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Illiniois State Natural History Survey

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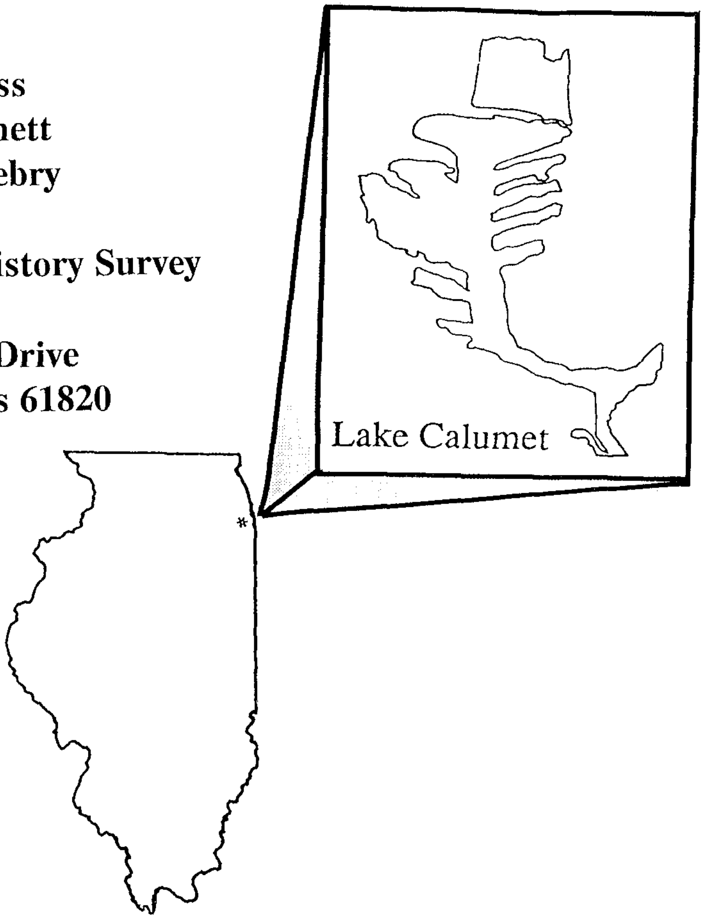

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Prepared for

the Illinois Hazardous Waste Research and Information Center

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ABSTRACT

Lake Calumet, located on Chicago's Far South Side, has been exposed to a wide range of industrial contaminants for approximately 110 years. Continued industrial activity and residues from past waste disposal practices, however, still threaten the Lake Calumet system. A study was initiated in 1986 by the Hazardous Waste Research and Information Center (HWRIC) of the Illinois Department of Energy and Natural Resources to Make a preliminary assessment of 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.

Results of the preliminary assessment showed that high concentrations of anthropogenic metals and polynuclear aromatic hydrocarbons (PAHs) were found in Lake Calumet sediments. These concentrations were generally higher than sediment samples in nearby waters. A majority of sediments were determined to be toxic by four biological screening assays *Photobacterium phosphoreum* , *Selenastrum capricornutum* , *Panagrellus redivivus* , and a microbial community that colonized artificial substrate. The preliminary study concluded that Lake Calumet is a severely disturbed system. Continued physical alteration has changed the lake's shape, reduced its surface area, and destroyed much of the surrounding natural wetland areas.

The current study addresses the recommendation from the preliminary study that chemical and toxicological analyses of Lake Calumet sediment should be continued. Special attention was paid to culverts and drainage ditches leading from past and current industrial or disposal sites into the lake and to the wetlands adjacent to the lake.

Chemical and toxicological data from the sediments in the areas adjacent to Lake Calumet indicate that contamination and toxicity are concentrated in these areas, relative to the sediments collected previously from Lake Calumet proper. To determine if a pattern of toxicity or contamination existed in the Lake Calumet area, geographical distribution maps were constructed from data collected throughout the two-year project. The maps resembled "fingerprints" and identified areas of concern

with regard to metal and PAH contamination and toxicity. The wetland areas east of Lake Calumet, and the drainage ditches west of the lake adjacent to the Calumet Expressway, warrant the most concern, based on these data.

To best identify the contaminant sources and hazards impacting the Lake Calumet ecosystem and the Far South Side of Chicago, data should be collected and analyzed for the following environmental parameters: 1) concentrations of harmful metals and organics in fish and waterfowl, 2) hydrogeological connection between wetlands, disposal sites, and the lake, 3) air monitoring to determine the contribution of atmospheric deposition of air pollutants to the terrestrial and aquatic ecosystem, 4) details of the waste disposal sites (past and present) including geographic coverage and potential pollutant export, and 5) further analysis of the hydrological and contaminant connection between Lake Calumet and the very important waterways of Lake Michigan and the Illinois River . The data reported in this study are merely yardstick measures of the extent of the disturbance. It is imperative that further research be conducted to determine the most effective methods to reduce the environmental hazards associated with the Calumet region.

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. 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 unequalled 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.

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. A study was initiated in 1986 by the Hazardous Waste Research and Information Center (HWRIC) of the Illinois Department of Energy and Natural Resources 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 results of that study are reported in the HWRIC publication " A Preliminary Environmental Assessment of the Contamination Associated with Lake Calumet, Cook County, Illinois" (HWRIC RR019).

Results of the preliminary assessment showed that high concentrations of anthropogenic metals and polynuclear aromatic hydrocarbons (PAHs) were found in Lake Calumet sediments. These concentrations were generally higher than sediment samples in nearby waters.

The relative toxic responses of *Photobacterium phosphoreum, Selenastrum capricornutum,* and *Panagrellus redivivus* to Lake Calumet sediment elutriates classified 57% (12 of 21) of the sampling stations as "highly toxic" (41-60% inhibition); the remainder (43%) were considered "moderately toxic" (11-40 % inhibition).

Exposure to sediment elutriate from 82% (18 of 22) of the sampling stations resulted in statistically significant changes in artificial substrate (microbial) communities. Measurements of the changes in photosynthesis and respiration were more sensitive than the measurement of reductions in numbers of species. Composite toxicity indices (based on the relative toxic responses of functional bioassays) classified 9% of the stations as "extremely toxic" (>300% inhibition), 23% as "highly toxic" (200-300% inhibition), 32% as "moderately toxic" (100-200% inhibition), and 18% as "weakly toxic" (0-100% inhibition); at 4 stations there was no statistically significant toxic response.

The preliminary study concluded that Lake Calumet is a severely disturbed system. Continued physical alteration has changed the lake's shape, reduced its surface area, and destroyed much of the surrounding natural wetland areas. Drainage is controlled by man-made channels (e.g., Pullman Creek) and the O'Brien Lock and Dam system. 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, waterfowl and humans is high. Alteration of the aquatic ecosystem through toxic effects of the contaminated sediments is probable. It is possible, based on conditions in Lake Calumet, that metals in the sediments could be released to the water column, impacting the long-term status of aquatic flora and fauna and also the water quality of the lake and other connected water systems.

The current study addresses the recommendation from the preliminary study that chemical and toxicological analyses of Lake Calumet sediment should be continued. Stations in wetlands, ponds, and small streams within the Lake

Calumet hydrologic system were studied in order to gain a more complete understanding of the situation. Special attention was paid to culverts and drainage ditches leading from past and current industrial or disposal sites into the lake and to the wetlands adjacent to the lake. Priority pollutant scans were run on a subsample of 10 stations to increase the likelihood that important contaminants are not being overlooked.

The objectives of continued toxicological and chemical analysis of the Lake Calumet sediments were 1) to determine the extent of sedimentary toxicity and contamination in the Lake Calumet area, 2) to construct a geographical distribution map of sedimentary toxicity and contamination to "fingerprint" areas of concern in the Lake Calumet system, and 3) to determine if these areas of concern are related to potential pollutant sources (e.g., waste disposal operations, highways, drainage ditches).

Over two years, sediments were collected from 66 sampling stations in and around Lake Calumet on four separate collection dates: November 20, 1986, April 28, 1987, September 25, 1987, and April 20, 1988 . Toxicological and chemical analyses were performed for these sediments. In the second year of study, 23 additional sediment samples were collected from the ditches and wetlands surrounding Lake Calumet. Chemical and toxicological data from these sediments indicate that contamination and toxicity are concentrated in these areas, relative to the sediments collected from Lake Calumet proper in 1986-1987.

The bulk sediments most contaminated with priority pollutant metals appear to be in the eastern wetlands and in the western ditch region. Most of the metals in Lake Calumet sediments are present at levels many times higher than average concentrations for Illinois lakes. The most contaminated stations show a similar pattern of metal contamination. Zinc, chromium and copper are the dominant priority pollutant metals in these samples.

Concentrations of priority pollutant metals measured in elutriates (sediment water extractions) from 10 sampling stations in the Lake Calumet region were generally below the detection limits of the analytical method. Copper, nickel, lead, and zinc were found at detectable levels but did not exceed the Illinois Pollution Control Board (IPCB) Water Quality Standards for Secondary Contact and Indigenous Aquatic Life; many of the elutriates, however, have concentrations above the IPCB Water Quality Standard for Lake Michigan. All of the elutriates contain elevated levels of lead, relative to Lake Michigan standards.

Metal contamination of sediments has been found in association with municipal wastewater operations, coal-fired power plants, landfill leachate, urban run-off, highway-runoff, mining and metal-working operations, airborne particulates, and industrial wastewaters. All of these activities have impacted Lake Calumet in the past and many are currently operating in the vicinity of the lake.

Sediment collected from a station located in Pullman Creek, the drainage ditch from the pumping station that handles run-off from the Calumet Expressway, contained over 50 ppm of total priority pollutant PAH compounds. A major source of PAHs is emissions from internal combustion engines used in transportation. This may explain the high levels near the expressway. The remaining stations measured for PAHs have levels ranging from 0.5 to 12.0 ppm. Levels exceeding 1 ppm indicate elevated PAH contamination relative to background PAH levels in "clean areas." Other sources of PAHs are coke production in the iron and steel industry; catalytic cracking in the petroleum industry; the manufacture of carbon black, coal tar pitch, and asphalt; heating and power generation; controlled refuse incineration; and open burning Most of these activities have occurred in the Lake Calumet area and could account for the higher levels of PAHs in the sediments. Certain PAHs are of particular concern because of their reported carcinogenicity. Recent studies show that sedimentary concentrations of select PAHs, similar to levels found at stations at Lake Calumet, induced mutagenicity in laboratory tests and evidence is increasingly strong that PAHs are a primary cause of neoplasia (tumor growth) in wild fish. Levels of PAHs were not found above detection limits in the elutriates prepared from 10 Lake Calumet sediments.

Concentrations of phthalate esters, in particular, bis (2-ethylhexyl) phthalate and di-n-butyl phthalate, were also found in the 10 sediment samples and corresponding elutriates analyzed for priority pollutants. It is highly probable that these compounds are contaminants of the chemical analysis procedure because phthalate esters were found in blanks as well as in the sediment and elutriate samples.

Cyanide was detected in sediment samples at values ranging from 0.25 to 3.40 $\mu g\ g^{-1}$; values in the elutriate ranged from less than 5 to 108 $\mu g\ L^{-1}$. Aqueous cyanide concentrations of 108 $\mu g\ L^{-1}$ have been reported to be toxic to the fish *Lepomis macrochirus* (bluegill).

Six areas of high toxicity (above 70 percent average response) were identified from single-species toxicity testing of the sediment elutriate.

- Site A is in the northern portion of the Eastern Wetlands. This site corresponds with an area of high metal contamination. Elutriate concentrations of metals from this area exceeded IPCB Lake Michigan Water Quality Standards for copper, lead, and zinc. Bulk sediment analyses showed that levels of zinc, chromium, and cobalt were elevated above Illinois background levels (Kelly and Hite 1981).

- Site B is also located in the Eastern Wetlands. This wetland area is near the location of several waste disposal facilities. Several of these waste sites have been reported to contain heavy metals or other hazardous wastes. More information regarding the nature of these wastes and disposal sites is necessary to determine the contribution of the wastes to the metal contamination. Zinc, lead, chromium, copper, and nickel were found in elevated concentrations at this site.

- Site C is a small area located in the Eastern Slip region close to stations that had high concentrations of arsenic, cobalt, lead, and zinc. Other stations tested from the Eastern Slip region were not as high in toxicity or metal contamination.

- Site D involves an area in the Western Shores & Slips region located near a sampling station station that had low concentrations of metals and relatively low concentrations of PAHs. No waste facilities appear to be in proximity to this area, however, the peninsula of land that extends into this site is new fill (since 1960) and consists mostly of slag. It is possible that this fill material contains toxic compounds that were not detected in chemical analysis.

- Site E is located in the deepest portion of Lake Calumet. Again, concentrations of metals and PAHs are low. The elutriate toxicity of this region is not apparently related to anything measured during the course of this study.

- Site F is located at the outfall of drainage ditches from both sides of the Calumet Expressway. Stations here had some of the highest concentrations of metals and a nearby waste disposal site has been identified to contain hazardous materials. These factors and the proximity to the Expressway may influence toxicity in this region.

All of these sites should be considered areas of concern for Lake Calumet by virtue of their high toxicity, whether or not toxicity can be related to measured contamination.

Substrate community response is similar to that of single-species tests. The inhibition of community function is dominant in the Eastern Wetland and Western Ditch regions of Lake Calumet. These regions correspond to Sites A and B identified as areas of concern in single-species toxicity.

It is beyond the scope of this study to determine where and how these sediments will effect the Lake Calumet, those of Lake Michigan, the Illinois River ecosystems. The results collected show that a percentage of the sediments were exceptionally damaging to three organisms from very different trophic levels and to an undefined number of species comprising an aquatic community. The elutriate test may overestimate the toxic potential of the sediments to organisms in the water column, but may underestimate the exposure to the whole sediment for important benthic biota. While conditions resembling the elutriation procedure are likely not to occur in Lake Calumet, information that nearly sixty sediment locations in and around Lake Calumet are capable of inducing toxicity should arouse concern.

Concentrations of zinc, lead, and copper in sediment elutriates exceeded water quality standards for some sampling locations in the lake and adjacent wetlands. Total composite toxicity was significantly correlated with levels of these metals, indicating that they may play a role in the toxicity reported for these areas. Other trace elements with significant correlation coefficients may also be related to toxicity but cannot be implicated with the data reported here.

To determine if a pattern of toxicity or contamination existed in the Lake Calumet area, geographical distribution maps were constructed from data collected during the two-year project. The maps resembled "fingerprints" and identified areas of concern with regard to metal and PAH contamination and toxicity (Figure A).

The proximity of many waste disposal facilities to Lake Calumet and the potential hydrological connection between the highly contaminated and toxic wetlands warrants concern. Regulating the disposal sites in the Lake Calumet region on a site-by-site basis would limit the effectiveness of the monitoring and remediation. Due to overlap or superposition of hazardous waste deposition sites over time, and to migration of contaminants within the region, the Lake Calumet area may have come to resemble a non-point source situation. The U S Environmental Protection Agency's evaluations of 42 potential Superfund sites in the region all yielded scores below the action level when done on an individual (site-by site) basis. When so many sites are in such close proximity, however, it may be more ecologically relevant to consider such an area as a single site, in which case the score might surpass the minimum for Superfund action.

To best identify the contaminant sources and hazards impacting in the Lake Calumet ecosystem and the Far South Side of Chicago, data should be collected and analyzed for the following environmental parameters:

1. concentrations of harmful metals and organics in fish and waterfowl,
2. hydrogeological connection between wetlands, disposal sites, and Lake Calumet,
3. air monitoring to determine the contribution of atmospheric deposition,
4. details of the waste disposal sites (past and present) including geographic coverage and potential pollutant export, and
5. further analysis of the hydrological and contaminant connection between Lake Calumet and the very important waterways of Lake Michigan and the Illinois River .

Lake Calumet is a severely disturbed ecosystem The data reported in this study are merely yardstick measures of the extent of the disturbance. It is imperative that further research be conducted to determine the most effective methods to reduce the environmental hazards associated with the Calumet region.

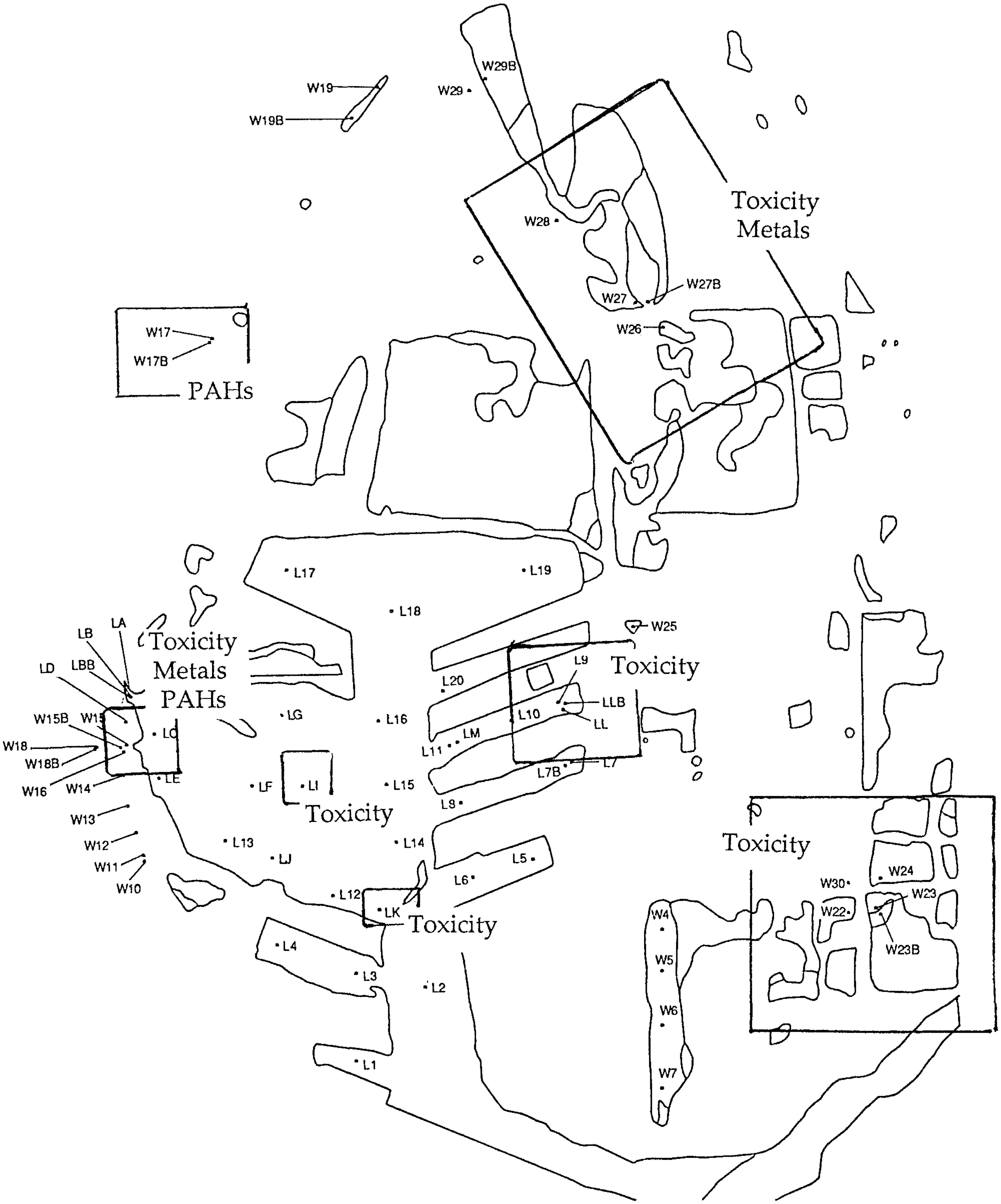


Figure A Areas of Concern In and Near Lake Calumet as Determined by Chemical and Toxicological Analysis

Chapter 1
Introduction

1.1 History of Lake Calumet

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 (Colten 1985).

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 unequalled 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 (Figure 1). 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 point source contamination, Lake Calumet is most likely impacted by a variety of nonpoint 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).

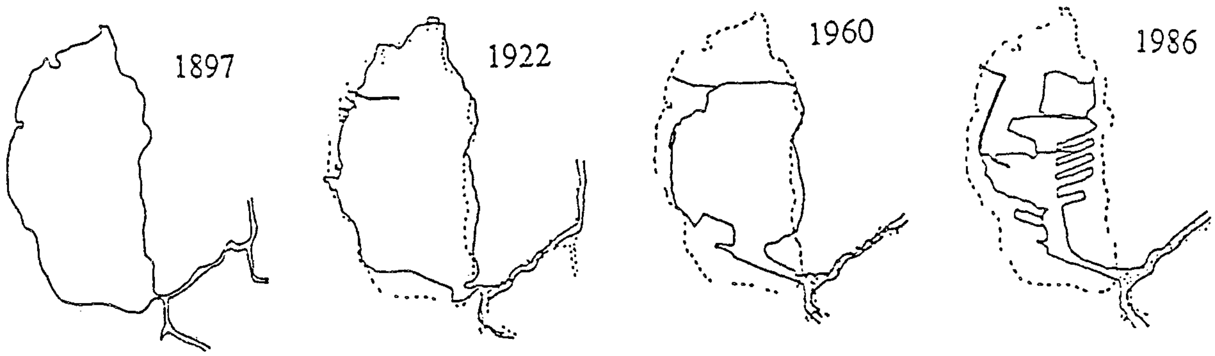


Figure 1. Alteration of Lake Calumet: 1897 - 1986 (from Colten 1985; and 1986 aerial photo)

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.

1.2 Preliminary Environmental Assessment of Lake Calumet

A study was initiated in 1986 by the Hazardous Waste Research and Information Center (HWRIC) of the Illinois Department of Energy and Natural Resources 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 results of that study are reported in the HWRIC publication "A Preliminary Environmental Assessment of the Contamination Associated with Lake Calumet, Cook County, Illinois" (Ross *et al.* 1988).

The preliminary assessment study was designed to evaluate the environmental status of Lake Calumet and was based upon the following objectives:

- determination of 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;

- determination of the movement of surface water, sediment, and pollutants in and around Lake Calumet and the dynamics of toxic chemicals in the surface water environment;

- determination of the contributions of contaminants to Lake Calumet *via* groundwater seepage;

- determination of the concentration and fugacity (the escaping tendency of an organic compound between phases) of a number of hazardous organic compounds in the sediments and water from different areas of Lake Calumet;

- determination of degradation rates of toxic organics and the isolation of the responsible microorganisms;

- determination of bioaccumulation of toxic metals in the aquatic plants found in the area; and

- determination of the toxic effect of sediment extracts to single-species assay organisms, *Photobacterium phosphoreum* (Microtox), *Selenastrum capricornutum* (green alga), and *Panagrellus redivivus* (nematode), and to the inhibition of the function of microbial communities.

Results of the preliminary assessment showed that high concentrations of anthropogenic metals and polynuclear aromatic hydrocarbons (PAHs) were found in Lake Calumet sediments. Metal concentrations were generally higher than sediment samples in nearby waters (Table 1). Total sediment PAH concentrations in Lake Calumet ranged from 0.3-9.2 mg kg $^{-1}$, similar to sediment concentrations in industrialized areas but higher than areas with low population density (i.e., Alaska; Table 2).

Table 1 Average Concentrations (in mg/kg unless otherwise noted) of Selected Elements in Sediments of Lake Calumet and in Sediments of Surrounding Water Systems

Elements	Lake[a] Calumet	Calumet[b] Harbor	Little[c] Cal. River	Lake[d] Michigan	Cal-Sag[c] Channel	Wolfe[e] Lake
Antimony (Sb)	2 4	–	--	1.1	–	–
Arsenic (As)	29 8	6 2	5 5	10.5	15	21
Bromine (Br)	4 2	–	–	33 0	–	–
Cadmium (Cd)	1 8	3 2	2 5	0 9	8 5	2 0
Chromium (Cr)	76 7	46 0	66	46 0	105 0	18 0
Copper (Cu)	57 5	44	88	22 0	125.0	27 0
Iron (Fe)	2.7%	–	2 9%	2 2%	3 4%	1 5%
Lead (Pb)	187 0	144	190 0	40	370 0	110 0
Nickel (Ni)	23 6	–	–	24	–	–
Phosphorus (P)	20 0	20 6	130.0	70.0	300 0	36 0
Selenium (Se)	0 7	–	–	1 2	–	–
Silver (Ag)	561 0 µg/kg	–	–	460 0 µg/kg--	–	
Sodium (Na)	470 0	–	–	458 0	–	–
Thallium (Th)	6.2	–	–	–	–	–
Zinc (Zn)	341 0	268 0	375.0	97 0	1100 0	255 0

a = Ross *et al* (1988)
b = USACE (1985)
c = IEPA (1984)
d= Cahill and Shimp (1984)
e = Kelly and Hite (1979)

Table 2 Concentrations (mg/kg) of Total Polynuclear Aromatic Hydrocarbons in U S Sediments (after Eisler 1987)

Cayuga Lake, Ithaca, NY (Deepwater)	1 26-2 50
Penebscot Bay, Maine	0 29-8 80
Casco Bay, Maine	0 21-14 43
Lake Erie	0 53-3 75
Adirondack Lakes	4 07-12 81
Alaska	0 005-1 13

No natural drainage channels into Lake Calumet were observed. Pullman Creek, (a small channel in the NW portion of the lake), and two storm sewers are the existing man-made drainage channels into the lake. Pullman Creek is not only a source of inflowing water but also of sediment. Production of methane was measured 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.

Composite toxicity indices (based on the relative toxic responses of *Photobacterium phosphoreum, Selenastrum capricornutum,* and *Panagrellus redivivus*, to Lake Calumet sediment elutriates) classified 57% (12 of 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.

Exposure to sediment elutriate from 82% (18 of 22) of the sampling stations resulted in statistically significant changes in microbial communities. Measurements of the changes in photosynthesis and respiration were more sensitive than the measurement of reductions 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 preliminary study concluded that Lake Calumet is a severely disturbed system. Continued physical alteration has changed the lake's shape, reduced its surface area, and destroyed most of the surrounding natural wetland areas. Drainage is controlled by man-made channels (e.g., Pullman Creek) and the O'Brien Lock and Dam system. 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, waterfowl 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.

Although Lake Calumet seems to be isolated by its own sluggish drainage system, its connection with Lake Michigan and with the Illinois River watershed cannot be ignored. The Calumet River, the Little Calumet River, and the Cal-Sag Channel may transport contaminants from the lake out of the Calumet region. 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.

1.3 Concepts of Toxicological Testing of Sediments

While chemical analyses of the whole sediment allow an inventory of the sediment contaminants to be constructed, the potential for biological availability or chemical mobility cannot be determined using bulk material measurements (Engler 1980). Bulk sediment material may, however, be the major exposure medium for organisms such as rooted aquatic plants and benthic organisms that recycle sedimentary material at the sediment-water interface. Sediment constituent mobility is a function of many factors. Even though a sediment may be grossly contaminated, the conditions which favor interaction between water and sediment may preclude significant movement of the contaminants into the water column (Brannon *et al.* 1980). Table 3 lists the "worst case" conditions that would favor release of anthropogenic metals into the water column. It is possible, based on these conditions, that metals in sediments from Lake Calumet could be released to the water column, impacting the long-term status of aquatic flora and fauna and also the water quality of the lake and other connected water systems.

Table 3 "Worst-Case" Conditions for Increased Release of Metals from Sediments into the Overlying Water Column (after Jennet *et al* 1980).

CONDITION	LAKE CALUMET
1 High concentrations of metals accumulated in sediments?	Yes[1]
2. Highly flocculent nature of surficial sediments?	Unknown
3. Highly reducing conditions?	Yes[1]
4 High degree of mixing at sediment-water interface?	Yes[1]
5 High complexing capabilities of overlying water?	Unknown[2]
6 Overlying waters rich in hydrogen ions (low pH)?	No[2]

[1] Ross *et al 1988* [2] William Fitzpatrick ISWS, personal communication

To simulate the short-term release of contaminants to the water column after disturbance of the sediment, the elutriate test, a water leach using one part sediment to four parts leaching water, was used. This technique has been used since 1973 and has been evaluated under an extremely wide range of conditions in marine, estuarine, and freshwater systems (Engler 1980). None of the extract procedures developed to measure the degree of chemical mobility of sediment constituents have been shown to be universally successful in defining chemical availability and exchangeability. The elutriate test will likely strip volatile compounds from the sediment and is limited to leaching under aerobic conditions (unless an inert compound, such as nitrogen (N_2), is used as the mixing gas). Some contaminants may be more readily released under anaerobic conditions; however, the anoxic regime is prohibitive for bioassay use. The elutriate test, however, was shown by Brannon *et al.* (1980) to be the most useful extract procedure in assessing water quality problems. Short-term extraction by elutriation was compared to long-term (4 month) leaching of contaminated dredge spoils. Significant statistical relationships ($p<0.05$) between long-term release and short-term sediment characterization were shown for five of eight metals in the elutriate test characterization. Bulk sediment analysis was successfully compared to only one metal released in long-term leaching (Brannon *et al.* 1980).

The liquid phase filtrate of the elutriate test may be used in bioassays as one way to evaluate the biological impact from the released sediment constituents and has been shown to project the earliest measure of toxicity of the sediment (Engler 1980). Elutriates from Lake Calumet sediments were used to assess biological response to contamination with four bioassay methods: luminescent inhibition of the marine bacterium *Photobacterium phosphoreum* (Microtox™), photosynthetic inhibition of the freshwater green alga *Selenastrum capricornutum*, developmental inhibition of the free-living nematode worm *Panagrellus redivivus*, and functional inhibition of aquatic microscopic communities (algae, diatoms, protozoans, etc.) cultured on artificial substrates.

1 3 1 *Single species testing*

The Microtox™ bacterial assay was developed on the principle that the luminescent properties of healthy cultures of *P. phosphoreum* will be inhibited upon exposure to toxic substances. The luminescence of cultures exposed to a series of dilutions of a sample is measured with the Microtox™ analyzer, a specially-designed fluorometer.

The protocol for the *S. capricornutum* assay is based on the principle that algae under normal conditions will use carbon from the surrounding medium to grow and photosynthesize. Under conditions of stress, including toxic aggression, photosynthesis will be inhibited and carbon consumption will decrease. In the laboratory, progressive inhibition of photosynthesis by increasing doses of test mixture is the measure of toxic response. This is easily measured using a ^{14}C-labeled HCO_3^- as a tracer in the carbon source pool.

The assay using the microscopic, free-living nematode *P. redivivus*, is based on the 96-hour growth cycle of the worm. Under normal conditions, a newly hatched juvenile will proceed through three molts to adulthood in 96 hours. If, at any of these molting points, the worm is stressed, it will remain in the lower, less demanding stage rather than molt. The assay exposes 10 replicate groups of 10 juveniles to a concentration of test material. After 96 hours, the survivorship and distribution of nematode lengths are measured relative to control tests. These measurements are a reflection of the lethal, inhibitory, or stimulatory nature of the mixture.

1 3.2 *Community toxicity testing.*

Relatively few studies have been undertaken to evaluate the effects of toxicants at the level of the community or ecosystem. Protozoa collected on artificial substrates (polyurethane foam blocks; 7.5 x 6.5 x 5 cm) represent intact communities made up of 30-40 interacting species of several trophic levels. The toxic responses (photosynthetic and respiratory changes) 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 exposed to toxic contamination when sediments are disturbed by dredging, by wave and wind action, or by bioturbation.

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 to compare with the results from Lake Calumet. However, in studies of microbial community response to sediment elutriates from an area of Waukegan (IL) Harbor which 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, with nutrients such as sucrose, and compounds containing nitrogen and phosphorus (Cairns *et al.* 1978) responded in much the same way as did the polyurethane foam (PF) block microbial communities In the Cairns *et al* . study the structure of the community was little changed by the various treatments. However, photosynthesis was inhibited by both copper and chromium and respiration was stimulated with the addition of sucrose (Cairns *et al.* 1978).

1 3.3 *Comparisons of toxicity tests*

Results of Microtox^{TM} assays have 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^{TM}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^{TM} 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^{TM}) in a comparison using 15 compounds.

The *S. capricornutum, P. phosphoreum,* and *P. redivivus* bioassays were also used in a study (Burnett and Ross, unpublished data) to identify the empirical relationship between sediment bioassays when exposed to sediments of varying types and degrees of contamination. Under conditions similar to those in Lake Calumet, all three assays were positively correlated with bioassays using *Daphnia magna, Ceriodaphnia dubia,* and the USEPA *S. capricornutum* bottle test The Kendall non-parametric rank order correlation coefficient τ (tau) values generated for comparisons between substrate community photosynthesis and the cladoceran, alga, and Microtox^{TM} bioassays were always negative, whereas, the τ values for substrate community respiration were positive. This is a desirable result because the usefulness of a multi-bioassay testing protocol would be reduced if all of the bioassays responded in a similar manner. The substrate community test is sensitive to factors not detected by single-species tests and *vice versa* (Table 4).

Table 4. Kendall τ Rank-order Correlation Coefficients for Eight Bioassays Performed on Six Sediment Samples of Varying Types and Degrees of Contamination (Burnett and Ross, unpublished data)

	Daphnia magna	*Ceriodaphnia*	*Selenastrum* I	*Selenastrum* II	Microtox™	*Panagrellus*	Substrate comm	
							photosyn	respir
Daphnia	X.XX	0 788*	0 741*	0 645*	0 501*	0 501*	-0 501*	0 501*
Ceriodaphnia		X XX	0 414	0.600*	0 467*	0 200	-0 467*	0 467*
Selenastrum I[1]			X XX	0 345	0 207	0 207	-0 207	0 207
Selenastrum II[2]				X XX	0 867*	0 333	-0 600*	0 333
Microtox					X XX	0 467	-0 467*	0 200
Panagrellus						X XX	-0 467*	0.467
Substrate community photosynthesis							X XX	-0 467*
Substrate community respiration								X XX

* significant at $p \leq 0\ 01$

[1] Standard Bottle (growth) Test

[2] ^{14}C uptake test

Chapter 2

Current Study

The current study addresses the recommendation from the preliminary study (Ross *et al.* 1988) that chemical and toxicological analyses of Lake Calumet sediment should be continued. Stations in wetlands, ponds, and small streams within the Lake Calumet hydrologic system were studied in order to gain a more complete understanding of the situation Special attention was paid to culverts and drainage ditches leading from past and current industrial or disposal sites into the lake. Priority pollutant scans were run on the sediments and elutriates from 10 selected sampling stations to increase the likelihood that important contaminants are not being overlooked.

The objectives of continued toxicological and chemical analysis of the Lake Calumet are 1) to determine the extent of sedimentary toxicity and contamination in the Lake Calumet area, 2) to construct a geographic distribution map of sedimentary toxicity and contamination to "fingerprint" areas of concern in the Lake Calumet system, and 3) to determine if these areas of concern are in proximity to potential pollutant sources (e.g., waste disposal operations, highways, drainage ditches).

Sediments were collected from 66 sediment stations in and around Lake Calumet on four separate collection dates: November 20, 1986, April 28, 1987, September 25, 1987, and April 20, 1988 (Table 5, Figure 2). The April 1988 collection was keyed to areas in and around Lake Calumet identified as highly contaminated (from the previous chemical and toxicological characterizations). Stations W17, W18, W19, W23, W27, and W29 from the September 1987 sample collection and stations LB and LL, sampled in November 1986, were chosen for additional chemical analyses because of the concentrations of metals assayed and the level of toxicity determined by previous testing. Station W15 (September 1987) and L7 (April 1987) were also chosen because these stations correspond to samples collected for surface water flow measurements and water column chemistry in a related HWRIC-sponsored study being conducted by the Illinois State Water Survey.

These 66 sediment stations can be divided into five regions:

1) **Western Ditches**. The samples collected from this region were taken from slow flowing drainage ditches along the frontage road adjacent to the Calumet Expressway (I-94).

2) **Western Shores/Slips**. These samples were collected along man-made shoreline and from constructed slips. Much of the adjacent land is based on construction rubble and slag.

3) **Open Lake**. These stations were the deepest sediments (6-10 feet) collected within Lake Calumet-proper.

4) **Eastern Slips**. The sediment stations from the eastern slips of Lake Calumet were separated by fingers of land built on construction rubble. The land near the slips is used predominantly for waste management and alternative disposal purposes.

5) **Eastern Wetlands**. The wetlands to the east of Lake Calumet consist of drainage ditches and marsh with stands of aquatic plants. Some of the sites are adjacent to railway. Most of the sites are on property where the Metropolitan Sanitary District of Greater Chicago (MSDGC) operates sludge drying beds and other waste management activities.

Table 5 also lists the toxicological and chemical analyses performed for the 66 sediment samples collected at Lake Calumet.

Table 5 Sampling, Toxicity Testing, and Chemical Analyses Performed on 66 Lake Calumet Sediments

		Toxicity tests					Chemical analyses	
sampling period	stations	*S capri-cornutum*	Micro-tox™	*P redivivus* mortality	*P redivivus* fitness	Substrate community	metals	organics
Nov-86	LA	X	X	X	X		X	PAHS
	LB	X	X	X	X		X	
	LC	X	X	X	X		X	
	LD	X	X	X			X	
	LE	X	X	X			X	
	LF	X	X	X	X		X	
	LG	X	X	X			X	
	LH	X	X	X	X		X	
	LI	X	X	X	X		X	
	LJ	X	X	X			X	
	LK	X	X				X	
	LL						X	
	LM	X	X	X			X	
Apr-87	L1	X	X	X	X		X	
	L2	X	X	X			X	
	L3	X	X	X			X	
	L4	X	X	X	X		X	
	L5	X	X	X			X	
	L6	X	X	X			X	
	L7	X	X	X	X		X	
	L8	X	X	X			X	
	L9	X	X	X	X		X	
	L10	X	X	X	X		X	
	L11	X	X		X		X	
	L12	X	X		X		X	
	L13	X	X		X		X	
	L14	X	X				X	
	L15	X	X		X		X	
	L16	X	X		X		X	
	L17	X	X		X		X	
	L18	X	X		X		X	
	L19	X	X				X	
	L20	X	X		X		X	
	W4				X		X	
	W5						X	
	W6				X		X	
	W7						X	
Sep-87	W10	X	X		X		X	
	W11	X	X		X		X	
	W12	X	X		X		X	
	W13	X	X	X	X		X	
	W14	X	X	X			X	

Table 5 continued

Toxicity tests

Chemical analyses

sampling period	stations	S capri-cornutum	Micro-tox™	P redivivus mortality	P redivivus fitness	Substrate community	metals	organics
Sept 1987 (cont)	W15	X	X	X		X	X	
	W16	X	X	X			X	
	W17	X	X	X			X	
	W18	X	X	X			X	
	W19	X	X	X		X	X	
	W22	X	X	X		X	X	
	W23	X	X	X		X	X	
	W24	X	X	X		X	X	
	W25	X	X	X		X	X	
	W26	X	X	X		X	X	
	W27	X	X	X		X	X	
	W28	X	X	X		X	X	
	W29	X	X	X		X	X	
	W30	X	X	X		X	X	
April-88	LBB	X	X		X		X	SV
	LLB	X	X		X		X	SV
	L7B	X	X		X		X	SV
	W15B	X	X		X		X	SV
	W17B	X	X		X		X	SV
	W18B	X	X		X		X	SV, V, P
	W19B	X	X		X		X	SV
	W23B	X	X		X		X	SV, V, P
	W27B	X	X		X		X	SV, V, P
	W29B	X	X		X		X	SV

PAH = polynuclear aromatic hydrocarbon scan, SV = semi-volatile priority pollutant scan, V = volatile priority pollutant scan, P = polychlorinated biphenyl and pesticide scan

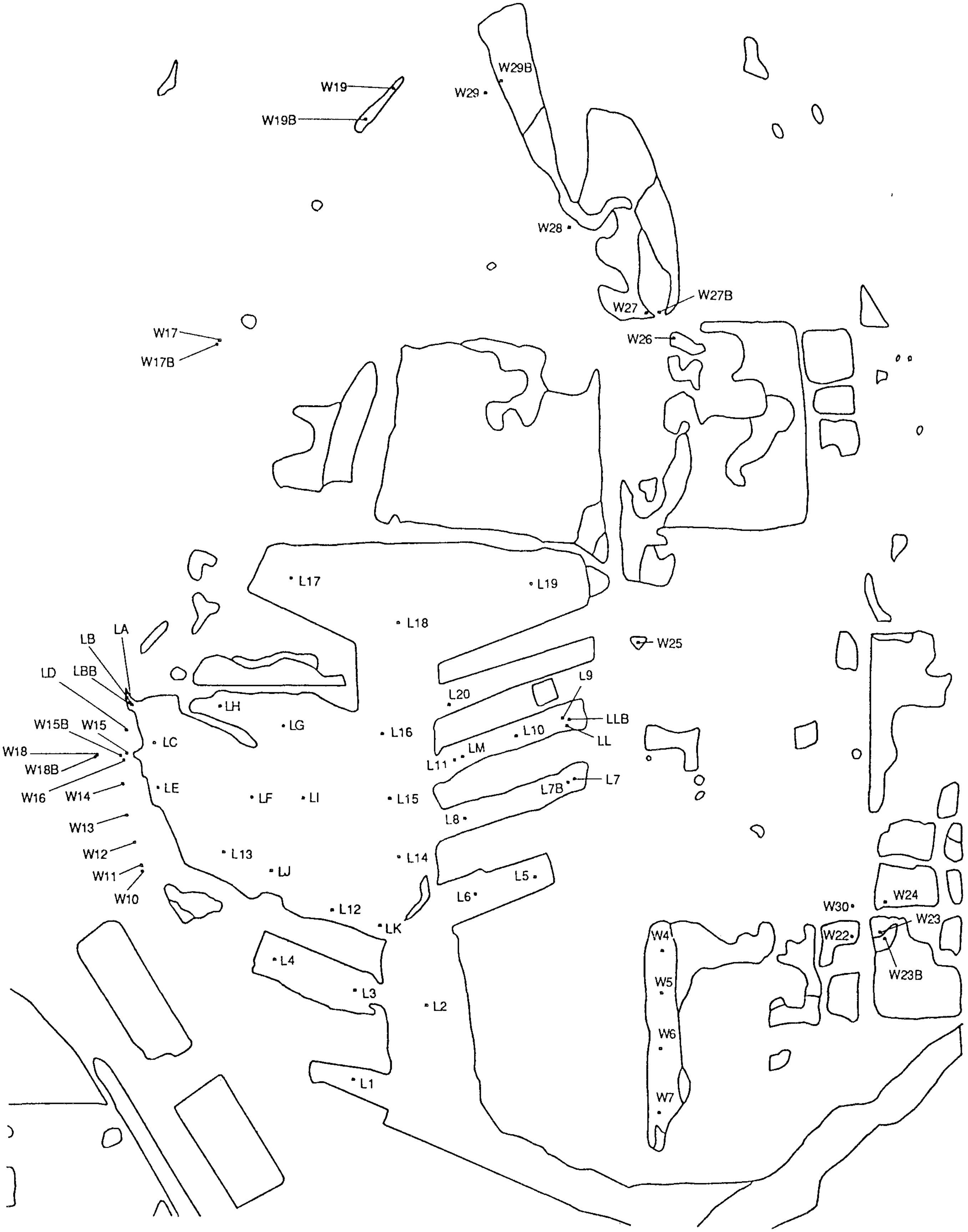


Figure 2 Locations of 66 Sediment Samples Collected at Lake Calumet: November 1986 to April 1988

Chapter 3
Materials and Methods

3.1 Sample Collection

Each sediment sample was collected by a stainless steel Ponar grab sampler that collects approximately 5000 mL of surficial sediment or a petite Ponar sampler that collects 1500 mL of sediment. The sample was transferred to a deep plastic tray, mixed by hand for homogeneity, and distributed to clean acid-washed bottles for storage. The samples were kept on ice in the field and were stored at $<4^{o}$ C in the dark at the laboratory for no more than 4 weeks.

3.2 Elutriation (US Army Corps of Engineers 1976)

Elutriates were prepared from the sediment sample by mixing 100 mL of sediment with 400 mL of triple-distilled water in a 2000 mL Pyrex™ beaker. Air was forced through this mixture for two hours to cause vigorous mixing. The liquid phase was filtered through a high purity #1 Whatman filter paper (nominal porosity: 11 µm) and through low absorption glass fiber filters (nominal porosity: 1.2 µm). The filtrate was used as test material in the toxicity tests.

3.3 Microtox™ Toxicity Test (Bulich 1977)

Aliquots (10 µL) of commercially available reconstituted *P. phosphoreum* were exposed in duplicate to 1.5 mL elutriate dilutions of 45.0, 22.5, 11.25, and 5.62 percent Dilutions were made with commercially available Microtox™ diluent (Table 6). The duplicate blank samples contained Microtox™ diluent and the aliquot of bacteria. Initial luminescence readings were taken before the addition of the elutriate and were repeated 5 and 15 minutes after exposure to the sample. The decrease in luminescence in test samples was calculated relative to the natural luminescent decay over time in the blank samples. A dose-response curve was constructed and percent response values calculated.

3.4 *Selenastrum capricornutum* ^{14}C uptake toxicity test (Ross *et al.* 1988)

Aliquots (200 μL) of a healthy *Selenastrum capricornutum* suspension were exposed in quadruplicate to 10 mL elutriate dilutions of 80, 60, 40, 20, 10 and 5 percent. Dilutions were made with triple-distilled water. Four replicates each of full strength elutriate and a control medium (triple-distilled water) were also prepared with the algae. One mL 10X PAAP (Provisional Algal Assay Protocol) media (Table 6) was added to each replicate. The test solutions were placed in a 20°C growth chamber with a 12 hr. light - 8 hr. dark-light regime for 20 hours to allow the algal cells to acclimate. At 20 hours each replicate was dosed with 0.575 μCi ^{14}C-sodium bicarbonate. After 4 hours of exposure to the radioisotope, 4 mLs were withdrawn from the test vessel and acidified with 1 drop 12 N HCl to convert unutilized HCO_3^- to CO_2. Each sample was bubbled for 5 minutes to fully purge the $^{14}CO_2$. Five mLs of gel-phase scintillation cocktail (Insta-Gel; Aquasol-2) were added to each sample to prepare for scintillation counting. Test samples were counted and a dose-response curve was calculated based on the ^{14}C-uptake inhibition relative to control values. Percent response was calculated.

3.5 *Panagrellus redivivus* development toxicity test (Samoiloff *et al.* 1980)

Ten replicates of 10 J2-phase (first juvenile stage outside mother) *Panagrellus redivivus* nematode worms were exposed to 0.5 mL of 50 percent elutriate. Dilutions were made with M9Y nutrient solution (Table 6). A control test was also run with 50 percent M9Y buffer as the blank solution. After 96 hours of exposure, surviving worms were counted and measured microscopically. Growth and maturity were determined by the number of worms that grew to adulthood and the proportion that remained in juvenile phases. A composite parameter, fitness, was calculated using the weighted average of the percent survival, percent growth, and percent maturity of each test population.

Table 6 Composition of Dilution and Nutrient Media for Single-Species Bioassays

	S capricorntum	*P. redivivus*
Microtox™ diluent[1]	PAAP medium (per L)[2]	liquid growth medium (per L)[3,4]
2% sodium chloride (NaCl)	14 7 g Mg $SO_4 \bullet 7H_2O$ 1 044 g K_2HPO_4 15.0 g $NaHCO_3$ 4.41 g $CaCl_2 \bullet 2H_2O$ 25 5 g $NaNO_3$ 10 0 g $MgCl_2 \bullet 6H_2O$ plus micronutrients (trace amounts boron, manganese, zinc, cobalt, copper, molybdenum, and iron salts)	6.0 g $Na_2PO_4 \bullet 7H_2O$ 3 0 g K_2HPO_4 5.0 g NaCl 0 04 g Mg SO_4 0 4 g dried Baker's yeast
in specially purified water	in triple distilled water	in triple distilled water

[1] commercially prepared by Microbics, Inc
[2] Stein (1973)
[3] Brenner (1974)
[4] Samoiloff *et al* (1980)

3.6 Substrate 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-hectare 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.

3.7 Substrate Community Process-level Bioassays

Changes in photosynthetic and respiration rates were evaluated by transferring 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.

The structure and biomass of the substrate communities varied with seasonal changes in water temperature and nutrient availability in the pond from which they were collected. We were forced by time constraints to run some bioassays when community biomass on pond substrates was so low that there was almost no photosynthetic or respiratory response in untreated bottles during an 8 hour test period. Tests were considered invalid when the dissolved oxygen gain in untreated bottles exposed to light was <0.5 mg L^{-1}. The initial dissolved oxygen levels in the diluted elutriate ranged from 6.0 to 8.0 mg L^{-1}.

3.8 Data Reduction

3.8.1 *Single species percent response*

The results of the Microtox™ and *S. capricornutum* assays for each sample were reduced by simple linear regression to generate a linear equation from which percent response (the effect of full strength elutriate relative to the control response) was extrapolated. The results of the *P. redivivus* test were reduced to fitness and percent mortality. Because these calculations are inherently based on percentage, the percent response (percent fitness or survival reduction) can be calculated by subtracting the percent survival or fitness value from 100.

3 8.2 *Substrate community 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 (ANOVA) (Sokal and Rohlf 1969). Differences were considered significant at $P \leq 0.05$. Data from substrate community bioassays were reduced to percent response so they could be compared. Pearson correlation coefficients, simple regression, and stepwise multiple regression techniques (Sokal and Rohlf 1969) were used to compare community responses with concentrations of toxic materials in sediments; $P \leq 0.05$ was used as the significance level

3.9 Chemical Analyses

Metals were determined as summarized in Table 7. Concentrations of total polynuclear aromatic hydrocarbons (PAHs), semi-volatile organic priority pollutants, and volatile organic priority pollutants were determined by EPA Methods 3550, 625, and 624, respectively

Table 7 Methods Used to Determine Trace, Minor, and Major Element Concentrations in Lake Calumet Sediments

Elements	Analytical System
November 1986 and April 1987	
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
September 1987 and April 1988	
Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, No, Na, Ni, P Pb, Sb, Se, Si, Sn, V, Zn, Hg	ICP
April 1988	
Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Th, V, Zn	EPA Method 200 0

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

Chapter 4
Results and Discussion

4.1 Metals

4 1 1 *Bulk sediment concentrations*

Figure 3 shows the sum of concentrations of priority pollutant metals (antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc) for the 56 sediment stations analyzed at Lake Calumet. In general, the concentrations of beryllium, silver, and thallium were below levels of environmental concern (IEPA 1988). The most contaminated stations appear to be W27 in the eastern wetlands and W16 in the western ditch region. Figure 4a shows the concentration of individual priority pollutant metals present in the sediment samples for W27 and W16. Background levels for most of these metals are shown in Figure 4b. Most of the metals in Lake Calumet sediments are present at levels many times higher than average concentrations for Illinois lakes (IEPA 1984). Stations W27 and W16 show a similar pattern of metal contamination. Zinc, chromium, and copper are the dominant priority pollutant metals in these samples. Metal concentrations determined from bulk sediment samples from Lake Calumet are listed in a tabular format in Appendix 1.

4 1 2 *Elutriate concentrations*

Concentrations of priority pollutant metals measured in elutriates from 10 stations in the Lake Calumet sampling region were generally below the detection limits of the analytical method. Copper, nickel, lead, and zinc were found at detectable levels but generally did not exceed the Illinois Pollution Control Board (IPCB) Water Quality Standards for Secondary Contact and Indigenous Aquatic Life (IEPA 1988); many of the elutriates, however, have concentrations above the IPCB Water Quality Standard for Lake Michigan (Table 8). All of the elutriates contain elevated levels of lead, relative to Lake Michigan standards). Bulk sediment sample W27, collected in the vicinity of W27B, had the highest concentration of bulk sediment metals of the 56 stations analyzed. Metal concentrations for elutriates prepared from Lake Calumet sediments are listed in a tabular format in Appendix 2.

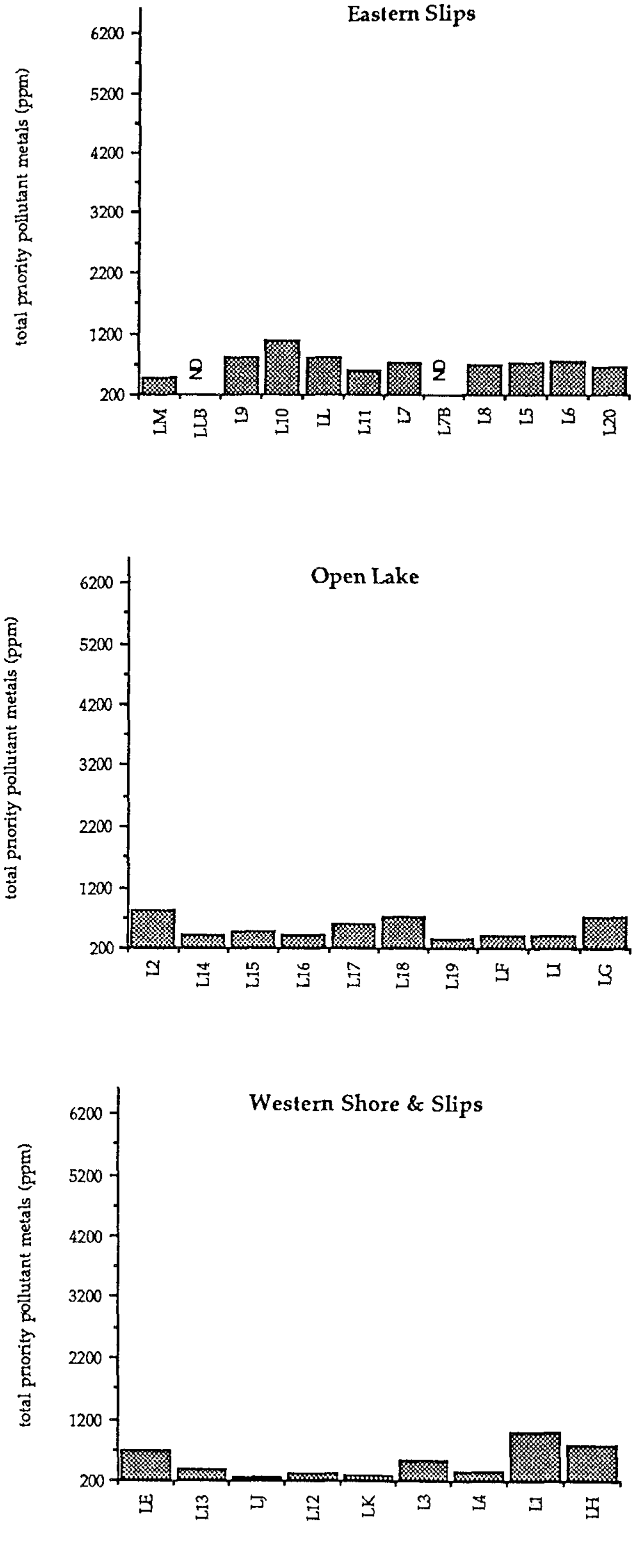
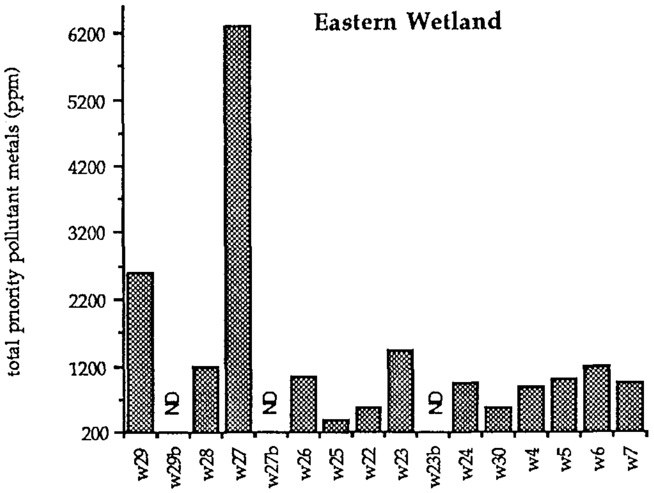


Figure 3 Total Priority Pollutant Metal Concentrations in Sediments from 56 Sampling Stations in Five Regions of Lake Calumet (ND=not determined)



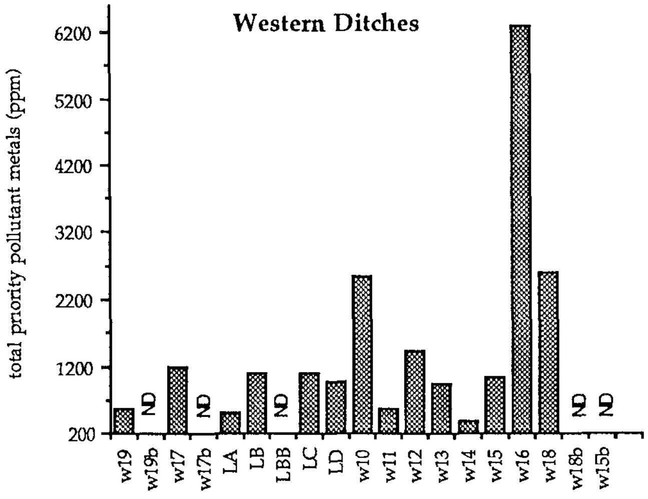


Figure 3, continued Total Priority Pollutant Metal Concentrations in Sediments from 56 Sampling Stations in Five Regions of Lake Calumet (ND=not determined)

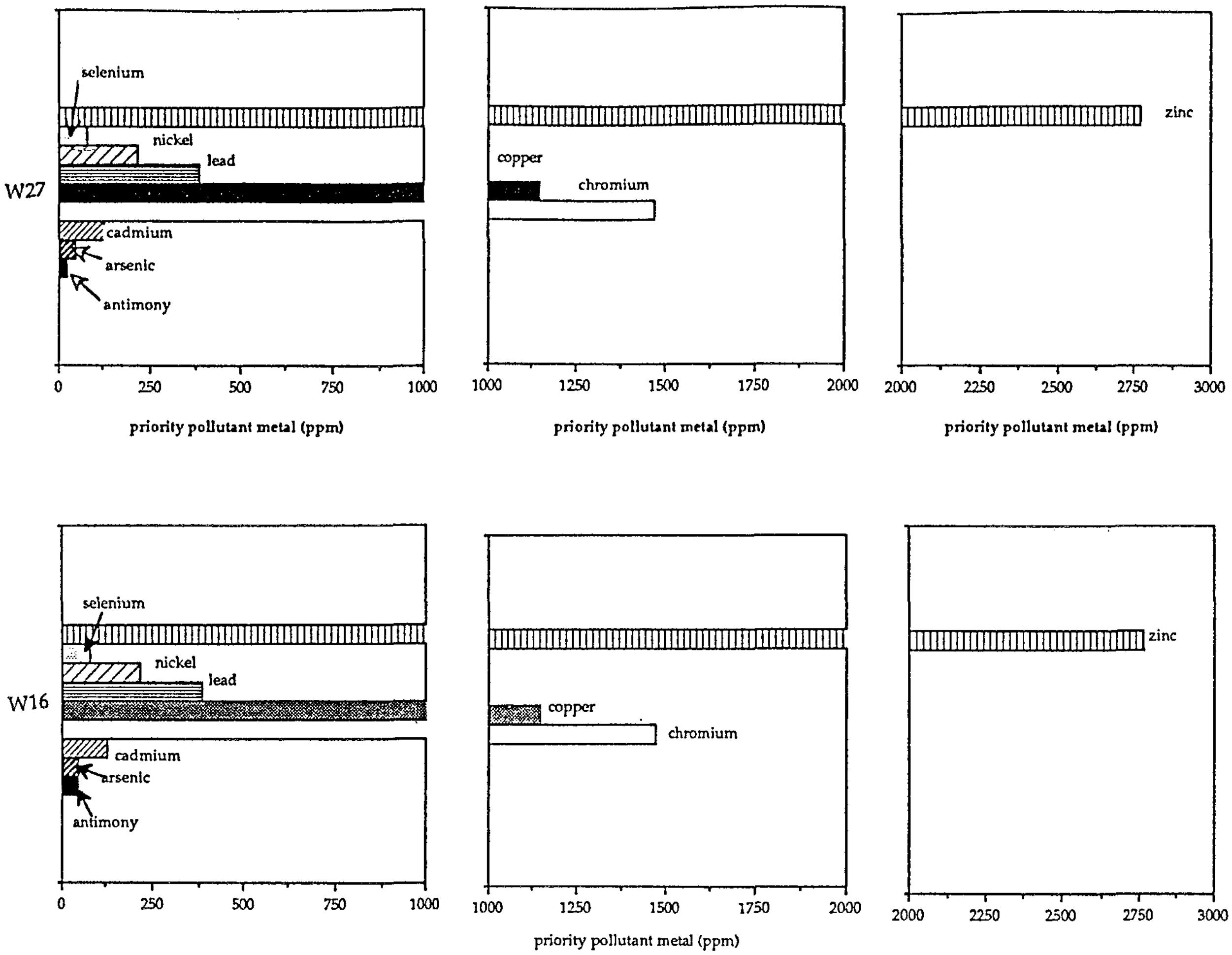


Figure 4a Concentrations of Individual Priority Pollutant Metals in Sediments from Lake Calumet Stations W27 and W16

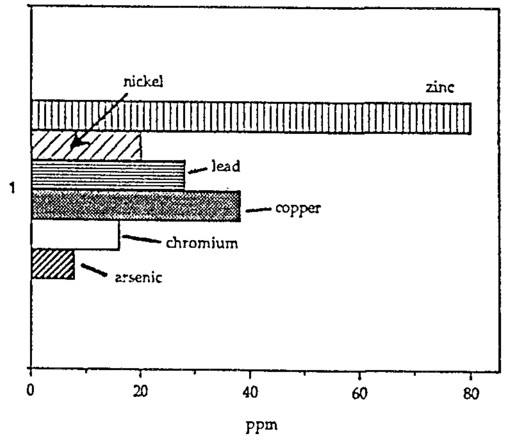


Figure 4b Background concentrations of priority pollutant metals (IEPA 1984)

Table 8 Concentrations (ppm) of Select Priority Pollutant Metals in Elutriates from Lake Calumet Sediments Compared to IPCB Standards for Secondary Contact and Indigenous Aquatic Life and for Lake Michigan (IEPA 1988).

Station	Cu	Ni	Pb	Zn
LBB	0.046*	0.023	0.030	0.070*
W18B	0.004	0.024	0.009*	0.075*
W17B	0.044*	0.008	0.009*	0.033*
W15B	0.009	0.008	0.009*	0.029*
W29B	0.176*	0.008	0.009*	0.087*
L7B	0.046*	0.057	0.009*	0.296*
W23B	0.014	0.008	0.009*	0.024*
W27B	0.131*	0.010	0.012*	0.096*
LLB	0.004	0.022	0.017*	0.040*
W19B	0.072*	0.008	0.009*	0.018
Secondary Standard	*1.00*	*1.00*	*0.10*	*1.00*
Lake Michigan Standard	*0.020*	*1.00*	*0.005*	*0.020*

*exceeds Lake Michigan Standard

4.1.3 *Regional significance*

Figure 5 shows the distribution of total priority pollutant metals in the Lake Calumet area, based on concentrations determined for the 56 sampling sites. Figure 6 also shows the locations of the 56 sampling sites as well as the locations of waste disposal operations from 1870 to the present. Metals are concentrated in the area close to W27. Other regions are less contaminated although total priority pollutant levels exceeding 500 ppm can be classified as moderately to highly elevated relative to Illinois background levels (Figure 4). Metal contamination of sediments has been found in association with municipal wastewater operations, coal-fired power plants, landfill leachate, urban run-off, highway-runoff, mining and metal-working operations, airborne particulates, and industrial wastewaters (Jennet *et al.* 1980). All of these activities have impacted Lake Calumet in the past (Colten 1985) and many are currently operating in the vicinity of the lake. The location of waste disposal sites does not appear to be related to locations of exceptionally high metals. Surface area and depth of disposal sites, soil permeability, and hydrological proximity may, however, influence the metal distribution in a manner not apparent from a simple surficial site map. The type of waste disposal operation (e.g. incinerator, lagoon, landfill) is also important in determining the impact of the site on the surrounding area. This in-depth information is not readily available, especially for the historical sites. A study, sponsored by HWRIC, is in progress to review the disposal operations in the Lake Calumet area. The conclusions of that study may clarify the role of waste disposal in the contamination of the Lake Calumet area.

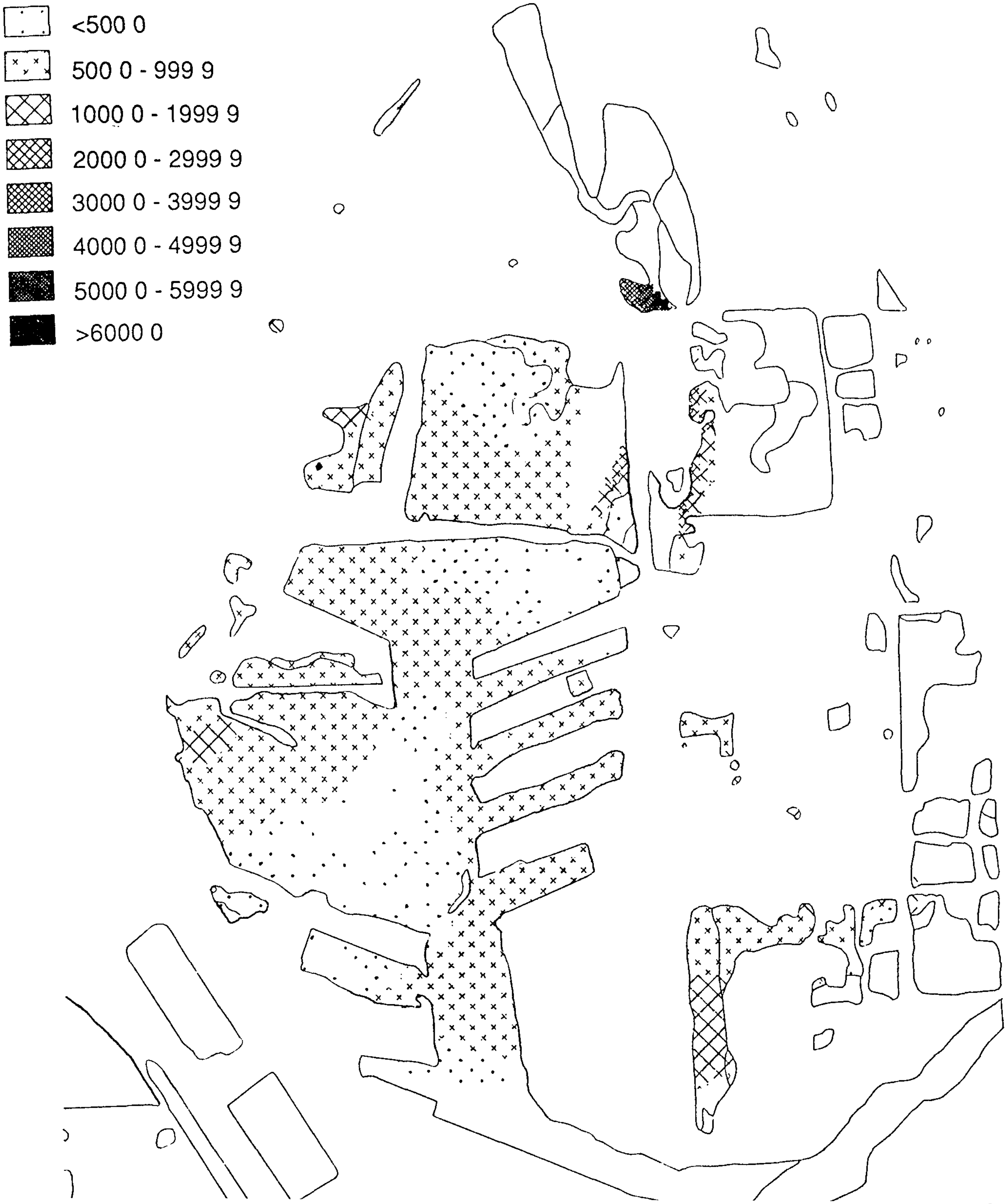


Figure 5a Geographical Distribution of Total Priority Pollutant Metals (ppm) in Sediments at Lake Calumet Based on Results from 56 Sediment Sampling Stations

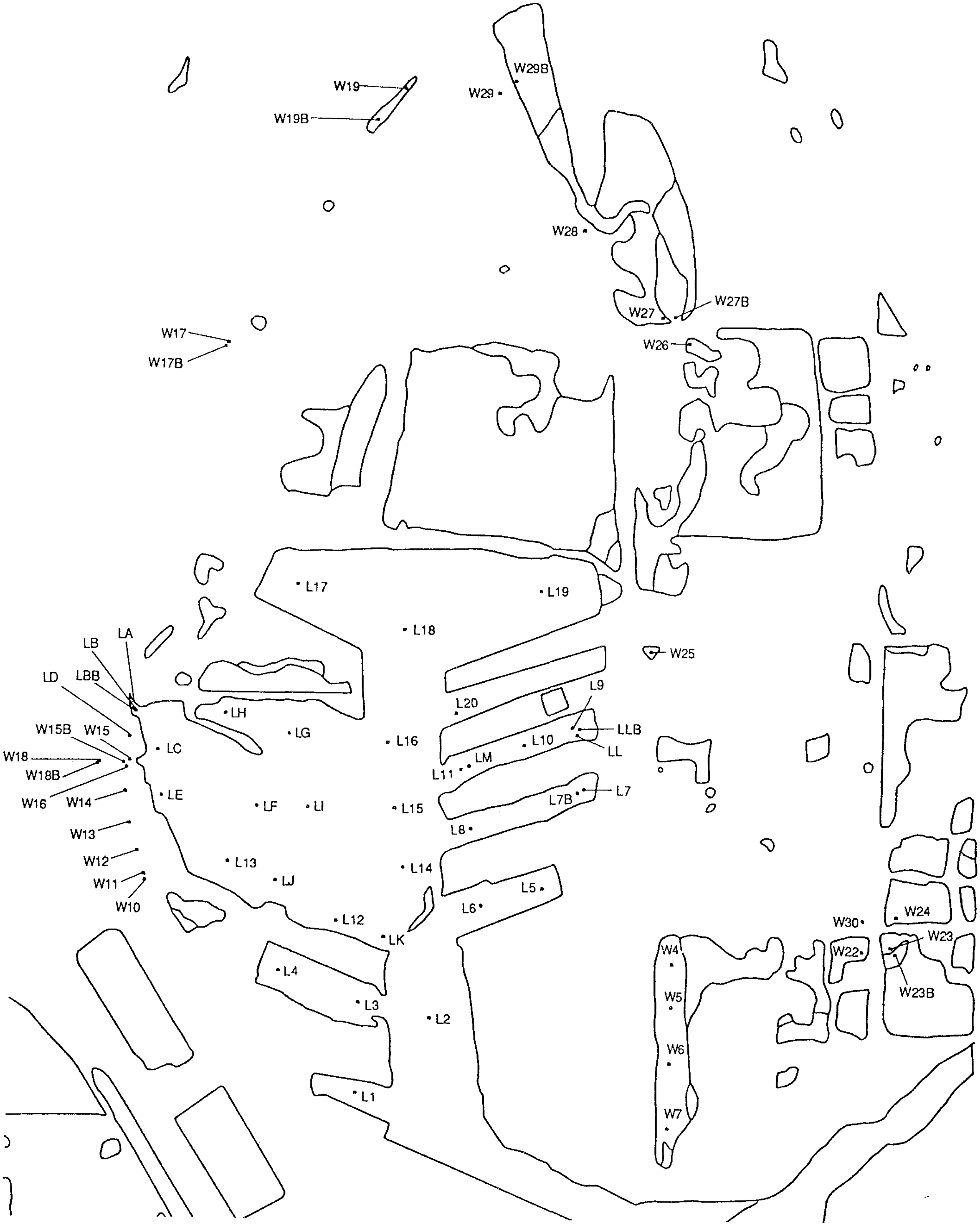


Figure 5b Locations of 66 Sediment Samples Collected at Lake Calumet: November 1986 to April 1988

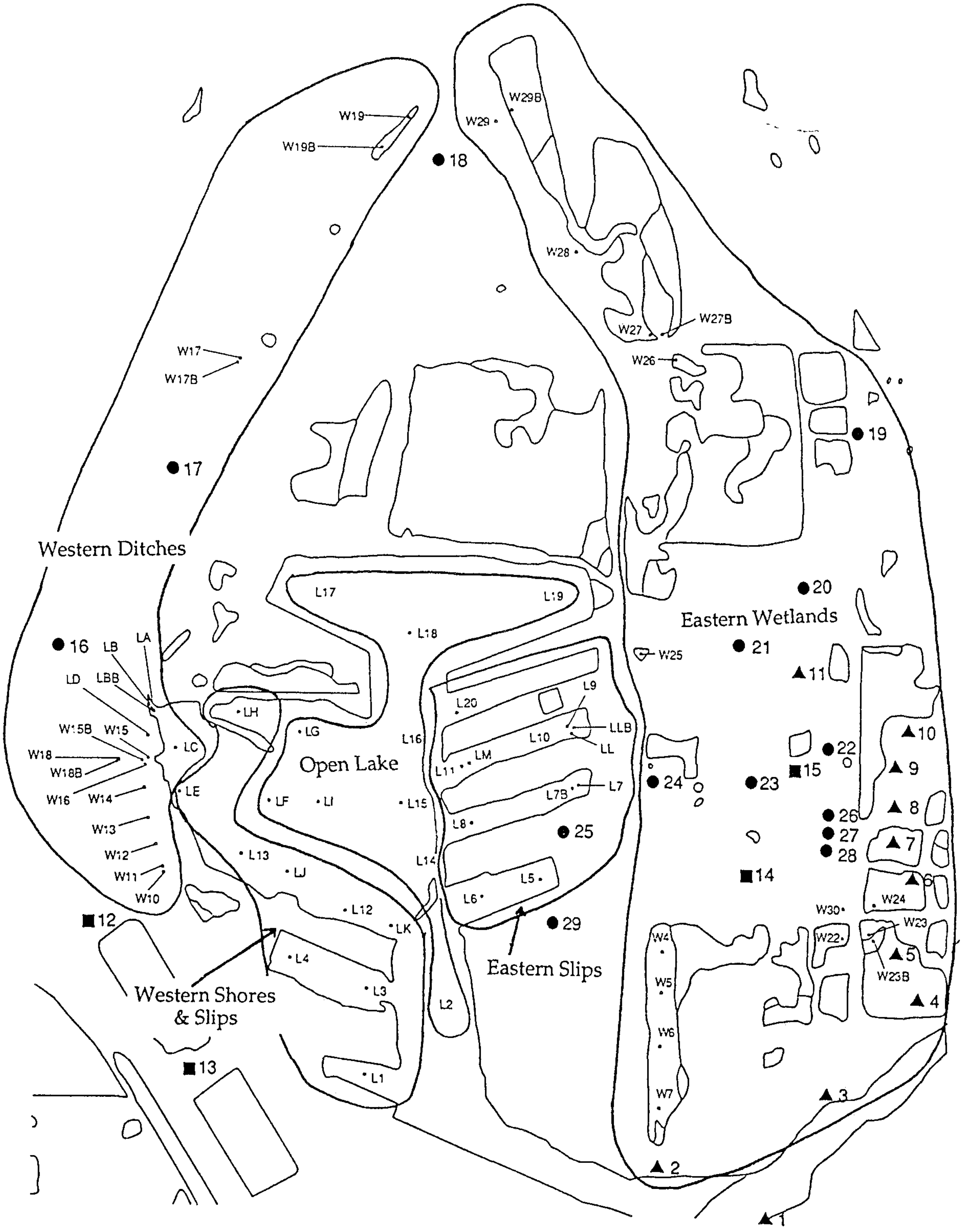


Figure 6 Locations of 60 Sediment Sampling Stations and Locations of Known Waste Disposal Operations from 1870 to Present ▲ (1870-1939), ■ (1940-1967), ● (current) Descriptions of these sites are given in Table 9

Table 9 Waste disposal site information. Site numbers refer to sites on Figures 6 and 10

Site No.	Year[a,b,c]	Contents	Reference
1	1929	lumber, stone, clay products	Colten 1985
2	1929	electrical, stone, clay, metals	Colten 1985
3	1929	electrical, stone, clay, metals	Colten 1985
4	1939	electrical, stone, clay, metals	Colten 1985
5	1939	primary metals	Colten 1985
6	1939	primary metals	Colten 1985
7	1939	primary metals	Colten 1985
8	1939	primary metals	Colten 1985
9	1939	primary metals	Colten 1985
10	1939	primary metals	Colten 1985
11	1939	primary metals	Colten 1985
12	1949	lumber, stone, clay products	Colten 1985
13	1949	municipal refuse	Colten 1985
14	1949	primary metals	Colten 1985
15	1963	municipal refuse	Colten 1985
16	---	hazardous/RCRA[1]	HWRIC database (4-88)
17	1970[a]	nonhazardous/illegal	HWRIC database (4-88)
18	1973[b]	nonhazardous/closed	HWRIC database (4-88)
19	---	nonhazardous	HWRIC database (4-88)
20	1970[a]	nonhazardous/illegal	HWRIC database (4-88)
21	1972[b]	nonhazardous/closed	HWRIC database (4-88)
22	1978[b]	nonhazardous/closed	HWRIC database (4-88)
23	1974[b]	nonhazardous/closed	HWRIC database (4-88)
24	1971[c]	nonhazardous	HWRIC database (4-88)
25	---	hazardous/RCRA[1]	HWRIC database (4-88)
26	---	nonhazardous	HWRIC database (4-88)
27	1978[c]	hazardous/RCRA[1]	HWRIC database (4-88)
28	1980[b]	hazardous/closed	HWRIC database (4-88)
29	1981[b]	nonhazardous/closed	HWRIC database (4-88)

[1] monitoring and permitted according to Resources Conservation and Recovery Act

[a] date discovered

[b] date closed

[c] date permitted

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4.2 PAHs

Concentrations of polynuclear aromatic hydrocarbons (PAHs) were determined for 23 Lake Calumet stations (Figure 7). Thirteen sediments (LA - LM) were analyzed for total PAH levels while the remaining determinations were part of base-neutral priority pollutant extractions. Sediment collected from station W17B contained over 50 ppm of total priority pollutant PAH compounds. This station was located in Pullman Creek, the drainage ditch from the pumping station that handles run-off from the Calumet Expressway. Figure 8, the distribution map of PAHs at Lake Calumet, also reflects this result. A major source of PAHs is emissions from internal combustion engines used in transportation. This may explain the high levels near the expressway. The remaining stations measured for PAHs have levels ranging from 0.5 to 12.0 ppm. Levels exceeding 1 ppm indicate elevated PAH contamination relative to levels in "clean areas" (see Table 2). Other sources of PAHs are coke production in the iron and steel industry; catalytic cracking in the petroleum industry; the manufacture of carbon black, coal tar pitch, and asphalt; heating and power generation; controlled refuse incineration; and open burning (Eisler 1987). Most of these activities have occurred in the Lake Calumet area and could account for the higher levels of PAHs in the sediments. Levels of PAHs were not found above detection limits in the elutriates prepared from 10 Lake Calumet sediments. Locations of waste disposal sites do not appear to be related to PAH contamination.

Select PAHs are of particular concern because of their potent carcinogenicity. The evidence implicating PAHs as an inducer of cancerous and precancerous lesions is becoming overwhelming and this class of substances is probably a major contributor to the recent increase in cancer rates reported for industrial nations (Eisler 1987). A study by Fabacher *et al.* (1988) showed that sedimentary concentrations (700 to 1900 ppb) of select PAHs (benzo(a)anthracene, benzo(a)pyrene, chrysene, fluoranthene, and fluorine), similar to levels found at stations at Lake Calumet (17B, 23B, 27B, BB, LB, 7B, and 15B), induced mutagenicity in laboratory tests. The authors conclude that evidence is increasingly strong that PAHs are a primary cause of neoplasia (tumor growth) in wild fish.

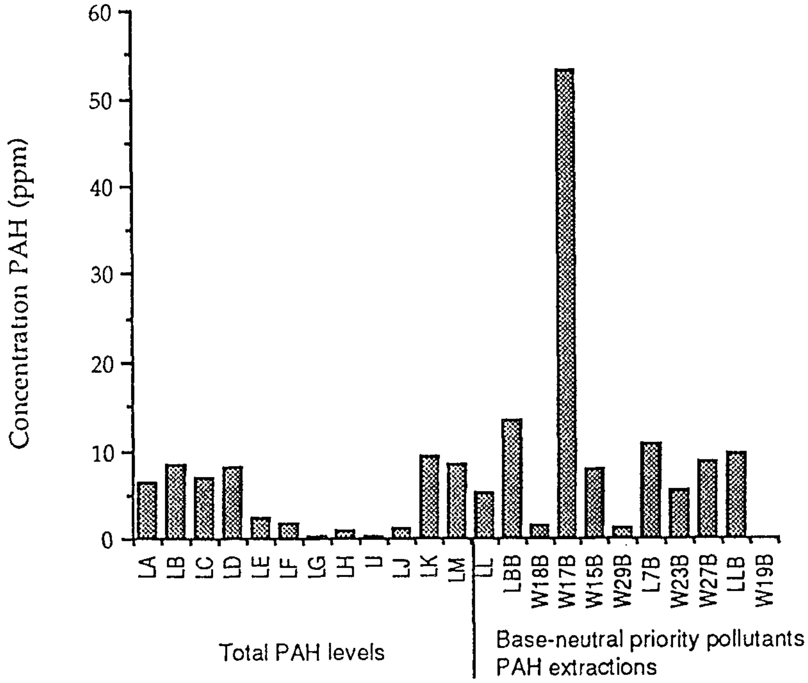


Figure 7 Concentrations of Total Polynuclear Aromatic Hydrocarbons from Sediments at Lake Calumet from 32 Sampling Stations

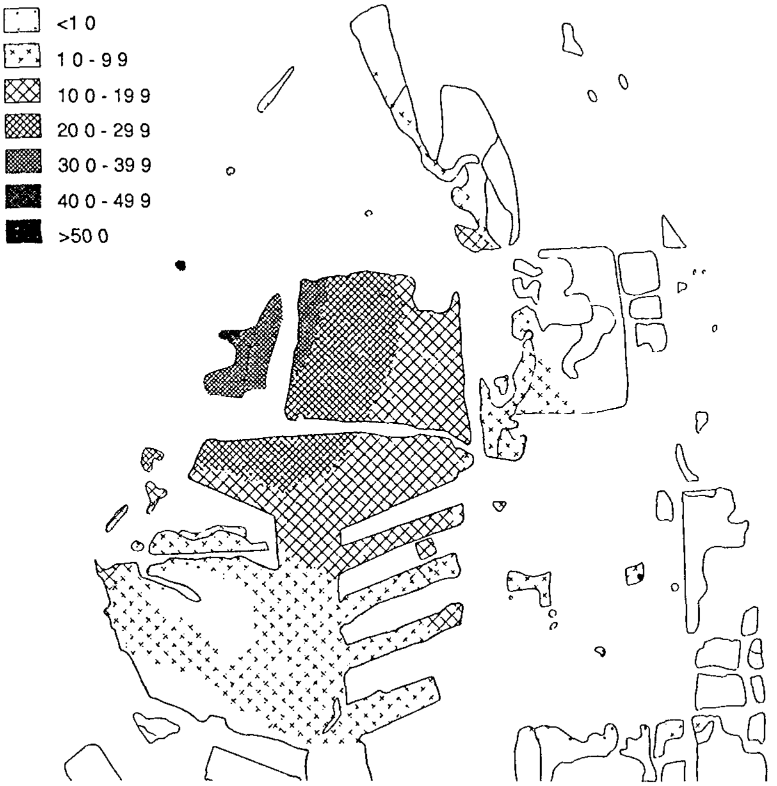


Figure 8a Geographic Distribution of Polynuclear Aromatic Hydrocarbons (ppm) in Sediments at Lake Calumet based on results from 23 Sampling Stations

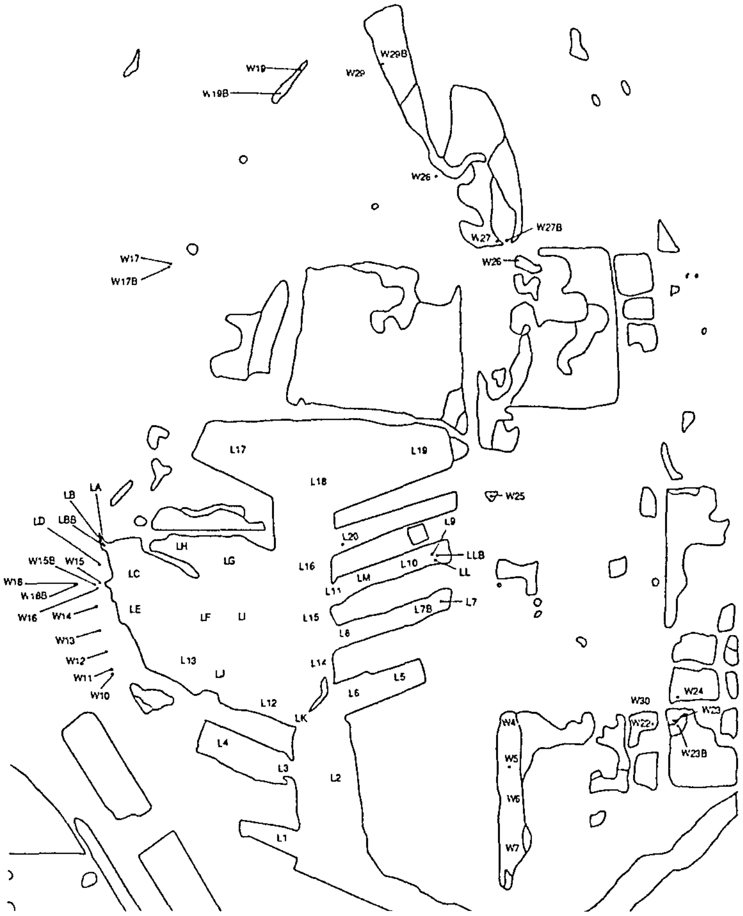


Figure 8b Locations of 66 Sediment Samples Collected at Lake Calumet: November 1986 to April 1988

4.3 Other Chemicals

Concentrations of phthalate esters, in particular, bis (2-ethylhexyl) phthalate and di-n-butyl phthalate, were also found in the 10 sediment samples and corresponding elutriates analyzed for priority pollutants. It is highly probable that these compounds are contaminants of the chemical analysis procedure because phthalate esters were found in blanks as well as in the sediment and elutriate samples.

Cyanide was detected in sediment samples at values ranging from 0 25 to 3.40 $\mu g\ g^{-1}$; values in the elutriate ranged from less than 5 to 108 $\mu g\ L^{-1}$. Aqueous cyanide concentrations of 108 $\mu g\ L^{-1}$ have been reported to be toxic to the fish *Lepomis macrochirus* (bluegill).

4.4 Limitations of Chemical Analyses

Characterizing the sediment by the presence or absence of priority pollutants is a yardstick measure of the anthropogenic activity in the area. This characterization, however, does not measure the many chemical by-products produced by chemical (other contaminants, hydrogen ion, light), biological (microbial degradation, benthic bioturbation), and physical (sediment structure, water flow, resuspension) interactions in close proximity to the sampling location. In addition, conditions influenced by these chemical, biological, and physical forces may be substantially different from sampling site to sampling site, based on many factors including wind velocity and direction, and water column depth. Monitoring all the factors influencing a single contaminant in a defined system requires lengthy research; the monitoring of the fate of a large number of contaminants exposed to varying conditions at many sites is a nearly impossible task. The chemical data collected in this two year study of Lake Calumet should be viewed as information about the environmental past and present of the lake. Lake Calumet sediments contain high concentrations of potentially hazardous priority pollutant metals and PAHs. Lake Calumet is not a closed system, and may impact the biota, possibly even humans, in the nearby vicinity. The Lake Calumet system may affect conditions in systems such as Lake Michigan and the Illinois River, to which Lake Calumet is hydrologically connected.

The cost of chemical analysis is prohibitive for collecting extensive chemical information from as large a set of sediment samples as were collected in this study. Even if cost were not a consideration, there is no guarantee that all of the chemicals that might be damaging to the ecosystem would be measured. There are 126 priority pollutants; many times that number of anthropogenic chemicals have been released into the environment as a whole, and probably into Lake Calumet in its 120-year industrial history.

4.5 Toxicity

Some of the limitations of chemical characterization of sediments can be overcome by using toxicological analyses to evaluate the hazard (toxic potential) of the sediment. An organism exposed to the sediment will be exposed to all the contaminants in the sample: metabolites, unknowns, complexes, etc. Furthermore, interactions (synergism, antagonism) between toxicants will be part of the exposure conditions. The organismal response should be a result of existing chemical, biological, and physical sediment conditions. The use of bioassay organisms can be considerably less expensive than chemical analysis and a hazard assessment can be constructed more readily and for more stations. Limitations arise from biological assessment also, however. Use of single bioassays, single-species bioassays, and laboratory bioassays eliminates the full effect of the "real world" : the many trophic levels of organisms that may inhabit or utilize a mere square inch of sediment; the temperature, pH, oxygen, and light regime of the sediment sample; and the inherent sensitivity or resistance of the resident species.

On a more technical scale, the use of elutriates, interstitial water, or even bulk sediment in laboratory tests necessitates disruption of the sediment ecosystem. Any or all of the chemical, biological, and physical conditions of the sediment can be disrupted causing a change, minute or extreme, in the toxic potential of the sediment.

The use, in the case of this study, of a battery of sediment elutriate bioassays is an attempt, in light of overwhelming complexities, to gain some understanding of the distribution of toxic potential from a number of sediments in and surrounding Lake Calumet. The results of toxicological bioassays of Lake Calumet sediment elutriates are presented graphically for single-species tests in Figure 9 and for substrate community tests in Figure 10. The sediment elutriate producing the highest toxicity for each set of tests in each region is listed in Table 10 Tabular data listing percent responses for each bioassay organism are given in Appendix 3.

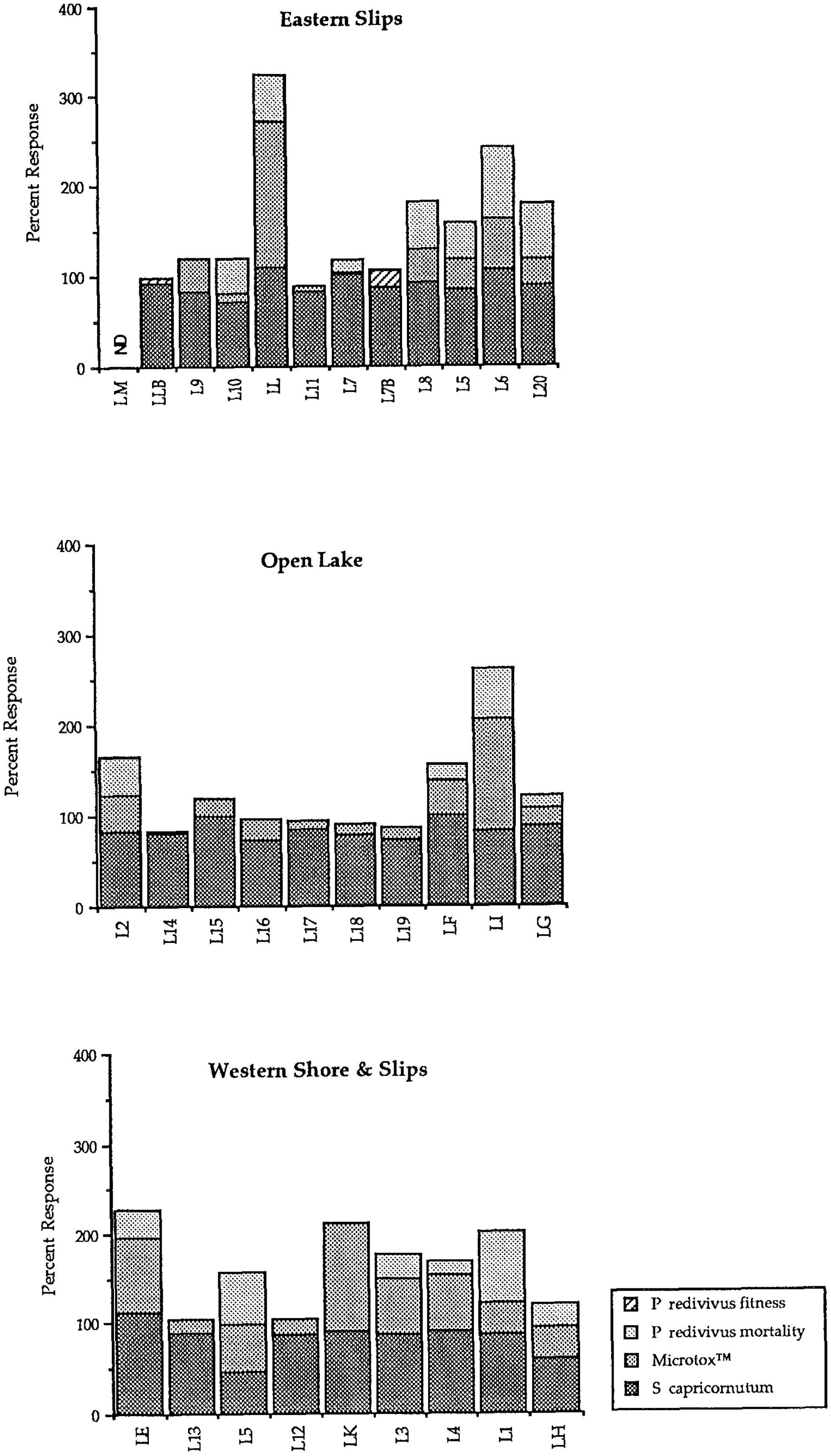
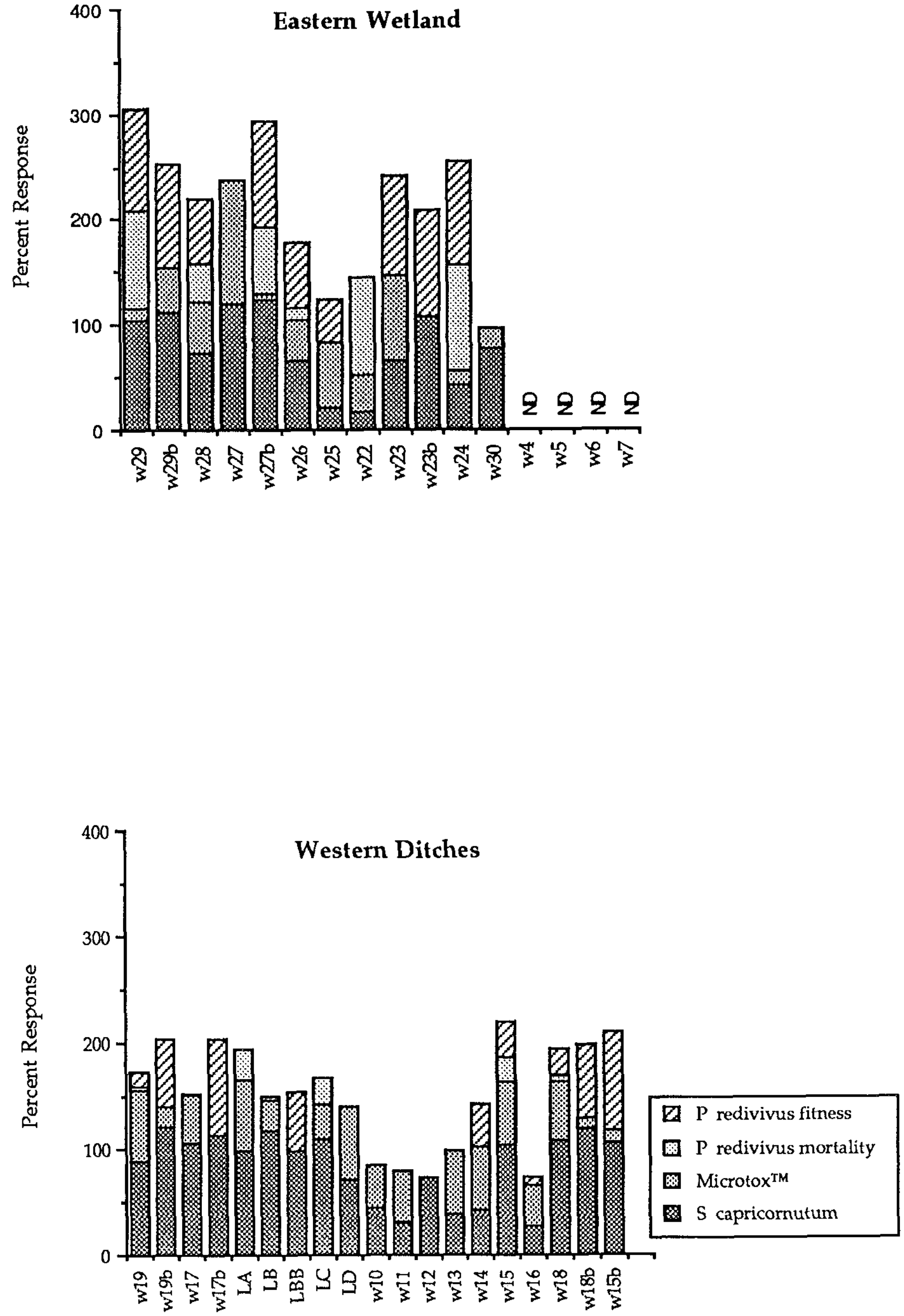


Figure 9 Single-species Toxicological Percent Response for Lake Calumet Elutriates ND=not determined


Eastern Wetland

Western Ditches

Figure 9, cont Single-species Toxicological Percent Response for Lake Calumet Elutriates ND=not determined

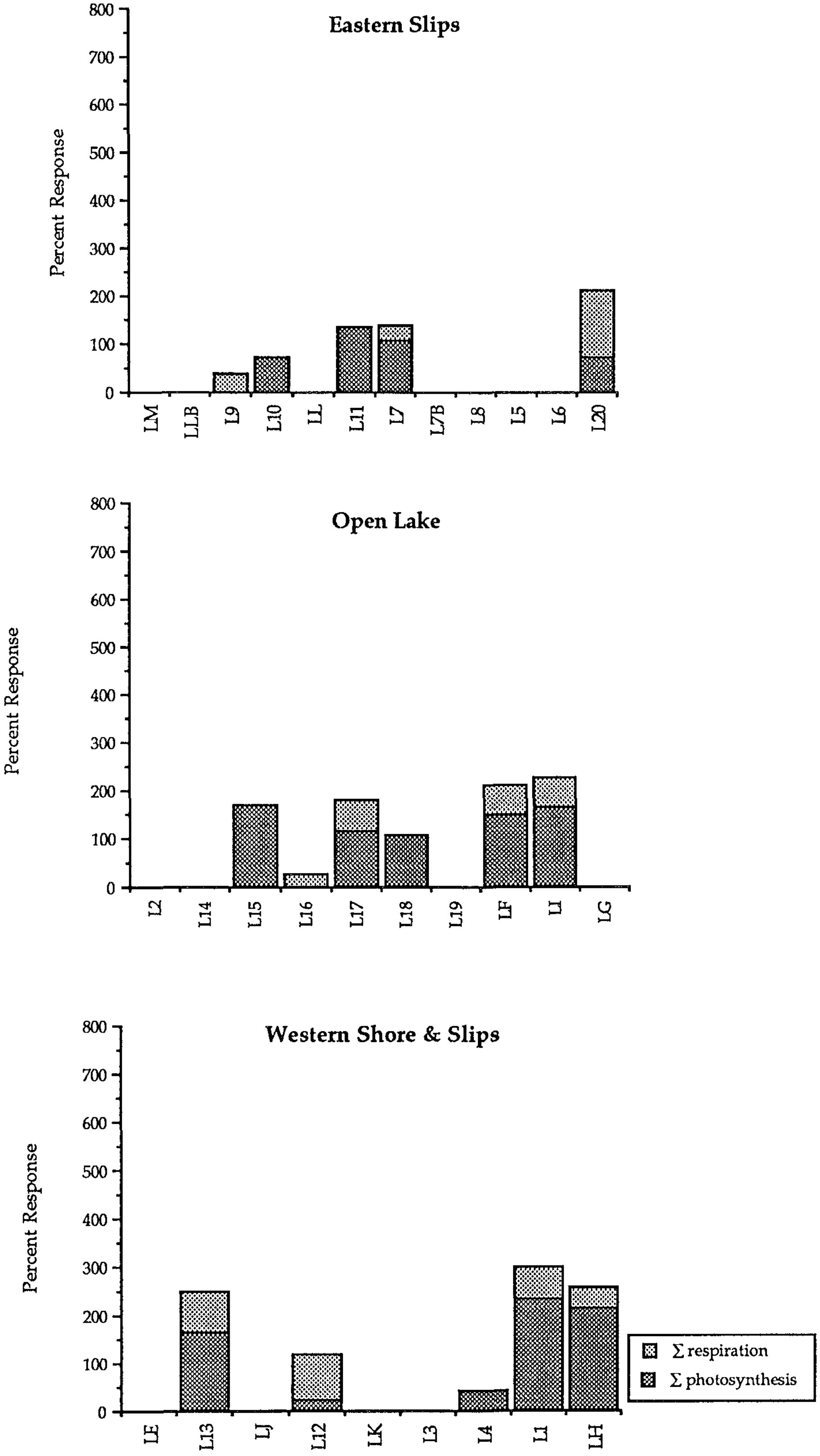
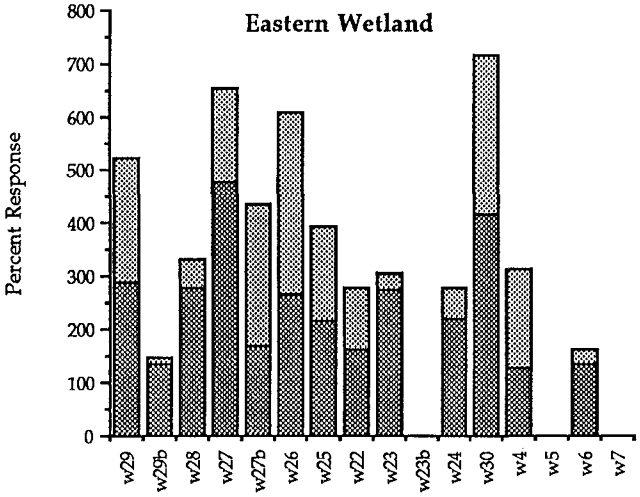


Figure 10 Substrate Community Toxicological Percent Response for Lake Calumet Elutriates



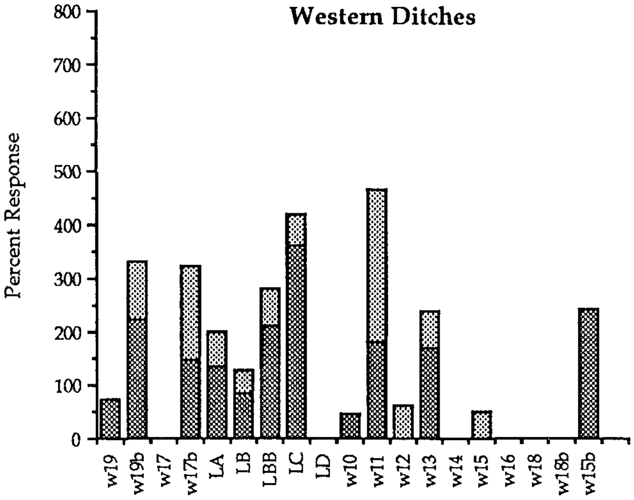


Figure 10, cont Substrate Community Toxicological Percent Response for Lake Calumet Elutriates

Table 10 Stations of Highest Toxicity to Organisms Used to Evaluate Contaminated Sediments at Lake Calumet in each of 5 Geographic Regions

	Single-species				Substrate community		
Region	*Selenastrum capricornutum*	Microtox™	*Panagrellus redivivus*	total[a]	photo-synthesis	respiration	total[b]
Eastern Slips	LL	LL	L6	LL	L11	L20	L20
Eastern Wetland	W27B	W27	W23B	W29	W27	W30	W30
Open Lake	L15	LI	LI	LI	L15	L17	LI
Western Ditches	W19B	LD	W15B	W15	LC	W11	W11
Western Shores	LE	LK	L1	LE	L12	L13	L1

[a] sum of response of S capricornutum, Microtox™, and P. redivivus
[b] sum of response of substrate community photosynthesis and respiration

Figure 11 shows the distribution of average toxicological response based on results of single-species bioassays performed on 60 sediments in and near Lake Calumet. Figure 11 also shows the locations of sampling sites and the locations of waste disposal operations from 1870 to the present. Information regarding these disposal sites is given in Appendix 4. Distribution maps of total priority metals and PAHs are repeated in Figure 12. Six areas of higher toxicity (above 70 percent response) are also identified in Figure 11.

- **Site A** is in the Eastern Wetlands near stations W27 and W29. This corresponds with an area of extreme metal contamination (Figure 12). Elutriate concentrations of metals from these stations (W27B, W29B) exceeded IPCB Lake Michigan Water Quality Standards for copper, lead, and zinc.

- **Site B** is also located in the Eastern Wetlands near station W23. This wetland area corresponds with the location of several waste disposal facilities. Several of these waste sites have been reported to contain heavy metals or other hazardous wastes (Colten 1985). More information (e.g. size, depth, permeability of surrounding soil, location of aquifers, specific chemistry, etc) regarding the nature of these wastes and disposal sites is necessary to determine the contribution of the wastes to the contamination.• **Site C** is a small area located in the Eastern Slip region close to station LL which had high concentrations of metals (Figure 5). Other stations tested from that slip were not as high in toxicity or metal contamination.

- **Site D** involves an area located near station LK. This station had low concentrations of metals and relatively low concentrations of PAHs. No waste facilities appear to be in proximity to this area, however, the peninsula of land that extends into this site is new fill (since 1960; Figure 1) and consists mostly of slag. It is possible that this fill material contains toxic compounds that were not detected in chemical analysis Also, sediment in runoff may be deposited behind this peninsula.

- **Site E** is located in the deepest portion of Lake Calumet near station LI. Again, concentrations of metals and PAHs are low. The toxicity of this region is not apparently related to anything measured during the course of this study.

- **Site F** is located at the outfall of drainage ditches from both sides of the Calumet Expressway Station W16 had one of the highest concentrations of metals and waste disposal site 16 has been identified to contain hazardous materials. These factors and the proximity to the Expressway may influence toxicity in this region.

All of these sites should be considered areas of concern for Lake Calumet by virtue of their high toxicity, whether or not toxicity can be related to measured contamination.

Substrate community response is similar to that of single-species tests. Toxicity is dominant in the Eastern Wetland and Western Ditch regions of Lake Calumet. Stations W27, W29, and W30 elicited the highest responses. These stations correspond to Sites A and B identified as areas of concern in single-species toxicity (Figure 11). Station W25 was also highly toxic to substrate communities. This station is in the vicinity of several waste disposal sites that may influence toxicity.

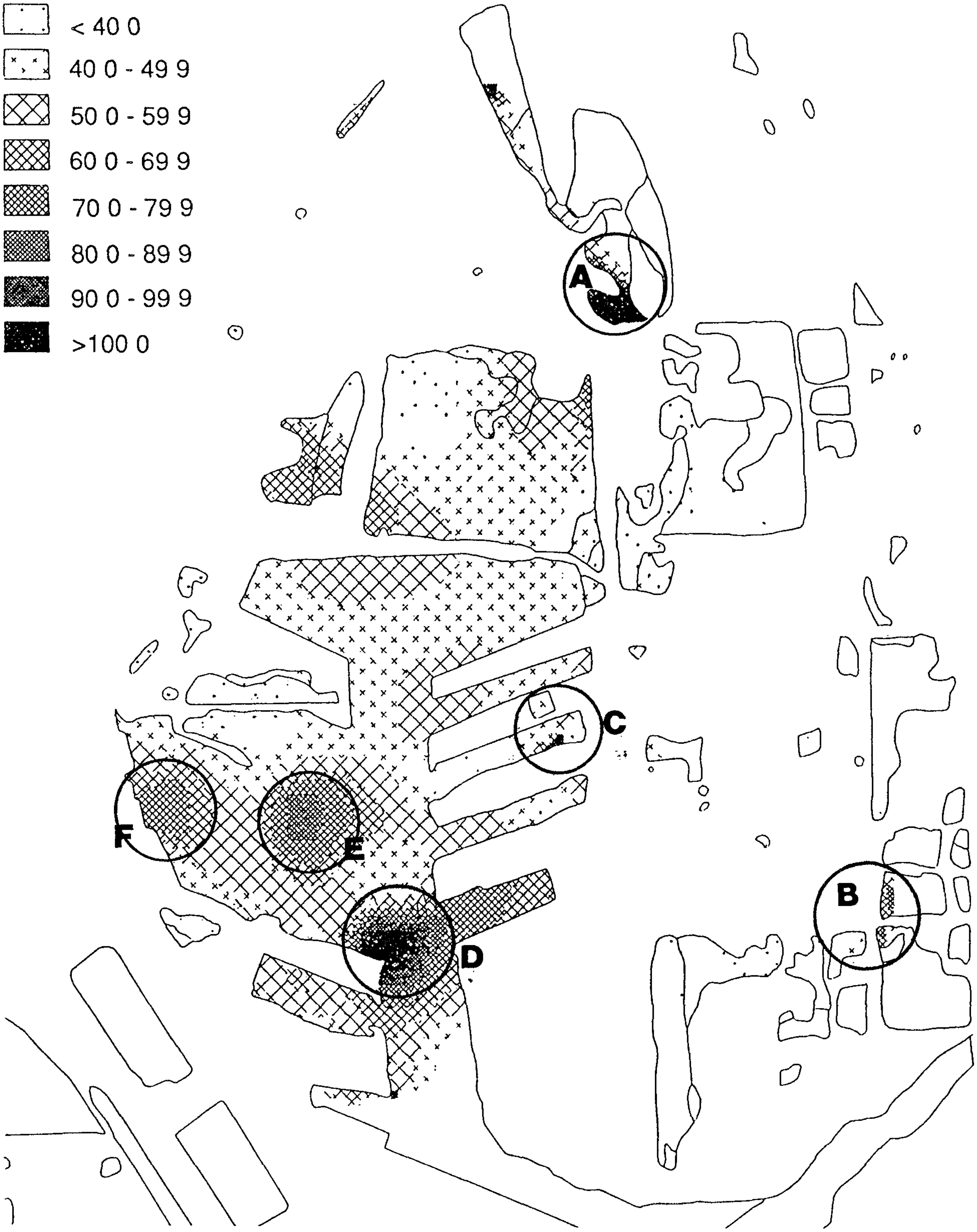
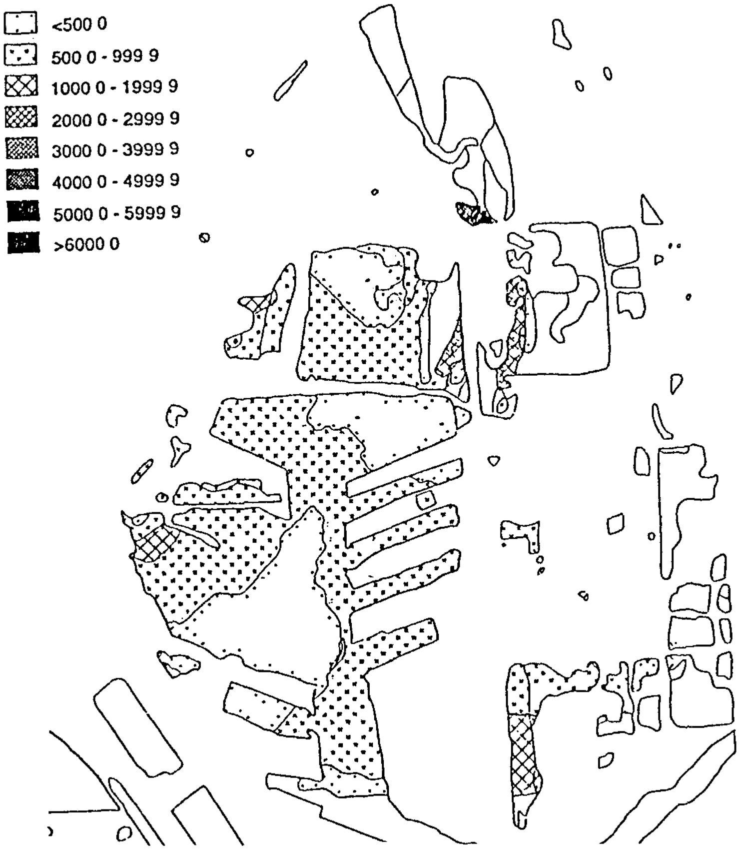
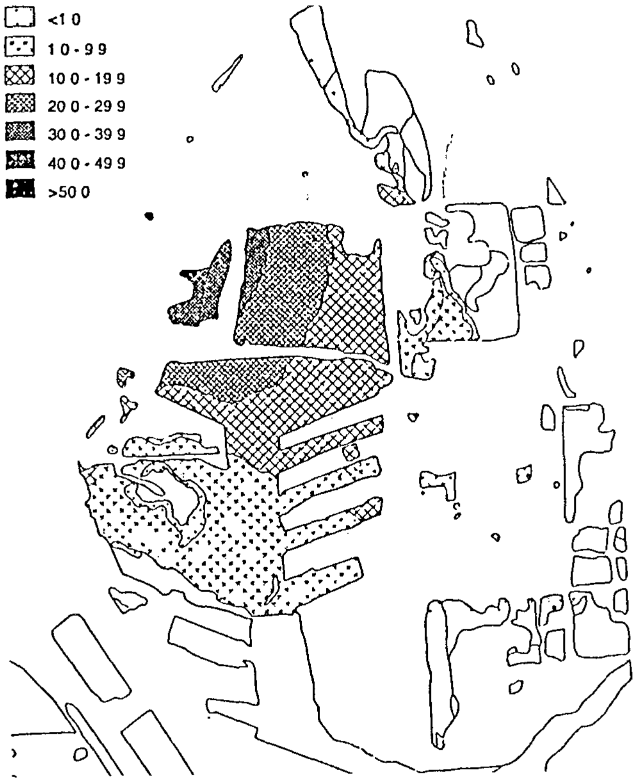


Figure 11. Geographic Distribution of Single-species Toxicity (average percent response) for Sediment Elutriates at Lake Calumet. Boxed regions are areas of high toxicity and are described in more detail in the text



Metals



PAHs

Figure 12 Geographical Distribution of Metal (from Figure 5), and PAH Contamination (from Figure 8)

It is beyond the scope of this study to determine where and how these sediments will effect the Lake Calumet ecosystem or those of Lake Michigan or the Illinois River. The results collected show that a certain percentage of the sediments were exceptionally damaging to three representative organisms from very different trophic levels and to an undefined number of species comprising an aquatic community. The elutriate test may overestimate the toxic potential of the sediments to organisms in the water column, but may underestimate the exposure to the whole sediment for important benthic biota. While conditions resembling the elutriation procedure are likely not to occur in Lake Calumet, information that nearly sixty sediment locations in and around Lake Calumet are capable of inducing toxicity should arouse concern.

Interpreting the data generated from chemical and toxicological analyses involves further limitations. The dose-response curve is a mainstay of toxicological research Values such as EC_{50} and percent response rely on the particular statistical analysis used to evaluate this curve. In the case of single-chemical tests or of well-defined mixtures of two or three chemicals, a probit analysis (log-probability) is generated. This analysis has been designed to most effectively describe the threshold effects of toxic chemicals. But because the sediment (or elutriate) contains many chemicals with the potential to exert a toxic effect, a simple linear regression may be the most conservative analyses by reason of its simplicity. The kind of effect produced by a chemical or group of chemicals may be different under each individual site condition and for each organism that is used. Several dose-responses for individual contaminants, as well as interactions between them, occur in a toxic effect of sediment constituents and combine to produce a sediment dose-response. The threshold effect can be determined only for the sediment (or elutriate) as a whole, not for the individual contaminants. (We have seen very few threshold-like dose-response curves in our elutriate bioassays.)

It is tempting to compare numbers from chemical tests with numbers from biological tests for corresponding sediments because the very basis of toxicology is the study of "cause and effect." Such comparisons must, however, be made cautiously. A positive correlation is generated when one parameter increases as another also increases (e.g. toxicity increases as lead concentrations increase) across a series of samples. This does not indict the second parameter as the cause of the first; only that the two vary in a similar manner. In conditions as complex as Lake Calumet, many contaminants may be positively correlated with toxicity at a small number of sites but be negatively related at others, generating a mid-range correlation coefficient for all the stations. Tables 11 and 12 list statistically significant nonparametric correlations generated when making comparisons between trace element chemistry for 10 Lake Calumet elutriates and toxicity tests. As determined in Table 8, concentrations of zinc, lead, and copper exceed IPCB secondary contact water quality standards. Significant correlations of toxicity with these metals indicate that they may play a role in the toxicity reported for these areas. Other trace elements with significant correlation coefficients may also be related to toxicity but cannot be implicated with the data reported here. This, again, reflects the localized conditions of the sediment. It is far beyond the scope and resources of this study to predict and interpret which contaminants will be toxic at which sites and under what conditions.

Table 11. Trace Elements in Elutriates from 10 Lake Calumet Sediments with Statistically Significant (p<0 01) Kendall's t Correlations when Compared to Single-species Bioassay Organism Response (in order of decreasing correlation)

Panagrellus redivivus	*Photobacterium phosphoreum*	*Selenastrum capricornutum*	Σ response
K	Mn	Na	K
B, Zn	Zn	Mn	Zn
Mo	K, Na	Mo	Mn
Pb	Ni	Pb	B, Ni, P
P, Ba, Mn	B, Ca	K	Cu, Na
Cu	Pb	B, P	Mo, Pb
Na	Mo	Fe	Ba
Ni	P	Cu	
		Si	
		Al	
		Ni	

Table 12 Trace Elements in Elutriates from 10 Lake Calumet Sediments with Statistically Significant (p<0 01) Kendall's t Correlations when Compared to Substrate Community Functional Response (in order of decreasing correlation)

respiration	photosynthesis	total significant
Na	B	Mo
B	K	Al, Fe, Na, Pb, Ca (negative)
K, Zn		Ba, Mn
P (negative)		

Chapter 5

Conclusions and Recommendations

In this second year of study, 23 additional sediment samples were collected from the ditches and wetlands surrounding Lake Calumet. Chemical and toxicological data from these sediments indicate that contamination and toxicity are concentrated in these areas, relative to the sediments collected previously from Lake Calumet proper.

To determine if a pattern of toxicity or contamination existed in the Lake Calumet area, geographic distribution maps were constructed from data collected throughout the two-year project. The maps resembled "fingerprints" and identified areas of concern with regard to metal and PAH contamination and toxicity:

- metal contamination: W27, W29 in the Eastern Wetlands.
- PAH contamination: W17 and areas around the Calumet Expressway.
- single-species toxicity: W27, W29 in the Eastern Wetlands,
  W23 in the Eastern Wetlands,
  LL in the Eastern Slips,
  LK in the Western Shore & Slips,
  LI in the Open Lake, and
  W15, W16 in the Western Ditches.
- substrate community toxicity: W30, W27, W25, W26 in the Eastern Wetlands.

The proximity of many waste disposal facilities to Lake Calumet and the potential hydrological connection between the highly contaminated and toxic wetlands warrants concern. Regulating the disposal sites in the Lake Calumet region on a site-by-site basis would limit the effectiveness of the monitoring and remediation. The history of contamination in the area is so long and so complex that it may unrealistic to expect that all potential point sources of contaminants could ever be identified and quantified. Due to overlap or superposition of hazardous waste deposition sites over time, and to migration of contaminants within the region, the Lake Calumet area may have come to resemble a non-point source situation. The U. S. Environmental Protection Agency's evaluations of forty-two potential Superfund sites in the region all yielded scores below the action level when done on an individual (site-by site) basis. When so many sites are in such close proximity, however, it may be more ecologically relevant to consider such an area as a single site, in which case the score might surpass the minimum for Superfund action.

To best identify the contaminant sources and hazards impacting the Lake Calumet ecosystem and the Far South Side of Chicago, data should be collected and analyzed for the following environmental parameters:

1. concentrations of harmful metals and organics in fish and waterfowl;
2. hydrogeological connection between wetlands, disposal sites, and Lake Calumet;
3. air monitoring to determine the contribution of atmospheric deposition,
4. details of the waste disposal sites (past and present) including geographic coverage and potential pollutant export; and
5. further analysis of the hydrological and contaminant connection between Lake Calumet and the very important waterways of Lake Michigan and the Illinois River .

Lake Calumet is a severely disturbed ecosystem. The data reported in this study are merely yardstick measures of the extent of the disturbance. It is imperative that further research is conducted to determine the most effective methods to reduce the environmental hazard associated with the Calumet region

Literature Cited

Brannon, J.M., R.H Plumb, Jr., and I. Smith Jr. 1980. Long-term release of heavy metals from sediments. pages 221-266 in Contaminants and Sediments Volume 2 (Robert A. Baker, editor). Ann Arbor Science Publishers. Ann Arbor, M I.

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., 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., 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., 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.

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

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.

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.

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

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.

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.

Fabacher, D.L. C.J. Schmitt, J.M. Besser, and M.J. Mac. 1988. Chemical characterization and mutagenic properties of polycyclic aromatic compounds in sediment from tributaries of the Great Lakes. Environ. Toxicol. Chem. 7: 529-543.

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.

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

IEPA. 1988. Illinois Water Quality Report 1986-1987. IEPA/WPC/88-002.

Jennett, J.C., S.W. Effler and B.G. Wixson 1980. Mobilization and toxicological aspects of sedimentary contaminants. pages 429-444 in Contaminants and Sediments Volume 1 (Robert A. Baker, editor). Ann Arbor Science Publishers. Ann Arbor, MI.

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

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

McCarthy, J.F. and D.K. Whitmore. 1985. Chronic toxicity of di-n-butyl and di-n-octyl phthalate to *Daphnia Magna* and the Fathead Minnow. Environ. Toxic. and Chem., Vol4,pp 167-179, 1985.

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.

Ross,P.E., M.S. Henebry, J.B. Risatti, T.J. Murphy, M. Demissie, and L C. Burnett with others. 1988a. A preliminary environmental assessment of the contamination associated with Lake Calumet, Cook County, Illinois, Illinois Hazardous Waste Resarch and Information Center Report RR019. Savoy, IL.

Ross,P.E., V. Jarry, and H. Sloterdijk. 1988b. A rapid bioassay using the green alga *Selenastrum capricornutum* to screen for toxicity in St. Lawrence River sediment elutriates. ASTM STP 988. American Society for Testing and Materials.

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.

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

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. 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.

APPENDICES

1. BULK SEDIMENT CHEMISTRY
    a. Eastern Slips
    b. Eastern Wetlands
    c. Open Lake
    d. Western Ditches
    e. Western Shores & Slips

2. ELUTRIATE CHEMISTRY

3. TOXICOLOGICAL DATA

<u>legend for chemical data</u>

J=estimated value
B=compound also detected in blank sample

BDL=below detection limit
NT=not tested

EASTERN SLIPS	LM	LLB	L9	L10	LL	L11	L7	L7B	L8	L5	L6	L20
Compounds (units)												
Acenaphthene (µg/Kg)		83						99J				
Anthracene (µg/Kg)		210						306J				
Benzo(a)Anthracene (µg/Kg)		848						953				
Benzo(b)Fluoranthene (µg/Kg)		1186						1228				
Benzo(k)Fluoranthene (µg/Kg)		1047						883				
Benzo(a)Pyrene (µg/Kg)		946						1136				
bis(2-ethyl hexyl)Phthalate (µg/Kg)		1221B						749B				
Chrysene (µg/Kg)		1071						1111				
Dibenzofuran (µg/Kg)		1						86J				
Fluoranthene (µg/Kg)		1390						1550				
Fluorene (µg/Kg)								162J				
2-Methylnaphthalene (µg/Kg)		1328						1086				
Phenanthrene (µg/Kg)		885						2131				
Pyrene (µg/Kg)		1956										
Hexachlorobenzene (µg/Kg)		303										
Al (%)	3.72		11.56	10.46		75	10.62		8.38	10.42	10.63	10.06
As (ppm)	22		21	23		23	19		21	18	19	19
B (ppm)	38		70	65		31	73		42	54	70	60
Ba (ppm)	414		448	439		421	419		418	450	454	401
Be (ppm)	<1		12	1.1		<1	12		1.1	12	1	<1
Ca (%)	5.64		8.43	8.31		7.62	8.63		8.01	9.55	8.77	8.86
Cd (ppm)	<1.5		<3	<3		<3	<2		<3	<2	<2	<3
Co (ppm)	11		18	16		12	17		14	15	15	15
Cr (ppm)	60		97	91		63	93		78	96	86	76
Cu (ppm)	35		72	67		45	53		58	56	51	54
Fe (%)	2.57		6.64	5.89		4.58	6.64		5.65	5.97	6.12	5.02
K (%)	1.92		3.09	2.96		2.28	2.85		2.4	2.98	3.08	29
Mg (%)	NT		4.6	4.82		4.59	4.88		4.88	5.14	5.03	5.47
Mn (%)	NT		0.11	0.11		0.09	0.11		0.09	0.14	0.14	0.11
Mo (ppm)	NT		20	19		15	02		0.18	02	0.21	22
Na (%)	0.53		05	0.58		0.71	0.58		0.66	0.55	0.55	0.65
Ni (ppm)	12		42	33		27	34		21	30	32	37
P (%)	0.05		0.12	0.12		0.11	0.12		0.12	0.16	0.15	0.12
Pb (ppm)	105		173	183		127	150		130	160	170	165
Sb (ppm)	1		2	1.7		12	1.3		1.3	12	1.3	1.9
Se (ppm)	<5		NT	NT		NT	NT		NT	NT	NT	NT
Si (%)	25.8		49.11	49.26		56.66	48.75		53.29	48.53	48.62	49.69
Sn (ppm)	10		11	10		5	9		9	12	11	11
V (ppm)	30		56	60		26	50		34	54	60	37
Zn (ppm)	229		409	388		320	363		380	361	379	299
Hg (ppb)	NT		NT	NT		NT	NT		NT	NT	NT	NT
CN (µg/g)							<25					

Appendix 1a. Eastern Slips Chemistry

EASTERN WETLANDS	W29	W29B	W28	W27	W27B	W26	W25	W22	W23	W23B	W24	W30	W4	W5	W6	W7
Compounds (units)																
Anthracene (µg/Kg)					250J				130J							
Benzo(a)Anthracene (µg/Kg)					790J				730J							
Benzo(b)Flouranthene (µg/Kg)		377			850J				730J							
Benzo(k)Flouranthene (µg/Kg)									530J							
Benzo(a)Pyrene (µg/Kg)		273			960J				720J							
bis(2-Ethylhexyl)Phthalate (µg/Kg)		5525B			740J				290J							
Chrysene (µg/Kg)					970J				800J							
Phenanthrene (µg/Kg)									517J							
Pyrene (µg/Kg)		330			1900				1330J							
Acenaphthene (µg/Kg)					200J											
Fluoranthene (µg/Kg)		283			1400J											
Fluorene (µg/Kg)					220J											
Phenanthrene (µg/Kg)					1300J											
Phenol (µg/Kg)		171														
Methylene Chloride (µg/Kg)										19B						
Acetone (µg/Kg)					147					36						
Chlorobenzene (µg/Kg)										8						
Al (%)	1.54		1.32	2.38	0.53	3.1	3.18	3.55	1.43	0.1375	1.47	2.43	9.42	9.69	8.88	6.39
As (ppm)	BDL		BDL	BDL	<4.7	BDL	BDL	BDL	BDL	16.7	BDL	BDL	15	13	15	16
B (ppm)	87		80.5	122	34.8	156	135	218	267	45.4	215	108	65	63	60	34
Ba (ppm)	273		190	630	210	314	146	218	253	30.2	160	176	435	443	432	353
Be (ppm)	25		6	BDL	0.85	1.5	1	2	1.5	0.3	1	3	BDL	BDL	BDL	BDL
Ca (%)	13.3		17	7.41	2.07	7.07	5.78	7.01	1.35	1.272	4.12	8.93	11.58	13.23	14.25	9.74
Cd (ppm)	45.5		23	128	3.62	16	6.5	10	16	1.24	12.5	7.5	BDL	BDL	BDL	BDL
Co (ppm)	BDL		BDL	BDL	4.31	BDL	BDL	BDL	BDL	2.17	BDL	BDL	16	17	16	16
Cr (ppm)	63		269	1470	50.5	169	52	108	186	76.7	137	82	111	121	116	129
Cu (ppm)	420		138	1150	59.9	113	BDL	17	178	18.1	64.5	28.5	65	62	74	61
Fe (%)	2.16		2.26	3.84	1.154	3.16	3.07	3.23	4.43	0.635	4.26	2.61	5.8	6.06	7.78	14.59
K (%)	0.419		2330	4190	901	9980	11100	13800	3990	418	4.5	0.84	2.82	2.93	2.6	1.92
Mg (%)	6.58		7.63	3.11	0.726	3.44	3.08	3.15	2.23	0.282	1.18	3	4.01	3.72	4.04	4.82
Mn (%)	0.124		0.264	0.158	0.034	0.122	0.116	0.126	0.245	0.0354	0.12	0.11	0.14	0.17	02	0.17
Mo (ppm)	BDL		BDL	BDL	8.02	BDL	BDL	BDL	BDL	6.67	BDL	BDL	30	34	31	36
Na (%)	BDL		BDL	BDL	660	BDL	BDL	BDL	2870	403	0.311	BDL	0.65	0.58	0.55	0.59
Ni (ppm)	95		44.5	219	19.7	46	33.5	48.5	46.5	29.1	60.5	45.5	37	48	36	45
P (%)	0.548		0.216	1.72		0.134	0.0362	0.0556	0.112		0.0974	0.0493	0.16	0.17	0.18	0.12
Pb (ppm)	213		58	387	115	111	BDL	BDL	202	34.5	83	BDL	184	217	242	194
Sb (ppm)	BDL		51.5	BDL	<3.8	BDL	25.5	BDL	BDL	<3.8	BDL	BDL	4.4	3.7	3.5	28
Se (ppm)	BDL		BDL	BDL	<3.0	BDL	BDL	BDL	BDL	<3.0	BDL	BDL	NT	NT	NT	NT
Si (%)	NT		NT	NT		NT	NT	NT	NT		NT	NT	40.04	35.52	35.06	40.56
Sn (ppm)	105		BDL	111		68	BDL	BDL	BDL		BDL	BDL	7	8	8	7
V (ppm)	56.5		59.5	84	13.8	85	86	79	70	10.7	52	97.5	38	53	30	20
Zn (ppm)	1040		482	2770	172	537	89	215	642	92.9	420	215	268	543	684	500
Hg (ppb)	1100		658	3150		796	88.7	106	637		190	199	NT	NT	NT	NT
CN (µg/G)		1.35			1.12					<25						

Appendix 1b. Eastern Wetlands Chemistry

OPEN LAKE	L2	L14	L15	L16	L17	L18	L19	LF	LI	LG
Compounds (units)										
Al (%)	11.3	6.01	8.98	6.4	9.05	10.3	8	5.32	10.92	4.57
As (ppm)	20	23	26	33	37	33	32	29	21	42
B (ppm)	93	48	53	28	50	61	41	33	80	58
Ba (ppm)	377	379	433	398	408	434	402	430	383	454
Be (ppm)	<1	<1	<1	<1	<1	<1	<1	<1	<1	2
Ca (%)	8.67	56	6.98	6.57	7.11	7.49	6.36	6.36	7.96	6.75
Cd (ppm)	<2	<3	<3	<2	<2	<2	<2	<1.5	<2	<1.5
Co (ppm)	16	10	14	9	14	17	12	14	21	14
Cr (ppm)	88	39	66	42	86	75	65	70	127	90
Cu (ppm)	48	28	34	30	44	50	23	48	73	62
Fe (%)	5.85	3.26	4.42	3.67	5.06	6.03	4.34	3	6.85	3
K (%)	3.26	1.92	2.92	2.06	2.63	2.92	2.48	2.74	3.14	2.52
Mg (%)	4.97	3.55	4.67	4.15	4.4	4.52	4.38	NT	4.76	NT
Mn (%)	0.15	0.08	0.08	0.07	0.09	0.11	01	NT	0.13	NT
Mo (ppm)	28	18	20	15	20	24	22	NT	31	NT
Na (%)	05	0.62	0.62	08	0.63	0.61	0.69	0.4	0.55	0.43
Ni (ppm)	29	<15	19	<7	23	27	10	27	36	33
P (%)	0.16	0.08	0.09	0.11	0.12	0.12	0.12	0.05	0.28	0.07
Pb (ppm)	170	84	89	80	130	170	80	109	200	180
Sb (ppm)	15	09	1	07	1.4	1.4	09	21	27	1.3
Se (ppm)	NT	NT	NT	NT	NT	NT	NT	1.3	NT	<5
Si (%)	48.81	66.36	55.63	64.84	55.9	51.44	60.17	22.8	48.88	20.4
Sn (ppm)	7	<5	<5	<5	6	9	<5	19	7	21
V (ppm)	76	213	239	228	286	349	132	44	79	68
Zn (ppm)	453	19	37	23	44	54	34	241	543	389
Hg (ppb)	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
CN (µg/g)			3.4							

Appendix 1c. Open Lake Chemistry

WESTERN DITCHES	W19	W19B	W17	W17B	LA	LB	LBB	LC	LD	W10	W11	W12	W13	W14	W15	W16	W18	W18B	W15B
Compounds (units)																			
Acenaphthylene (µg/Kg)				1150			120												
Anthracene (µg/Kg)				2797			370												
Benzo(a) pyrene (µg/Kg)				4523			1411												
Fluoranthene (µg/Kg)				10709														301J	3234
Fluorene (µg/Kg)				1660															
2-Methylnapthalene(µg/Kg)				13720															
Phenanthrene(µg/Kg)				13444			1583											198 J	
Pyrene (µg/Kg)				18865			2431											337 J	3796
Phenol (µg/Kg)		1527					242												
Benzo(a)Anthracene (µg/Kg)							1208												
Benzo(b) flouranthene (µg/Kg)							1398											168J	748
Benzo(k)Flouoranthene (µg/Kg)							1264												
bis(2-ethylhexyl)Phthalate (µg/Kg)							1987B											406 J	
Chrysene (µg/Kg)							1494											211 J	
1,2-Dichlorobenzene (µg/Kg)							2025											129 J	
Fluoranthene (µg/Kg)							3163												
4-Methylphenol (µg/Kg)							146												
Naphthalene (µg/Kg)																		110 J	
N-Nitroso-di-phenylamine (µg/Kg)																		138 J	
Al (%)	2.63		2.11		2.92	4.47		4.84	3.83	1.1		1.87	1.26	1.7	1.75	1.48	2.23	0.231	
As (ppm)	BDL		69		16	44		50	25	BDL		BDL	BDL	BDL	BDL	59.5	207	30.5	
B (ppm)	150		184		22	31		39	30	193		153	135	149	168	164	218	34.8	
Ba (ppm)	253		240		543	5.34		488	524	204		199	232	201	315	137	1230	233	
Be (ppm)	1.5		2.5		<1	<1		<1	<1	BDL		BDL	2.5	2.5	2	2	2	0.4	
Ca (%)	8.53		8.79		6.42	7.58		7.41	7.38	26.3		18.7	24.6	18.8	21.4	12.2	8.87	4.05	
Cd (ppm)	26.5		11		<1.5	3.6		29	<1.5	4.5		9.5	10	10.5	16	8	61	5.91	
Co (ppm)	BDL		BDL		7	12		14	9	BDL		BDL	BDL	BDL	BDL	BDL	BDL	2.97	
Cr (ppm)	282		179		54	116		110	71	62.5		95	103	168	85.8	100	203	20.1	
Cu (ppm)	237		117		42	115		104	60	35		37.5	87.5	35.5	53	37	191	37.6	
Fe (%)	3.96		3.34		1.58	2.78		2.92	2.15	1.32		2.18	1.65	2.23	2.11	2	5.65	1.11	
K (%)	0.839		0.69		1.5	2.14		2.37	1.85	0.374		0.651	0.429	0.597	0.617	0.542	0.814	0.022	
Mg (%)	3.31		3.85		NT	NT		NT	NT	1.95		2.37	1.93	2.32	1.97	3.46	2.91	0.651	
Mn (%)	0.199		0.16		NT	NT		NT	NT	0.097		0.134	0.12	0.218	0.119	0.0972	0.148	0.045	
Mo (ppm)	BDL		BDL		NT	NT		NT	NT	BDL		BDL	BDL	BDL	BDL	BDL	BDL	5.9	
Na (%)	12		BDL		0.51	0.44		0.41	0.55	0.266		BDL	BDL	BDL	BDL	BDL	BDL	0.131	
Ni (ppm)	69		34.5		12	29		27	22	21		40	BDL	25.5	23.5	22	60.5	9.5	
P (%)	1240		930		0.06	0.11		0.12	0.06	314		530	522	714	660	583	1370		
Pb (ppm)	615		289		320	316		298	373	104		117	262	140	175	114	1060	138	
Sb (ppm)	BDL		31.5		12	21		2.3	3.2	40		BDL	BDL	BDL	BDL	45.5	38	4.7	
Se (ppm)	BDL		BDL		<1	1.4		1.1	1.1	BDL		BDL	BDL	BDL	BDL	BDL	BDL	<3	
Si (%)	NT		NT		25.4	20.4		20.8	23.2	NA		NT	NT	NT	NT	NT	NT		
Sn (ppm)	79		180		31	42		44	24	BDL		BDL	BDL	BDL	BDL	BDL	84		
V (ppm)	109		84		25	37		60	35	27		67	54	93	70.5	63.5	97	15.9	
Zn (ppm)	1150		622		199	591		599	482	162		275	396	351	951	362	4800	975	
Hg (ppb)	860		600		NT	NT		NT	NT	60.5		87.6	116	236	146	115	579	NT	
CN (µg/G)	.92µg/G		1.25µg/G				.28µg/G										1.8µg/G		

Appendix 1d. Western Ditches Chemistry

WESTERN SHORES & SLIPS	LE	L13	LJ	L12	LK	L3	L4	L1	LH
Compounds (units)									
Al (%)	4.75	8.71	4.18	11.23	3.91	10.86	10.52	10.92	4.97
As (ppm)	31	36	20	22	23	14	15	21	44
B (ppm)	35	58	60	67	34	80	67	80	56
Ba (ppm)	455	377	371	470	452	406	491	383	473
Be (ppm)	<1	<1	1.2	<1	<1	<1	<1	<1	1.2
Ca (%)	7.25	8.73	6.56	7.88	5.09	12.3	7.84	7.96	6.56
Cd (ppm)	<1.5	<3	<1.5	<3	<1.5	<2	<3	<2	<1.5
Co (ppm)	14	16	14	15	9	16	14	21	15
Cr (ppm)	83	64	51	64	41	84	61	127	88
Cu (ppm)	58	43	37	33	13	36	34	73	77
Fe (%)	2.88	4.14	2.51	4.87	2.11	4.82	4.62	6.85	3.11
K (%)	2.45	2.88	2.38	3.29	2.16	3.17	3.24	3.17	2.58
Mg (%)	NT	5.72	NT	5.27	NT	4.6	4.58	4.76	NT
Mn (%)	NT	0.08	NT	0.11	NT	0.11	0.07	0.13	NT
Mo (ppm)	NT	24	NT	20	NT	26	22	31	NT
Na (%)	0.43	1.06	0.48	0.58	0.52	0.55	0.62	0.55	0.41
Ni (ppm)	30	21	14	22	12	28	21	36	25
P (%)	0.05	0.09	0.04	0.1	0.04	0.15	0.11	0.28	0.06
Pb (ppm)	206	76	70	91	90	120	64	200	206
Sb (ppm)	1.5	1.3	1.1	1	25	1.2	0.9	27	1.5
Se (ppm)	1	NT	<6	Nt	<5	NT	NT	NT	0.7
Si (%)	21.6	52.29	23	51.69	25.8	44.79	53.89	48.88	21.7
Sn (ppm)	30	6	7	<5	6	6	5	7	24
V (ppm)	36	37	39	43	37	12	48	79	76
Zn (ppm)	371	149	110	84	156	251	124	543	435
Hg (ppb)	NT	NT	NT	NT	NT	NT	NT	NT	NT

Appendix 1e. Western Shores Slips Chemistry

ELUTRIATE ANALYSIS	W17B-E	W18B-E	W19B-E	W23B-E	W27B-E	W29B-E	LBB-E	LLB-E	L7B-E	W15B-E
Compounds (units)										
bis(2-ethyl hexyl)Phthalate (µg/L)	23	22	26	43	74	27	31	17	41	17
Di-n-Butyl Phthalate (µg/L)	BDL	BDL	BDL	21	BDL	2J	1J	BDL	6	5J
Phenol (µg/L)	BDL	BDL	BDL	BDL	BDL	BDL	10J	BDL	BDL	BDL
2, 6-Dinitrotoluene (µg/L)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	5J	BDL	BDL
Al (%)	0.212	BDL	0.696	BDL	0.52	0.256		0.23	0.156	BDL
As (ppm)	0.027	BDL	BDL	BDL	BDL	BDL		BDL	BDL	BDL
B (ppm)	0.363	0.808	0.258	0.423	0.797	0.186		0.11	0.094	1.54
Ba (ppm)	0.09	0.092	0.146	0.052	0.182	0.042		0.13	0.128	0.085
Be (ppm)	BDL	BDL	BDL	BDL	BDL	BDL		BDL	BDL	BDL
Ca (%)	192	56.2	15.4	39.8	7.72	27.2		20.8	17.7	90
Cd (ppm)	BDL	BDL	BDL	BDL	BDL	0.032		BDL	BDL	BDL
Co (ppm)	0.007	BDL	0.003	BDL	0.002	BDL		BDL	BDL	0.002
Cr (ppm)	BDL	BDL	BDL	BDL	BDL	0.017		BDL	BDL	BDL
Cu (ppm)	0.044	BDL	0.072	0.014	0.131	0.176		BDL	0.046	0.009
Fe (%)	0.337	0.05	1.24	1.54	1.09	0.511		0.19	0.143	0.075
K (%)	9.69	11.9	12.9	14.6	35.4	13.6		3.5	4.36	17.7
Mg (%)	6.52	18.4	2.64	17.6	7.41	12		3.82	2.78	8.22
Mn (%)	0.028	0.038	0.338	0.017	0.074	0.204		0.01	0.01	0.72
Mo (ppm)	0.024	0.008	0.034	0.036	0.064	0.034		0.01	0.008	0.007
Na (%)	53.4	181	768	46.8	65.6	15.3		12.3	8.83	64.7
Ni (ppm)	0.008	0.008	0.023	0.01	0.022	0.057		BDL	BDL	0.008
P (%)	BDL	0.148	0.148	<BDL	0.181	1.4		BDL	BDL	BDL
Pb (ppm)	0.009	BDL	0.03	0.012	0.017	BDL		BDL	BDL	BDL
Sb (ppm)	0.026	BDL	0.019	BDL	BDL	BDL		BDL	BDL	BDL
Se (ppm)	BDL	BDL	BDL	BDL	BDL	BDL		BDL	BDL	BDL
Si (%)	1.74	1.59	1.47	0.785	0.99	1.02		1.28	0.797	1.38
Sn (ppm)	BDL	0.015	BDL	BDL	0.021	BDL		BDL	BDL	BDL
V (ppm)	BDL	BDL	BDL	BDL	BDL	BDL		BDL	BDL	BDL
Zn (ppm)	0.029	0.033	NT	0.096	0.04	0.296		0.02	0.024	0.087
Hg (ppb)								NT	NT	NT
CN (µg/g)	11	40	108	<5.2	18	26	16	<5	<5	<5

Appendix 2. Chemical analyses of elutriates

Eastern Slips toxicity

	STATION	S capricornutum	Microtox	P redivivus mortality	P redivivus fitness	Σ photosynthesis	Σ respiration
1	LM					0 000	0 000
2	LLB	92 610	0 000		6 381	0 000	0 000
3	L9	82 210	37 460			0 000	39 600
4	L10	71 290	9 210	37 930		73 500	0 000
5	LL	109 480	162 230	51 000		0 000	0 000
6	L11	82 210	6 340			135 300	0 000
7	L7	101 260	2 570	13 100		107 500	32 700
8	L7B	85 630	0 000		19 550	0 000	0 000
9	L8	92 470	36 530	51 720		0 000	0 000
10	L5	83 900	33 650	39 660		0 000	0 000
11	L6	105 920	55 210	78 330		0 000	0 000
12	L20	88 820	28 570	62 070		73 800	138 300

Eastern Wetland–toxicity

	Station	S capritornutum	Microtox™	P redivivus mortality	P redivivus fitness	Σ photosynthesis	Σ respiration
1	w29	104 480	11 030	93 060	95 980	290 000	235 000
2	w29b	112 130	42 350		99 240	133 000	12 000
3	w28	74 220	47 590	36 110	63 150	276 000	53 000
4	w27	120 660	117 280		0 000	477 000	176 000
5	w27b	123 150	6 200	63 640	100 000	168 000	268 000
6	w26	66 550	37 000	11 690	61 600	264 000	345 000
7	w25	20 350	63 570		40 070	217 000	175 000
8	w22	16 780	36 160	92 210	0 000	160 000	116 000
9	w23	65 180	80 840		95 500	274 000	29 000
10	w23b	107 630	0 600		100 000	0 000	0 000
11	w24	43 330	12 440	100 000	100 000	219 000	57 000
12	w30	77 690	18 500		0 000	417 000	300 000
13	w4					128 000	164 000
14	w5					0 000	0 000
15	w6					136 000	27 000
16	w7					0 000	0 000

Open Lake toxicity

	Station	S capricomutum	Microtox™	P redivivus mortality	P redivivus fitness	Σ photosynthesis	Σ respiration
1	L2	82 360	40 480	42 860		0 000	0 000
2	L14	80 990	1 400			0 000	0 000
3	L15	100 830	18 670			171 000	0 000
4	L16	73 270	22 740			0 000	26 800
5	L17	85 470	8 670			113 800	65 900
6	L18	79 130	11 110			107 300	0 000
7	L19	73 330	13 540			0 000	0 000
8	LF	99 100	39 480	18 000		148 800	63 800
9	LI	83 030	122 230	57 000		164 100	62 300
10	LG	88 730	19 620	13 000		0 000	0 000

Western Ditches–toxicity

	Station	S capricomutum	Microtox	P redivivus mortlaity	P redivivus fitness	Σphtsyn	Σ respiration
1	w19	88 610	66 250	5 560	12 960	73 500	0 000
2	w19b	121 030	18 860		64 360	224 000	108 000
3	w17	105 370	46 150	0 000	0 000	0 000	0 000
4	w17b	114 210	0 000		89 470	147 000	176 000
5	LA	98 730	67 080	28 000		135 700	64 900
6	LB	117 380	28 370	5 000		83 400	43 700
7	LBB	98 990	0 000		54 400	213 000	68 000
8	LC	109 230	33 590	24 000		362 700	55 300
9	LD	71 180	69 030	0 000		0 000	0 000
10	w10	43 630	41 780		0 000	45 000	0 000
11	w11	30 360	48 860		0 000	179 000	287 000
12	w12	73 270	0 000	0 000	0 000	0 000	62 000
13	w13	39 160	58 010		0 000	169 000	69 000
14	w14	42 230	60 360	0 000	39 970	0 000	0 000
15	w15	103 260	59 650	23 170	32 730	0 000	50 000
16	w16	27 720	37 930	0 000	8 320	0 000	0 000
17	w18	107 980	55 460	5 630	24 730	0 000	0 000
18	w18b	120 050	9 380		67 810	0 000	0 000
19	w15b	105 490	12 520		81 890	242 000	0 000

Western Shore & Slip–toxicity

	Station	S capricornutum	Microtox™	P redivivus mortality	P redivivus fitness	Σ photosynthesis	Σ respiration
1	LE	113 070	83 570	31 000		0 000	0 000
2	L13	89 680	14 850			164 800	84 700
3	LJ	45 720	52 610	59 000		0 000	0 000
4	L12	87 460	16 490			23 000	97 000
5	LK	91 290	121 030			0 000	0 000
6	L3	87 890	60 990	27 090		0 000	0 000
7	L4	90 610	62 870	15 270		40 900	0 000
8	L1	86 560	36 340	78 410		234 300	67 500
9	LH	60 460	34 020	25 000		215 000	40 800