that aerosol inputs of iron are *ca.* 25% of that added by soil erosion. Aqueous effluents from the iron and steel industries (Snow, 1974) and drainage from mines in the Northern Peninsula of Michigan (Businessmen for the Public Interest, 1972) might also be expected to contribute measurable quantities of iron to Lake Michigan.

Soluble forms of iron which might occur in Lake Michigan water include ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions as well as iron-organic complexes. Ferric hydroxides, oxides, and mixed phases are possible solid forms in which iron likely occurs in the Lake water.

Many of the data in Table 65 were collected by local and state agencies required to maintain records for state and federal drinking water regulations. The recommended limits on iron in drinking water and for protection of aquatic life are in Appendix B.

Considering the confusing regulations concerning forms and amounts of iron applicable to Lake Michigan water, the variability of reported values summarized in Table 65 is not surprising. Indeed, in many reports it was not clear whether soluble iron, total iron, or some intermediate form had been measured. In instances where measurement of soluble iron was specified, iron concentrations were generally less than 200 μg iron/l. The significance of these values is difficult to evaluate, however, for some samples were allowed to stand for considerable amounts of time before analysis (Kopp and Kroner, 1968; Copeland and Ayers, 1972). Storage of samples without appropriate preservative techniques can allow considerable changes in form (*e.g.* conversion of soluble ferric ion to ferric hydroxide precipitate).

Soluble iron concentrations are expected to be low under the conditions of pH and O_2 content of Lake Michigan water, since ferric hydroxides are only sparingly soluble (*e.g.* Stumm and Morgan, 1970). One might hope to gain more insight through knowledge of total iron concentrations. With the exception of data from Indiana Harbor summarized by Snow (1974), none of the iron data in Table 65 were clearly identified as total iron content. Thus our present knowledge of iron concentrations, both soluble and total, must be considered fragmentary at best because of nonuniformity in expression of results and lack of clear descriptions of what exactly was quantified. This lack of information hampers our understanding of the chemical behavior of a number of other trace metals, for the capacity of iron hydroxides to coprecipitate and sorb trace constituents is widely considered an important mechanism removing trace metals to the sediments (Jenne, 1968).

In contrast with the confusion on iron concentrations in Lake Michigan water, sediment data have been reported almost uniformly as total iron content (Callender, 1969; Shimp *et al.*, 1970, 1971; Leland *et al.*, 1973b; Copeland and Ayers, 1972). Callender (1969) said his data for total iron content (Table 66) showed insignificant variation in iron content with location in the Lake or with sediment depth. Total iron content was moderately correlated with total manganese content, showing that similar but not necessarily identical processes influenced their chemical behaviors in the sediments. Preliminary evidence indicated that about 40% of the total iron content occurred as precipitated oxides and hydroxides; by implication iron carbonates, sulfides, and silicates composed at least part of the remaining 60%. Estimates of the amount of iron associated with organic matter in the sediments were not indicated.

Interstitial iron content in all but the southern basin shows marked increases with sediment depth (Table 66). These phenomena are an indication of changing conditions within the sediment from a mildly oxidizing, slightly alkaline system (solid ferric hydroxides-oxides are stable) to a mildly reducing, slightly acidic system (solid ferric hydroxides-oxides are reduced to soluble ferrous iron) at depth. These changes are attributable at least in part to removal of O_2 by BOD and COD and to respiratory activities of benthic organisms releasing CO_2 (Eqs. 5-10).

Table 66. Iron Content in Lake Michigan Sediments*

	Total Fe, % dry weight of sediment		*Interstitial Fe, mg/l*	
	Surface Sediment	*Sediment at Depth*	*Surface Sediment*	*Sediment at Depth*
Southern basin	1.85	1.74	0.375	0.477
Divide area and northern basin	1.93	1.91	0.307	1.404
Green Bay	1.66	1.56	1.129	2.901

Summarized from Callender, 1969.

Leland *et al.* (1973b) summarized studies conducted by the Illinois State Geological Survey (Shimp *et al.*, 1970, 1971) on sediment composition in the southern basin. In contrast with the work of Callender (1969), Leland *et al.* (1973b) reported that the average total iron content in surficial sediments exceeded the average value for sediments 15-100 cm deep (2.83% *vs.* 2.49%). Total iron content in suspended matter collected 1 m above the bottom averaged 3.28%. The authors hypothesized that the higher values for iron in the surface sediment interval and suspended matter might indicate an increased rate of supply of iron. Alternatively, they suggested that reduction of iron to soluble ferrous ions within the sediment, upward migration of these diffusible ions, and subsequent reprecipitation as ferric hydroxides at the sediment surface might be important in accounting for observed changes in iron content with distance from the sediment-water interface.

In the southern basin, arsenic, bromine, chromium, copper, lead and zinc contents of surficial sediments are statistically related to iron content (Leland *et al.*, 1973b). One can speculate that these trace constituents were carried to the sediments in association with iron hydroxides and oxides, but experimental verification of this speculation is presently lacking.

Robbins and Edgington (1974) measured acid-extractable iron content in sediment cores (20 cm deep) collected on a transect from 9.6-40 km (6 to 25 mi) out from Grand Haven. They found some indications of surficial accumulation of iron, but also noted greater enrichments at depth in some cores. The authors did not offer an explanation of these observations, and their data are not strictly comparable with reported data because of the means of expression (acid-extractable iron instead of total iron).

As an interesting sidelight on iron content of Lake Michigan sediments, Perlow *et al.* (1974) looked at forms of iron in a sediment core collected 19 km northwest of Benton Harbor. Details of their experimental procedures are beyond the scope of this volume, but by sophisticated techniques they were able to identify a particular form of iron which they associated with air pollution inputs of iron from the complex of steel mills along the southern shore of the Lake. This particular form of iron was detectable only in sediments deposited since *ca.* 1915.

LEAD

Chemical forms and sources of input of lead and controls on its behavior have probably been more carefully studied than for any other non-essential trace element in Lake Michigan.

Lead is moderately toxic to mammals (Bowen, 1966); it apparently deposits in calcified tissue such as bone and acts as a cumulative poison (McKee and Wolf, 1963). Lead is very toxic for most plants (Bowen, 1966). The adverse effects of lead on aquatic organisms have been shown to be inversely related to the hardness of the water (McKee and Wolf, 1963; Kemp *et al.*, 1971; National Academy of Sciences ..., 1973). Lowered dissolved O_2 concentrations enhance lead toxicity to aquatic organisms.

Based on sedimentary characteristics of lead (see below), Edgington and Robbins (1976) have estimated that the burning of coal (averages 5 mg Pb/kg coal; Bowen, 1966) and leaded gasoline (contains 0.6 g Pb/l gasoline; Edgington *et al.*, 1974) currently contributes eight times more lead to Lake Michigan than is supplied by natural sources. The lead from combustion of coal and gasoline reaches the Lake partly through wet (Matson *et al.*, 1969--unpublished; Lazrus *et al.*, 1970; Ter Haar *et al.*, 1967; Gatz *et al.*, 1970) and dry (Gillette, 1972; Gillette and Winchester, 1972) aerosol deposition. Preliminary evidence (Edgington *et al.*, 1974) suggests that dry deposition accounts for about one-half of the total atmospheric input to the Lake. Tributary inputs also carry atmospheric lead to the Lake, especially streams which receive runoff from highways and other paved areas (*cf.* Van Loon, 1973; Jonasson, 1973).

Measurements of lead content in Lake Michigan water are summarized in Table 67. Excepting data collected by Risley and Fuller (1965, 1966) and Kopp and Kroner (1968), lead concentrations are in the vicinity of 5 μg Pb/l, the median value for fresh water given by Bowen (1966). The high values reported by Risley and Fuller (1965) may be biased by sampling near harbors and river mouths. Because samples were stored for a period of time before they were filtered and analyzed, the high values reported by Kopp and Kroner (1968) may contain procedural error.

Lead concentrations in inshore surface waters have been shown to be slightly higher in winter than in summer near Two Rivers and Oak Creek, Wisconsin (Limnetics, 1974) and Lake County, Illinois (Howe, 1973--personal communication). Other data (Industrial Bio-Test, 1972a, 1972c) are too variable to reveal seasonal trends. Possible causes for increases in lead concentrations during winter include burning of coal for heat and stirring of lead-containing bottom sediments by storms.

Except for the Risley and Fuller (1965, 1966) and Kopp and Kroner (1968) data, no values in Table 67 exceed the drinking water standard of 50 μg Pb/l adopted by the U. S. Public Health Service (1962), the National Academy of Sciences ... (1973), and the Environmental Protection Agency (1975b) (Appendix B, part 1). With the exceptions noted above, the limit of 30 μg Pb/1 recommended by the National Academy of Sciences ... (1973) (Appendix B, part 2) to protect aquatic life is not exceeded in the open water of the Lake.

Leland *et al.* (1973b) indicated that inorganic lead could be present in Lake Michigan as Pb^{2+}, $PbCO_3$, or some other hydrated lead carbonate. However, the authors felt that solubility considerations for lead minerals (*e.g.* $PbCO_3$) indicated mechanisms other than simple solubility determine lead concentrations. Noting the high statistical correlation between sedimentary organic carbon and lead contents (Shimp *et al.*, 1971; Leland *et al.*, 1973b), Leland *et al.* (1973b) suggested that organic complexes of lead and sorption of lead to organic particles were important factors influencing the removal of lead from lake water (*cf.* Ferguson and Bubela, 1974). Since lead and iron contents were correlated in Lake Michigan sediments, sorption onto preformed ferric hydroxides-oxides was also considered to influence the behavior of lead.

Matson *et al.* (1969--unpublished) used an experimental approach to characterize forms of lead in the Lake. In samples collected from the surface to 110 m at a station at 43°10', 86°15' [*sic*], they found that labile lead (free Pb^{2+} and metal ion complexes such as $PbCl^+$ and $PbOH^+$) was uniform (0.4 μg Pb/1) above the thermocline (midpoint of thermocline located at *ca.* 15 m on date of sampling). Samples below the thermocline varied between 0.1-0.4 μg Pb/1, with some indication of decreasing labile lead content with depth. They also measured total acid-exchangeable lead, or that lead which is released from complex form by exchange with acid,

$$PbL + 2\,H^+ \longrightarrow H_2L + Pb^{2+}\ , \qquad (35)$$

where PbL is a metal-organic ligand complex. Total acid-exchangeable lead content was lower above the thermocline ($\bar{x}$ = 0.5 μg Pb/1, range 0.3-0.6 μg Pb/1) than below ($\bar{x}$ = 1.4 μg Pb/1, range 1.0-1.6 μg Pb/1). Complexing materials (the L of PbL) in a sample taken from 80 m were thought to be of "intermediate molecular weight." From these and other data the authors hypothesized that lead, entering the Lake in some soluble inorganic form, complexes slowly with organic matter, accounting for higher free or labile lead concentrations above the thermocline. Higher concentrations of lead complexes (total acid-exchangeable lead) below the thermocline were then hypothesized to be due to biological transport downward by semiplanktonic benthos such as *Mysis*.

Both approaches (Matson *et al.*, 1969--unpublished; Leland *et al.*, 1973b) point to the importance of organic matter in relation to the chemical behavior of lead in the Lake. Organic matter is also related to sedimentary characteristics of lead (*cf.* Edgington *et al.*, 1974; Robbins and Edgington, 1975a; Edgington and Robbins, 1976).

Shimp *et al.* (1970, 1971) first reported that lead is accumulating in the most recently deposited sediments of the southern basin. This phenomenon was attributed to increased cultural activities in the watershed. Edgington *et al.* (1974), Robbins and Edgington (1975a, 1975b), and Edgington and Robbins (1976) have investigated in some detail the causes of this accumulation.

Table 67. Lead Content in Lake Michigan Water

Sample Description	Dates	Concentration Pb, µg/l		Reference
		Average	Range	
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City				
16 samples		<5[a]		
47 samples			9-80	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo				
36 samples		<5[a]		
3 samples			5-11	
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor				
33 samples		<5[a]		
3 samples			5-11	
On a line roughly between Sheboygan and Little Sable Point				
8 samples		<5[a]		
Samples collected:	1962-63			Risley and Fuller, 1966
Calumet Harbor, 7 samples			18-43	
Indiana Harbor, 8 samples			16-35	
Adjacent to Calumet and Indiana Harbors				
15 samples		<5[a]		
38 samples			9-80	
Semiannual composites from monthly samples collected at public water intakes:	Oct 1962-Sep 1967			Kopp and Kroner, 1968
Milwaukee				
7 composites		N.D.		
3 composites		13[b]	7-20[b]	
Gary				
6 composites		N.D.		
3 composites		34[b]	13-55[b]	
180 unfiltered samples collected by FWQA at unidentified locations	Aug-Oct 1970	<5[a]		Lake Mich. Enforcement Conf., 1972a
Single samples collected at water intakes:				Durum *et al.*, 1971
Evanston	7 Oct 1970	3[b]		
Chicago	7 Oct 1970	5[b]		
Milwaukee	7 Oct 1970	4[b]		
Whiting	13 Oct 1970	1[b]		
Gary	13 Oct 1970	1[b]		
Agnew, Mich.	22 Oct 1970	7[b]		
Monthly samples collected at intakes:	Oct 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		2	1-5	
Waukegan Generating Station		9	4-15	
North Chicago public water supply		2	1-3	
Samples collected ∿monthly at Lake County, Ill., public water intake:				Howe, 1973
12 samples	Oct 1970-Sep 1971	3	2-6	
4 samples	May 1972-Jun 1973	<1[a]		
9 samples	May 1972-Jun 1973	3	1-6	

Table 67. (contd.)

		Concentration Pb, μg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		<40		
Kenosha		<40		
Milwaukee (5 intakes)		<50[a]		
Port Washington		<50		
Racine		<40		
Sheboygan		<50		
Two Rivers		<50		
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun-Sep 1971	2	1-5	Industrial Bio-Test, 1972c
Samples collected between 0 and 110 m at 43°10', 86°15' [*sic*]:	Unspecified			Matson *et al.*, 1969
Labile lead, 10 samples		0.3	0.1-0.4	
Acid-exchangeable lead, 7 samples		1.0	0.3-1.6	
Single samples collected at a depth of 10 m near:	Unspecified			Allen *et al.*, 1970
Waukegan				
Free lead		0.2		
Acid-exchangeable lead		3.3		
Ludington				
Acid-exchangeable lead		0.6		
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		0.2[b]		
17 km (10.6 mi) offshore		0.9[b]		
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		2	<1-<10	
Effluent plume		2	<1-<10	
South of plant, 4.8 km (3 mi)		2	<1-<10	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		3	1-8	
North of plant, 1.6 km (1 mi)		4	1-8	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		3.1	0.5-5	
South of plant, 1.6 km (1 mi)		3	0.5-5	

[a] *Same value for all samples.*

[b] *Total soluble lead.*

In all cores (Edgington *et al.*, 1974; Edgington and Robbins, 1976), lead concentrations decreased with increasing sediment depth in a roughly exponential manner to an apparently constant value of *ca.* 23 mg/kg. Comparison of lead concentrations with time scales derived independently by radioactive dating techniques (Robbins and Edgington, 1975a) showed that major increases above the background of 23 mg Pb/kg correspond to the period (after 1930) when leaded gasoline came into general use (Edgington and Robbins, 1976). Smaller increases, evident even in the late 1800's, were related to burning of coal in the Chicago area.

There is little evidence of chemical mobility of lead (dissolution, diffusion, reprecipitation) once it is deposited in the sediments (Robbins and Edgington, 1975a), perhaps because of formation of insoluble lead sulfides or orthophosphates (Edgington and Robbins, 1976). The only post-depositional redistribution of lead is caused by predictable processes of physical mixing or benthic activity (Robbins and Edgington, 1975a).

MANGANESE

The essential trace nutrient manganese participates in the O_2-evolving system of photosynthesizing plants (Kessler, 1955) and in development of chloroplasts (Park, 1965). In animals, manganese is required for growth, reproduction, skeletal development, and for proper carbohydrate and lipid metabolism (Underwood, 1971). The minimum manganese concentration that supports photosynthesis and growth in the green alga *Chlorella pyrenoidosa* reportedly is 5.5 μg Mn/l (Eyster *et al.*, 1958). In contrast, Richter (1961) found blue-green algae require 10-50 μg Mn/l. Soluble manganese is only moderately toxic to aquatic organisms; data tabulated by Kemp *et al.* (1971) and McKee and Wolf (1963) indicate that concentrations less than *ca.* 5 mg Mn/l have few if any adverse effects on organisms such as water fleas, tadpoles, and channel catfish fingerlings.

Soil erosion and aerosol inputs have been estimated to contribute the same order-of-magnitude amounts of manganese to Lake Michigan (Winchester and Nifong, 1971; Klein, 1975). Manganese derived from natural soil erosional processes is likely transferred to the Lake largely in a particulate form (*cf.* Gibbs, 1973). Wet precipitation collected at Midway Field and O'Hare Field, Chicago, averaged 50 μg Mn/l and 30 μg Mn/l, respectively (Lazrus *et al.*, 1970). These values may not be representative of the entire Lake Michigan Basin, considering the large amounts of manganese emitted to the air by the iron and steel industries at the southern end of the Lake (Winchester and Nifong, 1971). Under certain conditions, manganese concentrations can be high in groundwater, but the importance of this source to Lake Michigan is unknown.

Like iron, manganese probably occurs in a number of chemical forms in Lake Michigan water. The occurrence of these forms is at least partly related to the presence of dissolved O_2. Possible soluble species include manganous ion (Mn^{2+}) and complexes of manganese with organic matter. Particulate forms include: various oxides, hydrous oxides, and hydroxides [*e.g.* MnO_2; $Mn(OH)_4$], manganese-containing minerals (*e.g.* rhodochrosite, $MnCO_3$), manganese ions adsorbed to or coprecipitated on other solid matter, and manganese in organic solids.

Determinations of manganese content in Lake Michigan water are summarized in Table 68. Soluble manganese concentrations are generally lower than the 12 μg Mn/l value indicated as the median for fresh water (Bowen, 1966); however, if the value of 12 μg Mn/l represents total manganese, then concentration data for Lake Michigan resemble this median concentration.

The recommended drinking-water limits, 0.05 mg Mn/l, on manganese (Appendix B, part 1) are based upon aesthetic considerations. Few values in Table 68 exceed that limit. The Illinois Pollution Control Board (1974) set a limit of 0.05 mg total Mn/l for the protection of aquatic life, but the National Academy of Sciences ... (1973) made no recommendation (Appendix B, part 2).

Industrial Bio-Test (1972a, 1972c), Howe (1973--personal communication), and Limnetics (1974) have reported seasonal surface-water variations in manganese concentrations at inshore stations along the western shore of the Lake. There is some indication that concentrations tend to be somewhat higher during winter months (November to April), but data scatter is too great to allow verification of this hypothesis. Resuspension of surficial sediments by winter storms might account at least in part for these higher values. Biological uptake may also affect manganese concentrations.

Manganese oxides are important in controlling the concentrations of other trace metals in water (Jenne, 1968). Manganese nodules found in the surficial sediments of the northern part of Lake Michigan and northern Green Bay concentrate cobalt, copper, zinc, barium, arsenic and cadmium (Edgington and Callender, 1970; Rossman *et al.*, 1972; Torrey and Edgington, 1973a). Sorption to or coprecipitation in manganese oxide-hydroxide coatings is proposed as at least one mechanism by which these trace elements are incorporated into Lake Michigan nodules.

Manganese concentrations in Lake Michigan sediments have been reported by Callender (1969), Shimp *et al.* (1970, 1971), Copeland and Ayers (1972), Robbins and Edgington (1974), Robbins *et al.* (1972a), and Robbins and Callender (1975). Callender (1969) sampled throughout the Lake (Table 69) and found about a four-fold increase in surficial-sediment manganese content from the southern basin to Green Bay. These data reflect the proximity of iron- and manganese-bearing materials in northern Michigan and Wisconsin. Preliminary evidence suggested virtually all of the sedimentary manganese was a manganese oxide-hydroxide, *e.g.* hausmannite (MnOOH).

Data collected by Callender (1969), Shimp *et al.* (1970, 1971), and Copeland and Ayers (1972) show that total manganese content is higher in the surficial sediments of the gray silt facies of the Waukegan member (Lineback and Gross, 1972) than in the brown silt facies (Table 70). This observation may be related to the association of manganese content with iron content (Callender, 1969; Shimp *et al.*, 1971). In turn, iron content showed a moderately strong correlation with organic carbon content (Callender, 1969). As discussed in the Organic Carbon section, Lineback and Gross (1972) attributed the abundance of some trace elements in the gray silt facies of the Waukegan member to the accumulation of organic matter.

Table 68. Manganese Content in Lake Michigan Water

		Concentration Mn, µg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Semiannual composites from monthly samples collected at public water intakes:	Oct 1962-Sep 1967			Kopp and Kroner, 1968
Milwaukee				
6 composites		N.D.		
4 composites		2.7[a]	0.3-7.4[a]	
Gary				
3 composites		N.D.		
6 composites		2.4[a]	0.7-5.5[a]	
Surface-water samples collected throughout Lake at stations sampled 3 times each:	Aug 1969-Jun 1970			Copeland and Ayers, 1972
12 inshore stations		0.98[a]	0.50-1.5[a]	
8 offshore stations		0.79[a]	0.45-1.4[a]	
Monthly samples collected at intakes:	Aug 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		5	<1-14	
Waukegan Generating Station		16	1-36	
North Chicago public water supply		7	<1-31	
Monthly samples collected at Lake County, Ill., public water intake	Sep 1970-Apr 1971 Oct 1971-Jun 1973	7 7	<1-24 <1-24	Howe, 1973
Single samples collected northwest of Grand River entrance, outside River plume	6 Oct 1970			Robbins *et al.*, 1972a
A station 1.0 km (0.62 mi) NW:				
Surface-water, soluble manganese		1.6		
Bottom-water, soluble manganese		3.4		
Surface-water, extractable particulate manganese		2.9		
Bottom-water, extractable particulate manganese		1.7		
A station 1.25 km (0.78 mi) NW:				
Bottom-water, soluble manganese		1.2		
Bottom-water, extractable particulate manganese		2.3		
Samples (3 replicate analyses) collected off Grand Haven	13-14 Sep 1971			Edgington *et al.*, 1972b
16 km (10 mi) west at a depth of:				
10 m (BNWL)*		1.14		
10 m (VD)*		1.11		
45 m		1.15		
60 m		1.28		
8 km (5 mi) west at a depth of:				
40 m		1.21		
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Oct 1971-Apr 1972		2-110	Industrial Bio-Test, 1972c
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		<40		
Kenosha		<40		
Milwaukee (5 intakes)		<40[b]		
Port Washington		<40		
Racine		<40		
Sheboygan		<40		
Two Rivers		<40		

Table 68. (contd.)

		Concentration Mn, μg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		0.3		
17 km (10.6 mi) offshore		0.4		
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers-- 3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		9	2-60	
Effluent plume		8	2-40	
South of plant, 4.8 km (3 mi)		9	1-25	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee-- 2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		20	5-30	
North of plant, 1.6 km (1 mi)		25	6-60	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis-- 2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		17	7-35	
South of plant, 1.6 km (1 mi)		20	5-33	

[a] *Total soluble manganese.*

[b] *Same value for all samples.*

BNWL = noncontaminating Niskin water bottle; VD = Van Dorn water bottle.

Table 69. Manganese Content in Lake Michigan Sediments*

	Total Mn, % dry weight of sediment		*Interstitial Mn, mg/l*	
	Surface Sediment	*Sediment at Depth*	*Surface Sediment*	*Sediment at Depth*
Southern basin	0.073	0.041	0.162	0.318
Divide area and northern basin	0.197	0.079	0.535	1.199
Green Bay	0.276	0.056	2.516	2.589

**Raw data from Callender, 1969.*

Table 70. Total Manganese Content* in Surficial Sediments of the Southern Basin of Lake Michigan

Eastern Area, Gray Silt Facies†			*Western Area, Brown Silt Facies*†			
No. of Samples	*Average*	*Range*	*No. of Samples*	*Average*	*Range*	*Raw Data Source*
8	0.096	0.028-0.178	8	0.059	0.020-0.157	Callender, 1969
17	0.082	0.023-0.442	29	0.043	0.019-0.164	Shimp *et al.*, 1970, 1971
5	0.036	0.012-0.053	2	0.027	0.026-0.028	Copeland and Ayers, 1972

* *% dry weight of sediment.*

† *Waukegan member, as described by Lineback and Gross, 1972.*

Robbins and Callender (1975) conducted a careful study of manganese content in a 40-cm core collected about 22 km (13 mi) northwest of Benton Harbor. One purpose of the study was to investigate whether surficial-sediment enrichment of manganese content (Callender, 1969; Robbins and Callender, 1975) was attributable to natural phenomena or whether the enrichment reflected cultural influences during recent times. They measured changes in total, acid-extractable, and interstitial manganese content with core depth. They characterized four regions by the dominant chemical processes occurring in those regions: (*i*) at the sediment-water interface soluble manganese (Mn^{2+}), diffusing upward from the interstitial water, reprecipitates by reaction with dissolved O_2; (*ii*) from 0-4 cm soluble manganese concentration is controlled primarily by diffusion and there is no increase or decrease of MnO_2; (*iii*) from 4-8 cm solid manganese is solubilized, presumably as manganese oxides are reduced to Mn^{2+}; (*iv*) at depths greater than 8 cm there is no further solubilization of manganese oxides and dissolved manganese approaches equilibrium concentrations.

Derivation and application of a mathematical model to their data allowed them to suggest that surficial enrichment of manganese occurs through steady-state recycling within a zone of variable depth in the surficial sediments. The model also showed that surficial-sediment enrichment of manganese can be treated quantitatively as a natural phenomenon, without considering cultural sources in the watershed.

Using solubility and rate data, Robbins and Callender predicted that rhodochrosite ($MnCO_3$) or some other manganese carbonate compound was the stable form of manganese at depths corresponding to the equilibrium zone, *i.e.* region (*iv*).

MERCURY

The toxicity of inorganic forms of mercury such as Hg^0 and Hg^{2+} to humans has been known for some time and was formerly associated mainly with occupational hazards (*e.g.* the Mad Hatter of Lewis Carroll's *Alice in Wonderland*). However, the demonstrated relationship between methyl mercuric ion (CH_3Hg^+) poisoning and Minamata disease focused public attention on mercury contamination of natural waters. Schroeder (1974) reported that methyl mercuric ion is fifty times more toxic than inorganic mercury (presumably to mammals). Limitations on mercury content in food and water are predicated on this fact.

Insufficient data are available to compute the relative importance of cultural and natural sources of mercury to Lake Michigan, but data from other Great Lakes may be used for comparison. Thomas (1973) estimated that nearly all of the mercury found in Lake Huron sediments is of natural origin, but cultural activities contribute two-thirds of the mercury found in surficial Lake Ontario sediments (Thomas, 1972). Fuel combustion and smelting processes release mercury to the atmosphere; this mercury can subsequently be transferred to water (Gavis and Ferguson, 1972). Its toxic properties account for its widespread use as a fungicide, bactericide, and slimicide in the manufacture of paints, seed dressings, and paper. Under conditions where there are no major point sources of mercury within a sewer system, sewage effluents probably are not major sources of mercury to Lake Michigan. Effluents from Wisconsin sewage plants (Konrad and Kleinert, 1974) discharging to Lake Michigan had mercury concentrations ranging from < 0.5 μg mercury/l (Kenosha, Manitowoc, South Milwaukee, and Two Rivers) to 1 μg mercury/l (Racine).

Only in the past decade have experimental techniques been developed that permit routine determinations of mercury content at low concentrations. Table 71 shows that, when mercury is detectable, it is often present at concentrations below 1 μg mercury/l. The higher concentrations near Point Beach Power Plant reported by Limnetics (1974) are at present inexplicable. Seasonal data on mercury concentrations (Industrial Bio-Test, 1972a, 1972c; Howe, 1973--personal communication; Limnetics, 1974) have been too contradictory to identify any recurring patterns.

Copeland and Ayers (1972) collected mercury data that allow comparison of concentrations at inshore and offshore locations. Total soluble mercury at nine inshore stations throughout the Lake averaged 0.032 μg mercury/l; at seven offshore stations the value was 0.020 μg mercury/l. This difference is statistically significant at the 99.5% confidence level. For perspective, averages for total soluble mercury in samples from the four International Great Lakes ranged from 0.13 μg mercury/l (Lake Ontario) to 0.18 μg mercury/l (Lake Superior) (Chau and Saitoh, 1973). Industrial sources of mercury to the four International Great Lakes were generally reflected in concentration data. It is not clear why total soluble mercury content in Lake Michigan (Copeland and Ayers, 1972) is apparently lower than in the other four Great Lakes (Chau and Saitoh, 1973).

Mercury concentrations found in Lake Michigan water (Table 71) have generally not exceeded the limit set by Indiana Stream Pollution Control Board (1973) for Lake Michigan water (5 μg total mercury/l) or the drinking water limit of 2 μg total mercury/l adopted by the National Academy of Sciences ... (1973) and the Environmental Protection Agency (1975b) (Appendix B, part 1). Almost none of the data in Table 71 meets the recommendations made by the National Academy of Sciences ... (1973) for the protection of aquatic life, namely, (*i*) no single value to exceed 0.2 μg total mercury/l and (*ii*) average total mercury concentrations not to exceed 0.05 μg/l (Appendix B, part 2). Serious consideration should be given to the possibility that natural background concentrations of mercury in Lake Michigan water may be higher than the limits recommended by the National Academy of Sciences ... (1973).

No studies have reported the form(s) in which mercury occurs in Lake Michigan water. From theory (Gavis and Ferguson, 1972), stable inorganic forms of mercury should include elemental mercury (Hg^0) and perhaps $Hg(OH)_2$. Other dissolved forms which may be present, although they are unstable, include methyl mercuric ion and dimethyl mercury (CH_3HgCH_3). Mercury in solution may also be associated with other, less well-defined, organic substances like fulvic matter (Andren and Harriss, 1975).

Comparing data collected by Copeland and Ayers (1972) with other data in Table 71 leads one to suggest that a major portion of the mercury present in Lake Michigan water is in some non-soluble form. Such a hypothesis agrees with observations made in the International Great Lakes (Chau and Saitoh, 1973). In Lake Erie, high concentrations of total soluble mercury were associated with low turbidity; there was little total soluble mercury in highly

Table 71. Mercury Content in Lake Michigan Water

Sample Description	Dates	Concentration Hg, μg/l		Reference
		Average	*Range*	
Surface-water samples collected throughout Lake at stations sampled 3 times each:	Aug 1969–Jun 1970			Copeland and Ayers, 1972
9 inshore stations		0.032[a]	0.022–0.042[a]	
7 offshore stations		0.020[a]	0.012–0.024[a]	
180 unfiltered samples collected by FWQA at unidentified locations	Aug–Oct 1970	<5[b]		Lake Mich. Enforcement Conf., 1972a
Single samples collected at water intakes:				Durum *et al.*, 1971
Evanston	7 Oct 1970			
Total mercury		<0.5		
Chicago	7 Oct 1970			
Total mercury		1.4		
Milwaukee	7 Oct 1970			
Dissolved mercury		<0.5		
Total mercury		<0.5		
Whiting	13 Oct 1970			
Dissolved mercury		<0.5		
Total mercury		<0.5		
Gary	13 Oct 1970			
Dissolved mercury		<0.5		
Total mercury		0.8		
Agnew, Mich.	22 Oct 1970			
Dissolved mercury		0.2		
Total mercury		0.7		
Monthly samples collected at intakes:	Oct 1970–Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		0.22	0.11–0.53	
Waukegan Generating Station		0.84	0.07–2.97	
North Chicago public water supply		0.56	0.06–3.00	
Samples collected ∿monthly at Lake County, Ill., public water intake:	Oct 1970–Jun 1973			Howe, 1973
11 samples		<0.05[b]		
20 samples		0.43	0.07–2.6	
Single samples collected at public water intakes:	1971			Baumeister, 1972
Kenosha		<0.2		
Milwaukee (5 intakes)		<0.2[b]		
Port Washington		<0.2		
Racine		<0.2		
Sheboygan		<0.2		
Two Rivers		<0.2		
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun 1971–Apr 1972	0.40	0.08–1.4	Industrial Bio-Test, 1972c
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers—3 areas (72 observations):	Nov 1972–Oct 1973			
North of plant, 3.2 km (2 mi)		0.3	<0.2–5	
Effluent plume		0.3	<0.2–4	
South of plant, 4.8 km (3 mi)		0.2	<0.2–20	

Table 71. (contd.)

		Concentration Hg, µg/l		
Sample Description	Dates	Average	Range	Reference
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		0.3	<0.2-2.8	
North of plant, 1.6 km (1 mi)		0.3	<0.2-2.3	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		0.34	0.1-1.5	
South of plant, 1.6 km (1 mi)		0.77	0.1-6	

[a] *Total soluble mercury.*

[b] *Same value for all samples.*

turbid samples. An association between mercury and particulate matter may be the reason. Additional evidence suggested mercury compounds were tightly bound to particles finer than 0.45 µm. Gavis and Ferguson (1972) pointed out the probable importance of sorptive removal of mercury to the sediments on iron oxides, clays, and sulfhydryl-containing suspended organic matter.

Kennedy *et al.* (1971) determined the mercury content of sediment samples from the southern basin of Lake Michigan and then compared their results with corresponding data for < 2 µm clay-size, organic carbon, and total sulfur content in the same samples. In the surface interval of 26 cores and grab samples, mercury and organic carbon concentrations were correlated ($r = 0.71$); likewise, mercury and total sulfur concentrations were related ($r = 0.71$). There was no clear relationship between mercury and the < 2 µm clay-size fraction. In Lakes Huron and Ontario, mercury content has similarly been shown to be correlated with organic carbon and sulfur concentrations (Thomas, 1972, 1973). The mercury-sulfur relationship suggested that mercury was sorbed by iron sulfides or that there was a relationship between mercury and organically bound sulfur. Kennedy *et al.* (1971) did not measure iron content in the samples they collected for mercury determinations, but Thomas (1973) suggested on the basis of statistical analysis that some of the mercury in Lake Huron sediments may be bound to an iron oxide-phosphorus complex.

Data on mercury content of surficial Lake Michigan sediments (Copeland and Ayers, 1972; Kennedy *et al.*, 1971) are insufficient to establish inshore-offshore trends. However, such trends have been identified in two other Great Lakes. Thomas (1972, 1973) measured total mercury content in surficial (0-3 cm) sediments of Lakes Huron and Ontario and found that there was a general trend for mercury concentrations to increase from the inshore area outward to the deep-water sediments. Natural and industrial sources of mercury could also be traced by mercury distributions in the sediments.

On the basis of samples from 30 stations in the southern basin of Lake Michigan, Kennedy *et al.* (1971) concluded that 17 cores showed an accumulation of mercury in the top few centimeters. The other 13 had fairly constant concentrations of mercury with sediment depth. All 30 cores had background concentrations of 30-60 µg mercury/kg of dry bulk sediment at sediment depths exceeding 10-15 cm. Fourteen of the 17 cores showing surficial mercury enrichment were collected in the gray silt facies of the Waukegan member (Lineback and Gross, 1972), along the eastern shore of the southern basin. Increases of mercury content with decreasing sediment depth in these 14 cores may be a reflection not only of the higher organic carbon content of sediments in the eastern part of the southern basin (*cf.* Callender, 1969; Shimp *et al.*, 1971), but also of decreasing organic carbon content with increasing sediment depth. Lineback and Gross (1972) presumed that observed surficial enrichment of mercury in Lake Michigan sediments resulted from introduction of materials to the Lake by industrial activities in the Basin. Similar increases in mercury content in cores from Lakes Erie and Ontario (Kemp *et al.*, 1974) also were attributed to increased mercury loadings, especially since 1950.

Once deposited, mercury probably has limited mobility; under reducing conditions, it is held as the highly insoluble HgS, whereas under oxidizing conditions it may be bound to ferric hydroxideoxide precipitates (Gavis and Ferguson, 1972) or iron oxide-phosphorus complexes (Thomas, 1973). Forms in which mercury could be mobile in the sediments include methyl mercuric ion and volatile dimethyl mercury; these compounds are both produced and degraded by microbial activities in sediments (Jernelöv and Martin, 1975). The contributions of CH_3Hg^+ and CH_3HgCH_3 to observed surficial enrichment have not been experimentally evaluated in Lake Michigan sediments.

MOLYBDENUM

Molybdenum is considered an essential trace element for plants and animals, but its utilization is not uniformly distributed among these organisms (Underwood, 1971). It is a key component of the enzyme xanthine oxidase in animals, but there is little evidence that molybdenum plays a role in any aspect of human health or disease. The toxicity of molybdenum is related to selenium and copper nutrition in animals, but most of the values listed by McKee and Wolf (1963) and the National Academy of Sciences ... (1973) were well above 10 mg/l of water or 10 mg/kg of food. Effects of molybdenum on aquatic animals have been little studied, but in one test fathead minnows were adversely affected by 46.7 mg Mo/l in soft water and by 246.6 mg Mo/l in very hard water.

All plants that reduce nitrate require molybdenum as a constituent of the enzyme nitrate reductase (Stanier *et al.*, 1970). It is also an integral part of the enzyme nitrogenase, by which certain algae and bacteria reduce molecular N_2 to NH_3. Bortels (1940) reported that blue-green algae using nitrate as their sole nitrogen source required 100 µg Mo/l. In contrast, Arnon (1958) said 10 µg/l was adequate for the blue-green alga *Anabaena*, and 0.1 µg/l was sufficient for the green alga *Scenedesmus*. Arnon also indicated that 1 µg/l was the limiting concentration of molybdenum for *Anabaena* growing with only N_2 as a nitrogen source. At very high concentrations, molybdenum can be toxic to plants. *Scenedesmus* is reportedly damaged by 54 mg Mo/l, and concentrations above 1 mg/l in irrigation water have injured certain sensitive plants (McKee and Wolf, 1963; National Academy of Sciences ..., 1973).

Lake Michigan likely receives most of its molybdenum from natural sources. Weathering and erosion of rocks and soils are the natural sources. Bowen (1966) reported that igneous rocks and shales typically contain 1-3 mg Mo/kg, while sandstones and limestones have 0.2-0.4 mg Mo/kg.

Molybdenum metal is used in special steel tools and in making electronic apparatus (McKee and Wolf, 1963). Molybdenum salts are used in manufacture of glass, ceramics, pigments, and fertilizers for leguminous crops. Wastes resulting from industrial uses of molybdenum might be a source to Lake Michigan. Winchester and Nifong (1971) calculated the amount of molybdenum that enters the Lake annually from stream influx and from aerosol deposition resulting from industrial activities in the Milwaukee-Chicago-Gary-Hammond area. Based on an assumed stream concentration of 1 µg Mo/l, they estimated that stream input is 33 metric tons/yr, while aerosol fallout is 4.6 metric tons/yr (assuming 10% transfer efficiency), largely from coal burning. It is possible that the estimate of Winchester and Nifong for stream input is low, since their assumed stream concentration is five to ten times less than tributary values reported by Robbins *et al.* (1972b).

The few available data on molybdenum concentrations in Lake Michigan water are presented in Table 72. The concentrations reported by Kopp and Kroner (1968) seem high, not only because they exceed the value presented by Turekian (1971) for unpolluted streams (1 µg Mo/l), but also because they exceed reported tributary concentrations (Robbins *et al.*, 1972b) by as much as an order of magnitude. Values presented by Copeland and Ayers (1972) and Robbins *et al.* (1972a) are perhaps the most reliable data available to date.

There are no regulations limiting molybdenum content in drinking water or in water for the protection of aquatic life.

Table 72. Molybdenum Content in Lake Michigan Water

Sample Description	*Dates*	*Concentration Mo, µg/l*		*Reference*
		Average	*Range*	
Semiannual composites from monthly samples collected at public water intakes:	Oct 1962-Sep 1967			Kopp and Kroner, 1968
Milwaukee				
4 composites		N.D.		
6 composites		54[a]	11-129[a]	
Gary				
2 composites		N.D.		
7 composites		35[a]	13-73[a]	
Surface-water samples collected throughout Lake at 20 inshore and offshore stations sampled ∿3 times each:	Aug 1969-Jun 1970			Copeland and Ayers, 1972
39 samples		N.D.		
14 samples		2.3[a]	1.1-4.8[a]	
Single samples collected northwest of Grand River entrance, outside River plume	6 Oct 1970			Robbins *et al.*, 1972a
A station 1.0 km (0.62 mi) NW:				
Surface-water, soluble molybdenum		2.7		
Bottom-water, soluble molybdenum		3.6		
A station 1.25 km (0.78 mi) NW:				
Bottom-water, soluble molybdenum		6.5		
Single sample collected offshore from Grand Haven	Unspecified	≤1[a]		Wahlgren *et al.*, 1972b

[a] *Total soluble molybdenum.*

The chemical forms of molybdenum in Lake Michigan water are unknown. At least one form may be an anion (*e.g.* $HMoO_4^-$, MoO_4^{2-}), considering the association (Rossman *et al.*, 1972) of molybdenum with the anion-attracting manganese portion of ferromanganese nodules.

Since molybdenum does not activate easily under neutron bombardment, it is not surprising that Copeland and Ayers (1972) were able to detect molybdenum in only one sediment sample, collected midway between Waukegan and South Haven. This sample had a molybdenum concentration of 12 ± 6 mg/kg dry sediment. This value may be high, because all the geologic formations tabulated by Bowen (1966) typically contained less than 3 mg Mo/kg.

NICKEL

Nickel is necessary for animals (Nielsen and Ollerich, 1974); it is essential for proper liver function and lipid metabolism. Nickel has also been found to be an essential constituent of at least one plant metalloenzyme (Dixon *et al.*, 1975).

At high concentrations, nickel has toxic properties. Nickel carbonyl, $Ni(CO)_4$, and nickel metal are carcinogens (Nielsen, 1971). Soluble nickel salts are relatively non-toxic to mammals (Nielsen, 1971). Aquatic organisms have varying sensitivities to nickel salts (McKee and Wolf, 1963), depending on species, pH of the water, hardness, alkalinity, and the type of nickel compound under consideration. Anderson (1948) found that 0.7 mg Ni/l immobilized *Daphnia magna* in Lake Erie water. All other reported concentrations for acute toxicities of nickel to aquatic animals (Kemp *et al.*, 1971) exceeded 0.7 mg/l.

Nickel is considered toxic to plants (Bowen, 1966), but there are occasional reports of improved growths or yields of various field crops, bacteria and algae upon addition of nickel salts (Nielsen, 1971).

Sources of nickel to Lake Michigan are largely from cultural activities in the watershed. Natural sources include weathering and erosion of rocks and soils. Bowen (1966) listed the following average concentrations in geologic materials: igneous rock, 75 mg Ni/kg; shales, 68 mg/kg; sandstones, 2 mg/kg; limestones, 20 mg/kg; and soils, 40 mg/kg. Higher concentrations are found in soils derived from serpentine. The same report stated that coal averaged 35 mg Ni/kg.

Konrad and Kleinert (1974) sampled effluents from eight sewage treatment plants discharging to Lake Michigan. The highest nickel concentration measured in these sewage effluents was 0.2 mg/l (Manitowoc) and the lowest was < 0.05 mg/l (South Milwaukee and Milwaukee's Jones Island).

Since metallic nickel is relatively inert chemically, it is used in corrosion-resistant materials, including electrodes, electrical connections, batteries, and spark plugs (National Academy of Sciences ..., 1973). Metallic nickel is also used as a catalyst in hydrogenation of organic compounds. Nickel salts furnish dyes for textile, ceramic, and ink manufacture. Mine wastes, electroplating plants, atmospheric emissions, and other industrial effluents add nickel to receiving water bodies. Plating plants in the Grand River basin are a major source of nickel to southern Lake Michigan (Robbins *et al.*, 1972a). Winchester and Nifong (1971) estimated that aerosol fallout from the burning of coal and fuel oil around the southwestern shore of the Lake is a significant source of nickel to Lake Michigan. The tributary concentrations of nickel assumed by Winchester and Nifong (1971) are an order of magnitude lower than measured concentrations (Table 73), but their estimate still shows aerosol inputs exceed tributary inputs by a ratio of at least five to one.

Few determinations of nickel for Lake Michigan are available. Almost all publications report less than 10 μg Ni/l (Table 73), which Bowen (1966) indicated was a typical value for fresh water. These data did not distinguish which chemical form of nickel was present. Garrels and Christ (1965) showed that Ni^{2+} is the stable inorganic form in oxygenated water below pH 9. Above pH 9 nickel oxides, hydroxides, and carbonates dominate.

Neither the U. S. Public Health Service (1962) nor the National Academy of Sciences ... (1973) recommended limits on nickel in drinking water (Appendix B, part 1). The National Academy of Sciences did suggest that for freshwater aquatic life a concentration lethal to 50% of the most sensitive important species in a locality should be determined in a 96-hr test (96-hr LC50) and then a factor of 0.02 should be multiplied by the 96-hr LC50 to arrive at a nickel concentration safe for aquatic life. The Lake Michigan Enforcement Conference report (1972a) tentatively suggested an upper limit of 700 μg Ni/l safe for fish, and 50-100 μg/l safe for zooplankton.

Shimp *et al.* (1970, 1971), Lineback and Gross (1972), Robbins *et al.* (1972a), Leland *et al.* (1973b) and Robbins and Edgington (1974) have reported nickel concentrations in sediments of the southern basin. Preliminary data (Shimp *et al.*, 1970) seemed to indicate that nickel accumulates in the upper few centimeters of these sediments. However, additional data (Shimp *et al.*, 1971; Lineback and Gross, 1972; Leland *et al.*, 1973b) indicated this accumulation, if it was present at all, was very slight; surficial concentrations were nonsignificantly different from the background values of *ca.* 32-35 mg/kg bulk dry sediment. The average nickel content of suspended matter collected 1 m above the Lake floor was 47 mg/kg bulk dry suspended matter (n = 12). Leland *et al.* (1973b) did not speculate why nickel concentrations were higher in suspended matter than in the surficial-sediment interval ($\bar{x}$ = 34 mg/kg bulk dry sediment, n = 24).

Shimp *et al.* (1971) found that nickel concentrations in sediments from southern Lake Michigan correlated somewhat better with iron oxide and perhaps clay content than with organic carbon or manganese oxide content. The relation of nickel with clay content may account for the somewhat higher average nickel concentrations in surficial sediments of the gray silt facies ($\bar{x}$ = 35 mg/kg dry sediment) than in the brown silt facies (27 mg/kg dry sediment) of the Waukegan member (Lineback and Gross, 1972).

Robbins *et al.* (1972a) and Robbins and Edgington (1974) also found no clear evidence of surficial nickel enrichment in sediments collected in the eastern part of the southern basin. Along a transect from Grand Haven, acid-extractable nickel content increased out to *ca.* 19.3-29.0 km (12-18 mi) and then decreased somewhat out to 40 km (25 mi) (Robbins and Edgington, 1974). The authors hypothesized that this pattern, which was seen in both surficial and sub-surface (to 20 cm) sediments, was somehow related to local variations in sedimentation rates.

Table 73. Nickel Content in Lake Michigan Water

Sample Description	Dates	Concentration Ni, μg/l Average	 Range	Reference
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City				
61 samples		<5[a]		
2 samples		5[a]		
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo				
36 samples		<5[a]		
3 samples		5[a]		
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor				
23 samples		<5[a]		
3 samples			3-6	
On a line roughly between Sheboygan and Little Sable Point				
3 samples		<5[a]		
5 samples		5[a]		
Samples collected:	1962-63			Risley and Fuller, 1966
Calumet Harbor, 7 samples		<5[a]		
Indiana Harbor, 8 samples		<5[a]		
Adjacent to Calumet and Indiana Harbors, 52 samples		<5[a]		
Whole Lake:	1962-63			USDOI, 1968
33 offshore samples		<5[a,b]		
28 offshore samples		5	5-7	
Monthly samples collected at intakes:	Aug 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply				
8 samples		<3		
1 sample		5		
Waukegan Generating Station				
9 samples		≤3		
North Chicago public water supply				
9 samples		≤3		
Samples collected ~monthly at Lake County, Ill., public water intake:	Sep 1970-Sep 1971, Sep 1972-Jun 1973			Howe, 1973
5 samples		<1		
17 samples		2	1-4	
Single samples collected northwest of Grand River entrance, outside River plume	6 Oct 1970			Robbins *et al.*, 1972a
A station 1.0 km (0.62 mi) NW:				
Surface-water, soluble nickel		4.2[c]		
Bottom-water, soluble nickel		5.5[c]		
A station 1.25 km (0.78 mi) NW:				
Bottom-water, soluble nickel		19.5[c,d]		
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		8.3[c]		
17 km (10.6 mi) offshore		7.7[c]		
Monthly averages for samples collected once a month over a 24 hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun-Sep 1971	2	1-3	Industrial Bio-Test, 1972c
Samples (3 replicate analyses) collected off Grand Haven	13-14 Sep 1971			Edgington *et al.*, 1972b
16 km (10 mi) west at a depth of:				

Table 73. (contd.)

		Concentration Ni, μg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
10 m (BNWL)*		6.28		
10 m (VD)*		5.61		
45 m		6.71		
60 m		6.16		
8 km (5 mi) west at a depth of:				
40 m		6.63		
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft) water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers--3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		7	<5-<50	
Effluent plume		6	<5-<50	
South of plant, 4.8 km (3 mi)		6	<5-<50	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee--2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		7	<5-25	
North of plant, 1.6 km (1 mi)		8	<5-25	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis--2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		11	5-25	
South of plant, 1.6 km (1 mi)		12	5-25	

[a] *Same value for all samples.*

[b] *Limit of detection.*

[c] *Total soluble nickel.*

[d] *This author questions whether this sample was outside the River plume.*

**BNWL = noncontaminating Niskin water bottle; VD = Van Dorn water bottle.*

USDOI = U. S. Department of the Interior.

SELENIUM

Plants do not require selenium, although several reports suggest it has stimulated growth in a few species not characterized as selenium accumulator species (Hemphill, 1972). In contrast, bacteria (Pinsent, 1954) and animals (Schwarz and Foltz, 1957) are known to require trace amounts of selenium. In mammals selenium is found in glutathione peroxidase, an enzyme of red blood cells (Rotruck *et al.*, 1973). Bacterial enzymes containing selenium include glycine reductase and formate dehydrogenase (Stadtman, 1974). All three of these selenium-containing enzymes catalyze oxidation-reduction reactions.

Selenium is more widely known for its animal toxicity. The narrow limits between concentrations necessary for health and concentrations causing toxicity have been recognized. The minimum requirement of higher animals for selenium is 0.04 mg/kg diet; furthermore, it is beneficial up to 0.1 mg/kg (Schwarz and Foltz, 1957). Above 4 mg/kg, selenium becomes toxic to animals. With the exception of hydrogen selenide, which is unstable in water (Coleman and Delevaux, 1957), selenite is the most toxic inorganic chemical form of selenium (Martin and Gerlach, 1972). The toxic characteristics of selenium are related to its oxidant properties. Because its properties of essentiality and toxicity both involve oxidation, selenium presents an apparent paradox: harmful biochemical oxidations will occur if the organism is presented with too little (deficiency) or too much (toxicity) selenium. Lakin (1973) reported that selenium deficiency in the diet of animals is more probable than toxicity of selenium.

Natural sources of selenium to Lake Michigan are relatively unimportant. The estimated abundance of selenium in shales is *ca.* 0.6 mg Se/kg, and about 0.2 mg/kg in soils (Bowen, 1966). Other geologic formations, whose erosion and weathering might carry selenium into Lake Michigan, are low in selenium. Sandstones, igneous rocks, and limestones contain 0.05-0.08 mg Se/kg. Coal and, to a lesser extent, petroleum often contain appreciable quantities of selenium because selenium is concentrated in the biological remains in these carbonaceous deposits (Lakin, 1973). On a global basis, vulcanism supplies large quantities of selenium to the environment, but this source is unimportant here.

Both industrial and municipal effluents carry selenium into the Lake. Selenium is used in manufacturing electrical rectifiers, decolorization of poor quality green glass, paint pigments, and a photocopying process (Levander, 1971). The largest source of selenium is probably aerosol fallout from the burning of fossil fuels (Winchester and Nifong, 1971; Klein, 1975). Selenium from fuel burning is likely added to Lake Michigan in particulate form, as Se^0 (relatively insoluble, slowly oxidized) and SeO_2 (reacts with water to form soluble selenite salts). Since the combustion products of selenium are particulate (Se^0 and SeO_2), unlike the gaseous combustion products of its chemical analogue sulfur (SO_2), one would expect selenium to be deposited much nearer to its emission source than SO_2 (Lakin, 1973). Another probable source of selenium to Lake Michigan is municipal sewage effluents. Baird *et al.* (1972) found 45 µg Se/l in three different sewage effluents from primary treatment, while secondary effluents from three separate sources ranged from 10 to 50 µg Se/l. Total selenium content in the final effluent from a tertiary treatment plant was reported as less than 1 µg Se/l (Tanner *et al.*, 1972).

Selenium determinations on Lake Michigan water samples are infrequent (Table 74). Wahlgren *et al.* (1972a) recorded total soluble selenium concentrations two to six times higher than the average value for natural waters (0.2 µg Se/l) reported by Turekian (1971). The data of Copeland and Ayers (1972) were less than half Turekian's value. It is not clear why the selenium concentrations reported by Wahlgren *et al.* (1972a) and Copeland and Ayers (1972) differ by at least an order of magnitude.

Some data suggest that inshore and offshore concentrations of selenium differ (Copeland and Ayers, 1972). A comparison of selenium and sulfur chemistry may suggest an explanation for this observation. Numerous organisms in inshore water are capable of converting more of the total sulfur to the particulate form than offshore. Since the biochemistry of selenium resembles that of sulfur, some enzyme systems requiring sulfur may incorporate selenium, a close chemical relative of sulfur (Stadtman, 1974). Hence, organisms in inshore water may be responsible for the lower soluble selenium concentrations compared with offshore water. Physical and chemical processes may also contribute to these apparent inshore-offshore differences as well.

Wahlgren *et al.* (1972a) and Copeland and Ayers (1972) did not determine the chemical form of selenium present in Lake Michigan water. Under equilibrium conditions, the stable forms between pH 6 and 10 include Se^0, $HSeO_3^-$,

Table 74. Total Soluble Selenium Content in Lake Michigan Water

Sample Description	Dates	Concentration Se, µg/l Average	Range	Reference
Stations throughout Lake sampled 3 times each:	Aug 1969-Jun 1970			Copeland and Ayers, 1972
12 inshore stations				
33 samples		0.081	0.016-0.17	
1 sample		N.D.		
8 offshore stations				
19 samples		0.096	0.078-0.14	
1 sample		N.D.		
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		0.5		
17 km (10.6 mi) offshore		1.3		

N.D. = not detected.

SeO_3^{2-}, and SeO_4^{2-}. Chemical forms also depend upon oxygen concentrations in the water. Microorganisms may mediate changes in the oxidation state of selenium in the water and sediment. One cannot *a priori* predict the chemical forms of selenium in Lake Michigan water, nor is it known what controls selenium concentrations in the water. Precipitation of more reduced forms (Se^0, SeO_2) as well as rates and ease of oxidation may control concentrations. As mentioned above, biochemical interactions may also influence measured selenium concentrations. For some insight on inorganic aspects of this problem, compare stability of sulfur forms in aqueous systems (p. 270 in Krauskopf, 1967) with that of selenium forms (Coleman and Delevaux, 1957).

The U. S. Public Health Service (1962) considered a selenium content of 0.01 mg/l too high for a drinking water source (Appendix B, part 1). The National Academy of Sciences ... (1973) made no specific recommendation on selenium content in fresh water for protection of fish and other aquatic life (Appendix B, part 2), but the Academy suggested that selenium be limited to 0.05 mg/l in water supplied to livestock.

Both Copeland and Ayers (1972) and Edgington *et al.* (1972a) used neutron activation analysis to measure selenium content in Lake Michigan sediment cores, although selenium is difficult to activate. Copeland and Ayers (1972) had difficulty detecting selenium in bulk sediments and in sediment particles of < 200 µm size. From a total of 39 surface sediment samples, selenium went undetected in 19, was reported as "less than" a given value in 8 samples, and was quantifiable in only 12. It was not possible to determine whether the apparent inshore-offshore difference in selenium content of water was also present in sediments.

Edgington *et al.* (1972a) measured selenium in three cores from Green Bay: midway between Marinette and Sturgeon Bay (Fig. 105a), just south of Little Bay de Noc (Fig. 105b), and in Big Bay de Noc (Fig. 105c). Edgington *et al.* performed a preliminary chemical separation (Edgington and Lucas, 1971) that allowed detection of low levels of selenium radioactivity. In all three cores studied, selenium was slightly higher at the sediment surface and decreased somewhat with depth. Below *ca.* 55 cm, selenium content increased markedly (Fig. 105a, c). The causes for these patterns are unknown. Oxidation and reduction of selenium species, as well as microbial activities involving selenium, are probable contributing factors. It is also possible that more than one geological stratum may have been penetrated by these cores.

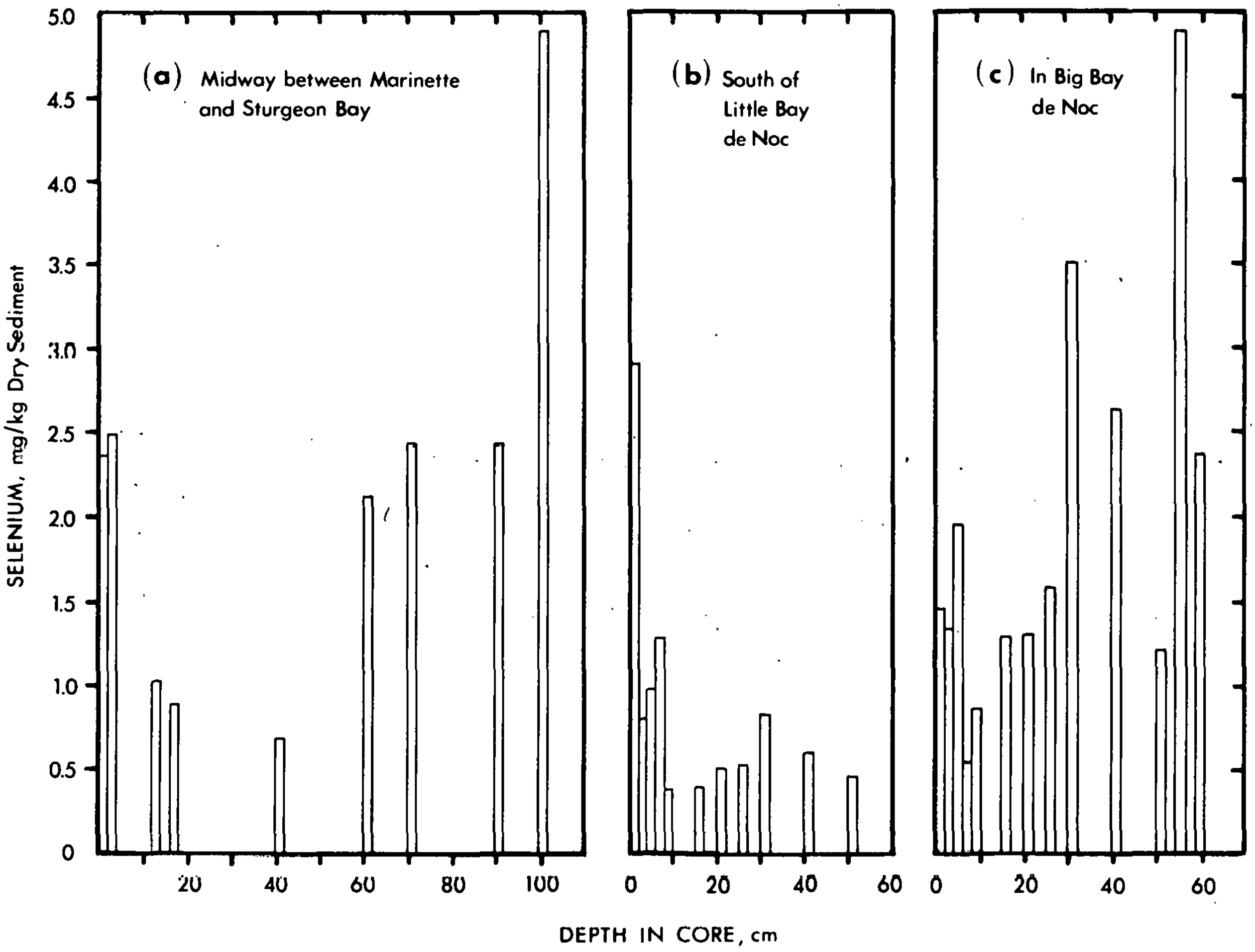


Fig. 105. Selenium Content in Three Sediment Cores from Green Bay. Data from Edgington *et al.* (1972a).

SILVER

Neither plants nor animals require silver. Ingested silver has a cosmetic effect in humans by causing permanent blue-gray discoloration of the skin, eyes, and mucous membranes if consumed in excess (U. S. Public Health Service, 1962).

Silver compounds are much more toxic to fish than to warm-blooded animals (Cooper and Jolly, 1970). Anderson (1948) found 4.8 μg Ag/l was the toxic threshold to sticklebacks held in Lake Erie waters, while 5.1 μg Ag/l produced immobilization in *Daphnia magna*. Sublethal effects on developing eggs may be more important than direct mortality (National Academy of Sciences ..., 1973).

There are few natural sources of silver to Lake Michigan. Igneous and sedimentary rocks typically contain 50-70 μg Ag/kg (Bowen, 1966), while soils average 100 µg/kg. Because most silver compounds have limited solubility and because soil colloids tend to adsorb silver strongly, weathering and erosion would transfer silver from rocks and soils into Lake Michigan predominantly in the particulate form. Gatz (1975) measured background silver concentrations in precipitation collected near Centralia, Illinois. Silver in rain and snow averaged 0.093 µg/l (range < 0.002-0.00250 µg/l). There was no strong evidence that dry deposited silver formed a large component of the precipitation samples.

Commercial and industrial use of silver provide the major source to Lake Michigan. In addition to its use in coins, silver finds wide use in photography, chemicals, jewelry and in manufacture of tableware. Silver has been used infrequently as a bacteriostat in water supply systems (McKee and Wolf, 1963). This array of uses can add small quantities of silver to the Lake. Winchester and Nifong (1971) estimated that tributaries carry 10 metric tons of silver annually to Lake Michigan, while aerosol inputs add 0.3 metric tons. In contrast, Klein (1975) computed that aerosol deposition (19 metric ton/yr) is a larger source of silver than soil erosion (0.5 metric ton/yr). If cloud seeding with AgI for the purpose of hail suppression, lightning suppression, or precipitation enhancement should ever become widespread around the Basin, then precipitation as a source of silver could become even more important.

Few determinations of silver concentration have been made in Lake Michigan (Table 75). With the exception of two values of 1.5 and 1.6 µg Ag/l, total soluble silver concentrations are about 0.3 µg Ag/l. Bowen (1966) reported that fresh water typically contains about 0.13 µg Ag/l. It is not clear why silver concentrations in Lake Michigan are higher.

Table 75. Total Soluble Silver Content in Lake Michigan Water

		Concentration Ag, µg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Semiannual composites from monthly samples collected at Milwaukee public water intake:	Oct 1962-Sep 1967			Kopp and Kroner, 1968
9 composites		N.D.		
1 composite		1.6		
Stations throughout Lake sampled 3 times each:	Aug 1969-Jun 1970			Copeland and Ayers, 1972
12 inshore stations		0.32	0.059-1.1	
8 offshore stations		0.32	0.18-1.2	
Single samples collected from public water intakes at Green Bay, Kenosha, Milwaukee (5 intakes), Port Washington, Racine, Sheboygan, and Two Rivers	1971	<40[a]		Baumeister, 1972
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		0.3		
17 km (10.6 mi) offshore		1.5		

[a] *Same value for all samples.*

N.D. = not detected.

Solubility of the most common silver salt, AgCl, apparently does not control silver concentrations in Lake Michigan. At the ionic strength of the Lake, 88.7 μg Ag/l would be in solution if the chloride content is 5 mg/l. Adsorption of silver ions to vegetation, detritus, clays, organic colloids and sediments (Cooper and Jolly, 1970) likely reduces the soluble silver concentration below the predicted value.

Based on aesthetics rather than toxicity to humans, the U. S. Public Health Service (1962) reported water containing more than 0.05 mg Ag/l was unfit for drinking (Appendix B, part 1). The National Academy of Sciences ... (1973) made no specific recommendation for limiting silver concentrations in fresh water for maintenance of fish and aquatic life (Appendix B, part 2).

Copeland and Ayers (1972) attempted to determine silver in surface sediments of Lake Michigan using neutron activation analysis. Of 19 samples, silver was quantifiable in eight. These eight averaged 0.7 mg Ag/kg bulk dry sediment (range 0.2-1.3 mg Ag/kg bulk dry sediment). This average value must be evaluated carefully, for it is nearly an order of magnitude higher than silver concentrations typically found in sedimentary rocks and soils.

VANADIUM

Vanadium reportedly is essential for photosynthesis in the green algae *Scenedesmus obliquus* and *Chlorella pyrenoidosa* (Arnon and Wessel, 1953; Meisch and Bielig, 1975) and is required by the mold *Aspergillus niger* (Schwarz and Milne, 1971). There is no firm evidence that higher plants require vanadium. Vanadium is essential to animals at 50-500 μg/kg diet (Hopkins and Mohr, 1974), where it is involved in lipid and hard-tissue metabolism. At higher concentrations, vanadium becomes toxic to animals (Underwood, 1971).

Sources of vanadium to Lake Michigan are both natural and cultural. Natural sources include weathering and erosion of soils and rocks in the Basin. Igneous rocks and shales average 130-135 mg V/kg (Bowen, 1966), while sandstones and limestones typically contain 20 mg V/kg. Soils average 100 mg V/kg. Alkaline humus in a soil may retain vanadium in an anionic form.

Cultural sources of vanadium to the Lake are by direct discharge as well as aerosol fallout. Vanadium metal is used in metallurgy to increase the hardness and malleability of steel (McKee and Wolf, 1963). Vanadium salts are used in glass manufacture, photography, and as a mordant in dyeing and printing textiles. More recently, vanadium has been used in catalytic converters to reduce hydrocarbon emissions from automobiles. Winchester and Nifong (1971) estimated that, compared with tribuary inputs (29 metric tons), the burning of coal and fuel oil around the southwestern shore of the Lake provides a significant aerosol source of vanadium to Lake Michigan (61 metric tons). Klein (1975) estimated that soil erosion contributes 540 metric tons of vanadium to the Lake each year, while aerosol deposition adds 120 metric tons.

Vanadium determinations in Lake Michigan water are summarized in Table 76. Wahlgren *et al.* (1972b) reported an upper limit of 1 μg total soluble V/l in water collected off Grand Haven. Total soluble vanadium in offshore and inshore surface-water samples collected throughout the Lake by Copeland and

Ayers (1972) averaged 0.23-0.24 µg V/l. Typical concentrations for vanadium in fresh water are 1 µg/l (Bowen, 1966). Wahlgren *et al.* (1972b) and Copeland and Ayers (1972) were not able to determine the chemical form of vanadium present in these samples. Using equilibrium data of Evans and Garrels (1958), one would predict that in oxygenated Lake Michigan waters between pH 6 and 10, V_2O_4 (solid) and soluble pentavalent vanadates, analogous to anionic phosphates, would be the stable forms.

Table 76. Total Soluble Vanadium Content in Lake Michigan Water

Sample Description	*Dates*	*Concentration V, µg/l*		*Reference*
		Average	*Range*	
Stations throughout Lake sampled 3 times each:	Aug 1969-Jun 1970			Copeland and Ayers, 1972
12 inshore stations				
32 samples		0.24	0.15-0.42	
2 samples		<0.15		
8 offshore stations				
19 samples		0.23	0.15-0.32	
1 sample		N.D.		
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		0.3		
17 km (10.6 mi) offshore		0.8		

N.D. = not detected.

Neither the U. S. Public Health Service (1962) nor the National Academy of Sciences ... (1973) suggested a limit on vanadium concentration in drinking water. There is no suggested limit on vanadium for protection of aquatic life (Appendix B).

Vanadium concentrations in Lake Michigan sediments have been determined by Shimp *et al.* (1970, 1971), Lineback and Gross (1972), Robbins *et al.* (1972a), Copeland and Ayers (1972), and Leland *et al.* (1973b). Samples from cores taken in the southern basin (Shimp *et al.*, 1971) had a median value of 55 mg V/kg dry sediment. There was no clear evidence that vanadium was accumulating in surficial sediments of the southern basin (Shimp *et al.*, 1971; Lineback and Gross, 1972), but the surficial vanadium content was higher along the eastern shore in the gray silt facies ($\bar{x}$ = 55 mg V/kg dry sediment) than in the brown silt facies ($\bar{x}$ = 38 mg/kg dry sediment) of the western part of the Waukegan member (Lineback and Gross, 1972). Vanadium concentrations in suspended matter collected 1 m above the Lake bottom were similar to or slightly higher ($\bar{x}$ = 56 mg/kg dry sediment; range, 26-72 mg/kg dry sediment) than in surficial sediments (Leland *et al.*, 1973b).

Preliminary data (Robbins *et al.*, 1972a) indicated that, offshore from Grand Haven, vanadium content in surficial sediments increased from 9.6 km (6 mi) to 24 km (15 mi) and then remained nearly constant to 40 km (25 mi). This trend has not yet been confirmed.

ZINC

The essential trace element zinc is an integral part of the metalloprotein enzymes carbonic anhydrase and alkaline phosphatase, which are essential for CO_2 metabolism and phosphorus utilization, respectively (Bowen, 1966). Zinc is also involved in the synthesis and metabolism of ribonucleic acids and proteins in microorganisms, plants, and higher animals (Underwood, 1971).

Quantities as low as 50 μg Zn/l yield maximal growth in the green alga *Chlorella pyrenoidosa* (Eyster *et al.*, 1958) and in blue-green algae (Allen and Arnon, 1955). Zinc concentrations of about 1 mg Zn/l in nutrient media are toxic to some plants (National Academy of Sciences ..., 1973). Zinc concentrations toxic to man are quite high (McKee and Wolf, 1963); no harm has been noted below 30 mg Zn/l. The greatest zinc susceptibility occurs in fish and other aquatic organisms, where zinc toxicity is inversely related to water hardness. Brungs (1969) tested the chronic effects of zinc on fathead minnow reproduction in hard water (200 mg/l as $CaCO_3$). Thirty μg Zn/l had no effect whereas 180 μg/l caused a 93% reduction in fecundity. *Daphnia magna* is more resistant to zinc than the fathead minnow (unpublished data cited by National Academy of Sciences ..., 1973).

Zinc is fairly abundant in nature (Hem, 1972). Weathering and erosion of geologic formations provide the natural supply of zinc to Lake Michigan. Worldwide, igneous rocks and shales typically contain 70-95 mg Zn/kg, while sandstones and limestones average 16-20 mg Zn/kg (Bowen, 1966). Coal and soils contain similar amounts of zinc (40-50 mg Zn/kg). Zinc in soil is fairly resistant to chemical weathering and little is removed by leaching, but zinc contained in coal is released to the atmosphere during combustion.

Metallic zinc is used in the production of brass and other alloys, as well as to galvanize pipe and hot water tanks (Hem, 1972). Zinc may dissolve from these galvanized containers and increase the soluble zinc content of the water (National Academy of Sciences ..., 1973). Zinc salts are used in rubber vulcanization, paint pigments, cosmetics, drugs, insecticides, and fertilizers.

Municipal sewage effluents can contain appreciable amounts of zinc. Konrad and Kleinert (1974) surveyed a number of primary and secondary sewage treatment plants in Wisconsin, including those at Kenosha, Racine, South Milwaukee, Milwaukee (both Jones Island and South Shore), Sheboygan, Manitowoc, and Two Rivers. Final effluent concentrations ranged from 0.12 mg Zn/l at South Milwaukee to 1.0 mg Zn/l at Sheboygan. The treatment plants at Kenosha, Manitowoc, and Milwaukee removed 50-80% of the influent zinc, while the others removed less than 20% of the incoming zinc. The Two Rivers sewage treatment plant did not remove any influent zinc. As tertiary treatment becomes more common in the Lake Michigan Basin, the amounts of zinc discharged in sewage effluents may decrease still further. For example, Tanner *et al.* (1972) found 3 μg Zn/l in the effluent of a tertiary treatment plant (presumably located in Washington state).

Both dry fallout and wet precipitation may contribute major quantities of zinc to Lake Michigan. Lazrus *et al.* (1970) collected wet precipitation at

32 sites in the United States from September 1966 to January 1967 and reported zinc averaged 107 μg/l, based on all stations. Extremely high concentrations at Midway and O'Hare fields were said to bias this average. Unfortunately, Lazrus *et al.* did not present raw concentration data to resolve this question. Van Loon (1973) compared zinc concentrations in precipitation in urban and rural areas. In metropolitan Toronto, soluble zinc concentrations averaged as much as 250 μg/l but north of the metropolitan area the average soluble zinc content of wet precipitation was ≤ 20 μg/l. Tanner *et al.* (1972) found that total zinc in rain collected during April at the Quillayute Indian reservation, in western Washington state, was 3 μg/l. Zinc in an ice core taken at Camp Century, Greenland, was < 1 μg/l. Winchester and Nifong (1971) estimated that pollution aerosol fallout, primarily from the iron and steel industries at the southern end of the Lake, added six times more zinc annually than stream input. Klein (1975) calculated that precipitation and dry fallout contribute twelve times more zinc to Lake Michigan than soil erosion does.

Zinc concentrations have been measured many times in Lake Michigan waters (Table 77). Several analytical methods used to develop data in Table 77 are inadequate for the very low zinc concentrations found in the Lake. Unsatisfactory methods include polarography (U. S. Dep. Inter., 1968), colorimetry (State of Michigan water intake data, cited by Lake Mich. Enforcement Conf., 1972a), and direct atomic absorption spectroscopy (Durum *et al.*, 1971; Baumeister, 1972). Greater success has been achieved with mass spectroscopy (Wahlgren *et al.*, 1972a, 1972b), neutron activation analysis (Copeland and Ayers, 1972), and solvent extraction followed by atomic absorption spectroscopy (Nienke, 1972--personal communication). In some instances samples have been stored for long periods before filtration or analysis. Zirino and Healy (1971) found that both Millipore and Gelman filters leach considerable quantities of zinc when filtering sea water. Nienke (1972--personal communication) found the same phenomenon in filtering Lake Michigan water through Millipore filters; the amount of zinc released also varied from one membrane filter to the next.

Another problem is common among the data cited in Table 77. Calvanized pipe releases zinc into the water passing through it. Many of these samples were obtained from intake pipes of various municipal water supplies. Zinc values reported at the Kenosha intake are high and variable (Table 78). Nienke (1972--personal communication) recorded that his sample was taken from a tap leading directly into the raw-water intake line in the treatment plant laboratory. Before the sample was collected, the plant operator flushed the tap until standing water in the line was drained. The zinc content in this sample was 45 μg/l, whereas the zinc concentration was only 10 μg/l in water collected at the entrance to the Kenosha Harbor, which Nienke sampled the same day as the treatment plant. Apparently, the zinc content in Lake Michigan water is increased by passing through the Kenosha water intake pipe. This mode of contamination may account for some of the other high zinc levels in Table 77.

Perhaps the most reliable determinations of zinc in Lake Michigan include those of Industrial Bio-Test (1972a), Nienke (1972--personal communication), and Limnetics (1974). Industrial Bio-Test (1972a) sampled the North Chicago water intake monthly from October 1970 to April 1971. During that time zinc concentrations fluctuated without pattern from 2 to 26 μg/l; the average value

Table 77. Zinc Content in Lake Michigan Water

Sample Description	Dates	Concentration Zn, μg/l Average	 Range	Reference
Samples collected:	1962-63			Risley and Fuller, 1965
South of a line from Calumet Harbor to Michigan City				
43 samples		$<5^a$		
20 samples			8-71	
Between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo				
37 samples		$<5^a$		
2 samples			8-32	
Between lines connecting Chicago to New Buffalo and Glencoe to Benton Harbor				
23 samples		$<5^a$		
3 samples			9-18	
On a line roughly between Sheboygan and Little Sable Point				
6 samples		$<5^a$		
2 samples			8-11	
Samples collected:	1962-63			Risley and Fuller, 1966
Calumet Harbor, 7 samples			25-53	
Indiana Harbor, 8 samples			9-87	
Adjacent to Calumet and Indiana Harbors				
43 samples		$<5^a$		
10 samples			8-71	
Whole Lake:	1962-63			USDOI, 1968
48 offshore samples		$<5^{a,b}$		
13 offshore samples		13	8-20	
Semiannual composites from monthly samples collected at public water intakes:	Oct 1962-Sep 1967			Kopp and Kroner, 1968
Milwaukee				
7 composites		13^c	$5-23^c$	
3 composites		N.D.		
Gary				
9 composites		25^c	$10-55^c$	
Samples collected at 11 public water intakes in Michigan	1967	$<100^{a,b}$		Lake Mich. Enforcement Conf., 1972a
Surface-water samples collected at stations throughout Lake sampled 3 times each:	Aug 1969-Jun 1970			Copeland and Ayers, 1972
12 inshore stations		20.8^c	$2.2-80^c$	
8 offshore stations		16.0^c	$1.9-62^c$	
Monthly samples collected at intakes:	Oct 1970-Apr 1971			Industrial Bio-Test, 1972a
Kenosha public water supply		160	43-450	
North Chicago public water supply		8	2-26	
Single samples collected northwest of Grand River entrance, outside River plume	6 Oct 1970			Robbins *et al.*, 1972a
A station 1.0 km (0.62 mi) NW:				
Surface-water, extractable particulate zinc		1.5		
Bottom-water, extractable particulate zinc		0.99		
A station 1.25 km (0.78 mi) NW:				
Bottom-water, extractable particulate zinc		0.8		

Table 77. (contd.)

		Concentration Zn, μg/l		
Sample Description	*Dates*	*Average*	*Range*	*Reference*
Single samples collected at water intakes:				Durum *et al.*, 1971
Evanston	7 Oct 1970	130[c]		
Chicago	7 Oct 1970	40[c]		
Milwaukee	7 Oct 1970	20[c]		
Whiting	13 Oct 1970	60[c]		
Gary	13 Oct 1970	<10[c]		
Agnew, Mich.	22 Oct 1970	70[c]		
Single samples collected at public water intakes:	1971			Baumeister, 1972
Green Bay		<10		
Kenosha		160		
Milwaukee (5 intakes)			<10-30	
Port Washington		20		
Racine		40		
Sheboygan		50		
Two Rivers		100		
Single samples collected at:	5 Feb 1971			Nienke, 1972
Waukegan breakwater		9.5		
Zion shoreline		9.5		
Monthly averages for samples collected once a month over a 24-hr period from the intake canal of Waukegan Generating Station, immediately inside the ice screen	Jun 1971-Apr 1972	15	<1-38	Industrial Bio-Test, 1972c
Samples (3 replicate analyses) collected off Grand Haven	13-14 Sep 1971			Edgington *et al.*, 1972b
16 km (10 mi) west at a depth of:				
10 m (BNWL)*		4.39		
10 m (VD)*		27.27		
45 m		3.59		
60 m		4.24		
8 km (5 mi) west at a depth of:				
40 m		3.97		
Single samples collected at:				Nienke, 1972
Waukegan breakwater	30 Nov 1971	16		
Kenosha water intake	30 Nov 1971	45		
Racine water intake	30 Nov 1971	41		
Beach at Shorewood, Wis.	26 Dec 1971	3.2		
Port Washington breakwater	26 Dec 1971	6.7		
Beach at Terry Andrae State Park (near Sheboygan)	26 Dec 1971	4.4		
Beach at Two Rivers	26 Dec 1971	1.1		
Beach at Whiting	13 Jan 1972	28		
Beach at Hammond	13 Jan 1972	22		
Port Washington breakwater	11 Apr 1972	9.7		
Beach at Terry Andrae State Park (near Sheboygan)	11 Apr 1972	8.7		
Single samples collected ∿48 km (30 mi) east of Kenosha at a depth of:	Late Apr 1972			Nienke, 1972
2 m		6.5		
50 m		8.1		
Single sample collected ∿16 km (10 mi) east of Sturgeon Bay at a depth of:	Early May 1972			Nienke, 1972
10 m		6.2		

Table 77. (contd.)

Sample Description	*Dates*	*Concentration Zn, µg/l*		*Reference*
		Average	*Range*	
Single samples collected offshore from Grand Haven:	Unspecified			Wahlgren *et al.*, 1972a
1.3 km (0.8 mi) offshore (mid-depth)		40[c]		
17 km (10.6 mi) offshore		96[c]		
Stations at 3.7, 5.5, and 7.3 m (12-, 18-, and 24-ft water-depth contours sampled monthly (2 replicates) at surface, middle, and bottom.				Limnetics, 1974
Point Beach Nuclear Plant, ∿11.2 km (7 mi) north of Two Rivers-- 3 areas (72 observations):	Nov 1972-Oct 1973			
North of plant, 3.2 km (2 mi)		4	<0.5-30	
Effluent plume		5	1-10	
South of plant, 4.8 km (3 mi)		4	<0.5-20	
Oak Creek Power Plant, ∿32 km (20 mi) south of Milwaukee-- 2 areas (72 observations):	Nov 1972-Oct 1973			
Effluent plume		7	<1-8	
North of plant, 1.6 km (1 mi)		7	<1-8	
Lakeside Power Plant, ∿8 km (5 mi) south of Milwaukee in St. Francis-- 2 areas (30 observations):	Nov, Dec 1972; Mar, May, Oct 1973			
Effluent plume		4.9	2-10.5	
South of plant, 1.6 km (1 mi)		5.2	2.5-10.5	

[a] *Same value for all samples.*

[b] *Limit of detection.*

[c] *Soluble zinc.*

* *BNWL = noncontaminating Niskin water bottle; VD = Van Dorn water bottle.*

N. D. = not detected.

USDOI = U. S. Department of the Interior.

Table 78. Zinc Content at the Kenosha Water Intake

Date	Concentration Zn, µg/l	Reference
(Unspecified) 1971	160	Baumeister, 1972
1 October 1970	200	Industrial Bio-Test, 1972a
5 November 1970	62	Industrial Bio-Test, 1972a
10 December 1970	97	Industrial Bio-Test, 1972a
13 January 1971	193	Industrial Bio-Test, 1972a
11 February 1971	113	Industrial Bio-Test, 1972a
26 March 1971	107	Industrial Bio-Test, 1972a
27 April 1971	363	Industrial Bio-Test, 1972a
30 November 1971	45	Nienke, 1972

for the seven months was 8 µg/l. Nienke (1972--personal communication) conducted the most extensive study to date on zinc in Lake Michigan. His work was confined largely to the western and southern part of the Lake. Nienke found that total zinc was generally less than 10 µg/l in unpolluted areas and in open waters. In spring 1972, Nienke noted that zinc concentrations, at a station 48 km (30 mi) east of Kenosha, were 6.5 µg/l and 8.1 µg/l at 2 m and 50 m, respectively. It is not known whether the difference in these two values was statistically significant. Open water samples in the southern basin (48 km east of Kenosha) did not differ appreciably from those in the northern basin (16 km east of Sturgeon Bay).

Nienke (1972--personal communication) sampled along a transect east of the Milwaukee Harbor entrance in March 1972 to establish the extent of pollution in inshore areas. Zinc concentrations were quite high, 80 µg/l, in the harbor area (Fig. 106). Fairly high concentrations were found at least 2.4 km (1.5 mi) offshore, and values slightly higher than open water persisted out to *ca.* 4.8 km (3.0 mi). Water close to shore was not well mixed, as reflected by zinc concentrations in surface (1 m) samples being much less than bottom samples at 0.40 and 0.80 km (0.25 and 0.5 mi) from shore.

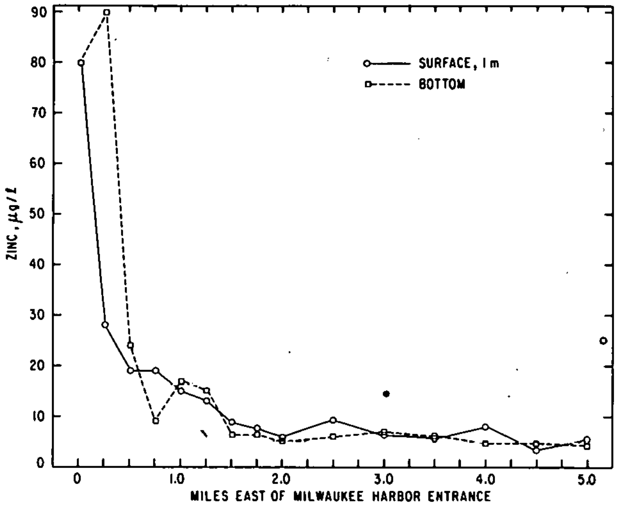


Fig. 106.

Distribution of Zinc Offshore from Milwaukee Harbor, March 1972. Data from Nienke (1972--personal communication).

Available data demonstrate seasonal trends for zinc in inshore waters. Zinc levels were highest in the Two Rivers area in February, March, and April (Fig. 107). During the summer months values were low, but increased slightly in autumn. Similar patterns were noted in the vicinity of Oak Creek, a southern suburb of Milwaukee (Fig. 108), but in the latter case higher absolute zinc concentrations were recorded. These seasonal patterns may be related to emission of aerosol zinc from the burning of fossil fuels during the heating season and/or to biochemical uptake during spring and summer; however, the exact cause or causes of this seasonal variation in zinc concentrations in inshore waters are unknown. Furthermore, it is also unknown if seasonal trends also occur in offshore waters.

Recommended limits on zinc in public drinking water supplies (Appendix B, part 1) are based on aesthetic rather than toxic considerations. Where aquatic life is to be managed, limitations on zinc (Appendix B, part 2) may be based on zinc toxicity to the most sensitive important species in the ecosystem, often a fish important for commercial and/or sport fishing.

The chemical forms of zinc in Lake Michigan waters have not been reported. It is probable that Zn^{2+}, $ZnHCO_3$, and the ion pairs $Zn(OH)_2{}^0$ and $ZnCO_3{}^0$ are the stable dissolved forms between pH 6 and 10. However, zinc can complex with organic materials (Hem, 1972). The significance of zinc complexation with organic matter in Lake Michigan is not known.

Purely on the basis of inorganic chemistry, Hem (1972) suggested that the solubility of the mineral willemite, Zn_2SiO_4, controls the amount of soluble zinc in natural waters. Lake Michigan, however, is a heterogeneous system,

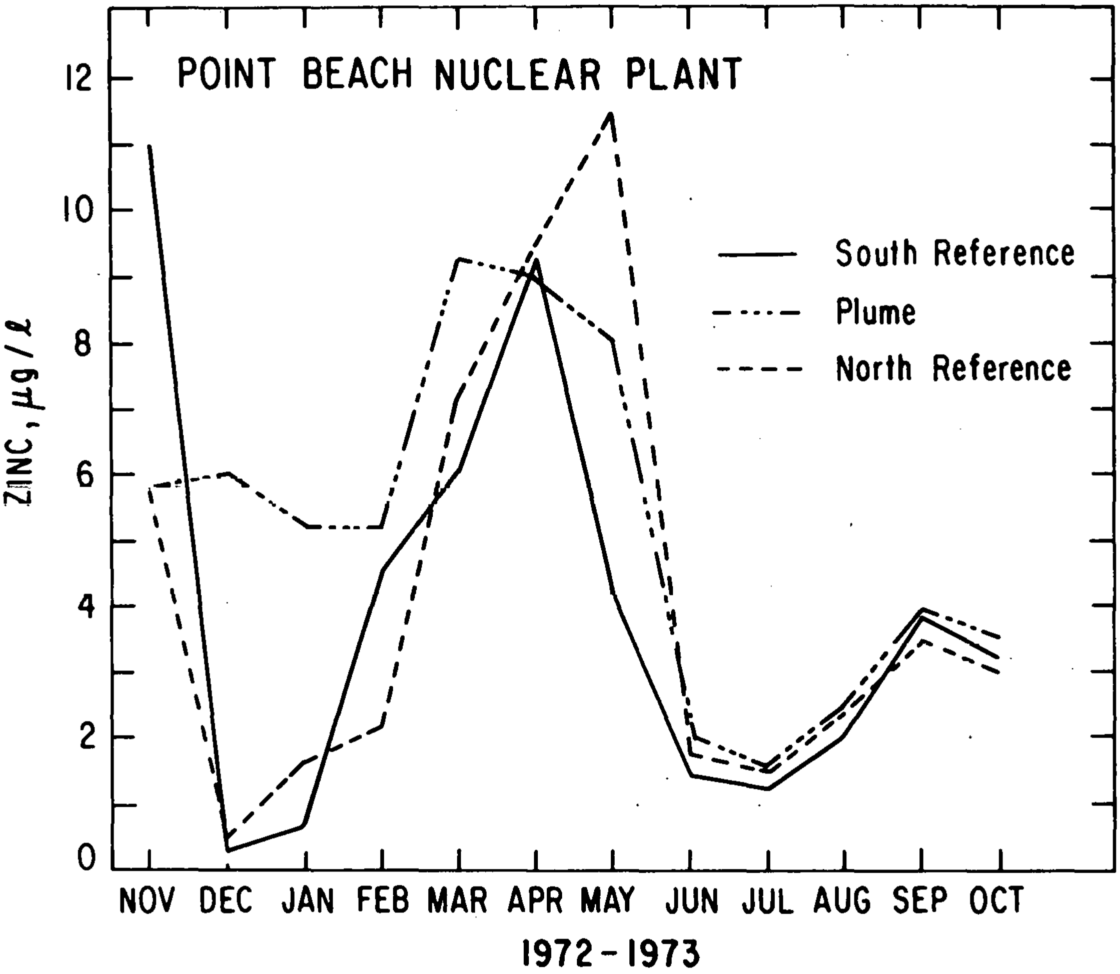


Fig. 107. Average Zinc Concentrations at Point Beach Nuclear Plant near Two Rivers. Modified from Limnetics (1974).

with inorganic and organic constituents as well as dissolved and particulate matter. Since hydrous iron and manganese oxides are well known for their sorptive capacity, Jenne (1968) suggested that they are important in controlling zinc concentrations in natural waters. Jenne also pointed out that organic matter, capable of complexing and/or chelating zinc, can determine the behavior of zinc in highly organic sediments and in sediments where oxidation-reduction or pH conditions allow the partial dissolution of hydrous iron and manganese oxides. Such conditions were observed in several of the cores described by Callender (1969), Leland *et al.* (1973b), and Shimp *et al.* (1970, 1971), notably in the eastern part of the southern basin and in Green Bay.

Zinc concentrations in Lake Michigan sediments have been reported by Edgington *et al.* (1972a), Robbins *et al.* (1972a), Copeland and Ayers (1972), Shimp *et al.* (1970, 1971), Lineback and Gross (1972), Leland *et al.* (1973b), and Robbins and Edgington (1974). In sediment cores taken in Green Bay and the southern basin (no cores were described in the northern basin), the investigators agreed that zinc concentrations are highest at the sediment

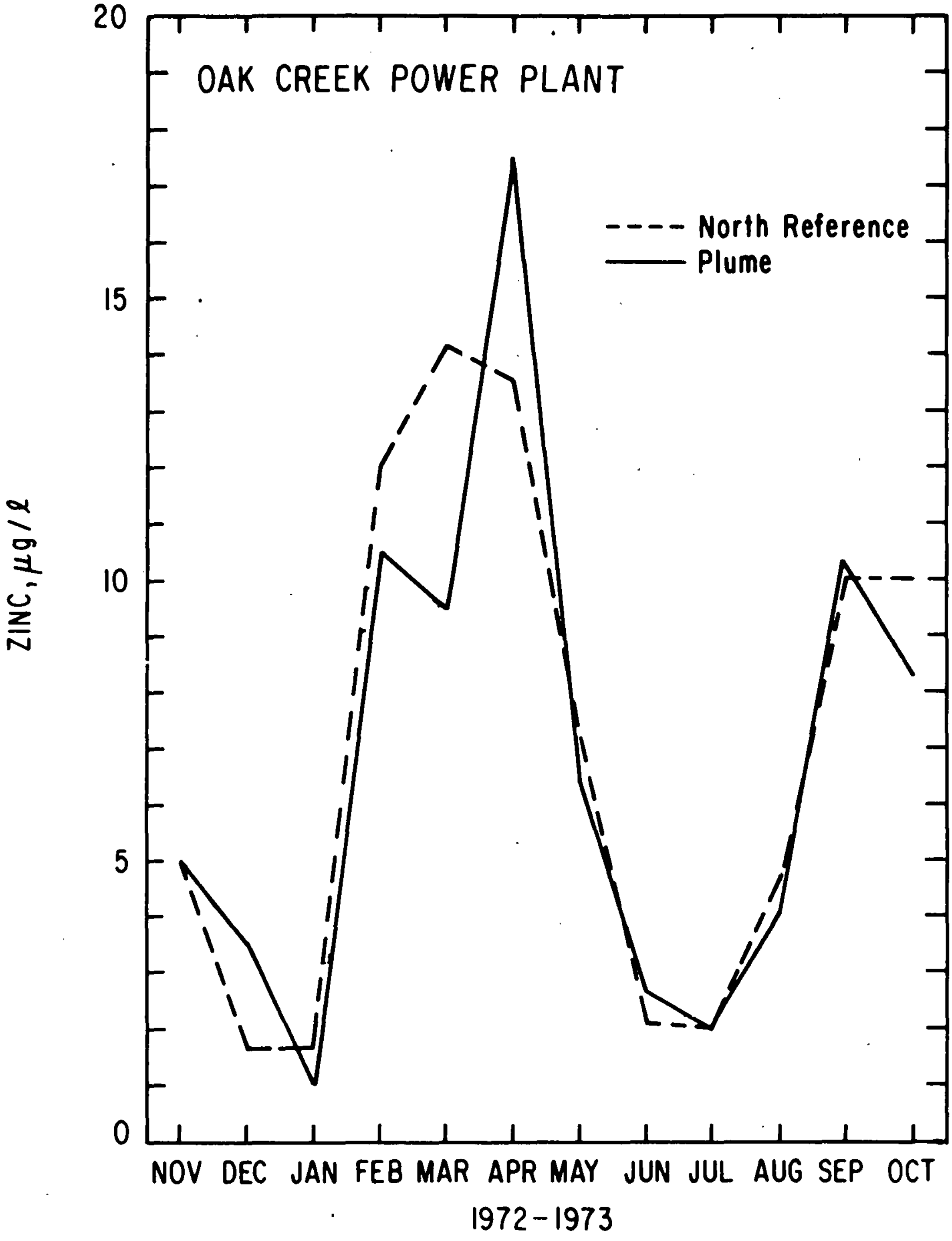
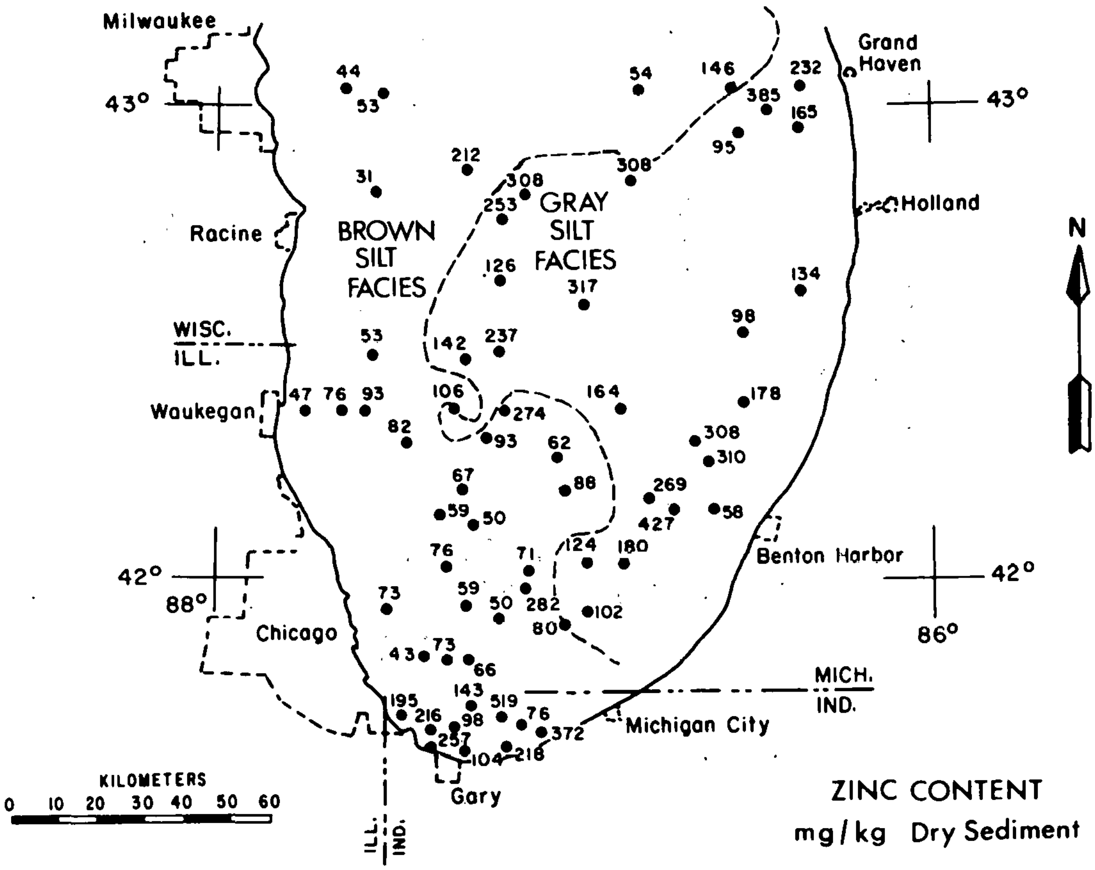


Fig. 108. Average Zinc Concentrations at Oak Creek Power Plant. Modified from Limnetics (1974).

surface and decrease rapidly with depth to a nearly constant level in sediments deposited since the last glaciation. Shimp *et al.* (1971) suggested that elevated zinc concentrations in the surface sediments of the southern basin (Fig. 109) were due at least in part to man's activities in the Basin. Statistical analysis of the relation of zinc to organic carbon content of the sediments revealed a good correlation. The statistical relationships between zinc and the proportion of < 2 μm clay-size particles, and zinc and the Fe_2O_3 and MnO content were poor. Lineback and Gross (1972) analyzed the data of Shimp *et al.* (1971) and computed that zinc in the topmost 2-3 cm averaged 123 mg/kg in the brown silt facies of the Waukegan member, along the western side of the southern basin (*cf.* Fig. 109), while zinc at the surface in the gray silt facies of the Waukegan member averaged 231 mg/kg. This marked difference was attributed to co-deposition of zinc, by sorption, with organic particles and with clay-size particles. Since the gray silt facies contains more clay and more organic carbon than the brown silt facies of the Waukegan member, the gray silt facies has a natural ability to accumulate a higher proportion of zinc. In addition, higher sediment deposition rates along the eastern side of the southern basin (*cf.* Robbins and Edgington, 1975a) afford less time for zinc losses to the water by diffusion and lower the chance for mixing and dilution with older sediments containing less zinc. In all the work done to date on zinc in Lake Michigan sediments, factors controlling the diagenetic behavior of zinc have not been identified.



ZINC CONTENT
mg/kg Dry Sediment

Fig. 109. Zinc Content in the Most Recent Sediments of Southern Lake Michigan. Modified from Leland *et al.* (1973b). Boundary of brown and gray silt facies of the Waukegan member from Lineback and Gross (1972).

OTHER ORGANIC CONSTITUENTS

PETROLEUM AND OTHER HYDROCARBONS

The presence of oil, greases, petroleum, and other hydrocarbons in Lake Michigan water is associated entirely with cultural and industrial sources. Potential contributors to oil pollution are agencies involved in production, transportation, handling, and use of oil, such as ships, oil-loading and unloading points, refineries, dumps, garages, and industries (McKee and Wolf, 1963). Petroleum pollution may be present as floating oils, emulsified oils, or a solution of the water-soluble portion of these oils (National Academy of Sciences ..., 1973).

Harmful effects of oil films include: interference with gas exchange (*cf.* Dissolved Oxygen section); coating bodies of water birds, leading to oil ingestion during preening and/or loss of buoyancy; adherence to gills of fish, which interferes with respiration; coating aquatic plants; fouling beaches with oil; and covering hulls of pleasure craft (National Academy of Sciences ..., 1973). Soluble substances released from floating or emulsified oils may kill fish and benthic organisms, taint the flesh of fish and waterfowl, and produce tastes and odors in drinking water. Oils may also be carried to bottom sediments with solid particles where they can alter benthic communities, destroy spawning areas, and concentrate organochlorine compounds (National Academy of Sciences ..., 1973). These sedimented oils may be released later during agitation (Snow, 1974). The high biochemical oxygen demand of petroleum oils may deoxygenate the water and kill fish and other aquatic organisms (McKee and Wolf, 1963).

The National Academy of Sciences ... (1973) pointed out that about 10% of the total amount of oil entering the marine environment comes from events like oil spills; the other 90% originates from normal operations of ships, oil-carrying tankers, refineries, and waste disposal. A similar estimate has not been made for Lake Michigan, but from the material reviewed below there seems to be little reason to think that accidental oil spills are the major source of oil pollution to the Lake.

Indiana Harbor and Calumet Harbor are sources of oil pollution to the southernmost part of Lake Michigan (Risley and Fuller, 1965; U. S. Dep. Inter., 1968; Snow, 1974). Risley and Fuller (1965) reported that oil and grease averaged 7.5 mg/l (range 0-240 mg/l) in 1962-1963 water samples collected south of a line from Calumet Harbor to Michigan City. Samples collected during the same period between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo averaged 1.5 mg/l (range 1.0-2.2 mg/l). Samples were not collected farther north than these areas.

The U. S. Department of the Interior (1968) collected data in 1962-1963 which showed that oil and grease concentrations in Indiana Harbor were much higher ($\bar{x}$ = 4.4 mg/l; range 0.4-29 mg/l) than in Calumet Harbor ($\bar{x}$ = 1.6 mg/l; range 0.1-3.4 mg/l). Snow (1974) confirmed that oil and grease concentrations continued to be higher in the Indiana Harbor area than in Calumet Harbor during 1965-1971. In Calumet Harbor oil and grease averaged 2.3 mg/l, while at the mouth of the Indiana Harbor Canal the average was 3.5 mg/l.

Snow (1974) reported there are daily oil spills and emissions into the Indiana Harbor Canal. Based on aerial observation, he stated that oil slicks were almost always visible in the Lake coming from the Indiana Harbor Canal, and the slicks were blown for many miles by the wind. These wind-blown oil spills and emissions have been documented at municipal water filtration plants around the southern tip of the Lake. In 1971 a high incidence of oil pollution seemed apparent. That year the following annual averages of oil and grease concentrations were recorded: Chicago South Water Filtration Plant, 4.8 mg/l; Hammond Water Filtration Plant, 5.6 mg/l; East Chicago Water Filtration Plant, 4.9 mg/l; and Gary Water Filtration Plant, 5.3 mg/l. Over the 1965-1971 period, the averages at each of these four plants were the same, 1.7-1.8 mg/l.

Because of the taste- and odor-causing properties of petroleum oils, these substances are an important consideration in preparing water for human consumption. The Chicago South Water Filtration Plant has kept records of the incidence of hydrocarbon odors in their raw water (Vaughn and Reed, 1973). From 1950 through 1971 the average number of days each year when hydrocarbon odors were detectable was 53. Vaughn and Reed (1973) suggested that maximum odors, as measured by threshold odor number, tended to decrease from 1965 to 1971. Maximum dosages of activated carbon, which is added to the water to adsorb odorous compounds, also tended to decrease during this period.

Many of the standards and criteria pertaining to oil and grease in Lake Michigan are expressed in somewhat indefinite terms like "virtually absent" or "no visible oil on the surface." Despite this shortcoming, it is obvious that water in the area encompassing Calumet Harbor and Indiana Harbor usually does not meet the limitations prescribed in Appendix B. Likewise, standards for odors and threshold odor numbers often are not met. It seems probable that other areas in Lake Michigan subject to oil pollution, such as the other major harbors, might also have difficulty meeting these standards and criteria.

Oil concentrations have been measured in sediments from Calumet Harbor and Indiana Harbor, frequently in connection with dredging operations. Four samples collected within Calumet Harbor in August 1968 contained between 3.2 and 6.2 mg oil/g dry sediment (0.3-0.6 weight %) (Illinois Sanitary Water Board, 1969). Sediment samples collected from eleven stations within the Indiana Harbor Canal on 14 June 1967 had an oil and grease content ranging from 3.7 to 17% and averaging 9.2% (Johnson *et al.*, 1968). It is reasonably certain that concentrations of oil and grease as high as these (National Academy of Sciences ..., 1973) contribute to the impoverished benthic fauna in the Indiana Harbor-Calumet Harbor area (*cf.* Howmiller, 1974).

ORGANOCHLORINE COMPOUNDS

Insecticides

Organochlorine insecticides, exemplified by DDT,* DDD,** DDE,† and dieldrin,†† came into use during the 1940's. Since that time, it has become

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**DDT: 1, 1, 1-trichloro-2, 2-bis(p-chlorophenyl)ethane.*

***DDD: 1, 1-dichloro-2, 2-bis(p-chlorophenyl)ethane.*

†DDE: 1, 1-dichloro-2, 2-bis(p-chlorophenyl)ethylene.

††Dieldrin: 1, 2, 3, 4, 10, 10-hexachloro-6, 7-epoxy-1, 4, 4a, 5, 6, 7, 8, 8a-octahydro-1, 4-endo-exo-5, 8-dimethanonaphthalene.

apparent that aquatic organisms react in a delayed and complicated manner to the toxic effects of these products.

At first, concern was expressed only for acute toxicities. By the mid-1950's, accumulating evidence indicated that organochlorine insecticides were causing damage other than by acute effects. Hunt and Bischoff (1960) traced the mortality of grebes (water birds whose main source of food is small aquatic animals including fish) to biological magnification of DDD applied periodically to Clear Lake, California, for the control of gnats. Burdick *et al.* (1964) correlated lake trout hatchery mortalities with the amount of DDT in the eggs. These and other studies demonstrated that insecticides have a widespread impact on natural fish and wildlife populations, attributable to a number of sublethal mechanisms.

At one time, organochlorine insecticides were widely used in the Lake Michigan Basin on forest land and non-croplands and for agricultural, industrial, and household purposes. Kleinert *et al.* (1968) indicated that in Wisconsin, DDT, DDD, and dieldrin were used to control one or more pests on various vegetables, tobacco, and fruits (especially apples and cherries). DDT was once the chemical of choice to control the insect vector of Dutch elm disease, and it is effective against mosquitoes. DDT and dieldrin have been used to control several household pests, and they also have been used during manufacture and drycleaning of woolens to protect against moths. These organochlorine insecticides were subsequently carried to Lake Michigan in runoff from treated lands, industrial discharges, and domestic sewage. Precipitation may also have been an important transport mechanism (Cohen and Pinkerton, 1966; Weibel *et al.*, 1966).

During the 1960's several state and federal governmental agencies developed monitoring programs on Lake Michigan to evaluate the effects of organochlorine insecticides on organisms in the Lake. Descriptions of DDT and dieldrin residues in fish samples comprise the bulk of the data available to date, although there are some data on water concentrations as well.

Three laboratories independently analyzed two samples of Lake water in summer 1968 for organochlorine insecticides (Lake Mich. Enforcement Conf., 1968). Samples collected 8 km (5 mi) west of Ludington and 40 km (25 mi) west of Saugatuck were similar. These concentrations were reported: DDT, 0.002 μg/l; DDD, 0.001 μg/l; DDE, 0.0005 μg/l; and dieldrin, 0.001 μg/l. Subsequently, water samples were analyzed by the Lake Michigan Basin Office of the Environmental Protection Agency (Lake Mich. Enforcement Conf., 1972b). Several conclusions were drawn on the basis of analysis of 21 samples collected from April 1970 to January 1971 at the Chicago Central Filtration Plant raw-water intake:

(*i*) The low levels of organochlorine insecticides in Lake Michigan water challenge the sensitivity of analytical techniques.

(*ii*) The presence of interfering compounds (*e.g.* phthalate esters and polychlorinated biphenyls) probably accounts for interpretations suggesting the presence of lindane, heptachlor, heptachlor epoxide, endrin, aldrin, and methoxychlor.

(*iii*) The concentration of total DDT (DDT plus DDD plus DDE) in southern Lake Michigan water is likely between 0.001 and 0.010 μg/l.

The Interstate Pesticides Committee (Lake Mich. Enforcement Conf., 1972b) concluded that there was a high statistical probability that total DDT concentrations at the Chicago Central Filtration Plant intake exceeded those in open Lake Michigan waters, although absolute values were possibly in error. Unusual variability in DDT concentrations in samples from six municipal water intakes in Wisconsin was attributed to wave action and currents in the inshore area. Total DDT concentrations in samples from 14 Michigan water intakes likewise were quite variable. Insufficient data were available to detect variations in organochlorine insecticide concentrations in water with season or depth. In an attempt to rationalize observed aqueous concentrations of organochlorine insecticides, the Committee conjectured that, although there has been fairly heavy use of the compounds in the Basin over the years, relatively little has reached the Lake; within the Lake, precipitation and/or degradation processes have been comparatively inefficient. The Committee did not present data to support these speculations.

Data reported by Schacht (1974) and the Lake Michigan Enforcement Conference (1972b) indicate that dieldrin concentrations in water are likely below 0.001 μg/l. Information on seasonal and geographic variations is not available.

Organochlorine insecticides are usually studied within various trophic levels, rather than in water, because complex relationships allow biological magnification to occur in a food chain. This approach permits better quantification, since analysis of aqueous concentrations introduces great analytical uncertainty.

One approach uses sessile organisms like mussels as monitors of stream inputs of organochlorine insecticides (Lake Mich. Enforcement Conf., 1972b). Mussels are not so easily used in open water, for they integrate chemical concentrations at one point only. In open water, fish are the best indicators of overall organochlorine insecticide concentrations because they move through widely distributed volumes of water. Even fish analyses are not simple procedures, for a number of independent variables may influence organochlorine insecticide concentrations, such as species, size and age of fish, location and season of year at which the fish is taken, differences in diet among different species, and portion of fish analyzed (whole body, fat, liver, other).

Data of Reinert and Bergman (1974) demonstrate the influences of fish size and sampling location on measured insecticide concentrations. Within each size class, total DDT concentrations in lake trout collected south of a line between Kewaunee and Ludington were higher than north of the line. Within either region, total DDT content increased with fish size; in both northern and southern regions lake trout longer than 40.5 cm (16 in.) had total DDT concentrations greater than 5 mg/kg, the tolerance level for DDT in human food established by the Food and Drug Administration (FDA). Coho salmon collected in late summer and fall of their second growing season in the Lake also contained DDT concentrations above the FDA tolerance level. These accumulations are related to the consumption of DDT-contaminated food (Reinert and Bergman, 1974; Reinert *et al.*, 1974), *e.g.* alewives typically contain 1-4 mg/kg total DDT (Reinert, 1970).

Veith (1973) analyzed 16 species of fish for DDT and DDT analogues. The fish were collected throughout Lake Michigan in 1971. DDT concentrations in alewives seemed to show no geographic variation, ranging from a low of 1.6 mg/kg near Waukegan to 5 mg/kg near the Manitou Islands. Carp and brown trout captured near Michigan City had higher total DDT levels than fish of the same species collected farther north. There seemed to be no geographic trend in DDT content in either chubs or coho salmon, although spring coho (1.6 mg/kg total DDT) contained 2.0-2.5 times less DDT than autumn coho. Large trout and salmon generally exceeded the FDA tolerance level of 5 mg/kg total DDT. Perch, smelt, whitefish, and suckers had less than 5 mg/kg total DDT.

To avoid the variations in organochlorine concentrations caused by differences in species, size and age of fish, diet, and location and season at which a fish is captured, the Great Lakes Fishery Laboratory (Bureau of Sport Fisheries and Wildlife, U. S. Department of the Interior, Ann Arbor, Michigan) instituted a sampling program that was confined to a single species, using fish within narrow size limits, collected from a particular area of the Lake at approximately the same time each year (Willford *et al.*, 1973--unpublished). Bloater chubs, 24.0-28.0 cm (9.4-11.0 in.) in length, captured near Saugatuck in the fall, were used for this program. In both 1969 and 1970, total DDT concentrations in bloaters averaged 9.9 mg/kg. Imposition of legal restrictions on DDT usage in the Lake Michigan Basin during 1969-1970 appeared to produce an almost immediate reduction in DDT levels. In 1971 total DDT averaged 6.2 mg/kg; and in 1972, 4.3 mg/kg. These declines were statistically significant at the 99% confidence level. Reinert (1974--personal communication) found that chubs analyzed in 1973 contained perhaps 3 mg/kg, and he suggested that DDT levels were also decreasing in Lake Michigan lake trout and coho salmon.

Analyses of fish collected in Lake Michigan generally have shown dieldrin concentrations less than 0.3 mg/kg (Willford *et al.*, 1973--unpublished; Lake Mich. Enforcement Conf., 1972b), the FDA tolerance level for dieldrin in human food.

Limits on DDT content in drinking water suggested by the National Academy of Sciences ... (1973) and the Michigan Water Resources Commission (1973) were 50 μg/l and 42 μg/l, respectively, and are at least three orders of magnitude higher than the typical concentration in Lake Michigan of < 0.01 μg/l (Reinert *et al.*, 1974). The National Academy of Sciences ... (1973) indicated that DDT concentrations below 0.002 μg/l should provide adequate protection for aquatic life (Appendix B, part 2). To protect higher trophic levels, total DDT concentrations on a wet-weight basis should not exceed 1 mg/kg in any aquatic plants or animals.

The National Academy of Sciences ... (1973) recommended limiting dieldrin in drinking water to less than 1 μg/l (Appendix B, part 1); the state of Michigan limit (Michigan Water Resources Commission, 1973) is higher (17 μg/l). Aquatic organisms, which are much more sensitive to organochlorine compounds than mammals, should be protected if dieldrin is present at less than 0.005 μg/l (Appendix B, part 2).

Leland *et al.* (1973a) conducted a survey of organochlorine insecticides in the sediments of southern Lake Michigan. They found that surficial (0-2 cm) sediment concentrations of total DDT were significantly related (r = 0.60) to the organic content of the sediments, as were dieldrin accumulations (r = 0.66). Organochlorine insecticides were more concentrated in the eastern part of the southern basin in the gray silt facies of the Waukegan member (Lineback and Gross, 1972) than in the brown silt facies; Leland *et al.* (1973a) attributed this observation to the higher organic matter content in the gray silt facies. Concentrations of DDT degradation products (DDD and DDE) were not so high as concentrations of DDT. In reducing sediments such as the gray silt facies along the eastern shore (Leland *et al.*, 1973b), DDD was the principal DDT degradation product found (Leland *et al.*, 1973a); DDD is formed by reductive dechlorination of DDT. In the more oxidizing sediments along the western shore and in the deepest regions of the southern basin, concentrations of DDE generally exceeded DDD; DDE is formed by dehydrochlorination of DDT under aerobic conditions.

The highest concentrations of total DDT and dieldrin were found in the central, or deepest, parts of the southern basin (as much as 175 μg/kg dry sediment and 10.4 μg/kg dry sediment, respectively). Leland *et al.* (1973a) assumed these compounds were transported to these deep areas in association with small finely divided particles by a natural sediment grading process.

Concentrations of all organochlorine insecticides decreased with increasing sediment depth to 12 cm (Leland *et al.*, 1973a). For example, the median concentration of total DDT in surface sediments was 18.5 μg/kg dry sediment; at 2-6 cm the median value was 6.3 μg/kg dry sediment; and at 6-12 cm the median was 3.4 μg/kg dry sediment. Comparable values for dieldrin were 2.0 μg/kg dry sediment, < 0.5 μg/kg dry sediment, and < 0.5 μg/kg dry sediment. These decreases were related to chemical degradation processes within the sediments and to recent human influences on the Lake.

Schacht (1974) analyzed 24 sediment samples, collected from Waukegan south to Chicago's Jackson Park, for total DDT and dieldrin content. Values were similar to those of Leland *et al.* (1973a). Five samples, collected near sewage treatment plant outfalls from Waukegan to Highland Park, averaged 2.8 μg/kg dry sediment of total DDT and 0.09 μg/kg dry sediment of dieldrin (Schacht, 1974). The other 19 stations, each less than 4.8 km (3 mi) from shore, averaged 7.8 μg/kg dry sediment of total DDT and 0.34 μg/kg dry sediment of dieldrin. Dividing these 19 samples into two groups, organochlorine insecticide concentrations were much lower at the 11 stations between Waukegan and Evanston (2.9 μg/kg dry sediment of total DDT, 0.10 μg/kg dry sediment of dieldrin) than the eight stations between Loyola University and Jackson Park (14.4 μg/kg dry sediment of total DDT, 0.78 μg/kg dry sediment of dieldrin).

Organochlorine insecticide concentration data from sediments outside the southern basin are not readily available. The Lake Michigan Enforcement Conference (1972b) reported that total DDT concentrations were high (0.1-1.0 mg/l) in sediments of the following tributaries to Lake Michigan: East River (Green Bay), Ahnapee River, Sheboygan River, Pike River (Wisconsin), Trail Creek (Indiana), and the Manistique River. Dieldrin concentrations were ≤ 0.005 mg/l in sediments of 58 of the tributaries sampled; in the other two, the Milwaukee and the Menomonee Rivers, dieldrin was 0.040 mg/l. The high value on the Milwaukee River may be related to dieldrin discharges by a wool processing plant near Grafton, Wisconsin (Lake Mich. Enforcement Conf., 1972b).

Polychlorinated Biphenyls

Within the past few years polychlorinated biphenyls (PCB's) have been identified in samples collected throughout the environment, particularly in organisms living in natural waters that receive waste effluents from urban centers. This toxic group of compounds has had widespread commercial use in several hundred products since the 1920's. PCB's have been used in plastics, wrapping paper (*e.g.* food packaging materials), carbon paper, printing inks, paints, resins, tires, hydraulic fluids, insulating fluids (closed-system heat exchangers), and dielectric fluids (capacitors) (Ahmed and Focht, 1973; National Academy of Sciences ..., 1973). At present, the only sources of PCB's to the Lake supposedly are leaks from closed-system transformers and capacitors (Veith, 1973).

Many of the problems of analysis for organochlorine insecticides are similar to those of PCB's. Aqueous concentrations are so low that available analytical techniques cannot measure them without prior concentration. Veith and Lee (1971) found PCB concentrations in Lake Michigan water were below the detection limit of 0.01 μg/l. Later, Veith (1973) estimated that PCB concentrations were less than 0.01 μg/l in the open water of the Lake and less than 0.10 μg/l in near-shore waters.

PCB concentrations in 26 water samples collected 0.8 km (0.5 mi) from shore were reported by the Lake Michigan Enforcement Conference (1972b). Two determinations were "off scale" and 16 were < 0.01 μg/l. High values were reported offshore from the Ahnapee River (0.051 μg/l), the East Twin River (0.020 μg/l), the Menominee River (0.015 μg/l), Oak Creek (0.027 μg/l), the Calumet River at Calumet City (0.056 μg/l), the Galien River (0.015 μg/l), the Paw Paw River (0.028 μg/l), and the Pentwater River (0.012 μg/l).

Biological magnification is also observed with PCB's. Indirect evidence suggests that a buildup of organochlorine compounds may be a threat to the future use or life of the biological resources of Lake Michigan (Veith, 1973). Johansson *et al.* (1970, cited by Veith, 1973) showed that 15 mg/kg of PCB's (lipid basis) in salmon eggs produced 50% mortality; eggs containing ≥ 25 mg/kg of PCB's (lipid basis) had 100% mortality. Such levels in eggs would be associated with concentrations in general body tissue, such as muscle, of 2.5 to 5.0 mg/kg. The FDA has established an interim tolerance value of 5 mg/kg of PCB's in food for human consumption.

Although continued stocking of certain fish from uncontaminated sources may avoid the problem of reproductive failure due to PCB accumulation in fish eggs, stocking does not settle the problem of PCB accumulation in growing fish. Numerous catches of fish from Lake Michigan, already in commercial channels, have been seized and withdrawn from human use because PCB residues exceeded the FDA interim tolerance level of 5 mg/kg (Veith, 1973).

Veith and Lee (1971) and Veith (1973) have analyzed Lake Michigan fish for the presence of PCB's. They have quantified these compounds by comparing each gas chromatogram to the most similar Arochlor mixture(s) and comparing the area under the chromatogram to an area-standard curve. Arochlor is the trade name given by Monsanto Company, the sole producer of PCB's in the United States, to its polychlorinated biphenyl mixtures. The last two digits of an

Arochlor mixture indicate percent chlorine, *e.g.* Arochlor 1254 contains 54% chlorine. For the most part, Arochlor 1254 was the PCB mixture most nearly resembling the PCB's isolated from Lake Michigan fish. In near-shore areas, fish were more likely to contain PCB's with less chlorine due to runoff from the watershed (Veith, 1973).

Veith (1973) analyzed about 800 Lake Michigan fish (13 species) collected in 1971 for PCB mixtures resembling Arochlor 1254. Mean concentrations ranged from 2.1 mg/kg (range 0.7-3.2 mg/kg; n = 35) in smelt to 15 mg/kg (range 9.9-24 mg/kg; n = 21) in chinook salmon. The larger species such as trout (brown, lake and rainbow) and salmon (coho and chinook) contained PCB's at concentrations two to three times higher than the 5 mg/kg tolerance level established by the FDA. Mean PCB concentrations in suckers, smelt, and whitefish were less than 5 mg/kg; and mean concentrations in alewife, carp, chub, and perch were about 5 mg/kg. As expected, greater concentrations of PCB's were found in the larger fish with greater percentages of fat.

The range of concentrations found within single species of Lake Michigan fish generally exceeded 100% (Veith, 1973). Although some of the variation in concentrations is attributable to analytical variability, a range of 100% indicates other factors are present which limit the usefulness of the mean concentrations presented. For example, Reinert (1970) found that observed tissue concentrations of organochlorine insecticides may be affected by lipid content, size of fish, season of capture, and aqueous organochlorine insecticide concentrations. These factors also likely influence PCB concentrations in fish.

Regional variations of PCB concentrations in Lake Michigan fish were suggested as another possible cause for the wide range of PCB concentrations in a single species (Veith, 1973). PCB concentrations generally were higher in alewives, brown trout, carp, lake trout, and whitefish from the southern basin than from the northern basin. Significant regional differences were less apparent in other species, often because insufficient samples were available.

Regional trends in PCB concentrations were more pronounced in an analysis of bottom fauna (Veith, 1973). In spring 1972, PCB content was 0.06 mg/kg wet weight in the amphipod *Pontoporeia* collected in 30.5 m (100 ft) of water near Sturgeon Bay, compared with 0.45 mg/kg wet weight in *Pontoporeia* collected offshore from Waukegan in 30.5 m of water. PCB concentrations in benthic fauna decreased with distance from shore; for example, PCB concentrations in *Pontoporeia* collected off Waukegan decreased from 0.89 mg/kg (8.2 m, or 27 ft) to 0.45 mg/kg (30.5 m, or 100 ft) to 0.34 mg/kg (45.7 m, or 150 ft).

PCB accumulations in fish may affect other animals which use Lake Michigan fish as a food source. Lake Michigan coho salmon containing PCB residues greater than 10 mg/kg caused reproductive failure in mink to which the fish were fed (Ringer *et al.*, 1972--unpublished). Veith (1973) summarized data from a number of sources that implicate a coincidence of high levels of organochlorine compounds with reproductive failure and subsequent population declines in fish-eating bird populations, such as herring gulls, bald eagles, and double-crested cormorants, in the Lake Michigan region.

To protect aquatic life, the National Academy of Sciences ... (1973) recommended that total PCB concentrations in unfiltered water should not exceed 0.002 μg/l at any time or place (Appendix B, part 2), and residues in general body tissues of any aquatic organisms should not exceed 0.5 mg/kg. Furthermore, the Academy recommended that PCB concentrations in birds and mammals dependent on fresh water should not be permitted to increase. Limitations on PCB's in drinking water were also discussed, but no concrete recommendation was made (Appendix B, part 1).

Schacht (1974) has reported sediment concentrations of PCB's in samples collected in the vicinity of five sewage treatment plant outfalls between Waukegan and Highland Park and in 19 lake bed samples collected from the northside of Waukegan south to the Jackson Park area of Chicago. Arochlor 1242 averaged 0.038 mg/kg dry sediment (range 0.010-0.106 mg/kg) in the five samples collected near sewage treatment plants; in these same samples Arochlor 1254 averaged 0.014 mg/kg dry sediment (range 0.007-0.027 mg/kg). The 19 lake bed stations averaged 0.019 mg/kg dry sediment (range N.D.-0.083 mg/kg) of Arochlor 1242 and 0.015 mg/kg dry sediment (range 0.002-0.046 mg/kg) of Arochlor 1254. Arochlor concentrations in lake bed sediments were notably higher near the Waukegan River and between Montrose Harbor and Navy Pier in Chicago.

There seem to be no readily available data on PCB content in Lake Michigan sediments outside the Chicago area. The Lake Michigan Enforcement Conference (1972b) estimated PCB concentrations in sediment samples collected in July 1969 from 40 tributaries to the Lake. Most concentrations were less than 0.1 mg/l. High values were recorded in the Calumet River at Calumet City (1.25 mg/l), the Menominee River (4.4 mg/l), the Milwaukee River (3.2 mg/l), the Sheboygan River (7.2 mg/l), the Ahnapee River (1.1 mg/l), and the Escanaba River (1.5 mg/l).

PHENOLS

Concentrations of phenol and phenolic compounds that are too low to affect fish physiology adversely may cause off-flavors in fish. The National Academy of Sciences ... (1973) compiled data which showed that pure phenol affects the taste of fish held in water containing 1,000 to 10,000 μg phenol/l. At 10-60 μg/l, 4-chlorophenol affects taste, and 2,4-dichlorophenol is noticeable at 1-5 μg/l. The Academy noted, "The taste of fish in most polluted situations is adversely affected by phenolics before acute toxic effects are observed."

People will probably reject drinking water supplies which smell or taste of phenols. Pure phenol has a threshold odor concentration of 4200 μg/l (Rosen *et al.*, 1962). A greater problem develops when phenol-containing water is chlorinated, because threshold odor concentrations for chlorinated phenols are lower than for pure phenol (*e.g.* 4-chlorophenol can be sensed at 250 μg/l) (Burttschell *et al.*, 1959).

Phenols in natural waters result largely from cultural activities. Domestic and animal wastes contain phenolic compounds (National Academy of Sciences ..., 1973). Wastes from petroleum, coke, and chemical industries are sources of phenolic compounds to aquatic systems.

As indicators of cultural activities, phenols may be expected to occur more frequently in inshore waters of Lake Michigan than offshore. This assumption may explain why the U. S. Department of the Interior (1968) did not sample offshore stations for phenols. In 1033 inshore samples, phenols averaged 2 μg/l. Within areas of restricted circulation, concentrations were sometimes higher. During 26 June-17 July 1963, phenol concentrations as high as 40 μg/l were detected in southern Green Bay within 16 km (10 mi) of where the Fox River enters. Near the mouth of the Milwaukee River concentrations from 5 to 8 μg phenol/l were found. Concentrations were near 3-4 μg/l throughout most of the Milwaukee Harbor, but outside the breakwater phenols were quickly diluted below the detection limit (1 μg/l).

Adjacent to Indiana Harbor, phenol concentrations averaged 3.1 μg/l in 1962-1963 (Risley and Fuller, 1966). Samples collected within Indiana Harbor averaged 33 μg phenol/l, and 12 samples collected in the Indiana Harbor Canal during the same period averaged 159 μg/l (U. S. Dep. Inter., 1968). Phenol concentrations were lowest in summer and highest in fall in Indiana Harbor; no samples were collected in winter. With restricted water movement during winter, phenol concentrations may reach high levels near shore, because phenols degrade less readily at lower temperatures.

Phenol determinations on 16 samples collected in Indiana Harbor in 1965 averaged 15 μg/l, less than half the 33 μg/l average for 1962-1963 (Risley and Fuller, 1966). This decrease was attributed to the season and water temperature when samples were collected, rather than to any improvement in water quality.

High levels of phenols found near Calumet and Indiana Harbors were due to waste discharges in that heavily industralized area (Risley and Fuller, 1965). High concentrations of phenols affected the quality of water withdrawn from this area for municipal water supplies, *e.g.* at Chicago's South Water Filtration Plant (Vaughn and Reed, 1973). During 1965-1970, 20% of the samples collected at that plant had phenol concentrations exceeding 3 μg/l, the single-value limit for Illinois at that time. In 1971, only 11% of the samples exceeded the single-value limit. Vaughn and Reed (1973) considered this decrease an encouraging sign of improving water quality.

Vaughn and Reed (1973) did not speculate why the frequency with which the phenol standard was exceeded decreased between 1971 and 1965-1970. Snow (1974) stated there has been a marked reduction in the amounts of phenols emitted from the Indiana Harbor Canal in the past ten years. There were still periodic releases of phenols that created taste and odor problems in the operation of Chicago, Hammond, East Chicago, and Gary water filtration plants, but Snow suggested that the average phenol concentrations were reduced enough that they were not a significant problem.

Industrial Bio-Test (1972a) collected inshore samples from Kenosha to North Chicago and analyzed them for phenols. From January 1970 to April 1971, phenol concentrations were less than 1 μg/l in 93% of the 232 samples analyzed. Only three of these 232 determinations were as high as 3 μg/l. Only samples collected in autumn (September to early December) had detectable phenols. Samples taken at three stations 9.6 km (6 mi) offshore from Zion, Illinois, from February 1970 to April 1971 (Industrial Bio-Test, 1972b), had less than the detection limit (1 μg phenol/l) in 88% of the samples. Like samples collected closer to shore, most of the samples in which phenols were detected were collected in autumn. The highest concentration was 12 μg/l on 11 November 1970. Since a duplicate determination yielded a phenol concentration of 1 μg/l, it is possible that the sample was contaminated or there was a typographical error.

Except in the Indiana Harbor Canal, phenol concentrations exceeding 100 μg/l have not been recorded in Lake Michigan; this concentration was recommended as an upper limit by the National Academy of Sciences ... (1973) to protect aquatic life from toxic effects of phenolic compounds. Most of the recorded phenol concentrations exceeding 1 μg/l in Lake Michigan have been in samples collected in harbors or near the mouths of polluted rivers. Otherwise, phenol concentrations in Lake Michigan are not likely to cause taste-and-odor problems in drinking water or to taint fish flesh (Appendix B).

CYANIDES

Hydrocyanic acid, HCN, is more toxic than the cyanide ion, CN^- (McKee and Wolf, 1963). At pH values of 8 or less, HCN is largely undissociated; thus, toxicity varies with pH. Temperature and dissolved oxygen concentrations also affect toxicity. Many sensitive fish are killed by free cyanide (CN^- plus HCN) concentrations of 0.01-0.05 mg cyanide/l, and most species die above 0.2 mg/l (National Academy of Sciences ..., 1973). McKee and Wolf (1963) stated that lower organisms are less sensitive to cyanide than fish. Doudoroff *et al.* (1966) demonstrated that the component toxic to fish in most solutions of complex metallocyanides (such as those resulting from metal cleaning and electroplating processes) is HCN; the complex ions are relatively harmless.

Cyanide sources to Lake Michigan have been associated with waste effluents from gas works and coke ovens, gas scrubbing at steel plants, metal cleaning and electroplating processes, and chemical industries (McKee and Wolf, 1963; Snow, 1974).

Cyanides are seldom detected in Lake Michigan except in polluted harbors or near the vicinity of harbor mouths. Snow (1974) indicated that the cyanide level in the Indiana Harbor Canal is harmful to aquatic life, but it is rapidly oxidized and diluted in the Lake. Samples collected from December 1965 through January 1970 in Indiana Harbor at the east breakwall inner light had cyanide concentrations ranging from 0 to 0.79 mg/l. Average annual values were $\leq$ 0.15 mg/l. Sixteen samples collected in Indiana Harbor in 1965 had an average cyanide concentration of 0.03 mg/l (Risley and Fuller, 1966). In a parallel study, cyanide content in Calumet Harbor averaged 0 mg/l (range 0-0.01 mg/l) in 1965.

Aside from harbors, cyanides present no apparent problem. Cyanide concentrations did not exceed 0.025 mg/l in any of the samples collected during 1965-1971 at Chicago's South Water Filtration Plant (Vaughn and Reed, 1973). All but three samples collected in this period were less than 0.010 mg/l. These three were only about 1.5% of the total number of samples tested.

At greater distances from harbors cyanide is uniformly undetectable. Cyanides were not present in measurable quantities at any of 12 water filtration plants from Waukegan to Chicago's South Water Filtration Plant in 1968 (Illinois Sanitary Water Board, 1969) or at five selected water treatment plants in 1969 (Illinois Sanitary Water Board, 1970). Industrial Bio-Test (1972a, 1972b) did not find any positive indication of the presence of cyanide at a level of ≥ 0.005 mg/l in 568 samples. These samples were collected at the Kenosha water treatment plant intake, the Waukegan Generating Station intake canal, the North Chicago water treatment plant intake, and three stations 9.6 km (6 mi) east of Zion, Illinois.

Cyanide concentrations in Indiana Harbor and the Indiana Harbor Canal (Snow, 1974; Risley and Fuller, 1966) have on occasion exceeded limits set for drinking water and for the protection of aquatic life (Appendix B).

BAY AREAS, INSHORE-OFFSHORE DIFFERENCES, AND LONGITUDINAL DIFFERENCES

GREEN BAY

Water Movement

Green Bay forms a relatively isolated portion of Lake Michigan (Fig. 110). Including Big and Little Bays de Noc, Green Bay has a surface area of 4212 km^2, a volume of 70 km^3, and a mean depth of 17 m (Fee--personal communication, cited by Ahrnsbrak and Ragotzkie, 1970). Tributaries to Green Bay (Table 79) are polluted to various degrees; however, the Fox River (the largest tributary to Green Bay) constitutes the major source of domestic and industrial wastes.

Table 79. Tributaries to Green Bay

River	*Flow, liters/sec*	*Reference*
Fox	117,245	USDOI, 1967
Big Suamico	1,157	Knowles *et al.*, 1964
Little Suamico	--	
Pensaukee	--	
Oconto	16,114	USDOI, 1967
Peshtigo	23,562	USDOI, 1967
Menominee	87,735	USDOI, 1967
Big Cedar	--	
Ford	9,176	USDOI, 1967
Escanaba	25,346	USDOI, 1967
Whitefish	6,429	USDOI, 1968
Rapid	2,266	USDOI, 1968
Sturgeon	--	
Total average guaged flow	287,929	

USDOI = U. S. Department of the Interior.

The pattern of water movement through the Bay is primarily determined by seiches acting on wind-driven circulation patterns; advective processes are much less important (Ahrnsbrak and Ragotzkie, 1970). Transport and flushing rates in the southern end of the Bay depend on the volume of Fox River discharge, while in the northern end rates are determined by the magnitude of inflowing lake currents (Modlin and Beeton, 1970).

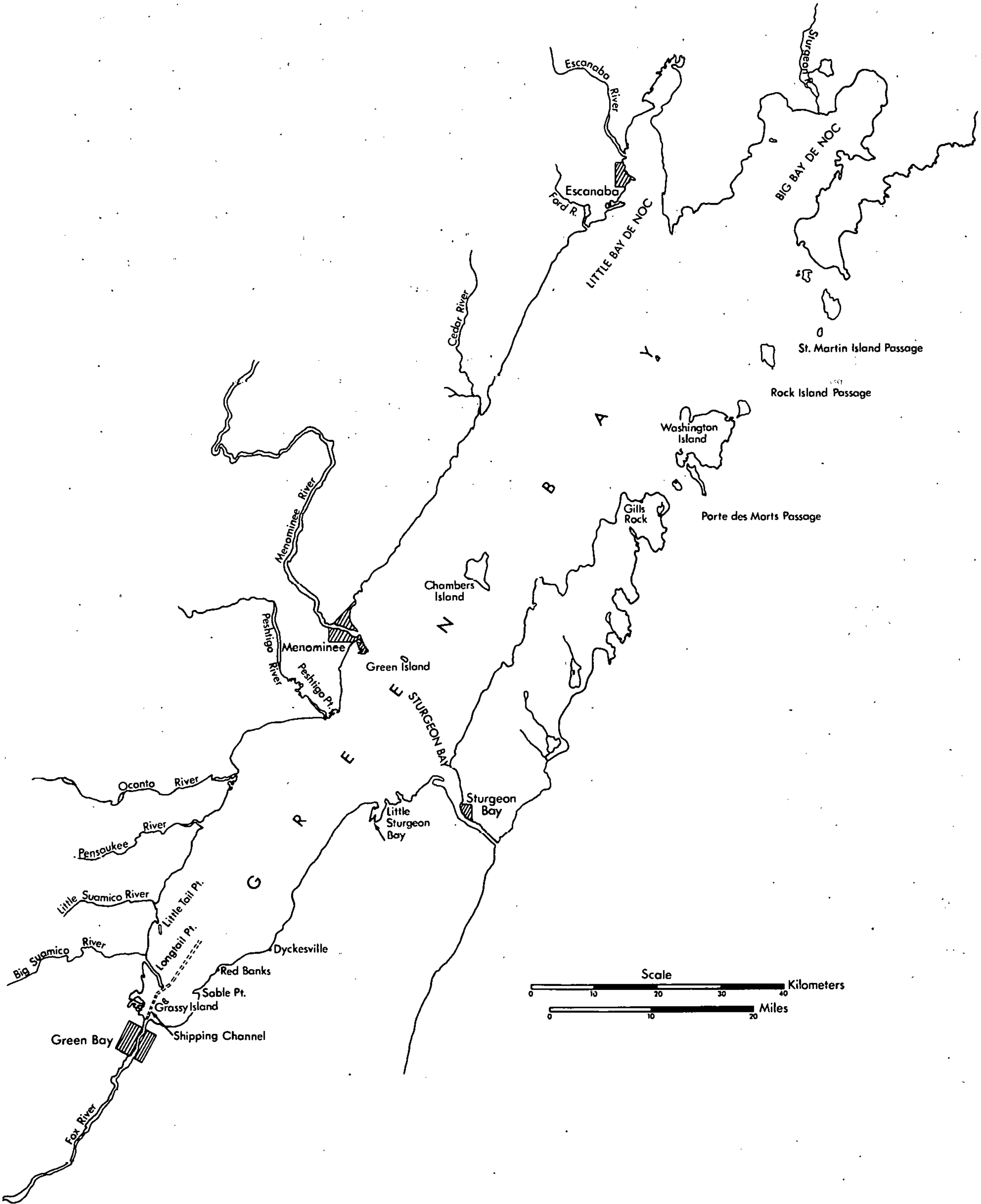


Fig. 110. Green Bay.

South of Long Tail Point, Fox River water constitutes 50-80% of the total water volume present (Ahrnsbrak and Ragotzkie, 1970). Under southerly winds, a plume of Fox River water can be traced 15-20 km northward along the east side of the Bay. In the summers of 1968 and 1969 Modlin and Beeton (1970) found that the Fox River plume remained along the eastern shore of the Bay, but wind directions were not specified. With northerly winds, Ahrnsbrak and Ragotzkie (1970) did not find a distinct plume of Fox River water.

North of Long Tail Point, the proportion of Fox River water decreases rapidly. More than 25 km north of the mouth of the river, values exceeding 25% of the total volume attributable to the Fox are seldom observed (Ahrnsbrak and Ragotzkie, 1970). Still farther north, the chemical effects of the Fox River are considerably reduced.

Current data in Big Rock Passage [Rock Island Passage ?] demonstrate a consistent reversal of flow every 12 hours due to seiche and tidal activity in the Bay and Lake (U. S. Dep. Inter., 1966b). Although the current reverses every 12 hours, the upper 18 m (60 ft) show a net outflow and the lower depths show a net inflow into the Bay. The net outflow is far greater than the inflow. This large volume of inflow water from Lake Michigan modifies the water quality of the Bay.

Temperature

In summer, Green Bay becomes thermally stratified weeks before the adjacent water of Lake Michigan (U. S. Dep. Inter., 1966b). Stratification in the Bay is separate from the main portion of the Lake.

Thermal stratification observed in Green Bay during summer apparently depends on the sampling site and date, and perhaps the investigator's skill as well. For example, Schraufnagel *et al.* (1968) reported no stratification 16 km (10 mi) north of the mouth of the Fox River in (August) 1966. At 24 and 41 km (15 and 25 mi) north of the Fox inlet the surface temperature at two stations was 21.1°C, while at the bottom the temperature was 12.8°C.

In mid-June 1962 the U. S. Department of the Interior (1966b) found sparse evidence of stratification at two stations about 28 km (17 mi) north of the mouth of the Fox River. Near a line from Sturgeon Bay to the mouth of the Menominee River, only partial stratification was evident, whereas stratification was obvious during mid-June at Big Rock Passage [Rock Island Passage ?].

In a longitudinal thermal profile on 16 July 1969 (Ahrnsbrak, 1971), evidences of stratification were noted within 25 km (15 mi) of the mouth of the Fox River. Two weeks later, in another longitudinal profile, no distinct thermocline was evident to a distance of 55 km (34 mi) from the mouth of the Fox River. In a transverse profile on 21 August, at a distance of 27 km (17 mi) from the mouth of the Fox River, surface temperatures exceeded 22°C while bottom temperatures were less than 16°C.

Unlike the major portion of Lake Michigan, Green Bay freezes each winter (Schraufnagel *et al.*, 1968). Ice cover of the Bay inhibits gas transfer and aggravates pollution problems in the Bay. Ice cover lasts from late December or early January into March or early April.

Ahrnsbrak (1971) observed a slight inverse thermocline under the ice in southern Green Bay in mid-February 1970. In the area between Long Tail Point and Sable Point surface temperatures were 0.2°C or less. Warmer, more dense water underlay the colder surface water, with the warmest water concentrated on the western side of the channel. Warmer water on the west side of the channel was also noted in a transect between Little Long Tail Point and Red Banks. In a third transect, between the mouth of the Little Suamico River and Dyckesville, warmer denser water was again located along the western shore, although the temperature contours were spread over nearly the entire channel instead of being focused on a small area. At a distance of 20 km (12 mi) the warmer water had shifted to the east side of the channel. These data indicate that colder less dense water from the Fox River enters Green Bay in winter and moves eastward, while warmer Lake Michigan water enters the northern part of the Bay and sinks as it flows southward along the western shore.

Specific Conductance

Evidence for the direction of current flows in Green Bay has been obtained from a nominally conservative property, specific conductance (*e.g.* Ahrnsbrak and Ragotzkie, 1970; Modlin and Beeton, 1970; Sager, 1971; Jayne and Lee, 1972--unpublished; Rousar and Beeton, 1973). The conductance values for tributaries to the Bay (Table 80) indicate the relative effect of river water on the Bay.

Near the mouth of the Fox, higher conductance is frequently noticed along the east shore of Green Bay than the west (Modlin and Beeton, 1970; Ahrnsbrak and Ragotzkie, 1970). The values along the east shore do not reflect the contribution of the Lake water, which is roughly 260-270 µmhos/cm at 25°C. Conductance values along the western shore (260-280 µmhos/cm) from the Cedar River to the Pensaukee River resemble those of the Lake rather than the conductance of the influent rivers (Table 80). These conductance values show that they are diluted by the Lake.

Table 80. Specific Conductance of Tributaries to Green Bay

	*Specific Conductance, µmhos/cm**		
River	*6 February 1971*	*July 1968*	*1954-55, 1960-61*
Fox	446	382	
Big Suamico		456	
Little Suamico		471	
Pensaukee	560	444	
Oconto	343	264	
Peshtigo	320	211	
Menominee	242	206	
Cedar	388		
Ford	360		
Escanaba	250		
Whitefish	299		
Lake Michigan			266

**Data for 6 February 1971 from Robbins et al., 1972b (presumably as µmhos/cm corrected to 25°C); data for July 1968 from Modlin and Beeton, 1970 (corrected to 25°C); averages for 1954-55 and 1960-61 from Beeton and Chandler, 1966.*

Sager (1971) also noted the importance of the Fox River discharge in determining the quality of the inner Bay, *i.e.* the area north of the Fox River mouth to Long Tail Point, including the Grassy Island chain just off the Fox River entrance. Using conductance measurements, Sager concluded the main flow of the Fox moves immediately to the east before traveling outward into the Bay, primarily along the east shore. Under north winds, river water is compressed along the east shore, while a strong south or east wind allows the river water mass to spread farther to the west.

Modlin and Beeton (1970) reported little variation in conductance with depth at least as far north as Gills Rock.

Transparency

High suspended solids concentrations reduce water transparency in lower Green Bay. Secchi depths (Schraufnagel *et al.*, 1968; Sager, 1971; Howmiller and Beeton, 1972) seldom exceed 2 m, especially in the southern portion of the Bay during summer. Sager (1971) reported suspended solids (TSS) ranging from 7 to 20 mg/l at the mouth of the Fox River, but Wiersma *et al.* (1974) found solids (TSS) as high as 50.5 mg/l in lower Green Bay.

Transparency increases gradually northeastward from the mouth of the Fox River, with the greatest increase noticed in the first several kilometers (Sager, 1971). The greater Secchi depths (improvement in water quality) at increasing distances from the city of Green Bay were attributed to dilution and sedimentation of suspended solids. Moore and Meyer (1969) supported the importance of the latter process with their finding that a significant portion of the southern part of Green Bay has become 0.6-1.2 m shallower in the past 19 years. One potential cause of low transparencies at stations close to the mouth of the Fox was the high phytoplankton concentrations. Another potential cause of low transparency considered by Sager (1971) was the resuspension of suspended solids from loose flocculent bottom sediments south of Long Tail Point. However, toward the central part of the Bay no marked increases in turbidity were observed following episodes of strong winds and associated wave action (Ahrnsbrak and Ragotzkie, 1970). Based on Secchi depth readings and determination of extinction coefficients, Howmiller and Beeton (1972) concluded that light penetrates deeper into Lake Michigan than into Green Bay. They distinguished two water masses in Green Bay by measuring light extinction; a clearer mass on the western side containing at least a portion of Lake Michigan water and a murkier mass on the eastern side of the Bay.

Dissolved Oxygen, BOD, and COD

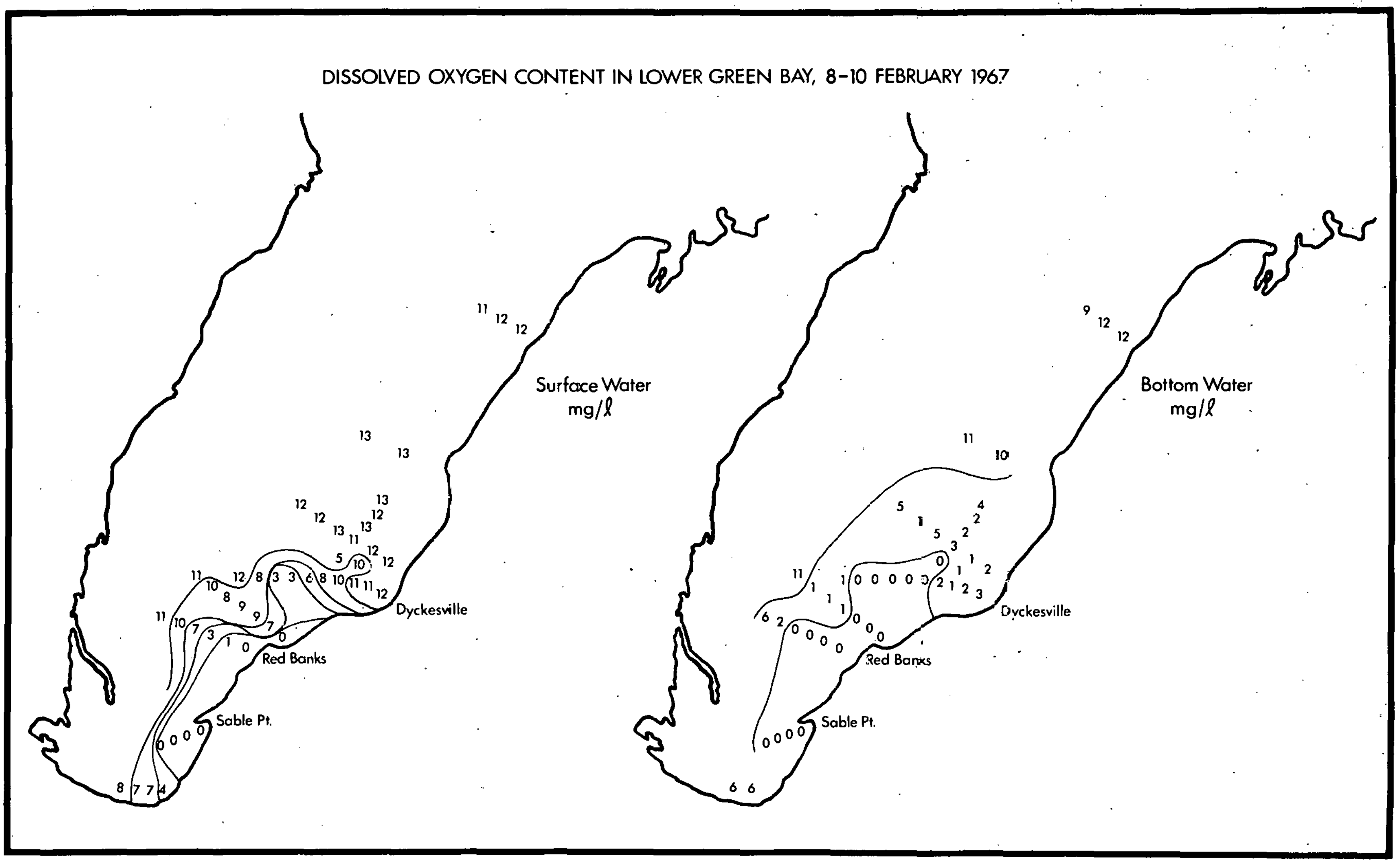
The water quality problems of Green Bay are most clearly manifested in the annual variations of the dissolved oxygen concentrations. Schraufnagel *et al.* (1968) have summarized oxygen concentrations in lower Green Bay as influenced by the Fox River during the past 30 years. Even in 1938-1939 discharge of the highly polluted Fox affected the dissolved oxygen concentration for some 32 km (20 mi) or more out into the Bay during the winter months. At that time, most of the oxygen-consuming material in the river was waste sulfite liquor discharged by numerous pulp and paper mills lining the lower Fox.

The U. S. Department of the Interior (1966b) found severe oxygen depletion in some areas of Green Bay, especially within 16 km (10 mi) of the mouth of the Fox River and near the entrance of the Peshtigo River. Problems in the lower Bay were derived from high organic loads discharged by the pulp and paper mills along the Fox and also to treated and untreated wastes discharged from municipalities. Waste discharge from the Peshtigo sewage treatment plant and paper mill effluents reportedly caused the degraded conditions near the city of Peshtigo.

The Wisconsin Department of Natural Resources conducted studies on the water quality of Green Bay during the summer of 1966 (Schraufnagel *et al.*, 1968). At the mouth of the Fox River, dissolved oxygen was depleted as the summer progressed and by August almost none remained in either the surface or the bottom waters. Gas bubbles and a pronounced H_2S odor were observed at that time. Oxygen reached a minimum of less than 1 mg/l on 12 August, remained low through September, but increased by October. The data collected in the area immediately east of the mouth of the Fox River reflected, in a muted fashion, the station at the mouth of the Fox; concentrations of oxygen were low, but somewhat higher than the incoming river water. West of the shipping channel, which enters the city of Green Bay, there was a minor influence of wastes on the summer dissolved oxygen concentrations. East of the shipping channel, the Fox River had a measurable influence. Near the Long Tail Point-Sable Point bar, oxygen concentrations were sufficient for fish, but oxygen content was depleted below saturation because of waste stabilization within that reach of the Bay. Beyond Long Tail Point and Sable Point, dissolved oxygen values did not appear to be affected during summer and fall. While the middle Bay (16 km from the mouth of the Fox River to Sturgeon Bay) did not show effects of waste discharge in surface waters, oxygen was low below the thermocline in waters deep enough to stratify. Depletion of O_2 in stratified bottom waters of the Bay was also noted at 64 and 80 km (40 and 50 mi) from the mouth of the Fox, but was less apparent at 113 km (70 mi).

On 8-10 February 1967 (Schraufnagel *et al.*, 1968), the dissolved oxygen concentrations in surface water within 5 km of the mouth of the Fox and near shore were adequate to sustain fish and other organisms (Fig. 111). Along the east side of the channel from Sable Point past Red Banks, dissolved oxygen was almost undetectable. A transect from Red Banks toward the center of the shipping channel showed increasing oxygen content. Channeling of the Fox River water along the east shore led to severe oxygen depletion. Off Dyckesville, surface waters near shore contained more than 10 mg/l dissolved oxygen. Offshore, dissolved O_2 was greatly reduced in the surface water. At the center of the channel, oxygen was high. Within 26 km (16 mi) of the mouth of the Fox, bottom-water concentrations were nearly undectable (Fig. 111).

By 9-10 March 1967 oxygen depletion was even more extensive under the ice (Schraufnagel *et al.*, 1968). Stations 29 km (18 mi) from the Fox River, which had no oxygen depletion in February, now had bottom-water concentrations less than 1 mg/l (Fig. 112). Only stations within a half mile of shore had bottom concentrations of oxygen exceeding 5 mg/l. Influence of the Fox River could still be seen 44 km (27 mi) north in bottom-water samples taken about one-half to one mile off the Door County peninsula shore where dissolved content oxygen was below 1 mg/l. Nearer shore there was enough oxygen to support fish life. The sharp boundaries in dissolved oxygen caused by the wastes supplied by the Fox River are noteworthy; the two stations pointed out by arrows in Figure 112,



DISSOLVED OXYGEN CONTENT IN LOWER GREEN BAY, 8-10 FEBRUARY 1967

Fig. 111. Dissolved Oxygen Content in Lower Green Bay, 8-10 February 1967. Data from Schraufnagel *et al.* (1968).

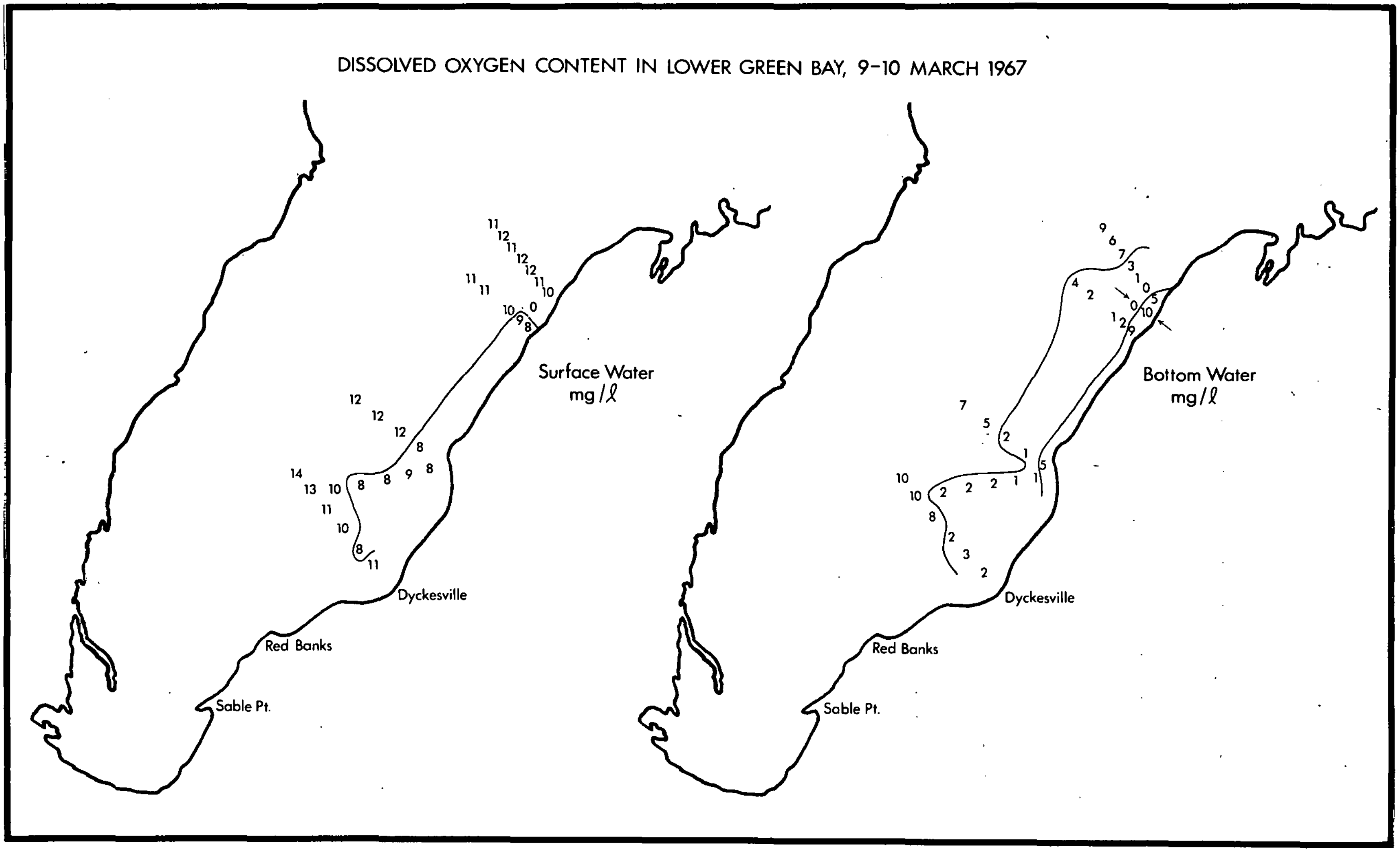


Fig. 112. Dissolved Oxygen Content in Lower Green Bay, 9-10 March 1967. Data from Schraufnagel *et al.* (1968).

with concentrations of 0 and 10 mg/l, were taken less than 250 m (800 ft) apart. In the middle and at least as far north as Sturgeon Bay, surface water oxygen concentrations remain high in winter (Fig. 112), but oxygen depletion becomes more noticeable with depth the longer the ice cover is on (Schraufnagel *et al.*, 1968).

Sager and Wiersma (1972) measured concentration distributions of COD as an indicator of oxygen-depleting material in lower Green Bay. Data for 3 August 1970 indicate organic matter concentrations decreased away from the Fox River mouth, reflecting dilution, sedimentation, and decomposition. During summer, the shallow, warm and potentially well-oxygenated lower Bay acts as a large oxidation pond for the organic matter brought in by the Fox River. Anoxic conditions were frequently observed in the immediate vicinity of the river mouth. In the remainder of the lower Bay, wind aeration of the water plus photosynthetic production of oxygen by dense algal growths permitted rapid oxidation of organic matter brought in by the Fox River.

Water from the Fox River can be traced into Green Bay with COD isopleths (Sager and Wiersma, 1972). River water with a COD exceeding 80 mg/l on 3 August 1970 moved to the east and then spread out northward, where it could be detected as a 40 mg/l isopleth for 24-32 km (15-20 mi) along the east shore.

With the physical barrier created by ice cover, much of a stream's reaeration ability is lost; low oxygen concentrations can develop great distances from the pollution source. These points are clearly shown in the data of Schraufnagel *et al.* (1968). Due to high decomposition rates in warm weather, critical dissolved oxygen conditions were found along the Fox River and out into the Bay for a distance of 3-5 km (2-3 mi). From mid-November to April, river concentrations of dissolved oxygen generally exceeded 5 mg/l. After prolonged ice cover of the Bay, however, low dissolved oxygen concentrations have extended for a distance of nearly 48 km (30 mi).

Phosphorus

Stations within 16 km (10 mi) from the mouth of the Fox River had an average total soluble phosphorus content of 65 μg PO_4-P/l during three weeks of early summer, 1963 (U. S. Dep. Inter., 1966b). Between Oconto and Sturgeon Bay total soluble phosphorus averaged 21 μg PO_4-P/l. From Menominee north to the entrance to the Bays de Noc, concentrations averaged 10 μg PO_4-P/l, with the lowest values recorded along the Door County peninsula north to Gills Rock. Levels within Big and Little Bays de Noc were 23-29 μg PO_4-P/l.

The Wisconsin Department of Natural Resources (Schraufnagel *et al.*, 1968) analyzed samples collected in August and October 1966 for total phosphorus. Four surface samples taken within 16 km (10 mi) of the mouth of the Fox River averaged 82 μg total PO_4-P/l, while five surface samples 32 and 48 km (20 and 30 mi) out averaged 65 μg total PO_4-P/l. There was no consistent difference between samples collected 1 m from the bottom and 1 m from the surface.

Schelske and Callender (1970) measured soluble reactive phosphate in seven samples collected at four stations in northern and central Green Bay during August 1969. Surface (2 m) and bottom (1 m above) water samples were taken. In northern Green Bay three samples were listed either as 0.0 or

< 0.5 μg PO_4-P/l; samples in Big and Little Bays de Noc were 0.7-0.8 μg PO_4-P/l. There was no consistent trend between surface and bottom samples. In the central portion of the Bay (roughly, from the mouth of the Oconto River north to Chambers Island) soluble reactive phosphate ranged from 0.5 to 4.2 μg PO_4-P, but no obvious trends were noted.

Phosphorus values in Green Bay during the summer of 1971 were reported in three papers. Rousar and Beeton (1973) sampled 21 stations within 48 km (30 mi) of the mouth of the Fox on 12 July. Sager and Wiersma (1972) sampled 25 stations monthly within 15.3 km (9.5 mi) of the Fox during open-water seasons of 1970-1971; details are presented in their paper for 20 July. Vanderhoef *et al.* (1972) presented averages of weekly samples on a transect in the ship channel during June, July, and August. Considering the variability among investigators and sampling methods, the agreement in Table 81 is noteworthy. Total phosphorus decreased with distance from the mouth of the Fox and apparently reached a constant value after 48 km (30 mi). Concentrations of soluble reactive phosphate are significant only in the first 16 km (10 mi); the low values for soluble reactive phosphorus more than 24 km (15 mi) out agree with those of Schelske and Callender (1970). Further conclusions of each of the three 1971 studies are considered below.

Table 81. Phosphorus Concentrations in Green Bay, Summer 1971*

	PO_4-P, μg/l					
	Rousar and Beeton (1973)		*Sager and Wiersma (1972)*		*Vanderhoef et al. (1972)*	
Miles from the Fox River Mouth	*Soluble Reactive*	*Total*	*Soluble Reactive*	*Total*	*Soluble Reactive*	*Total*
1	-	430				
1.5			16	230	15	-
2.0	-	350				
3.0-3.5			8	195	4	-
5.0-5.5			8	130	2	-
6.0-6.5	-	155			1	
7.0-8.0			< 8	100	13	-
9.0-10.0	-	58	< 8	65	3	-
11.5					4	-
12.3					5	-
14.7	-	52			3	-
19.0-21.0	-	41			2	-
29	-	40			1	-
36					3	-

**Based on a hypothetical or real transect conducted in the shipping channel.*
A blank indicates the investigators did not occupy a station in that reach.
A dash indicates no data were reported for the analysis in question.

Sager and Wiersma (1972) observed very high concentrations of soluble reactive phosphate south of the Grassy Island chain. The concentration gradient in the first few miles from the mouth of the Fox was considered steep (from 33 to less than 8 μg PO_4-P/l in 8 km). Generally, concentrations along the eastern half of the Bay were higher than those in the west. These lower values reflect the eastward dispersal of Fox River water and probably nutrient assimilation along the predominantly marshy western shore. Sager and Wiersma suggested the significantly higher soluble reactive phosphate concentrations in the southeastern corner of the Bay, rather than at the Fox River mouth, were evidence for phosphorus regeneration from the sediment by microbial activity or uptake and release by algae. The gradients in total phosphate concentrations with distance from the city of Green Bay (290 to 130 μg PO_4-P/l in 8 km) were not so steep as those for soluble reactive phosphate. Changes in total phosphate concentration appeared to more closely approximate dilution and dispersal of Fox River water in the Bay than did the distribution of soluble reactive phosphate.

Sridharan (1972) collected limited phosphorus data in southern Green Bay on 9 February 1969, when the lower Bay was covered with 75 cm of ice. South of Long Tail Point, soluble reactive phosphate ranged from 100 to 110 μg PO_4-P/1 at three stations. One station near Little Long Tail Point revealed a concentration of 60 μg PO_4-P/1. These values are three to six times higher than those of Sager and Wiersma (1972) at comparable sampling sites during summer. Total phosphorus concentrations in winter (Sridharan, 1972) were much more site-dependent than soluble reactive phosphate. Two stations, separated by less than 1.6 km, were sampled at the bottom (2-3 m) in the southeast corner of the Bay. Total phosphorus was 400 μg PO_4-P/1 at the deeper station, which is located farther from the Fox River mouth than the shallower station that had 700 μg PO_4-P/1. Stations just inside Long Tail Point and Little Long Tail Point both had total phosphorus concentrations of 300 μg PO_4-P/1. One can conclude from the data of Sridharan (1972) and Sager and Wiersma (1972) that under the ice two events may be occurring. First, the Fox River may contribute more phosphorus in winter than summer. Sager and Wiersma (1972) found soluble reactive phosphate concentrations at the Fox River inlet were highest from December to February, averaging 98 μg PO_4-P/1. Colder temperatures reduce the assimilation of soluble reactive phosphate by the river; there is also probably release or regeneration from river sediments, suspended solids, and plant material. Second, phosphorus may be released to the overlying water from the sediments of the Bay as dissolved oxygen is depleted under the ice (Mortimer, 1971).

Nitrogen

Ammonia

Like phosphorus, the ammonia-N values found in southern Green Bay near the mouth of the Fox River reflect the polluted, eutrophic state of that section of the Bay. Seventeen samples collected within 15 km (9 mi) of the Fox by the U. S. Department of the Interior (1966b) in early summer of 1963 averaged 460 μg NH_3-N/1. Schraufnagel *et al.* (1968) recorded average concentrations of 120 μg NH_3-N/1 at 6 and 16 km (4 and 10 mi) in August 1966; at one station 1.6 km from the Fox on 19 October of the same year, they found 460 μg NH_3-N/1. Within 16 km (10 mi) on the latter date the concentration had decreased to 50 μg HN_3-N/1. Mague (1971) found ammonia-N to be 700 μg NH_3-N/1 on 16 July 1970 at the mouth of the Fox River; ammonia-N decreased with distance up the ship channel and was 70 μg NH_3-N/1 at 19 km (12 mi). Mague's measurement at the river mouth agrees with the average Fox River mouth concentration recorded by Sager and Wiersma (1972) for summer 1970-1971 (700 μg NH_3^+-N/1). During 1972 Vanderhoef *et al.* (1974) found on the basis of weekly sampling during summer that ammonia-N at the Fox River mouth averaged 880 μg NH_3-N/1 but decreased rapidly with distance from the River. Within 10 km the concentration reached 80 μg NH_3-N/1 and remained at or below that value for 47 km. Within the same distance sampled by Vanderhoef *et al.* (1974), Mague (1971) found higher concentrations, reporting a range of 140-160 μg NH_3-N/1 for seven stations between Little Sturgeon Bay and the Grassy Islands on 26 August 1970.

In the central portion of the Bay, ammonia-N concentrations are usually much less than those found near the Fox River inlet. In the vicinity of Sturgeon Bay and Menominee the U. S. Department of the Interior (1966b) found ammonia-N concentrations of 170-180 μg NH_3-N/l in early summer 1963. A little south of Peshtigo, Schraufnagel *et al.* (1968) measured surface-water concentrations of 40-60 μg NH_3-N/l in 1966; concentrations were slightly higher south of Menominee, ranging from 80 to 100 μg NH_3-N/l. Mague (1971) sampled two stations in or near Sturgeon Bay and found 180-210 μg NH_3-N/l. Between Oconto and Sturgeon Bay, Schelske and Callender (1970) reported ammonia-N concentrations much lower than those of other investigators, only 10-20 μg NH_3-N/l in surface waters.

North of Chambers Island to the entrance to the Bays de Noc, the U. S. Department of the Interior (1966b) found ammonia-N values of 120-130 μg NH_3-N/l. These values were much higher than the 10-20 μg NH_3-N/l recorded by Schelske and Callender (1970) and also exceeded the 30-80 μg NH_3-N/l at the end of the Door County peninsula described by Schraufnagel *et al.* (1968).

Within Big Bay de Noc the surface-water ammonia-N levels measured by Schelske and Callender (1970) were only half those at 16 m, 20 *vs.* 40 μg NH_3-N/l; in Little Bay de Noc ammonia was 25 μg NH_3-N/l. The U. S. Department of the Interior (1966b) found much higher concentrations in both Big Bay de Noc (170 μg NH_3-N/l) and Little Bay de Noc (130 μg NH_3-N/l).

Nitrate

Three stations within 14.5 km (9 mi) of the mouth of the Fox had nitrate-N concentrations of 10 μg NO_3-N/l in early summer 1963 (U. S. Dep. Inter., 1966b). Schraufnagel *et al.* (1968) measured nitrate as 200 μg NO_3-N/l within 1.6 km (1 mi) of the Fox on 19 October 1966; seven other samples between 6.5 and 32 km (4 and 20 mi) averaged 60 μg NO_3-N/l in August and October. Mague analyzed water collected at the mouth of the Fox River on 16 July 1970 and found 560 μg NO_3-N/l; between the Grassy Islands and the city of Green Bay nitrate ranged between 80 and 100 μg NO_3-N/l. Vanderhoef *et al.* (1972) found nitrate-N averaged about 50 μg NO_3-N/l from the Grassy Islands to a station 24 km (15 mi) north of the mouth of the Fox; beyond that nitrate-N was $\leq$ 40 μg NO_3-N/l up to Sturgeon Bay and then probably increased north of that point. In contrast, Mague (1971) had found no consistent variation in nitrate-N concentration on 26 August 1970 in the area between the Grassy Islands and Sturgeon Bay; the range of values which Mague found was 50-120 μg NO_3-N/l.

Between Menominee and Sturgeon Bay, surface nitrate-N concentrations averaged 70 μg NO_3-N/l (Schraufnagel *et al.*, 1968). At two stations, samples were also taken at the bottom. Both stations showed that the surface-water samples were depleted with respect to the bottom waters (180-200 μg NO_3-N/l). Schelske and Callender (1970) found a similar depletion in central bay samples collected in 1969. The U. S. Department of the Interior (1966b) did not take bottom-water samples, but they also found low surface-water concentrations, 40 μg NO_3-N/l, around Sturgeon Bay.

North of Sturgeon Bay, there are very few data on nitrate-N concentrations in any season. The U. S. Department of the Interior (1966b) reported average concentrations from Chambers Island north to the entrances to the Bays de Noc of 100 µg NO_3-N/l in early summer 1966. Schraufnagel *et al.* (1968) measured nitrate-N near Washington Island on 21 October 1968 and found it to be identical with another surface-water sample taken in Lake Michigan at the Sturgeon Bay entry buoy. In the area between Gills Rock and Escanaba, Schelske and Callender (1970) reported that surface-water concentrations of nitrate-N in late August 1969 were depleted compared with bottom waters; surface-water samples ranged from 70-90 µg NO_3-N/l, while bottom waters were 160-210 µg NO_3-N/l.

In early summer 1963, the U. S. Department of the Interior (1966b) recorded 80 µg NO_3-N/l in Little Bay de Noc and 50 µg NO_3-N/l in Big Bay de Noc (presumably both were surface-water samples). Schelske and Callender (1970) reported no surface-water samples in these same places, but found nitrate-N was 130 µg NO_3-N/l in Little Bay de Noc (depth not recorded) and 170 µg NO_3-N/l at 16 m in Big Bay de Noc.

Organic Nitrogen

Schraufnagel *et al.* (1968) analyzed some scattered samples collected in August and October 1966. In the summer sampling period, surface waters ranged between 400 and 800 µg/l total organic-N in the zone from 6.5 to 65 km (4 to 40 mi) from the mouth of the Fox River. At 97 and 113 km (60 and 70 mi) and also at the Sturgeon Bay entry buoy in Lake Michigan, total organic-N was 220-260 µg NH_3-N/l. These latter samples are three times higher than comparable surface-water data reported by Robertson and Powers (1968) for the main body of Lake Michigan in August. At four stations in August 1966, bottom as well as surface waters were sampled. There was a consistent decrease in bottom concentrations of organic-N proceeding toward the open Lake. At 16 km (10 mi) from the mouth of the Fox, the bottom-water concentration of organic-N was 1010 µg NH_3-N/l; at 48 km (30 mi), 420 µg NH_3-N/l; at 64 km (40 mi), 260 µg NH_3-N/l; and at 113 km (70 mi), 240 µg NH_3-N/l. The October data clearly showed a decrease in organic-N with distance from the mouth of the Fox. At 1.6 km (1 mi), the concentration was 1570 µg NH_3-N/l; at 16 km (10 mi), 390 µg NH_3-N/l; at 64 km (40 mi), 290 µg NH_3-N/l; and at 97 and 113 km (60 and 70 mi), as well as Lake Michigan at the Sturgeon Bay entry buoy, 110 to 140 µg NH_3-N/l. These latter numbers are 1.3 to 1.6 times higher than the October data reported by Robertson and Powers (1968) for open Lake Michigan water.

Wiersma *et al.* (1974) measured organic-N monthly in the extreme southern end of Green Bay around the Fox River from January to October 1973. Concentrations ranged from 160 to 440 µg NH_3-N/l. The highest concentrations were recorded in August and September and the lowest in January.

Nitrogen Fixation

Although nitrogen fixation, measured by acetylene reduction (an indicator of N_2 reduction activity), is usually at or below the limit of detection for much of Lake Michigan (Peterson, 1973--personal communication), five years of evidence now show the importance of nitrogen fixation in Green Bay (Mague, 1971; Stewart *et al.*, 1971; Vanderhoef *et al.*, 1972; Vanderhoef *et al.*, 1974; Peterson and Burris, 1973--personal communication).

On 17 July 1969, Stewart *et al.* (1971) demonstrated high acetylene reduction activity at seven stations located between 11 and 23 km (7 and 14 mi) northeast of the Fox River mouth. There were no obvious spatial differences. Samples collected on 1 August 1969 between Chambers Island and the Escanaba area showed acetylene reduction activities one to two orders of magnitude lower in this location as compared with acetylene reduction in the southern Bay. Three transects from the east shore to the center of the channel, south of Sturgeon Bay, revealed less acetylene reduction occurred in the channel and more occurred along the east shore. In contrast, a transect from the city of Sturgeon Bay into Green Bay showed that acetylene reduction increased steadily away from shore. This observation was attributed to inhibition of algal growth inshore by the pollution generated by ship-building and other industrial activities near the city of Sturgeon Bay.

Mague (1971) performed a follow-up study in 1970. Acetylene reduction increased in samples as he approached the city of Green Bay. Maximal activity was detected between Long Tail Point and the Grassy Islands on all three sampling dates. Acetylene reduction dropped precipitously between the Grassy Islands and the mouth of the Fox River. This observation may confirm pollution effects noted by Stewart *et al.* (1971) at Sturgeon Bay.

Temperature increases and calm weather, combined with increased soluble reactive phosphate concentrations, initiate increases in acetylene reduction in Green Bay (Vanderhoef *et al.*, 1972). Most of the acetylene reduction recorded in 1971 was confined to the area within 21 km (13 mi) of the Fox River mouth. Stations located between 12 and 25 km (7.5 and 15.5 mi) from the mouth of the Fox had maximal acetylene reduction on 16 June 1971, and acetylene reduction was relatively negligible during the remainder of the summer. Two stations between Little Long Tail Point and Long Tail Point had low activities all summer. South of Long Tail Point, acetylene reduction was detected over the summer more consistently; peaks in activity were noted in both June and July.

Vanderhoef *et al.* (1972) calculated that biological reduction of N_2 contributed 94,000 kg of reduced nitrogen to the first 2 m of water in the lower 400 km^2 (15.4 mi^2) of Green Bay during a heavy algal growth lasting from 12 to 19 June 1971. Sager and Wiersma (1972) determined that during June to August 1971, the Fox River contributed an average of 20,575 kg/week (45,360 lb/week) of ammonia-N to the Bay; weekly contributions of total nitrogen were 285,768 kg N, or 630,000 lb. Thus during periods of intense nitrogen fixation activity, the reduced nitrogen formed by the algae (94,000 kg in a week) may exceed that contributed by the Fox River four or five times (20,575 kg). Reduced nitrogen formed by the algae may constitute an appreciable fraction (94,000 ÷ 285,768 = 0.33) of the total nitrogen carried into the Bay by the Fox River. This additional source of nitrogen can thus be significant to the nitrogen budget of Green Bay during periods of high algal activity.

Vanderhoef *et al.* (1974) found consistently higher levels of acetylene reduction in 1972 than they had in 1971. This result was attributed to the higher levels of phosphorus in 1972. Based on the higher levels of acetylene reduction and the values of inorganic nitrogen in the Fox River which they measured, Vanderhoef and coworkers concluded that the contribution of fixed nitrogen by N_2 fixation in the southernmost part of the Bay was nearly 40% of the total inorganic nitrogen ($NH_4^+ + NO_3^-$) carried in by the Fox during the period 14 June-17 August.

Peterson and Burris (1973--personal communication) did more intensive sampling near the Oconto River and around Menominee-Chambers Island in June 1973. As expected, inshore samples showed higher rates of acetylene reduction than offshore. In a transect between Sturgeon Bay and Menominee, N_2 fixation was occurring at significant rates everywhere except immediately north of Green Island. Samples collected to the northwest, east, and northeast of Chambers Island showed no acetylene reduction activity. Peterson (1973--personal communication) has suggested this was caused by the influence of northern Lake Michigan on that section of the Bay.

All studies have indicated that N_2 fixation was significant only near municipalities where nutrients are abundantly supplied. Beyond these centers, north of Chambers Island, N_2 fixation is presently an unimportant source of combined nitrogen to the water of Green Bay.

Silica

Concentrations of silica between the mouth of the Fox River and Sturgeon Bay ranged from 1.5 to 1.7 mg/l soluble reactive SiO_2 in early summer 1973 (U. S. Dep. Inter., 1966b). In the remainder of the Bay, including Big and Little Bays de Noc, the range was 2.0 to 2.4 mg SiO_2/l.

Schelske and Callender (1970) conducted a few silica analyses in northern and central Green Bay in August 1969. At three stations lying just outside the Bays de Noc, surface values averaged 0.46 mg soluble reactive silica per liter; two bottom samples were 1.04 and 1.20 mg/l. A single station midway between the city of Green Bay and Sturgeon Bay had surface and bottom concentrations of 0.25 and 1.84 mg SiO_2/l, respectively. In Sturgeon Bay, the comparable values were 0.78 and 3.24 mg SiO_2/l, while near Menominee the comparable values were 0.74 and 2.05 mg SiO_2/l. Since all these samples were taken in summer, the lower concentrations in surface waters are probably due to uptake of soluble reactive SiO_2 with conversion to particulate silica.

Rousar and Beeton (1973) observed an increase in surface water concentrations of soluble reactive silica from the Fox River (0.5 mg SiO_2/l) to the entrance light to the shipping channel (1.0 mg SiO_2/l) at 16 km (10 mi) on 12 July 1971. Out to 48 km (30 mi) from the mouth of the Fox, soluble reactive silica levels were higher on the east side of the Bay than in the middle. At 32 and 48 km (20 and 30 mi) from the Fox inlet, transect values at the east side exceeded concentrations in the west part of the Bay, and concentrations in the center were less than either the east or west sides.

The increase in concentration of SiO_2 described by Rousar and Beeton (1973), away from the city of Green Bay, may reflect either low diatom activity as the nitrogen and phosphorus of the Fox is diluted out or increasing influence by volume of Lake Michigan waters. The higher concentrations of silica along the eastern shore may indicate lower diatom activity caused by some adverse effect of the Fox River, which flows along the east shore of the Bay, or it may indicate that other algae are out-competing the diatoms for nutrients (*e.g.* see Vanderhoef *et al.*, 1974) so that diatoms are not present to use the soluble SiO_2.

GRAND TRAVERSE BAY

Grand Traverse Bay is a narrow inlet of Lake Michigan located in the Lower Peninsula of Michigan somewhat southwest of the Straits of Mackinac. The southern part of Grand Traverse Bay is divided approximately north-south by Old Mission Point into two nearly equal parts, the east arm and the west arm (Fig. 113). These two arms make up about half of the surface area of the entire Bay; the remaining half is more open than the southern half.

The Boardman River, the major tributary to the Bay, enters at the southern end of the west arm. Traverse City, the major population center of the area, has built up around the mouth of the Boardman. There are no large population centers along the east arm of Grand Traverse Bay or around the more open northern portion.

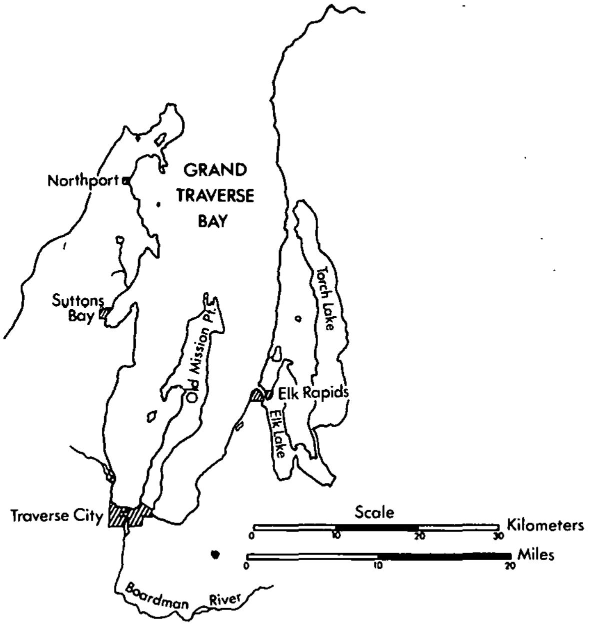


Fig. 113.

Grand Traverse Bay.

Previous Studies

Until the 1970's, there was little systematic research reported on the water quality or sediments of Grand Traverse Bay. Water quality problems in this Bay have been much less than in Green Bay, partly because the Boardman River drains an area with fewer people and industries than does the Fox River. The Boardman has an average flow of 7.22 m^3/sec (255 cfs) compared with the Fox River, 125.13 m^3/sec (4420 cfs) (U. S. Dep. Inter., 1968).

Lauff (1957) reported the results of a two-day survey, conducted 30-31 July 1954, of sediment characteristics, water transparency, temperature, soluble reactive silica and magnesium concentrations, and currents in Grand Traverse Bay. Influx of high-transparency water from Lake Michigan proper was evident at least as far south as the northern tip of Old Mission Point. Surface-water patterns of both magnesium and soluble reactive silica concentrations resembled the distributional pattern of water transparency. Temperature stratification in the Bay was reflected in vertical differences in silica concentrations. Soluble reactive silica was depleted in the surface water and high in the bottom water. Much of the surface water flowing from Lake Michigan into Grand Traverse Bay moved into the west arm; a smaller volume entered the east arm. Surface-water currents during the two-day sampling period showed several eddies; areas of probable upwelling of cold water and sinking of surface water were identified. In the east arm, deep-water circulation was minimal. The observed circulation patterns during this two-day survey were considered representative of the characteristic summer pattern in Grand Traverse Bay. Sediment deposition patterns reflected the circulation patterns. In deep areas, sediments consisted of fine particles, while in shallow water sediments were much coarser. An area along the southeastern shore of the west arm where there was an extensive sinking current was also evidenced by the fine sediments in that area. Reduction of current activity and turbulence during sinking carried these fine sediments to depths where there is little or no turbulence.

The U. S. Department of the Interior (1968) collected water samples for chemical analyses in the east and west arms of Grand Traverse Bay from 22 to 28 July 1964. They reported that contaminants were generally present in higher concentrations in the west arm, into which the Boardman River flows, than in the east arm; however, data were not presented in a manner which revealed these differences. The general water quality of Grand Traverse Bay was not considered significantly different from that in the adjacent inshore waters of the main portion of Lake Michigan.

In August 1969, samples were collected for nutrient analyses in the northern, more open part of Grand Traverse Bay as well as at other inshore and offshore stations in the northeastern part of Lake Michigan (Schelske and Callender, 1970). Silica, nitrate, and soluble reactive phosphate concentrations in Grand Traverse Bay resembled those in the northern part of the Lake, while ammonia content was somewhat higher in the Bay water than in the adjacent waters of the Lake.

Stoermer *et al.* (1972) compared primary productivity and nutrient concentrations in samples collected on 18 May 1970 with those collected on 20 June 1970. Productivity was highest in the west arm, lowest in the east arm, and intermediate in the open bay; nutrient concentrations were affected by biological uptake. High productivity in the west arm had been anticipated because of nutrient sources from Traverse City and the Boardman River. Intermediate values for primary productivity in the open Bay were attributed to (*i*) mixing of water from the east and west arms, and (*ii*) influx of water from the main body of Lake Michigan.

Modeling Efforts

Stoermer *et al.* (1972) said their study was designed to aid planning of a sampling program associated with a management-oriented project conducted by the University of Michigan Sea Grant Program. Under those auspices, several mathematical models describing various features of Grand Traverse Bay have been developed.

Water Circulation

A model which incorporated topography, wind effects, and seiching oscillations of Lake Michigan was developed to describe the circulation of Grand

Traverse Bay (Green, 1972). Field observations carried out by Johnson and Monahan (1971) were used to develop the model.

One of the results of model development (Green, 1972) was identification of a marked difference in circulation patterns in the east and west arms of the Bay. The model predicts that water in the west arm does not mix readily with the rest of the Bay due to a series of gyres and eddies which tend to inhibit mixing and increase detention times. In contrast, the water from the east arm appears to mix rather freely with the upper Bay. The water circulation model thus gives a physical reason for the difference in nutrient concentrations observed in the two arms (*cf.* Stoermer *et al.*, 1972), for the gyres and eddies in the west arm cause nutrients to accumulate there above the levels predicted by a theoretical detention time.

Coliform Distribution

The results of the water circulation model described by Green (1972) were used as the basis for modeling the dispersion of coliform bacteria in the west arm of the Bay (Canale, 1973; Canale and Green, 1972; Canale *et al.*, 1973b). In addition to water-movement equations, the model included a temperature-dependent equation to account for the (first-order) die-off of these bacteria. The model was verified by successfully simulating coliform distributions in the period 1963-1971 (Canale, 1973). The model could also be used to predict the effects on bacterial distributions of various management strategies, *e.g.* allowing boats to discharge sanitary wastes directly to the Bay.

Nutrient Distribution

Dissolved and particulate phosphorus, particulate nitrogen, dissolved organic nitrogen, ammonia, nitrate, and silica* distributions were incorporated in a dynamic model of phytoplankton production in the southern half of the west arm of Grand Traverse Bay (Canale *et al.*, 1973a). The model predicted changes in nutrient distributions due to water movements, temperature fluctuations, biological uptake and growth, death and decomposition, sediment regeneration, inorganic oxidation-reduction reactions (*e.g.* $NH_3 \rightleftharpoons NO_3^-$), exchange with Lake Michigan, and direct input from the Boardman River.

Canale *et al.* (1973a) found that the model they developed for nutrient distributions did not exactly match field data collected July 1970-December 1972 in Grand Traverse Bay. However, they considered the general agreement between the concentrations and trend of the data and model to be encouraging. Differences between model predictions and field data were attributed to several causes: (*i*) analytical errors, (*ii*) natural heterogeneity of the system, (*iii*) choice of inappropriate values for parameters in the model, and (*iv*) requirement of the model that data be averaged on a seasonal basis, obscuring the effects of short-term variations.

Using their dynamic model for phytoplankton production and nutrient distributions, Canale *et al.* (1973a) predicted that if population and industrial

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**The original paper (Canale et al., 1973a) did not state which silica species was included in the model, but from the context of the paper it is probable that soluble reactive silica was meant.*

and agricultural activity remained stable around Grand Traverse Bay, then a 90% reduction in phosphorus content of waste effluents discharged to the Boardman River or directly to the Bay would have relatively little effect on the southern part of the west arm. This prediction reflects the fact that the upper part of Grand Traverse Bay, not the Boardman River, is the major source of nutrients to the lower part of the west arm. That is, the sheer volume of input from Lake Michigan into the west arm contributes more nutrients than the Boardman River (volume × concentration = mass). However, the model was also able to show that if the residential population increased four-fold, accompanied by a doubling of industrial activity, then even if agricultural production remained stable the increased nutrient loads carried in by the Boardman River would cause significant increases in total dissolved phosphorus concentrations and decreases in silica concentrations in the west arm. Canale *et al.* (1973a) emphasized the usefulness of their model to forecast water quality in Grand Traverse Bay resulting from likely changes in residential, commercial, and industrial activities and from varying degrees of phosphorus effluent control in the Traverse City area.

INSHORE *VS*. OFFSHORE DIFFERENCES

Chemical substances are added to Lake Michigan primarily along the shoreline. Their sources are numerous: overland runoff and groundwater, tributaries carrying soluble and suspended matter, harbors, and industrial and municipal sewage outfalls. Because Lake Michigan is large and has diverse environments within it, there is no lakewide response to input of chemical additives. Instead, responses are local and regional, reflecting dilution and/or biological uptake. These processes account at least in part for the observed inshore-offshore (> 16 km) differences in concentrations of conservative substances, nutrients, and trace contaminants.

Differences in mixing processes contribute to observed inshore-offshore differences in chemical concentrations. For example, bottom topography and wind stresses combine to restrict offshore movement of inshore water. When thermal bars form they intensify these inshore-offshore differences. Inshore waters are so shallow that effects of storms may be felt at the bottom, but offshore sediments are affected directly only by the most violent storms if at all. These hydrodynamic processes contribute to inshore-offshore differences in sediment characteristics.

Conservative Substances

Total Dissolved Solids

Wind stirring of bottom sediments, input of municipal and industrial waste effluents, and influx of surface runoff likely contribute to inshore-offshore differences in total dissolved solids (TDS) values recorded in the southern basin (U. S. Dep. Inter., 1968; Industrial Bio-Test, 1972a, 1972b). TDS data collected from the shoreline intake of the Waukegan Generating Station averaged 171 mg/l (Industrial Bio-Test, 1972a), while samples collected at three stations east of the Waukegan area averaged 157 mg/l (Industrial Bio-Test, 1972b). Powers and Ayers (1967) indicated that total solids concentrations in offshore samples collected in the southern basin were much lower than at Michigan City and Whiting public water supply intakes. The U. S. Department of the Interior (1968) found that the average TDS concentration for offshore stations (155 mg/l) throughout the Lake in 1962-1963 was less than for inshore stations (175 mg/l). Almost half of the inshore stations were located close to Milwaukee or Calumet. The inshore-offshore difference was attributed to the chemical additives being discharged into Lake Michigan daily.

Data are not generally available on inshore-offshore differences in TDS concentrations in the divide area and northern basin.

Specific Conductance

The average offshore specific conductance value reported by the U. S. Department of the Interior (1968) for samples taken throughout the Lake was 25 μmhos/cm less than the inshore value (Table 5). Industrial Bio-Test (1972a) found that the specific conductance of samples collected from intakes at the Kenosha Water Treatment Plant, the Waukegan Generating Station, and the North Chicago Water Treatment Plant averaged 13-25 μmhos/cm higher than surface-water samples collected 9.6 km (6 mi) offshore in the vicinity of Waukegan (Industrial Bio-Test, 1972b).

Specific conductance values from Milwaukee and the divide area are presented in Figures 21 and 22. Near-shore synoptic studies conducted in April and June 1972 show that specific conductance values decreased sharply with increasing distance from shore at Milwaukee. South of Milwaukee Harbor, the high conductivities that Beeton and Barker (1974) attributed to industrial and municipal waste discharges are also a reflection of the prevailing southward-flowing currents during April to August (U. S. Dep. Inter., 1966a). Rousar (1973) and Holland and Beeton (1972) found no inshore-offshore differences in specific conductance along the car ferry track from Milwaukee to Ludington. However, their inshore stations were 4.8 km (3 mi) from shore, beyond the area where specific conductance decreases most rapidly with distance from shore (*cf.* Figs. 21 and 22).

Samples collected at five stations on a transect from Frankfort to Sturgeon Bay on 11 July 1971 revealed no significant ($P > 0.5$) inshore-offshore differences in specific conductance in this transect (Rousar and Beeton, 1973). Data of Beeton and Moffett (1964) showed no identifiable inshore-offshore differences in specific conductance values in the northern basin.

Sodium

Comparison of data collected from the Kenosha and North Chicago Water Treatment Plant intakes, the Waukegan Generating Station intake (Industrial Bio-Test, 1972a), and three stations 9.6 km (6 mi) offshore (Industrial Bio-Test, 1972b) suggests that sodium concentrations decrease offshore (*cf.* Table 37) in the southwestern part of the Lake.

Chloride

Data from the early 1960's (Beeton and Moffett, 1964; U. S. Dep. Inter., 1968) showed that inshore chloride concentrations in the southern basin were somewhat higher than offshore concentrations (Table 47). Decreasing chloride concentrations with distance from harbors and river mouths were evident (Risley and Fuller, 1966; U. S. Dep. Inter., 1968). Beeton and Barker (1974) investigated in more detail the variations in chloride concentrations with distance from shore around Milwaukee (Fig. 94). Their data revealed the effects of sewer outfalls as a chloride source. Seasonal variations in the extent of inshore-offshore chloride concentration gradients were evident, likely from winter street salting.

Several instances of marked differences in inshore-offshore chloride concentrations near Ludington and Manistee were identified in 1962-1963 (U. S. Dep. Inter., 1968). Values as high as 94 mg Cl^-/1 were found in that vicinity. The U. S. Department of the Interior (1968) attributed these high concentrations to industrial discharges near the mouth of the Manistee River.

Sulfate

Sulfate concentrations are generally lower offshore than inshore in the southern basin (Fig. 97). These differences may be caused partially by human activities in the area. For example, average sulfate concentrations in samples collected north of Milwaukee were only slightly higher inshore than 16 km (10 mi) offshore (Fig. 98), but south of Milwaukee the difference was pronounced. Beeton and Barker (1974) speculated that higher inshore values for sulfate south of Milwaukee reflected the southward flow of sulfate-containing effluents. In addition, sulfate concentrations dropped dramatically between Indiana Harbor (U. S. Dep. Inter., 1968) and the area adjacent to the Harbor (Risley and Fuller, 1966) during 1962-1963 (*cf.* Table 51).

Non-Conservative Substances

The distribution of non-conservative substances in Lake Michigan is affected primarily by the hydrodynamic processes and seasonal succession of the phytoplankton and zooplankton communities. There are insufficient data on non-conservative substances to allow a complete treatment of inshore-offshore variations of these chemicals; however, there is enough information on some selected parameters to give insight into the geographic distribution of non-conservative substances.

Dissolved Oxygen

Respiration (Eq. 5) and non-biochemical reactions (*e.g.* Eqs. 6 and 7) remove dissolved O_2 from Lake Michigan water. Major quantities of oxygen-consuming substances discharged to Lake Michigan are associated with municipal sewage effluents, pulp and paper manufacture, and metal refineries.

Risley and Fuller (1966) found that average dissolved O_2 concentrations (2.7 mg/1, 29% saturation) in Indiana Harbor during 1962-1963 were much less than in the adjacent inshore water of Lake Michigan (9.1 mg/1, 96% saturation). It is perhaps surprising that O_2 levels were near saturation at stations close to Indiana Harbor. Snow (1974) found no indication of oxygen depletion in STORET data from municipal water intakes at Chicago (South Plant), Hammond, Whiting, East Chicago, and Gary water plant intakes. Apparently, oxygen-consuming substances are oxidized and diluted quickly over a comparatively short distance. Snow suggested that measurements would need to be taken at the mouth of the Indiana Harbor Canal if O_2 depletion was to be detected.

The large quantities of municipal and industrial wastes discharged to the Lower Fox River and directly into Green Bay create O_2 concentration gradients in southern Green Bay. In winter, oxygen was depleted as far as 80 km (50 mi) from the mouth of the Fox River (Schraufnagel *et al.*, 1968). The problems associated with low O_2 and high BOD are exacerbated by mixing processes that may keep these waters near the eastern shore of Green Bay.

Organic Matter

Robertson and Powers (1965) showed that particulate organic matter concentrations were higher at stations 16 km (10 mi) from shore than at mid-lake in the southern basin, divide area, and northern basin. This observation was attributed to enhanced biological productivity closer to shore.

Ammonia

Inshore-offshore differences in ammonia concentrations are evident in Figure 45 and Table 22, especially in the vicinity of harbors and near the mouths of waste-laden tributaries. The U. S. Department of the Interior (1968) found inshore-offshore decreases in ammonia were especially noticeable along the western shore from northern Green Bay to Milwaukee, and from northern Chicago around the east side of the Lake north to Frankfort. Inshore-offshore differences are related to ammonia discharges by municipalities, steel mills, oil refineries, and chemical manufacturers (Snow, 1974).

Inshore buildup of ammonia has been noted around the Milwaukee Harbor (U. S. Dep. Inter., 1966a, 1968). Outside the Harbor breakwater, ammonia concentrations decreased within a mile or so to levels considered typical of open Lake water.

In the summer of 1969, surface-water samples were collected (Schelske and Callender, 1970) for ammonia determinations. These analyses revealed no inshore-offshore differences in either the southern or northern basins; however, the U. S. Department of the Interior (1968) found major inshore-offshore gradients. This is probably due to the latter organization's choice of sampling sites, largely near harbors and river mouths.

Nitrate

Differences in nitrate concentrations with distance from shore have been reported for Lake Michigan (U. S. Dep. Inter., 1968; Allen, 1973; Holland, 1969; Schelske and Callender, 1970; Industrial Bio-Test, 1972a, 1972b, 1972c; Lue-Hing, 1973--unpublished; Holland and Beeton, 1972; Rousar, 1973; Beeton and Barker, 1974). The average inshore concentration of nitrate (0.14 mg NO_3-N/1) was slightly higher than the offshore average (0.13 mg NO_3-N/1) in 1962-1963 (U. S. Dep Inter., 1968). Averaging may have made inshore-offshore differences less obvious (*cf.* Figs. 50 and 51), since nitrate variations with distance from shore depend on season.

The best demonstration of inshore-offshore differences in nitrate concentrations in the southern basin was provided by Beeton and Barker (1974). Figure 52 represents synoptic studies of surface-water nitrate concentrations around Milwaukee in June and January. At least part of the decrease in nitrate content with increasing distance east of Milwaukee Harbor in June (Fig. 10a) is due to simple dilution of harbor effluents, although biological uptake likely enhances the decrease. Since biological uptake of nitrate is minimal in January, the decrease in nitrate concentrations with increasing distance from shore (Fig. 10b) is attributable largely to dilution.

Allen (1973) determined surface-water (2-, 5-, and 10-m) nitrate concentrations in samples collected April-November 1965 in four areas: inshore Michigan (1-2 km offshore near Ludington), offshore Wisconsin (17-22 km offshore near Sturgeon Bay), and inshore Wisconsin (2-5 km offshore near Sturgeon Bay). Nitrate concentrations inshore near Ludington were about 10% less than the other three areas (data combined). This difference was attributed to the influence of the Pere Marquette River, which enters at Ludington. Statistical comparison of data from the other three areas showed no significant influence of sampling area on nitrate concentrations (Allen, 1973). There were no inshore-offshore differences in nitrate content along the car ferry track between Milwaukee and Ludington (Holland and Beeton, 1972; Rousar, 1973).

Phosphorus

Allen (1973) collected surface-water samples about every two weeks at two inshore stations near Ludington, two stations offshore from Ludington, two stations offshore from Sturgeon Bay, and two stations inshore near Sturgeon Bay from April to November 1965. Average total phosphorus concentration at the inshore Michigan area was higher (9.3 µg PO_4-P/1 *vs.* 6.3 µg PO_4-P/1) than the other three areas; this difference was attributed to the influence of the Pere Marquette River, which enters Lake Michigan at Ludington. Allen indicated that there were no marked differences in phosphorus levels for the other three open-lake areas.

Holland and Beeton (1972) and Rousar (1973) collected water samples along the car ferry track between Milwaukee and Ludington. Average total phosphorus concentrations at the station nearest Milwaukee were highest (14 µg PO_4-P/1) and most variable; the other four stations were lower (8-9 µg PO_4-P/1) and similar. In both reports high values near Milwaukee were attributed to nutrient loading from the Milwaukee metropolitan area and Milwaukee Harbor.

Beeton and Barker (1974) investigated in more detail the effects of Milwaukee and its harbor on inshore-offshore differences in phosphorus concentrations (Figs. 59 and 64). In general, they found a rapid decrease in phosphorus with increasing distance from shore. Evidence of phosphorus entering the Lake from sewer outfalls could generally be traced 1.6-3.2 km (1-2 mi) from shore, and on occasion could readily be found at 6.4-8.0 km (4-5 mi).

Some of the decrease in phosphorus concentrations with distance from shore is due to dilution, some to biological uptake. Wind mixing of bottom sediments may also play a role. Snow (1974) presented data collected at the Chicago South Water Filtration Plant (intake 3048 m, or 10,000 ft offshore) which showed a relationship between total phosphorus concentrations and wind speed, and total phosphorus concentrations and turbidity (Fig. 62). At greater distances from shore, wind mixing is less able to resuspend phosphorus-containing sediments (Figs. 65 and 66) and thus has less effect on total phosphorus concentrations than closer to shore.

Silica

Statistical analysis of raw data on soluble reactive silica concentrations collected by Beeton and Moffett (1964) shows no significant inshore-offshore differences in 1954, 1955, 1960, or 1961. In contrast, the U. S. Department of the Interior (1968) generally found that soluble reactive silica concentrations increased with distance from shore in the southern basin and divide area. Areas of low silica concentrations corresponded to regions of high phytoplankton populations, reflecting the greater abundance of silica-requiring diatoms inshore.

Soluble reactive silica concentrations in surface-water samples collected (Rousar and Beeton, 1973) between lines connecting Milwaukee to Grand Haven and Sturgeon Bay to Frankfort in July 1971 were significantly higher ($P < 0.025$) in offshore waters than inshore. On the car ferry track between Milwaukee and Ludington, both Holland and Beeton (1972) and Rousar (1973) found that surface-water soluble reactive silica concentrations were almost invariably lowest at the station nearest Milwaukee (4.8 km east of shore). Data from the other four stations (one-fourth, one-half, and three-fourths the distance between Milwaukee and Ludington; and 4.8 km west of Ludington) were generally higher and similar. Occasionally, in spring and early summer, concentrations at the station just west of Ludington were less than at the three offshore stations. All three papers (Rousar and Beeton, 1973; Holland and Beeton, 1972; Rousar, 1973) attributed inshore-offshore differences to incorporation of silica by the higher number of diatoms in the nearshore areas.

Soluble reactive silica data collected around Milwaukee by Beeton and Barker (1974) reveal that several factors influence variations in silica concentrations with distance from shore. Figure 70a, based on data collected in June, shows that silica concentrations increased with increasing distance from shore. These increases were more dramatic on the south side of Milwaukee than on the north side. Discharged into the Milwaukee Harbor and directly into the Lake, nutrient materials that stimulate diatoms to grow and utilize soluble reactive silica are generally carried south by the prevailing currents in that area in June (*cf.* U. S. Dep. Inter., 1966a). Since there are fewer sources of available nutrients on the north side of Milwaukee, silica is not lowered so much as on the south side. Nevertheless, both north and south sides of Milwaukee show increasing silica concentrations with distance from shore due to diatom uptake of silica near shore during the warm growing season. In winter, however, silica concentrations decrease with increasing distance from shore (Fig. 70b). In January, diatom growth is minimal; inshore-offshore decreases most nearly represent simple dilution and perhaps diminished effects of resuspension of bottom sediments at greater distances from shore.

Trace Contaminants

Phenols

Since phenolic compounds are unlikely to persist at great distances from the point of entry except during cold weather (Risley and Fuller, 1965), almost all the determinations of phenols in Lake Michigan have been made near the industrial complexes located along the shores of the southern basin. Inshore-offshore decreases in phenol around Chicago and Benton Harbor were evident in 1962-1963 data. Other data, collected along the shore from Calumet Harbor to Michigan City, were grouped in such a way that inshore-offshore differences could not be discerned. Risley and Fuller (1966) looked at the influence of pollutants from the Indiana Harbor on phenol content of the near-shore area of southwestern Lake Michigan. Average phenol concentrations within the Harbor in 1962-1963 were 33 μg/l (range 2.4-127 μg/l), while in the adjacent waters the average was 3.1 μg/l (range 0-72 μg/l).

Phenol levels also dropped rapidly with distance offshore from Milwaukee. The U. S. Department of the Interior (1966a, 1968) collected phenol data around Milwaukee in October 1962 and June 1963. At the mouth of the Milwaukee River phenols were 4-8 μg/l. Within 0.8 km (0.5 mi) phenols had dropped to 2.0-3.9 μg/l, and by 1.6 km (1 mi) east of shore almost all stations had less than 0.5 μg phenols/l.

Since there have been recent reductions in phenol concentrations around the Calumet area of Lake Michigan (Snow, 1974), it is likely that inshore-offshore differences in average phenol concentrations are less noticeable in the southwestern part of the Lake than they were in 1962-1963 (Risley and Fuller, 1965, 1966; U. S. Dep. Inter., 1968). Differences may still be pronounced around Milwaukee if source strengths have not been reduced in the intervening period.

Trace Metals

This volume has pointed out possible inshore-offshore differences in concentrations of several trace metals. Analysis of surface-water total soluble arsenic data, collected by Copeland and Ayers (1972), indicated that inshore concentrations were less than offshore; this difference may be related to similarities in phosphate and arsenate chemistry, leading to greater removal of soluble arsenate by organisms living in inshore areas. Analysis of total soluble selenium data showed that concentrations were higher offshore than inshore; this difference may have been due to similarities in sulfate and selenium chemistry, resulting in greater biological removal of selenite and selenate inshore than offshore.

In samples collected by Risley and Fuller (1966) lead was detected in 100% of the samples taken from Calumet and Indiana Harbors, while it was detected in 72% of samples from the adjacent waters. At least around areas where there are sources of metal pollution, zinc concentrations decrease with increasing distance from shore (Fig. 106). Inshore total soluble mercury concentrations, reported by Copeland and Ayers (1972) were significantly ($P = 0.005$) higher than offshore concentrations.

Edgington and Robbins (1976) cited data collected by the Michigan Department of Natural Resources which found that iron, zinc, copper, and chromium concentrations one mile from the mouth of the Grand and St. Joseph Rivers were markedly higher than ten miles offshore.

Sediments

Hough (1958) described in general terms the distribution of Great Lakes sediments. Four types of sediments were mentioned: gravel, sand, silt, and clay. These four size classifications are arranged in the order of water depth at which they are most frequently found, from gravel (shallowest) to clay (deepest). These depth distributions apparently result from (*i*) fractional settling of suspended particles according to their size and density, (*ii*) prevailing lake currents, and (*iii*) travel distance from shore (Leland *et al.*, 1973b).

In turn, particle sizes within a sediment have a bearing on the chemical composition of that sediment. For example, mercury has not accumulated near the surface of the sandy sediments along the southern and southwestern shores of the southern basin, while there is a surficial enrichment of mercury in the finer sediments farther from shore (Kennedy *et al.*, 1971). This observation is probably related to the fact that coarse sediments, which have a relatively small surface area for sorption, complexation, and ion exchange reactions, settle out in shallow areas; but fine-grained sediments, with a large surface area available for these reactions, are transported to deeper regions of Lake Michigan before they settle out. Leland *et al.* (1973b) reported that organic carbon content in near-shore sands is low (< 0.2 weight %) compared with high values (to *ca.* 5.0 weight %) in the silty clay of the offshore areas of the southern basin. There is also a definite relationship ($r = 0.65$) between < 2 μm clay-size material and organic carbon in southern basin sediments.

On a 40-km (25-mi) transect out of Grand Haven, Robbins and Edgington (1974) investigated inshore-offshore differences in the acid-soluble sediment content of calcium, magnesium, sodium, potassium, zinc, copper, and nickel. They found that certain groups of elements had features in common with respect to their distributions. For example, calcium and magnesium had their highest concentrations closest to shore; these decreased steadily with distance away from shore. Robbins and Edgington speculated that this distribution pattern might result from inshore deposition of biogenic calcareous matter (*e.g.* shell fragments) or of carbonate minerals washed in from the surrounding watershed.

In contrast, acid-soluble sodium and potassium concentrations tended to increase with distance from shore (Robbins and Edgington, 1974). These results were attributed to an increase in the clay content in sediments farther from shore. It was unclear in the original paper whether clay was used as a particle-size or a mineralogic designation, but sodium and potassium are both widely known for their ion-exchange reactions with clay minerals. As a sidelight, since the dominant mechanism for removal from water of Cs^+ is ion-exchange with clays (Robbins and Edgington, 1975a), one could also expect cesium deposition patterns to resemble those of potassium and sodium.

Acid-soluble chromium, zinc, copper, and nickel concentrations in sediments increased with distance from shore (Robbins and Edgington, 1974). The first three metals of this group reached maximal concentrations 19.2-28.8 km (12-18 mi) offshore. Robbins and Edgington (1974) suspected these results were related to sedimentation rates, and therefore deferred further interpretation of their data until information on these rates became available.

LONGITUDINAL DIFFERENCES

Chemical differences in samples collected in the southern basin, divide area, and northern basin are not so well characterized as inshore-offshore differences. Those differences which have been identified are based on comparisons of the southern basin with the divide area, or of the southern basin with the northern basin. Differences between the divide area and the northern basin have not been clearly established.

Conservative Substances

Risley and Fuller (1965) collected water samples along three transects in the southern basin (Calumet Harbor to Michigan City, Chicago to New Buffalo, and Glencoe to Benton Harbor) and along one transect to the divide area (Sheboygan to Little Sable Point) during 1962-1963. Samples were analyzed for conservative substances, nutrients, and pollutants that might be expected as a result of municipal and industrial activities in the watershed.

No clear north-to-south gradients were found in concentrations of alkalinity, specific conductance, potassium, calcium, magnesium, or sulfate (Risley and Fuller, 1965). However, average concentrations of both sodium and chloride decreased between the southern basin and divide area. Higher concentrations of these two ions along the three southern transects are quite likely related to the large human population, numerous industries, and the great areas of streets and highways around the Lake from Glencoe to Benton Harbor which are salted in winter. Lower concentrations of chloride and sodium in the transect from Sheboygan to Little Sable Point were related to the small number of streams and the absence of major waste inputs in that area.

Powers and Ayers (1967) compared sulfate, chloride, and total solids concentrations in samples from the southern basin and divide area. Like Risley and Fuller (1965), they found little if any geographic variations in sulfate content. Powers and Ayers confirmed that chloride levels were higher in the southern part of the Lake, but they considered the north-south gradient to be small. Differences in total solids data between the two areas were not evident.

Non-Conservative Substances

Risley and Fuller (1965) also compared the concentrations of biologically important substances in samples collected in the southern basin and divide area. They found that the average concentration of dissolved O_2 was lowest (9.2 mg/l) in the area south of a line from Calumet Harbor to Michigan City; the range also was greatest there (1.9-12 mg/l). The northernmost samples, collected in the Sheboygan-to-Little Sable Point transect, had the highest average concentration (13 mg/l) and the smallest range (10-15 mg/l). These differences were related to discharges of O_2-demanding wastes into the southern basin, and to dissimilarities in temperatures and depths in the two areas. Risley and Fuller did not indicate specifically when and at what depths samples were collected to make up these averages and ranges. Complementary information on percent O_2 saturation would have helped define these north-south differences more clearly.

This volume has indicated the possibility that BOD decreases, at least at inshore stations along the western shore, between the southern basin and the divide area (*cf.* Fig. 28a-e). Taken as a whole, the BOD data collected by Risley and Fuller (1965) on three transects across the southern basin showed a greater range (0.1-7.7 mg/l) than data collected on the transect between Sheboygan and Little Sable Point (0.6-3.0 mg/l); however, the average values for each of four transects were not appreciably different (1.2-1.6 mg/l).

Several groups (Risley and Fuller, 1965; Powers and Ayers, 1967; Schelske and Callender, 1970) have investigated geographic differences in nitrogen species in Lake Michigan. Risley and Fuller (1965) identified a decrease in ammonia concentrations between the southern basin and the divide area (depths and specific dates of sample collection were not indicated), while nitrate concentrations increased. Higher apparent ammonia concentrations in the southern basin were likely related to choice of sampling stations, near polluted harbors and municipal and industrial waste outfalls. Lower nitrate concentrations in the southern tip of the Lake, compared with the divide area, were attributed to nitrate uptake by phytoplankton, which were more numerous there.

The U. S. Department of the Interior (1968) analyzed samples from all parts of Lake Michigan for ammonia content, but their results are inconclusive with respect to longitudinal differences.

Powers and Ayers (1967) indicated their nitrate data, collected August-October 1962, April-June 1963, and April-November 1964, showed no appreciable concentration gradients along the axis of the Lake. However, the data they presented were averages of samples collected throughout the water column. If surface-water data had been analyzed separately, effects of biological uptake of nitrate in the southern areas of the Lake might have been evident.

Schelske and Callender (1970) analyzed for both ammonia and nitrate in water samples from the southern basin (July 1969) and the northern basin (August 1969). Statistical comparison of their offshore values for surface-water ammonia content demonstrates no difference between the northern and southern basins; however, inclusion of both inshore and offshore surface-water data in the computation shows that ammonia concentrations were significantly less (> 99% confidence level) in the southern basin. Since Schelske and Callender sampled much farther from shore (away from harbors and waste outfalls) than Risley and Fuller did, the lower ammonia concentrations that they reported in the southern basin are probably a result of biological uptake of this nutrient by phytoplankton. Statistical comparison of nitrate concentrations, including both inshore and offshore surface-water data, also shows there was a significant increase (98% confidence level) between the southern and northern basins.

Data presented by Risley and Fuller (1965) indicated a decrease in total phosphorus concentrations between the southern portion of Lake Michigan and the divide area. Again, waste discharges in the Glencoe-to-Benton Harbor area were said to account for these observations. Powers and Ayers (1967) and Schelske and Callender (1970) also measured phosphorus concentrations in the southern basin and divide area, and the southern and northern basins, respectively, but neither drew conclusions on possible north-south variations in their data. Offshore total soluble phosphorus concentration data presented by the U. S. Department of the Interior (1968) were similar in the southern basin, divide area, and northern basin.

There are distinct north-to-south variations in soluble reactive silica concentrations during the diatom growing seasons. Data of Risley and Fuller (1965) demonstrated that surface-water silica concentrations are lower in both spring and summer in the southern basin than in the divide area (no fall data were available for the divide area to allow comparison for that season). A similar north-south variation was found on 9-10 August 1955 (Ayers *et al.*, 1958, cited by Powers and Ayers, 1967). Surface-water concentrations of soluble reactive silica in samples collected in the southern basin (July 1969) were significantly less (> 99% confidence level) than in samples collected in the northern basin (August 1969); Schelske and Callender (1970) attributed this difference to the uptake of soluble reactive silica by diatoms, which are more numerous in the southern basin. Data of the U. S. Department of the Interior (1968) showed an increase in soluble reactive silica values between the southern basin and divide area, but there was no appreciable difference between the divide area and the northern basin.

Other Constituents

Risley and Fuller (1965) analyzed water samples, collected from the southern basin and divide area in 1962-1963, for contaminants that are known to be associated with municipal and industrial activities. Certain north-south gradients were anticipated because of the high degree of industrialization at the southwestern tip of Lake Michigan. Detection of alkyl benzene sulfonates (ABS), which were major constituents of synthetic detergents in the United States until 1965, was presumed to indicate the presence of domestic and commercial laundry wastes. Taken together, ABS data collected on three transects across the southern basin were much more variable (range 0 0.21 mg/l) than samples collected on a transect between Sheboygan and Little Sable Point (range 0.01-0.08 mg/l), but average values for the four transects were similar (0.02-0.05 mg/l).

The presence of phenols in natural waters generally results from industrial pollution. Thus Risley and Fuller (1965) were not surprised to find high concentrations of phenol near shore in the southern part of the Lake. Samples collected south of a line from Calumet Harbor in Michigan City averaged 2.0 μg phenol/l and ranged as high as 115 μg/l. These high levels of phenol were attributed to waste discharges in the heavily industralized area around Calumet and Indiana Harbors. All inshore samples collected north of a line from Calumet Harbor to Michigan City, but south of a line from Glencoe to Benton Harbor, were 4 μg/l or less; they averaged 1 μg/l. Inshore samples near Sheboygan contained 0 to 0.5 μg phenol/l; near Little Sable Point phenol concentrations were 1.0 μg/l.

Oil and grease, which also indicate industrial pollution, averaged 7.5 mg/l in samples collected south of a line from Calumet Harbor to Michigan City in 1962-1963 (Risley and Fuller, 1965); values as high as 240 mg/l were recorded. The average concentration of oil and grease dropped to 1.5 mg/l in samples collected between lines connecting Calumet Harbor to Michigan City and Chicago to New Buffalo. Presumably, oil and grease were present in negligible quantities farther north, since analyses for these contaminants were omitted for more northerly locations.

On occasion, the presence of certain trace metals indicates industrial pollution. Risley and Fuller (1965) were able to detect copper, cadmium, and chromium so infrequently that no comment can be offered on geographic variations of these metals. Lead was detected (as much as 80 μg/l) in 75% of the samples collected south of a line from Calumet Harbor to Michigan City and in 9% of the remaining samples from the southern basin. Lead was less than the 5 μg/l detection limit in all samples collected on the transect from Sheboygan to Little Sable Point. These observations are likely related to industrial activities around the southern tip of the Lake and to the great concentration in that area of automobiles using leaded gasoline.

The frequency with which nickel was detected by Risley and Fuller (1965) apparently increased between the southern basin and the divide area. The significance of this pattern is not known, because all samples recorded as positive for nickel (range 5-6 µg/l) were near the lower limit of detection (5 µg/l) for the analytical method. Zinc was detected in samples from all four transects of the Lake, but north-south variations were not evident.

Sediments

Longitudinal variations of major sedimentary components in the main body of Lake Michigan are considered in this section. Differences in trace constituents between the southern basin and divide area are also known, but these dissimilarities are best considered in terms of characteristics of the Waukegan member (*cf.* Lineback and Gross, 1972) or else in terms of inshore-offshore differences.

Callender (1969) found that the average bulk sediment content of calcium decreased between the southern basin and more northerly areas, while bulk magnesium concentrations were about the same throughout the main portion of the Lake. Likewise, interstitial calcium concentrations decreased between the southern basin and the divide area plus northern basin (Table 42), while interstitial magnesium concentrations may have increased slightly (Table 45). Callender did not indicate whether dissimilarities in the geology of the surrounding watershed or differences in chemical environment within the sediment, causing differences in chemical behavior, accounted for these north-south differences. Surficial bulk carbonate content was about the same throughout the main body of the Lake (Table 17).

Organic carbon content of Lake Michigan sediments is similar in the southern basin and the divide area plus northern basin (Table 20), both surficially and at depth (Callender, 1969). Average total Kjeldahl nitrogen concentrations increased progressively from the southern basin to the divide area to the northern basin, both in surficial and subsurface sediment samples. Average interstitial silica concentrations, both in surficial sediments and sediments at depth, increased 27 to 42%, respectively, between samples collected in the southern basin and more northerly stations.

Bulk iron concentrations varied insignificantly among the geochemical provinces of Lake Michigan (Table 66). Interstitial iron was about the same in sediment samples from the southern basin, divide area, and northern basin, but subsurface interstitial iron concentrations in the southern basin were only one-third those in the northern basin. Bulk manganese concentrations increased 2-3 times between the southern and northern basins (Table 69), a fact Callender (1969) attributed to the proximity of manganese-bearing geologic formations in northern Michigan and Wisconsin. Interstitial manganese concentrations also tripled between the southern and northern basins.

Interstitial sodium concentrations decreased from south to north, both in surface and subsurface sediments; Callender (1969) did not speculate whether this decrease is related to the south-to-north decrease in sodium concentrations in the overlying water (see above). Potassium concentrations in interstitial water decreased from south to north, but not significantly ($P > 0.05$). Chloride concentrations did not vary appreciably in surficial sediments from the main portion of the Lake, but interstitial chloride concentrations in sediments at depth decreased significantly (95% confidence level) between the southern and northern basins.

CHANGES IN WATER QUALITY AND SEDIMENT CHEMISTRY

This volume has been confined to a discussion of data collected during the past two decades, but an exception is now introduced. Data collected for about a century have shown noticeable changes in water quality and sediment characteristics of Lake Michigan. These chemical changes have preceded or accompanied changes in the biota of the Lake, such as alterations in the distribution and abundance of lake herring and whitefish, changes in species composition and abundance of benthic organisms, and increases in abundance and changes in species composition of phytoplankton (Beeton and Edmondson, 1972; Schelske and Stoermer, 1972). Since many of these changes coincided with population and industrial growth in the watershed, the question arises whether these changes in water quality and sediment characteristics are due to human activities.

WATER QUALITY--CONSERVATIVE SUBSTANCES

Total Dissolved Solids

Based on total dissolved solid (TDS) data, Beeton (1965) calculated that TDS content had increased from about 130 mg/l to 150 mg/l from 1895 to 1962 in Lake Michigan. Consideration of additonal data (Beeton, 1969) suggested that TDS content increased between 1877 and 1966 from 128 mg/l to 158 mg/l (Fig. 114). Beeton (1969) indicated that many of the data on which his computations were based had been collected from municipal water intakes, and may be more representative of the inshore zone. Changes in analytical methodology and their effects on observed trends were also considered.

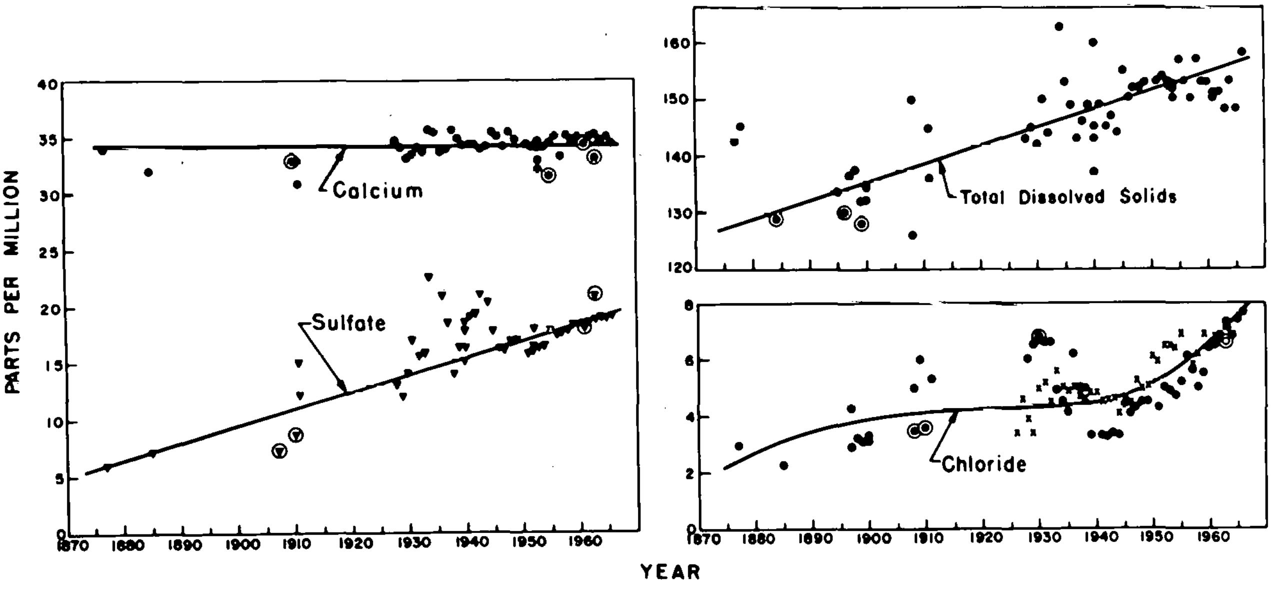

Fig. 114. Changes in the Chemical Characteristics of Lake Michigan over a Period of 90 Years. Data primarily from Milwaukee water intake, 1928-1966; circled points represent open-lake data; crosses represent chloride data from Chicago intake. Slightly modified from Beeton (1969) (with permission, see credits).

Powers and Ayers (1967) plotted statistical regression lines of total solids concentration *vs.* time for data collected at Grand Rapids, Chicago, and Milwaukee public water supply intakes. Chicago data showed a net increase of 14 mg/l (151 to 165 mg/l) from 1895 to 1962; about one-third (5 mg/l) of that increase was recorded between 1926 and 1962. At Milwaukee there was an increase of 7 mg/l (148 to 155 mg/l) from 1939 to 1962. At Grand Rapids the increase was about 15 mg/l (163 to 178 mg/l) from 1941 to 1961. Since open-lake values for total solids concentrations in the early to mid-1960's were similar to those at Chicago and Milwaukee public water intakes, Powers and Ayers (1967) inferred that inshore changes had been paralleled by offshore increases in total solids content.

Increases in TDS content from the 1870's to 1960's, noted by Beeton (1965, 1969), and increases in total solids concentrations, computed by Powers and Ayers (1967), are caused in large part by increased loadings of sulfate and chloride. These increases seem to be continuing into the 1970's (*cf.* Table 4).

Sodium and Potassium

Beeton (1965) concluded that sodium plus potassium concentrations remained constant from 1907 to 1962 in Lake Michigan; however, sodium plus potassium content had increased between 1877 and 1907. Beeton suggested that variations in analytic methods caused the apparent increase between 1877 and 1907. However, it is also possible the increase was related to population growth around Chicago. Considerable amounts of raw sewage were discharged to the Lake from the Chicago area before the Chicago Sanitary Canal was completed in 1900.

Table 38 indicates that potassium content in Lake Michigan water has been constant over the past twenty years. Table 37 suggests that sodium content has been increasing during that same period. Based on the data of Beeton and Moffett (1964), sodium concentrations may have increased as much as 20-25% over the past two decades. Some of this change may be related to increased usage of sodium chloride (*cf.* O'Connor and Mueller, 1970) as a deicing agent on roads and highways, and to industrial and municipal waste discharges.

Calcium and Magnesium

Analysis of magnesium and calcium data from Lake Michigan (Beeton, 1965, 1969; Powers and Ayers, 1967) suggests that no significant changes in calcium (Fig. 114) or magnesium concentrations have occurred over the past century. Powers and Ayers assumed that this lack of change reflects the slight effect that discharge of human wastes has on accumulation of calcium and magnesium in natural bodies of water.

Chloride

Chloride content has been increasing in Lake Michigan water for at least the past century (Ownbey and Willeke, 1965; Beeton, 1965, 1969; Powers and Ayers, 1967; Snow, 1974). Based on data from the Chicago and Milwaukee public water supply intakes, Beeton (1969) estimated that chloride concentrations had increased 6 mg/l (from 2 to 6 mg/l) in the period 1877-1966 (Fig. 114).

The rate of chloride accumulation has not been uniform. Beeton (1969) attributed a decrease in rate in the first decade of the twentieth century to completion of the Chicago Sanitary Canal in 1900. Powers and Ayers (1967) indicated that greater rates of accumulation of chloride in Lake Michigan water since 1948 accounted for increased chloride concentrations at Grand Rapids, Milwaukee, and Chicago.

Ownbey and Willeke (1965) computed that land runoff, perhaps including an appreciable fraction of the salt broadcast on highways for deicing, supplied 42% of the total amount of chloride reaching Lake Michigan in 1965. Industrial sources, including brine wastes from industries in Michigan, added 56%, while municipal inputs contributed less than 2%. They pointed out that removal of chlorides from municipal wastes would have little effect on chloride accumulation in the Lake, but suggested that control of industrial wastes and road salt might be effective.

O'Connor and Mueller (1970) analyzed trends in chloride concentrations in Lake Michigan water and attempted to assess the relative influence of various chloride sources. Their results showed that industrial wastes are and will continue to be the largest sources of chloride.

Sulfate

From 1877 to 1962 sulfate concentrations increased from 6 to 18 mg/l, the greatest increase of any ion in Lake Michigan (Beeton, 1965). Later Beeton (1969) revised this estimate downward to 13 mg/l (Fig. 114). Sulfate concentrations showed an increase from 13.8 to 18.6 mg/l at the Chicago public water supply intake from 1926 to 1962 (Powers and Ayers, 1967) and an increase from 18.9 to 27.8 mg/l at the Grand Rapids public water supply intake from 1941 to 1961. There was no distinct change at Milwaukee. However, a subset of Milwaukee data collected from 1948 to 1962, showed an increase in sulfate concentrations from 16.2 to 18.8 mg/l. The similarities in data on sulfate concentration at the Chicago and Milwaukee public water supply intakes with data collected at offshore stations suggested that inshore increases of sulfate concentrations were also occurring at offshore sites (Powers and Ayers, 1967).

Based on data collected from Chicago's South Water Filtration Plant, Snow (1974) suggested that sulfate concentrations have become constant, or perhaps decreased, since 1967.

Ownbey and Willeke (1965) computed land runoff contributed 40% of the total annual input of sulfate to Lake Michigan, precipitation added an estimated 7%, and the remaining 53% was attributed to municipal and industrial loads. Since natural sources were computed to add 47% of the total influent sulfate, Ownbey and Willeke said that curtailing cultural sources would have a limited effect on reducing the rate of sulfate accumulation.

The concentrations of total dissolved solids, total solids, sodium, chloride, and sulfate have increased in Lake Michigan water. The concentrations of other chemicals may be increasing while these conservative substances are accumulating.

WATER QUALITY--NON-CONSERVATIVE SUBSTANCES

Under natural conditions (over a short period), a lake is assumed to have a steady-state relationship with its surrounding watershed (Stumm and Stumm-Zollinger, 1971). That is,

$$I + P \simeq R + E \text{ ,} \qquad (36)$$

where I and E are the rates of import and export, respectively, of organic matter (or algal nutrients), P represents the rate of production of organic matter by photosynthesis, and R describes the rate of respiratory destruction of organic matter. When $P \simeq R$, photosynthetically produced organic matter is decomposed by respiratory activity and net production is small.

Addition of excess plant nutrients can produce an imbalance between P and R. When $P > (R + E - I)$, there is a progressive accumulation of plant material. If $R > (P + I - E)$, then plant material does not accumulate. Imbalances between P and R are symptoms of enrichment of a Lake with nutrients, or eutrophication.

Beeton (1965, 1969), Powers and Ayers (1967), Schelske and Stoermer (1971), and Beeton and Edmondson (1972) have recorded certain changes in chemical characteristics of Lake Michigan which they have interpreted as symptoms of cultural eutrophication. These symptoms indicate Lake Michigan is no longer in a steady-state, or equilibrium relationship with its watershed.

Dissolved Oxygen

One of the widely accepted indicators of lake eutrophication is hypolimnetic oxygen depletion during thermal stratification. Beeton (1969) said that in Lake Michigan dissolved O_2 is near saturation at all depths throughout the year. U. S. Department of the Interior (1968) data agreed in substance with Beeton (1969). Ayers *et al.* (1967) compared bottom-water dissolved O_2 values determined in autumn 1966 with data collected in autumn 1954, 1955, 1960, and 1961 (Beeton and Moffett, 1964). Ayers *et al.* (1967) suggested there had been a diminution of dissolved O_2 in bottom waters between 1964-1965 and 1966. However, statistical comparison performed by this author did not support this suggestion.

Nitrogen

Of the three forms of inorganic nigrogen discussed in this report (ammonia, nitrite, and nitrate), nitrate has the highest concentrations in Lake Michigan water (*cf*. Tables 22, 23, and 24).

Beeton (1969) found that average annual nitrate concentrations at the Milwaukee water plant declined from about 1936 to 1966, while albuminoid nitrogen (*ca*. total organic nitrogen) increased from 1928 to 1966 (Fig. 115). Beeton considered these changes indicated that a progressively greater amount of inorganic (nitrate) nitrogen was being tied up in the organic (albuminoid) form. One may speculate that photosynthesis, with attendant conversion of inorganic nitrogen to biomass, came to exceed respiration in the surface water from which Milwaukee draws its drinking water. Influx of excessive amounts of organic wastes or nutrients such as nitrogen or phosphorus (Stumm and Stumm-Zollinger, 1971) can cause this type of disturbance. For example, one might hypothesize that increased influx of phosphorus allowed more photosynthesis to take place, leading to enhanced conversion of inorganic nitrogen to albuminoid nitrogen.

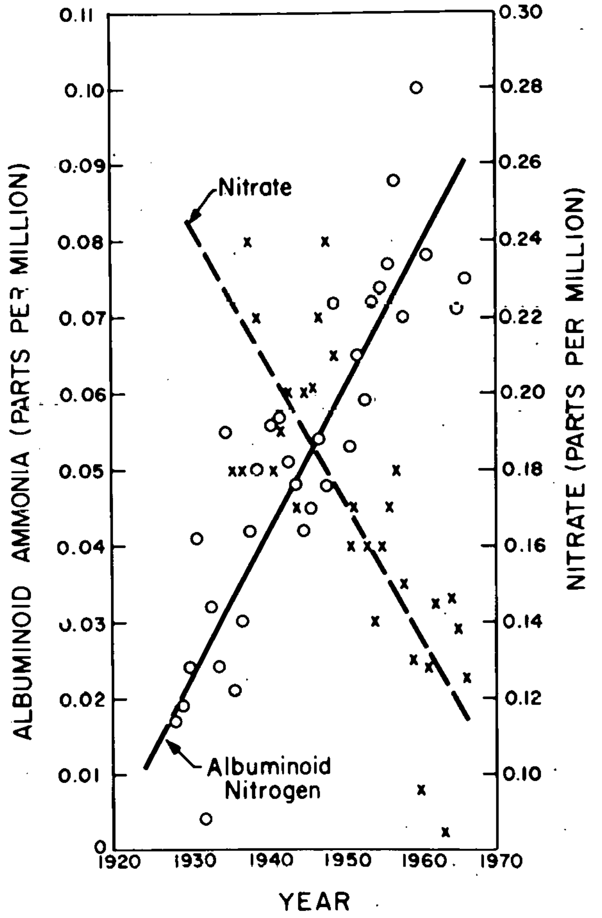

Fig. 115.

Changes in Nitrate-N (x) and Albuminoid Ammonia (o) at Milwaukee Water Intake in Lake Michigan over a Period of 38 Years (Beeton, 1969) (with permission, see credits).

Powers and Ayers (1967) also examined nitrate data collected from the Milwaukee public water intake and calculated that nitrate concentrations had declined from 0.20 to 0.14 mg NO_3^--N/l during the period 1939-1964. Powers and Ayers also calculated an increase (0.10 to 0.17 mg NO_3^--N/l) in nitrate concentration at the Chicago public water intake over the period 1926-1962. However, a subset of data (1955-1962) showed decreasing nitrate levels. Data examined by Powers and Ayers showed considerable variation around the computed regression lines. These authors thought that regressions on this parameter were not meaningful.

Reasons for the discrepancies between the conclusions of Beeton (1969) and Powers and Ayers (1967) on nitrate concentrations are not obvious. Different methods of data analysis, periods of record examined, and choice of data points to be included in regression equations may contribute to the discrepancies.

Phosphorus

Powers and Ayers (1967) said that phosphorus concentrations in samples collected from Chicago public water supply intakes have shown such marked fluctuations that no trends toward increasing or decreasing concentrations were evident. Beeton (1969) also could not find evidence of any change in phosphorus concentrations. He said that the few data available to him did not agree.

Total phosphorus concentrations at Chicago's South Water Filtration Plant increased rapidly in 1966 and 1967, and then decreased in 1968 and 1969 (Vaughn and Reed, 1973). Through 1970, 1971, and the first half of 1972, total phosphorus content increased consistently. A linear regression line fitted to total phosphorus data collected between July 1969 and June 1972 suggested that total phosphorus was increasing at this location at a rate of 5 μg P/l/yr. These changes were attributed to large and continuous inputs of phosphorus to the Lake. Vaughn and Reed (1973) speculated that the temporary drop in 1968-1969 was an indication that at least part of the phosphorus input is controllable.

Snow (1974) analyzed recent total phosphorus data collected at Chicago's South Water Filtration Plant. He indicated there had been a 20% decrease in total phosphorus content in these near-shore waters during 1972-1973. Snow pointed out that, taken by itself, the decrease was perhaps not statistically significant. However, in conjunction with the 40% decrease in phosphorus influx from the Indiana Harbor Canal, Snow considered the decrease in total phosphorus concentrations at the South Water Filtration Plant an encouraging sign that efforts to limit phosphorus inputs were having a beneficial effect in near-shore waters.

Silica

Powers and Ayers (1967) reported decreasing soluble reactive silica concentrations with time at Chicago (1926-1964), Milwaukee (1939-1964), and Grand Rapids (1944-1962) water supply intakes. They suggested that increased biological productivity, leading to increased incorporation of silica into diatom frustules, had resulted in lower concentrations of soluble reactive silica.

Schelske and Stoermer (1972) suggested that increased phosphorus inputs to Lake Michigan have stimulated diatom production. Parker and Edgington (1976--in press) suggested that a greater proportion of the total silica is being retained as biomass, accounting at least in part for reduced soluble reactive silica concentrations in the surface water of the Lake.

SEDIMENT CHARACTERISTICS

Frequently, without qualification, it is assumed that lake sediments are the historical record of what has happened within the lake and its watershed. The problems of interpreting this history are not always appreciated. The sediment record is seldom perfectly legible (*e.g.* Robbins and Edgington, 1976--in press; Robbins *et al.*, 1975b), and natural processes (diagenesis) within the sediment are changing the record continuously. However, some changes in the sediment can be unequivocal indications of alterations in Lake conditions.

Changes Attributable to Human Influences

Changes in the distribution of several elements in Lake Michigan sediment are attributable to human activities in the watershed. In sediment cores from the southern basin and divide area, lead concentrations are highest at the surface; they decrease to a nearly constant concentration at sediment depths corresponding to the early 1800's (Shimp *et al.*, 1970, 1971; Edgington *et al.*, 1974; Robbins and Edgington, 1975a, 1975b; Edgington and Robbins, 1976). Radioactive dating (Robbins and Edgington, 1975a) showed that most of the surface enrichment is associated with the period after 1930, when combustion of leaded automobile fuels became the major source of lead to the environment (Edgington and Robbins, 1976). Coal burning in the Chicago area, starting in the late 1800's, was also reflected by lesser increases in lead content of sediment. Even the conversion from coal to low-lead natural gas in Chicago-area homes and industries in the early 1960's could be identified in lead analyses of sediment cores (Edgington *et al.*, 1974). Since lead is nearly immobile once it is deposited in sediments, the surficial sediment accumulation of lead in Lake Michigan has been ascribed to human activities in the Basin.

A second change is increased surficial mercury content in sediment cores taken from the southern basin (Kennedy *et al.*, 1971; Lineback and Gross, 1972). Similar increases in mercury content in cores from Lakes Erie and Ontario (Kemp *et al.*, 1974) were releated to increased mercury loadings. Like lead, mercury is unlikely to be chemically mobile in Lake Michigan sediments. Mercury enrichment at the sediment surface indicates the influence of human activities on this sediment characteristic.

A third change is the surficial accumulation of chlorinated hydrocarbon insecticides, found in cores from the southern basin (Leland *et al.*, 1973a). Dieldrin, DDT, and DDT degradation products are most concentrated in the upper 2 cm of sediment at the water interface, but these insecticides frequently are detected at depths of 6-12 cm. Since these chlorinated hydrocarbon insecticides are only produced synthetically, their presence reflects the influence of our technological society on the Lake.

A fourth change that probably reflects human influences on the Lake is the surficial enrichment of bromine in sediment cores from the southern basin (Shimp *et al.*, 1970, 1971). This change may be related to the burning of leaded fuels containing ethylene dibromide.

Natural Changes

Not all changes in chemical characteristics with sediment depth are caused by human activities. The chemical behavior of each substance within the sediment must be understood before one can relate measured effects to causes.

Robbins and Callender (1975) showed that surficial sediment enrichment of manganese content in Lake Michigan sediments results entirely from natural processes; steady-state recycling of manganese between oxidized and reduced states accounted for observed changes in manganese forms (solid *vs.* solution) and concentrations with sediment depth.

Leland *et al.* (1973b) indicated that studies by Shimp *et al.* (1970, 1971) had shown that total iron content decreased with increasing sediment depth in Lake Michigan. Leland *et al.* suggested that these observations might be attributable to inorganic chemical properties of iron: reduction of solid ferric iron to soluble ferrous ions within the sediment, upward diffusion of these ions, and subsequent reprecipitation at the sediment surface as ferric oxides/hydroxides. Data available to Leland and coworkers were insufficient to allow verification of this suggestion.

Shimp *et al.* (1971) suggested that surficial copper accumulations (Robbins and Edgington, 1974; Robbins *et al.*, 1972a; Shimp *et al.*, 1970, 1971) in cores from the southern basin were due at least in part to cultural activities in the watershed. Cline and Upchurch (1973), however, showed that copper can accumulate at the surface of a lake sediment by natural processes.

Increases of interstitial soluble reactive silica concentrations with sediment depth, accompanied by decreases in diatom silica and amorphous silica concentrations, have been ascribed to natural processes (Robbins *et al.*, 1975a).

Other Recorded Changes

Callender (1969) proposed that increased organic productivity in Lake Michigan waters accounted for higher surficial sedimentary organic carbon content, while Schleicher and Kuhn (1970) implied that surficial sediment phosphorus accumulations were related to human activities in the Lake Michigan watershed. It is also possible that natural processes (diagenesis) account for these surficial enrichments (Williams and Mayer, 1972; *cf.* Shapiro *et al.*, 1971).

Ruch *et al.* (1970) reported that surficial accumulation of arsenic in sediment cores from the southern basin was a result of human activity in the watershed. Since phosphate and arsenate have similar chemical properties, it is possible that surficial arsenic enrichment is caused by the same chemical processes that produce surficial phosphorus enrichment (Williams and Mayer, 1972).

Shimp *et al.* (1970, 1971) suggested that surficial accumulations of chromium and zinc (*cf.* Edgington *et al.*, 1972a; Robbins *et al.*, 1972a; Robbins and Edgington, 1974) in the southern basin were caused at least in part by cultural activities in the watershed. The sedimentary behavior of these two elements at present is insufficiently known to allow verification of this suggestion.

CONCLUDING REMARKS

Despite the considerable amount of information reviewed in this report, there are still major deficiencies in our understanding of chemicals in Lake Michigan. An analytical approach can be used to reduce these deficiencies. That is, needs for further information can be identified and data collected to satisfy these needs. A second approach, which is complementary to the first, is synthetic. Available data can be assembled into a model, describing one or more dynamic aspects of Lake chemistry, and this model may then be used to predict future trends.

ANALYTICAL RESEARCH NEEDS

The order in which topics are presented in this section is not intended to indicate a priority for establishing research needs.

Analytical Methods

Many techniques used to analyze chemical constituents in Lake Michigan are not adequate for the dilute concentrations present in the Lake. For example, satisfactory techniques for analyzing Lake content of cadmium, chromium, copper, mercury, and nickel have been available only since about 1970. Techniques are not yet adequate for routine analysis of many trace constituents including cobalt, silver, selenium, molybdenum, iodine, bromine, and many of the organochlorine compounds.

The chemical forms of most substances found in Lake Michigan have not been determined, most often due to lack of a suitable analytical technique. Phosphorus and silica concentrations are reported as soluble reactive phosphorus and soluble reactive silica, respectively, because the exact forms in which these chemicals occur are unknown. The forms in which certain chemicals exist can be extremely important to the biota of the Lake; for example, the availability of certain trace nutrients (I^- *vs.* IO_3^-) may be altered. Organic complexes of trace metals may reduce their toxicity (*e.g.* copper-organic complexes) or may maintain them in solution at concentrations higher than predicted from inorganic chemistry (*e.g.* lead concentrations above and below the thermocline in the Lake). Results of experiments designed to identify various forms in which a chemical occurs in the Lake will help clarify biological interactions.

Much less is known about organic substances in Lake Michigan than about inorganic chemicals, partly because concerted efforts have not yet been directed toward developing analytical methods with sufficient sensitivity to identify and quantify dissolved and particulate organic substances which are used as food sources by microorganisms and zooplankton.

Spatial-Temporal Variations

Many of the samples discussed in this report were taken in a seemingly random fashion, with little concern for spatial and/or temporal variations. In all the categories discussed below, information is needed on inshore-offshore dissimilarities, surface- *vs.* bottom-water differences, northern *vs.* southern basin variations, and seasonal trends.

Air-Water Interactions

There is a need for field data, collected in the Lake Michigan Basin, to verify computed estimates of the importance to the Lake of aerosol deposition. Information on chemical forms as well as amounts is needed.

Sediment-Water Interactions

A number of papers have related cultural activities in the Lake Michigan watershed to the composition of suspended matter and surficial bottom sediments. Some of these findings have not yet been confirmed.

Enrichment and depletion of trace constituents in suspended matter are frequently discussed theoretically, but experimental data are needed to demonstrate the relationship between suspended matter and sediment composition. The diagenetic processes in sediments of Lake Michigan also need to be more carefully examined, in order to determine what compounds are enriched in the sediments naturally and which accumulate because of cultural inputs. Careful characterization of sediments, including stratigraphy, is needed in areas other than the southern basin.

Biological Assimilation and Accumulation

Standards, criteria, and objectives have been established for many chemical substances for the protection of Lake Michigan as a drinking water source and as a suitable environment for desirable aquatic life. However, few of these limits have been derived from experiments designed to identify levels of either essentiality or toxicity to organisms living in Lake Michigan. In a number of cases the chemical form which is essential or harmful is not known. Information is needed on the forms and concentrations of chemicals in Lake Michigan to set realistic standards and criteria. Evidence is also needed on possible synergistic interactions of toxic materials in the Lake.

Few studies have attempted to identify biological magnification of chemicals in Lake Michigan, although biological magnification of organochlorine compounds in Lake Michigan fish is known. Additional information on incorporation of chemicals at various trophic levels is needed. Work on organochlorine compounds should be continued and expanded to include other potentially toxic organic compounds.

Nutrients

In light of other changes which have already been observed in the Lake, dissolved oxygen concentrations in bottom waters should be monitored continually to detect incipient changes in trophic state.

Available phosphorus concentrations reportedly limit primary production in Lake Michigan. However, the extent to which phosphorus is limiting is presently unknown; this question cannot be answered without additional information on the rates at which phosphorus is cycled through the Lake. Additional research on these rates is needed, for if phosphorus is recycled into and out of biomass quickly then efforts to limit production by curtailing phosphorus sources may have little effect.

Likewise, information on silica cycling in Lake Michigan is fragmentary. There is information on rates at which silica enters the Lake and rates at which amorphous silica is resolubilized from the sediments to the overlying water. There are indications that grazing of diatoms by zooplankton enhances their dissolution and recycling but this information is preliminary and needs further elaboration. Further information regarding rates of reactions involving silica, diatoms, and bacteria would improve understanding of the silica cycle in Lake Michigan.

NEED FOR WATER RESOURCE MANAGEMENT PLANS

Increasing industrialization and population growth are creating new and expanding demands for uses of Lake Michigan. Present and future water users have two alternatives: (*i*) they can choose to continue the *status quo*, reacting when some detrimental effect can no longer be overlooked (*e.g.* recent regulatory action to reduce phosphorus discharges to limit primary production in the Lake), or (*ii*) they can choose to manage the uses of this valuable resource, for maintenance and enhancement of water quality through water resource management is more desirable than remedial attempts to restore water quality.

Mass Balance Studies

The objective of a mass balance study is to determine the amounts and forms of material entering, leaving, and remaining in Lake Michigan. The forms of materials entering and remaining in the Lake can be especially important to the biota. For example, phosphorus entering in the form of the mineral hydroxyapatite is not readily available to phytoplankton, complexed trace metals may have different toxicities from uncomplexed metals, and pesticides sorbed to particulate matter may be taken up more readily by zooplankton than free pesticides.

Information on forms of materials entering and remaining in Lake Michigan is generally unavailable and needs to be developed. Comprehensive mass balances have been compiled in only a few cases (*e.g.* sulfate and chloride). Further information is needed on the amounts of materials brought in by weathering and erosion, municipal and industrial waste effluents, aerosol deposition, urban and agricultural runoff, and other point and non-point sources.

Models

A mass balance study does not identify what happens to the substances in the Lake, the chemical and biochemical reactions involving these substances, and the effects of these substances on the biota of the Lake. These problems can be at least partially overcome by combining data from a mass balance study with other information into a predictive model.

Variations in conservative substances in Lake Michigan are presently of academic interest, since they have little if any relation to uses of the Lake. However, models based on conservative substances help to identify processes which will be important to models developed to evaluate management strategies that benefit the biota of the Lake.

It is conceivable that a dynamic model of Lake Michigan, involving nutrients, could be developed with little additional data collection, especially if data from the sources tabulated by Beeton and Strand (1975) could be assembled and collated for incorporation. More likely, however, some new sampling programs will need to be designed and executed to identify spatial and temporal variations before a useful nutrient model will become available. More data on mass balances and physical, chemical, and biological processes affecting mass balances will be necessary before most of the trace contaminants in Lake Michigan can be modeled.

ACKNOWLEDGEMENTS

The author expresses appreciation to those staff members in the Division of Environmental Impact Studies, Argonne National Laboratory, who assisted in the preparation of this volume. Credit is given for extensive editorial assistance during all stages of report preparation. This included the laborious task of preparing figures, most of which were composed and redrawn from rough sketches, and of improving the accuracy and format of tables. Any errors of fact and judgement that remain are the responsibility of this author. The author also wishes to acknowledge the cooperation of the Department of Civil and Environmental Engineering, University of Wisconsin--Madison.

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APPENDIX A.
CALCULATION OF THE THEORETICAL DETENTION TIME

Watching the water pass through the Straits of Mackinac gives no clue to the amount of time required for any particular parcel of water, or indeed the entire volume of Lake Michigan, to flow out through the Straits. Because the physical properties of each parcel of water resemble those of the next, we would rapidly run into problems trying to keep track of our chosen parcel of water. All would look the same.

If there is a chemical tracer present, *X* in this case, then there is no need to follow the progress of any parcel of water. Instead, we can monitor the concentration of *X* at the Straits and calculate the detention time of water in Lake Michigan.

We know the rate of change in concentration *C* of *X* with time *t* in a volume *V* of lake water is some function of the rate and concentration of *X* added to the Lake, less the rates of removal, and the concentration of *X* in the Lake. If the Lake itself is perfectly mixed so that the concentration *C* of *X* is everywhere the same, then the change in concentration of *X* with time at the Straits of Mackinac can be described mathematically as:

$$V\frac{dC}{dt} = R_iC_i - R_dC - VR_rC - VR_sC - VR_eC \ , \tag{A.1}$$

where V = Lake volume, km^3,
t = time, yr,
C = concentration of *X* in the Lake water, kg/km^3,
R_i = volume rate of input, km^3/yr,
C_i = concentration of *X* in input, kg/km^3,
R_d = volume rate of discharge, including the Straits of Mackinac and the Chicago diversion, km^3/yr,
R_r = a summary term, representing the rates of all reactions, both chemical and biochemical, which remove *X* from solution in Lake Michigan, yr^{-1},
R_s = a summary term, representing the rates of all reactions which remove *X* from Lake Michigan by sedimentation, yr^{-1},
R_e = a summary term, representing the rates of all reactions that remove *X* from Lake Michigan by evaporation or volatilization, yr^{-1}.

For a conservative substance *X*, R_r and R_s and R_e are all zero and the equation reduces to,

$$\frac{dC}{dt} = R_iC_i - R_dC \ . \tag{A.2}$$

If all inputs of *X* are suddenly stopped (R_i = 0), then the equation becomes,

$$V\frac{dC}{dt} = - R_dC \ . \tag{A.3}$$

5

To calculate the concentration C at any time t after inputs of X ceased at $t = 0$, we can write the integral and set limits:

$$\int_{C_o}^{C} \frac{dC}{C} = - \int_{o}^{t} \frac{R_d}{V}\, dt ,$$

$$t = - \frac{V}{R_d} \ln \frac{C}{C_o} .$$

For our conservative substance X, or for the water in Lake Michigan, we can now compute the amount of time required for the concentration of X to be reduced to half its initial concentration. Using discharge (at the Straits, 42.8 km^3/yr; at Chicago, 2.9 km^3/yr) and volume (4920 km^3) data supplied by Mortimer (1975), we calculate:*

$$t_{\frac{1}{2}} = - \frac{4920\ km^3}{45.7\ km^3/yr} (\ln 0.5) ,$$

or,

$$t_{\frac{1}{2}} = 74.6\ yr.$$

Similarly, the time required for the concentration of X to be reduced to a quarter of its initial value is calculated to be 149.2 yr. In 100 years, $\frac{C}{C_o} = 0.396$.

**Rainey (1967) performed similar calculations, but his mean outflow of 5×10^6 l/sec (= 158 km^3/yr) may be too high.*

APPENDIX B. PART 1.
DRINKING WATER STANDARDS AND CRITERIA

Values expressed in mg/l except turbidity (JTU or TU), color (platinum-cobalt units), threshold odor number (units), and pH (units). Values are maximum permissible concentrations except dissolved oxygen which is minimum permissible concentration. Metal concentrations are designated as total or soluble only where clearly indicated as such in the original source. N.R. inidcates parameter considered but no recommendation offered; hyphen indicates parameter not considered. Ess. absent = essentially absent.

	USPHS Drinking Water Standards 1962		*EPA Int. Prim. Drinking Water Stds. 1975*	*NAS-NAE Water Quality Criteria 1972*	*Drinking Water Standards*			
Parameter	*Recommended*	*Mandatory*			*Illinois*	*Indiana*	*Michigan*	*Wisconsin*
Turbidity	5		1^a	N.R.	5^b	5^b	N.R.	5^b
Color	15		-	75	15^b	15^b	75	15^b
Odor	-		-	Ess. absent	-	-	Ess. absent	-
Threshold odor number	3		-	-	3^b	3	-	3^b
Total dissolved solids (monthly average)	500		-	N.R.	500	750 500	500	750 500
Dissolved O_2 (monthly average)	-		-	N.R.	-	-	≥3 ≥4	
pH range	-		-	5.0-9.0	-	-	6.0-8.5	6.0-9.0
Alkalinity	-		-	N.R.	-	-	a/	-
Ammonia-N	-		-	0.5	-	-	0.5	-
Nitrate-N	10		10	10	10^b	10^b	-	10^b
Nitrite-N	-		-	1	-	-	-	-
Nitrate-N + Nitrite-N	-		-	-	10	-	10	-
Phosphate	-		-	N.R.	-	-	N.R.	-
Sodium	-		-	N.R.	-	-	-	-
Hardness	-		-	N.R.	-	-	-	-
Chloride (monthly average)	250		250	250	250	250^b	 50	250^b
Sulfate	250		-	250	250	250^b	250	250^b
Arsenic	0.01	0.05	0.05			0.01^b	0.05	0.01^b
Arsenic, Total				0.1	0.01			
Barium		1.0	1.0	1.0		1.0^b	1.0	1.0^b
Barium, Total					1.0			
Boron	-		-	N.R.	-	-	1.0	-
Cadmium		0.01	0.01	0.01		0.01^b	0.01	0.01^b
Cadmium, Total					0.01			
Chromium			0.05					
Chromium, Hexavalent		0.05			0.05^b	0.05^b	0.05	0.05^b
Chromium, Total				0.05				
Copper	1.0		-	1.0	1.0^b	1.0^b	1.0	1.0^b
Fluoride	a/		a/	a/	b/	b/	a/	b/
Iron	0.3		-			0.3^b		0.3^b
Iron, Soluble				0.3			0.3	
Iron, Total					0.3			
Lead		0.05	0.05	0.05		0.05^b	0.05	0.05^b
Lead, Total					0.05			
Manganese	0.05		-			0.05^b		0.05^b
Manganese, Soluble				0.05			0.05	
Manganese, Total					0.05			
Mercury	-		0.002		-	-	-	-
Mercury, Total				0.002				

APPENDIX B. PART 1. (contd.)

Parameter	USPHS Drinking Water Standards 1962: Recommended	USPHS Drinking Water Standards 1962: Mandatory	EPA Int. Prim. Drinking Water Stds. 1975	NAS-NAE Water Quality Criteria 1972	Drinking Water Standards: Illinois	Drinking Water Standards: Indiana	Drinking Water Standards: Michigan	Drinking Water Standards: Wisconsin
Selenium		0.01	0.01	0.01	0.01[b]	0.01[b]	0.01	0.01[b]
Silver		0.05	0.05	N.R.	0.05[b]	0.05[b]	0.05	0.05[b]
Uranyl ion	-		-	N.R.	-	-	5.0	-
Zinc	5.0		-	5.0	5.0[b]	5.0[b]	5.0	5.0[b]
Alkyl benzene sulfonates	0.5		-	-	0.5[b]	0.5[b]	-	0.5[b]
Methlyene blue active substances	-		-	0.5	0.5	-	0.5	-
Carbon-chloroform extract	0.2		0.7	0.3	0.2	0.2[b]	0.15	0.2[b]
Carbon-alcohol extract	-		-	1.5	-	-	-	-
Oil (hexane-solubles or equivalent)	-		-	-	0.1	-	-	-
Oil and grease	-		-	Ess. absent	-	-	Ess. absent	-
Cyanide	0.01	0.2	0.2	0.2	0.01	0.01[b]	0.20	0.01[b]
Phenols	0.001		-	0.001	0.001	0.001[b]	0.001	0.001[b]
Aldrin	-		-	0.001	-	-	0.017	-
Chlordane	-		0.003	0.003	-	-	0.003	-
DDT	-		-	0.05	-	-	0.042	-
Dieldrin	-		-	0.001	-	-	0.017	-
Endrin	-		0.0002	0.0005	-	-	0.001	-
Heptachlor	-		0.0001	0.0001	-	-	0.018	-
Heptachlor epoxide	-		0.0001	0.0001	-	-	0.018	-
Lindane	-		0.004	0.005	-	-	0.056	-
Methoxychlor	-		0.1	1.0	-	-	0.035	-
Toxaphene	-		0.005	0.005	-	-	0.005	-
Polychlorinated biphenyls, Total	-		-	N.R.	-	-	-	-
2,4-D	-		0.1	0.02	-	-	-	-
2,4,5-T	-		-	0.002	-	-	-	-
2,4,5-TP (Silvex)	-		0.01	0.03	-	-	-	-
2,4-D + 2,4,5-T + 2,4,5-TP	-		-	-	-	-	0.1	-

---

[a] See text for discussion and clarification.

[b] Value represents recommendation that water should comply with standards of the U. S. Public Health Service, 1962.

Sources: U. S. Public Health Service, 1962; Environmental Protection Agency (U. S.), 1975b; National Academy of Sciences . . ., 1973; Illinois Pollution Control Board, 1974; Indiana Stream Pollution Control Board, 1973; Michigan Water Resources Commission, 1973; Wisconsin Administrative Code, 1973.

APPENDIX B. PART 2.
STANDARDS, CRITERIA AND OBJECTIVES FOR THE PROTECTION OF AQUATIC LIFE IN LAKE MICHIGAN

Values expressed in mg/l except color (platinum-cobalt units), threshold odor number (units), pH (units), and oxygen (mg/l or % saturation). Values are maximum permissible concentrations except dissolved oxygen and alkalinity which are minimum permissible concentrations. Element concentrations are designated as total or soluble only where clearly indicated as such in the original source. N.R. indicates parameter considered but no recommendation offered; hyphen indicates parameter not considered. Subst. absent = substantially absent; Virt. absent = virtually absent.

	NAS-NAE Water Quality Criteria	*U. S.-Canada Great Lakes Water Quality Agreement*	*Water Quality Standards*			
Parameter	*1972*	*1972**	*Illinois*	*Indiana*	*Michigan*	*Wisconsin*
Turbidity (suspended solids)	25[a,b]	c/	c/	c/	c/	-
Color (monthly average)	a/	-	c/	15 5	c/	-
Odor	-	Subst. absent	c/	c/	c/	-
Threshold odor number (daily average)	-	-	-	8 4	-	-
Total dissolved solids (monthly average)	a/	200	180	200 172	750 500	-
Dissolved O_2 (daily average)	a/	6.0	90%	80% 90%	6.0	5.0
pH range	6.5-8.5[e]	6.7-8.5	7.0-9.0	7.5-8.5	6.7-8.5	6.0-9.0
Free CO_2	N.R.	-	-	-	25	-
Alkalinity	a/	-	-	-	-	-
Ammonia-N (monthly average)	0.017	-	0.02	0.05 0.02	-	f/
Nitrate-N + Nitrite-N	-	-	10.0	-	-	-
Phosphorus	-	a/	0.007		-	-
Phosphorus, Total (monthly average)				0.04 0.03		
Hardness	N.R.	-	-	-	-	-
Chloride (monthly average)	-	-	12.0	15 10	-	-
Sulfides, Total	0.002	-	-	-	f/	f/
Sulfate (monthly average)	-	-	24.0	50 26	-	-
Aluminum	N.R.	-	-	-	f/	f/
Arsenic	-	-		0.05	f/	f/
Arsenic, Total			0.01			
Barium	-	-		1.0	f/	f/
Barium, Total			1.0			
Boron	-	-		-	f/	f/
Boron, Total			1.0			
Cadmium	g/	-		0.01	f/	f/
Cadmium, Total			0.01			
Chromium		-			f/	f/
Chromium, Total	0.05					
Chromium, Hexavalent			0.05	0.05		
Chromium, Trivalent			1.0			
Copper	a/	-		-	f/	f/
Copper, Total			0.02			
Fluoride (monthly average)	-	-	1.4	1.0	f/	f/

APPENDIX B. PART 2. (contd.)

Parameter	NAS-NAE Water Quality Criteria 1972	U. S.-Canada Great Lakes Water Quality Agreement 1972*	Water Quality Standards			
			Illinois	Indiana	Michigan	Wisconsin
Iron	-					f/
Iron, Soluble (monthly average)				0.30 0.15	0.3	
Iron, Total		0.3	0.3			
Lead	0.03	-		0.05	f/	f/
Lead, Total			0.05			
Manganese	-	-		-	f/	f/
Manganese, Total			0.05			
Mercury		-			f/	f/
Mercury, Total (average value)	0.0002 0.00005		0.0005	0.005		
Nickel	a/	-		-	f/	f/
Nickel, Total			1.0			
Selenium	-	-		0.01	f/	f/
Selenium, Total			0.01			
Silver	-	-		0.05	f/	f/
Silver, Total			0.005			
Zinc	a/	-	1.0	-	f/	f/
Alkyl benzene sulfonates (daily average)	-	-	-	-	1.0	f/
Methylene blue active substances	-	-	0.5	-	-	-
Linear alkylate sulfonates	0.2	-	-	-	0.2	f/
Carbon-chloroform extract	-	-	0.2	-	-	-
Oil	a,h/	Subst. absent	h/	h/	-	-
Oil (hexane-solubles or equivalent)	a/	-	0.1	-	-	-
Cyanide	0.005	-	0.01	0.01	f/	f/
Phenols (monthly average)	0.1[i]	Subst. absent	0.001	0.003 0.001	Virt. absent	f/
Aldrin	0.00001	-	-	-	f/	f/
Chlordane	0.00004	-	-	-	f/	f/
DDT	0.000002	-	-	-	f/	f/
Dieldrin	0.000005	-	-	-	f/	f/
Endrin	0.000002	-	-	-	f/	f/
Heptachlor	0.00001	-	-	-	f/	f/
Lindane	0.00002	-	-	-	f/	f/
Methoxychlor	0.000005	-	-	-	f/	f/
Toxaphene	0.00001	-	-	-	f/	f/
Polychlorinated biphenyls, Total	0.000002	-	-	-	f/	f/
Other biocides	a/	-	-	-	f/	f/

Although the Treaty between the United States and Canada (U. S. Treaties, etc., 1972) does not apply to Lake Michigan, those objectives are included for comparison.

[a] *See text for discussion and clarification.*

[b] *Maximum concentration of 25 mg/l suspended solids offers a high level of protection.*

[c] *None other than of natural origin.*

[d] *Limit recommended for cold-water streams and oligotrophic lakes.*

APPENDIX B. PART 2. (contd.)

[e] *Nearly maximum level of protection.*

[f] *Permissible levels shall be resolved in accordance with the methods specified in "Water Quality Criteria, Report of the National Technical Advisory Committee to the Secretary of the Interior, April 1, 1968."*

[g] *Aquatic life should be protected in hard water (total hardness = >100 mg/l as* $CaCO_3$*) if cadmium is ≤0.03 mg/l, and in soft water (≤100 mg* $CaCO_3$*/l) if cadmium is ≤0.004 mg/l. Habitats should be safe for crustaceans or eggs and larvae of salmon if cadmium is ≤0.003 mg/l in hard water or ≤0.0004 mg/l in soft water.*

[h] *No visible oil on surface.*

[i] *Applies only to fish.*

Sources: National Academy of Sciences . . .,1973; U. S. Treaties, etc., 1972; Illinois Pollution Control Board, 1974; Indiana Stream Pollution Control Board, 1973; Michigan Water Resources Commission, 1973; Wisconsin Administrative Code, 1973.

APPENDIX C, PART 1.
OXYGEN CONTENT AND SATURATION, 20 SEPTEMBER-2 OCTOBER 1966*

Station	*Water Depth, m*	*Sample Depth*	*Temperature, °C*	*O_2, mg/l*	*O_2, % saturation*
AEC-4	177	Surface	17.2	9.4	102
		5 m off bottom	3.8	10.4	82
AEC-5	171	Surface	13.5	9.5	95
		1 m off bottom	4.7	10.5	84
AEC-6	236	Surface	18.0	9.1	100
		2 m off bottom	4.2	10.9	87
AEC-7	278	Surface	18.5	9.0	100
		8 m off bottom	4.2	10.8	86
A-3	68	0.4 m off bottom	5.5	8.1	67
A-4	135	0.4 m off bottom	4.0	9.8	77
C-3	81	0.4 m off bottom	4.4	10.5	84
C-5	152	0.4 m off bottom	4.4	11.6	92
C-7	54	0.4 m off bottom	6.3	8.3	72
E-5	177	0.4 m off bottom	4.3	10.6	84

*From Ayers *et al.*, 1967.

APPENDIX C, PART 2.
OXYGEN CONTENT AND SATURATION, MID-SEPTEMBER TO MID-OCTOBER, 1954-55 AND 1960-61*

Station	*Water Depth m*	*Inshore or Offshore*	*Sample Depth, m*	*Temperature, °C*	*O_2, mg/l*	*O_2, % saturation*
1954						
13	73	I	70	4.1	10.5	83
12	91	0	90.6	4.4	10.8	86
11	73	0	70	4.3	9.0	73
14	75	0	70	4.4	10.6	85
15	157	0	156.7	3.8	11.0	86
19	73	0	70	4.8	9.9	80
18	128	0	bottom	4.1	10.9	87
17	73	0	70	4.7	9.7	78
13	73	I	70	4.4	10.0	80
12	91	0	90.6	4.2	11.3	90
11	73	0	70	4.3	10.9	87
1	73	I	70	4.3	11.4	91
2	146	0	bottom	3.9	12.0	95
3	73	I	70	4.4	11.3	90
1955						
34	73	I	70	3.8	10.9	86
33	265	0	250	3.75	11.7	92
32	73	I	70	5.0	11.0	94
1	73	I	70	4.7	11.2	90
2	146	0	135	3.9	10.7	83
3	73	I	70	3.95	11.2	88
1960						
12d	128	0	125	4.1	9.7	76
1961						
8f	73	I	70	4.5	10.8	86
8g	260	0	251	3.65	10.5	82
7d	73	I	70	6.6	10.6	90
8f	72	I	70	3.9	9.7	76

*Data (except % saturation) from Beeton and Moffett, 1964. Percent saturation data in part from Ayers *et al.*, 1967. This author corrected and expanded the data from Ayers *et al.*, 1967, based on the data of Beeton and Moffett, 1964.*

CREDITS

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	Beeton, A. M., and J. M. Barker. 1974. *Investigation of the influence of thermal discharge from a large electric power station on the biology and near-shore circulation of Lake Michigan - Part A: Biology.* Univ. Wisconsin--Milwaukee, Center for Great Lakes Studies Spec. Rep. 18. Figures 21, 22, 52, 59, 64, and 94 reproduced with permission of University of Wisconsin--Milwaukee, Center for Great Lakes Studies.
21	(*Fig. 30*)
22	(*Fig. 38*)
52a	(*Fig. 41*)
52b	(*Fig. 61*)
59	(*Fig. 64*)
64	(*Fig. 63*)
94a	(*Fig. 31*)

Figure	
94b	(*Fig. 39*)
94c	(*Fig. 46*)
94d	(*Fig. 67*)
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114	p. 158 (*Fig. 4*)
115	p. 159 (*Fig. 5*)

REFERENCES CITED

Unpublished references and personal communications are indicated by an asterisk (*).

Ahmed, M., and D. D. Focht. 1973. *Degradation of polychlorinated biphenyls by two species of Achromobacter.* Can. J. Microbiol. 19:47-52.

Ahrnsbrak, W. F. 1971. *A diffusion model for Green Bay, Lake Michigan.* Ph.D. Thesis. Univ. Wisconsin--Madison. 105 pp.

__________, and R. A. Ragotzkie. 1970. *Mixing processes in Green Bay.* Proc. 13th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 880-890.

Alexander, G. B., W. M. Heston, and H. K. Iler. 1954. *The solubility of amorphous silica in water.* J. Phys. Chem. 58:453-455.

Allen, H. E. 1973. *Seasonal variation of nitrogen, phosphorus, and chlorophyll a in Lake Michigan and Green Bay, 1965.* U. S. Bur. Sport Fish. Wildl. Tech. Pap. 70. 23 pp.

__________, W. R. Matson, and K. H. Mancy. 1970. *Trace metal characterization in aquatic environments by anodic stripping voltammetry.* J. Water Pollut. Control Fed. 42:573-581.

Allen, M. B., and D. I. Arnon. 1955. *Studies on nitrogen-fixing blue-green algae. I. Growth and nitrogen fixation by Anabaena cylindrica Lemm.* Plant Physiol. 30:366-372.

American Heart Association. 1957. *Your 500 milligram sodium diet.* New York (pamphlet). (As cited by Terry, 1974).

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. 1971. *Standard methods for the examination of water and wastewater.* 13th ed. Am. Public Health Assoc., Washington, D. C. 874 pp.

Anderson, B. G. 1948. *The apparent thresholds of toxicity to Daphnia magna for chlorides of various metals when added to Lake Erie water.* Trans. Am. Fish. Soc. 78:96-113.

Andren, A. W., and R. C. Harriss. 1975. *Observations on the association between mercury and organic matter dissolved in natural waters.* Geochim. Cosmochim. Acta 39:1253-1257.

Angino, E. E., L. M. Magnuson, T. C. Waugh, O. K. Calle, and J. Bredfeldt. 1970. *Arsenic in detergents.* Science 168:389-390.

Anonymous. 1975. *Effect of trace metals on sea lions probed.* Chem. Eng. News 53(46):34.

Antia, N. J., C. D. McAllister, T. R. Parsons, K. Stephens, and J. D. H. Strickland. 1963. *Further measurements of primary production using a large-volume plastic sphere.* Limnol. Oceanogr. 8:166-183.

Arnon, D. I. 1958. *The role of micronutrients in plant nutrition with special reference to photosynthesis and nitrogen assimilation.* In: C. A. Lamb, O. G. Bentley, and J. M. Beattie (eds.), *Trace elements.* Academic Press, New York. pp. 1-32.

__________, and G. Wessel. 1953. *Vanadium as an essential element for green plants.* Nature 172:1039-1040.

Ayers, J. C. 1962. *Great Lakes waters, their circulation and physical and chemical characteristics.* In: *Great Lakes basin.* Am. Assoc. Adv. Sci. Publ. 71:71-89.

__________. 1970. *Lake Michigan environmental survey.* Univ. Michigan, Great Lakes Res. Div. Spec. Rep. 49. 14 pp.

__________, D. C. Chandler, G. H. Lauff, C. F. Powers, and E. B. Henson. 1958. *Currents and water masses of Lake Michigan.* Univ. Michigan, Great Lakes Res. Div. Publ. No. 3. 169 pp. (As cited by Powers and Ayers, 1967).

__________, E. F. Stoermer, and P. McWilliam. 1967. *Recently noticed changes in the biology-chemistry of Lake Michigan.* In: J. C. Ayers and D. C. Chandler (eds.), *Studies on the environment and eutrophication of Lake Michigan.* Univ. Michigan, Great Lakes Res. Div. Spec. Rep. 30. pp. 95-111.

Azam, F., B. B. Hemmingsen, and B. E. Volcani. 1974. *Role of silicon in diatom metabolism. V. Silicic acid transport and metabolism in the heterotrophic diatom Nitzschia alba.* Arch. Microbiol. 97:103-114.

Baird, R. B., S. Pourian, and S. M. Gabrielian. 1972. *Determination of trace amounts of selenium in wastewaters by carbon rod atomization.* Anal. Chem. 44:1887-1889.

Balch, R. F., K. M. Mackenthun, W. M. Van Horn, and T. F. Wisniewski. 1956. *Biological studies of the Fox River and Green Bay.* Wis. Comm. Water Pollut. Bull. WP102 (mimeo). 74 pp.

Bandurski, R. S. 1965. *Biological reduction of sulfate and nitrate.* In: J. Bonner and J. E. Varner (eds.), *Plant biochemistry.* Academic Press, New York. pp. 467-490.

Baumeister, R. 1972. *Chemical analyses of selected public drinking water supplies (including trace metals).* Wis. Dep. Nat. Resour. Tech. Bull. No. 53. 16 pp.

__________. 1973. Personal communication (Wisconsin Department of Natural Resources, Madison).

Beeton, A. M. 1962. *Light penetration in the Great Lakes.* Proc. 5th Conf. Great Lakes Res., Great Lakes Res. Div. Publ. No. 9, Univ. Michigan. pp. 68-76.

__________. 1965. *Eutrophication of the St. Lawrence Great Lakes.* Limnol. Oceanogr. 10:240-254.

__________. 1969. *Changes in the environment and biota of the Great Lakes.* In: *Eutrophication: causes, consequences, correctives.* National Academy of Sciences, Washington, D. C. pp. 150-187.

__________, and J. W. Moffett. 1964. *Lake Michigan chemical data, 1954-55, 1960-61.* U. S. Fish Wildl. Serv. Data Rep. No. 6. 102 pp.

__________, and W. T. Edmondson. 1972. *The eutrophication problem.* J. Fish. Res. Board Can. 29:673-682.

__________, and J. M. Barker. 1974. *Investigation of the influence of thermal discharge from a large electric power station on the biology and near-shore circulation of Lake Michigan - Part A: Biology.* Univ. Wisconsin--Milwaukee, Center for Great Lakes Studies Spec. Rep. 18. 140 pp.

__________, and J. W. Strand. 1975. *Sources of water quality, lake level, ice, water temperature and meteorological data for the St. Lawrence Great Lakes.* Univ. Wisconsin--Madison Sea Grant College Program Advisory Rep. No. 10. 189 pp.

Bingham, F. T. 1973. *Boron in cultivated soils and irrigation waters.* In: E. L. Kothny (ed.), *Trace elements in the environment.* Adv. Chem. Ser. 123:130-138.

Black, J. J., and C. L. Simpson. 1974. *Thyroid enlargement in Lake Erie coho salmon.* J. Natl. Cancer Inst. 53:725-729.

Bond, G. 1967. *Fixation of nitrogen by higher plants other than legumes.* Annu. Rev. Plant Physiol. 18:107-126.

Bortels, H. 1940. *Über die Bedeutung die Molybdäns für stickstoffbindende Nostocaceen.* Arch. Mikrobiol. 11:155-186.

Bowen, H. J. M. 1966. *Trace elements in biochemistry.* Academic Press, New York. 241 pp.

Braman, R. S., and C. C. Foreback. 1973. *Methylated forms of arsenic in the environment.* Science 182:1247-1249.

Brungs, W. A. 1969. *Chronic toxicity of zinc to the fathead minnow, Pimephales promelas Rafinesque.* Trans. Am. Fish. Soc. 98:272-279.

Burdick, G. E., E. J. Harris, H. J. Dean, T. M. Walker, J. Skea, and D. Colby. 1964. *The accumulation of DDT in lake trout and the effect on reproduction.* Trans. Am. Fish. Soc. 93:127-136.

Burton, J. D., T. M. Leatherland, and P. S. Liss. 1970. *The reactivity of dissolved silicon in some natural waters.* Limnol. Oceanogr. 15:473-476.

Burttschell, R. H., A. A. Rosen, F. M. Middleton, and M. B. Ettinger. 1959. *Chlorine derivatives of phenol causing taste and odor.* J. Am. Water Works Assoc. 51:205-214.

Businessmen for the Public Interest. 1972. *Lake Michigan major industrial polluter inventory.* Chicago, Ill. 14 pp.

Callender, E. 1969. *Geochemical characteristics of Lakes Michigan and Superior sediments.* Proc. 12th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 124-160.

Canale, R. P. 1973. *Model of coliform bacteria in Grand Traverse Bay.* J. Water Pollut. Control Fed. 45:2358-2371.

__________, and A. W. Green, Jr. 1972. *Modeling the spatial distribution of coliforms in Grand Traverse Bay.* Proc. 15th Conf. Great Lakes Res., Int Assoc. Great Lakes Res. pp. 719-728.

__________, S. Nachiappan, D. J. Hineman, and H. E. Allen. 1973a. *A dynamic model for phytoplankton production in Grand Traverse Bay.* Proc. 16th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 21-33.

__________, R. L. Patterson, J. J. Gannon, and W. F. Powers. 1973b. *Water quality models for total coliform bacteria in Grand Traverse Bay.* J. Water Pollut. Control Fed. 45:325-336.

Chau, Y. K., and H. Saitoh. 1973. *Mercury in the international Great Lakes.* Proc. 16th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 221-232.

Cline, J. T., and S. B. Upchurch. 1973. *Mode of heavy metal migration in the upper strata of lake sediment.* Proc. 16th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 349-356.

Cohen, J. M., and C. Pinkerton. 1966. *Widespread translocation of pesticides by air transport and rain-out.* In: *Organic pesticides in the environment.* Adv. Chem. Ser. 60:163-176.

Coleman, R. G., and M. Delevaux. 1957. *Occurrence of selenium in sulfides from some sedimentary rocks of the western United States.* Econ. Geol. 52:499-527.

Conn, E. E., and P. K. Stumpf. 1966. *Outlines in biochemistry.* 2nd ed. John Wiley & Sons, Inc., New York. 468 pp.

Cooper, C. F., and W. C. Jolly. 1970. *Ecological effects of silver iodide and other weather modification agents: a review.* Water Resour. Res. 6:88-98.

Copeland, R. A., and J. C. Ayers. 1972. *Trace element distributions in water, sediment, phytoplankton, zooplankton and benthos of Lake Michigan: a baseline study with calculations of concentration factors and buildup of radioisotopes in the food web.* Environmental Research Group, Ann Arbor, Mich. ERG Spec. Rep. No. 1. 271 pp.

Corner, E. D. S. 1973. *Phosphorus in marine zooplankton.* Water Res. 7:93-110.

Crecelius, E. A. 1975. *The geochemical cycle of arsenic in Lake Washington and its relation to other elements.* Limnol. Oceanogr. 20:441-451.

Csanady, G. T. 1975. *Physical limnology of Lake Michigan. Part 2, Diffusion and dispersion.* Environmental status of the Lake Michigan region, Vol. 2. Argonne National Laboratory ANL/ES-40. pp. 103-121.

Danckwerts, P. V. 1970. *Gas-liquid reactions.* McGraw-Hill Book Co., New York. 276 pp.

Degens, E. T. 1970. *Molecular nature of nitrogenous compounds in sea water and recent marine sediments.* In: D. W. Hood (ed.), *Symposium on organic matter in natural waters.* Univ. Alaska, Inst. Mar. Sci. Occas. Publ. No. 1. pp. 77-106.

Devey, D. G., and N. Harkness. 1973. *The significance of man-made sources of phosphorus: detergents and sewage.* Water Res. 7:35-54.

Diénert, F., and F. Wandenbulcke. 1923. *Sur la dosage de silice dans les eaux.* C. R. Acad. Sci. Paris 176:1478-1480.

Dixon, N. E., C. Gazzola, R. L. Blakeley, and B. Zerner. 1975. *Jack bean urease (EC 3.5.1.5). A metalloenzyme. A simple biological role for nickel?* J. Am. Chem. Soc. 97:4131-4133.

Doudoroff, P., G. Leduc, and C. R. Schneider. 1966. *Acute toxicity to fish of solutions containing complex metal cyanides, in relation to concentrations of molecular hydrocyanic acid.* Trans. Am. Fish. Soc. 95:6-22.

Downing, A. L., and G. A. Truesdale. 1955. *Some factors affecting the rate of solution of oxygen in water.* J. Appl. Chem. 5:570-581.

Drongowski, R. 1972. *Thyroid and LDH activity in coho salmon from West Coast and Lake Michigan regions.* M.S. Thesis. Western Michigan Univ. (As cited by Black and Simpson, 1974).

Dugger, W. M. 1973. *Functional aspects of boron in plants.* In: E. L. Kothny (ed.), *Trace elements in the environment.* Adv. Chem. Ser. 123:112-129.

Durum, W. H., J. D. Hem, and S. G. Heidel. 1971. *Reconnaissance of selected minor elements in surface waters of the United States, October 1970.* U. S. Geol. Surv. Circ. No. 643. 49 pp.

Edgington, D. N., and E. Callender. 1970. *Minor element geochemistry of Lake Michigan ferromanganese nodules.* Earth Planet. Sci. Lett. 8:97-100.

___________, and H. F. Lucas, Jr. 1971. *A semi-automatic method of neutron activation analysis with application to environmental studies.* In: *Nuclear techniques in environmental pollution.* International Atomic Energy Agency, Vienna. pp. 311-322.

___________, M. M. Thommes, and E. Callender. 1972a. *Studies of recent sedimentation in Green Bay.* Radiol. Physics Div. Annu. Rep., Environmental Research, January-December 1971, Argonne National Laboratory Rep. ANL-7860, Part III. pp. 64-76.

__________, M. A. Wahlgren, E. Callender, and J. A. Robbins. 1972b. *The environmental intercalibration/intercomparison program.* Radiol. Physics Div. Annu. Rep., Environmental Research, January-December 1971, Argonne National Laboratory Rep. ANL-7860, Part III. pp. 77-79.

__________, J. A. Robbins, and J. O. Karttunen. 1974. *The distribution of* ^{210}*Pb and stable lead in Lake Michigan sediments.* Radiol. Environ. Res. Div. Annu. Rep., Ecology, January-December 1973, Argonne National Laboratory Rep. ANL-8060, Part III. pp. 63-76.

__________, and J. A. Robbins. 1976. *Records of lead deposition in Lake Michigan sediments since 1800.* Environ. Sci. Technol. 10:266-274.

Elliott, G. H., and J. A. Elliott. 1969. *Small-scale model of the "thermal bar."* Proc. 12th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 553-557.

Emerson, S., W. Broecker, and D. W. Schindler. 1973. *Gas-exchange rates in a small lake as determined by the radon method.* J. Fish. Res. Board Can. 30:1475-1484.

Environmental Protection Agency (U. S.). 1971. *Algal assay procedure bottle test.* National Environmental Research Center, Corvallis, Ore. 82 pp.

__________. 1973. *Water programs: guidelines establishing test procedures for analysis of pollutants.* Fed. Regist. 38(199):28758-28760.

__________. 1975a. *Process design manual for suspended solids removal.* Rep. No. EPA 625/1-75-003a. Technology Transfer Office, Washington, D. C. 1 vol.

__________. 1975b. *Interim primary drinking water standards.* Fed. Regist. 40(51):11990-11998.

Epstein, E., M. Bryans, D. Mezei, and D. Patterson. 1974. *Lower Green Bay: an evaluation of existing and historical conditions.* U. S. Environmental Protection Agency Region V Enforcement Div., Great Lakes Initiative Contract Program Rep. No. EPA-905/9-74-006. 281 pp.

Evans, H. T., Jr., and R. M. Garrels. 1958. *Thermodynamic equilibria of vanadium in aqueous systems as applied to the interpretation of the Colorado Plateau ore deposits.* Geochim. Cosmochim. Acta 15:131-149.

Eyster, H. C., T. E. Brown, and H. A. Tanner. 1958. *Mineral requirements for Chlorella pyrenoidosa under autotrophic and heterotrophic conditions.* In: C. A. Lamb, O. G. Bentley, and J. M. Beattie (eds.), *Trace elements.* Academic Press, New York. pp. 157-174.

Fair, G. M., J. C. Geyer, and D. A. Okun. 1968. *Water and wastewater engineering. Vol. 2. Water purification and wastewater treatment and disposal.* John Wiley & Sons, Inc., New York. Chap. 20, p. 17.

Fanning, K. A., and M. E. Q. Pilson. 1974. *The diffusion of dissolved silica out of deep-sea sediments.* J. Geophys. Res. 79:1293-1297.

Ferguson, J., and B. Bubela. 1974. *The concentration of Cu(II), Pb(II) and An(II) from aqueous solutions by particulate algal matter*. Chem. Geol. 13:163-186.

Ferguson, J. F., and J. Gavis. 1972. *A review of the arsenic cycle in natural waters*. Water Res. 6:1259-1274.

Ferrante, J. G., J. I. Parker, and J. S. Marshall. 1975. *Role of copepod fecal pellets in the vertical transport of freshwater diatoms*. Radiol. Environ. Res. Div. Annu. Rep., Ecology, January-December 1974, Argonne National Laboratory Rep. ANL-75-3, Part III. pp. 1-8.

__________, and J. I. Parker. 1976. *Transport of diatom frustules by copepod fecal pellets to the sediments of Lake Michigan*. Limnol. Oceanogr. (in press).

Fisher, D. J. 1973. *Geochemistry of minerals containing phosphorus*. In: E. J. Griffith, A. Beeton, J. M. Spencer, and D. T. Mitchell (eds.), *Environmental phosphorus handbook*. John Wiley & Sons, Inc., New York. pp. 141-152.

Fitzgerald, G. P., M. S. Torrey, and G. C. Gerloff. 1975. *Green Bay self-purifies algal nutrients*. Water Sewage Works 122(6):58-61.

Fogg, G. E. 1973. *Phosphorus in primary aquatic plants*. Water Res. 7:77-91.

__________, and D. F. Westlake. 1955. *The importance of extracellular products of algae in freshwater*. Verh. int. Ver. Limnol. 12:219-232.

Forsberg, C., D. Jinnerot, and L. Davidson. 1967. *The influence of synthetic detergents on the growth of algae*. Vatten 23:2-16.

Foster, R. F. 1963. *Environmental behavior of chromium and neptunium*. In: V. Schultz and A. W. Klement, Jr. (eds.), *Radioecology*. Reinhold Publishing Co., New York. pp. 569-576.

Friberg, L., M. Piscator, and G. Nordberg. 1971. *Cadmium in the environment: a toxicological and epidemiological appraisal*. Rep. No. APTD-0681, Access No. PB 199 795, NTIS, Springfield, Va. 53 pp.

Frye, J. C., and N. F. Shimp. 1973. *Major, minor and trace elements in sediments of Late Pleistocene Lake Saline compared with those in Lake Michigan sediments*. Ill. State Geol. Surv. Environ. Geol. Notes No. 60. 14 pp.

Gardiner, J. 1974a. *The chemistry of cadmium in natural water--I. A study of cadmium complex formation using the cadmium specific-ion electrode*. Water Res. 8:23-30.

__________. 1974b. *The chemistry of cadmium in natural water--II. The adsorption of cadmium on river muds and naturally occurring solids*. Water Res. 8:157-164.

Garrels, R. M., and C. L. Christ. 1965. *Solutions, minerals, and equilibria*. Harper & Row, New York 450 pp.

Gast, J. A., and T. G. Thompson. 1958. *Determination of the alkalinity and borate concentration of sea water.* Anal. Chem. 30:1549-1551.

Gatz, D. F. 1975. *Background silver concentrations in Illinois precipitation and river water.* J. Appl. Meteorol. 14:217-221.

__________, R. F. Selman, R. K. Langs, and R. B. Holtzman. 1970. *Automatic sequential rain sampler for scavenging studies.* In: *Precipitation scavenging (1970).* U. S. Atomic Energy Commission, Div. Tech. Inf., CONF-700601, NTIS, Springfield, Va. pp. 239-244.

Gavis, J., and J. F. Ferguson. 1972. *The cycling of mercury through the environment.* Water Res. 6:989-1008.

Gerloff, G. C. 1968. *The comparative boron nutrition of several green and blue-green algae.* Physiol. Plant. 21:369-377.

__________, G. P. Fitzgerald, and F. Skoog. 1950. *The mineral nutrition of Coccochloris peniocystis.* Am. J. Bot. 37:835-840.

__________, G. P. Fitzgerald, and F. Skoog. 1952. *The mineral nutrition of Microcystis aeruginosa.* Am. J. Bot. 39:26-32.

Gibbs, R. J. 1973. *Mechanisms of trace metal transport in rivers.* Science 180:71-73.

Gillette, D. A. 1972. *A study of aging of lead aerosols--II: a numerical model simulating coagulation and sedimentation of a lead aerosol in the presence of an unleaded background aerosol.* Atmos. Environ. 6:451-462.

__________, and J. W. Winchester. 1972. *A study of aging of lead aerosols--I: observations.* Atmos. Environ. 6:443-450.

Goldberg, E. D. 1965. *Minor elements in sea water.* In: J. P. Riley and G. Skirrow (eds.), *Chemical oceanography.* Vol. 1. Academic Press, New York. pp. 163-196.

Goldschmidt, V. M. 1954. *Geochemistry.* Clarendon Press, Oxford, Eng. 730 pp.

Goryunova, S. V., and T. U. Maksudov. 1971. *Cobalt requirements of certain nitrogen-fixing blue-green algae.* Mikrobiologiya 40:297-304.

Green, A. W. 1972. *Water circulation modeling.* Univ. Michigan Sea Grant Program Annu. Rep. 1971-1972. p. 26.

Guillard, R. R. L., P. Kilham, and T. A. Jackson. 1973. *Kinetics of silicon-limited growth in the marine diatom Thalassiosira pseudonana Hasle and Heimdal (= Cyclotella nana Hustedt).* J. Phycol. 9:233-237.

Hambidge, K. M. 1971. *Chromium nutrition in the mother and the growing child.* In: W. Mertz and W. E. Cornatzer (eds.), *Newer trace elements in nutrition.* Marcel Dekker, Inc., New York. pp. 169-194.

Harder, H., and W. Flehmig. 1970. *Quarzsynthese bei tiefen Temperaturen.* Geochim. Cosmochim. Acta 34:295-305.

Hatcher, R. F., and B. C. Parker. 1974. *Microbiological and chemical enrichment of freshwater-surface microlayers relative to the bulk-subsurface water.* Can. J. Microbiol. 20:1051-1057.

Healey, F. P. 1973. *Inorganic nutrient uptake and deficiency in algae.* CRC Crit. Rev. Microbiol. 3:69-113.

Hellebust, J. A. 1965. *Excretion of some organic compounds by marine phytoplankton.* Limnol. Oceanogr. 10:192-216.

Hem, J. D. 1959. *Study and interpretation of the chemical characteristics of natural waters.* U. S. Geol. Surv. Water-Supply Pap. 1473. 269 pp.

__________. 1972. *Chemistry and occurrence of cadmium and zinc in surface water and groundwater.* Water Resour. Res. 8:661-679.

Hemphill, D. D. 1972. *Availability of trace elements to plants with respect to soil-plant interaction.* Ann. N. Y. Acad. Sci. 199:46-61.

Herbes, S. E., H. E. Allen, and K. H. Mancy. 1975. *Enzymatic characterization of soluble organic phosphorus in lake water.* Science 187:432-434.

Hoglund, B., and S. A. Spigarelli. 1972. *Studies of the sinking plume phenomenon.* Proc. 15th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 614-624.

*Holland, D. 1975. Personal communication (Public Water Department, City of Kenosha, Wis.).

Holland, R. E. 1969. *Seasonal fluctuations of Lake Michigan diatoms.* Limnol. Oceanogr. 14:423-436.

__________, and A. M. Beeton. 1972. *Significance to eutrophication of spatial differences in nutrients and diatoms in Lake Michigan.* Limnol. Oceanogr. 17:88-96.

Hooper, F. F. 1973. *Origin and fate of organic phosphorus compounds in aquatic systems.* In: E. J. Griffith, A. Beeton, J. M. Spencer, and D. T. Mitchell (eds.), *Environmental phosphorus handbook.* John Wiley & Sons, Inc., New York. pp. 179-201.

Hoover, T. E., and D. C. Berkshire. 1969. *Effects of hydration on carbon dioxide exchange across an air-water interface.* J. Geophys. Res. 74:456-464.

Hopkins, L. L., Jr., and H. E. Mohr. 1974. *Vanadium as an essential nutrient.* Fed. Proc. 33:1773-1775.

Hough, J. L. 1958. *Geology of the Great Lakes.* University of Illinois Press, Urbana. 313 pp.

*Howe, P. H. 1973. Personal communication (Commonwealth Edison, P. O. Box 767, Chicago, Illinois).

Howmiller, R. P. 1974. *Appendix A: A review of selected research on the biology and sediments of southern Lake Michigan with particular reference to the Calumet area.* In: R. H. Snow, *Water pollution investigation: Calumet area of Lake Michigan.* Vol. 2. U. S. Environmental Protection Agency Region V Enforcement Div., Great Lakes Initiative Contract Program Rep. No. EPA-905/9-74-011-A. NTIS, Springfield, Va. pp. A/1-A/77.

__________, and A. M. Beeton. 1972. *Report on a cruise of the R/V Neeskay in central Lake Michigan and Green Bay, 8-14 July 1971.* Univ. Wisconsin--Milwaukee, Center for Great Lakes Studies Spec. Rep. 13. 71 pp.

Hunt, E. G., and A. I. Bischoff. 1960. *Inimical effects on wildlife of periodic DDD applications to Clear Lake.* Calif. Fish Game 46:91-106.

Hurd, D. C. 1973. *Interactions of biogenic opal, sediment and seawater in the central equatorial Pacific.* Geochim. Cosmochim. Acta 37:2257-2282.

Hutchinson, G. E. 1957. *A treatise on limnology.* Vol. 1. John Wiley & Sons, Inc., New York. 1015 pp.

Illinois Pollution Control Board. 1974. *Rules and regulations. Chapter 3: Water pollution and Amendments R-72-4 and R-73-1.* Illinois Environmental Protection Agency (mimeo). 46 pp.

Illinois Sanitary Water Board. 1969. *1968 surveys of Lake Michigan open water quality and lakebed.* Springfield, Illinois. 35 pp.

__________. 1970. *1969 surveys of Lake Michigan open water quality and lakebed.* Springfield, Illinois. 39 pp.

Indiana Stream Pollution Control Board. 1973. *Water quality standards. Regulation SPC 4-R: Lake Michigan and contiguous harbor areas.* (mimeo) 5 pp.

__________. 1974. *Preliminary report of phosphorus trends at municipal sewage treatment plants and in Indiana streams for years 1971, 1972, and 1973.* Indianapolis, Ind. 10 pp.

Industrial Bio-Test, Inc. 1972a. *Evaluation of thermal effects in southwestern Lake Michigan (January 1970-April 1971).* Inshore Water Quality Evaluation, Project II, IBT No. W8955, Part A-Chemistry, January 1970-April 1971. Rep. to Commonwealth Edison Co., Chicago, Ill. 99 pp.

__________. 1972b. *Evaluation of thermal effects in southwestern Lake Michigan (January 1970-April 1971).* Field Sampling Program, Project VII, IBT No. W8960, Part D-Offshore Water Quality, February 1970-April 1971. Rep. to Commonwealth Edison Co., Chicago, Ill. 140 pp.

__________. 1972c. *Preoperational thermal monitoring program of Lake Michigan (1971-1972).* Intake-discharge experiments at Waukegan Generating Station, Project XI, IBT No. W9861, Water Quality Section, May 1971-April 1972. Rep. to Commonwealth Edison Co., Chicago, Ill. 222 pp.

__________. 1972d. *Preoperational thermal monitoring program of Lake Michigan near the Kewaunee Nuclear Power Plant, January 1971-December 1971.* IBT No. W9438. Rep. to Commonwealth Edison Co., Chicago, Ill. 88 pp. & appendices.

*Jayne, J. C., and G. F. Lee. 1972. *Phosphate transfer through lower Green Bay--exchange between water and sediments.* Paper presented at 15th Conf. Great Lakes Res., Madison, Wis.

Jenkins, D. 1968. *The differentiation, analysis, and preservation of nitrogen and phosphorus forms in natural waters.* In: *Trace inorganics in water.* Adv. Chem. Ser. 73:265-280.

Jenne, E. A. 1968. *Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides.* In: *Trace inorganics in water.* Adv. Chem. Ser. 73:337-387.

Jernelöv, A., and A.-L. Martin. 1975. *Ecological implications of metal metabolism by microorganisms.* Annu. Rev. Microbiol. 29:61-77.

Johannes, R. E., and K. L. Webb. 1970. *Release of dissolved organic compounds by marine and fresh water invertebrates.* In: D. W. Hood (ed.), *Symposium on organic matter in natural waters.* Univ. Alaska, Inst. Mar. Sci. Occas. Publ. No. 1. pp. 257-273.

Johansson, N. S., S. Jensen, and M. Olsson. 1970. *PCB indications of effects on salmon.* PCB Conference, Swedish Salmon Institute, Stockholm, September 1970 (mimeo). pp. 59-68. (As cited by Veith, 1973).

Johnson, G. V., P. A. Mayeux, and H. J. Evans. 1966. *A cobalt requirement for symbiotic growth of Azolla filiculoides in the absence of combined nitrogen.* Plant Physiol. 41:852-855.

Johnson, R. G., and E. C. Monahan. 1971. *Current meter observations of the circulation in Grand Traverse Bay of Lake Michigan: mooring methods and initial results.* Univ. Michigan Sea Grant Program Tech. Rep. No. 18. 58 pp.

Johnson, W. D., F. K. Kawahara, L. E. Scarce, F. D. Fuller, and C. Risley, Jr. 1968. *Identification of residual oil pollutants in surface waters of the southern end of Lake Michigan.* Proc. 11th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 550-564.

Jonasson, I. R. 1973. *Migration of trace metals in snow.* Nature 241:447-448.

Jones, B. F., V. C. Kennedy, and G. W. Zellweger. 1974. *Comparison of observed and calculated concentrations of dissolved Al and Fe in stream water.* Water Resour. Res. 10:791-793.

Jørgensen, E. G. 1953. *Silicate assimilation by diatoms.* Physiol. Plant. 6:301-315.

Joussot-Dubien, J., and A. Kadiri. 1970. *Photosensitized oxidation of ammonia by singlet oxygen in aqueous solution and in seawater.* Nature 227:700-701.

Junge, C. E. 1958. *The distribution of ammonia and nitrate in rain water over the United States.* Trans. Am. Geophys. Union 39:241-248.

Kanamori, S., and K. Sugawara. 1965. *Geochemical study of arsenic in natural waters. I. Arsenic in rain and snow.* J. Earth Sci. Nagoya Univ. 13:23-35.

Kanwisher, J. 1963. *On the exchange of gases between the atmosphere and the sea.* Deep-Sea Res. 10:195-207.

Kato, K. 1969. *Behavior of dissolved silica in connection with oxidation-reduction cycle in lake water.* Geochem. J. 3:87-97.

Kemp, A. L. W., and A. Mudrochova. 1972. *Distribution and forms of nitrogen in a Lake Ontario sediment core.* Limnol. Oceanogr. 17:855-867.

__________, C. B. J. Gray, and A. Mudrochova. 1972. *Changes in C, N, P, and S in the last 140 years in three cores from Lakes Ontario, Erie, and Huron.* In: H. E. Allen and J. R. Kramer (eds.), *Nutrients in natural waters.* John Wiley & Sons, Inc., New York. pp. 251-279.

__________, T. W. Anderson, R. L. Thomas, and A. Mudrochova. 1974. *Sedimentation rates and recent sediment history of Lakes Ontario, Erie and Huron.* J. Sediment. Petrol. 44:207-218.

Kemp, H. T., J. P. Abrams, and R. C. Overbeck. 1971. *Effect of chemicals on aquatic life. Water quality criteria data book.* Vol. 3. U. S. Environmental Protection Agency, Water Pollut. Control Res. Ser. No. 18050GWV05/71. U. S. Government Printing Office, Washington, D. C. 528 pp.

Kennedy, E. J., R. R. Ruch, and N. F. Shimp. 1971. *Distribution of mercury in unconsolidated sediments from southern Lake Michigan.* Ill. State Geol. Surv. Environ. Geol. Notes No. 44. 18 pp.

Kennedy, V. C., G. W. Zellweger, and B. F. Jones. 1974. *Filter pore-size effects on the analysis of Al, Fe, Mn, and Ti in water.* Water Resour. Res. 10:785-790.

Kessler, E. 1955. *On the role of manganese in the oxygen-evolving system in photosynthesis.* Arch. Biochem. Biophys. 59:527-529.

Kilham, P. 1971. *A hypothesis concerning silica and the freshwater planktonic diatoms.* Limnol. Oceanogr. 16:10-18.

Kittredge, J. S., M. Horiguchi, and P. M. Williams. 1969. *Aminophosphonic acids: biosynthesis by marine phytoplankton.* Comp. Biochem. Physiol. 29:859-863.

Klass, E., D. W. Rowe, and E. J. Massaro. 1974. *The effect of cadmium on population growth of the green alga Scenedesmus quadracauda.* Bull. Environ. Contam. Toxicol. 12:442-445.

Klein, D. H. 1975. *Fluxes, residence times, and sources of some elements to Lake Michigan.* Water Air Soil Pollut. 4:3-8.

Kleinert, S. J., P. E. Degurse, and T. L. Wirth. 1968. *Occurrence and significance of DDT and dieldrin residues in Wisconsin fish.* Wis. Dep. Nat. Resour. Tech. Bull. No. 41. 43 pp.

Kliewer, M., and H. J. Evans. 1963. *Cobamide coenzyme contents of soybean nodules and nitrogen fixing bacteria in relation to physiological conditions.* Plant Physiol. 38:99-104.

Kluesener, J. W. 1972. *Nutrient transport and transformations in Lake Wingra.* Ph.D. Thesis. Univ. Wisconsin--Madison. 242 pp.

Knowles, D. B., F. C. Dreher, and G. W. Whetstone. 1964. *Water resources of the Green Bay area, Wisconsin.* U. S. Geol. Surv. Water-Supply Pap. 1499-G. 67 pp.

Konrad, J. G., and S. J. Kleinert. 1974. *Removal of metals from waste waters by municipal sewage treatment plants.* Wis. Dep. Nat. Resour. Tech. Bull. No. 74. 7 pp.

Kopp, J. F., and R. C. Kroner. 1968. *Trace metals in waters of the United States: a five year summary of trace metals in rivers and lakes of the United States (Oct. 1, 1962-Sept. 30, 1967).* U. S. Department of the Interior, Fed. Water Pollut. Control Adm., Div. Pollut. Surveillance, Cincinnati, Ohio. 1 vol.

Kramer, J. R. 1967. *Equilibrium models and composition of the Great Lakes.* In: *Equilibrium concepts in natural water systems.* Adv. Chem. Ser. 67:243-254.

Kratz, W. A., and J. Myers. 1955. *Nutrition and growth of several blue-green algae.* Am. J. Bot. 42-282-287.

Krauskopf, K. B. 1956. *Dissolution and precipitation of silica at low temperatures.* Geochim. Cosmochim. Acta 10:1-26.

__________. 1967. *Introduction to geochemistry.* McGraw-Hill Book Co., New York. 721 pp.

Kuenzler, E. J., and J. P. Perras. 1965. *Phosphatases of marine algae.* Biol. Bull. (Woods Hole) 128:271-284.

Ladewski, T. B., and E. F. Stoermer. 1973. *Water transparency in southern Lake Michigan in 1971 and 1972.* Proc. 16th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 791-807.

Lagerwerff, J. V., and A. W. Specht. 1970. *Contamination of roadside soil and vegetation with cadmium, nickel, lead, and zinc.* Environ. Sci. Technol. 4:583-586.

Lake Michigan Enforcement Conference, Interstate Pesticides Committee. 1968. *Report on pesticides in Lake Michigan.* U. S. Department of the Interior, Fed. Water Pollut. Control Adm., Great Lakes Region, Chicago. 44 pp.

__________. 1972a. *Report on selected trace metals in the Lake Michigan basin.* 87 pp.

__________. 1972b. *An evaluation of DDT and dieldrin in Lake Michigan.* U. S. Environmental Protection Agency, Off. Res. Monit. Rep. No. EPA-R3-72-003. 139 pp.

Lakin, H. 1973. *Selenium in our environment.* In: E. L. Kothny (ed.), *Trace elements in the environment.* Adv. Chem. Ser. 123:96-111.

Latimer, W. M. 1952. *Oxidation potentials.* 2nd ed. Prentice-Hall, Inc., Englewood Cliffs, N. J. 392 pp.

Lauff, G. H. 1957. *Some aspects of the physical limnology of Grand Traverse Bay.* Univ. Michigan, Great Lakes Res. Inst. Publ. No. 2. 56 pp.

Lauwers, A. M., and W. Heinen. 1974. *Bio-degradation and utilization of silica and quartz.* Arch. Microbiol. 95:67-78.

Lawton, G. W., and W. Busse. 1966. *Drinking water--a source of sodium: results of a survey of Wisconsin communities.* Wis. Med. J. 65:259-264.

Lazrus, A. L., E. Lorange, and J. P. Lodge, Jr. 1970. *Lead and other metal ions in United States precipitation.* Environ. Sci. Technol. 4:55-58.

Lean, D. R. S. 1973. *Phosphorus dynamics in lake water.* Science 179:678-680.

Leland, H. V., W. N. Bruce, and N. F. Shimp. 1973a. *Chlorinated hydrocarbon insecticides in sediments of southern Lake Michigan.* Environ. Sci. Technol. 7:833-838.

__________, S. S. Shukla, and N. F. Shimp. 1973b. *Factors affecting distribution of lead and other trace elements in sediments of southern Lake Michigan.* In: P. C. Singer (ed.), *Trace metals and metal-organic interactions in natural waters.* Ann Arbor Science Publishers, Ann Arbor, Mich. pp. 89-129.

Levander, O. A. 1971. *Factors that modify the toxicity of selenium.* In: W. Mertz and W. E. Cornatzer (eds.), *Newer trace elements in nutrition.* Marcel Dekker, Inc., New York. pp. 57-83.

Lewin, J. C. 1961. *The dissolution of silica from diatom walls.* Geochim. Cosmochim. Acta 21:182-198.

__________. 1962. *Silicification.* In: R. A. Lewin (ed.), *Physiology and biochemistry of algae.* Academic Press, New York. pp. 445-455.

__________. 1966. *Physiological studies of the boron requirement of the diatom Cylindrotheca fusiformis Reimann and Lewin.* J. Exp. Bot. 17:473-479.

Limnetics, Inc. 1974. *An environmental study of the ecological effects of the thermal discharges from Point Beach, Oak Creek, and Lakeside Power Plants on Lake Michigan.* Commissioned by Wisconsin Electric Power Co., Milwaukee. 2 vol.

Lin, K. W., and J. L. Blum. 1973. *Adaptation to eutrophic conditions by Lake Michigan algae*. Univ. Wisconsin--Madison, Water Resour. Cent. Tech. Rep. WIS-WRC 73-03. 23 pp.

Lineback, J. A., H. J. Ayer, and D. L. Gross. 1970. *Stratigraphy of unconsolidated sediments in the southern part of Lake Michigan*. Ill. State Geol. Surv. Environ. Geol. Notes No. 35. 35 pp.

__________, and D. L. Gross. 1972. *Depositional patterns, facies, and trace element accumulation in the Waukegan member of the Late Pleistocene Lake Michigan formation in southern Lake Michigan*. Ill. State Geol. Surv. Environ. Geol. Notes No. 58. 25 pp.

Lisk, Donald J. 1972. *Trace metals in soils, plants, and animals*. Adv. Agron. 24:267-325.

Liss, P. S. 1973. *Processes of gas exchange across an air-water interface*. Deep-Sea Res. 20:221-238.

Lodge, J. P., Jr., J. B. Pate, W. Basbergill, G. S. Swanson, K. C. Hill, E. Lorange, and A. L. Lazrus. 1968. *Chemistry of United States precipitation: final report on the national precipitation sampling network*. Laboratory of Atmospheric Sciences, National Center for Atmospheric Research, Boulder, Col. 66 pp.

Loucks, R. H., and J. W. Winchester. 1969. *Pollution contributions to the atmospheric inventory of chlorine and bromine in aerosols over continental U. S. A.* In: D. D. Hemphill (ed.), *Trace substances in environmental health*. Vol. III. Proc. Univ. Missouri 3rd Annu. Conf., Columbia, Mo. pp. 233-250.

*Lue-Hing, C. 1973. *Water quality trends in inshore water of southwestern Lake Michigan*. Paper presented at 16th Conf. Great Lakes Res., Huron, Ohio.

Lund, J. W. G. 1950. *Studies on Asterionella formosa Hass. II. Nutrient depletion and the spring maximum*. J. Ecol. 38:15-35.

__________. 1969. *Phytoplankton*. In: *Eutrophication: causes, consequences, correctives*. National Academy of Sciences, Washington, D. C. pp. 306-330.

Mague, T. H. 1971. *Field assessment of N_2-fixation by legumes and blue-green algae with the acetylene reduction technique*. Ph.D. Thesis. Univ. Wisconsin--Madison. 173 pp.

__________, and R. H. Burris. 1973. *Biological nitrogen fixation in the Great Lakes*. BioScience 23:236-239.

Manny, B. A., and C. A. S. Hall. 1969. *Diurnal changes in stratification and dissolved oxygen in the surface waters of Lake Michigan*. Proc. 12th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 622-634.

Martin, J. L., and M. L. Gerlach. 1972. *Selenium metabolism in animals*. Ann. N. Y. Acad. Sci. 192:193-199.

*Matson, W. R., H. E. Allen, and P. Rekshan. 1969. *Trace metal organic complexes in the Great Lakes.* Paper presented at Div. of Water, Air and Waste Chemistry, American Chemical Society, Minneapolis, Minn.

McKee, J. E., and H. W. Wolf (eds.). 1963. *Water quality criteria.* 2nd ed. Resources Agency of California, State Water Quality Control Board, Sacramento. Publ. No. 3A. 548 pp.

Meisch, H.-U., and H.-J. Bielig. 1975. *Effect of vanadium on growth, chlorophyll formation and iron metabolism in unicellular green algae.* Arch. Microbiol. 105:77-82.

Merck Index. 8th ed. 1968. Merck & Co., Inc., Rathway, N. J. 1713 pp.

Mertz, W. 1969. *Chromium occurrence and function in biological systems.* Physiol. Rev. 49:163-239.

__________, and E. E. Roginski. 1971. *Chromium metabolism: the glucose tolerance factor.* In: W. Mertz and W. E. Cornatzer (eds.), *Newer trace elements in nutrition.* Marcel Dekker, Inc., New York. pp. 123-153.

__________, E. W. Toepfer, E. E. Roginski, and M. M. Polansky. 1974. *Present knowledge of the role of chromium.* Fed. Proc. 33:2275-2280.

Michigan Water Resources Commission. 1973. *General rules. Part 4: Water quality standards (proposed rules 9/25/73).* Michigan Department of Natural Resources (mimeo). 17 pp.

Modlin, R. F., and A. M. Beeton. 1970. *Dispersal of Fox River water in Green Bay, Lake Michigan.* Proc. 13th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 468-476.

Moore, A. W., G. N. McDermott, M. A. Post, J. W. Mandia, and M. B. Ettinger. 1961. *Effects of chromium on the activated sludge process.* J. Water Pollut. Control Fed. 33:54-72.

Moore, J. R., and R. P. Meyer. 1969. *Progress report on the geological-geophysical survey of Green Bay, 1968.* Univ. Wisconsin--Madison Sea Grant Program Tech. Rep. No. 1. 16 pp.

Morris, J. C., and W. Stumm. 1967. *Redox and equilibria and measurements of potentials in the aquatic environment.* In: *Equilibrium concepts in natural water systems.* Adv. Chem. Ser. 67:270-285.

Mortimer, C. H. 1941. *The exchange of dissolved substances between mud and water, I and II.* J. Ecol. 29:280-329.

__________. 1942. *The exchange of dissolved substances between mud and water in lakes, III and IV.* J. Ecol. 30:147-201.

__________. 1971. *Chemical exchanges between sediments and water in the Great Lakes--speculations on probable regulatory mechanisms.* Limnol. Oceanogr. 16:387-404.

__________. 1975. *Physical limnology of Lake Michigan. Part 1, Physical characteristics of Lake Michigan and its responses to applied forces.* Environmental status of the Lake Michigan region, Vol. 2. pp. 13-102.

Mount, D. I. 1968. *Chronic toxicity of copper to fathead minnows (Pimephales promelas Rafinesque).* Water Res. 2:215-223.

__________, and C. F. Stephen. 1969. *Chronic toxicity of copper to the fathead minnow (Pimephales promelas) in soft water.* J. Fish. Res. Board Can. 26:2449-2457.

*Murphy, T. J., and D. J. Cesarotti. 1974. *Phosphorus inputs from the atmosphere.* Paper presented at 37th Annual Meeting, American Society of Limnology and Oceanography, Seattle, Wash.

National Academy of Sciences-National Academy of Engineering Committee on Water Quality Criteria. 1973. *Water quality criteria 1972.* U. S. Environmental Protection Agency Rep. No. EPA-R3-73-033. U. S. Government Printing Office, Washington, D. C. 594 pp.

Nemerow, N. L. 1963. *Theories and practices of industrial waste treatment.* Addison-Wesley Publishing Co., Inc., Reading, Mass. 557 pp.

Nicholas, D. J. D., D. J. Fisher, W. J. Redmond, and M. Osborne. 1964. *A cobalt requirement for nitrogen fixation, hydrogenase, nitrite and hydroxylamine reductases in Clostridium pasteurianum.* Nature 201:793-795.

Nielsen, F. H. 1971. *Studies on the essentiality of nickel.* In: W. Mertz and W. E. Cornatzer (eds.), *Newer trace elements in nutrition.* Marcel Dekker, Inc., New York. pp. 215-253.

__________, and D. A. Ollerich. 1974. *Nickel: a new essential trace element.* Fed. Proc. 33:1767-1772.

*Nienke, G. E. 1972. Personal communication (University of Wisconsin--Stevens Point).

Noble, V. E., and R. F. Anderson. 1968. *Temperature and current in the Grand Haven, Michigan, vicinity during thermal bar conditions.* Proc. 11th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 470-479.

__________, and A. Michaelis. 1968. *Winter temperature data from Federal Water Pollution Control Administration buoy stations, Lake Michigan, winters of 1962-63 and 1963-64; Lake Huron, winter of 1965-66.* Univ. Michigan, Great Lakes Res. Div. Spec. Rep. 39. 387 pp.

O'Connor, D. J., and J. A. Mueller. 1970. *A water quality model of chlorides in Great Lakes.* J. Sanit. Eng. Div. Proc. Am. Soc. Civ. Eng. 96(SA4): 955-975.

O'Kelley, J. C. 1968. *Mineral nutrition of algae.* Annu. Rev. Plant Physiol. 19:89-112.

__________, and R. G. Wetzel. 1973. *Interaction of yellow organic acids with calcium carbonate in freshwater.* Limnol. Oceanogr. 18:490-493.

Ownbey, C. R., and G. E. Willeke. 1965. *Long-term solids buildup in Lake Michigan water.* Proc. 8th Conf. Great Lakes Res., Great Lakes Res. Div. Publ. No. 13, Univ. Michigan. pp. 141-152.

Paasche, E. 1973a. *Silicon and the ecology of marine plankton diatoms. I. Thalassiosira pseudonana (Cyclotella nana) grown in a chemostat with silicate as limiting nutrient.* Mar. Biol. (Berl.) 19:117-126.

__________. 1973b. *Silicon and the ecology of marine plankton diatoms. II. Silicate-uptake kinetics in five diatom species.* Mar. Biol. (Berl.) 19:262-269.

__________. 1975. *Growth of the plankton diatom Thalassiosira nordenskioeldii Cleve at low silicate concentrations.* J. Exp. Mar. Biol. Ecol. 18:173-183.

Page, A. L., F. T. Bingham, and C. Nelson. 1972. *Cadmium absorption and growth of various plant species as influenced by solution cadmium concentration.* J. Environ. Qual. 1:288-291.

Pardi, R. 1972. *The role of organic films in controlling gas exchange.* M.S. Thesis. Queens College, New York. (As cited by Emerson *et al.*, 1973).

Park, R. B. 1965. *The chloroplast.* In: J. Bonner and J. E. Varner (eds.), *Plant biochemistry.* Academic Press, New York. pp. 124-150.

Parker, J. I., and J. G. Ferrante. 1975. *Vertical transport of particulate material in Lake Michigan by the lorica of Codonella cratera.* Radiol. Environ. Res. Div. Annu. Rep., Ecology, January-December 1974, Argonne National Laboratory Rep. ANL-75-3, Part III. pp. 9-12.

__________, and D. N. Edgington. 1976. *Concentration of diatom frustules in Lake Michigan sediment cores.* Limnol. Oceanogr. (in press).

Parsons, T. R. 1963. *Suspended organic matter in sea water.* Prog. Oceanogr. 1:203-239.

Peck, H. D., Jr. 1970. *Sulfur requirements and metabolism of microorganisms.* In: O. H. Muth and J. E. Oldfield (eds.), *Symposium: sulfur in nutrition.* Avi Publishing Co., Inc., Westport, Conn. pp. 66-79.

Penrose, W. R. 1974. *Arsenic in the marine and aquatic environments: analysis, occurrence and significance.* CRC Crit. Rev. Environ. Control 4:465-482.

Perlow, G. J., W. Potzel, and D. Edgington. 1974. *Serial study of Lake Michigan sediments by ^{57}Fe Mössbauer spectroscopy.* J. Phys. (Paris), Colloq. C6 Suppl. 12, Tome 35:547-548.

Peters, R., and D. Lean. 1973. *The characterization of soluble phosphorus released by limnetic zooplankton.* Limnol. Oceanogr. 18:270-279.

*Peterson, R. B. 1973. Personal communication (Department of Biochemistry, University of Wisconsin--Madison).

*__________, and R. H. Burris. 1973. Personal communication (Department of Biochemistry, University of Wisconsin--Madison).

Philbert, F. J. 1973. *The effect of sample preservation by freezing prior to chemical analysis of Great Lakes waters.* Proc. 16th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 282-293.

Pinsak, A. 1972. *Physical characteristics.* In: *Great Lakes Basin Framework Study. App. 4, Limnology of lakes and embayments.* Draft No. 2, Vol. 1. pp. 313-416.

Pinsent, J. 1954. *The need for selenite and molybdate in the formation of formic dehydrogenase by members of the coli-aerogenes group of bacteria.* Biochem. J. 57:10-16.

Pomeroy, R. D., and H. Cruse. 1969. *Hydrogen sulfide odor threshold.* J. Am. Water Works Assoc. 61:677.

Pourbaix, M. J. N. 1963. *Atlas d'équilibres électrochimiques.* Gauthier-Villars, Paris. 644 pp.

Powers, C. F., and J. C. Ayers. 1967. *Water quality and eutrophication trends in southern Lake Michigan.* In: J. C. Ayers and D. C. Chandler (eds.), *Studies on the environment and eutrophication of Lake Michigan.* Univ. Michigan, Great Lakes Res. Div. Spec. Rep. 30. pp. 142-178.

Provasoli, L. 1958. *Nutrition and ecology of protozoa and algae.* Annu. Rev. Microbiol. 12:279-308.

__________. 1969. *Algal nutrition and eutrophication.* In: *Eutrophication: causes, consequences, correctives.* National Academy of Sciences, Washington, D. C. pp. 574-593.

Purushothaman, A., D. Chandramohan, and R. Naterajan. 1974. *Distribution of silicate dissolving bacteria in the Vellar Estuary.* Curr. Sci. (Bangalore) 43:282-283.

Quin, L. D. 1965. *The presence of compounds with a carbon-phosphorus bond in some marine invertebrates.* Biochemistry 4:324-330.

Rainey, R. H. 1967. *Natural displacement of pollution from the Great Lakes.* Science 155:1242-1243.

Rattonetti, A. 1974. *Determination of soluble cadmium, lead, silver, and indium in rainwater and stream water with the use of flameless atomic absorption.* Anal. Chem. 46:739-742.

Reinert, R. E. 1970. *Pesticide concentrations in Great Lakes fish.* Pestic. Monit. J. 3:233-240.

*__________. 1974. Personal communication (Seminar presented at the Laboratory of Limnology, Univ. Wisconsin--Madison, 29 May 1974).

__________, and H. L. Bergman. 1974. *Residues of DDT in lake trout (Salvelinus namaycush) and coho salmon (Oncorhynchus kisutch) from the Great Lakes.* J. Fish. Res. Board Can. 31:191-199.

__________, L. J. Stone, and H. L. Bergman. 1974. *Dieldrin and DDT: accumulation from water and food by lake trout (Salvelinus namaycush) in the laboratory.* Proc. 17th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 52-58.

Richter, G. 1961. *Auswirkungen von Mangan-Mangel auf Wachstum und Photosynthese bei der Blaualge Anacystis nidulans.* Planta (Berl.) 57:202-214.

Riley, G. A. 1963. *Organic aggregates in seawater and the dynamics of their formation and utilization.* Limnol. Oceanogr. 8:372-381.

*Ringer, R. K., R. J. Aulerich, and M. Zabik. 1972. *Effect of dietary polychlorinated biphenyls on growth and reproduction of mink.* Paper presented at Div. of Water, Air and Waste Chemistry, 164th National Meeting of American Chemical Society, New York, August 1972.

Risley, C., Jr., and F. D. Fuller. 1965. *Chemical characteristics of Lake Michigan.* Proc. 8th Conf. Great Lakes Res., Great Lakes Res. Div. Publ. No. 13, Univ. Michigan. pp. 168-174.

__________, and F. D. Fuller. 1966. *Chemical findings from pollution studies in the Calumet area of Indiana and Illinois and the adjacent waters of Lake Michigan.* Proc. 9th Conf. Great Lakes Res., Great Lakes Res Div. Publ. No. 15, Univ. Michigan. pp. 423-429.

Robbins, J. A., E. Callender, M. A. Wahlgren, and D. N. Edgington. 1972a. *Environmental chemistry: Grand River studies.* Radiol. Physics Div. Annu. Rep., Environmental Research, January-December 1971, Argonne National Laboratory Rep. ANL-7860, Part III. pp. 80-100.

__________, E. Landstrom, and M. Wahlgren. 1972b. *Tributary inputs of soluble trace metals to Lake Michigan.* Proc. 15th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 270-290.

__________, and D. N. Edgington. 1974. *The distribution of trace elements in the clay-silt sediments off Grand Haven.* Radiol. Environ. Res. Div. Annu. Rep., Ecology, January-December 1973, Argonne National Laboratory Rep. ANL-8060, Part III. pp. 77-84.

__________, and E. Callender. 1975. *Diagenesis of manganese in Lake Michigan sediments.* Am. J. Sci. 275:512-533.

__________, and D. N. Edgington. 1975a. *Determination of recent sedimentation rates in Lake Michigan using Pb-210 and Cs-137.* Geochim. Cosmochim. Acta 39:285-304.

__________, and D. N. Edgington. 1975b. *Stable lead geochronology of fine-grained sediments in southern Lake Michigan.* Radiol. Environ. Res. Div. Annu. Rep., Ecology, January-December 1974, Argonne National Laboratory Rep. ANL-75-3, Part III. pp. 32-39.

__________, D. N. Edgington, J. Gustinis, and J. O. Karttunen. 1975a. *Geochronology of Lake Michigan sediments: anomalies in lead-210 distributions.* Radiol. Environ. Res. Div. Annu. Rep., Ecology, January-December 1974, Argonne National Laboratory Rep. ANL-75-3, Part III. pp. 40-50.

__________, D. N. Edgington, and J. I. Parker. 1975b. *Distribution of amorphous diatom frustule, and dissolved silica in a lead-210 dated core from southern Lake Michigan.* Radiol. Environ. Res. Div. Annu. Rep., Ecology, January-December 1974, Argonne National Laboratory Rep. ANL-75-3, Part III. pp. 19-31.

__________, and D. N. Edgington. 1976. *Depositional processes and the determination of recent sedimentation rates in Lake Michigan.* Proceedings of the 2nd Conference on the Great Lakes, Interagency Committee for Marine Science and Engineering (in press).

Robertson, A., and C. F. Powers. 1965. *Particulate organic matter in Lake Michigan.* Univ. Michigan, Great Lakes Res. Div. Publ. No. 13. pp. 175-181.

__________, and C. F. Powers. 1967. *Comparison of the distribution of organic matter in the five Great Lakes.* In: J. C. Ayers and D. C. Chandler (eds.), *Studies on the environment and eutrophication of Lake Michigan.* Univ. Michigan, Great Lakes Res. Div. Spec. Rep. 30. pp. 1-18.

__________, and C. F. Powers, 1968. *The distribution of organic nitrogen in Lake Michigan.* Pap. Mich. Acad. Sci. Arts Lett. 53:137-151.

__________, C. F. Powers, and J. Rose. 1971. *Distribution of chlorophyll and its relation to particulate organic matter in the offshore waters of Lake Michigan.* Proc. 14th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 90-101.

Robertson, O. H., and A. L. Chaney. 1953. *Thyroid hyperplasia and tissue iodine content in spawning rainbow trout: a comparative study of Lake Michigan and California sea-run trout.* Physiol. Zool. 26:328-340.

Rodgers, G. K. 1966. *The thermal bar in Lake Ontario, Spring 1965 and Winter 1965-66.* Proc. 9th Conf. Great Lakes Res., Great Lakes Res. Div. Publ. No. 15, Univ. Michigan. pp. 369-374.

Rosen, A. A., J. B. Peter, and F. M. Middleton. 1962. *Odor thresholds of mixed organic chemicals.* J. Water Pollut. Control Fed. 34:7-14.

Rossmann, R., E. Callender, and C. J. Bowser. 1972. *Inter-element geochemistry of Lake Michigan ferromanganese nodules.* Proc. 24th Int. Geol. Congress Montreal Section 10. pp. 336-341.

Rotruck, J. T., A. L. Pope, H. E. Ganther, A. B. Swanson, D. G. Hafeman, and W. G. Hoekstra. 1973. *Selenium: biochemical role as a component of glutathione peroxidase.* Science 179:588-590.

Rousar, D. C. 1973. *Seasonal and spatial changes in primary production and nutrients in Lake Michigan.* Water Air Soil Pollut. 2:497-514.

__________, and A. M. Beeton. 1973. *Distribution of phosphorus, silica, chlorophyll a, and conductivity in Lake Michigan and Green Bay.* Trans. Wis. Acad. Sci. Arts Lett. 61:117-140.

Ruch, R. R., E. J. Kennedy, and N. F. Shimp. 1970. *Distribution of arsenic in unconsolidated sediments from southern Lake Michigan.* Ill. State Geol. Surv. Environ. Geol. Notes No. 37. 16 pp.

Sager, P. E. 1971. *Nutritional ecology and community structure of the phytoplankton of Green Bay.* Univ. Wisconsin--Madison, Water Resour. Cent. Tech. Completion Rep. OWRR A-017-WIS. 31 pp.

__________, and J. H. Wiersma. 1972. *Nutrient discharges to Green Bay, Lake Michigan from the lower Fox River.* Proc. 15th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 132-148.

Schacht, R. A. 1974. *Pesticides in the Illinois waters of Lake Michigan.* U. S. Environmental Protection Agency, Off. Res. Dev., Rep. No. EPA-660/3-74-002. U. S. Government Printing Office, Washington, D. C. 55 pp.

Schelske, C. L., and E. Callender. 1970. *Survey of phytoplankton productivity and nutrients in Lake Michigan and Lake Superior.* Proc. 13th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 93-105.

__________, and E. F. Stoermer. 1971. *Eutrophication, silica depletion, and predicted changes in algal quality in Lake Michigan.* Science 173:423-424.

__________, E. F. Stoermer, and L. E. Feldt. 1971. *Nutrients, phytoplankton productivity and species composition as influenced by upwelling in Lake Michigan.* Proc. 14th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 102-113.

__________, and E. F. Stoermer. 1972. *Phosphorus, silica, and eutrophication of Lake Michigan.* In: G. E. Likens (ed.), *Nutrients and eutrophication: the limiting-nutrient controversy.* Special Symposia Vol. 1, American Society of Limnology and Oceanography. pp. 157-171.

__________, and J. C. Roth. 1973. *Limnological survey of Lakes Michigan, Superior, Huron, and Erie.* Univ. Michigan, Great Lakes Res. Div. Publ. No. 17. 108 pp.

Schiff, J. A., and R. C. Hodson. 1973. *The metabolism of sulfate.* Annu. Rev. Plant Physiol. 24:381-414.

Schink, D. R., K. A. Fanning, and M. E. Q. Pilson. 1974. *Dissolved silica in the upper pore waters of the Atlantic Ocean floor.* J. Geophys. Res. 79: 2243-2250.

Schleicher, J. A., and J. K. Kuhn. 1970. *Phosphorus content in unconsolidated sediments from southern Lake Michigan.* Ill. State Geol. Surv. Environ. Geol. Notes No. 39. 15 pp.

Schraufnagel, F. H., L. A. Lueschow, G. Karl, L. A. Montie, J. Lissack, and J. R. McKersie. 1968. *Report on an investigation of the pollution in the Lower Fox River and Green Bay made during 1966 and 1967.* Wisconsin Department of Natural Resources, Div. Resour. Dev. 77 pp.

Schroeder, H. A. 1965. *Cadmium as a factor in hypertension.* J. Chronic Dis. 18:647-656.

__________. 1973. *The trace elements and man.* Devin-Adair Company, Old Greenwich, Conn. 180 pp.

__________. 1974. *The poisons around us.* Indiana University Press, Bloomington. 144 pp.

*Schwab, G. M., and P. L. Katz. 1975. *Nearshore dispersion of pollutants from the Calumet region of Lake Michigan: model and data.* Paper presented at Div. of Environmental Chemistry, American Chemical Society, Philadelphia, Pa.

Schwarz, K. 1974. *Recent dietary trace element research, exemplified by tin, fluorine, and silicon.* Fed. Proc. 33:1748-1757.

__________, and C. M. Foltz. 1957. *Selenium as an integral part of Factor 3 against dietary necrotic liver degeneration.* J. Am. Chem. Soc. 79:3292-3293.

__________, and D. B. Milne. 1971. *Growth effects of vanadium in the rat.* Science 174:426-428.

Seydel, I. S. 1972. *Distribution and circulation of arsenic through water, organisms and sediments of Lake Michigan.* Arch. Hydrobiol. 71:17-30.

Shapiro, J., W. T. Edmondson, and D. E. Allison. 1971. *Changes in the chemical composition of sediments of Lake Washington, 1958-1970.* Limnol. Oceanogr. 16:437-452.

Shen, H. S., and C. S. Chen. 1965. *Relation between black-foot disease and the pollution of drinking water by arsenic in Taiwan.* Adv. Water Pollut. Res. 1:173-190.

Shimp, N. F., J. Witters, P. D. Potter, and J. A. Schleicher. 1969. *Distinguishing marine and freshwater muds.* J. Geol. 77:566-580.

__________, H. V. Leland, and W. A. White. 1970. *Distribution of major, minor and trace constituents in unconsolidated sediments from southern Lake Michigan.* Ill. State Geol. Surv. Environ. Geol. Notes No. 32. 19 pp.

__________, J. A. Schleicher, R. R. Ruch, D. B. Heck, and H. V. Leland. 1971. *Trace element and organic carbon accumulation in the most recent sediments of southern Lake Michigan.* Ill. State Geol. Surv. Environ. Geol. Notes No. 41. 25 pp.

*Shiomi, M. T., and K. W. Kuntz. 1973. *Great Lakes precipitation chemistry. Part I. Lake Ontario Basin.* Paper presented at 16th Conf. Great Lakes Res., Huron, Ohio.

Siever, R., and N. Woodward. 1973. *Sorption of silica by clay minerals.* Geochim. Cosmochim. Acta 37:1851-1880.

Skirrow, G. 1965. *The dissolved gases--carbon dioxide.* In: J. P. Riley and G. Skirrow (eds.), *Chemical oceanography.* Vol. 1. Academic Press, New York. pp. 227-322.

Smith, S. H. 1968. *That little pest, the alewife.* Limnos 1:13-20.

Snow, R. H. 1974. *Water pollution investigation: Calumet area of Lake Michigan.* Vol. 1. U. S. Environmental Protection Agency Region V Enforcement Div., Great Lakes Initiative Contract Program Rep. No. EPA-905/9-74-011-A. NTIS, Springfield, Va. 307 pp.

Sridharan, N. 1972. *Aqueous environmental chemistry of phosphorus in lower Green Bay, Wisconsin.* Ph.D. Thesis. Univ. Wisconsin--Madison. 312 pp.

Stadtman, T. C. 1974. *Selenium biochemistry.* Science 183:915-922.

Stanier, R. Y., M. Doudoroff, and E. A. Adelberg. 1970. *The microbial world.* 3rd ed. Prentice-Hall, Inc., Englewood Cliffs, N. J. 873 pp.

Stewart, W. D. P. 1971. *Physiological studies on nitrogen-fixing blue-green algae.* Plant Soil Spec. Issue:377-391.

__________, T. Mague, R. H. Burris, and G. P. Fitzgerald. 1971. *Nitrogenase activity in Wisconsin lakes of differing degrees of eutrophication.* New Phytol. 70:497-509.

Stiff, M. J. 1971. *The chemical states of copper in polluted fresh water and a scheme of analysis to differentiate them.* Water Res. 5:585-599.

Stoermer, E. F., C. L. Schelske, M. A. Santiago, and L. E. Feldt. 1972. *Spring phytoplankton abundance and productivity in Grand Traverse Bay, Lake Michigan, 1970.* Proc. 15th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 181-191.

Strickland, J. D. H., and T. R. Parsons. 1968. *A practical handbook of seawater analysis.* Fish Res. Board Can. Bull. No. 167. 310 pp.

Stumm, W., and J. J. Morgan. 1962. *Stream pollution by algal nutrients.* Proc. 12th Annu. Conf. Sanit. Eng. Univ. Kansas--Lawrence. pp. 16-26. (As cited by Vollenweider, 1968).

__________, and J. J. Morgan. 1970. *Aquatic chemistry.* Wiley-Interscience, New York. 583 pp.

__________, and E. Stumm-Zollinger. 1971. *Chemostasis and homeostasis in aquatic ecosystems; principles of water pollution control.* In: *Nonequilibrium systems in natural water chemistry.* Adv. Chem. Ser. 106:1-29.

Sugawara, K., T. Koyama, and K. Terada. 1958. *Co-precipitation of iodide ions by some metallic hydrated oxides with special reference to iodine accumulation in bottom water layers and in interstitial water of muds in some Japanese lakes*. J. Earth Sci. Nagoya Univ. 6:52-61.

Sverdrup, H. U., M. W. Johnson, and R. H. Fleming. 1942. *The oceans: their physics, chemistry and general biology*. Prentice-Hall, Inc., Englewood Cliffs, N. J. 1087 pp.

Tanner, T. M., L. A. Rancitelli, and W. A. Haller. 1972. *Multielement analysis of natural waters by neutron activation, group chemical separations, and gamma-ray spectrometric techniques*. Water Air Soil Pollut. 1:132-143.

Ter Haar, G., R. B. Holtzman, and H. Lucas, Jr. 1967. *Lead and lead-210 in rainwater*. Nature 216:353-355.

Terry, R. C., Jr. 1974. *Road salt, drinking water, and safety*. Ballinger Publishing Co., Cambridge, Mass. 163 pp.

Thomas, N. A., K. Hartwell, and W. Miller. 1972. *Technical Working Rep. No. 3, Grosse Ile Laboratory*. U. S. Environmental Protection Agency. (As cited by Snow, 1974).

Thomas, R. L. 1972. *The distribution of mercury in the sediments of Lake Ontario*. Can. J. Earth Sci. 9:636-651.

__________. 1973. *The distribution of mercury in the surficial sediments of Lake Huron*. Can. J. Earth Sci. 10:194-204.

Tiffany, M. A., J. W. Winchester, and R. H. Loucks. 1969. *Natural and pollution sources of iodine, bromine, and chlorine in the Great Lakes*. J. Water Pollut. Control Fed. 41:1319-1329.

Torrey, M. S., and D. N. Edgington. 1973a. *Trace element assemblages in Lake Michigan manganese nodules*. Radiol. Environ. Res. Div. Annu. Rep., Ecology, January-December 1972, Argonne National Laboratory Rep. ANL-7960, Part III. pp. 54-63.

*__________, and D. N. Edgington. 1973b. Unpublished data.

Truesdale, V. W. 1975. *"Reactive" and "unreactive" iodine in seawater--a possible indication of an organically bound iodine fraction*. Mar. Chem. 3:111-119.

Turekian, K. K. 1971. *Geochemical distribution of elements*. In: *McGraw-Hill encyclopedia of science and technology*. Vol. 4. McGraw-Hill Book Co., New York. pp. 627-630.

Underwood, E. J. 1971. *Trace elements in human and animal nutrition*. 3rd ed. Academic Press, New York. 543 pp.

U. S. Department of the Interior. 1966a. *Comprehensive water pollution control program for the Lake Michigan Basin--Milwaukee area, Wisconsin*. Fed. Water Pollut. Control Admin., Great Lakes-Illinois River Basins Project, Region V, Chicago. 1 vol.

__________. 1966b. *Comprehensive water pollution control program for the Lake Michigan Basin--Green Bay area, Michigan and Wisconsin.* Fed. Water Pollut. Control Admin., Great Lakes-Illinois River Basins Project, Region V, Chicago. 1 vol.

__________. 1967. *Water quality investigations, Lake Michigan basin: lake currents.* Fed. Water Pollut. Control Admin. Tech. Rep., Great Lakes Region, Chicago. 364 pp.

__________. 1968. *Water quality investigations, Lake Michigan basin: physical and chemical quality conditions.* Fed. Water Pollut. Control Admin. Tech. Rep., Great Lakes Region, Chicago. 81 pp.

U. S. Geological Survey. 1972. *1970 water resources data for Wisconsin.* Water Resour. Div., Madison. 259 pp.

__________. 1973. *1971 water resources data for Wisconsin.* Water Resour. Div., Madison. 225 pp.

__________. 1974a. *1972 water resources data for Wisconsin.* Water Resour. Div., Madison. 262 pp.

__________. 1974b. *1973 water resources data for Wisconsin.* Water Resour. Div., Madison. 262 pp.

U. S. Public Health Service. 1962. *Public Health Service drinking water standards, revised 1962.* Public Health Service Publ. No. 956. U. S. Government Printing Office, Washington, D. C. 61 pp.

U. S. Treaties, etc. 1972. *Great Lakes water quality agreement, with annexes and texts and terms of reference, between the United States of America and Canada, signed at Ottawa April 15, 1972.* Treaties and Other International Acts Ser, 7312. U. S. Government Printing Office, Washington, D. C. 69 pp.

Upchurch, S. B. 1972. *Natural weathering and chemical loads in the Great Lakes.* Proc. 15th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 401-415.

Vanderhoef, L. N., B. Dana, D. Emerich, and R. H. Burris. 1972. *Acetylene reduction in relation to levels of phosphate and fixed nitrogen in Green Bay.* New Phytol. 71:1097-1105.

__________, C.-Y. Huang, R. Musil, and J. Williams. 1974. *Nitrogen fixation (acetylene reduction) by phytoplankton in Green Bay, Lake Michigan, in relation to nutrient concentrations.* Limnol. Oceanogr. 19:119-125.

Van Loon, J. C. 1973. *Toronto's precipitation analyzed for heavy metal content.* Water Pollut. Control 3(2):38-41.

Vaughn, J. C., and P. A. Reed. 1973. *Progress report on water quality of Lake Michigan near Chicago.* Water Sewage Works 120(5):73-80.

Veith, G. D. 1973. *Chlorinated hydrocarbons in fish from Lake Michigan.* U. S. Environmental Protection Agency, Water Qual. Off., Project No. 16020 PBE. 129 pp.

__________, and G. F. Lee. 1971. *PCB's in fish from the Milwaukee region.* Proc. 14th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 157-169.

Vollenweider, R. A. 1968. *Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular reference to nitrogen and phosphorus as factors in eutrophication.* OECD Rep. DAS/CS1/68.27. Paris. 192 pp.

Wahlgren, M. A., D. N. Edgington, and F. F. Rawlings. 1972a. *Determination of selected trace elements in natural water samples using spark source mass spectroscopy.* Radiol. Physics Div. Annu. Rep., Environmental Research, January-December 1971, Argonne National Laboratory Rep. ANL-7860, Part III. pp. 55-63.

__________, D. N. Edgington, F. F. Rawlings, and J. J. Rawls. 1972b. *Trace element determinations on Lake Michigan tributary water samples using spark source mass spectrometry.* Proc. 15th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 298-305.

Waller, R. M., and W. B. Allen. 1975. *Great Lakes Basin Framework Study. App. 3, Geology and ground water.* Public Information Office, Great Lakes Basin Commission, Ann Arbor, Mich. 152 pp.

Warner, T. B., and D. J. Bressan. 1973. *Direct measurement of less than 1 part-per-billion fluoride in rain, fog and aerosols with an ion-sensitive electrode.* Anal. Chim. Acta 63:165-173.

Webb, J. L. 1966. *Enzyme and metabolic inhibitors.* Vol. 3. Academic Press, New York. pp. 595-793.

Webb, K. L., and R. E. Johannes. 1967. *Studies on the release of dissolved free amino acids by marine zooplankton.* Limnol. Oceanogr. 12:376-382.

Weibel, S. R., R. B. Weidner, J. M. Cohen, and A. G. Christianson. 1966. *Pesticides and other contaminants in rainfall and runoff.* J. Am. Water Works Assoc. 58:1075-1084.

Weiler, R. R. 1974. *Exchange of carbon dioxide between the atmosphere and Lake Ontario.* J. Fish. Res. Board Can. 31:329-332.

Weinberger, L. W., D. G. Stephan, and F. M. Middleton. 1966. *Solving our water problems--water renovation and reuse.* Ann. N. Y. Acad. Sci. 136:131-154.

Welch, P. S. *Limnology.* 2nd ed. McGraw-Hill Book Co., New York. 538 pp.

Weschler, M. C., S. A. Spigarelli, and D. N. Edgington. 1972. *The measurement of major nutrients and water quality parameters at Point Beach - 1971.* Radiol. Physics Div. Annu. Rep., Environmental Research, January-December 1971, Argonne National Laboratory Rep. ANL-7860, Part III. pp. 103-108.

Wetzel, R. G. 1972. *The role of carbon in hard-water marl lakes.* In: G. E. Likens (ed.), *Nutrients and eutrophication: the limiting-nutrient controversy.* Special Symposia Vol. 1, American Society of Limnology and Oceanography. pp. 84-97.

__________, P. H. Rich, M. C. Miller, and H. L. Allen. 1972. *Metabolism of dissolved and particulate detrital carbon in a temperate hard-water lake.* Mem. Ist. Ital. Idrobiol. 29(Suppl.):185-243.

Wiersma, J. H., I. K. Iskandar, L. J. Schwartz, and C. C. Weber. 1974. *The effect of a fossil fuel power plant on water quality.* Abstracts, 17th Conf. Great Lakes Res., Hamilton, Ontario. pp. 248-249.

*Willford, W. A., J. F. Carr, and R. J. Hesselberg. 1973. *Pesticide residues in Lake Michigan bloaters (Coregonus hoyi) 1969-1972.* Paper presented at Lake Michigan Toxic Substances Committee Meeting, Columbia, Mo., 21-23 May 1973.

Williams, J. D. H., and T. Mayer. 1972. *Effects of sediment diagenesis and regeneration of phosphorus with special reference to Lakes Erie and Ontario.* In: H. E. Allen and J. R. Kramer (eds.), *Nutrients in natural waters.* John Wiley & Sons, Inc., New York. pp. 281-315.

Winchester, J. W. 1969. *Pollution pathways in the Great Lakes.* Limnos 2:20-24.

__________. 1970. *Chemical equilibria of iodine in Great Lakes waters.* Proc. 13th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 137-140.

__________, and G. D. Nifong. 1971. *Water pollution in Lake Michigan by trace elements from pollution aerosol fallout.* Water Air Soil Pollut. 1:50-64.

Wisconsin Administrative Code. 1973. *Chapter NR 102, Water quality standards for Wisconsin surface waters.* Wis. Regist., September 1973, No. 213. pp. 9-16.

Wisconsin Committee on Water Pollution. 1965. *Wisconsin surface water quality, 1961-1964.* Madison, Wis. (mimeo). 96 pp.

Wisconsin Department of Natural Resources. 1969. *State of Wisconsin surface water quality monitoring data, 1965-68.* Wisconsin Department of Natural Resources, Div. Environ. Prot., Madison. 97 pp.

__________. 1973. *State of Wisconsin surface water quality monitoring data, 1969-72.* Wisconsin Department of Natural Resources, Div. Environ. Prot., Madison. 53 pp.

Wood, J. M. 1974. *Biological cycles for toxic elements in the environment.* Science 183:1049-1052.

Wood, W. W. 1970. *Chemical quality of Michigan streams.* U. S. Geol. Surv. Circ. 634. 21 pp.

Yamagata, N., and I. Shigematsu. 1970. *Cadmium pollution in perspective.* Bull. Inst. Public Health (Tokyo) 19:1-27. (As cited by Friberg *et al.*, 1971).

Zirino, A., and M. L. Healy. 1971. *Voltammetric measurement of zinc in the northeastern tropical Pacific Ocean.* Limnol. Oceanogr. 16:773-778.

ADDITIONAL REFERENCES

Aston, S. R., D. Bruty, R. Chester, and R. C. Padgham. 1973. *Mercury in lake sediments: a possible indicator of technological growth.* Nature 241:450-451.

Beeton, A. M., and D. C. Chandler. 1963. *The St. Lawrence Great Lakes.* In: D. G. Frey (ed.), *Limnology in North America.* University of Wisconsin Press, Madison. pp. 535-558.

Biggs, R. B., J. C. Miller, and M. J. Otley. 1972. *Trace metals in several Delaware watersheds: a progress report.* University of Delaware Water Resources Center, Newark. 37 pp.

Burns, N. M., and C. Ross. 1972. *Project Hypo - discussion of findings.* In: N. M. Burns and C. Ross (eds.), *Project Hypo: an intensive study of the Lake Erie Central Basin hypolimnion and related surface water phenomena.* U. S. Environmental Protection Agency Tech. Rep. TS-05-71-208-24. pp. 120-126.

Carlisle, E. M. 1974. *Silicon as an essential element.* Fed. Proc. 33:1758-1766.

Chau, Y. K. 1973. *Complexing capacity of natural water--its significance and measurement.* J. Chromatogr. Sci. 11:579.

__________, R. Gächter, and K. Lum-Shue-Chan. 1974. *The determination of complexing capacity in lake waters.* J. Fish. Res. Board Can. 31:1515-1519.

__________, and K. Lum-Shue-Chan. 1974. *Determination of labile and strongly bound metals in lake water.* Water Res. 8:383-388.

Craig, L. S. 1972. *The Sea Grant Program in the Great Lakes area.* Proc. 1st Fed. Conf. on the Great Lakes. Great Lakes Basin Commission, Public Inf. Off., EPA Agreement No. EPA-1AG-140(D). pp. 150-156.

Duursma, E. K. 1970. *Organic chelation of* ^{60}*Co and* ^{65}*Zn by leucine in relation to sorption by sediments.* In: D. W. Hood (ed.), *Symposium on organic matter in natural waters.* Univ. Alaska, Inst. Mar. Sci. Occas. Publ. No. 1. pp. 387-397.

Garrels, R. M., and M. E. Thompson. 1962. *A chemical model for sea water at 25°C and one atmosphere total pressure.* Am. J. Sci. 260:57-66.

Hopkins, L. L., Jr., and H. E. Mohr. 1971. *The biological essentiality of vanadium.* In: W. Mertz and W. E. Cornatzer (eds.), *Newer trace elements in nutrition.* Marcel Dekker, Inc., New York. pp. 195-213.

Leary, R. D., and D. T. Lundy. 1973. *Lake Michigan gets help.* Water Wastes Eng. 10(9):64-67.

Otsuki, A. and R. G. Wetzel. 1972. *Coprecipitation of phosphate with carbonates in a marl lake.* Limnol. Oceanogr. 17:763-767.

Schroeder, D. C. 1973. *Transformations of chromium in natural waters.* M.S. Thesis. Univ. Wisconsin--Madison. 86 pp.

Schwab, G. M., and P. L. Katz. 1974. *A model for the study of episodes in the dispersion of a conservative pollutant in Lake Michigan.* Proc. 17th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 837-845.

Slowey, J. F., and D. W. Hood. 1971. *Copper, manganese and zinc concentrations in Gulf of Mexico waters.* Geochim. Cosmochim. Acta 35:121-138.

Syrett, P. J. 1962. *Nitrogen assimilation.* In: R. A. Lewin (ed.), *Physiology and biochemistry of algae.* Academic Press, New York. pp. 171-188.

Thomann, R. V., R. P. Winfield, and D. M. Di Toro. 1974. *Modeling of phytoplankton in Lake Ontario.* Proc. 17th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 135-149.

Warburton, J. A., and L. G. Young. 1968. *Neutron activation measurements of silver in precipitation from locations in western North America.* J. Appl. Meteorol. 7:444-448.

Wood, K. G. 1970. *Carbonate equilibria in Lake Erie.* Proc. 13th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res. pp. 744-750.

__________, and J. Verduin. 1972. *Correlation between CO_2 and O_2 concentrations in Lake Erie, U.S.A.* Arch. Hydrobiol. 71:1-16.

Zoller, W. H., G. E. Gordon, E. S. Gladney, and A. G. Jones. 1973. *The sources and distribution of vanadium in the atmosphere.* In: E. L. Kothny (ed.), *Trace elements in the environment.* Adv. Chem. Ser. 123:31-47.