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Amendment: Assessme of Ecotoxicological Hazard of Waukegan Harbor Sediments

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Illinois State and Water Survey

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HWRIC RR-052

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TABLE OF CONTENTS

Tables

Figures

EXECUTIVE SUMMARY

Waukegan Harbor is located on the western shore of Lake Michigan, approximately 36 miles north of Chicago and 9 miles south of the Illinois-Wisconsin border. Since 1975, Waukegan Harbor has been recognized as being heavily contaminated (primarily Slip 3), with polychlorinated biphenyls (PCBs). In 1948, the Johnson Motors Division of Outboard Marine Corporation (OMC) began purchasing a polychlorinated biphenyl (PCB)-containing hydraulic fluid called Pydraul, manufactured by Monsanto, for use in high-pressure diecast machines. Pydraul leaked steadily from these machines into a floor drainage system, which ultimately emptied into Waukegan Harbor and Lake Michigan. About 8 million pounds of Pydraul were purchased between 1948 and 1971 and OMC estimates that 900,000 pounds may have been discharged to the harbor (Mason and Hanger 1981). In 1971, after evidence accumulated that exposure to PCBs might be hazardous to human health and to the environment, Monsanto voluntarily restricted sales of PCB containing fluids like Pydraul. In 1979, all PCB sales were banned in the United States.

In 1981, Waukegan Harbor was placed on the federal National Priorities List (NPL) as a target for clean-up as mandated by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Superfund Amendments and Reauthorization Act (SARA). OMC was declared the Potentially Responsible Party (PRP) and was thus liable under CERCLA for cleanup costs. A Consent Decree specifying OMC's obligations to remedial action in Waukegan Harbor was signed in early 1989. Remedial action under CERCLA/SARA is currently in place and in progress at the Harbor.

Waukegan Harbor has also been identified as one of 42 Areas of Concern (AOCs) in the Great Lakes by the International Joint Commission (U.S /Canada). The AOCs are areas where beneficial uses of a waterbody are "impaired". The Great Lakes Water Quality Agreement stipulates that a local authority (the State of Illinois, in the case of Waukegan Harbor) shall produce a remedial action plan for each AOC, detailing what needs to be done to restore the area to an acceptable level of beneficial use.

A 1986 study funded by the Illinois Department of Energy and Natural Resources, through the Hazardous Waste Research and Information Center reported that total PCB concentrations in harbor sediments were found to vary from 5 to 17,251 ppm . The highest concentrations were found in Slip 3 near the PCB outfall from OMC and decreased away from the outfall into the outer harbor. Toxic responses were measured at various levels, but the magnitude of the total PCB concentration did not correlate with the magnitude of the toxic effect.

That total PCB concentrations could not be directly correlated with toxic response was not surprising since aquatic ecosystems are seldom contaminated with a single class of chemical. Rather, there are a number of compounds and sources contaminating most systems. Any system near human activity will likely contain contaminating chemicals and their by-products. The major problem in such environments is to determine which specific components pose the greatest long- and short-term risks to biological systems. The question of which chemicals are present is secondary; the primary objective is to establish which compounds at what concentrations in a particular system pose the greatest risk. Waukegan Harbor has been exposed to a point source of PCBs, but it is possible they are not the only toxic compounds in the harbor sediments. A second study was initiated to determine the concentrations of several other contaminants in Waukegan Harbor sediments. Sediments were collected from 23 stations in the harbor and concentrations were determined for oil and grease and for 22 major, minor, and trace elements. In addition, specific lower weight PCB congeners reported to be toxic were chromatographically resolved, identified, and semi-quantified in sediment samples from five stations. A priority pollutant scan was made of sediments collected in proximity to two stations which had, respectively, high and moderate toxicity responses as reported in the previous study.

Chemical analyses of the whole sediment allow an inventory of sediment contaminants to be constructed; however, biological availability cannot be determined from bulk material measurements. Sediment constituent mobility depends on many factors. Even though a sediment may be grossly contaminated, the conditions which control interaction between water and sediment may preclude significant movement into the water column and *vice versa* .

Percentages of oil and grease were determined from all stations sampled in the harbor. Concentrations ranged from 0.3% to 5.19%, with the highest values occurring in Slip 3 and in the areas immediately outside the slip Average concentrations of nine metals in Waukegan Harbor sediments were compared with sediments from other commercial areas in the Great Lakes and to a pollution classification index for Great Lakes Harbor sediments. Waukegan Harbor sediments are heavily polluted with respect to cadmium (4 stations), copper (20 stations), manganese (14 stations), lead (21 stations), and zinc (13 stations) and moderately polluted with respect to iron (17 stations)

Sediments collected in proximity to stations J and K were screened for the presence of 135 organic compounds or families of compounds, including priority pollutants. Of these compounds, fifteen were found to occur in Station J sediments. Seven of these fifteen also occurred at Station K, but were generally in concentrations that were an order of magnitude or more lower, except for the Aroclors (commercial PCB mixtures) An estimate of the amounts of commonly occurring,

lower chlorinated PCBs and toxic congeners (up to pentachlorobiphenyl), were identified at five harbor stations. The most predominant toxic congener at these stations, based on peak height, may be 3,4,4'- trichlorobiphenyl.

To simulate the short-term release of contaminants to the water column after disturbance of the sediment, the elutriate test, a water leachate obtained from mixing one part sediment to four parts leaching water, was used. Elutriates from Waukegan Harbor sediments were used to determine biological response to contamination with three toxicity test methods: luminescent inhibition of the marine bacterium *Photobacterium phosphoreum* (Microtox™), photosynthetic inhibition of the green alga *Selenastrum capricornutum*, and developmental inhibition of the nematode worm *Panagrellus redivivus* .

The three toxicity tests were performed on elutriates of the sediments collected and, therefore, represent the toxic response to the "bioavailable" contaminants in the sediments. Because of this distinction, "hot spots" in the Harbor as determined by chemical analysis and those determined by toxicological analysis may differ. An analysis of variance (ANOVA) of the results of the toxicity tests identified three areas of high toxicity and four areas of low toxicity in Waukegan Harbor. The responses to stations WH1, WH9, and WH10 were significantly ($p<0.05$) more toxic than stations WH2, WH3, WH11, and WH15. There were no significant differences in toxicity within the remaining stations.

There was a significant difference, however, between the toxicity tests. Responses of the *S capricornutum* assay were significantly different from either the Microtox™ or *P redivivus* assays. The mean (x) of the algal test across the 23 stations is 58.38, while those of the Microtox™ and *P. redivivus* tests are 34.79 and 32.32, respectively. These assays are surrogates for different ecological functions, each of which has different sensitivity and discriminatory ability.

Metal (priority pollutant metals Be, Cd, Cr, Cu, Pb, Ni, and Zn) hot spots were identified by ANOVA as stations WH13 and WH7. Stations with statistically significant lower priority pollutant metal contamination were identified as WH2, WH4, WH21, and WH22 The area of the Harbor that includes stations WH5 through WH9, WH13, WH14, and WH17 is the most contaminated by priority pollutant metals. Station WH9 corresponds to an area of high toxicity and high metal concentrations while stations WH2, WH3, WH11, and WH15 (low toxicity stations) were lower in metal contamination.

A concern in the preceding study was the presence of oils and grease in Waukegan Harbor sediments. The presence of oils and grease in the sediments may reduce the solubility and, thus the

bioavailability of many of the sediment contaminants, especially in the elutriation procedure. To determine if differences in toxicity existed in elutriates of sediments with varying oils and grease percentages, the 23 stations were divided into three groups according to oils and grease content. Sediments in Group I had concentrations exceeding 3%, oils and grease concentrations in Group II fell between 1% and 3%, and Group III had less than 1% oils and grease content. A one-factor ANOVA showed that there were no significant differences in toxicity between these regions of oils and grease contamination.

The presence of PCBs remains the primary environmental issue at Waukegan Harbor. Relative qualification of "toxic" congeners suggests that station WH8 has the most complete spectrum of chlorinated biphenyls. Station WH8 was not itself overly toxic although it is located in a region with other stations of higher toxicity (WH9 and WH10) Station WH5 is more toxic and yet the PCB profile showed that it is slightly less contaminated with congeners except for 2,4,4' and 3,4,4'; 2,3,3',6. These congeners are also present at the same relative quantities at station WH3, defined previously as a low toxicity station.

General observations from the two studies in Waukegan Harbor serve to reject a hypothesis from the first study: "concentrations of certain pollutants can be used to predict the response of the organisms. " This hypothesis may hold for limited laboratory studies with one or two chemicals and strictly defined testing conditions but cannot be supported from this complex environmental sampling study. Instead, we put forth that chemical analysis cannot predict biological response (or *vice versa*) and assert that biological testing is an integral part of determining the hazard of a contaminated site such as Waukegan Harbor.

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 Waukegan Harbor should be viewed as information about the environmental past and present of the Harbor. Waukegan Harbor sediments contain high concentrations of potentially

hazardous priority pollutant metals and PCBs. The Harbor is not a closed system, and may impact the biota, possibly even humans, in the nearby vicinity.

Waukegan Harbor continues to be a site of intense environmental focus. The cleanup plan mandated by Superfund legislation (CERCLA/SARA) is in place and in progress But the Harbor is also targetted as an Area of Concern (AOC) by the International Joint Commission. The AOC classification is independent of CERCLA/SARA scoring and jurisdiction. The Remedial Action Plan required by the Great Lakes Water Quality Agreement must also consider non-PCB pollutants and evaluate the impact of the contaminated site relative to the entire Great Lakes region. Based on the results of the studies reported here, we strongly recommend that biological testing (toxicity, bioaccumulation, etc) be included as a partner in evaluating the effectiveness of the Superfund cleanup and in any assessment of further environmental damage, both within Waukegan Harbor and throughout the Great Lakes ecosystem

Chapter 1. INTRODUCTION

Waukegan Harbor is located on the western shore of Lake Michigan, approximately 36 miles north of Chicago and 9 miles south of the Illinois-Wisconsin border. The city of Waukegan with a population of about 66,000 surrounds the harbor. The harbor is a commercial area, a center for charter boat fishing, and also a major port for pleasure boats. Lining the harbor are commercial and industrial facilities such as two Outboard Marine Company Plants (Numbers 1 and 2) and National Gypsum Company, as well as a private marina at the north end and a municipal marina at the south end. The east side of the harbor is the former site of a General Motors foundry. The total area of the harbor is about 37 acres with water depths ranging to 25 feet in the main harbor; in Slip 3 at the north end, which is the site of heavy PCB contamination, water depths are generally less than 10 feet (Figure 1) According to Mason and Hangar (1981), the harbor sediments consist of an upper, soft "muck" containing organic matter and fine silt, a sand layer and lastly, a silty clay, "hard pan" layer. The muck horizon is about 0 to 10 feet thick, and the sand layer ranges from 0 to 9 feet thick.

Since 1975, Waukegan Harbor has been recognized as being heavily contaminated (primarily Slip 3), with polychlorinated biphenyls (PCBs). In the past, the sources of PCBs into Lake Michigan were primarily from industrial discharges. In 1975, the Johnson Motors Division of Outboard Marine Corporation (OMC) in Waukegan was accused of discharging PCBs into Waukegan Harbor and into a ditch leading to Lake Michigan known as the North Ditch. It appears that in 1948, the Johnson Motors Division of Outboard Marine Corporation began purchasing a polychlorinated biphenyl (PCB)-containing hydraulic fluid called Pydraul, manufactured by Monsanto, for use in high-pressure diecast machines. Pydraul leaked steadily from these machines into a floor drainage system, which ultimately emptied into Waukegan Harbor and Lake Michigan. About 8 million pounds of Pydraul were purchased between 1948 and 1971 and OMC estimates that 900,000 pounds may have been discharged to the harbor (Mason and Hanger 1981). In 1971, after evidence accumulated that exposure to PCBs might be hazardous to human health and to the environment, Monsanto voluntarily restricted sales of PCB containing fluids like Pydraul. In 1979, all PCB sales were banned in the United States.

In 1981, Waukegan Harbor was placed on the federal National Priorities List (NPL) as a target for clean-up as mandated by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Superfund Amendments and Reauthorization Act (SARA) OMC was declared the Potentially Responsible Party (PRP) and was thus liable under CERCLA for cleanup costs. A Consent Decree specifying OMC's obligations to remedial action in Waukegan

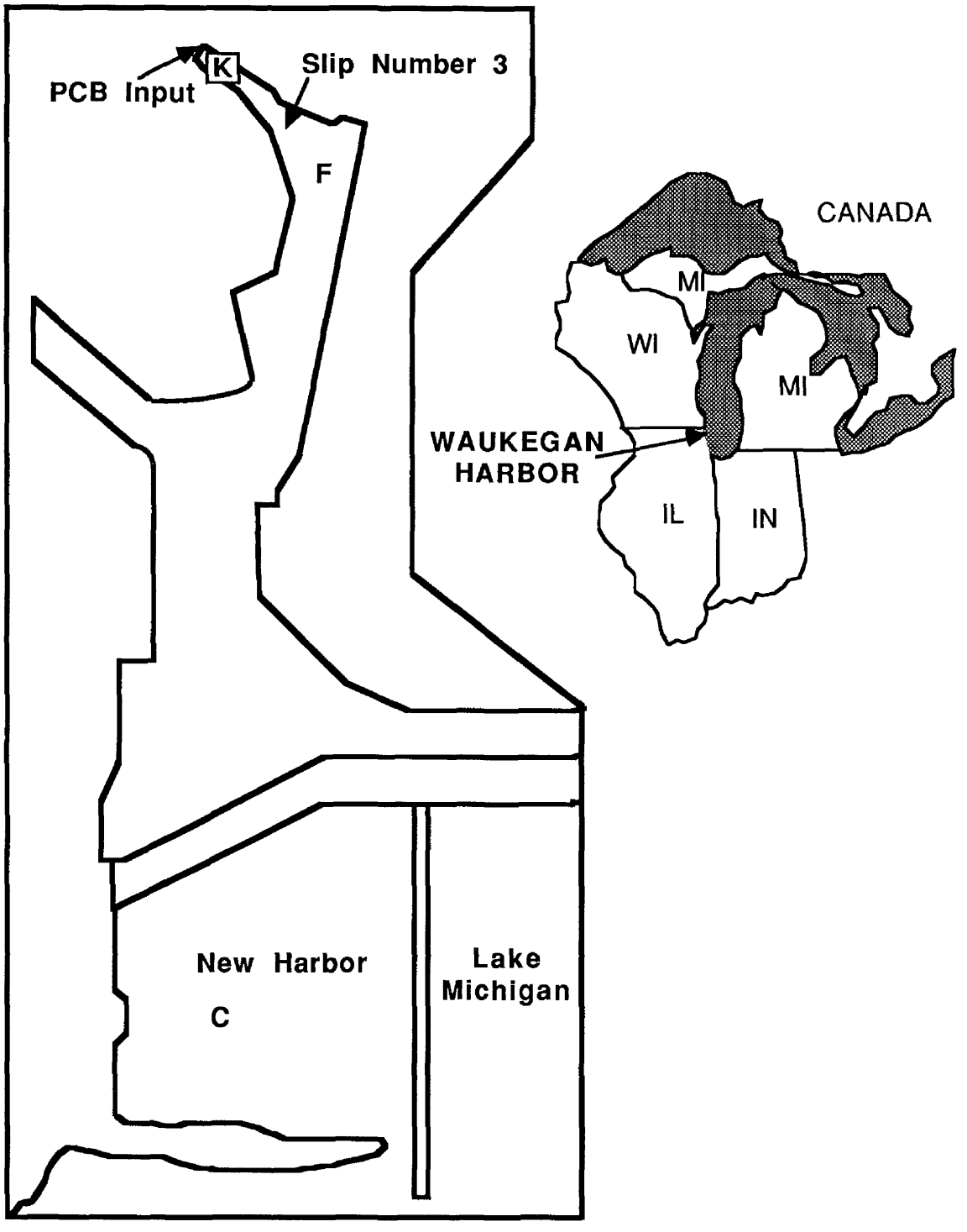

Figure 1. Location of Waukegan Harbor, Waukegan, Illinois.

Harbor was signed in early 1989. Remedial action under CERCLA/SARA is currently in place and in progress at the Harbor.

Waukegan Harbor has also been identified as one of 42 Areas of Concern (AOCs) in the Great Lakes by the International Joint Commission (U.S./Canada). The AOCs are areas where beneficial uses of a waterbody are "impaired". The Great Lakes Water Quality Agreement stipulates that a local authority (the State of Illinois, in the case of Waukegan Harbor) shall produce a remedial action plan for each AOC, detailing what needs to be done to restore the area to an acceptable level of beneficial use.

In July of 1986, because of the substantial PCB contamination in Waukegan Harbor, an ecotoxicological assessment of the sediments in the harbor was funded by the Illinois Department of Energy and Natural Resources (ENR), through the Hazardous Waste Research and Information Center (HWRIC). This study was undertaken by researchers from the Illinois State Geological Survey (ISGS), the Illinois Natural History Survey (INHS), and the State Water Survey (ISWS) who based the objectives for their research on the following hypotheses. (1) the concentrations of certain pollutants can be used to predict the response of test organisms to sediment elutriates in a suite of bioassays, and (2) the toxic responses observed are attributable to specific compounds or groups of compounds found in the sediments. To test these hypotheses, sediment samples were collected from 24 stations in Waukegan Harbor and the following tasks performed:

1) The concentrations of total PCBs in the sediment samples were determined.

2) Acute, short term, bioassays utilizing an elutriate from each Waukegan Harbor sediment sample were performed for the luminescent bacterium *Photobacterium phosphoreum,* (Microtox™), the green alga *Selenastrum capricornutum,* and the free-living nematode *Panagrellus redivivus* . Bioassay results and PCB values were statistically compared to assess biohazard.

3) Bioassays using protozoan community structure as an index of toxicity were performed both *in situ* (at Waukegan Harbor) and in the laboratory.

4) Phytoassay methods using tests of duckweed, lettuce, and millet were performed (on 21 of the 24 sediment samples).

Total PCB concentrations in harbor sediments were found to vary from 5 to 17,251 ppm (Risatti 1989; Ross *et al* 1988). The highest concentrations were found in Slip 3 near the PCB outfall from OMC and decreased away from the outfall into the outer harbor. Toxic responses were measured at various levels, but the magnitude of the total PCB concentration did not correlate with the magnitude of the toxic effect (Ross *et al* 1988).

That total PCB concentrations could not be directly correlated with toxic response was not surprising since aquatic ecosystems are seldom contaminated with a single class of chemical Rather, there are a number of compounds and sources contaminating most systems. Any system near human activity will likely contain contaminating chemicals and their by-products. The major problem in such environments is to determine which specific components pose the greatest long- and short-term risks to biological systems The question of which chemicals are present is secondary; the primary objective is to establish which compounds at what concentrations in a particular system pose the greatest risk (Samoiloff *et al* 1983). Waukegan Harbor has been exposed to a point source of PCBs, but it is possible they are not the only toxic compounds in the harbor sediments. The current study was proposed to address the following recommendation stated in the Ross *et al.* (1988) report:

> "Because of the highly toxic nature of sediments at many stations, even some with only moderate PCB levels, a more thorough investigation of other contaminants should be performed before the cause of the acute toxicity in the Harbor sediments can be determined. This investigation should include analyses for lead, aluminum, and oils and grease (all of which could be expected as waste products of local industry)."

In this current project, we have determined the concentrations of several other contaminants in Waukegan Harbor sediments and have attempted to relate sediment toxicity to these measurements. Sediments were collected from 23 stations in the harbor and concentrations were determined for oil and grease and for 22 major, minor and trace elements. In addition, specific lower weight PCB congeners reported to be toxic (Duinker *et al* , 1988) were chromatographically resolved, identified and semi-quantified in sediment samples from five stations. A priority pollutant scan was made of sediments collected in proximity to two stations which had, respectively, high and moderate toxicity responses as reported in the previous study (Ross *et al.* 1989).

Ecotoxicological testing is an approach that focuses on the combined effects of environmental contaminants on organisms. Biological effects produced by the total mix of contaminants resulting from synergistic or antagonistic action of the various constituents (contaminants, byproducts of contaminants, and natural components) of the ecosystem can be measured. The range of biological effects produced by mixed contaminants is compounded by significant differences in sensitivity to the contaminants by different species in the environment. These differences are due to many factors, including differences in patterns of toxicant / nutrient uptake and differences in ability to detoxify contaminants. The effect of a contaminant or group of contaminants cannot be predicted for the entire ecosystem if only one organism is used in the

biological assays. To gather the most information on ecosystem toxicity, a determination of the susceptibility of as many component organisms as is economically and reasonably possible should be performed. A comprehensive hazard assessment requires acute toxicity data, using a variety of species occupying several trophic levels. While such short-term effects as increased mortality or reduced function are the most severe effects of environmental contamination, more subtle long-term effects such as carcinogenesis, mutagenesis, reproductive success and the disruption of normal developmental activities may present a major risk for organisms associated with the contaminated environment and their progeny. Assays which help assess long-term risks are also important in ecotoxicological assessment.

Chemical analyses of the whole sediment allow an inventory of sediment contaminants to be constructed; however, biological availability cannot be determined from bulk material measurements (Engler 1980). Sediment constituent mobility depends on many factors. Even though a sediment may be grossly contaminated, the conditions which control interaction between water and sediment may preclude significant movement into the water column and *vice versa* (Brannon *et al.* 1980).

To simulate the short-term release of contaminants to the water column after disturbance of the sediment, the elutriate test, a water leachate obtained from mixing one part sediment to four parts leaching water, was used. This technique, in use since 1973, has been evaluated under an extremely wide range of conditions in marine, estuarine, and freshwater systems (Engler 1980). None of the extraction procedures developed to measure the degree of chemical mobility of sediment constituents has been shown to be universally successful in defining chemical availability and exchangeability. The elutriate test may strip volatile compounds from the sediment and is limited to leaching under aerobic conditions unless 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 use in biological testing. The elutriate test was shown by Brannon *et al.* (1980) to be the most useful extraction procedure in assessing water quality problems resulting from heavy metal contaminants. Brannon *et al* (1980) compared short-term extraction by elutriation 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 toxicity tests to determine the impact of the released sediment constituents on biological systems and has been reported to project the earliest measure of toxicity of the sediment (Engler 1980). Elutriates from Waukegan Harbor

sediments were used to determine biological response to contamination with three toxicity test methods: luminescent inhibition of the marine bacterium *Photobacterium phosphoreum* (Microtox™), photosynthetic inhibition of the green alga *Selenastrum capricornutum*, and developmental inhibition of the nematode worm *Panagrellus redivivus* .

The Microtox™ assay was developed on the principle that the luminescent properties of healthy cultures of *P phosphoreum* will be inhibited upon exposure to toxic substances (Bulich *et al* , 1981). The luminescence of cultures exposed to a series of dilutions of elutriate sample is measured with the Microtox™ analyzer, a specially-designed fluorometer.

The protocol for the *S. capricornutum* assay (Ross *et al* , 1989) 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 the elutriate is the measure of toxic response in this protocol This is measured using a ^{14}C-isotope as a tracer in the carbon source pool.

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

The responses of *S capricornutum* and *P phosphoreum* have been reported to be similar to those of several commonly used bioassay organisms such as rainbow trout, fathead minnow, and *Daphnia magna* (Bulich *et al* 1981; Curtis *et al* 1982; Qureshi *et al* 1982) *S capricornutum* , *P. phosphoreum* , and *P redivivus* bioassays were also used in a study (Burnett, 1989) 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 Waukegan Harbor, all three assays were positively correlated with bioassays using *Daphnia magna, Ceriodaphnia dubia,* and the USEPA *S capricornutum* bottle test. Burnett (1989) also determined that the *S capricornutum* and *P redivivus* assays were among (out of thirteen different testing methods) the most sensitive (ability to detect a toxicant) and discriminatory (ability to distinguish between samples of varying toxicity) toxicity tests. The Microtox™ test was more discriminatory than acute measures of mortality (*D magna, C dubia* , etc.) but less sensitive.

Chapter 2. METHODS AND PROCEDURES

SAMPLE COLLECTION

Sediment samples were collected from 23 stations (Figure 2) in Waukegan Harbor on April 27, 1987. Samples were collected with hand operated Ponar and petite Ponar dredges in depths ranging from 10 to 23 feet. Approximately 5000 mL of surficial sediment were collected each time with the Ponar and about 1500 mL with the petite Ponar. Several samples were collected from each location and immediately placed into a large, plastic basin, homogenized, put into clean, acid-washed glass containers and sealed. Samples were kept on ice in the field and during transportation; in the laboratory, they were stored at 4°C until used for chemical analyses or toxicity testing

CHEMISTRY

Elemental Analyses: Approximately 0.1 gm of each sample was weighed into a 60 mL linear polyethylene bottle. To each sample was added 1.5 mL of aqua regia (1:3:1 - HNO_3: HCL: H_2O by volume) and 2.5 mL 48% HF. The bottles were tightly capped and placed on a steam bath for two hours . Carbonaceous material remained undissolved in some samples. Twenty-five milliliters of boric acid solution (50 gm H_3BO_3 L^{-1}) was added to each sample. The sample was then transferred to a 50 mL volumetric flask, diluted to volume with deionized water and transferred to its original container for storage. Reagent blanks were routinely included in the procedure.

Solutions were analyzed for major, minor, and trace element concentrations by inductively coupled plasma (ICP) emission spectrometry and atomic absorption spectrophotometry (AAS). The ICP spectrometer used was a Thermo Jarrell-Ash Mark III 1100 vacuum spectrometer. An HF resistant torch and mixing chamber was used in place of the normal quartz torch and mixing chamber. The ICP spectrometer was used to determine aluminum (Al), barium (Ba), beryllium (Be), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), potassium (K), lanthanum (La), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), silicon (Si), strontium (Sr), titanium (Ti), vanadium (V), and zinc (Zn). For improved detection limits, a Perkin-Elmer Model 306 atomic absorption spectrophotometer was used to determine cadmium (Cd), nickel (Ni), and lead (Pb).

Quality control was maintained by calibrating each instrument against multi-element solutions containing known concentrations of the elements of interest. Both instruments were calibrated prior to and during usage with blanks and standards; however, recovery measurements

from the matrix were not made. Before samples were analyzed using the ICP spectrometer, calibration standards were analyzed as unknowns. In using both the ICP spectrometer and the AA spectrophotometer, an International Atomic Energy Agency (IAEA) lake sediment standard sample (SdL-1) was analyzed. Table 1 indicates the literature values (Abbey 1983) and the values obtained by either ICP or AAS for the various elements.

The ISGS results for Mg in the IAEA lake sediment standard were found to be lower than documented. Consequently, the determined values for this element in Waukegan Harbor sediments are expected to be lower than the actual concentrations. We currently have no explanation for the low recoveries of this element. Recovery of molybdenum is not given because this element was not included in the IAEA SL-1 standard, and measured values were inexplicably higher than analytical standards.

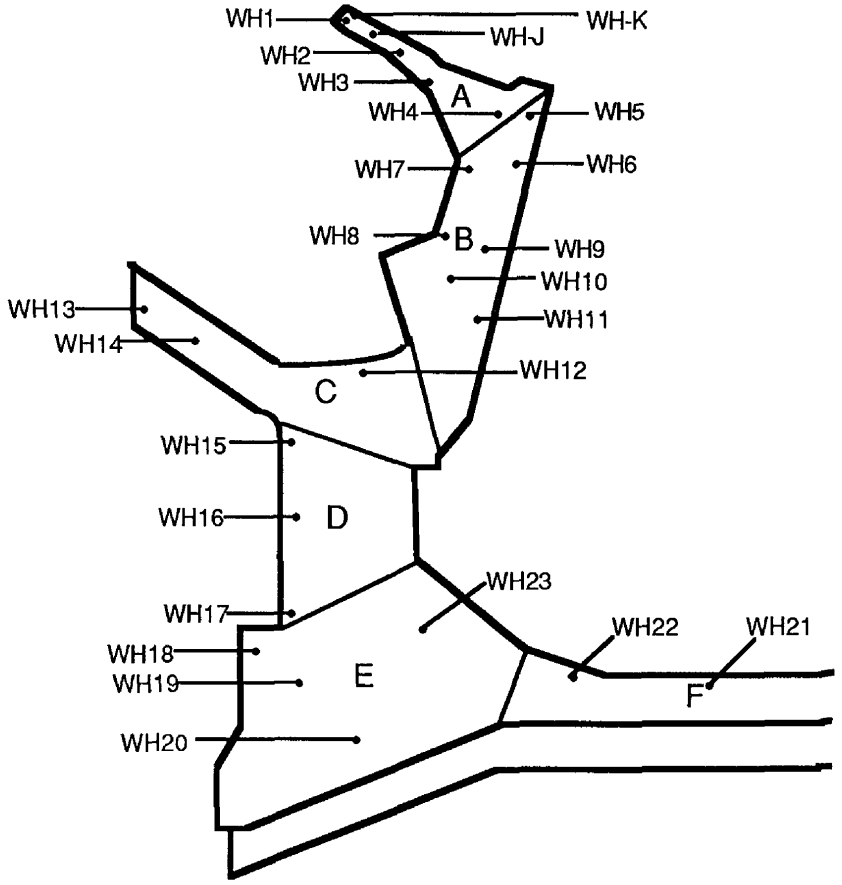

Figure 2 Location of Stations Sampled in Waukegan Harbor

Table 1 Comparison of ISGS Analytical Results for Twenty-one Metals in IAEA Lake Standard (SL-1), with Expected IAEA Values (mg/Kg unless specified)

Element	IAEA	ISGS	Element	IAEA	ISGS
Al (%)	8 89	8 77	**Mg** (%)	2 90	0 58
Ba	640 00	610 00	**Mn** (%)	0 34	0 36
Be	-.-	2 95	**Na** (%)	0 17	0 14
Ca (%)	0 25	0 26	**Ni**	45.00	34 00
Cd	0.26	<1 30	**Pb**	38 00	43 00
Co	20 00	18 00	**Si** (%)	-.-	41 77
Cr	105 00	87.00	**Sr**	80 00	73 00
Cu	30 00	35 00	**Ti** (%)	0 52	0 45
Fe (%)	6 74	5 60	**V**	170 00	180 00
K (%)	1 50	1 30	**Zn**	220 00	200 00
La	53 00	50 00			

Oils and grease. A modified soxhlet extraction-gravimetric method (Standard Methods for the Examination of Water and Wastewater 1982) was used for oil and grease analysis. Sediments were dried for 3-4 days at ambient temperature, crushed with a porcelain pestle and mortar, then passed through a 100 mesh sieve. The crushed sediment (~20 g) was then put into a Whatman cellulose extraction thimble (19mm x 90mm) and weighed. Glass wool was added to prevent loss of sample during extraction.

A 500 mL round bottom flask was cleaned using solvents, dried in an oven, cooled, and tared. Eighty mL of trichlorotrifloroethane (TCFE) was added to the flask and the flask connected to the soxhlet apparatus containing the sample thimble and a condenser. After the sample was extracted for 4 h at 20 cycles h^{-1}, a Snyder column was connected to the extraction flask and the solvent distilled. A vacuum was drawn on the flask for approximately 10 minutes to remove residual solvent and the flask weighed to determine oil and grease levels. Three blanks were run (residues found were 0.00 - 0.01 g) and three stations (WH1, WH21, and WH23) were randomly selected and run in duplicate.

PCB Analyses. PCBs were extracted from sediments using a slight modification of the method described by Goerlitz and Law (1974). A flow sheet outlining the procedure used is shown in Figure 3. To eliminate sub-sampling bias, sediments and deionized water (dH_2O), in equal volumes, (vol/vol) were homogenized in a blender. Hexachlorobenzene (HCB) was added to all

samples to monitor recovery efficiency. HCB was used because it co-extracts with PCBs, has a good response factor on the electron capture detector (ECD), and does not co-elute with any of the polychlorinated biphenyl congeners. PCBs were extracted by adding an equal volume of a mixture of 20 mL acetone and 60 mL hexane to 25 g dry sediment and placed on a gyrating shaker for 20 minutes at 150 rpm. The extract was centrifuged at 5000 rpm for 8 minutes and decanted into a separatory funnel. Sediments were extracted by repeating this procedure three times and combining all extracts. Periodically, a sample was randomly selected and extracted for a fourth time to determine if there were any PCBs still present in the sample. PCBs were never found in the fourth extract, indicating that all extractable PCBs were removed by the threefold extraction procedure. The extract was back washed with 250 mL of dH_2O, the non-polar and aqueous phases were separated, and the non-polar extract dried by the addition of 0.5 g Na_2SO_4. The extract was concentrated by refluxing, at 90-95°C, in a 500 mL round bottom flask with a 3-ball Snyder column. The concentrate was then cleaned-up on a Florisil column using nanograde hexane (Mallinckrodt, Inc., Paris, KY) as eluent. Clean-up procedure followed EPA guidelines for organochlorine pesticides and for PCBs (Fed. Reg. 1979). After clean-up, the PCB extracts were put into serum bottles, closed with teflon liners, and sealed with aluminum crimps. Extracts were stored in the dark at 4°C until analysis

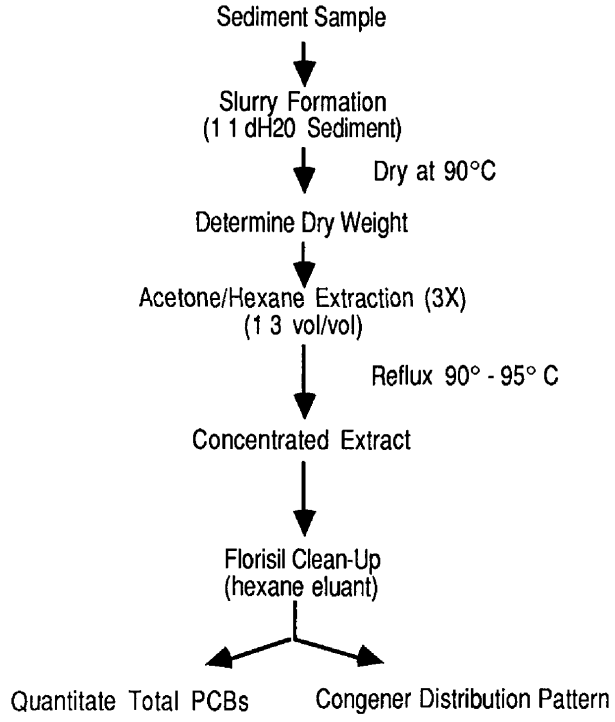

Figure 3 Flow Chart Depicting Protocol to Extract PCBs from Sediments

Gas Chromatography. High-resolution capillary gas chromatography (HRGC) was performed on a Varian Model 3500 gas chromatograph equipped with a ^{63}Ni electron capture detector (ECD) interfaced to a Varian 4270 Integrator, and a Finnegan MAT 700 ion trap detector (ITD) operated through an IBM PC-AT. A 30 meter fused silica capillary column (0.25 mm i.d.) coated with DB-5 (J & W Scientific) was used to separate PCB congeners. Carrier gas was ultra high purity (UHP) helium with a flow rate of 2.0 mL min^{-1} at 80°C; ECD make-up gas was ultra high purity (UHP) N_2 at 20 or 30 mL min^{-1} depending on desired sensitivity. Split/splitless (s/s) and on-column injection (OCI) methods were both used for congener separations. The ECD temperature was set at 300°C and the injector temperature was set at 300°C for s/s mode and at 150°C for OCI. To determine PCB congener distribution patterns, the following program was developed: injection at 80°C, hold 1 minute, ramp from 80-160°C at 20° min^{-1}, hold 1 minute; ramp from 160-270°C at 4°min^{-1}, hold 5 minutes.

Priority Pollutants. Sediments in proximity to stations J and K (Slip 3) were collected for determination of concentrations of volatile organics, base neutral and acid fractions, pesticides, PCBs (as Aroclors) and cyanide because sediments collected at these two stations had high levels of PCBs (Risatti, 1989) but differed greatly in toxicity responses (Ross *et al.* 1988). Immediately after collection, samples were put into clean, glass containers (which had been sealed prior to use) resealed and placed on ice. Samples were then shipped from the collection site, on ice, using Federal Express overnight service, to the CH2M Hill Company analytical laboratory in Montgomery, Alabama. EPA chain of custody procedures were used throughout; the elapsed time from sample collection to acceptance by the contractor's analytical personnel was less than 24 hours. The CH2M Hill laboratory is an EPA certified laboratory; sediments were analyzed using procedures described in USEPA Methods 8080, 8240, 8270 and 9020 (Test Methods for Evaluating Solid Waste, 1982) and Method 7 (Federal Register, 1979).

TOXICITY TESTING

Elutriation (USACE 1976). Elutriates were prepared from the sediment sample by mixing 100 mL of sediment with 400 mL of triple-distilled water. Air was forced for two hours through this mixture to cause vigorous churning for two hours. The liquid phase was filtered first through #1 Whatman filter paper (nominal porosity: 11 µm) and through glass fiber filters (nominal porosity· 1.2 µm). The filtrate was used as test material in the toxicity tests.

Microtox™ toxicity test (Bulich 1982). Aliquots (10 µL) of commercially available reconstituted *P phosphoreum* culture 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 2) The duplicate blank samples contained Microtox™ diluent and the 10µl 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 (response at full-strength elutriate divided by control response; multiplied by 100) were calculated.

***Selenastrum capricornutum* 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; Table 2) media was added to each replicate. The test solutions were placed in a 20°C growth chamber with a 12 hr. light - 8 hr. dark 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 HCO3- and CO_3^- to CO_2. Each sample was then bubbled with air for 5 minutes to fully remove any free ^{14}C. 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.

***Panagrellus redivivus* toxicity test (Samoiloff *et al.* 1980).** Ten replicates of 10 L1 juvenile-phase *Panagrellus redivivus* nematode worms were exposed to 0.5 mL of 50 percent elutriate. Dilutions were made with M9Y nutrient solution (Table 2). 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 (Samoiloff *et al* 1980).

Table 2 Composition of Dilution and Nutrient Media for Single-Species Bioassays

Microtox™ diluent	*S capricornutum* PAAP medium (per L)	*P redivivus* liquid growth medium (per L)
2% sodium chloride (NaCl)	14 7 g Mg $SO_4 \cdot 7H_2O$ 1 044 g $K_{2H}PO_4$ 15 0 g $NaHCO_3$ 4 41 g $CaCl_2 \cdot 2H_2O$ 25 5 g $NaNO_3$ 10 0 g $MgCl_2 \cdot 6H_2O$ plus micronutrients (trace amounts boron, manganese, zinc, cobalt, copper, molybdenum, and iron salts)	6 0 g $Na_2PO_4 \cdot 7H_2O$ 3 0 g $K_{2H}PO_4$ 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

Chapter 3. RESULTS AND DISCUSSION

CHEMISTRY

Oil and Grease. Percentages of oil and grease were determined from all stations sampled in the harbor (Table 3). Concentrations ranged from 0.3% to 5.19%, with the highest values occurring in Slip 3 and in the areas immediately outside the slip. There are a number of small boat moorings associated with the marina at this location. Consequently, these areas are subjected to heavy boating activity which, at this time at least, is probably the major source of oil and grease. Prior to 1975, there may also have been an input of machine fluids from the adjacent Outboard Marine Company plant. Small boats as well as commercial freighters and industrial activity may account for the above average levels in the vicinity of Slip 1. ENCOTEC (1976) reported concentrations of oil and grease from eight harbor stations that are generally lower (range of 0.18 percent to 3.9 percent) than the values we found Their two highest concentrations (0.97 percent and 3.9 percent) were from Slip 1 stations.

Not surprisingly, the concentration pattern of oil and grease in the harbor is similar to that observed by Risatti (1989) and Ross *et al* (1988) for PCB concentrations These authors suggested that there was movement of PCBs out of Slip 3 into the lower harbor and that currents seemed to be concentrating PCB-bearing sediments on the west side of the harbor.

Table 3 Total Oils and Grease Levels in Waukegan Harbor Samples Collected on April 27, 1987 Stations WH1, WH21 and WH23 are Averages of Duplicate Values

Sample	% Oil & Grease	Sample	% Oil & Grease	Sample	% Oil & Grease
WH-1	3 5	WH-9	0 9	WH-17	1 2
WH-2	3 7	WH-10	2.9	WH-18	1 5
WH-3	4 3	WH-11	0 5	WH-19	0 5
WH-4	3 0	WH-12	0 3	WH-20	0 5
WH-5	3 7	WH-13	0 8	WH-21	0.9
WH-6	0 9	WH-14	1 2	WH-22	0 4
WH-7	5 1	WH-15	2 7	WH-23	0 6
WH-8	3 2	WH-16	1 2		

Metals Analyses. The concentrations of 22 major, minor and trace metals from 23 stations are listed in Table 4. Although only a few of the metals listed are toxic to some degree, the concentrations of all the metals analyzed were included to serve as a reference for future work on the harbor sediments.

Table 4 Elemental Analysis of Waukegan Harbor Sediments Collected on 27 April 1987 (in ppm unless otherwise noted).

Station	Elements										
	Al (%)	Ba	Be	Ca (%)	Cd	Co	Cr	Cu	Fe (%)	K (%)	La
WH-1	1 88	230	1 6	7 1	<1 3	10 0	9	120	4 0	1 0	27
WH-2	2 11	260	1 8	6 4	<1 3	4 8	2	86	2 2	1 1	20
WH-3	2 46	280	1 7	7 1	<1 3	4 8	3	178	1 8	1 2	21
WH-4	2 34	280	1 6	6 3	<1.3	3 1	1	57	1 3	1 2	20
WH-5	3 70	290	1 8	5 6	3 8	9.0	7	210	2 5	1 7	30
WH-6	3 54	290	1 8	5 5	4 0	6 2	6	230	2 4	1 7	28
WH-7	3 99	290	1 8	5 4	4 9	9 8	9	150	2 7	1 9	32
WH-8	3 87	290	1 7	5 7	4 9	9.4	8	120	2 4	1 7	31
WH--9	3 93	280	1.9	5 7	5 5	10 0	8	120	2 3	1 8	32
WH--10	3 59	290	1 8	6 1	4 0	7 1	6	100	2 1	1 7	30
WH--11	3 64	290	1 8	6 0	6 5	7 5	7	96	2 1	1 7	30
WH--12	3 04	280	1 8	6 6	23 0	7 5	1	76	1 9	1 4	27
WH--13	3 67	280	2 2	6 7	50 0	10 0	2	120	2 4	1 7	32
WH--14	3 56	290	1 8	6 9	38 0	9 2	2	100	2 2	1 6	31
WH--15	3 77	280	1 8	6 5	4 4	8 4	7	78	2 5	1 6	32
WH--16	3 92	280	1 8	6 4	2 1	7.6	6	86	2 1	1 8	33
WH--17	3 39	280	1 8	6 3	14 0	0 0	1	93	2 1	0 8	31
WH--18	2 67	290	1 8	6 9	<1 3	0 0	9	48	1 6	0 7	24
WH--19	3 69	280	1.8	6 7	2 2	0 0	1	86	2 1	1 0	32
WH--20	3 38	320	1 8	7 2	1 7	0 0	1	72	1 8	0 9	29
WH--21	2 68	270	1 7	8 7	<1 3	0 0	9	40	1 5	0 8	28
WH--22	2 85	280	1 8	8 2	<1 3	0 0	9	45	1 5	0 8	28
WH--23	3 30	300	1 8	8 0	5 7	0.0	1	89	2 0	0 9	31

(continued)

Table 4 (cont) Elemental Analysis of Waukegan Harbor Sediments Collected on 27 April 1987 (in ppm unless noted otherwise)

Station	Elements										
	Mg (%)	Mn	Mo	Na (ppt)	Ni	Pb	Si (%)	Sr	V	Zn	Ti
WH--1	4	840	24	5800	8	54	49	110	180	210	5400
WH--2	3	530	28	3300	8	36	53	120	83	130	2600
WH--3	4	460	18	3100	8	150	46	110	45	300	2100
WH--4	3	440	22	3600	11	99	57	120	42	81	1750
WH--5	3	460	18	3100	26	260	39	100	90	270	2200
WH--6	3	460	20	3400	24	240	42	100	85	260	2000
WH--7	4	470	17	1000	19	330	40	100	83	330	2200
WH--8	4	500	19	7300	25	290	40	110	82	280	2200
WH--9	4	490	15	1200	23	280	40	110	43	270	2100
WH-10	4	480	19	1600	16	210	40	100	83	210	2200
WH--11	4	510	18	1500	24	270	40	110	41	210	2000
WH--12	4	540	25	2200	24	280	44	120	83	200	2000
WH--13	4	580	20	1200	32	420	38	110	84	370	2100
WH--14	4	560	26	2500	27	370	40	120	73	290	2100
WH--15	4	610	18	2500	19	190	40	120	84	200	2100
WH--16	4	590	13	2100	13	200	38	110	73	200	2100
WH--17	4	480	22	2900	13	280	43	110	77	240	2100
WH--18	4	440	31	3700	8	140	48	110	63	110	1700
WH--19	4	550	17	3000	19	130	42	100	94	200	2100
WH--20	4	540	30	3000	16	100	42	130	52	160	1800
WH--21	5	570	32	3300	19	60	41	110	58	90	1600
WH--22	5	540	36	2900	13	110	41	110	52	98	1800
WH--23	5	580	24	2500	16	150	39	110	74	220	1900

In Table 5, the average Waukegan Harbor concentrations for eight metals of geochemical or environmental interest are compared to values found in sediments from Lake Calumet, Calumet Harbor, Little Calumet River, Lake Michigan, Cal-Sag Channel and Wolf Lake. Except for the Cal-Sag Channel, Waukegan Harbor has the highest concentrations of cadmium, copper, and lead. Waukegan Harbor sediments on the average are about 3.5 times lower in chromium than sediments from surrounding areas and are also relatively low in zinc.

Table 5. Average Concentrations (N=23) of Selected Metals (in ppm unless otherwise noted) in Sediments of Waukegan Harbor and in Sediments of Nearby Water Systems

Elements	Waukegan Harbor	Lake[e] Calumet	Calumet[a] Harbor	Little[b] Cal River	Lake[c] Michigan	Cal-Sag[b] Channel	Wolf[d] Lake
Cadmium	8 0	1 8	3 2	2.5	0 9	8 5	2 0
Chromium	5 0	76 7	46 0	66.0	46 0	105 0	18 0
Copper	104 0	57 5	44 0	88 0	22 0	125 0	27 0
Iron (%)	2 2	2 7	- -	2 9	2 2	3 4	1 5
Lead	202 0	187 0	144 0	190 0	40 0	370 0	110 0
Nickel	17.0	23 6	- -	- -	24 0	-.-	-.-
Sodium	2900 0	470 0	- -	-.-	458 0	- -	- -
Zinc	214 0	341 0	268 0	375 0	97 0	1100 0	255 0

a = USACE (1985)
b = IEPA (1984)
c = Cahill and Shimp (1984)
d = Kelly and Hite (1981)
e = Risatti and Sheridan (1988)

The concentrations and relative distributions of aluminum, cadmium, cobalt, copper, lead and zinc at the various stations, are illustrated by the histograms in Figures 6 and 7. Especially interesting are stations 1-7, which are located in Slip 3 and immediate vicinity, and stations 12-15 which are located in and just outside of Slip 1 (station 12). The most unusual distribution is that of cadmium where values at stations 12, 13, and 14 are, on the average,10 times greater than values elsewhere in the harbor. Lead and zinc are also higher in Slip 1, which suggests that the cadmium values may be related to paint manufacture or disposal. The occurrences of lead and zinc are related and a regression analyses of lead versus zinc gives a correlation of R = 0 79. Copper is slightly more elevated in the area of Slip 3, possibly because of copper containing marine paints used as biocides on boat hulls.

Average concentrations of nine metals in Waukegan Harbor sediments were also compared with sediments from other commercial areas in the Great Lakes and to a pollution classification index for Great Lakes Harbor sediments (Table 6) Harbor sediments are heavily polluted with respect to cadmium (4 stations), copper (20 stations), manganese (14 stations), lead (21 stations), and zinc (13 stations) and moderately polluted with respect to iron (17 stations).

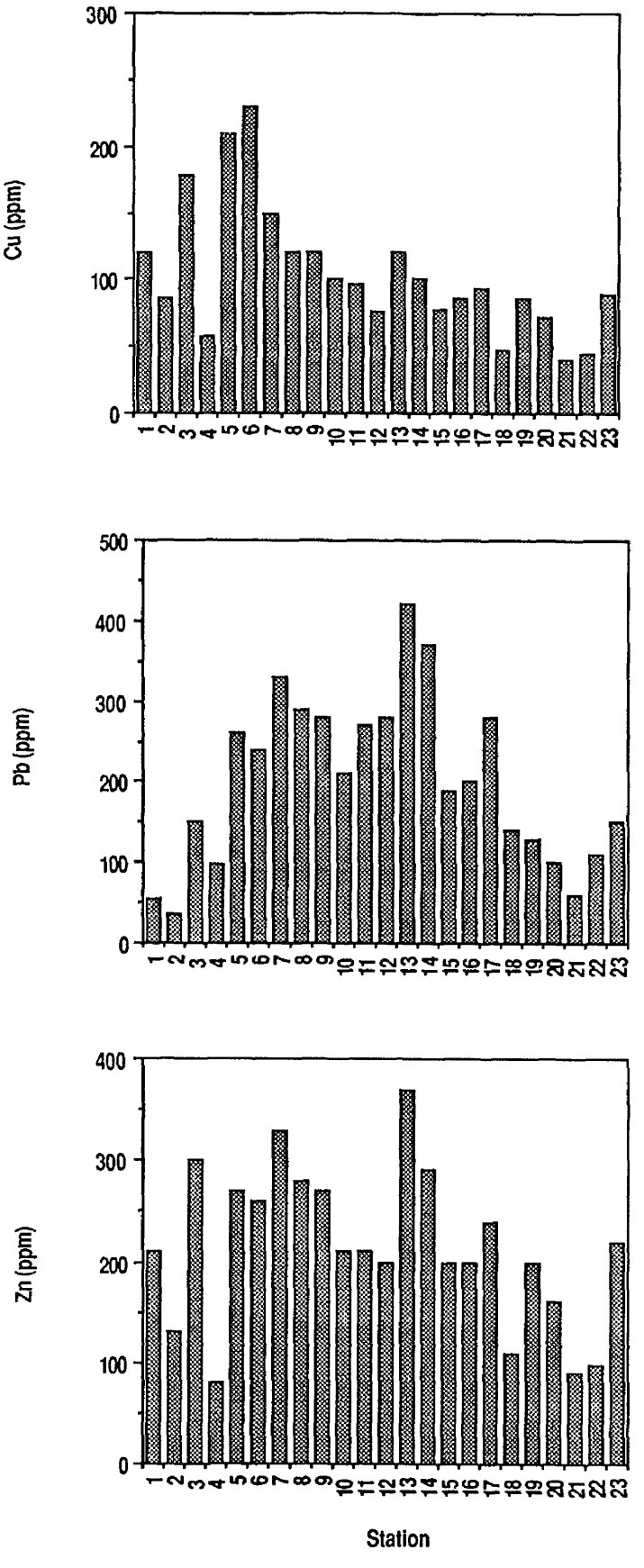

Figure 5 Concentrations of Copper, Lead, and Zinc in 23 Sediment Samples from Waukegan Harbor

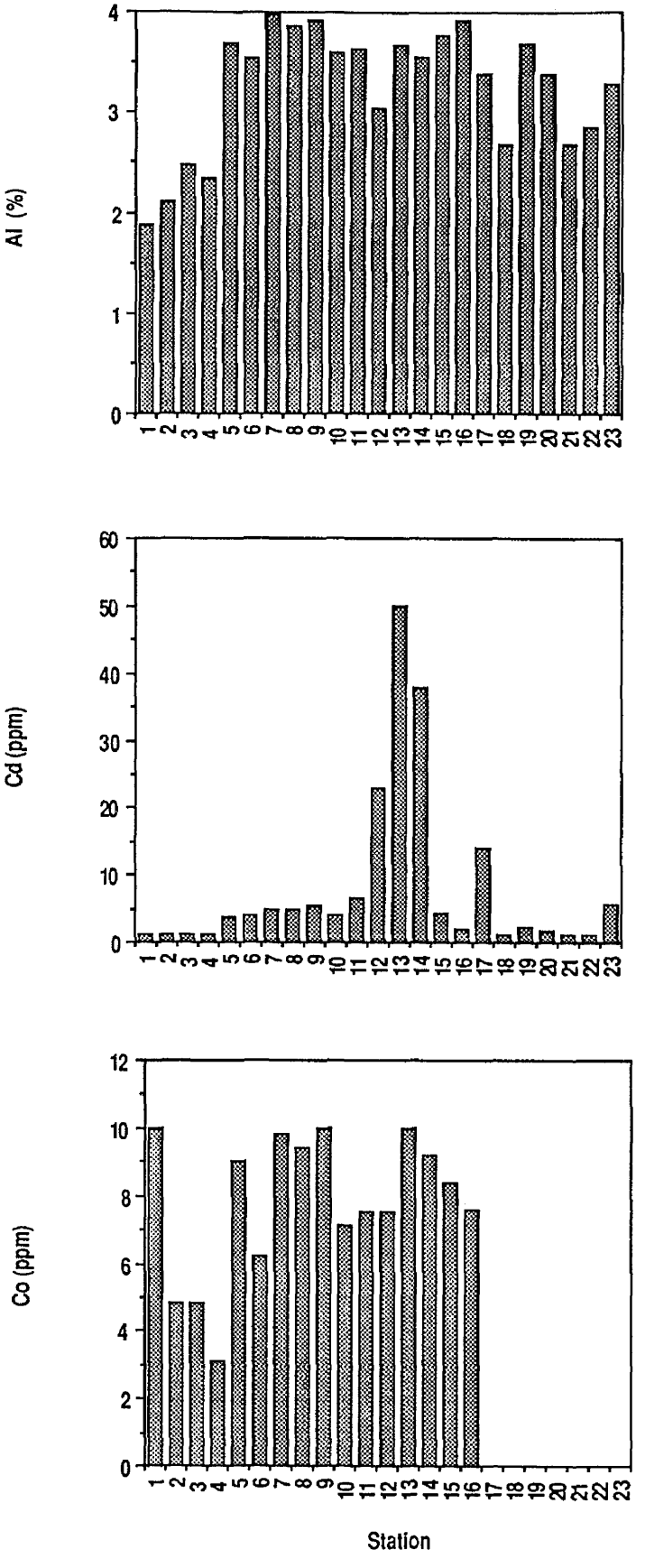

Figure 4 Concentrations of Aluminum, Cadmium, and Cobalt in 23 Sediment Samples from Waukegan Harbor

Table 6 Comparison of Average Concentrations of Selected Metals in Sediments of Waukegan Harbor with Sediments of Several Similar Localities in the Great Lakes

Element	Waukegan Harbor	Toronto Harbor	Hamilton Harbor	Lake St Clair	Heavily * Polluted
Cd	8 0	8 0	19 0	--	>6 0
Co	5 0	34 0	36 0	--	-- --
Cr	5 0	137 0	539 0	--	>75 0
Cu	104 0	94 0	216 0	16 0	>50 0
Fe (%)	2 2	4 0	12 0	--	>2 5
Mn	531 0	610 0	3355 0	--	>500 0
Ni	17 0	62 0	106 0	21 0	>50 0
Pb	202 0	297 0	756 0	26 0	>60 0
Zn	214 0	303 0	5440 0	45 0	>200 0

* Guidelines for the pollution classification of Great Lakes harbor sediments, 1982.

Priority Pollutant Analyses. Sediments collected in proximity to stations J and K (see Figure 2) were screened for the presence of 135 organic compounds or families of compounds, including priority pollutants. A list of these compounds, except cyanide, which was not found at either station, is given in Appendices 1-6. Of these compounds, fifteen were found to occur in Station J sediments Seven of these fifteen also occurred at Station K, but were generally in concentrations that were an order of magnitude or more lower (Table 7), except for the Aroclors (commercial PCB mixtures)

Table 7 Concentrations and Comparison of Compounds Identified in Sediments in Proximity to Stations J and K

Compounds	MDL[1] (ppm)	Station J (ppm)	Station K (ppm)
Pentachlorophenol	0 8	7	*
Phenanthrene	0.8	29	*
Fluoranthene	0 8	64	1 0
Pyrene	0 8	25	0.5**
Benzo (a) anthracene	0 8	23	0 4**
Benzo (b) fluoranthene	0 8	22	*
Benzo (k) fluoranthene	0 8	14	*
Benzo (a) pyrene	0 8	22	*
Chrysene	0 8	23	0 9
Bis (2-ethylhexyl) phthalate	0 8	1400	*
Di-m-octyl phthalate	0 8	7	*
Arochlor 1221	10 0	140	220 0
Arochlor 1248	2 0	36	44 0
Arochlor 1260	1 0	7	9 0
Total Xylenes	5.0	4.7**	*

[1] MDL = Method Detection Limit * = Below Method Detection Limit ** = Presence indicated but less than MDL

Polychlorinated Biphenyl (PCB) Distributions. In the previous report (Ross *et al* 1988), only total PCB concentrations were determined at the various stations and not the distribution of specific congeners. Reports of PCB toxicity suggest that lower-chlorinated congeners are more toxic to tested organisms (Eisler 1986) than are the more highly chlorinated congeners. Although this is generally true for laboratory test organisms in natural systems, the PCBs (13) thought to be most toxic range from trichlorobiphenyls to heptachlorobiphenyls (Duinker *et al* 1988). In Waukegan Harbor, some of these more mobile, toxic isomers might be present in sediments further away from the outfall and may explain increased toxicity in the middle of the harbor.

An estimate of the amounts of commonly occurring, lower chlorinated PCBs and toxic congeners (up to pentachlorobiphenyl), identified at five harbor stations is given in Table 8. This list is necessarily qualitative at this time because of the varying PCB concentrations at the stations, and because standards were not available for all congeners in order to correct for response times The predominant commercial PCB mixtures which contaminated the harbor were Aroclors 1242 and 1248 (D. Stallings, personal communication). The most predominant toxic congener at these stations, based on peak height, may be 3,4,4'- trichlorobiphenyl. We could not unequivocally identify this congener because it co-elutes with 2,2',3,4 - and 2,3,3',6 - tetrachlorobiphenyl. Of these three congeners, 2,3,3',6 - tetrachlorobiphenyl occurs as a major peak in Aroclor 1242 and as a minor peak in Aroclor 1248 (Sissons and Welti, 1971, Erickson, 1986), 3,4,4'- tetrachlorobiphenyl occurs as a minor peak in Aroclor 1242 (Sissons and Welti, 1971) and 2,2',3,4 - tetrachlorobiphenyl does not occur in either Aroclor 1242 or 1248 (Erickson, 1986).

Table 8 Estimated Relative Quantities of Selected Lower Chlorinated and Reported Toxic * PCB Congeners Occurring in Sediments from Stations in Waukegan Harbor

PCB Congeners †	Stations 3	5	8	16	22
2, 2', 2,6	-	-	-	-	+
2,3'	-	-	-	-	-
2,4'; 2,3	-	tr	tr	-	-
2,2',6	++++	++	++	++++	++
4,4', 2,2',5	+	+	++	+	tr
2,4,2'	+++	++	+++	+	+++
2,6,3'	+	+	+	+	+
2,4',6, 2,2',3	+++++	++	+++	+	+
2,3',4,	+	++	+++	+	+
2,4',5	+	++	+++	+	+
2,4,4'	+++++	+++++	+++++	++	++
2,2',5,5'	+	+++	+++++	++	+
2,2',4',5	+	+++	+++++	++	+
2,2',4,4'	+	+++	+++++	++	+
* 3,4,4',2,3,3',6	+++++	+++++	+++++	+++++	+++++
*3,3',4,4', 2,3,3'4',6	+	+	+	+	tr
*3,4,4',5	-	-	-	-	-
*2,3',4,4',5	-	-	-	-	-
*2,3,4,4',5	-	-	-	-	-
*2,3,4,4',5	-	-	-	-	-
*2,3,3',4,4' , 2,2,',3,3',4,6'	++	+	+	+	+

† possibly present co-eluting congeners are listed for unresolved peaks

(tr) = trace amounts , (-) = not present

TOXICOLOGY

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 is a result of existing chemical, biological, and physical sediment conditions. The use of bioassay organisms can be considerably less expensive than chemical analysis. Because of the lower cost, a hazard assessment can be constructed more readily and for more stations. Limitations also arise from biological assessment, 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 Waukegan Harbor.

The responses of the three toxicity tests (Microtox, *S capricornutum* , and *P redivivus*) used to determine the toxic potential of the Waukegan Harbor sediments are listed in Table 9. The toxicity tests were performed on elutriates (as discussed in the introduction) of the sediments collected and, therefore, represent the toxic response to the "bioavailable" contaminants in the sediments. Because of this distinction, "hot spots" in the Harbor as determined by chemical analysis and those determined by toxicological analysis may differ.

An analysis of variance (ANOVA; Sokal and Rohlf, 1969) of the results of the toxicity tests identified three areas of high toxicity and four areas of low toxicity in Waukegan Harbor (Figure 6) The responses to stations WH1, WH9, and WH10 were significantly ($p<0.05$) more toxic than stations WH2, WH3, WH11, and WH15 There were no significant differences in toxicity within the remaining stations.

There was a significant difference, however, between the toxicity tests. Responses of the *S capricornutum* assay were significantly different from either the Microtox™ or *P. redivivus* assays The mean (x) of the algal test across the 23 stations is 58.38, while those of the Microtox™ and *P redivivus* tests are 34.79 and 32.32, respectively. These assays are surrogates for different ecological functions, each of which has different sensitivity and discriminatory ability.

Metal (priority pollutant metals: Be, Cd, Cr, Cu, Pb, Ni, and Zn) hot spots were identified by ANOVA as stations WH13 and WH7 (Figure 6). Stations with statistically significant lower priority pollutant metal contamination were identified as WH2, WH4, WH21, and WH22. The area of the Harbor that includes stations WH5 - WH9, WH13, WH14, and WH17 is the most contaminated by priority pollutant metals. Station WH9 corresponds to an area of high toxicity and high metal concentrations while stations WH2, WH3, WH11, and WH15 (low toxicity stations) were lower in metal contamination.

Table 9 Percent Response of Toxicity Tests to Elutriates from 23 Sediment Samples Collected at Waukegan Harbor

Station	*S capricornutum*	Microtox™	*P redivivus*	Sum all responses
WH1	105 92	72 24	17 77	195 93
WH2	-30 01	33 11	4 28	7 38
WH3	-2 66	57 95	0 20	55 49
WH4	77 80	27 08	26 37	131 25
WH5	35 23	50 01	73.94	159.18
WH6	99 45	28 65	47 09	175 19
WH7	64 71	22.40	47 4	134 51
WH8	53 43	10 34	44 59	108 36
WH9	57 08	111 59	40 69	209 36
WH10	70 60	114 88	49.96	235.44
WH11	30 08	0 74	15.41	46 23
WH12	74 19	30 46	5 08	109 73
WH13	95.26	28 30	31 10	154 66
WH14	68 00	18.30	32 36	118 66
WH15	-1 00	25 64	35 29	59 93
WH16	82 15	40 66	*	*
WH17	77 02	28 51	*	*
WH18	88 57	28 74	*	*
WH19	-1 00	45 33	*	*
WH20	105 87	9 85	44 85	160 57
WH21	72 24	1 75	22 70	96 69
WH22	60 24	2 40	31 50	94 14
WH23	36 56	11 25	43 55	91 36

*not performed

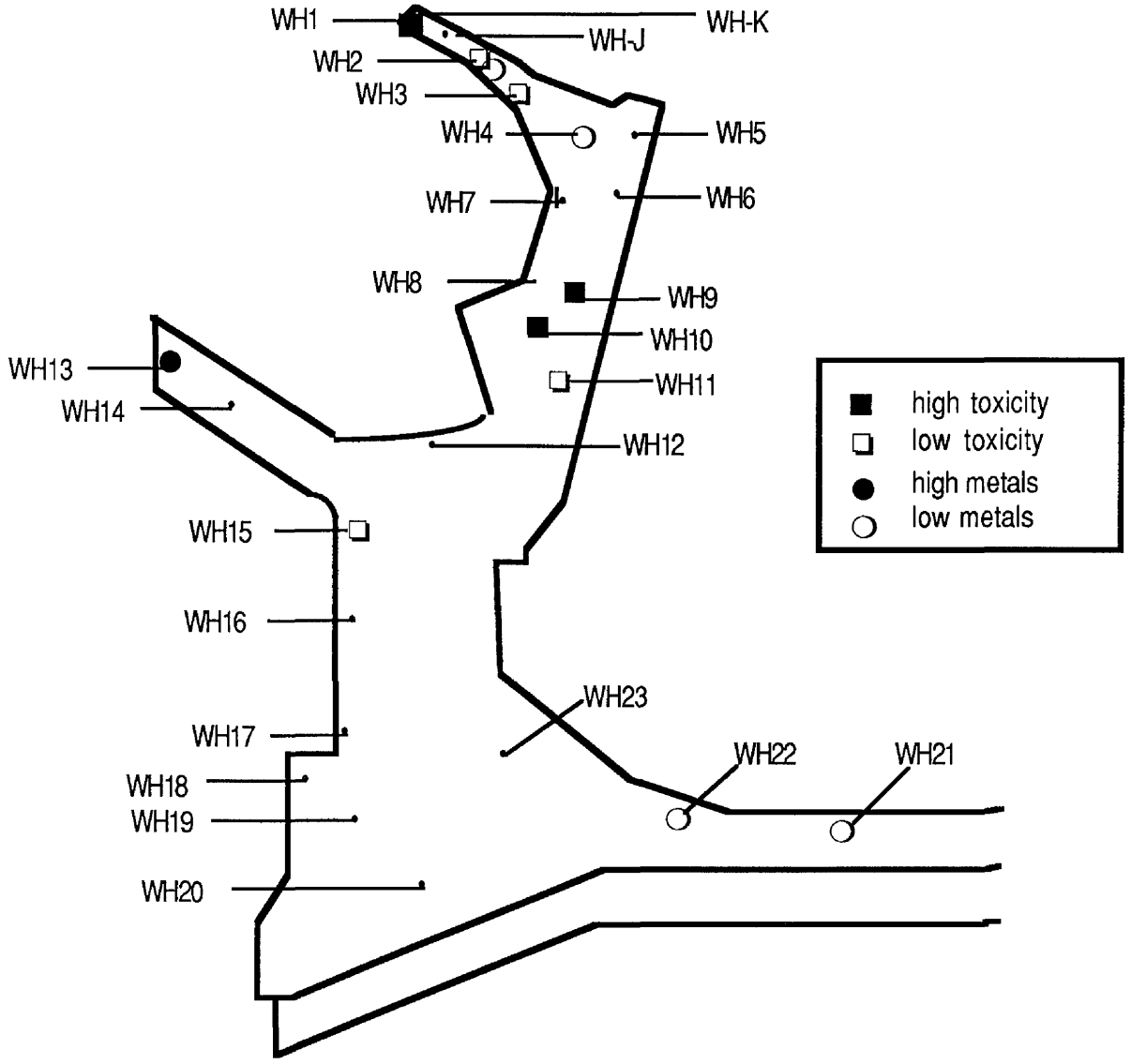

Figure 7 Distribution of High and Low Toxicity Areas and Dtations with High and Low Priority Pollutant Metal Concentrations (see text, relative to results from other stations)

A concern in the preceding study (Ross *et al* 1988) was the presence of oils and grease in Waukegan Harbor sediments. These contaminants were quantified in this study (Table 3). The presence of oils and grease in the sediments may reduce the solubility and, thus the bioavailability of many of the sediment contaminants, especially in the elutriation procedure. To determine if differences in toxicity existed in elutriates of sediments with varying oils and grease percentages, the 23 stations were divided into three groups according to oils and grease content. Sediments in Group I had concentrations exceeding 3%, oils and grease concentrations in Group II fell between 1% and 3%, and Group 3 had less than 1% oils and grease content. A one-factor ANOVA showed that there were no significant differences in toxicity between these regions of oils and grease contamination

The presence of PCBs remains the primary environmental issue at Waukegan Harbor. The relative qualification of "toxic" congeners in Table 8 suggests that station WH8 has the most complete spectrum of chlorinated biphenyls Station WH8 was not itself overly toxic although it is located in a region with other stations of higher toxicity (WH9 and WH10). Station WH5 is more toxic and yet the PCB profile shows that it is slightly less contaminated with congeners except for 2,4,4' and 3,4,4';2,3,3',6. These congeners are also present at the same relative quantities at station WH3, defined previously as a low toxicity station.

Chapter 4. CONCLUSIONS AND RECOMMENDATIONS

General observations from the two studies in Waukegan Harbor serve to reject a hypothesis from the first study: "concentrations of certain pollutants can be used to predict the response of the organisms...(Ross et al. 1988)." This hypothesis may hold for limited laboratory studies with one or two chemicals and strictly defined testing conditions but cannot be supported from this complex environmental sampling study Instead, we put forth that chemical analysis cannot predict biological response (or *vice versa*) and assert that biological testing is an integral part of determining the hazard of a contaminated site such as Waukegan Harbor.

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 Waukegan Harbor should be viewed as information about the environmental past and present of the Harbor. Waukegan Harbor sediments contain high concentrations of potentially hazardous priority pollutant metals and PCBs. The Harbor is not a closed system, and may impact the biota, possibly even humans, in the nearby vicinity.

Waukegan Harbor continues to be a site of intense environmental focus. The cleanup plan mandated by Superfund legislation (CERCLA/SARA) is in place and in progress. But the Harbor is also targeted as an Area of Concern (AOC) by the International Joint Commission. The AOC classification is independent of CERCLA/SARA scoring and jurisdiction. The Remedial Action Plan required by the Great Lakes Water Quality Agreement must also consider non-PCB pollutants and evaluate the impact of the contaminated site relative to the entire Great Lakes region. Based on the results of the studies reported here, we strongly recommend that biological testing (toxicity, bioaccumulation, etc.) be included as a partner in evaluating the effectiveness of the Superfund cleanup and in any assessment of further environmental damage, both within Waukegan Harbor and throughout the Great Lakes ecosystem.

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APPENDICES

Appendix 1.Acid compounds analyzed in sediments from stations J and K

STATION K			STATION J		
Compounds	MDL[1] PPM	Conc. PPM	Compounds	MDL[1] PPM	Conc. PPM
Phenol	0.8	BMDL[2]	Phenol	0.8	BMDL[2]
2-Chlorophenol	0.8	BMDL	2-Chlorophenol	0.8	BMDL
O-Cresol	0.8	BMDL	O-Cresol	0.8	BMDL
M & P-Cresol	0.8	BMDL	M &P-Cresol	0.8	BMDL
2-Nitrophenol	0.8	BMDL	2-Nitrophenol	0.8	BMDL
2,4-Dimethylphenol	0.8	BMDL	2,4-Dimethylphenol	0.8	BMDL
2,4-Dichlorophenol	0.8	BMDL	2,4-Dichlorophenol	0.8	BMDL
Benzoic Acid	4.0	BMDL	Benzoic Acid	4.0	BMDL
4-Chloro-3-methylphenol	0.8	BMDL	4-Chloro-3-methylphenol	0.8	BMDL
2,4,6-Trichlorophenol	0.8	BMDL	2,4,6-Trichlorophenol	0.8	BMDL
2,4,5-Trichlorophenol	0.8	BMDL	2,4,5-Trichlorophenol	0.8	BMDL
2,4-Dinitrophenol	4.0	BMDL	2,4-Dinitrophenol	4.0	BMDL
4-Nitrophenol	4.0	BMDL	4-Nitrophenol	4.0	BMDL
2-Methyl-4,6-dinitrophenol	4.0	BMDL	2-Methyl-4,6-dinitrophenol	4.0	BMDL
Pentachlorophenol	0.8	BMDL	Pentachlorophenol	0.8	BMDL

(1) MDL = Method Detection Limit
(2) BMDL = Below Method Detection Limit

Appendix 2.Concentrations of base/neutral compounds in sediments from Station J.

Compounds	MDL[1] PPM	Conc. PPM
Aniline	0.8	BMDL[2]
Bis(2-chloroethyl)ether	0.8	BMDL
1,3-Dichlorobenzene	0.8	BMDL
1,4-Dichlorobenzene	0.8	BMDL
Benzyl Alcohl	0.8	BMDL
1,2-Dichlorobenzene	0.8	BMDL
Bis(2-chloroisopropyl)ether	0.8	BMDL
Hexachloroethane	0.8	BMDL
N-nitroso-di-n-propylamine	0.8	BMDL
Nitrobenzene	0.8	BMDL
Isophorone	0.8	BMDL
Bis(2-chloroethoxy)methane	0.8	BMDL
1,2,4-Trichlorobenzene	0.8	BMDL
Naphthalene	0.8	BMDL
4-Chloroaniline	0.8	BMDL
Hexachlorobutadiene	0.8	BMDL
2-Methylnaphthalene	0.8	BMDL
Hexachlorocyclopentadiene	0.8	BMDL
2-Chloronaphthalene	0.8	BMDL
3-Nitroaniline	4.0	BMDL
Acenaphthylene	0.8	BMDL
Dimethyl phthalate	0.8	BMDL
2,6-Dinitrotolvene	0.8	BMDL
2-Nitroaniline	4.0	BMDL
Acenaphthene	0.8	BMDL
Dibenzofuran	0.8	BMDL
2,4-Dinitrotolvene	0.8	BMDL
Fluorene	0.8	BMDL
4-Chlorophenyl phenyl ether	0.8	BMDL
4-Nitroaniline	4.0	BMDL
Diethyl phthalate	0.8	BMDL
N-nitrosodiphenylamine	0.8	BMDL[2]
1,2-Diphenylhydrazine	0.8	BMDL
4-Bromophenyl phenyl ether	0.8	BMDL
Hexachlorobenzene	0.8	BMDL
Phenanthrene	0.8	29
Anthracene	0.8	BMDL
Dibutyl phthalate	0.8	BMDL
Fluoranthene	0.8	64
Pyrene	0.8	25
Benzidine	4.0	BMDL
Butyl benzyl Phthalate	0.8	BMDL
2,3,7,8-Tetrachlorodibenzo-p-dioxin	0.8	BMDL
Benzo (a) anthracene	0.8	23
Chrysene	0.8	23
3,3'-Dichlorobenzidine	4.0	BMDL
Bis(2-ethylexyl)phthalate	0.8	1400
Di-n-octyl phthalate	0.8	7
Benzo (b) fluoranthene	0.8	22
Benzo (k) fluoranthene	0.8	14
Benzo (a) pyrene	0.8	22
Indeno (1,2,3-cd) pyrene	0.8	BMDL
Dibenzo (a,h) anthracene	0.8	BMDL
Benzo (g,h,i) perylene	0.8	BMDL

SURROGATE RECOVERIES	% REC.
05-Nitrobenzene	67
2-Fluorobiphenyl	78
D10-Pyrene	52
D14-Terphenyl	56

(1) MDL = Method Detection Limit
(2) BMDL = Below Method Detection Limit

Appendix 3. Concentrations of base/neutral compounds in sediments from Station K.

Compounds	MDL[1] PPM	Conc. PPM
Aniline	0.8	BMDL[2]
Bis(2-chloroethyl)ether	0.8	BMDL
1,3-Dichlorobenzene	0.8	BMDL
1,4-Dichlorobenzene	0.8	BMDL
Benzyl Alcohl	0.8	BMDL
1,2-Dichlorobenzene	0.8	BMDL
Bis(2-chloroisopropyl)ether	0.8	BMDL
Hexachloroethane	0.8	BMDL
N-nitroso-di-n-propylamine	0.8	BMDL
Nitrobenzene	0.8	BMDL
Isophorone	0.8	BMDL
Bis(2-chloroethoxy)methane	0.8	BMDL
1,2,4-Trichlorobenzene	0.8	BMDL
Naphthalene	0.8	BMDL
4-Chloroaniline	0.8	BMDL
Hexachlorobutadiene	0.8	BMDL
2-Methylnaphthalene	0.8	BMDL
Hexachlorocyclopentadiene	0.8	BMDL
2-Chloronaphthalene	0.8	BMDL
3-Nitroaniline	4.0	BMDL
Acenaphthylene	0.8	BMDL
Dimethyl phthalate	0.8	BMDL
2,6-Dinitrotolvene	0.8	BMDL
2-Nitroaniline	4.0	BMDL
Acenaphthene	0.8	BMDL
Dibenzofuran	0.8	BMDL
2,4-Dinitrotolvene	0.8	BMDL
Fluorene	0.8	BMDL
4-Chlorophenyl phenyl ether	0.8	BMDL
4-Nitroaniline	4.0	BMDL
Diethyl phthalate	0.8	BMDL

SURROGATE RECOVERIES	% REC.
05-Nitrobenzene	79
2-Fluorobiphenyl	72
D10-Pyrene	52
D14-Terphenyl	53

Compounds	MDL[1] PPM	Conc. PPM
N-nitrosodiphenylamine	0.8	BMDL[2]
1,2-Diphenylhydrazine	0.8	BMDL
4-Bromophenyl phenyl ether	0.8	BMDL
Hexachlorobenzene	0.8	BMDL
Phenanthrene	0.8	BMDL
Anthracene	0.8	BMDL
Dibutyl phthalate	0.8	BMDL
Fluoranthene	0.8	1.0
Pyrene	0.8	*0.5
Benzidine	4.0	BMDL
Butyl benzyl Phthalate	0.8	BMDL
2,3,7,8-Tetrachlorodibenzo-p-dioxin	0.8	BMDL
Benzo (a) anthracene	0.8	*0.4
Chrysene	0.8	0.9
3,3'-Dichlorobenzidine	4.0	BMDL
Bis(2-ethylexyl)phthalate	0.8	BMDL
Di-n-octyl phthalate	0.8	BMDL
Benzo (b) fluoranthene	0.8	BMDL
Benzo (k) fluoranthene	0.8	BMDL
Benzo (a) pyrene	0.8	BMDL
Indeno (1,2,3-cd) pyrene	0.8	BMDL
Dibenzo (a,h) anthracene	0.8	BMDL
Benzo (g,h,i) perylene	0.8	BMDL

(1) MDL = Method Detection Limit
(2) BMDL = Below Method Detection Limit
* Presence indicated but less than MDL

Appendix 4. Pesticides and PCBs determined in sediments from Stations J and K.

Station J			Station K		
Compounds	MDL[1] PPM	Conc. PPM	Compounds	MDL[1] PPM	Conc. PPM
Aldrin	0.25	BMDL[2]	Aldrin	0.25	BMDL[2]
alpha-BHC	0.25	BMDL	alpha-BHC	0.25	BMDL
beta-BHC	0.5	BMDL	beta-BHC	0.5	BMDL
delta-BHC	0.25	BMDL	delta-BHC	0.25	BMDL
gamma-BHC	0.25	BMDL	gamma-BHC	0.25	BMDL
Chlordane	1.25	BMDL	Chlordane	1.25	BMDL
4,4'-DDD	0.5	BMDL	4,4'-DDD	0.5	BMDL
4,4'-DDE	0.5	BMDL	4,4'-DDE	0.5	BMDL
4,4'-DDT	0.5	BMDL	4,4'-DDT	0.5	BMDL
Dieldrin	0.5	BMDL	Dieldrin	0.5	BMDL
Endosulfan I	0.5	BMDL	Endosulfan I	0.5	BMDL
Endosulfan II	0.5	BMDL	Endosulfan II	0.5	BMDL
Endosulfan Sulfate	0.5	BMDL	Endosulfan Sulfate	0.5	BMDL
Endrin	0.5	BMDL	Endrin	0.5	BMDL
Endrin Aldehyde	0.5	BMDL	Endrin Aldehyde	0.5	BMDL
Endrin Ketone	0.5	BMDL	Endrin Ketone	0.5	BMDL
Heptachlor	0.25	BMDL	Heptachlor	0.25	BMDL
Heptachlor Epoxide	0.25	BMDL	Heptachlor Epoxide	0.25	BMDL
4,4'-Methoxychlor	1	BMDL	4,4'-Methoxychlor	1	BMDL
Toxaphene	6.25	BMDL	Toxaphene	6.25	BMDL
PCB - 1016	4	BMDL	PCB - 1016	4	BMDL
PCB - 1221	10	140	PCB - 1221	10	220
PCB - 1232	10	BMDL	PCB - 1232	10	BMDL
PCB - 1242	4	BMDL	PCB - 1242	4	BMDL
PCB - 1248	2	36	PCB - 1248	2	44
PCB - 1254	1	BMDL	PCB - 1254	1	BMDL
PCB - 1260	1	7	PCB - 1260	1	9

(1) MDL = Method Detection Limit
(2) BMDL = Below Method Detection Limit

Appendix 5. Volatile compounds determined in sediments from Station J.

Compounds	MDL[1] PPM	Conc. PPM	Compounds	MDL[1] PPM	Conc. PPM
Chloromethane	5	BMDL[2]	Tolvene	5	BMDL[2]
Bromomethane	5	BMDL	Chlorobenzene	5	BMDL
Vinyl chloride	5	BMDL	Ethyl Benzene	5	BMDL
Chloroethane	5	BMDL	Styrene	5	BMDL
Methylene chloride	5	ND [3]	Total Xylenes	5	4.7
Trichlorofluormethane	5	BMDL	Acrylonitrile	100	BMDL
Acetone	10	BMDL	Acrolein	100	BMDL
Carbon disulfide	5	BMDL			
1,1-Dichloroethene	5	BMDL			
1,1-Dichloroethane	5	BMDL			
Trans-1,2-dichloroethene	5	BMDL			
Chloroform	5	BMDL			
2-Butanone	10	BMDL			
1,2-Dichloroethane	5	BMDL			
1,1,1-Trichloroethane	5	BMDL			
Carbon tetrachloride	5	BMDL			
Vinyl acetate	10	BMDL			
Bromodichloromethane	5	BMDL			
1,2-Dichloropropane	5	BMDL			
Trans-1,3-dichloropropene	5	BMDL			
Trichloroethene	5	BMDL			
Benzene	5	BMDL			
Dibromochloromethane	5	BMDL			
1,1,2-Trichloroethane	5	BMDL			
Cis-1,3-dichloropropene	10	BMDL			
2-Chloroethylvinylether	10	BMDL			
Bromoform	5	BMDL			
4-Methyl-2-pentanone	10	BMDL			
2-Hexanone	10	BMDL			
Tetrachloroethene	5	BMDL			
1,1,2,2-Tetrachloroethane	5	BMDL			
SURROGATE RECOVERIES	% REC.				
D4-1,1-Dichloroethane	81				
D8-Tolvene	102				
1,4-Bromofluorobenzene	107				

(1) MDL = Method Detection Limit
(2) BMDL = Below Method Detection Limit
(3) ND = Not Determined
* Present be less than MDL

Appendix 6. Volatile compounds determined in sediments from Station K.

Compounds	MDL[1] PPM	Conc. PPM	Compounds	MDL[1] PPM	Conc. PPM
Chloromethane	5	BMDL[2]	Tolvene	5	BMDL[2]
Bromomethane	5	BMDL	Chlorobenzene	5	BMDL
Vinyl chloride	5	BMDL	Ethyl Benzene	5	BMDL
Chloroethane	5	BMDL	Styrene	5	BMDL
Methylene chloride	5	ND [3]	Total Xylenes	5	BMDL
Trichlorofluormethane	5	BMDL	Acrylonitrile	100	BMDL
Acetone	10	BMDL	Acrolein	100	BMDL
Carbon disulfide	5	BMDL			
1,1-Dichloroethene	5	BMDL			
1,1-Dichloroethane	5	BMDL			
Trans-1,2-dichloroethene	5	BMDL			
Chloroform	5	BMDL			
2-Butanone	10	BMDL			
1,2-Dichloroethane	5	BMDL			
1,1,1-Trichloroethane	5	BMDL			
Carbon tetrachloride	5	BMDL			
Vinyl acetate	10	BMDL			
Bromodichloromethane	5	BMDL			
1,2-Dichloropropane	5	BMDL			
Trans-1,3-dichloropropene	5	BMDL			
Trichloroethene	5	BMDL			
Benzene	5	BMDL			
Dibromochloromethane	5	BMDL			
1,1,2-Trichloroethane	5	BMDL			
Cis-1,3-dichloropropene	10	BMDL			
2-Chloroethylvinylether	10	BMDL			
Bromoform	5	BMDL			
4-Methyl-2-pentanone	10	BMDL			
2-Hexanone	10	BMDL			
Tetrachloroethene	5	BMDL			
1,1,2,2-Tetrachloroethane	5	BMDL			
SURROGATE RECOVERIES	% REC.				
D4-1,1-Dichloroethane	96				
D8-Tolvene	105				
1,4-Bromofluorobenzene	94				

(1) MDL = Method Detection Limit
(2) BMDL = Below Method Detection Limit
(3) ND = Not Determined