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The partitioning and distribution of zinc, nickel, chromium and copper in western Lake Erie sediments.

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THE PARTITIONING AND DISTRIBUTION OF Zn, Ni, Cr, AND Cu IN WESTERN LAKE ERIE SEDIMENTS

By
By Bryan Matthew MacFarlane

A thesis
submitted to the
College of Graduate Studies and Research
through the Department of Earth Sciences
in partial fulfillment of the requirements
for the degree of Master of Science
at the University of Windsor

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ABSTRACT

Previous research on trace metals in aquatic sediments have employed non-selective extractants which do not address the partitioning of trace metals. Partitioning data is important in environmental geochemistry because it can reveal a great deal of information about the source and distribution of the trace metals. A sequential extraction procedure was designed to examine the partitioning of anthropogenically derived Zn, Ni, Cr, and Cu in western Lake Erie sediment. The <63 micron size fraction of twenty surficial sediment samples were subjected to a three step extraction procedure that examined trace metals: 1)adsorbed on the surface of sediment grains and/or bound to carbonates, using 1.0M Na-Acetate; 2) bound to organic matter, using 0.1 M Na-pyrophosphate; and 3) bound to Fe-Mn oxides, using 1.0 M Hydroxylamine hydrochloride.

The results of the sequential extraction indicate that Fe-Mn oxides are the dominant scavengers of Zn, Ni, Cr, and Cu throughout the study area. The data also indicate that organic matter plays only a minor role in the partitioning of Zn and Ni, but a much more significant role for Cr and Cu. Additionally, the data indicate that adsorptive type bonding is minimal for Cr but much more important for Zn, Ni, and Cu. The partitioning of Zn and Ni was quite similar throughout the study area and both elements show an increase in metals associated with adsorption type bonding near the mouth of the Detroit River. The partitioning of Cr and Cu throughout the study area was much more variable and no clear trends were observed.

The highest trace metal concentrations are found at the western edge of Lake Erie along the American shoreline. Trace metals derived from industrial activity along the American shoreline of the Detroit River are restricted to the American shoreline of Lake Erie, due to current directions. An increase in trace metal concentrations was also observed offshore from the town of Leamington. The lowest trace metal concentrations were observed at sites near the shipping channel. It is believed that lake freighters are causing erosion of the bottom sediments that inhibits the accumulation of anthropogenically derived trace metals.

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CHAPTER 1

INTRODUCTION

Western Lake Erie is located at the end of the Huron-Erie corridor, a waterway that flows through an area of intense industrial activity and borders a number of large urban centres. The intense industrial activity and the large urban centres contribute significant amounts of trace metals into the waterway that eventually end up in the sediments of western Lake Erie. Numerous studies have investigated trace metal concentrations in the sediments of western Lake Erie but no research has been conducted on the partitioning of the trace metals within the sediment.

Chemical extraction procedures exist that can selectively remove trace metals associated with the various sediment forming components. These extraction procedures can be sequenced in such a way as to remove elements selectively from the various components that constitute a sediment. This approach to chemical extraction is called sequential and has been performed on samples from western Lake Erie in order to determine the partitioning and distribution pattern of Zn, Ni, Cr, and Cu within the sediments.

1.1 Importance of the Study

Western Lake Erie is surrounded by a large human population and is home to a large commercial fresh water fish industry. Trace metal pollution in the sediments of western Lake Erie is a concern in this area but little information is available regarding the partitioning and distribution of the trace metals. Partitioning data can reveal information regarding what types of sediment-forming components the trace metals are associated with and how they are associated with them. Distribution patterns can reveal the source(s) and transportation paths of the trace metals in western Lake Erie and can indicate areas of relatively high trace metal concentrations. This information, in conjunction with other studies, may help in determining if the trace metals in sediments of western Lake Erie posses a potential risk to organisms in and around the lake.

1.2 Objectives of the Study

The objectives of this thesis were:

1) Determine the selectivity of some of the reagents employed in the sequential extraction procedure and to ensure that the procedure was conducted under controlled operating conditions;

2) Use the data from the sequential extraction procedure to determine the partitioning and distribution of Fe, Mn, Ca, and Mg in western Lake Erie sediments;

3) Use the data from the sequential extraction procedure to determine the partitioning and distribution of Zn, Ni, Cr, and Cu in western Lake Erie sediments; and

4) Examine some of the characteristics of the sediment to determine what role if any they have on the partitioning and distribution Zn, Ni, Cr, and Cu in western Lake Erie.

CHAPTER 2

STUDY AREA

2.1 Geographic Setting

Lake Erie is the smallest of the Great Lakes by volume and the southernmost lake in the Great Lakes system (Figure 1). The surface area is over 25,000 km^2, the volume of the lake is 470 km^3 and its surface is 174 m above sea level (Sly, 1976). It is connected to Lake Huron via the Huron-Erie Corridor (St.Clair River-Lake St. Clair-Detroit River) and to Lake Ontario by the Niagara River. The lake has been divided into three basins based on bathymetry (Figure 2). These are the western, central and eastern basins (Sly, 1976). The western basin is the smallest with a surface area of 3,680 km^2, which represents less than 15% of the total surface area of the lake (Sly, 1976). The average depth of the western basin is 7.6 m (Burns, 1976b) which is much less than the average depths of the central and eastern basin which are 25 m and 64 m, respectively (Sly, 1976).

2.2 Bedrock Geology

The bedrock geology of the Lake Erie basin consists of a thick sequence of Paleozoic sedimentary rocks overlying a Precambrian crystalline basement. The Paleozoic sediments consist of Upper Silurian and Lower Devonian dolomites, limestones, and shales (Figure 3). No sedimentary successions which date between early Carboniferous and the Pleistocene exist in the area and it is thought that the region was largely subject to subaerial weathering and erosion during the Tertiary and early Quaternary times (Sly, 1976).

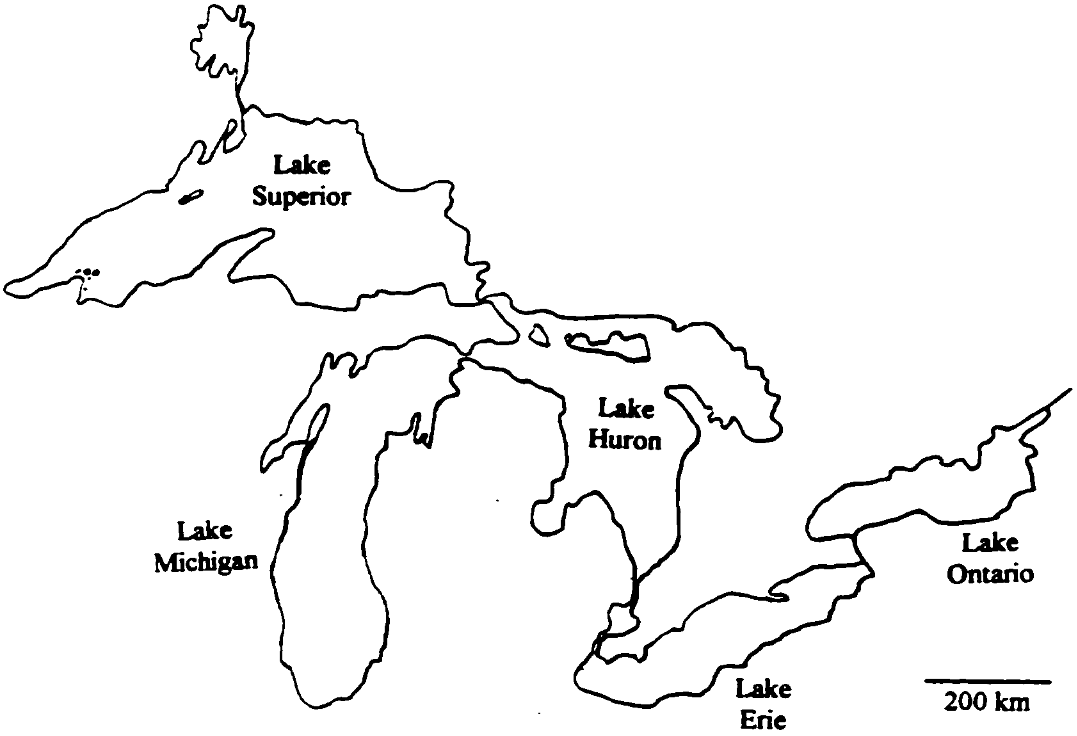

Figure 1: Map of the Great Lakes

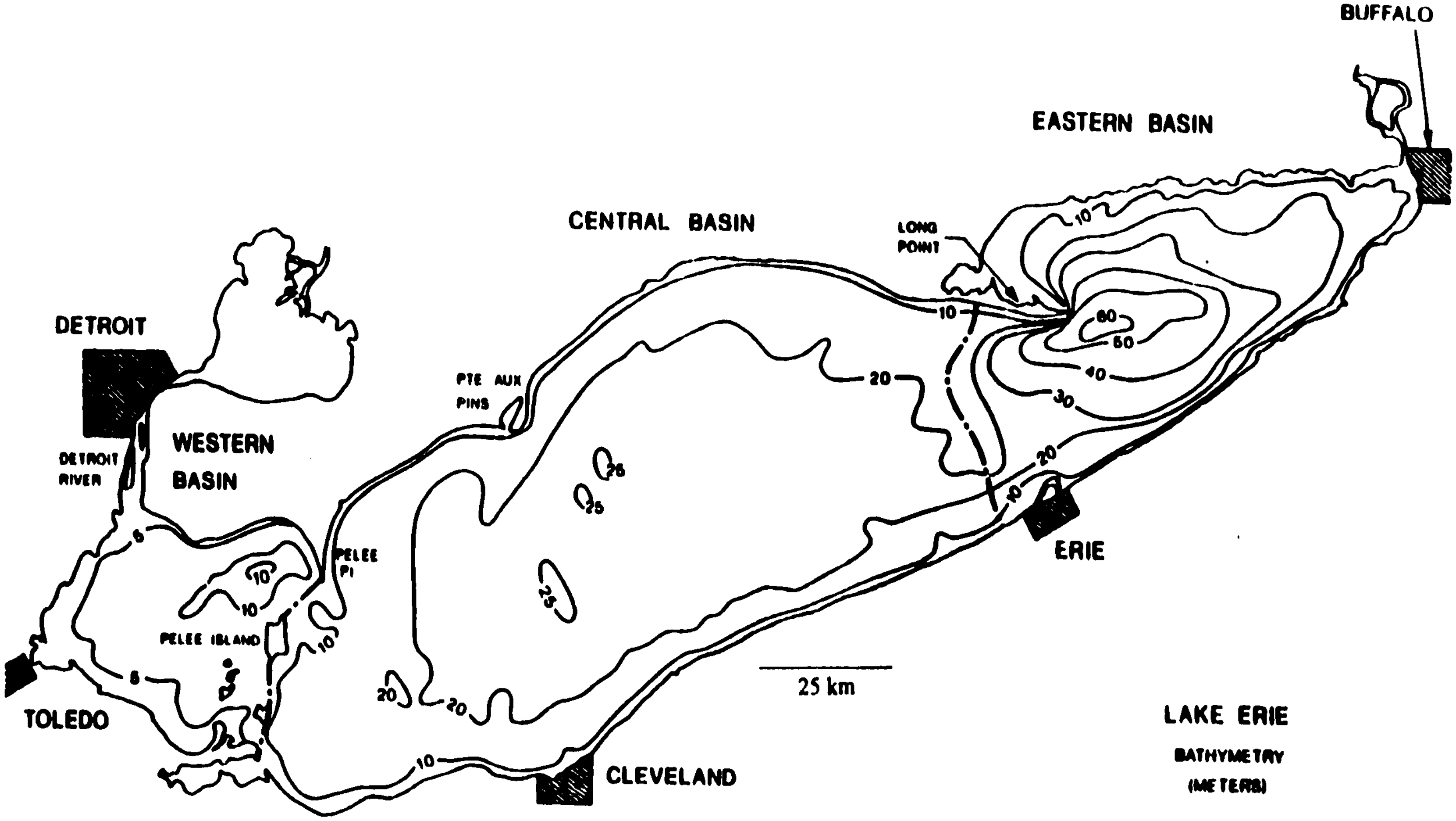

Figure 2: Bathymetry of Lake Erie (Sly, 1976).

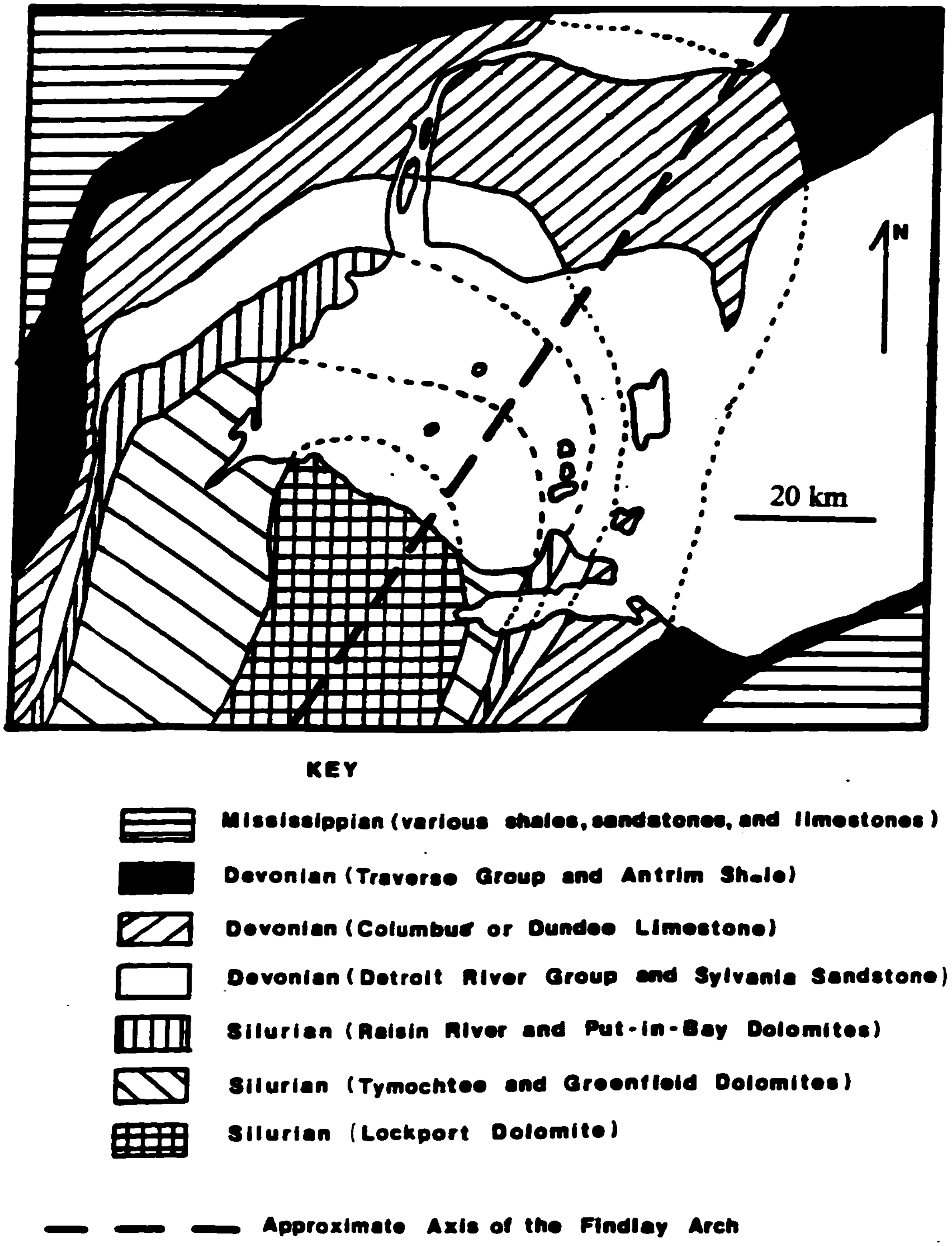

Figure 3: Geologic map of the western end of Lake Erie, with both Paleozoic rock distribution and the location of the Findlay Arch (Pryzwara, 1978).

An important structural feature that cuts across the western portion of the basin is the Findlay Arch (Figure 3). This arch, which up-warps a rim of Lower Devonian - dolomitic rocks, largely controls the form of western Lake Erie (Sly, 1976). The most notable feature of the arch is the underwater rise and the chain of islands that separates the western and central basins of the lake (Sly, 1976).

2.3 Quaternary Evolution of Lake Erie

The formation of the Lake Erie basin may have begun in the Tertiary Period (Hough, 1958). Reconstruction of early drainage patterns in the area suggests that one tributary of the Proto-St. Lawrence aligned itself along the axis of the present day lake (Sly, 1976). The main driving force for the formation of Lake Erie and the other Great Lakes was the continental glacial activity during the Quaternary Period. The shape and orientation of the Lake Erie basin was controlled by the pre-existing Tertiary drainage and the Appalachian highlands located to the south that deflected the flow of the continental ice sheets westward along the trend of the basin (Barnett, 1985). Glacial activity, besides scouring out the basin, also caused differential rock stress as a result of ice loading. These stresses were not uniform and this resulted in the lowering of the eastern and central portion of the basin relative to the western basin (Sly, 1976).

Approximately 14,500 B. P. the continental ice sheets started to retreat and with this retreat, a complex history of lake development was initiated in the area (Calkin and Feenstra, 1985). Within the Erie basin a series of eight proglacial (ice-dammed) and nonglacial low lake phases occurred as a result of repeated ice-marginal readvances, crustal warping due to glacial unloading and reloading, and downcutting of lake outlets during the retreat of continental glaciation in the region (Calkin and Feenstra, 1985). Early Lake Erie formed some 12,400 B. P. and not until 3,400 B.P. did the lake achieve a depth that was within 4 m of the present day lake (Calkin and Feenstra, 1985)

2.4 Modern Lake Erie

As the glaciers retreated they left a large amount of glacial infill within the basin. This infill varies from less then 13 m in the western basin to more than 40 m in the eastern basin of the lake (Sly, 1976). This glacial infill consists of coarse tills and fine-grained glacio-lacustrine clays that were deposited during the retreat of the glaciers. The mineralogy of the glacial infill is dominantly carbonates from local sources but a small proportion consists of igneous and metamorphic rock fragments from more distant sources (Przywara, 1978). Above the glacial infill are post-glacial sediments that range in thickness from 8 m in the western area to 26 m in the east (Sly 1976). The mineralogy of the modern sediments in the western basin, as determined by Thomas (1968), is dominated by quartz, feldspars and clay minerals which combined can contribute up to 80% of the total, with the remaining fraction being carbonates (dolomite and calcite) and organic matter in that order of significance. The clay minerals consist of approximately 70-80% illite and 20-30% chlorite and kaolinite (Thomas, 1976).

2.5 Basin Dynamics

The Western basin of Lake Erie is a very complex basin which in part is due its small volume relative to its large surface area. Minor fluctuations in air temperature, wind velocity, precipitation, and barometric pressure can cause significant changes in the characteristics of the water column and resuspend surficial sediments (Bartish, 1984). Therefore, due to the impact that daily variations in meteorological factors have on the western basin, the most accurate description of the basin dynamics is that they are highly variable (Bartish, 1984).

The main source of water inflow into the Western basin of Lake Erie is the Detroit River which accounts for over 94% of the inflow (Przywara, 1978). The remaining water is derived mainly from minor tributaries from its drainage basin that has an area of almost 29,000 km^2 (Figure 4). The majority of the drainage basin is located in Michigan, Ohio and a small part of Indiana; only three small creeks drain Essex County. The largest river in the drainage basin is the Maumee River which drains northeastern Ohio and southeastern Michigan and enters the lake near Toledo, Ohio.

The Detroit and Maumee Rivers are largely responsible for the sediments that enter the lake. The Detroit river contributes 1.4x10^9 kg/yr which is slightly less than the Maumee River's contribution of 1.8x10^9 kg/yr (Kemp et al. 1976). It should be noted that the flow rate of the Maumee river is about 1/40th of the Detroit River (Przywara, 1978). Slight differences exist between the sediments carried by both rivers. Sediments from the Detroit River tend to be mostly silt and clay sized with very little sand, while the Maumee River has a higher proportion of sand (Przywara, 1978). This is due to the Maumee River draining a flat glacial till plain which in places is covered by glaciolacustrine silts, clays and small sand ridges (Nwankwo and Walters, 1980). The entire input of sediment into the western basin is 4.4x10^9 kg/yr and the total export to the

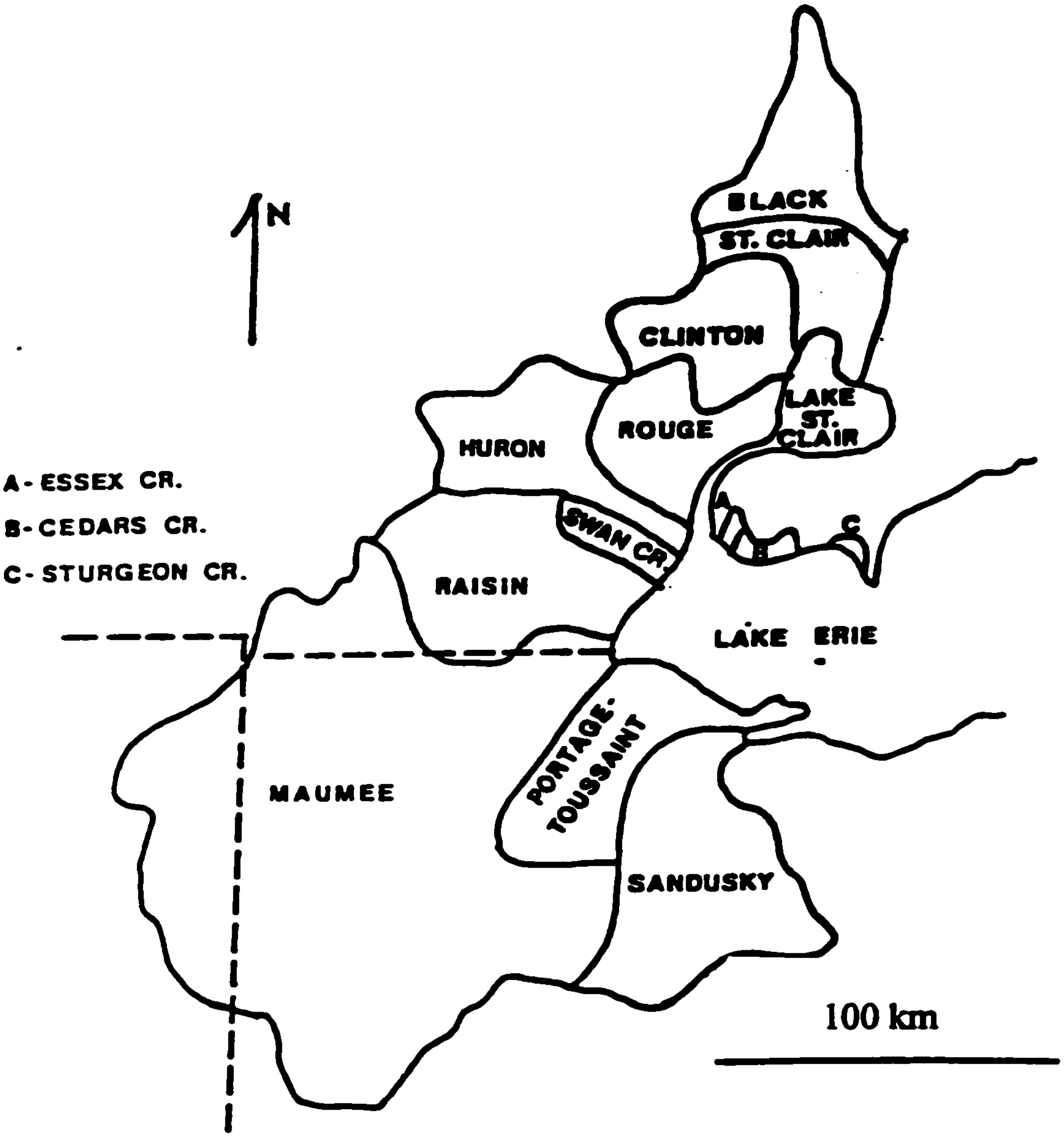

Figure 4: Drainage basin of western Lake Erie (Pryzwara, 1978).

central basin which is mainly through the south passage (Figure 7), is only $0.3\text{x}10^9$ kg/yr, producing a rate of sediment accumulation of $4.1\text{x}10^9$ kg/yr (Yahney, 1978).

Thomas et al. (1976) studied the surficial sediments of Lake Erie and concluded that in the western basin there is a high input of fine-grained sediment, and a low input of coarse-grained materials. Most of this fine-grained material remains in the western basin as little export to the Central basin occurs. Since the western basin is shallow, wave action tends to produce mixing and suspension followed by redeposition of the bottom sediments. This has been reported by Walters et al. (1974) and Williams et al. (1976b) who noted sediment mixing up to sediment depths of 14-20 cm.

The average sedimentation rate varies within the western basin but is highest at the mouths of the Detroit and Maumee Rivers. Data from Kemp et al. (1976) indicate a sedimentation rate of 6.9-7.6 mm/yr while another report by Walters and Herdendorf (1975) determined the sedimentation rate to be as high as 17.5 mm/yr. Variations are probably due to sampling location, methodology, and the complex dynamics of the western basin but it is apparent that the sedimentation rate is quite high.

Current directions are considered to be very complex in the western basin but are dominated by the Detroit and Maumee River inflows as well as wind velocity (Yahney 1978). The action of the Detroit and Maumee Rivers can be observed by the sediment plumes that extend into the western basin (Figure 5). Both plumes split up into a number of smaller plumes as they enter the western basin. Besides the sediment plumes, the Detroit and Maumee Rivers dominate the flow directions of the surface and bottom currents in the western portion of the western basin (Figure 6). In the eastern portion of the western basin near Pelee Island far from the effects of the Detroit and Maumee Rivers

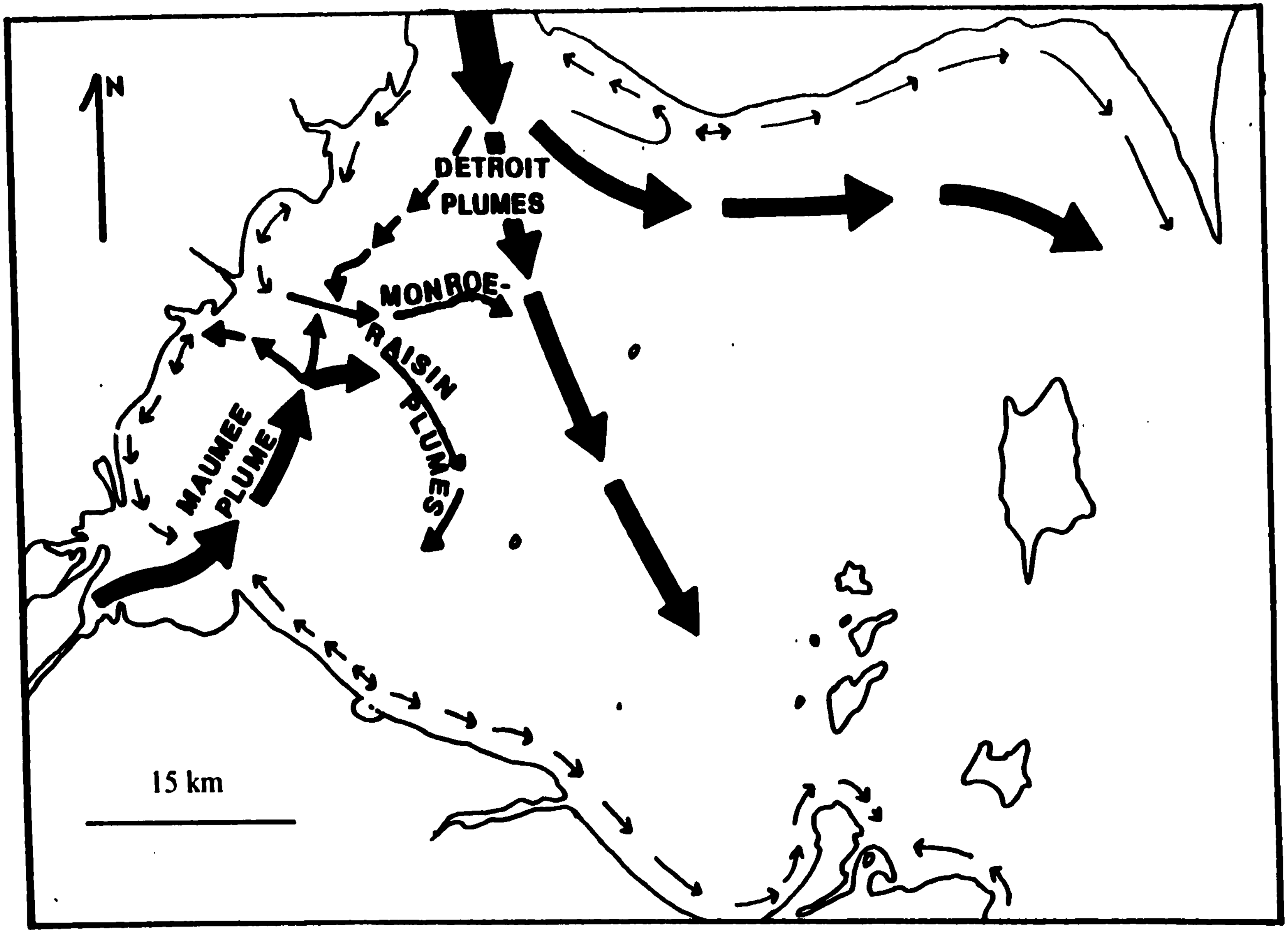

Figure 5: Generalized sediment transport in the western basin (Pryzwara, 1978).

the surface flow is dominated by the wind. The winds on average blow from the southwest but can originate from any directions and this results in quite variable surface flow patterns (Yahney, 1978).

Thermal stratification is an important phenomenon that occurs in the western basin of Lake Erie, but is very difficult to observe (Bartish, 1984). In the western basin thermal stratification occurs by two processes; meteorological, and hydromechanical (Bartish, 1984). Meteorological thermal stratification occurs during periods of high temperature and low wind velocities when a layer of warm water lies above a cooler and denser column of water. In the case of hydromechanical thermal stratification, a cooler mass of water from the central basin flows under the western basin water mass, resulting in a stratified condition (Bartish, 1984). In both situations, thermal stratification causes a rapid depletion of oxygen in the bottom waters creating an anoxic environment. Although thermal stratification in the western basin is ephemeral, sporadic, and localized in horizontal extent and therefore difficult to observe, it is an important phenomenon that occurs in the western basin and may have an important effect on the distribution of nutrients and trace metals within the basin.

2.6 Human Influence on Lake Erie

Human activity over the past few hundred years has had a significant impact on the water quality of Lake Erie. The amount of silt entering the lake has increased as much as three fold since 1850 (Kemp et al. 1974). This increase is the result of clearing, ditching and tiling of large areas of land around the basin for agriculture. The increase in silt input results in the in-filling of harbors and channels, destruction of some types of

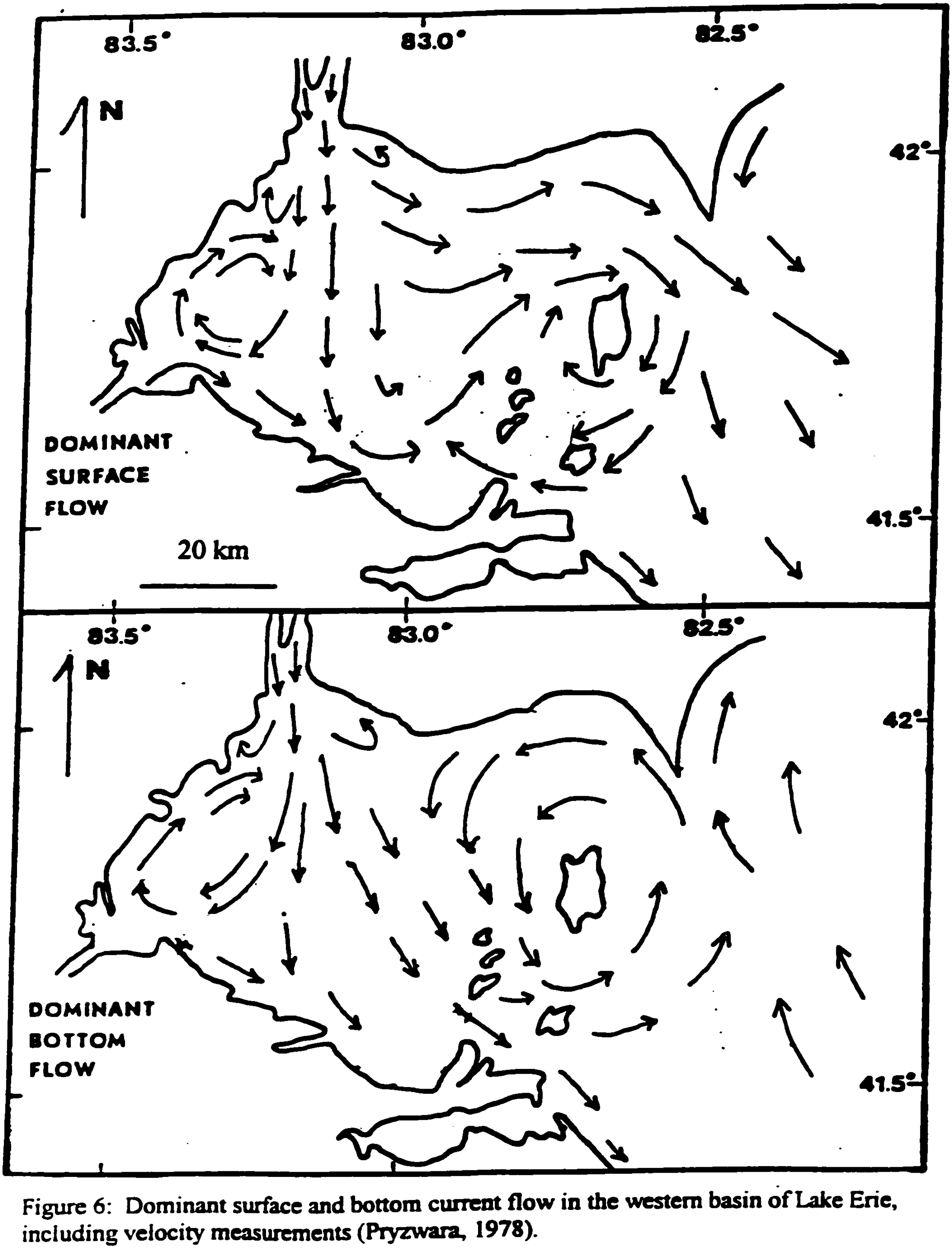

Figure 6: Dominant surface and bottom current flow in the western basin of Lake Erie, including velocity measurements (Pryzwara, 1978).

aquatic organisms and clouding of the water. An increase in the amount of nutrient elements (N and P) derived from municipal and agricultural runoff have dramatically altered Lake Erie. In the western basin and parts of the central basin the surface became coated with green algae during the late 1960's and early 1970's (Sweeney 1993). The sport and commercial fishing catches declined dramatically and populations of sheephead and carp rose. Sechi disk measures of water clarity registered readings greater than 9 m in 1928 and were reduced to 7-14 cm. in the 1960's and 1970's (Sweeney 1993). Steps were initiated to reduce nutrient loading by limiting phosphate content in detergents, changing farming practices and upgrading sewage treatment plants. These steps have resulted in a reduction of the amount of nutrients that enter the lake, but levels are still considered well above natural levels (Sweeny 1993).

The introduction of a large variety of organic chemicals and an increase in the concentration of a number of transition metals entering Lake Erie due to human activity has had a less visible yet still important affect on the lake ecosystem. The primary sources of the transition metals and organic chemicals are from industrial and municipal activity. Transition metals are also derived from the weathering of sediments. Geological weathering is the source for the baseline or background levels and is dependent on the geology of the area. Mudroch et al. (1988) have reviewed a number of studies that have measured background levels of some transition metals in western Lake Erie and found low levels indicating that no natural sources exist for the high levels that are currently found in the surficial sediments. Industrial effluent is the main source of the transition metals in western Lake Erie. Areas of intensive industrial activity are found in Detroit, Windsor and Sarnia. A number of transition metals are used extensively in electroplating, steel production, catalysts for petrochemical process, and a wide variety of other industrial activities. Atmospheric fallout derived from the burning of fossil fuels and cement production are also a source of transition metals. The urban centres surrounding the western basin are home to a number of cement producers, foundries, coal-fired power plants and a large number of automobiles. The fallout enters the lake directly by deposition on the surface of the lake or through storm runoff. In the case of storm runoff, the fallout is first deposited within the drainage basin and is washed into the lake via the tributaries during a rain or snow melting event.

A number of studies have been conducted on the western basin of Lake Erie to determine the concentration of trace metals within the sediment. For an excellent review, refer to Mudroch et al. (1988). The trace metals studied are those that are extensively used in industrial activity and include As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn. These studies generally conclude that the highest concentrations of these metals are found near the mouth of the Detroit River at the river-lake interface (Mudroch, 1985; Lum and Gammon, 1985). The results of these studies have been compared to the results of this study and can be found in the discussion.

A number of studies have used sediment cores to measure changes in elemental concentration with depth (Walters Jr., et al. 1974; Wolery and Walters Jr., 1974; Kemp et al. 1976; Nriagu et al. 1979). In all cases, a decrease in trace metal concentration with depth occurs while major element concentrations tend to remain generally uniform with depth. Preliminary research on the partitioning of trace metals in Lake Erie and the Detroit River concluded that most of the trace metals are associated with Fe-Mn oxides and that the concentration of trace metals increases downstream in the Detroit River towards Lake Erie (MacFarlane et al. 1996; Shwetz et al. 1997).

CHAPTER 3

METHODS OF INVESTIGATION

3.1 Sample Collection and Preservation

Sediment samples were collected from April through September of 1996 using boats provided by the Great Lakes Institute for Environmental Research (G.L.I.E.R.). The sampling sites were taken at the intersections of a 9 x 9 km grid with precise locations being determined in the field with the use of a Global Positioning System unit (Figure 7). A total of twenty sites covering the north and western sections of the western basin of Lake Erie were used in this study. All sediment samples were obtained from the lake bottom using a Petite Ponar grab sampler. Immediately after the sediment samples were brought to the surface they were wet sieved through a 63 micron nylon mesh. Small amounts of lake water were used in order to facilitate the wet sieving process. After a sufficient amount of sediment was wet sieved, the sample was placed in a polyethylene bag, placed in a cooler, taken back to the lab, and frozen until later analysis. A bulk sediment sample was also taken for mineralogical analysis and was also stored in a polyethylene bag and frozen until analysis.

3.2 Sequential Extraction Procedure

Geochemical analysis of sediment has progressed from the simple technique of total element analysis to more complex techniques involving the determination of how elements are partitioned within sediment. Partitioning data can provide information regarding what types of sediment-forming material with which an element may be associated with. In lacustrine sediments the most common materials are: 1) detrital

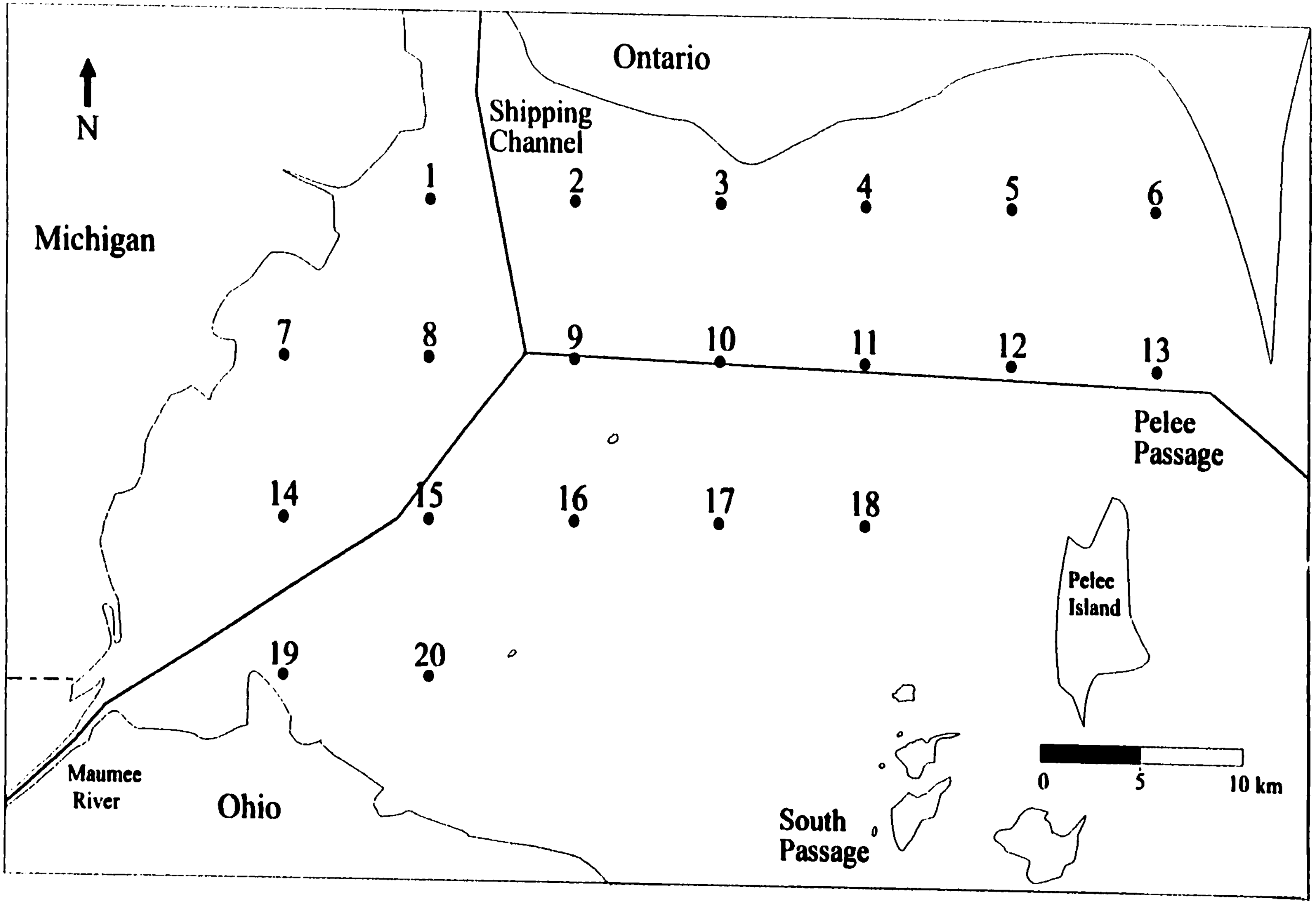

Figure 7. Map of the western basin of Lake Erie showing location of the sample sites and shipping channels.

grains such as quartz and feldspars; 2) products of weathering such as clay minerals; 3) organic matter, and 4) authigenic precipitates that may be discrete grains or coatings on existing minerals. Partitioning data can also reveal information regarding how an element is associated with the various sediment forming materials. Elements may be: 1) adsorbed; 2) coprecipitated with authigenic minerals; 3) complexed by organic matter, and 4) incorporated in crystalline minerals (Forstner and Wittmann, 1983). Partitioning data can potentially reveal a great deal of information regarding the mobility and the possible source(s) of an element. For example, trace metals incorporated in detrital grains are involved in strong chemical bonding and are relatively immobile. In addition, the primary detrital grains are relatively stable in the lacustrine environment. On the other hand an element that is adsorbed onto the surface of an authigenic Mn-oxide is much more mobile since adsorption type bonding involves electrostatic attraction which is much weaker than chemical bonding. In addition the Mn-oxide itself is subject to dissolution in reducing conditions that are commonly encountered in the lacustrine environment. Determining the possible source(s) of an element contained in a sediment is complicated and requires a knowledge of the mineralogy, type(s) of element associations (e.g. adsorption or coprecipitation), and transportation pathways.

The most important components in terms of trace metal partitioning are the Fe-Mn oxides and organic matter (Chao, 1984). A large number of Fe and Mn oxides, hydroxides, and oxyhydroxides with varying degrees of crystallinity exist in the lacustrine environment. It is very difficult to distinguish among the various types and in addition, the oxides of Fe and Mn tend to form together as mixed oxides and therefore it is easier to study them together (Forstner and Wittmann, 1983). For convenience the term Fe-Mn oxides will be used when discussing this group. Organic matter consists of the remains of biologically-produced compounds and synthetic organic substances. A wide variety of organic substances exists in the lacustrine environment but no distinction between the various substances will be made in this study.

A large number of chemical extraction techniques have been developed to study the partitioning of elements between the various components of a sediment. These extraction techniques are referred to as selective extractions or partial dissolution techniques (Chao, 1984). The basic idea is that the reagents employed will (1) dissolve a specific component of the sediment (e.g. organic matter or carbonates) releasing elements that were associated with that sediment-forming component, or (2) the reagents will selectively remove those elements that are adsorbed to the surface of sediment-forming components. The choice of which sediment-forming component(s) to study and which reagent(s) to use is highly dependent on the objectives of the project and the composition of the sediment being studied. It is possible to apply the selective extraction techniques in sequence to remove elements from a specific component while minimizing the removal of elements from the other components. This type of procedure is called a selective sequential extraction and was first proposed by Chester and Hughes (1967). Since then many studies have been conducted using a variety of reagents. Chao (1984) and Hall et al. (1996a) provide excellent summaries of the numerous extraction procedures found in the literature. There is no general agreement in the literature on which procedure is the 'best'. The most appropriate procedure is determined by the objectives of the study, the composition of the sediment and the elements that are to be studied. The most commonly employed selective sequential extraction procedure to date is that of Tessier (1979). This procedure has been extensively studied and forms the basis for the majority of the selective sequential extraction procedures found in the recent literature (Howard and Shu, 1995; Stone and Droppo 1996; Li et al. 1995; Hall et al. 1996a). Of course, limitations exist with selective sequential extractions. A number of studies have shown that resorption of released elements occurs and that problems exist with the selectivity of the reagents used (Kheboian and Bauer, 1987; Xiao-Quan and Bin, 1993). The selectivity of the reagents is a problem because it is unrealistic to assume that a reagent will only attack one specific type of material. In addition, the results are highly dependent on such factors as reagent strength, reaction time, temperature, and a number of other factors and, therefore, most authors report results as operationally defined (Hall et al., 1996a; Howard and Shu, 1995). Despite these drawbacks, it is thought that selective sequential extractions are still very useful if the data are collected and interpreted carefully (Tessier and Campbell, 1988; Forstner, 1989).

The method chosen for this study is a modification of the procedure developed by Hall et al. (1996a) which is based on the procedure of Tessier et al. (1979). The procedure consists of three extractions which are designed to examine: 1) elements adsorbed onto the surface of sediment forming material and bound to carbonates (AEC); 2) elements bound to organic matter; and 3) elements bound to Fe-Mn oxides. These fractions were chosen because trace metals associated with anthropogenic trace metal pollution are expected to be found in these fractions. Figure 8 is a flow chart of the sediment analysis procedure, in addition a detailed description of the procedure can be found in Appendix I. Na-Acetate was chosen for the first reagent because it has been extensively used in previous studies for the dissolution of carbonates and has also been used to remove elements adsorbed on the surface of sediment-forming material (Han and Banin, 1995; Hall et al. 1996a; Chao, 1984; Tessier et al. 1981). In addition, it has been shown that Na-Acetate does not attack Fe-Mn oxides or organic matter (Chao, 1984). It was decided to extract elements from organic matter in the second step because the reagents employed for the dissolution of Fe-Mn oxides can also attack organic matter (Chao, 1984). Na-pyrophosphate was chosen as the second reagent because it is considered the most selective of the reagents used to destroy organic matter (Hall et al. 1996b). And finally, hydroxylamine hydrochloride was chosen as the reagent for the third step because it has been used extensively for the dissolution of Fe-Mn oxides (Tessier et al. 1979; Chao and Zhou, 1983; Hall et al. 1996a).

All reagents used for the sequential extraction procedure were of Analar grade and de-ionized water (resistivity 18 M ohms • cm) was used throughout the study. All pipettes, tubes and containers were soaked in 13% nitric acid for 24 hours followed by 24 hours in de-ionized water and finally rinsed three times with de-ionized water. All supernatants were filtered through Whatman #40 filter paper that was rinsed twice in 5% nitric and three times with de-ionized water. Sediment samples were first thawed to room temperature and then homogenized. After homogenization, approximately 10 grams of sediment was taken for the sequential extraction. Porewater was removed first by centrifuging at 7000 rpm for 15 minutes. After removal of the porewater a 0.5 gram subsample was collected from the centrifuge tube and used for the sequential extraction. Extractions were performed in batches of nine which consisted of one blank, one internal reference sample (SED), one certified reference standard (LKSD-4), and six samples. The internal reference material (SED) consisted of a large bulk sample of Lake Erie

SEDIMENT ANALYSIS PROCEDURE

Porewater Removal

Bulk sediment sieved to isolate the
<63 µm size fraction

↓

Porewater removed by
centrifugation at 7 000 rpm for 15 minutes

↓

0.5 gram subsampled from dewatered sediment

↓

Sodium Acetate Extraction

10 mL of 1.0 M NaOAC (adjusted to pH 5 with concentrated HNO_3)
Agitated for 6 hours at room temperature
Centrifuged at 6 000 rpm for 10 minutes
Supernatant filtered into 60 mL polypropylene bottle
Sediment rinsed with 2.5 mL of deionized water and centrifuged twice
Rinse water filtered and added to supernatant

↓

Sodium Acetate extraction repeated
Supernatant filtered and added to previous supernatant
Sediment rinsed rinsed with 2.5 mL of deionized water and centrifuged twice
Rinse water filtered and added to supernatant

Figure 8: Flow chart of the of the sediment analysis procedure.

Sodium Pyrophosphate Extraction

Add 35 mL of 0.1 M $Na_4P_2O_7$ (adjusted to pH 10 with concentrated HNO_3)
to the sediment previously reacted with the sodium acetate reagent
Agitated for 1 hour at room temperature
Centrifuged at 6 000 rpm for 10 minutes
Supernatant filtered into a 125 mL polypropylene bottle

Sodium Pyrophosphate extraction repeated
Supernatant filtered and added to previous supernatant
Sediment rinsed with 2.5 mL of deionized water and centrifuged twice
Rinse waters filtered and added to supernatant

Hydroxylamine Hydrochloride Extraction

Add 15 mL of 1.0 M $HN_2OH.HCL$ (adjusted to pH 2 with concentrated HNO_3)
to the sediment previously reacted with the sodium pyrophosphate reagent
Placed in 90 °C water bath for 3 hour and occasionally agitated
Centrifuged at 6 000 rpm for 10 minutes
Supernatant filtered into 60 mL polypropylene bottle
Sediment rinsed with 5.0 mL of 25% HOAc solution and centrifuged twice
Rinse water filtered and added to supernatant

Hydroxylamine Hydrochloride extraction repeated
Placed in 90 °C water bath for 1.5 hours and occasionally agitated
Supernatant filtered and added to previous supernatant
Sediment rinsed with 5.0 mL of 25% HOAc solution and centrifuged twice
Rinse water filtered and added to supernatant

Figure 8 (continued)

sediment that was collected with a Petite Ponar grab sampler. The sample was dried, crushed, and homogenized. The results for the internal reference material forms the basis for the quality control on the procedure.

The elements chosen for this study were Fe, Mn, Ca, Mg, Zn, Ni, Cr, and Cu. The major elements Fe, Mn, Ca, and Mg were chosen because they are the main elements of Fe-Mn oxides and carbonates. The trace elements studied were chosen because these metals are used extensively in industry in this area.

Solutions were analyzed at the University of Windsor using an ARL Maxim ICP-OES. The sodium acetate and hydroxlyamine hydrochloride solutions were analyzed without dilution but due to the high salt content, the sodium pyrophosphate had to be diluted before analysis. The instrument was calibrated using known standards and corrected for drift by analyzing a known standard after each batch of nine samples. An in-house reference solution was also analyzed to check precision and accuracy of the instrument.

In order to obtain more information about the mineralogical and chemical changes that were taking place during the sequential extraction procedure, duplicates of three samples were compromised by removing a small amount of sediment after each step of the extraction procedure. The sediment was subjected to x-ray diffraction analysis which is discussed below. In addition, the pH of the supernatants were measured and compared to the pH of fresh reagent. The pH measurements were done to determine if the reactions took place within the recommended pH ranges of the particular extraction procedure.

3.3 X-Ray Diffraction Analysis of the Sequential Extraction Residues

Three samples were selected to determine the mineralogical changes that occurred to the sediments during the sequential extraction procedure. It was not known how much variation with respect to mineralogy existed within the study area and therefore, the three sites chosen were thought to represent the various sub-environments of the western basin. The three samples selected were from the mouth of the Detroit River (site 1), from Pigeon Bay located west of Point Pelee and away from these river inputs (site 6), and near the mouth of the Maummee River (site 19). In order to determine the mineralogical changes that occurred during the sequential extraction procedure, small amounts of sediment were removed from the centrifuge tubes after each step of the procedure was completed. The reacted sediments subsamples were then smeared on glass slides and allowed to air-dry. A small amount of sediment was also taken before the procedure started to determine the original mineralogy. A total of seven glass slide preparations were created for each sample. The reacted sediments were then analyzed at the University of Windsor using an x-ray diffractometer with power settings of 40 kV, and 20 mA using CuKα radiation. Samples were scanned from $3°2\theta$ to $60°2\theta$ at a 0.5° step interval and a scan rate of 1° per minute. The identification of minerals was aided by the use of computer software and the Joint Committee on Powder Diffraction Standards (J.C.P.D.S.) search manuals.

3.4 Major Element Procedure

The <63 micron size fraction of the sediment samples were analyzed for major elements (Si, Al, Fe, Mg, Ca, Na, K, Ti, and Mn) using the alkali-fusion technique (Z.

Chen, personal comm.). A 0.5 gram sample that had been dried at 100°C for 24 hours was mixed with 1.0 gram of lithium metaborate and 0.5 grams of lithium tetraborate in a graphite crucible. The contents were thoroughly mixed and then the graphite crucible was placed in a muffle furnace at 900°C for 30 minutes. At the 20 and 25 minute periods the graphite crucibles were stirred to ensure complete homogenization of the sample. After 30 minutes the melt was poured into a polyethylene beaker containing 150 mL of de-ionized water, 10 mL of 0.8% ethylediaminetetraacetic acid (EDTA) solution and 10 mL of concentrated HNO_3. A stirring bar was added and the sample stirred until complete dissolution was achieved (approx. 30 minutes). The solution was then filtered through a dry #42 filter paper into a 500 mL polyethylene bottle and the solution brought to 250 mL with de-ionized water. Solutions were analyzed in batches of nine with seven samples, one blank and one standard reference material (LKSD-4). The solutions were analyzed at the University of Windsor using an ARL Maxim ICP-OES. The instrument was calibrated using matrix matched standards and corrected for drift by analyzing a known standard after each batch of nine samples. An in-house reference solution was also analyzed to check precision and accuracy of the instrument. Loss on ignition was also performed on the dried sediment samples. Sediment samples were dried in an oven overnight at 100 °C. One gram of dried sediment was measured into a porcelain crucible of known weight and the crucible was placed in an oven at 1000°C for 30 minutes. The difference in weight, before and after ignition is the loss calculated as a percent.

3.5 Total Carbon, Nitrogen and Sulphur Analysis

Total carbon, nitrogen, and sulphur were determined with a CE Instruments EA-1110 Elemental Analyzer at the University of Ottawa. The samples were placed on a automatic sampler with standards at the beginning and end of the batch. A sample is dropped in a combustion tube and 'dynamic flash combustion' occurs at 1800°C. The gases are separated in a packed column GC and measured on a TCD detector. The precision of the method for carbon, nitrogen and sulphur is +/- 0.3%, 0.1%, and 0.2%, respectively.

3.6 Grain-Size Analysis

Grain-size analysis was done on the bulk sediment samples with a Laser CILAS 715-B granulometer at the University of Uppsala, Sweden. Reproducibility expressed as one standard deviation was <5%. All samples were passed through a 200 micron sieve before the analysis. The amount of the >200 micron size is not given because most samples contained shell fragments which can give rise to a bimodal distribution (Aldahan, personal comm.).

CHAPTER 4

RESULTS

4.1 Sequential Extraction Procedure

One of the experiments conducted during the sequential extraction procedure was the comparison of the pH of fresh reagent to that of reagent that had reacted with the sediment used in this study. This was done to determine if the reactions took place within the desired pH range of the particular extraction procedure. The sediment samples used were the same samples that were compromised to obtain the XRD sample. The results of this experiment are given in Table 1 and indicate that the difference in pH between fresh reagent and reagent that has reacted with the sediment is very small. In each step the pH of the final supernatants were well within the recommended pH ranges for the extractions as suggested by Chao (1984) and Han and Banin (1995).

The solid detection limits for each element studied are given in Table 2. A range of solid detection limits is given because the measured values are based on the instrument detection limit, the water content, and weight of each sediment sample. Since the water content and weight of each sample varied, the solid detection limit was calculated for each individual sediment sample. Concentrations below the solid detection limit are reported as <DL. Results of the sequential extraction procedure are found in Appendix II. Results of mean, standard deviation and relative standard deviation (RSD) from the analysis of SED the internal reference material (Lake Erie sediment) are given in Table 3. Table 4 summarizes the ranges in concentration that were found in each of the three steps of the extraction procedure. The sequential extraction procedure produced a large

Table 1: Initial pH of reagents and pH of supernatants after completion of 2nd treatment with reagents.

	AEC Extraction		Organic Extraction		Fe-Mn oxide Extraction	
	Initial pH	Final pH	Initial pH	Final pH	Initial pH	Final pH
Batch						
1	5.2	5.3	10.4	10.0	1.1	0.9
2	5.2	5.3	10.3	9.4	1.1	1.0
5	5.2	5.2	10.0	9.8	1.1	1.1
6	5.2	5.3	10.2	9.5	1.1	1.0
9	5.2	5.3	10.1	9.7	1.1	1.0
10	5.2	5.3	10.1	10.0	1.1	1.1
11	5.2	5.3	10.1	10.0	1.1	1.0

Table 2: Minimum and Maximum Solid Detection Limits for the three extractions. Refer to text for explanation. Concentrations in μg/g.

Element	AEC Extraction		Organic Extraction		Fe-Mn oxide Extraction	
	Min.	Max.	Min.	Max.	Min.	Max.
Fe	72	271	112	510	79	335
Mn	0.1	0.7	0.3	1.8	0.2	0.7
Ca	7.7	34.6	16.5	75.2	10.3	40.8
Mg	8.2	36.6	23.4	106	13.3	52.1
Zn	0.6	2.9	1.4	6.5	0.9	3.8
Ni	0.7	3	0.8	4.7	0.7	2.8
Cr	0.4	1.6	0.5	2.1	0.3	2
Cu	2.7	14.3	1	6.5	0.5	2.3

Table 3: Mean, standard deviation (in μg/g) and Relative Standard Deviation (in percent) for Fe, Mn, Ca, Mg, Zn, Ni, Cr, and Cu in the three extractions and Aqua Regia digest. Based on replicate analysis of internal reference material SED (n=10).

Element	AEC Extraction			Organic Extraction			Fe-Mn oxide Extraction			Sum of Three Extractions			Aqua Regia Digest [1]		
	Mean	SD	RSD	Mean	SD	RSD	Mean	SD	RSD	Mean	SD	RSD	Mean	SD	RSD
Fe	2000	120	6.0	2970	206	6.9	25600	3400	13.3	31500	3300	10.4	30200	1230	4.1
Mn	306	21.3	7.0	17.3	1.3	7.5	309	33.3	10.8	650	32	4.9	572	7.3	1.3
Ca	18800	1130	6.0	1190	109	9.2	21100	2410	11.4	42000	1800	4.3	30800	411	1.3
Mg	8700	569	6.5	836	76	9.1	15700	1650	10.5	26000	660	2.5	22200	531	2.4
Zn	101	5.5	5.4	16.4	2.2	13.4	201	17.3	8.6	326	11.5	3.5	296	9.9	3.4
Ni	16.1	0.9	5.6	3.6	0.6	16.7	47.4	4.8	10.1	66.6	6.1	9.1	65.9	3.1	4.7
Cr	7.8	0.4	5.1	18.1	2.2	12.2	75.2	7.9	10.5	104	7.8	7.5	100	2.8	2.8
Cu	22.6	2.0	8.8	20.7	0.7	3.4	53	5.4	10.2	98.4	4.9	5.0	89.3	2.0	2.3

[1] Values obtained from G.L.I.E.R. laboratory (n=4).

Table 4: Summary of min., max, and median values (μg/g) obtained in each extraction step from Lake Erie seJiments.

Element	AEC Extraction			Organic Extraction			Fe-Mn oxide Extraction			Sum of Three Extractions		
	Min.	Max.	Median	Min.	Max.	Median	Min.	Max.	Median	Min.	Max.	Median
Fe	1030	3890	1870	1870	5800	3410	12300	29200	24800	15500	37900	29700
Mn	178	464	289	9.6	24	15	154	315	251	342	774	536
Ca	9640	30000	19300	<DL	1570	1070	1810	33100	10700	13300	49300	31100
Mg	4240	13100	7740	486	1160	938	4880	23100	8970	10800	30000	17800
Zn	8.1	209	71	<DL	25.2	11	73.5	201	150	91	389	228
Ni	3	31	13	<DL	6.8	3	13.3	54	36	16	88	49
Cr	<DL	20.3	4	<DL	38.7	23	10.3	115	52	10.3	173	74
Cu	<DL	24.5	12	3.5	23	12	<DL	61.6	24	11.3	106	48

number of results and it is difficult to observe patterns and trends when the data is kept in this raw format. Therefore, the data has been presented visually to convey the information in a simple and easy to understand format. Two types of bar charts were created to display the data. The first type of bar chart displays the results from each extraction step as a percent of the total of the three extraction steps (Figures 9 and 10). These charts are used to examine the partitioning of the elements and to examine the variations in the partitioning throughout the study area. The second type of bar chart displays the sum of three extractions steps in µg/g (Figures 11 and 12). These charts are used to examine the variations in total extractable element concentrations throughout the study area.

4.2 X-Ray Diffraction Analysis Of The Sequential Extraction Residues

The results of the XRD analysis are strictly qualitative and abundances of the individual minerals were not determined. Partial plots of the XRD analysis for the three samples are given in Figures 13, 14, and 15. The detectable minerals of the untreated sediments are: quartz, dolomite, calcite, feldspars, chlorite, and illite. The only variation observed in the untreated sediments is the lack of a detectable calcite peak in the ite six sample (Figure 14). The only observed change to the XRD patterns of the sediments after the first sodium acetate extraction step was the loss of the calcite peaks for samples from sites one and nineteen (Figures 13 and 15). The XRD traces of the second sodium acetate extraction show a slight decrease in the dolomite peak (Figures 13 to 15). This may or may not be due to partial dissolution of dolomite. The XRD patterns of the organic extraction steps show no apparent change in mineralogy (Figures 13 to 15).

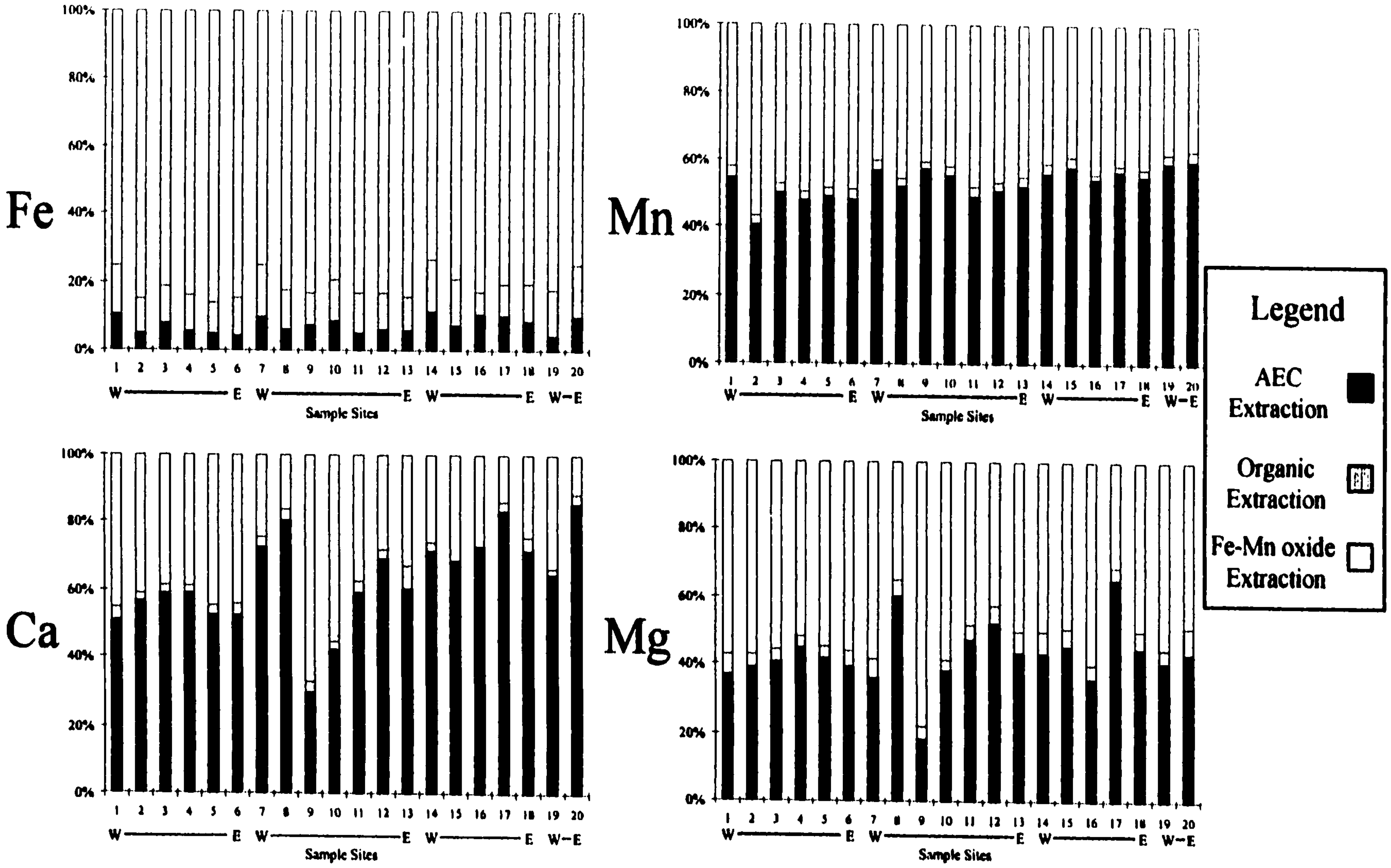

Figure 9: Bar charts showing the results of the sequential extractions for Fe, Mn, Ca, and Mg. Each fraction is expressed as a percent of the sum of the three extractions. Refer to Figure 7 for location of samples sites. Sites with W or E beneath are located at the western and eastern edges of the sampling area.

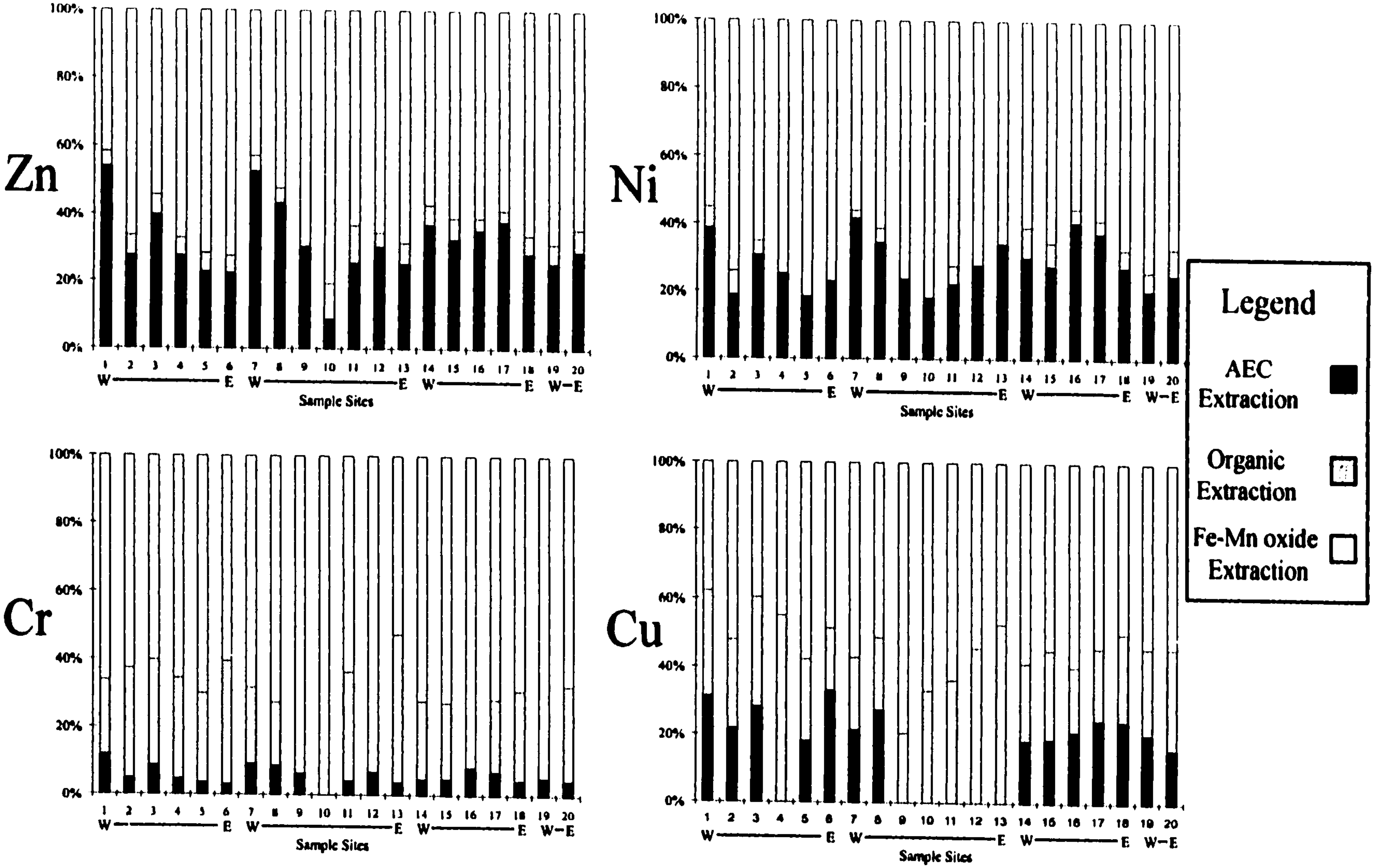

Figure 10: Bar charts showing the results of the sequential extraction for Zn, Ni, Cr, and Cu. Each fraction is expressed as a percent of the sum of the three extractions. Refer to Figure 7 for location of samples sites. Sites with W or E beneath are located at the western and eastern edges of the sampling area.

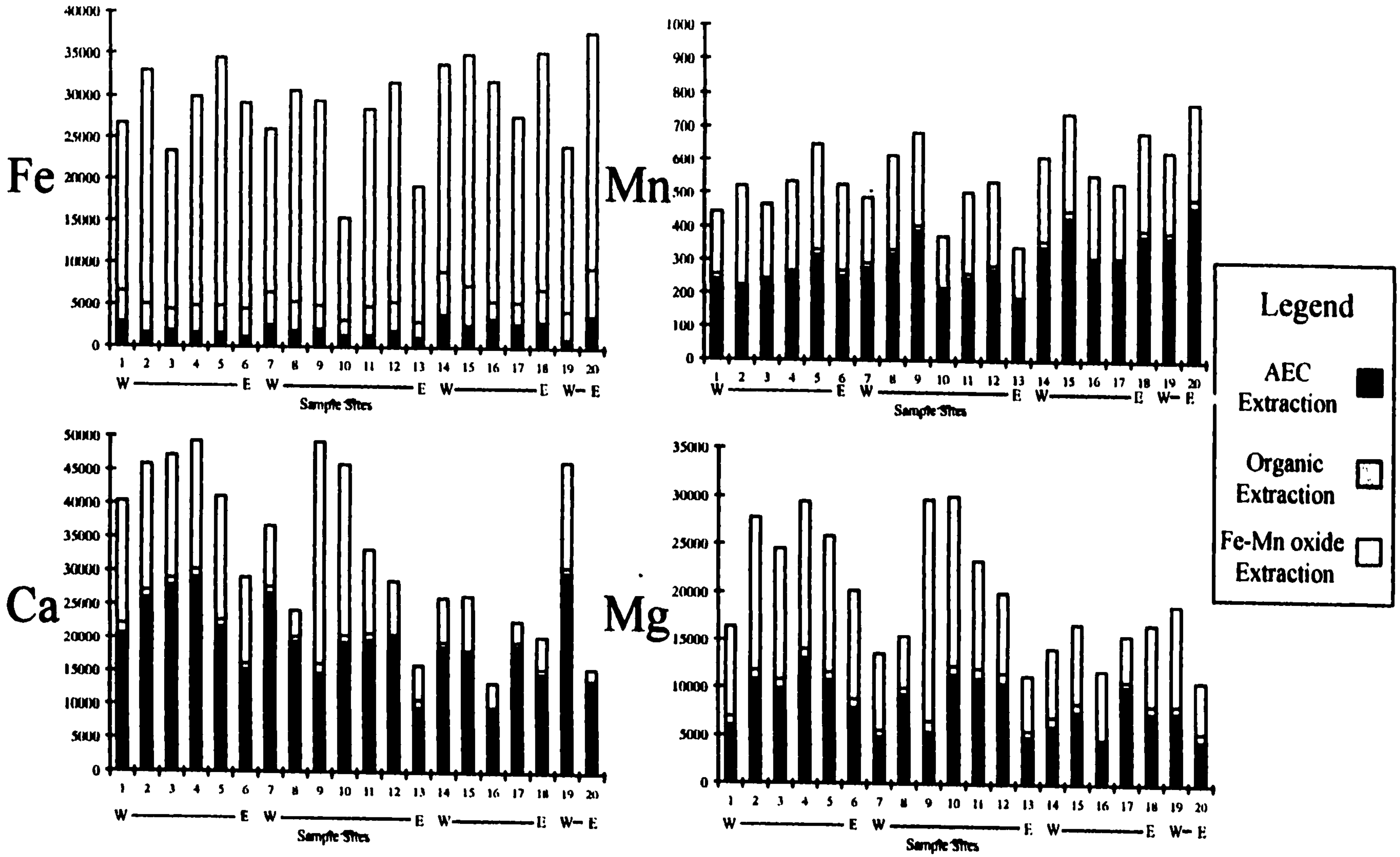

Figure 11: Bar charts showing the results of the sequential extractions for Fe, Mn, Ca, and Mg. Results are in µg/g. Refer to Figure 7 for location of samples sites. Sites with W or E beneath are located at the western and eastern edges of the sampling area.

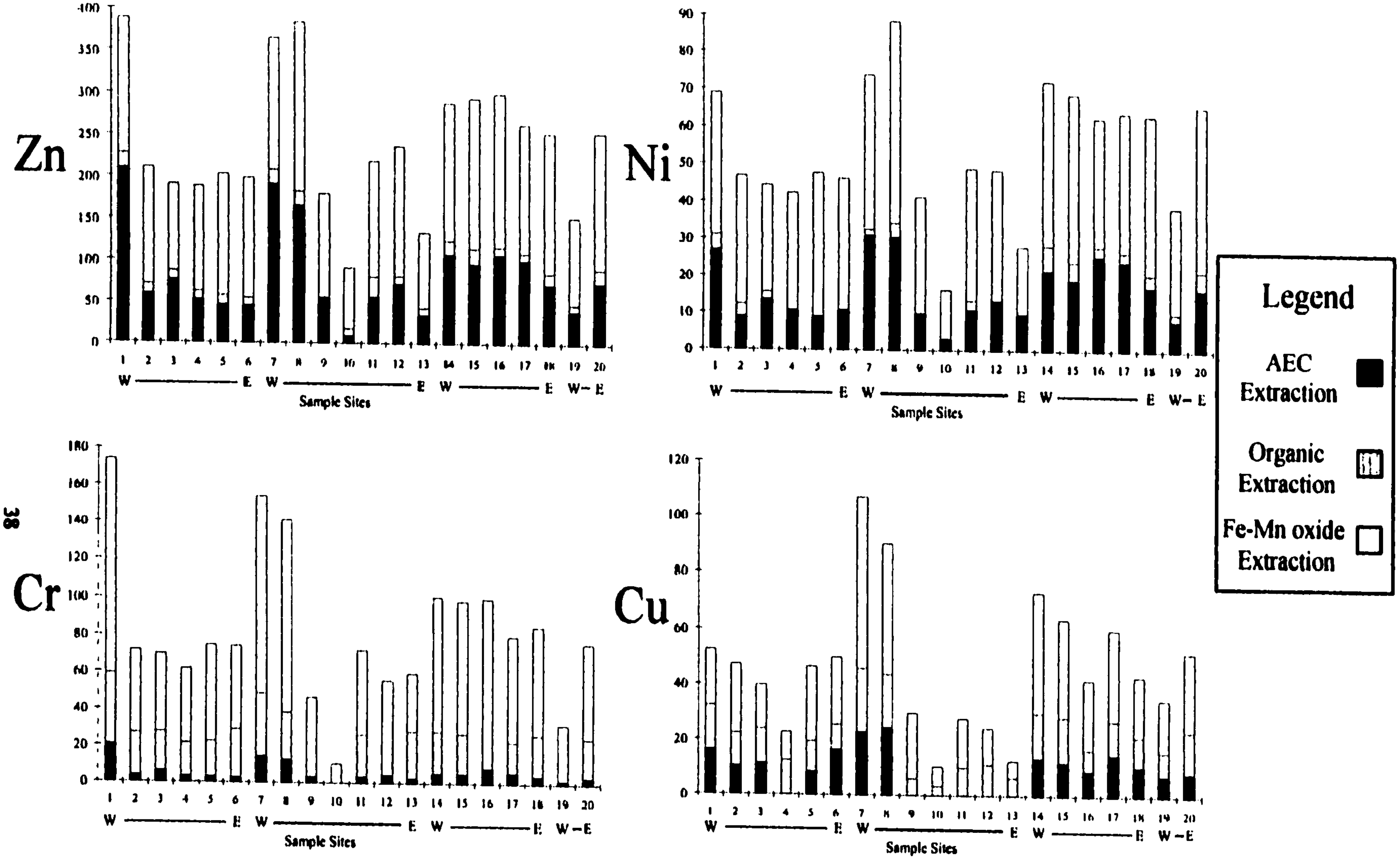

Figure 12: Bar charts showing the results of the sequential extraction for Zn, Ni, Cr, and Cu. Results are in μg/g. Refer to Figure 7 for location of samples sites. Sites with W or E beneath are located at the western and eastern edges of the sampling area.

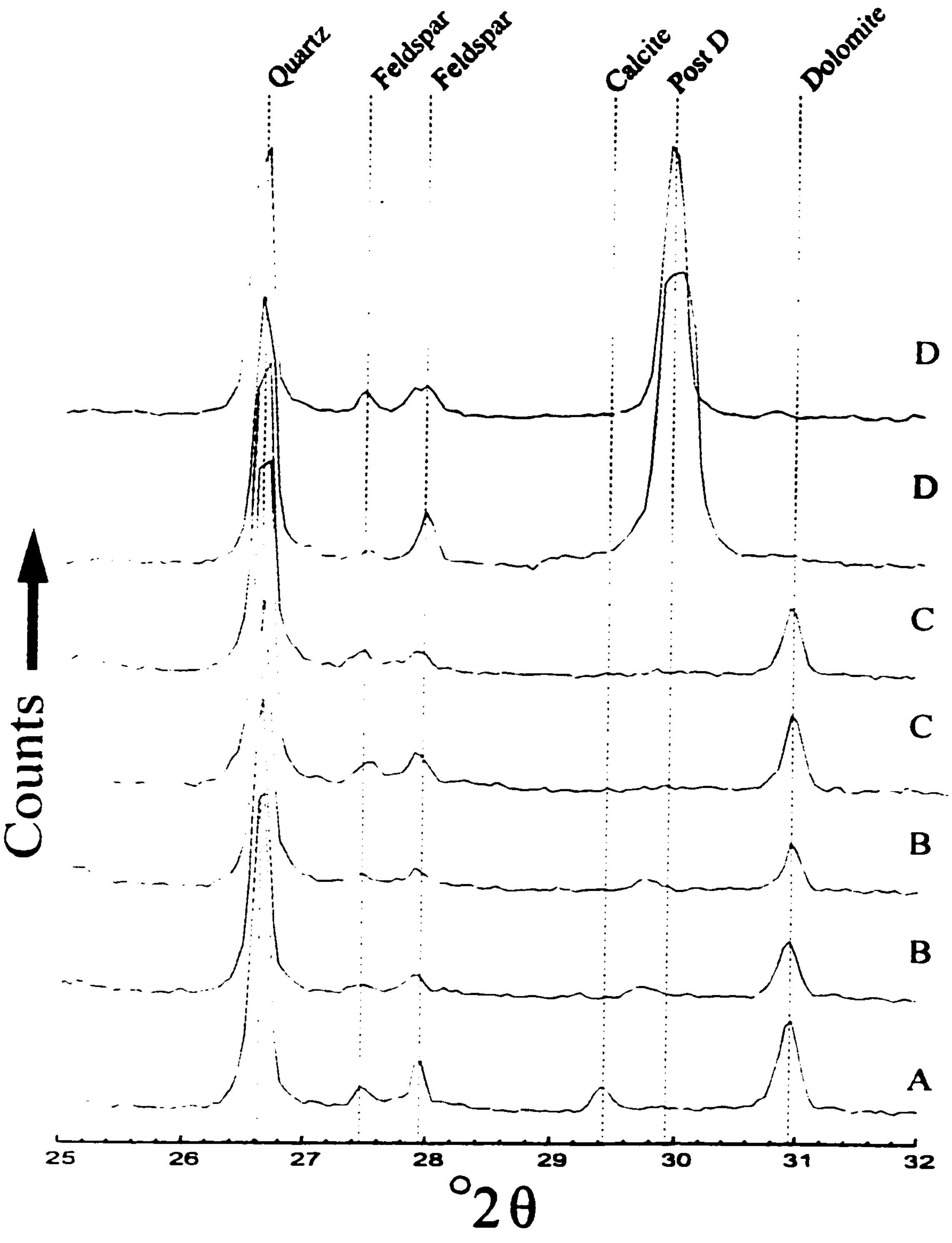

Figure 13. X-Ray diffraction patterns of residues from site one. A) untreated B) after treatment with NaOAC C) after treatment with $Na_4P_2O_7$ D) after treatment with $NH_2OH \cdot HCL$.

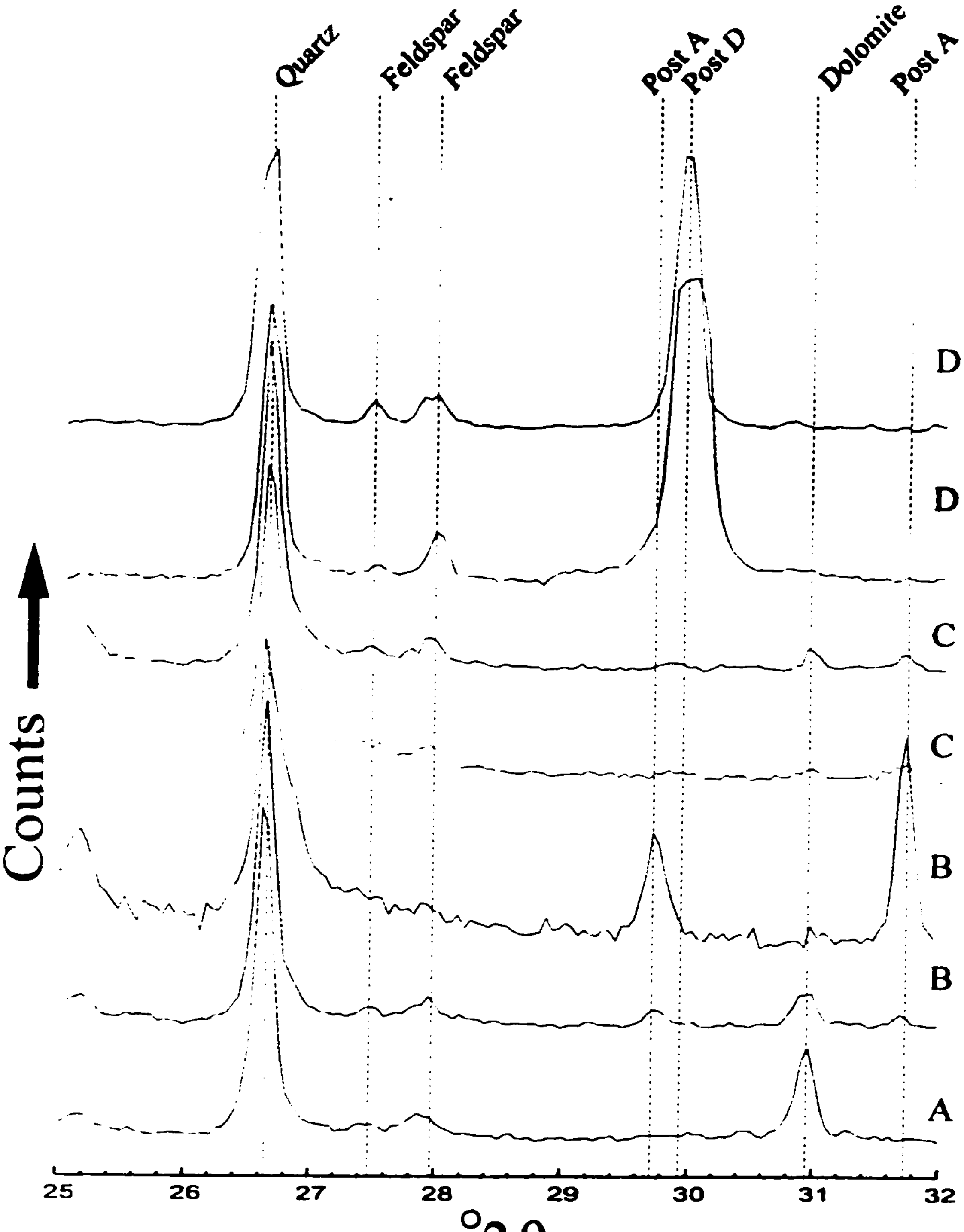

Figure 14. X-Ray diffraction patterns of residues from site six. A) untreated B) after treatment with NaOAC C) after treatment with $Na_4P_2O_7$ D) after treatment with $NH_2OH \cdot HCL$.

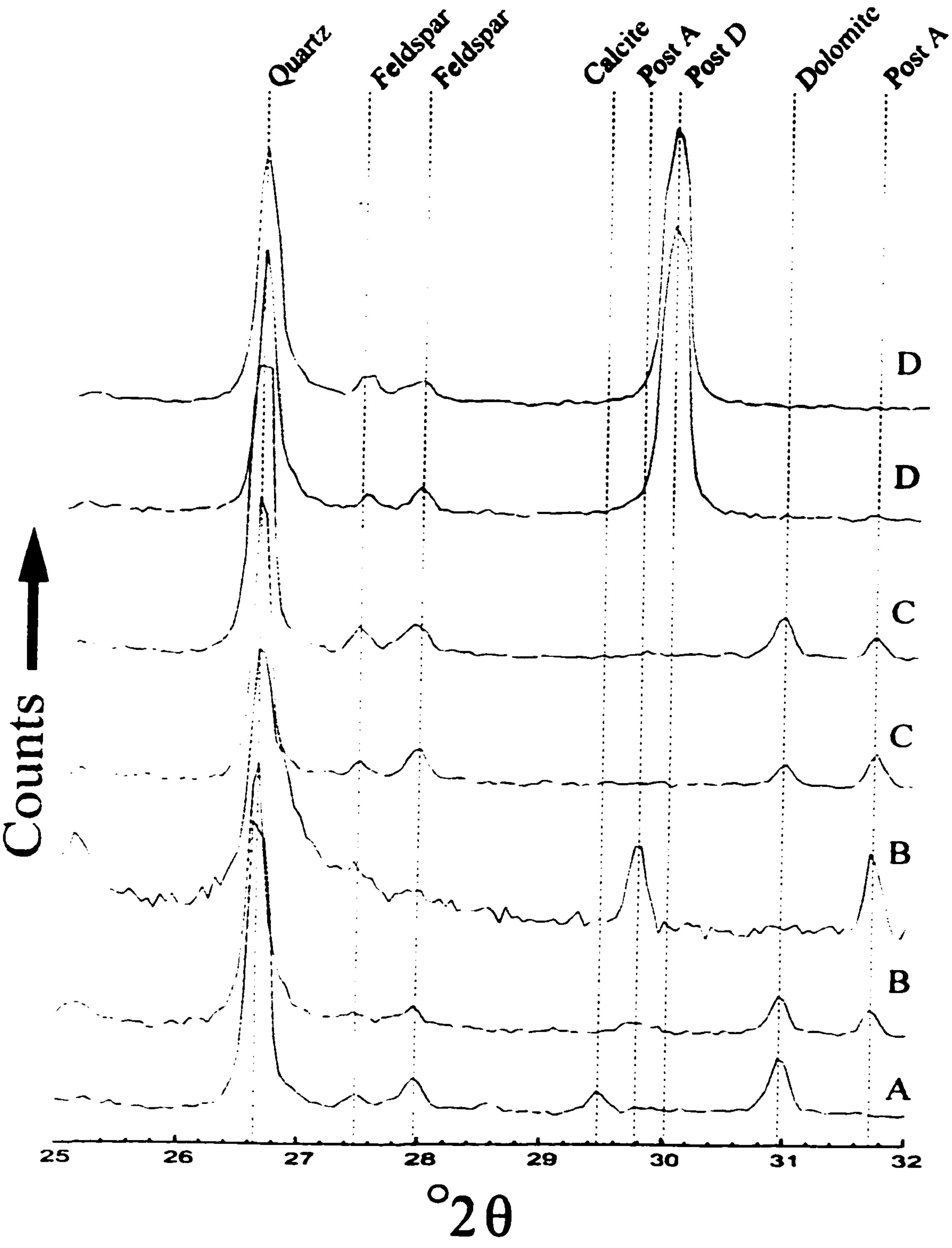

Figure 15. X-Ray diffraction patterns of residues from site nineteen. A) untreated B) after treatment with NaOAC C) after treatment with $Na_4P_2O_7$ D) after treatment with $NH_2OH \cdot HCL$.

The XRD patterns of the hydroxylamine hydrochloride step show that the dolomite peaks from the three sites are no longer present (Figures 13 to 15). No other changes in mineralogy were observed from the XRD patterns.

A number of unexplained peaks were observed in the XRD patterns from all the samples. Peaks at 29.75 and 31.7° 2θ are observed in samples six and nineteen after the second treatment with sodium acetate and an unexplained peak also occurs after the hydroxylamine hydrochloride treatments in all three samples at 29.95 °2θ (Figures 13 to 15).

4.3 Major Element Analysis

Results of the major element analysis are given in Table 5 and are presented as oxides of the major elements. The precision of the procedure, based on the relative standard deviation of replicate analysis of the certified reference material LKSD-4 is less than 5% for all elements (Table 5). The accuracy of the procedure as determined by the difference in percent between the certified value of LKSD-4 and the value obtained in this study are given in Table 5. The accuracy of the procedure is quite good for all elements except Mn. The results are not surprising in that the dominant oxide is SiO_2 followed by Al_2O_3, Fe_2O_3, MgO, CaO, and K_2O in order of significance. The remaining oxides account for very little of the total.

Table 5: Results of the major element analsysis for Lake Erie sediments and certified reference material expressed as a percent of the total.

SITE	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	L.O.I.	Total
1	49.95	0.55	9.49	6.20	0.07	4.29	7.25	0.80	2.21	15.8	96.6
2	50.06	0.67	11.87	5.26	0.06	4.32	5.59	0.66	2.82	16.3	97.6
3	49.30	0.62	11.10	4.98	0.06	4.36	6.00	0.77	2.56	14.2	94.0
4	46.32	0.56	9.43	3.93	0.06	4.40	6.10	0.75	2.25	17.4	91.2
5	51.62	0.65	11.10	4.76	0.07	4.61	5.55	0.79	2.67	15.1	96.9
6	51.13	0.69	12.38	5.75	0.09	3.90	4.76	0.74	2.82	14.5	96.8
7	50.55	0.61	11.92	5.45	0.08	3.00	5.61	0.71	2.72	13.2	93.9
8	51.52	0.74	13.28	6.00	0.07	3.94	3.82	0.69	3.14	12.4	95.6
9	51.34	0.62	10.52	4.59	0.07	4.34	5.50	0.84	2.48	13.1	93.4
10	53.16	0.71	11.94	5.14	0.07	4.59	4.85	0.78	2.98	12.0	96.2
11	50.78	0.69	12.17	5.36	0.07	4.22	4.47	0.71	2.89	13.5	94.9
12	54.02	0.74	13.34	5.76	0.07	3.82	3.67	0.73	3.11	13.6	98.9
13	52.64	0.72	13.13	5.70	0.08	3.47	3.28	0.72	3.05	13.1	95.9
14	51.21	0.71	13.83	6.16	0.08	3.22	3.90	0.60	3.06	15.1	97.9
15	51.96	0.70	12.69	5.83	0.09	3.97	4.87	0.74	2.94	14.2	98.0
16	51.84	0.74	13.73	6.40	0.08	3.88	3.79	0.65	3.29	13.8	98.2
17	49.13	0.69	12.90	6.13	0.08	3.77	4.12	0.64	3.01	13.4	93.9
18	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
19	55.26	0.71	12.18	5.38	0.08	3.37	5.31	0.83	2.74	12.8	98.6
20	51.15	0.73	15.30	6.66	0.10	3.03	2.83	0.52	3.36	16.0	99.7
Certified Reference Material (n=5)											
LKSD-4 (avg.)	39.79	0.30	5.36	3.96	0.06	0.92	1.78	0.76	0.82	N/A	N/A
LKSD-4 (Cert.)	41.60	N/A	5.90	4.10	0.10	0.90	1.80	0.70	0.80	43.6	N/A
LKSD-4 (RSD)	1.6%	1.6%	1.7%	1.2%	1.2%	1.9%	1.9%	2.7%	1.4%	N/A	N/A
LKSD-4 (Diff.)	4.4%	N/A	9.2%	3.5%	37.2%	-1.7%	0.8%	-8.9%	-2.6%	N/A	N/A

4.4 Total Carbon, Nitrogen, and Sulphur Analysis

The results for the carbon, nitrogen, and sulphur analysis are given in Table 6. The results show that total carbon varies between 3.1 and 4.7% The highest values tend to be found at the mouth of the Detroit River and along the Ontario shoreline from sites three, four, and five. The lowest values are found in the open lake areas and near the Maumee River. Nitrogen values show little variation and the highest values tend to be found in the open-lake area. No sulphur was detected.

4.5 Grain-Size Analysis

Results of the grain-size analysis are give in Table 7. Calculations of mean, sorting and skewness are based on the formula by Folk and Ward (1957). In addition, histograms for each site are located in Appendix III. Mean grain size varied from 4.5 ϕ at the mouth of the river to 7.1 ϕ at sample location seventeen which is found in the open-lake portion of the study area. Sorting which is a measure of the spread of grain-size distribution was poor for all but samples seven and twenty, which were very poor. Skewness which is a measure of the symmetry of the distribution ranged from positive-skewed (> +0.30), to negative-skewed (-0.1 to - 0.3). Other measurements reported in Table 7 are the percentage of material in a given grain-size fraction The percent fine sand represents only the percentage of grains between 200 μm and 64 μm since material greater than 200 μm was not measured because most samples contained shell fragments which can give rise to a bimodal distribution.

Table 6: Results of the total carbon, nitrogen, and sulphur analysis from the western Lake Erie sediments in weight %.

SITE	Carbon %	Nitrogen %	Sulphur %
1	4.7	0.1	<0.2
2	4.1	0.2	<0.2
3	4.3	0.1	<0.2
4	4.2	0.1	<0.2
5	4.2	0.2	<0.2
6	3.5	0.2	<0.2
7	4.5	0.2	<0.2
8	3.5	0.1	<0.2
9	3.6	0.1	<0.2
10	3.3	0.1	<0.2
11	3.8	0.2	<0.2
12	3.4	0.2	<0.2
13	3.2	0.2	<0.2
14	3.6	0.2	<0.2
15	3.8	0.2	<0.2
16	3.7	0.2	<0.2
17	4.2	0.2	<0.2
18	3.4	0.2	<0.2
19	3.3	0.1	<0.2
20	3.1	0.3	<0.2

Table 7: Results of the grain-size analysis for Lake Erie sediments.

Site	Mean ϕ	Sorting ϕ	Skewness ϕ	Percent Fine Sand	Percent Silt	Percent Clay	Percent <63 μm
1	4.5	1.9	0.4	39.8	50.1	10.1	60.2
2	6.6	1.6	0.2	1.6	69.3	29.1	98.4
3	6.2	1.8	0.2	4.3	71.8	23.9	95.7
4	6.2	1.8	0.2	3.5	71.6	24.9	96.5
5	6.1	1.8	0.1	4.1	71.4	24.5	95.9
6	6.6	1.7	0.2	2.2	67.8	30	97.8
7	5.6	2.1	0.2	16	62.9	21.1	84
8	6.7	1.5	0.1	0.8	64.6	34.6	99.2
9	6.1	1.9	0.1	7.5	69.5	23	92.5
10	6.6	1.7	0.2	0	73.9	26.1	100
11	6.6	1.6	0.2	0	68.7	31.3	100
12	6.9	1.5	0.0	0	70.3	29.7	100
13	6.7	1.8	-0.1	1.8	62.7	35.5	98.2
14	6.9	1.5	-0.1	3.2	62.6	34.2	96.8
15	5.3	2.2	0.2	31.7	48.3	20	68.3
16	7.1	1.2	0.1	0	59.5	40.5	100
17	7.0	1.8	0.0	0	62.7	37.3	100
18	6.7	1.5	0.1	0	62.1	37.9	100
19	6.1	1.8	0.1	5.3	70.4	24.3	94.7
20	5.9	2.5	-0.2	24.5	45.2	30.3	75.5

CHAPTER 5

DISCUSSION

5.1 Characterization of the Western Lake Erie Sediments

The characterization of the sediments from the study area is based on the results from the analyses of grain-size distributions, major elements, and the total carbon and nitrogen. This of course does not constitute a complete sediment analysis but the above data in conjunction with other published reports are sufficient for the purposes of this project.

The histogram patterns (Appendix III) have been used as the basis for subdividing the sample sites into three groups which are shown in Figure 16. The first subdivision consists of those sites with a positive-skew grain-size distribution which consists of sites 1, 3, 4, 5, 7, 9, 10, and 11. For convenience this group will be referred to as the Positive-Skew subdivision. In general, these sites are located in the nearshore regions of the lake except for samples 9 and 10 which are found in the open-lake area (Figure 16). Samples 3, 4, and 5 of the Positive-Skew subdivision are located just south of the Ontario shoreline and this area has been described by Herdendorf (1970a) as a region of erosion or non-deposition. The current action in this area causes winnowing of the bottom sediments which would create the positive-skew observed at these sites. Site 1, located close to the American shoreline, is situated in a lag-deposit zone (Przywara, 1978). The nearshore bottom sediments are subjected to winnowing and subaqeuous erosion caused by the inflow from the Detroit River. Here the combination of local currents and the relative shallowness of the area result in the removal of most of the fine-grained sediments (Kemp, 1975). Site 7, which is located to the northeast of Monroe,

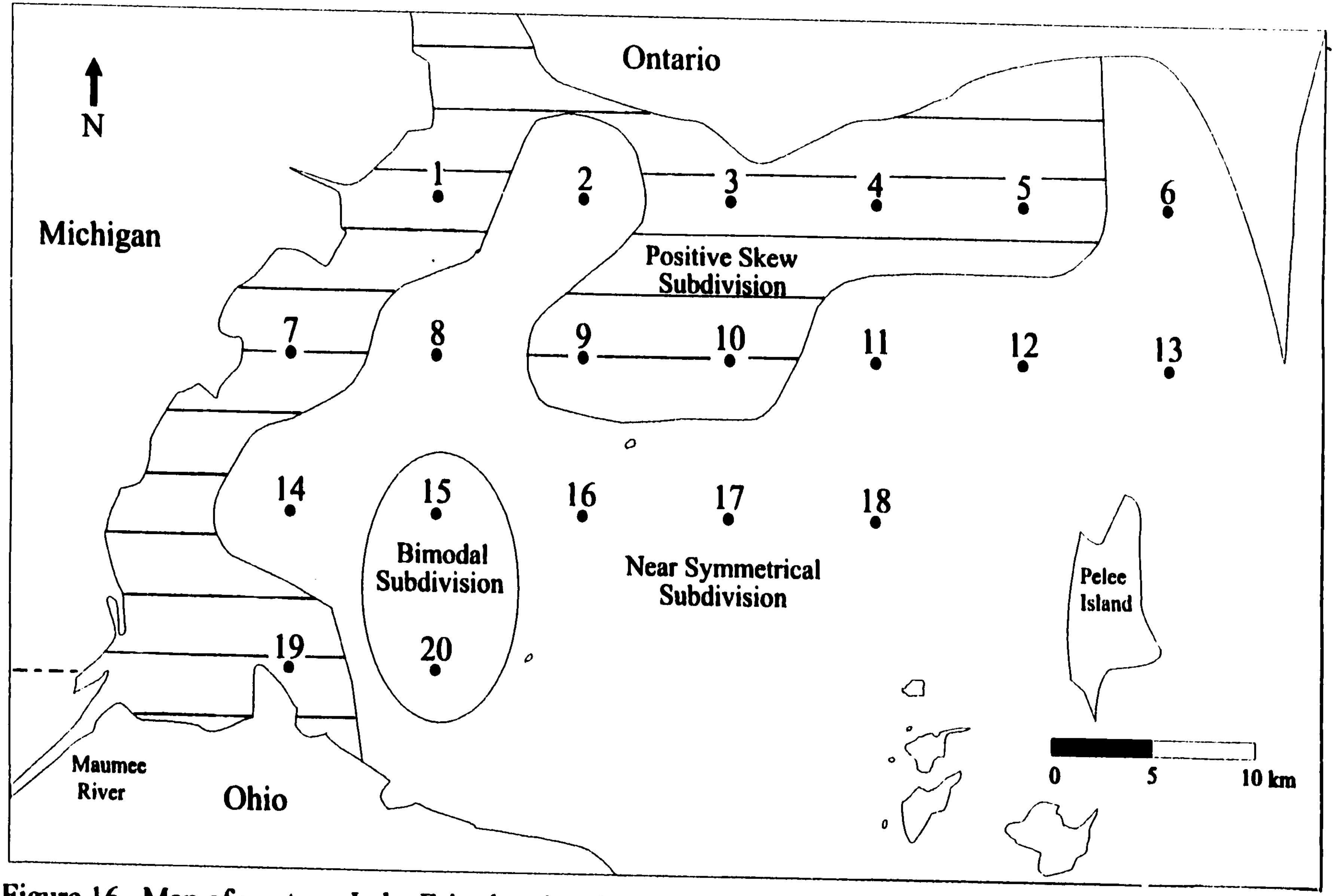

Figure 16. Map of western Lake Erie showing the three subdivisions based on grain-size data.

Michigan is located in an area of subaqueous erosion (Walters, 1974), and again this erosion removes the fine-grained sediment leaving the characteristic positive-skew distribution of a lag deposit. Site 19 is located to the northeast of Cedar Point in relatively shallow water (< 5 m) and once again is located in an area of erosion or non-deposition according to Herdendorf (1970a). Sites 9 and 10 are quite interesting in that the mechanism that creates the positive-skew is thought to be the result of human induced actions and not natural processes. Sites 9 and 10 are located less than 100 metres from the east-west shipping channels (Figure 7). It has been observed by Holcombe et al. (1997) that dual parallel channels underlie the main shipping lanes in the western basin. These channels are the result of eastbound and westbound shipping traffic that resuspend the underlying bottom sediments by the action of the propeller blades. The resuspended fine-grained sediments will tend to settle much slower than the coarse-grained sediments and will be drawn away from the shipping lane by current action. This results in the selective removal of the fine-grained sediment which would create the positive-skew observed. Site 11 is also located less than 100 metres from the shipping lane but it is located in water that is approximately one metre deeper than sites 9 and 10 and it appears that sediment resuspension and the subsequent transport is minimal or does not occur. Evidence for this is seen in the histogram of site 11 which is nearly symmetrical (Appendix III).

The second subdivision consists of sediments that have a distinct bimodal distribution and consists of sites 15 and 20 and will be referred to as the Bimodal subdivision. These sites are located on a sand deposit found in the western edge of the western basin (Figure 16). According to Nwankwo and Walters, Jr., (1980), "the sand deposit formed from glacial outwash, and was perhaps modified by wave action and supplemented by the modern deposits from the Raisin River." The sand deposit is overlain in places by a thin layer of recent silt and clay-sized sediments (Nwankwo and Walters, Jr. 1980). It is thought that the bimodal distribution is the result of the Ponar grab sampler collecting both the overlying fine-grained sediments and the underlying sand deposit combining the two distinct sediment types into one sample. However, it was not possible to identify the two distinct sediment types in the field and it is likely that sediment resuspension and bioturbation has also mixed these two populations. Thomas et al. (1976) has indicated that sediment resuspension caused by wave action and bioturbation continually reworks the sediments in this area.

The last group, which contains the remaining sample sites, all have a near-symmetrical distribution and are found away from the direct influence of the rivers, shoreline, and shipping channels and will be referred to as the Near Symmetrical subdivision. These sediments also have the finest grain size and lowest sorting values, which is to be expected in the lower energy open-lake environment.

In addition to examining histogram patterns, the mean grain size, sorting, and skewness have also been examined. Figure 17 is a scatter plot of mean grain size versus sorting and Figure 18 is a scatter plot of mean grain size versus skewness. In general as grain size decreases (phi increases) the sorting and skewness values decrease. From Figures 17 and 18, it is observed that the sediments from the different subdivisions tend to group together. Sediments from the Near Symmetrical subdivision have the closest grouping as would be expected since these sediments are all found in the open-lake area and are subjected to a similar energy regime. These sediments have the highest phi values and lowest sorting and skewness values. Sediments from the Positive-skew distribution show a wide range of mean grain size but a narrow range in sorting and

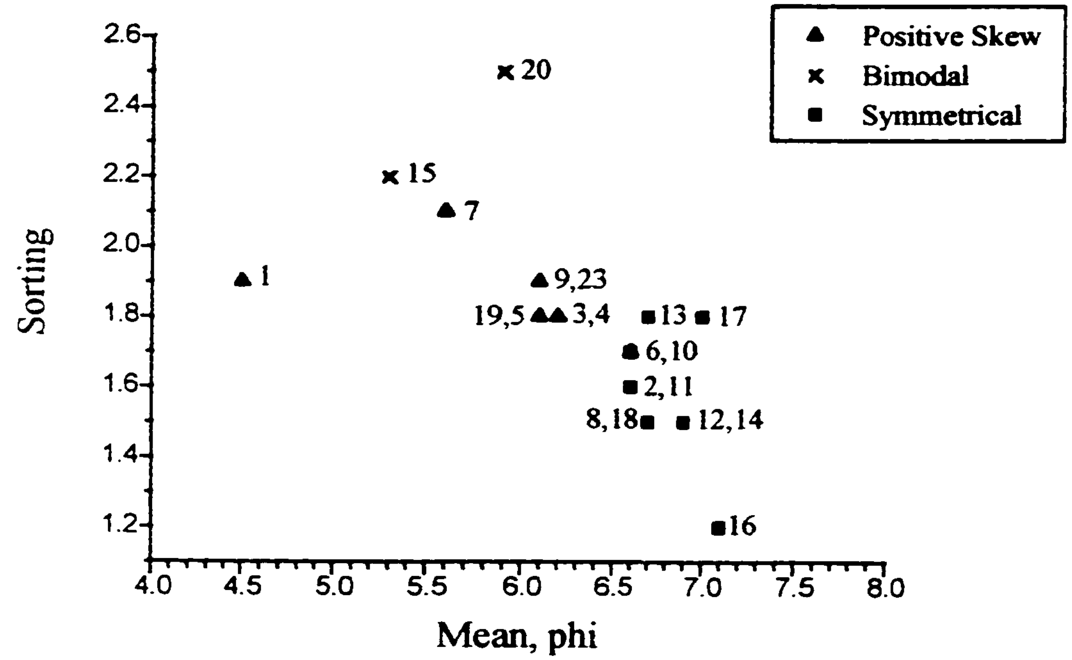

Figure 17: Scatter Plot of Mean Grain Size versus Sorting

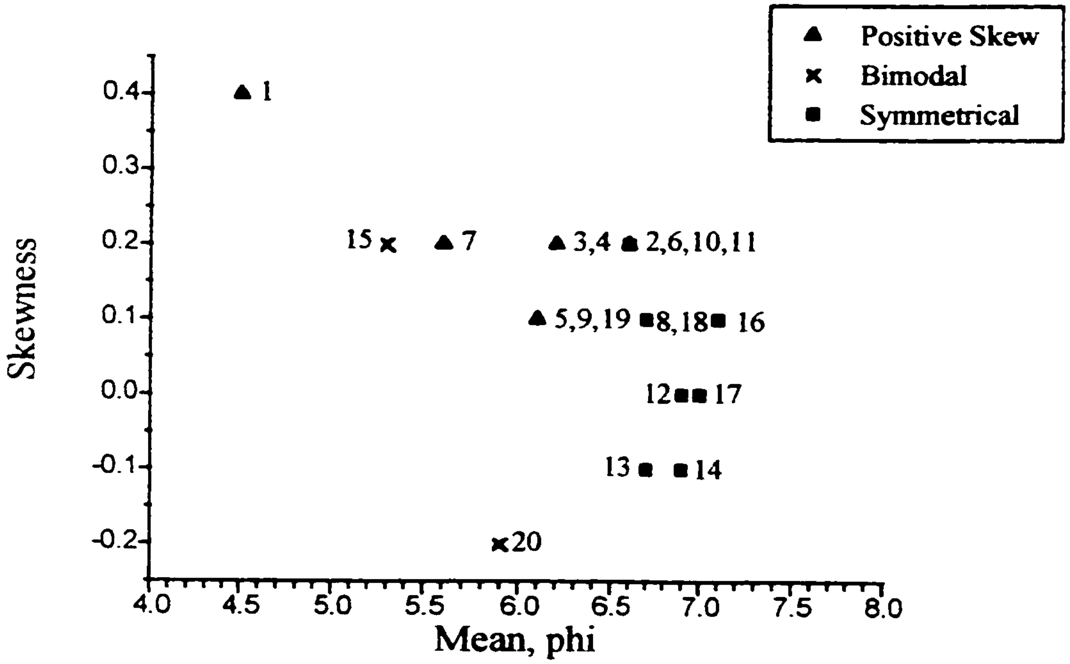

Figure 18: Scatter Plot of Mean Grain Size versus Skewness

skewness. The wide range in grain size is due to the different energy environments found along the shoreline. Sites near the Detroit River would be subjected to higher current velocities which would deposit coarser material and remove the finer material, resulting in a coarser mean grain size. Sediments from the Bimodal subdivision do not plot close to each other. This can be explained since each site is composed of differing amounts of the sand and recent fine-grain sediment populations.

Examination of the geochemical data obtained on the sediments from western Lake Erie support the division of the sample sites based on grain-size analysis and reveal a number of interesting observations. Figure 19 is a scatter plot of total Ca versus Mg from the major element analysis and shows that the samples tend to cluster into the previously stated subdivisions. It is assumed that detrital calcite and dolomite are the main sources of the Ca and Mg. Other sources of Ca are from the shells of organisms and from feldspars. Very little shell material was observed in the bulk samples and was mostly removed before sieving. As for the feldspar it is considered a minor component of the sediments and would contribute very little Ca as compared to the carbonates. Other sources of Mg are from the minerals chlorite, pyroxenes, and amphiboles. The amount of Mg derived from these minerals is also considered minimal since chlorite accounts for less than 20% of the clay-sized fraction and the total amount of heavy minerals account for less than 10% of the sand-sized fraction (Yahney, 1978; Kemp et al. 1976). From Figure 19 it is observed that the Near Symmetrical subdivision group together except for site 2 which plots close to samples 3, 4, 5, 9, and 10 of the Positive-skew subdivision. These samples are all located near the Ontario shoreline and probably have a similar sediment source and therefore would be expected to plot close to one another. Sites 7 and 19 also plot near each other and again probably have a similar sediment source. This is

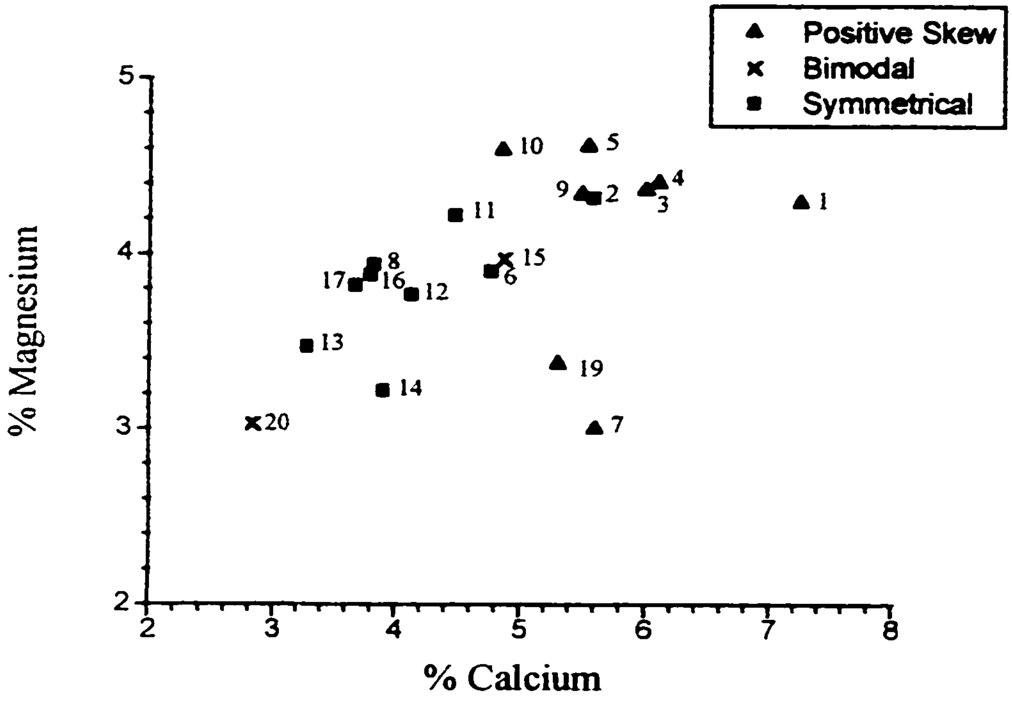

Figure 19: Scatter Plot of Total Calcium versus Magnesium

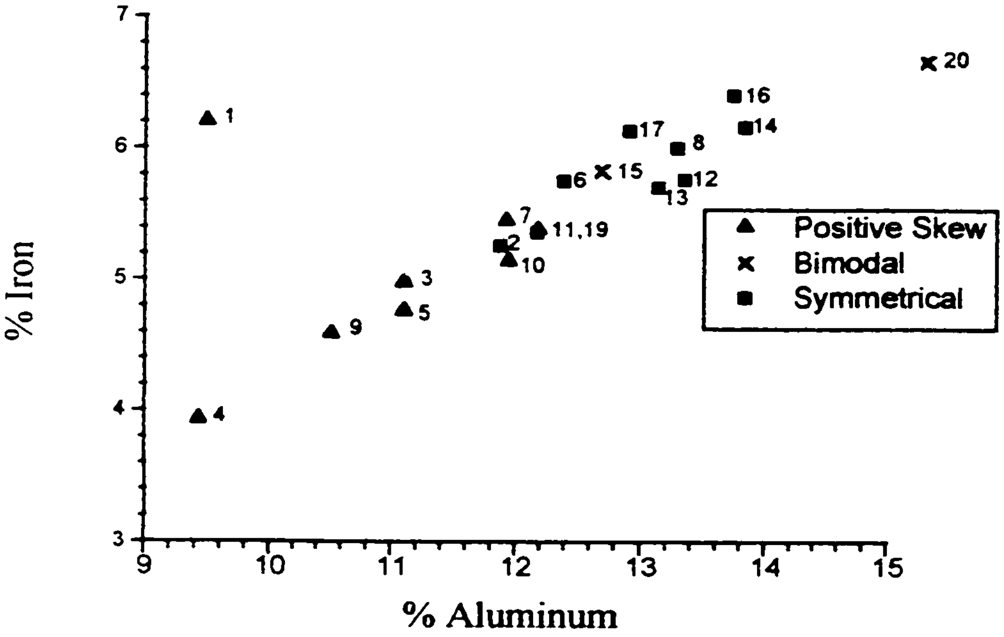

Figure 20: Scatter Plot of Total Aluminum versus Iron

probably due to the proximity of both samples to the Michigan shoreline. Sites 15 and 20 of the Bimodal subdivision do not plot near each other and this is probably due to the samples consisting of different amounts of the sand deposit and the recent sediments.

Examination of Al versus Fe (Figure 20) reveals a strong trend of increasing Al with increasing Fe content. The main source of the Al is thought to be from the clay minerals. Besides being incorporated into the clay minerals Fe also exists as an oxide and it has been observed that Fe-oxides are nearly always associated with clay minerals in sediment (Forstner and Wittmann, 1983). The sites from the Near Symmetrical subdivision have the highest values of Al and Fe while the sites from the Positive-skew subdivision have the lowest. This is expected since sediments from the Near Symmetrical subdivision have the highest clay content (Table 7). A notable exception is site 1 which has a much higher amount of Fe for its corresponding Al content. This can be explained by the presence of Fe-rich particles of anthropogenic origin. A sediment sample from 1 one was examined with a scanning electron microscope and a number of particles that were mainly composed of Fe and O were found. These Fe-rich particles also had a pitted appearance and it is thought that they are of an anthropogenic origin. These particles probably originate from the foundries located along the Detroit River.

Figure 21 is a scatter plot of total carbon versus nitrogen. Samples 1, 3, 4, 5, and 7 have the highest total carbon content. Total carbon includes organic and inorganic carbon and unfortunately it is not known if the high total carbon concentrations reflect higher amounts of carbonates or organic matter. Examination of Figure 21 reveals that sites 1, 3, 4, 5, and 7 also have the highest amount of calcium and therefore would be expected to have high total carbon values since carbonates are the main source of Ca. On the other hand, these sites are near the Detroit River and the Ontario shoreline. Organic matter from sewage treatment plants located along the Detroit River and agricultural runoff, rich in nutrients from the agricultural areas of Essex county, may increase the amount of organic matter at sites 1, 3, 4, 5, and 7. It is probable that these sites have both high organic carbon and carbonate carbon contents. Figure 21 also reveals that, in general, the sediments from the Near Symmetrical subdivision have the highest nitrogen values. As stated earlier these samples are found in the open-lake environment. Research by Frink (1969) found that in eutrophic lakes the highest nitrogen values are located in the centre of the lake. This is because most of the nitrogen is organic nitrogen and research by Wood (1964) observed that organic matter has nearly the same density as water and only tends to settle out in deeper water. Kemp (1971) found that over 90% of the nitrogen in Lake Erie was organic nitrogen and therefore would tend to settle in the open-lake area.

5.2 Evaluation of the Sequential Extraction Procedure

The precision of the data as stated earlier is based on the results from the replicate analysis of SED, the internal reference material. The results indicate that the RSDs for the major elements from the AEC and organic extractions are all <10% (Table 3). An RSD below 10% is considered acceptable for precision (Vander Voet and Riddle 1993). The RSD for the major elements from the Fe-Mn-oxide extraction are of poorer quality and are between 10% and 13% (Table 3) but for the purpose of this study they are acceptable. The precision of the trace metal data in general is not as good as the major element data and this largely due to the low concentrations involved (Table 3). The results indicate that the RSDs for the AEC extraction are all <10% and RSDs for the organic and Fe-Mn oxide extractions are higher but are still below 15% with the

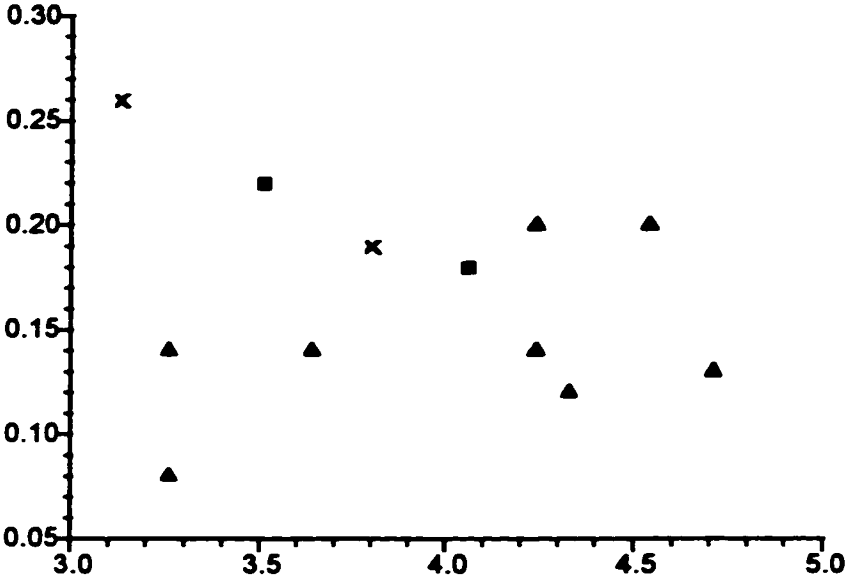

Figure 21: Scatter plot of Total Carbon versus Nitrogen

exception of Ni from the organic extraction, which is 16.7% (Table 3). As with the major element data the precision of the data is acceptable for the purposes of this study.

Besides determining the partitioning of trace metals in Lake Erie sediments a certified reference material (LKSD-4) and an internal reference material (SED) was subjected to the sequential extraction procedure. This was done to evaluate the sequential extraction procedure and allow for comparisons between other studies. LKSD-4, created by the Canada Centre for Mineral and Energy Technology (CANMET) is a composite sample of lake sediments from three lakes located in the Canadian Shield. Hall et al. (1996c) also subjected LKSD-4 to a sequential extraction procedure that employed the same AEC extraction that was used in this study. The results obtained from the AEC extractions from both studies are given in Table 8. The difference in metal concentrations between the two studies is <15% for all metals studied except for Cr and Cu. The large differences are largely due to the very low concentrations of extractable Cr and Cu.

Table 8: LKSD-4 concentrations obtained from the AEC step from this study as compared to Hall et al. (1996c). Concentrations in μg/g.

Element	This Study[1]	Hall et al. [2] (1996c)	Difference %
Fe	275±22	260±0	5.8
Mn	271±20	233±2	15.9
Ca	7250±511	6800 ±440	6.6
Zn	62.7±4.9	68±1	-7.8
Ni	4.5±0.5	4.8±0.1	-6.3
Cr	1.1±0.1	.89 ±0.1	23.6
Cu	1.2±0.7	<0.5	N/A

[1] n=14

[2] n=3

It was known in advance that the concentrations obtained from the sum of the three extractions for LKSD-4 would be lower than the certified concentrations since the procedure was designed to not attack the more resistant silicate and sulphide fractions and the certified concentrations are from a total digestion. However, Hall et al. (1996c) also subjected LKSD-4 to a similar sequential extraction procedure that in addition to examining the fractions studied in this procedure, also examined the silicate and sulphide fractions. Therefore, in theory if the average sum of the three extractions from this study are added to the average silicate and sulphide fractions obtained by Hall et. al (1996c) they should be close to the certified values. The concentrations obtained by adding the results of the two studies are intended to be used only as an approximation and are given in Table 9. The results suggest that since the addition of these two studies produces values that are close to the literature value for a total digestion the sequential extraction procedure employed in this study probably did not attack the silicate or sulphide fractions to a significant extent. Thus, the sequential extraction procedure employed in this study gives results that can be used to examine the partitioning of anthropogenically derived trace metals in oxidized aquatic sediments, because it excludes the silicate and sulphide fractions.

Table 9: LKSD-4 concentrations obtained in this study as compared to Hall et. al. (1996c) and literature values. Concentrations in μg/g.

Element	Sum[1]	Silicates[2]	Sulphides[2]	Sum + Silicates[2] +Sulphides[2]	Literature Value[3]
Fe	14300± 2200	4440± 5	5460± 10	24200	28500± 2000
Mn	405± 27	84± 1	17± 1	506	464± 30
Ca	8720± 542	5180± 13	210± 2	14113	12900± 1400
Zn	172± 12	11± 1	14± 0	197	194± 19
Ni	23± 2.1	5.4± 0.2	6± 0.2	34.4	31± 5
Cr	18.4± 1.9	12.6± 0.4	6± 0.3	37	33± 6
Cu	16.7± 3.8	3± 0.1	13.4± 0.2	33.1	31± 4

[1] Sum of the three extractions from this study. (n=14).

[2] Results from Hall et al. (1996c). (n=3).

[3] Lynch (1996).

The internal reference material (SED) used in this study is also used by the G.L.I.E.R. laboratory. However, the G.L.I.E.R. laboratory uses an aqua regia digest for sediment analysis. Aqua regia, a mixture of HCl and HNO_3 in a ratio of 3 to 1 by volume is a non-selective extractant that attacks various inorganic and organic phases in soils and sediments (Chao, 1984). It is commonly used in exploration and environmental geochemistry studies and therefore, it is important to compare the results of the sequential extraction to that of the aqua regia digest in order to evaluate the robustness of the sequential extraction procedure. The element concentrations from the addition of the three extractions and the concentrations obtained from the aqua regia digest are given in Table 3 and it appears that the mean concentrations are similar. If the standard deviations are taken into account there is overlap between the two studies for Fe, Ni, Cr, and Cu. The concentrations of Mn, Ca, Mg, and Zn from the aqua regia digest are much lower than the concentrations obtained from this study and this discrepancy may be due to readsorption or a weakness of the aqua regia digest.

5.3 Behaviour of Ca, Mg, Fe, and Mn in Western Lake Erie Sediments

The partitioning of Ca and Mg during the sequential extraction can be explained by the reactions of calcite and dolomite to the three reagents used. It is assumed that the majority of the Ca and Mg recovered from steps one and three of the procedure are from the dissolution of carbonates. The other possible sources of Ca such as feldspars can be ruled out since the XRD analysis indicates that feldspars were not dissolved during the sequential extraction procedure. In addition, Loring (1976) states that Na-Acetate leaves the silicate minerals intact. As for Mg, it is assumed that the majority of Mg is derived from the dissolution of calcite containing Mg and the dissolution of dolomite. Other minerals containing Mg in Lake Erie sediments include hornblende, pyroxene and chlorite but none of the reagents used react with silicate minerals (Chao, 1984). Ca and Mg may also be associated with organic matter. According to Engstrom and Wright (1984) Ca and Mg have a strong affinity for organic ligands such as humic and fulvic acids. Bowen, (1966) states that Ca and Mg are 'loosely' bonded to humic material. The term 'loosely' is ambiguous but, according to Forstner and Wittmann (1983), the attractive forces between metal ions with organic matter range from 'weak' (adsorption) to 'strong' (metal chelation and complexation). Therefore, it is possible that Bowen (1966) is referring to the adsorption of Ca and Mg onto the surface of organic matter. If this is the case, Ca and Mg would be removed during the AEC extraction because Na-Acetate can remove elements adsorbed onto organic matter (Chao, 1984). It is impossible to tell how much of this 'loosely' bonded Ca and Mg, if any, was derived from the organic matter.

As previously stated, XRD analysis indicated that calcite was completely dissolved after the AEC extraction (Figures 13 and 15). A small amount of dolomite may have been dissolved during the AEC extraction as indicated by a reduction of the dolomite peaks (Figures 13 to 15). The majority of the dolomite was not dissolved until the Fe-Mn oxide extraction. A similar result was obtained by Han and Banin (1995) using Na-acetate with the same extraction conditions. Therefore, the Ca and Mg extracted in the AEC extraction is likely dominantly from the dissolution of calcite and a minor amount of dolomite. The Ca and Mg extracted in the Fe-Mn oxide extraction is entirely from the dissolution of dolomite. Pearson linear correlation coefficients between Ca and Mg from the Fe-Mn oxide extraction indicate a strong linear relationship (Table 10). This indicates that the concentration of Ca and Mg are linearly related to each other and this can only be explained by the dissolution of dolomite which has a fixed ratio of Ca:Mg. The Pearson linear correlation coefficient between Ca and Mg from the AEC extraction is not significantly different from zero and this is because the source of the Ca and Mg is from adsorption onto organic matter and the dissolution of both calcite and dolomite. In each case the ratio of Ca and Mg would be different and since the amount of calcite, dolomite, and organic matter varies at each site the ratio of Ca:Mg extracted in the AEC extraction would vary and no linear relationship would be expected.

The proportion of Ca and Mg extracted during the organic extraction did not exceed 10% (Figure 10). This indicates that very little Ca and Mg is bound to organic matter by stronger bonding such as chelation or complexation. As stated earlier it is possible that Ca and Mg are 'loosely' bonded to organic matter which would have been removed during the AEC extraction.

The partitioning of Ca and Mg throughout the western basin of Lake Erie as stated earlier is mainly controlled by the amount of calcite and dolomite within the sediment. Therefore, variations in the partitioning of Ca and Mg between sample sites is a reflection

Table 10: Pearson linear correlation coefficient matrices for major and trace elements from the three extraction steps.

AEC Extraction

	Fe	Mn	Ca	Mg	Zn	Ni	Cr
Mn	0.55						
Ca	-0.36	-0.19					
Mg	-0.53	-0.38	0.54				
Zn	0.50	0.08	0.08	-0.37			
Ni	0.63	0.21	-0.11	-0.43	**0.92**		
Cr	0.32	-0.17	0.10	-0.29	**0.96**	**0.81**	
Cu	-0.05	-0.31	0.08	-0.05	**0.74**	**0.71**	0.65

Organic Extraction

	Fe	Mn	Ca	Mg	Zn	Ni	Cr
Mn	**0.92**						
Ca	-0.51	-0.38					
Mg	0.23	0.33	0.45				
Zn	0.63	0.55	0.01	0.30			
Ni	**0.77**	**0.69**	-0.34	0.33	0.39		
Cr	0.07	0.03	0.48	-0.01	0.31	-0.09	
Cu	0.67	0.46	-0.28	-0.11	0.56	0.28	0.42

Fe-Mn oxide Extraction

	Fe	Mn	Ca	Mg	Zn	Ni	Cr
Mn	**0.93**						
Ca	-0.27	-0.05					
Mg	-0.11	0.11	**0.96**				
Zn	**0.71**	0.54	-0.58	-0.53			
Ni	**0.71**	0.63	-0.50	-0.46	**0.92**		
Cr	0.25	0.06	-0.39	-0.48	**0.79**	**0.70**	
Cu	-0.04	-0.19	-0.43	-0.43	0.15	0.09	0.20

[1] Values that are significantly different from zero at the 0.001 probability level are bold faced. (n=20)

of the slight changes in calcite and dolomite contents within the sediment.

Both Fe and Mn are found in lake sediments as elements associated with detrital minerals and as components of authigenic oxides and organic substances and the partitioning data should reflect this. The proportion of Mn extracted during the AEC extraction was much higher than the proportion of Fe (Figure 9). The relatively high proportion of Mn extracted by Na-Acetate has been observed by others (Tessier et al. 1981; McIsaac et al. 1982). A number of possible sources exist for the Fe and Mn that was extracted during the AEC extraction. Studies by Tessier et al. (1979) and Loring (1976) have concluded that the Na-Acetate reagent does not attack silicate minerals or Fe-Mn oxides. In addition, Grossman and Millet (1961) reported that organic carbon concentrations in non-calcareous soils were unchanged after contact with this solution for nine weeks. Therefore it is unlikely that the reagent employed attacked organic matter or Fe-Mn oxides but it must be stressed that the selectivity of the reagents is not perfect and the possibility always exists that unintended components of the sediments may be attacked during any of the steps. One possible source of the Fe and Mn is from the dissolution of detrital carbonates. It is well known that carbonates can incorporate minor amounts of other elements such and Fe and Mn by substitution. Unfortunately, no data exists for the concentration of Fe and Mn in carbonates derived from the local bedrock. Another possible source of Fe and Mn in the AEC extraction is that the Fe and Mn may be adsorbed onto the surface of sediment forming material. It should be noted that the sediments were obtained with a Ponar grab sampler. This device takes a sediment sample of the upper 10 cm of the sediment. In most lakes the upper few cm of the sediments are under oxidizing conditions and the Fe and Mn will exist as oxides or complexed with organic matter (Engstrom and Wright, 1984). Below this upper layer, oxygen consumption by microbial activity and the diagenesis of inorganic chemical species leads to reducing conditions. Under reducing conditions the solubility of Fe and Mn increases, Mn much more than Fe. The exact chemical configuration of Fe and Mn below the oxidized surface is uncertain but Williams et al. (1971a) suggest that most Fe exists as a hydrated form of amorphous ferrous hydroxide and that Mn may be soluble and adsorbed onto the surface of Fe-oxides or weakly bonded (adsorbed) to organic matter. It is expected that this Mn adsorbed onto the Fe-oxides and weakly bonded to organic matter would be extracted during the AEC extraction and that the Fe oxides would be dissolved during the Fe-Mn oxide extraction. It should be remembered though that the sediments were brought to the surface after sampling and exposed to the atmosphere. It was observed that the samples underwent a slight colour change from gray to brown upon exposure to the atmosphere indicating oxidation of the sediments but what affect this had on the measured partitioning of Fe and Mn is unknown.

It is apparent from the above discussion that the possible source(s) of Mn in the AEC extraction is from both the dissolution of detrital carbonates and the removal of soluble Mn adsorbed onto Fe-oxides and weakly bonded to organic matter, but it is impossible to determine how much came each of the sources. Since most of the Fe exists as an oxide which would not be extracted during the AEC extraction, the likely source of Fe is from the dissolution of detrital carbonates.

The organic extraction recovered between 6% and 15% of the Fe and less than 3% of the Mn from the sediment samples (Figure 9). This indicates that very little Fe and Mn is complexed or chelated with organic matter. However, examination of Table 10 indicates that the Pearson linear correlation coefficients between Fe and Mn show a strong linear relationship. There is no explanation why Fe and Mn associated with organic matter should behave in such a linear relationship. However, this type of linear relationship is also observed in the Fe-Mn oxide extraction which is intended to dissolve Fe-Mn oxides. In addition this linear relationship was also reported by Tessier et al. (1981) using the same reagent (Hydroxylamine Hydrochloride) to dissolve Fe-Mn oxides. Therefore it is possible that minor dissolution of Fe-Mn oxides occurred during the organic extraction. It has been observed by McKeague (1967) that Na-pyrophosphate does not dissolve Fe-Mn oxides, provided the pH remains above seven. The pH data from Table 1 indicates that the pH was always above seven, ruling out this possibility. However, Chao (1984) states that because of the highly dispersive state of the suspension resulting from treatment with Na-pyrophosphate at pH 10, strong centrifugation is necessary to separate the supernatant solution (McKeague, 1967). Jeanroy and Guillet, (1981) reported ferruginous particles in their Na-pyrophosphate extracts and it was observed that the Na-pyrophosphate supernatants from this study did contain minor amounts of suspended particles even after strong centrifugation and filtering.

The Fe-Mn oxide extraction recovered the largest proportions of Fe and Mn from the sediments (Figure 9). The source of this Fe and Mn is from the dissolution of Fe-Mn oxides and dolomite but it is impossible to determine the proportion of Fe and Mn derived from each source. The Pearson linear correlation coefficient between Fe and Mn indicate a strong linear relationship (Table 10). As stated earlier this strong linear relationship was also reported by Tessier et al. (1981) who attributed it to the dissolution of Fe-Mn oxides.

The partitioning of Fe and Mn throughout western Lake Erie shows only slight variation. The slight variations reflect the different amounts of carbonate, Fe-Mn oxides, organic matter and the varying physio-chemical conditions that exist between sample sites. It is interesting to note that even though a large number of variables affect the partitioning of Fe and Mn only slight variations are observed throughout western Lake Erie. This is probably due to the relatively homogenous nature of the sediment.

5.4 Behaviour of Zn, Ni, Cr, and Cu in Western Lake Erie Sediments

As stated earlier Na-Acetate does not attack organic matter or Fe-Mn oxides and therefore the trace metals recovered during the AEC extraction were likely derived from the minor dissolution of detrital carbonates or were adsorbed on the surface of the sediment-forming components. Data from Wedapohl (1978) indicate that the concentration of Zn, Ni, Cr, and Cu in detrital carbonates is quite low (Wedapohl 1978). In addition, carbonates account for between 10% and 40% of the sediment and therefore, the contribution of trace metals from the dissolution of minor amounts of detrital carbonates is considered minimal (Lee et al. 1981). The Pearson correlation coefficients for the trace metals pairs show strong linear correlations (Table 10). This same observation was made by Tessier et al. (1981) using the same reagent and concluded that the metals were adsorbed onto Fe-Mn oxides and organic matter. Thus, it appears that adsorption of trace metals onto Fe-Mn oxides and organic matter is the main source of the trace metals from the AEC extraction. Studies on the adsorption of trace metals onto hydrous metal oxides have demonstrated that adsorption involves cation exchange of H^+ ions from the hydroxide groups with trace metals (Forstner and Wittmann, 1983). The adsorption of trace metals onto organic matter is much more complicated since a wide variety of organic substances exist in the lacustrine environment. Although Fe-Mn oxides and organic matter are considered the most important substances for the adsorption of trace metals, clay minerals and carbonates can also adsorb trace metals. Adsorption onto clay minerals is caused by charge imbalances created by broken bonds around the edges of the Si-Al units. These broken bonds predominantly occur on noncleavage surfaces and the number of broken bonds increases as the particle size decreases (Forstner and Wittmann, 1983). Charge imbalances can also be created by the substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and divalent cations for Al^{3+} in the octahedral layer (Forstner and Wittmann, 1983). This process of substitution can leave behind unbalanced charges, which are balanced by adsorbed cations principally K^+. These cations include H^+ ions, trace metals, and other cations. The involvement of H^+ ions indicates the importance of pH in the role of adsorption. Trace metals and H^+ ions compete in adsorption and as the pH decreases the amount of trace metals adsorbed decrease and under extreme acidic conditions adsorbed trace metals cations are completely released (Forstner and Wittmann, 1983). Although adsorption of trace metals onto clay minerals does occur, it is considered to be relatively insignificant (Forstner and Wittmann, 1983). The most important role of clay minerals in trace metal adsorption is that of providing a mechanical substrate for the precipitation and flocculation Fe-Mn oxides and organic matter (Jenne, 1976). Carbonates are capable of adsorbing trace metals but they must compete with Fe-Mn oxides and organic matter (Chao, 1984). The adsorption of trace elements by carbonates is considered important only in arid environments were there is a lack of Fe-Mn oxides and organic matter (Chao, 1984). Overall the relative order of importance of adsorption type bonding for the trace metals examined in the study area appears to be: Zn>Ni>Cu>Cr (Figure 10).

The results from the organic extraction indicates that Cu has a relatively strong affinity for organic matter as compared to the other trace metals (Figure 10). A number of studies have shown that Cu has the greatest affinity to organic matter compared to Zn and Ni (Rashid, 1974; Stone and Droppo 1996; Tessier et al. 1981). It has been reported that, in the presence of organic matter, Cu(II) forms an inner sphere complex which is the most stable organic complex among the bivalent transition metal cations (Elliott et al. 1986). The data suggest that Cr also has a relatively strong affinity for organic matter but this association has not been previously reported in the literature (Figure 10). Only minor proportions (≤10%) of Zn and Ni were extracted during the second step indicating that organic matter plays only a minor role in the partitioning of Zn and Ni in western Lake Erie sediments (Figure 10).

Trace metals derived from the Fe-Mn oxide extraction step are those that were coprecipitated with Fe-Mn oxides. Trace metals adsorbed onto the surface of Fe-Mn oxides would have been removed during the AEC extraction. It has also been demonstrated that this step also dissolves dolomite. However, it is thought that the contribution of trace metals from the dissolution of dolomite is insignificant compared to the contribution from Fe-Mn oxides. A high proportion of trace metals associated with an Fe-Mn oxide extraction step is common (Tessier et al. 1981; Hall et al. 1996a; Stone and Droppo 1996 etc.). Forstner and Whitman (1983) state that Fe-Mn oxides under oxidizing conditions, constitute significant sinks for trace metals in aquatic systems. This is due to their ubiquitous occurrence and their low degree of crystallinity. This low degree of crystallinity is created by the alternate dissolution and precipitation caused by changes in the redox conditions. The low degree of crystallinity facilitates the nonstoichiometric incorporation of trace metals into the Fe-Mn oxides (Kuhnel et el. 1975). All four metals studied had the highest proportions extracted from the third step indicating that Fe-Mn oxides play an important role in the partitioning of these trace metals in western Lake Erie.

Overall, it appears that the partitioning of Zn and Ni is quite similar throughout western Lake Erie (Figure 10). Both elements have similar proportions recovered in the three extractions and the patterns of partitioning between samples sites are quite similar. The partitioning of Cu is much more variable but this is mainly due to a number of samples having values below the solid detection limit in the AEC extraction which produced misleading partitioning data for some samples (Figure 10). The partitioning of Cr in the study area is quite different from the other trace metals studied (Figure 10). The partioning patterns observed are controlled by the physio-chemical characteristics of the lake and the numerous sources of the trace metals which are mainly from industrial activity.

A number of researchers studying the partitioning of trace metals in sediments for environmental purposes mention the bioavailability and mobility of trace metals (Stone and Droppo 1996; Hall et. al 1996; Li et al. 1994). It is thought that bioavailability and mobility of a trace metal in sediment decrease in order of availability from the AEC extraction to the Fe-Mn oxide extraction because the strength of the extraction reagents used increases (Harrison et al. 1981; Tessier and Campbell, 1987). However, as it has been pointed out, the results are operationally defined and are only relative in nature. In addition, a multitude of factors influence the mobility and uptake of trace metals by organisms. Therefore, it unwise to use only the results of a sequential extraction to make claims about the mobility and bioavailability of trace metals in sediments.

A number of studies have examined the concentrations of trace metals in Lake Erie sediments (Mudroch et. al. 1988). However, it is difficult to make direct comparisons between the results of this study with that of others on Lake Erie sediments since different extraction techniques, sampling methods, and sample locations were used as well as the fact that the studies have been conducted over the last thirty years. However, most of the analytical techniques employed a non-selective partial extraction using HCL and or HNO_3. Table 11 is a comparison between the sum of the three extractions from this study with ranges in surficial sediments of Lake Erie that are reported in the literature. Table 11 indicates that the sum of the three extractions fall within the range of reported trace metal concentrations in Lake Erie.

Table 11: Comparison between the sum of the three extractions from this study with concentrations in surface sediments of Lake Erie from other studies. Concentrations in μg/g.

Element	Sum of Three Extractions		Reported Concentrations in Surface Sediments[1]	
	Min.	Max.	Min.	Max.
Zn	91	389	18	536
Ni	16	88	16	150
Cr	10.3	173	12	362
Cu	11.3	106	5	207

[1] After Mudroch et al. (1988).

One important aspect of the trace metal data that must be addressed is the role of grain size. It is well established that grain size has an influence on the metal concentration (Forstner and Wittmann, 1983). Trace metals are mainly found in the silt to clay sized fraction and the coarser material is considered to be relatively devoid of trace metals (Tessier et al. 1981; Stone and Droppo 1996). The only way to study the variations in trace metal concentrations caused by anthropogenic loading is to remove the variations caused by grain size. This was done by examining only the <63 μm fraction. However, by removing the coarser material the actual total trace metal distribution is lost and the trace metal concentrations measured only apply to the <63 micron fraction and not the total sediment. Within the study area it is observed that sites of the Positive-Skew and Bimodal subdivisions tend to have low percentages of material that is <63 microns while sediment of the Near Symmetrical subdivision have the highest percentages and are 100% for many sites (Table 7; Figure 16). Therefore, the trace metal concentrations of sites designated as Near Symmetrical are probably very similar to the trace metal concentrations expected from a bulk sediment sample. The measured trace metal concentrations of sites designated as Positive-Skew and Bimodal are probably much higher than the concentrations that would be measured from a bulk sediment sample. This is because the coarse detrital material would dilute the overall concentration of trace metals.

Although the trace metal data may not reflect the true concentration of trace metals within the study area, by removing the variations caused by grain size, the trace metal data can be used to study the distribution patterns and possible sources of the trace metals. Examination of Figure 12 indicates that the highest concentrations of Zn, Ni, Cr, and Cu are found at sites 1, 7, 8, 14, and 15. These sites are located at the western edge of Lake Erie along the American shoreline. Extensive industrial activity is located all along the American shoreline of the Detroit River and this is the primary source for the trace metals entering Lake Erie (Mudroch 1985; Lum and Gammon, 1985). Due to a midchannel water mass, low in temperature, that bisects the Detroit River, trace metals originating along the American shoreline are restricted to the American shoreline (Walters Jr. et al. 1972). Examination of Figure 6 indicates that the dominant surface and bottom currents restrict this water mass to the western section of the basin. This is confirmed since sites 1, 7, 8, 14, and 15 are located in this area and have the highest trace metal concentrations found in the study area. Lum and Gammon (1985) also found the high trace metal concentrations on the American shoreline at the mouth of the Detroit River. Carter and Hites (1992) studied the fate and transport of 2,4-di-*tert*-pentylphenol (24DP), an hydrophobic organic chemical derived from a single point source along the Detroit River. Hydrophobic organic chemicals, like trace metals, tend to be associated with fine-grained particles and accumulate in the sediment. Carter and Hites (1992) concluded that the majority of the 24DP is accumulating in the western basin of Lake Erie and the highest concentrations were found in an area 20-30 km from the mouth of the Detroit River. It appears that trace metals are also behaving in a similar way. Sites 2 through 6 located near the Ontario shoreline display a relatively constant concentration for each element studied and the concentrations are roughly half of what is observed on the American shoreline (Figure 12). This large difference can be explained by the midchannel water mass that bisects the Detroit River preventing trace metals originating on the American shoreline from migrating towards the Canadian side. In addition, there is very little industrial activity along the Canadian shoreline of the Detroit River as compared to the American shoreline. Sites 9 and 10 have the lowest trace metal concentrations observed in the study area. (Figure 12). As stated earlier, sites 9 and 10 are located less than 100 metres from the east-west shipping channels and the lake freighters erode and resuspend the lake bottom. Therefore, the sediments at sites 9 and 10 are undergoing erosion and this greatly reduces the accumulation of anthropogenically derived trace metals. The trace metal concentrations at sites 9 and 10 are similar to the range for background concentrations of trace metals reported in Lake Erie sediments by Mudroch et al. (1988). However, it is important to realize that the shipping channel is very narrow and that sediments a short distance north or south from the channel are expected to have trace metal concentrations that are much higher and comparable to the surrounding sample sites. The trace metal concentrations obtained at site 13 are also quite low compared to the other sample sites. The low trace metal concentrations observed at site 13 are largely due to the fact that this site is furthest away from the Detroit River. The dominant current velocities of western Lake Erie are probably responsible for the relatively high trace metal concentrations found at sites 16, 17, 18, and 20. Figures 5 and 6 indicate a general southeast direction of migration for sediment and water originating from the Detroit River. This southeast direction of flow would tend to carry sediments contaminated with trace metals towards the South Passage. Site 19 located near the mouth of the Maumee River has a much lower trace metal loading value than the surrounding sample sites. Examination of Figure 6 indicates that outflow from the Maumee River travels close to the shoreline near site 19. Thus, it appears that the Maumee River is not a major source for trace metals in Lake Erie.

The sum of the three extractions for each metal from the sample sites has also been examined. This may indicate which sample sites have the highest total metal concentrations. In order to display this information in a single diagram a simple calculation was performed. For each element the sum of the three extractions were examined and the highest concentration was set as a normalizing value. All the sums from the samples were divided by the normalizing value, so, the highest value would be one and all other sites would be some value less than one. This was done for each of the four metals studied and the values were added. Since four trace metals were examined, the maximum theoretical value would be four. The values were then plotted on a map of the study area (Figure 22). This is a very simplistic approach but the results can be used to determine the sites that have the highest trace metal concentrations. Figure 22 confirms the high concentrations of trace metals located at the western edge of Lake Erie.

Sites 1, 7, 8, 14, and 15 are clearly the most contaminated with respect to the trace metals. These sites have values that are approximately six times the value obtained at site 10. Figure 22 also reveals a general pattern of decreasing metal concentrations from west-east. This trend is expected since the Detroit River is the main source for trace metals entering Lake Erie. An exception to this trend occurs at sites 5 and 6 which show a slight increase in the trace metal concentration. It is not known why the trace metal concentration increase at sites 5 and 6 but the municipalities of Leamington and Kingsville are located just inland of these sites and may be a possible source of trace metal input. It should be noted however, that these values are much lower than those observed along the American shoreline.

The results of the sequential extraction procedure have shown that overall the greatest percentage of the extractable Zn, Ni, Cr, and Cu are associated with the Fe-Mn oxide extraction step. As stated earlier, elements associated with this step are considered the least mobile as compared with the other two extraction steps since the reagent used was the strongest. This behaviour will persist provided that oxidizing conditions persist in western Lake Erie since Fe-Mn oxides are subject to dissolution in reducing conditions. However, reducing conditions appear to be an uncommon phenomenon in western Lake Erie. Thus, the bulk of the trace metals appear to be relatively immobile. The highest trace metal concentrations as well as the highest proportion of trace metals involved in adsorptive type bonding are found in this area. This indicates a large amount of relatively immobile elements that would be potentially bioavailable to organisms residing within the sediment, exist in this area. The mobility of the trace metals associated with organic matter is difficult to asses since a large number of organic molecules exist in the lacustrine environment. It is interesting to note that besides the areas near the mouth of the Detroit River and sites 9 and 10 which are affected by the shipping channel, the trace metal concentrations are relatively uniform throughout the study area. This suggest a quite homogenous system with respect to trace metal concentrations. This is probably due to the continual resuspension and redistribution of the fine-grained sediment, combined with the low export of sediment to the central basin.

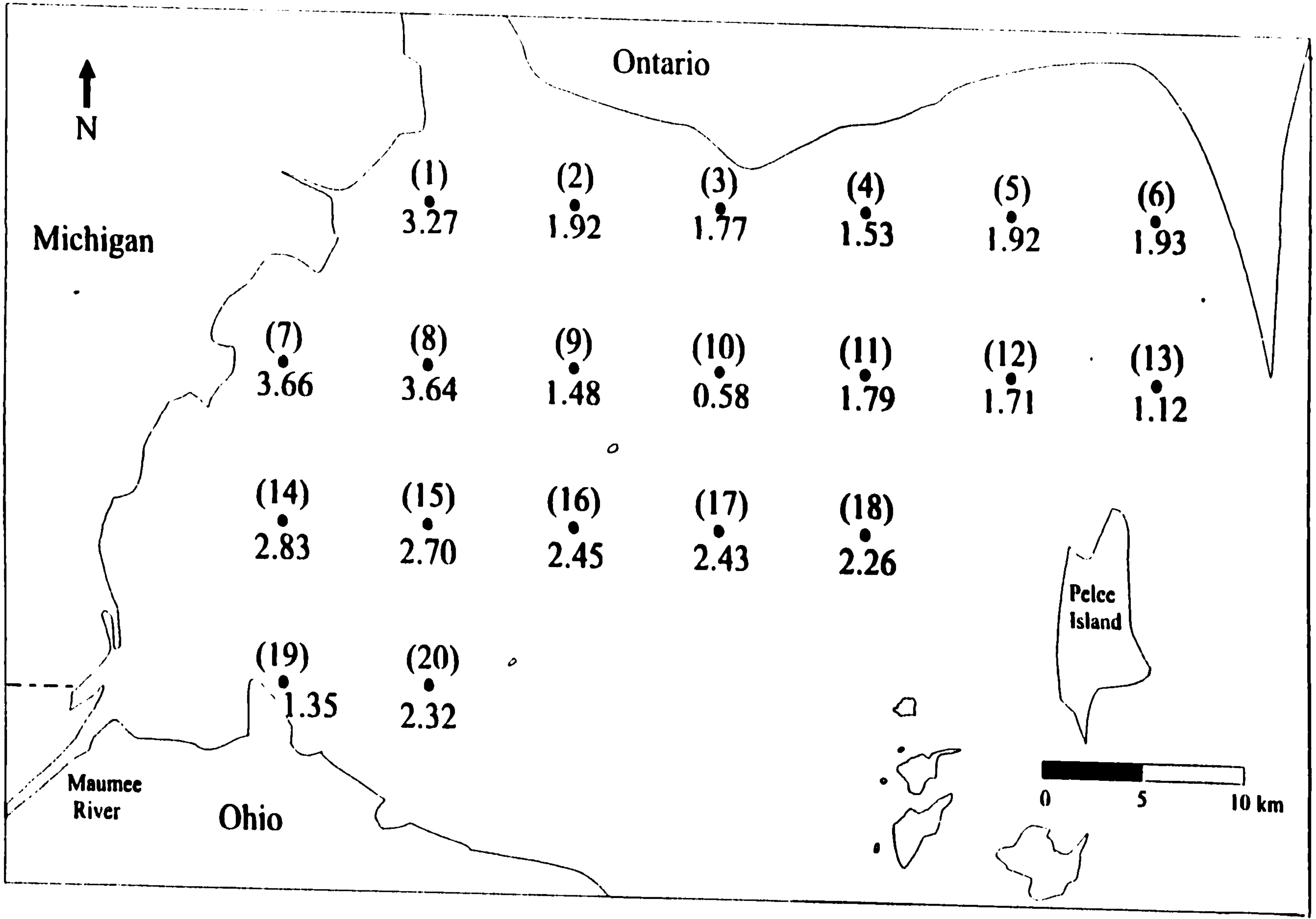

Figure 34. Map of the western basin of Lake Erie with trace metal loading values. Sample sites are in brackets.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

(1) Examination of histogram patterns from the grain-size data reveal that three distinct sediment types exist in Lake Erie. The first group consists of sites that have a positive-skew distribution. These sites are found near the shoreline and the positive-skew is created by the strong current velocities found in this area which selectively remove the fine-grained sediments. Exceptions to this are found at two sites that are located near the shipping lane. The positive-skew distribution at these sites is thought to be created by the lake freighters. The ships scour the lake bottom and resuspend the fine-grained sediments which are carried away by the currents. The second subdivision consists of sites with a bimodal distribution and are the result of mixing of a glacial sand deposit and the more recent fine-grained sediments derived from the rivers that enter the lake. The third subdivision consists of sites with a near symmetrical grain-size distribution. These sites are located in the open-lake environment.

(2) The results from the major element, total carbon, and nitrogen analyses reinforce the subdivisions based on the grain-size data.

(3) Examination of the sediments residues after each step of the sequential extraction procedure indicate that calcite was completely dissolved and dolomite may have been partially dissolved during the first step of the procedure. No changes in mineralogy were observed during the second extraction step and dolomite was completely dissolved during the third step. No other changes in mineralogy were

observed but a number of unexplained peaks appeared after the second and third step of the procedure.

(4) Results from analyses of LKSD-4 a certified reference material suggest that the sequential extraction procedure does not attack sulphides and silicates, indicating that this procedure is an excellent technique for examining the partitioning of anthropogenically derived trace metals in aquatic sediments.

(5) The partitioning data for the major elements indicates that Ca and Mg were mainly extracted during the first and third extraction step. This was expected since most of the Ca and Mg is found in calcite and dolomite. The partitioning of Fe and Mn indicates that most of the Fe exists as an oxide as very little was removed from the first and second steps. The partitioning of Mn was quite different from Fe. The partitioning data indicates that Mn is either adsorbed onto the surface of Fe-oxides and organic matter or exists as an oxide. Very little Fe and Mn was extracted from the second step suggesting that organic matter played a minor role. However, it was observed that the small proportion of Fe and Mn that was extracted may have be due to ferruginous solid particles that existed in the supernatants.

(6) The partitioning of the trace metals indicates that Fe-Mn oxides are the most important sediment forming component that trace metals are associated with in western Lake Erie. The partitioning data indicate that the behaviour of Zn and Ni are quite similar. The partitioning data indicates organic matter is an important scavenger of Cr and Cu.

(7) Partitioning patterns reveal the highest amount of adsorbed metals are found near the mouth of the Detroit River. This may be related to discharge of industrial waste along the Detroit River.

(8) The trace metals originating from point sources along the American shoreline are restricted to the western portion of the western basin of Lake Erie because of current flow. This area has the highest trace metal concentrations observed.

(9) A general pattern of decreasing trace metal loading from west to east is observed in western Lake Erie. The only exception to this located at sites located in the north-east corner of the study area where a slight increase is observed. This may, or may not, be related to their close proximity of Leamington and Kingsville. Sites 9 and 10 have the lowest trace metal loading value and this is due their proximity to the shipping channel.

(10) It appears that the Maumee River is not a significant source for trace metals in western Lake Erie.

6.2 Recommendations

(1) The partitioning of Pb and Cd should also be examined since these elements are used extensively in industrial activity and previous research has indicated that high concentrations have been found in the sediments of western Lake Erie. Their partitioning data is unknown and required in order to examine the mobility and potential bioavailability of these elements.

(2) Examination of sediment cores from western Lake Erie should be undertaken. Sediment cores can be used to study the vertical distribution of trace metals within the

lake sediment. This data can be used to examine the changes in trace metal inputs over time as well as element mobility within the sediments vertically. Redox conditions may vary with depth and this can affect the partitioning of the trace metals.

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APPENDIX I
SEDIMENT ANALYSIS PROCEDURE

Preparation of Reagents

1.0 M Sodium Acetate (NaOAc)

1) Dissolve 82.03 grams of BDH AnalaR grade sodium acetate into 1 L of deionized water.
2) Adjust pH to 5.0 with addition of AnalaR grade concentrated HNO_3.

0.1 M sodium pyrophosphate ($Na_4P_2O_7$)

1) Dissolve 44.6 gram of BDH ACS Assured sodium pyrophosphate in 1 L of deionized water.
2) Adjust pH to 10.0 with addition of BDH AnalaR grade concentrated HNO_3.

1.0 M Hydroxylamine Hydrochloride ($NH_2OH.HCL$)

1) Dissolve 69.49 of BDH AnalaR grade hydroxylamine hydrochloride in deionized water.
2) Adjust pH to 2.0 with BDH AnalaR grade concentrated HNO_3.

Porewater Removal

1) Approximately 10 grams of wet sediment was placed in a 50mL polypropylene centrifuge tube and centrifuged for 15 minutes at 7,000 rpm.
2) Decant supernatant.

Sediment samples were run in batches of nine which consisted of six samples, one blank, one certified reference material (LKSD-4), and one internal reference material (SED).

AEC Extraction

1) A 0.5 g sample of dewatered sediment was weighted into a 50 mL Oak Ridge polycarbonate centrifuge tube and 10mL of the 1.0 M NaOAc (sodium acetate) solution was added.

2) The centrifuge tube was placed in a horizontal shaker for six hours at room temperature.

3) The samples were centrifuge for 10 minutes at 6,000 rpm.

4) The supernatant was filtered through a #40 Whatman filter paper (pre-rinsed once with 5% nitric acid and three times with de-ionized water) into a pre-weighed 60mL low density polyethylene bottle.

5) 2.5 mL of de-ionized water was added to the sediment in the centrifuge tube and the tube was again centrifuged for 10 minutes at 6,000 rpm.

6) The supernatant was filtered through the same filter paper and into the same bottle as the previous supernatant.

7) Sep 5 and 6 were repeated.

8) Steps 1 through 6 were repeated.

9) After the final rinse the weight of the bottle was recorded and the weight of the empty bottle was subtracted to obtain the solution weight.

Organic Extraction

1) 35 mL of the 0.1 M $Na_4P_2O_7$ (sodium pyrophosphate) solution was added to the centrifuge tube containing the sediment used in the AEC extraction.

2) The centrifuge tube was placed in a horizontal shaker for one hour at room temperature.

3) The samples were centrifuged for 10 minutes at 6,000 rpm.

4) The supernatant was then filtered through a #40 Whatman filter paper (pre-rinsed once with 5% nitric acid and three times with de-ionized water) into a pre-weighed 60mL low density polyethylene bottle.

5) Steps 1 through 4 were repeated.

6) 2.5 mL of de-ionized water was added to the sediment in the centrifuge tube and the tube was again centrifuged for 10 minutes at 6,000 rpm.

7) The supernatant was filtered through the same filter paper and into the same bottle as the previous supernatant.

8) The weight of the bottle was recorded and the weight of the empty bottle was subtracted to obtain the solution weight.

Fe-Mn oxide Extraction

1) 15 mL of the 1.0M $NH_2OH.HCL$ (hydroxylamine hydrochloride) solution was added to the centrifuge tube containing the sediment from the organic extraction.

2) The centrifuge tubes were placed into a water-bath at 90° for three hours.

3) The centrifuge tubes were carefully opened every half-hour to vent gas.

4) The samples were centrifuged for 10 minutes at 6,000 rpm.

5) The supernatant is then filtered through a #40 Whatman filter paper (pre-rinsed once with 5% nitric acid and three times with de-ionized water) into a pre-weighed 60mL low density polyethylene bottle.

5) 5 mL of BDH ACS assured 25% HOAc (glacial acetic acid) in de-ionized water was added to the sediment in the centrifuge tube and the tube was again centrifuged for 10 minutes at 6,000 rpm.

6) The supernatant was filtered through the same filter paper and into the same bottle as the previous supernatant.

7) Step 5 and 6 were repeated.

8) Steps 1 through 7 were repeated.

9) After the final rinse the weight of the bottle was recorded and the weight of the empty bottle was subtracted to obtain the solution weight.

APPENDIX II:
ANALYTICAL RESULTS

Table A1: **Fe, Mg, Ca, and Mg concentrations from the sequential extraction procedure for Lake Erie sediments.**

	Iron (µg/g)				Manganese(µg/g)			
SITE	Extraction 1	Extraction 2	Extraction 3	Sum	Extraction 1	Extraction 2	Extraction 3	Sum
1	2820	3800	20100	26720	241	16.1	186	443
2	1570	3460	28000	33030	210	14.0	296	520
3	1820	2600	19000	23420	232	13.1	220	465
4	1590	3280	25100	29970	255	13.2	266	534
5	1560	3280	29700	34540	316	16.8	315	648
6	1160	3370	24700	29230	252	16.7	257	526
7	2550	4010	19600	26160	277	15.0	195	487
8	1840	3620	25300	30760	319	15.8	281	616
9	2160	2830	24500	29490	392	15.2	277	684
10	1350	1870	12300	15520	207	10.3	157	375
11	1390	3470	23700	28560	246	15.2	243	504
12	1910	3490	26400	31800	271	15.0	251	537
13	1100	1970	16300	19370	178	10.5	154	342
14	3890	5190	24900	33980	343	19.6	250	613
15	2600	4830	27700	35130	430	22.6	290	742
16	3390	2150	26500	32040	302	9.6	246	557
17	2800	2660	22300	27760	301	9.6	221	532
18	3040	3970	28400	35410	378	17.5	292	687
19	1030	3360	19900	24290	372	17.1	239	628
20	3790	5800	28300	37890	464	24.0	286	774

	Calcium (µg/g)				Magnesium (µg/g)			
SITE	Extraction 1	Extraction 2	Extraction 3	Sum	Extraction 1	Extraction 2	Extraction 3	Sum
1	20600	1550	18200	40350	6020	983	9400	16403
2	26000	1100	18800	45900	10800	1050	15960	27810
3	27800	1200	18200	47200	9900	935	13700	24535
4	29100	1130	19100	49330	13100	1030	15300	29430
5	21600	1200	18300	41100	10700	949	14200	25849
6	15200	1020	12800	29020	7900	941	11400	20241
7	26700	1050	9020	36770	4870	769	7990	13629
8	19400	857	3940	24197	9300	733	5420	15453
9	14600	1570	33100	49270	5450	1160	23100	29710
10	19300	1170	25500	45970	11400	957	17700	30057
11	19700	1140	12400	33240	11000	1090	11300	23390
12	19900	749	8050	28699	10500	1090	8540	20130
13	9640	1100	5210	15950	4890	723	5710	11323
14	18700	707	6770	26177	6100	965	7170	14235
15	18200	<DL	8280	26480	7590	924	8300	16814
16	9720	<DL	3600	13320	4240	486	7170	11896
17	18800	713	3140	22654	10200	592	4880	15672
18	14600	825	5010	20435	7440	935	8450	16825
19	30000	837	15600	46437	7590	756	10500	18846
20	13300	481	1810	15591	4630	870	5300	10800

Table A2: **Zn, Ni, Cr, and Cu concentrations from the sequential extraction procedure for Lake Erie sediments.**

	Zinc (µg/g)				Nickel (µg/g)			
SITE	Extraction 1	Extraction 2	Extraction 3	Sum	Extraction 1	Extraction 2	Extraction 3	Sum
1	209	17.9	162	389	26.7	4.3	38	69.0
2	57.5	13.1	140	211	8.8	3.3	34.6	46.7
3	75.8	11.1	104	191	13.5	2.0	28.9	44.4
4	51.6	10.3	127	189	10.6	<DL	31.8	42.4
5	45.8	11.3	146	203	8.8	<DL	38.8	47.6
6	43.9	10.2	144	198	10.7	<DL	35.6	46.3
7	191	17.2	156	365	31.0	1.7	41.3	74.1
8	166	17.4	201	384	30.5	3.9	54.0	88.5
9	54.5	<DL	126	181	9.8	<DL	31.6	41.4
10	8.1	9.4	73	91	3.0	<DL	13.3	16.3
11	55.2	25.2	139	219	10.9	2.7	35.5	49.0
12	71.0	10.4	155	236	13.5	<DL	35.1	48.6
13	33.6	8.5	92	134	9.7	<DL	18.5	28.2
14	107	17.5	165	289	21.7	6.8	44.0	72.4
15	95.8	18.8	180	294	19.1	4.9	45.1	69.1
16	106	10.8	183	300	25.6	2.7	34.5	62.8
17	100	9.4	155	264	24.0	2.6	37.5	64.1
18	71.0	14.7	167	253	17.2	3.5	42.7	63.4
19	38.7	9.2	105	153	7.9	2.2	28.7	38.8
20	73.1	17.7	163	254	16.5	5.2	44.1	65.9

	Chromium (µg/g)				Copper (µg/g)			
SITE	Extraction 1	Extraction 2	Extraction 3	Sum	Extraction 1	Extraction 2	Extraction 3	Sum
1	20.3	38.7	115	174	16.3	16.2	19.8	52.4
2	3.4	23.4	44.8	71.5	10.2	12.4	24.5	47.0
3	5.9	21.8	41.8	69.5	11.2	12.9	15.8	39.9
4	2.9	18.4	40.5	61.8	<DL	12.6	10.3	22.9
5	2.7	19.7	52.1	74.5	8.3	11.4	26.8	46.5
6	2.2	27.0	44.7	73.9	16.5	9.3	24.2	49.9
7	14.1	34.9	105	154	22.8	23.0	61.0	106.8
8	12.0	26.5	102	141	24.5	19.4	46.0	89.9
9	3.0	<DL	43.6	46.6	<DL	6.2	24.0	30.2
10	<DL	<DL	10.3	10.3	<DL	3.5	7.0	10.5
11	3.0	23.2	45.5	71.7	<DL	10.2	17.9	28.1
12	3.8	<DL	52.0	55.8	<DL	11.3	13.4	24.7
13	2.2	26.1	31.1	59.3	<DL	6.7	6.0	12.7
14	4.9	23.3	72.5	101	13.4	16.8	43.0	73.3
15	4.7	22.3	71.6	98.6	12.0	16.9	35.0	63.9
16	8.1	<DL	91.7	99.9	8.9	8.1	25.2	42.2
17	5.6	17.2	57	79.7	14.8	12.8	32.6	60.2
18	3.7	22.7	58.7	85.2	10.5	11.2	21.7	43.5
19	1.7	<DL	30.6	32.2	7.2	9.0	19.1	35.3
20	3.3	21.5	51.2	75.9	8.3	15.5	28.2	52.0

Table A3: **Fe, Mn, Ca, and Mg concentrations from the sequential extraction procedure for the internal reference material (SED).**

	Iron (µg/g)					Manganese (µg/g)			
Sample	Extraction 1	Extraction 2	xtraction	Sum	Sample	Extraction 1	Extraction 2	Extraction 3	Sum
1	2148	2980	27836	32964	1	309	18.2	319	647
2	1954	N/A	22310	N/A	2	295	N/A	268	N/A
3	1892	N/A	22479	N/A	3	293	N/A	268	N/A
4	2008	3102	21711	26821	4	288	18.1	275	582
5	1851	2736	30749	35336	5	285	16.4	353	655
6	1884	3348	29921	35153	6	286	19.3	349	654
7	2014	2813	23507	28333	7	331	16.2	306	653
8	2100	2857	26996	31953	8	334	15.7	334	684
9	2182	2926	24908	30016	9	335	17.0	311	662
	Calcium (µg/g)					Magnesium (µg/g)			
Sample	Extraction 1	Extraction 2	xtraction	Sum	Sample	Extraction 1	Extraction 2	Extraction 3	Sum
1	18441	1386	19976	39803	1	8333	955	16873	26161
2	18974	N/A	17548	N/A	2	9043	N/A	13445	N/A
3	19011	N/A	17255	N/A	3	9165	N/A	13268	N/A
4	18275	1290	22218	41783	4	8738	915	15366	25019
5	17347	1114	22671	41131	5	8036	757	17845	26638
6	17028	1085	22583	40697	6	7801	867	17795	26463
7	19539	1115	24418	45072	7	8738	774	16195	25707
8	20666	1187	21384	43237	8	9631	790	15488	25909
9	19522	1174	22025	42721	9	8778	797	15376	24951

Table A4: Zn, Ni, Cr, and Cu concentrations from the sequential extraction procedure for the internal reference material (SED).

	Zinc (µg/g)			
Sample	Extraction 1	Extraction 2	Extraction 3	Sum
1	103	16.0	213	331
2	100	N/A	180	N/A
3	97	N/A	178	N/A
4	97	20.7	193	310
5	93	15.1	225	334
6	98	18.0	224	339
7	104	14.9	196	315
8	110	15.1	210	335
9	108	14.8	195	318

	Nickel (µg/g)			
Sample	Extraction 1	Extraction 2	Extraction 3	Sum
1	16.5	3.7	49.0	69.2
2	15.6	N/A	42.6	N/A
3	15.4	N/A	40.9	N/A
4	15.8	3.7	41.0	60.6
5	N/A	3.1	52.7	N/A
6	14.6	4.4	51.7	70.6
7	16.8	3.0	48.0	67.8
8	17.2	3.0	53.0	73.2
9	16.9	4.1	48.2	69.1

	Chromium (µg/g)			
Sample	Extraction 1	Extraction 2	Extraction 3	Sum
1	8.1	19.4	79.6	107
2	7.8	N/A	66.0	N/A
3	7.7	N/A	63.8	N/A
4	7.6	16.9	67.8	92
5	7.3	18.8	84.0	110
6	7.3	21.8	85.2	114
7	8.1	15.7	75.0	99
8	8.4	18.6	81.3	108
9	8.2	15.8	74.4	98

	Copper (µg/g)			
Sample	Extraction 1	Extraction 2	Extraction 3	Sum
1	25.8	20.2	52.4	98.4
2	23.0	N/A	47.4	N/A
3	22.6	N/A	44.1	N/A
4	20.3	20.2	51.2	91.8
5	21.5	20.4	49.9	91.8
6	20.1	22.0	58.0	100
7	21.3	20.2	58.5	100
8	23.8	20.7	60.1	105
9	25.2	21.2	55.8	102

Table A5: Fe, Mn, Ca, and Mg concentrations from the sequential extraction procedure for LKSD-4.

	Iron (µg/g)					Manganese (µg/g)			
Sample	Extraction 1	Extraction 2	Extraction 3	Sum	Sample	Extraction 1	Extraction 2	Extraction 3	Sum
LKSD-4	295	2902	10578	13800	LKSD-4	264	22.7	107	394
LKSD-4	285	2698	11659	14700	LKSD-4	258	20.5	109	387
LKSD-4	272	3483	10666	14300	LKSD-4	260	27.1	106	393
LKSD-4	282	3326	11075	14900	LKSD-4	259	26.3	111	397
LKSD-4	255	3329	11479	15100	LKSD-4	250	30.3	115	395
LKSD-4	231	3221	9888	13300	LKSD-4	253	24.2	106	383
LKSD-4	273	2989	8750	12000	LKSD-4	260	23.5	92	375
LKSD-4	275	2717	8552	11600	LKSD-4	251	21.2	87	359
LKSD-4	257	3214	16496	19968	LKSD-4	261	26.3	148	436
LKSD-4	300	2962	8609	11900	LKSD-4	303	22.3	91	416
LKSD-4	304	2350	10999	13653	LKSD-4	300	18.8	125	444
LKSD-4	241	3152	11831	15223	LKSD-4	285	28.7	125	439
LKSD-4	293	3086	11872	15300	LKSD-4	292	25.8	123	441
LKSD-4	293	2747	8493	11400	LKSD-4	299	19.2	97	416

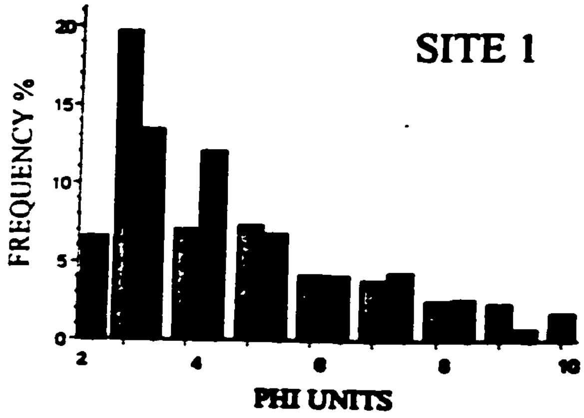
	Calcium (µg/g)					Magnesium (µg/g)			
Sample	Extraction 1	Extraction 2	Extraction 3	Sum	Sample	Extraction 1	Extraction 2	Extraction 3	Sum
LKSD-4	7089	767	1044	8899	LKSD-4	551	77.5	2338	2967
LKSD-4	6976	685	1162	8824	LKSD-4	539	67.8	2335	2942
LKSD-4	7041	697	721	8460	LKSD-4	540	37.8	2141	2650
LKSD-4	7026	660	759	8445	LKSD-4	541	37.8	2095	2610
LKSD-4	6674	813	860	8347	LKSD-4	512	32.7	2265	2790
LKSD-4	6728	657	797	8182	LKSD-4	524	31.5	2043	2580
LKSD-4	6961	623	699	8282	LKSD-4	544	27.3	1620	2180
LKSD-4	6744	369	659	7773	LKSD-4	522	N/A	1542	N/A
LKSD-4	6934	690	981	8605	LKSD-4	530	29.7	2893	3430
LKSD-4	7993	605	774	9373	LKSD-4	597	28.2	1535	2150
LKSD-4	8226	507	872	9605	LKSD-4	630	25.5	2195	2851
LKSD-4	7489	797	955	9241	LKSD-4	573	30.4	2401	3005
LKSD-4	7784	703	873	9360	LKSD-4	591	34.3	2130	2700
LKSD-4	7817	584	811	9212	LKSD-4	593	23.0	1640	2200

Table A6: Zn, Ni, Cr, and Cu concentrations from the sequential extraction procedure for LKSD-4.

	Zinc (µg/g)					Nickel (µg/g)			
Sample	Extraction 1	Extraction 2	Extraction 3	Sum	Sample	Extraction 1	Extraction 2	Extraction 3	Sum
LKSD-4	61.4	23.4	81.6	166	LKSD-4	4.5	4.2	13.1	21.9
LKSD-4	59.9	21.3	77.8	159	LKSD-4	4.5	3.7	13.2	21.4
LKSD-4	62.4	34.9	N/A	N/A	LKSD-4	4.7	4.5	15.0	24.2
LKSD-4	62.7	32.9	86.6	182	LKSD-4	4.5	4.6	14.6	23.6
LKSD-4	57.5	28.4	89.8	176	LKSD-4	4.3	3.9	15.5	23.7
LKSD-4	54.7	24.8	89.3	169	LKSD-4	3.6	1.9	14.8	20.2
LKSD-4	60.5	21.6	75.3	157	LKSD-4	4.4	N/A	12.1	N/A
LKSD-4	58.5	19.5	69.9	148	LKSD-4	4.5	N/A	11.3	N/A
LKSD-4	60.6	26.0	103.8	190	LKSD-4	4.3	4.7	16.7	25.7
LKSD-4	67.2	28.6	80.4	176	LKSD-4	4.7	4.2	11.9	20.8
LKSD-4	69.1	18.6	94.8	182	LKSD-4	5.0	3.3	16.6	N/A
LKSD-4	62.7	29.0	90.7	182	LKSD-4	4.0	3.9	17.1	19.5
LKSD-4	67.3	24.7	91.6	172	LKSD-4	4.8	4.7	16.4	25.9
LKSD-4	72.6	20.9	74.1	160	LKSD-4	5.6	3.9	12.8	22.3

	Chromium (µg/g)					Copper (µg/g)			
Sample	Extraction 1	Extraction 2	Extraction 3	Sum	Sample	Extraction 1	Extraction 2	Extraction 3	Sum
LKSD-4	1.1	8.8	7.7	17.6	LKSD-4	0.7	5.9	7.8	14.5
LKSD-4	1.1	9.2	8.1	18.5	LKSD-4	2.0	5.7	4.9	12.6
LKSD-4	1.1	10.1	7.4	18.6	LKSD-4	2.1	7.1	11.4	20.6
LKSD-4	1.1	9.9	7.6	18.5	LKSD-4	1.5	7.2	6.1	14.9
LKSD-4	1.0	9.9	8.6	19.5	LKSD-4	0.3	6.7	7.9	14.9
LKSD-4	0.9	11.3	7.3	19.5	LKSD-4	1.1	4.8	9.2	15.0
LKSD-4	1.1	8.9	6.4	16.3	LKSD-4	1.3	3.2	10.8	15.3
LKSD-4	1.0	N/A	6.3	N/A	LKSD-4	1.4	1.5	5.3	8.3
LKSD-4	1.2	11.8	10.8	23.8	LKSD-4	0.0	7.3	14.3	21.6
LKSD-4	1.3	8.7	7.2	17.1	LKSD-4	0.9	6.3	14.8	22.0
LKSD-4	1.3	8.4	8.2	18.0	LKSD-4	0.7	4.8	12.4	18.0
LKSD-4	1.0	8.9	8.8	18.6	LKSD-4	1.0	6.7	11.8	19.5
LKSD-4	1.1	8.2	8.1	17.4	LKSD-4	0.8	7.4	10.2	18.3
LKSD-4	1.3	8.6	6.2	16.1	LKSD-4	2.5	6.2	9.3	18.1

APPENDIX III
HISTOGRAMS OF GRAIN-SIZE DISTRIBUTIONS FROM WESTERN LAKE ERIE SEDIMENTS


SITE 1
FREQUENCY %
20
15
10
5
0
2
4
6
8
10
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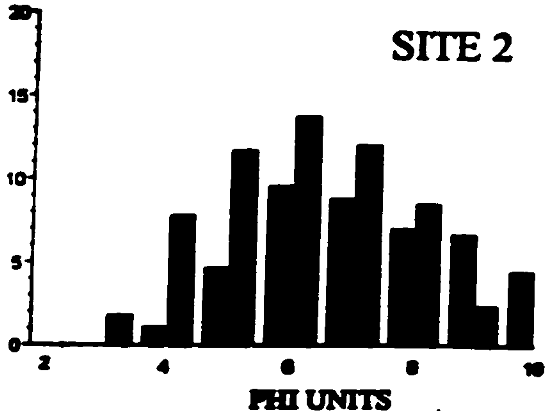
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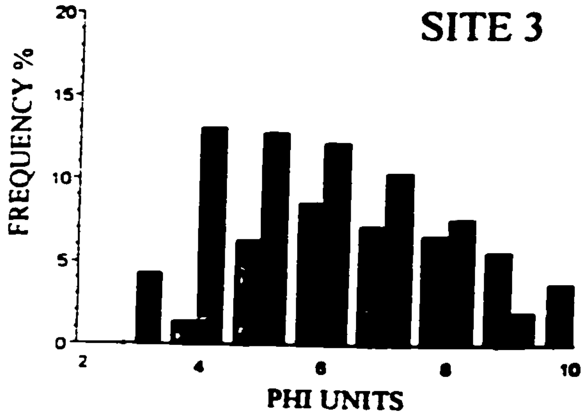
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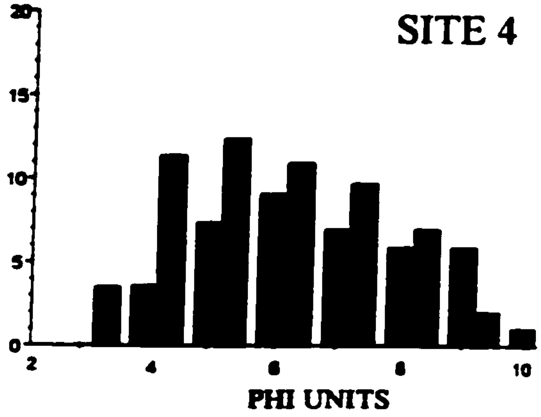
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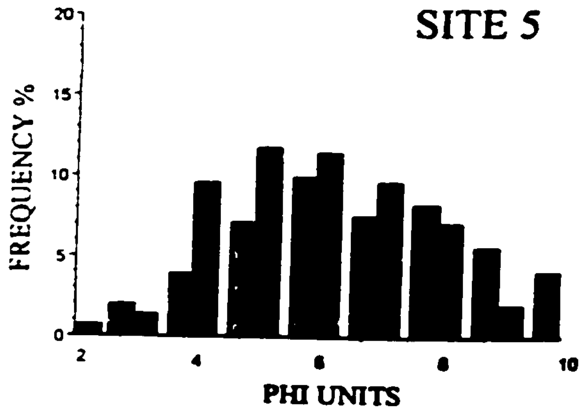
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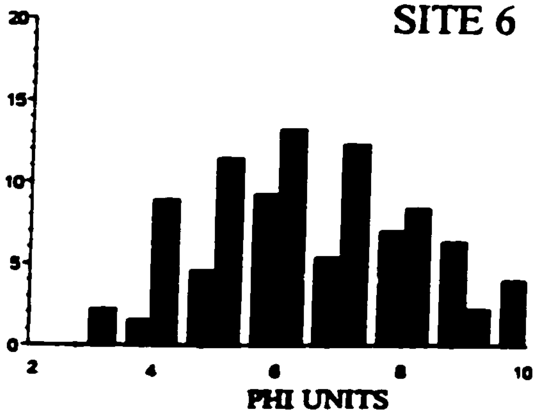
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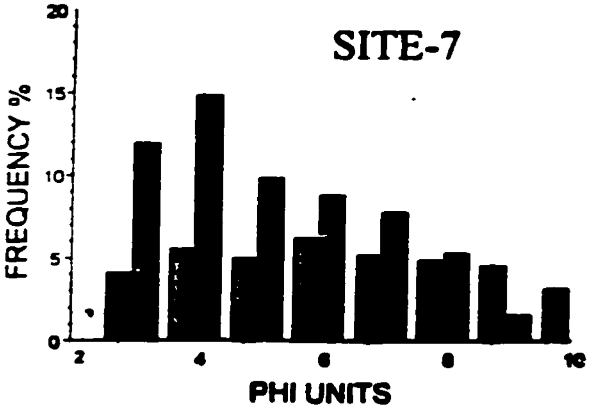
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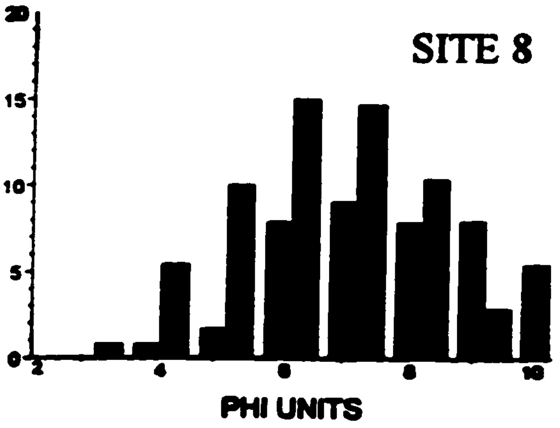
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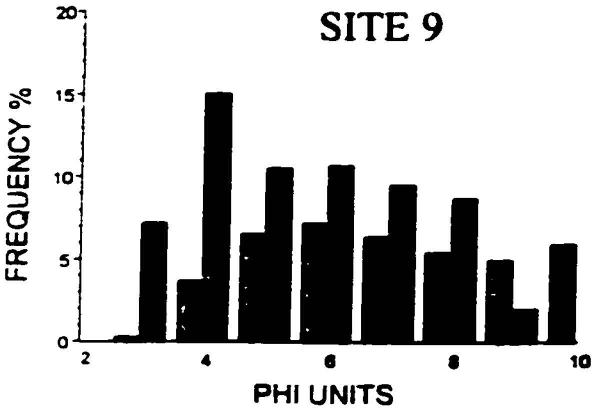
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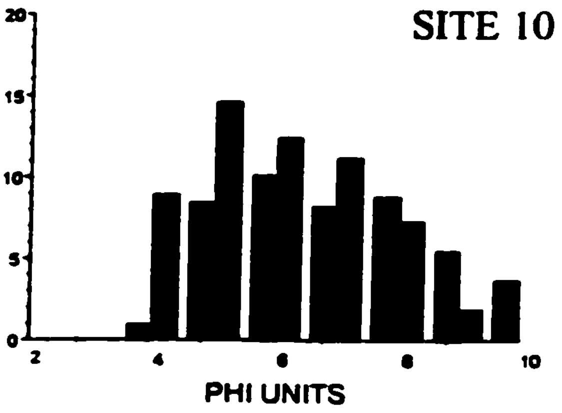
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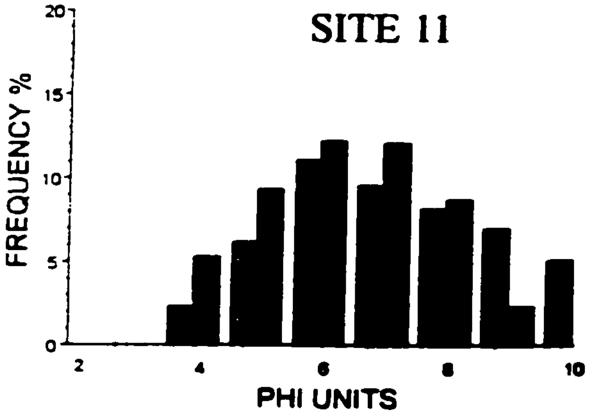
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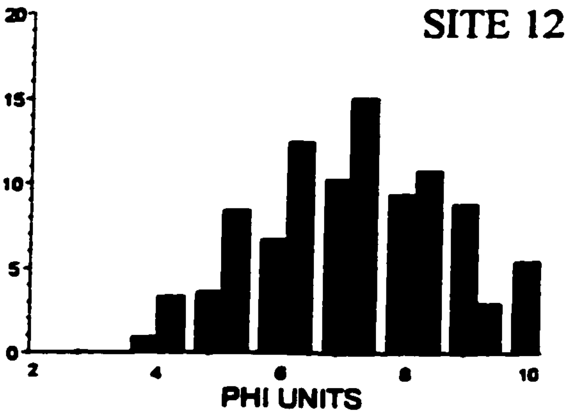
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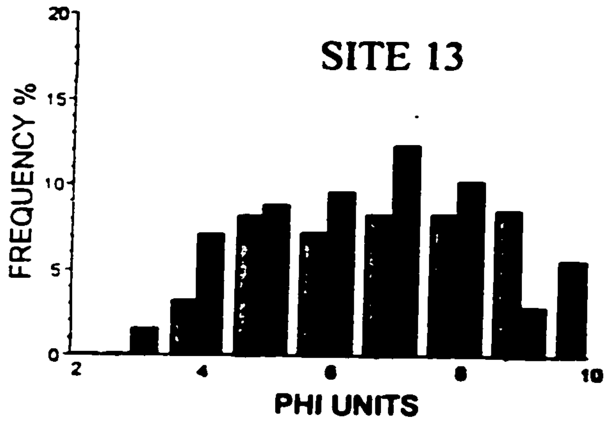
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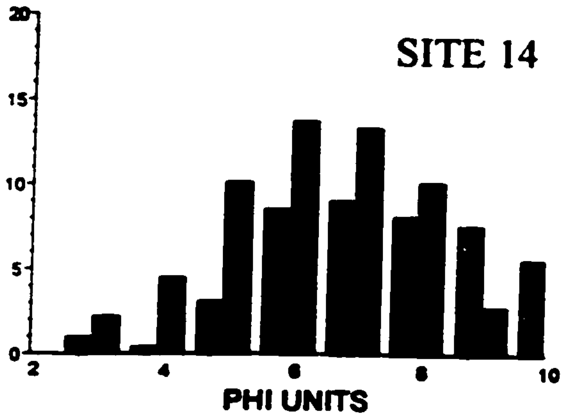
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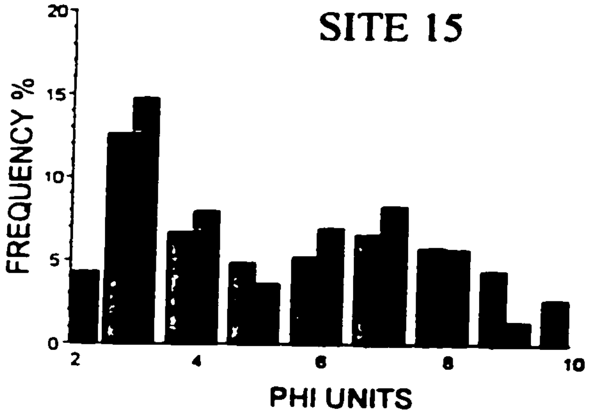
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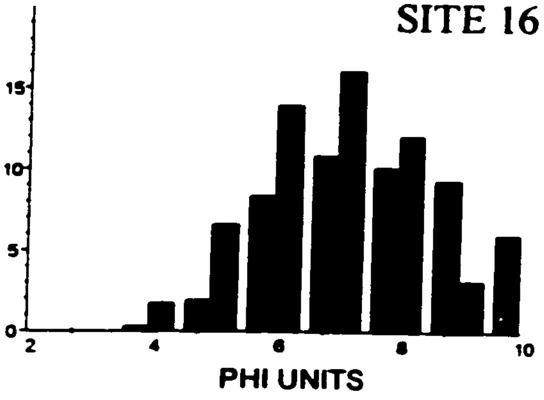
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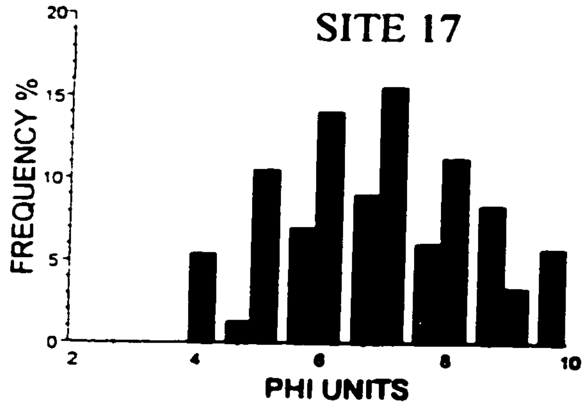
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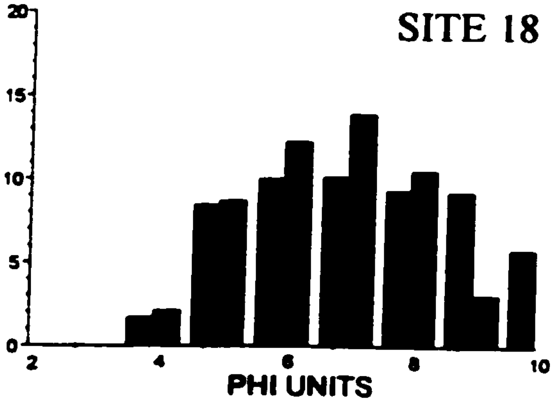
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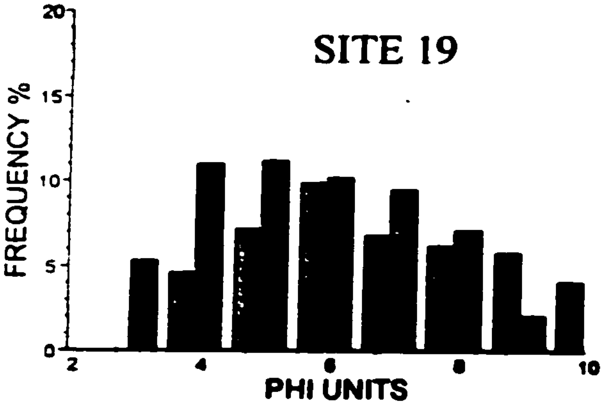
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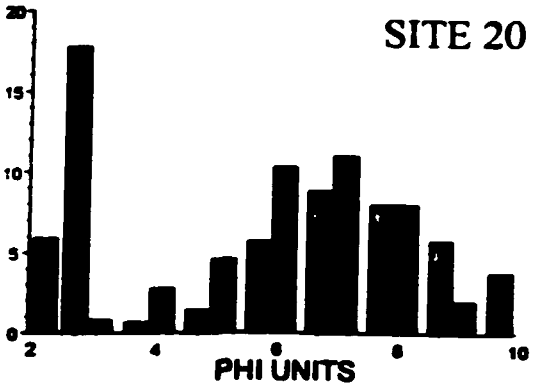
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PHI UNITS

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