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# A Preliminary Environmental Assessment of the Contamination Associated with Lake Calumet, Cook County, Illinois

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Illinois Waste Management and Research Center

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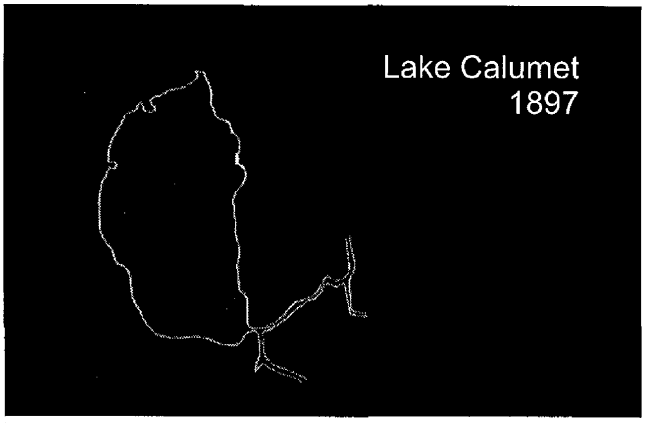


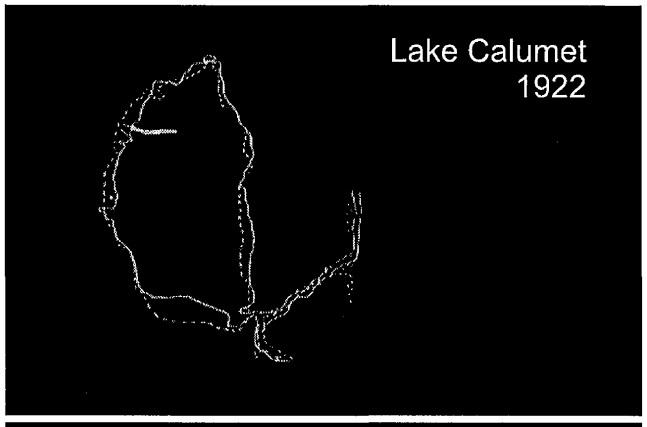


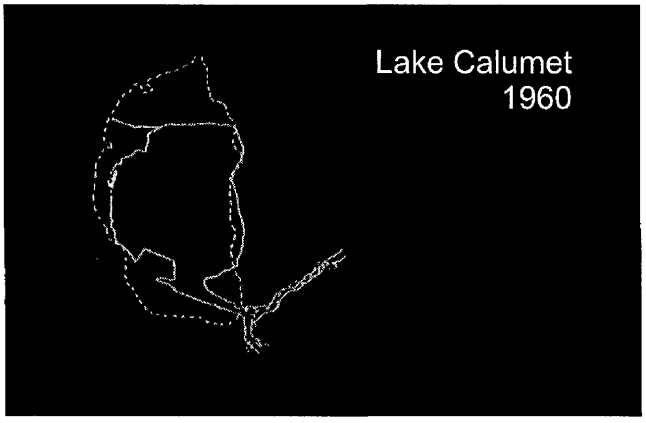


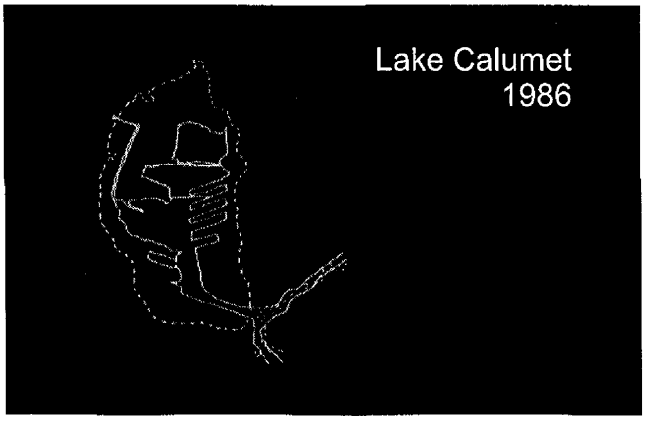


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# ABSTRACT

An environmental profile of Lake Calumet (Chicago, Cook Co., IL) was constructed from a review of technical reports, newspaper articles, and historical studies. From this profile, the need for a more complete study of the contamination of the Lake Calumet area was recognized. In Fiscal Year 1987 (FY'87) the Illinois Department of Energy and Natural Resources (DENR), through the Hazardous Waste Research and Information Center (HWRIC), funded a multidisciplinary study involving researchers from the Illinois State Natural History (INHS), Geological (ISGS), and Water Surveys (ISWS) and DePaul University.

The FY'87 study focussed on the various basins within Lake Calumet proper. Study objectives were: (1) determination of the horizontal distribution of metals and organic contaminants in lake sediments; (2) study of the physical transport of contaminants by surface water and ground water; (3) investigation of the fugacity of selected organic compounds in sediments and water; (4) determination of microbial degradation rates of toxic organic compounds; (5) estimation of metal bioaccumulation rates in macrophytes; and, (6) assessment of overall sediment toxicity by laboratory and field biosssays. Sediment samples were collected at 33 stations within the lake.

Principal findings of this study are: (1) concentrations of toxic metals and organics are generally far above background levels and higher than in nearby water bodies; (2) surface drainage into the lake is entirely through man-made channels; (3) wind-driven resuspension of sediment particles is continual; (4) methane production in sediments confirms the presence of anaerobic microbial communities, which are more numerous in near-shore areas; (5) macrophyte species known to be bioaccumulators of heavy metals were found; (6) all sediment sampling stations produced toxic responses in single-species bioassays, with over half the stations classified as "highly toxic"; and, (7) community-level bioassays showed toxic effects at 71% of the stations.

These results suggest that Lake Calumet is a severely disturbed ecosystem that may present a danger to the surrounding community. The investigators recommend further research in the areas of sediment chemistry and toxicology, groundwater hydrology and chemistry, sediment resuspension, historical loading (isotope studies), bioaccumulation, literature and database searching, atmospheric deposition, and risk assessment. In particular, the database should be expanded to include stations from wetlands, ponds, and small streams within the Lake Calumet drainage basin. The level of effort required to respond to all of the above recommendations would be considerably higher than that allotted in FY'87.

# Executive Summary

Lake Calumet, located 15 miles south of downtown Chicago, is the vestige of a huge lake formed approximately 13,500 years ago from the meltwater of retreating glaciers. The prehistoric lake (which covered the area of present-day Chicago) receded, leaving a low, flat plain with a poorly developed drainage pattern. Stony Island, a rocky outcrop north of Lake Calumet, prevented the deposition of course materials that eventually would have filled in the lake. Instead, fine silt and clays and later organic sediments accumulated in the lake bottom.

Although the high water table and flat, low topography provided an inadequate site for large-scale construction, entrepreneurs in 1869 promoted the Calumet area as an unequaled location for industrial development. Proximity to water for shipping and processing, to railroads for inland transport, and to many potential and expanding markets overshadowed the natural flaws of the area for many industrialists, particularly iron and steel manufacturers.

After a century of industrialization, Lake Calumet's surface area has been substantially reduced. Some of the lake has been filled in with landfills and some "improved" for navigation. The east side of the lake is currently lined with waste disposal facilities, and the west side is bordered by the busy Calumet Expressway (I-94) and a ditch (Pullman Creek) filled with the runoff from the expressway and nearby industries. In addition to the effects of past contamination, Lake Calumet is most likely impacted by a variety of non-point toxicant sources: leaching and dispersal from sediments; highway runoff, including spills; surface runoff from industrial properties contiguous to the lake or drainage areas; seepage of contaminated groundwater from dumps, landfills, waste lagoons, and underground storage tanks; rain scour and dust fall; and perhaps illegal dumping.

Lake Calumet has been exposed to a wide range of industrial contaminants for approximately 110 years. Through increasing regulations, some of the pollution has been reduced. Continued industrial activity and residues from past waste disposal practices, however, still threaten the Lake Calumet system.

The study reported here was initiated to evaluate the physical, chemical, and biological processes that influence the environmental quality of Lake Calumet and the surrounding area and to predict the ecological effects of the contamination associated with lake sediments. The objectives for this preliminary environmental assessment of contamination associated with Lake Calumet are as follows:

• To determine the horizontal distribution of concentrations of heavy metals, total organic carbon (TOC), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and phenolic compounds in Lake Calumet sediments;

• To investigate the movement of surface water, sediment, and pollutants in and around Lake Calumet and to define the dynamics of toxic chemicals in the surface water environment;

• To estimate the contributions of contaminants to the lake *via* groundwater seepage;

• To determine the concentration and fugacity of a number of hazardous organic compounds in the sediments and water from different areas of Lake Calumet;

• To determine microbial degradation rates of toxic organics and to isolate the responsible microorganisms;

• To determine if toxic metals in the sediments and water column of Lake Calumet are bioaccumulated in the aquatic plants found in the area; and

• To measure the toxic effect of sediment extracts to single-species assay organisms, *Photobacterium phosphoreum* (Microtox™), *Selenastrum capricornumtum* (green alga), and *Panagrellus redivivus* (nematode), and to the structure and function of microbial communities.

Results of the preliminary assessment include:

• High concentrations of anthropogenic metals and polycyclic aromatic hydrocarbons (PAHs) were found in Lake Calumet sediments. These concentrations were generally higher than sediment samples in nearby waters.

• In an evaluation of surface water in Lake Calumet, no natural drainage channels were observed. Pullman Creek, a smaller channel in the NE portion of the lake, and two storm sewers are the existing man-made drainage channels for the lake. Pullman Creek is not only a source of inflowing water but also of sediment.

• Organic compounds in the water column were at levels too low for one type of experimental fugacity measurement, but polychlorinated biphenyls were detected in the sediment at levels appropriate for measurement.

• Methane was produced in Lake Calumet sediments, thereby confirming the presence of anaerobic microbial communities. Aerobic and anaerobic bacteria were found in greater numbers at sampling stations near the shoreline of Lake Calumet than at stations in deeper water.

• Lake Calumet wetlands support a population of macrophyte species that have been documented as bioaccumulators of heavy metals.

• Composite toxicity indices (based on the relative toxic responses of *Photobacterium phosphoreum* , *Selenastrum capricornutum* , and *Panagrellus redivivus* ) classified 57% (12/21) of the stations as "highly toxic"; the remainder (43%) were considered "moderately toxic." The toxic responses had a slight statistical correlation with total PAH concentrations in the sediment. Predictions of elutriate chemistry indicate that lead (Pb) might have the potential to exceed water quality standards if released from Lake Calumet sediments.

• Exposure to sediment elutriate from 82% (18/22) of the stations resulted in statistically significant changes in microbial communities with the functional endpoints, photosynthesis and respiration, more sensitive than reduction in numbers of species. Composite toxicity indices (based on the relative toxic responses of functional bioassays) classified 9% of the stations as "extremely toxic," 23% as "highly toxic," 32% as "moderately toxic," and 18% as "weakly toxic"; at 4 stations there was no statistically significant toxic response. Photosynthetic and total microbial community response had strong statistical correlations with metal concentrations in the sediment.

The research described in this study indicates that Lake Calumet is a severely disturbed system. Continued physical alteration has changed the lake's shape, reduced its surface area, and destroyed the surrounding natural wetland areas. Drainage is controlled by man-made channels (e.g., Pullman Creek) and the O'Brien Lock and Dam system. Pullman Creek has been identified as a source of pollutants as well as inflowing water. Chemical compounds common to industry in the Calumet region since the 1870s have concentrated in the sediments of the lake and, consequently, the potential for bioaccumulation in aquatic plants, invertebrates, fish, and perhaps, water fowl and humans is high. Alteration of the aquatic ecosystem through toxic effects of the contaminated sediments is probable.

The presence of waste landfills, major highways, refineries, scrap metal operations, and other industrial activities continues to threaten the Lake Calumet ecosystem. Atmospheric deposition, highway and industrial run-off, and continued alteration of the shoreline and surrounding wetlands may add to the pollution of the lake or induce further sediment disturbance and drainage problems. Changes in the physiochemical nature of the lake by current activities may result in the release of

contaminants deposited in previous years.

Although Lake Calumet seems to be isolated by the O'Brien Lock and Dam and its own sluggish drainage system, its connection with Lake Michigan and with the Illinois River watershed cannot be ignored. Some of the contaminants found in the sediments of Lake Calumet are likely to be found in the soil, water, and air in surrounding areas. The Calumet River and the Cal-Sag Channel may transport contaminants from the lake out of the Calumet region. A ground water connection with the lake is, as yet, unidentified but may play a role in the transport of pollutants in or out of the lake. Resuspension of Lake Calumet sediments is readily accomplished by wind-induced flow and storm events that scour the bottom, transporting sediments to other locations in the lake.

After a year of preliminary study, the investigators feel that further research should be carried out in the following areas:

Continued chemical and toxicological analyses of surface sediment. The existing knowledge base should be expanded in two ways. First, more stations within Lake Calumet proper should be studied to permit greater resolution in contaminant and toxicity mapping. Second, stations in wetlands, ponds, and small streams within the Lake Calumet hydrologic system should be studied in order to gain a more complete understanding of the situation. Special attention should be paid to culverts and drainage ditches leading from past and current industrial or disposal sites into the lake. In addition to chemicals already analyzed, priority pollutant scans should be run on a few selected stations to ensure that important contaminants are not being ignored.

Continued data collection for sediment resuspension. The clearly demonstrated importance of particulate mobilization raises three questions that should be addressed. First, is there a prevalent pattern of particle transport within Lake Calumet? Second, do particles originating in Lake Calumet sediments affect water quality in the Calumet River system and in Lake Michigan? Third, do storm events cause predictable contaminant relocation patterns? More precise data on sediment relocation is needed to answer these questions.

Contaminant input from groundwater. A study of groundwater flow patterns in and around the lake should be undertaken to estimate the importance of continued contaminant input from sub-surface sources.

Historical loading. The historical dimension of contaminant input to the system should be investigated by studying vertical sediment cores at selected stations. Core horizons can be dated by the Cesium-137 or Lead-210 methods, and chemical and toxicological analyses can then be

performed on material deposited in various time periods. The effectiveness of this approach may be compromised if thehigh degree of lateral transport noted above obscures vertical deposition patterns, making historical trends impossible to detect.

Bioaccumulation. The level of bioaccumulatory substances in the sediment justifies analyses of aquatic plants and the initiation of a fish and invertebrate sampling program. Flesh analysis should include metals, PAHs, PCBs, and select pesticides. Fish analysis is especially critical because human consumption of Lake Calumet fish could present a health risk. (During the April 1987 sampling trip, 18 fishermen were seen in one afternoon.)

Literature and data base research. Although a good deal of information has been summarized in the Colten (1985) report and in this document, more sources should be explored. In particular, data from monitoring wells (Illinois Environmental Protection Agency) and internal environmental quality programs (Metropolitan Sanitary District of Greater Chicago) should be accessed.

Atmospheric deposition. In order to complete the study of contamination sources, the role of atmospheric deposition should be evaluated.

Public health. The existing public health data base (Illinois Public Health Dept.) should be re-examined when current studies are completed. These data should be compared with contaminant and toxicological data to determine whether correlations exist. The need for further epidemiological studies should also be evaluated at that time.

# Chapter 1
# An Environmental Profile of Lake Calumet

## 1.1 Historical Perspective

Lake Calumet, located 15 miles south of downtown Chicago (Figure 1.1), is the vestige of a huge lake formed approximately 13,500 years ago from the meltwater of retreating glaciers. The prehistoric lake (which covered the area of present-day Chicago) receded, leaving a low, flat plain with a poorly developed drainage pattern (Figure 1.2). Stony Island, a rocky outcrop north of Lake Calumet, prevented the deposition of course materials that eventually would have filled in the lake. Instead, fine silt and clays and later organic sediments accumulated in the lake bottom (Colten 1985).

Prior to industrialization, the shallow sand aquifers absorbed rainwater and runoff, discharging it into the marshy areas surrounding Lake Calumet. Acting like sponges, the organic swamp deposits held the water levels in hydraulic balance with Lake Calumet, which, in turn, was in balance with Lake Michigan. The Calumet River, formed by the confluence of the Grand Calumet and Little Calumet rivers, received the outflow of Lake Calumet and then flowed into Lake Michigan. When it was surveyed in 1834, Lake Calumet was 3.5 miles long (north-south) and 1.5 miles wide. The surrounding marshes were as much as 2 feet deep and the lake was only 6 to 10 feet deep.

Although the high water table and flat, low topography provided an inadequate site for large-scale construction, entrepreneurs in 1869 promoted the Calumet area as an unequaled location for industrial development. Proximity to water for shipping and processing, to railroads for inland transport, and to many potential and expanding markets overshadowed the natural flaws of the area for many industrialists, particularly iron and steel manufacturers. Two primary metal industries, two building materials manufacturers, four food processing industries, and one chemical-petroleum manaufacturer were sited on the west bank of Lake Calumet in 1897. By 1913, five primary metal industries resided on the west bank (Colten 1985). As industrial activity in the Calumet area increased, so did the uncontrolled disposal of waste. Liquid wastes were directed into nearby water; these wastes were usually untreated, although they were sometimes diluted with non-contact waste water. Solid refuse was taken to nearby vacant land and dumped. Little concern was expressed about the hazardous quality of industrial by-product, and health authorities directed most of their attention to the problems of biological wastes, both domestic and industrial.

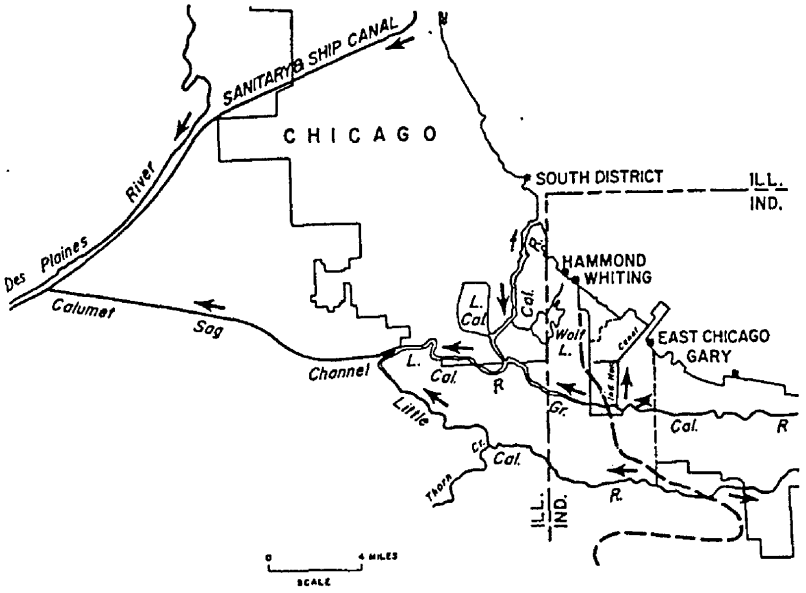


Figure 1.1 Location of Lake Calumet.

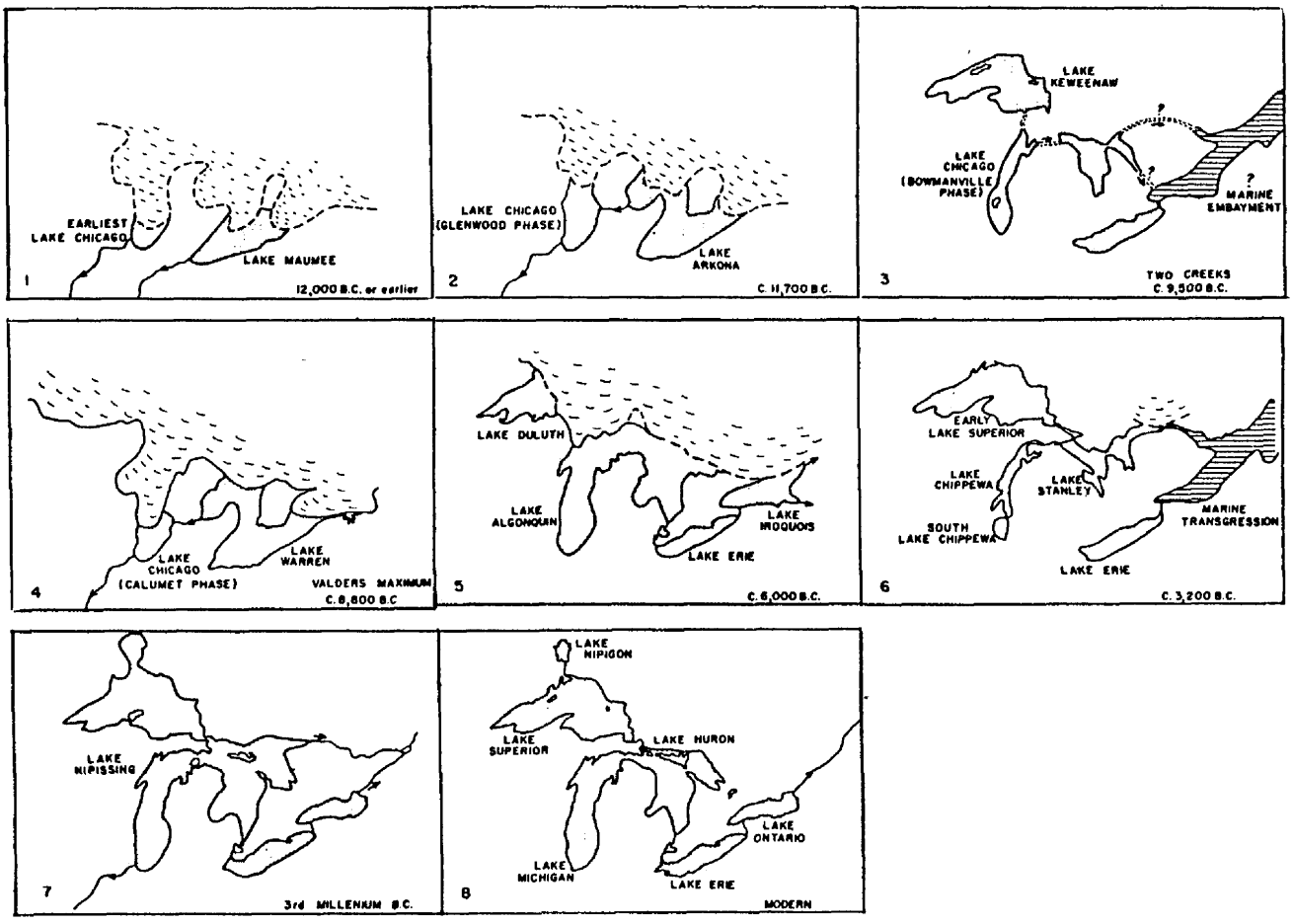


Figure 1.2 Glacial history of the Great Lakes (from Wetzel 1983).

Some manufacturers sought to improve their property by filling the marshland with solid waste, primarily slag (the fused refuse separated from a metal in smelting) and/or dredge spoils from the lake and river. By 1882, over 30 acres of land had been created in the Lake Calumet area by the combination of natural and human deposition, and eventually 300 acres were built up (Colten 1985). Waste streams probably contained huge quantities of phenols, cyanides, and heavy metals (Colten 1985). Coal was the primary fuel in most factories and fly ash added to the atmospheric pollution and solid waste in the area. Chemical components of fly ash from Illinois coals included high concentrations of zinc, nickel, rubidium, cesium, chromium, cobalt, and uranium in addition to amounts of most other metals (Suloway *et al.* 1983).

In 1922, the flow of the Calumet River was reversed to preserve the integrity of Lake Michigan waters. The construction of the Cal-Sag channel allowed diversion of industrial effluents from Lake Michigan to the Illinois River and eventually into the Mississippi River . Concurrently, research into the treatment of domestic wastes led to the construction of sewage systems and treatment facilities. Industrial waste, however, continued to pour untreated into the streams of the Calumet area. Storm runoff sporadically forced the current of the waste-laden Calumet River toward Lake Michigan, threatening drinking-water supplies. The Great Depression probably had a much greater effect on reducing water pollution than did the new wastewater treatment programs of the 1920s. When production levels dropped, waste production also fell and pollution problems decreased (Colten 1985).

After 1940, land disposal became the most widely accepted and economic means of waste disposal. In addition to slag and other material that had long been handled in this way, sludges from treatment facilities were transported to nearby dumps in the marshland of the Calumet area (Colten 1985). In 1940, the City of Chicago built a dike at 110th Street across Lake Calumet in order to use the open space to the north as a garbage dump. In 1954, citizens protesting the odors and fires from the dump found that the untreated leachate from the dump was flowing into the lake, swamps, and streams (IEPA 1986). Although the landfill is now nearing capacity, it has been in continuous operation since its opening and has filled in the northern quarter of Lake Calumet (Colten 1985). Materials excavated from some of the landfills include construction and building debris, ashes from incinerators, cinders, clay, brick, wood, paper, steel-making process slag, organic and inorganic materials, general bulk refuse, excavation spoil, and industrial wastes (ENCAP 1979). Samples taken from landfill sites (USACE 1985) contained elevated levels of most heavy metals and PAHs (polycyclic aromatic hydrocarbons).

## 1.2 Current Environmental Status

Figure 1.3 illustrates the impact on Lake Calumet of over a century of industrialization. Some of the lake has been filled in with landfills and some "improved" for navigation. The east side of the lake is currently lined with waste disposal facilities, and the west side is bordered by the busy Calumet Expressway (I-94) and a ditch (Pullman Creek) filled with the runoff from the expressway and nearby industries. In addition to the effects of past contamination, Lake Calumet is most likely impacted by a variety of non-point toxicant sources: leaching and dispersal from sediments; highway runoff, including spills; surface runoff from industrial properties contiguous to the lake or drainage areas; seepage of contaminated groundwater from dumps, landfills, waste lagoons, and underground storage tanks; rain scour and dust fall; and perhaps illegal dumping (USEPA 1985).

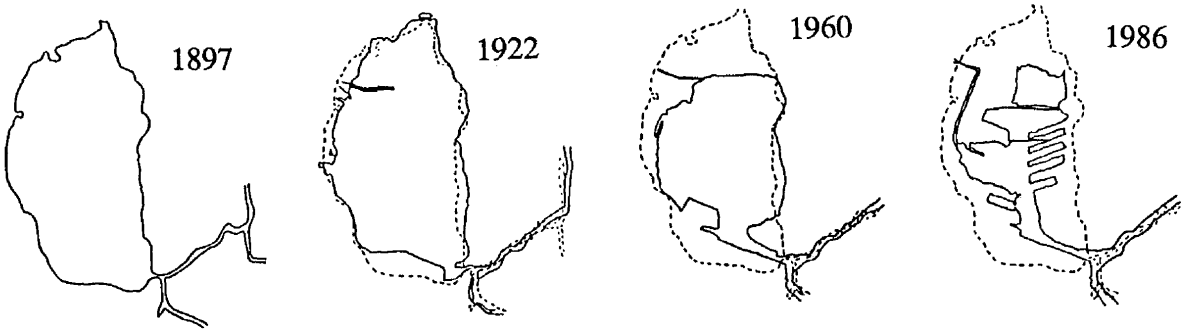


Figure 1.3 Alteration of Lake Calumet: 1897 - 1986.

A 1986 survey of volatile organic compounds (VOC) entering the Calumet Sewage Treatment plant included dichloromethane, 1,1,1-trichloroethane, acetone, isopropanol, toluene, and a vinyl toluene isomer. Dichloromethane, 1,1,1-trichloromethane, acetone, and toluene were also present in large quantities in the primary sludge sampled from the treatment plant (MSDGC, unpublished data ). In a separate study of the VOC component of the Calumet Sewage Treatment Plant influent, Namkung and Rittmann (1986) noted the presence of benzene, chlorobenzene, chloroform, 1,2-dichlorethane, ethylbenzene, methylene chloride, tetrachlorethylene, toluene, 1,1,1-trichloroethane, 1,2-*trans* -dichloroethylene, and trichloroethylene. Industries dealing with petroleum refining, gum and wood chemicals, metal degreasing , or dry cleaning may be sources of VOCs in the Calumet area because of the large amounts of toluene and benzene in the Calumet Treatment Plant influent (Namkung and Rittmann 1986).

A study completed by the Illinois Environmental Protection Agency (IEPA) in 1986 contains an overview of the status of land, water and air pollution in the Lake Calumet area. Contaminants frequently encountered in the study are listed in Table 1.1. Land pollution may stem from the 31 (operating or retired) landfills and waste handling facilities in the study area. Most of the sites are generally in compliance with IEPA permit conditions; however, three sites are cited in litigation with the IEPA and the Illinois Attorney General and ten sites are either not operating or are regulated through other agencies and are not required to be permitted with the IEPA Division of Land Pollution Control.

Table 1.1 Chemicals encountered during the IEPA *Southeast Chicago Study* (1986).

| Land Pollution | Water Pollution | Air Pollution |
|---|---|---|
| Arsenic | Ammonia | Sulfur dioxide |
| Barium | Lead | Carbon monoxide |
| Cadmium | Zinc | Nitrogen oxides |
| Chromium | Cyanide | Ozone |
| Copper | Chromium VI | Lead |
| Iron | PCB | Sulfates |
| Lead | Hexachlorocyclohexane | Nitrates |
| Manganese | Heptachlor | Copper |
| Mercury | Chlordanes | Iron |
| Nickel | DDT and analogs | Manganese |
| Selenium | Dieldrin | Toluene |
| Silver | Endrin | Benzene |
| Zinc | trans-Nonachlor | Xylenes |
| Benzene | | Acetone |
| Toluene | | Arsenic |
| Xylenes | | Beryllium |
| Ethylbenzene | | Cadmium |
| Pyridine | | Chromium |
| Methylpyridine | | Nickel |
| Dibutylphthalate | | Mineral spirits |
| | | Hexane |
| | | Isopentane |
| | | Isopropyl alcohol |
| | | Naphtha |
| | | Methyl ethyl ketone |
| | | Methanol |
| | | Methylene chloride |
| | | Phenol |

Key factors influencing the water quality of Lake Calumet included the use of the lake for deep draft navigation, the regulation of flow by the O'Brien lock, and the susceptibility of the Calumet River to changes in flow direction during storm events and of Lake Calumet to local conditions, storm drainage, and seepage water (IEPA 1986).

Facilities that probably contribute to air pollution in the area include steel mills, chemical plants, auto assembly plants, and a hazardous waste incinerator. Monitoring of the air detected toluene, benzene, xylene, acetone, arsenic, beryllium, cadmium, chromium, and nickel (IEPA 1986, Gatz & Sweet 1987).

Monitoring the concentrations of certain anthropogenic compounds in the flesh of fish from an impacted waterway can indicate the presence of persistent compounds in the water column. A fish contaminant analysis for Lake Calumet, including pesticides and organics that are routinely checked by the IEPA in the fish of Illlinois, is given in Table 1.2. Studies measuring levels of toxic metals in fish from Lake Calumet have not been published.

Table 1.2 Fish Contaminant Analysis in mg $kg^{-1}$ for Lake Calumet (IEPA 1986).

| Parameter | Action Level | Largemouth Bass | Carp | White Crappie |
|---|---|---|---|---|
| PCB (1254) | 5.0 | 0.219 | 0.631 | 0.263 |
| Hexachlorobenzene | -- | Tr | Tr | Tr |
| Hexachlorocyclohexanes | -- | Tr | Tr | Tr |
| Heptachlor epoxide | 0.3 | Tr | Tr | Tr |
| Chlordanes | 0.3 | Tr | 0.014 | Tr |
| DDT and analogs | 5.0 | 0.018 | 0.069 | 0.022 |
| Dieldrin | 0.3 | Tr | Tr | Tr |
| Endrin | -- | Tr | -- | -- |
| trans-Nonachlor | -- | Tr | Tr | Tr |
| Percent fat | -- | 1.6 | 2.8 | 1.2 |

Tr=trace amounts

The fish fauna from Lake Calumet and its adjacent wetlands were assessed in 1981 and 1982 (Greenfield and Rogner 1984). A total of 27 fish species from 10 families was collected the sampling area (Table 1.3). The number of species had apparently decreased at sites with the most

extensive habitat modifications. Table 1.3 also lists the fish species recorded from the Lake Calumet area from 1876 to 1980 by various authors. A comparison of the current species with historical records shows a relative reduction in diversity over time in the lake. The current fish community in Lake Calumet, however, remains diverse. A score of 48 was calculated for the lake based on Karr's index of integrity (Karr 1981) to evaluate the quality of the fish fauna. This score is comparable to scores obtained for the Fox River and falls within the "good" range (Greenfield and Rogner 1984).

Five species of birds listed on the Illinois endangered list but not on the Federal list have been found in the Lake Calumet area: yellow rail, black-crowned night heron, American bittern, red-shouldered hawk, and marsh hawk (Equitable Environmental Health 1978). Continued habitat degradation and contaminated food could affect the future status of these birds.

Sediment sampling parameters from four sampling stations on nearby rivers and a lake (Figure 1.4) exposed to similar environmental conditions as Lake Calumet are listed in Table 1.4. Sediment quality criteria and standards are currently being developed by the USEPA. Until these standards are published, pollutant concentrations can be compared to background levels from a statewide chemical survey of Illinois sediments (Kelly and Hite 1979). The concentrations determined for each compound in Table 1.4 are assigned a value based on the relative level of elevation over this background (Table 1.5).

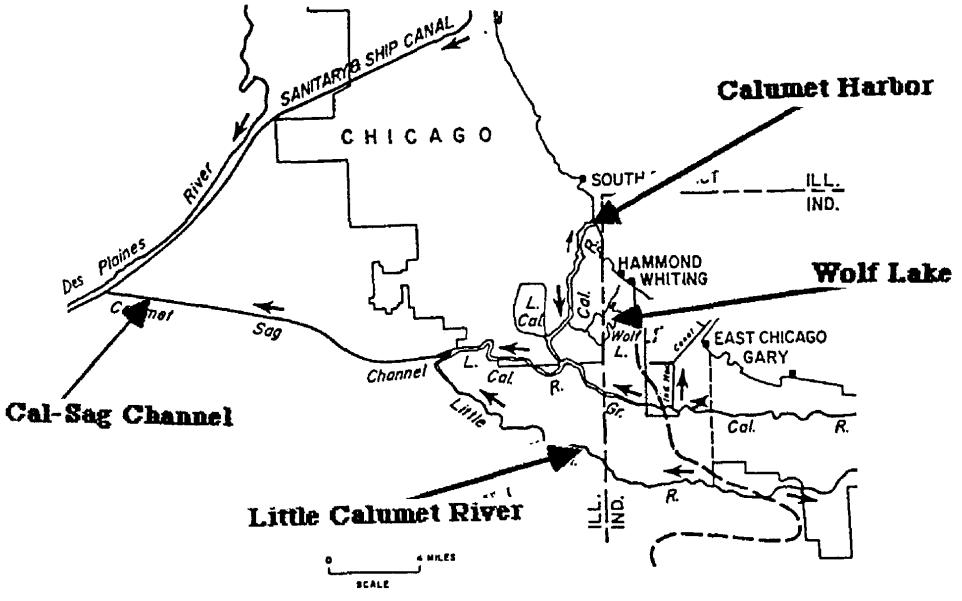


Figure 1.4 Stations sampled for sediment chemistry near Lake Calumet.

Table 1.3 Past and present fish species found in Lake Calumet (Greenfield and Rogner 1984).

| Fish collected by various studies 1876 - 1980 | Year(s) collected* | Fish collected Sept. 1981 through Aug. 1982 |
|---|---|---|
| *Acipenser flavescens* | 1 | |
| *Lepisosteus osseus* | 1 | *Umbra limi* |
| *Amia calva* | 2,3 | *Alosa psuedoharengus* |
| *Alosa pseudoharengus* | 5,6,7 | *Dorosoma cepedianum* |
| *Dorosoma cepedianum* | 5,6,7 | *Oncorhynchus tshawytscha* |
| *Umbra limi* | 3 | *Osmerus mordax* |
| *Esox americanus vermiculatus* | 2,5 | *Carassius auratus* |
| *Esox lucius* | 2,3,5 | *Cyprinus carpio* |
| *Catostomus commersoni* | 2 | *Notemigonus crysoleucas* |
| *Ictiobus niger* | 3 | *Notropis atherinoides* |
| *Ictiobus bubalus* | 3 | *Notropis hudsonius* |
| *Carpoides velifer* | 3 | *Notropis spilopterus* |
| *Erymyzon succetta* | 2,3 | *Notropis stramineus* |
| *Pimephales notatus* | 3,4,5,6,7 | *Pimephales promelas* |
| *Pimephales promelas* | 5,7 | *Carpoides cyprinus* |
| *Carassius auratus* | 4,5,6,7 | *Ictalurus melas* |
| *Cyprinus carpio* | 4,5,6,7 | *Ictalurus punctatus* |
| *Notemigonus crysoleucas* | 2,3,4,7 | *Lepomis cyanellus* |
| *Notropis emiliae* | 3 | *Lepomis gibbosus* |
| *N. stramineus* | 7 | *L. cyanellus X L. gibbosus* |
| *N. heterolepis* | 3 | *Lepomis humilis* |
| *N. heterodon* | 1,3 | *Micropterus salmoides* |
| *N. blennius* | 3 | *Pomoxis annularis* |
| *N. hudsonius* | 3,6,7 | *Pomoxis nigromaculatus* |
| *N. spilopterus* | 3 | *Etheostoma nigrum* |
| *N. atherinoides* | 3,6,7 | *Perca flavescens* |
| *Ictalurus natalis* | 2,4 | *Aplodinotus grunniens* |
| *Noturs gyrinus* | 2 | |
| *Apherdoderus sayanus* | 1 | |
| *Fundulus diaphanus* | 3 | |
| *Fundulus dispar* | 3,4 | |
| *Labidesthes sicculus* | 3 | |
| *Pomoxis annularis* | 3 | |
| *Pomoxis nigromaculatus* | 2,3,6,7 | |
| *Ambliplites rupstris* | 3,5 | |
| *Lepomis cyanellus* | 1,5,6,7 | |
| *Lepomis humilis* | 6,7 | |
| *Lepomis magalotis* | 3 | |
| *Lempomis macrochirus* | 1,2,3,5,6,7 | |
| *Lepomis gibbosus* | 3,4,6,7 | |
| *Micropterus salmoides* | 1,2,3,5,6,7 | |
| *Perca flavescens* | 1,2,3,5,6,7 | |
| *Percina caprodes* | 1,3 | |
| *Etheostoma nigurm* | 3 | |
| *Etheostoma camurum* | 3 | |
| *Morone chrysops* | 3 | |

* 1=1876, 2=1910, 3=1920, 4=1941, 5=1975, 6=1978, 7=1980

Table 1.4 Chemistry of sediments near Lake Calumet (see Figure 1.4 for sampling locations).

| Parameter | Wolf Lake [a] Value | Rank | Calumet Harbor [b] Value | Rank | Cal-Sag Channel [c] Value | Rank | Little Calumet River [c] Value | Rank |
|---|---|---|---|---|---|---|---|---|
| COD(mg $kg^{-1}$) (chemical oxygen demand) | 90000 | 0 | 86000 | 0 | 150000 | 2 | 141000 | 2 |
| Total Kjedahl Nitrogen (mg $kg^{-1}$) | 2250 | 0 | 860 | 0 | 3200 | 1 | 3500 | 2 |
| Total Volatile Solids (%) | 5.75 | 0 | 9.5 | 2 | 8.6 | 1 | 8.7 | 1 |
| Total Phosphorus (mg $kg^{-1}$) | 360 | 1 | 206 | 1 | 3000 | 3 | 1300 | 2 |
| Arsenic (mg $kg^{-1}$) | 21 | 3 | 6.2 | 0 | 15 | 2 | 5.5 | 0 |
| Chromium (mg $kg^{-1}$) | 18 | 1 | 46 | 3 | 105 | 4 | 66 | 4 |
| Copper (mg $kg^{-1}$) | 27 | 0 | 44 | 1 | 125 | 3 | 88 | 2 |
| Iron (mg $kg^{-1}$) | 14900 | 0 | -- | -- | 33500 | 3 | 29000 | 2 |
| Lead (mg $kg^{-1}$) | 110 | 4 | 144 | 4 | 370 | 4 | 190 | 4 |
| Manganese (mg $kg^{-1}$) | 820 | 0 | 948 | 0 | 470 | 0 | 540 | 0 |
| Mercury (mg $kg^{-1}$) | 0.06 | 0 | 0.4 | 4 | 0.89 | 4 | 0.85 | 4 |
| Zinc (mg $kg^{-1}$) | 255 | 3 | 268 | 3 | 1100 | 4 | 375 | 4 |
| Cadmium (mg $kg^{-1}$) | 2.0 | 2 | 3.2 | 3 | 8.5 | 3 | 2.5 | 3 |

[a] Kelly and Hite 1979
[b] USACE 1985
[c] IEPA 1984

Table 1.5 Classification of Illinois sediments relative to background mean values ( after IEPA 1984)[a].

| | Not elevated 0 | Slightly elevated 1 | Elevated 2 | Highly elevated 3 | Extreme 4 |
|---|---|---|---|---|---|
| COD(mg $kg^{-1}$) | <90000 | >90000 | >132000 | >215000 | >380000 |
| Total Kjedahl Nitrogen (mg $kg^{-1}$) | <2300 | >2300 | >3200 | >5100 | >8800 |
| Total Volatile Solids (%) | <6.5 | >6.5 | >8.8 | >13 | >22 |
| Total Phosphorus (mg $kg^{-1}$) | <80 | >80 | >1100 | >1700 | >3000 |
| Arsenic (mg $kg^{-1}$) | <8.0 | >8.0 | >11 | >17 | >28 |
| Chromium (mg $kg^{-1}$) | <16 | >16 | >23 | >38 | >60 |
| Copper (mg $kg^{-1}$) | <38 | >38 | >60 | >100 | >200 |
| Iron (mg $kg^{-1}$) | <18000 | >18000 | >23000 | >32000 | >50000 |
| Lead (mg $kg^{-1}$) | <28 | >28 | >38 | >60 | >100 |
| Manganese (mg $kg^{-1}$) | <1300 | >1300 | >1800 | >2800 | >5000 |
| Mercury (mg $kg^{-1}$) | <0.07 | >0.07 | >0.10 | >0.17 | >0.30 |
| Zinc (mg $kg^{-1}$) | <80 | >80 | >100 | >170 | >300 |
| Cadmium (mg $kg^{-1}$) | <0.5 | >0.5 | >1.0 | >2.0 | >20.0 |
| Chlordane (µg $kg^{-1}$) | <5 | >5 | >6 | >10 | >40 |
| Sum DDT (µg $kg^{-1}$) | <6.0 | >6.0 | >10 | >35 | >200 |
| Dieldrin (µg $kg^{-1}$) | <3.5 | >3.5 | >6 | >10 | >25 |
| Heptachlor Epoxide (µg $kg^{-1}$) | <1.0 | >1.0 | >1.5 | >3 | >9 |
| PCBs (µg $kg^{-1}$) | <20 | >20 | >50 | >200 | >1500 |

[a] Ranges of concentrations displayed and resultant groupings are based on one, two, four, and eight standard deviations from background mean. Cadmium, Chlordane, DDT, Dieldrin, Heptachlor Epoxide and PCB groupings are based on 50, 65, 80, and 95% distributions for all samples.

## 1.3 Predictions for Lake Calumet

Because the contaminants listed in Table 1.1 are prevalent in the industrial setting near Lake Calumet, they have the potential to enter the water column of Lake Calumet *via* overland runoff, surface water transport, atmospheric depostion, industrial flow, or groundwater contribution (Figure 1.5). The water-related fate of these compounds can involve physical, chemical, and biological processes that act individually or in combination depending on the structure of the chemical and on the structure and function of the aquatic system. In 1979, the USEPA completed a literature study of the water-related environmental fate of 129 priority pollutants. The mechanisms involved in the fate of a pollutant in an aquatic system were identified (Callahan and Slimak 1979) as follows:

*Transport processes*:

1. Volatilization--an important pathway for chemicals with high vapor pressures or low solubilities.

2. Sorption--in general, the more hydrophobic a chemical is the more likely it is to be sorbed to sediment.

*Chemical processes:*

3. Photolysis--photochemical transformations may occur by one or more processes, depending on the chemical structure and substances in the environment; photolysis occurs at wavelengths greater than 290 nm.

4. Oxidation--may occur as a result of oxidizing chemicals formed during photochemical processes in natural waters.

5. Hydrolysis--usually promoted by acidic conditions.

*Biological processes*:

6. Bioaccumulation--is especially important for hydrophobic chemicals that can be partitioned into fat and lipid tissues; bioaccumulation can produce significant ecological effects.

7. Biotransformation and Biodegradation--result from enzyme-catalyzed transformation of chemicals.

Table 1.6 lists the transport and fate of priority pollutants encountered in studies of the Lake Calumet area. Arsenic, cadmium, chromium, copper, lead, nickel, selenium, silver, zinc, DDT, dieldrin, PCBs, di-n-butyl phthalate, and PAHs are the priority pollutants most likely to be identified in the sediments of Lake Calumet.

In summary, Lake Calumet has been exposed to a wide range of industrial contaminants for approximately 110 years. Through increasing regulations, some of the pollution has been reduced. Continued industrial activity and residues from past waste disposal practices, however, still threaten the Lake Calumet system. The study reported here was initiated to evaluate the physical, chemical, and biological processes that influence the environmental quality of Lake Calumet and the surrounding area and to predict the ecological effects of the contamination associated with lake sediments.

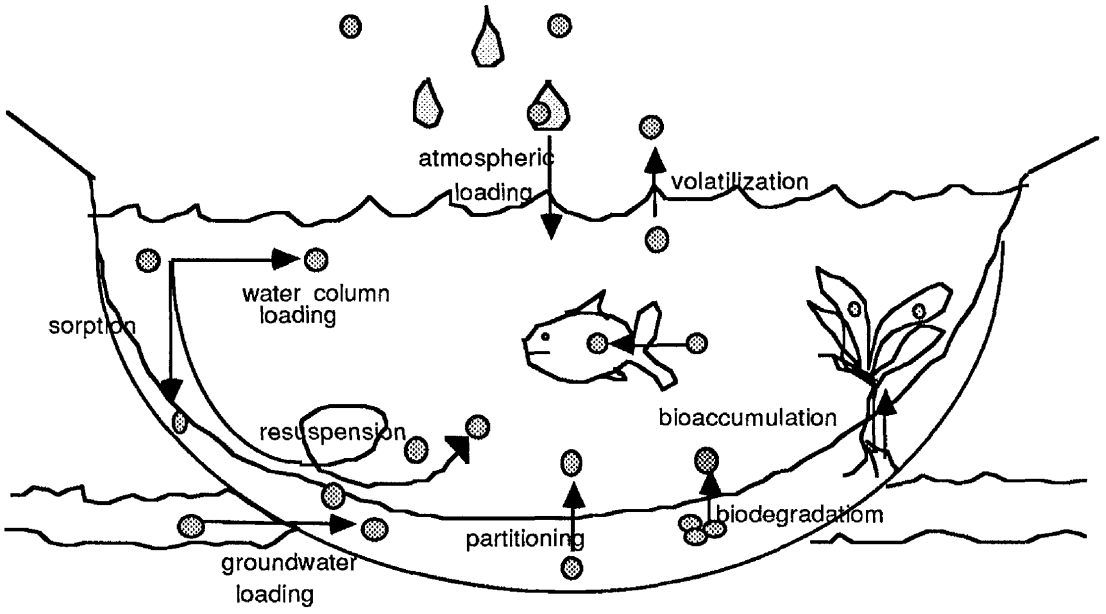


Figure 1.5 Transport and fate of contaminants in the aquatic environment.

Table 1.6 Estimated transport and fate of priority pollutants encountered in the Lake Calumet area (after Callahan and Slimak 1979).

| Chemical | Is the process important for aquatic transport? | | | Is the process important in determining aquatic fate? | | | |
|---|---|---|---|---|---|---|---|
| | Vola-tilization | Sorption | Transport downstream | Photolysis | Speciation | Bioaccu-mulation | Biodegra-dation |
| Arsenic | Y | Y | Y | N | Y | Y | Y |
| Cadmium | N | Y | Y | N | Y | Y | N |
| Chromium | N | Y | Y | N | Y | Y | N |
| Copper | N | Y | Y | N | Y | Y | N |
| Cyanide | Y | N | N | Y | U | N | Y |
| Lead | U | Y | Y | U | Y | Y | Y |
| Mercury | Y | Y | Y | Y | Y | Y | Y |
| Nickel | N | Y | Y | N | Y | N | Y |
| Selenium | U | Y | Y | N | Y | U | Y |
| Silver | N | Y | Y | N | Y | U | N |
| Zinc | N | Y | Y | N | Y | Y | N |
| DDT | Y | Y | U | U | U | Y | U |
| Dieldrin | U | Y | U | U | N | Y | U |
| Endrin | U | U | U | U | N | Y | U |
| Heptachlor | U | N | U | U | Y | U | N |
| Hexachlor-cyclohexane | U | U | U | N | N | U | N |
| PCBs | Y | Y | U | U | N | Y | N |
| Benzene | Y | U | U | N | N | N | U |
| Toluene | Y | U | U | N | N | N | U |
| Phenol | U | N | U | Y | N | N | Y |
| Di-n-butyl-phthalate | N | Y | Y | N | N | U | U |
| PAHs | U | Y | U | Y | N | N | Y |

Y=yes, N=no, U=uncertain

# Chapter 2
# Study Objectives and Fieldwork

## 2.1 Study Objectives

The preceding literature review and environmental profile of Lake Calumet document the need for a more complete study of the contamination of Lake Calumet and for an assessment of the associated ecological hazard. Lake sediments can contain magnified concentrations of chemicals (especially anthropogenic compounds) from years of exposure. Investigations of sediment chemistry, transport, and toxicity help to predict short- and long-term effects on the surrounding ecosystem and to identify hazardous pollutants and point sources. In a complex environment such as a lake, physical, chemical, and biological factors must be investigated.

The report that follows includes the results of the first year of study on the processes and effects occuring in Lake Calumet. Each study objective, as indicated below, correlates with one or more of the chapters that follow.

1) To determine the horizontal distribution of concentrations of heavy metals, total organic carbon (TOC), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and phenolic compounds in Lake Calumet sediments (Chapter 3);

2) To investigate the movement of surface water, sediment, and pollutants in and around Lake Calumet and to define the dynamics of toxic chemicals in the surface water environment (Chapter 4, Sections 4.1 - 4.4);

3) To estimated the contributions of contaminants to the lake *via* groundwater seepage (Chapter 4, Section 4.5);

4) To determine the concentration and fugacity of a number of hazardous organic compounds in the sediments and water from different areas of Lake Calumet (Chapter 5);

5) To determine microbial degradation rates of toxic organics and to isolate the responsible microorganisms (Chapter 6);

6) To determine if toxic metals in the sediments and water column of Lake Calumet are bioaccumulated in the aquatic plants found in the area (Chapter 7); and

7) To measure the toxic effect of sediment extracts to single-species assay organisms, *Photobacterium phosphoreum* (Microtox$^{TM}$), *Selenastrum capricornumtum* (green alga), and *Panagrellus redivivus* (nematode), and to the structure and function of microbial communities (Chapters 8 and 9).

Chapter 10 summarizes the research conducted and presents the conclusions drawn from the study as a whole. It makes recommendations for continued research to meet the objectives of this study and for new research that will add to the growing data base on Lake Calumet.

## 2.2 Fieldwork

Measurements and samples were collected at Lake Calumet at various times during the research year by various investigators. Table 2.1 summarizes these field activities. Figure 2.1 identifies the sampling stations.

Table 2.1. Field activities at Lake Calumet, 1 August 1986 - 31 July 1987.

| Date | Activity | Sample labels | Participants |
|---|---|---|---|
| 4 - 5 Sept. 1986 | drainage/flow investigation | -------- | ISWS |
| 23 Oct. 1986 | reconnaisance/sediment sampling | LCAL D | ISGS, INHS, DPU |
| 1 Nov. 1986 | protozoan colonization studies | -------- | INHS |
| 20 Nov. 1986 | sediment sampling | LCAL A-C, E-M | ISGS, INHS, DPU |
| 6 Jan. 1987 | water column sampling | ------- | DPU |
| 6 Apr. 1987 | water column sampling | ------- | DPU |
| 7 Apr. 1987 | sonar profiles of lake bed | ------- | ISWS |
| 15 Apr. 1987 | in-lake flow measurements | ------- | ISWS |
| 16 Apr. 1987 | total lake discharge measurements, sonar profiles of lake bed | ------- | ISWS |
| 28 Apr. 1987 | sediment sampling | LCAL 1-20, WCAL 4-7 | ISGS, INHS, DPU |
| 1 July 1987 | macrophyte collection | A1-3, B1, C1, D1, E1, F1-4, G1, H1-5 | INHS |

ISWS = Illinois State Water Survey INHS = Illinois Natural History Survey
DPU = DePaul University ISGS = Illinois State Geological Survey

Sediments were collected with a Ponar grab sampler, manually mixed for homogenization, distributed to glass jars, and iced in the field. In the laboratory, the samples were stored in the dark at 4 $^{o}$C until they were used for chemical determination or toxicological characterization (maximum storage: 8 weeks).

Other measurement and collection activities are described in detail in the chapters of the report.

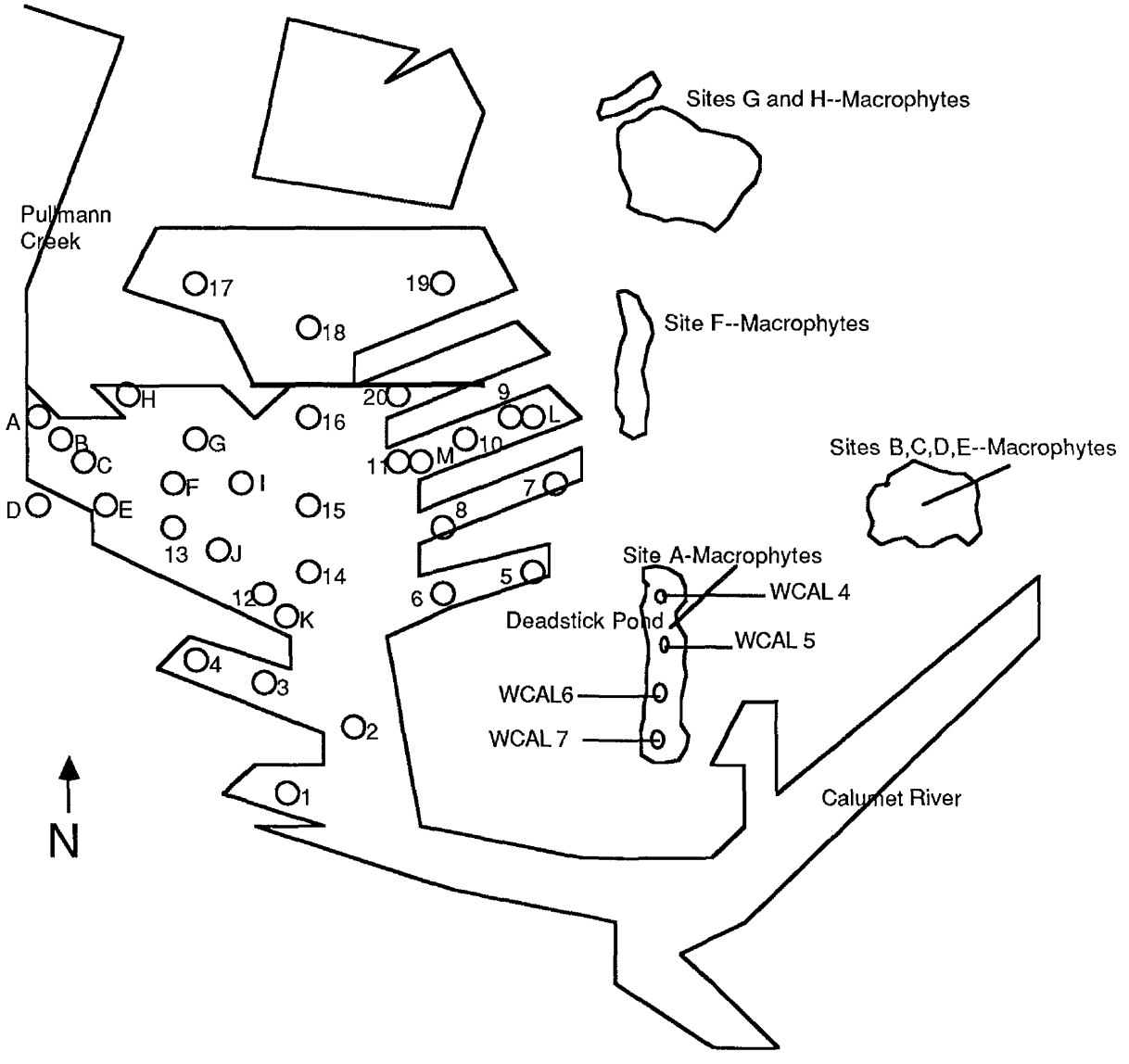


Figure 2.1. Sampling Locations for Fiscal Year 1987 at Lake Calumet. Lettered stations in the lake-proper were collected in November 1986. Numbered stations were collected in April 1987. The prefix LCAL for numbered stations in the lake-proper has been dropped in this map; LCAL 1 = 1.

# Chapter 3
# Sediment Chemistry

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## 3.1 Introduction

The investigation of the sediments at the bottom of a lake provides a record of events that have influenced the lake and its associated drainage basin. The most recent sediments in a lake reflect human impact on the surrounding drainage area and direct discharges to the lake itself.Thus, inorganic and organic chemical analyses of lake sediments are frequently used to distinguish the sources of inputs to a lake.

In this study we have determined the concentration of 44 major, minor, and trace elements insediments from 37 stations in Lake Calumet (Figure 3.1). During the first phase of sampling in November 1986, thirteen stations (A-M) were sampled; during the second phase, sediments from 25 stations (LCAL 1 - 20 and WCAL 4 - 7) were collected.

Because no single analytical method is accurate for all elements, several analytical techniques appropriate for specific elements were used. The instrumental methods used are summarized in Table 3.1. In addition to elemental analyses, total organic carbon, polycyclic aromatics, and chloro-, nitro-, and methyl-phenols were determined.

## 3.2 Materials and Methods

### 3.2.1. Sample preparation.

Surficial sediments from 37 stations were collected and maintained as described in Chapter 2. Samples, which had been stored at 4°C, were homogenized and sub-sampled (approx. 50 g) for elemental analysis. After wet weights were determined, sub-samples were dried at ambient temperature, ground to pass a 100 mesh sieve, and stored in glass bottles at 23°C until needed.

### 3.2.2. Instrumental neutron activation (INAA).

Gamma activities of the samples (0.500 g, 110°C dried sediment) were compared with those of multi-elemental calibration standards prepared by evaporating aliquots of standard solution onto a Whatman Cellulose Powder, CF-11. Samples and standards were irradiated with thermal neutrons in the Advanced TRIGA Mark II reactor at the University of Illinois. Gamma intensity measurements were carried out at the Illinois State Geological Survey (ISGS) using Ge(Li) detectors

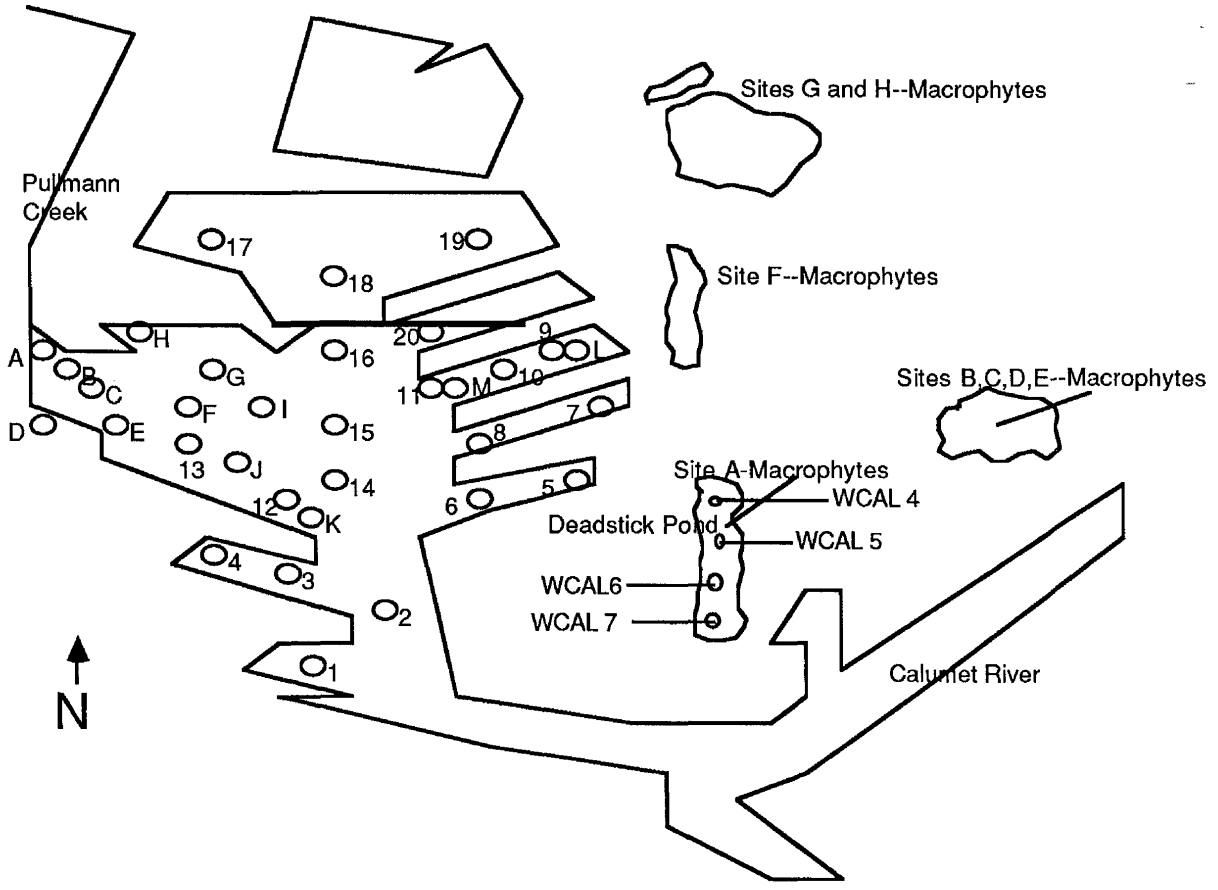


Figure 3.1. Location of sampling stations in Lake Calumet (November 1986, April 1987).

Table 3.1. Methods used to determine trace, minor, and major element concentrations in Lake Calumet sediments.

| Elements | Methods |
|---|---|
| Cd, Cu, Pb, Zn, Ni | AA |
| Br, Ce, Cr, Cs, Eu, Ga, Hf, La, Lu, Mn, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, W, Yb | INAA |
| Fe, K, Na | INAA, XRF |
| Ag, Co | OEP, INAA |
| B, Be, Ge, Tl, V | OEP |
| Si, Al, Ca, Ti, P | XRF |
| Ba, Mo, Sn, Sr, Zr | XES |
| Total Organic Carbon | Coulometrics |

INAA=Instrumental neutron activation analysis
XRF=X-ray fluorescence analysis
OEP=Optical emission spectrochemical analysis, photographic
AA=Atomic absorption analysis
XES=X-ray emission spectroscopy
Coulometrics=Coulometrics carbon analysis system

fitted with automatic sample changers, multichannel analysers, and magnetic tape data recording. Data reduction and calculation of the results were accomplished with the aid of computer facilities of the University of Illinois. Accuracy was verified by analyzing NBS-certified reference materials and International Atomic Energy Agency (IAEA) round- robin soil and sediment samples.

3.2.3. X-ray fluorescence analysis (XRF).

Samples (approx. 125 mg) were ashed at 750°C and mixed with 2 g of $Li_2B_4O_7$ and 125 mg of $La_2O_3$. This mixture was then fused at 1000°C in covered graphite crucibles; a pellet was made by mixing the crushed beads with a Somar mix binder and pressing at 400,000 psi. The pellet was analyzed using the optimum setting recommended for a Rigaku - 3371 Vacuum X-ray spectrometer. A set of synthetic and natural calibration standards was used to insure accuracy and to establish a calibration line. Matrix corrections were made for each element, taking into account absorption and enhancement effects. The practical detection limits by weight percent were: $SiO_2$ (2%), $Al_2O_3$

(1%), CaO (0.1%), $Fe_2O_3$ (0.1%), $TiO_2$ (0.1%), $P_2O_5$ (0.1%), and MgO (1%). Reference materials were analyzed to check accuracy and precision.

3.2.4. Atomic adsorption analysis (AA).

Duplicate samples (100 mg) of 500°C ash were digested by placing into 60 mL capped plastic (HPE) bottles, adding 1.5 mL aqua regia and 2.5 mL of concentrated HF, and steaming for 2 hours. Bottles were then removed and 25 mL of 5% $H_3BO_3$ solution was added. After cooling, 200 mL of Ca (500 mg/mL) was added, and the final solution was diluted to 50 mL. Measurements were made using a Perkin Elmer Model 306 Atomic Absorption Spectrophotometer at settings recommended by the manufacturer. Calibration curves were calculated for each set of analyses using standard solutions. Analyses of standard reference materials were used to evaluate the accuracy and precision of the technique.

3.2.5. Energy dispersive X-ray fluorescence (EDX).

For energy dispersive X-ray fluorescence, a 500-mg sample ashed at 500°C was placed in a polyethylene cup and sealed with a piece of Mylar film 0.0040 mm thick. The cup was inverted to obtain a uniform layer of ash and exposed to monochromatic radiation from secondary targets of Dy or Sn. Count rates were obtained on samples and standards that had been corrected for background and blanks. Concentrations were calculated from a plot of count rate versus concentrations for a series of standards.

3.2.6. Optical emission spectrochemical analysis (OE).

A 20-mg sample ashed at 500°C was mixed with 80 mg of graphite powder in a Wig-L-Bug mill. A 15 mg aliquot was then transferred to a graphite electrode (Ultra Carbon 100-L), compressed, and vented to obtain reproducible and stable geometry of the electrode charge during arc excitation. A reference standard was exposed with each group of samples.

3.2.7. Total organic carbon (TOC).

Organic carbon was determined by difference from the independent measurement of total and inorganic carbon. Total and inorganic carbon were determined by using a Coulometrics Carbon Analysis System. Total carbon was determined by coulometrically titrating the amount of $CO_2$ that was released from a sample combusted in an oxygen atmosphere at 950°C. Inorganic carbon was determined by titrating the amount of $CO_2$ released from a sample to which 2N HCl had been added. Accuracy and precision were checked by running NBS reference samples.

3.2.8. Analysis of organic constituents.

Concentrations of polycyclic aromatic compounds (PAHs) and phenolic compounds were extracted and analyzed by GC/MS following EPA Methods 3550 and 8220. Limits of detection for PAHs, chlorophenols and methylphenols were 300 ug/kg; detection limits for nitrophenol is 1600 ug/kg.

Polychlorinated biphenyls were extracted from sediments, perchlorinated to decachlorobiphenyl and analyzed by capillary gas chromatography as described by Risatti and Sheridan (1987).

## 3.3. Results and Discussion.

The compilation of 44 major, minor, and trace elements from the 37 stations is given in Appendices 3.1and 3.3. Average values have been calculated and are listed as are the available average values reported for Lake Michigan samples. Concentrations for several elements (Ag, Be, Cd, and Se) were below detection limits for four or more stations and averages for these elements should be viewed as unreliable. In Table 3.2, the average concentrations for eight elements that are of geochemical or environmental interest are compared to values found in sediments from Calumet Harbor, the Little Calumet River, Lake Michigan, the Cal-Sag Channel, and Wolf Lake. Except for arsenic, the Cal-Sag Channel has the highest concentrations of these elements. Lake Calumet, however, has the highest concentration of arsenic and the second highest level of chromium. Lead and zinc values are similar to those found in the Little Calumet River. Except for cadmium, concentrations of these elements in Calumet Harbor are generally lower than those found in Lake Calumet. This may be due to poor transfer of sediments from the lake to the harbor or to the more frequent dredging of the harbor for commercial ship traffic. The higher cadmium levels in the harbor may be due to road dust being deposited over a relatively smaller area.

Table 3.2. Average concentrations (in ppm unless otherwise noted) of selected elements in sediments of Lake Calumet and in sediments of surrounding water systems.

| Elements | Lake Calumet | Calumet[a] Harbor | Little[b] Cal. River | Lake[c] Michigan | Cal-Sag[b] Channel | Wolf[e] Lake |
|---|---|---|---|---|---|---|
| Antimony | 2.4 | -- | -- | 1.1 | -- | -- |
| Arsenic | 29.8 | 6.2 | 5.5 | 10.5 | 15 | 21 |
| Bromine | 4.2 | -- | -- | 33.0 | -- | -- |
| Cadmium | 1.8 | 3.2 | 2.5 | 0.9 | 8.5 | 2.0 |
| Chromium | 76.7 | 46.0 | 66 | 46.0 | 105.0 | 18.0 |
| Copper | 57.5 | 44 | 88 | 22.0 | 125.0 | 27.0 |
| Iron (%) | 2.7 | -- | 2.9 | 2.2 | 3.4 | 1.5 |
| Lead | 187.0 | 144 | 190.0 | 40 | 370.0 | 110.0 |
| Nickel | 23.6 | -- | -- | 24 | -- | -- |
| Phosphorus | 20.0 | 20.6 | 130.0 | 70.0 | 300.0 | 36.0 |
| Selenium | 0.7 | -- | -- | 1.2 | -- | -- |
| Silver (ppb) | 561.0 | -- | -- | 460.0 | -- | -- |
| Sodium | 470.0 | -- | -- | 458.0 | -- | -- |
| Thallium | 6.2 | -- | -- | -- | -- | -- |
| Zinc | 341.0 | 268.0 | 375.0 | 97.0 | 1100.0 | 255.0 |

a = USACE (1985)
b = IEPA (1984)
c = Cahill and Shimp (1984)
d = Kelly and Hite (1979)

The concentrations of arsenic, bromine, cadmium, copper, lead, nickel, sodium, tin, and zinc in sediments at the various stations in Lake Calumet are illustrated by the histograms in Figures 3.2 - 3. 4. Cadmium levels (Figure 3.3) are below detection limits (<1.5 ppm) at all stations except B and C. These stations are both located at the mouth of the drainage canal (Figure 3.1), which carries, in part, runoff from the nearby Calumet Expressway (I-94). Cadmium is probably contained in the fine particles of road dust that are washed into the canal and eventually deposited in the lower energy environment of the lake (Stations B and C).

Concentrations of bromine (Figure 3.3), copper, lead, tin, and zinc (Figure 3. 2), and organic carbon and chromium (Figure 3.5) have similar distribution patterns. The highest values for these elements are generally found at stations B, C, or D, a finding which suggests that these elements are transported from their source by the drainage canal that empties into the lake (Figure 3.1).

Organic carbon levels are also higher at these stations (Figure 3.4), and the areal distribution map (Figure 3.5) shows a general trend of organic carbon decreasing away from the mouth of the canal.

Areal distribution maps of chromium (Figure 3.5), copper, and lead (Figure 3.6), and arsenic and zinc (Figure 3.7) also show that the higher values of these elements tend to be clustered near the mouth of the drainage canal. These elements also have a strong positive correlation with organic

carbon (Table 3.3). Cahill and Shimp (1984) found similar correlations with organic carbon for these elements in Lake Michigan sediments, and they concluded that the accumulation of these elements was related to organic-rich, fine-grained sedimentation.

Bromine, which has average values about 8 times lower than those reported for Lake Michigan sediments (Table 3.2), has a moderately positive (0.62) correlation with organic carbon. However, the distubution of bromine is somewhat puzzling. The highest values occur at stations A, B, and D while concentrations in sediments from the other stations are well within normal background levels.

Sodium levels are approximately the same as values reported for Lake Michigan (Cahill 1981). The high values of 610 ppm and 550 ppm found at stations A and D, respectively, are probably from the use of road salt during the winter. Inexplicably, the highest value (620 ppm) was recorded at station K which incidentally also had very high toxicity levels (Chapter 8).

Concentration values of major, minor, and trace elements from the sediment samples collected in April 1987 (stations LCAL 1-20 and WCAL 4-7) and from sediments collected in November 1986 (stations A-M),were treated statistically using factor analyses to summarize relationships between variables in a factor matrix (Appendix 4).These elemental relationships grouped into five factors which can be attributed to specific sources and associations (Table 3.4).

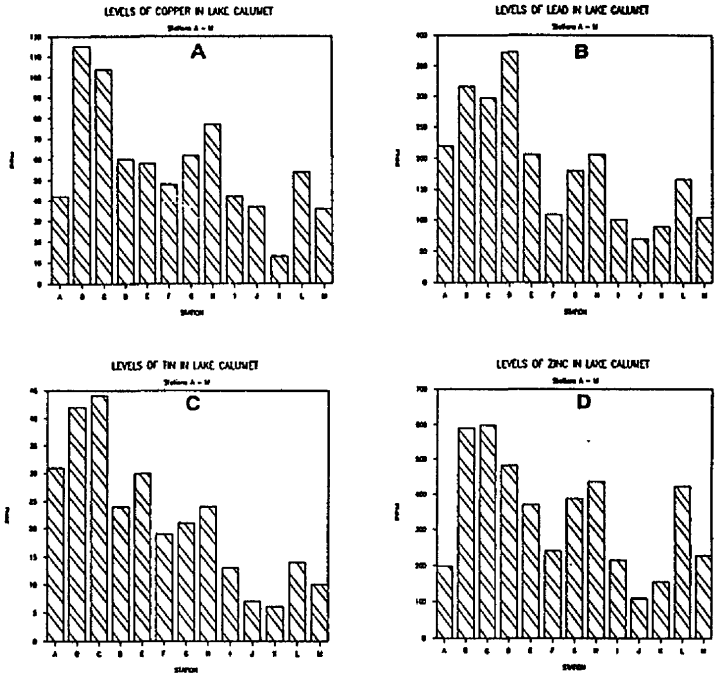


Figure 3.2. Concentrations of copper (A), lead (B), tin (C), and zinc (D) in dried sediments from 13 sampling stations at Lake Calumet.

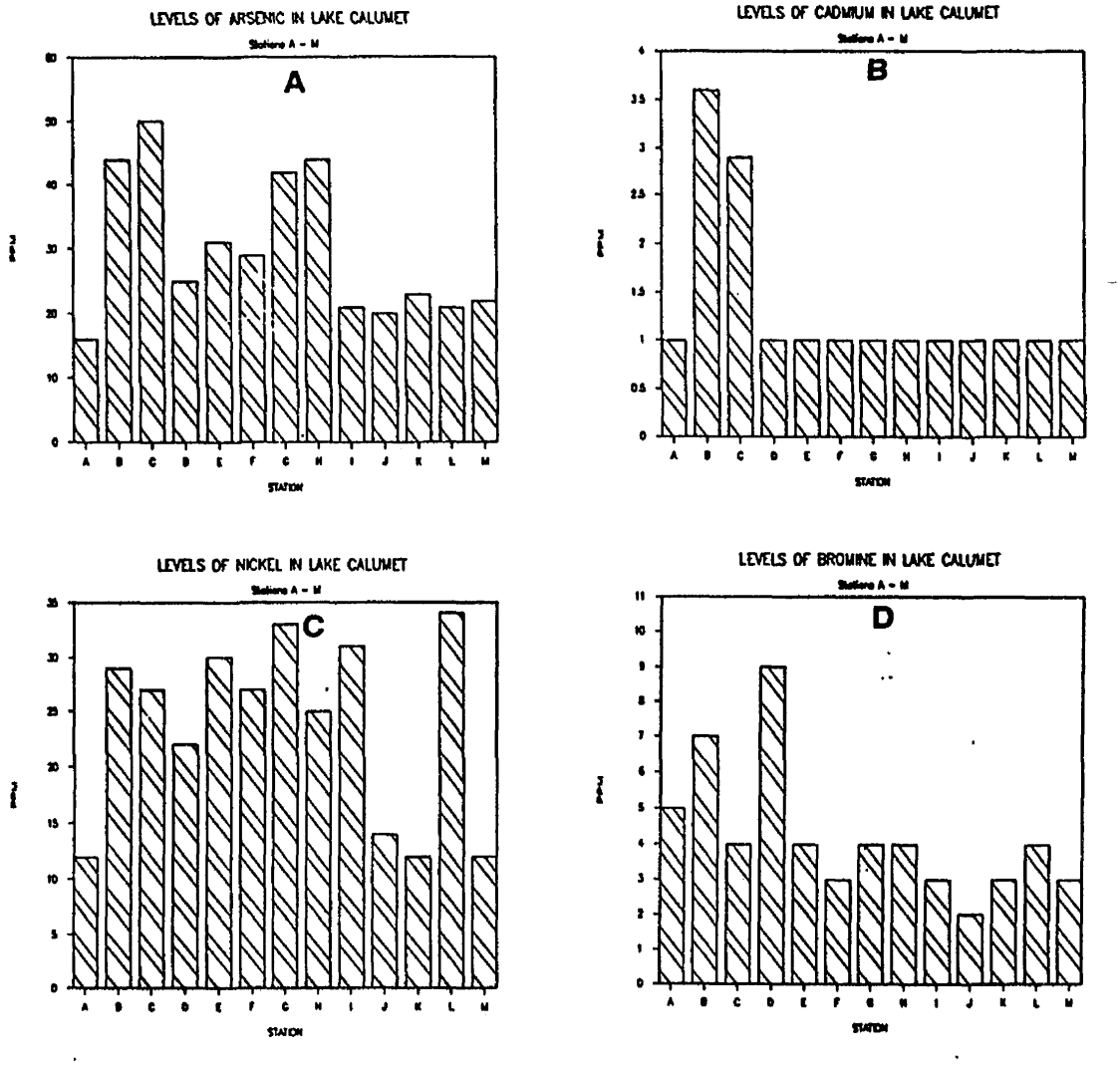


Figure 3.3. Concentrations of arsenic (A), cadmium (B), nickel (C), and bromine (D) in dried sediments from 13 sampling stations at Lake Calumet.

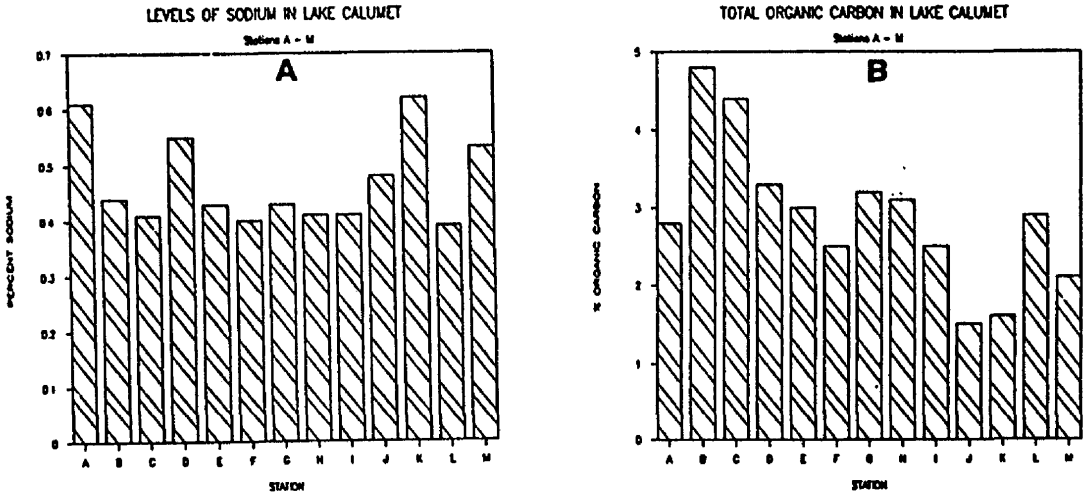


Figure 3.4. Concentrations of sodium (A) and total organic carbon (B) in dried sediments from 13 sampling stations at Lake Calumet.

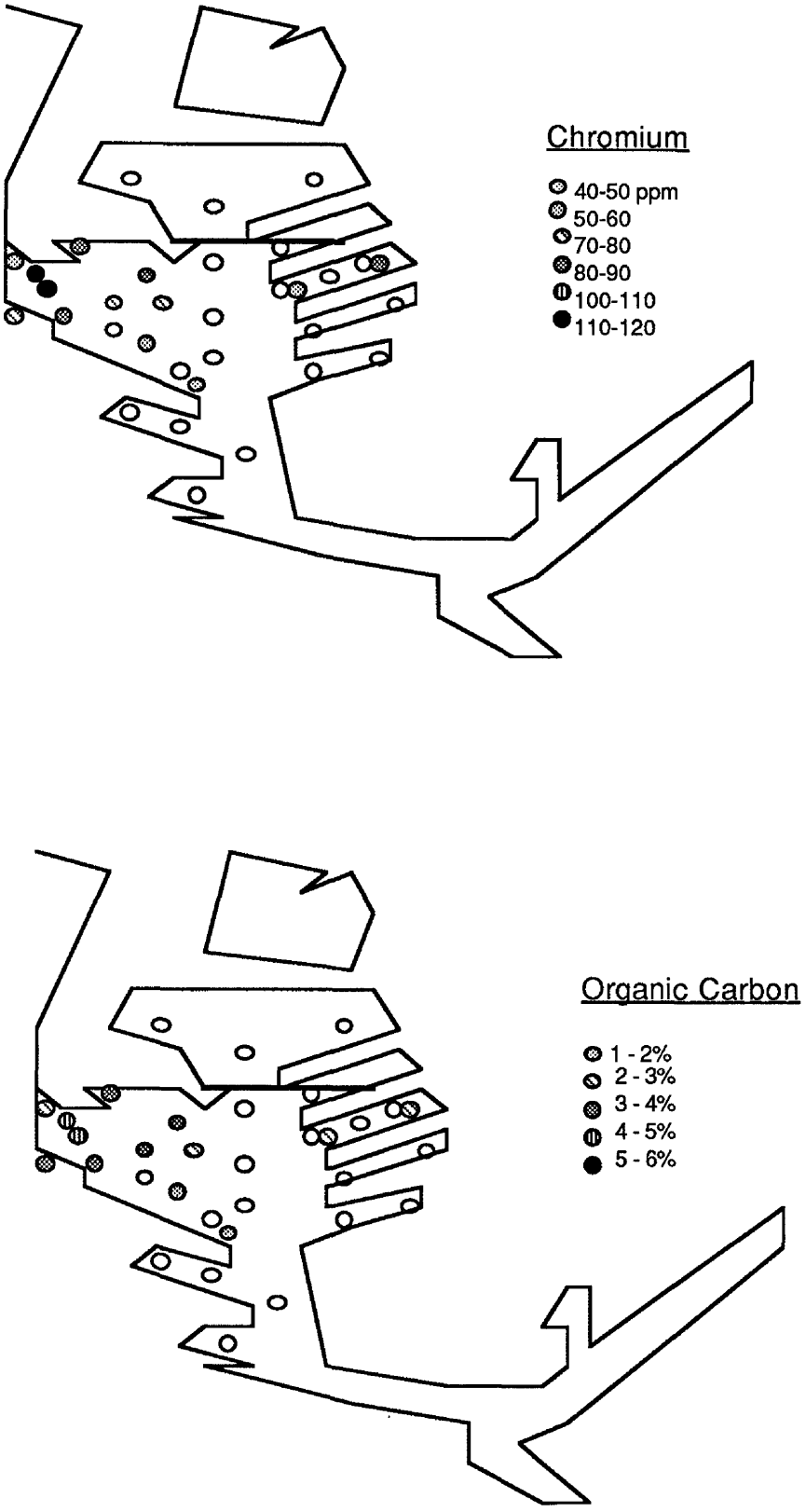


Figure 3.5. Distributions of chromium and organic carbon in Lake Calumet sediments.

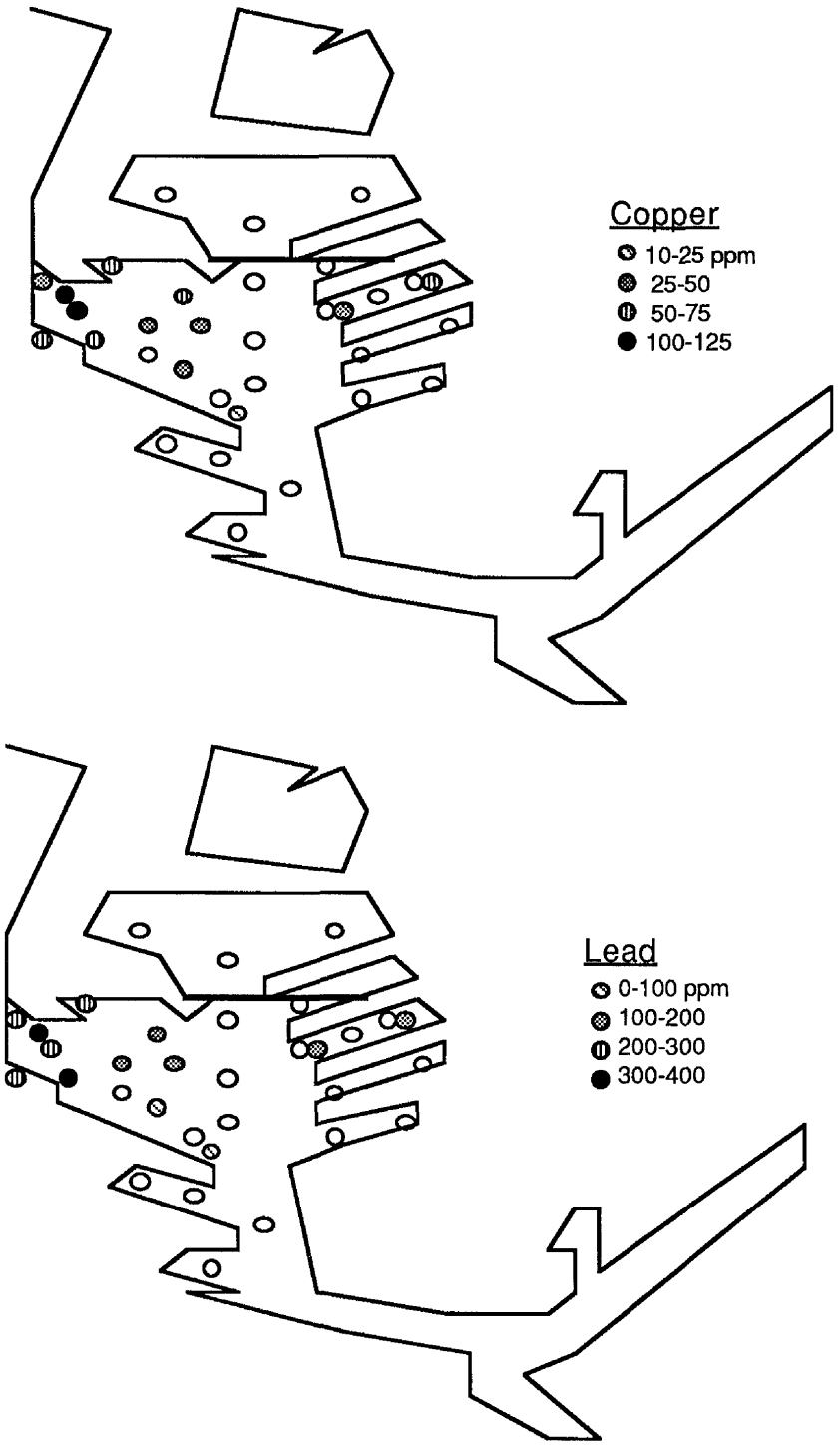


Figure 3.6. Distributions of copper and lead in Lake Calumet sediments.

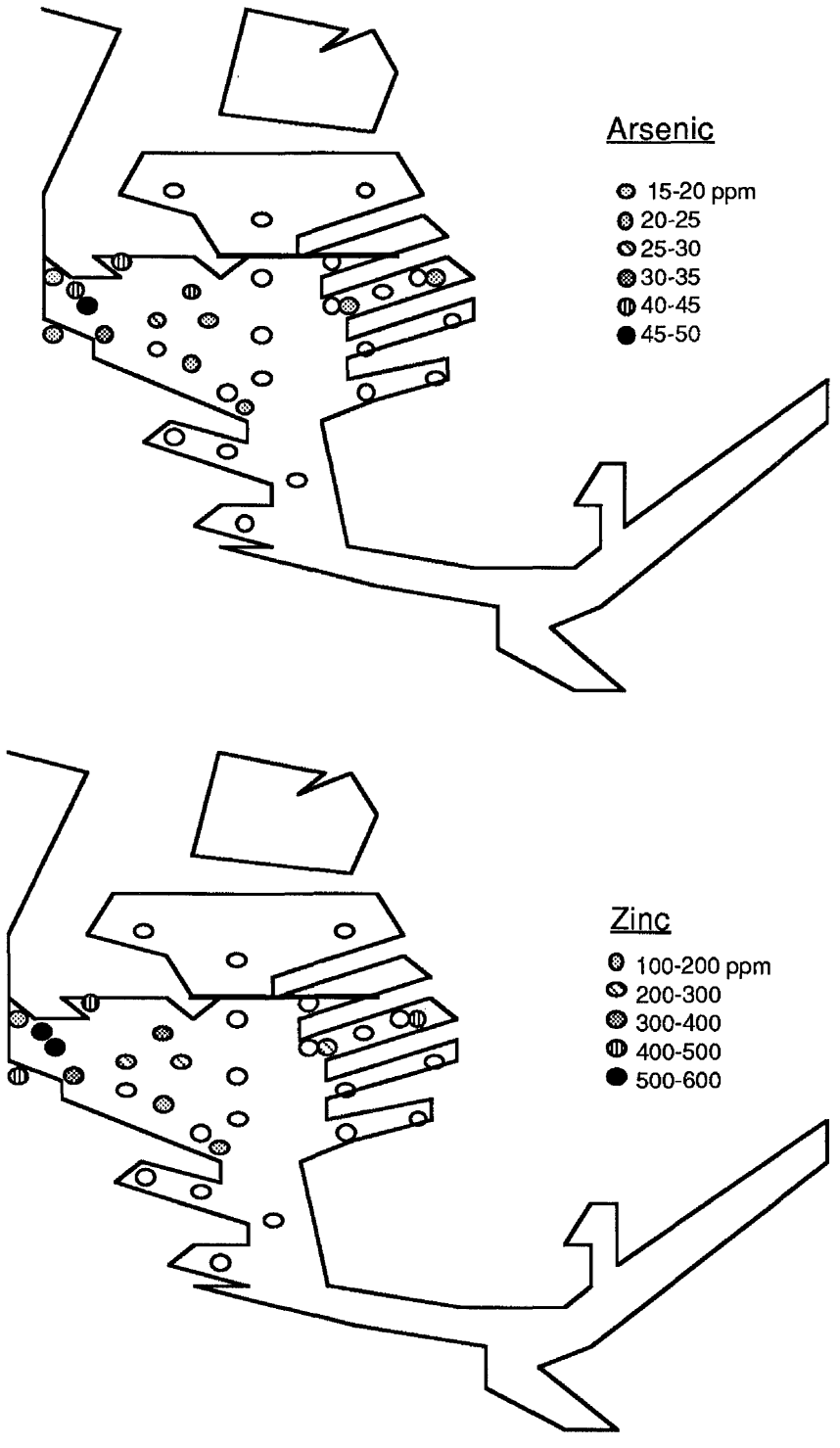


Figure 3.7. Distributions of arsenic and zinc in Lake Calumet sediments.

Table 3.3 Correlations of trace elements in Lake Calumet sediments with organic carbon.

| Element | Correlation Coefficient |
|---|---|
| Cu | 0.95 |
| Zn | 0.93 |
| Cr | 0.91 |
| Pb | 0.84 |
| As | 0.75 |
| Br | 0.62 |
| Be | 0.44 |
| Ni | 0.39 |
| Ga | 0.28 |
| La | 0.26 |
| Sc | 0.22 |
| V | 0.17 |
| Co | 0.10 |

Table 3.4. Factor analyses of elements in Lake Calumet sediments

| FACTOR | ELEMENTS | SOURCE | ASSOCIATION |
|---|---|---|---|
| 1 | Al,B,Ce,Co,Cs,Eu,Ga,K, La,Li,Lu,Rb,Sc,Sm, Ta,Tb,Th,Ti,V,Yb | Soil erosion | Fine grained material |
| 2 | Br,Ca,C-total,C-inorg, C-org,Cr,Mn,Mo,Ni,Sb Sr,Zn, | Anthropogenic | Fine grained material |
| 3 | As,Cu,P,Pb,Sn | Anthropogenic | Industrial, Biocides |
| 4 | Fe,W | Anthropogenic | Steel production |
| 5 | Mg | Anthropogenic | Slag weathering |

The first factor consists of elements that are primarily of geological origin. Their occurrence in Lake Calumet is probably due to erosion and weathering and to transport by wind and water to the lake basin. Factor 2 elements appear to be related to organic and inorganic carbon. The concentration of several of these elements may be due to coating of organic carbon on silt and clay-sized sediments.The distribution of zinc and the occurence of antimony suggest an anthropogenic source for the elements in this grouping. The elements of factor 3, arsenic, copper,l ead, phosphorous, and tin, are generally associated with anthropogenic activity. The sources of copper, lead, and tin are probably metal smelting, steel production, and chemical and paint manufacturing. Arsenic and possibly tin,may have accumulated from fungicides and pesticides.Iron and tungsten in facotr 4 and magnesium in factor 5, probably occur because of the extensive steel industry that existed in the Calumet area. The presence of magnesium may be related to the use of slag as a lake fill material or from the erosion of slag piles.

Organic analysis of the sediments indicated that levels of nitro-, chloro-, and methyl-phenols were below detection limits of 1600 ug/kg for nitro-phenols and 330 ug/kg for chloro- and methyl-phenols. Polychlorinated biphenyl (PCB) concentrations are currently being determined by perchlorination. Concentrations of total polycyclic aromatic hydrocarbons (PAHs) for stations A - M are shown in Figure 3.8. Values ranged from 340 ppb for station G to 9,640 ppb for station K. The lowest values were found for stations E-J, where average values were about 86% lower than those for stations A - D and K - M. The source of PAHs for stations A - D is probably discharge from the drainage canal (Figure 3.9). The high values at L and M may be from the former waste pits located just to the north of these stations (Figure 3.1). The anomalously high values for station K cannot be explained. Previous studies of lake sediments indicate that PAHs are generally of anthropogenic origin (Wakeham *et al.* 1980a, 1980b), primarily from combustion of fossil fuels (especially coal) and from petroleum spills (Laflamme and Hites 1978; Hase and Hites 1976).

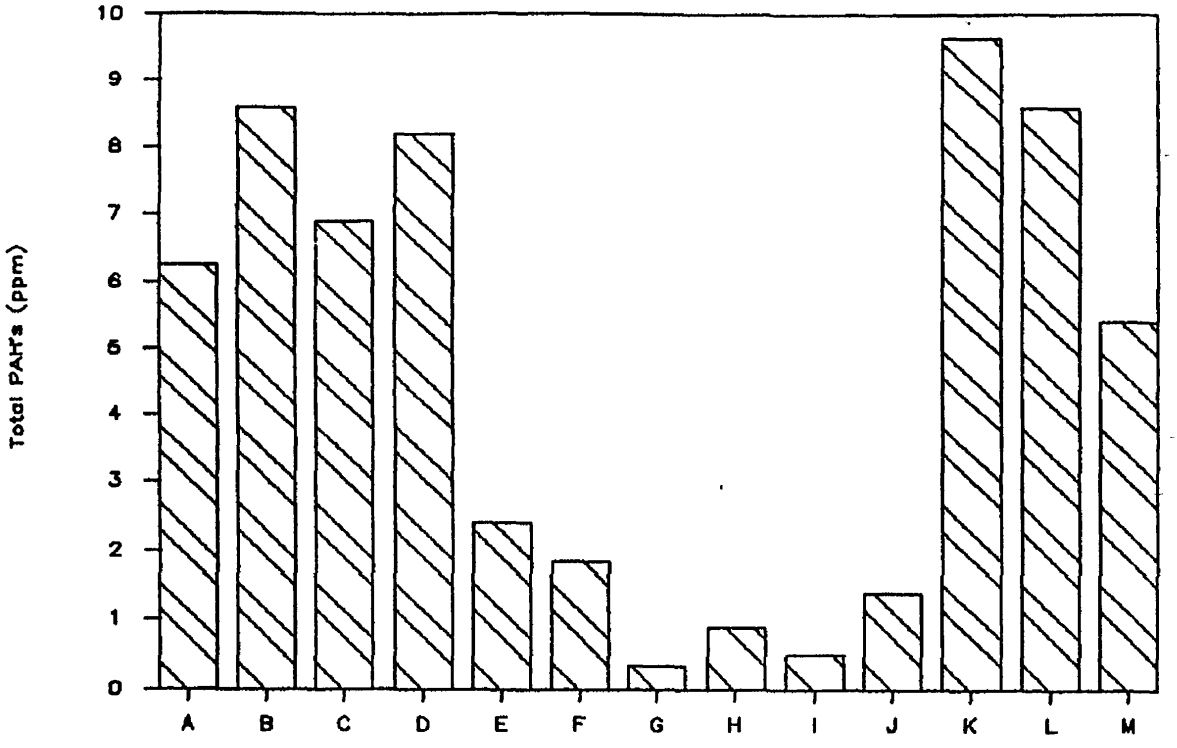


Figure 3.8. Concentrations of PAHs in dried sediments from 13 sampling stations in Lake Calumet.

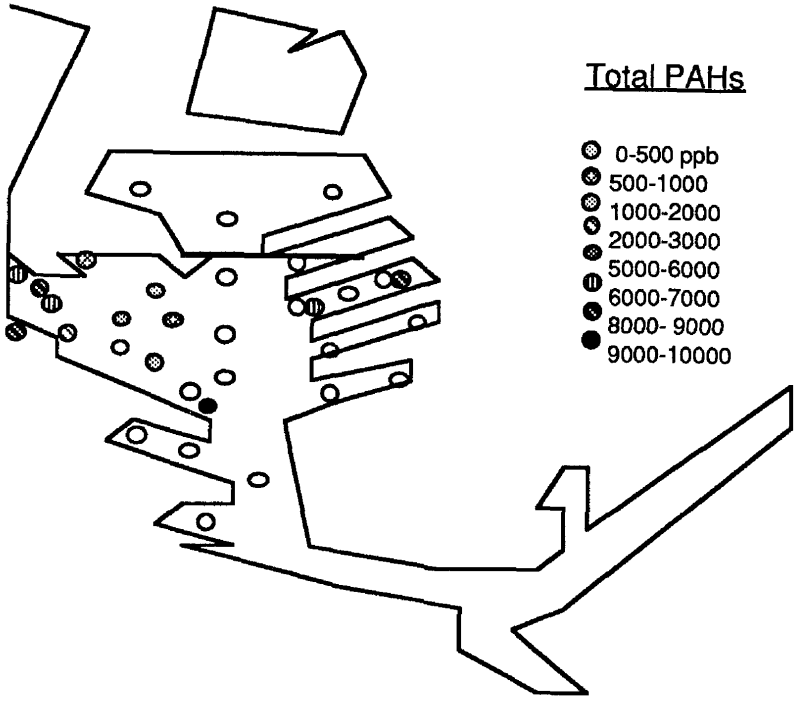


Figure 3.9. Distributions of PAHs in Lake Calumet sediments.

# Chapter 4
# Physical Transport Processes: Surface Water and Ground Water

Surface Water
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Groundwater
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## 4.1 Introduction

### 4.1.1 Project description

The accumulation of sediment and pollutants in stream channels and lakes of the Calumet area has been a major concern for a long time. Various studies have documented high levels of contaminants in the sediments of streams and lakes in the area. Fine sediments and particulate and absorbed pollutants deposited in lakebeds and stream channels are frequently resuspended by water velocities induced by winds and waterborne traffic. The resuspension and movement of sediment and pollutants may be major long-term sources of contaminants in Lake Calumet and the interconnected stream channels.

Lake Calumet, a remnant of a much larger lake system which covered much of northeastern Illinois during prehistoric times after the retreat of the glaciers, is one of the few natural open bodies of water still in existence in the Chicago area. Lake Calumet and its watershed are part of a larger drainage system generally known as the Calumet area. The Calumet area, located in northeastern Illinois and northwestern Indiana, is flat and poorly drained. The primary outlets for water from the Calumet area are the Calumet, Grand Calumet, and Little Calumet rivers in Illinois, and the Indiana Ship Canal and Burns Ditch in Indiana. Surface drainage flows either into Lake Michigan through the Calumet River, the Indiana Ship Canal, or Burns Ditch or into the Illinois River Waterway through the Cal-Sag Channel. The flows and water surface elevations in each of the above channels and in Lake Michigan interact to determine the flow patterns and directions of drainage. In general, the flow in the drainage basin is sluggish and sedimentation problems result. Regular dredging is required to maintain navigation and to reduce flooding.

In this study the movement of surface water, sediment, and pollutants in and around Lake Calumet was investigated. A literature review was conducted to describe the watershed, the drainage pattern

into the lake, the hydraulics of flow in and out of the lake, sediment transport and accumulation, the dredging history, pollutant transport, the accumulation and flushing of pollutants, and water quality. The findings are presented below, along with results from recent field investigations of hydraulics, surface drainage patterns, and bottom sediment movement.

## 4.2 Background

### 4.2.1 Location of study area

The Calumet area is located in northeastern Illinois and northwestern Indiana, just south of Lake Michigan (Figure 4.1). The area shares similar geologic, topographic, physiographic, and hydrologic characteristics that distinguish it, in many respects, from the rest of Illinois and Indiana.

Lake Calumet and its watershed located in southeastern Chicago form the northwestern limit of the Calumet area. Lake Calumet is connected to Lake Michigan and to the Little Calumet River by the Calumet River, which runs in a north-south direction from Lake Michigan to the Little Calumet River.

### 4.2.2 Hydrology and hydraulics

#### *4.2.2.1 Watershed*

The watershed of the Calumet area is shown in Figure 4.2. The watershed, hydrology and drainage pattern of the Little Calumet River were described by the U.S. Army Corps of Engineers (1982a). For the most part, the watershed is flat. The surfacial geologic characteristics of the area were formed about 20,000 years ago by glacial and fluvial action. Following the retreat of the Wisconsinan glaciers, a vast lake covered much of northeastern Illinois and northwestern Indiana. This lake eventually receded into present-day Lake Michigan and exposed a flat lakebed now occupied by the sluggish drainage system known as the Calumet area. The soils of the area are formed on sandy lakebed deposits underlain by the stony clay Valparaiso Moraine.

Before Lake Michigan receded to its modern shoreline the depression occupied by Lake Calumet was formed because Stony Island, a rock outcrop (Figure 4.3) deflected southerly lake currents to the east. To the west of the lake is the Toleston Beach Ridge (Figure 4.3) which is about 10 to 15 feet above the lake plain (Colten 1985). To the east and south of the lake, a well-drained area with several sandy ridges ran parallel to the Lake Michigan shoreline. The Calumet River meandered between two of these ridges, and Wolf Lake to the east was located between others. As early as 1834, Lake Calumet was only 6 to 10 feet deep (Colten 1985). Its size and depth varied depending on Lake Michigan's water level.

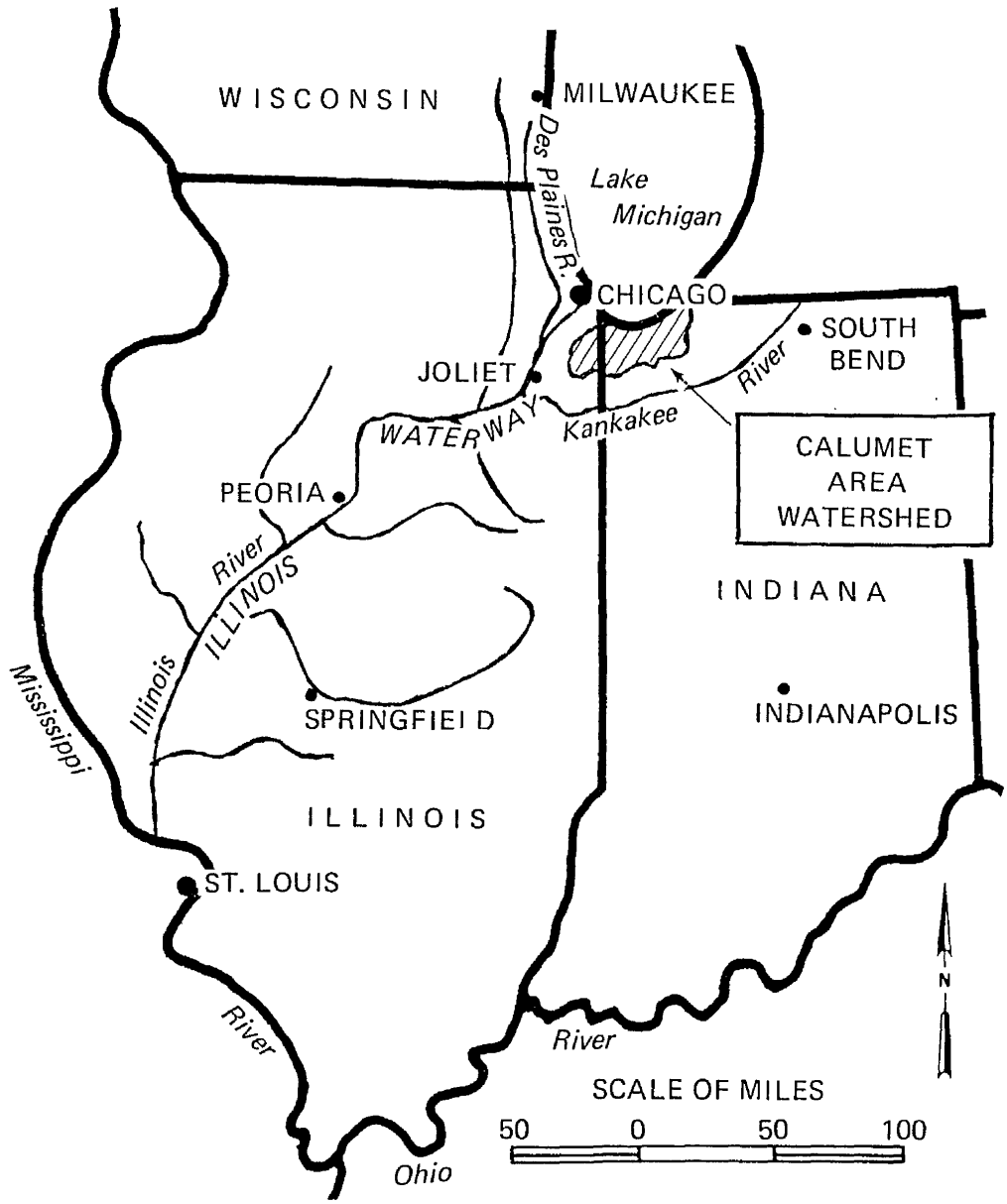


Figure 4.1. Location of Calumet area.

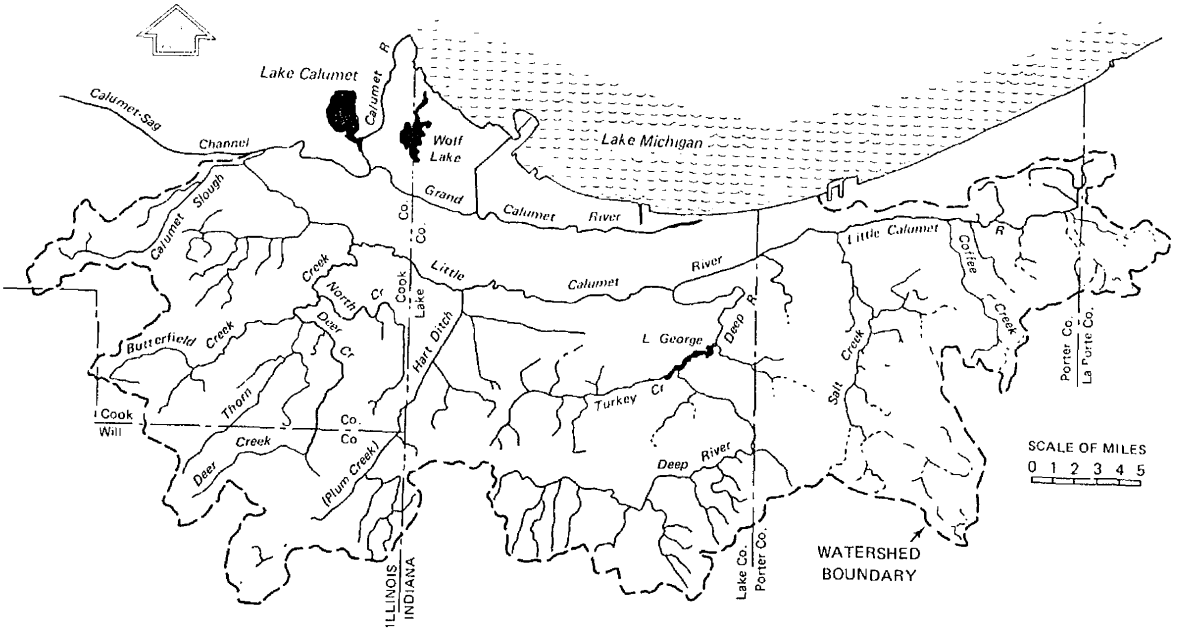


Figure 4.2. Streams and drainage pattern in the Calumet area watershed.

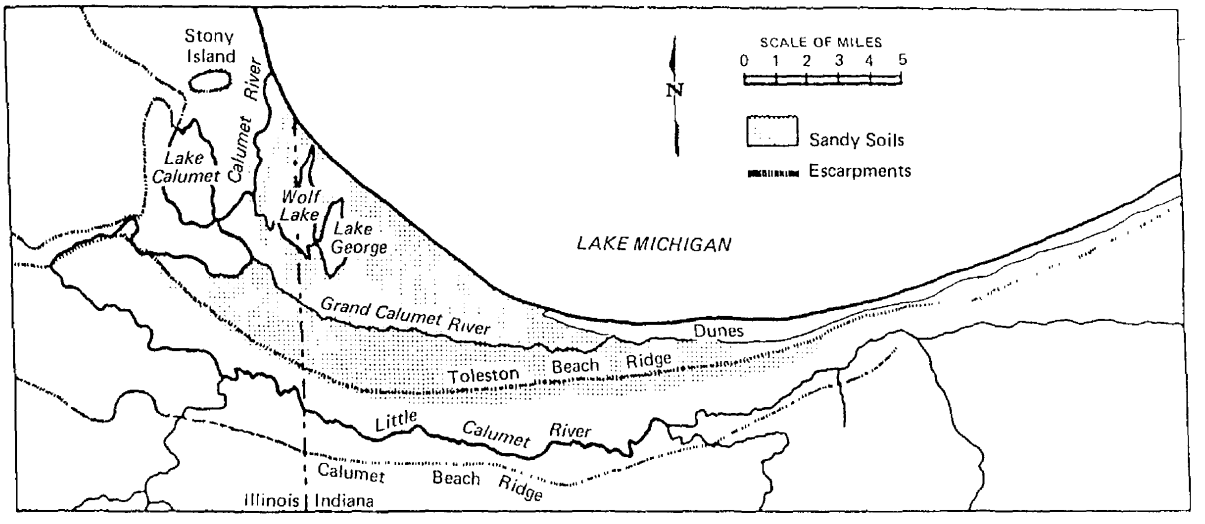


Figure 4.3 Topographic features of the Calumet area.

*4.2.2.2 Drainage pattern*

The main rivers of the Calumet area are the Calumet River, the Grand Calumet River, and the Little Calumet River. Most of the watershed drains through many smaller streams that discharge directly into the Little Calumet River. Burns Ditch and the Burns Waterway connect the Little Calumet River to Lake Michigan. The Grand Calumet River is connected to Lake Michigan through the Indiana Harbor Canal. Both the Grand and Little Calumet Rivers are connected to the Calumet River, which eventually joins Lake Michigan.

Hart Ditch (Figure 4.2), one of the major tributaries of the Little Calumet River, has a drainage area of 71.2 square miles. It serves as an outlet of Plum Creek at the point where they join at U.S. Route 30 and drains a portion of Lake County in Indiana. High points in the bed of the Little Calumet River to the east of Hart Ditch cause low flows from Hart Ditch to move westward in the river toward Illinois. During flood events, the flow is divided: a portion of it moves westward and the rest eastward.

West of Hart Ditch most of the drainage into the Little Calumet is from Illinois. The major tributary in Illinois is Thorn Creek. Deep River, Turkey Creek, and Duck Creek are tributaries of the central portion of the Little Calumet River. Deep River has a drainage area of 151.1 square miles and drains a major portion of Lake County in Indiana. A dam across Deep River at Hobart created Lake George. The dam has an uncontrolled concrete ogee spillway 114 feet in length, which provides a storage capacity in the lake capable of reducing peak flood discharges by 20 percent. High flows from Deep River at its confluence with the Little Calumet River cause temporary flow reversals of the Little Calumet River. This drainage pattern is shown in Figure 4.2.

Burns Ditch is the extension of the Little Calumet River from the mouth of Deep River eastward to Burns Waterway, which connects Burns Ditch to Lake Michigan. The Little Calumet River to the east of Burns Ditch has two tributaries (Salt Creek and Coffee Creek) with a total drainage area of 151.0 square miles. Their watersheds consist mostly of farmlands and grasslands.

*4.2.2.3 Flow into and out of Lake Calumet*

The streamflow pattern in the Lake Calumet area is controlled by several factors. These include the level of Lake Michigan, storm runoff in the drainage basin, and the O'Brien Lock and Dam (Figure 4.3) on the Calumet River. The possible flow directions are shown in Figure 4.3. The flow pattern that influences Lake Calumet is that of the Calumet River. The flow direction is from Lake Michigan toward Lake Calumet when the gates at the lock and dam are open for navigation. At all other times, including storm runoff, flows are towards Lake Michigan.

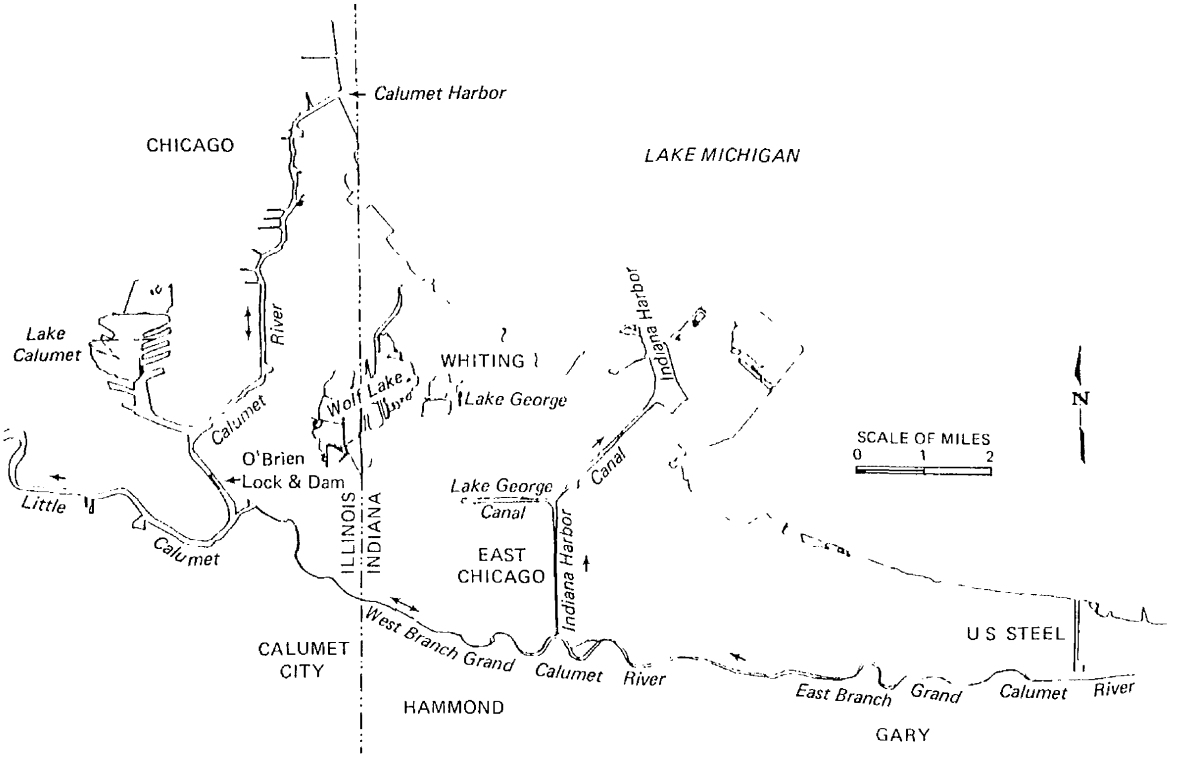


Figure 4.4. Stream channels and flow directions in the Lake Calumet, Calumet, and Grand Calumet Rivers and Indiana Harbor area.

4.2.3 Sediment and pollutant transport

*4.2.3.1 Sediment sources*

The sources of sediment in the Calumet area were studied by the USACE (1983). Their study concentrated on the Little Calumet River and found that most of the suspended sediment is contributed to the river by combined sewer overflows, sewage treatment plant discharges, and surface water runoff. Sewer outlets are located along the river in both Indiana and Illinois. Surface water runoff comes primarily from urbanized and industrialized areas, although some of the tributaries have agricultural watersheds that contribute sediment. The low flow velocity of the river results in the deposition of most of the suspended sediment in the stream channels..

*4.2.3.2 Sedimentation and dredging*

Sedimentation of the surface water in the Calumet area has resulted from erosion in the watershed, municipal wastes, erosion of channel banks, and littoral sand input from Lake Michigan and causes extensive problems to navigation. The U.S. Army Corps of Engineers (USACE 1982b) addressed the need for periodic dredging and disposal of sediments in order to maintain navigation in the Calumet River and Harbor. The U.S. Environmental Protection Agency classified sediment from the Calumet area waters as unsuitable for open channel disposal; therefore, the U.S. Army Corps of Engineers constructed and and has begun to operate confined disposal facilities sufficient to hold the anticipated material from ten years of dredging. Several alternatives for the location of these disposal facilities were discussed by USACE (1982b).

*4.2.3.3 Pollutant sources*

The pollutant sources in the Calumet area were studied by the USACE (1983) and by Hydroqual (1985). The USACE study concentrated specifically on the Little Calumet River and was designed to investigate improving the quality of the river and adjacent area by removing the polluted benthic sediments from the river. The Hydroqual study concentrated on the Grand Calumet River.

The land in the area surrounding Little Calumet River is highly industrialized and urbanized. Several facilities discharge domestic and industrial waste to the river (USACE 1983). Sediment loading from the Indiana portion of the watershed is also significant. The major pollutant load is due to combined sewer overflows. In the downstream part of the Little Calumet River, 47 percent of the Biological Oxygen Demand (BOD) load is attributed to combined sewer overflows; however, about 2,500 of the nearly 7,000 tons of BOD entering the Little Calumet River system each year and about one-third of the ammonia load are estimated to have originated in Indiana. In addition to point source pollutant loads, non-point pollutant sources resulting from fertilizer applications and septic systems were also mentioned in the USACE report. Because of the low

stream bed gradient, the velocity of the flow in the rivers is relatively low. As a result, sediment and pollutants settle to the bottom, reaeration rates are low, and algal growth is enhanced.

Hydroqual (1985) found elevatedconcentrations of priority pollutants in the sediments in the vicinity of U.S. Steel outfalls and near the East Chicago outfall in the Grand Calumet River. Heavy metal concentrations were slightly less than those found by USEPA in 1972; however, the concentrations were considered to be fatal for fish.

*4.2.3.4 Pollutant accumulation*

USACE (1983) assessed the water quality of the Little Calumet River based on sampling programs conducted by the Illinois EPA (IEPA) that showed the water quality of the Little Calumet River and its tributaries to be very poor. High values were found for BOD, fecal coliform bacteria, phosphorus, and nitrogen. Excessive bacterial input into the river from human and animal wastes was also considered to be part of the problem.

Colten (1985) presented an historical review of industrial wastes in the area around Lake Calumet. According to Colten, the Calumet region was altered greatly between 1869 and 1921 through direct modifications of the environment by private industry and the Army Corps of Engineers (dredging, etc.) and through the indirect effects of industrial waste disposal. The dredging of the Calumet River, the potential development of a harbor, and the existence of open land attracted many industries to the region. Its development resulted in the dumping of untreated industrial wastes into the water courses and the destruction of many of the wetlands in the area.

*4.2.3.5 Pollutant transport*

Information on the transport of pollutants out of Lake Calumet is not available; however, some information on pollutant transport out of the larger Calumet area into Lake Michigan and the Cal-Sag Channel to the Illinois Waterway can be found in the literature. Hydroqual (1985) summarized the effects of pollutant transport on the water quality of Lake Michigan. Pollutant plumes were observed in Lake Michigan at the outflows of Indiana Harbor and Grand Calumet Harbor and at the mouths of Burns Ditch and Trail Creek. Within a radius of a few miles around these outlets, the pollutant levels in Lake Michigan were elevated. For example, Figure 4.5 shows that concentrations of chloride increase at stations near the south shore of Lake Michigan relative to those stations farther from the shore. However, according to Hydroqual (1985) evidence does not suggest that the Indiana Harbor outflow causes significant contamination of Lake Michigan. This conclusion was based on data shown in Figure 4.6, which shows chloride concentrations at two stations, one in the Indiana Harbor Canal and another in Lake Michigan about two miles out from the outflow. Hydroqual (1985) also reported other studies that used near-shore data to estimate the

dilution factors between concentrations in Indiana Canal concentrations offshore. The dilution factors were 5 and 10 at distances of 1 and 3 miles, respectively, from the mouth of Indiana Harbor. However, the accumulation of pollutants in the near-shore sediments of Lake Michigan has not been investigated in detail.

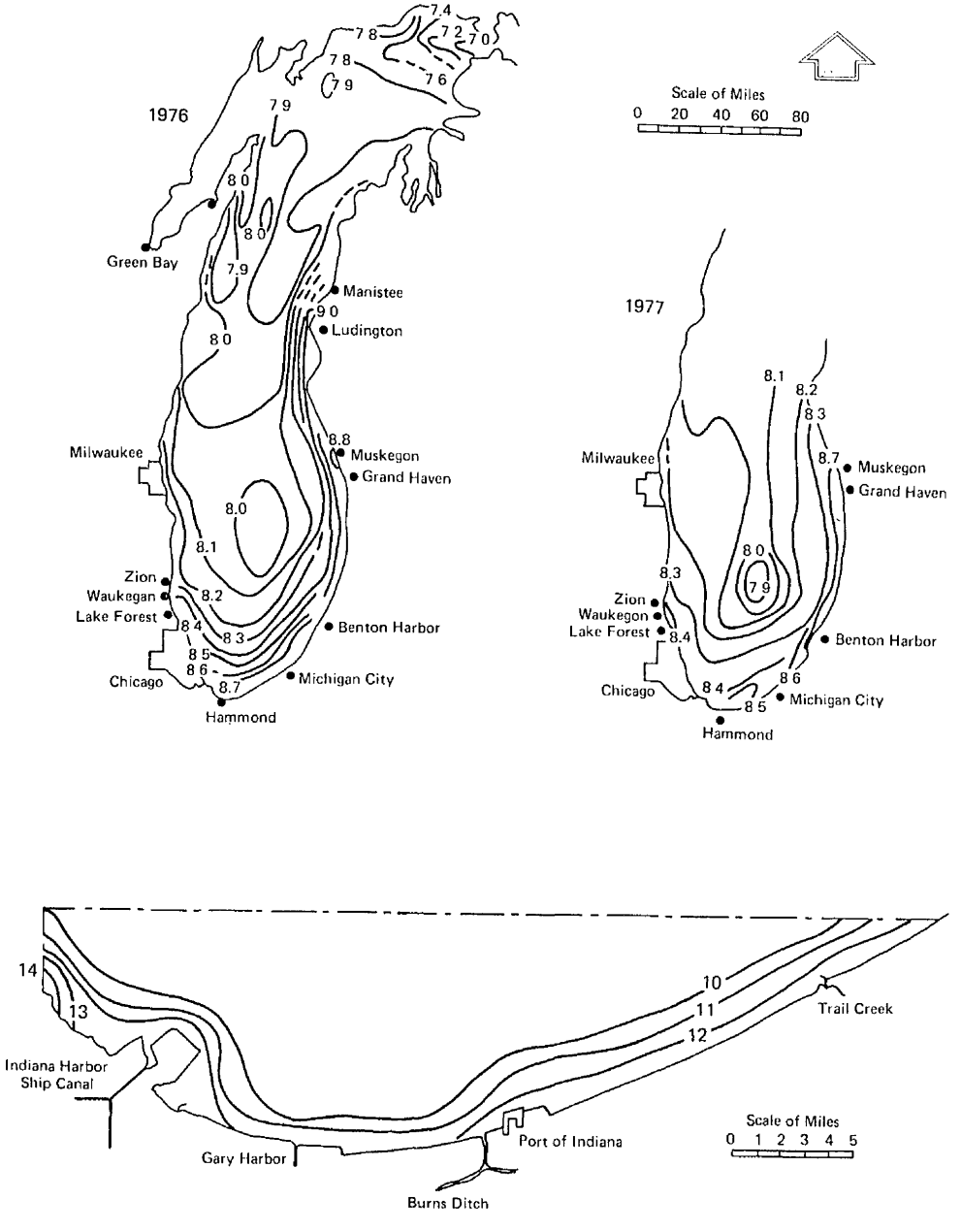


Figure 4.5. Concentrations of chlorides in mg $L^{-1}$ in Lake Michigan (Hydroqual 1985).

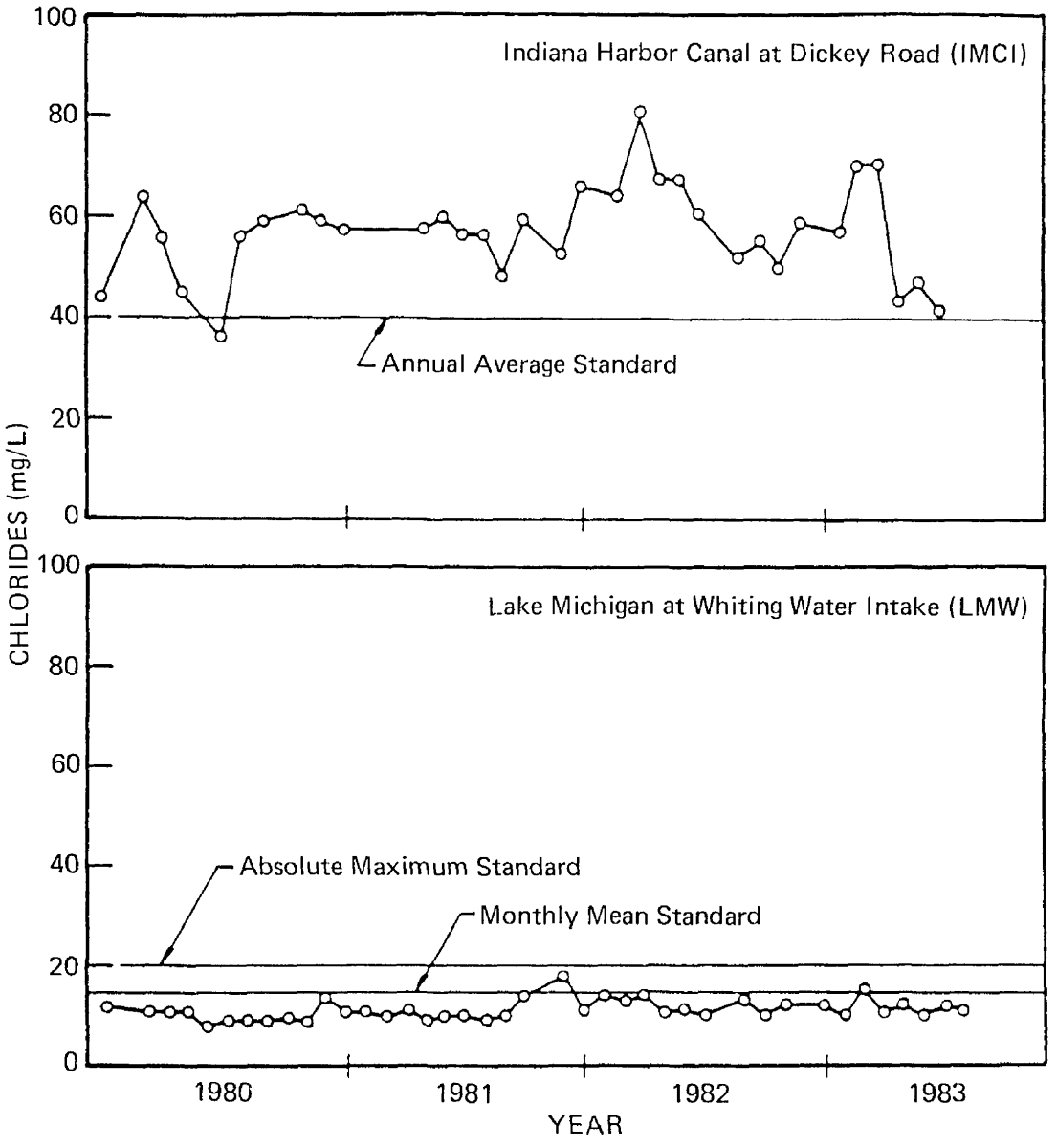


Figure 4.6. Comparison of chloride concentrations in Indiana Harbor Canal and Lake Michigan (Hydroqual 1985).

## 4.3 Data Collection and Results

Since only limited and general information is available on the hydrologic and hydraulic characteristics of Lake Calumet, field data were needed to define the physical dynamics of the lake and its watershed. Because of continuous changes in the surrounding area, field investigations were also required to define the drainage pattern around the lake and the flow pattern and movement of sediment and pollutants in the lake.

The data collection had two major components. The first dealt with drainage pattern and flow measurements; the second dealt with resuspension and movement of bottom materials in the lake. Three field data collection trips were taken to the Lake Calumet area: September 4 to 5 1986, April 6 to 7, and April 15 to 16, 1987. The methods used and the results obtained are presented in the following sections.

### 4.3.1 Drainage pattern and flow investigation

Field data were collected to determine the regional drainage pattern associated with Lake Calumet and to investigate in-lake flow patterns. Knowledge of water movement into,within, and out of the lake is essential to understand the processes of transport and deposition of sediment and pollutants. Waters are delivered to the lake from the watershed by drainage channels and storm sewers. These channels and sewers not only convey water but also contain entrained sediment and pollutants and dissolved pollutants carried by runoff waters.

#### *4.3.1.1 Drainage into Lake Calumet*

Surface drainage into the lake was investigated during each field trip. Reconnaissance was conducted by driving around the lake's perimeter and by walking into areas where access by vehicle was limited. Although the lake had received surface drainage from the surrounding areas in pre-settlement times, no evidence of natural drainage channels was observed. Currently all drainage into the lake is from man-made channels.

Surface drainage into the lake consists of runoff from the areas immediately adjacent to the lake, from the highway system to the west, and from a small area to the west of Interstate 94, as shown in Figure 4.7. The size of the area, including the lake, is about 3,700 acres. The surface area of the lake is 782 acres. Its watershed is primarily landfill, industrial areas, and highway. The major inflow to the lake from surface drainage is through an unnamed drainage channel parallel to Interstate 94. For discussion purposes, this channel will be termed "Pullman Creek" (for the Pullman neighborhood to the west of the lake). Pullman Creek conveys storm water runoff from

drainage ditches and from Interstate highway storm sewer water pumped into the creek at the Illinois Department of Transportation pump station near the junction of Pullman Creek and the Interstate (Figure 4.8). Another major drainage channel flowing into the lake is located in the its northeast corner. Two storm sewer outfalls have been identified: one empties into one of the boat slips on the east side of the lake, and the other empties into the Calumet River near the inlet to the lake. Other outfalls, that we have not been able to identify, may be discharging into the lake. Stormwater runoff from the highway area and from areas west of the Interstate flows into the lake via Pullman Creek channel. Surface drainage from the other areas of the watershed either is held in storage in the marsh areas east of the lake or runs into Lake Calumet via small drainage channels.

*4.3.1.2 Flow pattern in Lake Calumet*

The normal flow pattern that results from storm events is shown in Figure 4.8. Inflow from Pullman Creek channel and drainage delivered into the other basins of the lake eventually flows into Basin 1. As shown in Figure 4.8, the outlet of the lake is the harbor access channel at the south end of the lake. There is evidence of significant flow between Basin 2 and Basin 1 and between the small west bay and Basin 1. These areas are connected by openings in the separating causeways that are seven feet deep or more. The depth of the causeway openings are about two feet deeper than the average depth of the lake.

Total discharge from the lake was measured on April 16, 1987. The discharge rate at the harbor access channel was 473 cubic feet per second or 306 million gallons per day. This rate was due to a storm/runoff event and wind-induced circulation and is probably much larger than the average outflow rate.

The in-lake flow pattern was observed to be heavily influenced by wind. At 1:40 p.m. on April 15, 1987, flow direction in Pullman Creek was toward the Interstate and away from the lake. The velocity in the channel at the frontage road culvert near the pump station was approximately 0.5 feet per second. At 4:30 p.m. on the same date, the flow direction was toward the lake at a velocity of 2 feet per second. The wind was from the north-northeast and gusting. When sustained gusts occurred, flow was toward the lake. When the wind calmed, the flow was up the channel toward the Interstate. Velocity measurements performed in Pullman Creek showed large variations in velocity, direction, and magnitude of flow over time. Velocity readings from a measurement point in the middle of the channel varied from 0.35 to -0.06 feet per second (the negative value indicates upstream flow) on April 15, 1987. Pulses of reversing flow direction caused by wind-induced circulation were also observed in the connecting channels through the causeway openings between Basin 1 and Basin 2, and Basin 1 and the West Bay. An implication of the observed wind-induced flow in the lake is that sediment and pollutants delivered to the lake from an inflow source can be

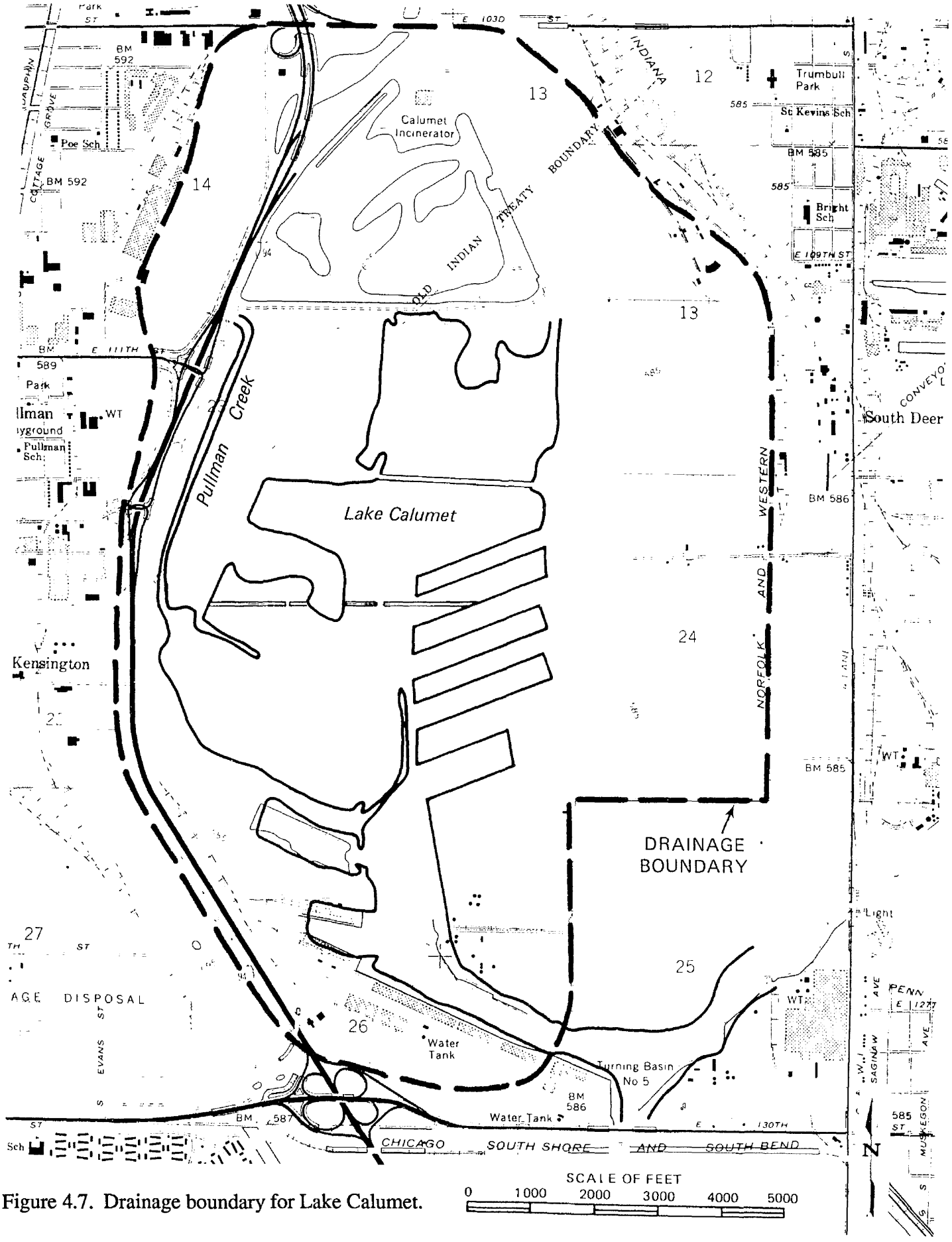


Figure 4.7. Drainage boundary for Lake Calumet.

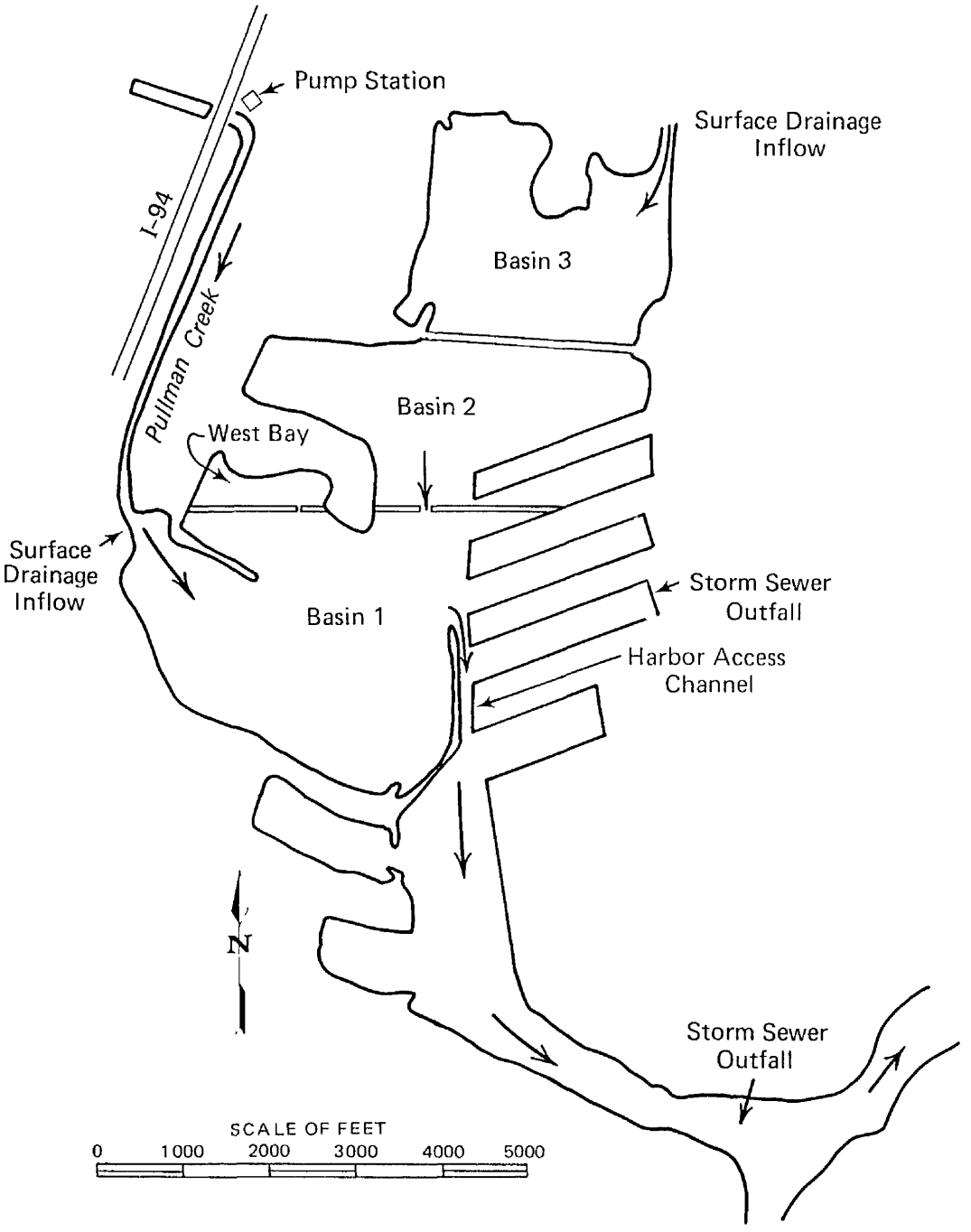


Figure 4.8. Flow into and out of Lake Calumet.

transported throughout the lake. Suspended and dissolved materials delivered to the lake from the storm sewer outfall on the east side of the lake or from Pullman Creek can be transported from Basin 1 to Basin 2 or to the small west bay (Figure 4.8).

### 4.3.2 Resuspension and movement of bottom materials

#### *4.3.2.1 Data collection procedure*

Three primary collection techniques were used to quantify flow, velocity, suspended sediment concentration, and lake/channel morphology. Flow and velocity were measured with a digital velocity meter. Suspended sediment concentration samples were obtained through the dip sample technique. Lake and channel morphology were measured with a sounding pole and a recording sonar meter.

Flow and velocity were measured with a Marsh-McBirney Model 201 velocity meter, a solid-state electromagnetic meter that provides a digital readout of water velocity at the measurement point of the meter's probe. The meter's probe was positioned within the water column by using either a standard wading rod or a cable/winch/crane assembly attached to the data collection boat. Either method provides accurate readings of the meter's probe depth and allow precise measurements of changes in velocity with depth. The discharge measurement techniques used were developed by the U.S. Geological Survey (USGS) (Buchanan and Sommers 1969) and the American Society for Testing and Materials (Standard practices for Open-Channel Flow Measurements of Water by Velocity-Area Method, designation D 3858-79).

Sediment concentration samples were obtained through the dip sample technique in which a prepared sampling bottle was immersed in the water by hand or in a weighted bottle holder. A sampler was developed for this project that allows sampling from any location in the water column. Named the Calumet Sampler, it consists of an intake, sample hose, pump, and cable/winch/crane assembly. The intake was modified from the US-DH59 iso-kinetic depth integrating sampler developed by the USGS. It is a streamlined bronze casting 15 inches long and 24 pounds in weight. The US-DH59 provided a weight on the sampling line to hold the intake at a set elevation in the water column. The intake nozzles manufactured for the US-DH59 were used on the modified sampler. The modified US-DH59 sampler was connected to the peristaltic pump with a vinyl hose and was aligned in the water column with a standard cable/winch/crane assembly that allowed a direct reading of the depth of the intake below the water surface. The Calumet Sampler was developed to obtain rapid sampling of the water column during rapidly changing conditions so that concentration changes with depth and time could be assessed. This sampler will be used in future field trips to measure concentration changes associated with navigation and wind events.

Lake and channel morphology was measured by using a standard 2-inch-diameter sounding pole constructed in 8-foot segments. The pole is graduated in 0.1 foot increments and depth is read directly on the pole at the water surface. A Lowrance Model X-15A Computer Chart Recording Sonar was the principal tool for measuring lake and channel bed profiles. An 8-degree sonar transducer was used with the sonar unit. To provide reliable measurements of depth on the sonar charts, the sonar unit was calibrated for transducer submergence depth each time it was installed on the workboat. The sonar was used to measure changes in depth with distance along a measurement line. Line endpoints were identified in the field and marked on an aerial photo. The chart in the sonar unit was annotated with data related to date, time, location, and end points to facilitate the interpretation of the data from the charts. Total distances and the distance between points on the sonar chart were scaled from aerial photos.

*4.3.2.2 Movement of bottom materials*

Bottom materials in the lake are resuspended by velocities generated by inflow to the lake and by flow within the lake. Sonar data were used to determine the profile of the lake and to assess the scour and depositional features in the lakebed morphology. A profile of the lake and Pullman Creek is shown in Figure 4.9. The lakebed at the mouth of Pullman Creek shows a delta formation, which indicates deposition of materials carried by the creek's inflow. This delta accumulation is indicated by the bulge of the lakebed at the junction of the creek and the lake (Figure 4.9). Scour of the lakebed is indicated in Figure 4.9 in the area just upstream of the mouth of Pullman Creek. This area is 1.5 feet deeper than the surrounding lakebed because of the scouring effects of inflow from the creek. Another feature of the lake that can be seen in this figure is the relatively flat bottom of the harbor area that was produced by dredging.

Sonar profiles measured the changes in the lakebed over time. On April 7 and 16, 1987, sonar runs were made of Pullman Creek. Results indicated that 2,500 cubic feet of sediment, equivalent to 44 tons of sediment, had been deposited in the channel during this period (Figure 4.10). Several areas of the channel had experienced scouring during this interval. A large area of the channel 4,500 feet from the pump station lost nearly three feet of depth by scouring. This material was resuspended by the inflowing waters of the channel and carried into Lake Calumet. It is likely that over this time period, most of the channel experienced scouring. The deposition in the channel occurred in the later portions of a storm/runoff event. These results indicate that Pullman Creek serves not only as a conveyance for inflowing water, sediment, and pollutants, but also as a source of sediment and pollutants delivered to the lake during storm/runoff events. Resuspension of bottom materials was also seen in the areas of the causeway openings between the basins of the lake. Sonar profiles of the areas near the openings show that scouring to a depth several feet below the surrounding

lakebed was caused by the velocities generated by flow between the basins, as can be seen in Figure 4.11. This figure is a plot of the sonar data from a cross-sectional profile 100 feet south of the causeway separating Basin 1 and Basin 2. These data indicate that significant flow and movement of bed materials are occurring between the connected basins of the lake.

The scour and deposition observed in the lake indicate that resuspension of bottom materials is a significant source of pollutants and that it is an important mechanism of pollutant transport in Lake Calumet.

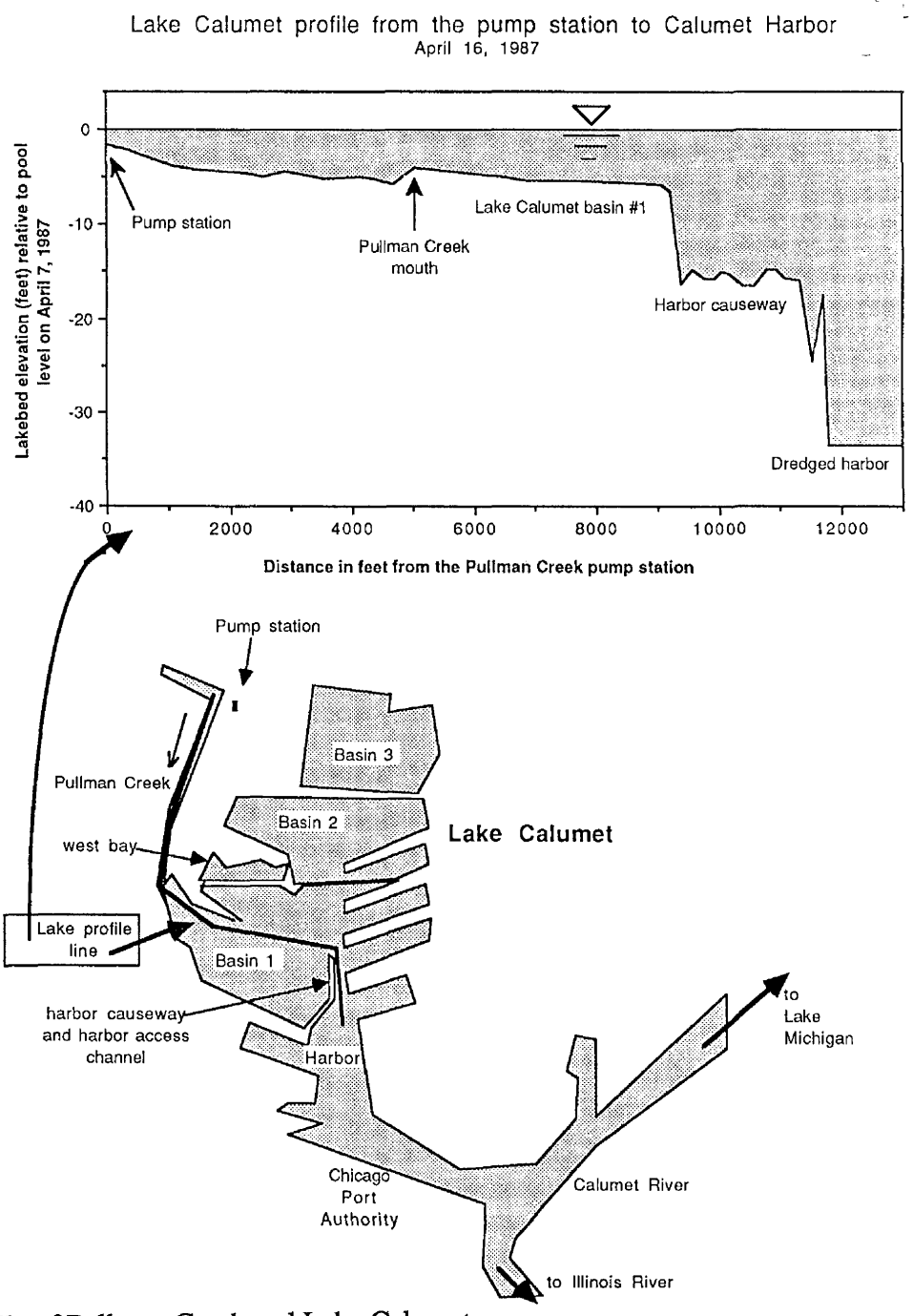


Figure 4.9. Bed profile of Pullman Creek and Lake Calumet

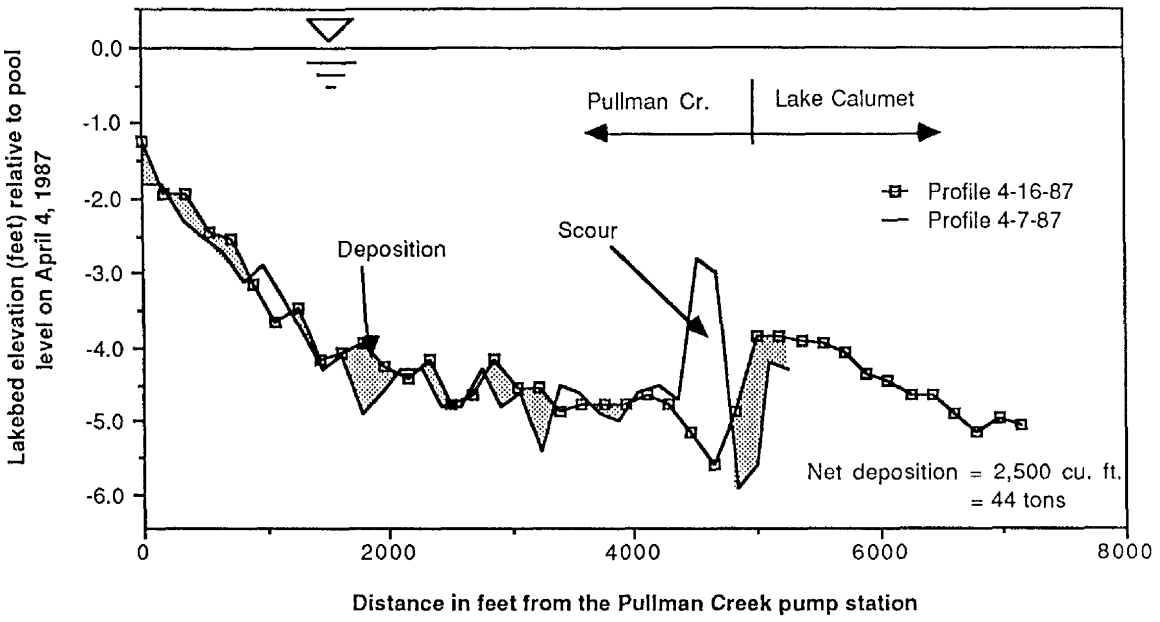


Figure 4.10. Pullman Creek profiles on April 7 and 16, 1987, showing scour and deposition in the creek channel.

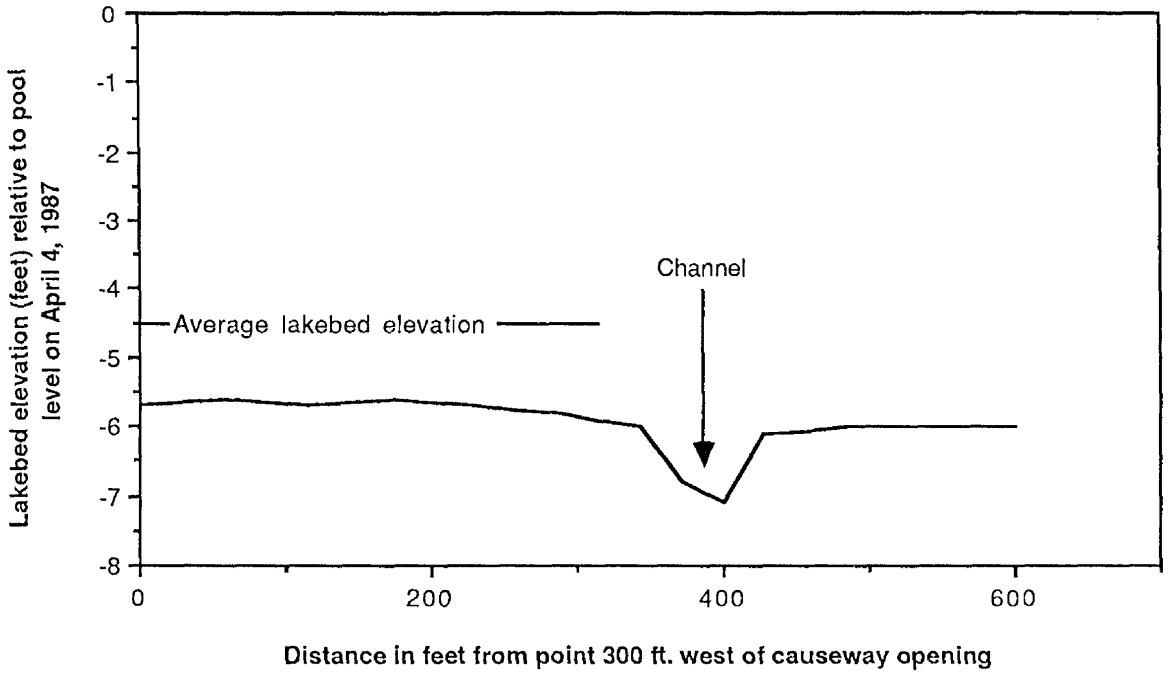


Figure 4.11. Lake Calumet bed profile, 100 feet south of the causeway opening between Basins 1 and 2.

## 4.4 Ground-Water Seepage Studies

### 4.4.1 Study objective

In an assessment of the environmental hazards posed to Lake Calumet, ground-water pathways were recognized as a potential contributor to the total contaminant loading of the lake bottom sediments. Numerous sites of potential ground-water contamination exist within close proximity to the lake. A summary of the locations of waste handling facilities near Lake Calumet is shown in Figure 4.12 (a brief description of the sites represented by circled numbers on the map can be found in Illinois Environmental Protection Agency 1986). Numerous other facilities that handle hazardous materials are located in the Lake Calumet area and could pose similar threats to ground-water quality.

Compared to most surface water investigations, ground-water studies are costly. The expenses involved in drilling and sampling monitoring wells are usually much greater than those required for investigating more "accessible" environments. Due to limited funding for this preliminary environmental assessment, a scaled-down effort was initiated to study interactions between ground water and surface water at Lake Calumet. Emphasis in this preliminary assessment was placed on evaluating the feasibility of techniques for determining ground-water seepage rates into Lake Calumet. A brief discussion of the local geohydrology, ground-water movement near lake environments, and techniques used for the determination of ground-water seepage into surface water bodies follows.

### 4.4.2 Geohydrology of the Lake Calumet area

The geology and ground-water hydrology of northeastern Illinois have been extensively studied and interpreted by several investigators (Bretz 1939-1955; Suter *et al.* 1959; Willman 1971; Schicht et al. 1976; Gilkeson et al. 1983; Sasman et al. 1982; Visocky et al. 1985). Principal emphasis in recent years has been placed on declining ground- water levels in the Cambrian and Ordovician aquifers and the potential for water supply for northeastern Illinois communities. These reports, along with records for local industrial and domestic wells, provide a firm basis for describing the geohydrology of the Lake Calumet area.

The geology of the Lake Calumet area is generally characterized by unconsolidated Quaternary material unconformably underlain by thick sections of sedimentary rocks. The Quaternary deposits are composed principally of lake plain sediments, lacustrine silts and clays, and some sand and gravel. Sandy beach ridges along Lake Michigan appear in areas just to the east and

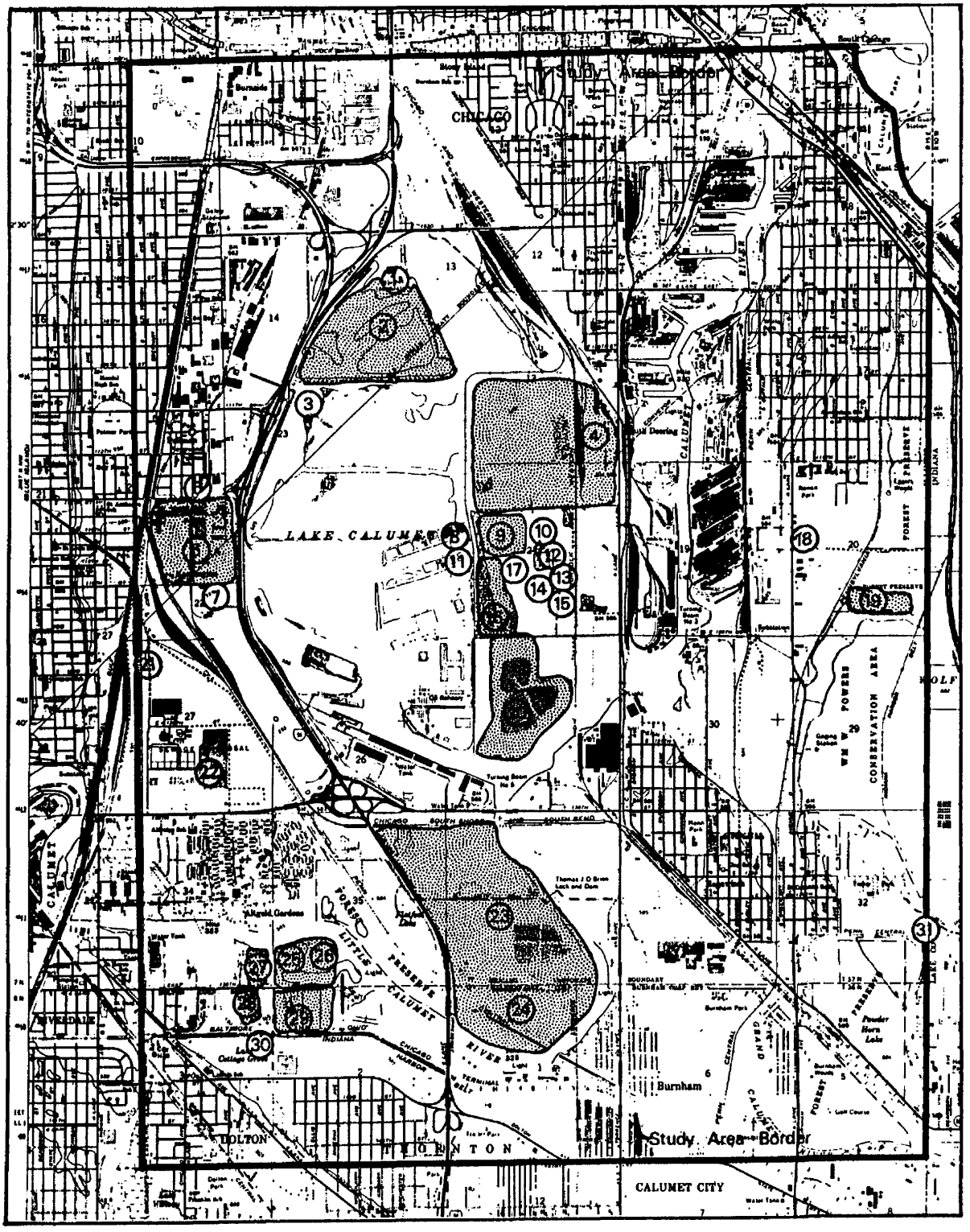


Figure 4.12. Geographic distribution of landfills and waste handling facilities in the south Chicago area (from IEPA 1986).

south of Lake Calumet. Much of the area adjacent to Lake Calumet has been filled by materials of various origins including demolition debris (e.g., concrete rubble, stone) and incinerator ash. Depth to bedrock in undisturbed areas is approximately 65-80 feet. Well records indicate thin deposits (5-10 feet) of sand and gravel at the bedrock surface. These unconsolidated materials do not readily yield water to wells and are not considered a viable resource even for domestic supplies.

The bedrock surface is dolomite of Silurian age. Rocks of the Pennsylvanian, Mississippian, and Devonian systems are not present in the area (Figures 4.13 and 4.14). Most small capacity wells in the area are completed in the dolomite and reach depths of 300-400 feet. Well yields range from 5-30 gallons/minute. Approximately 200 feet of Maquoketa Shale separates the dolomite from the underlying Glenwood-St. Peter Sandstone and other Cambrian-Ordovician aquifers. The thick sequence of shale greatly limits the local movement of water downward to underlying formations. Recharge to these deeper formations is received in portions of north-central Illinois and southern Wisconsin. Wells completed in the Glenwood-St. Peter and underlying formations at depths over 1,000 feet are capable of yielding in excess of 500 gallons/minute. According to Kirk *et al.* (1985), total ground-water withdrawals in 1984 for the six townships surrounding Lake Calumet (T.36-38N.,R.14- 15E.) were only 244,000 gallons/day. Nearly all (more than 99 percent) of these withdrawals were due to industrial withdrawals from Cambrian-Ordovician aquifers.

4.4.3 Ground-Water Occurrence and Movement near Lake Environments

Ground water is an integral part of the hydrologic cycle (Figure 4.13). Most precipitation reaching the surface of the earth evaporates or flows overland to lakes and streams; a smaller portion infiltrates the soil. The amount of water that infiltrates from a given storm is dependent upon such factors as the amount and intensity of precipitation, the slope of the land surface, the permeability of the soil (the amount of pore space open to the flow of water), the type and density of plant growth on the soil, and antecedent moisture conditions.

Water infiltrating the soil may evaporate or be used by plants and transpired. The remainder percolates downward through the pore spaces of the soil or rock, eventually reaching a zone where all pore spaces are saturated. The surface of this zone of saturation is called the "water table." All water below the water table is referred to as ground water. The water table is a surface which can be approximated by the elevation of water surfaces in wells that just penetrate the saturated zone. The position of the water table will fluctuate in response to rainfall recharge, evapotranspiration, and ground-water withdrawals (pumpage).

| SYSTEM | SERIES | GROUP OR FORMATION | HYDROLOGIC UNITS | | LOG | THICKNESS (FT.) | DESCRIPTION |
|---|---|---|---|---|---|---|---|
| Quaternary | Pleistocene | | Glacial drift aquifers | | | 0-350+ | Unconsolidated glacial deposits - pebbly clay (till), silt, and gravel. Alluvial silts and sands along streams. |
| Pennsylvanian | | Carbondale Tradewater | | | | 0-175 | Shale; sandstones, fine-grained; limestones; coal; clay. |
| Mississippian | Kinderhook | | | | | 0-365 | Shale, green and brown, dolomitic; dolomite, silty. |
| Devonian | | | | | | 0-25 | Shale, calcareous; limestone beds, thin. |
| Silurian | Niagaran | Port Byron<br>Racine<br>Waukesha<br>Joliet | Silurian | Shallow dolomite aquifs | | 0-465 | Dolomite, silty at base, locally cherty. |
| | Alexandrian | Kankakee<br>Edgewood | | | | | |
| Ordovician | Cincinnatian | Maquoketa | Maquoketa | | | 0-250 | Shale, gray or brown; locally dolomite and/or limestone, argillaceous. |
| | Mohawkian | Galena<br>Decorah<br>Platteville | Galena-Platteville | | | 220-350+ | Dolomite and/or limestone, cherty.<br>Dolomite, shale partings, speckled.<br>Dolomite and/or limestone, cherty, sandy at base. |
| | Chazyan | Glenwood<br>St. Peter | Glenwood-St. Peter | Cambrian-Ordovician Aquifer | | 100-650 | Sandstone, fine- and coarse-grained; little dolomite; shale at top.<br>Sandstone, fine- to medium-grained; locally cherty red shale at base. |
| | Prairie du Chien | Shakopee<br>New Richmond<br>Oneota | Prairie du Chien | | | 0-340 | Dolomite, sandy, cherty (oolitic); sandstone.<br>Sandstone, interbedded with dolomite.<br>Dolomite, white to pink, coarse-grained, cherty (oolitic), sandy at base. |
| Cambrian | St. Croixian | Trempealeau | Trempealeau | | | 0-225 | Dolomite, white, fine-grained, geodic quartz, sandy at base. |
| | | Franconia | Franconia | | | 45-175 | Dolomite, sandstone, and shale, glauconitic, green to red, micaceous. |
| | | Ironton<br>Galesville | Ironton-Galesville | | | 105-270 | Sandstone, fine- to medium-grained, well sorted, upper part dolomitic. |
| | | Eau Claire | Eau Claire (upper and middle beds) | | | 235-450 | Shale and siltstone, dolomitic, glauconitic; sandstone, dolomitic, glauconitic. |
| | | Mt. Simon | Sandstones Eau Claire (lower) & Mt. Simon | Mt. Simon | | 2000± | Sandstone, coarse-grained, white, red in lower half; lenses of shale and siltstone, red, micaceous. |
| | | | | | | | Precambrian |

Figure 4.13. Stratigraphic column for the Chicago region (frum Suter *et al*. 1959).

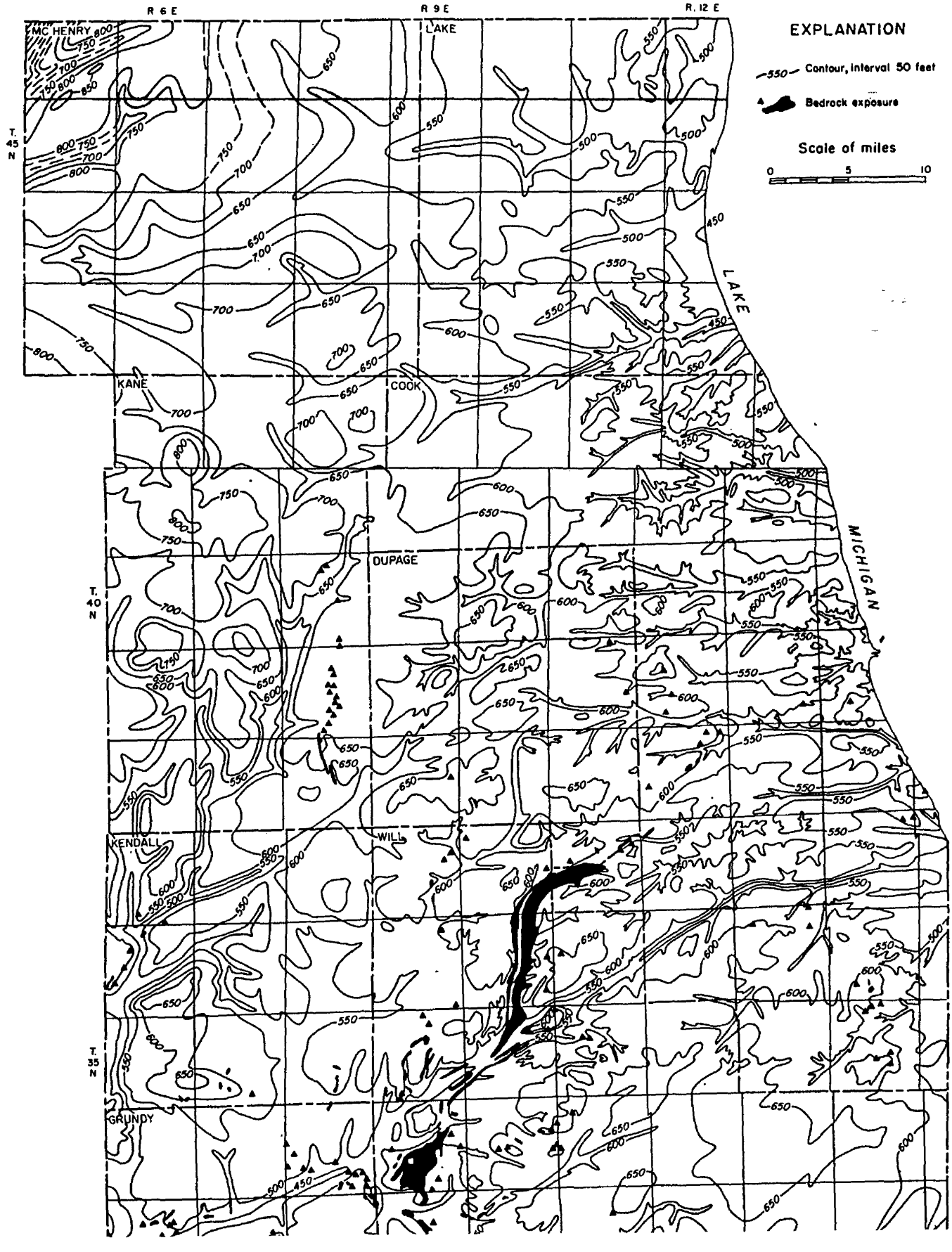


Figure 4.14. Bedrock topography of northeastern Illinois (from Suter *et al.* 1959).

Under natural conditions, the water table forms a surface that resembles a subdued and smoother configuration of the overlying land surface topography. The water table which is at higher elevations beneath upland areas and at lower elevations in valleys intersects the ground surface along perennial streams, springs, and lakes, that are natural areas of ground-water discharge.

Ground water moves in a fashion somewhat analogous to surface water, only at much slower rates. While surface water moves downhill in response to gravity, ground water moves down-gradient from areas of higher potential energy to areas of lower potential energy. This potential energy is measured as the ground-water elevation (or head) in a well tapping the aquifer or geologic zone of interest. Ground water flows from recharge zones, where infiltration occurs, to discharge zones, where ground water discharges into streams and lakes (Figure 4.15). Ground-water discharge can be a significant portion of the total flow of a stream or river. The flow in a perennial stream after extended periods without precipitation is due, in large part, to ground-water discharge. The direction of ground-water movement can be estimated from a map of the potentiometric surface, i.e., a contour map of the elevations of water levels in observation wells. Ground-water flow will be perpendicular to the contours of the potentiometric surface.

Depending on the position of a surface water body (in this case, a lake) in relation to the ground-water system and the nature of the underlying and surrounding geologic materials, two scenarios describing the ground water/surface water interaction are possible (Figure 4.16). In one case, the lake receives ground-water seepage through part of its bed and discharges water to the ground through another part. In the other case, ground water discharges to the lake on all sides.

Numerous investigations have been conducted to evaluate ground water/ surface water interactions near lake environments. McBride and Pfannkuch (1975) and Lee *et al.* (1980) concluded that, for two shallow sandy lakebeds they investigated in Minnesota and Canada, ground-water seepage was greatest at the shoreline and decreased exponentially with distance from shore. In addition, Lee *et al.* found that ground-water lake discharge occurred primarily from spring through fall with the greatest rates in the spring and fall, coinciding with the principal ground-water recharge seasons. Due to the low-lying character of the topography in the Lake Calumet area, water table elevations are very near the land surface. The water table elevation changes in response to climatic conditions and are readily observed by surface water elevations in the lake and surrounding ditches. Ground-water elevations in dolomite wells range

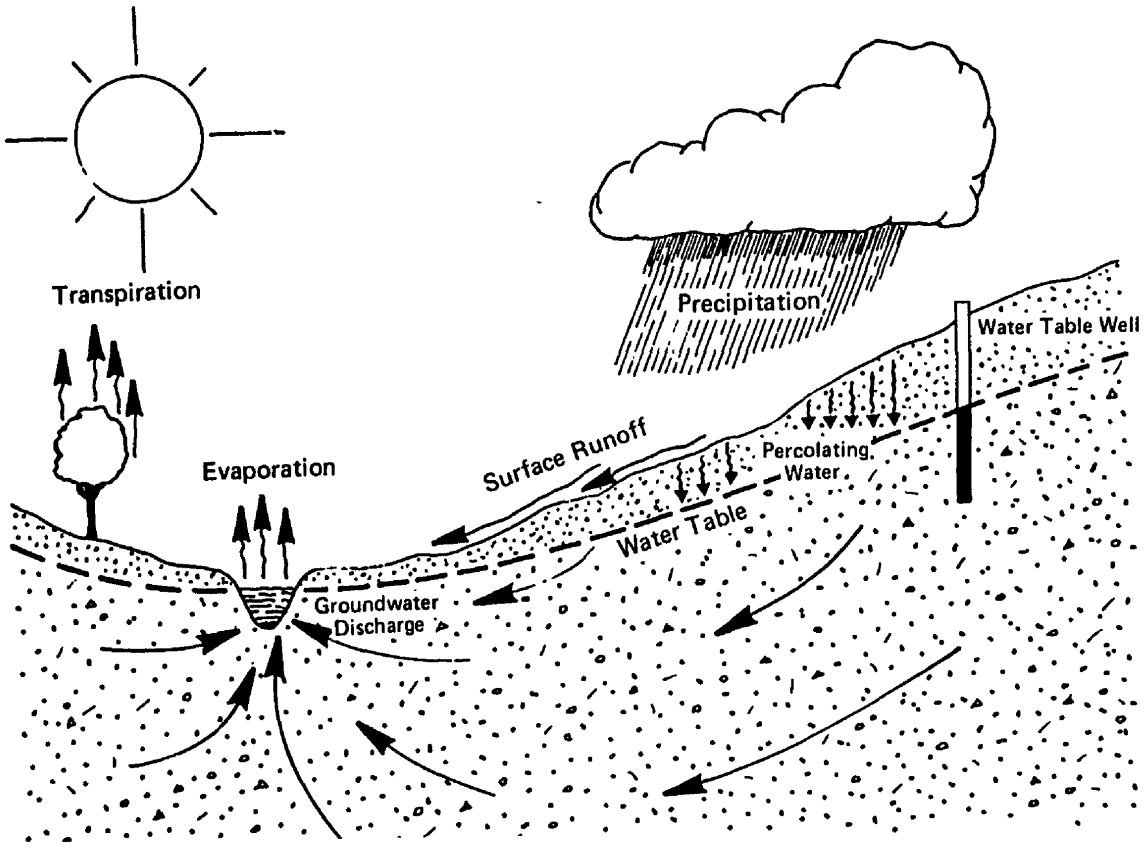


Figure 4.15. Generalized hydrologic cycle

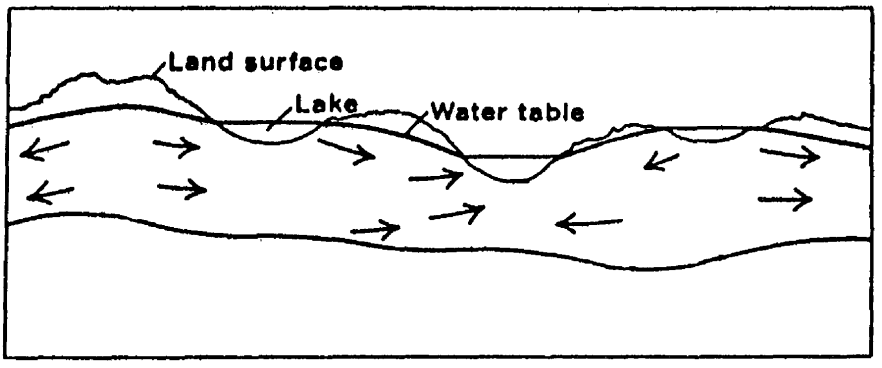


Figure 4.16. Relation between lakes and ground-water flow (adapted from McBride and Pfannkuch 1975).

from 20-40 feet below ground surface, indicating an overall downward movement of ground water to recharge the underlying dolomite bedrock. However, no studies have been conducted specifically to map the direction of ground-water movement near Lake Calumet or the relative contribution of ground-water flow into the lake.

4.4.4 Measurement of ground-water seepage into lakes

Studies by Lee (1977) represent some of the few investigations where ground-water seepage rates through lakebeds were physically measured. A summary of seepage measurements from Lee (1977) appears in Table 4.1. Ground-water discharge was measured using seepage meters placed in the lake bottom sediments at various locations around the lake perimeter and on traverses extending into the lake from the shoreline. A seepage meter (Figure 4.17.) consists of a 55-gallon drum cut in half and outfitted with a tap or port on the closed end over which a deflated plastic bag can be placed. The cylinder is placed open-end down into the sediment until its top is approximately 2 cm above the sediment surface.

Table 4.1. Seepage measurements at various locations (from Lee 1977)

| Locations | Seepage velocity ($\mu m\ s^{-1}$) | Number of measurements | Bottom type | Water depth (m) |
|---|---|---|---|---|
| Lake Sallie, MN | 0.01-2.58 | 494 | sand and gravel | 0.2 -2.0 |
| Lake Movil, MN | 1.0 | 3 | gravel | 1.0 |
| Lake Mendota, MN | 0.32-0.46 | 2 | sand | 0.7 |
| Minas Basin, NS | 0.5-1.4 | 6 | sand, silt | 1.5-2.0 |
| Bogue Sound, NC | 0.32 | 1 | sand | 0.9 |
| Duke Marine Lab, NC | -0.1-0.8 | 44 | sand | 0.1-1.5 |

Seepage flux can be measured directly by measuring the time and change of water volume in the bag connected to the cylinder. The bulk or Darcy ground-water velocity is calculated by dividing the volume of water collected by the cross-sectional area of the seepage meter and the time over which the water was collected. An average interstitial velocity can then be calculated by dividing the Darcy velocity by the sediment porosity.

Seepage rates can also be measured indirectly by the use of "minipiezometers" (Lee and Cherry 1978). Generally, piezometers are small wells used to measure ground-water heads in discrete zones of an aquifer or geologic unit. The minipiezometer is even smaller in size and is often installed manually rather than with well drilling equipment ( Figure 4.18). As described by Lee

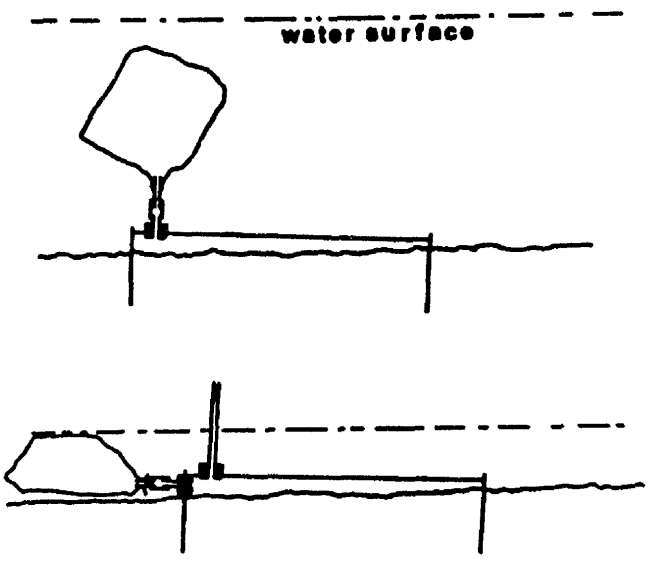


Figure 4.17. Full section views of seepage meter showing placement in deep (2-3 m) and shallow (less than 0.5 m) water (from Lee and Cherry 1978).

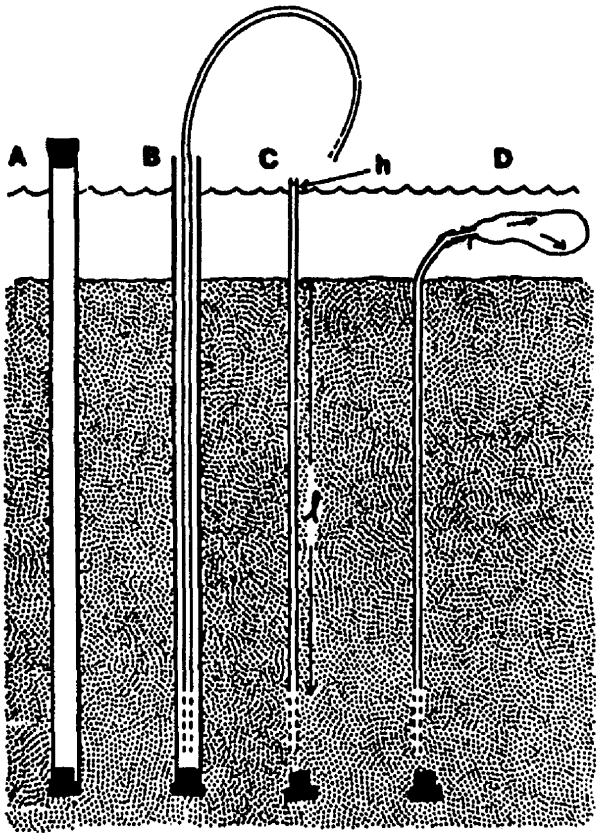


Figure 4.18. General features and method of installation of a minipiezometer: (A) casing driven into the sediment; (B) plastic tube with screened tip inserted in the casing; (C) plastic tube is a piezometer and indicates differential head; (h) with respect to surface water, (D) plastic bag attached to the piezometer collects sediment-porewater (from Lee and Cherry 1978).

and Cherry (1978) the minipiezometer is installed by driving a pipe into a lakebed to the desired depth, inserting a smaller diameter screened tube into the pipe, and withdrawing the pipe leaving the screened tube in place. The difference between the water level in the screened tube and the lake level is proportional to the ground-water discharge into (or out of) the lake. A higher water level in the tube denotes ground-water movement into the lake; a higher lake level means water movement from the lake to the ground. Newer methods for measuring ground-water heads with pressure transducers have been recently introduced (Bennett et al. 1987).

Subsequent to the head measurement, falling- or constant-head permeability tests (Hvorslev 1951; Lambe and Whitman 1969) are performed to derive the hydraulic conductivity of the lakebed. With these measurements, the seepage rate can be calculated using Darcy's Law:

$$v = K.dh/dl$$

where,

v = Darcy velocity,
K = hydraulic conductivity,

dh/dl = hydraulic gradient or the difference in measured water levels divided by the depth of the piezometer screen below the sediment-water interface.

A more conventional approach than the use of minipiezometers driven into the lake bottom is the measurement of water levels in wells and piezometers around the lake periphery and in areas not adjacent to the lake. A contour map of ground-water elevations can be used to define ground-water flow direction and, ground-water contributions to the lake can then be calculated through the use of Darcy's Law.

4.4.5. Assessment of Feasibility of Ground-Water Seepage Techniques

Unfortunately, the previously described methods have serious limitations when conditions are less than ideal. As mentioned by Lee (1977), "the method [seepage meters] will probably find its greatest application where surface waters lie in high to moderately permeable material....In fine, low permeability sediments, groundwater velocity may be too low to measure with this technique, or flow may be restricted to distinct springs or leaks." In addition, Lee and Cherry (1978) point out that sediments containing large rocks will likely bend piezometer drive-casings, greatly increasing the difficulty in placing minipiezometers.

Reconnaissance of the Lake Calumet shoreline encountered both of the previously described conditions. In most cases, the near-shore environment consists of demolition rubble (e.g., concrete, stone) placed as fill to enlarge the land area around the lake. In such areas, placement

of minipiezometers or seepage meters is not feasible. In several other areas, the lake bottom sediments are largely fine-grained materials and organic matter that would severely limit the usefulness of seepage meters. In only one area along the southwestern corner of the lake did it appear that such methods could be realistically attempted. Extrapolation of results from this limited area of the lake could be made but should be used with caution. In particular, ground-water quality samples collected from the southwestern part of the lake may not be representative of ground-water seepage into other parts of the lake because the southwestern part of the lake is somewhat removed from most sources of potential contamination (see Figure 4.12).

4.4.6. Future ground-water investigations at Lake Calumet

Owing to the tentative feasibility of using seepage meters and minipiezometers in Lake Calumet, we recommend a thorough review of available ground-water information from surrounding waste disposal facilities. For example, the Illinois Environmental Protection Agency requires all hazardous waste disposal facilities to collect ground-water elevation measurements to determine the ground-water flow direction beneath their facility (a determination of upgradient and downgradient positions for monitoring well locations is the goal of these measurements) as part of the regulations under RCRA (the Resource Conservation and Recovery Act). If enough facilities surrounding Lake Calumet have complied with these regulations and sufficient correlation between separate facilities can be made, it may be possible to link the separate ground-water contour maps prepared for each facility into one map that generally describes ground-water flow conditions around the entire lake. Then, calculations of ground-water seepage to the lake can be made for different cross- sectional areas around the lake.

Information review would also be useful for determining the presence of potential contaminants in ground water and the location of such contaminants. Sampling of future installations (e.g., monitoring wells) near those locations can then be directed toward the determination of those same contaminants as well as related compounds. Futhermore, a review of the information being collected under current regulations would be useful in determining the adequacy of the regulations. If the data collected under the regulations are not useful, then changes in the regulations may be necessary. Where possible, actual ground-water seepage measurements in portions of the lake are important. Physical measurements should be compared with seepage rates calculated from ground-water elevation contour maps. Estimates of ground-water contribution to the lake from such measurements, even if for only a portion of the lake, can also be used to describe the relative contributions of surface water and ground water to the lake water budget. In addition, ground-water quality samples collected from seepage measuring devices would be useful for comparison with monitoring well data. If the water quality of

nearby monitoring wells is similar to that collected from the ground-water seepage devices, then the monitoring well data may be useful for estimating ground-water quality contributions to the lake. However, if the water quality is dissimilar, then the physical, chemical, and biological processes affecting ground-water quality between sampling locations (i.e., dry-land monitoring well vs. in-lake seepage device) may need to be more closely investigated.

Finally, as funds become available, the installation and sampling of monitoring wells should be conducted in areas for which there is little information. Monitoring wells completed in separate vertical intervals would be valuable for determining the movement of ground water and potential contaminants to the underlying dolomite aquifer.

# Chapter 5
# Chemical Transport Processes

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## 5.1 Introduction

A number of toxic chlorinated hydrocarbons are present in the water and sediments of Lake Calumet. These compounds may directly affect people through the air or water, or indirectly by contaminating fish or waterfowl which are then consumed. These toxics may also be transported from the lake in the water, on particulates, or in the air, thereby contaminating areas remote from the lake. To determine if a toxics problem exists in, or is caused by Lake Calumet, more needs to be known about the chemicals present.

The movement and effects of all chemical molecules and ions in the environment are determined by their chemical availability--their chemical activity or fugacity (Mackay 1979; Mackay and Peterson 1981). Therefore, to compare and relate toxicities and to calculate and estimate transport between different phases, the chemical availability of the compounds of interest needs to be known.

The advantage of working with chemical availabilities rather than concentrations is that chemical availability is the thermodynamic driving force behind the movement of compounds. Thus if water and sediments are in contact, compounds migrate from the phase where their chemical availability is the highest to the other phase. At equilibrium, the chemical activity is the same in both phases. For some materials, chiefly ions, there are readily available and easily used specific-ion electrodes that directly measure chemical availability. Unfortunately, no such sensors exist for high molecular weight, non-polar, chlorinated organic compounds, the compounds of interest in this study.

## 5.2 Goals and Objectives

The goal of this portion of the Lake Calumet Project was to understand more completely the chemical availability of some of the toxic, non-polar, chlorinated organic compounds in the Lake Calumet system.

The objectives were as follows:

1) To develop methods to measure the chemical availability of toxics in water and sediment samples from Lake Calumet.

2) To measure chemical availability of toxics on samples from Lake Calumet.

3) To estimate the loss rate of toxics from the sediments and waters of Lake Calumet to the atmosphere.

## 5.3 Background

When several different phases (water, sediments, air, *etc.*) are in contact, organic compounds will migrate between them so that their chemical availability is the same in each phase (in equilibrium). Thus, determining the chemical availability of a compound in one phase gives its chemical availability in all of the phases in equilibrium.

Because there are no direct methods of determining the chemical availability of organic compounds, fugacities have to be inferred from concentration measurements. However, the chemical availability for the same concentration of a compound in two phases may differ by a factor of a million or more. The more soluble a compound is, the lower its tendency to evaporate. As a result its chemical availability is lower.

In water, the chemical availability of a compound is proportional to the concentration of that compound in true solution. The particles in solution usually contain much greater concentrations of the compounds of interest and can significantly affect the measured concentrations. Because there are no methods to remove all of the particles from water samples, determining the concentrations of the organic compounds that have a low water solubility is not yet possible. With sediment samples, the relationship of chemical availability to concentration depends on the composition of the sediment and is expected to vary greatly from sample to sample in the diverse sediments from Lake Calumet.

Determining the chemical availability of compounds in the vapor phase has the fewest complications. Because the chemical availability is proportional to its vapor pressure (=atm/RT), one need only determine the vapor pressure of the compound in the air sample to know its chemical availability. Because the chemical availability is the same for all phases in equilibrium, determining chemical availabilities in the vapor phase serves as the basis for determining the chemical availabilities of the compounds in all samples.

Given the chemical availability (CA) of a compound in the vapor phase, its concentration can be calculated in an equilibrated water phase. Since the CA in the two phases is the same, the ratio of the concentrations is the ratio of the solubility of the compound in the two phases (Mackay and Peterson 1981). This ratio is the Henry'sLaw constant (HLC), and it is known for many of the compounds of interest.

$$\text{At equilibrium: } CA_{(AIR)}=CA_{(WATER)}\text{;} \qquad HLC = \frac{\text{Conc. in air (atm)}}{\text{Conc. in water (mol/m}^3\text{)}}$$

Chemical availability (CA) information is also needed to determine the exchange rate of the compounds of interest between water and air. The tendency of a compound in water to evaporate is directly proportional to the difference in chemical availability of the compounds between air and water. The net gain or loss of material is (Liss & Slater 1974) as follows:

$$\text{Flux} = K_{OL} * (CA_{(WATER)} - CA_{(AIR)})$$

where $K_{OL}$ is the overall mass transfer coefficient. $K_{OL}$ is a function of the HLC, which includes the vapor pressure of the compound, and is thus temperature dependant. The $K_{OL}$ is also dependant on the wind speed and molecular weight of the compound.

In addition to chemical availability measurements, sediment and water samples were analyzed directly to determine what compounds were present and to compare the concentrations found with those reported for samples from other locations.

## 5.4 Methods and Procedures

### 5.4.1 Sample collections

The sediment samples used were portions of the samples collected as described in Chapter 2. Water samples were collected during the sediment collection cruises and on three occasions from along the west shore of the lake. Rocks along the shore permitted sampling away from the immediate shore. The particular rock used was accessible from shore, about 3 m from shore, and in water about 0.5 m deep. Clean, 4-liter bottles were immersed below the surface to collect the water. The wind was onshore when the samples were collected.

5.4.2 Analyses

The solvents used in the project were pesticide grade. The Florisil™ was activated by baking at 600°C and storing at 130°C. The chlorinated organic compounds were determined in the sediment samples by extracton in a soxhlet extractor with hexane and methylene chloride. The extracts were chromatographed on Florisil. The fractions eluted with hexane and hexane + 20% methylene chloride contained the compounds of interest.

The chlorinated organic compounds were determined in the water samples by extracting them with methylene chloride. The extracts were concentrated, dissolved in hexane, and then cleaned-up by chromatography on Florisil, as above.

Dry sediments were needed for fugacity measurements. To minimize the loss of organics, the sediments were dried over calcium chloride in a desiccator at room temperature.

Non-polar chlorinated organic compounds measured in this project were identified and quantified by gas chromatography. The compounds were separated on a 30-m, wide-bore (0.75 mm), bonded-phase (DB-5) capillary column. Detection was by a $Ni^{63}$ electron capture detector. Peaks were integrated using a digital electronic integrator (Supergrator-3); their retention times were determined relative to internal standards of tribromobenzene (TBB) and octachloronaphthalene (OCN). Compounds were identified by comparing them to the retention times and peak patterns of standards run under identical conditions. The PCBs were quantified by first determining the response factors for 54 resolved peaks in the PCB chromatogram. These response factors were then applied to the appropriate PCB peak in the chromatogram of the sample to determine the amount of PCBs present in each peak. These amounts were summed to give the total amount present.

5.4.3 Availability Measurements

Methods and procedures had to be developed to determine the vapor pressure of the chlorinated organics in the sediment and water samples. Two different approaches, batch and flow through, were taken. In the batch approach, a sample was equilibrated with air, the air was collected, and the compounds of interest were determined. The starting point for these efforts was a report by Yin and Hassett (1986) on determining the availability of mirex in Lake Ontario water. The flow-through approach continuously passed air through a very large sample to equilibrate a large volume of air.The batch method was simpler to run but was limited by sample size.

The apparatus built for the water equilibration was checked by running blanks and then water solutions of standards for which partitioning behavior was known. When satisfactory results were obtained from these efforts, measurements were begun on samples from Lake Calumet. A blank air sample was run before each experiment. The column was cleaned by refluxing acetone and then hexane in it between each experiment.

## 5.5 Results

The first order of business was to devise the techniques and the equipment necessary to make the availability measurements. Batch experiments using 5-gal carboys were set-up for both the water and sediment samples. For the water measurements, a measured amount of cleaned air was bubbled through and equilibrated with the water and then the air was passed through a tube filled with an absorber (Florisil™) for the organic compounds. From the amount collected on the absorber and the amount of air used, concentrations of the compounds in the air were calculated. The amounts of compounds collected in these experiments were below the limits of detection and the technique was abandoned.

### 5.5.1 Water

For the flow-through method, a column was needed that would permit counter-current air and water flows, provide an area of water surface large enough for air/water exchange to occur, and offer sufficient residence time for the air and water to permit equilibration. A variety of columns and column packings were tried. The column design that evolved was 1.5 m long and4 cm in diameter; 1.2 m of its length were packed with metal (copper) sponge. The column was operated with water flows of ≈10 l/hr and air flows of ≈120 l/hr. Residence times in the column were ≈40 sec. for water and ≈45 sec. for air. Flows were such that about 10% of the compounds with HLCs $= 2x10^{-4}$ $atm_*m^3/mol$ (similar to the PCBs) would be stripped from the water. Air residence time was about four times the air/water equilibration half-life . We believed that this method would provide sufficient material to analyze without causing a significant change in the water concentrations. A greater proportion of compounds with higher HLCs would partition into the air (which could deplete the water), while a smaller proportion of those with a lower HLC would do so.

The flow-through method was used for the sample measurements because of the relative ease of handing large air flows and water volumes. The column design was refined and tested, and the first experiment was run. The results are shown in Table 5.1. A large water sample (≈96 l) was

collected from Lake Calumet, and 7 liters of were analyzed. The remainder of the sample (≈89 l) was run through the column and equilibrated with air (1.19$m^3$) over an 8-hour period.

These results are in essential agreement with expectations. On an average, only 32% of the PCBs and 48% of the HCB in the water were available (column 6). The less soluble (higher molecular weight; higher peak #) compounds should be more associated with the particulates and therefore be less available, and this trend is seen in the PCB data. The HCB results, though different, fit quite well. The HLC for the HCB is higher by a factor of ten than it is for the PCBs, and the ratio of the concentration in the air to the amount in the water is much higher for the HCB than for the PCBs, column 7.

**Table 5.1.** Chemical Availability (CA) of a number of compounds in water as determined from air equilibration experiments.

| Peak | [Water]Meas. (ng/l) | [Air]Meas. (ng/m3) | Air CA (atm.; meas.) | Water CA (ng/l; calc) | Water CA [Water]Meas | [Air]Meas. [Water]Meas. |
|---|---|---|---|---|---|---|
| HCB | 0.54 | 13.5 | $1.13x10^{-12}$ | 0.26 | 0.48 | 24.7 |
| 11 | 0.48 | 1.8 | $1.7x10^{-13}$ | 0.22 | 0.46 | 3.7 |
| 15 | 0.48 | 1.2 | $1.1x10^{-13}$ | 0.15 | 0.31 | 2.5 |
| 20 | 0.076 | 0.32 | $2.6x10^{-14}$ | 0.040 | 0.53 | 4.3 |
| 21 | 0.070 | 0.31 | $2.5x10^{-14}$ | 0.038 | 0.55 | 4.4 |
| 24 | 0.30 | 0.88 | $7.0x10^{-14}$ | 0.11 | 0.36 | 2.9 |
| 28 | 0.27 | 0.44 | $3.5x10^{-14}$ | 0.055 | 0.20 | 1.6 |
| 30 | 0.33 | 0.88 | $6.5x10^{-14}$ | 0.11 | 0.33 | 2.6 |
| 33 | 0.36 | 0.48 | $3.5x10^{-14}$ | 0.06 | 0.17 | 1.33 |
| 37 | 0.11 | 0.26 | $1.9x10^{-14}$ | 0.033 | 0.31 | 2.5 |
| 40 | 0.16 | 0.15 | $1.1x10^{-14}$ | 0.018 | 0.11 | 0.9 |
| ΣPCBs | 2.65 | 6.7 | $5.4x10^{-14}$ | 0.84 | Avg. =0.32 | Avg. =2.53 |

The concentrations of HCB and the PCBs found in the water sample are shown in column 2; those in the air sample are shown in column 3. The availability of the compounds in the air (converting ng/$m^3$ to atm) is shown in column 4. The calculated availability of the compounds in the water (availability in air/HLC; moles/$m^3$ converted to ng/l) is given in column 5. The HLC used for HCB was $1.3x10^{-3}$ atm*$m^3$/mol (Strachan and Eisenreich 1987) and for the PCBs was $2x10^{-4}$ atm*$m^3$/mol (Murphy et al. 1986). The total amount of the PCBs in the sample was summed, and these results, and the calculations done on them, are shown in the last row of the table.

Scatter is due to analytical errors in determining low concentrations, interference by other compounds in the sample, and the use of a single HLC for each of the PCB compounds. Of these errors, the analytical errors are the largest.

5.5.2 Sediments

Preliminary calculations for the sediment measurements indicated that the batch method using 5-gal carboys would not give sufficient sample for analysis. Therefore, a flow-through set-up was constructed by loosely packing glass tubes with a mixture of dried sediment and glass wool. The rationale for using this packing was that it presented a high surface area of sediment for equilibration with the air but did not impede the air flow. A typical tube used was 0.9 cm ID, had a packed length of 60 cm , and contained ≈10 g of sediment; the transit time of the air through the packed volume was ≈2 min. To maintain an even temperature, the tubes were jacketed, and water from a constant temperature bath was circulated through the jacket. Larger diameter tubes were also tried. Nitrogen gas from cylinders was used in place of air because of its convenience and purity. It was cleaned by passing it through Florisil™ before it entered the equilibration tube. After leaving the tube, the nitrogen passed through a Florisil™ absorber which removed the organics for analysis.

Experiments run so far have used total air volumes of 0.3-1.0 $m^3$; however, significant amounts of the compounds of interest have not been detected. Thus the availabilities are lower than anticipated and lower than the water samples. For instance, if 5 $ng/m^3$ of PCBs could be detected in the air, and the PCB concentration in the sediment is 0.5 mg/kg, then the availability of the PCBs in the sediments is less than 1 part in $10^6$ ($5 \times 10^{-14}$). These experiments are easier to run than the water determinations but take more time (1-2 weeks). The techniquehas promise, but more experimentation is needed to define the air flow rates, sediment amounts, and residence times that will measure these low availabilities.

In anticipation of getting CA from the sediments and to help choosing the sediments to measure, the concentrations of chlorinated hydrocarbons in many of the sediments have been determined. HCB and chlordane have not been detected in any of the sediments analyzed. PCBs equal to or greater than 0.1 mg/kg (ppm) were found in samples B (0.9mg/kg), C (3 mg/kg), F (0.1 mg/kg), H (0.5 mg/kg) and I (0.2 mg/kg). Samples 9, 10, 11, and 14 had concentrations below 0.1 mg/kg.

## 5.6 Discussion

The initial results for the chemical availabilities in the water sample indicate that only about one-third of the PCBs and half of the HCB in the samples was available to evaporate, partition, or

be absorbed by an organism. The preliminary sediment measurements indicate that less than 2 ppm of the PCBs present were available. More measurements need to be made to determine what typical values are.

Comparisons between the chemical availability of the PCBs and their concentrations should prove interesting. We would be surprised if comparisons between the chemical availability for samples did not differ from the comparisons of the concentrations. They may even differ in a random fashion—some higher, some lower. However, they may prove to be closer to one another than the concentration results. If so, the sediments in the system would be closer to equilibrium (or uniform availability and toxicity) than the concentration results indicate.

It is surprising that our preliminary results indicate that the availabilities of the compounds in the samples measured are lower in the sediments than in the water. If true, these results suggest a net transport of toxics to the sediments of Lake Calumet rather than out of the sediments.At this time, errors in the sediment measurements are also a good possibility. Winter should provide an opportunity to check this situation when ice cover prevents evaporation. The availabilities in the water and in the sediments then should be closer to equilibrium. Because of the warm winter during 1986-87, ice cover was patchy and thin, and samples could not be collected. We hope to be able to collect such samples during the winter of 1987-88.

# Chapter 6
# Microbial Processes

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## 6.1.Introduction.

Aerobic microbial degradation of priority pollutants has received extensive attention with the advent of synthetic organic chemicals and toxic wastes (Chakrabarty 1982). Anaerobic biodegradation of natural organic macromolecules has received increased attention in recent years, because many of these compounds are considered renewable energy resources (e.g., Hungate 1982 , Bryant 1976 , Lettinga *et al.* 1977). However, little information exists regarding the role of anaerobic bacteria in the transfomation and biodegradation of priority pollutants. The absence of such data has led to questions concerning the fate of priority pollutants in both anaerobic and microaerophilic environments.

A three-step approach to investigating microbial processes in sediments from Lake Calumet was undertaken. First, selected stations were used to study the rates of methane formation in anaerobic sediments. Methane production was monitored because the methane-producing bacteria occupy an essential position in the anaerobic food chain; many natural and synthetic compounds (including priority pollutants) are broken down entirely or in part to methanogenic substrates (Balch *et al.* 1979 , Boyd and Shelton 1984 , Healy and Young 1979 , Horowitz *et al.* 1982 , Kaiser and Hanselmann 1982 , Schink and Pfennig 1982 , Suflita *et al.* 1982). Since methane is a stable and unique end product, its concentration indicates the extent of anaerobic degradation processes.

Second, in order to determine the extent of the over-all microbial population, the total number of bacteria in the sediments were enumerated by direct counts using a microscopic enumeration technique.

Finally, aerobic and anaerobic bacterial degradation experiments were initiated to determine the fate of several priority pollutants. Compounds that are being investigated are anthracene, phenanthrene, 2-chloro, 3-chloro, and 4-chloro-phenols, and di-, tri-, and tetra-chloroethylene. Anthracene and phenanthrene were detected in Lake Calumet sediments (330-850 µg/Kg and 400-1300 µg/Kg, respectively) and were selected for the biodegradation study as representatives of the polycyclic aromatic hydrocarbons. Chlorinated phenols and chlorinated ethylenes are common halogenated pollutants. Although none of these compounds were detected in Lake Calumet, these compounds

were selected to study the sediment biodegradative potential for halogenated compounds. The persistence of specific pollutants directly reflects the degradation potential of the microbial communities.

## 6.2. Materials and Methods.

### 6.2.1. Methane production from anaerobic sediments.

Rates of biological methane production were determined in sediments from Stations A - M in Lake Calumet (Figure 6.1). Anaerobic culture tubes with rubber stoppers were tared, and placed in an anaerobic chamber (Coy Mfg., Ann Arbor, MI). Undiluted sediments from each station were placed into duplicate culture tubes. The tubes were stoppered and gases exchanged by flushing with $N_2$ for 5 minutes. The tubes were then weighed to determine the wet weight of the sediment, pressurized to 20 psi with $N_2$, and incubated at 30°C in an anaerobic chamber. Methane was measured weekly using a Hewlett-Packard Sigma 1 gas chromatograph equipped with a CTR packed column and a flame ionization detector.

### 6.2.2. Bacterial enumeration.

Sediment from each station, was blended with an equal volume of filtered $dH_2O$ for approximately 2 minutes to form a slurry. The dry weight of the slurry was determined in triplicate. A 1.0 mL aliquot of the slurry was added to 200 mL of filtered $dH_2O$ containing 1.85% formaldehyde. This solution was stored in plastic bottles at 4°C until ready to be used for direct counts.

The bacterial enumeration procedure of Hobbie *et al.* (1977) was followed for all counts. Nucleopore A filters (0.2 /μm pore size, 25 mm diameter) were stained by soaking for 2 - 24 hours in a 0.2% Irgalan Black (Ciba-Geigy Corp.) solution containg 2% acetic acid. Stained filters were rinsed in filtered $dH_2O$ and placed on a damp Millipore filter (0.45 μm, 25 mm) in a filter holder.Appropriate dilutions of the preserved samples were made, and 500 μL of the diluted sample was placed in a test tube containing 1.5 mL of 0.01% Acridine Orange (Sigma Chemical) solution and incubated for 1 - 2 minutes. The stained sample was then added to the filter tower and a vacuum applied. The test tube was rinsed with 2 mL filtered $dH_2O$, and the rinse was added to the filter tower.

After filtration, the stained filter was removed and placed on a drop of immersion oil on a slide. Another drop of oil and a coverslip were then placed on the filter and the slide was examined under

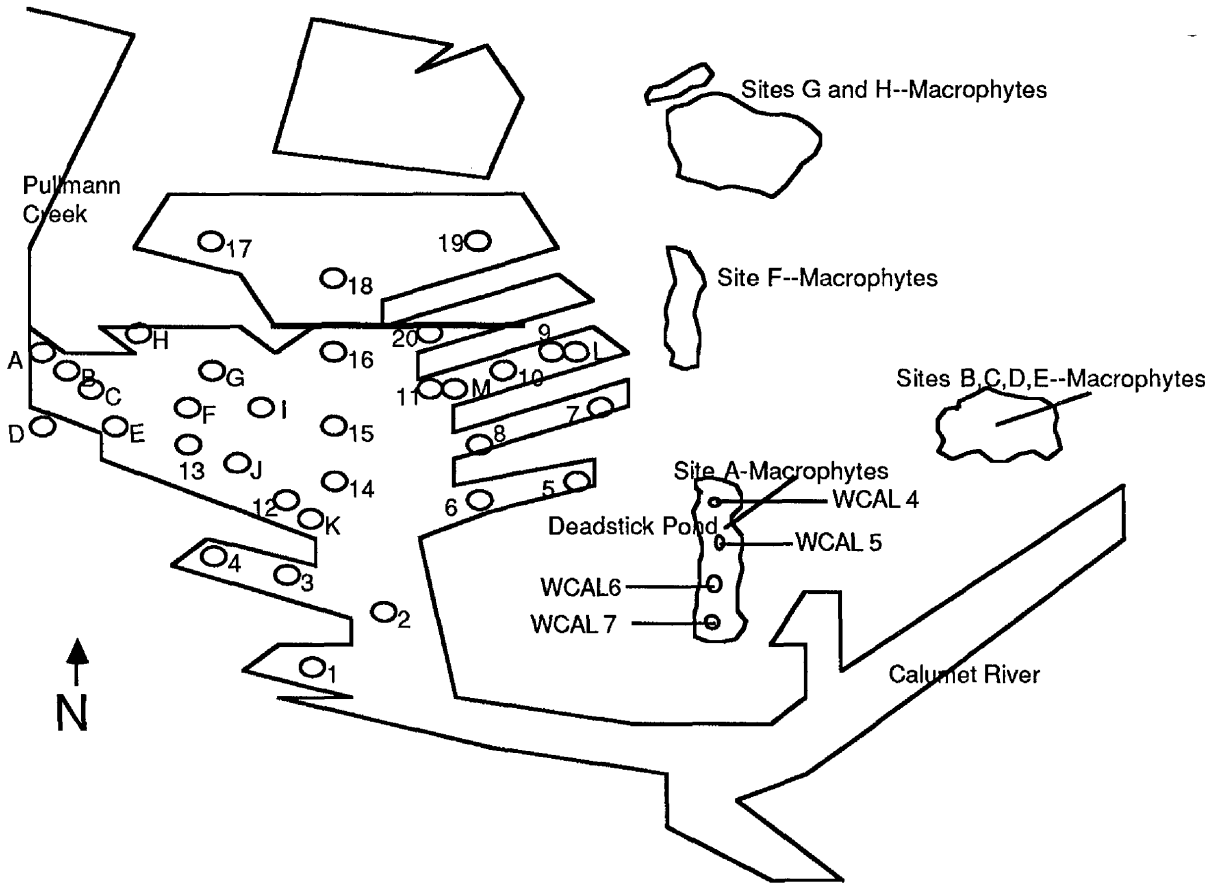


Figure 6.1. Station locations in Lake Calumet and surrounding wetlands.

oil immersion using a planachromat objective with a Zeiss 487709 filter set. Bacteria which fluoresced both green and red were counted in ten fields (grids) from each sample. The following calculation was used to determine the number of cells/g dry weight sediment:

(1.) Cells / mL slurry = (ave # cells/field)(dilution factor) $(2.22 \times 10^4)(2)$

(2.) # cells / g dry wt. sediment = (cells /mL slurry) / (g dry wt sediment / mL slurry)

The acridine orange solution and all water used for dilutions and for rinsing of filters and glassware were filtered through a 0.2 /μm Nucleopore or Millipore filter before use. Water blanks were run each day.

### 6.3. Results and Discussion

6.3.1. Methane production from anaerobic sediments.

Methane concentrations were followed for 9 weeks in the culture tubes stored in the anaerobic chamber. As Figure 6.2 indicates, significant levels of methane were formed in all station sediments, with levels stabilizing after approximately 50 days. The decrease in the level of $CH_4$ in Station G may have been due to an inaccurate gas measurement or, less likely, to gas seepage with subsequent $CH_4$ formation.

These stations are broken into three groups based upon the amount of $CH_4$ formed. Stations B, G, and L stabilized above 3% within 7 weeks and comprise group 1. Stations A, C, D, E and I formed between 2 and 3% methane and comprise group 2. Stations F, H, J, K, and M formed less than 2.0% $CH_4$ and comprise group 3 (Table 6.1).

The mean values of % $CH_4$ formation for groups 1, 2, and 3 are 3.73, 2.56, and 1.48 % respectively. Groups 1 and 2 produced 152% and 73% more $CH_4$, respectively, than group 3, and group 1 produced 46% more $CH_4$ than group 2. On the basis of these data, the anaerobic degradation processes in Stations B, G, and L are approximately 1.7-fold more active than those in Stations A, C, D, E, and I, and approximately 2.5-fold more active than those in Stations F, H, J, K, and M. Although these values correlate well with the total levels of organic carbon, the principle classes of compounds involved in the degradative processes are not apparent.

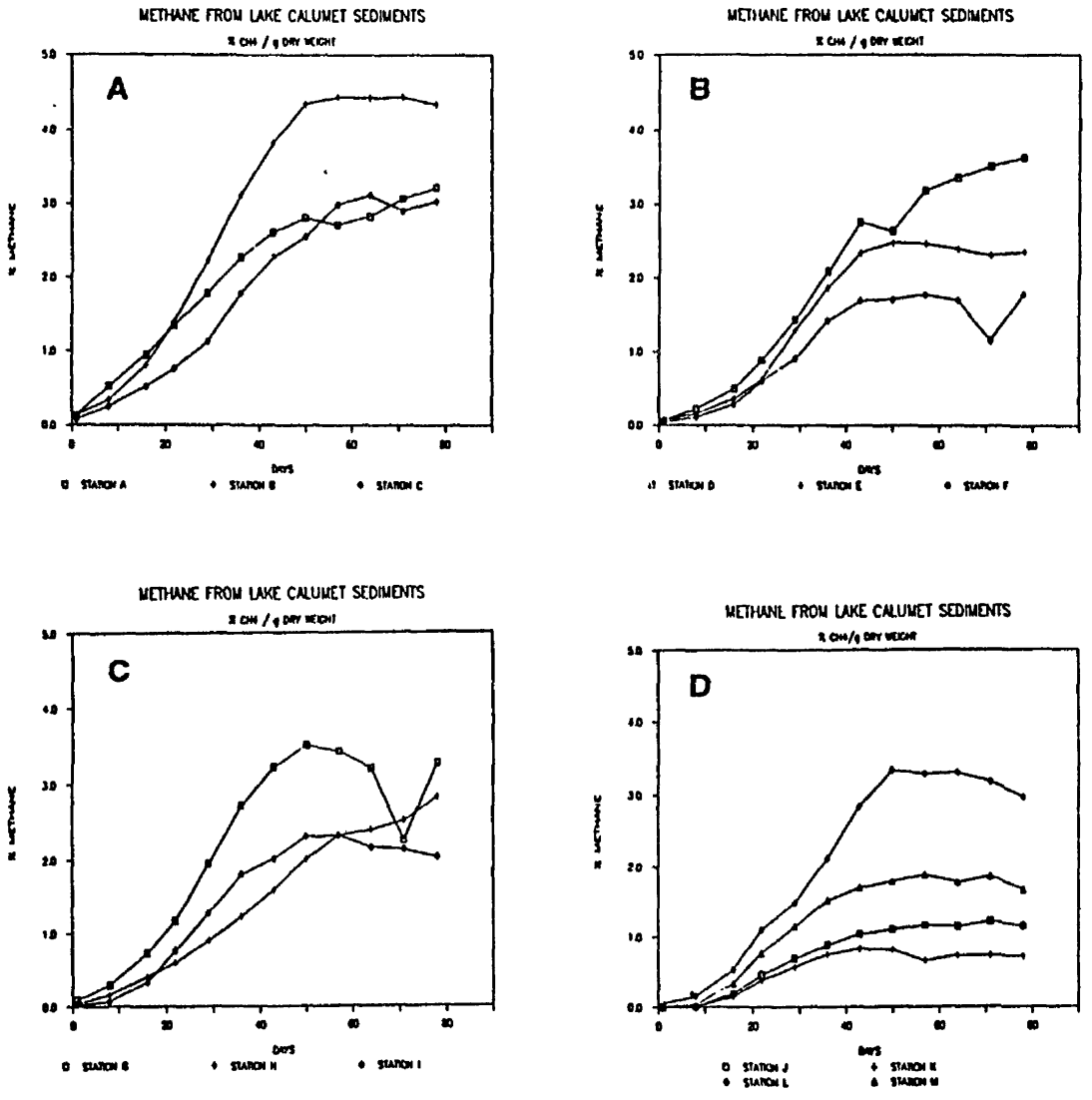


Figure 6.2. Methane production in sediments from 13 stations of Lake Calumet; values represent duplicates.

Table 6.1. Methane production from Lake Calumet anaerobic sediments.

| Station | % Total Organic Carbon | % $CH_4$/ g dry wt* (day 50) |
|---|---|---|
| A | 2.8 | 2.81 ± 0.23 |
| B | 4.8 | 4.36 ± 0.26 |
| C | 4.4 | 2.56 ± 0.33 |
| D | 3.3 | 2.65 ± 1.05 |
| E | 3.0 | 2.48 ± 0.23 |
| F | 2.5 | 1.72 ± 0.47 |
| G | 3.2 | 3.50 ± 0.25 |
| H | 3.1 | 2.00 ± 0.91 |
| I | 2.5 | 2.31 ± 0.63 |
| J | 1.5 | 1.10 ± 0.04 |
| K | 1.6 | 0.81 ± 0.11 |
| L | 2.9 | 3.34 ± 0.04 |
| M | 2.1 | 1.78 ± 0.18 |

* All values were averages of duplicates

6.3.2. Bacterial enumeration.

The major problem in direct microscopic enumeration is the difficulty of refilling the chamber with fluid (Norris and Powell 1961). We have attempted to overcome this problem by using a filtration/staining approach (Hobbie *et al.* 1977). Table 6.2 contains these data with standard deviations that were calculated. Lamp failure prevented repetition of all samples.

These data are divided into three groups based on sample collection periods and locations. Samples labelled LCAL 1 - 20, and WCAL 4 - 7 were collected on April 28 1987. Samples from stations A-M were collected in late November 1986. Enumerations focused on samples collected on April 28, 1987. These samples were preserved immediately after returning to the laboratory and stored at $4^{o}C$ until analysis.

Samples labelled LCAL 1 - 20 indicate lower bacterial numbers in sediments from stations in central regions of the lake away from shores and slips. For example, Stations 12,13,14,15,17, and 19 which are located well off-shore, have bacterial counts of less than $6.5 \times 10^{+8}$ cells/g dry sediment. On the other hand, stations located within slips (Stations 5, 6, 7, 9, 10, and 20) have bacterial counts that range between $6.7 - 15.0 \times 10^{+8}$ cells/g dry sediment. . Exceptions include Station 4, which is located deep within a slip, but has a low cell count, and Stations 2 and 18, which have high cell counts despite being in open water. Station 16 follows this general pattern since it has a high cell count and is located just off the mid-lake ridge.

Table 6.2. Total organic carbon (%TOC) and bacterial enumerations by direct counts from Lake Calumet sediments.

| Station | % TOC | Direct counts (x $10^8$ cells/g dry wt.) |
|---|---|---|
| LCAL 1* | 2.7 | 4.68 ± 0.2 |
| 2 | 2.6 | 31.90 ± 5.80 |
| 3 | 2.0 | 11.10 |
| 4 | 1.6 | 2.15 |
| 5 | 2.6 | 6.67 ± 0.88 |
| 6 | 2.7 | 12.30 |
| 7 | 3.0 | 14.50 |
| 8 | 3.6 | 4.85 ± 1.59 |
| 9 | 2.6 | 7.06 |
| 10 | 3.1 | 8.17 ± 1.84 |
| 11 | 2.7 | 5.18 |
| 12 | 1.7 | 4.32 |
| 13 | 1.8 | 6.46 ± 0.94 |
| 14 | 1.1 | 1.70 |
| 15 | 2.2 | 6.02 |
| 16 | 1.6 | 16.10 |
| 17 | 3.5 | 6.31 |
| 18 | 2.4 | 10.10 |
| 19 | 1.9 | 4.40 |
| 20 | 2.6 | 10.50 |
| WCAL 4* | 5.5 | 14.07 ± 4.10 |
| 5 | 5.6 | 22.60 ± 1.98 |
| 6 | 5.4 | 14.30 ± 2.30 |
| 7 | 5.7 | 32.70 |
| A** | 2.8 | ND |
| B | 4.8 | 6.65 ± 2.18 |
| C | 4.4 | 5.78 |
| D | 3.3 | 4.03 ± 0.38 |
| E | 3.0 | 2.82 |
| F | 2.5 | 3.40 |
| G | 3.2 | ND |
| H | 3.1 | ND |
| I | 2.5 | 3.66 |
| J | 1.5 | 2.54 ± 0.22 |
| K | 1.6 | 2.32 |
| L | 2.9 | 7.92 ±1.92 |
| M | 2.1 | 4.40 |

ND=not determined

*Samples stored at 4°C for 1 week before preservation. Standard deviations based on triplicates.

**Samples stored at 4°C for 6 months before preservation. Standard deviations based on duplicates.

Grab samples collected from a shallow wetland southeast of the lake (Figure 6.1) were labelled WCAL 4 - 7. These samples contained substantially higher numbers of bacteria (Table 6.2).

After the above samples were analyzed, enumerations were performed on the older sediments from Stations A - M since extra samples were available. These samples had been collected months before delivery of the fluorescence microscope and therefore were considered less reliable for enumeration studies. As a group they reflect lower cell numbers (Table 6.2) due to cell loss over the long storage period, but comparisons within the group again substantiate that higher cell numbers occur near shore and in slips. Stations B, C, D, L, and M had cell counts greater than 4.0 x $10^8$ cells/g dry sediment; samples collected further from the shore (Stations F, I, J, and K) had cell counts of less than 3.7 x $10^8$ cells/g dry sediment. An exception was Station E which is located near shore and had a relatively low cell count of 2.82 x $10^8$ cells/g dry sediment (Figure 6.2).

It is interesting to note that Stations B and L had the highestconcentrations of $CH_4$, bacterial numbers, and % TOC in this group; Stations J and K had the lowest values for all these parameters. Apparently, stations located closer to shoreline and in the slips contain greater levels of organic carbon and correspondingly higher levels of bacterial numbers. Water and soil run-off, currents, erosion, plant foliage, and debris in the near shore zone results in an organically rich matrix that can support a larger microbial population. However, the impact of these microbial communities on in-situ priority pollutants can only be determined by direct analyses of those pollutants.

6.3.3. Data correlation.

Table 6.3 contains correlation coefficients calculated from the percent total organic carbon (% TOC), methane production, and bacterial enumeration data collected from these studies. A high degree of concomitant variance was observed with the exception of the % TOC vs. the number of bacteria from Stations LCAL 1 - 20 ($r = 0.401$). While this correspondence is moderately positive, the same comparison for Stations A - M and WCAL 4 - 7 indicated a significant degree of correspondence ($r = 0.831$ and 0.935, respectively). While fewer points are more likely to be aligned, the larger number of data points for the LCAL 1 - 20 group may account for greater scattering and therefore error. Also, enumeration data from Stations LCAL 2 and 16 exhibit low degrees of correspondence to the remainder of the data. Comparing % $CH_4$ to TOC and to bacterial number also gave correlation coefficients that suggested high degrees of relationship.

## 6.4. Discussion.

These data indicate that microbial degradation of organic matter is actively occuring in the anaerobic sediments of Lake Calumet. Levels of methane and levels of bacterial numbers correlate well with percent organic carbon in the sediments and indicate that complex microbial food chains in the sediments are converting carbon compounds to anaerobic end products. Although organic compounds are being actively metabolized in the lake sediments, we do not yet know if polycyclic aromatic hydrocarbons, chlorinated phenols, or chlorinated ethylenes are being degraded. Several specific compounds from each of these groups are presently being studied in the laboratory to determine if microorganisms occurring in the aerobic and anaerobic sediments of Lake Calumet have the potential to metabolize these compounds.

Table 6.3. Correlation coefficients for total organic carbon, methance production, and bacterial enumeration from Lake Calumet sediments.

| Comparison | Stations | Correlation Coefficient |
|---|---|---|
| % Methane *vs.* # bacteria | A-M | 0.844 |
| % Methane *vs.* % TOC | A-M | 0.800 |
| % TOC *vs.* # bacteria | A-M | 0.831 |
| | LCAL 1-20 | 0.401 |
| | WCAL 4-7 | 0.935 |

*Correlation coefficient calculated from 10 of the 13 samples. Bacterial enumerations were not available for stations A, G, and H.

# Chapter 7
# Biological Uptake

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## 7.1 Introduction

Aquatic macrophytes are important in the functioning of freshwater aquatic systems. They produce oxygen, provide cover for young-of-the-year prey fish species and substrate for fish food organisms, and function in sediment stabilization (Wright *et al.* 1981, Bennett 1971, Wiley and Gorden 1984). They also modify the physical and chemical characteristics of the aquatic system they inhabit (Sculthorpe 1967, Hutchinson 1975, Dawson *et al.* 1978). Modification of sediment and water chemistry is often accomplished by substance uptake and release (Hill 1979, Smith and Adams 1986, Jaynes and Carpenter 1986).

Aquatic macrophytes are accumulators that concentrate toxic substances as well as essential nutrients from their surrounding media. Amounts concentrated are determined largely by substance availability in the environment, morphology of the plant species, and prevailing edaphic factors (Gerloff and Fishbeck 1973, Cowgill 1974, Mayes and McIntosh 1977, Mudroch and Capobianco 1979, Schierup and Larsen 1981, Campbell *et al.* 1985, Everard and Denny 1985). Uptake from sediments is generally greater than uptake from the water column primarily because substance concentrations are higher in sediments (Welsh and Denny 1980, Willford et al.1987). Rhizomes, roots, and root hairs provide a large surface area for uptake, and the substances remain in contact with macrophytes for extended periods of time. Because macrophytes often accumulate large amounts of toxic materials and are able to survive, investigators have proposed that they may be useful as indicator species for certain pollutants and be useful in remediation (Aulio 1980, Franzin and McFarlane 1980)

Lake Calumet and the surrounding area have a long history of pollution, and samples from the area have notably elevated levels of various toxic substances (USEPA 1985, USACE 1982, 1985). Chemical analyses revealed high levels of lead, zinc, and chromium in Lake Calumet sediments

(see Chapter 3). Although no sediment samples from vegetated areas have been analyzed, vegetated sediments are probably contaminated as well. Consequently, resident macrophyte populations will likely contain toxic substances.

Recent studies suggest that macrophytes provide a pathway for movement of nutrients and toxic substances from deeper sediments to the water column and top sediments (Howard-Williams and Lenton 1975, Welsh and Denny 1976, McIntosh *et al.* 1978, Gabrielson *et al.* 1984, Campbell *et al.* 1985, Smith and Adams 1986). This mobilization occurs when substances are accumulated by roots and rhizomes and acropetally translocated to stems and leaves. During plant senescence, substances may be leached into the water column in a form available for uptake by planktonic organisms or may become available to benthic organisms in decomposing particulate matter. Exposure to and biomagnification of substances once buried then becomes possible. It is this process of uptake, translocation, and leaching that may increase exposure of aquatic organisms to toxic substances and, therefore, may limit aquatic life inhabiting the lake and surrounding wetlands, and other life dependant on these water resources (e.g., waterfowl).

Determination of existing toxic substance levels in macrophytes and other ecosystem components is an important first step in assessing a pollution problem, but other steps must be taken if the impacts of toxic substances are to be fully assessed. The larger questions need to be addressed as well: (1) Are pollutants accumulated by macrophytes directly toxic to aquatic life (i.e., pose an environmental hazard)? (2) Does uptake increase toxicity by providing an alternate route of exposure, by transforming contaminants into more toxic compounds, or by enhancing bioavailability (Lee *et al.* 1987)? Rapid screening tests using bacteria (Microtox™ ) and algae (*Selenastrum capricornutum* ) provide a reliable mechanism of assessing the toxicity of accumulated materials to aquatic biota under prevailing conditions (see Chapter 8).

### 7.2 Purpose

The purpose of this portion of the Lake Calumet study is to provide preliminary information on the accumulation of selected toxic substances by aquatic macrophytes in the Lake Calumet area. The questions to be addressed follow:

1. What concentrations of heavy metals, PCBs, and organic pesticides are present in aquatic macrophytes inhabiting the lake and adjacent wetland areas?
2. What concentrations of these toxic substances are present in the sediments inhabited by the macrophytes?
3. How do the concentrations in sediments and macrophyte tissues compare to each other and to

other available data?

These data will improve our understanding of the pollution problem in the Lake Calumet area, show how resident aquatic macrophytes accumulate and cycle pollutants in the system, and aid in evaluating the potential for remediation. Other agencies interested in the environmental effects of pollutants in Lake Calumet will also find these data valuable. The U.S. Army Corps of Engineers is preparing a Special Area Management Plan for the Lake Calumet area (Slowinski, 1987) that will suggest development alternatives and will include a habitat evaluation of the wetland areas (Cowardin *et al.* 1979). Since the quality of aquatic habitat is often governed by the presence and characterisitcs of macrophytes, these data will provide important information for evaluating habitat quality.

### 7.3 Sample Collection

Lake Calumet sampling stations contained no macrophytic vegetation in October 1986 or in April 1987. On 1 July 1987, seventeen macrophyte specimens were collected from eight wetland sites in the vicinity of Lake Calumet. Macrophytes collected include Typha sp., Zannichellia palustris, Potamogeton sp., Potamogeton crispus, Potamogeton pectinatus, Phragmites communis, Ceratophyllum demersum, Eleocharis sp., Juncus sp., and Lythrum salicaria (Table 7.1). Whole plants were air dried and subsamples of each plant part (root, shoots/stems, leaves, and reproductive structures) were fixed in gluteraldehyde and frozen in preparation for analyses using EDX equipment at the Illinois Natural History Survey. In addition, whole plants from each sample were frozen and delivered to the Illinois Natural History Survey Chemical Laboratory for inductively coupled plasma analyses.

Sediment samples from one wetland area, Deadstick Pond, were collected prior to the 1 July macrophyte sampling (Figure 2.1). Subsequently, sediment samples have been collected from the other wetland areas. A full report will be prepared after sediment and macrophyte samples have been analyzed.

The above collections and analyses are designed to provide preliminary information necessary to the design of a more complete study. When the chemical analyses are complete, a study design will be developed that will compare Calumet area macrophytes with those from other sites, both polluted and unpolluted, and provide specific information on the toxicity of the substances accumulated and recycled by the macrophytes.

## 7.4 Determination of Metals by X-ray Energy Dispersive Microanalysis (EDX)

EDX is cabable of identifying metals with the atomic number of sodium (11) or greater. Sites of accumulation in plants may be recordable with the combined techniques of Scanning Electron Microscopy (SEM) and EDX. Sample sizes from 1 to 5mm square will be examined with SEM and EDX. Preparation may be from air-dried plant parts or plant parts fixed with gluteraldehyde and freeze-dried. The dried materials are then coated with carbon in a vacuum evaporator. Recording of data is by photographing the spectrum display or hardcopy printout of the spectrum. When appropriate, localization and distribution of minerals may be obtained by photographing the image on the display. Dot maps are espcially useful for recording location and distribution of elements.

Table 7.1. Macrophyte samples collected in wetlands near Calumet Lake on 1 July 1987. The first letter of each sample label indicates the collection site as listed at the bottom of the table and Figure 2.1.

| Sample Label | Plant Species | Plant parts |
|---|---|---|
| A1 | Typha sp. | whole plant |
| A2 | Zannichellia plaustris | whole plant |
| A3* | Potamogeton sp. | whole plant |
| B1 | Phragmites communis | whole plant |
| C1 | Phragmites communis | whole plant |
| D1 | Zannichellia palustris | whole plant |
| E1* | Potamogeton sp. | whole plant |
| F1 | Potamogeton crispus | whole plant |
| F2 | Ceratophyllum demersum | whole plant |
| F3 | Potamogeton pectinatus | whole plant |
| F4* | Potamogeton sp. | whole plant |
| G1 | Phragmites communis | whole plant |
| H1 | Typha sp. | whole plant |
| H2 | Phragmites communis | whole plant |
| H3 | Eleocharis sp. | whole plant |
| H4 | Juncus sp. | whole plant |
| H5 | Lythrum salicaria | stems, no roots |

Collection sites -
Site A - Deadstick Pond
Site B - E. 122nd Street, W. of RR tracks, S. of 122nd
Site C - E. 122nd Street, W. of RR tracks, N. of 122nd
Site D - E. 122nd Street, E. of RR tracks, N. of 122nd
Site E - E. 122nd Street, E. of RR tracks, S. of 122nd
Site F - Fishing pond, north end
Site G - Top of wetlands (Phgragmites bed), ditch near RR tracks running thru wetlands
Site H - Incinerator Site/ NW Railroad, bedrock ditch

* Narrow-leaved pondweed believed to be Potamogeton foliosus.

# Chapter 8
# Ecological Effects: Single Species Toxicity Testing

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## 8.1 Introduction

Contaminants in Lake Calumet could be released into the water column by several routes. Microbial action in the sediment may reduce persisitent molecules to the more water-soluble metabolites. Organisms living at the sediment-water interface may resuspend and cycle contaminated sediments. Phytoplankton and other plants may accumulate contaminants from the sediments or water column, releasing them when plant cells rupture or die.

Due to the poor drainage and shallow nature of Lake Calumet, physical processes that disturb the sediment will probably resuspend settled contaminants. Disruptive processes in an aquatic environment include violent water movement caused by passing boats, storms, or strong winds. To simulate these processes, the elutriate test, a water leach using one part sediment to four parts leaching water, was used. This technique, developed as an accurate method to predict which components of the sediment will be released to the water column, has been used since 1973 and has been evaluated under an extremely wide range of conditions in marine, estuarine, and freshwater systems (Engler 1980). Bulk analysis (solvent extraction which strips contaminants from the sediment) cannot be used to predict the chemical concentrations that will be found in the water column and available to the organisms there. For the same reason, the bulk sediment analysis is more predictive for the exposure of organisms at the benthic (sediment-water) interface (Hoke and Prater 1980). Bioassays using the filtered liquid-phase from the elutriation test have been shown to project the earliest measure of the toxicity of the sediment (Engler 1980). The liquid-phase elutriates from 32 sediment samples in Lake Calumet were used to determine biological response to contamination.

The sediments in Lake Calumet have been altered by disturbance and contamination; however, chemical characterization of the sediment does not, in itself, prove that an ecological threat exists. Selective chemical analyses also have the potential to "overlook" minute concentrations of contaminants or those that are not suspected to occur (Ross 1987). For example, chlorinated dibenzofurans have been found associated with Aroclor PCB mixtures in amounts below standard detection limits, but they are known to be orders of magnitude more toxic than the Aroclors (McKinney 1976, Eisler 1986). Laboratory experiments that exposed organisms to elutriates from

the whole sediment can aid in assessing the hazard associated with composite contamination.

The many organisms that make up the biotic component in the aquatic ecosystem vary in basic structure, organization, and metabolism. The effect of a contaminant or group of contaminants cannot be predicted for the entire ecosystem if only one organism is used in the biological assay. To gather the most information on ecosystem toxicity, the susceptibility of as many component organisms as is economically and reasonably possible should be determined. Any comprehensive hazard assessment will require acute toxicity data from a variety of species that occupy several trophic levels (LeBlanc 1984). While the short-term responses such as increased mortality or reduced function are the most severe endpoints of environmental contamination, more subtle long-term effects such as carcinogenisis, mutagenesis, and the disruption of normal developmental activities may present a major risk to the organisms associated with the contaminated environment and to their progeny. Assays that help assess the long-term risks are also important in ecotoxicological assessment (Samoiloff *et al.* 1980).

The assay organisms chosen to perform an ecotoxicological assessment of Lake Calumet sediments include the luminescent marine bacterium *Photobacterium phosphoreum* (Microtox™), the freshwater green alga *Selenastrum capricornutum*, and the free-living nematode worm *Panagrellus redivivus* .

The Microtox™ assay measures luminescence of P. phosphoreum. Inhibition of this luminescence is considered a toxic response. Results of Microtox™ assays has been compared to those of standard assays using rainbow trout (*Salmo gairdneri* ), fathead minnow (*Pimephales promelas* ), bluegill (*Lepomis macrochirus* ), sheepshead minnow (*Cyprinidon variegatus* ) and cladoceran (*Daphnia magna* ) for a variety of pure compounds and complex environmental samples. In most cases, Microtox™ results showed equal sensitivity to the compounds tested (Bulich *et al.* 1981, Curtis *et al.* 1982, Quereshi *et al.* 1982). Bulich *et al.* (1981) concluded that the Microtox™ $EC_{50}$ data are comparable with 24- to 96-hour fish data. *D. magna, S. gairdneri*, and *P. promelas* were reported by DeZwart and Sloof (1983) to be 2.54, 2.04, and 1.99 times more sensitive than *P. phosphoreum*, respectively.

The *S. capricornutum* assay measures the photosynthesis of an algal culture. Inhibition of photosynthesis is considered a toxic response. The sensitivity of *S. capricornutum* was compared with the cladoceran *D. magna, L. macrochirus*, the saltwater alga *Skeletonema costatum*, the marine zooplankton *Mysidopsis bahia*, and *C. variegatus* by LeBlanc (1984) for 19 non-pesticide organic compounds. Generally, *S. capricornutum* was equally or more sensitive than *D. magna, L. macrochirus* , and *C. variegatus* . *S. capricornutum* was found by DeZwart and Sloof (1983)

to be, on average, 1.09 times more sensitive than *P. phosphoreum* (Microtox™) in a comparison using 15 compounds.

These findings indicate that the Microtox™ and *S. capricornutum* tests are comparable to the more conventional freshwater assays and could be considered superior if the ease, speed, and cost-effectiveness of the protocols were also compared.

The *Panagrellus redivivus* developmental assay is capable of detecting lethal, semilethal, inhibitory, mutagenic, or stimulatory environmental conditions (Samoiloff *et al.* 1983). Nematodes, in general, are unlikely candidates for strictly acute test protocols because they are one of the hardiest groups of organisms in the ecosystem. Laboratory-cultured organisms are, however, more sensitve to changing environmental conditions (Samoiloff and Bogaert 1984). The *P. redivivus* protocol includes a measurement of survival but also continues to follow the developmental progress of a test population of worms. The nematode must complete three molts from the smallest juvenile stage to the adult stage. At each molt, the worm entrains itself to the environmental conditions, molting only if conditions are favorable for continued growth. Under environmental stress, a population of *P. redivivus* contains a higher proportion of juvenile stages than is found in an unstressed environment (Samoiloff and Bogaert 1984). Using this assay, the effects of long-term exposure to an environmental sample can be measured (Samoiloff *et al.* 1980). Acute mortality, acute sub-lethal effects, chronic mortality, chronic sub-lethal effects, and phenotoxic effects can be differentiated or combined into one composite parameter called fitness that represents the overall health of the tested population. Like the Microtox™ and algal tests, this protocol is rapid, simple, and cost-effective.

Each bioassay was performed on elutriates from samples of 32 sites in Lake Calumet. Results were compared statistically between the assays, with the bulk sediment concentrations, and with the elutriate conditions as defined by Champoux and co-workers (1986).

## 8.2 Materials and Methods

### 8.2.1. Elutriation (U.S. Army Corps of Engineers 1976)

One part mixed sediment was added to 4 parts distilled water in an acid-washed glass container. To suspend the sediment in the water, air was bubbled through the system for two hours. After a settling period of approximately 4 hours, the elutriate was filtered through a glass fiber filter (nominal porosity: 1.2 μm) and then diluted appropriately for the bioassays.

8.2.2. *Photobacterium phosphoreum* (Microtox™) bioassay (Bulich 1977)

An aliquot of the 100% concentration of elutriate from each Lake Calumet station was used with the Beckman Microtox Analyzer and the 2:1 dilution series protocol as described by Bulich (1982) and Beckman, Inc. (1982). Each test was performed for two replicates, each with 4 dilutions (45, 22.5, 11.25, 5.63%). The luminescence loss was calculated for a 15-minute, 15°C test and a linear regression was performed. An $EC_{50}$ value (the concentration at which 50% luminescent inhibition was observed) was obtained from the regression equation.

8.2.3. *Selenastrum capricornutum* bioassay (Ross *et al.*, in press)

This bioassay involves the calculation of a photosynthesis inhibition curve for each elutriate. An aliquot of elutriate, six dilutions of elutriate (5, 10, 20, 40, 60, 80 percent), and a control are used for each test; results are expressed as percentages of control photosynthesis. The algal culture is incubated at 25°C for at least six days before the test. In this study, a 20% dilution of the algal culturing medium was used as a diluent for the elutriate. Four replicates of 100 mL of each elutriate dilution were inoculated with 2 mL of viable *S. capricornutum*. The algae were allowed to acclimate to the elutriate concentrations for 20 hours at 25°C under a constant light source. After the acclimation period, 5 μCi of sodium bicarbonate $^{14}C$ were introduced to each flask. After 4 hours of exposure to the radioisotope, a 4 mL aliquot of each sample was acidified with 1 drop concentrated HC1 and all unincorporated $^{14}C$ was bubbled off. The radioactivity of the samples was measured using a Packard Tri-Carb 2000CA Liquid Scintillation Analyzer. The percent photosynthetic inhibition was calculated by dividing each sample radioactivity (dpm) by the mean of the control sample's radioactivity (dpm) and multiplying by 100. A linear regression comparing elutriate concentration and percent photosynthetic inhibition was performed for each station. The $EC_{50}$ value was taken to be the elutriate concentration at which 50 percent photosynthetic inhibition occurred, as described by the regression equation.

8.2.4. *Panagrellus redivivus* bioassay (Samoiloff *et al.* 1980)

The *Panagrellus redivivus* bioassay was performed for each sediment sample. This rapid, simple, long-term toxicity assay is described in detail by Samoiloff *et al.*, (1980). Briefly, the assay utilizes the four post-embryonic stages of the nematode, each characterized by a specific size range. Animals of the smallest post-embryonic stage are introduced to the contaminant. Growth from one stage to the next requires normal physiological and informational processes; growth is inhibited when these processes are blocked or inhibited. The stage distribution of test and control animals represents the primary set of data from which toxicity is determined. The stage distribution can be analyzed to provide evidence for lethality, semilethality and inhibition. A composite parameter,

"fitness" can be calculated for all tests. Low fitness denotes strong toxic response. Lake Calumet elutriates were tested at 50%.

8.2.5 Data analysis

The results of the Microtox™ and *S. capricornutum* assays for each station were reduced by simple linear regression (Figure 8.1) to slope, EC50 (the concentration of elutriate at which the effective response of the organism was reduced by 50%) and percent response (the effect of full strength elutriate relative to the control response). Because the percent response for both organisms is based on the same unit scale, only these results are reported for simplified comparison.

The results of the *P. redivivus* test are reduced to percent survival and fitness. Because these caluclutations are inherently based on percentage, the percent response (percent mortality or fitness reduction) can be calculated by subtracting the percent survival or fitness value from 100.

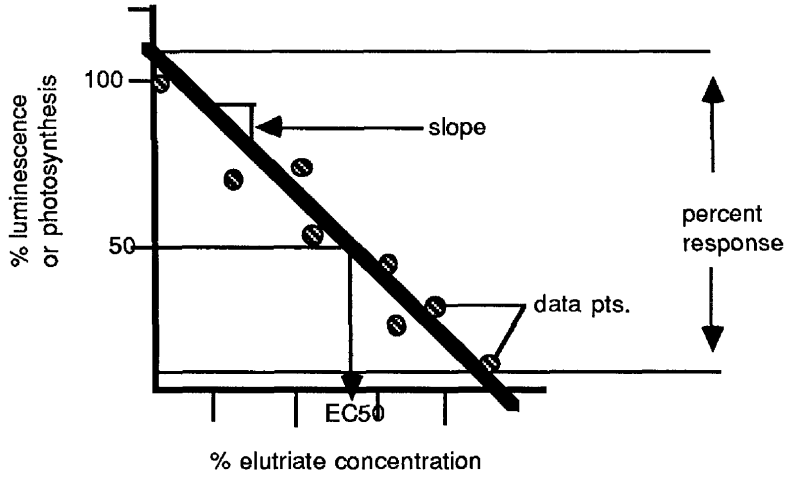


Figure 8.1. Data reduction for Microtox™ and *S. capricornutum* assays.

Each percent response value for each station and assay can then be separated into classes of relative toxicity (Table 8.1). The assignment of a toxicological class allows the data to be reduced to five classes and simplifies a qualitative hazard assessement.

Table 8.1. Classification of percent response to relative toxicity values (after Williams *et al.* 1986).

| Percent response | Toxicological class | Numerical assignment | Max. composite toxicity index[a] |
|---|---|---|---|
| 0 - 5 | No response | 0 | 0 |
| 6 - 10 | Slightly toxic | 1 | 3 |
| 11 - 40 | Moderately toxic | 2 | 6 |
| 41- 60 | Highly toxic | 3 | 9 |
| 61 - 100 | Extremely toxic | 4 | 12 |

[a] Maximum composite toxicity index is the highest score possible in the toxicological class when the three assay responses are summed.

## 8.3 Results

### 8.3.1 Microtox™ bioassays

Luminescent inhibition (Table 8.2) ranged from 1.4 to 162.23% (the ocurrence of values greater than 100% is a factor of the extrapolation of the linear regression between data points). The majority (18/32) of Lake Calumet stations were in the "moderately toxic" category; 2 stations were classified as "highly toxic" and 7 as "extremely toxic."

### 8.3.2 *Selenastrum capricornutum* (green algae) bioassays

The inhibition of photosynthesis of *S. capricornutum* cultures exposed to elutriates of Lake Calumet sediments (Table 8.3) ranged from 45.72 to 117.38%. Most stations (30/32) elicited an "extremely toxic" response; the remaining two stations were categorized as "highly toxic."

### 8.3.3. *Panagrellus redivivus* (nematode) bioassays

The results of the *P. redivivus* test (Table 8.4) for Lake Calumet sediment elutriates were scored as percent mortality based only on survival data. Collection of length data for stations 1-20 are in progress as are full tests for stations 12 - 20. The mortality values for 50% elutriate tested ranged from 0 to 78.41%. Classification of the response varied from "no response" (2/21 stations), "moderately toxic" (11/21 stations), "highly toxic" (5/21 stations), and "extremely toxic" (3/21 stations). The high and extreme toxicity of eight stations is somewhat surprising for mortality data because the nematode is generally hardy. These stations (I,J,L,1,2,5,6,and 7) should be examined further.

Table 8.2. Values of Percent response and toxicological classification for the Microtox™ bioassay from 32 sampling stations in Lake Calumet.

| Station | Percent response | Toxicological class |
|---|---|---|
| A | 67.08 | 4 |
| B | 28.37 | 2 |
| C | 33.59 | 2 |
| D | 69.03 | 4 |
| E | 83.57 | 4 |
| F | 39.48 | 2 |
| G | 19.62 | 2 |
| H | 34.02 | 2 |
| I | 122.23 | 4 |
| J | 52.61 | 3 |
| K | 121.03 | 4 |
| L | 162.63 | 4 |
| 1* | 36.34 | 2 |
| 2 | 40.48 | 2 |
| 3 | 60.99 | 4 |
| 4 | 62.87 | 3 |
| 5 | 33.65 | 2 |
| 6 | 36.12 | 2 |
| 7 | 26.62 | 2 |
| 8 | 36.53 | 2 |
| 9 | 37.46 | 2 |
| 10 | 9.21 | 1 |
| 11 | 6.34 | 1 |
| 12 | 16.49 | 2 |
| 13 | 14.85 | 2 |
| 14 | 1.40 | 0 |
| 15 | 18.67 | 2 |
| 16 | 22.74 | 2 |
| 17 | 8.67 | 1 |
| 18 | 11.11 | 2 |
| 19 | 2.01 | 0 |
| 20 | 28.57 | 2 |

*Numbered stations are equivalent to 'LCAL' stations ; LCAL 1=1

Table 8.3. Values of percent response and toxicological classification for the *S. capricornutum* bioassay from 32 sampling stations in Lake Calumet.

| Station | Percent response | Toxicological Class |
|---|---|---|
| A | 98.73 | 4 |
| B | 117.38 | 4 |
| C | 109.23 | 4 |
| D | 71.18 | 4 |
| E | 113.07 | 4 |
| F | 99.10 | 4 |
| G | 88.73 | 4 |
| H | 60.46 | 3 |
| I | 83.05 | 4 |
| J | 45.72 | 3 |
| K | 91.29 | 4 |
| L | 109.48 | 4 |
| 1* | 84.75 | 4 |
| 2 | 82.38 | 4 |
| 3 | 87.89 | 4 |
| 4 | 90.61 | 4 |
| 5 | 83.90 | 4 |
| 6 | 105.92 | 4 |
| 7 | 101.26 | 4 |
| 8 | 92.47 | 4 |
| 9 | 82.21 | 4 |
| 10 | 71.29 | 4 |
| 11 | 82.21 | 4 |
| 12 | 87.46 | 4 |
| 13 | 89.68 | 4 |
| 14 | 80.99 | 4 |
| 15 | 100.83 | 4 |
| 16 | 73.27 | 4 |
| 17 | 85.47 | 4 |
| 18 | 79.13 | 4 |
| 19 | 73.33 | 4 |
| 20 | 88.82 | 4 |

*Numbered stations are equivalent to 'LCAL' stations ; LCAL 1=1

Table 8.4. Values of percent response and toxicological classification for the *P. redivivus* bioassay from 32 sampling stations in Lake Calumet.

| Station | Percent response | Toxicological class |
|---|---|---|
| A | 28.00 | 2 |
| B | 5.00 | 0 |
| C | 24.00 | 2 |
| D | 0.00 | 0 |
| E | 31.00 | 2 |
| F | 18.00 | 2 |
| G | 13.00 | 2 |
| H | 25.00 | 2 |
| I | 57.00 | 3 |
| J | 59.00 | 3 |
| K | -- | -- |
| L | 51.00 | 3 |
| 1* | 78.41 | 4 |
| 2 | 42.86 | 3 |
| 3 | 27.09 | 2 |
| 4 | 15.27 | 2 |
| 5 | 78.33 | 4 |
| 6 | 62.07 | 4 |
| 7 | 51.72 | 3 |
| 8 | 39.66 | 2 |
| 9 | 37.93 | 2 |
| 10 | -- | -- |
| 11 | 13.10 | 2 |

*Numbered stations are equivalent to 'LCAL' stations ; LCAL 1=1

8.3.4 Data summary and assay comparisons

Table 8.5 summarizes the toxicological classifications for the three bioassays. The sum of the three assay classes for each sediment is termed the "composite toxicity index."

Table 8.5. Summary of data for Microtox™, *S. capricornutum*, and *P. redivivus* bioassays.

| Station | Composite Toxicity Index | Σ percent response |
|---|---|---|
| A | 10 | 193.81 |
| B | 6 | 150.75 |
| C | 8 | 166.82 |
| D | 8 | 140.21 |
| E | 10 | 232.64 |
| F | 8 | 156.58 |
| G | 8 | 121.35 |
| H | 7 | 119.48 |
| I | 11 | 262.28 |
| J | 9 | 157.33 |
| K | * | 212.32** |
| L | 11 | 322.71 |
| 1*** | 9 | 199.50 |
| 2 | 9 | 165.72 |
| 3 | 10 | 185.97 |
| 4 | 9 | 168.75 |
| 5 | 10 | 195.88 |
| 6 | 10 | 204.11 |
| 7 | 9 | 179.60 |
| 8 | 8 | 168.66 |
| 9 | 8 | 157.60 |
| 10 | * | * |
| 11 | 7 | 101.65 |

*cannot be calculated without *P. redivivus* assay data
**based only on Microtox™ and *S. capricornutum* assays.
** *Numbered stations are equivalent to 'LCAL' stations ; LCAL 1=1

Comparisons of results among Microtox™/algal, Microtox™/nematode, and algal/nematode assays failed to generate a correlation between organism responses. In general, the algal bioassay was most sensitive, followed by the Microtox™ assay. The nematode assay (due probably to the less senstive scoring of mortality) was generally the least sensitive assay. This variability of response is not surprising when the many biological differences between the organisms are noted, further supporting the need to test more than one species.

8.3.5 Bioassay response relative to the distribution of sediments

Figures 8.2 through 8.5 provide a schematic representation of toxicity in Lake Calumet sediments. The majority of "highly toxic" stations (Figure 8.5) appear to be distributed in the slips or near the shore. Most of the land separating the slips has been constructed with slag and construction rubble, and toxic compounds associated with the man-made land as well as with the run-off from industrial property that might well influence sediment toxicity.

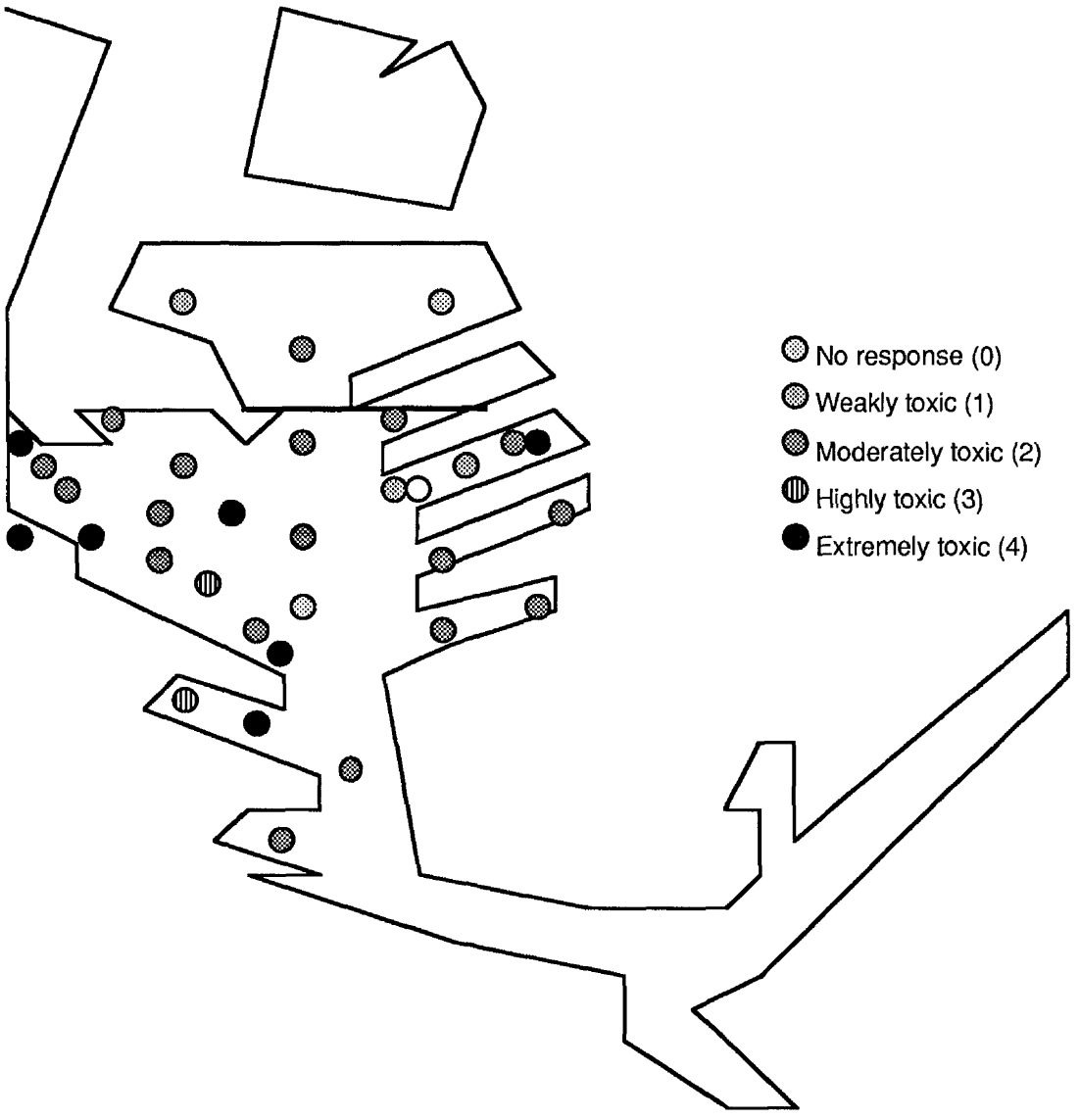


Figure 8.2. Classification of percent response Microtox™ values for Lake Calumet sediments. Open station circles indicate that the test was not performed for the station.

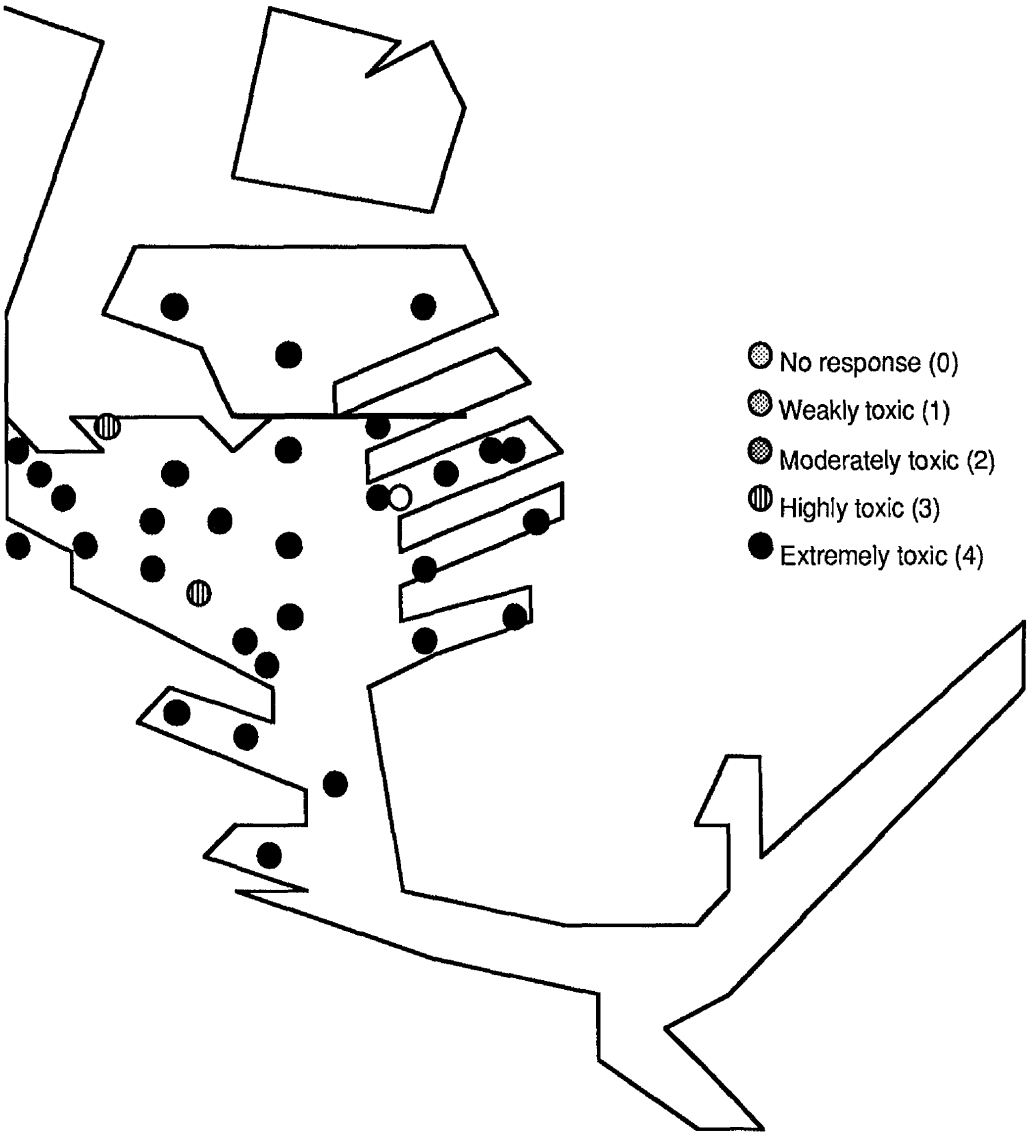


Figure 8.3. Classification of percent response values from algal assays for Lake Calumet sediments. Open station circles indicate that the test was not performed for the station.

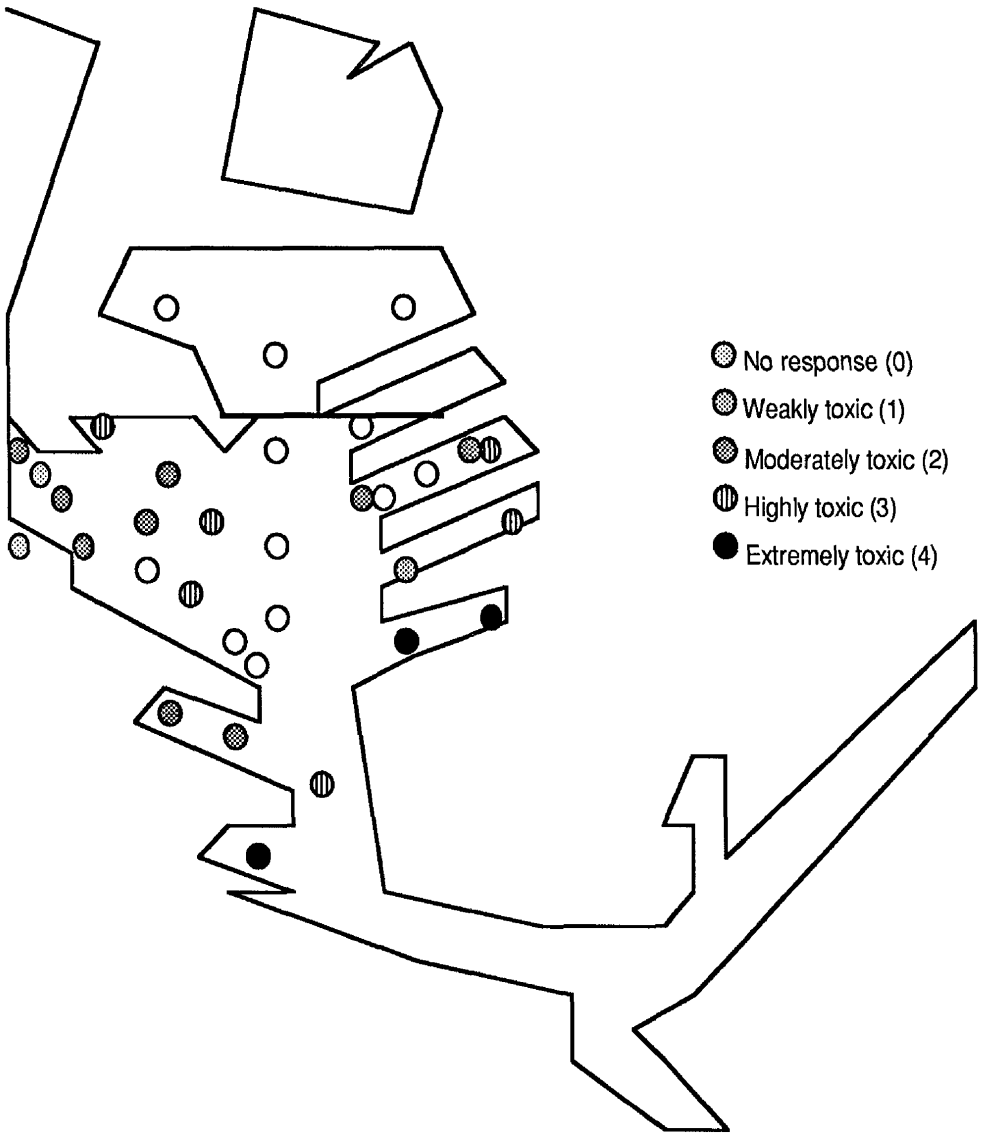


Figure 8.4. Classification of percent response values from nematode assays for Lake Calumet sediments. Open station circles indicate that the test was not performed for the station.

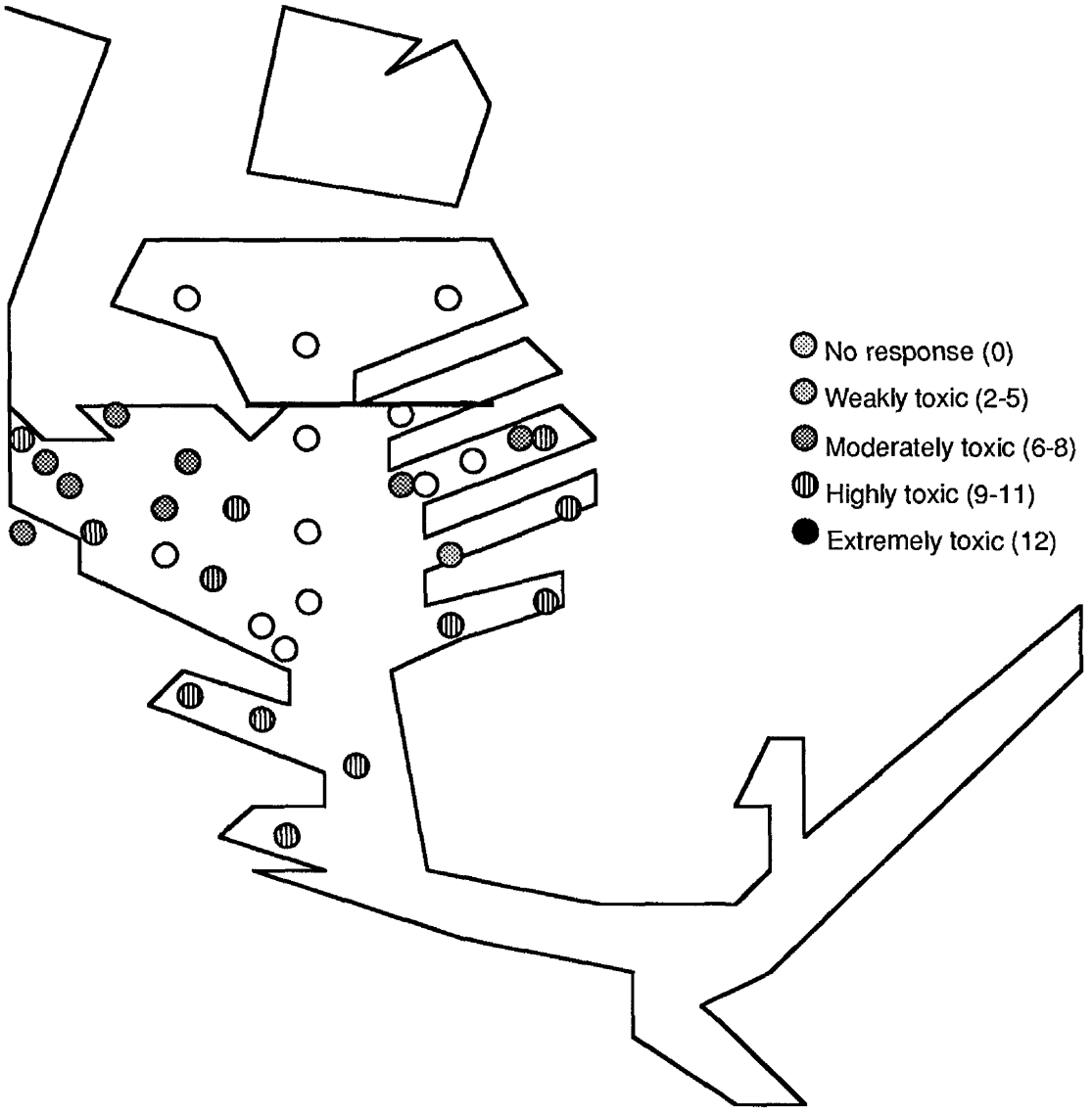


Figure 8.5. Composite toxicity for Lake Calumet sediments. Open station circles indicate that all the tests were not performed for the station.

8.3.6 Bioassay response in relations to the chemical composition of sediments

Concentrations of several metals, total polycyclic aromatic hydrocarbons, and total organic carbon for Lake Calumet sediments from Stations A through M are given in Chapter 3. Determining the relationship between the chemical components of the sediments and the bioassay response helps predict which contaminants, if any, are the source of toxicity to the assay organisms. Mixtures, such as Lake Calumet sediment, are extremely complex and a determination of all the compounds likely to affect the outcome of the bioassay is probably impossible or at least, very expensive. In comparing, the concentrations of only five metals (Cu, Pb, Zn, As, and Cr) and one class of organic compounds (PAHs) in Lake Calumet sediments, strong correlations cannot therefore be expected.

When two variables, such as metal concentration and bioassay response, are compared by simple linear regression, Pearson's product-moment correlation coefficient (**r**) is commonly calculated to find how much variability is explained by the regresssion equation. Pearson's **r** represents the square root of the proportion of the total variance that is attributable to the regression. The sum of the five metals ($\Sigma$ metals), total PAHs, and the sum of both $\Sigma$ metals and total PAHs ($\Sigma$ chemistry) were compared to the percent response values form Microtox™, *S. capricornutum*, and *P. redivivus* assays and to the sum of the percent response values from these assays ($\Sigma$ assays). The values of Pearson's **r** can be used to examine trends, if not correlations, between these factors (Table 8.6). These **r** values indicate that the regression equations are influenced by experimental variability and other factors, some of which may be additional sediment contaminants. Sediment heterogeneity and differing bioassay sensitivity can affect the variability in these screening tests (Williams *et. al.* 1986). Further chemical characterization and comparison with assay results should improve the correlation.

Table 8.6 . Pearson's **r** (correlation coefficient) values for comparisons of bioassay and chemical parameters.

| | Microtox™ | S. capricornutum | P. redivivus | $\Sigma$ assays |
|---|---|---|---|---|
| $\Sigma$ metals | -0.39 | +0.40 | -0.68 | -0.28 |
| Total PAHs | +0.33 | +0.44 | -0.33 | +0.25 |
| $\Sigma$ chemistry | +0.29 | +0.46 | -0.37 | +0.22 |

*8.3.6.1. Elutriate chemistry*

Individual chemical determinations for the elutriates from Lake Calumet sediments were not performed in this project. Champoux *et al.*. (1986) reported values of the net release of

compounds from Lake Saint Louis sediments in Quebec. Using the ratio of elutriate concentration:bulk sediment concentration for several chemicals, we computed crude estimates of the release of similar chemicals in Lake Calumet. These predications can then be compared to water quality standards (Table 8.7). This comparison may help to better assess the factors contributing to toxicity as reported in this chapter.

Estimated elutriate concentrations of select metals show only lead (Pb) concentrations above recommended levels. The individual characteristics of the aquatic system constitute the major influence on the release of metals and organics from the sediments. Salinity, pH, redox conditions, microbial activities, disturbance events (i.e. dredging, navigation, storms) and lake morphology are

Table 8.7. Ratio of elutriate:sediment chemistry (from Champoux *et al.* 1986) applied to Lake Calumet sediment chemistry (Chapter 3) and compared to Illinois water quality standards for secondary contact (IEPA 1984).

| Parameter | Elutriate:Sediment ratio | Lake Calumet range (ppb) | Illinois standard(ppb) | Lake Calumet "violations" |
|---|---|---|---|---|
| Cd | 0.001 | 1.5 - 3.6 | 150 | 0 |
| Cu | 0.001 | 13 - 115 | 1000 | 0 |
| Ni | 0.001 | 12 -33 | 1000 | 0 |
| Pb | 0.001 | 70 - 316 | 100 | 11 |
| Zn | 0.001 | 110 - 599 | 1000 | 0 |
| As | 0.0005 | 8 - 25 | 1000 | 0 |

several of the parameters that can influence release of sediment contaminants (Forstner and Prosi 1979). Contaminant partitioning is a function of sediment characteristics, including grain size and organic content (Chapman 1986). Lake Saint Louis in Quebec may differ substantially in water chemistry from Lake Calumet, and the estimates in Table 8.7 may be inaccurate. The increased biological response to the PAHs in the sediment may be due to the release from the sediments of lower molecular weight PAHs (2 or 3 rings) , which are also implicated in higher toxicity (Eisler 1987). These lighter molecules are more water soluble and more mobile in the aquatic environment; therefore, they are more available to the organisms in the water column. It is not clear, however, whether environmental release of these smaller PAHs can reach the magnitude associated with laboratory toxicity.

## 8.4 Conclusions

Most sediments from Lake Calumet elicit a toxicological response from three single-species biological assays. Pinpointing the source of this toxicity is difficult in a complex media like sediment and in a disturbed environment like Lake Calumet. Although additional chemical characterization will allow further comparisons between the components of the sediment and the toxic response, the exact source of the toxicity may never be known. The three assays are, more realistically, screening tests for areas of particular concern. Further use of these tests for the toxicological characterization of Lake Calumet sediments and the surrounding wetlands should strengthen the hazard assessment of the lake environment.

# Chapter 9
# Ecological Effects: Microbial Community Toxicity Testing

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## 9.1 Introduction

The microbial community that colonizes artificial substrates includes a variety of organisms, ranging from bacteria to small metazoans such as insect larvae. This community is a composite of the communities inhabiting natural substrates (Henebry and Cairns 1984). Because protozoa (complex, single-celled organisms) are ubiquitous in the aquatic environment and cosmopolitan in their distribution, a mature community of about 30-40 species representative of those in an entire ecosystem colonize artificial substrates within a period of 2-3 weeks (Cairns *et al.* 1979).

Toxicity tests measuring the effect of single chemicals on single biological species (e.g., studies of the effect of copper on fathead minnows) have been the primary source of data for evaluating the environmental hazard of chemicals (National Research Council 1981); however, the goal of most hazard evaluation is to assess or predict the degree of risk of toxic substances to organisms in an ecosystem. As appreciation of the complexity of ecosystems has increased, so has concern over bias in hazard assessments based solely on the response of isolated single species, which often are not found in the ecosystem being studied (Cairns 1984, Odum 1984).

The Protozoa include representatives of virtually every functional group--primary producers, grazers, filter feeders, and predators (Pratt and Cairns 1985). The responses of this diverse group of microorganisms may be similar to the responses of the broader community of organisms in a system such as Lake Calumet (e.g., algae, shellfish, and fish). The use of these communities is scientifically valid because protozoa represent important components of aquatic food chains in both freshwater and marine ecosystems (Barsdate *et al.* 1974, Goldman 1983). Most of the photosynthesis and respiration in many aquatic ecosystems is microbial (Pritchard and Bourquin 1984). Photosynthesis and respiration are excellent measures of system behavioir and are consistent, sensitive to man-made perturbations, and easily compared in both laboratory and field situations (Beyers 1964, Cooke 1974).

The objectives of this study were to evaluate the responses of microbial communities, particularly protozoans, to elutriates of selected Lake Calumet sediments.

## 9.2 Materials and Methods

### 9.2.1 Test communities

Protozoan communities were collected on identical polyurethane foam (PF) block substrates (7.5 x 6.5 x 5 cm) at an assumed "clean" site, a 0.08-ha artificial pond (Illinois Natural History Survey [INHS] Pond 12) that had no history of toxic contamination. After mature communities developed (2-4 weeks, Cairns *et al.* 1979) PF blocks were transferred to the laboratory and acclimated to a 16-hour light (≈1500 lux), 8-hour dark regime at 23°C for 48-96 hours.

### 9.2.2 Species reduction bioassays

For each test evaluating changes in numbers of species, three PF block substrates were exposed to a concentration of elutriate and three substrates (controls) to filtered pond water in separate 1000-mL acid washed beakers. After 48 hours and 7 days, PF blocks were removed from beakers, and each substrate was sampled by squeezing it over a clean collecting vessel to remove 135±10 mL water and microorganisms. The contents were allowed to settle, and the number of colonizing species were determined by repeated subsampling and microscopic observation. Taxa were identified, to species when possible, using standard taxonomic references (e.g., Kudo 1966). These methods and their repeatability are described in detail in Cairns *et al.* (1979). Protozoan species were classified into trophic (feeding) types (Pratt and Cairns 1985), similar to the classification scheme used for aquatic macroinvertebrates (Cummins 1973).

### 9.2.3 Process-level bioassays

Changes in photosynthetic and respiration rates were evaluated by transferring 12 or 18 replicate mature microbial PF block communities from INHS Pond 12 into 150-mL glass biochemical oxygen demand (B.O.D.) bottles. To measure photosynthesis, three bottles containing communities and sediment elutriate and three bottles containing communities in filtered pond water (controls) were exposed to ≈ 1500 lux light for 8 hours. Dissolved oxygen (D.O.) in the bottles was measured with a YSI model 51B dissolved oxygen meter (equipped with a probe and a power stirrer designed for use in the bottles) at the beginning and end of the experiments. Photosynthesis rates were evaluated as gain in D.O.; respiration rates were evaluated as 8-hour D.O. loss in dark bottles. Because of the amount of water associated with communities from the PF block substrates could be reduced to only ≈ 35 mL the highest concentration of elutriate tested in the bottles was ≈ 74%.

9.2.4 Data analysis

Differences in numbers of protozoan species and changes in microbial photosynthesis and respiration rates in control and treated systems were tested using parametric analysis of variance (AOV) (Sokal and Rohlf 1969). Differences were considered significant at $P \leq 0.05$. Data from all types of bioassays were reduced to percent response so they could be compared (the percent response for all bioassays is based on the same scale). Pearson correlation coefficients, simple regression and stepwise multiple regression techniques (Sokal and Rohlf 1969) were used to compare microbial community responses with concentrations of toxic materials in sediments; $P \leq 0.05$ was used as the significance level.

## 9.3 Results

9.3.1 Species reduction bioassays

Numbers of protozoan species (a meaurement of community structure) were significantly reduced in 100% elutriate from two of five stations in 48-h tests and from one of five stations in 7-d tests (Table 9.1). These time-consuming bioassays using community structure as the endpoint were so much less sensitive than the process-level tests that they were discontinued after testing sediments from the five stations listed in Table 9.1.

Table 9.1. Percentage difference between numbers of protozoan species in control and test systems (percent response) in static community bioassays with 100% concentrations of sediment elutriates.

| Station | 48-hour test | 7-day test |
|---|---|---|
| A | -1.7 | -23.1 |
| B | -32.2* | -18.2 |
| 1 | -29.6* | -31.0* |
| 2 | -20.5 | -13.5 |
| 4 | -8.8 | -12.5 |

* Significant difference in numbers of species ($a$= 0.05).

9.3.2 Process-level bioassays

Process-level (functional) end points (photosynthesis, respiration) were more sensitive than reduction in species diversity. Greater than 100% reductions in photosynthesis resulted when communities in elutriate exposed to light consumed rather than produced oxygen; control

communities exposed to light produced oxygen in all tests. Exposure to 74% elutriate from 15 of 22 stations resulted in significant reductions in community photosynthesis (Table 9.2); a lower concentration of elutriate (37%) produced significant reductions in community photosynthesis at 12 of the stations (Table 9.2), indicating that sediments at those stations were more toxic. Significant changes in community respiration were observed in tests with elutriate (74%) from 12 of the 22 stations (Table 9.2). Respiration was enhanced by exposure to elutriates from most stations but not from Stations 7, 8, 9, and 10.

Table 9.2. Percentage difference in oxygen liberation and oxygen consumption (percent response) between control and test systems during 8-hour incubations with sediment elutriates of 37 % and 74%.

| | Photosynthetic Response | | Respiratory Response | |
|---|---|---|---|---|
| Station | 37% | 74% | 37% | 74% |
| A | -49.3 | -86.4* | +2.4 | +64.9* |
| B | -63.3 | -83.4* | -27.0 | +43.7* |
| C | -153.4* | -209.3* | +8.0 | +55.3* |
| F | -24.6 | -148.8* | +8.0 | +63.8* |
| H | -57.7* | -157.3* | +36.1 | +40.8* |
| I | -97.4* | -66.7* | -8.0 | +62.3* |
| 1 | -72.5* | -161.8* | +47.7 | +67.5* |
| 2 | N.D. | -35.2 | N.D. | +45.0 |
| 4 | -21.1 | -40.9* | +2.6 | +20.9 |
| 5 | -4.6 | -23.9 | +9.6 | +31.1 |

(Table 9.1, continued)

| Station | Photosynthetic Response | | Respiratory Response | |
|---|---|---|---|---|
| | 37% | 74% | 37% | 74% |
| 7 | -58.9* | -48.6* | +12.0 | -32.7* |
| 8 | +25.0 | -13.3 | -5.8 | -41.3 |
| 9 | +8.2 | -2.8 | -9.4 | -39.6* |
| 10 | -31.6* | -41.9* | -10.7 | -3.6 |
| 11 | -64.8* | -70.5* | -21.6 | +5.3 |
| 12 | +20.5 | +2.5 | +71.7 | +25.3 |
| 13 | -70.9* | -93.9* | +69.8 | +84.7* |
| 15 | -105.3* | -65.7* | +18.1 | +8.5 |
| 16 | +0.3 | -10.9 | +26.8* | +26.2 |
| 17 | -53.1* | -60.7* | +32.6* | +33.3* |
| 18 | -33.5* | -73.8* | +15.7 | +5.2 |
| 20 | -41.1* | -32.7* | +40.0* | +98.3* |

* Significant difference in dissolved oxygen values between control and test systems ($a$ =0.05). Each value is the mean of three replicates.

9.3.3. Distribution of toxicity in Lake Calumet

Stations with the highest cumulative toxicity, calculated by adding together the significant responses in all four of the process-level bioassays regardless of sign (+ or -), were C>1>H>13>I>20>F (Fig. 9.1A, 9.1.B); all of these sediments produced cumulative community responses greater than 200%.

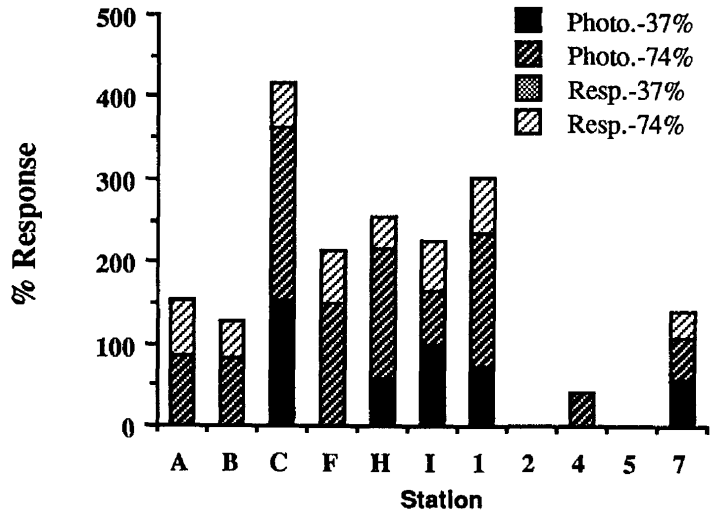


Figure 9.1.A. Cumulative (significant) percent response for the four microbial community functional bioassays (Stations A through 7).

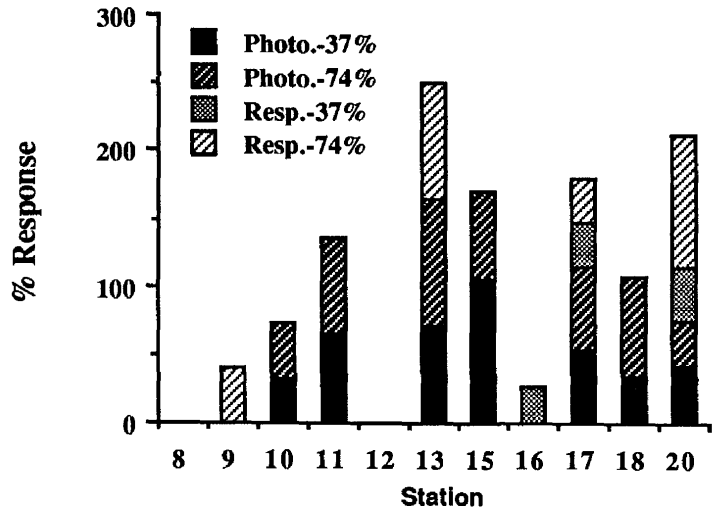


Figure 9.1B. Cumulative (significant) percent response for the four community functional bioassays (Stations 8 through 20).

Cumulative percent response values were assigned to five toxicological classes (Table 9.3), using a system similar to that in the section on single species bioassays (Chapter 8). At this time we do not know how the toxicological classes in this system may correlate with, for example, effects on fish populations; the classes presented in Table 9.3 are only for the purpose of ranking the relative toxicity of stations in Lake Calumet to microbial communities from INHS Pond 12.

Table 9.3. Classification of cumulative percent response to relative toxicity values.

| Percent response | Toxicological class | Numerical assignment |
|---|---|---|
| 0% | No response | 0 |
| 0-100% | Weakly toxic | 1 |
| 100-200% | Moderately toxic | 2 |
| 200-300% | Highly toxic | 3 |
| >300% | Extremely toxic | 4 |

Figure 9.2 provides a schematic representation of toxicity in Lake Calumet sediments based on the toxicity to microbial communities. The station ranked as extremely toxic on the northwest side of the lake was at inflow of Pullman Creek, which receives storm water runoff from Interstate-94 and areas west of the interstate (Chapter 3 of this report). The extremely toxic station on the southwest side of the lake was in an area that appeared to have a high potential for receiving storm water runoff, although no inputs were identified.

9.3.4 Microbial community response in relation to chemical composition in sediments

The cumulative percent response of the four process-level bioassays ($\Sigma$ microbial response) correlated significantly with the concentrations of 5 heavy metals found in substantial amounts in Lake Calumet (Table 9.4) The strongest correlation was between $\Sigma$ microbial response and copper concentration ($r = 0.851$). The sum of community photosynthetic response ($\Sigma$ photosynthetic response, the cumulative response of the photosynthetic assays with 37% and 74% concentrations of elutriate) correlated equally as well as $\Sigma$ microbial response with copper concentration ($r = 0.849$), and correlated more strongly with concentrations of lead, tin, zinc, arsenic and nickel (Table 9.4).

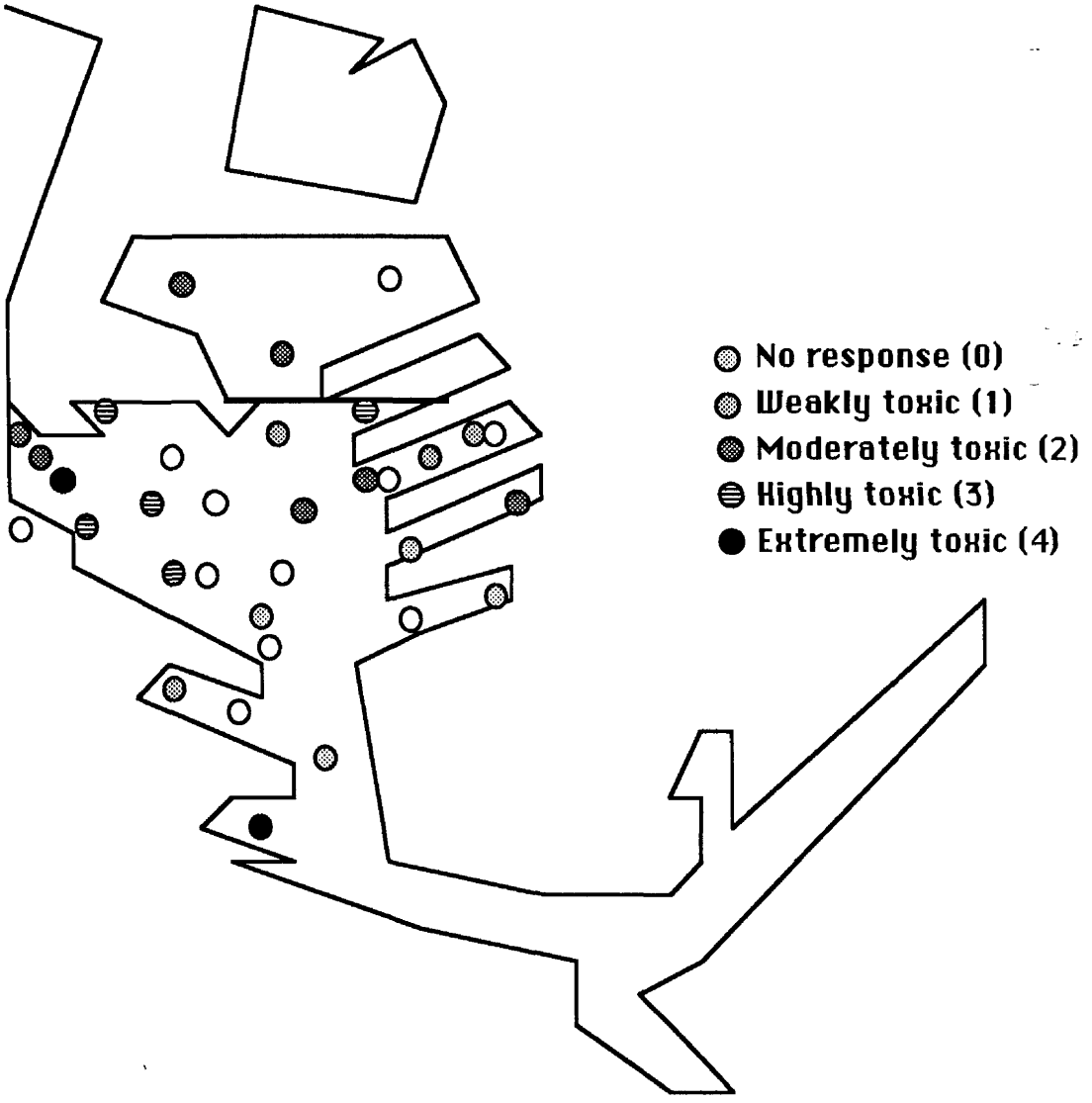


Figure 9.2. Classification of percent response microbial community values for Lake Calumet sediments. Open circles indicate a station where no test was performed

Table 9.4. Correlations (Pearson coefficients) between microbial community responses and sediment metal concentrations.

| | Cu | Pb | Sn | Zn | As | Ni | Σ Photo. | Σ Resp. |
|---|---|---|---|---|---|---|---|---|
| Cu | 1 | | | | | | | |
| Pb | .814 | 1 | | | | | | |
| Sn | .446 | .564 | 1 | | | | | |
| Zn | .926 | .771 | .23 | 1 | | | | |
| As | .611 | .303 | .312 | .403 | 1 | | | |
| Ni | .244 | -.061 | -.321 | .424 | -.224 | 1 | | |
| Σ Photo. | .849* | .635* | .609* | .714* | .658* | -.031 | 1 | |
| Σ Resp. | .031 | -.018 | .138 | -.179 | -.056 | .031 | .038 | 1 |
| Σ Microb. | .851* | .626* | .585* | .672* | .656* | .031 | .947* | .308 |

* Significant correlations ($a$ =0.05); Cu = copper, Pb = lead, Sn = tin, Zn = zinc, As = arsenic, Ni = nickel, Σ Photo. = sum of photosynthetic response, Σ Resp. = sum of respiratory response, Σ Microb. = sum of the microbial community response.

There were no significant correlations between the sum of community respiratory response (Σ respiratory response, the cumulative response of the respiratory assays with 37% and 74% concentrations of elutriate) and any metals (Table 9.4). The Σ microbial response correlated strongly with Σ photosynthetic response (r = 0.947) but not with Σ respiratory response.

Simple linear regressions were used to test the significance of the relationships of Σ microbial response, Σ photosynthetic response and Σ respiratory response with concentrations of metals. The best regressions for Σ microbial response andΣ photosynthetic response are presented as examples (Fig. 9.3); there were no significant regressions between respiratory response and any metals. Data from stations at which microbial community responses were not significant (Table 9.2) or where concentrations of a metal were below detection limits (Chapter 3) were not used in regressions (or in the previous correlations) because the community response or the metal concentration would have a value of zero. The values of community response and metal concentrations were not really zero, but simply below significance/detection limits. Therefore, 15 stations were used in the regressions with copper with tin (Fig. 9.3) instead of the 22 stations that were used in microbial assays (Table 9.2).

Variables which showed significant relationships in simple regressions were analyzed using stepwise multiple regression (Fig. 9.4).The best one-variable model for Σ photosynthetic response

was with copper ($r^2 = 0.511$), and the best overall fit ($r^2 = 0.739$) resulted when all the metals were included in the model (Fig. 9.4). The best one-variable model for $\Sigma$ microbial response was with tin ($r^2 = 0.416$) and the best overall regression coefficient ($r^2 = 0.555$) was the same for both 3 and for 4 metals (Fig. 9.4); the regression between $\Sigma$ microbial response and zinc was not significant.

## 9.4 Discussion

### 9.4.1 Effect of Lake Calumet sediments on microbial communities

Most studies do not attempt to evaluate the effects of toxicants at the level of the community or ecosystem. Protozoa collected on artificial substrates represent intact communities made up of 30-40 interacting species of several trophic levels. The toxic responses displayed by this group of organisms (which includes producers, herbivores and predators) may mimic the types of changes that could occur in other populations of organisms in Lake Calumet that may be exposed to toxic contamination when sediments are disturbed by dredging or by wave and wind action. The photosynthetic and respiratory responses of the total microbial community colonizing the substrates (the Protozoa, the algae, the bacteria and the small metazoans) may be representative of types of changes that could occur in the larger Lake Calumet ecosystem.

The fact that photosynthesis was significantly affected by elutriates from more stations (68%, 15/22) than affected respiration (55%) suggests that contamination in Lake Calumet generally had a greater impact on autotrophic than on heterotrophic organisms. Further, this finding illustrates the type and amount of information provided by these microbial community tests. Community photosynthesis decreased with exposure to elutriate from all stations, but respiration generally increased. That increase in respiration rates suggests that whereas metals in the sediments may have inhibited photosynthesis by autotrophic microorganisms in the community (the filamentous and unicellular algae, and phototrophic protozoa), nutrients in the sediments stimulated the activities of heterotrophs (the bacteria and bactivorous protozoa).

Inhibition of community respiration occurred only with exposure to elutriates from Stations 7-10. Elutriates from none of these stations produced great inhibition of photosynthesis; and only one of these stations, Station 7, was classified as even moderately toxic based on cumulative percent response values. Metal concentrations at these stations were neither

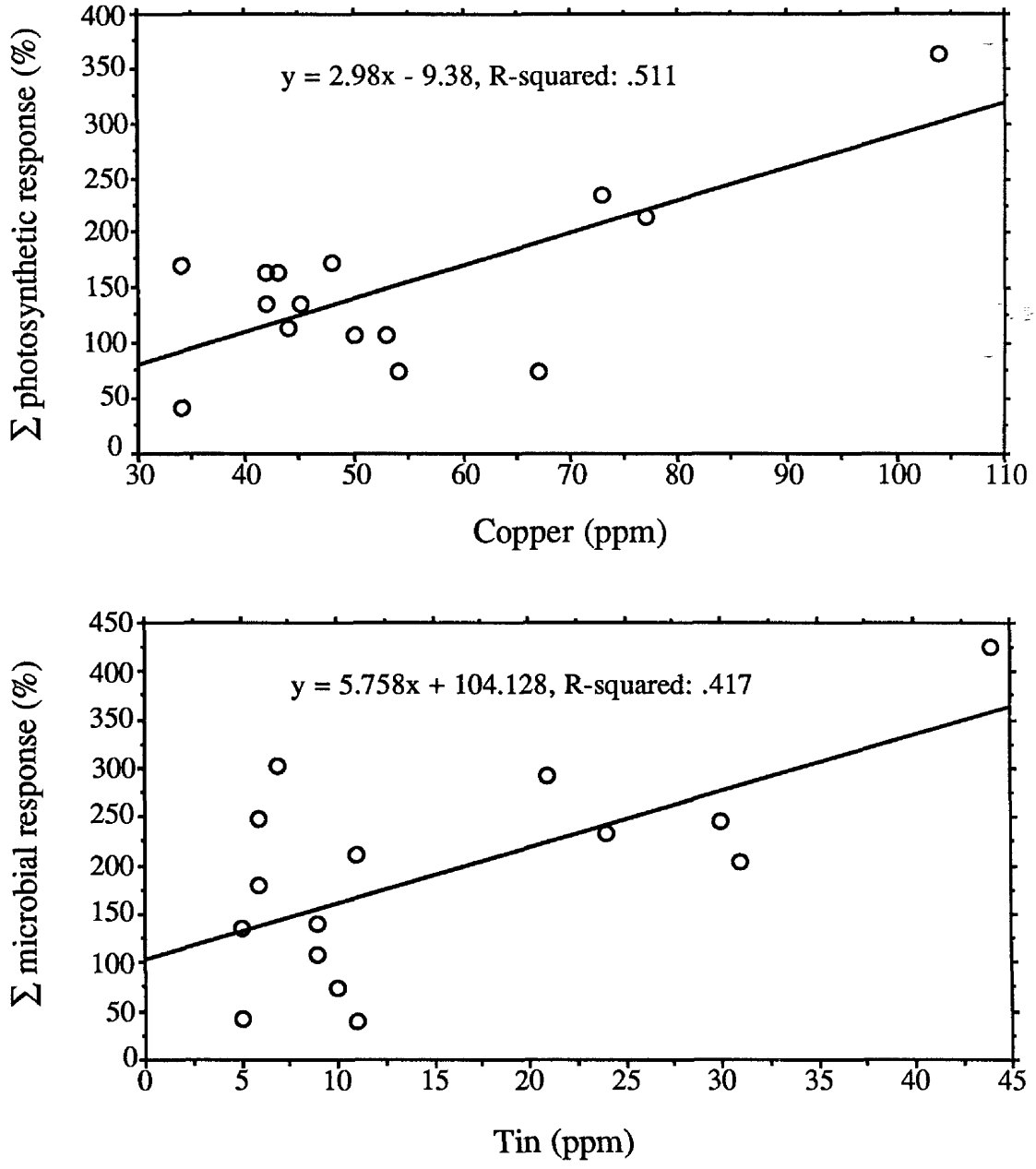


Figure 9.3. Regressions of photosynthetic response and Σ microbial response with metals concentrations in Lake Calumet sediments.

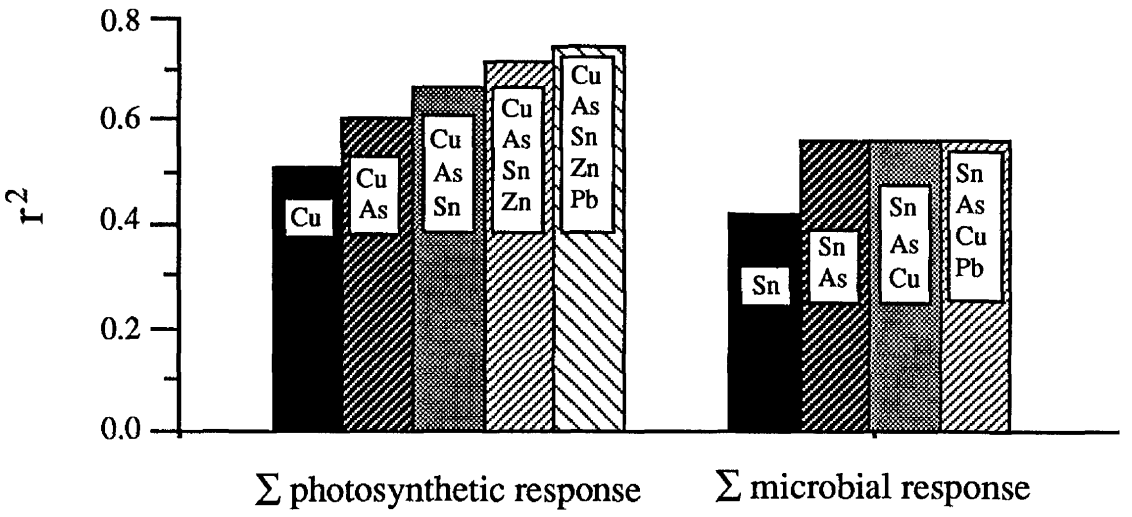


Figure 9.4. Stepwise multiple regressions of Σ photosynthetic response and Σ microbial community response with sediment metal concentrations. Cu = copper, Pb = lead, Sn = tin, Zn = zinc, As = arsenic.

particularly high nor particularly low (Chapter 3 of this report). Organic carbon values at these stations were also in the middle range for Lake Calumet (Chapter 3), so the reduction in community respiration does not appear to be due to a lack of organic material to respire. The sediment samples are still being analyzed for polyaromatic hydrocarbons and other toxic organics (Chapter 3). At this time, the inhibition of community respiration cannot be attributed to any specific group of toxic compounds, but it appears that there was something different about Stations 7-10.

9.4.2 Bioassay response in relation to chemical composition in sediments

The strong Pearson correlations and relatively high regression coefficients between Σ photosynthetic response and metal concentrations, and the general reduction in these values when the Σ respiratory response was added (to make up the Σ microbial response), indicates that the main response of the microbial communities in this study of Lake Calumet was a reduction in photosynthesis with increased metal concentrations in the sediments. Heavy metals, copper in particular, are well-documented inhibitors of photosynthesis (Steemann-Nielsen and Wium-Anderson 1970), and copper is a commonly used algacide. Therefore, it is not surprising that Σ photosynthetic response correlated most strongly with copper concentration. The Σ respiratory response correlated weakly (and not significantly) with the concentration of organic carbon in the sediments. No other nutrient concentrations in the sediments (e.g., nitrogen and phosphorus) were measured.

9.4.3 Comparisons with other studies

Tests comparing changes in photosynthesis and respiration of microbial communities developed on artificial substrates and exposed to elutriates of contaminated sediments are relatively new (Ross *et al.* 1987, Henebry and Ross 1987a), so there are few studies with which to compare the results from Lake Calumet. However, in studies of microbial community response to sediment elutriates from an area of Waukegan (IL) Harbor that was heavily contaminated with polychlorinated biphenyls (PCBs), photosynthesis was also inhibited while respiration was stimulated (Henebry and Ross 1987b).

Microbial communities on glass slides in artificial streams dosed with copper and chromium compounds and with nutrients such as sucrose and compounds containing nitrogen and phosphorus (Cairns *et al.* 1978) responded in much the same way as did the PF block microbial communities. In the Cairns *et al.* study the structure of the community was little changed by the various treatments. However, respiration was significantly stimulated with the addition of sucrose, and photosynthesis was significantly inhibited by both copper and chromium (Cairns *et al.* 1978).

When PF block microbial communities from INHS Pond 12 were exposed to copper chloride ($CuCl_2$), photosynthesis was reduced 97% in a concentration containing 0.66 ppm copper ion ($Cu^{++}$) and 55% in a 0.066 ppm concentration of $Cu^{++}$ (Henebry, unpublished). In that same series of tests, community respiration was reduced 58% in the 0.66 ppm concentration of $Cu^{++}$, but respiration was not significantly reduced in the 0.066 ppm $Cu^{++}$ concentration. Both photosynthesis and respiration of microbial communities from INHS Pond 12 were sensitive to relatively low levels of copper; however, photosynthesis was inhibited by a significantly lower concentration than was required to inhibit respiration.

Tests using the reduction in number of protozoan species as the endpoint were run with elutriates from only a few stations in Lake Calumet. Those species-reduction bioassays were time consuming and were less sensitive than the photosynthesis and respiration tests. The greatest (and only statistically significant) reduction in number of species occurred with exposure to 100% concentrations of sediment elutriate from stations B (32.2%) and 1 (31.0%). A 20% reduction in number of species in protozoan communities is considered biologically significant (Cairns *et al.* 1980, Cairns and Pratt 1985); therefore, Lake Calumet sediments may be moderately toxic in terms of altering community structure. Similarly, 100% concentrations of Waukegan Harbor sediment elutriate were required to significantly reduce numbers of species in protozoan communities, but colonization of barren islands and photosynthesis were inhibited by concentrations as low as 10% (Ross *et al.* 1987). Bioassays using the colonization rate of barren artificial islands by protozoa are

more sensitive to metals and other toxic substances than are species reduction tests (Cairns *et al.* 1980, Cairns and Pratt 1985), but take from 2-4 weeks to run and are even more labor intensive than species reduction tests.

9.4.4 Suggestions for further work

The information provided by this series of microbial community tests is more complex than that generated by single species bioassays. While the data from microbial community tests result in more realistic predictions concerning the impact of sediment contamination on Lake Calumet, caution must be exercised. The investigator must look at different endpoints and make judgements based on knowledge of community and ecosystem ecology. For example, the increase in respiration associated with exposure to elutriates from most stations might lead to the conclusion that Lake Calumet sediments were not toxic to the microbial communities but actually enhanced their activities. In reality, those increases probably incidcated that one or more nutrients that promote heterotrophic activities were present in higher amounts than at other stations, thereby masking the toxic effect of the contaminants at those stations. The decrease in photosynthesis at most stations probably provides a more accurate picture of the distribution of toxic materials in Lake Calumet sediments. To test the relationship between the stimulation of community activities by nutrients and the inhibition of activities by toxic substances, microbial communities should be exposed to various combinations of such toxic materials as heavy metals and varying levels of such nutrients as dissolved organic carbon, nitrogen and phosphorus.

Bioassays using microbial communities need to be performed on a variety of toxic metals and organics that have been used in bioassays with more standard organisms in order to compare the sensitivity of the microbial communities with that of such organisms as fish. It would also be useful to directly compare the responses of microbial communities with those of standard bioassay organisms by conducting simultaneous tests with split samples of contaminated sediments.

One advantage of using PF block protozoan communities for ecotoxicological studies is that *in situ* tests may be efficiently conducted with indigenous or indigenous-type organisms. Effects of toxic substances in laboratory tests may not be representative of effects on actual ecosystems. In studies of contamination in Waukegan Harbor (Ross *et al.* 1987) *in situ* tests allowed direct observation of the effects of sediment contamination, and confirmed predictions about changes in community structure based on laboratory tests. Unfortunately, during the first year of this work on Lake Calumet, artificial substrates placed in the lake were removed by vandals. Although the laboratory bioassays provided useful information, future studies should include monitoring of changes in indigenous-type protozoan communities collected at clean sites and transferred to Lake Calumet.

# Chapter 10
# Summary, Conclusions, and Recommendations

## 10.1 Summary

This study examined some of the physical, chemical, and biological processes occurring in Lake Calumet and sought to identify sources and effects of contamination from over a century of industrial development in the Calumet area.

### 10.1.1. Sediment chemistry

High concentrations of anthropogenic metals and polycyclic aromatic hydrocarbons (PAHs) were found in Lake Calumet sediments. These concentrations were generally higher than sediment samples in nearby waters.

### 10.1.2. Physical transport processes

In an evaluation of surface water in Lake Calumet, no natural drainage channels were observed. Pullman Creek, a smaller channel in the NE portion of the lake, and two storm sewers are the existing man-made drainage channels for the lake. Pullman Creek is not only a source of inflowing water but also of sediment.

### 10.1.3. Chemical transport processes

Organic compounds in the water column were at levels too low for one type of experimental fugacity measurement, but polychlorinated biphenyls were detected in the sediment at levels appropriate for measurement.

### 10.1.4. Microbiological processes

Methane was produced in Lake Calumet sediments, thereby confirming the presence of anaerobic microbial communities. Aerobic and anaerobic bacteria were found in greater numbers at sampling stations near the shoreline of Lake Calumet than at stations in deeper water.

### 10.1.5. Biological uptake

Lake Calumet wetlands support a population of macrophyte species that have been documented as bioaccumulators of heavy metals.

10.1.6 Single-species toxicity tests

Composite toxicity indices (based on the relative toxic responses of *Photobacterium phosphoreum* , *Selenastrum capricornutum* , and *Panagrellus redivivus* ) classified 57% (12/21) of the stations as "highly toxic"; the remainder (43%) were considered "moderately toxic." The toxic responses had a slight statistical correlation with total PAH concentrations in the sediment. Predictions of elutriate chemistry indicate that lead (Pb) might have the potential to exceed water quality standards if released from Lake Calumet sediments.

10.1.7. Microbial community toxicity tests

Exposure to sediment elutriate from 82% (18/22) of the stations resulted in statistically significant changes in microbial communities with the functional (photosynthesis and respiration) endpoints more sensitive than endpoints measuring reduction in numbers of species. Composite toxicity indices (based on the relative toxic responses of functional bioassays) classified 9% of the stations as "extremely toxic," 23% as "highly toxic," 32% as "moderately toxic," and 18% as "weakly toxic"; at 4 stations there was no statistically significant toxic response. Photosynthetic and total microbial community response had strong statistical correlations with metal concentrations in the sediment.

## 10.2 Conclusions

The research described in this study indicates that Lake Calumet is a severely disturbed system. Continued physical alteration has changed the lake's shape, reduced its surface area, and destroyed the surrounding natural wetland areas. Drainage is controlled by man-made channels (e.g., Pullman Creek) and the O'Brien Lock and Dam system. Pullman Creek has been identified as a source of pollutants as well as inflowing water. Chemical compounds common to industry in the Calumet region since the 1870s have concentrated in the sediments of the lake and, consequently, the potential for bioaccumulation in aquatic plants, invertebrates, fish, and perhaps, water fowl and humans is high. Alteration of the aquatic ecosystem through toxic effects of the contaminated sediments is probable.

Resuspension of Lake Calumet sediments is readily accomplished by wind-induced flow and storm events that scour the bottom and transport sediments to other locations in the lake.

The presence of waste landfills, major highways, refineries, scrap metal operations, and other industrial activities continues to threaten the Lake Calumet ecosystem. Atmospheric deposition, highway and industrial run-off, and continued alteration of the shoreline and surrounding wetlands may add to the pollution of the lake or induce further sediment disturbance and drainage problems.

Changes in the physiochemical nature of the lake by current activities may result in the release of contaminants deposited in previous years.

Although Lake Calumet seems to be isolated by the O'Brien Lock and Dam and its own sluggish drainage system, its connection with Lake Michigan and with the Illinois River watershed cannot be ignored. Some of the contaminants found in the sediments of Lake Calumet are likely to be found in the soil, water, and air in surrounding areas. The Calumet River and the Cal-Sag Channel may transport contaminants from the lake out of the Calumet region. A groundwater connection with the lake is, as yet, unidentified but may play a role in the transport of pollutants in or out of the lake.

The results from this year of study should provide a data base to support continued research on Lake Calumet and the surrounding region. Additional data will allow further conclusions on the environmental status of Lake Calumet.

### 10.3 Recommendations

Further research should be carried out in the following areas:

**Continued chemical and toxicological analyses of surface sediment:**. The existing knowledge base should be expanded in two ways. First, more stations within Lake Calumet proper should be studied to permit greater resolution in contaminant and toxicity mapping. Second, stations in wetlands, ponds, and small streams within the Lake Calumet hydrologic system should be studied in order to gain a more complete understanding of the situation. Special attention should be paid to culverts and drainage ditches leading from past and current industrial or disposal sites into the lake. In addition to chemicals already analyzed, priority pollutant scans should be run on a few selected stations to ensure that important contaminants are not being ignored.

**Continued data collection for sediment resuspension**. The clearly demonstrated importance of particulate mobilization raises three questions that should be addressed. First, is there a prevalent pattern of particle transport within Lake Calumet? Second, do particles originating in Lake Calumet sediments affect water quality in the Calumet River system and in Lake Michigan? Third, do storm events cause predictable contaminant relocation patterns? More precise data on sediment relocation is needed to answer these questions.

**Contaminant input from groundwater**. A study of groundwater flow patterns in and around the lake should be undertaken to estimate the importance of continued contaminant input from sub-surface sources.

**Historical loading.** The historical dimension of contaminant input to the system should be investigated by studying vertical sediment cores at selected stations. Core horizons can be dated by the Cesium-137 or Lead-210 methods, and chemical and toxicological analyses can then be performed on material deposited in various time periods. The effectiveness of this approach may be compromised if the high degree of lateral transport noted above obscures vertical deposition patterns, making historical trends impossible to detect.

**Bioaccumulation.** The level of bioaccumulatory substances in the sediment justifies analyses of aquatic plants and the initiation of a fish and invertebrate sampling program. Flesh analysis should include metals, PAHs, PCBs, and select pesticides. Fish analysis is especially critical because human consumption of Lake Calumet fish could present a health risk. (During the April 1987 sampling trip, 18 fishermen were seen in one afternoon.)

**Literature and data base research.** Although a good deal of information has been summarized in the Colten (1985) report and in this document, more sources should be explored. In particular, data from monitoring wells (IEPA) and internal environmental quality programs (MSDGC) should be accessed.

**Atmospheric deposition.** In order to complete the study of contamination sources, the role of atmospheric deposition should be evaluated.

**Public health.** The existing public health data base (Illinois Public Health Dept.) should be re-examined when current studies are completed. These data should be compared with contaminant and toxicological data to determine whether correlations exist. The need for further epidemiological studies should also be evaluated at that time.

# Chapter 11
# Literature Cited


American Society for Testing and Materials. 1982. Annual Book of ASTM Standards, Part 31, Water.

Aulio, K. 1980. Accumulation of copper in fluvial sediments and yellow water lilies (Nuphar lutea) at varying distances from a metal processing plant. Bull. Environ. Contam. Toxicol. 25: 713-717.

Balch, W.E., G.E. Fox, L.J. Magrum, C.R. Woese, and R.S. Wolfe. 1979. Methanogens: Reevaluation of a Unique Biological Group. Microbiol. Reviews 43: 260-293.

Barsdate, R.J., R.T. Prentki, and F. Fenchel. 1974. Phosphorus cycle of model ecosystems; significance for decomposer food chains and the effect of bacterial grazers. Oikos 25: 239-251.

Beckman Instruments, Inc. 1982. Microtox system operating manual. Microbics Operations, Carlsbad, CA.

Bendell-Young, L.I. and H.H. Harvey. 1986. Metal concentration and calcification of bone of White Sucker (Catostomas commersoni) in relation to lake pH. Water, Air and Soil Pollution 30: 657-664.

Bennett, G. W. 1971. Management of lakes and ponds. Van Nostrand Reinhold Co., NY.

Bennett, P., D.I. Siegel, A.I. Veeger, and P.C. Jones. 1987. Abstract, A pressure probe for determining lake-ground water interaction. Eos. 68: 319-320.

Beyers, R.J. 1964. The microcosm approach to ecosystem ecology. Am. Biol. Teach. 26: 491-497.

Boyd, S.A. and D.R. Shelton. 1984. Anaerobic biodegradation of chlorophenols in fresh and acclimated sludge. Appl. Environ. Microbiol. 47:272-277.

Bretz, J.H. 1939-1955. Geology of the Chicago Region, Part I: General; Part II: The Pleistocene. Ill. State Geol. Survey Bull. 65.

Bryant, M.P. 1976. The microbiology of anaerobic degradation and methanogenesis with special reference to sewage. Pages 107-117 in Proceedings of the Microbial Energy Conversion Symposium. Gottingen, F.R.G.

Buchanan, T.J., and W.P. Sommers. 1969. Discharge measurements at gaging stations. Book 3, Chapter A8 in Techniques of Water Resource Investigations of the United States Geological Survey.

Bulich, A. A. 1982. A practical and reliable method for monitoring the toxicity of aquatic samples. Process Biochemistry March/April: 45-47.

Bulich, A.A., M.W. Greene, and D. L. Isenberg. 1981. Reliability of the bacterial luminescence assay for determination of the toxicity of pure compounds and complex effluents. ASTM STP 737. American Society for Testing and Materials. pp. 338-347.

Cahill, R.A. 1981. Geochemistry of recent Lake Michigan sediments. Ill. State Geol. Survey Circ. 517, 94 pp.

Cahill, R.A., and N.F. Shimp. 1984. Inorganic contaminants in Lake Michigan sediments. In Toxic Contaminants in the Great Lakes, eds. J.O. Nriagu and M.S. Simmons. J. Wiley and Sons.

Cairns, J. Jr. 1984. Multispecies toxicity testing. Environ.Toxicol. and Chem. 3: 1-3.

Cairns, J. Jr., K. L. Dickson, E. Benfield, and A. L. Buikema. 1978. The Development of Biological Indices for Identifying and Evaluating Impacts of Pollutants on Freshwater Ecosystems. Summary Report to United States Department of Energy, Washington, DC, June 1978.

Cairns, J. Jr., K.M. Hart, and M.S. Henebry. 1980. The effects of a sublethal dose of copper sulfate on the colonization rate of freshwater protozoan communites. Amer. Mid. Nat.104: 93-101.

Cairns, J, Jr., D.L. Kuhn, and J.L. Plafkin. 1979. Protozoan colonization of artificial substrates. pages 34-57 in R.L. Weitzel, [ed.] Methods and Measurements of Periphyton Communities: A Review, American Society for Testing and Materials, Philadelphia, PA.

Cairns, J. Jr., and J.R Pratt. 1985. Multispecies toxicity testing using indigenous organisms -- a new, cost-effective approach to ecosystem protection. pages 149-159 in 1985 Environmental Conference, TAPPI Proceedings, ISSN 0272-7269. TAPPI Press, Atlanta GA.

Callahan, Michael A. and Michael Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. EPA-440/4-79-029. USEPA.

Campbell, P.G.C., A. Tessier, M. Bisson, and R. Bougie. 1985. Accumulation of copper and zinc in the yellow water lily, *Nuphar variegatum* : Relationships to metal partitioning in the adjacent lake sediments. Canadian Journal of Fisheries and Aquatic Sciences 42:23-32.

Chakrabarty, A.M. 1982. Biodegradation and Detoxification of Environmental Pollutants. CRC Press, Inc., BocaRaton, FL.

Champoux, L., P. Ross, V. Jarry, H. Sloterdijk, A. Mudroch, and Y. Couillard. 1986. Libèration par èlutriation des contaminants des sèdiments du lac Saint-Louis (fleuve Saint-Laurent Quèbec). Revue internationale des sciences de l'eau 2: 95-107.

Colten, C.E. 1985. Industrial Wastes in the Calumet Area, 1869-1970: An Historical Geography. Illinois Dept. of Energy and Natural Resources. Hazardous Waste Research and Information Center Report RR 001. Savoy, IL.

Cooke, G.D. 1974. Aquatic laboratory microsystems and communities. pages 47-86 in J. Cairns, Jr., [ed.] Structure and Function of Freshwater Microbial Communities. Virginia Polytechnic Institute and State University Press, Blacksburg, VA.

Cowardin, L.M., V. Carter, F.C. Golet, and E.T. LaRoe. 1979. Classification of wetlands and deepwater habitats of the United States. U.S. Fish Wildl. Serv. Biol. Serv. Prog., FWS/OBS-79/31.

Cowgill, U.M. 1974. The hydrogeochemistry of Linsley Pond, North Branford, Connecticut. II. The chemical composition of the aquatic macrophytes. Archive fur Hydrobiologia Supplement 1:1-119.

Cummins, K.W. 1973. Trophic relations of aquatic insects. Ann. Rev. Entomol. 18: 183-206.

Curtis, Carolanne, Ann Lima, S.J. Lozano, and G. D. Veith. 1982. Evaluation of a bacterial bioluminescence bioassay as a method for predicting acute toxicity of organic chemicals to fish. ASTM STP 766. American Society for Testing and Materials. pp. 170-178.

Dawson, F. H., E. Castellano, and M. Ladle. 1978. Concept of species succession in relation to river vegetation and management. Verh. Internat. Verin. Limnol. 20:1429-1434.

DeZwart, D. and W. Sloof. 1983. The Microtox™ as an alternative assay in the acute toxicity assessment of water pollutants. Aquatic Toxicology 4: 129-138.

Eisler, R. 1986. Polychlorinated biphenyl hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Fish and Wildlife Service Biological Report 85(1.7). Patuxent Wildlife Research Center, Laurel, MD.

Eisler, R. 1987. Polycyclic aromatic hydrocarbon hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Fish and Wildlife Service Biological Report 85(1.11). Patuxent Wildlife Research Center, Laurel, MD.

EnCap, Inc.1981. Habitat Evaluation of Lake Calumet. Chicago, IL.

Engler, Robert M. 1980. Prediction of pollution potential through geochemical and biological procedures: development of regulation guidelines and criteria for the discharge of dredged and fill material. pages 143-169 in Contaminants and Sediments Volume 1 (Robert A. Baker, editor). Ann Arbor Science Publishers. Ann Arbor, MI.

Equitable Environmental Health. 1978. Ecological Analysis of the Lake Calumet Development Area. Chicago, Illinois.

Everard, M., and P. Denny. 1985. Flux of lead in submerged plants and its relevance to a freshwater system. Aquatic Botany 21:185-193.

Franzin, W. G., and G. A. MacFarlane. 1980. An analysis of the aquatic macrophyte, *Myriophyllum exalbescens*, as an indicator of metal contamination of aquatic ecosystem near a base metal smelter. Bull. Environ. Contam. Toxicol. 24: 597-605.

Gabrielson, J.O., M.A. Perkins, and E.B. Welsh. 1984. The uptake, translocation and release of phosphorus by *Elodea densa*. Hydrobiologia 111: 43-48.

Gerloff, G.C. and K.A. Fishbeck. 1973. Plant content of elements as a bioassay of nutrient availability in lakes and streams. Pages 159-176 in G.E. Glass, ed. Bioassay Techniques and Environmental Chemistry, Ann Arbor Science Publishers, MI.

Gilkeson, R.H., K. Cartwright, J.B. Cowart, R.B. Holtzman. 1983. Hydrogeologic and Geochemical Studies of Selected Natural Radioisotopes and Barium in Groundwater in Illinois. Illinois State Geological Survey Contract Report 1983-6. 93 pp.

Greenfield, D.W. and J.D. Rogner. 1984. An assessment of the fish fauna of Lake Calumet and its adjacent wetlands, Chicago, Illinois: Past, present, and future. Trans. of Illinois Academy of Sciences 77: 77-93.

Goldman, J.C. 1983. p. 17-18 in Oceanic Nutrient Cycles. WHOI Annual Report.

Hase, A. and R.A. Hites. 1976. On the origin of polycyclic aromatic hydrocarbons in recent sediments. Geochimica Cosmo. Acta. 40: 1141-1143.

Healy, J.B., and L.Y. Young. 1979. Anaerobic Biodegradation of Eleven Aromatic Compounds to Methane. Appl. Environ. Microbiol. 38: 84-89.

Henebry, M.S., and J. Cairns, Jr. 1984. Protozoan colonization rates and trophicstatus of some freshwater wetland lakes. J. Protozool. 31: 456-467.

Henebry, M.S. and P. Ross. 1987a. Changes in the structure of protozoan communities exposed to contaminated sediments. International Symposium: Cellular Impacts in Ecotoxicology, Lyon, France, 19-22 May. Abstract.

Henebry, M.S. and P. Ross. 1987b. Use of protozoan community tests for estimating ecotoxicological hazard. Third International Symposium, Toxicity Testing Using Microbial Systems., Valencia, Spain, 11-15 May. Abstract.

Hill, B. H. 1979. Uptake and release of nutrients by aquatic macrophytes. Aquatic Botany 7:87-93.

Hobbie, J.E., R.J. Daley, and S. Jasper. 1977. Use of nucleopore filters for counting bacteria by fluorescence microscopy. Applied and Environ. Microbiol. 33:1225-1228.

Hoke, Robert A. and Bayliss L. Prater. 1980. Relationship of per cent mortality of four species of aquatic biota from 96-hour sediment bioassays of five Lake Michigan harbors and elutriate Chemistry of the Sediments. Bull. Environ. Contam. Toxicol. 25: 394-399.

Horowitz, A., D.R. Shelton, C.P. Cornell, and J.M. Tiedje. 1982. Anaerobic degradation of aromatic compounds in sediments and digested sludge. Dev. Ind. Microbiol. 23: 435-444.

Howard-Williams, C. and G.M. Lenton. 1975. The role of the littoral zone in the functioning of a shallow tropical lake ecosystem. Freshwater Biology 5: 445-459.

Hungate, R.E. 1982. Methane formation and cellulose digestion--biochemical ecology and microbiology of the rumen ecosystem. Experientia 38:189-182.

Hutchinson, G.E. 1975. A Treatise on Limnology. Vol III Limnological Botany. John Wiley & sons, New York.

Hvorslev, M.J. 1951. Time lag and soil permeability in groundwater observations. U.S. Army Waterways Experiment Station Bulletin 36.

Hydroqual, Inc. 1985. Grand Calumet River Wasteload Allocation Study.

IEPA. 1984. Illinois Water Quality Report 1982-1983. IEPA/WPC/84-024.

IEPA. 1986. The Southeast Chicago Study: An Assessment of Environmental Pollution and Public Health Impacts. IEPA/ENV/86-008. 150+ pp.

Jaynes, M.L. and S.R. Carpenter. 1986. Effects of vascular and nonvascular macrophytes on sediment redox and solute dynamics. Ecology 67: 875-882.

Kaiser, J.P. and K.W. Hanselmann. 1982. Fermentative metabolism of substituted monoaromatic compounds by a bacterial community from anaerobic sediments. Arch. Microbiol. 133: 185- 194.

Karr, J.R., 1981. Assessment of biotic integrity using fish communities. Fisheries 6: 21-27.

Kelly, M.H. and R.L. Hite. 1981. Chemical analysis of surficial sediments from 63 Illinois Lakes, Summer 1979. IEPA. Springfield, Illinois.

Kirk, J.R., K.J. Hlinka, R.T. Sasman, and E.W. Sanderson. 1985. Water withdrawals in Illinois, 1984. Illinois State Water Survey Circular 163.

Kudo, R.R. 1966. Protozoology, 5th ed. Charles C. Thomas, Springfield, Illinois, 1174 pp.

Laflamme, R.E. and R.A. Hites. 1978. The global distribution of polycyclic aromatic hydrocarbons in recent sediments. Geochimica Cosmo. Acta. 42: 289-303.

Lambe, T.W., and R.V. Whitman. 1969. Soil Mechanics. John Wiley and Sons, Inc., New York. 553 pp.

Larsen, V.J. and H.H. Schierup. 1981. Macrophyte cycling of zinc, copper, lead and cadmium in the littoral zone of a polluted and a non-polluted lake. II. Seasonal changes in heavy metal content of above-ground biomass and decomposing leaves of *Phragmites australis*. Aquatic Botany 11: 211-230.

LeBlanc, G. A. 1984. Interspecies relationships in acute toxicity of chemicals to aquatic organisms. Environmental Toxicology and Chemistry 3:47-60.

Lee, C.R., R.K. Peddicord, B.L. Folsom, and J.G. Skogerboe. 1987. The use of bioassay and associated tests in dredged material and disposal management. Hydrobiologia 149: 81-86.

Lee, D.R. 1977. A device for measuring seepage flux in lakes and estuaries. Limnol. Oceanogr. 22: 140-147.

Lee, D.R. 1980. Groundwater-solute influx. Limnol. Oceanogr. 25: 183-186.

Lee, D.R. and J.A. Cherry. 1978. A field exercise on gorundwater flow using seepage meters and mini-piezometers. Jour. Geological Education 27: 6-10.

Lee, D.R., J.A. Cherry, and J.F. Pickens. 1980. Groundwater transport of a salt tracer through a sandy lakebed. Limnol. Oceanogr. 25: 45-61.

Leland, H.V., S.S. Shukla, and N.F. Shimp. 1973. Factors affecting distribution of lead and other trace elements in sediments of southern Lake Michigan. pages 89-138 in Trace metals and metal-organic interactions in natural waters. Ann Arbor Science, Ann Arbor, MI.

Lettinga, G., K.C. Pette, R. de Vletter and E. Wind. 1977. Anaerobic treatment of sugarbeet waste water in a $6m^3$ pilot plant. $H_2O$ 10: 526.

Liss, P. S. and Slater, P. G. 1974. Flux of Gases across the Air-Sea Interface. Nature 247: 181-184.

Mackay, D. 1979. Finding fugacity feasible. Envir. Sci. & Tech. 13: 1218-23.

Mackay, D. and Peterson, S. 1981. Calculating fugacity. Envir. Sci. & Tech. 15: 1006-14.

Mayes, Roger A. and Alan W. McIntosh. 1977. Uptake of cadmium and lead by a rooted aquatic macrophyte (*Elodea canadensis*). Ecology 58: 1176-1180.

McBride, M.S. and H.O. Pfannkuch. 1975. The distribution of seepage within lakebeds. Jour. Research U.S. Geol. Survey 3: 505-512.

McIntosh, A.W., B.K. Shephard, R.A. Mayes, G.J. Atchison, and D.W. Nelson. 1978. Some aspects of sediment distribution and macrophyte cycling of heavy metals in a contaminated lake. Journal of Envirnomental Quality 7:301-305.

McKinney, J. D. 1976. Toxicology of selected symmetrical hexachlorobiphenyl isomers: correlating biological effects with chemical structure. Pages 73-76 *in* Proceedings, USEPA National Conference on Polychlorinated Biphenyls, Chicago, IL, November 1975.

Miller, G.E., I. While and G. Hitchin. 1983. Patterns of accumulation of selected metals in members of soft-water macrophyte flora of central Ontario lakes. Aquatic Botany 15: 53-64.

Mudroch, A. and J.A. Capobianco. 1979. Effects of mine effluent on uptake of Co, Ni, Cu, As, Zn, Cd, Cr, and Pb by aquatic macrophytes. Hydrobiologia 64:223-231.

Murphy, T. J., Mullin, M. D. and Meyer, J. A. 1986. Equilibration of PCBs and toxaphene with air and water. Envir. Sci. & Tech. 21: 155-62.

Namkung,E. and B.E. Rittmann. 1986. A study of VOC emmissions from the Calumet sewage treatment plant in the Chicago area. ILENR/RE-AQ-86/15. Illinois Department of Energy and Natural Resources, Springfield, IL.

National Research Council. 1981. Testing for effects of chemicals on ecosystems. National Academy Press, Washington, D.C.

Norris, K.P. and E.O. Powell. 1961. J.R. Microsc. Soc. 80:107-119.

Odum, E.P. 1984. Mesocosm. Bioscience 34: 558-562.

Pratt, J.R., and J. Cairns, Jr. 1985. Functional groups in the Protozoa: roles in differing ecosystems. J. Protozool. 32: 415-423.

Quereshi, A.A., K.W. Flood, S.R. Thompson, S.M. Janhurst, C.S. Inniss, and D.A. Rokosh. 1982. Comparison of a luminescent bacterial test with other bioassays for determining toxicity of pure compounds and complex effluents. ASTM STP 766. American Society for Testing and Materials. pp. 179-195.

Risatti, J. Bruno, and W.G. Sheridan. 1987. Rates of microbial dechlorination of polychlorinated biphenyls (PCBs) in anaerobic sediments from Waukegan Harbor. Report to Hazardous Waste Research andInformation Center, Savoy, Il.

Ross. P.E., 1987. Ecotoxicology for Illinois. IN Ecotoxicology for Illinois: Establishing the research agenda. Illinois Hazardous Waste Research and Information Center Report RR 015, Savoy IL

Ross, P. E., M.S. Henebry, W. Wang, and L.C. Burnett. 1987. Assessment of ecotoxicological hazard of Waukegan Harbor sediments. Final Report to the Hazardous Waste Research and Information Center, Savoy, Illinos, December 1987.

Ross, P., V. Jarry, and H. Sloterdijk. 1987. A rapid bioassay using the green alga *Selenstrum capricornutum* to screen for toxicity in St. Lawrence River sediment elutriates. Accepted by ASTM.

Samoiloff, M. R. and T. Bogeart. 1984. The use of nematodes in marine ecotoxicology. *in* G. Personne, E. Jaspers, and C. Claus editors. Ecotoxicological testing for the marine environment, Vol. 1. State University of Ghent and Institute of Marine Scientific Research, Brendene, Belgium.

Samoiloff, M. R., and P. G. Wells. 1984. Future trends in marine ecotoxicology. Pages 733-750 *in* G. Personne, E. Jaspers, and C. Claus editors. Ecotoxicological testing for the marine environment, vol. 1. State University of Ghent and Institute of Marine Scientific Research, Brendene, Belgium.

Samoiloff, M. R., S. Schulz, Y. Jordan, K. Denich, and E. Arnott. 1980. A rapid simple long-term toxicity assay for aquatic contaminants using the nematode *Panagrellus redivivus*. Canadian Journal of Fisheries and Aquatic Sciences 37:1167-1174.

Samoiloff, M.R., J. Bell, D.A. Birkholz, G.R.B Webster, E. Arnott, R. Pulak, and A. Madrid. 1983. Combined bioassay-chemical fractionation scheme for the determination and ranking of toxic chemicals in sediments. Environ. Sci. Technol. 17: 329-334.

Sasman, R.T., C.R. Benson, R.S. Ludwigs, and T.L. Williams. 1982. Water-level trends, pumpage, and chemical quality in the Cambrian-Ordivician aquifer in Illinois, 1971-1980. Illinois State Water Survey Circular 154.

Schicht, R.J., J.R. Adams, and J.B. Stall. 1976. Water Resources Availability, Quality, and Cost in Northeastern Illinois. Illinois State Water Survey Report of Investigation 83. 90 pp.

Schierup, H.H. and V.J. Larsen. 1981. Macrophyte cycling of zinc, copper, lead and cadmium in the littoral zone of a polluted and a non-polluted lake. I. Availability, uptake, and translocation of heavy metals in *Phragmites australis*. Aquatic Botany 11: 197-210.

Schink, B. and N. Pfennig. 1982. Fermentation of trihydroxy- benzenes by*Pelobacter acidigallici* gen. nov. sp. nov., a new strictly anaerobic, non-spore forming bacterium. Arch. Microbiol. 133:195-201.

Sculthorpe, C.D. 1967. The Biology of Aquatic Vascular Plants. Edward Arnold Publishers Ltd. London.

Slowinski, Thomas. Chicago district, U.S. Army Corps of Engineers, 219 S. Dearborn, Chicago, IL 60604. Personal communication with W. Garrison, August, 1987.

Smith, C.S., and M.S. Adams. 1986. Phosphorus transfer from sediments by *Myriophyllum spicatum*. Linmol. Ocean. 31: 1312-1321.

Sokal, R.R, and F.J. Rohlf. 1969. Biometry. W. H. Freeman and Company, San Francisco, California.

Strachan, W. M. J. and Eisenreich, S. J. 1987. Mass balancing of toxic chemicals in the Great Lakes: The role of atmospheric deposition. A report of a Workshop held at the Guild Inn, Scarborough, Ontario, October 29-31, 1986. International Joint Commission, 100 Ouelette St, Windsor, Ontario.

Sulflita, J.M., A. Horowitz, D.R. Shelton and J.M. Tiedje. 1982. Dehalogenation: A novel pathway for the anaerobic biodegradation of haloaromatic compounds. Science 218: 1115-1117.

Suloway, J., T. Skelly, W. Roy, D. Dickerson, R. Schuller, and R. Griffin. 1983. Chemical and toxicological properties of coal fly ash. IDENR. Environmental Geology Notes 105. Champaign, Illinois.

Suter, M., R.E. Bergstrom, H.F. Smith, G.H. Emrich, W.C. Walton, T.E. Larson. 1959. Ground-Water Resources of the Chicago Region, Illinois. Cooperative Ground-Water Report 1. Illinois State Water and Geological Surveys. 89 pp.

Sweet,C.W. and D.F. Gatz. 1987. Atmospheric research and monitoring study of hazardous substances: Second Annual Report. RR 014. Illinois Hazardous Waste Research and Information Center, Savoy, Illinois.

USACE. 1976. Ecological evaluation of proposed discharge of dredged or fill material into navigable waters. Misc. papeer D-76-17. U.S. Army Engineer Waterways Experiment Station, Vicksburg,MS.

USACE, Chicago District, Final Environmental Impact Statement, May 1982, Chicago Area Confined Disposal Facility and Maintenance Dredging in Cook County, Illinois.

USACE, Chicago District. 1982. Phase I, General Design Memorandum, Little Calumet River, Indiana, Technical Volume E, Hydrology and Hydraulics, July.

USACE. 1983. Phase II Letter Report, Little Calumet River, Illinois, Technical Appendices.

USACE. 1985. Draft Environmental Impact Statement: Section 10 and Section 404 Permit for a sanitary landfill in a wetland adjacent to Lake Calumet, Chicago, Cook County, IL. Chicago, IL.

USEPA. 1986. Gas chromatography/mass spectrometry for semivolatile organics: Capillary column technique. Method 8270, USEPA.

USEPA. 1986. Sonication Extraction, Method 3550. USEPA.

Visocky, A.P., M.G. Sherrill, and K. Cartwright. 1985. Geology, hydrology, and water quality of the Cambrian and Ordovician systems in Northern Illinois. Illinois State Geological and Water Surveys Cooperative Groundwater Report 10. 136 pp.

Wakeham, S.G., C. Schaffner and W. Giger. 1980a. Polycyclic aromatic hydrocarbons in recent lake sediments I. Compounds having anthropogenic origins. Geochimica Cosmo. Acta. 44: 403-413.

Wakeham, S.G., C. Schaffner and W. Giger. 1980b. Polycyclic aromatic hydrocarbons in recent lake sediments II. Compounds derived from biogenic precursors during early diagenesis. Geochimica Cosmo. Acta. 44: 415-429.

Welsh, R.P.H. and P. Denny. 1980. The uptake of lead and copper by submerged aquatic macrophytes in two English lakes. J. Ecology 68: 443-445.

Welsh, R.P.H. and P. Denny. 1976. Waterplants and the recycling of heavy metals in an English lake. Proc. Conf. Trace Substances and Environmental Health 10: 217-223.

Wetzel, R.G. 1983. Limnology. 2nd edition. Saunders College Publishing. Philadelphia, PA.

Wiley, M. J., and R. W. Gorden. 1984. Biological control of aquatic macrophytes by herbivorous carp. Part 2. Biology and ecology of herbivorous carp. Final report, Federal Aid Project F-37-R. Aq. Biol. Tech. Rep. 1984(11). Ill. Nat. Hist. Survey, Champaign.

Willford, W.A., M.J. Mac, and R.J. Hesselberg. 1987. Assessing the bioaccumulation of contaminants from sediments by fish and other aquatic organisms. Hydrobiologia 149: 107-111.

Williams, L.G., P.M. Chapman, and T.C. Ginn. 1986. A comparative evaluation of marine sediment toxicity using bacterial luminescence, oyster embryo, and amphipod sediment bioassays. Marine Environmental Research 19: 225-249.

Willman, H.B. 1971. Summary of the Geology of the Chicago Area. Illinois State Geological Survey Circular 460. 77

Wright, J. F., P. D. Hiley, S. F. Ham, and A. D. Berrie. 1981.Comparison of three mapping procedures developed for river macrophytes. Freshwater Biology 11(4): 369-380.

# Appendices

Appendix 1. Elemental analysis of Lake Calumet surficial sediments from 13 stations.

| STATION | ELEMENTS | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | AG | Al (%) | As | B | Ba | Be | Br | Ca (%) | Cd | Ce | Co |
| A | 1.1 | 2.92 | 16 | 22 | 543 | <1 | 5.0 | 6.42 | <1.5 | 25 | 7 |
| B | 1.8 | 4.47 | 44 | 31 | 534 | <1 | 7.0 | 7.58 | 3.6 | 38 | 12 |
| C | 1.5 | 4.84 | 50 | 39 | 488 | <1 | 4.0 | 7.41 | 2.9 | 45 | 14 |
| D | 0.5 | 3.83 | 25 | 30 | 524 | <1 | 9.0 | 7.38 | <1.5 | 32 | 9 |
| E | 0.6 | 4.75 | 31 | 36 | 455 | <1 | 4.0 | 7.25 | <1.5 | 45 | 14 |
| F | 0.3 | 5.32 | 29 | 33 | 430 | <1 | 3.0 | 6.36 | <1.5 | 45 | 14 |
| G | 0.9 | 4.57 | 42 | 58 | 454 | 2.0 | 4.0 | 6.75 | <1.5 | 50 | 14 |
| H | 0.6 | 4.97 | 44 | 56 | 473 | 1.2 | 4.0 | 6.56 | <1.5 | 50 | 15 |
| I | <.3 | 4.89 | 21 | 60 | 434 | 1.6 | 3.0 | 6.03 | <1.5 | 51 | 16 |
| J | <.2 | 4.18 | 20 | 60 | 371 | 1.2 | 2.0 | 6.56 | <1.5 | 46 | 14 |
| K | <.2 | 3.91 | 23 | 34 | 452 | <1 | 3.0 | 5.09 | <1.5 | 28 | 9 |
| L | <.6 | 5.45 | 21 | 55 | 420 | 1.3 | 4.0 | 6.57 | <1.5 | 49 | 15 |
| M | <.2 | 3.72 | 22 | 38 | 414 | <1 | 3.0 | 5.64 | <1.5 | 32 | 11 |
| L.C. AVG. | 0.562 | 4.45 | 29.8 | 42.4 | 461 | | 4.23 | 4.71 | 1.76 | 41.2 | 12.6 |
| L.M. AVG. | 0.46 | 3.82 | 10.5 | | 494 | | 33 | 2.84 | 0.9 | 48 | 9 |

| | Cr | Cs | Cu | Eu | Fe (%) | Ga | Hf | K (%) | La | Lu | Na (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 54 | 2.0 | 42 | 0.4 | 1.58 | 8 | 3.1 | 1.60 | 15 | 0.15 | 0.61 |
| B | 116 | 4.7 | 115 | 0.8 | 2.78 | 10 | 4.5 | 2.14 | 24 | 0.27 | 0.44 |
| C | 110 | 5.9 | 104 | 0.9 | 2.92 | 13 | 4.7 | 2.37 | 30 | 0.30 | 0.41 |
| D | 71 | 3.6 | 60 | 0.6 | 2.15 | 8 | 3.7 | 1.85 | 18 | 0.23 | 0.55 |
| E | 83 | 5.7 | 58 | 0.8 | 2.88 | 10 | 4.9 | 2.45 | 25 | 0.35 | 0.43 |
| F | 70 | 6.0 | 48 | 1.0 | 3.00 | 13 | 4.6 | 2.74 | 31 | 0.31 | 0.40 |
| G | 90 | 6.7 | 62 | 1.1 | 3.00 | 15 | 5.6 | 2.52 | 34 | 0.41 | 0.43 |
| H | 88 | 6.8 | 77 | 0.9 | 3.11 | 11 | 5.2 | 2.58 | 27 | 0.33 | 0.41 |
| I | 75 | 6.1 | 42 | 0.9 | 3.10 | 11 | 5.3 | 2.77 | 27 | 0.31 | 0.41 |
| J | 51 | 4.0 | 37 | 0.9 | 2.51 | 9 | 5.6 | 2.38 | 27 | 0.27 | 0.48 |
| K | 41 | 2.8 | 13 | 0.6 | 2.11 | 10 | 3.3 | 2.16 | 17 | 0.20 | 0.62 |
| L | 89 | 7.5 | 54 | 0.9 | 3.64 | 12 | 4.8 | 2.53 | 27 | 0.30 | 0.39 |
| M | 60 | 4.1 | 36 | 0.7 | 2.57 | 8 | 5.2 | 1.92 | 17 | 0.26 | 0.53 |
| L.C. AVG. | 76.8 | 5.07 | 57.5 | 0.81 | 2.72 | 10.6 | 4.65 | 1.92 | 24.5 | 0.28 | 0.47 |
| L.M. AVG. | 46 | 2.9 | 22 | 0.8 | 2.17 | 10 | 5.1 | 1.83 | 23 | 0.2 | 0.459 |

| | Ni (%) | P | Pb | Rb | Sb | Sc | Se | Si | Sm | Sn | Sr (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 12 | 0.06 | 220 | 52 | 1.2 | 3.9 | <1 | 25.4 | 2.1 | 31 | 101 |
| B | 29 | 0.11 | 316 | 69 | 2.1 | 7.0 | 1.4 | 20.4 | 4.3 | 42 | 103 |
| C | 27 | 0.12 | 298 | 84 | 2.3 | 8.1 | 1.1 | 20.8 | 5.1 | 44 | 104 |
| D | 22 | 0.06 | 373 | 65 | 3.2 | 6.0 | 1.1 | 23.2 | 2.9 | 24 | 118 |
| E | 30 | 0.05 | 206 | 83 | 1.5 | 8.2 | 1.0 | 21.6 | 4.4 | 30 | 93 |
| F | 27 | 0.05 | 109 | 86 | 2.1 | 8.4 | 1.3 | 22.8 | 5.6 | 19 | 89 |
| G | 33 | 0.07 | 180 | 103 | 1.3 | 9.0 | <.5 | 20.4 | 5.7 | 21 | 93 |
| H | 25 | 0.06 | 206 | 94 | 1.5 | 9.0 | 0.7 | 21.7 | 5.1 | 24 | 91 |
| I | 31 | 0.05 | 101 | 94 | 1.0 | 9.2 | 1.2 | 22.0 | 4.6 | 13 | 79 |
| J | 14 | 0.04 | 70 | 73 | 1.1 | 7.4 | <.6 | 23.0 | 5.3 | 7 | 76 |
| K | 12 | 0.04 | 90 | 69 | 2.5 | 4.8 | <.5 | 26.8 | 3.0 | 6 | 95 |
| L | 34 | 0.06 | 167 | 89 | 1.5 | 9.0 | 1.3 | 21.3 | 5.3 | 14 | 98 |
| M | 12 | 0.05 | 105 | 71 | 1.0 | 5.9 | <.5 | 25.8 | 2.9 | 10 | 95 |
| L.C. AVG. | 23.6 | 0.03 | 187 | 79.4 | 2.35 | 7.38 | 0.7 | 22.7 | 4.33 | 21.9 | 95 |
| L.M. AVG. | 24 | 0.07 | 40 | 85 | 1.1 | 6.6 | 1.2 | 31.4 | 3.7 | | 132 |

Appendix 1. Continued.

| | Ta | Tb | Th | Ti | Tl | U | V | W | Yb | Zn (%) | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 0.3 | 0.26 | 3.2 | 0.16 | 6 | 1.4 | 25 | 1.0 | 1.1 | 199 | 86 |
| B | 0.6 | 0.46 | 6.0 | 0.31 | 7 | 2.3 | 37 | 1.7 | 1.9 | 591 | 131 |
| C | 0.7 | 0.54 | 7.2 | 0.35 | 5 | 4.0 | 60 | 2.1 | 2.5 | 599 | 141 |
| D | 0.5 | 0.36 | 4.9 | 0.24 | 8 | 3.0 | 35 | 2.5 | 1.5 | 482 | 115 |
| E | 0.7 | 0.60 | 7.2 | 0.35 | 8 | 4.0 | 36 | 1.7 | 2.3 | 371 | 159 |
| F | 0.7 | 0.50 | 7.3 | 0.40 | 8 | 4.0 | 44 | 2.0 | 2.2 | 241 | 166 |
| G | 0.8 | 0.60 | 8.2 | 0.36 | 7 | 4.0 | 68 | 2.0 | 1.5 | 389 | 168 |
| H | 0.8 | 0.80 | 7.7 | 0.38 | 4 | 4.0 | 76 | 1.8 | 1.6 | 436 | 166 |
| I | 0.8 | 0.60 | 7.8 | 0.38 | 6 | 5.0 | 76 | 1.7 | 2.7 | 217 | 179 |
| J | 0.7 | 0.50 | 6.6 | 0.32 | 7 | 5.0 | 39 | 1.0 | 2.4 | 110 | 179 |
| K | 0.4 | 0.40 | 3.9 | 0.18 | 7 | 3.0 | 37 | 1.5 | 0.9 | 156 | 103 |
| L | 0.7 | 0.50 | 7.7 | 0.37 | 5 | 3.5 | 68 | 1.8 | 1.6 | 423 | 161 |
| M | 0.4 | 0.40 | 5.0 | 0.24 | 3 | 3.0 | 30 | 1.7 | 1.9 | 229 | 150 |
| L.C. AVG. | 0.62 | 0.50 | 6.36 | 0.19 | 6.23 | 3.55 | 48.5 | 1.73 | 1.85 | 341.0 | 146 |
| L.M. AVG. | 0.5 | 0.5 | 5.8 | 0.18 | | | | 1.1 | 1.7 | 97 | 138 |

Appendix 2. Concentrations of total carbon, inorganic carbon, and organic carbon in Lake Calumet surficial sediments from 37 stations.

| | CARBON | | |
|---|---|---|---|
| STATIONS | AVG TC (%) | AVG INC (%) | OC (%) |
| L-1 | 5.4 | 2.7 | 2.7 |
| L-2 | 5.4 | 2.8 | 2.6 |
| L-3 | 5.5 | 3.5 | 2.0 |
| L-4 | 4.3 | 2.7 | 1.6 |
| L-5 | 5.7 | 3.1 | 2.6 |
| L-6 | 5.5 | 2.8 | 2.7 |
| L-7 | 5.8 | 2.8 | 3.0 |
| L-8 | 6.5 | 2.9 | 3.6 |
| L-9 | 5.4 | 2.8 | 2.6 |
| L-10 | 5.9 | 2.8 | 3.1 |
| L-11 | 5.4 | 2.7 | 2.7 |
| L-12 | 4.5 | 2.8 | 1.7 |
| L-13 | 5.2 | 3.4 | 1.8 |
| L-14 | 3.2 | 2.1 | 1.1 |
| L-15 | 4.9 | 2.7 | 2.2 |
| L-16 | 4.1 | 2.5 | 1.6 |
| L-17 | 6.0 | 2.5 | 3.5 |
| L-18 | 5.8 | 2.6 | 2.4 |
| L-19 | 4.2 | 2.3 | 1.9 |
| L-20 | 5.9 | 2.3 | 2.6 |
| W-4 | 8.6 | 3.1 | 5.5 |
| W-5 | 9.0 | 3.4 | 5.6 |
| W-6 | 9.0 | 3.6 | 5.4 |
| W-7 | 9.0 | 3.3 | 5.7 |
| A | 5.5 | 2.7 | 2.8 |
| B | 8.1 | 3.3 | 4.8 |
| C | 7.2 | 2.8 | 4.4 |
| D | 6.6 | 3.3 | 3.3 |
| E | 6.2 | 3.2 | 3.0 |
| F | 5.4 | 2.9 | 2.5 |
| G | 6.2 | 3.0 | 3.2 |
| H | 6.0 | 2.9 | 3.1 |
| I | 5.4 | 2.9 | 2.5 |
| J | 4.8 | 3.3 | 1.5 |
| K | 4.2 | 2.6 | 1.6 |
| L | 5.8 | 2.9 | 2.9 |
| M | 4.6 | 2.5 | 2.1 |

Appendix 3. Elemental analysis of Lake Calumet surficial sediments from 24 stations taken on April 28, 1987.

| STATION | ELEMENTS | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ag | Al % | As | B | Ba | Be | Br | Ca % | Cd | Ce | Co | Cr |
| LCAL 1 | <1 | 10.92 | 21 | 80 | 383 | <1 | 5 | 7.96 | <2 | 67 | 21 | 127 |
| LCAL 2 | <1 | 11.30 | 20 | 93 | 377 | <1 | 5 | 8.67 | <2 | 49 | 16 | 88 |
| LCAL 3 | <1 | 10.86 | 14 | 80 | 406 | <1 | 4 | 12.30 | <2 | 57 | 16 | 84 |
| LCAL 4 | <1 | 10.52 | 15 | 67 | 491 | <1 | 2.5 | 7.84 | <3 | 43 | 14 | 61 |
| LCAL 5 | <1 | 10.42 | 18 | 54 | 450 | 1.2 | 4.2 | 9.55 | <2 | 45 | 15 | 96 |
| LCAL 6 | <1 | 10.63 | 19 | 70 | 454 | 1 | 4 | 8.77 | <2 | 46 | 15 | 86 |
| LCAL 7 | <1 | 10.62 | 19 | 73 | 419 | 1.2 | 3.5 | 8.63 | <2 | 44 | 17 | 93 |
| LCAL 8 | <1 | 8.38 | 21 | 42 | 418 | 1.1 | 4 | 8.01 | <3 | 35 | 14 | 78 |
| LCAL 9 | <1 | 11.56 | 21 | 70 | 448 | 1.2 | 3.8 | 8.43 | <3 | 47 | 18 | 97 |
| LCAL 10 | <1 | 10.46 | 23 | 65 | 439 | 1.1 | 3.5 | 8.31 | <3 | 45 | 16 | 91 |
| LCAL 11 | <1 | 7.50 | 23 | 31 | 421 | <1 | 4 | 7.62 | <3 | 39 | 12 | 63 |
| LCAL 12 | <1 | 11.26 | 22 | 67 | 470 | <1 | 4 | 7.88 | <3 | 43 | 15 | 64 |
| LCAL 13 | <1 | 8.71 | 36 | 58 | 377 | <1 | 3.4 | 8.73 | <3 | 63 | 16 | 64 |
| LCAL 14 | <1 | 6.01 | 23 | 48 | 379 | <1 | 3 | 5.60 | <3 | 31 | 10 | 39 |
| LCAL 15 | <1 | 8.98 | 26 | 53 | 433 | <1 | 3.4 | 6.98 | <3 | 46 | 14 | 66 |
| LCAL 16 | <1 | 6.40 | 33 | 28 | 398 | <1 | 3 | 6.57 | <2 | 30 | 9 | 42 |
| LCAL 17 | <1 | 9.05 | 37 | 50 | 408 | <1 | 3 | 7.11 | <2 | 44 | 14 | 86 |
| LCAL 18 | <1 | 10.30 | 33 | 61 | 434 | <1 | 3.5 | 7.49 | <2 | 42 | 17 | 75 |
| LCAL 19 | <1 | 8.00 | 32 | 41 | 402 | <1 | 2 | 6.36 | <2 | 35 | 12 | 65 |
| LCAL 20 | <1 | 10.06 | 19 | 60 | 401 | <1 | 4 | 8.86 | <3 | 52 | 15 | 76 |
| WCAL 4 | <1 | 9.42 | 15 | 65 | 435 | <1 | 16 | 11.58 | <3 | 52 | 16 | 111 |
| WCAL 5 | <1 | 9.69 | 13 | 63 | 443 | <1 | 22 | 13.23 | <3 | 55 | 17 | 121 |
| WCAL 6 | <1 | 8.88 | 15 | 60 | 432 | <1 | 21 | 14.25 | <3 | 53 | 16 | 116 |
| WCAL 7 | <1 | 6.39 | 16 | 34 | 353 | <1 | 8 | 9.74 | <3 | 44 | 16 | 129 |

| STATION | Cs | Cu | Eu | Fe % | Ga | Ge | Hf | K % | La | Li | Lu | Mg % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LCAL 1 | 9.7 | 73 | 0.74 | 6.85 | 13 | 17 | 5.5 | 3.17 | 26 | 44 | 0.37 | 4.76 |
| LCAL 2 | 7.5 | 48 | 0.92 | 5.85 | 14 | 9 | 4.6 | 3.26 | 29 | 43 | 0.32 | 4.97 |
| LCAL 3 | 6.6 | 36 | 0.74 | 4.82 | 14 | 8 | 4.1 | 3.17 | 26 | 39 | 0.36 | 4.60 |
| LCAL 4 | 5.2 | 34 | 0.87 | 4.62 | 13 | <5 | 5.4 | 3.24 | 23 | 39 | 0.29 | 4.58 |
| LCAL 5 | 6.5 | 56 | 0.82 | 5.97 | 14 | <5 | 4.8 | 2.98 | 24 | 40 | 0.35 | 5.14 |
| LCAL 6 | 6.7 | 51 | 0.89 | 6.12 | 12 | <5 | 4.7 | 3.08 | 24 | 42 | 0.29 | 5.03 |
| LCAL 7 | 7.5 | 53 | 0.85 | 6.64 | 12 | <5 | 5.6 | 2.85 | 25 | 46 | 0.4 | 4.88 |
| LCAL 8 | 4.8 | 58 | 0.73 | 5.65 | 10 | <5 | 4.8 | 2.40 | 19 | 23 | 0.3 | 4.88 |
| LCAL 9 | 8.5 | 72 | 1 | 6.64 | 13 | <5 | 4.6 | 3.09 | 27 | 46 | 0.39 | 4.60 |
| LCAL 10 | 7.8 | 67 | 0.9 | 5.89 | 13 | <5 | 4.9 | 2.96 | 27 | 42 | 0.37 | 4.82 |
| LCAL 11 | 3.9 | 45 | 0.6 | 4.58 | 8 | <5 | 4.5 | 2.28 | 25 | 22 | 0.25 | 4.59 |
| LCAL 12 | 5.2 | 33 | 0.9 | 4.87 | 14 | <5 | 4.2 | 3.29 | 25 | 46 | 0.36 | 5.27 |
| LCAL 13 | 4.7 | 43 | 1.1 | 4.14 | 12 | <5 | 6.2 | 2.88 | 23 | 30 | 0.34 | 5.72 |
| LCAL 14 | 2.8 | 28 | 0.9 | 3.26 | 10 | <5 | 8.2 | 1.92 | 26 | 11 | 0.29 | 3.55 |
| LCAL 15 | 4.4 | 34 | 0.9 | 4.42 | 11 | <5 | 4.9 | 2.92 | 24 | 30 | 0.35 | 4.67 |
| LCAL 16 | 2.6 | 30 | 0.7 | 3.67 | 8 | <5 | 4.1 | 2.06 | 16 | 18 | 0.22 | 4.15 |
| LCAL 17 | 5.9 | 44 | 1 | 5.06 | 12 | <5 | 4.8 | 2.63 | 24 | 31 | 0.3 | 4.40 |
| LCAL 18 | 7 | 50 | 1 | 6.03 | 14 | <5 | 4.5 | 2.92 | 28 | 38 | 0.15 | 4.52 |
| LCAL 19 | 3.8 | 23 | 0.8 | 4.34 | 10 | 8 | 7.6 | 2.48 | 20 | 26 | 0.32 | 4.38 |
| LCAL 20 | 6.2 | 54 | 0.8 | 5.02 | 12 | 10 | 5.4 | 2.90 | 26 | 36 | 0.35 | 5.47 |
| WCAL 4 | 6.5 | 65 | 0.7 | 5.88 | 10 | 9 | 4.2 | 2.82 | 22 | 41 | 0.33 | 4.01 |
| WCAL 5 | 7.1 | 62 | 0.6 | 6.06 | 12 | <5 | 3.8 | 2.93 | 22 | 43 | 0.3 | 3.72 |
| WCAL 6 | 6 | 74 | 0.61 | 7.78 | 10 | <5 | 3.4 | 2.60 | 21 | 37 | 0.26 | 4.04 |
| WCAL 7 | 3.5 | 61 | 0.5 | 14.59 | 9 | 9 | 4.2 | 1.92 | 17 | 24 | 0.26 | 4.82 |

| STATION | Mn % | Mo | Na % | Ni | P % | Pb | Rb | Sb | Sc | Si % | Sm | Sn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LCAL 1 | 0.13 | 31 | 0.55 | 36 | 0.28 | 200 | 127 | 2.7 | 11 | 48.88 | 4.5 | 7 |
| LCAL 2 | 0.15 | 28 | 0.5 | 29 | 0.16 | 170 | 93 | 1.5 | 10 | 48.81 | 4.9 | 7 |
| LCAL 3 | 0.11 | 26 | 0.55 | 28 | 0.15 | 120 | 104 | 1.2 | 10 | 44.79 | 4.3 | 6 |
| LCAL 4 | 0.07 | 22 | 0.62 | 21 | 0.11 | 64 | 105 | 0.9 | 9.2 | 53.89 | 4.4 | 5 |
| LCAL 5 | 0.14 | 20 | 0.55 | 30 | 0.16 | 160 | 87 | 1.2 | 9.3 | 48.53 | 4.6 | 12 |
| LCAL 6 | 0.14 | 21 | 0.55 | 32 | 0.15 | 170 | 98 | 1.3 | 9.5 | 48.62 | 4.6 | 11 |
| LCAL 7 | 0.11 | 20 | 0.58 | 34 | 0.12 | 150 | 94 | 1.3 | 10 | 48.75 | 4.8 | 9 |
| LCAL 8 | 0.09 | 18 | 0.66 | 21 | 0.12 | 130 | 77 | 1.3 | 7.6 | 53.29 | 4 | 9 |
| LCAL 9 | 0.11 | 20 | 0.5 | 42 | 0.12 | 173 | 106 | 2 | 11 | 49.11 | 4.9 | 11 |
| LCAL 10 | 0.11 | 19 | 0.58 | 33 | 0.12 | 183 | 92 | 1.7 | 9.7 | 49.26 | 4.7 | 10 |
| LCAL 11 | 0.09 | 15 | 0.71 | 27 | 0.11 | 127 | 67 | 1.2 | 6.3 | 56.66 | 4.1 | 5 |
| LCAL 12 | 0.11 | 20 | 0.58 | 22 | 0.10 | 91 | 106 | 1 | 9.7 | 51.69 | 4.2 | <5 |
| LCAL 13 | 0.08 | 24 | 1.06 | 21 | 0.09 | 76 | 80 | 1.3 | 8.8 | 52.29 | 4.3 | 6 |
| LCAL 14 | 0.08 | 18 | 0.62 | <15 | 0.08 | 84 | 61 | 0.9 | 5.3 | 66.36 | 5.2 | <5 |
| LCAL 15 | 0.08 | 20 | 0.62 | 19 | 0.09 | 89 | 92 | 1 | 8.2 | 55.63 | 4.4 | <5 |
| LCAL 16 | 0.07 | 15 | 0.8 | <7 | 0.11 | 80 | 62 | 0.7 | 4.6 | 64.84 | 2.9 | <5 |
| LCAL 17 | 0.09 | 20 | 0.63 | 23 | 0.12 | 130 | 88 | 1.4 | 8.3 | 55.90 | 4.5 | 6 |
| LCAL 18 | 0.11 | 24 | 0.61 | 27 | 0.12 | 170 | 68 | 1.4 | 9.2 | 51.44 | 4.9 | 9 |
| LCAL 19 | 0.10 | 22 | 0.69 | 10 | 0.12 | 80 | 77 | 0.9 | 7.3 | 60.17 | 4 | <5 |
| LCAL 20 | 0.11 | 22 | 0.65 | 37 | 0.12 | 165 | 86 | 1.9 | 9 | 49.69 | 4.3 | 11 |
| WCAL 4 | 0.14 | 30 | 0.65 | 37 | 0.16 | 184 | 100 | 4.4 | 9.5 | 40.04 | 3.6 | 7 |
| WCAL 5 | 0.17 | 34 | 0.58 | 48 | 0.17 | 217 | 113 | 3.7 | 10 | 35.52 | 3.6 | 8 |
| WCAL 6 | 0.20 | 31 | 0.55 | 36 | 0.18 | 242 | 95 | 3.5 | 8.7 | 35.06 | 3.4 | 8 |
| WCAL 7 | 0.17 | 36 | 0.59 | 45 | 0.12 | 194 | 65 | 2.8 | 6.5 | 40.56 | 2.9 | 7 |

| STATION | Sr | Ta | Tb | Th | Ti % | Tl | U | V | W | Yb | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LCAL 1 | 89 | 0.8 | 0.7 | 9 | 0.58 | 8 | 3.6 | 79 | 1.6 | 2 | 543 | 149 |
| LCAL 2 | 90 | 0.7 | 0.7 | 7.9 | 0.60 | 7 | 4.3 | 76 | 2.2 | 2.5 | 453 | 139 |
| LCAL 3 | 123 | 0.8 | 0.5 | 7.9 | 0.54 | 4 | 4.3 | 12 | 1.6 | 2.3 | 251 | 123 |
| LCAL 4 | 106 | 0.7 | 0.4 | 7.1 | 0.47 | 8 | 3.9 | 48 | 1 | 1.6 | 124 | 159 |
| LCAL 5 | 105 | 0.7 | 0.8 | 7.3 | 0.55 | 9 | 3.3 | 54 | 2 | 1.6 | 361 | 165 |
| LCAL 6 | 100 | 0.8 | 0.5 | 7.5 | 0.56 | 9 | 3.6 | 60 | 1.9 | 1.5 | 379 | 162 |
| LCAL 7 | 106 | 0.9 | 0.7 | 8.7 | 0.60 | 5 | 5.8 | 50 | 1.8 | 2.8 | 363 | 182 |
| LCAL 8 | 99 | 0.5 | 0.5 | 5.8 | 0.43 | 9 | 3.5 | 34 | 1.3 | 2 | 380 | 175 |
| LCAL 9 | 105 | 0.8 | 0.7 | 8 | 0.63 | 6 | 6.2 | 56 | 2.3 | 2.9 | 409 | 166 |
| LCAL 10 | 95 | 0.7 | 0.7 | 7.2 | 0.57 | 6 | 4.4 | 60 | 1.5 | 2.4 | 388 | 165 |
| LCAL 11 | 96 | 0.5 | 0.4 | 6.8 | 0.40 | 8 | 3 | 26 | 1.7 | 1.7 | 320 | 170 |
| LCAL 12 | 87 | 0.7 | 0.5 | 7.2 | 0.52 | 5 | 4.7 | 43 | 1.5 | 2.3 | 84 | 144 |
| LCAL 13 | 79 | 0.7 | 0.6 | 7.6 | 0.54 | 6 | ND | 37 | 2.5 | 2.7 | 149 | 190 |
| LCAL 14 | 89 | 0.5 | 0.4 | 4.1 | 0.39 | 6 | 3.6 | 19 | 1.6 | 1.6 | 213 | 165 |
| LCAL 15 | 87 | 0.7 | 0.5 | 7.3 | 0.49 | 5 | 4 | 37 | 1.8 | 2.1 | 239 | 170 |
| LCAL 16 | 97 | 0.3 | 0.4 | 4.6 | 0.30 | 5 | 2 | 23 | 2.2 | 1.4 | 228 | 147 |
| LCAL 17 | 90 | 0.7 | 0.5 | 7 | 0.46 | 6 | ND | 44 | 2.4 | 1.9 | 286 | 154 |
| LCAL 18 | 93 | 0.7 | 0.7 | 6.9 | 0.55 | 6 | 2.9 | 54 | 2 | 1.4 | 349 | 168 |
| LCAL 19 | 88 | 0.5 | 0.4 | 5.5 | 0.46 | 4 | 2.9 | 34 | 1.8 | 1.7 | 132 | 177 |
| LCAL 20 | 87 | 0.7 | 0.6 | 7.2 | 0.56 | 7 | 2 | 37 | 1.7 | 1.7 | 299 | 171 |
| WCAL 4 | 173 | 0.7 | 0.6 | 7.1 | 0.44 | 4 | 5 | 38 | 1.4 | 1.5 | 268 | 117 |
| WCAL 5 | 196 | 0.7 | 0.5 | 7.4 | 0.44 | 8 | 3.6 | 53 | 2 | 1.6 | 543 | 99 |
| WCAL 6 | 225 | 0.6 | 0.4 | 6.6 | 0.43 | 6 | 4.3 | 30 | 2.2 | 1.5 | 684 | 106 |
| WCAL 7 | 121 | 0.4 | 0.7 | 5.2 | 0.32 | 4 | 5.8 | 20 | 2.3 | 1.2 | 500 | 113 |

Appendix 4. Orthogonally rotated factor matrix for elements in Lake Calumet sediments.

| | FACTOR 1 | FACTOR 2 | FACTOR 3 | FACTOR 4 | FACTOR 5 |
|---|---|---|---|---|---|
| SC | .95613 | .21176 | -.08080 | .08223 | .00417 |
| TH | .93768 | .09399 | .02158 | .10213 | .16104 |
| TA | .93479 | .02645 | .05125 | .00813 | .16710 |
| AL2O3 | .93242 | .08459 | -.08890 | -.12088 | -.04743 |
| LI | .91412 | .26794 | .07080 | -.09628 | .09851 |
| CS | .91084 | .23883 | .12500 | .05463 | -.11242 |
| K2O | .90996 | -.02351 | -.09846 | -.24722 | .18507 |
| TIO2 | .87151 | -.14318 | .24128 | .00646 | .32516 |
| RB | .85826 | .26072 | -.17340 | -.06853 | -.16185 |
| CO | .83404 | .30983 | -.09444 | .35083 | .03495 |
| B | .82665 | .09328 | -.32882 | .07869 | -.15631 |
| GA | .81492 | -.10290 | .07819 | -.06160 | -.21741 |
| LA | .78964 | -.18881 | .27791 | .02958 | .25776 |
| SM | .76951 | -.34172 | .23129 | .12820 | .28827 |
| CE | .75760 | .33449 | -.10568 | .20378 | .19767 |
| NA2O | -.74332 | -.35996 | -.10567 | -.00847 | -.33045 |
| V | .73129 | -.02938 | .31357 | -.10137 | -.04421 |
| LU | .72245 | -.06269 | -.02897 | .24280 | .12638 |
| TB | .66132 | .08350 | .17090 | .41247 | .12601 |
| EU | .65764 | -.52182 | .19100 | .17869 | .16979 |
| YB | .55544 | -.22171 | -.00308 | .17508 | .39633 |
| TOTC | .02012 | .90136 | .28173 | .14466 | .11669 |
| BR | -.05584 | .88813 | -.06993 | .00300 | -.19503 |
| CAO | .14007 | .86626 | .04911 | -.17659 | .24728 |
| SR | -.05534 | .86495 | -.13759 | -.00236 | -.26102 |
| ORGC | -.01507 | .85565 | .35206 | .18629 | -.02728 |
| SB | -.01343 | .84641 | .11024 | .03658 | -.10738 |
| SIO2 | -.38344 | -.83861 | -.13232 | .02658 | -.29431 |
| MNO | .12048 | .83762 | -.00433 | .07640 | .00775 |
| NI | .24524 | .76065 | -.17736 | .35027 | -.01182 |
| CR | .42195 | .74828 | .35167 | .24116 | -.04000 |
| ZN | .17155 | .74125 | .55142 | .14445 | -.14137 |
| INC | .13824 | .70419 | -.08325 | -.06255 | .58611 |
| ZR | .41487 | -.69019 | .03206 | .32693 | .24057 |
| HF | .17456 | -.60192 | .05640 | .43132 | -.02298 |
| MO | .17060 | .53906 | .09844 | .03816 | .45772 |
| AS | -.05078 | -.38642 | .81106 | .07912 | .00126 |
| SN | -.10705 | .13517 | .80079 | -.38267 | .31638 |
| CU | .25914 | .51107 | .73444 | .01835 | .12492 |
| PB | -.04999 | .60785 | .66956 | -.20067 | .05070 |
| P2O5 | .24180 | .47096 | .60891 | -.19900 | -.17592 |
| BA | -.11689 | .15005 | .41630 | -.73546 | -.00778 |
| FE2O3 | .16707 | .53721 | -.10453 | .63010 | -.03694 |
| U | .47137 | .19669 | -.18091 | .49556 | .21162 |
| W | .06968 | .17998 | .32941 | .45243 | .02248 |
| TL | .13602 | .02990 | .02988 | -.39005 | .08581 |
| MGO | .26784 | -.20632 | .12827 | -.12874 | .83062 |

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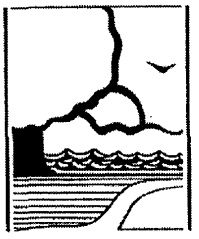

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# Acknowledgements

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# ABSTRACT

An environmental profile of Lake Calumet (Chicago, Cook Co., IL) was constructed from a review of technical reports, newspaper articles, and historical studies. From this profile, the need for a more complete study of the contamination of the Lake Calumet area was recognized. In Fiscal Year 1987 (FY'87) the Illinois Department of Energy and Natural Resources (DENR), through the Hazardous Waste Research and Information Center (HWRIC), funded a multidisciplinary study involving researchers from the Illinois State Natural History (INHS), Geological (ISGS), and Water Surveys (ISWS) and DePaul University.

The FY'87 study focussed on the various basins within Lake Calumet proper. Study objectives were: (1) determination of the horizontal distribution of metals and organic contaminants in lake sediments; (2) study of the physical transport of contaminants by surface water and ground water; (3) investigation of the fugacity of selected organic compounds in sediments and water; (4) determination of microbial degradation rates of toxic organic compounds; (5) estimation of metal bioaccumulation rates in macrophytes; and, (6) assessment of overall sediment toxicity by laboratory and field biosssays. Sediment samples were collected at 33 stations within the lake.

Principal findings of this study are: (1) concentrations of toxic metals and organics are generally far above background levels and higher than in nearby water bodies; (2) surface drainage into the lake is entirely through man-made channels; (3) wind-driven resuspension of sediment particles is continual; (4) methane production in sediments confirms the presence of anaerobic microbial communities, which are more numerous in near-shore areas; (5) macrophyte species known to be bioaccumulators of heavy metals were found; (6) all sediment sampling stations produced toxic responses in single-species bioassays, with over half the stations classified as "highly toxic"; and, (7) community-level bioassays showed toxic effects at 71% of the stations.

These results suggest that Lake Calumet is a severely disturbed ecosystem that may present a danger to the surrounding community. The investigators recommend further research in the areas of sediment chemistry and toxicology, groundwater hydrology and chemistry, sediment resuspension, historical loading (isotope studies), bioaccumulation, literature and database searching, atmospheric deposition, and risk assessment. In particular, the database should be expanded to include stations from wetlands, ponds, and small streams within the Lake Calumet drainage basin. The level of effort required to respond to all of the above recommendations would be considerably higher than that allotted in FY'87.

# Executive Summary

Lake Calumet, located 15 miles south of downtown Chicago, is the vestige of a huge lake formed approximately 13,500 years ago from the meltwater of retreating glaciers. The prehistoric lake (which covered the area of present-day Chicago) receded, leaving a low, flat plain with a poorly developed drainage pattern. Stony Island, a rocky outcrop north of Lake Calumet, prevented the deposition of course materials that eventually would have filled in the lake. Instead, fine silt and clays and later organic sediments accumulated in the lake bottom.

Although the high water table and flat, low topography provided an inadequate site for large-scale construction, entrepreneurs in 1869 promoted the Calumet area as an unequaled location for industrial development. Proximity to water for shipping and processing, to railroads for inland transport, and to many potential and expanding markets overshadowed the natural flaws of the area for many industrialists, particularly iron and steel manufacturers.

After a century of industrialization, Lake Calumet's surface area has been substantially reduced. Some of the lake has been filled in with landfills and some "improved" for navigation. The east side of the lake is currently lined with waste disposal facilities, and the west side is bordered by the busy Calumet Expressway (I-94) and a ditch (Pullman Creek) filled with the runoff from the expressway and nearby industries. In addition to the effects of past contamination, Lake Calumet is most likely impacted by a variety of non-point toxicant sources: leaching and dispersal from sediments; highway runoff, including spills; surface runoff from industrial properties contiguous to the lake or drainage areas; seepage of contaminated groundwater from dumps, landfills, waste lagoons, and underground storage tanks; rain scour and dust fall; and perhaps illegal dumping.

Lake Calumet has been exposed to a wide range of industrial contaminants for approximately 110 years. Through increasing regulations, some of the pollution has been reduced. Continued industrial activity and residues from past waste disposal practices, however, still threaten the Lake Calumet system.

The study reported here was initiated to evaluate the physical, chemical, and biological processes that influence the environmental quality of Lake Calumet and the surrounding area and to predict the ecological effects of the contamination associated with lake sediments. The objectives for this preliminary environmental assessment of contamination associated with Lake Calumet are as follows:

• To determine the horizontal distribution of concentrations of heavy metals, total organic carbon (TOC), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and phenolic compounds in Lake Calumet sediments;

• To investigate the movement of surface water, sediment, and pollutants in and around Lake Calumet and to define the dynamics of toxic chemicals in the surface water environment;

• To estimate the contributions of contaminants to the lake *via* groundwater seepage;

• To determine the concentration and fugacity of a number of hazardous organic compounds in the sediments and water from different areas of Lake Calumet;

• To determine microbial degradation rates of toxic organics and to isolate the responsible microorganisms;

• To determine if toxic metals in the sediments and water column of Lake Calumet are bioaccumulated in the aquatic plants found in the area; and

• To measure the toxic effect of sediment extracts to single-species assay organisms, *Photobacterium phosphoreum* (Microtox™), *Selenastrum capricornumtum* (green alga), and *Panagrellus redivivus* (nematode), and to the structure and function of microbial communities.

Results of the preliminary assessment include:

• High concentrations of anthropogenic metals and polycyclic aromatic hydrocarbons (PAHs) were found in Lake Calumet sediments. These concentrations were generally higher than sediment samples in nearby waters.

• In an evaluation of surface water in Lake Calumet, no natural drainage channels were observed. Pullman Creek, a smaller channel in the NE portion of the lake, and two storm sewers are the existing man-made drainage channels for the lake. Pullman Creek is not only a source of inflowing water but also of sediment.

• Organic compounds in the water column were at levels too low for one type of experimental fugacity measurement, but polychlorinated biphenyls were detected in the sediment at levels appropriate for measurement.

• Methane was produced in Lake Calumet sediments, thereby confirming the presence of anaerobic microbial communities. Aerobic and anaerobic bacteria were found in greater numbers at sampling stations near the shoreline of Lake Calumet than at stations in deeper water.

• Lake Calumet wetlands support a population of macrophyte species that have been documented as bioaccumulators of heavy metals.

• Composite toxicity indices (based on the relative toxic responses of *Photobacterium phosphoreum* , *Selenastrum capricornutum* , and *Panagrellus redivivus* ) classified 57% (12/21) of the stations as "highly toxic"; the remainder (43%) were considered "moderately toxic." The toxic responses had a slight statistical correlation with total PAH concentrations in the sediment. Predictions of elutriate chemistry indicate that lead (Pb) might have the potential to exceed water quality standards if released from Lake Calumet sediments.

• Exposure to sediment elutriate from 82% (18/22) of the stations resulted in statistically significant changes in microbial communities with the functional endpoints, photosynthesis and respiration, more sensitive than reduction in numbers of species. Composite toxicity indices (based on the relative toxic responses of functional bioassays) classified 9% of the stations as "extremely toxic," 23% as "highly toxic," 32% as "moderately toxic," and 18% as "weakly toxic"; at 4 stations there was no statistically significant toxic response. Photosynthetic and total microbial community response had strong statistical correlations with metal concentrations in the sediment.

The research described in this study indicates that Lake Calumet is a severely disturbed system. Continued physical alteration has changed the lake's shape, reduced its surface area, and destroyed the surrounding natural wetland areas. Drainage is controlled by man-made channels (e.g., Pullman Creek) and the O'Brien Lock and Dam system. Pullman Creek has been identified as a source of pollutants as well as inflowing water. Chemical compounds common to industry in the Calumet region since the 1870s have concentrated in the sediments of the lake and, consequently, the potential for bioaccumulation in aquatic plants, invertebrates, fish, and perhaps, water fowl and humans is high. Alteration of the aquatic ecosystem through toxic effects of the contaminated sediments is probable.

The presence of waste landfills, major highways, refineries, scrap metal operations, and other industrial activities continues to threaten the Lake Calumet ecosystem. Atmospheric deposition, highway and industrial run-off, and continued alteration of the shoreline and surrounding wetlands may add to the pollution of the lake or induce further sediment disturbance and drainage problems. Changes in the physiochemical nature of the lake by current activities may result in the release of

contaminants deposited in previous years.

Although Lake Calumet seems to be isolated by the O'Brien Lock and Dam and its own sluggish drainage system, its connection with Lake Michigan and with the Illinois River watershed cannot be ignored. Some of the contaminants found in the sediments of Lake Calumet are likely to be found in the soil, water, and air in surrounding areas. The Calumet River and the Cal-Sag Channel may transport contaminants from the lake out of the Calumet region. A ground water connection with the lake is, as yet, unidentified but may play a role in the transport of pollutants in or out of the lake. Resuspension of Lake Calumet sediments is readily accomplished by wind-induced flow and storm events that scour the bottom, transporting sediments to other locations in the lake.

After a year of preliminary study, the investigators feel that further research should be carried out in the following areas:

Continued chemical and toxicological analyses of surface sediment. The existing knowledge base should be expanded in two ways. First, more stations within Lake Calumet proper should be studied to permit greater resolution in contaminant and toxicity mapping. Second, stations in wetlands, ponds, and small streams within the Lake Calumet hydrologic system should be studied in order to gain a more complete understanding of the situation. Special attention should be paid to culverts and drainage ditches leading from past and current industrial or disposal sites into the lake. In addition to chemicals already analyzed, priority pollutant scans should be run on a few selected stations to ensure that important contaminants are not being ignored.

Continued data collection for sediment resuspension. The clearly demonstrated importance of particulate mobilization raises three questions that should be addressed. First, is there a prevalent pattern of particle transport within Lake Calumet? Second, do particles originating in Lake Calumet sediments affect water quality in the Calumet River system and in Lake Michigan? Third, do storm events cause predictable contaminant relocation patterns? More precise data on sediment relocation is needed to answer these questions.

Contaminant input from groundwater. A study of groundwater flow patterns in and around the lake should be undertaken to estimate the importance of continued contaminant input from sub-surface sources.

Historical loading. The historical dimension of contaminant input to the system should be investigated by studying vertical sediment cores at selected stations. Core horizons can be dated by the Cesium-137 or Lead-210 methods, and chemical and toxicological analyses can then be

performed on material deposited in various time periods. The effectiveness of this approach may be compromised if thehigh degree of lateral transport noted above obscures vertical deposition patterns, making historical trends impossible to detect.

Bioaccumulation. The level of bioaccumulatory substances in the sediment justifies analyses of aquatic plants and the initiation of a fish and invertebrate sampling program. Flesh analysis should include metals, PAHs, PCBs, and select pesticides. Fish analysis is especially critical because human consumption of Lake Calumet fish could present a health risk. (During the April 1987 sampling trip, 18 fishermen were seen in one afternoon.)

Literature and data base research. Although a good deal of information has been summarized in the Colten (1985) report and in this document, more sources should be explored. In particular, data from monitoring wells (Illinois Environmental Protection Agency) and internal environmental quality programs (Metropolitan Sanitary District of Greater Chicago) should be accessed.

Atmospheric deposition. In order to complete the study of contamination sources, the role of atmospheric deposition should be evaluated.

Public health. The existing public health data base (Illinois Public Health Dept.) should be re-examined when current studies are completed. These data should be compared with contaminant and toxicological data to determine whether correlations exist. The need for further epidemiological studies should also be evaluated at that time.

## 1.2 Current Environmental Status

Figure 1.3 illustrates the impact on Lake Calumet of over a century of industrialization. Some of the lake has been filled in with landfills and some "improved" for navigation. The east side of the lake is currently lined with waste disposal facilities, and the west side is bordered by the busy Calumet Expressway (I-94) and a ditch (Pullman Creek) filled with the runoff from the expressway and nearby industries. In addition to the effects of past contamination, Lake Calumet is most likely impacted by a variety of non-point toxicant sources: leaching and dispersal from sediments; highway runoff, including spills; surface runoff from industrial properties contiguous to the lake or drainage areas; seepage of contaminated groundwater from dumps, landfills, waste lagoons, and underground storage tanks; rain scour and dust fall; and perhaps illegal dumping (USEPA 1985).

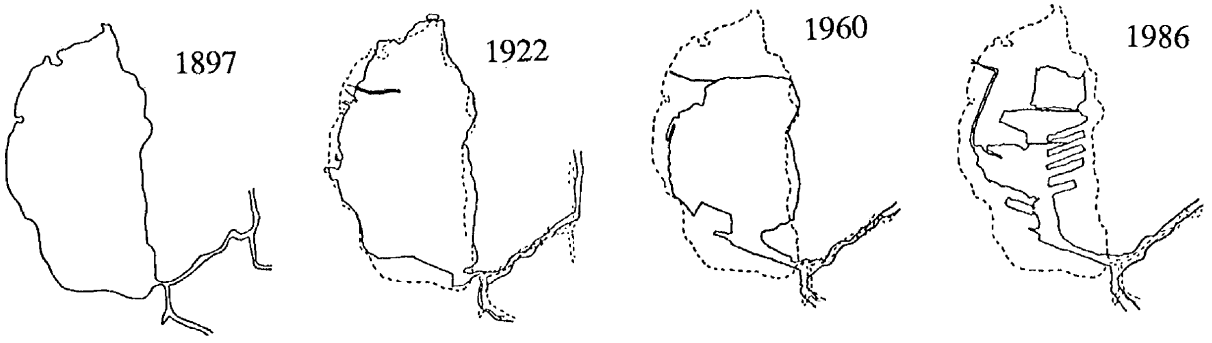


Figure 1.3 Alteration of Lake Calumet: 1897 - 1986.

A 1986 survey of volatile organic compounds (VOC) entering the Calumet Sewage Treatment plant included dichloromethane, 1,1,1-trichloroethane, acetone, isopropanol, toluene, and a vinyl toluene isomer. Dichloromethane, 1,1,1-trichloromethane, acetone, and toluene were also present in large quantities in the primary sludge sampled from the treatment plant (MSDGC, unpublished data ). In a separate study of the VOC component of the Calumet Sewage Treatment Plant influent, Namkung and Rittmann (1986) noted the presence of benzene, chlorobenzene, chloroform, 1,2-dichlorethane, ethylbenzene, methylene chloride, tetrachlorethylene, toluene, 1,1,1-trichloroethane, 1,2-*trans* -dichloroethylene, and trichloroethylene. Industries dealing with petroleum refining, gum and wood chemicals, metal degreasing , or dry cleaning may be sources of VOCs in the Calumet area because of the large amounts of toluene and benzene in the Calumet Treatment Plant influent (Namkung and Rittmann 1986).

extensive habitat modifications. Table 1.3 also lists the fish species recorded from the Lake Calumet area from 1876 to 1980 by various authors. A comparison of the current species with historical records shows a relative reduction in diversity over time in the lake. The current fish community in Lake Calumet, however, remains diverse. A score of 48 was calculated for the lake based on Karr's index of integrity (Karr 1981) to evaluate the quality of the fish fauna. This score is comparable to scores obtained for the Fox River and falls within the "good" range (Greenfield and Rogner 1984).

Five species of birds listed on the Illinois endangered list but not on the Federal list have been found in the Lake Calumet area: yellow rail, black-crowned night heron, American bittern, red-shouldered hawk, and marsh hawk (Equitable Environmental Health 1978). Continued habitat degradation and contaminated food could affect the future status of these birds.

Sediment sampling parameters from four sampling stations on nearby rivers and a lake (Figure 1.4) exposed to similar environmental conditions as Lake Calumet are listed in Table 1.4. Sediment quality criteria and standards are currently being developed by the USEPA. Until these standards are published, pollutant concentrations can be compared to background levels from a statewide chemical survey of Illinois sediments (Kelly and Hite 1979). The concentrations determined for each compound in Table 1.4 are assigned a value based on the relative level of elevation over this background (Table 1.5).

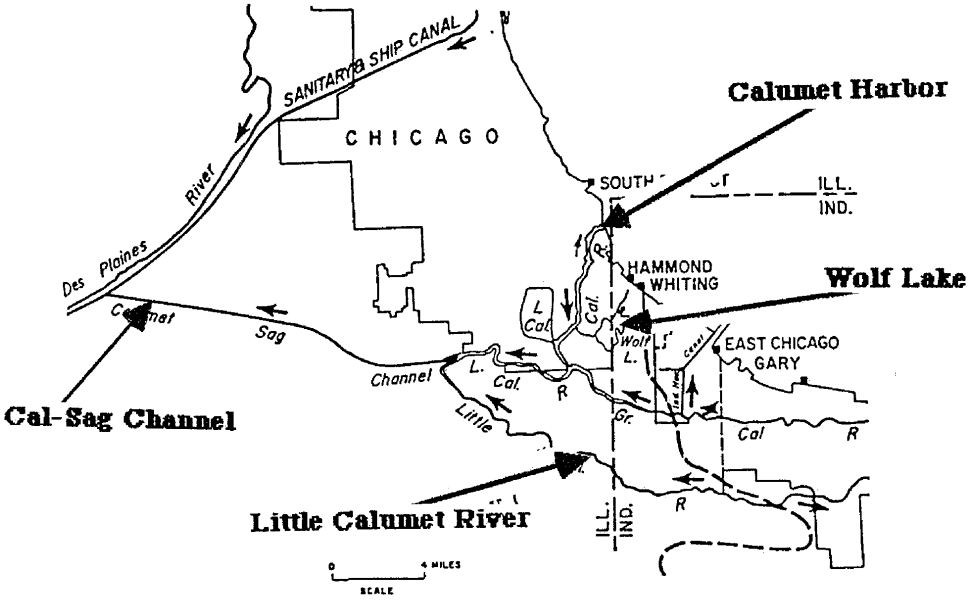


Figure 1.4 Stations sampled for sediment chemistry near Lake Calumet.

carbon (Table 3.3). Cahill and Shimp (1984) found similar correlations with organic carbon for these elements in Lake Michigan sediments, and they concluded that the accumulation of these elements was related to organic-rich, fine-grained sedimentation.

Bromine, which has average values about 8 times lower than those reported for Lake Michigan sediments (Table 3.2), has a moderately positive (0.62) correlation with organic carbon. However, the distubution of bromine is somewhat puzzling. The highest values occur at stations A, B, and D while concentrations in sediments from the other stations are well within normal background levels.

Sodium levels are approximately the same as values reported for Lake Michigan (Cahill 1981). The high values of 610 ppm and 550 ppm found at stations A and D, respectively, are probably from the use of road salt during the winter. Inexplicably, the highest value (620 ppm) was recorded at station K which incidentally also had very high toxicity levels (Chapter 8).

Concentration values of major, minor, and trace elements from the sediment samples collected in April 1987 (stations LCAL 1-20 and WCAL 4-7) and from sediments collected in November 1986 (stations A-M),were treated statistically using factor analyses to summarize relationships between variables in a factor matrix (Appendix 4).These elemental relationships grouped into five factors which can be attributed to specific sources and associations (Table 3.4).

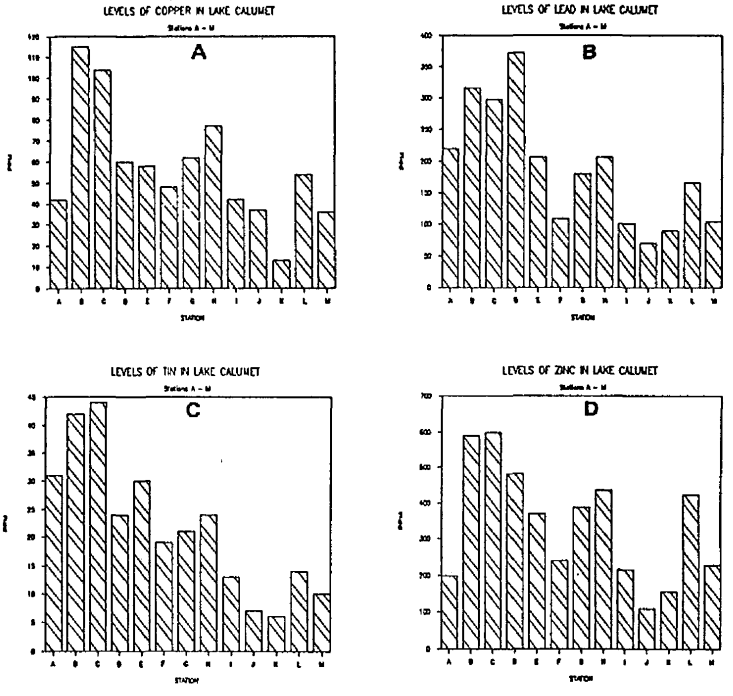


Figure 3.2. Concentrations of copper (A), lead (B), tin (C), and zinc (D) in dried sediments from 13 sampling stations at Lake Calumet.

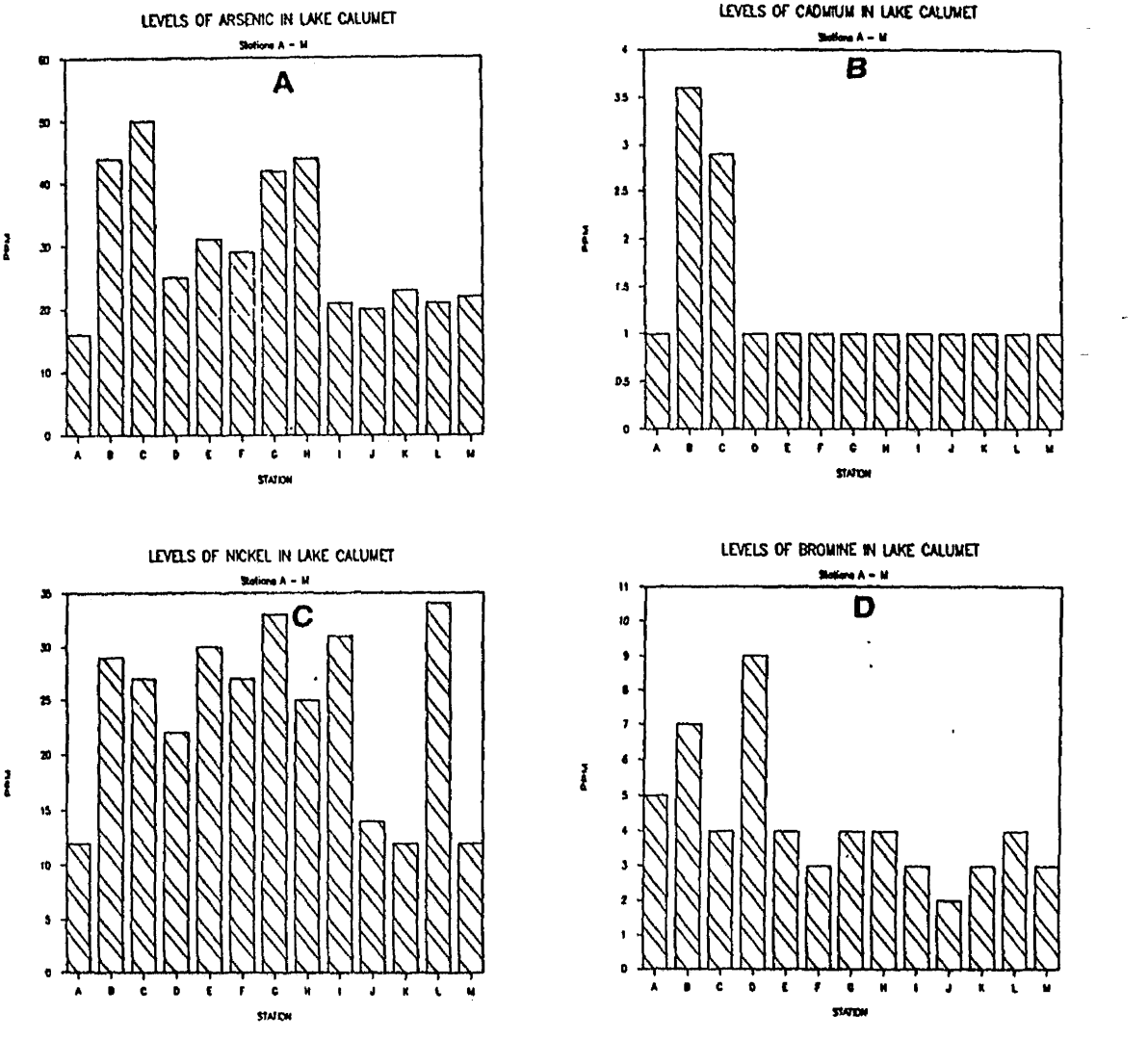


Figure 3.3. Concentrations of arsenic (A), cadmium (B), nickel (C), and bromine (D) in dried sediments from 13 sampling stations at Lake Calumet.

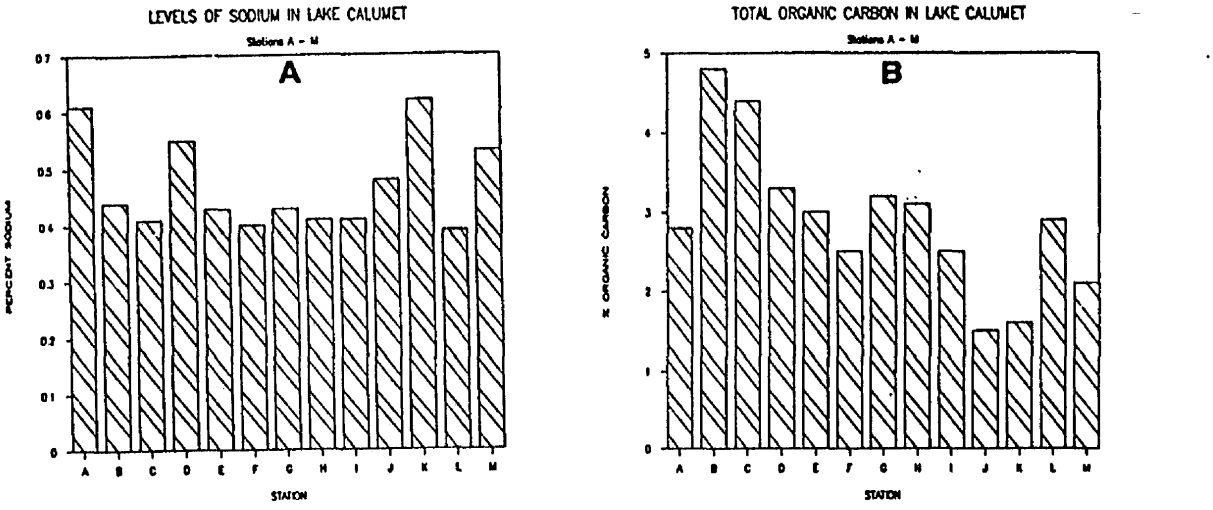


Figure 3.4. Concentrations of sodium (A) and total organic carbon (B) in dried sediments from 13 sampling stations at Lake Calumet.

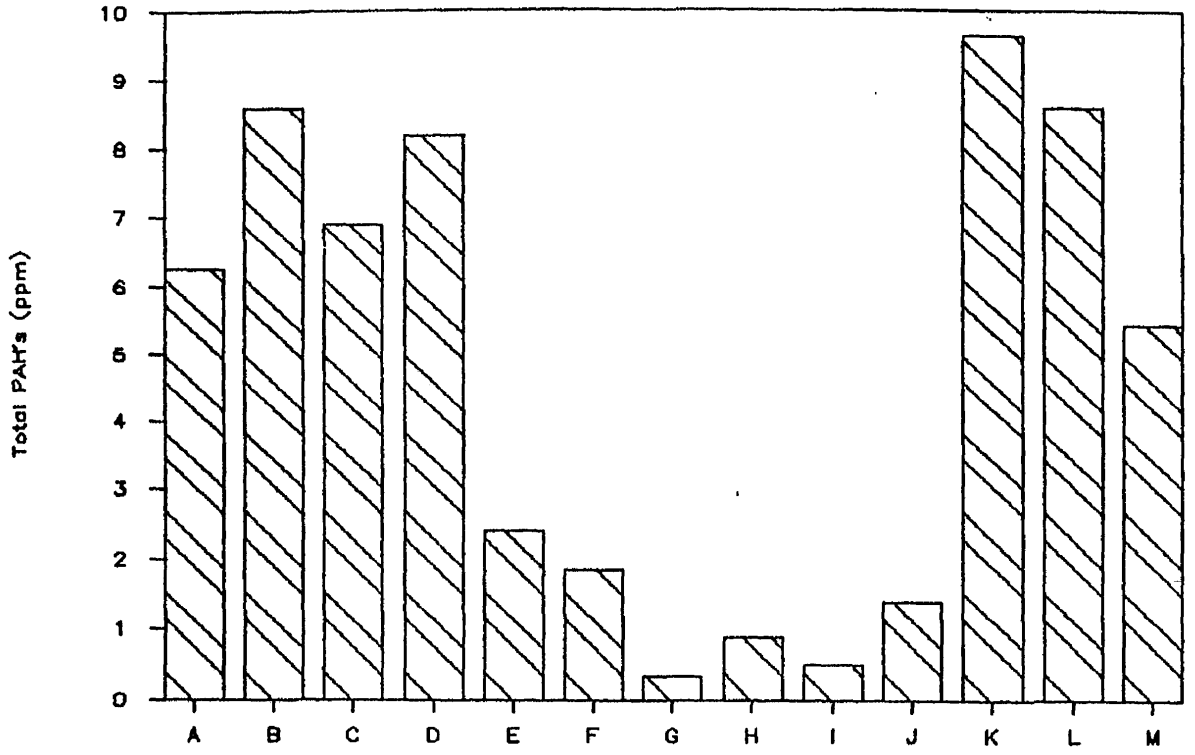


Figure 3.8. Concentrations of PAHs in dried sediments from 13 sampling stations in Lake Calumet.

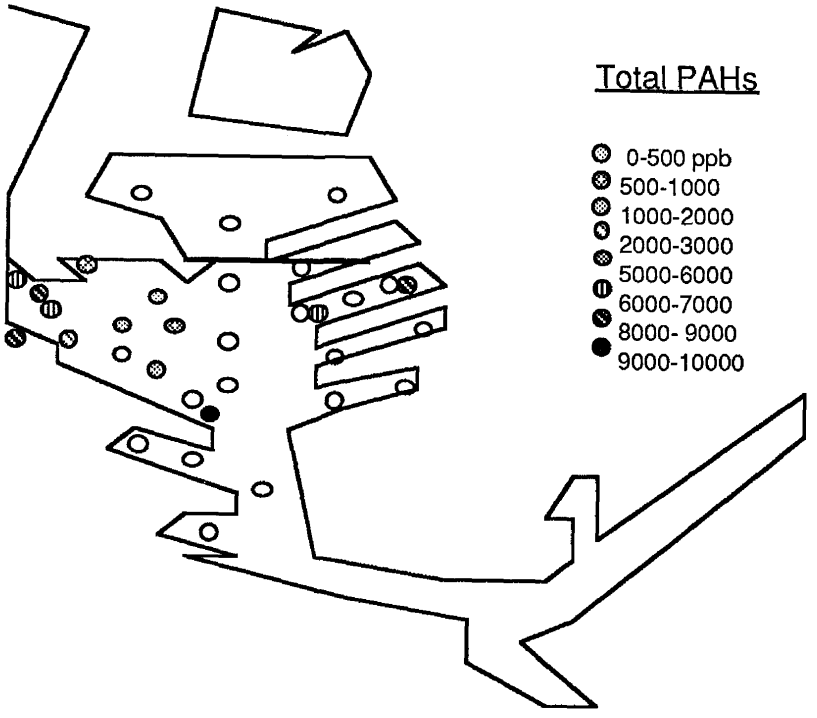


Figure 3.9. Distributions of PAHs in Lake Calumet sediments.

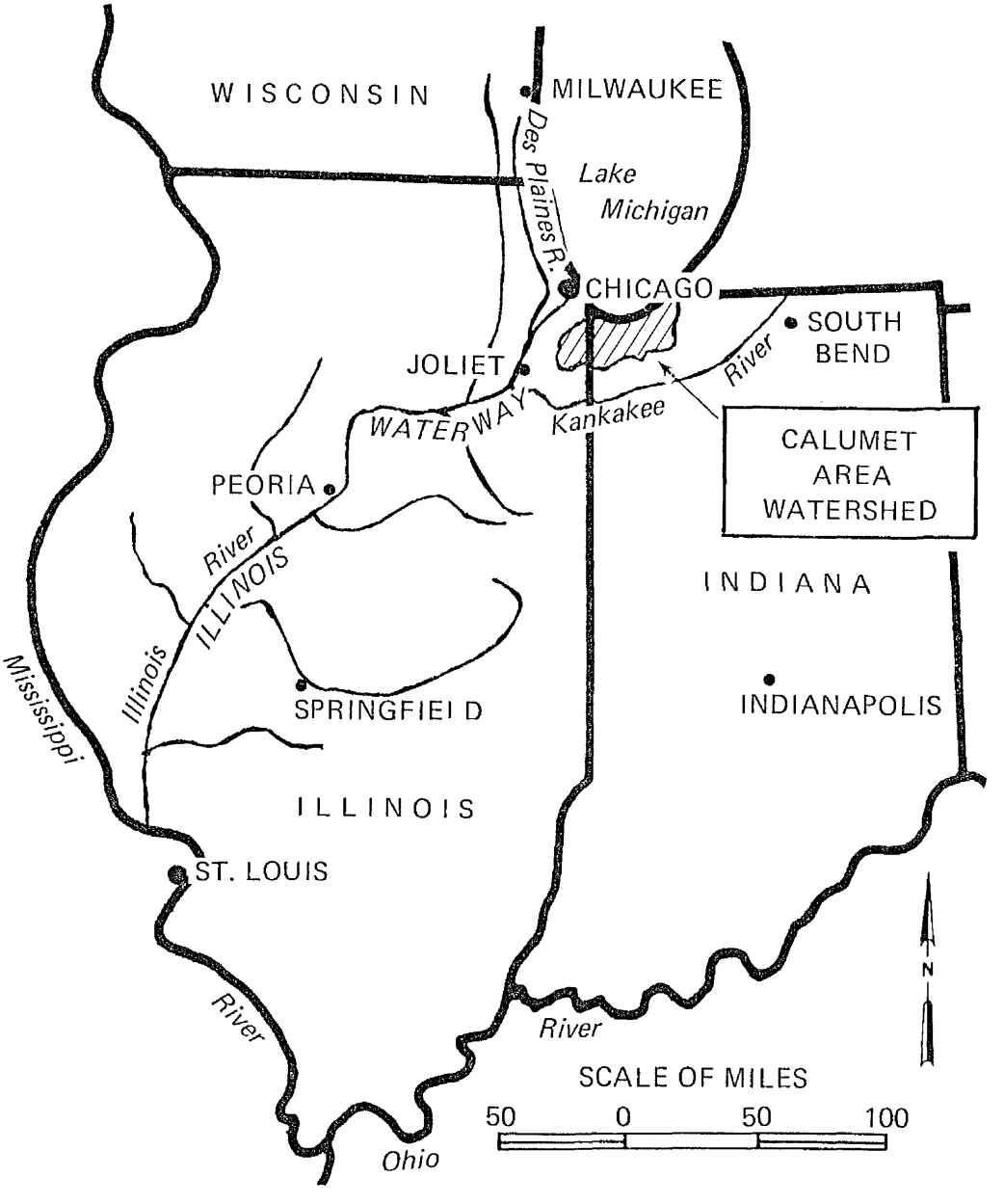


Figure 4.1. Location of Calumet area.

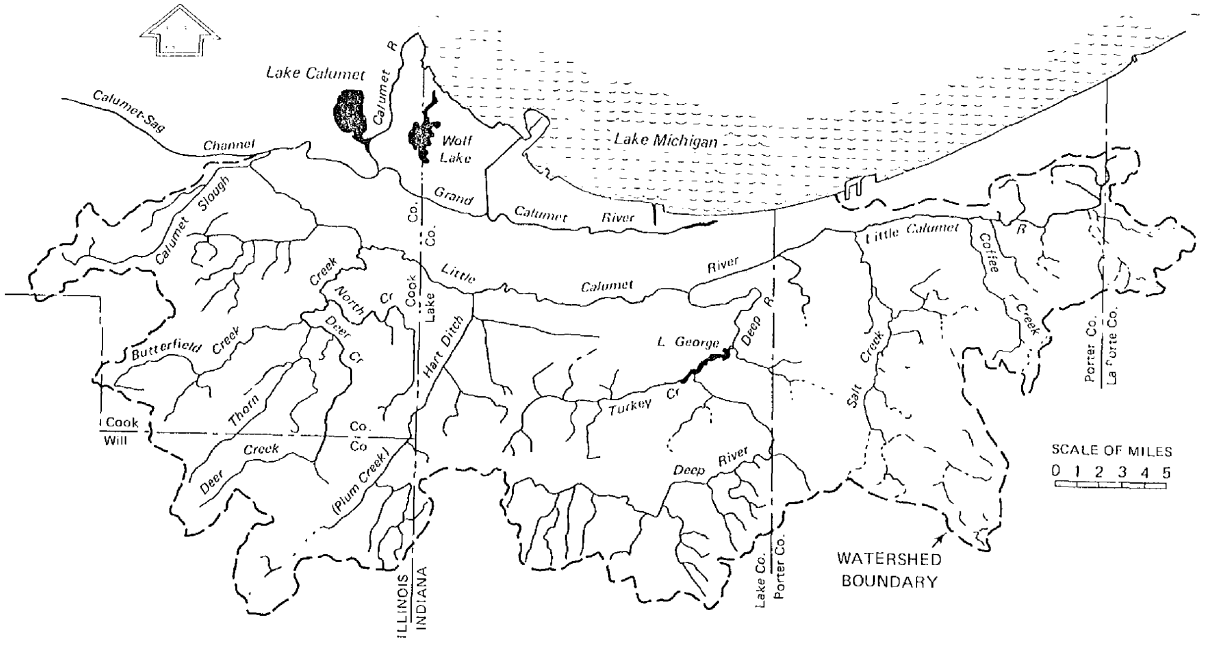


Figure 4.2. Streams and drainage pattern in the Calumet area watershed.

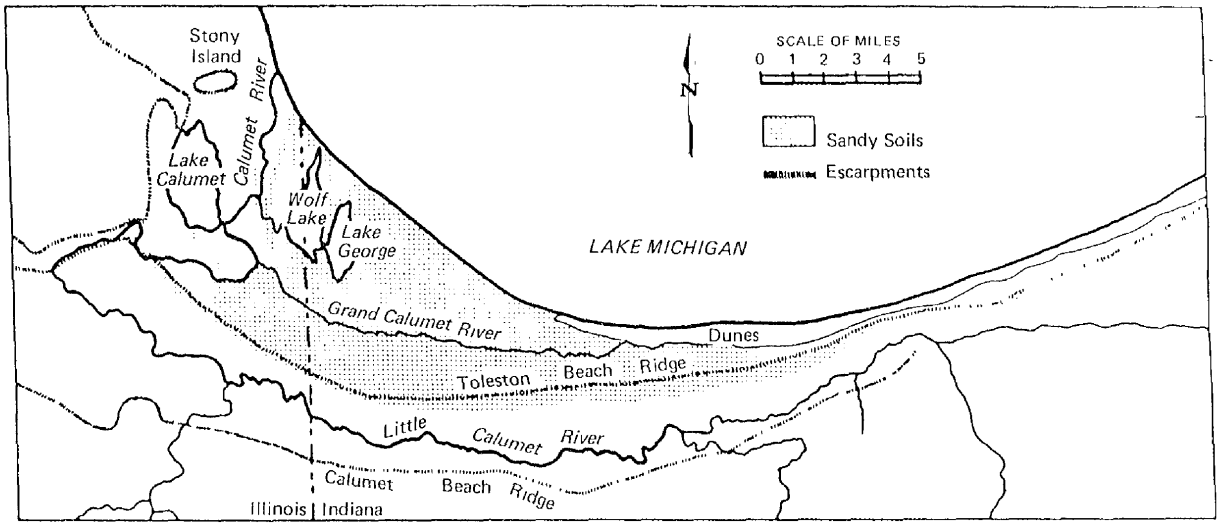


Figure 4.3 Topographic features of the Calumet area.

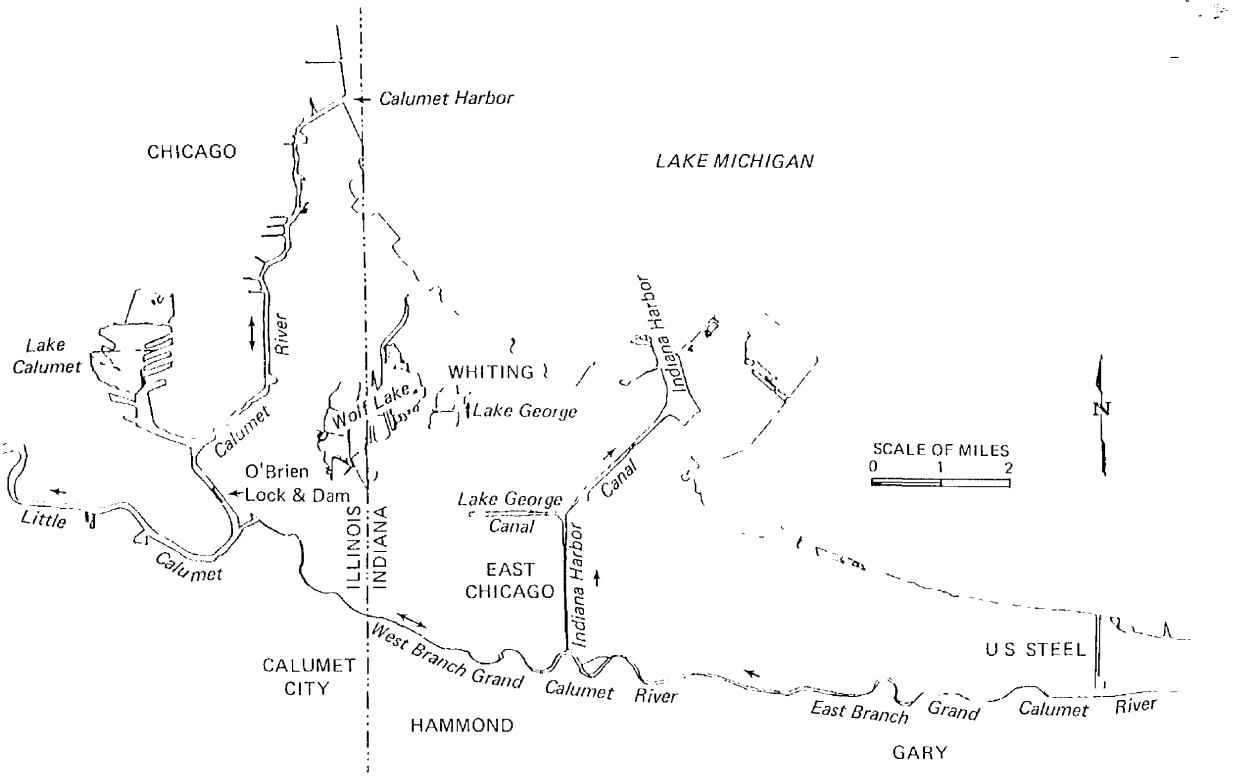


Figure 4.4. Stream channels and flow directions in the Lake Calumet, Calumet, and Grand Calumet Rivers and Indiana Harbor area.

dilution factors between concentrations in Indiana Canal concentrations offshore. The dilution factors were 5 and 10 at distances of 1 and 3 miles, respectively, from the mouth of Indiana Harbor. However, the accumulation of pollutants in the near-shore sediments of Lake Michigan has not been investigated in detail.

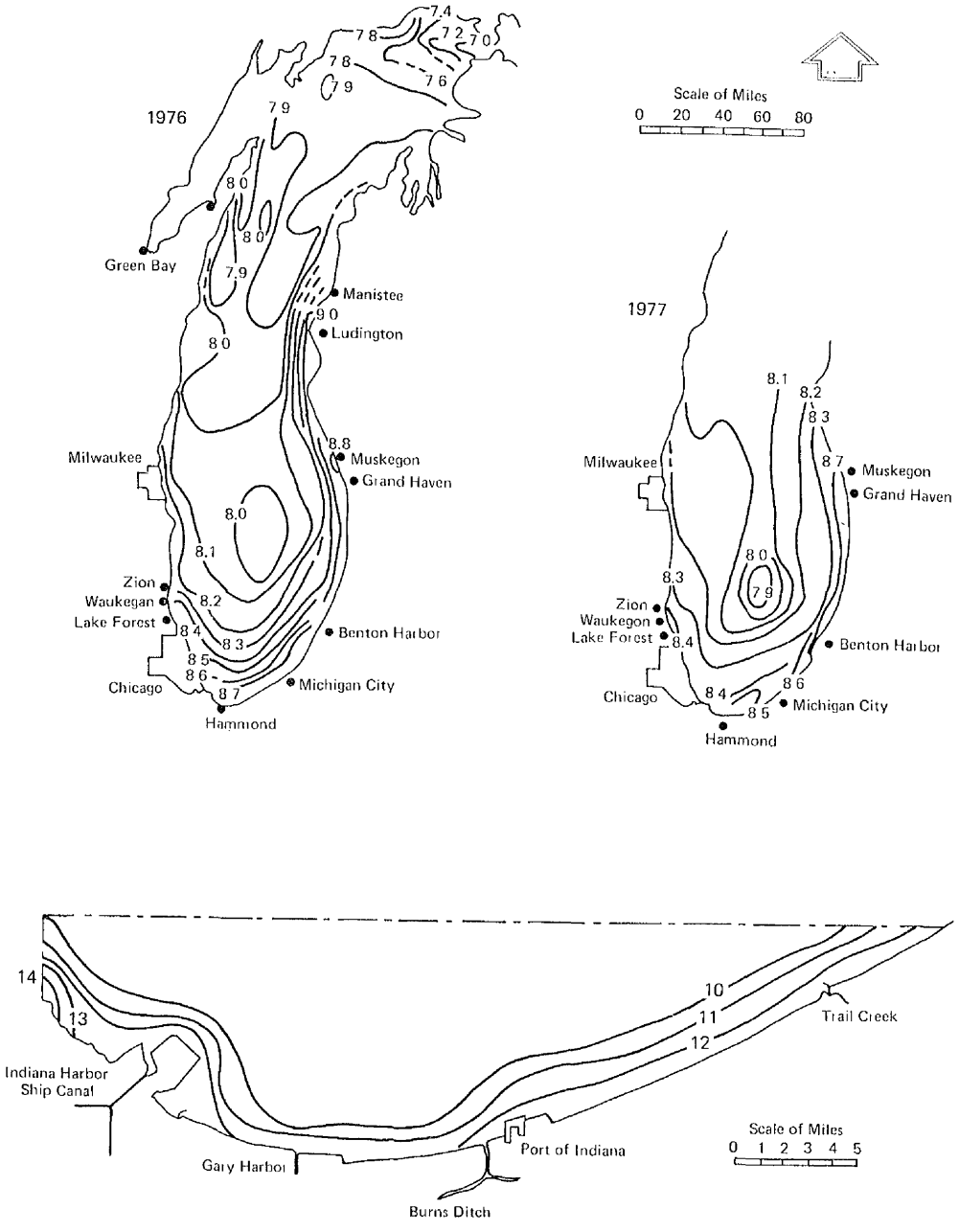


Figure 4.5. Concentrations of chlorides in mg $L^{-1}$ in Lake Michigan (Hydroqual 1985).

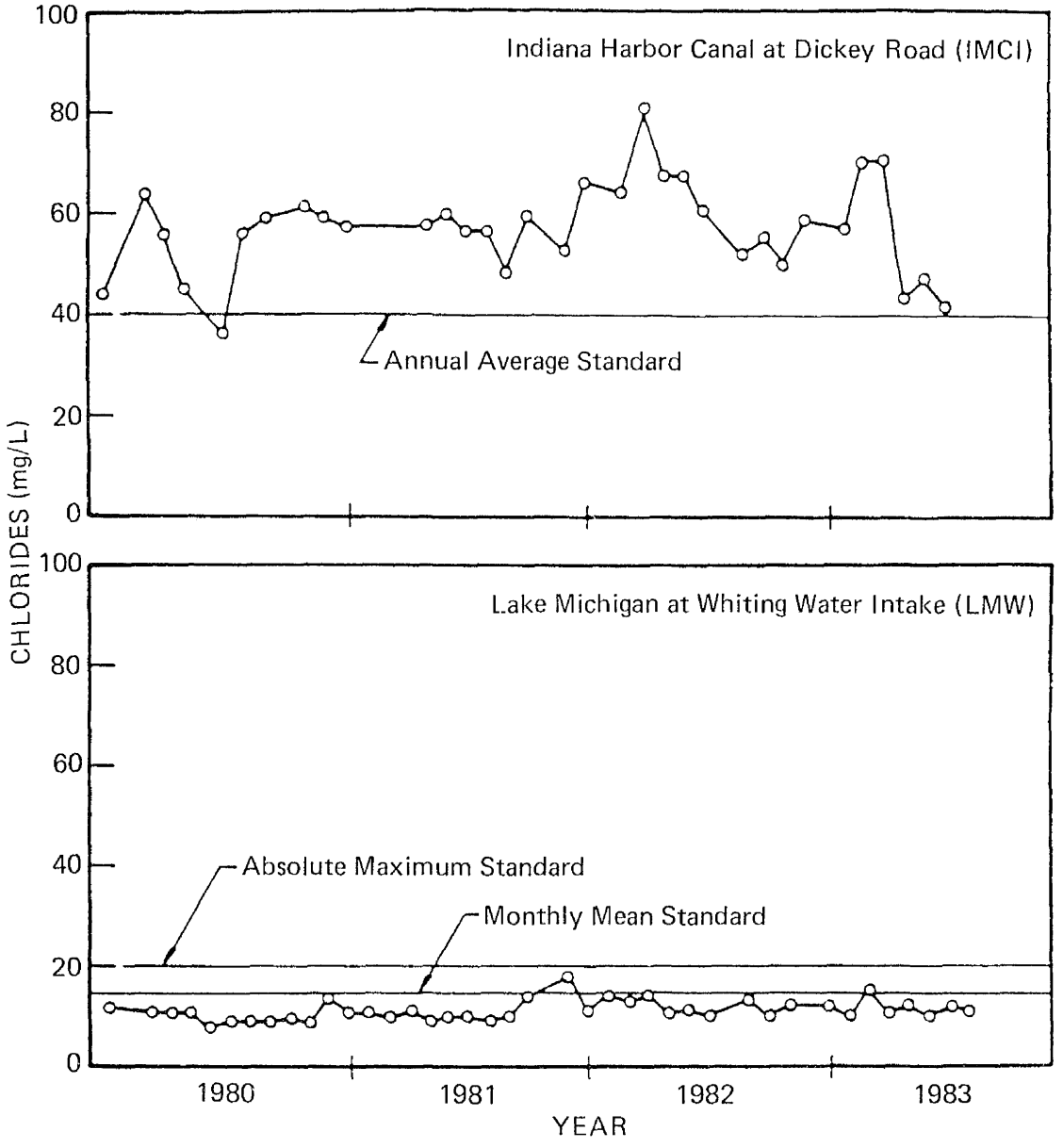


Figure 4.6. Comparison of chloride concentrations in Indiana Harbor Canal and Lake Michigan (Hydroqual 1985).

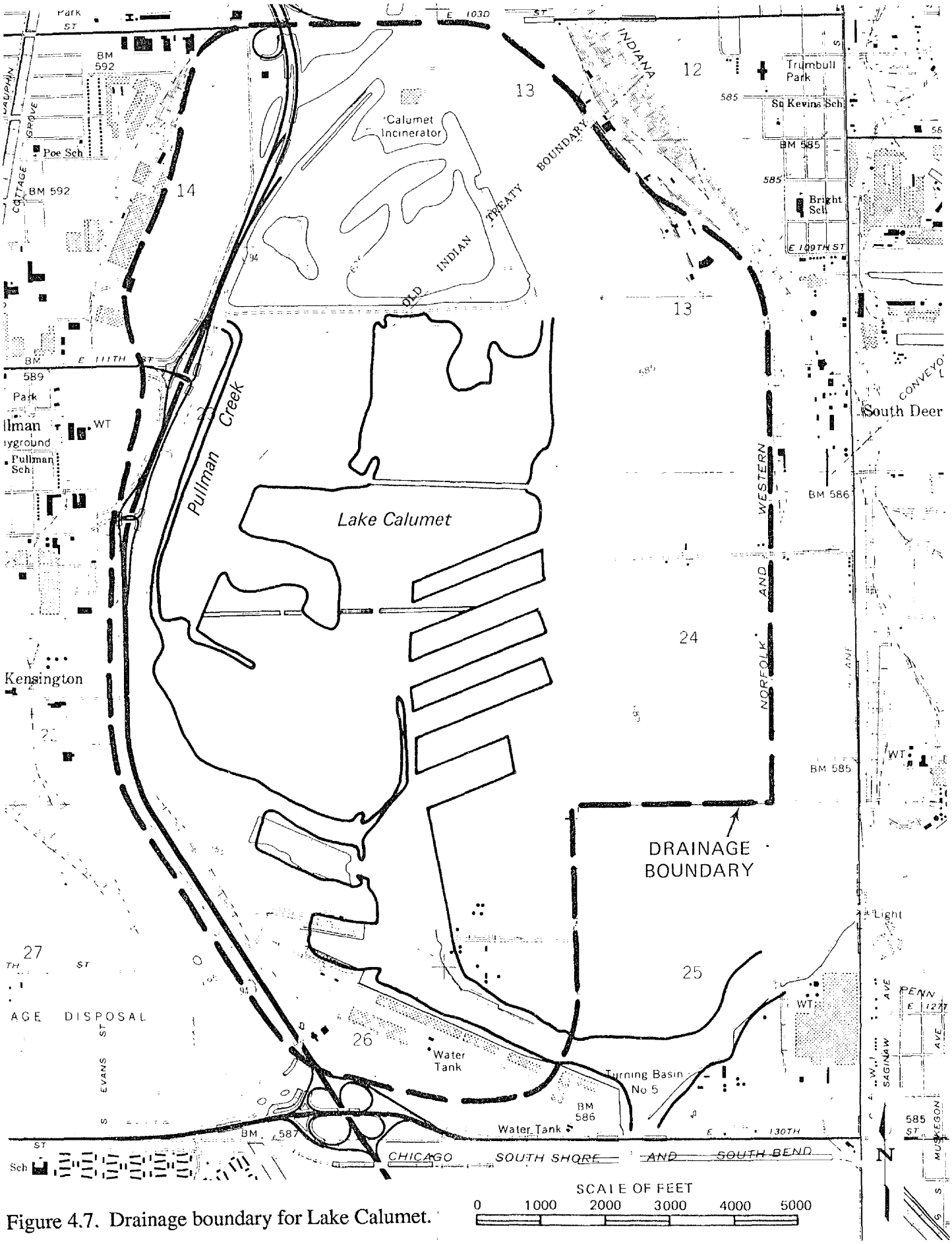


Figure 4.7. Drainage boundary for Lake Calumet.

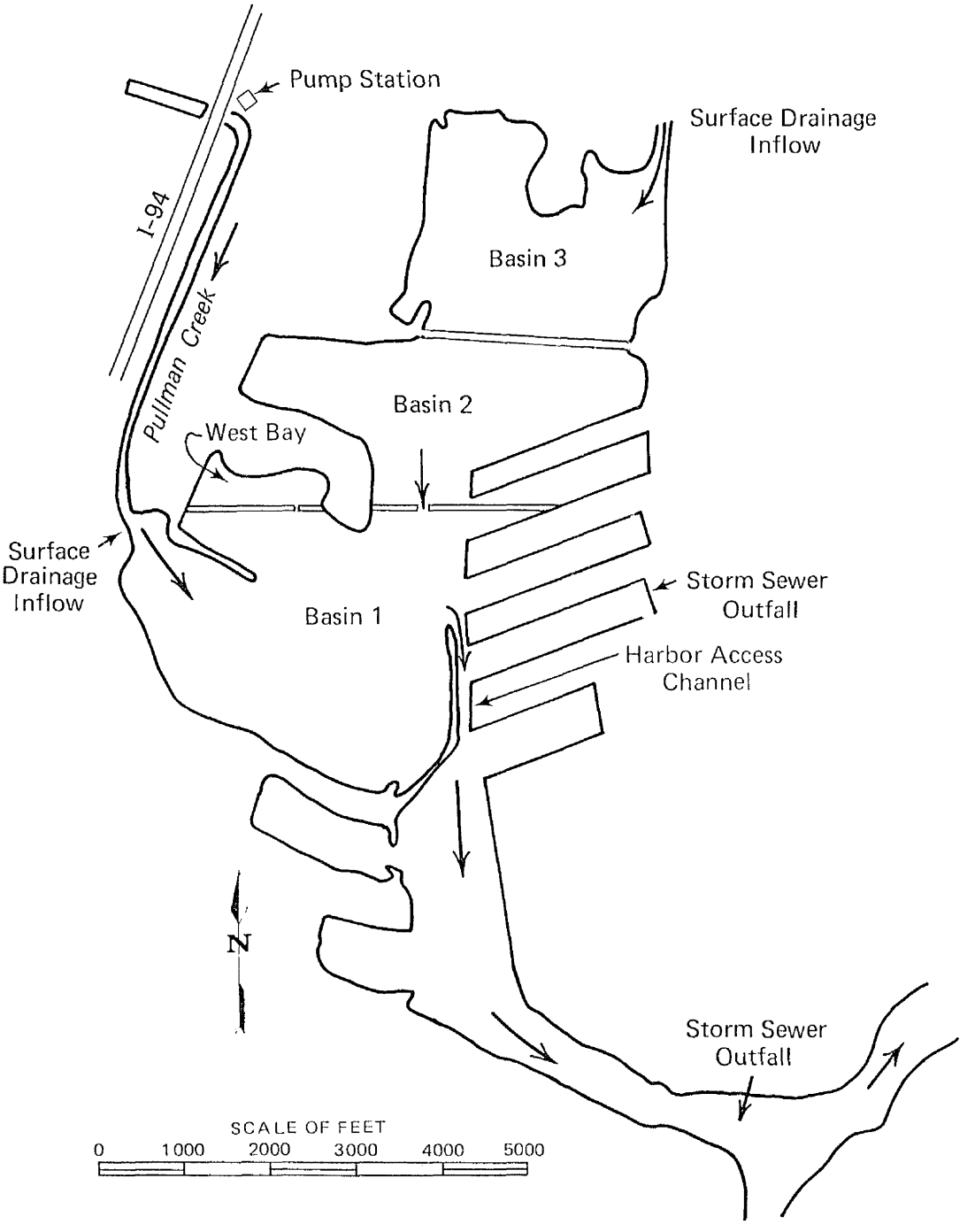


Figure 4.8. Flow into and out of Lake Calumet.

lakebed was caused by the velocities generated by flow between the basins, as can be seen in Figure 4.11. This figure is a plot of the sonar data from a cross-sectional profile 100 feet south of the causeway separating Basin 1 and Basin 2. These data indicate that significant flow and movement of bed materials are occurring between the connected basins of the lake.

The scour and deposition observed in the lake indicate that resuspension of bottom materials is a significant source of pollutants and that it is an important mechanism of pollutant transport in Lake Calumet.

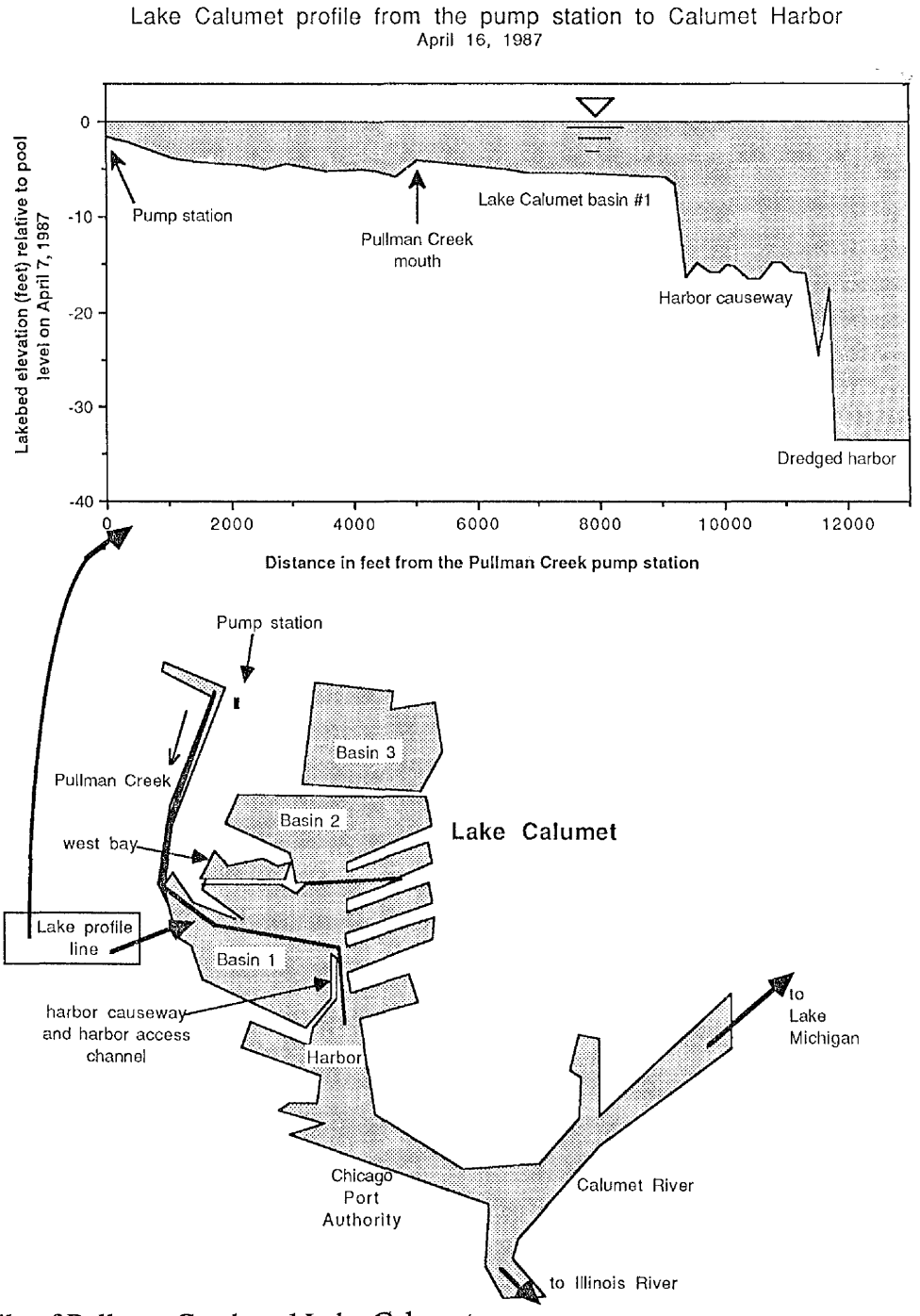


Figure 4.9. Bed profile of Pullman Creek and Lake Calumet

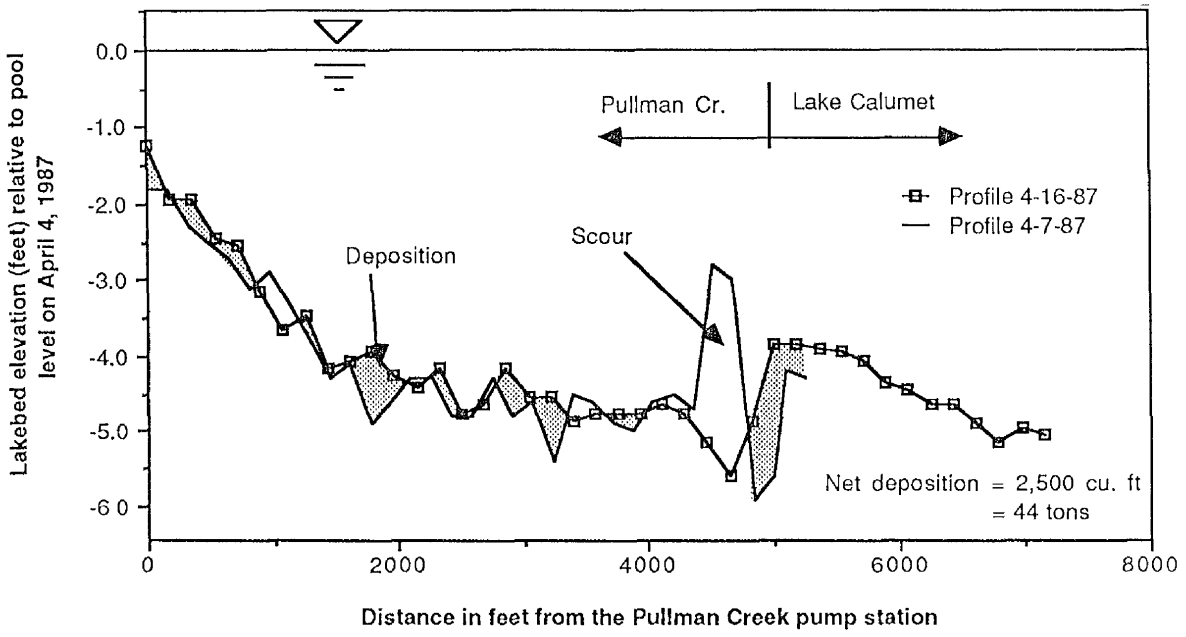


Figure 4.10. Pullman Creek profiles on April 7 and 16, 1987, showing scour and deposition in the creek channel.

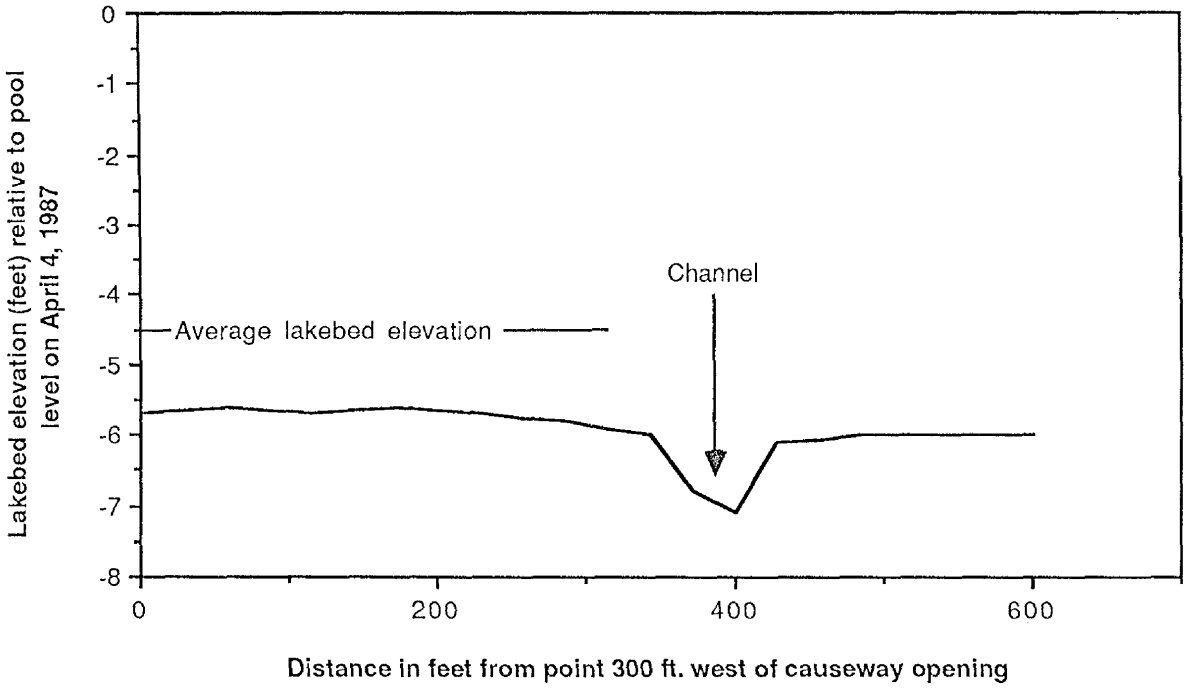


Figure 4.11. Lake Calumet bed profile, 100 feet south of the causeway opening between Basins 1 and 2.

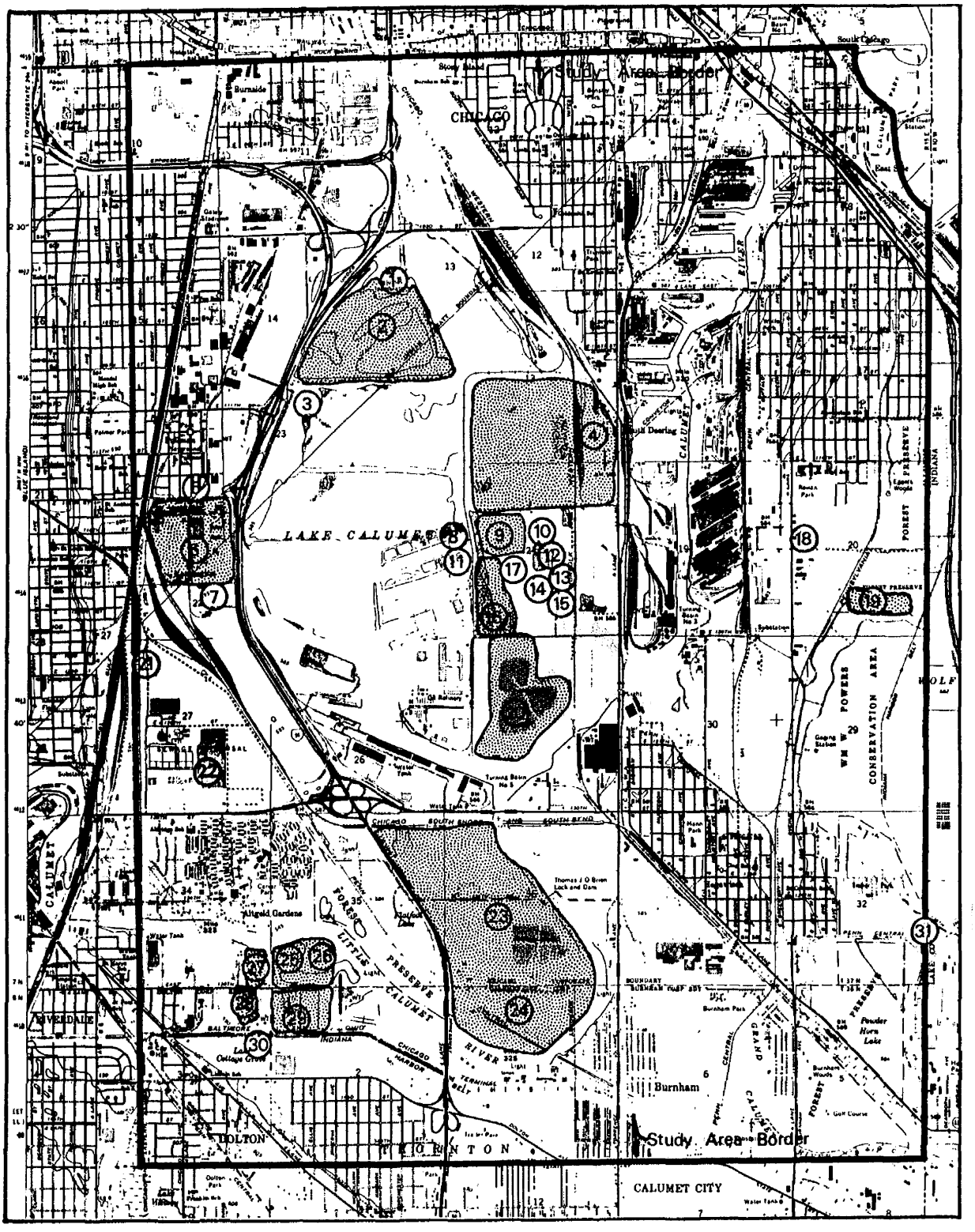


Figure 4.12. Geographic distribution of landfills and waste handling facilities in the south Chicago area (from IEPA 1986).

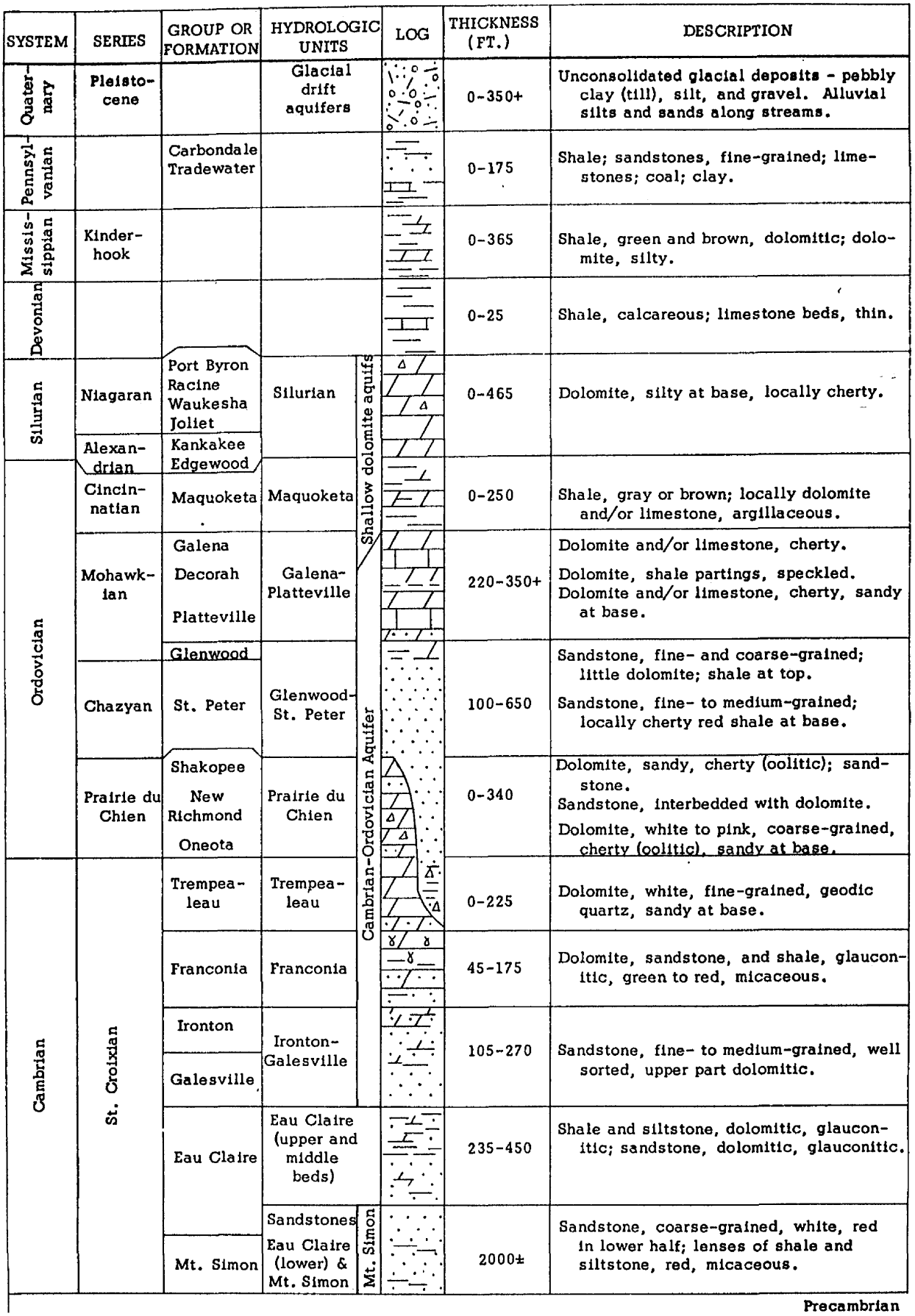


Figure 4.13. Stratigraphic column for the Chicago region (frum Suter *et al* . 1959).

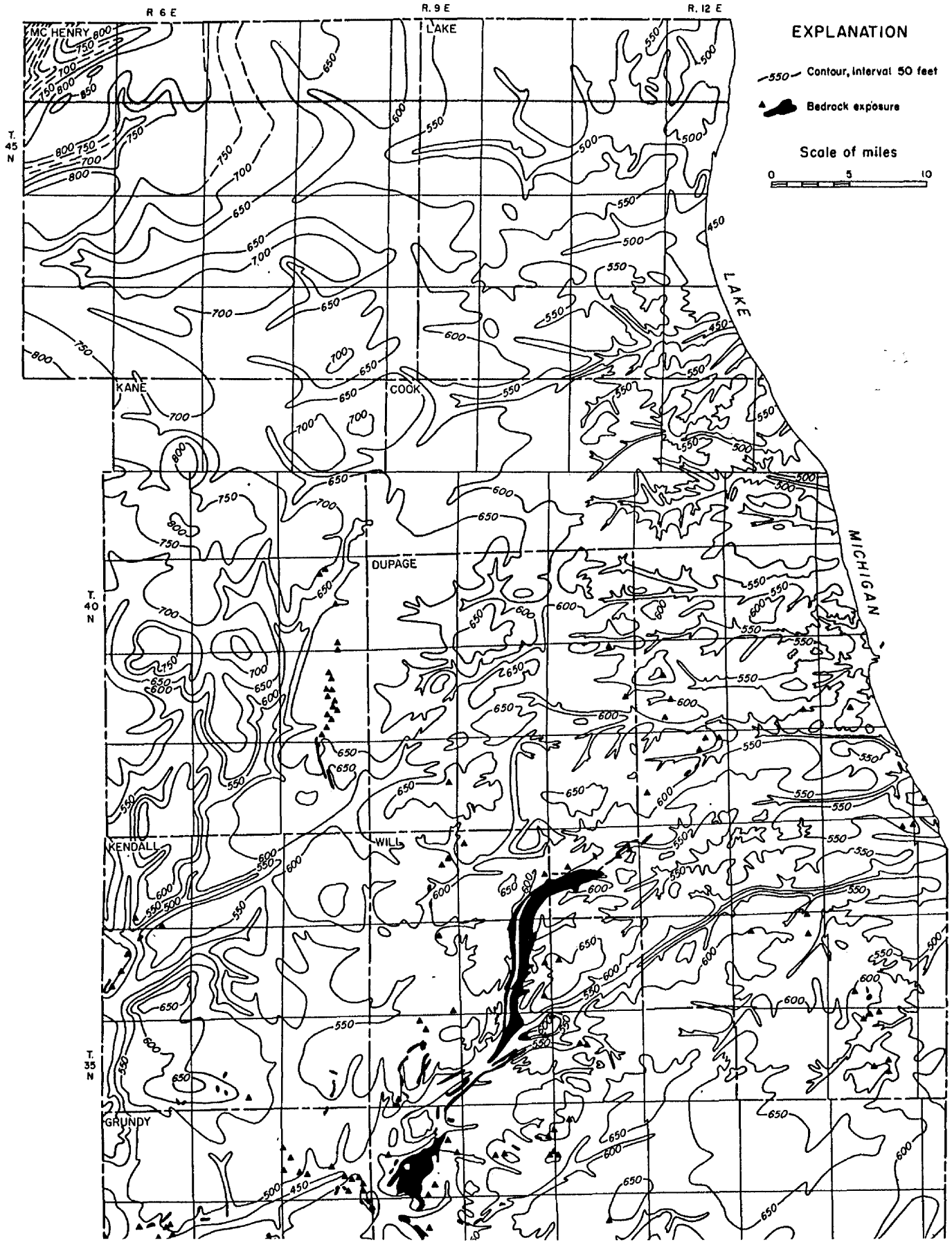


Figure 4.14. Bedrock topography of northeastern Illinois (from Suter *et al.* 1959).

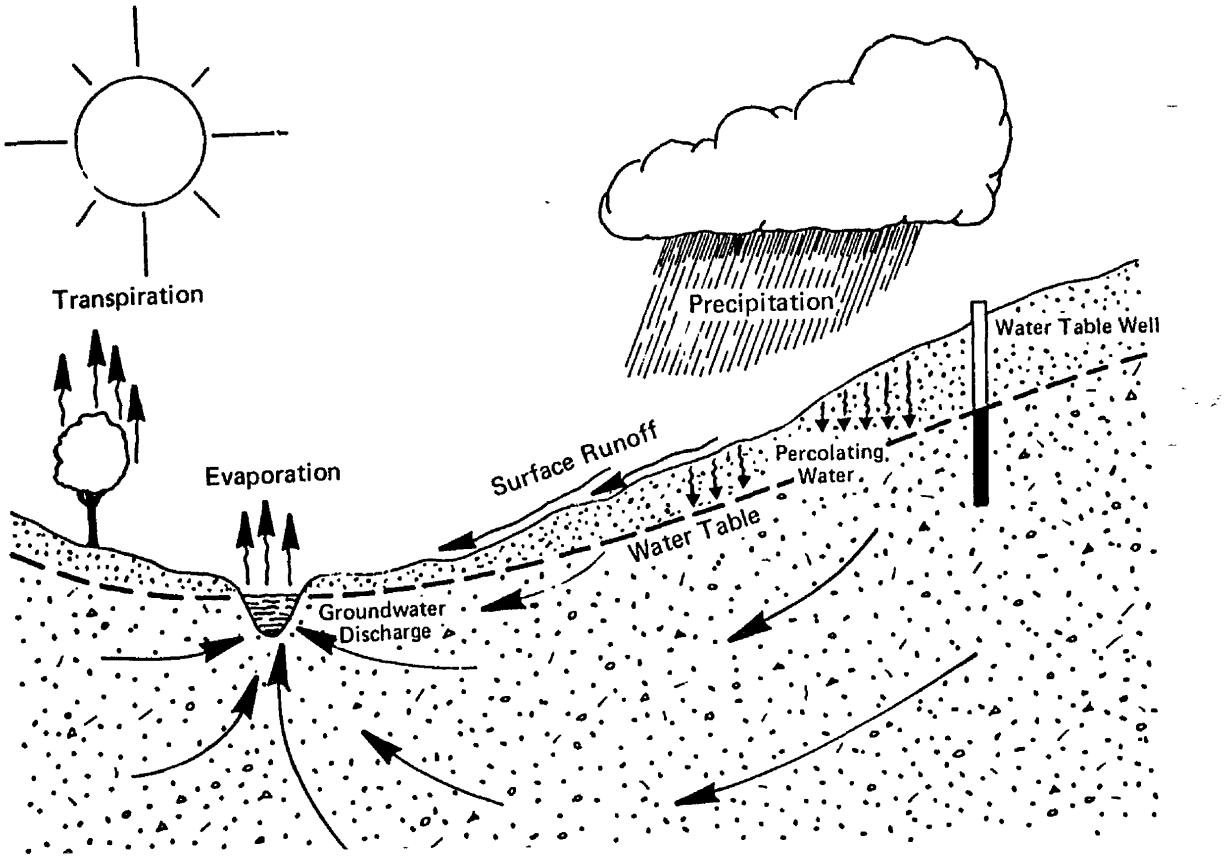


Figure 4.15. Generalized hydrologic cycle

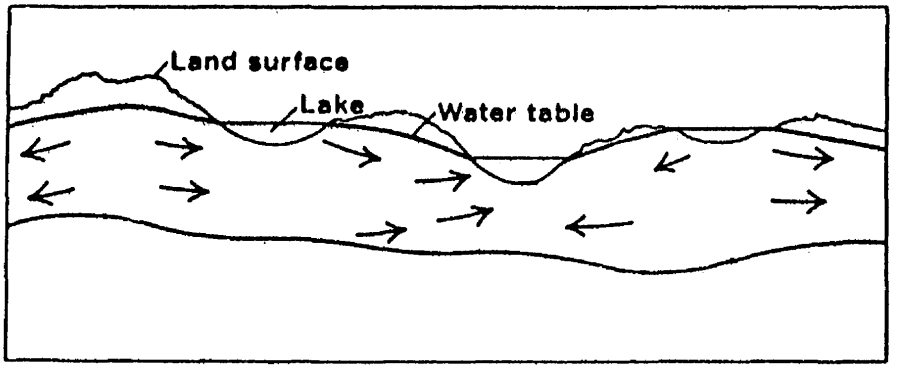


Figure 4.16. Relation between lakes and ground-water flow (adapted from McBride and Pfannkuch 1975).

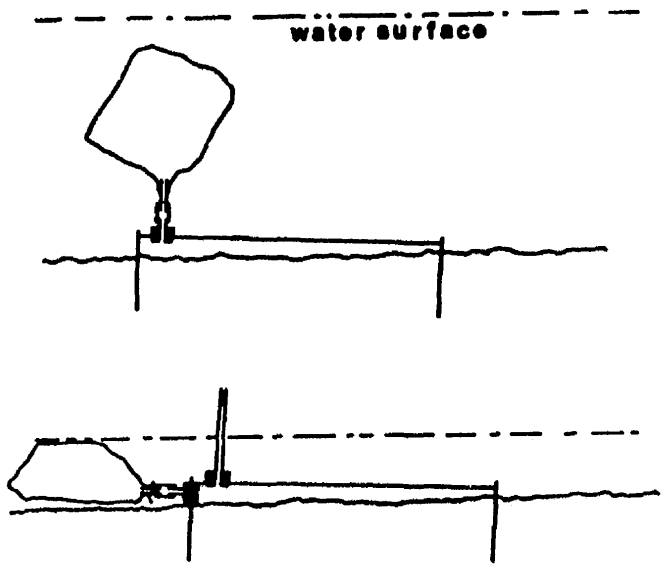


Figure 4.17. Full section views of seepage meter showing placement in deep (2-3 m) and shallow (less than 0.5 m) water (from Lee and Cherry 1978).

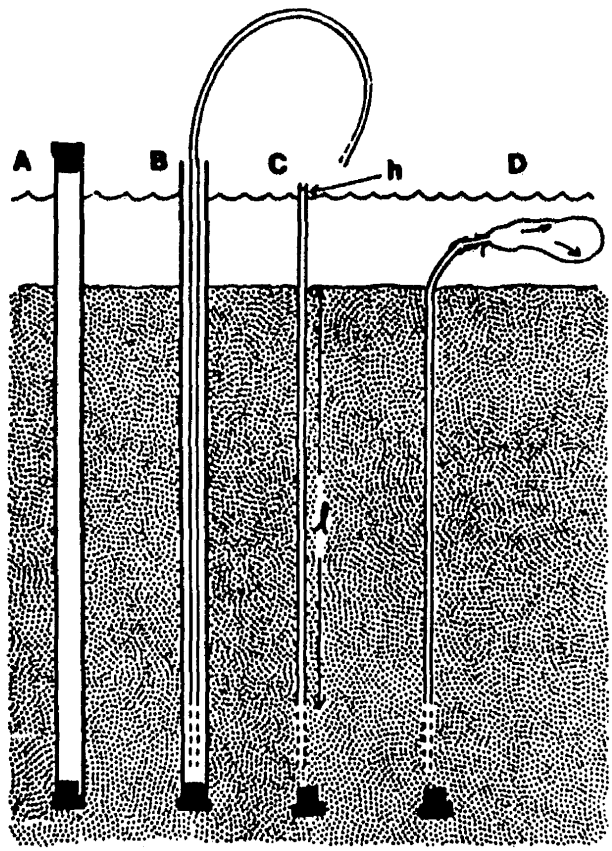


Figure 4.18. General features and method of installation of a minipiezometer: (A) casing driven into the sediment; (B) plastic tube with screened tip inserted in the casing; (C) plastic tube is a piezometer and indicates differential head; (h) with respect to surface water, (D) plastic bag attached to the piezometer collects sediment-porewater (from Lee and Cherry 1978).

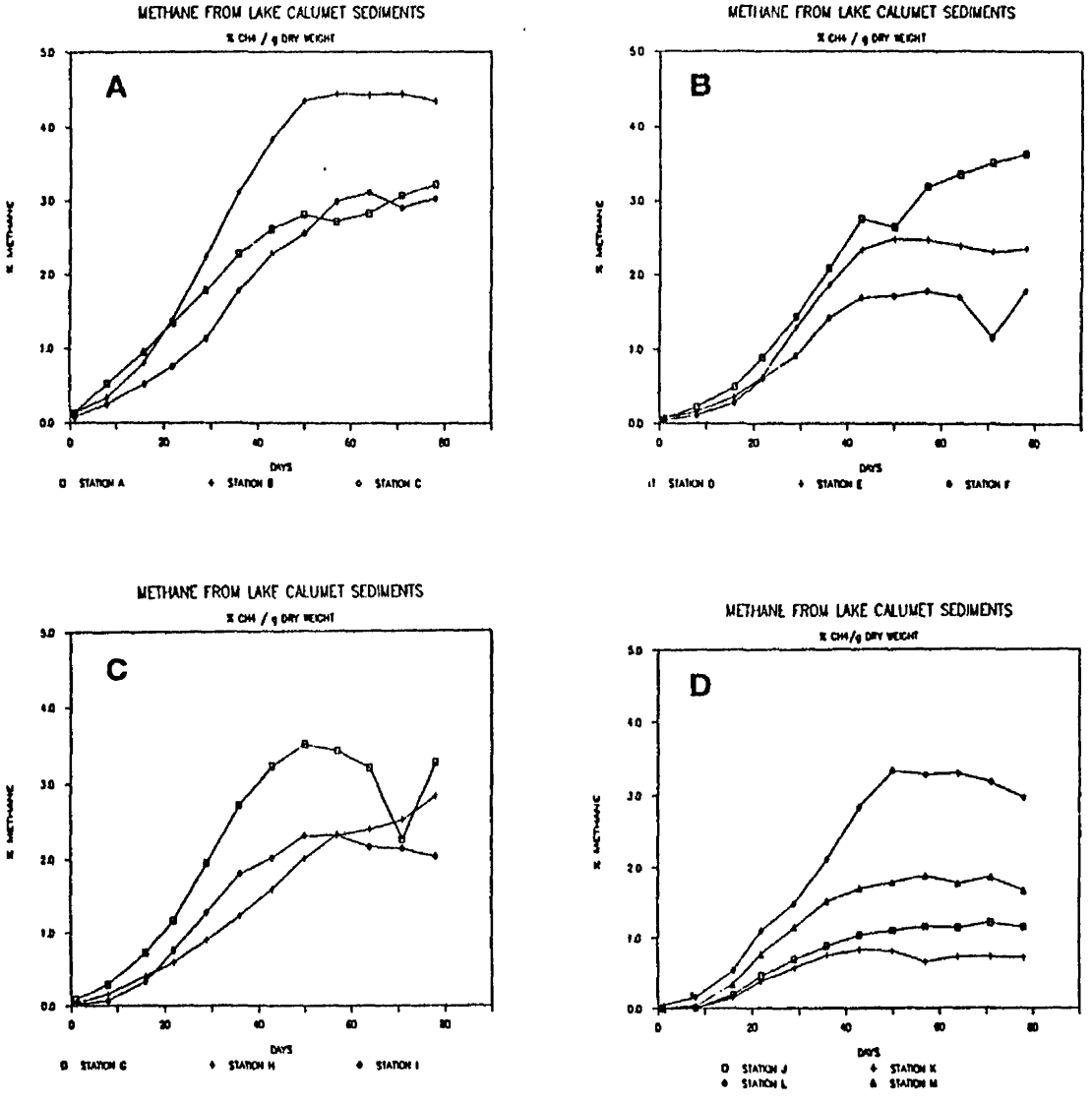


Figure 6.2. Methane production in sediments from 13 stations of Lake Calumet; values represent duplicates.

compounds from Lake Saint Louis sediments in Quebec. Using the ratio of elutriate concentration:bulk sediment concentration for several chemicals, we computed crude estimates of the release of similar chemicals in Lake Calumet. These predications can then be compared to water quality standards (Table 8.7). This comparison may help to better assess the factors contributing to toxicity as reported in this chapter.

Estimated elutriate concentrations of select metals show only lead (Pb) concentrations above recommended levels. The individual characteristics of the aquatic system constitute the major influence on the release of metals and organics from the sediments. Salinity, pH, redox conditions, microbial activities, disturbance events (i.e. dredging, navigation, storms) and lake morphology are

Table 8.7. Ratio of elutriate:sediment chemistry (from Champoux *et al.* 1986) applied to Lake Calumet sediment chemistry (Chapter 3) and compared to Illinois water quality standards for secondary contact (IEPA 1984).

| Parameter | Elutriate:Sediment ratio | Lake Calumet range (ppb) | Illinois standard(ppb) | Lake Calumet "violations" |
|---|---|---|---|---|
| Cd | 0.001 | 1.5 - 3.6 | 150 | 0 |
| Cu | 0.001 | 13 - 115 | 1000 | 0 |
| Ni | 0.001 | 12 -33 | 1000 | 0 |
| Pb | 0.001 | 70 - 316 | 100 | 11 |
| Zn | 0.001 | 110 - 599 | 1000 | 0 |
| As | 0.0005 | 8 - 25 | 1000 | 0 |

several of the parameters that can influence release of sediment contaminants (Forstner and Prosi 1979). Contaminant partitioning is a function of sediment characteristics, including grain size and organic content (Chapman 1986). Lake Saint Louis in Quebec may differ substantially in water chemistry from Lake Calumet, and the estimates in Table 8.7 may be inaccurate. The increased biological response to the PAHs in the sediment may be due to the release from the sediments of lower molecular weight PAHs (2 or 3 rings) , which are also implicated in higher toxicity (Eisler 1987). These lighter molecules are more water soluble and more mobile in the aquatic environment; therefore, they are more available to the organisms in the water column. It is not clear, however, whether environmental release of these smaller PAHs can reach the magnitude associated with laboratory toxicity.

## 8.4 Conclusions

Most sediments from Lake Calumet elicit a toxicological response from three single-species biological assays. Pinpointing the source of this toxicity is difficult in a complex media like sediment and in a disturbed environment like Lake Calumet. Although additional chemical characterization will allow further comparisons between the components of the sediment and the toxic response, the exact source of the toxicity may never be known. The three assays are, more realistically, screening tests for areas of particular concern. Further use of these tests for the toxicological characterization of Lake Calumet sediments and the surrounding wetlands should strengthen the hazard assessment of the lake environment.

# Chapter 9
# Ecological Effects: Microbial Community Toxicity Testing

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## 9.1 Introduction

The microbial community that colonizes artificial substrates includes a variety of organisms, ranging from bacteria to small metazoans such as insect larvae. This community is a composite of the communities inhabiting natural substrates (Henebry and Cairns 1984). Because protozoa (complex, single-celled organisms) are ubiquitous in the aquatic environment and cosmopolitan in their distribution, a mature community of about 30-40 species representative of those in an entire ecosystem colonize artificial substrates within a period of 2-3 weeks (Cairns *et al.* 1979).

Toxicity tests measuring the effect of single chemicals on single biological species (e.g., studies of the effect of copper on fathead minnows) have been the primary source of data for evaluating the environmental hazard of chemicals (National Research Council 1981); however, the goal of most hazard evaluation is to assess or predict the degree of risk of toxic substances to organisms in an ecosystem. As appreciation of the complexity of ecosystems has increased, so has concern over bias in hazard assessments based solely on the response of isolated single species, which often are not found in the ecosystem being studied (Cairns 1984, Odum 1984).

The Protozoa include representatives of virtually every functional group--primary producers, grazers, filter feeders, and predators (Pratt and Cairns 1985). The responses of this diverse group of microorganisms may be similar to the responses of the broader community of organisms in a system such as Lake Calumet (e.g., algae, shellfish, and fish). The use of these communities is scientifically valid because protozoa represent important components of aquatic food chains in both freshwater and marine ecosystems (Barsdate *et al.* 1974, Goldman 1983). Most of the photosynthesis and respiration in many aquatic ecosystems is microbial (Pritchard and Bourquin 1984). Photosynthesis and respiration are excellent measures of system behavioir and are consistent, sensitive to man-made perturbations, and easily compared in both laboratory and field situations (Beyers 1964, Cooke 1974).

The objectives of this study were to evaluate the responses of microbial communities, particularly protozoans, to elutriates of selected Lake Calumet sediments.

## 9.2 Materials and Methods

### 9.2.1 Test communities

Protozoan communities were collected on identical polyurethane foam (PF) block substrates (7.5 x 6.5 x 5 cm) at an assumed "clean" site, a 0.08-ha artificial pond (Illinois Natural History Survey [INHS] Pond 12) that had no history of toxic contamination. After mature communities developed (2-4 weeks, Cairns *et al.* 1979) PF blocks were transferred to the laboratory and acclimated to a 16-hour light (≈1500 lux), 8-hour dark regime at 23°C for 48-96 hours.

### 9.2.2 Species reduction bioassays

For each test evaluating changes in numbers of species, three PF block substrates were exposed to a concentration of elutriate and three substrates (controls) to filtered pond water in separate 1000-mL acid washed beakers. After 48 hours and 7 days, PF blocks were removed from beakers, and each substrate was sampled by squeezing it over a clean collecting vessel to remove 135±10 mL water and microorganisms. The contents were allowed to settle, and the number of colonizing species were determined by repeated subsampling and microscopic observation. Taxa were identified, to species when possible, using standard taxonomic references (e.g., Kudo 1966). These methods and their repeatability are described in detail in Cairns *et al.* (1979). Protozoan species were classified into trophic (feeding) types (Pratt and Cairns 1985), similar to the classification scheme used for aquatic macroinvertebrates (Cummins 1973).

### 9.2.3 Process-level bioassays

Changes in photosynthetic and respiration rates were evaluated by transferring 12 or 18 replicate mature microbial PF block communities from INHS Pond 12 into 150-mL glass biochemical oxygen demand (B.O.D.) bottles. To measure photosynthesis, three bottles containing communities and sediment elutriate and three bottles containing communities in filtered pond water (controls) were exposed to ≈ 1500 lux light for 8 hours. Dissolved oxygen (D.O.) in the bottles was measured with a YSI model 51B dissolved oxygen meter (equipped with a probe and a power stirrer designed for use in the bottles) at the beginning and end of the experiments. Photosynthesis rates were evaluated as gain in D.O.; respiration rates were evaluated as 8-hour D.O. loss in dark bottles. Because of the amount of water associated with communities from the PF block substrates could be reduced to only ≈ 35 mL the highest concentration of elutriate tested in the bottles was ≈ 74%.

9.2.4 Data analysis

Differences in numbers of protozoan species and changes in microbial photosynthesis and respiration rates in control and treated systems were tested using parametric analysis of variance (AOV) (Sokal and Rohlf 1969). Differences were considered significant at $P \leq 0.05$. Data from all types of bioassays were reduced to percent response so they could be compared (the percent response for all bioassays is based on the same scale). Pearson correlation coefficients, simple regression and stepwise multiple regression techniques (Sokal and Rohlf 1969) were used to compare microbial community responses with concentrations of toxic materials in sediments; $P \leq 0.05$ was used as the significance level.

## 9.3 Results

9.3.1 Species reduction bioassays

Numbers of protozoan species (a meaurement of community structure) were significantly reduced in 100% elutriate from two of five stations in 48-h tests and from one of five stations in 7-d tests (Table 9.1). These time-consuming bioassays using community structure as the endpoint were so much less sensitive than the process-level tests that they were discontinued after testing sediments from the five stations listed in Table 9.1.

Table 9.1. Percentage difference between numbers of protozoan species in control and test systems (percent response) in static community bioassays with 100% concentrations of sediment elutriates.

| Station | 48-hour test | 7-day test |
|---|---|---|
| A | -1.7 | -23.1 |
| B | -32.2* | -18.2 |
| 1 | -29.6* | -31.0* |
| 2 | -20.5 | -13.5 |
| 4 | -8.8 | -12.5 |

* Significant difference in numbers of species ($a$= 0.05).

9.3.2 Process-level bioassays

Process-level (functional) end points (photosynthesis, respiration) were more sensitive than reduction in species diversity. Greater than 100% reductions in photosynthesis resulted when communities in elutriate exposed to light consumed rather than produced oxygen; control

communities exposed to light produced oxygen in all tests. Exposure to 74% elutriate from 15 of 22 stations resulted in significant reductions in community photosynthesis (Table 9.2); a lower concentration of elutriate (37%) produced significant reductions in community photosynthesis at 12 of the stations (Table 9.2), indicating that sediments at those stations were more toxic. Significant changes in community respiration were observed in tests with elutriate (74%) from 12 of the 22 stations (Table 9.2). Respiration was enhanced by exposure to elutriates from most stations but not from Stations 7, 8, 9, and 10.

Table 9.2. Percentage difference in oxygen liberation and oxygen consumption (percent response) between control and test systems during 8-hour incubations with sediment elutriates of 37 % and 74%.

| | Photosynthetic Response | | Respiratory Response | |
|---|---|---|---|---|
| Station | 37% | 74% | 37% | 74% |
| A | -49.3 | -86.4* | +2.4 | +64.9* |
| B | -63.3 | -83.4* | -27.0 | +43.7* |
| C | -153.4* | -209.3* | +8.0 | +55.3* |
| F | -24.6 | -148.8* | +8.0 | +63.8* |
| H | -57.7* | -157.3* | +36.1 | +40.8* |
| I | -97.4* | -66.7* | -8.0 | +62.3* |
| 1 | -72.5* | -161.8* | +47.7 | +67.5* |
| 2 | N.D. | -35.2 | N.D. | +45.0 |
| 4 | -21.1 | -40.9* | +2.6 | +20.9 |
| 5 | -4.6 | -23.9 | +9.6 | +31.1 |

(Table 9.1, continued)

| Station | Photosynthetic Response | | Respiratory Response | |
|---|---|---|---|---|
| | 37% | 74% | 37% | 74% |
| 7 | -58.9* | -48.6* | +12.0 | -32.7* |
| 8 | +25.0 | -13.3 | -5.8 | -41.3 |
| 9 | +8.2 | -2.8 | -9.4 | -39.6* |
| 10 | -31.6* | -41.9* | -10.7 | -3.6 |
| 11 | -64.8* | -70.5* | -21.6 | +5.3 |
| 12 | +20.5 | +2.5 | +71.7 | +25.3 |
| 13 | -70.9* | -93.9* | +69.8 | +84.7* |
| 15 | -105.3* | -65.7* | +18.1 | +8.5 |
| 16 | +0.3 | -10.9 | +26.8* | +26.2 |
| 17 | -53.1* | -60.7* | +32.6* | +33.3* |
| 18 | -33.5* | -73.8* | +15.7 | +5.2 |
| 20 | -41.1* | -32.7* | +40.0* | +98.3* |

* Significant difference in dissolved oxygen values between control and test systems ($a$ =0.05). Each value is the mean of three replicates.

9.3.3. Distribution of toxicity in Lake Calumet

Stations with the highest cumulative toxicity, calculated by adding together the significant responses in all four of the process-level bioassays regardless of sign (+ or -), were C>1>H>13>I>20>F (Fig. 9.1A, 9.1.B); all of these sediments produced cumulative community responses greater than 200%.

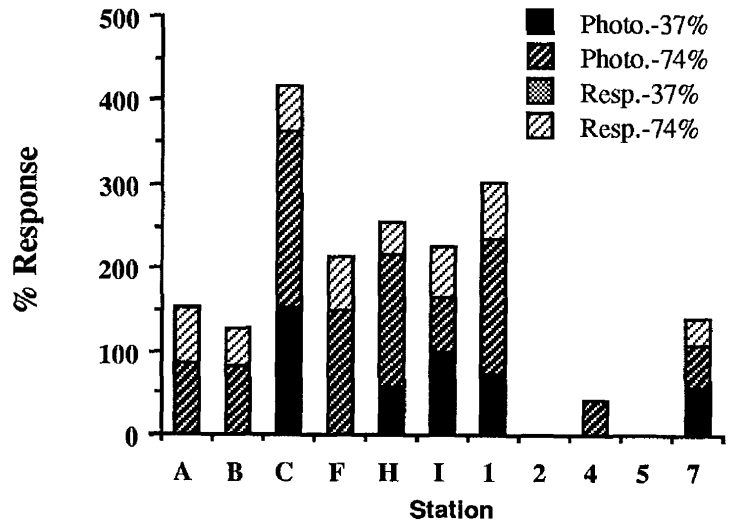


Figure 9.1.A. Cumulative (significant) percent response for the four microbial community functional bioassays (Stations A through 7).

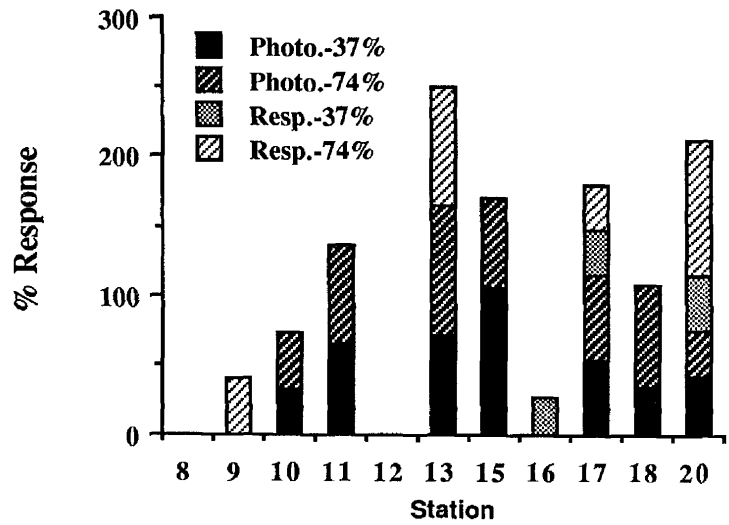


Figure 9.1B. Cumulative (significant) percent response for the four community functional bioassays (Stations 8 through 20).

Cumulative percent response values were assigned to five toxicological classes (Table 9.3), using a system similar to that in the section on single species bioassays (Chapter 8). At this time we do not know how the toxicological classes in this system may correlate with, for example, effects on fish populations; the classes presented in Table 9.3 are only for the purpose of ranking the relative toxicity of stations in Lake Calumet to microbial communities from INHS Pond 12.

Table 9.3. Classification of cumulative percent response to relative toxicity values.

| Percent response | Toxicological class | Numerical assignment |
|---|---|---|
| 0% | No response | 0 |
| 0-100% | Weakly toxic | 1 |
| 100-200% | Moderately toxic | 2 |
| 200-300% | Highly toxic | 3 |
| >300% | Extremely toxic | 4 |

Figure 9.2 provides a schematic representation of toxicity in Lake Calumet sediments based on the toxicity to microbial communities. The station ranked as extremely toxic on the northwest side of the lake was at inflow of Pullman Creek, which receives storm water runoff from Interstate-94 and areas west of the interstate (Chapter 3 of this report). The extremely toxic station on the southwest side of the lake was in an area that appeared to have a high potential for receiving storm water runoff, although no inputs were identified.

9.3.4 Microbial community response in relation to chemical composition in sediments

The cumulative percent response of the four process-level bioassays ($\Sigma$ microbial response) correlated significantly with the concentrations of 5 heavy metals found in substantial amounts in Lake Calumet (Table 9.4) The strongest correlation was between $\Sigma$ microbial response and copper concentration ($r = 0.851$). The sum of community photosynthetic response ($\Sigma$ photosynthetic response, the cumulative response of the photosynthetic assays with 37% and 74% concentrations of elutriate) correlated equally as well as $\Sigma$ microbial response with copper concentration ($r = 0.849$), and correlated more strongly with concentrations of lead, tin, zinc, arsenic and nickel (Table 9.4).

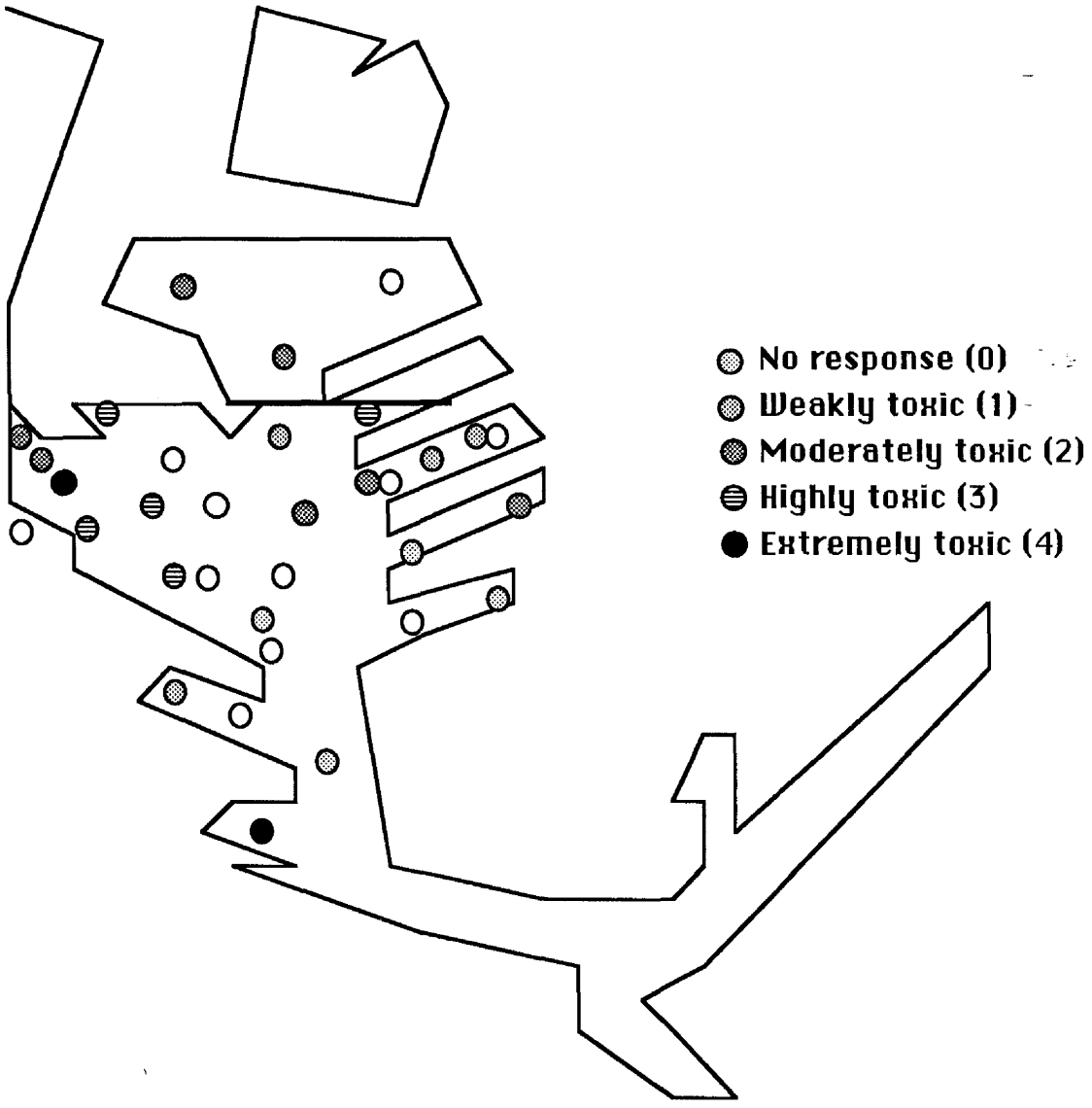


Figure 9.2. Classification of percent response microbial community values for Lake Calumet sediments. Open circles indicate a station where no test was performed

Table 9.4. Correlations (Pearson coefficients) between microbial community responses and sediment metal concentrations.

| | Cu | Pb | Sn | Zn | As | Ni | Σ Photo. | Σ Resp. |
|---|---|---|---|---|---|---|---|---|
| Cu | 1 | | | | | | | |
| Pb | .814 | 1 | | | | | | |
| Sn | .446 | .564 | 1 | | | | | |
| Zn | .926 | .771 | .23 | 1 | | | | |
| As | .611 | .303 | .312 | .403 | 1 | | | |
| Ni | .244 | -.061 | -.321 | .424 | -.224 | 1 | | |
| Σ Photo. | .849* | .635* | .609* | .714* | .658* | -.031 | 1 | |
| Σ Resp. | .031 | -.018 | .138 | -.179 | -.056 | .031 | .038 | 1 |
| Σ Microb. | .851* | .626* | .585* | .672* | .656* | .031 | .947* | .308 |

* Significant correlations ($a$ =0.05); Cu = copper, Pb = lead, Sn = tin, Zn = zinc, As = arsenic, Ni = nickel, Σ Photo. = sum of photosynthetic response, Σ Resp. = sum of respiratory response, Σ Microb. = sum of the microbial community response.

There were no significant correlations between the sum of community respiratory response (Σ respiratory response, the cumulative response of the respiratory assays with 37% and 74% concentrations of elutriate) and any metals (Table 9.4). The Σ microbial response correlated strongly with Σ photosynthetic response (r = 0.947) but not with Σ respiratory response.

Simple linear regressions were used to test the significance of the relationships of Σ microbial response, Σ photosynthetic response and Σ respiratory response with concentrations of metals. The best regressions for Σ microbial response andΣ photosynthetic response are presented as examples (Fig. 9.3); there were no significant regressions between respiratory response and any metals. Data from stations at which microbial community responses were not significant (Table 9.2) or where concentrations of a metal were below detection limits (Chapter 3) were not used in regressions (or in the previous correlations) because the community response or the metal concentration would have a value of zero. The values of community response and metal concentrations were not really zero, but simply below significance/detection limits. Therefore, 15 stations were used in the regressions with copper with tin (Fig. 9.3) instead of the 22 stations that were used in microbial assays (Table 9.2).

Variables which showed significant relationships in simple regressions were analyzed using stepwise multiple regression (Fig. 9.4).The best one-variable model for Σ photosynthetic response

was with copper ($r^2 = 0.511$), and the best overall fit ($r^2 = 0.739$) resulted when all the metals were included in the model (Fig. 9.4). The best one-variable model for $\Sigma$ microbial response was with tin ($r^2 = 0.416$) and the best overall regression coefficient ($r^2 = 0.555$) was the same for both 3 and for 4 metals (Fig. 9.4); the regression between $\Sigma$ microbial response and zinc was not significant.

## 9.4 Discussion

### 9.4.1 Effect of Lake Calumet sediments on microbial communities

Most studies do not attempt to evaluate the effects of toxicants at the level of the community or ecosystem. Protozoa collected on artificial substrates represent intact communities made up of 30-40 interacting species of several trophic levels. The toxic responses displayed by this group of organisms (which includes producers, herbivores and predators) may mimic the types of changes that could occur in other populations of organisms in Lake Calumet that may be exposed to toxic contamination when sediments are disturbed by dredging or by wave and wind action. The photosynthetic and respiratory responses of the total microbial community colonizing the substrates (the Protozoa, the algae, the bacteria and the small metazoans) may be representative of types of changes that could occur in the larger Lake Calumet ecosystem.

The fact that photosynthesis was significantly affected by elutriates from more stations (68%, 15/22) than affected respiration (55%) suggests that contamination in Lake Calumet generally had a greater impact on autotrophic than on heterotrophic organisms. Further, this finding illustrates the type and amount of information provided by these microbial community tests. Community photosynthesis decreased with exposure to elutriate from all stations, but respiration generally increased. That increase in respiration rates suggests that whereas metals in the sediments may have inhibited photosynthesis by autotrophic microorganisms in the community (the filamentous and unicellular algae, and phototrophic protozoa), nutrients in the sediments stimulated the activities of heterotrophs (the bacteria and bactivorous protozoa).

Inhibition of community respiration occurred only with exposure to elutriates from Stations 7-10. Elutriates from none of these stations produced great inhibition of photosynthesis; and only one of these stations, Station 7, was classified as even moderately toxic based on cumulative percent response values. Metal concentrations at these stations were neither

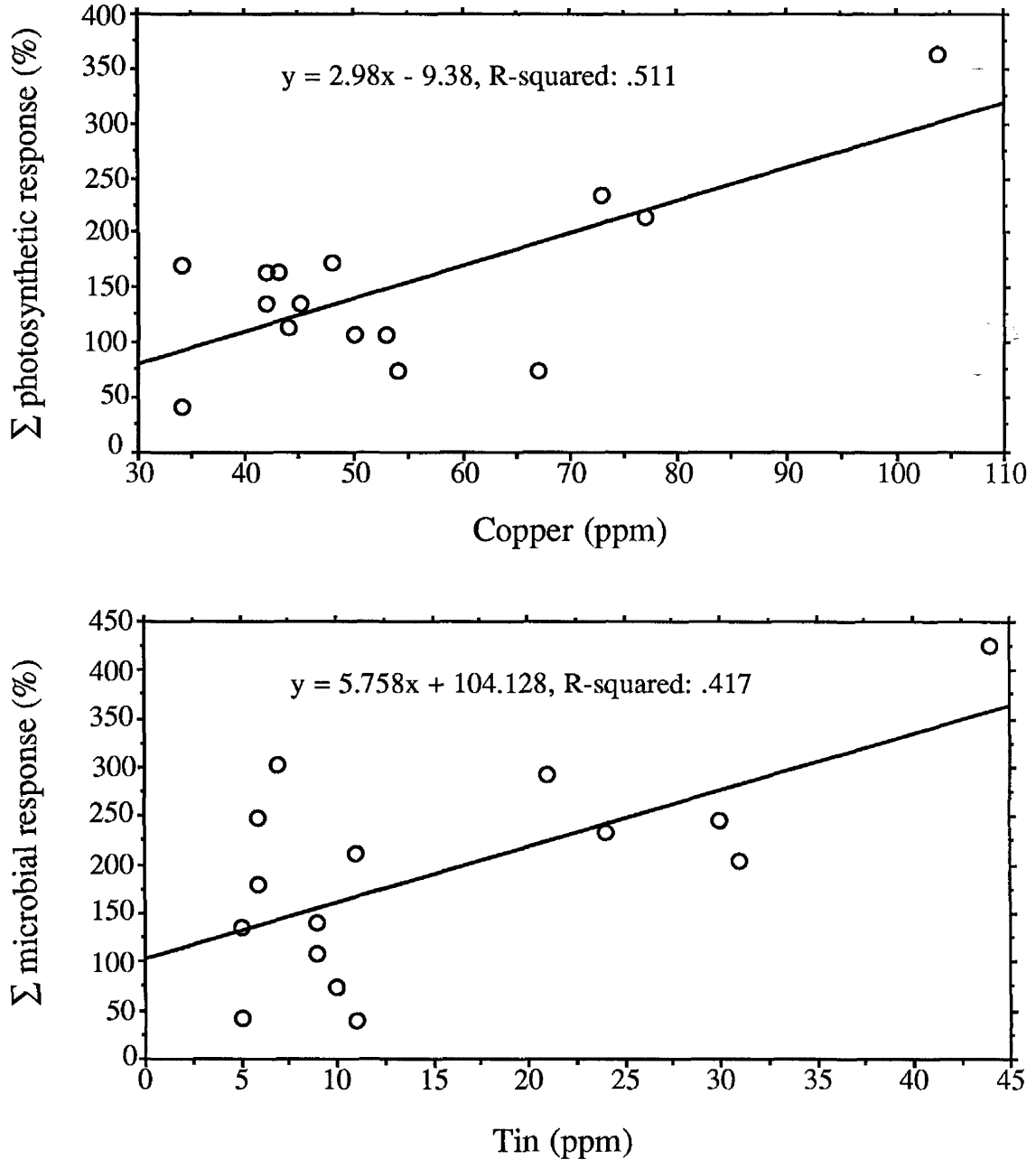


Figure 9.3. Regressions of photosynthetic response and Σ microbial response with metals concentrations in Lake Calumet sediments.

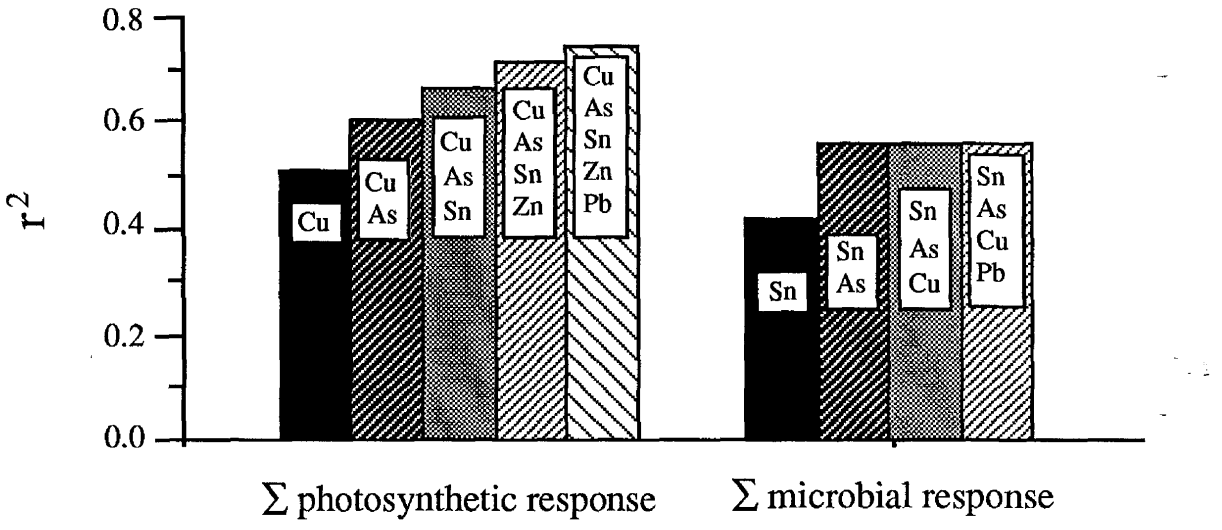


Figure 9.4. Stepwise multiple regressions of Σ photosynthetic response and Σ microbial community response with sediment metal concentrations. Cu = copper, Pb = lead, Sn = tin, Zn = zinc, As = arsenic.

particularly high nor particularly low (Chapter 3 of this report). Organic carbon values at these stations were also in the middle range for Lake Calumet (Chapter 3), so the reduction in community respiration does not appear to be due to a lack of organic material to respire. The sediment samples are still being analyzed for polyaromatic hydrocarbons and other toxic organics (Chapter 3). At this time, the inhibition of community respiration cannot be attributed to any specific group of toxic compounds, but it appears that there was something different about Stations 7-10.

9.4.2 Bioassay response in relation to chemical composition in sediments

The strong Pearson correlations and relatively high regression coefficients between Σ photosynthetic response and metal concentrations, and the general reduction in these values when the Σ respiratory response was added (to make up the Σ microbial response), indicates that the main response of the microbial communities in this study of Lake Calumet was a reduction in photosynthesis with increased metal concentrations in the sediments. Heavy metals, copper in particular, are well-documented inhibitors of photosynthesis (Steemann-Nielsen and Wium-Anderson 1970), and copper is a commonly used algacide. Therefore, it is not surprising that Σ photosynthetic response correlated most strongly with copper concentration. The Σ respiratory response correlated weakly (and not significantly) with the concentration of organic carbon in the sediments. No other nutrient concentrations in the sediments (e.g., nitrogen and phosphorus) were measured.

9.4.3 Comparisons with other studies

Tests comparing changes in photosynthesis and respiration of microbial communities developed on artificial substrates and exposed to elutriates of contaminated sediments are relatively new (Ross *et al.* 1987, Henebry and Ross 1987a), so there are few studies with which to compare the results from Lake Calumet. However, in studies of microbial community response to sediment elutriates from an area of Waukegan (IL) Harbor that was heavily contaminated with polychlorinated biphenyls (PCBs), photosynthesis was also inhibited while respiration was stimulated (Henebry and Ross 1987b).

Microbial communities on glass slides in artificial streams dosed with copper and chromium compounds and with nutrients such as sucrose and compounds containing nitrogen and phosphorus (Cairns *et al.* 1978) responded in much the same way as did the PF block microbial communities. In the Cairns *et al.* study the structure of the community was little changed by the various treatments. However, respiration was significantly stimulated with the addition of sucrose, and photosynthesis was significantly inhibited by both copper and chromium (Cairns *et al.* 1978).

When PF block microbial communities from INHS Pond 12 were exposed to copper chloride ($CuCl_2$), photosynthesis was reduced 97% in a concentration containing 0.66 ppm copper ion ($Cu^{++}$) and 55% in a 0.066 ppm concentration of $Cu^{++}$ (Henebry, unpublished). In that same series of tests, community respiration was reduced 58% in the 0.66 ppm concentration of $Cu^{++}$, but respiration was not significantly reduced in the 0.066 ppm $Cu^{++}$ concentration. Both photosynthesis and respiration of microbial communities from INHS Pond 12 were sensitive to relatively low levels of copper; however, photosynthesis was inhibited by a significantly lower concentration than was required to inhibit respiration.

Tests using the reduction in number of protozoan species as the endpoint were run with elutriates from only a few stations in Lake Calumet. Those species-reduction bioassays were time consuming and were less sensitive than the photosynthesis and respiration tests. The greatest (and only statistically significant) reduction in number of species occurred with exposure to 100% concentrations of sediment elutriate from stations B (32.2%) and 1 (31.0%). A 20% reduction in number of species in protozoan communities is considered biologically significant (Cairns *et al.* 1980, Cairns and Pratt 1985); therefore, Lake Calumet sediments may be moderately toxic in terms of altering community structure. Similarly, 100% concentrations of Waukegan Harbor sediment elutriate were required to significantly reduce numbers of species in protozoan communities, but colonization of barren islands and photosynthesis were inhibited by concentrations as low as 10% (Ross *et al.* 1987). Bioassays using the colonization rate of barren artificial islands by protozoa are

more sensitive to metals and other toxic substances than are species reduction tests (Cairns *et al.* 1980, Cairns and Pratt 1985), but take from 2-4 weeks to run and are even more labor intensive than species reduction tests.

### 9.4.4 Suggestions for further work

The information provided by this series of microbial community tests is more complex than that generated by single species bioassays. While the data from microbial community tests result in more realistic predictions concerning the impact of sediment contamination on Lake Calumet, caution must be exercised. The investigator must look at different endpoints and make judgements based on knowledge of community and ecosystem ecology. For example, the increase in respiration associated with exposure to elutriates from most stations might lead to the conclusion that Lake Calumet sediments were not toxic to the microbial communities but actually enhanced their activities. In reality, those increases probably incidcated that one or more nutrients that promote heterotrophic activities were present in higher amounts than at other stations, thereby masking the toxic effect of the contaminants at those stations. The decrease in photosynthesis at most stations probably provides a more accurate picture of the distribution of toxic materials in Lake Calumet sediments. To test the relationship between the stimulation of community activities by nutrients and the inhibition of activities by toxic substances, microbial communities should be exposed to various combinations of such toxic materials as heavy metals and varying levels of such nutrients as dissolved organic carbon, nitrogen and phosphorus.

Bioassays using microbial communities need to be performed on a variety of toxic metals and organics that have been used in bioassays with more standard organisms in order to compare the sensitivity of the microbial communities with that of such organisms as fish. It would also be useful to directly compare the responses of microbial communities with those of standard bioassay organisms by conducting simultaneous tests with split samples of contaminated sediments.

One advantage of using PF block protozoan communities for ecotoxicological studies is that *in situ* tests may be efficiently conducted with indigenous or indigenous-type organisms. Effects of toxic substances in laboratory tests may not be representative of effects on actual ecosystems. In studies of contamination in Waukegan Harbor (Ross *et al.* 1987) *in situ* tests allowed direct observation of the effects of sediment contamination, and confirmed predictions about changes in community structure based on laboratory tests. Unfortunately, during the first year of this work on Lake Calumet, artificial substrates placed in the lake were removed by vandals. Although the laboratory bioassays provided useful information, future studies should include monitoring of changes in indigenous-type protozoan communities collected at clean sites and transferred to Lake Calumet.

# Chapter 10
# Summary, Conclusions, and Recommendations

## 10.1 Summary

This study examined some of the physical, chemical, and biological processes occurring in Lake Calumet and sought to identify sources and effects of contamination from over a century of industrial development in the Calumet area.

### 10.1.1. Sediment chemistry

High concentrations of anthropogenic metals and polycyclic aromatic hydrocarbons (PAHs) were found in Lake Calumet sediments. These concentrations were generally higher than sediment samples in nearby waters.

### 10.1.2. Physical transport processes

In an evaluation of surface water in Lake Calumet, no natural drainage channels were observed. Pullman Creek, a smaller channel in the NE portion of the lake, and two storm sewers are the existing man-made drainage channels for the lake. Pullman Creek is not only a source of inflowing water but also of sediment.

### 10.1.3. Chemical transport processes

Organic compounds in the water column were at levels too low for one type of experimental fugacity measurement, but polychlorinated biphenyls were detected in the sediment at levels appropriate for measurement.

### 10.1.4. Microbiological processes

Methane was produced in Lake Calumet sediments, thereby confirming the presence of anaerobic microbial communities. Aerobic and anaerobic bacteria were found in greater numbers at sampling stations near the shoreline of Lake Calumet than at stations in deeper water.

### 10.1.5. Biological uptake

Lake Calumet wetlands support a population of macrophyte species that have been documented as bioaccumulators of heavy metals.

10.1.6 Single-species toxicity tests

Composite toxicity indices (based on the relative toxic responses of *Photobacterium phosphoreum* , *Selenastrum capricornutum* , and *Panagrellus redivivus* ) classified 57% (12/21) of the stations as "highly toxic"; the remainder (43%) were considered "moderately toxic." The toxic responses had a slight statistical correlation with total PAH concentrations in the sediment. Predictions of elutriate chemistry indicate that lead (Pb) might have the potential to exceed water quality standards if released from Lake Calumet sediments.

10.1.7. Microbial community toxicity tests

Exposure to sediment elutriate from 82% (18/22) of the stations resulted in statistically significant changes in microbial communities with the functional (photosynthesis and respiration) endpoints more sensitive than endpoints measuring reduction in numbers of species. Composite toxicity indices (based on the relative toxic responses of functional bioassays) classified 9% of the stations as "extremely toxic," 23% as "highly toxic," 32% as "moderately toxic," and 18% as "weakly toxic"; at 4 stations there was no statistically significant toxic response. Photosynthetic and total microbial community response had strong statistical correlations with metal concentrations in the sediment.

## 10.2 Conclusions

The research described in this study indicates that Lake Calumet is a severely disturbed system. Continued physical alteration has changed the lake's shape, reduced its surface area, and destroyed the surrounding natural wetland areas. Drainage is controlled by man-made channels (e.g., Pullman Creek) and the O'Brien Lock and Dam system. Pullman Creek has been identified as a source of pollutants as well as inflowing water. Chemical compounds common to industry in the Calumet region since the 1870s have concentrated in the sediments of the lake and, consequently, the potential for bioaccumulation in aquatic plants, invertebrates, fish, and perhaps, water fowl and humans is high. Alteration of the aquatic ecosystem through toxic effects of the contaminated sediments is probable.

Resuspension of Lake Calumet sediments is readily accomplished by wind-induced flow and storm events that scour the bottom and transport sediments to other locations in the lake.

The presence of waste landfills, major highways, refineries, scrap metal operations, and other industrial activities continues to threaten the Lake Calumet ecosystem. Atmospheric deposition, highway and industrial run-off, and continued alteration of the shoreline and surrounding wetlands may add to the pollution of the lake or induce further sediment disturbance and drainage problems.

Changes in the physiochemical nature of the lake by current activities may result in the release of contaminants deposited in previous years.

Although Lake Calumet seems to be isolated by the O'Brien Lock and Dam and its own sluggish drainage system, its connection with Lake Michigan and with the Illinois River watershed cannot be ignored. Some of the contaminants found in the sediments of Lake Calumet are likely to be found in the soil, water, and air in surrounding areas. The Calumet River and the Cal-Sag Channel may transport contaminants from the lake out of the Calumet region. A groundwater connection with the lake is, as yet, unidentified but may play a role in the transport of pollutants in or out of the lake.

The results from this year of study should provide a data base to support continued research on Lake Calumet and the surrounding region. Additional data will allow further conclusions on the environmental status of Lake Calumet.

### 10.3 Recommendations

Further research should be carried out in the following areas:

**Continued chemical and toxicological analyses of surface sediment:**. The existing knowledge base should be expanded in two ways. First, more stations within Lake Calumet proper should be studied to permit greater resolution in contaminant and toxicity mapping. Second, stations in wetlands, ponds, and small streams within the Lake Calumet hydrologic system should be studied in order to gain a more complete understanding of the situation. Special attention should be paid to culverts and drainage ditches leading from past and current industrial or disposal sites into the lake. In addition to chemicals already analyzed, priority pollutant scans should be run on a few selected stations to ensure that important contaminants are not being ignored.

**Continued data collection for sediment resuspension.** The clearly demonstrated importance of particulate mobilization raises three questions that should be addressed. First, is there a prevalent pattern of particle transport within Lake Calumet? Second, do particles originating in Lake Calumet sediments affect water quality in the Calumet River system and in Lake Michigan? Third, do storm events cause predictable contaminant relocation patterns? More precise data on sediment relocation is needed to answer these questions.

**Contaminant input from groundwater**. A study of groundwater flow patterns in and around the lake should be undertaken to estimate the importance of continued contaminant input from sub-surface sources.

**Historical loading.** The historical dimension of contaminant input to the system should be investigated by studying vertical sediment cores at selected stations. Core horizons can be dated by the Cesium-137 or Lead-210 methods, and chemical and toxicological analyses can then be performed on material deposited in various time periods. The effectiveness of this approach may be compromised if the high degree of lateral transport noted above obscures vertical deposition patterns, making historical trends impossible to detect.

**Bioaccumulation.** The level of bioaccumulatory substances in the sediment justifies analyses of aquatic plants and the initiation of a fish and invertebrate sampling program. Flesh analysis should include metals, PAHs, PCBs, and select pesticides. Fish analysis is especially critical because human consumption of Lake Calumet fish could present a health risk. (During the April 1987 sampling trip, 18 fishermen were seen in one afternoon.)

**Literature and data base research.** Although a good deal of information has been summarized in the Colten (1985) report and in this document, more sources should be explored. In particular, data from monitoring wells (IEPA) and internal environmental quality programs (MSDGC) should be accessed.

**Atmospheric deposition.** In order to complete the study of contamination sources, the role of atmospheric deposition should be evaluated.

**Public health.** The existing public health data base (Illinois Public Health Dept.) should be re-examined when current studies are completed. These data should be compared with contaminant and toxicological data to determine whether correlations exist. The need for further epidemiological studies should also be evaluated at that time.

# Chapter 11
# Literature Cited


American Society for Testing and Materials. 1982. Annual Book of ASTM Standards, Part 31, Water.

Aulio, K. 1980. Accumulation of copper in fluvial sediments and yellow water lilies (Nuphar lutea) at varying distances from a metal processing plant. Bull. Environ. Contam. Toxicol. 25: 713-717.

Balch, W.E., G.E. Fox, L.J. Magrum, C.R. Woese, and R.S. Wolfe. 1979. Methanogens: Reevaluation of a Unique Biological Group. Microbiol. Reviews 43: 260-293.

Barsdate, R.J., R.T. Prentki, and F. Fenchel. 1974. Phosphorus cycle of model ecosystems; significance for decomposer food chains and the effect of bacterial grazers. Oikos 25: 239-251.

Beckman Instruments, Inc. 1982. Microtox system operating manual. Microbics Operations, Carlsbad, CA.

Bendell-Young, L.I. and H.H. Harvey. 1986. Metal concentration and calcification of bone of White Sucker (Catostomas commersoni) in relation to lake pH. Water, Air and Soil Pollution 30: 657-664.

Bennett, G. W. 1971. Management of lakes and ponds. Van Nostrand Reinhold Co., NY.

Bennett, P., D.I. Siegel, A.I. Veeger, and P.C. Jones. 1987. Abstract, A pressure probe for determining lake-ground water interaction. Eos. 68: 319-320.

Beyers, R.J. 1964. The microcosm approach to ecosystem ecology. Am. Biol. Teach. 26: 491-497.

Boyd, S.A. and D.R. Shelton. 1984. Anaerobic biodegradation of chlorophenols in fresh and acclimated sludge. Appl. Environ. Microbiol. 47:272-277.

Bretz, J.H. 1939-1955. Geology of the Chicago Region, Part I: General; Part II: The Pleistocene. Ill. State Geol. Survey Bull. 65.

Bryant, M.P. 1976. The microbiology of anaerobic degradation and methanogenesis with special reference to sewage. Pages 107-117 in Proceedings of the Microbial Energy Conversion Symposium. Gottingen, F.R.G.

Buchanan, T.J., and W.P. Sommers. 1969. Discharge measurements at gaging stations. Book 3, Chapter A8 in Techniques of Water Resource Investigations of the United States Geological Survey.

Bulich, A. A. 1982. A practical and reliable method for monitoring the toxicity of aquatic samples. Process Biochemistry March/April: 45-47.

Bulich, A.A., M.W. Greene, and D. L. Isenberg. 1981. Reliability of the bacterial luminescence assay for determination of the toxicity of pure compounds and complex effluents. ASTM STP 737. American Society for Testing and Materials. pp. 338-347.

Cahill, R.A. 1981. Geochemistry of recent Lake Michigan sediments. Ill. State Geol. Survey Circ. 517, 94 pp.

Cahill, R.A., and N.F. Shimp. 1984. Inorganic contaminants in Lake Michigan sediments. In Toxic Contaminants in the Great Lakes, eds. J.O. Nriagu and M.S. Simmons. J. Wiley and Sons.

Cairns, J. Jr. 1984. Multispecies toxicity testing. Environ.Toxicol. and Chem. 3: 1-3.

Cairns, J. Jr., K. L. Dickson, E. Benfield, and A. L. Buikema. 1978. The Development of Biological Indices for Identifying and Evaluating Impacts of Pollutants on Freshwater Ecosystems. Summary Report to United States Department of Energy, Washington, DC, June 1978.

Cairns, J. Jr., K.M. Hart, and M.S. Henebry. 1980. The effects of a sublethal dose of copper sulfate on the colonization rate of freshwater protozoan communites. Amer. Mid. Nat.104: 93-101.

Cairns, J, Jr., D.L. Kuhn, and J.L. Plafkin. 1979. Protozoan colonization of artificial substrates. pages 34-57 in R.L. Weitzel, [ed.] Methods and Measurements of Periphyton Communities: A Review, American Society for Testing and Materials, Philadelphia, PA.

Cairns, J. Jr., and J.R Pratt. 1985. Multispecies toxicity testing using indigenous organisms -- a new, cost-effective approach to ecosystem protection. pages 149-159 in 1985 Environmental Conference, TAPPI Proceedings, ISSN 0272-7269. TAPPI Press, Atlanta GA.

Callahan, Michael A. and Michael Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. EPA-440/4-79-029. USEPA.

Campbell, P.G.C., A. Tessier, M. Bisson, and R. Bougie. 1985. Accumulation of copper and zinc in the yellow water lily, *Nuphar variegatum* : Relationships to metal partitioning in the adjacent lake sediments. Canadian Journal of Fisheries and Aquatic Sciences 42:23-32.

Chakrabarty, A.M. 1982. Biodegradation and Detoxification of Environmental Pollutants. CRC Press, Inc., BocaRaton, FL.

Champoux, L., P. Ross, V. Jarry, H. Sloterdijk, A. Mudroch, and Y. Couillard. 1986. Libèration par èlutriation des contaminants des sèdiments du lac Saint-Louis (fleuve Saint-Laurent Quèbec). Revue internationale des sciences de l'eau 2: 95-107.

Colten, C.E. 1985. Industrial Wastes in the Calumet Area, 1869-1970: An Historical Geography. Illinois Dept. of Energy and Natural Resources. Hazardous Waste Research and Information Center Report RR 001. Savoy, IL.

Cooke, G.D. 1974. Aquatic laboratory microsystems and communities. pages 47-86 in J. Cairns, Jr., [ed.] Structure and Function of Freshwater Microbial Communities. Virginia Polytechnic Institute and State University Press, Blacksburg, VA.

Cowardin, L.M., V. Carter, F.C. Golet, and E.T. LaRoe. 1979. Classification of wetlands and deepwater habitats of the United States. U.S. Fish Wildl. Serv. Biol. Serv. Prog., FWS/OBS-79/31.

Cowgill, U.M. 1974. The hydrogeochemistry of Linsley Pond, North Branford, Connecticut. II. The chemical composition of the aquatic macrophytes. Archive fur Hydrobiologia Supplement 1:1-119.

Cummins, K.W. 1973. Trophic relations of aquatic insects. Ann. Rev. Entomol. 18: 183-206.

Curtis, Carolanne, Ann Lima, S.J. Lozano, and G. D. Veith. 1982. Evaluation of a bacterial bioluminescence bioassay as a method for predicting acute toxicity of organic chemicals to fish. ASTM STP 766. American Society for Testing and Materials. pp. 170-178.

Dawson, F. H., E. Castellano, and M. Ladle. 1978. Concept of species succession in relation to river vegetation and management. Verh. Internat. Verin. Limnol. 20:1429-1434.

DeZwart, D. and W. Sloof. 1983. The Microtox™ as an alternative assay in the acute toxicity assessment of water pollutants. Aquatic Toxicology 4: 129-138.

Eisler, R. 1986. Polychlorinated biphenyl hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Fish and Wildlife Service Biological Report 85(1.7). Patuxent Wildlife Research Center, Laurel, MD.

Eisler, R. 1987. Polycyclic aromatic hydrocarbon hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Fish and Wildlife Service Biological Report 85(1.11). Patuxent Wildlife Research Center, Laurel, MD.

EnCap, Inc.1981. Habitat Evaluation of Lake Calumet. Chicago, IL.

Engler, Robert M. 1980. Prediction of pollution potential through geochemical and biological procedures: development of regulation guidelines and criteria for the discharge of dredged and fill material. pages 143-169 in Contaminants and Sediments Volume 1 (Robert A. Baker, editor). Ann Arbor Science Publishers. Ann Arbor, MI.

Equitable Environmental Health. 1978. Ecological Analysis of the Lake Calumet Development Area. Chicago, Illinois.

Everard, M., and P. Denny. 1985. Flux of lead in submerged plants and its relevance to a freshwater system. Aquatic Botany 21:185-193.

Franzin, W. G., and G. A. MacFarlane. 1980. An analysis of the aquatic macrophyte, *Myriophyllum exalbescens*, as an indicator of metal contamination of aquatic ecosystem near a base metal smelter. Bull. Environ. Contam. Toxicol. 24: 597-605.

Gabrielson, J.O., M.A. Perkins, and E.B. Welsh. 1984. The uptake, translocation and release of phosphorus by *Elodea densa*. Hydrobiologia 111: 43-48.

Gerloff, G.C. and K.A. Fishbeck. 1973. Plant content of elements as a bioassay of nutrient availability in lakes and streams. Pages 159-176 in G.E. Glass, ed. Bioassay Techniques and Environmental Chemistry, Ann Arbor Science Publishers, MI.

Gilkeson, R.H., K. Cartwright, J.B. Cowart, R.B. Holtzman. 1983. Hydrogeologic and Geochemical Studies of Selected Natural Radioisotopes and Barium in Groundwater in Illinois. Illinois State Geological Survey Contract Report 1983-6. 93 pp.

Greenfield, D.W. and J.D. Rogner. 1984. An assessment of the fish fauna of Lake Calumet and its adjacent wetlands, Chicago, Illinois: Past, present, and future. Trans. of Illinois Academy of Sciences 77: 77-93.

Goldman, J.C. 1983. p. 17-18 in Oceanic Nutrient Cycles. WHOI Annual Report.

Hase, A. and R.A. Hites. 1976. On the origin of polycyclic aromatic hydrocarbons in recent sediments. Geochimica Cosmo. Acta. 40: 1141-1143.

Healy, J.B., and L.Y. Young. 1979. Anaerobic Biodegradation of Eleven Aromatic Compounds to Methane. Appl. Environ. Microbiol. 38: 84-89.

Henebry, M.S., and J. Cairns, Jr. 1984. Protozoan colonization rates and trophicstatus of some freshwater wetland lakes. J. Protozool. 31: 456-467.

Henebry, M.S. and P. Ross. 1987a. Changes in the structure of protozoan communities exposed to contaminated sediments. International Symposium: Cellular Impacts in Ecotoxicology, Lyon, France, 19-22 May. Abstract.

Henebry, M.S. and P. Ross. 1987b. Use of protozoan community tests for estimating ecotoxicological hazard. Third International Symposium, Toxicity Testing Using Microbial Systems., Valencia, Spain, 11-15 May. Abstract.

Hill, B. H. 1979. Uptake and release of nutrients by aquatic macrophytes. Aquatic Botany 7:87-93.

Hobbie, J.E., R.J. Daley, and S. Jasper. 1977. Use of nucleopore filters for counting bacteria by fluorescence microscopy. Applied and Environ. Microbiol. 33:1225-1228.

Hoke, Robert A. and Bayliss L. Prater. 1980. Relationship of per cent mortality of four species of aquatic biota from 96-hour sediment bioassays of five Lake Michigan harbors and elutriate Chemistry of the Sediments. Bull. Environ. Contam. Toxicol. 25: 394-399.

Horowitz, A., D.R. Shelton, C.P. Cornell, and J.M. Tiedje. 1982. Anaerobic degradation of aromatic compounds in sediments and digested sludge. Dev. Ind. Microbiol. 23: 435-444.

Howard-Williams, C. and G.M. Lenton. 1975. The role of the littoral zone in the functioning of a shallow tropical lake ecosystem. Freshwater Biology 5: 445-459.

Hungate, R.E. 1982. Methane formation and cellulose digestion--biochemical ecology and microbiology of the rumen ecosystem. Experientia 38:189-182.

Hutchinson, G.E. 1975. A Treatise on Limnology. Vol III Limnological Botany. John Wiley & sons, New York.

Hvorslev, M.J. 1951. Time lag and soil permeability in groundwater observations. U.S. Army Waterways Experiment Station Bulletin 36.

Hydroqual, Inc. 1985. Grand Calumet River Wasteload Allocation Study.

IEPA. 1984. Illinois Water Quality Report 1982-1983. IEPA/WPC/84-024.

IEPA. 1986. The Southeast Chicago Study: An Assessment of Environmental Pollution and Public Health Impacts. IEPA/ENV/86-008. 150+ pp.

Jaynes, M.L. and S.R. Carpenter. 1986. Effects of vascular and nonvascular macrophytes on sediment redox and solute dynamics. Ecology 67: 875-882.

Kaiser, J.P. and K.W. Hanselmann. 1982. Fermentative metabolism of substituted monoaromatic compounds by a bacterial community from anaerobic sediments. Arch. Microbiol. 133: 185- 194.

Karr, J.R., 1981. Assessment of biotic integrity using fish communities. Fisheries 6: 21-27.

Kelly, M.H. and R.L. Hite. 1981. Chemical analysis of surficial sediments from 63 Illinois Lakes, Summer 1979. IEPA. Springfield, Illinois.

Kirk, J.R., K.J. Hlinka, R.T. Sasman, and E.W. Sanderson. 1985. Water withdrawals in Illinois, 1984. Illinois State Water Survey Circular 163.

Kudo, R.R. 1966. Protozoology, 5th ed. Charles C. Thomas, Springfield, Illinois, 1174 pp.

Laflamme, R.E. and R.A. Hites. 1978. The global distribution of polycyclic aromatic hydrocarbons in recent sediments. Geochimica Cosmo. Acta. 42: 289-303.

Lambe, T.W., and R.V. Whitman. 1969. Soil Mechanics. John Wiley and Sons, Inc., New York. 553 pp.

Larsen, V.J. and H.H. Schierup. 1981. Macrophyte cycling of zinc, copper, lead and cadmium in the littoral zone of a polluted and a non-polluted lake. II. Seasonal changes in heavy metal content of above-ground biomass and decomposing leaves of *Phragmites australis*. Aquatic Botany 11: 211-230.

LeBlanc, G. A. 1984. Interspecies relationships in acute toxicity of chemicals to aquatic organisms. Environmental Toxicology and Chemistry 3:47-60.

Lee, C.R., R.K. Peddicord, B.L. Folsom, and J.G. Skogerboe. 1987. The use of bioassay and associated tests in dredged material and disposal management. Hydrobiologia 149: 81-86.

Lee, D.R. 1977. A device for measuring seepage flux in lakes and estuaries. Limnol. Oceanogr. 22: 140-147.

Lee, D.R. 1980. Groundwater-solute influx. Limnol. Oceanogr. 25: 183-186.

Lee, D.R. and J.A. Cherry. 1978. A field exercise on gorundwater flow using seepage meters and mini-piezometers. Jour. Geological Education 27: 6-10.

Lee, D.R., J.A. Cherry, and J.F. Pickens. 1980. Groundwater transport of a salt tracer through a sandy lakebed. Limnol. Oceanogr. 25: 45-61.

Leland, H.V., S.S. Shukla, and N.F. Shimp. 1973. Factors affecting distribution of lead and other trace elements in sediments of southern Lake Michigan. pages 89-138 in Trace metals and metal-organic interactions in natural waters. Ann Arbor Science, Ann Arbor, MI.

Lettinga, G., K.C. Pette, R. de Vletter and E. Wind. 1977. Anaerobic treatment of sugarbeet waste water in a $6m^3$ pilot plant. $H_2O$ 10: 526.

Liss, P. S. and Slater, P. G. 1974. Flux of Gases across the Air-Sea Interface. Nature 247: 181-184.

Mackay, D. 1979. Finding fugacity feasible. Envir. Sci. & Tech. 13: 1218-23.

Mackay, D. and Peterson, S. 1981. Calculating fugacity. Envir. Sci. & Tech. 15: 1006-14.

Mayes, Roger A. and Alan W. McIntosh. 1977. Uptake of cadmium and lead by a rooted aquatic macrophyte (*Elodea canadensis*). Ecology 58: 1176-1180.

McBride, M.S. and H.O. Pfannkuch. 1975. The distribution of seepage within lakebeds. Jour. Research U.S. Geol. Survey 3: 505-512.

McIntosh, A.W., B.K. Shephard, R.A. Mayes, G.J. Atchison, and D.W. Nelson. 1978. Some aspects of sediment distribution and macrophyte cycling of heavy metals in a contaminated lake. Journal of Envirnomental Quality 7:301-305.

McKinney, J. D. 1976. Toxicology of selected symmetrical hexachlorobiphenyl isomers: correlating biological effects with chemical structure. Pages 73-76 *in* Proceedings, USEPA National Conference on Polychlorinated Biphenyls, Chicago, IL, November 1975.

Miller, G.E., I. While and G. Hitchin. 1983. Patterns of accumulation of selected metals in members of soft-water macrophyte flora of central Ontario lakes. Aquatic Botany 15: 53-64.

Mudroch, A. and J.A. Capobianco. 1979. Effects of mine effluent on uptake of Co, Ni, Cu, As, Zn, Cd, Cr, and Pb by aquatic macrophytes. Hydrobiologia 64:223-231.

Murphy, T. J., Mullin, M. D. and Meyer, J. A. 1986. Equilibration of PCBs and toxaphene with air and water. Envir. Sci. & Tech. 21: 155-62.

Namkung,E. and B.E. Rittmann. 1986. A study of VOC emmissions from the Calumet sewage treatment plant in the Chicago area. ILENR/RE-AQ-86/15. Illinois Department of Energy and Natural Resources, Springfield, IL.

National Research Council. 1981. Testing for effects of chemicals on ecosystems. National Academy Press, Washington, D.C.

Norris, K.P. and E.O. Powell. 1961. J.R. Microsc. Soc. 80:107-119.

Odum, E.P. 1984. Mesocosm. Bioscience 34: 558-562.

Pratt, J.R., and J. Cairns, Jr. 1985. Functional groups in the Protozoa: roles in differing ecosystems. J. Protozool. 32: 415-423.

Quereshi, A.A., K.W. Flood, S.R. Thompson, S.M. Janhurst, C.S. Inniss, and D.A. Rokosh. 1982. Comparison of a luminescent bacterial test with other bioassays for determining toxicity of pure compounds and complex effluents. ASTM STP 766. American Society for Testing and Materials. pp. 179-195.

Risatti, J. Bruno, and W.G. Sheridan. 1987. Rates of microbial dechlorination of polychlorinated biphenyls (PCBs) in anaerobic sediments from Waukegan Harbor. Report to Hazardous Waste Research andInformation Center, Savoy, Il.

Ross. P.E., 1987. Ecotoxicology for Illinois. IN Ecotoxicology for Illinois: Establishing the research agenda. Illinois Hazardous Waste Research and Information Center Report RR 015, Savoy IL

Ross, P. E., M.S. Henebry, W. Wang, and L.C. Burnett. 1987. Assessment of ecotoxicological hazard of Waukegan Harbor sediments. Final Report to the Hazardous Waste Research and Information Center, Savoy, Illinos, December 1987.

Ross, P., V. Jarry, and H. Sloterdijk. 1987. A rapid bioassay using the green alga *Selenstrum capricornutum* to screen for toxicity in St. Lawrence River sediment elutriates. Accepted by ASTM.

Samoiloff, M. R. and T. Bogeart. 1984. The use of nematodes in marine ecotoxicology. *in* G. Personne, E. Jaspers, and C. Claus editors. Ecotoxicological testing for the marine environment, Vol. 1. State University of Ghent and Institute of Marine Scientific Research, Brendene, Belgium.

Samoiloff, M. R., and P. G. Wells. 1984. Future trends in marine ecotoxicology. Pages 733-750 *in* G. Personne, E. Jaspers, and C. Claus editors. Ecotoxicological testing for the marine environment, vol. 1. State University of Ghent and Institute of Marine Scientific Research, Brendene, Belgium.

Samoiloff, M. R., S. Schulz, Y. Jordan, K. Denich, and E. Arnott. 1980. A rapid simple long-term toxicity assay for aquatic contaminants using the nematode *Panagrellus redivivus*. Canadian Journal of Fisheries and Aquatic Sciences 37:1167-1174.

Samoiloff, M.R., J. Bell, D.A. Birkholz, G.R.B Webster, E. Arnott, R. Pulak, and A. Madrid. 1983. Combined bioassay-chemical fractionation scheme for the determination and ranking of toxic chemicals in sediments. Environ. Sci. Technol. 17: 329-334.

Sasman, R.T., C.R. Benson, R.S. Ludwigs, and T.L. Williams. 1982. Water-level trends, pumpage, and chemical quality in the Cambrian-Ordivician aquifer in Illinois, 1971-1980. Illinois State Water Survey Circular 154.

Schicht, R.J., J.R. Adams, and J.B. Stall. 1976. Water Resources Availability, Quality, and Cost in Northeastern Illinois. Illinois State Water Survey Report of Investigation 83. 90 pp.

Schierup, H.H. and V.J. Larsen. 1981. Macrophyte cycling of zinc, copper, lead and cadmium in the littoral zone of a polluted and a non-polluted lake. I. Availability, uptake, and translocation of heavy metals in *Phragmites australis*. Aquatic Botany 11: 197-210.

Schink, B. and N. Pfennig. 1982. Fermentation of trihydroxy- benzenes by*Pelobacter acidigallici* gen. nov. sp. nov., a new strictly anaerobic, non-spore forming bacterium. Arch. Microbiol. 133:195-201.

Sculthorpe, C.D. 1967. The Biology of Aquatic Vascular Plants. Edward Arnold Publishers Ltd. London.

Slowinski, Thomas. Chicago district, U.S. Army Corps of Engineers, 219 S. Dearborn, Chicago, IL 60604. Personal communication with W. Garrison, August, 1987.

Smith, C.S., and M.S. Adams. 1986. Phosphorus transfer from sediments by *Myriophyllum spicatum*. Linmol. Ocean. 31: 1312-1321.

Sokal, R.R, and F.J. Rohlf. 1969. Biometry. W. H. Freeman and Company, San Francisco, California.

Strachan, W. M. J. and Eisenreich, S. J. 1987. Mass balancing of toxic chemicals in the Great Lakes: The role of atmospheric deposition. A report of a Workshop held at the Guild Inn, Scarborough, Ontario, October 29-31, 1986. International Joint Commission, 100 Ouelette St, Windsor, Ontario.

Sulflita, J.M., A. Horowitz, D.R. Shelton and J.M. Tiedje. 1982. Dehalogenation: A novel pathway for the anaerobic biodegradation of haloaromatic compounds. Science 218: 1115-1117.

Suloway, J., T. Skelly, W. Roy, D. Dickerson, R. Schuller, and R. Griffin. 1983. Chemical and toxicological properties of coal fly ash. IDENR. Environmental Geology Notes 105. Champaign, Illinois.

Suter, M., R.E. Bergstrom, H.F. Smith, G.H. Emrich, W.C. Walton, T.E. Larson. 1959. Ground-Water Resources of the Chicago Region, Illinois. Cooperative Ground-Water Report 1. Illinois State Water and Geological Surveys. 89 pp.

Sweet,C.W. and D.F. Gatz. 1987. Atmospheric research and monitoring study of hazardous substances: Second Annual Report. RR 014. Illinois Hazardous Waste Research and Information Center, Savoy, Illinois.

USACE. 1976. Ecological evaluation of proposed discharge of dredged or fill material into navigable waters. Misc. papeer D-76-17. U.S. Army Engineer Waterways Experiment Station, Vicksburg,MS.

USACE, Chicago District, Final Environmental Impact Statement, May 1982, Chicago Area Confined Disposal Facility and Maintenance Dredging in Cook County, Illinois.

USACE, Chicago District. 1982. Phase I, General Design Memorandum, Little Calumet River, Indiana, Technical Volume E, Hydrology and Hydraulics, July.

USACE. 1983. Phase II Letter Report, Little Calumet River, Illinois, Technical Appendices.

USACE. 1985. Draft Environmental Impact Statement: Section 10 and Section 404 Permit for a sanitary landfill in a wetland adjacent to Lake Calumet, Chicago, Cook County, IL. Chicago, IL.

USEPA. 1986. Gas chromatography/mass spectrometry for semivolatile organics: Capillary column technique. Method 8270, USEPA.

USEPA. 1986. Sonication Extraction, Method 3550. USEPA.

Visocky, A.P., M.G. Sherrill, and K. Cartwright. 1985. Geology, hydrology, and water quality of the Cambrian and Ordovician systems in Northern Illinois. Illinois State Geological and Water Surveys Cooperative Groundwater Report 10. 136 pp.

Wakeham, S.G., C. Schaffner and W. Giger. 1980a. Polycyclic aromatic hydrocarbons in recent lake sediments I. Compounds having anthropogenic origins. Geochimica Cosmo. Acta. 44: 403-413.

Wakeham, S.G., C. Schaffner and W. Giger. 1980b. Polycyclic aromatic hydrocarbons in recent lake sediments II. Compounds derived from biogenic precursors during early diagenesis. Geochimica Cosmo. Acta. 44: 415-429.

Welsh, R.P.H. and P. Denny. 1980. The uptake of lead and copper by submerged aquatic macrophytes in two English lakes. J. Ecology 68: 443-445.

Welsh, R.P.H. and P. Denny. 1976. Waterplants and the recycling of heavy metals in an English lake. Proc. Conf. Trace Substances and Environmental Health 10: 217-223.

Wetzel, R.G. 1983. Limnology. 2nd edition. Saunders College Publishing. Philadelphia, PA.

Wiley, M. J., and R. W. Gorden. 1984. Biological control of aquatic macrophytes by herbivorous carp. Part 2. Biology and ecology of herbivorous carp. Final report, Federal Aid Project F-37-R. Aq. Biol. Tech. Rep. 1984(11). Ill. Nat. Hist. Survey, Champaign.

Willford, W.A., M.J. Mac, and R.J. Hesselberg. 1987. Assessing the bioaccumulation of contaminants from sediments by fish and other aquatic organisms. Hydrobiologia 149: 107-111.

Williams, L.G., P.M. Chapman, and T.C. Ginn. 1986. A comparative evaluation of marine sediment toxicity using bacterial luminescence, oyster embryo, and amphipod sediment bioassays. Marine Environmental Research 19: 225-249.

Willman, H.B. 1971. Summary of the Geology of the Chicago Area. Illinois State Geological Survey Circular 460. 77

Wright, J. F., P. D. Hiley, S. F. Ham, and A. D. Berrie. 1981.Comparison of three mapping procedures developed for river macrophytes. Freshwater Biology 11(4): 369-380.

# Appendices

Appendix 1. Elemental analysis of Lake Calumet surficial sediments from 13 stations.

| STATION | ELEMENTS | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | AG | Al (%) | As | B | Ba | Be | Br | Ca (%) | Cd | Ce | Co |
| A | 1.1 | 2.92 | 16 | 22 | 543 | <1 | 5.0 | 6.42 | <1.5 | 25 | 7 |
| B | 1.8 | 4.47 | 44 | 31 | 534 | <1 | 7.0 | 7.58 | 3.6 | 38 | 12 |
| C | 1.5 | 4.84 | 50 | 39 | 488 | <1 | 4.0 | 7.41 | 2.9 | 45 | 14 |
| D | 0.5 | 3.83 | 25 | 30 | 524 | <1 | 9.0 | 7.38 | <1.5 | 32 | 9 |
| E | 0.6 | 4.75 | 31 | 36 | 455 | <1 | 4.0 | 7.25 | <1.5 | 45 | 14 |
| F | 0.3 | 5.32 | 29 | 33 | 430 | <1 | 3.0 | 6.36 | <1.5 | 45 | 14 |
| G | 0.9 | 4.57 | 42 | 58 | 454 | 2.0 | 4.0 | 6.75 | <1.5 | 50 | 14 |
| H | 0.6 | 4.97 | 44 | 56 | 473 | 1.2 | 4.0 | 6.56 | <1.5 | 50 | 15 |
| I | <.3 | 4.89 | 21 | 60 | 434 | 1.6 | 3.0 | 6.03 | <1.5 | 51 | 16 |
| J | <.2 | 4.18 | 20 | 60 | 371 | 1.2 | 2.0 | 6.56 | <1.5 | 46 | 14 |
| K | <.2 | 3.91 | 23 | 34 | 452 | <1 | 3.0 | 5.09 | <1.5 | 28 | 9 |
| L | <.6 | 5.45 | 21 | 55 | 420 | 1.3 | 4.0 | 6.57 | <1.5 | 49 | 15 |
| M | <.2 | 3.72 | 22 | 38 | 414 | <1 | 3.0 | 5.64 | <1.5 | 32 | 11 |
| L.C. AVG. | 0.562 | 4.45 | 29.8 | 42.4 | 461 | | 4.23 | 4.71 | 1.76 | 41.2 | 12.6 |
| L.M. AVG. | 0.46 | 3.82 | 10.5 | | 494 | | 33 | 2.84 | 0.9 | 48 | 9 |

| | Cr | Cs | Cu | Eu | Fe (%) | Ga | Hf | K (%) | La | Lu | Na (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 54 | 2.0 | 42 | 0.4 | 1.58 | 8 | 3.1 | 1.60 | 15 | 0.15 | 0.61 |
| B | 116 | 4.7 | 115 | 0.8 | 2.78 | 10 | 4.5 | 2.14 | 24 | 0.27 | 0.44 |
| C | 110 | 5.9 | 104 | 0.9 | 2.92 | 13 | 4.7 | 2.37 | 30 | 0.30 | 0.41 |
| D | 71 | 3.6 | 60 | 0.6 | 2.15 | 8 | 3.7 | 1.85 | 18 | 0.23 | 0.55 |
| E | 83 | 5.7 | 58 | 0.8 | 2.88 | 10 | 4.9 | 2.45 | 25 | 0.35 | 0.43 |
| F | 70 | 6.0 | 48 | 1.0 | 3.00 | 13 | 4.6 | 2.74 | 31 | 0.31 | 0.40 |
| G | 90 | 6.7 | 62 | 1.1 | 3.00 | 15 | 5.6 | 2.52 | 34 | 0.41 | 0.43 |
| H | 88 | 6.8 | 77 | 0.9 | 3.11 | 11 | 5.2 | 2.58 | 27 | 0.33 | 0.41 |
| I | 75 | 6.1 | 42 | 0.9 | 3.10 | 11 | 5.3 | 2.77 | 27 | 0.31 | 0.41 |
| J | 51 | 4.0 | 37 | 0.9 | 2.51 | 9 | 5.6 | 2.38 | 27 | 0.27 | 0.48 |
| K | 41 | 2.8 | 13 | 0.6 | 2.11 | 10 | 3.3 | 2.16 | 17 | 0.20 | 0.62 |
| L | 89 | 7.5 | 54 | 0.9 | 3.64 | 12 | 4.8 | 2.53 | 27 | 0.30 | 0.39 |
| M | 60 | 4.1 | 36 | 0.7 | 2.57 | 8 | 5.2 | 1.92 | 17 | 0.26 | 0.53 |
| L.C. AVG. | 76.8 | 5.07 | 57.5 | 0.81 | 2.72 | 10.6 | 4.65 | 1.92 | 24.5 | 0.28 | 0.47 |
| L.M. AVG. | 46 | 2.9 | 22 | 0.8 | 2.17 | 10 | 5.1 | 1.83 | 23 | 0.2 | 0.459 |

| | Ni (%) | P | Pb | Rb | Sb | Sc | Se | Si | Sm | Sn | Sr (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 12 | 0.06 | 220 | 52 | 1.2 | 3.9 | <1 | 25.4 | 2.1 | 31 | 101 |
| B | 29 | 0.11 | 316 | 69 | 2.1 | 7.0 | 1.4 | 20.4 | 4.3 | 42 | 103 |
| C | 27 | 0.12 | 298 | 84 | 2.3 | 8.1 | 1.1 | 20.8 | 5.1 | 44 | 104 |
| D | 22 | 0.06 | 373 | 65 | 3.2 | 6.0 | 1.1 | 23.2 | 2.9 | 24 | 118 |
| E | 30 | 0.05 | 206 | 83 | 1.5 | 8.2 | 1.0 | 21.6 | 4.4 | 30 | 93 |
| F | 27 | 0.05 | 109 | 86 | 2.1 | 8.4 | 1.3 | 22.8 | 5.6 | 19 | 89 |
| G | 33 | 0.07 | 180 | 103 | 1.3 | 9.0 | <.5 | 20.4 | 5.7 | 21 | 93 |
| H | 25 | 0.06 | 206 | 94 | 1.5 | 9.0 | 0.7 | 21.7 | 5.1 | 24 | 91 |
| I | 31 | 0.05 | 101 | 94 | 1.0 | 9.2 | 1.2 | 22.0 | 4.6 | 13 | 79 |
| J | 14 | 0.04 | 70 | 73 | 1.1 | 7.4 | <.6 | 23.0 | 5.3 | 7 | 76 |
| K | 12 | 0.04 | 90 | 69 | 2.5 | 4.8 | <.5 | 26.8 | 3.0 | 6 | 95 |
| L | 34 | 0.06 | 167 | 89 | 1.5 | 9.0 | 1.3 | 21.3 | 5.3 | 14 | 98 |
| M | 12 | 0.05 | 105 | 71 | 1.0 | 5.9 | <.5 | 25.8 | 2.9 | 10 | 95 |
| L.C. AVG. | 23.6 | 0.03 | 187 | 79.4 | 2.35 | 7.38 | 0.7 | 22.7 | 4.33 | 21.9 | 95 |
| L.M. AVG. | 24 | 0.07 | 40 | 85 | 1.1 | 6.6 | 1.2 | 31.4 | 3.7 | | 132 |

Appendix 1. Continued.

| | Ta | Tb | Th | Ti | Tl | U | V | W | Yb | Zn (%) | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 0.3 | 0.26 | 3.2 | 0.16 | 6 | 1.4 | 25 | 1.0 | 1.1 | 199 | 86 |
| B | 0.6 | 0.46 | 6.0 | 0.31 | 7 | 2.3 | 37 | 1.7 | 1.9 | 591 | 131 |
| C | 0.7 | 0.54 | 7.2 | 0.35 | 5 | 4.0 | 60 | 2.1 | 2.5 | 599 | 141 |
| D | 0.5 | 0.36 | 4.9 | 0.24 | 8 | 3.0 | 35 | 2.5 | 1.5 | 482 | 115 |
| E | 0.7 | 0.60 | 7.2 | 0.35 | 8 | 4.0 | 36 | 1.7 | 2.3 | 371 | 159 |
| F | 0.7 | 0.50 | 7.3 | 0.40 | 8 | 4.0 | 44 | 2.0 | 2.2 | 241 | 166 |
| G | 0.8 | 0.60 | 8.2 | 0.36 | 7 | 4.0 | 68 | 2.0 | 1.5 | 389 | 168 |
| H | 0.8 | 0.80 | 7.7 | 0.38 | 4 | 4.0 | 76 | 1.8 | 1.6 | 436 | 166 |
| I | 0.8 | 0.60 | 7.8 | 0.38 | 6 | 5.0 | 76 | 1.7 | 2.7 | 217 | 179 |
| J | 0.7 | 0.50 | 6.6 | 0.32 | 7 | 5.0 | 39 | 1.0 | 2.4 | 110 | 179 |
| K | 0.4 | 0.40 | 3.9 | 0.18 | 7 | 3.0 | 37 | 1.5 | 0.9 | 156 | 103 |
| L | 0.7 | 0.50 | 7.7 | 0.37 | 5 | 3.5 | 68 | 1.8 | 1.6 | 423 | 161 |
| M | 0.4 | 0.40 | 5.0 | 0.24 | 3 | 3.0 | 30 | 1.7 | 1.9 | 229 | 150 |
| L.C. AVG. | 0.62 | 0.50 | 6.36 | 0.19 | 6.23 | 3.55 | 48.5 | 1.73 | 1.85 | 341.0 | 146 |
| L.M. AVG. | 0.5 | 0.5 | 5.8 | 0.18 | | | | 1.1 | 1.7 | 97 | 138 |

Appendix 2. Concentrations of total carbon, inorganic carbon, and organic carbon in Lake Calumet surficial sediments from 37 stations.

| | CARBON | | |
|---|---|---|---|
| STATIONS | AVG TC (%) | AVG INC (%) | OC (%) |
| L-1 | 5.4 | 2.7 | 2.7 |
| L-2 | 5.4 | 2.8 | 2.6 |
| L-3 | 5.5 | 3.5 | 2.0 |
| L-4 | 4.3 | 2.7 | 1.6 |
| L-5 | 5.7 | 3.1 | 2.6 |
| L-6 | 5.5 | 2.8 | 2.7 |
| L-7 | 5.8 | 2.8 | 3.0 |
| L-8 | 6.5 | 2.9 | 3.6 |
| L-9 | 5.4 | 2.8 | 2.6 |
| L-10 | 5.9 | 2.8 | 3.1 |
| L-11 | 5.4 | 2.7 | 2.7 |
| L-12 | 4.5 | 2.8 | 1.7 |
| L-13 | 5.2 | 3.4 | 1.8 |
| L-14 | 3.2 | 2.1 | 1.1 |
| L-15 | 4.9 | 2.7 | 2.2 |
| L-16 | 4.1 | 2.5 | 1.6 |
| L-17 | 6.0 | 2.5 | 3.5 |
| L-18 | 5.8 | 2.6 | 2.4 |
| L-19 | 4.2 | 2.3 | 1.9 |
| L-20 | 5.9 | 2.3 | 2.6 |
| W-4 | 8.6 | 3.1 | 5.5 |
| W-5 | 9.0 | 3.4 | 5.6 |
| W-6 | 9.0 | 3.6 | 5.4 |
| W-7 | 9.0 | 3.3 | 5.7 |
| A | 5.5 | 2.7 | 2.8 |
| B | 8.1 | 3.3 | 4.8 |
| C | 7.2 | 2.8 | 4.4 |
| D | 6.6 | 3.3 | 3.3 |
| E | 6.2 | 3.2 | 3.0 |
| F | 5.4 | 2.9 | 2.5 |
| G | 6.2 | 3.0 | 3.2 |
| H | 6.0 | 2.9 | 3.1 |
| I | 5.4 | 2.9 | 2.5 |
| J | 4.8 | 3.3 | 1.5 |
| K | 4.2 | 2.6 | 1.6 |
| L | 5.8 | 2.9 | 2.9 |
| M | 4.6 | 2.5 | 2.1 |

Appendix 3. Elemental analysis of Lake Calumet surficial sediments from 24 stations taken on April 28, 1987.

| STATION | ELEMENTS | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ag | Al | As | B | Ba | Be | Br | Ca | Cd | Ce | Co | Cr |
| | | % | | | | | | % | | | | |
| LCAL 1 | <1 | 10.92 | 21 | 80 | 383 | <1 | 5 | 7.96 | <2 | 67 | 21 | 127 |
| LCAL 2 | <1 | 11.30 | 20 | 93 | 377 | <1 | 5 | 8.67 | <2 | 49 | 16 | 88 |
| LCAL 3 | <1 | 10.86 | 14 | 80 | 406 | <1 | 4 | 12.30 | <2 | 57 | 16 | 84 |
| LCAL 4 | <1 | 10.52 | 15 | 67 | 491 | <1 | 2.5 | 7.84 | <3 | 43 | 14 | 61 |
| LCAL 5 | <1 | 10.42 | 18 | 54 | 450 | 1.2 | 4.2 | 9.55 | <2 | 45 | 15 | 96 |
| LCAL 6 | <1 | 10.63 | 19 | 70 | 454 | 1 | 4 | 8.77 | <2 | 46 | 15 | 86 |
| LCAL 7 | <1 | 10.62 | 19 | 73 | 419 | 1.2 | 3.5 | 8.63 | <2 | 44 | 17 | 93 |
| LCAL 8 | <1 | 8.38 | 21 | 42 | 418 | 1.1 | 4 | 8.01 | <3 | 35 | 14 | 78 |
| LCAL 9 | <1 | 11.56 | 21 | 70 | 448 | 1.2 | 3.8 | 8.43 | <3 | 47 | 18 | 97 |
| LCAL 10 | <1 | 10.46 | 23 | 65 | 439 | 1.1 | 3.5 | 8.31 | <3 | 45 | 16 | 91 |
| LCAL 11 | <1 | 7.50 | 23 | 31 | 421 | <1 | 4 | 7.62 | <3 | 39 | 12 | 63 |
| LCAL 12 | <1 | 11.26 | 22 | 67 | 470 | <1 | 4 | 7.88 | <3 | 43 | 15 | 64 |
| LCAL 13 | <1 | 8.71 | 36 | 58 | 377 | <1 | 3.4 | 8.73 | <3 | 63 | 16 | 64 |
| LCAL 14 | <1 | 6.01 | 23 | 48 | 379 | <1 | 3 | 5.60 | <3 | 31 | 10 | 39 |
| LCAL 15 | <1 | 8.98 | 26 | 53 | 433 | <1 | 3.4 | 6.98 | <3 | 46 | 14 | 66 |
| LCAL 16 | <1 | 6.40 | 33 | 28 | 398 | <1 | 3 | 6.57 | <2 | 30 | 9 | 42 |
| LCAL 17 | <1 | 9.05 | 37 | 50 | 408 | <1 | 3 | 7.11 | <2 | 44 | 14 | 86 |
| LCAL 18 | <1 | 10.30 | 33 | 61 | 434 | <1 | 3.5 | 7.49 | <2 | 42 | 17 | 75 |
| LCAL 19 | <1 | 8.00 | 32 | 41 | 402 | <1 | 2 | 6.36 | <2 | 35 | 12 | 65 |
| LCAL 20 | <1 | 10.06 | 19 | 60 | 401 | <1 | 4 | 8.86 | <3 | 52 | 15 | 76 |
| WCAL 4 | <1 | 9.42 | 15 | 65 | 435 | <1 | 16 | 11.58 | <3 | 52 | 16 | 111 |
| WCAL 5 | <1 | 9.69 | 13 | 63 | 443 | <1 | 22 | 13.23 | <3 | 55 | 17 | 121 |
| WCAL 6 | <1 | 8.88 | 15 | 60 | 432 | <1 | 21 | 14.25 | <3 | 53 | 16 | 116 |
| WCAL 7 | <1 | 6.39 | 16 | 34 | 353 | <1 | 8 | 9.74 | <3 | 44 | 16 | 129 |

| STATION | Cs | Cu | Eu | Fe | Ga | Ge | Hf | K | La | Li | Lu | Mg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | % | | | | % | | | | % |
| LCAL 1 | 9.7 | 73 | 0.74 | 6.85 | 13 | 17 | 5.5 | 3.17 | 26 | 44 | 0.37 | 4.76 |
| LCAL 2 | 7.5 | 48 | 0.92 | 5.85 | 14 | 9 | 4.6 | 3.26 | 29 | 43 | 0.32 | 4.97 |
| LCAL 3 | 6.6 | 36 | 0.74 | 4.82 | 14 | 8 | 4.1 | 3.17 | 26 | 39 | 0.36 | 4.60 |
| LCAL 4 | 5.2 | 34 | 0.87 | 4.62 | 13 | <5 | 5.4 | 3.24 | 23 | 39 | 0.29 | 4.58 |
| LCAL 5 | 6.5 | 56 | 0.82 | 5.97 | 14 | <5 | 4.8 | 2.98 | 24 | 40 | 0.35 | 5.14 |
| LCAL 6 | 6.7 | 51 | 0.89 | 6.12 | 12 | <5 | 4.7 | 3.08 | 24 | 42 | 0.29 | 5.03 |
| LCAL 7 | 7.5 | 53 | 0.85 | 6.64 | 12 | <5 | 5.6 | 2.85 | 25 | 46 | 0.4 | 4.88 |
| LCAL 8 | 4.8 | 58 | 0.73 | 5.65 | 10 | <5 | 4.8 | 2.40 | 19 | 23 | 0.3 | 4.88 |
| LCAL 9 | 8.5 | 72 | 1 | 6.64 | 13 | <5 | 4.6 | 3.09 | 27 | 46 | 0.39 | 4.60 |
| LCAL 10 | 7.8 | 67 | 0.9 | 5.89 | 13 | <5 | 4.9 | 2.96 | 27 | 42 | 0.37 | 4.82 |
| LCAL 11 | 3.9 | 45 | 0.6 | 4.58 | 8 | <5 | 4.5 | 2.28 | 25 | 22 | 0.25 | 4.59 |
| LCAL 12 | 5.2 | 33 | 0.9 | 4.87 | 14 | <5 | 4.2 | 3.29 | 25 | 46 | 0.36 | 5.27 |
| LCAL 13 | 4.7 | 43 | 1.1 | 4.14 | 12 | <5 | 6.2 | 2.88 | 23 | 30 | 0.34 | 5.72 |
| LCAL 14 | 2.8 | 28 | 0.9 | 3.26 | 10 | <5 | 8.2 | 1.92 | 26 | 11 | 0.29 | 3.55 |
| LCAL 15 | 4.4 | 34 | 0.9 | 4.42 | 11 | <5 | 4.9 | 2.92 | 24 | 30 | 0.35 | 4.67 |
| LCAL 16 | 2.6 | 30 | 0.7 | 3.67 | 8 | <5 | 4.1 | 2.06 | 16 | 18 | 0.22 | 4.15 |
| LCAL 17 | 5.9 | 44 | 1 | 5.06 | 12 | <5 | 4.8 | 2.63 | 24 | 31 | 0.3 | 4.40 |
| LCAL 18 | 7 | 50 | 1 | 6.03 | 14 | <5 | 4.5 | 2.92 | 28 | 38 | 0.15 | 4.52 |
| LCAL 19 | 3.8 | 23 | 0.8 | 4.34 | 10 | 8 | 7.6 | 2.48 | 20 | 26 | 0.32 | 4.38 |
| LCAL 20 | 6.2 | 54 | 0.8 | 5.02 | 12 | 10 | 5.4 | 2.90 | 26 | 36 | 0.35 | 5.47 |
| WCAL 4 | 6.5 | 65 | 0.7 | 5.88 | 10 | 9 | 4.2 | 2.82 | 22 | 41 | 0.33 | 4.01 |
| WCAL 5 | 7.1 | 62 | 0.6 | 6.06 | 12 | <5 | 3.8 | 2.93 | 22 | 43 | 0.3 | 3.72 |
| WCAL 6 | 6 | 74 | 0.61 | 7.78 | 10 | <5 | 3.4 | 2.60 | 21 | 37 | 0.26 | 4.04 |
| WCAL 7 | 3.5 | 61 | 0.5 | 14.59 | 9 | 9 | 4.2 | 1.92 | 17 | 24 | 0.26 | 4.82 |

| STATION | Mn % | Mo | Na % | Ni | P % | Pb | Rb | Sb | Sc | Si % | Sm | Sn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LCAL 1 | 0.13 | 31 | 0.55 | 36 | 0.28 | 200 | 127 | 2.7 | 11 | 48.88 | 4.5 | 7 |
| LCAL 2 | 0.15 | 28 | 0.5 | 29 | 0.16 | 170 | 93 | 1.5 | 10 | 48.81 | 4.9 | 7 |
| LCAL 3 | 0.11 | 26 | 0.55 | 28 | 0.15 | 120 | 104 | 1.2 | 10 | 44.79 | 4.3 | 6 |
| LCAL 4 | 0.07 | 22 | 0.62 | 21 | 0.11 | 64 | 105 | 0.9 | 9.2 | 53.89 | 4.4 | 5 |
| LCAL 5 | 0.14 | 20 | 0.55 | 30 | 0.16 | 160 | 87 | 1.2 | 9.3 | 48.53 | 4.6 | 12 |
| LCAL 6 | 0.14 | 21 | 0.55 | 32 | 0.15 | 170 | 98 | 1.3 | 9.5 | 48.62 | 4.6 | 11 |
| LCAL 7 | 0.11 | 20 | 0.58 | 34 | 0.12 | 150 | 94 | 1.3 | 10 | 48.75 | 4.8 | 9 |
| LCAL 8 | 0.09 | 18 | 0.66 | 21 | 0.12 | 130 | 77 | 1.3 | 7.6 | 53.29 | 4 | 9 |
| LCAL 9 | 0.11 | 20 | 0.5 | 42 | 0.12 | 173 | 106 | 2 | 11 | 49.11 | 4.9 | 11 |
| LCAL 10 | 0.11 | 19 | 0.58 | 33 | 0.12 | 183 | 92 | 1.7 | 9.7 | 49.26 | 4.7 | 10 |
| LCAL 11 | 0.09 | 15 | 0.71 | 27 | 0.11 | 127 | 67 | 1.2 | 6.3 | 56.66 | 4.1 | 5 |
| LCAL 12 | 0.11 | 20 | 0.58 | 22 | 0.10 | 91 | 106 | 1 | 9.7 | 51.69 | 4.2 | <5 |
| LCAL 13 | 0.08 | 24 | 1.06 | 21 | 0.09 | 76 | 80 | 1.3 | 8.8 | 52.29 | 4.3 | 6 |
| LCAL 14 | 0.08 | 18 | 0.62 | <15 | 0.08 | 84 | 61 | 0.9 | 5.3 | 66.36 | 5.2 | <5 |
| LCAL 15 | 0.08 | 20 | 0.62 | 19 | 0.09 | 89 | 92 | 1 | 8.2 | 55.63 | 4.4 | <5 |
| LCAL 16 | 0.07 | 15 | 0.8 | <7 | 0.11 | 80 | 62 | 0.7 | 4.6 | 64.84 | 2.9 | <5 |
| LCAL 17 | 0.09 | 20 | 0.63 | 23 | 0.12 | 130 | 88 | 1.4 | 8.3 | 55.90 | 4.5 | 6 |
| LCAL 18 | 0.11 | 24 | 0.61 | 27 | 0.12 | 170 | 68 | 1.4 | 9.2 | 51.44 | 4.9 | 9 |
| LCAL 19 | 0.10 | 22 | 0.69 | 10 | 0.12 | 80 | 77 | 0.9 | 7.3 | 60.17 | 4 | <5 |
| LCAL 20 | 0.11 | 22 | 0.65 | 37 | 0.12 | 165 | 86 | 1.9 | 9 | 49.69 | 4.3 | 11 |
| WCAL 4 | 0.14 | 30 | 0.65 | 37 | 0.16 | 184 | 100 | 4.4 | 9.5 | 40.04 | 3.6 | 7 |
| WCAL 5 | 0.17 | 34 | 0.58 | 48 | 0.17 | 217 | 113 | 3.7 | 10 | 35.52 | 3.6 | 8 |
| WCAL 6 | 0.20 | 31 | 0.55 | 36 | 0.18 | 242 | 95 | 3.5 | 8.7 | 35.06 | 3.4 | 8 |
| WCAL 7 | 0.17 | 36 | 0.59 | 45 | 0.12 | 194 | 65 | 2.8 | 6.5 | 40.56 | 2.9 | 7 |

| STATION | Sr | Ta | Tb | Th | Ti % | Tl | U | V | W | Yb | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LCAL 1 | 89 | 0.8 | 0.7 | 9 | 0.58 | 8 | 3.6 | 79 | 1.6 | 2 | 543 | 149 |
| LCAL 2 | 90 | 0.7 | 0.7 | 7.9 | 0.60 | 7 | 4.3 | 76 | 2.2 | 2.5 | 453 | 139 |
| LCAL 3 | 123 | 0.8 | 0.5 | 7.9 | 0.54 | 4 | 4.3 | 12 | 1.6 | 2.3 | 251 | 123 |
| LCAL 4 | 106 | 0.7 | 0.4 | 7.1 | 0.47 | 8 | 3.9 | 48 | 1 | 1.6 | 124 | 159 |
| LCAL 5 | 105 | 0.7 | 0.8 | 7.3 | 0.55 | 9 | 3.3 | 54 | 2 | 1.6 | 361 | 165 |
| LCAL 6 | 100 | 0.8 | 0.5 | 7.5 | 0.56 | 9 | 3.6 | 60 | 1.9 | 1.5 | 379 | 162 |
| LCAL 7 | 106 | 0.9 | 0.7 | 8.7 | 0.60 | 5 | 5.8 | 50 | 1.8 | 2.8 | 363 | 182 |
| LCAL 8 | 99 | 0.5 | 0.5 | 5.8 | 0.43 | 9 | 3.5 | 34 | 1.3 | 2 | 380 | 175 |
| LCAL 9 | 105 | 0.8 | 0.7 | 8 | 0.63 | 6 | 6.2 | 56 | 2.3 | 2.9 | 409 | 166 |
| LCAL 10 | 95 | 0.7 | 0.7 | 7.2 | 0.57 | 6 | 4.4 | 60 | 1.5 | 2.4 | 388 | 165 |
| LCAL 11 | 96 | 0.5 | 0.4 | 6.8 | 0.40 | 8 | 3 | 26 | 1.7 | 1.7 | 320 | 170 |
| LCAL 12 | 87 | 0.7 | 0.5 | 7.2 | 0.52 | 5 | 4.7 | 43 | 1.5 | 2.3 | 84 | 144 |
| LCAL 13 | 79 | 0.7 | 0.6 | 7.6 | 0.54 | 6 | ND | 37 | 2.5 | 2.7 | 149 | 190 |
| LCAL 14 | 89 | 0.5 | 0.4 | 4.1 | 0.39 | 6 | 3.6 | 19 | 1.6 | 1.6 | 213 | 165 |
| LCAL 15 | 87 | 0.7 | 0.5 | 7.3 | 0.49 | 5 | 4 | 37 | 1.8 | 2.1 | 239 | 170 |
| LCAL 16 | 97 | 0.3 | 0.4 | 4.6 | 0.30 | 5 | 2 | 23 | 2.2 | 1.4 | 228 | 147 |
| LCAL 17 | 90 | 0.7 | 0.5 | 7 | 0.46 | 6 | ND | 44 | 2.4 | 1.9 | 286 | 154 |
| LCAL 18 | 93 | 0.7 | 0.7 | 6.9 | 0.55 | 6 | 2.9 | 54 | 2 | 1.4 | 349 | 168 |
| LCAL 19 | 88 | 0.5 | 0.4 | 5.5 | 0.46 | 4 | 2.9 | 34 | 1.8 | 1.7 | 132 | 177 |
| LCAL 20 | 87 | 0.7 | 0.6 | 7.2 | 0.56 | 7 | 2 | 37 | 1.7 | 1.7 | 299 | 171 |
| WCAL 4 | 173 | 0.7 | 0.6 | 7.1 | 0.44 | 4 | 5 | 38 | 1.4 | 1.5 | 268 | 117 |
| WCAL 5 | 196 | 0.7 | 0.5 | 7.4 | 0.44 | 8 | 3.6 | 53 | 2 | 1.6 | 543 | 99 |
| WCAL 6 | 225 | 0.6 | 0.4 | 6.6 | 0.43 | 6 | 4.3 | 30 | 2.2 | 1.5 | 684 | 106 |
| WCAL 7 | 121 | 0.4 | 0.7 | 5.2 | 0.32 | 4 | 5.8 | 20 | 2.3 | 1.2 | 500 | 113 |

Appendix 4. Orthogonally rotated factor matrix for elements in Lake Calumet sediments.

| | FACTOR 1 | FACTOR 2 | FACTOR 3 | FACTOR 4 | FACTOR 5 |
|---|---|---|---|---|---|
| SC | .95613 | .21176 | -.08080 | .08223 | .00417 |
| TH | .93768 | .09399 | .02158 | .10213 | .16104 |
| TA | .93479 | .02645 | .05125 | .00813 | .16710 |
| AL2O3 | .93242 | .08459 | -.08890 | -.12088 | -.04743 |
| LI | .91412 | .26794 | .07080 | -.09628 | .09851 |
| CS | .91084 | .23883 | .12500 | .05463 | -.11242 |
| K2O | .90996 | -.02351 | -.09846 | -.24722 | .18507 |
| TIO2 | .87151 | -.14318 | .24128 | .00646 | .32516 |
| RB | .85826 | .26072 | -.17340 | -.06853 | -.16185 |
| CO | .83404 | .30983 | -.09444 | .35083 | .03495 |
| B | .82665 | .09328 | -.32882 | .07869 | -.15631 |
| GA | .81492 | -.10290 | .07819 | -.06160 | -.21741 |
| LA | .78964 | -.18881 | .27791 | .02958 | .25776 |
| SM | .76951 | -.34172 | .23129 | .12820 | .28827 |
| CE | .75760 | .33449 | -.10568 | .20378 | .19767 |
| NA2O | -.74332 | -.35996 | -.10567 | -.00847 | -.33045 |
| V | .73129 | -.02938 | .31357 | -.10137 | -.04421 |
| LU | .72245 | -.06269 | -.02897 | .24280 | .12638 |
| TB | .66132 | .08350 | .17090 | .41247 | .12601 |
| EU | .65764 | -.52182 | .19100 | .17869 | .16979 |
| YB | .55544 | -.22171 | -.00308 | .17508 | .39633 |
| TOTC | .02012 | .90136 | .28173 | .14466 | .11669 |
| BR | -.05584 | .88813 | -.06993 | .00300 | -.19503 |
| CAO | .14007 | .86626 | .04911 | -.17659 | .24728 |
| SR | -.05534 | .86495 | -.13759 | -.00236 | -.26102 |
| ORGC | -.01507 | .85565 | .35206 | .18629 | -.02728 |
| SB | -.01343 | .84641 | .11024 | .03658 | -.10738 |
| SIO2 | -.38344 | -.83861 | -.13232 | .02658 | -.29431 |
| MNO | .12048 | .83762 | -.00433 | .07640 | .00775 |
| NI | .24524 | .76065 | -.17736 | .35027 | -.01182 |
| CR | .42195 | .74828 | .35167 | .24116 | -.04000 |
| ZN | .17155 | .74125 | .55142 | .14445 | -.14137 |
| INC | .13824 | .70419 | -.08325 | -.06255 | .58611 |
| ZR | .41487 | -.69019 | .03206 | .32693 | .24057 |
| HF | .17456 | -.60192 | .05640 | .43132 | -.02298 |
| MO | .17060 | .53906 | .09844 | .03816 | .45772 |
| AS | -.05078 | -.38642 | .81106 | .07912 | .00126 |
| SN | -.10705 | .13517 | .80079 | -.38267 | .31638 |
| CU | .25914 | .51107 | .73444 | .01835 | .12492 |
| PB | -.04999 | .60785 | .66956 | -.20067 | .05070 |
| P2O5 | .24180 | .47096 | .60891 | -.19900 | -.17592 |
| BA | -.11689 | .15005 | .41630 | -.73546 | -.00778 |
| FE2O3 | .16707 | .53721 | -.10453 | .63010 | -.03694 |
| U | .47137 | .19669 | -.18091 | .49556 | .21162 |
| W | .06968 | .17998 | .32941 | .45243 | .02248 |
| TL | .13602 | .02990 | .02988 | -.39005 | .08581 |
| MGO | .26784 | -.20632 | .12827 | -.12874 | .83062 |