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Investigations in the Great Lakes and the Gulf of Maine

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Jane M. Matty

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Major professor

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INFLUENCE OF EARLY DIAGENESIS ON THE GEOCHEMICAL CYCLING OF ARSENIC AND MERCURY

Investigations in the Great Lakes and the Gulf of Maine

by

Jane M. Matty

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ABSTRACT

INFLUENCE OF EARLY DIAGENESIS ON THE GEOCHEMICAL CYCLING OF ARSENIC AND MERCURY

Investigations in the Great Lakes and the Gulf of Maine

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Jane M. Matty

The geochemical cycles of arsenic and mercury in aquatic systems are strongly influenced by the association of these elements with particulate matter. In aquatic basins, arsenic and mercury are scavenged by particulate matter, which settles to the bottom, where it is subjected to the physical, chemical and biological processes of early diagenesis. The effects of these processes on arsenic and mercury were investigated in selected depositional basins of Lake Michigan, Lake Superior, and the Gulf of Maine.

Sediment cores were collected and sectioned at 1 cm intervals, porewaters were separated by centrifuging, and sediments subjected to sequential chemical extractions. Porewaters and sediment leachates were analyzed for arsenic and mercury. Alkalinity, pH, and ferrous iron of porewaters, and the organic carbon content of sediments was also determined.

As sediment is buried, changes in the partitioning of mercury and arsenic among different phases of sediment occur, indicating that both elements are mobilized and repartitioned during early diagenesis in all of the sites examined. Concentration gradients of arsenic in porewaters indicate that there is a flux of arsenic from the sediments to the sediment-water interface via porewater at most sites. Concentration gradients of mercury in porewaters are more complicated than those for arsenic, but there are gradients suggesting some flux of mercury to the sediment-water interface at all of the Great Lakes sites, although not in the Gulf of Maine. The upward diffusive fluxes of mercury and arsenic released during early diagenesis are responsible for the observed repartitioning of these elements in buried sediments, and for the enrichment of surface sediments in these metals. Diagenetic enrichment of surface sediments is more efficient in freshwater than in the marine setting, and more effective for mercury than for arsenic. This enhances the potential bioavailability of these metals. Permanent burial of arsenic and mercury in sediments is governed by the formation of authigenic minerals, particularly sulfides, in the reduced zone of sediments.

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I. INTRODUCTION

The geochemical cycling of elements is a fundamental theme of geochemistry. Understanding the controls on geochemical cycling of elements allows geochemists to interpret elemental distribution patterns in rocks and other geologic materials, and thereby gain insight into geologic processes. An understanding of geochemical cycles is also of substantial practical value. The geochemical cycles of elements have influenced the earth's surface environment throughout geologic time, and have themselves been altered by changes in that environment (Faure, 1991). Knowledge of the cycles of toxic elements, what controls them, and how they respond to perturbations is essential for environmental scientists researching such elements.

One environmental issue which generates a good deal of public concern is the pollution of aquatic environments. In order to comprehend the problem fully and develop practical guidelines for the control and cleanup of toxic substances in aquatic systems, the behavior and fate of contaminants must be understood. This requires adequate knowledge of the geochemical cycles of the contaminating elements.

Mercury and arsenic are toxic; they are also ubiquitous in aquatic environments, with both natural and anthropogenic sources. Fish consumption in some areas is proscribed or limited because concentrations of mercury in fish are elevated, even when concentrations in water bodies are low. The concentrations of many contaminants (including mercury and arsenic) in water bodies are generally low due to efficient scavenging by particulate matter in the water column. Particles adsorb dissolved contaminants from the water column, eventually settle, and are incorporated into the bottom sediments. Their associated contaminants are thus removed from the water column. This process has been regarded as a "self-cleansing" mechanism for polluted aquatic systems (e.g. Förstner and Wittmann, 1983; Hart, 1982); however, there is substantial evidence indicating that this is not the complete cycle. The occurrence of elevated concentrations

of mercury in fish, relative to concentrations in water bodies, indicates that there is some process (or processes) at work facilitating the transfer of mercury from particulate matter to the biota.

Scavenging and burial provide an adequate description of contaminant behavior only on long (i.e. geologic) time scales. On shorter time scales, the behavior of contaminants such as hydrophobic organic compounds and heavy metals has been linked to the dynamic behavior and short-term cycling of particulate matter in lakes and oceans (e.g. Baker and Eisenreich, 1989; Honeyman et al., 1988). It is the short term behavior that governs the bioavailability of contaminants, while the long term behavior controls the permanent removal of contaminants from aquatic ecosystems. Processes occurring at the sediment-water interface are of particular importance, as this geochemical boundary has been found to exert the greatest control on the cycling of many elements in shallow aquatic systems such as lakes and coastal marine embayments (Santschi, 1988). This project is an investigation into the geochemical cycles of arsenic and mercury in aquatic environments (the Great Lakes and the Gulf of Maine).

Mercury and Arsenic in Aquatic Environments

Mercury and arsenic are introduced to aquatic environments from both natural and anthropogenic sources. The principal pathways are via the atmosphere (particularly for mercury) and weathering processes. The major natural sources of mercury and arsenic are sulfide ores and minerals. Anthropogenic sources of mercury and arsenic include a variety of industrial and manufacturing processes, the burning of fossil fuels, and municipal sewage effluent. Because mercury and some of its compounds are highly volatile, there is a constant flux to the atmosphere from ores, soils, and volcanic emissions. Mercury in the atmosphere is adsorbed by particulate matter and removed by rainfall or dry deposition, thus providing a flux to aquatic systems. The major pathway for the transport of arsenic to aquatic environments is by weathering processes, rates of which can be substantially accelerated by anthropogenic activities. It is estimated that up to 50% of the mercury currently cycled through the atmosphere is of anthropogenic origin; the anthropogenic sources of arsenic are approximately 2.5 times the natural contribution from weathering (Faust and Aly, 1981; Moore and Ramamoorthy, 1984).

THE SCAVENGING PROCESS

Like other trace metals, mercury and arsenic are readily scavenged from the water column by particles (Förstner, 1982; Förstner and Wittmann, 1983). Metals can enter an aquatic basin already adsorbed to particles, or they can be scavenged from the water column by suspended and settling particles within the basin. This represents a major pathway in the biogeochemical cycling of trace contaminants (Hart, 1982). The particulate matter in aquatic systems can be thought of as comprising two distinct fractions, an inert portion (consisting primarily of detrital silicate minerals) and a reactive--or hydromorphic--portion (including clay minerals, carbonates, sulfide minerals, hydrous iron and manganese oxides, and organic matter). The phases most important in scavenging dissolved metals from solution are fine-grained organic matter and iron-manganese oxides (Förstner and Wittmann, 1983). Dissolved contaminants scavenged from the water column are incorporated into the hydromorphic fraction, which is capable of taking up or releasing metals (Gibbs, 1977). Contaminants associated with the hydromorphic fraction are likely to be bioavailable and chemically reactive in aquatic and sedimentary environments (Förstner and Wittmann, 1983; Allan, 1986).

The removal of contaminants from the water column by scavenging is, however, neither complete nor permanent. The efficiency of scavenging by particles has been found to be related to the concentration of particles in water, the concentration of the element, the nature of the surfaces available, and the affinity of the element for the available surfaces (Salomons and Förstner, 1984; Honeyman et al., 1988). The capacity for sorption of trace elements by particulate matter has been found to be limited by competition for sorption sites by major elements (Frenet, 1981; Rae and Aston, 1982; Förstner and Wittmann, 1983). It is also uncertain whether increases in the anthropogenic input of pollutants are being balanced by increased removal by the scavenging process (Sigg et al., 1987). The presence of complexing agents in solution and the alteration of solid phase surfaces due to changes in redox conditions (dissolution of iron and manganese hydroxides) or pH (dissolution of carbonates and hydroxides; desorption of metals) have also been found to alter sorption capacities (Förstner and Wittmann, 1983).

ROLE OF PARTICLE CYCLING

Since mercury and arsenic are associated with particulate matter, their cycling is linked to the cycling of particles in aquatic systems. A conceptual model for the cycling of particles and their associated metals in lakes and oceans is shown in Figure 1. Particle flux has been found to control concentrations and residence times of particle-reactive elements in lakes (Santschi, 1984). Processes modifying particles in water bodies can influence the residence times of elements, (Santschi, 1984; Whitfield and Turner, 1987; Bacon and Rutgers van der Loeff, 1989), the bioavailability of contaminants (Elder, 1988), and the proportion of deposited metal that is retained in the sedimentary record (Shaw et al., 1990).

Particulate matter in aquatic systems is derived from atmospheric deposition, river inputs, resuspension of bottom sediments, and biological production. Although distributed throughout the water column, particles are often concentrated in several distinct layers. The first is an upper nepheloid layer which develops at the thermocline where higher density water below slows the settling of particles (Rea et al., 1981). Below the nepheloid layer, a high concentration of particles can occur in the benthic nepheloid layer (BNL) which extends several meters upward from the bottom (e.g. Biscaye and Eittreim, 1974; Feely et al., 1974; Eadie et al., 1983). Below the BNL particles are present in the sediment column. In depositional basins and other areas where currents are minimal, particles also occur in a layer between the BNL and the sediment column: the "fluff", or sediment boundary layer (SBL), where particles are in physical contact with one another, yet remain sufficiently diffuse to be resuspended very easily (Wilson et al., 1986; Sweerts et al., 1986).

Significant compositional differences have been observed between layers, in both lacustrine and marine environments (Meade et al., 1975; Eadie, 1984; Eadie and Robbins, 1987). The composition of particle layers within the water column has been observed to vary spatially and change seasonally (Sandilands and Mudroch, 1983; Eadie and Robbins, 1987; Tsunogai and Uematsu, 1978). This can lead to seasonal and spatial variations in the distribution of particle-associated metals. In addition, the chemical composition of suspended particles comprising these layers may differ from that of actively settling particles in the water column (Eadie and Robbins,

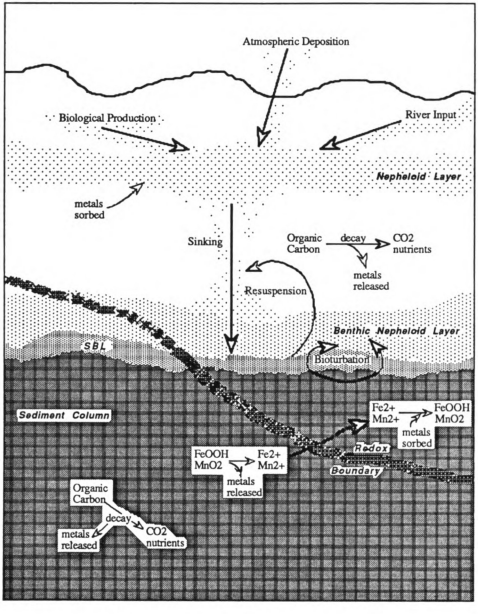


Figure 1. Conceptual model of particle cycling and metal interactions in aquatic systems.

1987; Honeyman et al., 1988). Masuzawa et al. (1989) have found settling particles to change composition as they settle into deeper waters. There is evidence that settling particles develop from populations of suspended particulate matter; this process has been linked to the transfer of particle-reactive pollutants and nutrients to bottom sediments in lakes (O'Melia, 1985; 1987).

Significant processes believed to occur within the nepheloid and BNL include photosynthesis and respiration, precipitation and dissolution, adsorption and desorption, aggregation and disaggregation, and biological uptake and decomposition (Honeyman et al., 1988). These processes can result in the uptake or release of metals within the various particle layers, and therefore influence residence times of metals in aquatic systems. Such processes can significantly retard the permanent burial of scavenged chemical species (Csanady, 1986). For example, Peterson and Carpenter (1983) attribute arsenic enrichment in deep waters of an anoxic fjord to the release of arsenic from decomposing organic matter in deep waters. Many of these processes probably occur in the SBL as well, but because of sampling difficulties, the nature of particles and processes within the SBL are largely unknown (Pedersen et al., 1986). McKee et al. (1989a) have demonstrated that the SBL is important in the cycling of trace elements in Lake Superior.

Depositional basins, where fine-grained sediments are actively accumulating, are significant sites for the cycling of contaminants in lakes and oceans. Hydrodynamic processes result in the selective transport of fine-grained sediments to deep areas where currents are minimal; this process in known as sediment focusing (Hilton et al., 1986). Since contaminants are primarily associated with fine-grained particles (Förstner and Wittmann, 1983), focusing results in the accumulation of contaminants primarily in areas where fine-grained sediments accumulate (Eadie and Robbins, 1987; Loring, 1975).

Physical processes occurring near the sediment surface (within the SBL and upper sediment column) include bioturbation and resuspension; these processes can affect element cycling. Wave-induced resuspension has been documented in both lacustrine (Håkanson, 1982; Matty et al., 1987) and marine environments (Baker and Feely, 1978; Lampitt, 1985). Resuspension can also result from current activity (e.g. Johnson et al., 1984; Lampitt, 1985). Bioturbation results in the resuspension of bottom sediments (Nowell et al., 1981) and in the mixing of the upper

layers of the sediment column (Aller, 1978; Förstner and Wittmann, 1983). These processes can result in the transfer of elements from the sediment to the water column in two ways. Resuspension (wave- or current-induced, or via bioturbation) increases the residence time of particles in the water column. This increases the extent of alteration of and potential release of contaminants from particulate matter. This process has been shown to be responsible for the recycling of mercury-polluted sediments in the Wabigoon River system of northwestern Ontario (Allan, 1986). Resuspension and bioturbation can also release porewaters from the sediment column. Since porewaters are typically enriched in metal contaminants due to diagenetic reactions, this can result in a flux of dissolved metals to the overlying water (Förstner and Wittmann, 1983). Although the mobilization of contaminants from bottom sediments may be only a fraction of the total amount accumulated, this may represent a substantial environmental impact (Jennett et al., 1980). The accumulation of mercury by fish exposed to resuspended sediments (under simulated dredging conditions) has been documented (Seelye et al., 1982).

MICROBIAL PROCESSES

Microbially-mediated processes (in addition to those which drive early diagenesis) affect both mercury and arsenic in aquatic environments. These processes can alter residence times of mercury and arsenic in the water column, and increase bioavailability. The release of mercury from sediments has been linked to processes which generate volatile forms of mercury, most of which are microbially-mediated. Aerobic bacteria can oxidize HgS, producing soluble Hg^{2+}. This can then be converted to elemental mercury, methyl mercury, or dimethyl mercury via the detoxification mechanisms of other bacteria (Wood, 1974). Microorganisms can also degrade methyl mercury by reduction to elemental mercury (Spangler et al., 1973; Wood, 1974), and humic acids have also been found to produce elemental mercury from mercuric ions (Alberts et al., 1974). Elemental mercury and dimethyl mercury are volatile, and may be lost from the sediments; methyl mercury is readily taken up by organisms (Wood, 1974).

Microbial processes can also effect the release of arsenic from sediments by the production of volatile methylated compounds (Wood, 1974; Faust et al., 1987; Sanders, 1985). However,

Andreae (1979) found no evidence for the biomethylation of arsenic in the interstitial waters of oxic or anoxic marine sediments, and Aggett and O'Brien (1985) found no methylated arsenic species in lake sediments where conditions should have favored their formation. Additional microbiological processes which occur in sediments can result in the oxidation of arsenite to arsenate by aerobic bacteria, the reduction of arsenate to arsenite, and the reduction of both arsenite and arsenate to volatile arsine (Faust et al., 1987).

Effects of Early Diagenesis

Early diagenetic reactions occurring in the upper layers of sediments can be important in the remobilization of heavy metals (Berner, 1976; 1980). Changes in particle surfaces and changes in metal speciation which occur during early diagenesis can remobilize bound metals (Shaw et al., 1990). As the sediments become buried, the continuing decay of organic matter lowers the redox potential of the sediment. Eventually, iron and manganese oxides begin to dissolve and elements are released. The dissolved iron, manganese, and associated elements build up in the porewater and diffuse upward. When the iron and manganese reach oxygenated water they are reoxidized, precipitate as oxides, and scavenge some of the dissolved elements. Elements can continue to diffuse upward to where they can be taken up by biota or scavenged by iron-manganese oxides and organic material; this occurs throughout the sediment column, but principally in the uppermost layers of sediment and in the sediment boundary layer. Any dissolved element which diffuses out of the sediment column can be scavenged by particulate matter in the BNL, thus increasing the metal content of the upper layers of sediment and the SBL, and producing metal concentration profiles which resemble the effects of anthropogenic input. This set of processes constitutes the redox cycles of iron and manganese, which have been shown to influence the behavior of several elements (e.g. Salomons and Förstner, 1984; Balistrieri and Murray, 1986; McKee et al., 1989a; Belzile and Tessier, 1990).

Much of the biogenic detritus (a major carrier of particle-associated elements) reaching the sea floor is degraded at the sediment-water interface (Gerringa, 1990). This indicates that the transport of metals to sediments by settling particles may not directly contribute to permanent

metal accumulation in the sediment column; it has been suggested that the uptake of metal from porewaters may be the primary link between detrital flux and metal accumulation in sediments (Shaw et al., 1990).

Analysis of the partitioning of elements among the various hydromorphic fractions of the bottom sediment, and in the interstitial waters and overlying waters, can be used to deduce the effects of diagenetic chemical changes on the associated elements (e.g. Takamatsu et al., 1985; Moore et al., 1988; Holm, 1988; Farmer and Lovell, 1986; Graybeal and Heath, 1984; Lerman and Brunskill, 1971; Jennett et al., 1980; McKee et al., 1989a). Partitioning of elements among the hydromorphic phases is most usually defined operationally by the chemical methods used to extract the element from the sediment (Martin et al., 1987).

Arsenic in sediments and porewaters appears to follow the diagenetic cycles of iron and manganese, although there is some controversy as to whether arsenic is adsorbed onto hydrous iron and manganese oxides or coprecipitated with them. Farmer and Lovell (1986) found substantial enrichment of arsenic in the top few centimeters of sediment in Loch Lomond, Scotland, which could not be attributed to any anthropogenic source. Based on element concentrations in the sediments determined by selective extraction procedures, and on porewater profiles, they came to the following conclusions: [1] arsenic is associated with amorphous iron compounds in oxic surface sediments, where it is either adsorbed onto or coprecipitated with ferric oxides and hydroxides; [2] under reducing conditions lower in the sediment column, iron compounds are reduced and dissolved, releasing adsorbed arsenic (or accompanied by the reduction and solubilization of arsenic compounds); [3] both iron and arsenic migrate upward in the porewaters to the oxidized zone, where precipitation and adsorption (or coprecipitation) again take place; and [4] these processes produce a diagenetic zone of arsenic enrichment near the surface of the sediments. Holm (1988) found a similar association of arsenic with ferric oxide-hydroxide complexes in sediments. He determined that arsenate (AsO_4^{3-}) was adsorbed to the surface of these complexes in the same manner as phosphate ions. Aggett and Roberts (1986) determined that arsenate and phosphate are co-precipitated with hydrous iron oxides in lake sediments rather than adsorbed onto existing surfaces. Moore et al. (1988) found that arsenic

concentrations in porewaters of reservoir sediments were controlled by the solubility of iron and manganese oxyhydroxides in the oxidized zone and of metal sulfides in the reduced zone. Microbial sulfate reduction and decomposition of ferric oxide-hydroxides can also result in the release of arsenic from sediments (Holm, 1988).

It has been suggested that mercury in sediments is not affected by diagenesis. For example, Rossmann (1986) concluded that mercury was not affected to any substantial degree by diagenesis in Lake Superior. This was based on a study of the total mercury content of sediments. Total metal profiles can resemble the effects of changing inputs (such as increased pollution) even when studies of partitioning among hydromorphic phases indicate diagenetic remobilization is responsible (e.g. McKee et al., 1989a). There is also some experimental evidence for the immobility of mercury in sediments: experiments lasting up to 6 months indicated no diagenetic release of mercury from sediments of a model marine ecosystem (Santschi et al., 1987). Six months, however, is not a long time relative to sedimentation and burial rates and remobilization of mercury may take longer. Other studies have found evidence for the diagenetic remobilization of mercury. In an investigation of the partitioning of mercury in the hydromorphic fractions of sediment from Lake Superior, Strunk (1991) determined that most of the mercury was associated with the oxidizable (organic matter and sulfides) and base soluble (humic and fulvic acid) phases of the sediment, with lesser amounts in the acid soluble (iron and manganese oxide) phases. Concentration profiles of mercury in the base soluble and strongly acid soluble phases suggest that mercury is mobilized from both phases by diagenetic reactions; however, the fate of the mercury released by such processes was not determined. A similar distribution of mercury among the hydromorphic phases of sediments from the Palos Verdes shelf was documented by Eganhouse et al. (1978). They determined that the enrichment of mercury in surficial sediments appeared to be due to diagenetic reactions. Indirect evidence for diagenetic remobilization of mercury has been detected in the Atlantic Ocean by Gill and Fitzgerald (1988), who propose the release of mercury from sediments by diagenetic reactions as the most reasonable explanation for elevated concentrations of mercury in some ocean waters. Evidence for the diagenetic remobilization of mercury has also been found in fluvial (Jackson et al., 1982) and estuarine

environments (Lindberg and Harriss, 1974). Detailed porewater profiles are lacking from all of these studies. Bothner et al. (1980) found evidence for fluxes of dissolved mercury out of contaminated marine sediments under anoxic conditions in *in situ* bell jar experiments; they attribute these fluxes to the release of mercury following dissolution of iron and manganese oxides.

These studies described above indicate that both arsenic and mercury may be released from sediments following burial due to early diagenesis. Although early diagenetic processes may recycle mercury and arsenic within the upper layers of sediment, remobilization processes are not efficient enough to preclude the permanent burial of sediment-bound elements altogether. The proportion of an element which becomes permanently buried is a function of the diagenetic processes and the hydromorphic phase(s) sequestering the element. Phases which appear to be particularly important in the permanent burial of elements are refractory organic matter, sulfides, metastable iron and manganese oxides, and clays (Förstner and Wittmann, 1983).

Objectives

This project was designed to investigate basic controls on geochemical cycling of mercury and arsenic in aquatic environments. The goal was to identify the geochemical processes operating in the sediments, and to determine how these processes influence the cycling of mercury and arsenic. The hypothesis investigated was that as particles move from one layer to another (from the SBL to the sediment column, and with increasing depth in the sediments) toward permanent burial, the composition and chemical character of the particles change. The processes that cause these changes influence the cycling of mercury and arsenic, by sequestering these elements within the sediments, by releasing them from sediments, or by repartitioning them among different phases of the sediment.

This was pursued by examining the distributions of mercury and arsenic among the waters and particulate matter of different types of aquatic environments. Changes in the composition, mercury and arsenic content, and partitioning that occur between layers can be used to identify

processes at work. By examining the behavior of two different elements that respond to different conditions and processes in different ways, and by studying these in several diverse settings that undergo different processes to different degrees, a more complete understanding of geochemical cycling should be obtained. Toward this end, two different elements were chosen (arsenic and mercury) and several different sample locations. Sample sites were selected so that variations in diagenetic processes might be observed on several scales, even when employing identical procedures and techniques. One coastal marine and several lake sites were chosen to examine differences in diagenesis between freshwater and marine environments. Within the freshwater environment, two different lakes were selected, and two different sites in each lake. Locations chosen for this study were selected depositional basins of Lake Michigan, Lake Superior, and the Gulf of Maine.

II. METHOD OF STUDY

The approach and general methodology used in this study are described here. Details of sampling, sample preparation, and analytical procedures are presented in Appendix 1.

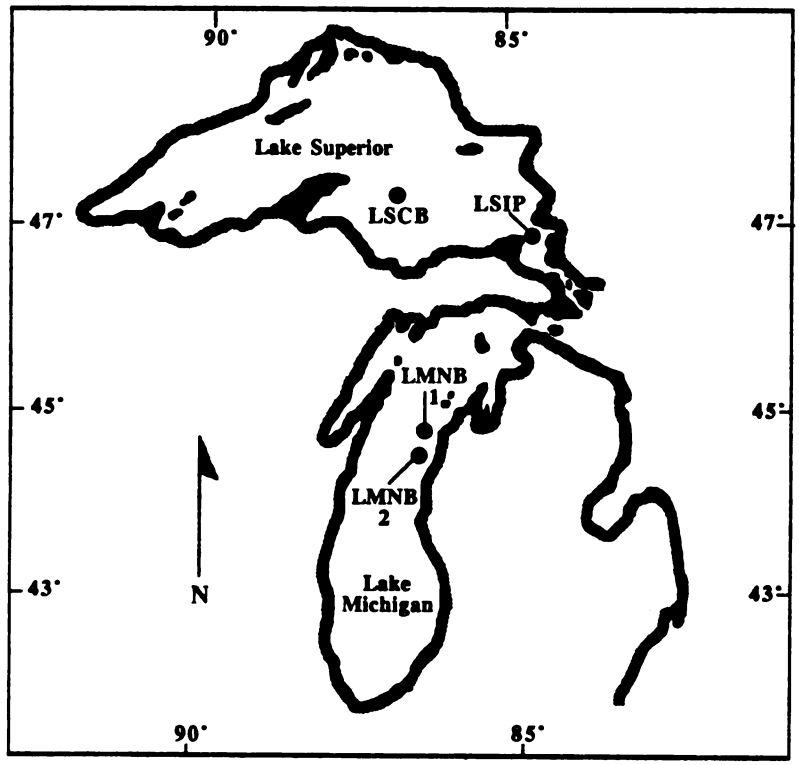
Sampling

SAMPLE SITES

Deep basins where fine-grained sediments are actively accumulating were chosen as sites for collection of samples. These areas represent locations where the majority of sediment-bound contaminants accumulate due to the process of sediment focusing. Locations of sample sites are shown in Figure 2.

The Laurentian Great Lakes were chosen to represent the freshwater environment; three sites with different sedimentological and geochemical characteristics were selected: (1) the Caribou Basin of Lake Superior, which is 335 m deep, with a slow sedimentation rate and a well-defined redox zone within the sediment column; (2) the Ile Parisienne Basin in Lake Superior, which is 160 m deep, with a rapid sedimentation rate, and a weakly-defined redox zone within the sediment column; and (3) the North (Algoma) Basin of Lake Michigan, which is 200 m deep, with a high sedimentation rate, a high organic matter content, and a redox zone near the sediment-water interface.

One depositional basin within the Gulf of Maine was included in this study: the Murray Basin. The Gulf of Maine was chosen as a suitable site for this study because it is similar to the Laurentian Great Lakes in several important respects. Both the physical setting and the particle dynamics in the gulf resemble those of the Great Lakes; these similarities are discussed below.



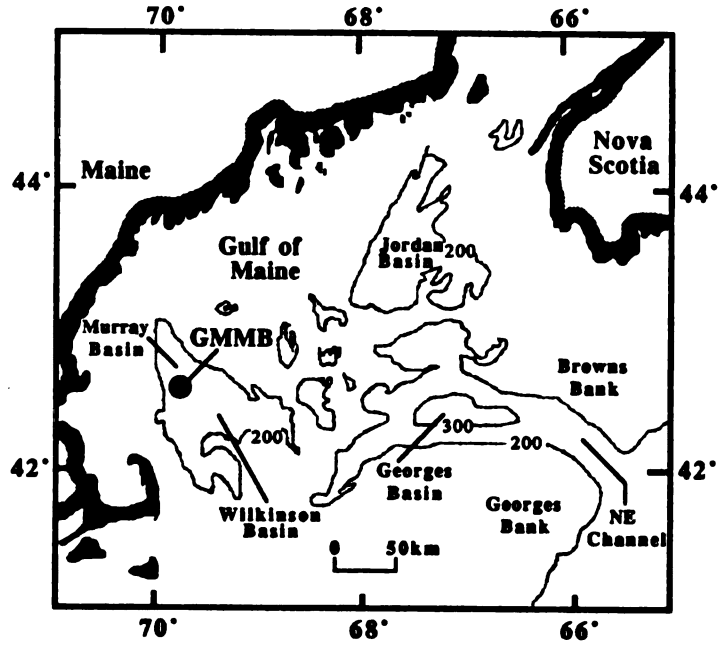


Figure 2. Locations of sample sites in (a) the Great Lakes and (b) the Gulf of Maine.

Because of the partially enclosed nature of the gulf, most of the particles delivered to or generated in the gulf will remain there, eventually accumulating in the depositional basins (Spinrad, 1986). Nepheloid layers have been observed at the thermocline (about 25 m depth) and near the bottom (Spinrad, 1986), corresponding to those in the Great Lakes. A third nepheloid layer has also been observed, associated with the base of the Maine Intermediate Water (Spinrad, 1986). Seasonal influences on the concentration and distribution of suspended particulate matter, such as those observed in the Great Lakes (Baker and Eisenreich, 1989), are pronounced in the Gulf of Maine (Spencer and Sachs, 1970; Spinrad, 1986).

Circulation in the Gulf of Maine is quite different from that in the Great Lakes and may affect the cycling of particulate matter and associated contaminants. The gulf is a relatively enclosed basin; the exchange of waters with the Atlantic Ocean is confined mostly to the Northwest Channel (Brooks, 1985). Oceanic water entering though the Northeast Channel is warmer and saltier than other water masses in the gulf. This forms the Maine Bottom Water (MBW), which flows into the deepest parts of the basins (Brooks, 1985). During the summer stratified period, the Maine Surface Water (MSW) and Maine Intermediate Water (MIW) overlie the MBW (Hopkins and Garfield, 1979; Brooks, 1985). These layers are less saline than the MBW (Brooks, 1985). The MIW is cooler than the MSW or MBW during summer stratification (Hopkins and Garfield, 1979). Density differences in the water column are mainly controlled by salinity rather than temperature (Brooks, 1985). This would account for the concentration of particulate matter which has been observed at the base of the MIW: particle settling is slowed at the interface with the denser, more saline MBW. During the winter, the MSW cools and is mixed with the MIW, forming a single water mass (Hopkins and Garfield, 1979).

Contaminants entering the Gulf of Maine from the Atlantic Ocean via the MBW may accumulate with particulate matter in the deep basins via sediment focusing. For example, Gill and Fitzgerald (1988) observed that concentrations of mercury in water samples from the Gulf of Maine were lower than in samples from the adjacent continental slope, and suggested that the gulf may be a sink for mercury entering from the Atlantic Ocean.

SAMPLE COLLECTION

Sampling for this project made use of a research ship, the R/V *Seward Johnson* (equipped with a gravity coring system and suitable laboratory space) and submersible, the DSRV *Johnson-Sea-Link II* (equipped with a mechanical arm and nepheloid/SBL sampling system, as described in McKee et al., 1989a). Samples taken included column waters, water and suspended material in the nepheloid, benthic nepheloid, and SBL layers, and bottom sediments with associated porewaters. Samples of benthic nepheloid and SBL were collected via the suction filtration apparatus designed for the submersible. Although some nepheloid and benthic nepheloid particulate matter was collected at each site, there was not enough to process for chemical analysis. Box cores (15 cm x 15 cm x 40 cm, stainless steel) and short cores (7.6 cm butyrate) were also collected from the submersible. In addition to samples collected from the submersible, long cores were collected by gravity coring from the surface ship. All of the cores used for pH, alkalinity, arsenic, and mercury analyses were taken by gravity coring procedures, and are designated "gc".

CLEAN PROCEDURES

Precautions were taken to prevent contamination from any of the sampling, processing, or analytical procedures. Details of clean procedures are described in Appendix 1. Samples for mercury and arsenic analysis only came in contact with material which had been acid-cleaned and stored in plastic bags. Only distilled deionized water (DDW) was used for cleaning and sample processing. Gloves were worn at all times while handling samples, sample processing equipment, or sample containers. Care was taken to avoid airborne contamination and most shipboard sample processing was performed in closed plastic glove-bags purged with nitrogen gas. Sample processing in the laboratory was performed within clean hoods supplied with filtered air (passed through a Class 100 filter).

SHIPBOARD SAMPLE PROCESSING

Sample containers and all sample-processing equipment were acid-cleaned before use (see Appendix 1). All samples collected for arsenic analysis, and samples from the Gulf of Maine

collected for mercury analysis, were processed in an inert atmosphere (utilizing N_2-filled glove bags). Collection and processing of samples for mercury analysis was performed under oxidizing conditions (open to the atmosphere) at the Great Lakes sites; this was intended to prevent the loss of volatile reduced mercury (Strunk, 1991).

Cores were stored at 4°C (approximate *in situ* temperature) and sectioned within a few hours of collection. The sections were transferred to acid-cleaned 50 mL polyallomer centrifuge tubes and centrifuged at 15,000 rpm (using a chilled centrifuge head to keep the temperature near 4°C) to separate the porewaters from the sediment. Following removal of porewater, sediment samples were stored frozen in the centrifuge tubes.

Porewaters were removed from centrifuged samples by syringe, filtered through acid-cleaned 0.4 µm Nucleopore membrane filters, acidified to pH < 2 with sub-boiling distilled Ultrex™ nitric acid, and stored in acid-cleaned polyethylene bottles. Samples to be analyzed for mercury were also preserved with gold (chloroauric acid) and hermetically sealed following the procedures of Moody et al. (1976) as recommended by Gill and Fitzgerald (1987). All water sample bottles were sealed in plastic bags and stored in a cold room at 4°C. Procedural blanks were carried through all processing steps.

pH and alkalinity were measured on one sediment core from each site, which was sectioned exposed to the atmosphere. pH was measured by inserting a spear-tip electrode (Orion Ross combination pH) into the wet sediment before removing each section. Alkalinity was measured in porewater samples using an apparatus designed for small-volume titrations; results were converted to mg/L HCO_3^-.

Sequential Extractions

Sequential chemical extractions were employed to examine the partitioning of mercury and arsenic among the hydromorphic phases of the sediment. In this procedure, samples are treated with a series of successively harsher chemicals to remove metals from the sediment. Metals are released in response to the change in chemical environment produced by the extractant, so "phases" are really operationally defined. Each extraction, however, is believed to affect primarily

one (or more) physical phase of the sediment, which responds to the extractant; thus each operationally-defined phase roughly corresponds to a physical portion of the sediment. Although there is some controversy surrounding the use of sequential chemical extractions to examine partitioning of metals in sediment (e.g., Rendell et al., 1980; Tipping et al., 1985; Nirel et al., 1985; Rapin et al., 1986; Kersten and Förstner, 1987; Kheboian and Bauer, 1987; Loring and Rantala, 1988; Rauret et al., 1989; Papp et al., 1991), there is a general consensus that--as long as limitations are noted--useful insights into metal partitioning can be gained by use of this type of procedure (e.g., McKee et al., 1989a; Prohic and Kniewald, 1987; Martin et al., 1987; Boust et al., 1988; Belzile et al., 1989; Aggett and Roberts 1986; Salomons and Förstner, 1984; Santschi et al., 1987; El Ghobary and Latouche, 1986; Belzile and Tessier, 1990). The extraction solutions, conditions, and sediment phases theoretically affected are summarized in Table 1. All reagents used were analytical reagent grade, prepared with distilled deionized water.

ARSENIC

Arsenic was extracted from the hydromorphic phases of sediments following the procedures determined by McKee (1989a); these procedures were modified from Tessier et al. (1979) and Gephart (1982) and are summarized in Table 1. The duration of each extraction step was verified for arsenic by steady-state analysis (see Appendix 1). Samples were thawed in a refrigerator, but not dried. Aliquots were placed in acid-cleaned tared centrifuge tubes, weighed, and treated with (1) magnesium chloride solution to remove the exchangeable arsenic [EX fraction]; (2) sodium acetate/acetic acid to dissolve carbonates and remove arsenic associated with the weak-acid soluble phase [WAS fraction]; (3) hydroxylamine hydrochloride in nitric acid to release arsenic associated with the easily reducible phases [ER fraction]; (4) hydroxylamine hydrochloride in acetic acid to extract arsenic associated with the moderately reducible phases [MR fraction]; and (5) hydrogen peroxide and nitric acid, followed by ammonium acetate, to release arsenic associated with the oxidizable phases [OX fraction]. All processing was performed under an inert (N_2) atmosphere until the final (oxidizing) step. Leachates were analyzed as described below.

Table 1

Summary of Methods Used for Sequential Chemical Extractions

SEDIMENT SUBSTRATE	CHEMICAL PHASE	EXTRACTION SOLUTION*	EXTRACTION CONDITIONS
		A. Arsenic (from McKee, 1990)	
Clay Minerals	Exchangeable EX	1.0 M $MgCl_2$, 7 pH 10 mL	20°C, 1 hour
Carbonates	Weak-Acid Soluble WAS	1.0 M NaAc, 5 pH 10 mL	20°C, 5 hours
Mn Oxides	Easily Reducible ER	0.1 M $NH_2OH \cdot HCl$ in 0.01 N HNO_3 25 mL	20°C, 1/2 hour
Fe Oxides	Moderately Reducible MR	0.04 M $NH_2OH \cdot HCl$ in 25% (v/v) HAc 20 mL	90°C, 5 hours
Organics & Sulfides	Oxidizable OX	30% H_2O_2, 2 pH, 8 mL 0.02 N HNO_3, 3 mL then add	85°C, 5 hours
		3.2 M NH_4Ac, 5 mL then add H_2O to make 25 mL	20°C, 1 hour
		B. Mercury (from Strunk, 1991)	
Clay Minerals	Exchangeable EX	10% KCl 15 mL	20°C, 1 hour
Humic & Fulvic Acids	Base Soluble BS	0.1 N NaOH 15 mL	20°C, 30 hours
Fe & Mn Oxides	Acid Soluble AS	1.0 N HCl 10 mL	20°C, 6 hours
Organics & Sulfides	Oxidizable OX	30% H_2O_2, 2 pH, 7 mL 0.02 N HNO_3, 2 mL then add 4 mL	50°C, 5 hours
		2.0 M NH_4Cl in 20% HNO_3 then add H_2O to make 25 mL	20°C, 1 hour

*Volumes optimized for 1.0 g sample.

MERCURY

Mercury was extracted from the hydromorphic fractions of the sediments using the selective chemical extraction procedures determined by Strunk (1991). Samples were prepared as for arsenic, then treated with (1) potassium chloride to remove exchangeable mercury [EX fraction]; (2) sodium hydroxide to remove base-soluble mercury [BS fraction]; (3) hydrochloric acid to remove acid-soluble mercury [AS fraction]; and (4) hydrogen peroxide and nitric acid, followed by ammonium chloride in nitric acid to extract oxidizable mercury [OX fraction]. Leachates were analyzed immediately, as described below.

Analytical Procedures

ARSENIC

Arsenic in liquid samples was analyzed by graphite furnace atomic absorption, utilizing a Perkin-Elmer Zeeman/5100 with Zeeman background correction and autosampler. Stabilized temperature platform furnace (STPF) procedures were followed (see Appendix 1). Using STPF techniques, graphite furnace analyses are interference-free, and highly stable and repeatable (Beaty, 1988). Blanks and standards were prepared in extraction solutions (for leachates) or in distilled deionized water (for water samples). Each analysis was performed in triplicate.

MERCURY

Mercury in samples was analyzed by hydride-reduction/flow-injection, using a Perkin-Elmer *Zeeman/5100* with *MHS/FIAS-200* equipped with autosampler. Preconcentration of mercury in water samples was performed by amalgamation onto gold using the Perkin-Elmer Amalgam System accessory. Blanks and standards were prepared in extraction solutions (for leachates) or in distilled deionized water (for water samples). Each analysis was performed in triplicate.

ORGANIC CARBON

The organic carbon content of sediment samples was measured in splits of the core samples which were used for chemical extractions for arsenic, following the modified Walkley-Black titration procedure of Gaudette et al. (1974).

III. RESULTS

Samples of sediment, porewater, and column water were collected at two sites in the North Basin of Lake Michigan, and at each of the other sites (see Figure 2). Preliminary shipboard descriptions of sediment cores are presented in Appendix 2 (Table A2-1). We were unable to collect adequate samples of SBL sediment from the Gulf of Maine (this layer was abesent at the time of sampling), or of particulate matter from the nepheloid or BNL at any of these sites (due to equipment problems) to perform chemical analyses. Results of chemical analyses are presented in Appendix 3.

Site Characterization

Supplemental data on dissolved iron in porewaters, organic carbon content of sediments, and the pH and alkalinity of porewaters were acquired to aid in characterizing each site. Iron, organic carbon, pH, and alkalinity can all be used to examine the extent and effects of early diagenesis in sediments. Changes in these parameters can be used to help identify the early diagenetic processes occurring and how they affect mercury and arsenic.

FERROUS IRON

Profiles of Fe(II) in porewater are shown in Figure 3. These data were provided by J.D.McKee (unpublished data). At all sites, dissolved ferrous iron is undetectable at the sediment-water interface, and concentrations increase in porewater at some depth below. This increase occurs very near the surface in Lake Michigan and Ile Parisienne, but much deeper in the sediments in Caribou Basin and the Gulf of Maine. At each of the lake sites, there is a narrow zone of lower iron concentration just below the the initial peak; below this the concentrations increase once again.

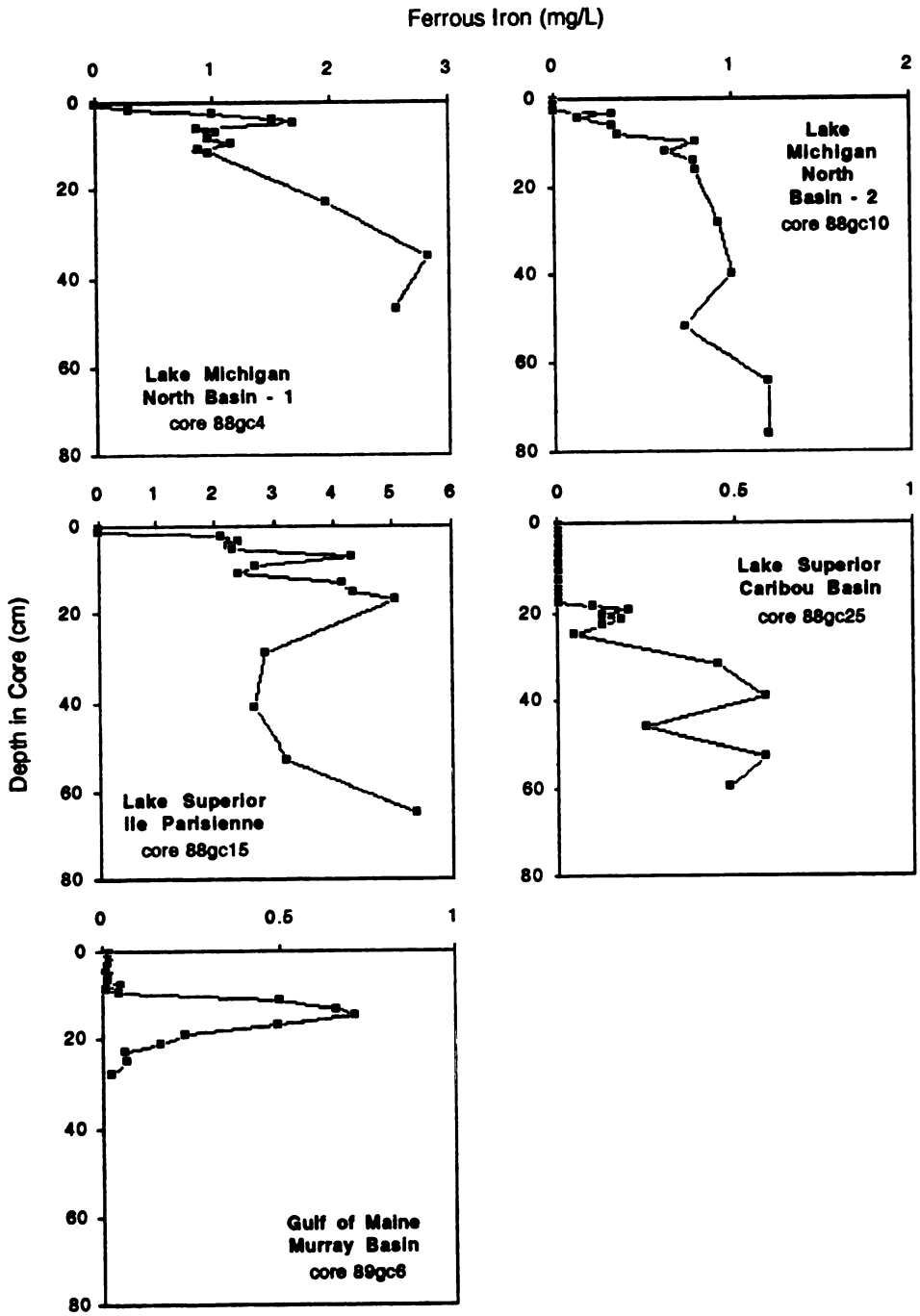


Figure 3. Ferrous iron in porewater.

Maximum values of Fe(II) are highest in Ile Parisienne and lowest in the Caribou Basin. There is also much more iron in Lake Michigan site 1 than in site 2 samples. In the Gulf of Maine, Fe(II) is restricted to a layer, between about 10 and 20 cm depth. In all of the lake sites, concentrations are variable, but tend to continue increasing with depth in the sediment.

Oxidation Potentials

Profiles of ferrous iron in porewater can be used to delineate the various redox zones in the sediment column: where ferrous iron is absent, sediments are more oxidizing, although O_2 may be absent near the base of this zone (Berner, 1980). This environment extends to a depth of 1 cm at Lake Michigan site 1 (LMNB-1), a depth of 3 cm at Lake Michigan site 2 (LMNB-2), a depth of 2 cm at Ile Parisienne (LSIP), a depth of 18 cm at Caribou Basin (LSCB), and a depth of 9 cm at the Gulf of Maine site (GMMB). The redox horizon, where iron is reduced and iron oxides dissolve to produce ferrous iron, is indicated by a peak in porewater Fe (II) concentrations. This occurs at a depth of 5 cm at LMNB-1, a depth of 10 cm at LMNB-2, a depth of 7 cm at LSIP, a depth of 19 cm at LSCB, and at a depth of 15 cm at GMMB. Above the redox horizon, ferrous iron diffuses upward along the concentration gradient, is oxidized, and is precipitated as iron oxides. This constitutes the redox cycle of iron which has been found to influence the behavior of many metals (Förstner and Wittmann, 1983).

pH

pH profiles of sediments are displayed in Figure 4. In the Lake Michigan cores, pH of surficial sediments is distinctly lower than in bottom waters, rapidly increases below the uppermost sediments, then drops off slightly with increasing depth. At site 1 the pH rises to a maximum of 7.6 at 6 cm depth. This is significantly higher than its value in bottom waters (6.8). At site 2 the increase in pH is to a maximum of 7.3, not much higher than the pH of the bottom water (7.1). pH then decreases only slightly with depth, reaching a constant value of 7.0 at about 60 cm depth.

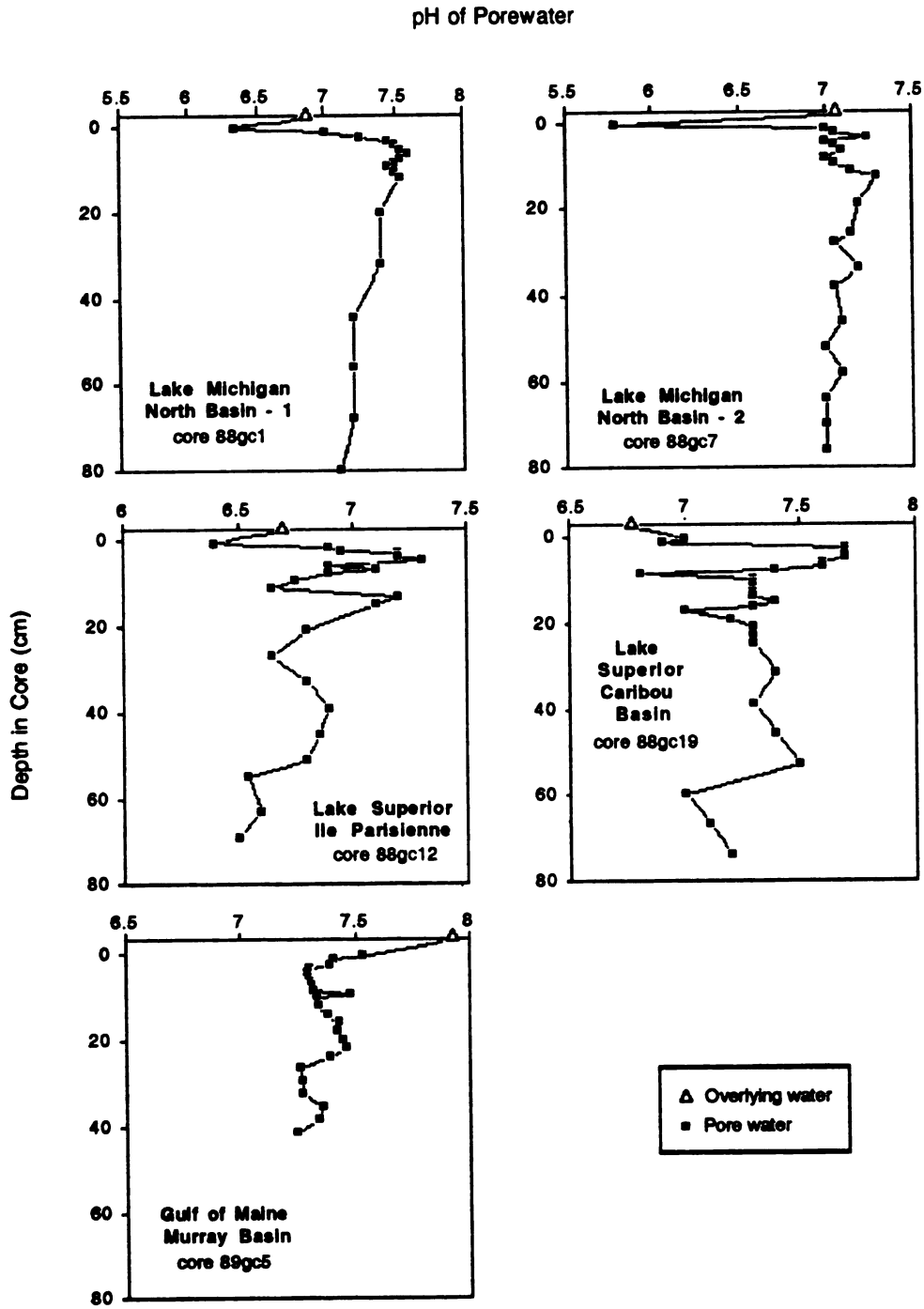


Figure 4. pH of sediments.

In Lake Superior samples, pH is much more variable with depth in the sediment column than in the Lake Michigan samples. The decrease in pH from overlying water to surface sediments is slightly less for Ile Parisienne, and much less of Caribou Basin than that seen in Lake Michigan. There is no consistent trend with depth in either of the Lake Superior cores, although the fluctuations decrease somewhat below 20 cm depth in both cores.

In sediment from the Gulf of Maine, pH of the surficial sediment is lower than that of the bottom waters, and continues dropping to a depth of 4 cm. Values then remain fairly constant, with a slight increase with depth until 22 cm, then pH begins to decrease somewhat. The total degree of variability in pH in this marine sample is lower than that observed in Lake Superior or Lake Michigan.

ALKALINITY

Profiles of porewater alkalinity are shown on Figure 5. In the Lake Michigan samples, alkalinity shows a relatively rapid increase in the first few cm, then a slight but continued increase with depth. At site 1 all values in the sediment are higher than in the lake bottom waters; at site 2 porewater alkalinity at the sediment surface is identical to that of the bottom water, but is higher at all subsequent depths in the sediment. In the Lake Superior samples, porewater alkalinity shows an initial decrease below lake bottom water values, then a continuous increase in alkalinity with depth. At Ile Parisienne the rate of increase in alkalinity is rapid below the minimum value at 3 cm depth, then slows with depth. In the Caribou Basin alkalinity increases slowly until a depth of approximately 30 cm, then increases more rapidly. Alkalinity in bottom waters and near-surface interstitial waters of Lake Michigan is nearly three times as high as in Lake Superior. The total increase in alkalinity with depth in the sediments is greater for the Lake Superior samples.

Gulf of Maine porewater alkalinity drops initially from the bottom water value, continues dropping slightly until a depth of 5 cm, then increases, drops sharply at 9 cm, then increases further with depth, to a maximum value of 433 mg/L HCO_3^-. Below a depth of ~15 cm, alkalinity is much higher than in the lakes, and the total increase in alkalinity is substantially higher.

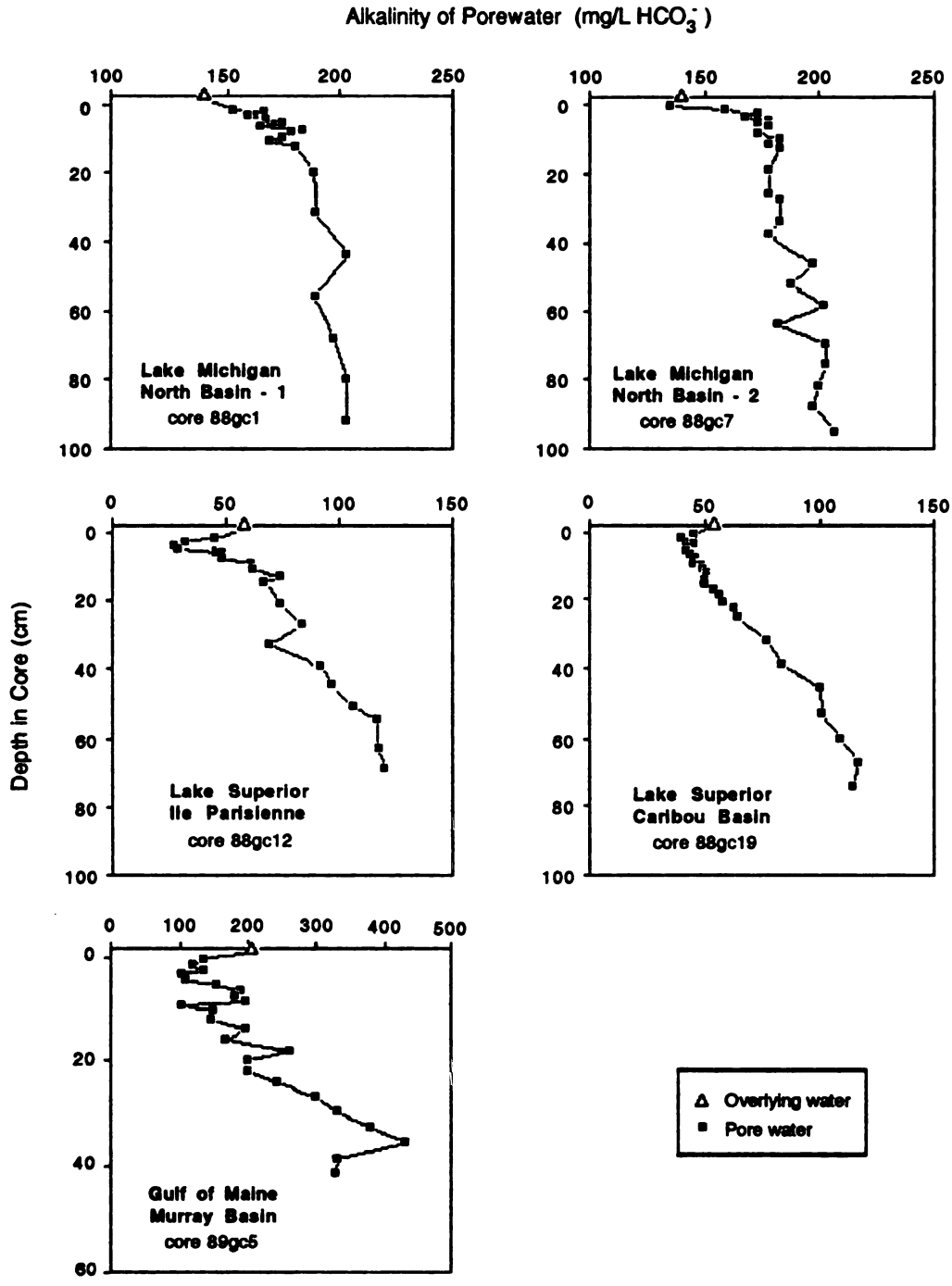


Figure 5. Alkalinity of porewater.

ORGANIC CARBON

Profiles of organic carbon content are shown in Figure 6. In Lake Michigan, values in near-surface sediments are slightly greater than 3 % (w/w) organic carbon, decreasing fairly rapidly at first, then more slowly with depth. Values seem to stabilize at about 2 % deep in the sediments. There is an excursion to over 3 % organic carbon at ~10 cm depth at site 1. At site 1 the organic carbon content of the SBL is lower than that of the uppermost layers of the sediment column; at site 2 the values in SBL and surficial sediments are very similar.

In Lake Superior, values of organic carbon are highest in the SBL samples, and decrease rapidly in the sediment column. Values then fluctuate somewhat, and in both areas seem to stabilize at about 1.5 % at depth. Ile Parisienne has a lower organic carbon content in near-surface sediments than any of the other lake sites.

Organic carbon in the Gulf of Maine site is slightly lower at the surface than deeper in the core, and there is very little variation in the organic carbon content with depth. The organic carbon content of Gulf of Maine sediments is lower than that of Lake Michigan sediments, and similar to that of more deeply buried Lake Superior sediments.

Partitioning of Arsenic

SEDIMENTS

Results of chemical extractions are displayed in Figures 7-11. In the SBL and uppermost layers of sediment, the moderately reducible (MR) and oxidizable (OX) phases sequester by far the most arsenic. As burial depth increases, the total amount of arsenic extracted from the sediments decreases, and the proportion associated with the MR and OX phases decreases as well. The degree of enrichment of the surficial layers in arsenic relative to deeper sediments is greater in the Great Lakes than in the Gulf of Maine.

The relationship between concentrations of arsenic in the SBL and in the uppermost core sediment varies between sites. In Lake Michigan, concentrations are lower in the SBL than in the core top samples at site 1, and approximately equal at site 2. In Lake Superior, the SBL is

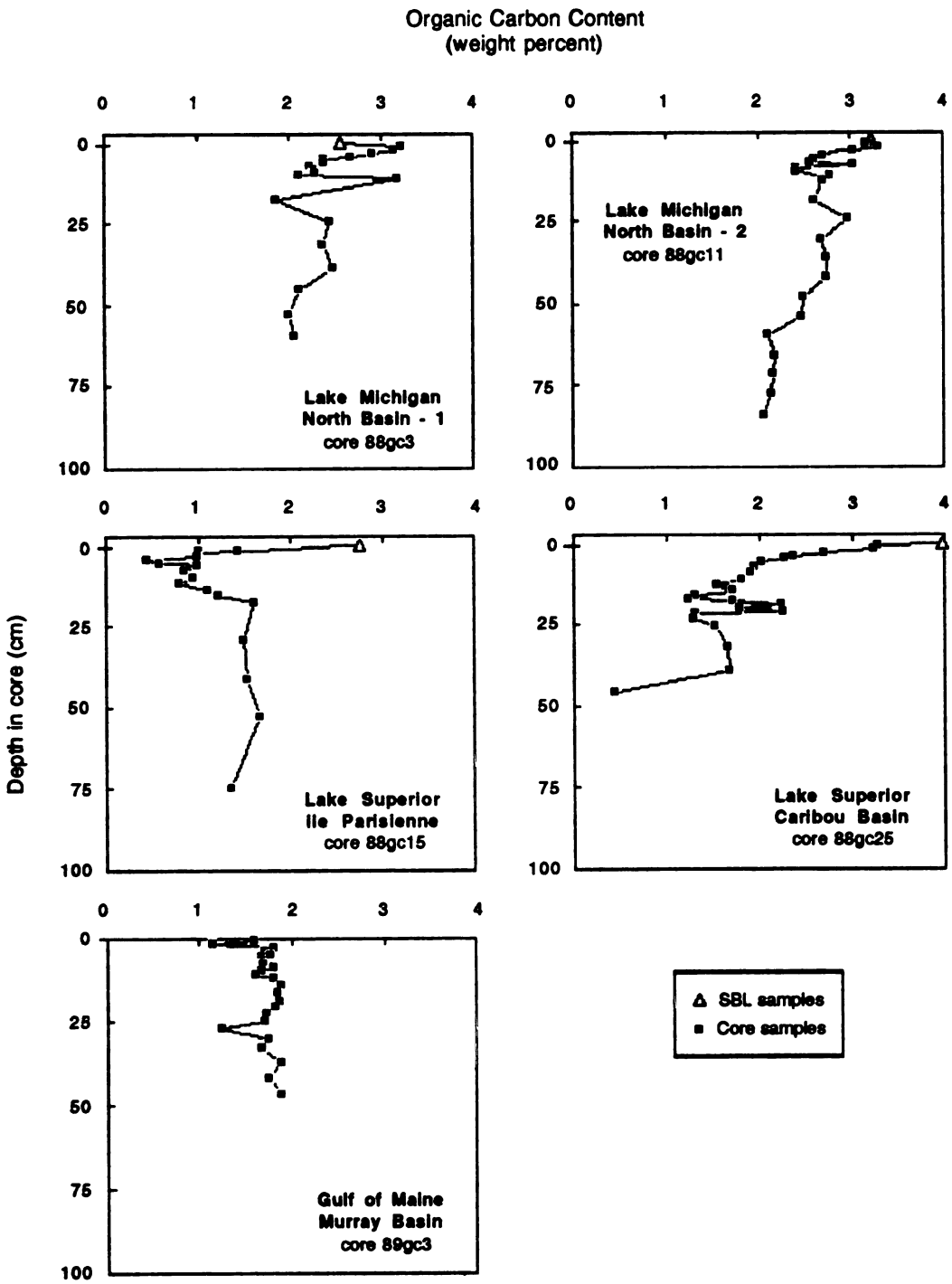


Figure 6. Organic carbon content of sediment.

Depth in Core (cm)

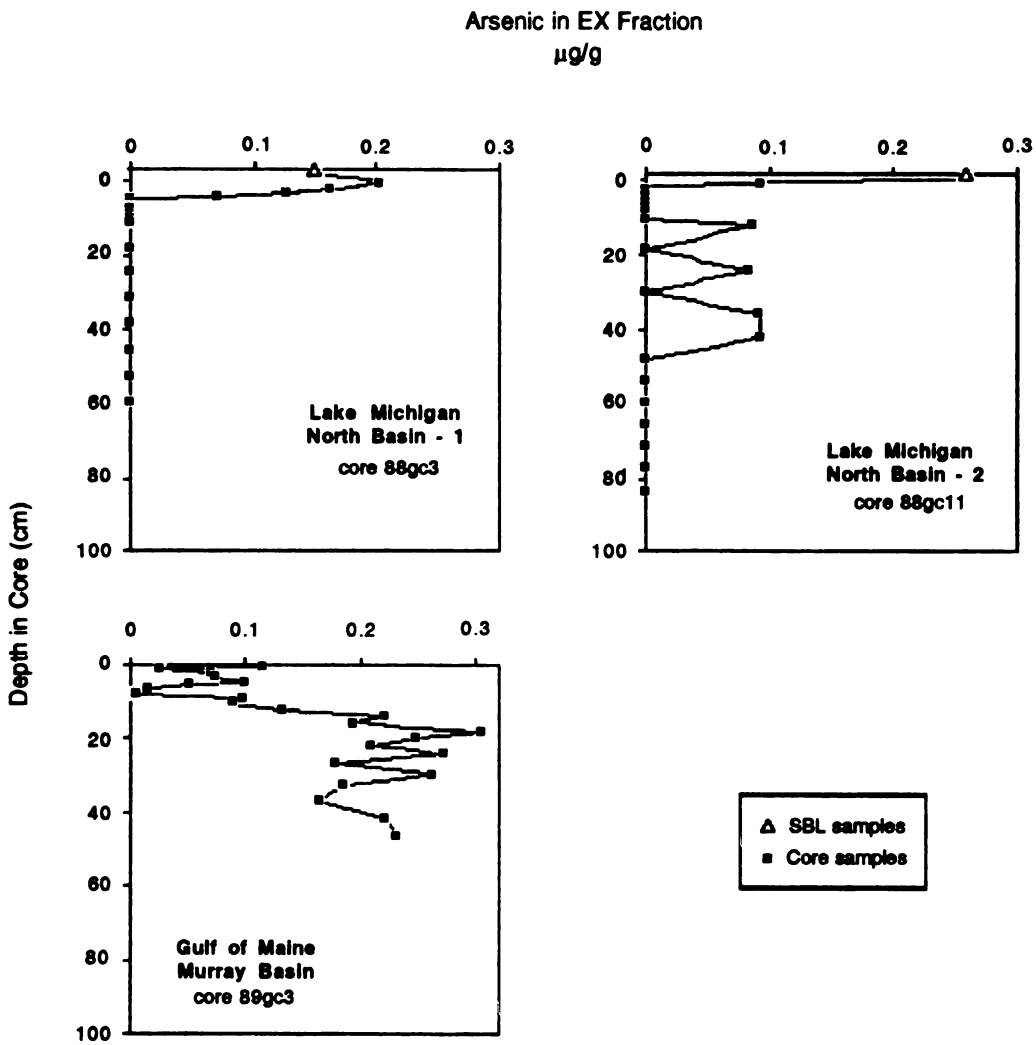


Figure 7. Arsenic extracted from the EX fraction of sediment.

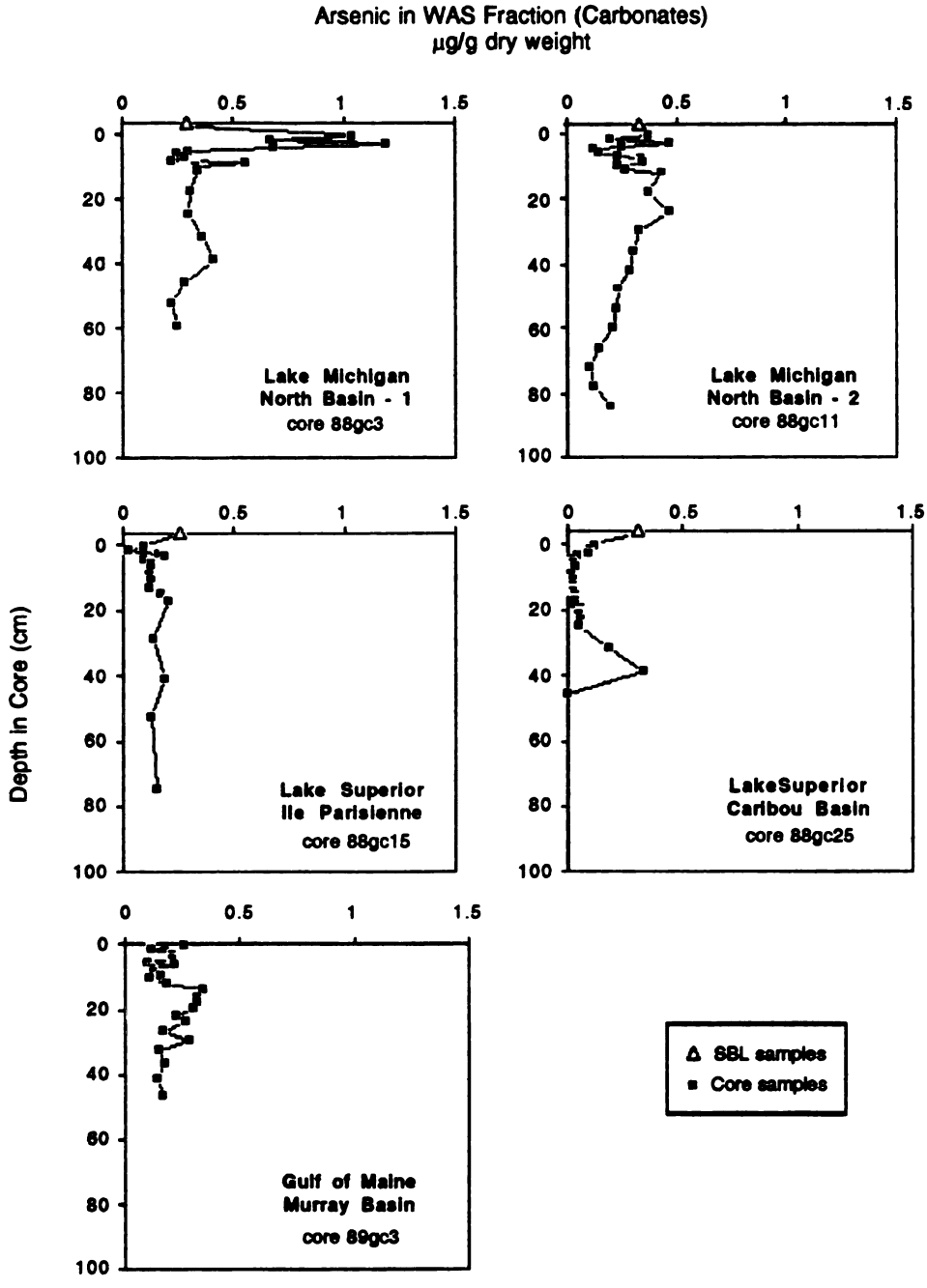


Figure 8. Arsenic extracted from the WAS fraction of sediment.

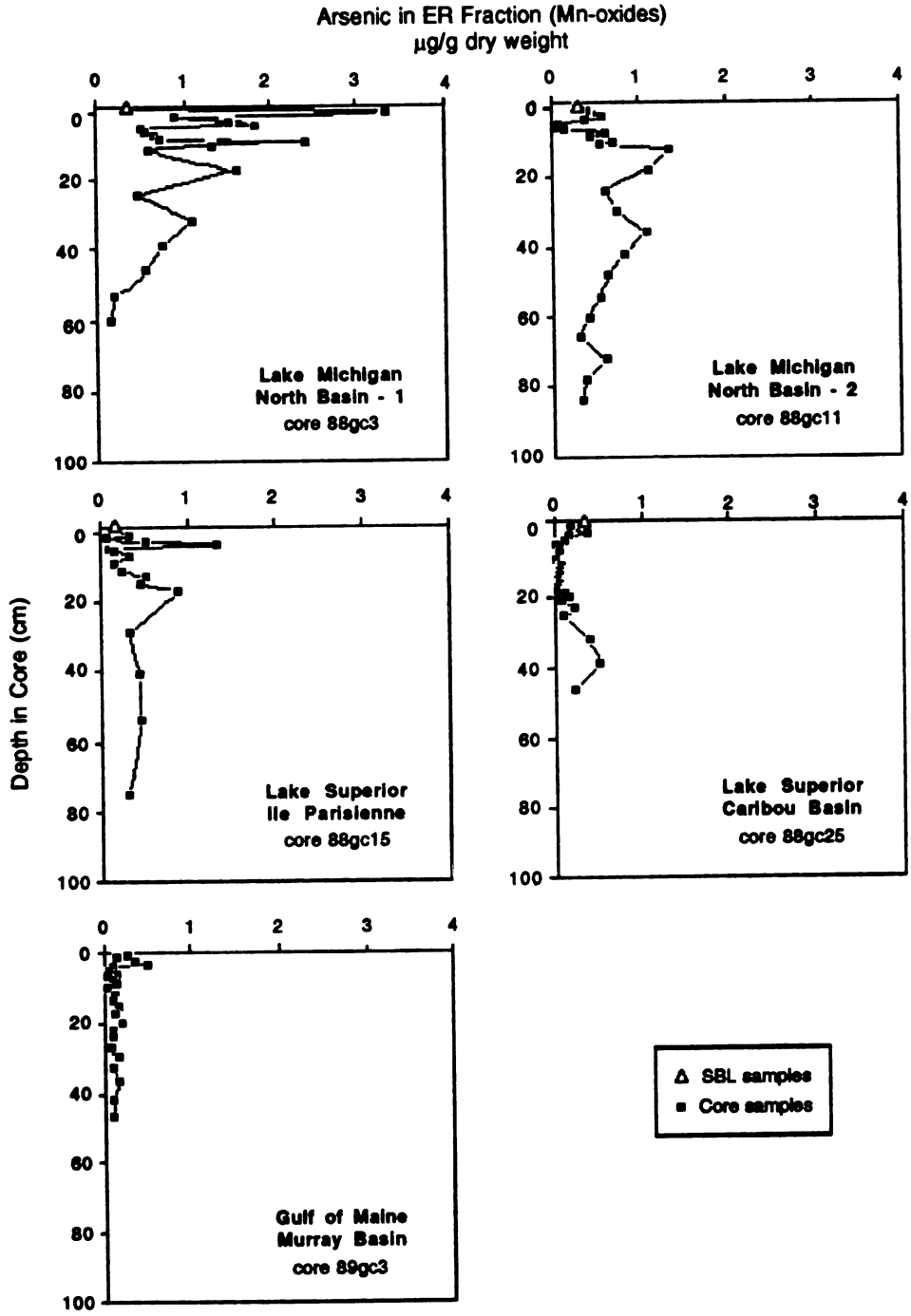


Figure 9. Arsenic extracted from the ER fraction of sediment.

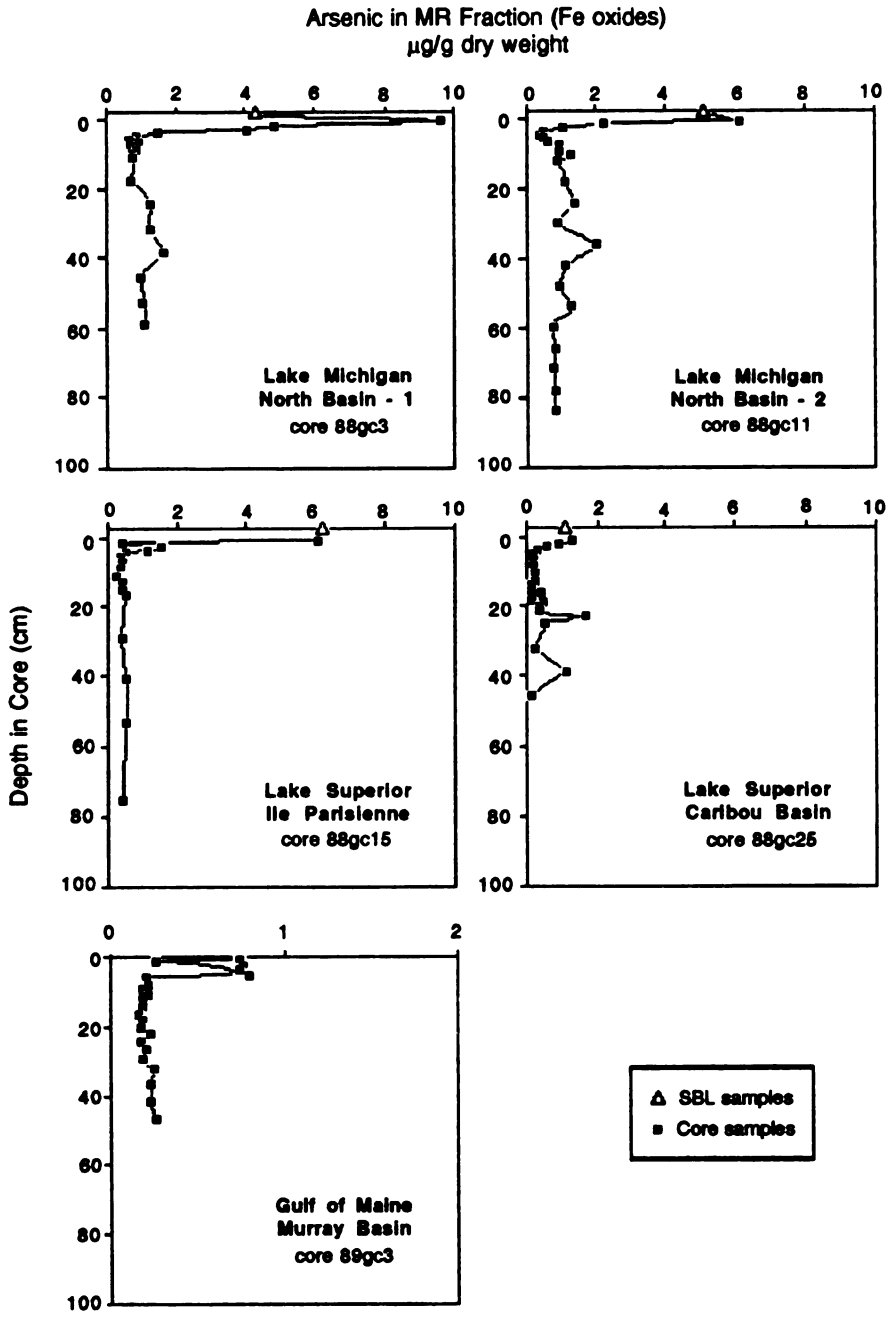


Figure 10. Arsenic extracted from the MR fraction of sediment.

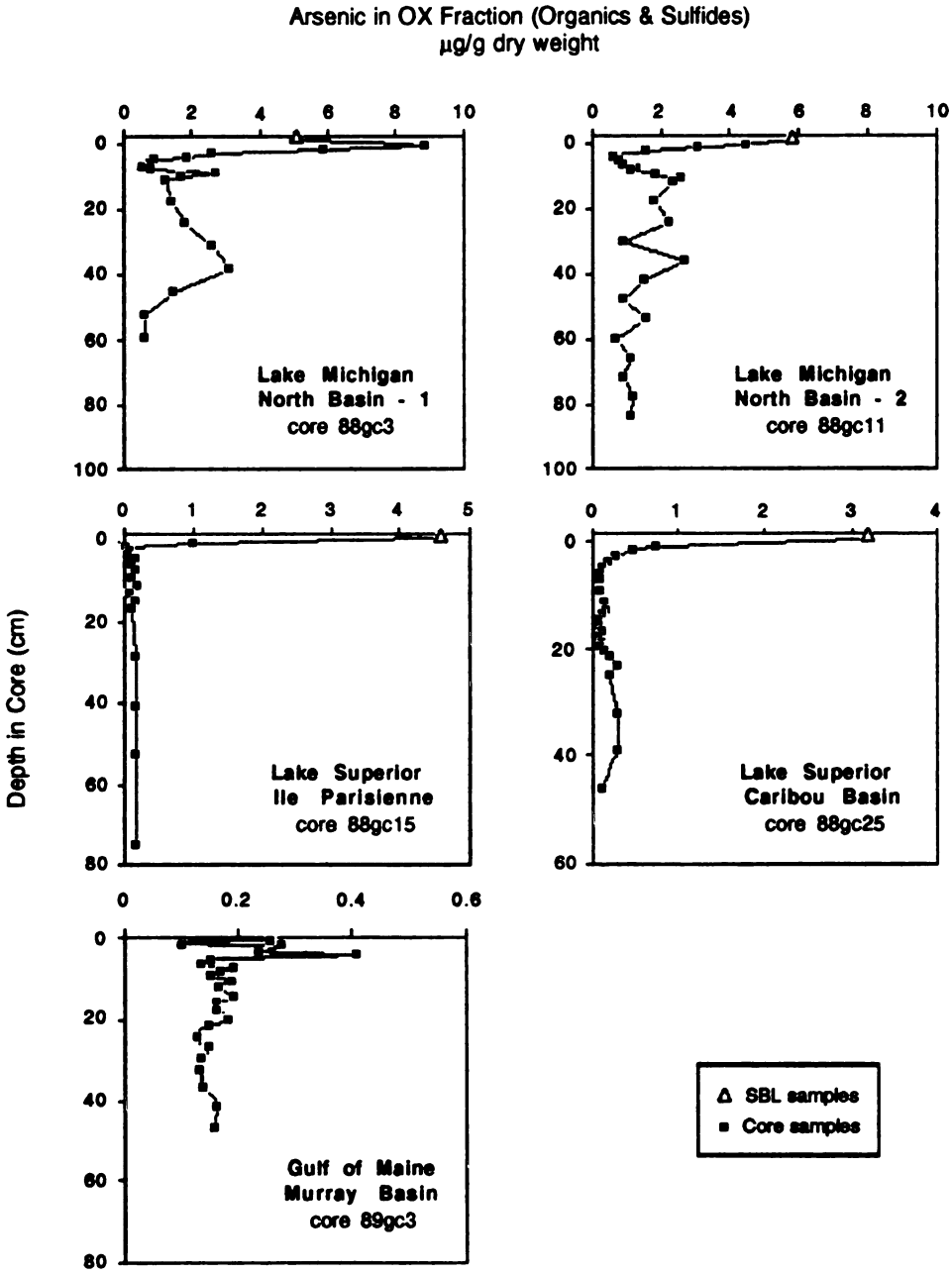


Figure 11. Arsenic extracted from the OX fraction of sediment.

distinctly enriched in arsenic compared with the top-most core sediments; in both locations the total extractable arsenic in the SBL is nearly twice the total extractable arsenic in the uppermost core sample.

At all of the sites, below the surficial enriched zone there is a layer where total extractable arsenic concentrations are at a minimum; the position of this layer corresponds to the redox zone. Total extractable arsenic concentrations increase again below this depth. In most cases, there is a distinct secondary maximum below this minimum at the redox zone, then lower concentrations again, and some additional peaks in total extractable arsenic concentration.

The exchangeable (EX) fraction is insignificant in sequestering arsenic in the lake sediments, but is a major phase holding arsenic in the gulf sediments. The proportion of arsenic extracted from the exchangeable fraction is small but not insignificant in oxidized sediments of the gulf, drops to nearly zero in the redox zone, and is the major contributor of extractable arsenic from the reduced sediments (see Figure 7).

The weak-acid soluble (WAS) fraction contributes a small amount of arsenic in the Great Lakes; not surprisingly, its contribution is larger in the Gulf of Maine, where carbonate sediments are more abundant (Figure 8). WAS arsenic is also more abundant in Lake Michigan than in Lake Superior, where modern sediments do not contain carbonates.

In the lakes, the easily reducible (ER) and MR fractions contribute comparable amounts of arsenic, except in the uppermost layer where MR contributes much more, and at a few locations deeper in the sediments where ER concentrations exceed MR concentrations (Figures 9 and 10). In the Gulf of Maine, the ER fraction consistently contributes less than the MR fraction.

In Lake Michigan, the oxidizable (OX) fraction (Figure 11) is at least as important as either the ER or MR fractions in holding arsenic in sediments; in Lake Superior it is noticeably less important than these phases, contributing approximately the same amount of arsenic as does the WAS phase. In Gulf of Maine sediments, arsenic from the OX fraction is approximately equal to that from the ER and MR fractions.

Total extractable arsenic (Figure 12) is highest in Lake Michigan sediments, with near-surface concentrations exceeding 10 μg/g (23 μg/g at site 1 and 11 μg/g at site 2), and declining to a

baseline level of about 3-4 μg/g. These values are similar to total arsenic concentrations reported for Lake Michigan by Mudroch et al. (1988): 5-15 μg/g in surficial sediments and 5-8 μg/g as a background level. In Lake Superior, total arsenic at the sediment surface shows considerable enrichment (to ~7.5 μg/g) at the Ile Parisienne site, but little enrichment (to ~2.2 μg/g) at the Caribou Basin site; baseline values seem to be about 1 μg/g. Overall total extractable arsenic is lower in Lake Superior than in Lake Michigan. In the Gulf of Maine, total extractable arsenic reaches a maximum of 1.6 μg/g at the sediment surface, shows a second peak of 1.7 μg/g at 3.5 cm depth, and shows a baseline value of about 1 μg/g.

POREWATER

Arsenic concentrations in porewater tend to be low near the sediment-water interface, and higher deeper in the sediment column (Figure 13). At the Caribou Basin site of Lake Superior, the low arsenic concentrations extend to about 13 cm below the sediment-water interface; at each of the other sites there is a distinct concentration gradient near the surface suggesting a flux of arsenic upward toward the sediment-water interface.

Lake Michigan site 1 exhibits a nearly classical profile of porewater arsenic: increasing rapidly from a low concentration at the sediment-water interface to a high concentration at the redox zone, with the porewater maximum value occurring immediately below the surface zone of sediment enrichment. At other sites, the maximum porewater concentration occurs at a greater depth below the zone of surface enrichment, although in Lake Michigan site 2 and Ile Parisienne there are peaks (not the largest) immediately below the enriched layer. Multiple peaks in porewater profiles are evident in all of the locations, most notably in the LMNB-2 and LSIP sites.

Although sediment concentrations of arsenic are low in the Gulf of Maine, porewater concentrations are much higher than in the lakes. Concentrations of arsenic in sediments of the Great Lakes are on the order of 1000 times the porewater arsenic concentrations; in the Gulf of Maine, sediment concentrations are about 100 times the porewater values. Porewater arsenic in the gulf seems to increase continuously with depth rather than reaching a maximum value as

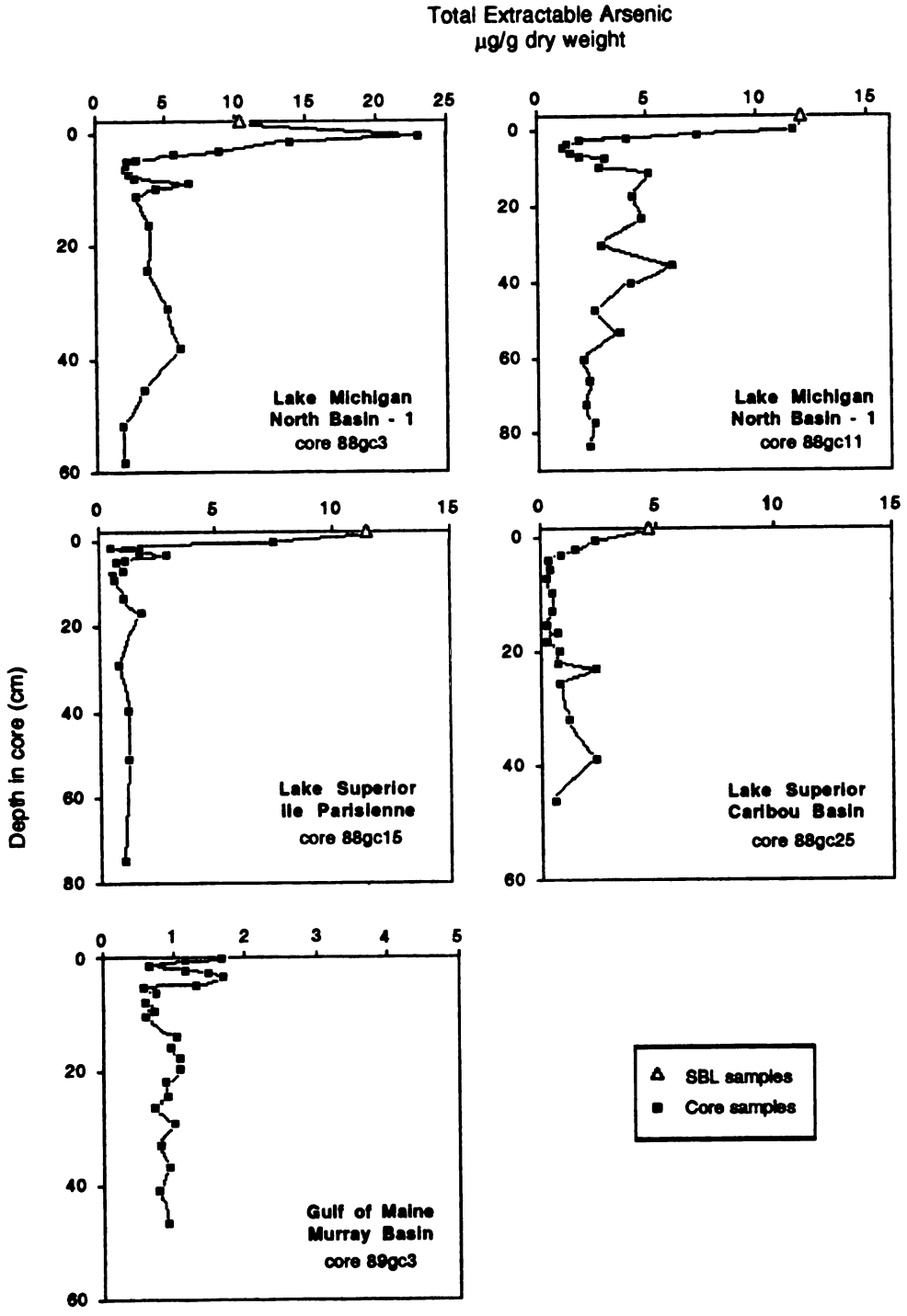


Figure 12. Total extractable arsenic.

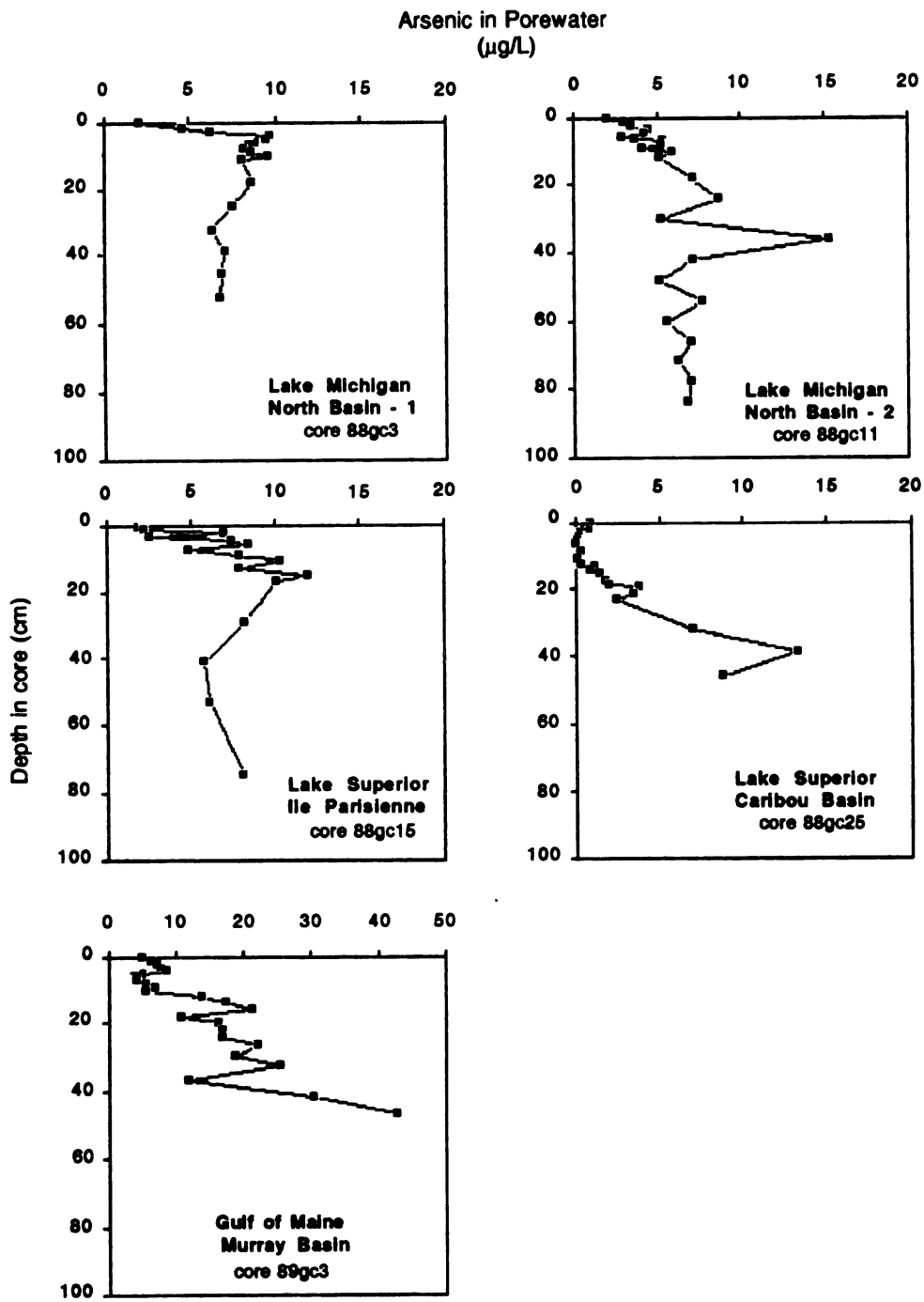


Figure 13. Arsenic in porewater.

appears to be the case in all of the lake sites. Below the redox zone, porewater shows an inverse relationship to total extractable arsenic.

Partitioning of Mercury

SEDIMENTS

Results of chemical extractions for mercury are displayed in Figures 14-16. Mercury was not detected in the exchangeable fraction of any core. Most of the extractable mercury in all of these cores is associated with the oxidizable fraction, although the base-soluble and acid-soluble fractions contribute significant amounts of mercury in the uppermost layers of sediment. At all of the sites, total extractable mercury (Figure 17) is highly enriched in the uppermost layers of sediment, and concentrations decrease rapidly to a background level of approximately 20 ng/g. This is similar to the results of Strunk (1991) for mercury in sediments of Lake Superior.

Profiles of mercury in the base soluble (BS) and acid soluble (AS) fractions are very similar to one another, particularly in the two Lake Michigan sites and in Ile Parisienne of Lake Superior (Figures 14 and 15). In both of these fractions, mercury is high near the sediment-water interface, and drops rapidly to very low values. The depth at which this occurs is identical for the two fractions in both Lake Michigan sites and in the Ile Parisienne samples, but in the Caribou Basin and Gulf of Maine cores, the depth at which concentrations drop to near-zero is somewhat deeper for the acid-soluble phase than for the base-soluble phase.

In all of the lake samples, mercury in the oxidizable (OX) fraction increases from the sediment-water interface to a maximum near the surface, decreases to a minimum immediately below this enriched zone, then increases again to a second maximum before dropping to a relatively constant value (Figure 16). In Lake Michigan, the upper enriched layer is thicker, and more distinctly enriched in mercury than in Lake Superior. In all lake sites, the zone of OX enrichment occurs directly below the enrichment in the AS and BS fractions. In the gulf, mercury in the OX fraction is enriched in the uppermost sample, and nearly constant below this depth.

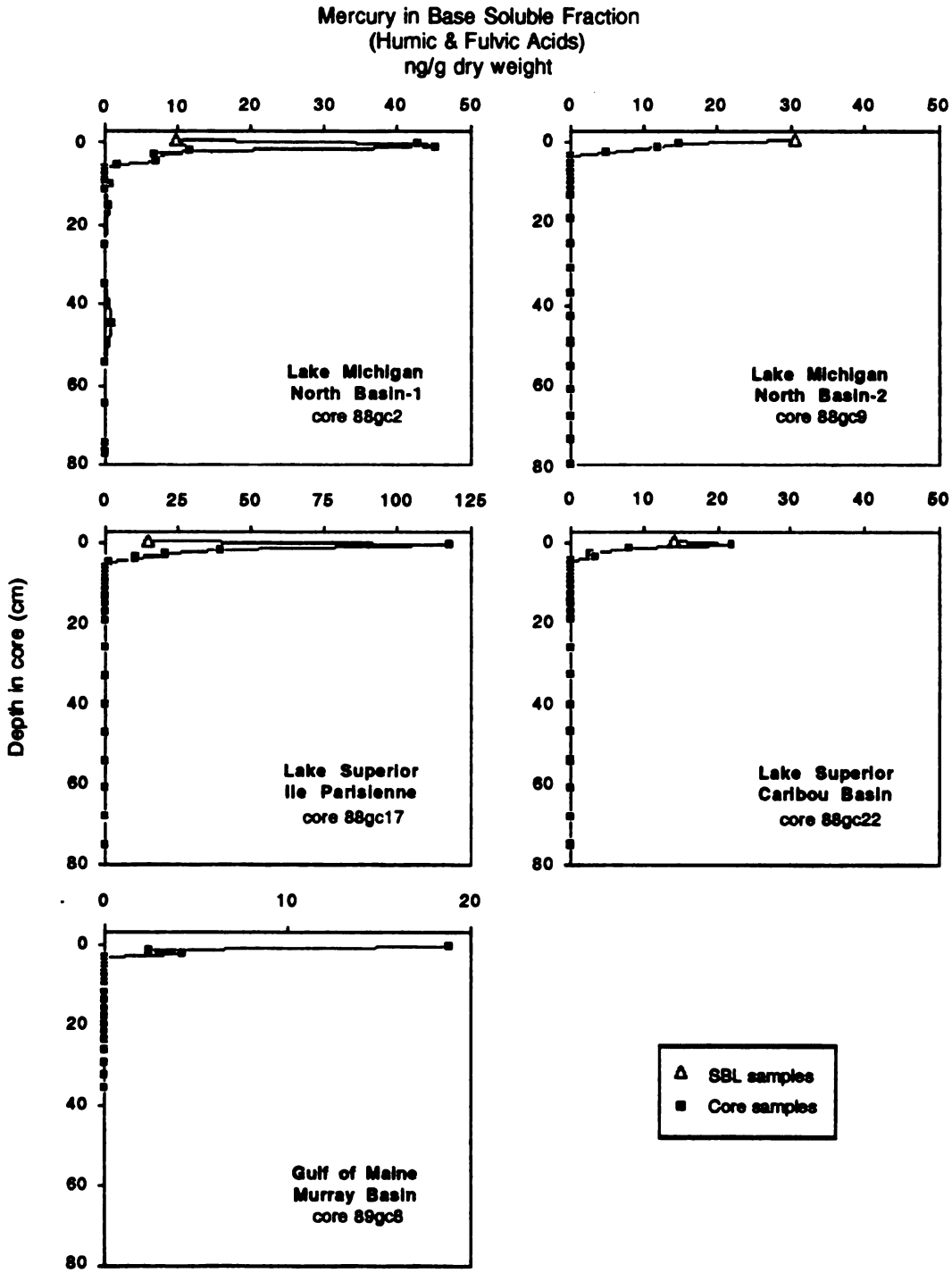


Figure 14. Mercury extracted from the BS fraction of sediment.

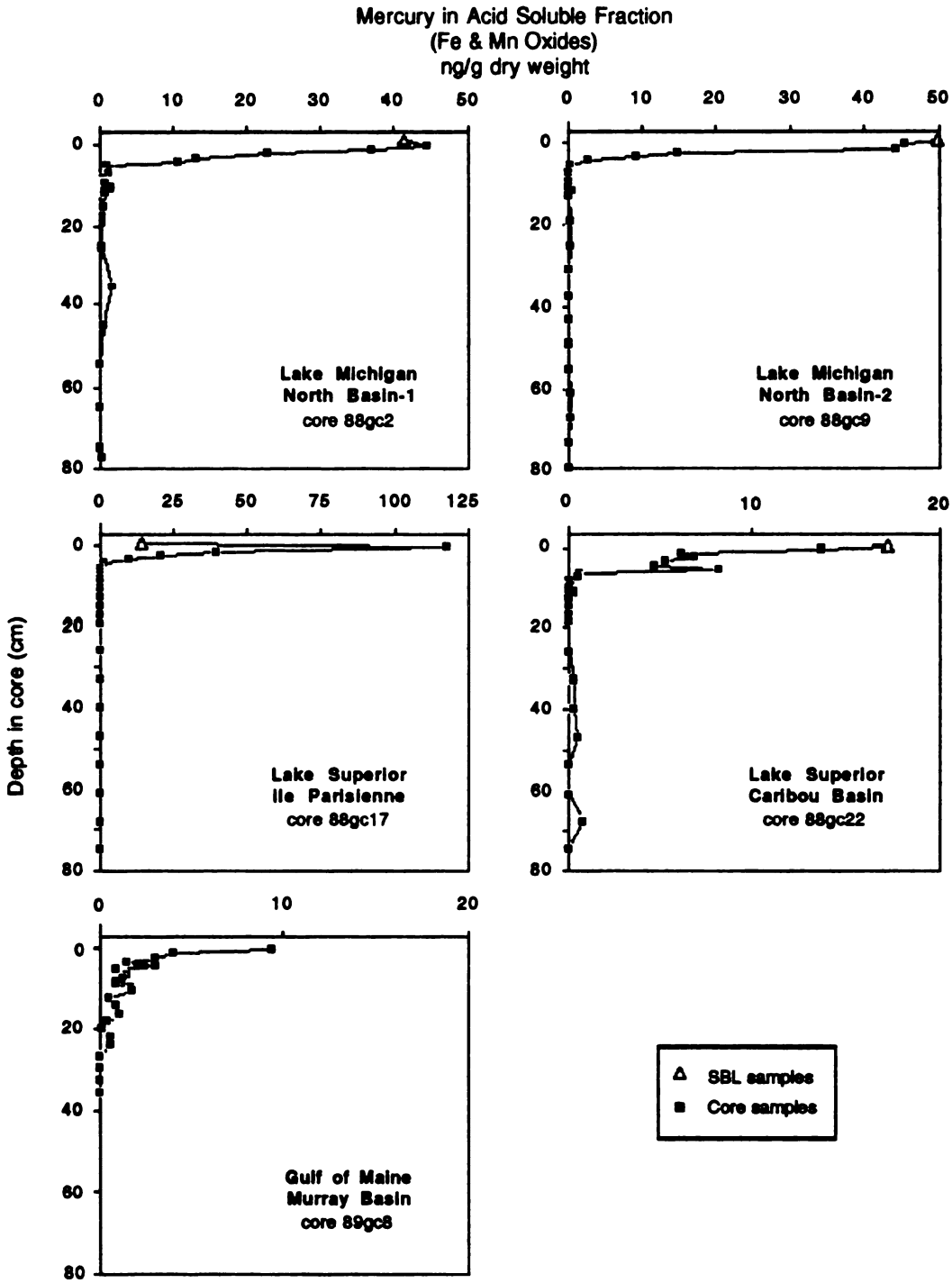


Figure 15. Mercury extracted from the AS fraction of sediment.

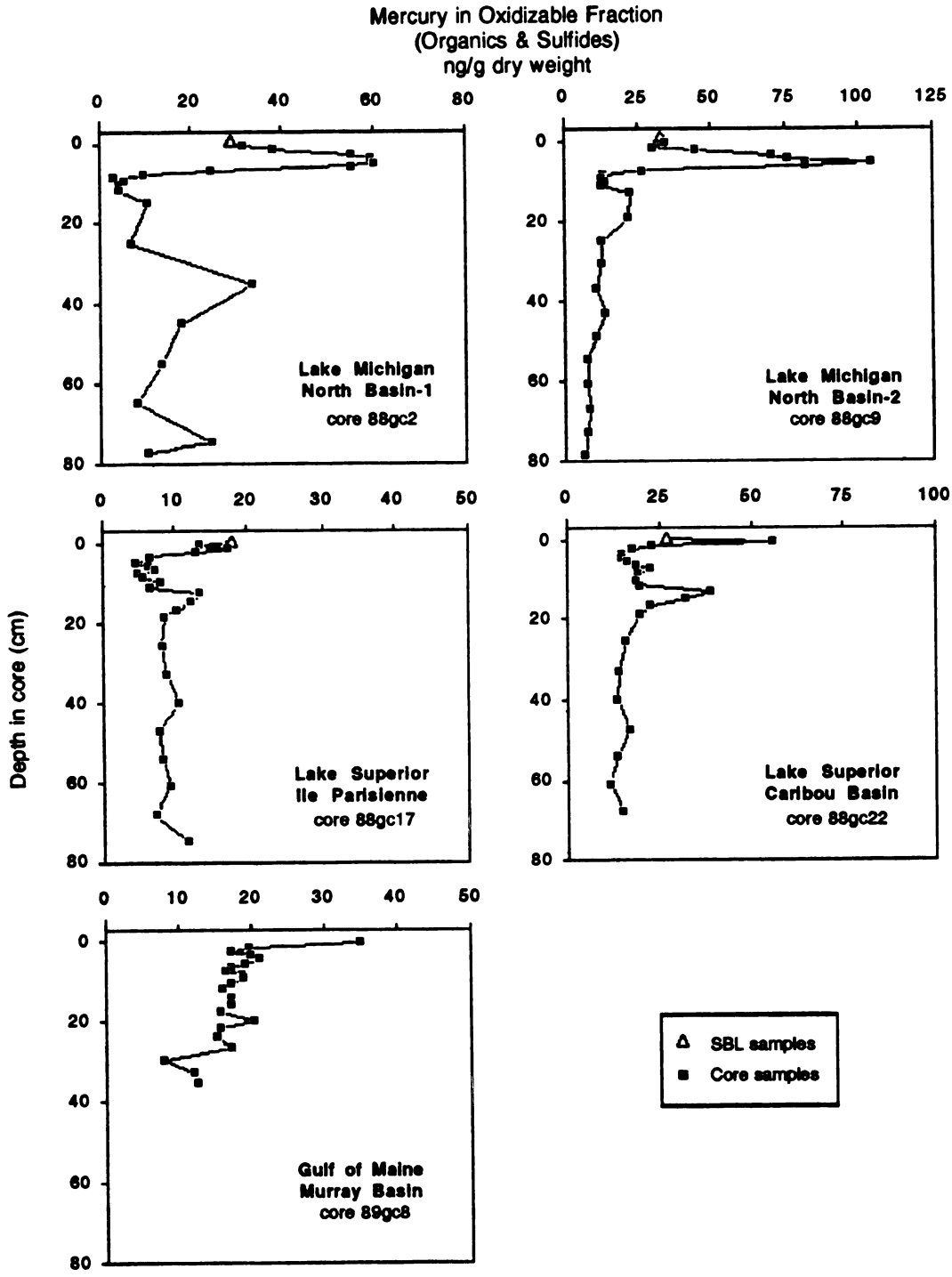


Figure 16. Mercury extracted from the OX fraction of sediment.

Profiles of total extractable mercury (Figure 17) are very similar to OX profiles, with additional enrichment of surficial sediments reflecting contributions of the BS and AS phases. Total extractable mercury is highest in the SBL sample only in site 2 of Lake Michigan; at the other three lake sites the SBL has lower total mercury than the uppermost sediments. Lake Michigan site 2 also displays the most distinct sub-surface maximum, reflecting the highest maximum values in mercury from the OX fraction.

Values of total mercury in sediments of Lake Michigan's depositional basins have been reported in the range 0.030 to 0.380 μg/g in surface sediments; values reported for Lake Superior range from 0.094 to 0.160 μg/g in surface sediments, and 0.044 to 0.68 μg/g for "background" levels (Mudroch et al., 1988). Results from this study are comparable, although baseline concentrations of total extractable mercury are generally lower (~0.02 μg/g).

POREWATER

Mercury porewater profiles in the lakes exhibit high concentrations near the surface, a zone of low/minimum concentration below this, then higher concentrations again at depth in the cores (Figure 18). These minima in dissolved mercury do not correspond to the major enriched zones in the total extractable sediment mercury; they do correspond to secondary maxima in the oxidizable fraction (see Figure 16), although the porewater minima span a greater depth distribution.

Mercury concentrations in the Lake Superior Caribou Basin core are much higher than in the other cores; also the minimum concentration is higher than that in the other lake locations. The Lake Superior profile more closely resembles the Lake Michigan profiles, although peaks below the minimum are higher in Ile Parisienne.

In the Gulf of Maine core, dissolved mercury is uniformly low in porewaters, although slightly higher in the vicinity of the redox zone (near 15 cm depth) and lower near the sediment surface and deeper in the core.

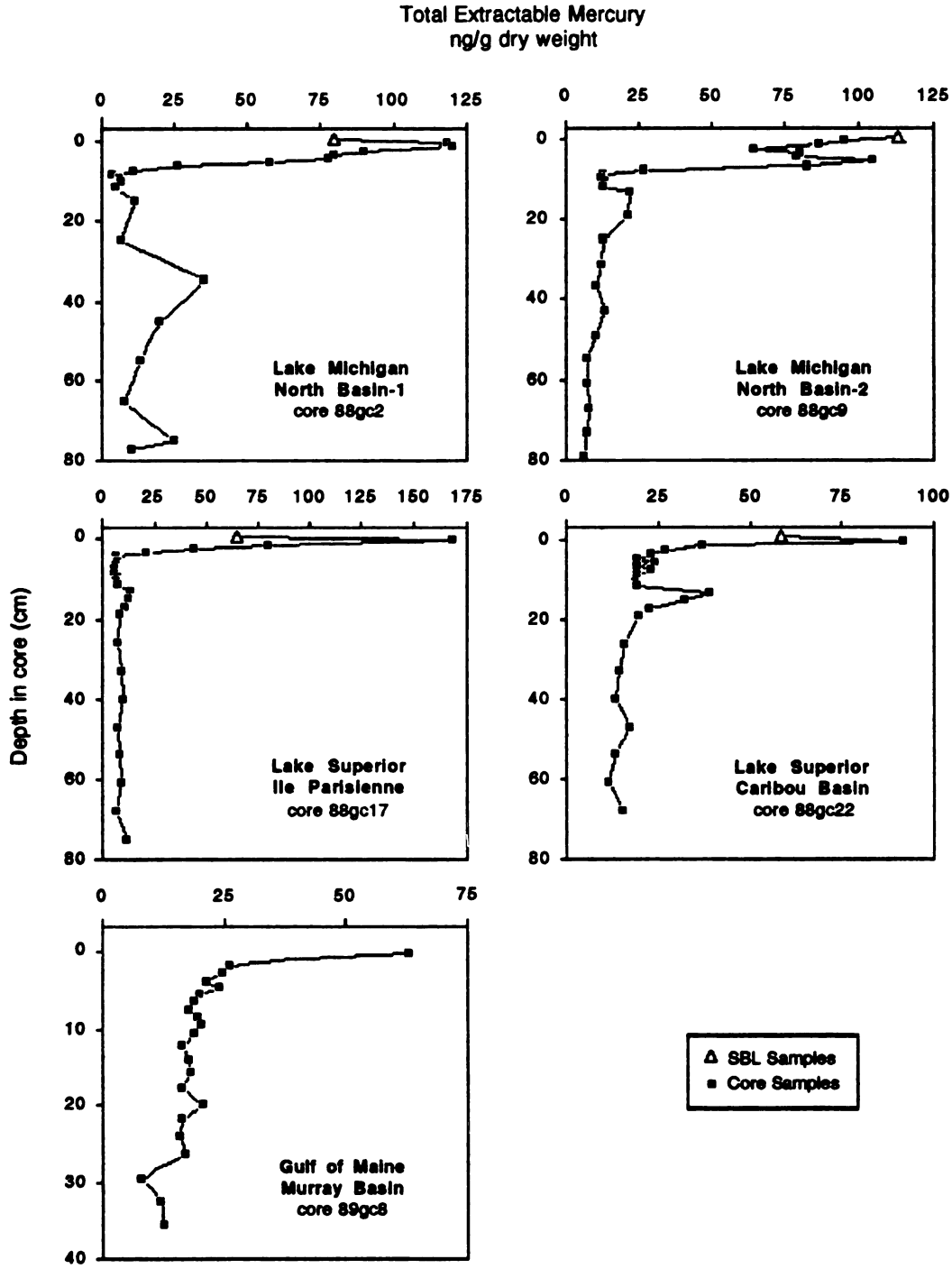


Figure 17. Total extractable mercury.

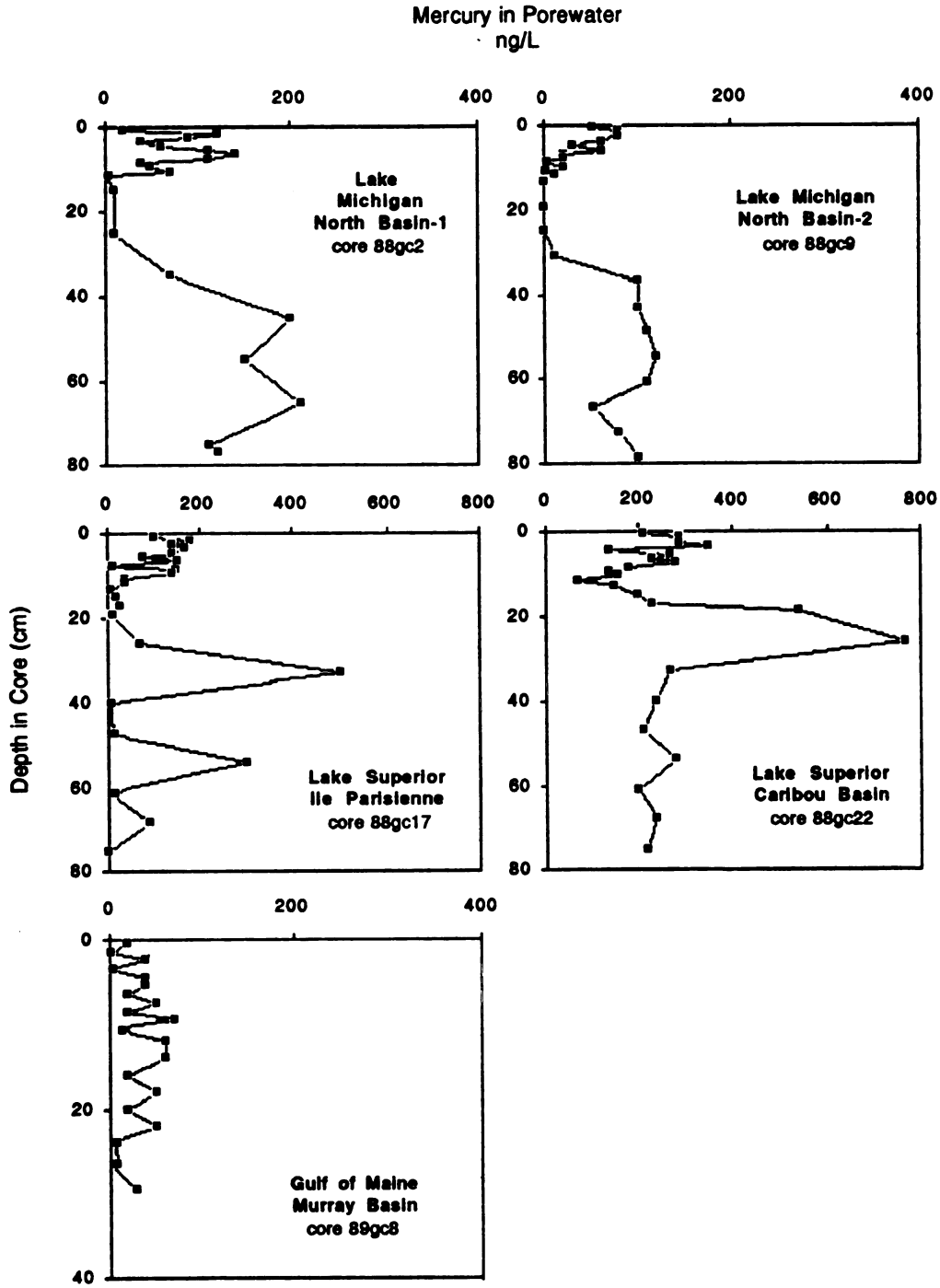


Figure 18. Mercury in porewater.

IV. DISCUSSION

Examination of the data shows several interesting results:

- Changes in the partitioning of mercury and arsenic which accompany increasing burial depth indicate that both elements are mobilized and repartitioned during early diagenesis at all of the sites investigated.
- Mercury and arsenic behave differently during early diagenesis. The repartitioning of mercury appears to be more extensive than is that of arsenic. The "enrichment" of mercury near the sediment-water interface relative to deeper sediments is also more prominent.
- Concentration gradients of arsenic in porewaters indicate that there is a flux of arsenic from the sediments to the sediment-water interface via porewater at all of the sites except the Caribou Basin of Lake Superior.
- Concentration profiles of mercury in porewaters are more complicated than those for arsenic, but there are gradients suggesting some flux of mercury toward the sediment-water interface at all of the Great Lakes sites. There does not appear to be a significant upward flux of mercury from sediments of the Gulf of Maine.
- The apparent upward diffusive fluxes of mercury and arsenic released during early diagenesis contribute to the enrichment of surface sediments in these metals. High concentrations of mercury and arsenic exist in surface sediments even when porewater gradients are not distinct. Enrichment appears to be greater in the Great Lakes sites than in the Gulf of Maine.
- There is notable variability in diagenetic conditions among sites. Evidence for differences is provided by data for organic carbon, ferrous iron, pH and alkalinity of sediments and porewaters.

These are discussed in detail in the following sections. To facilitate comparisons, summaries of geochemical data from each sample site are presented in Figures 19-23.

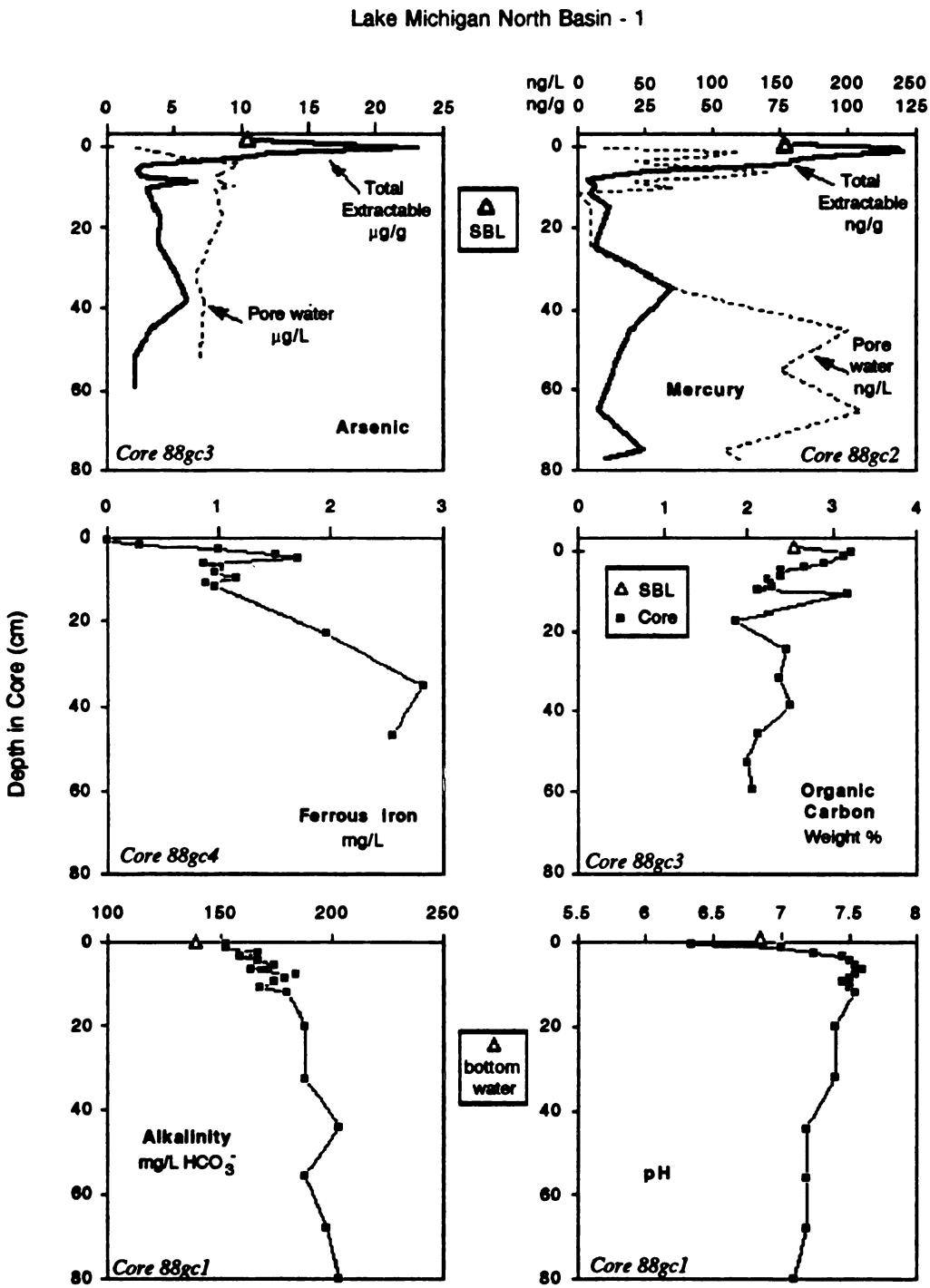


Figure 19. Summary of chemical data: Lake Michigan North Basin - 1.

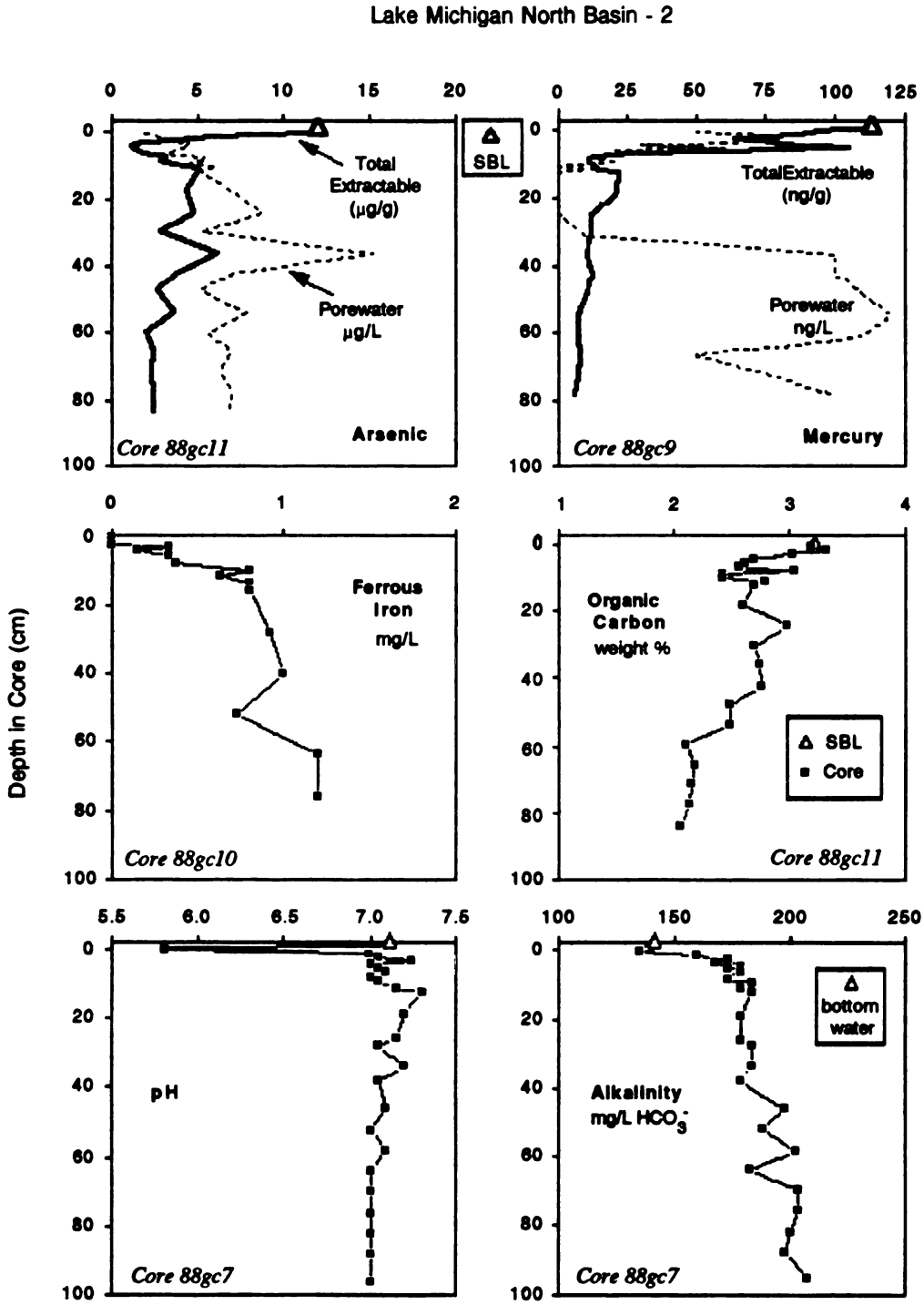


Figure 20. Summary of chemical data: Lake Michigan North Basin - 2.

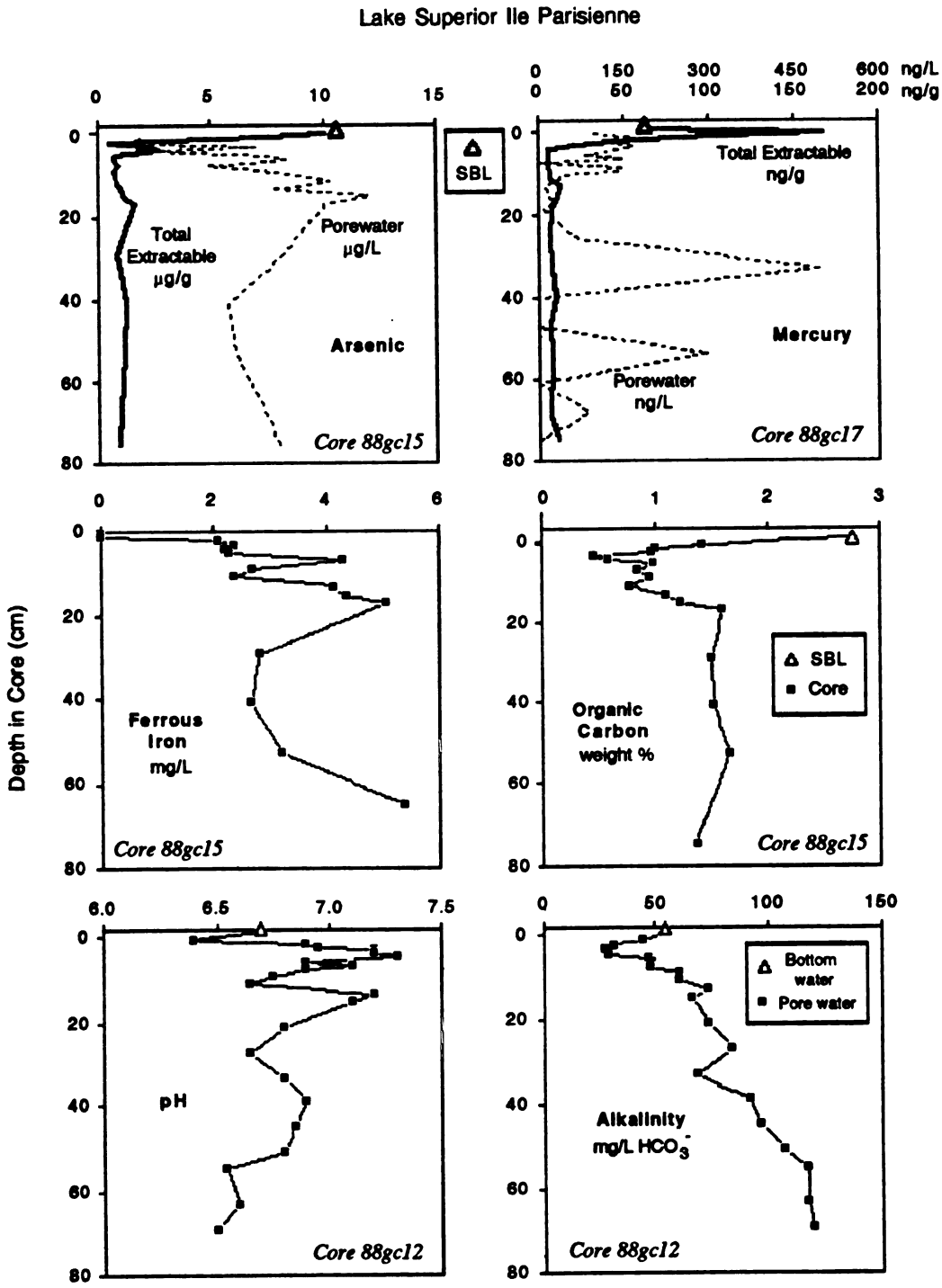


Figure 21. Summary of chemical data: Lake Superior Ile Parisienne.

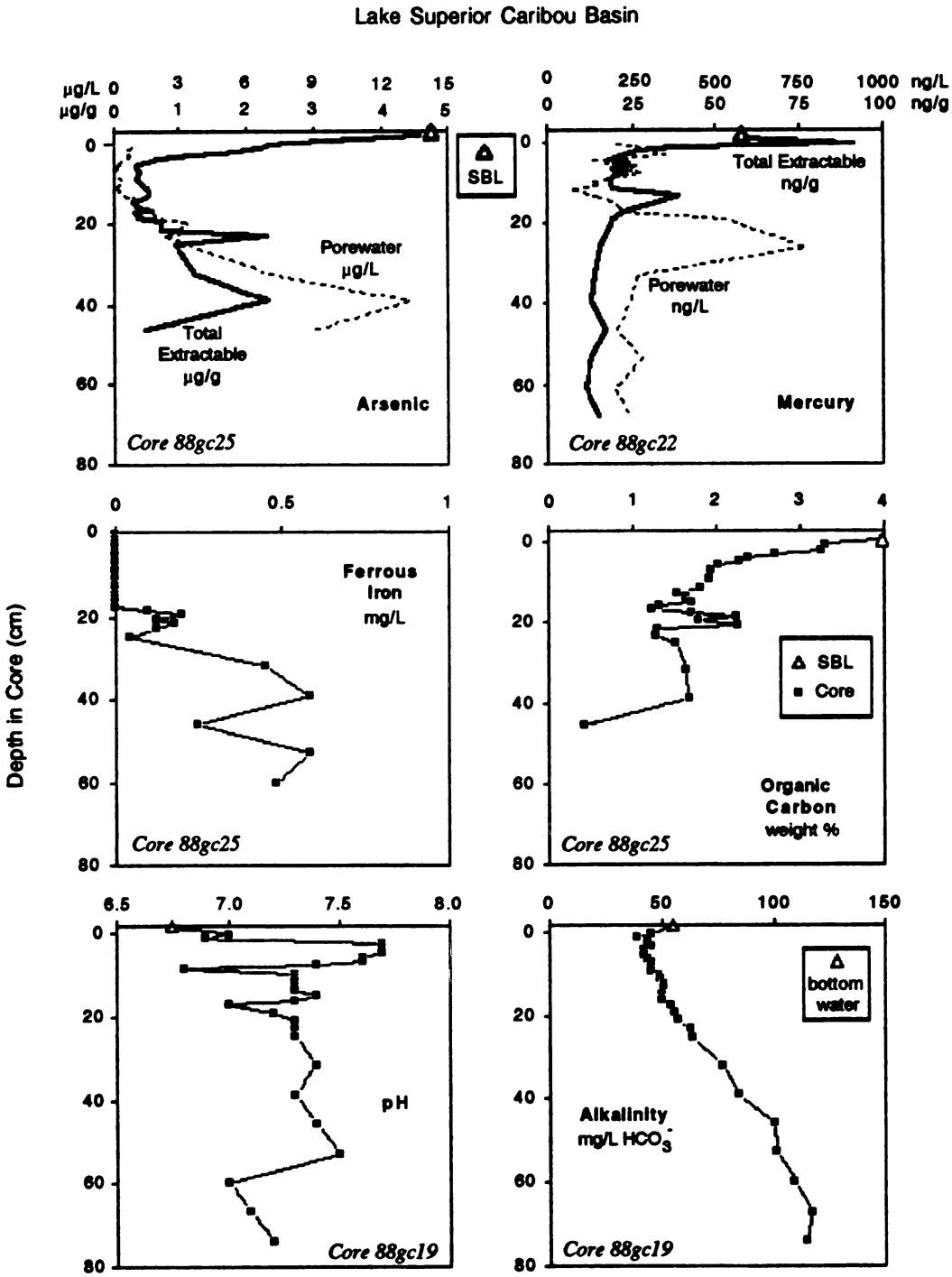


Figure 22. Summary of chemical data: Lake Superior Caribou Basin.

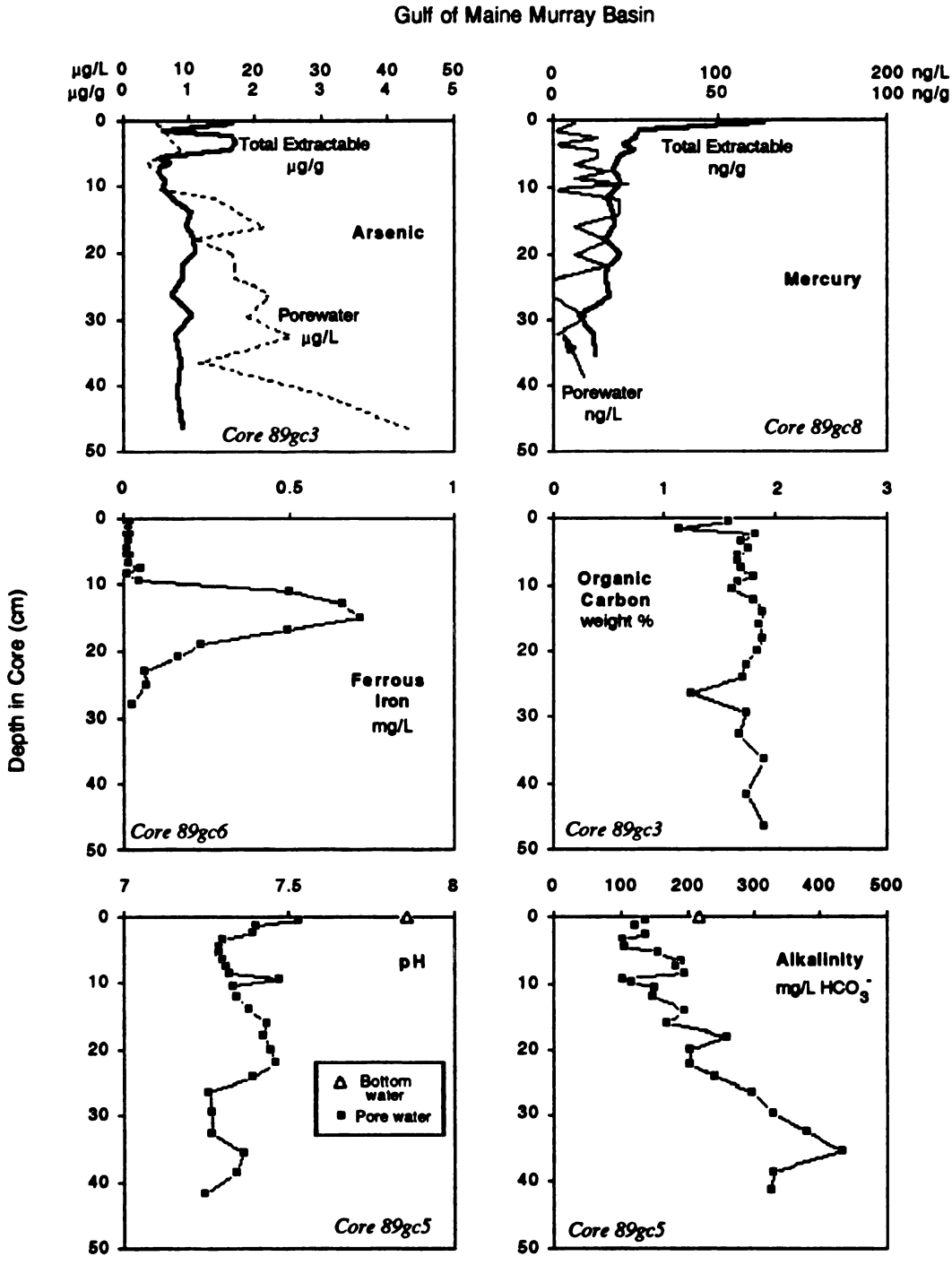


Figure 23. Summary of chemical data: Gulf of Maine Murray Basin.

Diagenetic Processes: Evidence and Effects

EARLY DIAGENESIS OF ARSENIC

The influence of early diagenesis on arsenic can be determined by examining profiles of arsenic concentrations in sediments and porewaters. Profiles of total extractable arsenic in sediments, although produced in part by diagenetic processes, they do not reveal much about these processes. Changes in partitioning of arsenic among the hydromorphic fractions of the sediment are also caused by early diagenesis, but these do provide evidence for the operation of individual processes.

Oxidized Zone

The redox cycling of iron is one of the principal influences on diagenesis of arsenic. There are three lines of evidence for this, as follows. First, total arsenic is enriched in the upper layers of the sediment column at all of the sites (Figure 12). This type of enrichment has been attributed to the adsorption of upward-diffusing porewater arsenic by iron oxides in the oxidized zone of sediments (Farmer and Lovell, 1986; Belzile, 1988; Belzile and Tessier, 1990). The enriched zone lies above the iron redox zone (defined by the appearance of dissolved ferrous iron in porewater) in all of the sites.

Second, profiles of arsenic from the moderately reducible (MR) fraction of sediment (Figure 10) show distinct enrichment of the upper, oxidized layers of sediment. Since arsenic from this fraction is primarily associated with iron oxides, the evident enrichment in the MR fraction is consistent with the adsorption of upward-diffusing arsenic from porewater. .This supports the idea that arsenic is associated with the redox cycling of iron. The enrichment of arsenic in the easily reducible fraction is less distinct, suggesting that manganese oxides play a minor role in the redox cycling of arsenic. This is consistent with the results of other investigations (e.g. Aggett and Roberts, 1986).

Third, porewater profiles of dissolved arsenic (Figure 13) support this explanation. At all of the sites, there is a general gradient of dissolved arsenic from high values in the reduced zone to

lower values in the oxidized zone. Dissolved arsenic is produced during the reductive dissolution of iron oxides, and diffuses up along the concentration gradient toward the oxidized zone, where arsenic is removed from the porewater by adsorption onto solid phases. This is shown by the abrupt decrease in porewater arsenic within the enriched zone at all sites (except for the Caribou Basin, where the redox zone is quite deep in the sediment column). In the Lake Michigan sites, in Ile Parisienne, and in the Gulf of Maine the porewater arsenic gradient is quite steep just below the sediment-water interface, suggesting that significant diffusive fluxes out of the sediments are possible; this is discussed further below.

At the Caribou Basin site, the gradient of porewater arsenic shows that diffusion should occur from the reducing sediments up to just above the redox zone (about 15 cm depth). This depth coincides with a slight enrichment of arsenic in the MR and oxidizable (OX) fractions. Above this, porewater arsenic concentrations are very low, suggesting nearly complete removal of dissolved arsenic from the porewater in and above the redox zone. Relatively high arsenic concentrations do exist in the surface sediments, even though porewater gradients indicate that redox cycling does not provide arsenic to the sediment surface. The degree of enrichment of surface sediments relative to "background" concentrations is much less at this site than is observed at other lake sites. Also, there are two depths (at ~25 cm and ~40 cm) where total extractable arsenic is equal to concentrations found at the sediment surface. These facts suggest that, in the Caribou Basin, concentrations at the sediment surface are elevated due to some process other than redox cycling.

Degradation of organic matter also plays an important role in arsenic diagenesis. Above the redox zone, organic matter is first degraded aerobically. The decay of organic matter releases associated arsenic, contributing to the increase in porewater arsenic just below the sediment-water interface which occurs at all of the sites. In general, oxidizable arsenic profiles (Figure 11) closely resemble those of organic carbon content (Figure 6). In the Great Lakes sites there is a distinct zone of decreasing organic carbon content immediately below the sediment water interface, extending to a depth of several cm; there is a corresponding sharp decline in arsenic associated with the OX fraction in all of the Lakes sites. A similar decrease in concentrations of

cadmium in near-surface sediments of the Laurentian Trough has been noted, and attributed to the aerobic degradation of organic matter (Gobeil et al., 1987; Gratton et al., 1990). There appears to be a strong link between arsenic and organic matter. This relationship is most evident in the Lake Michigan sediments, as can be seen in a plot of arsenic concentration versus organic carbon content (Figure 24a). Additionally, there is a considerable decrease in oxidizable arsenic between the SBL and the tops of cores in Lake Superior, suggesting that arsenic is lost from easily oxidizable organic matter that is largely decomposed before being buried in the sediment column. This decrease is not noted in Lake Michigan, where the organic carbon content of the SBL is similar to (LMNB-2) or lower than (LMNB-1) that of the surface sediments. This difference is discussed in more detail in the section on diagenetic variability. In the Gulf of Maine, there is also a sharp decrease in OX arsenic just below the sediment-water interface, even though no concomitant decrease in organic carbon content is observed. This suggests that the loss of arsenic from the OX phase is caused by some process other than simple degradation of organic matter.

Other phases sequestering arsenic do not show such clear distribution patterns. Patterns are most evident in profiles from Lake Michigan site 1, where exchangeable (EX), weak-acid soluble (WAS), and easily reducible (ER) fractions show enrichment in upper layers. The arsenic enrichment of these phases probably results from the uptake of arsenic from porewater--arsenic provided by the decay of organic matter and arsenic which diffused upward from the reduced sediments. The adsorption of arsenic from porewaters appears to be very effective within the oxidized layers of sediment: most of the arsenic released from decomposing organic matter is transferred to other solid phases rather than accumulating in the porewater. The fact that the MR fractions of the SBL samples do not show additional enrichment over the upper layers of the core sediments also indicates that adsorption is efficient within these upper layers, removing upward-diffusing arsenic from porewaters before it reaches the SBL. Sundby et al. (1986) found that diffusion of metals out of fjord sediments did not occur even though porewater concentrations were higher than those of overlying waters; they attributed this to fixation of metals by oxygen diffusing into the sediment.

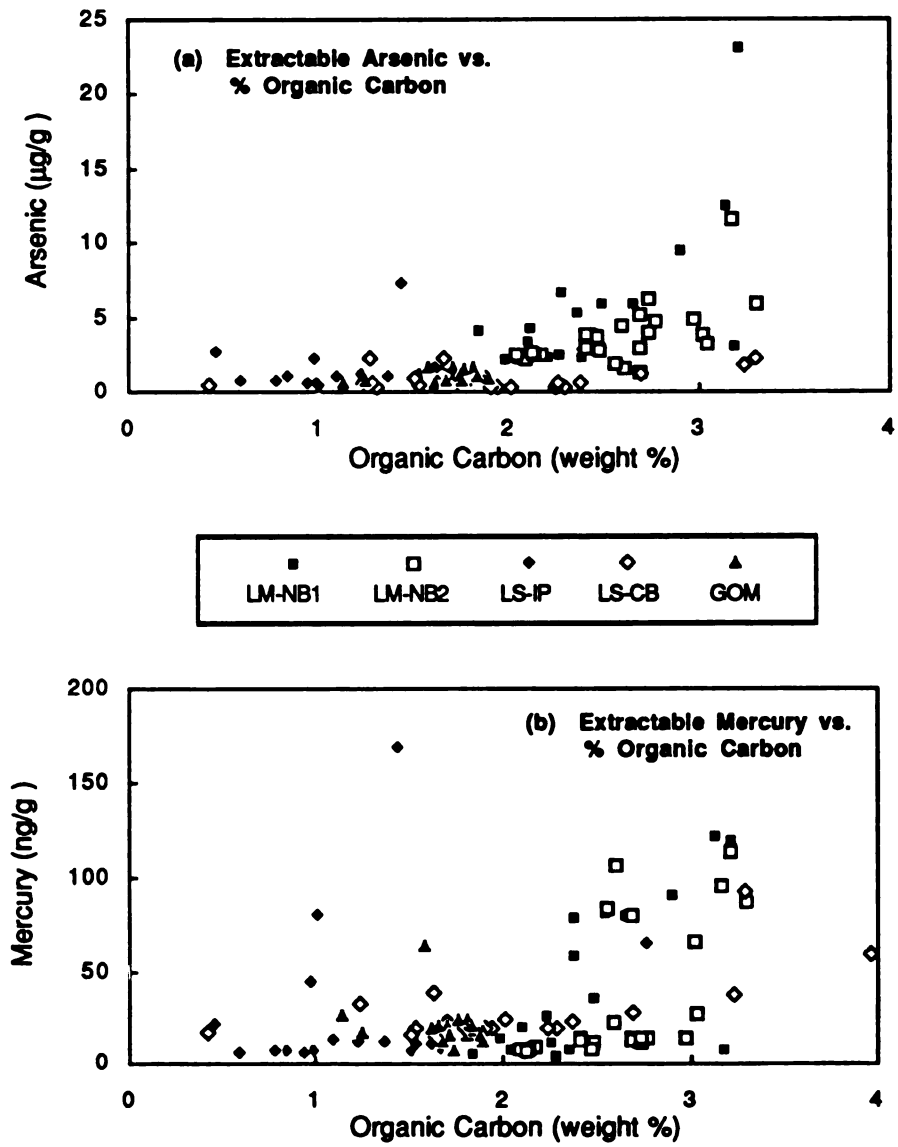


Figure 24. Relationship between sediment organic carbon content and (a) total extractable arsenic, and (b) total extractable mercury in sediment.

The same patterns of arsenic distribution among the EX, WAS, and ER fractions are not as clear in Lake Michigan site 2, however, even though arsenic concentrations in SBL samples and "background" concentrations of these fractions are similar for the two sites (Figures 7-9). Total arsenic profiles are similar, except for the degree of enrichment of the uppermost sediments, but comparisons of the EX, WAS, and ER fractions show lack of enrichment, and MR and OX fractions show less enrichment than is seen for LMNB-1. One possible explanation is that the surface enrichment at LMNB-2 has been obscured by bioturbation. The porewater profiles (Figures 19 and 20) are also quite different. At LMNB-1, dissolved arsenic increases rapidly below the sediment-water interface to a maximum at 4 cm depth (just below the zone of sediment enrichment) then decreases slowly with depth, with few minor excursions from this general trend. The site 2 profile shows an initial peak just below the enriched sediment layer, then numerous higher concentration peaks at depth. This type of profile may be caused by bioturbation and bioirrigation (Belzile, 1988). These processes can also enhance the fluxes of dissolved metals out of the sediments (Gratton et al., 1990); this may account for the lesser degree of enrichment of surficial sediments at LMNB-2 relative to LMNB-1. Thus the differences in both sediment and porewater arsenic profiles may be caused by differences in the degree of bioturbation at the two sites. The Ile Parisienne site also shows some evidence of bioturbation (multiple peaks in porewater arsenic). Effects of bioturbation on arsenic diagenesis are discussed further below.

In the Caribou Basin core, the peak in sediment-bound arsenic at ~25 cm depth is associated with a strongly enriched zone in the MR phase (Figure 10) and slight enrichment in the ER and OX phases (Figures 9 and 11). This layer is the redox crust, a layer distinct in appearance from overlying and underlying sediments, where a concentration of iron oxides is developed just above the iron reduction zone. This layer coincides with the top of a large gradient in porewater arsenic (see Figure 22), and may represent uptake of arsenic released from below. Just above this zone, at ~20 to 24 cm depth, are small peaks in ferrous iron, dissolved arsenic, and organic carbon (Figure 22). This layer consists of sediments that are mottled in appearance (see Table A2-1), and may represent a relict redox horizon. This may have developed due to relatively recent changes in conditions in this basin, such as variations in organic matter inputs which can alter the effective

depth of oxygen penetration (Pedersen et al., 1986); a similar explanation has been proposed to explain manganese profiles in the Caribou Basin (McKee et al., 1989b). This does not explain the increased organic carbon content of this zone, however. Jahnke et al. (1989) noted the presence of a deep "reaction layer" which was enriched in organic carbon in many sites in suboxic sediments of the eastern equatorial Atlantic ocean. This layer is believed to be a relict organic-rich layer that is still decaying, possibly a turbidite deposit (Jahnke et al., 1989).

To summarize, the elevated concentrations of arsenic in the upper layers of sediment are partly due to the fact that sediments being deposited contain more arsenic associated with organic matter than do those that have been buried; partly due to the repartitioning of arsenic within the oxidized layers as organic matter decays and the released arsenic is taken up by other phases; and partly due to fixation of arsenic provided from reduced sediments below via porewater fluxes.

Reduced Sediments

Below the redox zone other processes control arsenic distributions in sediment and porewater. Here, the marine environment is quite different from the freshwater setting. This is due in part to differences in mineralogy, and in part to differences in water chemistry.

Partitioning of arsenic among the hydromorphic sediment phases is different below the redox zone in all of the sites. In the lake sediments, total extractable arsenic concentrations show a minimum just below the redox horizon, increase somewhat below this, becoming more or less constant with depth. Arsenic in the WAS fraction decreases slightly but steadily with increasing depth in sediments of the Lake Michigan sites. This can be explained by the slow dissolution of carbonate minerals as burial depth increases, which is consistent with pH profiles from Lake Michigan (Figure 4), that indicate buffering of pH, probably by carbonate mineral dissolution. There is also a decline in the ER arsenic concentration in the Lake Michigan sites. This may indicate continuing dissolution of manganese oxides with depth of burial. Alternatively, this may result from loss of amorphous iron oxides. There is some evidence that the easily reducible extraction can release metals from some amorphous iron oxides (Tipping et al., 1985) and there is ample evidence that iron oxides, although thermodynamically unstable, can persist well into the

reduced zone of sediments (e.g. Canfield, 1989; Wesrin et al., 1991), continuing to release sorbed metals as they slowly dissolve.

Arsenic appears to be being released from a strongly enriched layer at ~40 cm depth in the Lake Superior Caribou Basin core. This sample was no different in appearance from surrounding sediments (see Table A2-1). All of the extractable phases exhibit enrichment at this depth, and a large peak in porewater arsenic also occurs, with steep gradients above and below. Similar enriched zones with coinciding porewater peaks also occur in the reduced sediments of the other lake sites (at ~10 cm in LMNB-1, at ~40 cm in LMNB-2, and at ~20 cm depth in LSIP). This indicates that arsenic in the reduced zone is not immobile, but can be transferred between different phases and different depths in the sediment.

In the Gulf of Maine, the EX and WAS phases become the dominant sequesterers of arsenic below the redox zone. The transfer of a large proportion of the extractable arsenic from the reducible phases which dominate in the oxidized zone to exchangeable sites may happen because the number of sorption sites is reduced via the dissolution of iron and manganese oxides and the decay of reactive organic matter. Arsenic in known to adsorb preferentially onto iron oxides over other substrates (Crecelius et al., 1975; Sadiq, 1990). In the marine environment, where porewater is of substantially higher ionic strength than in freshwater settings, there is more competition for sorption sites (Förstner and Wittmann, 1983). Some experimental work on sorption capacities of SBL sediment from Lake Superior (J.D. McKee, pers. comm.) support the idea that sorption sites can become saturated, and that sites on oxides are preferable to exchangeable sites. These experiments showed that small amounts of copper added to the sediment were adsorbed by oxides, but that when greater amounts were added, copper was adsorbed by oxides up to a certain limit, then appeared in the WAS and EX phases. The loss of sorption sites may also contribute to the high concentrations of arsenic in porewaters of this site.

Authigenic mineral formation appears to influence dissolved arsenic profiles. Porewater arsenic concentrations in the lake sites do not increase continuously with depth, suggesting that concentrations may be limited by incorporation into or adsorption onto authigenic phases. In general, below the redox zone, porewater arsenic profiles resemble those of ferrous iron in all of

the lake sites, but not in the Gulf of Maine (see Figures 19-23). Similar trends in the relationship between iron and arsenic profiles were found by Belzile (1988) in sediments from sites of varying salinity in the Laurentian Trough. Peterson and Carpenter (1986), however, found evidence for removal of dissolved arsenic to solid phases in reduced zones of marine but not lacustrine sites.

In the Gulf of Maine site, iron sulfide formation appears to be responsible for removing iron quantitatively from porewaters; this is typical of marine environments where there is excess sulfide to convert reactive iron to FeS_2 (Berner, 1980) or to an FeS precursor (Schoonen and Barnes, 1991b).,Arsenic concentrations, however, just keep on increasing with burial depth. The first large peak in dissolved arsenic coincides with the iron peak, indicating release of arsenic from dissolving iron oxides. Arsenic is depleted from the porewaters for a few cm below this horizon, but then begins increasing again whereas iron concentrations remain low. There is a general inverse relationship between profiles of solid-phase arsenic and dissolved arsenic below the iron peak (Figure 23) indicating some relationship between sediments and porewater arsenic, but it is not clear which phase(s) may be involved.

Belzile (1988) found that in marine sediments of the Laurentian Trough, pyrite formation played a significant role in controlling arsenic concentrations in both sediment and porewater; arsenic was incorporated into growing pyrite crystals. However, profiles of dissolved arsenic in the seaward-most samples show continuous increase with depth, to 35 cm at least, well below the iron peak (Belzile, 1988), much like the Gulf of Maine core. Sadiq (1990) found that As(III) sulfides (realgar, AsS) were stable in anoxic marine settings where pH + pe < 4.5, whereas As(V) as $Fe_3(AsO_4)_2$ was stable for pH + pe > 5. He concluded that arsenic sulfide formation should control porewater arsenic concentrations in sulfidic marine sediments by removing arsenite from porewater (Sadiq, 1990); similar conclusions were reached by Moore et al. (1988). Perhaps the formation of arsenic sulfides occurs deeper in the sediments than was sampled in this core, where more strongly reducing conditions develop and pH + pe can drop below 4.5. Since there appears to be sufficient sulfide available to remove iron from porewaters, and iron is available in much higher concentrations than arsenic, it seems unlikely that sulfide concentrations are limiting the formation of arsenic sulfides.

In Gulf of Maine sediments, arsenic in the oxidizable fraction (where arsenic contributed from sulfides should appear) is essentially constant below the redox zone (see Figure 11). The base of the dissolved iron peak (just below 20 cm depth) indicates where maximum pyrite formation is expected; it appears to have little effect on the profiles of OX arsenic or dissolved arsenic (Figure 23). It is possible that uptake of arsenic by pyrite is balanced by loss of arsenic from organic phases, since the OX extraction procedure does not distinguish between organics and sulfides.

EARLY DIAGENESIS OF MERCURY

Data from this study reveal that diagenetic processes do affect mercury in sediments; in fact, the diagenetic recycling of mercury is more effective than is that of arsenic. The diagenetic behavior of mercury is different from that of arsenic in a number of respects. The porewater profiles of the two metals are not at all alike, indicating that different processes control the distributions of these two dissolved components. Changes in the partitioning of mercury among the solid phases are also different from that of arsenic.

Oxidized Zone

Above the redox zone, the base soluble (BS) and acid soluble (AS) fractions contain substantial amounts of mercury, as does the oxidizable (OX) fraction; below this zone nearly all of the mercury is associated with the OX fraction (Figures 14-16). This suggests that mercury is very efficiently removed from the AS and BS fractions by processes operating in the oxidized upper layer, and by the onset of reducing conditions.

The redox cycling of iron exerts considerable influence on the behavior of mercury. The nearly complete loss of mercury from iron and manganese oxides (AS fraction, Figure 15) noted for all sites was also observed by Strunk (1991) and is different from the behavior shown by arsenic or by other metals (e.g. McKee et al., 1989a). Forbes et al. (1974) found that mercury bonds on goethite surfaces were less stable than those of other metals adsorbed to oxides. As iron oxides begin to dissolve under reducing conditions, the tenuously bound mercury may be readily

released. This may account for mercury being removed almost completely from the AS fraction during early diagenesis.

The degradation of organic matter also affects mercury. The extensive loss of mercury from the BS fraction (humic/fulvic acids; see Figure 14) may be due to the fact that these compounds (or their bonds to mercury) are readily broken down during early diagenesis. Readily decomposable organic matter has been found to constitute up to 45% of organic matter deposited in Lake Superior sediments (Klump et al., 1989). This loss of BS mercury is in contrast to the results of Strunk (1991) who found that the BS fraction contributed significant amounts of mercury to deeper sediments in several locations of Lake Superior. It is unlikely that the methods used are responsible for this discrepancy, because identical extraction procedures were employed. In one core, from the Ile Parisienne area, mercury was found to be essentially absent from the BS fraction below the redox zone (Strunk, 1991); perhaps this is a feature that varies spatially as a result of contrasts in organic matter inputs. Small-scale spatial variations in the nature of organic matter accumulating in depositional basins have been observed (Silverberg et al., 1985; Klump et al., 1989) and related to differences in diagenesis of metals (Iricanin et al., 1985; Gobeil et al., 1987). This is discussed in more detail in the section on diagenetic variability below.

Mercury in the OX fraction of Lake Michigan samples increases with depth in the oxidizing zone, reaching a maximum at the depth corresponding to peak iron dissolution, then drops quickly to a low values before showing a secondary peak within the reduced sediment layer. The pattern of enrichment in the OX fraction occurring directly below the enrichment in the AS and BS fractions suggests that mercury released by decay of humic/fulvic acids and by reduction of iron/manganese oxides is taken up by some component of the oxidizable fraction. The depth of the upper enriched layer corresponds to the bottom of the zone of rapid organic matter degradation shown by the organic carbon profiles in the Lake Michigan and Ile Parisienne sites (Figures 19-21). This indicates that as the more reactive organic matter is degraded, mercury released from it is accumulated by some other component of the oxidizable fraction. Below this zone, mercury in the OX fraction drops to a minimum, and organic carbon becomes more constant.

Within the zone of rapid organic matter decomposition, porewater concentrations fluctuate, but in general show an initial increase below the sediment-water interface, followed by a decrease in concentration. This is consistent with the release of mercury from the AS and BS phases and subsequent uptake by the OX phase within this zone. A plot of organic carbon vs. mercury content of sediments (Figure 24b) shows a correlation between organic carbon and total extractable mercury at high levels of organic carbon (particularly for the Lake Michigan sites). This reflects the retention of mercury in the upper layers where organic carbon content is generally highest. A similar pattern was observed for cadmium in the Laurentian Trough (Gobeil et al., 1987); they attributed the loss of cadmium to aerobic oxidation of organic matter and estimated that 80% of the total cadmium flux to the sediments was returned to the water column via upward diffusion. Porewater profiles of suggest that fluxes of mercury out of the sediment may also be occurring; this is discussed in the section on fluxes below.

Mercury has been found to form complexes with dissolved, colloidal, and particulate organic carbon (Falchuk et al., 1977; Cline et al., 1973; Mantoura et al., 1978). Hallberg (1982) found experimental evidence that chelating agents are concentrated in upper sediment layers above the redox layer, and suggested that they may react with heavy metals there, sweeping them out of the system before they have time to be fixed as sulfides. This would tend to keep mercury in the upper oxidized portions of the sediment, and/or to return it to the water column. Lindberg and Harriss (1974) also found a significant correlation between dissolved organic carbon and dissolved mercury in porewaters of estuarine sediments, and that this association decreased with increasing depth in the sediments. This association can explain the very efficient retention of mercury in the upper layers of sediment: mercury released by the decay of solid-phase labile organic matter is complexed by dissolved organic carbon. Such complexes may then be transferred to solid phases by flocculation (Cline et al., 1973), by coagulation or aggregation of colloids (Morel and Gschwend, 1987), or by scavenging of colloids onto sediments (Santschi et al., 1987).

Similar behavior has been observed for iodine by Kennedy and Elderfield (1987). They found that the association of iodine with organic matter was responsible for retaining iodine near

the sediment-water interface of pelagic marine sediments. Iodine released from decomposing organic matter was rapidly removed onto reactive organic matter at the sediment surface (Figure 25). Retention of iodine in the sediments was found to depend on the presence of newly deposited reactive organic matter (Kennedy and Elderfield, 1987). It is possible that the same mechanism affects mercury cycling in sediments: variations in the reactive organic matter content of surficial sediments could influence mercury enrichments at the sediment-water interface.

This is one possible explanation for the lower enrichment of the surface sediment of the Gulf of Maine. Organic carbon content is quite low, suggesting there may be less reactive organic matter at this site than at the Great Lakes sites. Another possible explanation is the higher salinity of the marine environment. Lindberg and Harriss (1974) found that higher salinity resulted in lower mercury-complexing capacity of dissolved organic matter in porewaters. This could also contribute to the lesser degree of enrichment of surficial sediments in the Gulf of Maine.

Reduced Sediments

Below the redox zone, mercury appears to be influenced by sulfide mineral formation. The smaller secondary peaks in OX mercury occurring in the reduced zone of all the lake sites may be due to uptake of mercury into some sulfide phase. In the Gulf of Maine the formation of sulfides in reduced sediments results in uniformly low concentrations of dissolved mercury, but in the Great Lakes this leads to somewhat more complicated behavior. Although there is not much sulfate in lake waters, and sulfate reduction is considered to be a minor contributor to organic matter decomposition (Carlton et al., 1989), sulfate reduction does occur (Tisue et al., 1988) and authigenic sulfide minerals have been identified in modern sediments of the Great Lakes (Dell, 1972; Sly and Thomas, 1974). Several studies have found that sulfate reduction can be important in oligotrophic lake sediments with low organic matter input (Capone and Kiene, 1988, and references cited therein). Evidence for the influence of sulfides on mercury in the lakes is provided by mercury porewater profiles, as discussed below.

First, porewater mercury profiles in the lakes (Figure 18) show minima at depths which generally correspond to secondary maxima in oxidizable mercury (Figure 16; see also Figures 19-22). This suggests that mercury released from dissolving iron and manganese oxides which

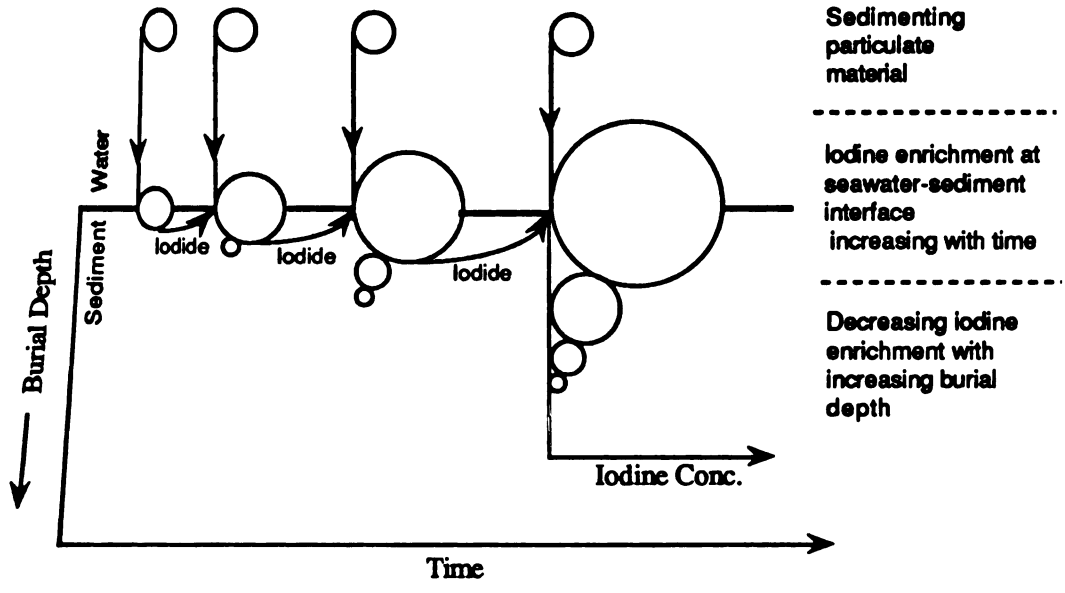


Figure 25. Cartoon of iodine cycling at the sediment-water interface (from Kennedy and Elderfield, 1987).

diffuses downward is taken up by some component of the oxidizable fraction. This occurs below the depth of rapid organic matter oxidation, where organic carbon levels are relatively low (see Figure 6). The other principle phase affected by the oxidizable extraction is sulfides.

Sulfate reduction typically occurs in sediments below the zone of iron reduction (Berner, 1976; 1980). In marine environments where sulfate reduction is the major process of organic carbon oxidation, iron tends to be removed from porewater by precipitation of pyrite (Capone and Kiene, 1988). In the lakes there is often more iron than sulfide, so formation of iron sulfide minerals will effectively remove sulfide, allowing excess Fe(II) to accumulate in the porewater. This explains the continuous increase in ferrous iron with depth in the lake sediments, in contrast to the narrow zone of ferrous iron in the Gulf of Maine core.

In lakes, sulfate reduction is generally completed within a few cm of the sediment-water interface, and once sulfate is depleted the remaining sulfide is precipitated as highly insoluble FeS minerals (Berner, 1980; 1985). In the zone of sulfate reduction and sulfide generation, mercury may be incorporated into HgS, or may be adsorbed onto FeS minerals (Hyland et al., 1990). Kuivila and Murray (1984) found that the depth where sulfate concentrations in lake sediments reached a background level (i.e. where sulfate reduction was essentially completed) corresponded to the depth where a change in slope of the alkalinity profile occurred, to a less rapid rate of increase in alkalinity. Examination of alkalinity profiles from the Great Lakes (Figure 5) shows such trends in alkalinity, with the change in slope occurring at ~9 cm in LMNB-1, ~6 cm in LMNB-2, ~13 cm in LSIP and ~46 cm in LSCB. These depths are all several cm below the apparent zone of iron reduction (see Figures 19-21), and may indicate the base of the zone of sulfate reduction. These depths correspond to depths where mercury in porewater starts dropping to minimum values, i.e. the top of the mercury minimum zone, in Lake Michigan and Lake Superior Ile Parisienne. This is consistent with the hypothesis that mercury is removed from porewater by the formation of sulfide minerals, at least in these three sites. Below this zone, no sulfide forms, so dissolved mercury will not be removed from the porewater by this process. In the Caribou Basin, there is no distinct minimum in porewater mercury; it is possible that sulfide formation is limited in this location.

Second, dissolved mercury profiles in the lake sites display a general inverse relationship with ferrous iron profiles below the redox zone (Figure 26). Mercury in porewater tends to increase initially below the sediment-water interface, then concentrations decrease in the zone where ferrous iron concentrations increase (Figures 19-22). Then the iron concentrations drop off somewhat, and mercury concentrations peak. Below this, mercury concentrations decrease and iron concentrations increase once again. This inverse relationship is essentially the opposite of that between ferrous iron and arsenic, and suggests that some type of competition between iron and mercury for sulfide may exist.

The formation of pyrite requires more than just the presence of reduced iron and sulfide ions. Schoonen and Barnes (1991a,b) have found that the nucleation of pyrite is inhibited under typical conditions of early diagenesis, and FeS_2 forms only after conversion involving several steps, from FeS precursors through Fe_2S_3 to FeS_2. Morse and Cornwell (1987) found that identifiable iron sulfides in anoxic marine sediments were almost always pyrite; they suggest that if precursors are present they must be as coatings or as submicron particles. Other studies suggest that iron monosulfides form first when the pH is near neutral, but pyrite forms first at pH values below 6.5 (Drever, 1988). Values of pH approach 6.5 in some samples of LSIP, but all other areas have pH > 6.5 in the reduced sediment (Figure 4).

One explanation for this behavior is that HgS forms in the shallower depths where sulfate reduction first occurs. HgS is more insoluble than the various FeS minerals (based on values of solubility products; see Table 2). Therefore, as mercury sulfide precipitates, virtually all of the mercury supplied to the porewater in this zone may be removed. Because mercury is present at trace levels only, the formation of HgS does not remove all of the sulfide. Deeper in the sediments FeS is converted to Fe_2S_3, which is much more insoluble than HgS, so iron is removed from porewater (to some extent), sulfide is used up, and any released mercury could appear dissolved in porewater once again. The solubility of FeS_2 is somewhat lower than that of HgS, but much closer in magnitude than either FeS or Fe_2S_3.

Extending this hypothesis, solubilities of other trace metal sulfides could be used to predict trends in porewater profiles. Lead sulfide solubility is close to those of iron monosulfides, so

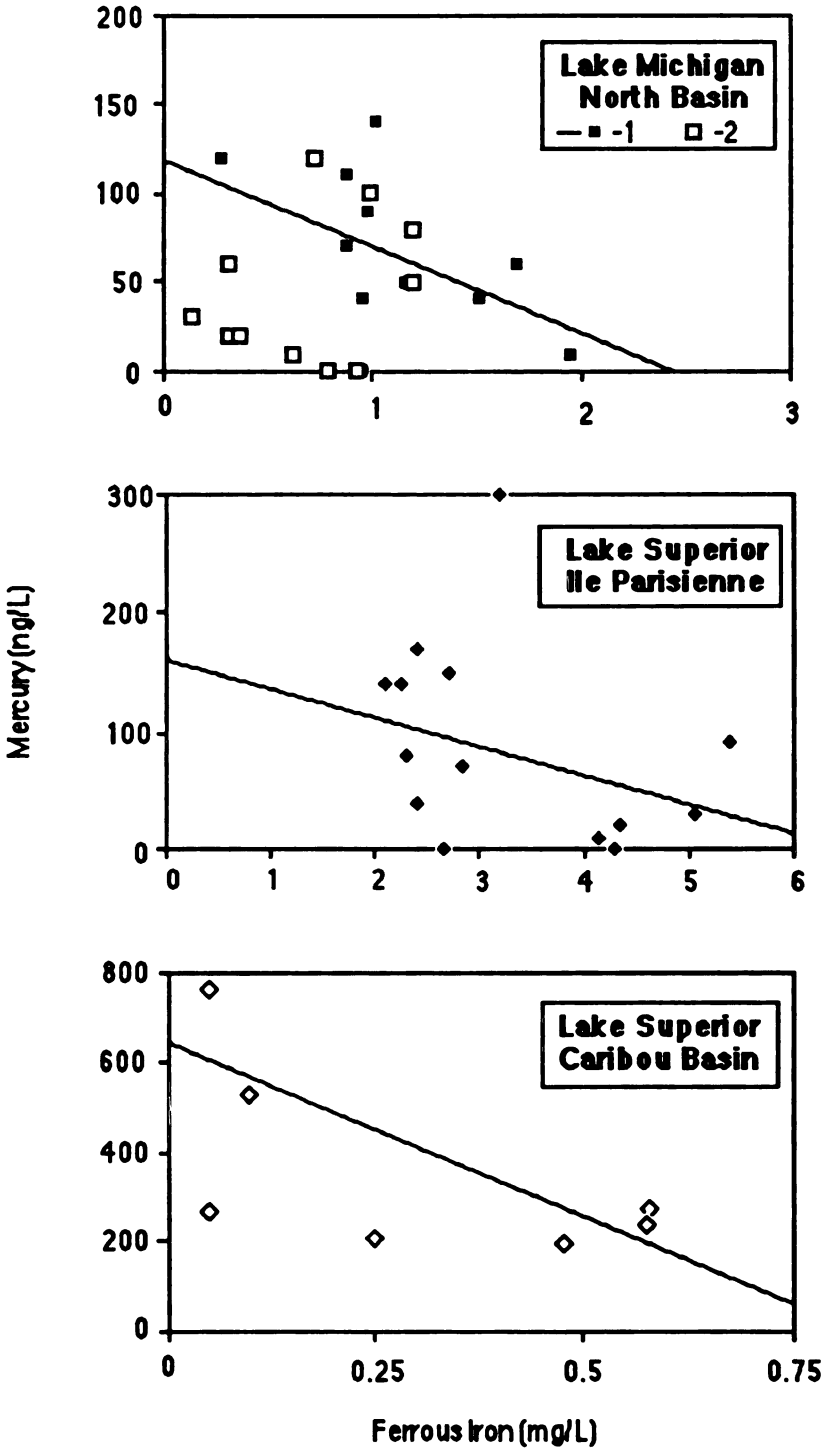


Figure 26. Relationship between ferrous iron and dissolved mercury in porewater of reduced sediments, Great Lakes samples.

Table 2

Solubility product constants of some sulfide minerals at 25°C
(from Faure, 1991)

Mineral		pK_{sp}	Mineral		pK_{sp}
α-HgS	cinnabar	53.0	Cu_2S	chalcocite	48.5
Hg_2S		54.8	PbS	galena	17.5
$Fe_{.95}S$	pyrrhotite	17.4	CdS	greenockite	27.0
FeS	troilite	16.2	α - ZnS	sphalerite	24.7
Fe_2S_3	greigite	88.0	β - ZnS	wurtzite	22.5
FeS_2	pyrite	42.5	α - NiS		19.4
FeS_2	marcasite	41.8	γ - NiS		26.6

lead would not form instead of sulfides of the more abundant iron, and lead profiles would more closely resemble those of Fe(II). Solubilities of cadmium, zinc, and nickel sulfides are slightly lower than those of FeS minerals, with α - NiS being closest to FeS. These metals should be affected by sulfide in the same manner as mercury (i.e. inversely related to Fe). Mercury sulfide is more insoluble than any of these sulfides, so should be able to precipitate even though mercury concentrations in porewater may be much lower than those of other metals.

Lead in porewaters from the Laurentian Trough has been found to correspond to ferrous iron profiles (Gobeil and Silverberg, 1989), whereas cadmium shows an inverse relationship with iron: concentrations are high near the sediment surface, decrease to undetectable values below the redox zone, then increase again deep in the core (Figure 27; Gobeil et al., 1987; Gobeil and Silverberg, 1989). These data support the hypothesis that metal-sulfide formation affects trace metal concentrations in porewater.

An alternative explanation is that adsorption onto iron sulfide minerals is controlling the concentrations of mercury. Sulfide minerals are excellent scavengers of divalent cations of mercury, lead, zinc, and cadmium (Jean and Bancroft, 1986). Mercury adsorption onto FeS minerals may be controlling dissolved mercury in marine porewaters as well (Hyland et al.,

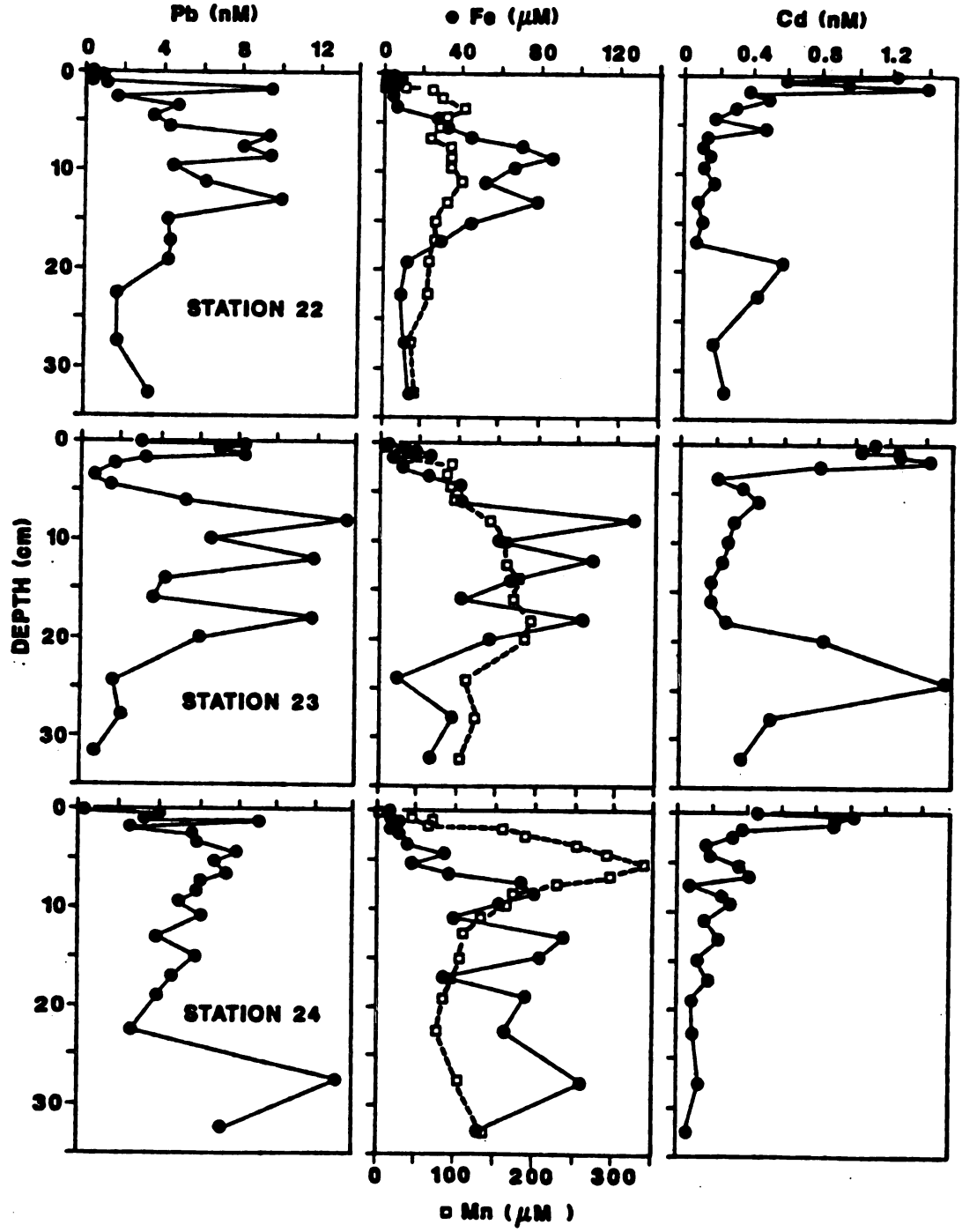


Figure 27. Dissolved Pb, Fe, Mn, and Cd in porewater from the Laurentian Trough (from Gobeil and Silverberg, 1989)

1990). It is more difficult to resolve the inverse relationship between dissolved iron and dissolved mercury, however, if this is what is controlling porewater mercury concentrations.

An alternative explanation for the mercury porewater profiles is that some volatile mercury species forms at this zone in the sediments. It is possible that mercury is reduced to elemental mercury, which is volatile and may escape from the sediments. It is also possible that dimethyl mercury could be formed, perhaps by microbial processes.

FLUXES TO THE SEDIMENT-WATER INTERFACE

As described above, there is evidence suggesting diffusive fluxes of arsenic and mercury may be occurring from porewaters into overlying waters in many of the sites investigated. Porewater gradients in arsenic at all sites but the Caribou Basin of Lake Superior, and mercury gradients in the lake sites indicate that fluxes out of the sediment are possible. Arsenic concentrations in Lake Superior water have been found to be highest in deep waters; this has been attributed to arsenic regeneration from bottom sediments (Rossmann, 1986). Total mercury in epilimnetic waters of Lake Superior has been reported to average 44 ng/L in the eastern portion of the lake (Rossmann, 1986). These values are much lower than uppermost porewater samples for Lake Superior, indicating that a flux of mercury from sediments might be possible.

Rates of organic matter degradation have been found to increase with increasing sediment deposition rates (Johnson et al., 1982). This results in increased fluxes of nutrients to the water column (Johnson et al., 1982) and should result in more rapid cycling of diagenetically-cycled elements. Rates of bioturbation have also been related to rates of organic matter decomposition and general diagenetic recycling (Gratton et al., 1990). Deeper water should allow more decomposition of organic matter before it reaches the sediments, reducing rates of degradation in the sediments (Klump et al., 1989). Thus greatest fluxes of mercury and arsenic from the sediments would be expected in shallower waters where sedimentation rates, organic matter accumulation rates, and bioturbation rates are the greatest.

In the following sections, the diffusive fluxes and sedimentation fluxes of arsenic and some of the consequences of these fluxes are estimated. These calculations are not performed for mercury

because of the manner in which mercury is recycled during early diagenesis. Since most of the mercury is released from sediments very near the sediment-water interface, and appears to be removed again almost immediately, fluxes calculated from porewater concentration gradients would not be meaningful.

Diffusive Fluxes

Vertical diffusive fluxes can be estimated using Fick's first law for one dimension:

$$J = \phi \cdot D_s \cdot (\partial C/\partial z)$$

where J = the diffusion flux, ϕ = the porosity, D_s is the diffusion coefficient, and $(\partial C/\partial z)$ is the concentration gradient (Berner, 1980). To calculate the flux for arsenic, several assumptions must be made: 1) viscosity and charge coupling effects are negligible; 2) arsenate and arsenite anions are the only arsenic species present, and they have identical diffusional properties; 3) there is no solid-phase consumption of dissolved arsenic near the sediment-water interface; and 4) arsenic concentration gradients are linear so that $\partial C/\partial z$ is equal to $\Delta As / \Delta z$ (Peterson and Carpenter, 1986). D_s is estimated from the diffusion coefficient for the arsenate anion at infinite dilution, D_o, estimated for 4°C from the data of Li and Gregory (1974) by assuming a linear change with temperature between 0°C and 25°C (Peterson and Carpenter, 1986), and using the relationship $D_s = D_o \cdot \phi^2$ (Lerman, 1977) to approximate the effects of sediment tortuosity.

Calculations of diffusive fluxes (Table 3) show that the flux of arsenic from the sediments at site 1 of Lake Michigan is more than twice that at site 2. The organic carbon content is approximately the same in surface sediments of these sites, the sedimentation rates are reportedly similar (Christensen and Chien, 1981), and bioturbation (based on porewater arsenic profiles) appears to be greater at site 2 than at site 1; thus the relative values of diffusive flux are the opposite of what might be expected. This phenomenon could be explained if the concentration gradient at site 2 has been reduced by mixing of porewaters with more dilute lake water due to bioturbation and bioirrigation. Sedimentation rates at Ile Parisienne are nearly four times those for Lake Michigan (see Table 4), which could account for the highest flux value in this location.

Although organic carbon content is low (probably due to dilution by terrestrial inorganic sediments), the sedimentation rate and bioturbation rates are high enough that much sediment-

Table 3

Parameters Used for Calculation of Diffusive Fluxes of Arsenic

Site	ø	D_s	Δz	ΔAs	J
LMNB-1	0.93	134	4.0	7.5×10^{-3}	0.234
LMNB-2	0.93	134	3.5	2.5×10^{-3}	0.089
LSIP	0.93	134	2.5	5.1×10^{-3}	0.254
GMMB	0.93	134	4.5	3.6×10^{-3}	0.100

ø = porosity; $D_s = D_o \cdot ø^2$, and $D_o = 155$ cm^2/yr at 4°C (estimated from data of Li and Gregory, 1974); Δz = depth (cm) to first concentration peak; ΔAs = difference in dissolved arsenic concentration (μg/cm^3) from the sediment surface to depth Δz; and J = diffusive flux (μg/cm^2 · yr).

bound arsenic is released within the upper few cm of the sediment column (Δz is nearest the sediment surface at this site), and much is able to diffuse up toward the sediment surface.

These calculated fluxes represent estimates only, since several of the assumptions are not strictly true. Although arsenate is generally predominant in oxidized waters, arsenite can also be present, as can methylated arsenic species (Crecelius, 1975; Andreae, 1979; Huang et al., 1982; Peterson and Carpenter, 1986; Brannon and Patrick 1987). There also appears to be significant incorporation of dissolved arsenic into solid phases in the near-surface sediments. Concentration gradients are probably not linear, but may appear so due to the 1 cm sampling interval. More closely spaced samples could reveal steeper concentration gradients. These calculations do not take into account the effects of bioturbation; however, Sweerts et al. (1991) found that the relationship between D_s and D_o did not change much with porosity and that effects of bioturbation on predictability of D_s were only significant in sediments with very high invertebrate populations. Several studies have found that measured fluxes of dissolved metals out of sediments do not agree with fluxes calculated from porewater profiles (e.g. Westerlund et al., 1986; Sundby et al., 1986;

Berelson et al., 1990). Fluxes of dissolved metals that are redox sensitive are strongly dependent on the flux of oxygen into the sediments across the sediment-water interface rather than on pore-water gradients alone (Sundby et al., 1986). Nonetheless, differences between fluxes calculated for the different sites may provide some useful information, and differences between upward diffusive fluxes of dissolved species and downward fluxes of sediment-bound metals can provide estimates of the proportion that is recycled from the sediment column. This is described below.

Sedimentation Fluxes

Fluxes of arsenic arriving at the sediment surface can be estimated as the product of the mass sedimentation rate and the arsenic concentration of the SBL, which represents freshly deposited material (McKee et al., 1989b):

$$F_s = R \cdot [As]_o$$

where F_s is the sedimentation flux, R is the mass sedimentation rate, and $[As]_o$ is the total extractable arsenic concentration in the SBL. Hermanson and Christensen (1991) have determined mass sedimentation rates for northern Lake Michigan as 1.33×10^{-2} g/cm$^2 \cdot$ yr for LMNB-1 (their site NLM-E) and 1.37×10^{-2} g/cm$^2 \cdot$ yr for LMNB-2 (their site NLM-B). Sedimentation rates for northern Lake Michigan have also been reported as 8.8×10^{-3} g/cm$^2 \cdot$ yr (Christensen and Chien, 1981). Rates have been estimated for Lake Superior Ile Parisienne Basin as 7.0×10^{-2} g/cm$^2 \cdot$ yr (Kemp et al., 1978) and 6.5×10^{-2} g/cm$^2 \cdot$ yr (Krezoski, 1989). Sedimentation rates are not available for the Gulf of Maine; ^{210}Pb studies have been unsuccessful due to extensive bioturbation in this area (Brower, 1984 cited in Hines et al., 1991).

Calculated sedimentation fluxes are shown in Table 4. Downward fluxes are similar for the two Lake Michigan sites. These values are higher than the sedimentation flux for arsenic in northern Lake Michigan (0.088 μg/cm$^2 \cdot$ yr) calculated by Christensen and Chien (1981). If their sedimentation rate (8.8 mg/cm$^2 \cdot$ yr) is used for these calculations, sedimentation fluxes of arsenic are closer to their result. A much higher flux is found for the Ile Parisienne site; this is largely a function of the sedimentation rate, as arsenic concentrations in the SBL are fairly similar for all three sites.

Table 4

Parameters Used for Calculation of Sedimentation Fluxes of Arsenic

Site	R	$[As]_o$	F_s	J	J/F_s
LMNB-1	1.33×10^{-2}	10.2	0.136	0.234	1.72
	8.8×10^{-3}	10.2	0.090	0.234	2.60
LMNB-2	1.37×10^{-2}	11.8	0.162	0.089	0.55
	8.8×10^{-3}	11.8	0.104	0.089	0.86
LSIP	7.0×10^{-2}	11.3	0.791	0.254	0.32
	6.5×10^{-2}	11.3	0.735	0.254	0.35

R = sedimentation rate in $g/cm^2 \cdot yr$; $[As]_o$ = total extractable arsenic in SBL sample (μg/g); F_s = sedimentation flux in $\mu g/cm^2 \cdot yr$; J is the diffusive flux from Table 3. J/F_s represents proportion recycled.

The proportion of sedimented arsenic that is recycled by early diagenetic processes can be estimated as the ratio of the upward diffusive flux, J, to the downward sedimentation flux, F_s (Table 4). These values appear to be quite high for Lake Michigan: 55 - 86 % for site 2, and over 100 % for site 1. This last value suggests that sedimentation fluxes are underestimated, or diffusion fluxes are over-estimated. At this site, the SBL contained less than half the total extractable arsenic of the uppermost core sample. It is possible that this SBL sample is not representative of typical arsenic sedimentation fluxes at this site. If the concentration from the top of the sediment core, 22.8 μg/g, is used in the calculations, F_s becomes 0.201 $\mu g/cm^2 \cdot yr$, and J/F_s becomes 1.16 for the lower sedimentation rate of Christensen and Chen (1981), still indicating greater than 100 % recycling, suggesting some error in the calculations. For the higher sedimentation rate of Hermanson and Christensen (1991), F_s becomes 0.304 $\mu g/cm^2 \cdot yr$ and J/F_s becomes 0.77. This represents a more reasonable number, but it is probable that the arsenic concentration in the core top sample does not represent freshly deposited material. This concentration more likely results from enrichment by adsorption of upward diffusing arsenic, as discussed below.

In all three of these sites, the concentration of arsenic in the SBL and the concentration in porewaters of reduced sediments are similar (~11 μg/g and ~8 μg/L, respectively), while the "background" concentration of arsenic in the sediment is higher in the Lake Michigan sites (~4 μg/g) than in the Ile Parisienne site (<2 μg/g). These facts suggest that recycling is more effective in the Ile Parisienne site, as would be expected from the higher sedimentation rate and shallower water depth. Yet the calculations show the least proportion of arsenic recycled at this site.

There are several potential sources of error in these calculations. Uncertainties associated with diffusive fluxes are described above. Sedimentation rates are commonly determined from ^{210}Pb dates, and this method was used by Christensen and Chien (1981) and by Hermanson and Christensen (1991). Lead is known to be mobilized during early diagenesis (McKee et al., 1989a,b) and recently, ^{210}Pb was found to be redistributed in lake sediments (Benoit and Hemond, 1991). The sedimentation rate for Ile Parisienne calculated by Kemp et al. (1978) was determined from the total mass of sediment deposited above the *Ambrosia* horizon (dated at 1890 in this region). This rate would be averaged over the entire time interval, but it is similar to the rate reported by Krezoski (1989), based on ^{210}Pb data. Despite the many uncertainties, these calculations suggest that significant proportions of arsenic reaching the sediments can be recycled by diagenetic processes.

Role of Fluxes in Enrichment of Surface Sediments

The influence of upward diffusive fluxes on enrichment of sediments near the sediment-water interface can be estimated by calculating the amount of arsenic contributed by the diffusive flux to the sediment arriving at the sediment-water interface. The only suitable site for this calculation is Lake Michigan North Basin site 1. This site has an upward diffusive flux at the sediment-water interface and a concentration of arsenic in the SBL lower than that in the uppermost sediment column. This allows the SBL to be used as an estimate of incoming arsenic content, and the uppermost sediment core sample to be used as the enriched layer resulting from adsorption of diffusing arsenic. The sedimentation rate is 8.8 $mg/cm^2 \cdot yr$, and the concentration of arsenic in the SBL sediment is 1.02 μg/g. Therefore, for one cm^2 of lake bottom for one year, 8.8 mg of sediment accumulates, which contains a total of 0.090 μg of arsenic. To this would be added

0.234 μg of arsenic from the diffusive flux over that square cm for 1 year. If all of this arsenic were sorbed by the 8.8 mg of sediment, the total mass of arsenic would become 0.324 μg, resulting in an arsenic concentration of 36.8 μg/g. This is higher than the observed concentration of 22.8 μg/g in the uppermost core sample, but indicates that enrichment of sediment by diffusive fluxes is certainly possible. The recycling of arsenic from the sediments, and adsorption of upward-diffusing arsenic by sediments near the sediment-water interface would tend to retain arsenic near the sediment surface.

IMPLICATIONS FOR BIOAVAILABILITY

One important consequence of the retention of deposited mercury and arsenic near the sediment surface is that these elements remain available for uptake by benthic organisms for longer periods of time than if they were buried and removed from the sediment-water interface. The activities of benthic organisms themselves have been found to promote recycling near the sediment surface (e.g. Cross et al., 1975; Aller, 1978), enhancing potential bioavailability.

Recent newspaper reports (e.g. Lange, 1991) cite the widespread nature of mercury contamination in North American lakes and their fish populations. Mercury finds its way into the food chain primarily as methyl mercury (Stokes and Wren, 1987). Methyl mercury is formed in sediments by bacterial action (Wood, 1974), and the rates of production of methyl mercury have been found to depend on the rate of supply of dissolved mercury to the microbes (Mikac et al., 1985; Olson and Cooper, 1974). This supply will depend on early diagenetic processes releasing mercury near the sediment-water interface. The fact that most of the mercury reaching the bottom sediments is retained near the surface enhances the chances for methylation and subsequent entry into the food chain. Gill and Fitzgerald (1988) find evidence that the scavenging of mercury by settling particles in the ocean is so effective that any mercury regenerated (for example, by organic matter decay in the benthic nepheloid layer) is quickly removed from solution, maintaining relatively low levels of dissolved mercury in the deep ocean. This would also tend to keep mercury near the sediment-water interface, enhancing its potential bioavailability to benthic organisms. These phenomena suggest that the problem of mercury contamination could persist

for a long time; as long as even small amounts of mercury are discharged to lakes (directly or via atmospheric transport), relatively high concentrations of mercury will remain available to benthic organisms.

Analysis of Diagenetic Variability

Differences in diagenetic parameters were observed on four scales: differences between the lakes and the ocean, differences between the two lakes, differences between depositional basins within a lake, and differences between sample sites within a single depositional basin. Observed differences range from distinct to subtle, and there were also numerous similarities among these sites. Factors contributing to diagenetic variability include differences in water depth, differences in rates of bioturbation, variations in the supply of reactive organic carbon, and variations in overall sedimentation rate, as well as differences in water chemistry and sediment mineralogy; these are discussed below.

Initial evidence for the variability among diagenetic environments was provided by porewater alkalinity profiles from the Great Lakes sites (Figure 5). Alkalinity of interstitial waters is largely controlled by early diagenetic reactions (Ben-Yaakov, 1973; Seuss, 1979; Kuivila and Murray, 1984; Anderson et al., 1986), so differences in alkalinity profiles should reflect differences in diagenetic processes. Although the relative contributions of individual diagenetic reactions to changes in the alkalinity of sediment interstitial waters in lacustrine environments are variable, changes in alkalinity and pH are generally attributable to the decomposition of organic matter, and indicate the extent of early diagenesis in lake sediments. Additional evidence for diagenetic conditions at the different sites is provided by data for ferrous iron in porewaters and by the organic carbon content of the sediments.

Diagenetic variability has been observed in the Laurentian Trough by Gobeil et al. (1987). They found differences in iron and manganese profiles between closely spaced cores collected at one site; these differences were regarded as relative stretching or compression of the profiles. This was attributed to variations in the depth distribution of diagenetic reactions caused by differences in rates of organic matter input, oxygen consumption, and distribution of benthic

organisms (Gobeil et al., 1987). The variability displayed among the five sites of this study is wider, but can be largely explained by these same variables. Differences in diagenetic processes result in variations in the behavior of mercury and arsenic undergoing early diagenesis. Variations in site characteristics and mercury and arsenic concentrations are summarized in Table 5.

GREAT LAKES VS. GULF OF MAINE

Although the dimensions and energy inputs of lakes and oceans are very different, processes controlling biogeochemical cycles of elements are similar, so the two systems can be compared (Santschi, 1988). The marine environment is chemically quite different from the freshwater environment. Particularly important differences in terms of early diagenesis are: the presence of higher concentrations of sulfate in seawater; the higher pH and alkalinity of seawater; and the higher ionic strength of seawater.

Higher concentrations of sulfate allow sulfate reduction to play a more important role in early diagenesis. In the Wilkinson Basin, which adjoins the Murray Basin in the Gulf of Maine (see Figure 2), sulfate reduction has been found to be the dominant biogeochemical process at depths below ~ 11 cm in short sediment cores (Hines et al., 1991). The Gulf of Maine could be characterized as a sulfidic environment, whereas the Great Lakes are non-sulfidic according to the classification of Berner (1981). The more active sulfate reduction influences porewater profiles, particularly for mercury, and helps to retain elements in the sediments.

Dissolved arsenic and mercury concentrations in porewaters are governed by different phenomena in the two settings. Below the redox zone, in the lakes, the profiles of porewater arsenic and ferrous iron are similar; the porewater profile of arsenic in the gulf is not as closely related to ferrous iron. Similar results were observed by Belzile (1988) in the Laurentian Trough, an estuarine setting: profiles of arsenic and iron in porewater from the seaward-most site resemble the profiles from the Gulf of Maine, while profiles from the most freshwater-influenced site show more similarity to the Great Lakes sites. This is due to the active removal of iron from porewaters in reduced sediment of the Gulf of Maine, most likely due to the formation of iron sulfide minerals. Although sulfides do appear to be forming in the Great Lakes sites, there is

Table 5

Summary of Site Characteristics That Influence Early Diagenesis

SITE	Water Depth	Sed. Rate	Redox depth	% OC SBL	% OC core top	As Max	As Bkg	As E.F.	% As recycled	Hg Max	Hg Bkg	Hg E.F.
LMNB-1	252	13.3	5	2.55	3.21	23	3.6	6.3	172	119	14	8.5
LMNB-2	275	13.7	10	3.22	3.17	12	3.5	3.3	55	113	12	9.4
LSIP	122	70	7	2.76	1.44	12	1.1	10	32	168	9	18.7
LSCB	330	2.5	19	3.96	3.29	4.9	1.2	4.1	--	92	16	5.8
GMMB	284	--	15	--	1.58	1.6	0.7	2.4	--	63	17	3.7

Water depth in meters. Sedimentation rates ($mg/cm^2 \cdot yr$) for Lake Michigan from Hermanson and Christensen (1991), for Lake Superior from Kemp et al. (1978). Redox depth = depth (cm) to ferrous iron peak. % OC = Weight percent organic carbon in sediment. Max = maximum concentration of total extractable arsenic (μg/g) or mercury (ng/g) in SBL or core top. Bkg = average concenration of total extractable arsenic (μg/g) or mercury (ng/g) in reduced sediments. E.F.= "Enrichment factor" = ratio between max and bkg concentrations (see Figure 28). % As recycled = J/F_s (upward diffusive flux / sedimentation flux of arsenic, from Table 4).

much more iron than sulfide, so iron concentrations are controlled by other mineral equilibria. For mercury, concentrations are very low everywhere in the Gulf of Maine porewaters, due to precipitation of sulfides. In the Lakes, dissolved mercury concentrations are higher in reduced sediments, again due to the much lower sulfide content.

The higher pH, alkalinity, and ionic strength influence the partitioning of arsenic among the hydromorphic phases of the sediment. In the lakes, the easily reducible, moderately reducible, and oxidizable fractions are the major sequesterers of arsenic; in the Gulf the exchangeable and weak-acid soluble phases contain most of the arsenic. The presence of carbonate minerals in the Gulf of Maine sediments, which persist in deep sediments due to the higher pH and alkalinity of these waters, may contribute to the greater amount of arsenic in the WAS fraction. Below the redox zone, the EX fraction of the Gulf sediments contains the most extractable arsenic; in the lakes, any arsenic in the EX fraction disappears in the reduced zone. This sorption of arsenic onto exchangeable sites in the marine setting is probably related to the "saturation" of other sorption sites by more abundant elements, as discussed in the section on diagenesis of arsenic, above. The higher ionic strength of the marine environment appears to affect both the partitioning of arsenic, and the total amount of arsenic that is sorbed to sediments. The higher arsenic porewater concentrations, and the lower ratio of maximum to background concentrations in sediments (Table 5) suggest that arsenic released by early diagenetic processes is not as readily taken up by other phases in the Gulf of Maine as it is in the Great Lakes.

Mercury partitioning among sediment phases is similar in both environments, and does not seem to be influenced by the same factors as arsenic. The biggest difference observed in sediment-bound mercury is that the maximum concentrations at the sediment-water interface are higher in the lakes, although the average concentration in reduced sediments is highest in the Gulf of Maine (Table 5). This results in a ratio of maximum to background mercury concentrations that is lowest in the Gulf of Maine. The same contrast in "enrichment factors" (ratio of maximum to background concentrations) is observed for arsenic; this is shown graphically in Figure 28.

There are several possible explanations for greater "enrichment factors" (Figure 28) observed in the freshwater sites than in the marine setting. As discussed earlier, concentrations of arsenic

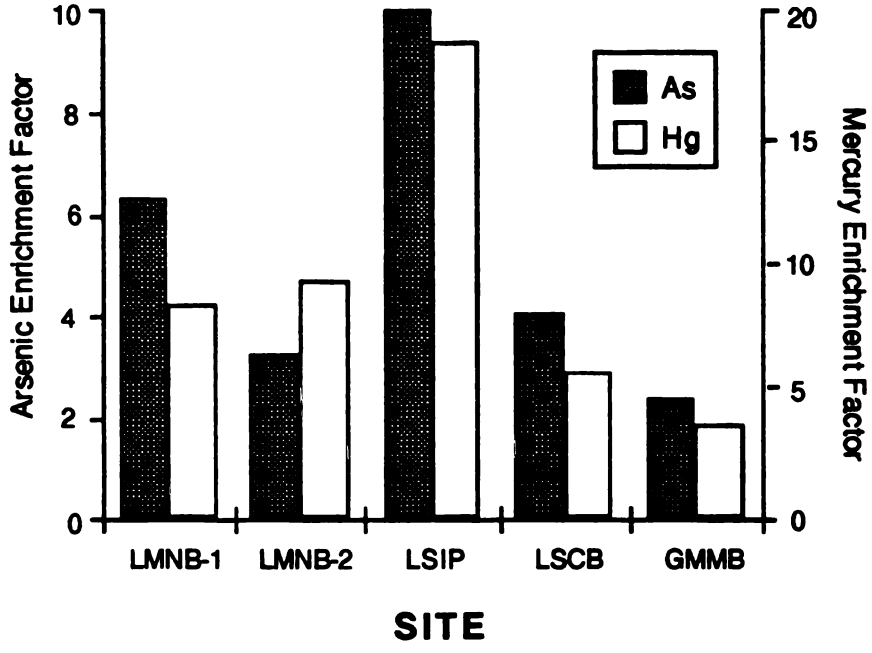


Figure 28. Enrichment factors for arsenic and mercury (from Table 5).

and mercury near the sediment-water interface are higher than in more deeply buried sediments due to several processes: higher concentrations in freshly deposited material, recycling within the upper oxidized sediment layers, and adsorption of dissolved arsenic and mercury diffusing up from deeper in the sediment column.

One possible explanation is that the Murray Basin is not a site of active sediment focusing; concentrations of arsenic and mercury are low at the sediment surface because fresh material with higher concentrations is not accumulating. The absence of a distinctive SBL layer at this site supports this erosion/non-deposition idea. Organic carbon concentrations are very low at the top of the core, also suggesting this is possible. It is conceivable that erosive action has removed SBL and upper layer of sediment, with its more reactive organic matter. The basins of the Gulf of Maine are known to be accumulating sediment, however (Spinrad, 1986), suggesting this is not the best explanation. The profiles of mercury in sediment also indicate that sediments are actively accumulating here. There is an enriched layer at the sediment surface, with high mercury concentrations in the base soluble and acid soluble phases, and in the sediment immediately below this, the oxidizable phase is a highly enriched in mercury. This is the same pattern as observed for the uppermost layers of sediment in the lakes, where distinct SBLs and higher concentrations of organic matter are present. If erosion was occurring or sediment had not been recently deposited, these characteristic surface layers would be removed as well.

The low concentrations of organic carbon at the sediment surface may be due to dilution by terrigenous organic material, as noted for nearshore basins of Lake Superior by Klump et al. (1989). Evidence that the suspended sediment in deep waters of the Gulf of Maine is dominated by silicates (Spencer and Sachs, 1970) suggests significant dilution of organic matter is possible. Hines et al. (1991) found evidence that organic matter deposition was lower in the Wilkinson Basin than in other areas of the Gulf of Maine. Mayer et al. (1988) found that sedimentary organic matter in basins of the Gulf with water depths exceeding 70 m was dominantly refractory material. They also find evidence that organic matter reaching the bottom in deep waters of the Gulf of Maine is present mainly as coatings on mineral grains, and is therefore more resistant to microbial breakdown (Mayer et al., 1988). These findings indicate that recent sediment is

accumulating, and a lack of freshly deposited sediment cannot be the cause of the lower "enrichment" of arsenic and mercury in Gulf of Maine surface sediments.

A second possibility is that changes in inputs of arsenic and mercury have varied among sites. Recent inputs of these elements worldwide have increased relative to historical background levels due to anthropogenic activities. If this increase was smaller in the Gulf than in the lakes, the resulting "enrichment" in more recent sediments would be smaller as well.

A third possible explanation for the lower degrees of enrichment in Gulf of Maine sediments is that mercury and arsenic are transferred more completely to the deeper, reduced sediments; they are recycled less effectively. This may be the case for mercury, which is removed from porewater by sulfide formation below the redox zone. This process appears to be so effective that very little dissolved mercury is available for diffusion up toward the surface. The fact that concentrations of mercury in reduced sediments are highest for the Gulf of Maine, even though concentrations in in surface sediments are lowest (Table 5), indicates that mercury is buried more efficiently in marine sediments than in the Lakes.

Arsenic is not affected in the same manner, however. Porewater arsenic concentrations are very high, producing a steep gradient, and potentially substantial diffusive fluxes, from the reduced zone toward the sediment surface. In the upper 50 cm of sediment, at least, there is enough available arsenic in Gulf porewaters that it is taken up by the exchangeable sites. "Background" extractable arsenic concentrations are also lowest in the Gulf of Maine; the average background concentration of total extractable arsenic is about 60% of that in Lake Superior and only about 20% of that in Lake Michigan (see Table 5). These facts suggest that arsenic may be buried more effectively in the lake sites than in the ocean. Arsenic that is transferred in to the reduced sediments does not seem to be precipitated as a sulfide (as discussed in the section on arsenic diagenesis, above) but it may be sorbed onto iron sulfide surfaces. Kornicker and Morse (1991) found that rates of sorption onto pyrite decreased with increasing ionic strength, but that rates of desorption were not affected by ionic strength. Both sorption and desorption reaction rates were found to increase with increasing pH. The higher pH and much higher ionic strength

of the marine environment would lead to less sorption onto pyrite, and faster desorption. This would reduce the metal retention capacity of these sediments relative to freshwater sediment.

A fourth possible explanation for the lower enrichment factors in the Gulf of Maine is that mercury and arsenic released by diagenetic processes within the sediments diffuse upward, but are not readsorbed and retained within the sediment column as efficiently as in the lakes. Instead, they are released to the overlying water column. The dearth of reactive organic matter in upper layers of sediment which is typical for deep waters of the Gulf of Maine (Mayer et al., 1988) would reduce the number of sorption sites available. This would certainly contribute to the lower enrichment of arsenic and mercury in surface sediments of the Gulf of Maine compared to the Great Lakes.

It appears most likely that some of the arsenic released from sediments in the Gulf of Maine by diagenetic processes is returned to the water column, which is why enrichments are lower than those seen in the Great Lakes. Not all of the arsenic is released, as there is significant uptake of arsenic by iron and manganese oxides in the oxidized layers of sediment; it is just that less of the recycled arsenic is retained in the sediment than is the case for the lakes. Since both maximum and background concentrations are lowest in the Gulf, it is also possible that less arsenic is being deposited here than in the Great Lakes.

For mercury, the lower enrichments appear to be caused by a combination of factors. Recycling within the surface layers is much less intense in the Gulf of Maine than in the Great Lakes, because of the lack of reactive organic matter to take up released mercury. There is also apparently a greater burial of mercury in the sediment column due to the uptake of dissolved mercury by the formation of sulfide minerals. Thus, although maximum concentrations of mercury are lowest at this site, indicating concentrations of mercury being deposited are lowest, the amount of mercury buried in deeper sediments is highest, indicated by the highest background values of sediment-bound mercury.

Although arsenic and mercury are affected unequally by differences between freshwater and marine sites, the net result is the same: lower enrichment in the Gulf of Maine. The consequences of this result are different for the two elements, however. Because arsenic is retained by marine

sediments less effectively, its residence time in the water column will be longer than in lakes, all other things being equal. The opposite is true for mercury, which is more effectively buried in marine sediments.

The low abundance of reactive organic matter at the sediment-water interface is largely responsible for the lower enrichment in both cases. This may be the factor which Gulf of Maine sediments have in common with Caribou Basin sediments. In some ways, the Caribou Basin of Lake Superior is more like the Gulf of Maine than like the other lake sites. This similarity is discussed further below.

VARIABILITY AMONG GREAT LAKES SITES

Lake Michigan vs. Lake Superior

Differences between Lake Michigan and Lake Superior that can influence early diagenesis include differences in pH and alkalinity of lake waters and porewaters (Figures 4 and 5), and the difference in carbonate mineral content of the sediments: Lake Michigan sediments contain carbonate minerals, while modern Lake Superior sediments do not (Lineback et al., 1979; Dell, 1972). Other factors influencing diagenesis vary as much or more between the two Lake Superior sites as between the two lakes, so are discussed later.

Although the profiles of mercury in sediments and porewaters of the Great Lakes sites vary, no consistent differences between the two lakes are evident. The "background" concentrations of sediment-bound mercury are quite similar in all four sites; perhaps this reflects dominantly atmospheric inputs of mercury which may have been relatively consistent throughout the region. According to Mudroch et al. (1988), the reported range of mercury concentrations in sediments of Lake Superior falls within the range reported for Lake Michigan sediments, also indicating no inter-lake differences. There are also no distinct trends observed in the partitioning of mercury among hydromorphic phases of sediments in the two lakes.

There are some distinct differences between the two lakes in terms of arsenic partitioning. Lake Michigan shows an overall higher concentration of arsenic in the sediments than Lake Superior. This most likely reflects higher inputs to Lake Michigan than to eastern Lake Superior.

There is more arsenic in the weak-acid soluble fraction of Lake Michigan sediments (Figure 8), which is probably related to the presence of carbonate minerals in Lake Michigan.

A larger proportion of the sediment-bound arsenic is in the oxidizable fraction in Lake Michigan; in Lake Superior sediments the oxidizable fraction contains little arsenic below the uppermost sediment layers (Figure 11). This may in part reflect the higher organic content of deeper sediments in Lake Michigan. Although the organic carbon content of Lake Superior surficial sediments is comparable to that of Lake Michigan, the organic carbon content at depth remains above 2 % in Lake Michigan, but drops below 2 % fairly quickly in Lake Superior sediments (Figure 6). Sediment-bound arsenic also shows a more distinct correlation with sediment organic carbon content in Lake Michigan (Figure 24a).

In both Lake Michigan sites, the organic carbon content of the SBL is not much higher than that of core-top sediments, whereas in both Lake Superior sites there is a significant decrease in organic carbon from the SBL to the top of the sediment column (Figure 6). The same pattern is observed for arsenic in the oxidizable fraction of these sediments (Figure 11). This indicates that more organic carbon decays at the sediment-water interface in Lake Superior, and most of the arsenic associated with organic matter is released. In contrast, less organic matter decays at the sediment-water interface of Lake Michigan, and more organic carbon, with more associated arsenic, is buried into deeper sediments.

Johnson et al. (1982) found that the decay rate *vs.* accumulation rate of organic carbon in Lake Superior was related to sedimentation rate. Similarly, Klump et al. (1989) found that the decomposition of labile organic matter in areas of Lake Superior with low sediment accumulation rates occurred largely in the water column and at the sediment-water interface. Yet Ile Parisienne has the highest sedimentation rate of all these sites and the Caribou Basin the lowest (the rate for LSIP is nearly 30 times the rate for LSCB; Table 5), so sedimentation rates cannot account for these observed differences between the two lakes. The different patterns displayed for organic carbon and between arsenic and organic carbon in the two lakes may be due to differences in the nature of the organic matter accumulating. Kemp and Johnston (1979) found the proportions of more reactive components of organic matter (amino acids, amino sugars, and carbohydrates)

varied among Lakes Ontario, Erie, and Huron. It is possible that Lakes Michigan and Superior accumulate different proportions of the various organic components as well, and that this accounts for the differences in organic carbon burial and in organic-associated arsenic between the two lakes.

The largest differences among all the lake samples are between Caribou Basin and the rest; in many respects Ile Parisienne more closely resembles Lake Michigan than it does the Caribou Basin. This is discussed further below.

Lake Superior: Ile Parisienne vs. Caribou Basin

The Ile Parisienne Basin and the Caribou Basin of Lake Superior are very different (see Table 5 and Figures 21-22). Ile Parisienne has a sedimentation rate nearly 30 times that of Caribou Basin. The redox zone in LSIP is much nearer the sediment surface than in LSCB. LSIP has higher concentrations of mercury and arsenic in surficial sediments, hence much higher enrichment factors than the Caribou Basin. LSIP is the shallowest site sampled and LSCB is the deepest. LSIP is quite near shore whereas LSCB is more distant.

Klump et al. (1989) found that the transition from nearshore to deep basins in Lake Superior was accompanied by a decrease in the fraction of readily-decomposable organic matter deposited on the lake bottom. They found that 40% of organic matter that was deposited in a nearshore shallow bay was recycled, whereas only 15% was recycled in a deep basin; this was attributed to an increase in the extent of remineralization within the water column. Thus differences in water depth can influence diagenesis by influencing the amount of labile organic matter that reaches the sediments and drives rapid early diagenesis. The nearshore bay with the highest proportion of organic matter recycled was also found to have the lowest surface organic carbon content, due to dilution by terrigenous inorganic matter (Klump et al., 1989). These trends are observed in the two Lake Superior sites.

The organic carbon content of LSIP sediments is lower than in LSCB; this indicates dilution by inorganic matter. The organic content of LSIP sediment drops off faster than it does in LSCB, suggesting rapid decomposition of the organic matter that accumulates. Early diagenetic recycling

also appears to be much more effective in the LSIP site, as indicated by the much higher "enrichment factors" for this site relative to all of the other sites.

Higher fluxes of metabolizable organic carbon to sediments have been found to result in increased rates of release of remineralized constituents to sediment porewaters so that porewater gradients steepen (Klump et al., 1989). This would be expected to affect mercury and arsenic associated with organic matter as well as nutrients; therefore, recycling and porewater gradients of these elements would be expected to be steeper in areas with high fluxes of reactive organic matter. This is a logical explanation for the observed differences between LSIP (with a high rate of organic carbon accumulation) and LSCB (with a low rate or organic carbon accumulation). Johnson et al. (1982) found a relationship between the decay rate of organic carbon and the total sedimentation rate in Lake Superior that was consistent with trends observed in marine pelagic sediments; this may be indicated also by the similarities between the Caribou Basin and the Gulf of Maine sediments.

The role of reactive organic matter at the sediment surface in recycling mercury in sediments can be observed in these sites. LSCB sediments with higher percent organic carbon, but lower total organic carbon accumulation rates has less recycling of mercury (Figure 28). Values of mercury in surface sediments are lowest of all the lake sites and values in reduced sediments are highest of all lake sites, resulting in the lowest enrichment factor of all the lake sites.

Davison (1985) found that the proximity of the redox boundary to the sediment-water interface greatly influenced rates of elemental recycling of iron and manganese. The redox boundary is much deeper in the Caribou Basin than in any of the other lake sites. It is also fairly deep in the Gulf of Maine. Depth of the redox boundary is determined by sedimentation rate, organic carbon accumulation rates, and oxygen diffusion rates (Davison, 1985). Organic matter reaching the bottom of Lake Superior was found to have a relatively uniform stoichiometry for the reactive component, indicating a similar source in different parts of the lake (Klump et al., 1989); this could account for the similarities in organic carbon behavior of these two sites relative to the Lake Michigan sites.

Lake Michigan North Basin: 2 sites

There are some definite differences between sediment cores taken in the two sites in the North Basin of Lake Michigan. Profiles of both dissolved arsenic and dissolved iron show multiple subsurface maxima; these may be caused by bioturbation. This seems to be an important difference between these two sites: site 1 has experienced little bioturbation while site 2 seems to be more extensively bioturbated. Hermanson and Christensen (1991) report evidence for sediment mixing in sites close to both LMNB-1 and LMNB-2. This supports the notion of patchy distributions of organisms and bioturbation in deep benthic environments.

Arsenic data show significant differences in enrichment patterns within near-surface sediments and in porewater profiles. There is greater total enrichment of extractable arsenic at the surface at site 1 than at the surface in site 2. Almost twice as much total extractable arsenic is found in the uppermost sample at site 1; this enrichment is observed in all of the fractions. There is about twice as much arsenic in the EX, WAS, and OX fractions, more than twice as much in the ER fraction, and slightly less than twice as much in the MR fraction at site 1 relative to site 2. The ER fraction actually shows a depletion in arsenic in near-surface sediments at site 2. The "background" concentration of arsenic in porewater is similar at both sites, approximately 7 μg/L. However, the near-surface gradient of porewater arsenic is much steeper at site 1; values reach a maximum of nearly 10 μg/L within 5 cm at site 1, then stabilize with a slight decline in arsenic at increasing depths. At site 2, concentrations increase steadily to a depth of about 35 cm, then stabilize. This suggests a more significant flux of arsenic from the sediment at site 1 than at site 2, the opposite of what would be expected due to bioturbation.

Lake Superior Caribou Basin: cores collected by submersible

During the final submersible dive in the Caribou Basin of Lake Superior (1988), it was noticed that in some areas the reddish-colored redox layer (enriched in iron oxides) was visible at the sediment surface, whereas in other nearby areas it was not. Several shore "punch" cores were collected along an east-to-west transect across the basin to examine the extent of variability in depth to the redox layer. Generalized descriptions of these cores, taken within 100 m of one another, are shown in Figure 29. In the eastern-most core (LD-2) two redox layers are evident at

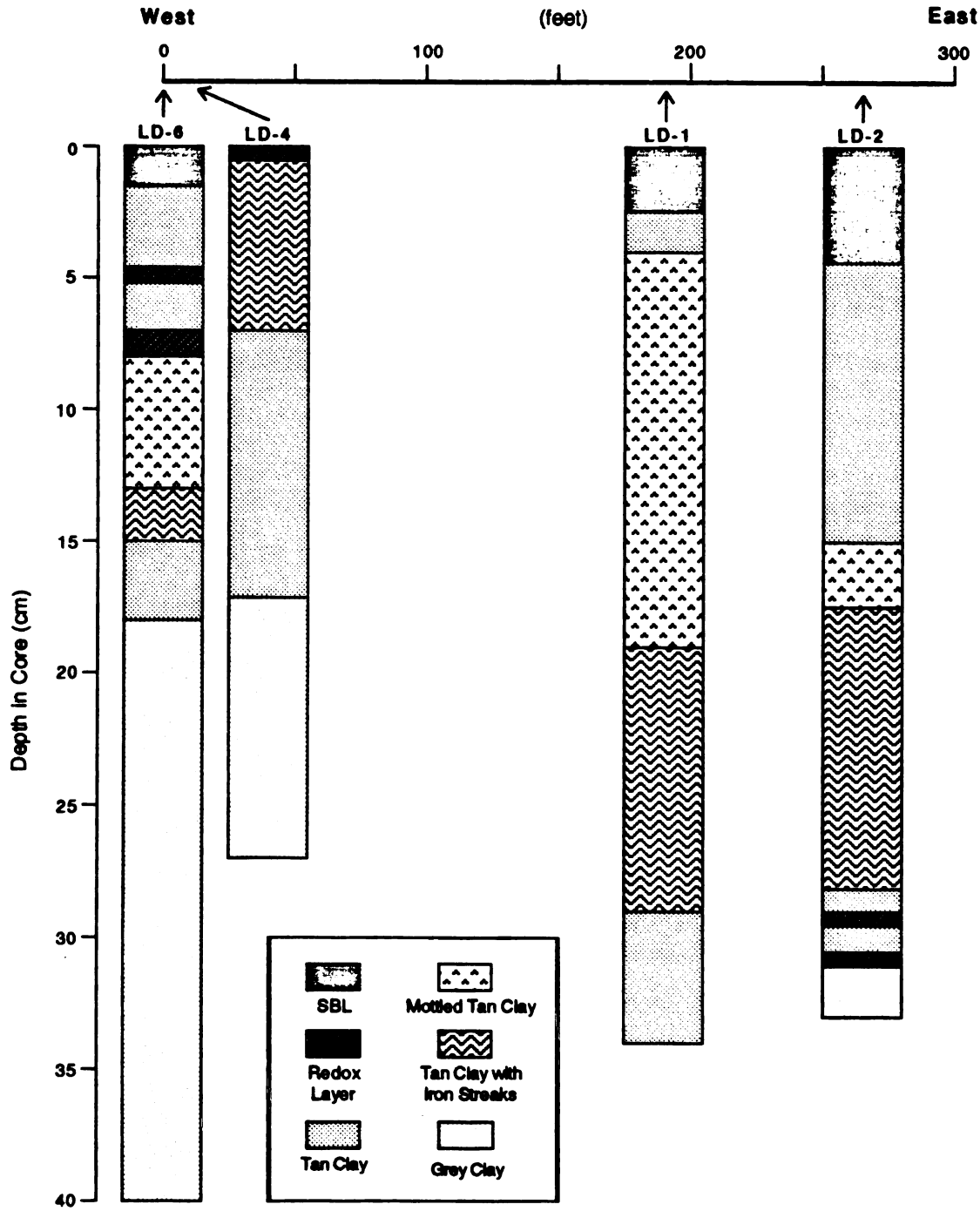


Figure 29. Cores collected by submersible from Lake Superior Caribou Basin.

a depth of about 30 cm. In the western-most (LD-6), two redox layers are present between 5 and 10 cm depth. In core LD-1 no redox layer is observed; this core is 35 cm long. In LD-4, only about 3 m east of LD-6, a thin redox layer is present at the sediment surface. The extent of the variability observed was surprising. The variations may be due to erosion by strong winter currents, such as those observed in other deep areas of Lake Superior by Flood (1989).

These cores suggest that the sediments and diagenetic processes in deep basins of lakes are not necessarily homogeneous, even across small areas. Therefore, conclusions about sediments and diagenetic processes based on one core may not be representative of the basin.

POTENTIAL FOR SEASONAL VARIATIONS

Seasonal variability in diagenetic parameters has been observed in nearshore marine environments, where it related to temperature-dependent rates of microbially mediated organic matter oxidation (Klump and Martens, 1989) or to temperature-related variations in the intensity of bioturbation (Martin and Sayles, 1987). In these areas temperature fluctuations can exceed 20°C annually. Bottom water temperatures in deep basins of Lakes Michigan and Superior are fairly constant, so such factors are unlikely to be important in these sites. Seasonal variations in inputs of sediment, organic matter, and metals, and in lake circulation patterns may be expected, however (e.g. Pocklington and Tan, 1987).

Annual ice-out and overturn events in Lake Superior waters have been found to have a substantial impact on particle transport and the dynamics of particles, organic matter, and associated hydrophobic organic contaminants (Baker and Eisenreich, 1989). They noted pulses of inorganic particles input following spring ice-out, which were concentrated in shallow near-shore areas. This could contribute to the high sedimentation rate and low organic carbon content of sediments of Ile Parisienne Basin. Baker and Eisenreich (1989) also found that settling of particles was enhanced during summer stratification due to coagulation and fecal pellet production, and that resuspension of benthic material was potentially great during fall overturn. Evidence for the presence of strong currents in Lake Superior during the winter has been found (Flood, 1989).

These processes would be expected to affect arsenic and mercury, and other metals as well. Sedimentation fluxes of metals would be greatest during summer months, and during fall and winter when the lakes are isothermal and currents may be active sediment-bound contaminants can be resuspended from the lake bottoms and reintroduced to column waters, potentially increasing residence times and bioavailability. Johnson (1991) found seasonal variations in dissolved metal concentrations in Georgian Bay, Lake Huron which were related to higher river inputs during spring. Similar seasonal variations might also be expected in the Gulf of Maine, but little seasonal variation in the distribution of suspended inorganic particles has been observed (Spencer and Sachs, 1970).

V. SUMMARY AND CONCLUSIONS

Role of Diagenesis in Geochemical Cycling

Early diagenesis exerts considerable influence on the geochemical cycles of arsenic and mercury in aquatic systems. Processes operating above the redox zone are important in determining potential bioavailability and recycling elements to the water column, whereas processes operating below the redox zone are important in fixing metals in the sediments, transferring them to the next reservoir and creating the historical sedimentary record.

Arsenic and mercury display several similarities as they undergo early diagenesis. They are both present in higher concentrations in upper layers of the sediment. They are both released from the sediment by aerobic degradation of organic matter. They are both strongly influenced by iron redox cycles. And both elements are subject to transfer between solid phases above and below redox zone; this involves transport via porewater along concentration gradients.

The presence of higher concentrations in upper layers of sediment indicate that much of what is buried in the sediment remains near the sediment surface or returns to the sediment surface. This has profound consequences for the bioavailability of these elements. As long at they remain near the sediment-water interface, they are potentially bioavailable. Bioturbation and bioirrigation have been found to enhance diagenetic fluxes (Belzile, 1988); thus elements can be made most available in areas where there are more organisms to ingest them. Mercury is very effectively retained near the sediment-water interface by reactions with labile organic matter; this results in enrichments of mercury in surface sediments relative to deeper sediments that are approximately twice as great as enrichments of arsenic. The total enrichment of both arsenic and mercury in surface sediments relative to deeper sediments appears to depend most on the nature of the organic

matter accumulating at the sediment surface. Rapid accumulation of labile (reactive) organic matter promotes strong enrichment.

The dissolution of iron oxides and the changes in redox conditions associated with this cycle are major influences on both arsenic and mercury (as well as many other trace elements). Profiles of sediment-bound arsenic and mercury show a minimum in concentration coincident with the base of redox zone. This is present to some degree in all phases at all sites and indicates that much of the sediment-bound metal reaching the redox zone is removed from sediments and transferred to the porewater. Some of this moves back up into the oxidized zone via diffusion, some is transferred into the reduced zone.

Below the redox zone, arsenic and mercury continue to be released from the sediments due to the continuing decay of organic matter (which is predominant for mercury) and the continuing dissolution of iron and manganese oxides (which is predominant for arsenic). In the marine environment, iron oxides can be reduced by reaction with sulfide to form iron sulfide minerals, or can be reduced microbially to produce dissolved Fe(II). Other metals can be adsorbed onto or or coprecipitated with the forming iron sulfides (which mercury seems to do), or can be released to solution due to the reduction of the iron oxide (which As seems to do). The presence of sulfide in reduced sediments promotes burial of mercury, but not of arsenic.

Conclusions

The goal of this project was to identify the geochemical processes operating in the sediments of the sites investigated, and to determine how these processes influence the cycling of mercury and arsenic. Several processes were identified: the aerobic decay of organic matter (which releases sorbed mercury and arsenic), the sorption of mercury and arsenic onto fresh organic matter at the sediment-water interface (which contributes to enrichment of surface sediments), the reductive dissolution of iron and manganese oxides (which releases arsenic and mercury at the redox zone, allowing them to diffuse upward toward the sediment surface or to be transferred to

other solid phases within the sediment column), and the formation of sulfide minerals (which can permanently fix mercury and arsenic in the sediment column) are the most important.

These processes are not new; their importance in early diagenesis and elemental cycling is well documented. The identification of specific influences of individual processes (particularly for mercury), and the recognition of the roles played by variations in diagenetic environments are new. These results provide some meaningful insights into the role of early diagenesis in the geochemical cycling of arsenic and mercury in aquatic environments.

APPENDICES

APPENDIX 1

METHODS

Sampling Procedures

CLEAN PROCEDURES

Water: Deionized water (mixed resin) was further purified by distillation in a Corning model AG-11 still. The distilled-deionized water (DDW) was stored in acid-cleaned polyethylene carboys until use. DDW was used in all cleaning, processing, and analysis steps.

Sample containers: Bottles, centrifuge tubes, and syringes were cleaned before use by soaking in 10% HCl (analytical reagent grade) in a water bath maintained at 60°C for 12-24 hours, rinsing 4 times in DDW, soaking in DDW for 24 hours, then rinsing again in DDW and allowing to dry in a clean hood. Containers were then capped and sealed in plastic bags for transportation to sampling sites. Gloves were worn at all times while handling sample containers.

Filters: 0.4 μm pore diameter Nucleopore polycarbonate membrane filters used for filtration of water samples were cleaned by soaking in 10% HCl at room temperature for 24 hours, then rinsed 4 times in DDW, soaked in DDW for 24 hours, rinsed again in DDW, then stored in DDW in acid-cleaned polyethylene containers until use. Filters were handled with acid-cleaned plastic forceps.

Sample processing equipment: All other equipment (spatulas, scoops, etc.) used in sample processing was cleaned by soaking in 10% HCl at room temperature for $\geq$ 12 hours and rinsing 4 times in DDW. Acid-cleaned equipment was stored in plastic bags.

CORE SAMPLES

All of the cores used for analyses were gravity cores, retrieved in 7.5 cm diameter butyrate core liners using a Benthos gravity corer deployed from the R/V *Seward Johnson*. Cores were capped with plastic caps, stored upright in a cold room at 4°C (approximate *in situ* temperature), and sectioned within 2-3 hours of collection. Sediment was extruded using a hydraulic extrusion device; this can be done in a nitrogen-filled glove bag as required (for mercury, arsenic, and iron samples). As each section was extruded, the outer portion of the sediment which had been in contact with the core tube was removed. Samples were 1 cm thick (near the top or the core) or greater (toward the base of the core) slices of sediment, which were immediately transferred to acid-cleaned 50 mL polyallomer centrifuge tubes.

SBL SAMPLES

Sediment boundary layer (SBL) samples were collected via the submersible *Johnson-Sea-Link II*. The mechanical arm was waved gently to suspend SBL sediment, which could then be pumped through Tygon tubing attached to the mechanical arm, through filter paper held on teflon-coated filter holders. At the surface, the filters were removed, and SBL sediments washed from the filter; this wash water was then removed by centrifugation in acid-cleaned 50 mL polyallomer centrifuge tubes. SBL samples were stored frozen.

SAMPLE PROCESSING

Sediment samples were centrifuged for 15 minutes at 15,000 rpm (using a chilled centrifuge head to keep the temperature near 4°C) to separate the porewaters from the sediment. In a nitrogen-filled glove bag, porewaters were removed from centrifuged samples by syringe, filtered through acid-cleaned 0.4 μm Nucleopore membrane filters, then acidified to pH < 2 with sub-boiling distilled Ultrex™ nitric acid, and stored in acid-cleaned polyethylene bottles. Water samples to be analyzed for mercury were also preserved with gold (as chloroauric acid, such that 10 ng Au was added to each mL of sample) and hermetically sealed (using a wrench), following the procedures of Moody et al. (1976). All water sample bottles were sealed in plastic bags and stored in a cold room maintained at 4°C. Following removal of porewater, sediment samples

were stored frozen in the centrifuge tubes, which were placed in plastic bags. Sediment and water samples were transported to the laboratory packed in coolers with dry ice.

pH and Alkalinity

pH and alkalinity were determined for one sediment core from each site, which was sectioned in air. pH was measured by inserting a spear-tip electrode (Orion Ross combination pH) into the wet sediment before removing each section. The electrode was calibrated with pH 7 and pH 4 standard solutions, and the calibration verified with pH 7 standard every few measurements. Recalibration was performed as necessary. Sections were processed as described above, and porewater separated for alkalinity analysis.

Alkalinity was measured in 3 mL aliquots of porewater samples, which were titrated with 0.017 N HNO_3 to an endpoint of 4.5 pH (Great Lakes) or 4.2 pH (Gulf of Maine). Appropriate endpoints were determined by examination of titration curves for several samples at each site. Titrations were performed using an apparatus designed for small-volume titrations (Figure A1-1). Acid was added using a Brinkmann digital micro-dispenser, in 25 µL increments (Lake Superior samples) or 50 µL (Lake Michigan and Gulf of Maine samples). Volume increments of acid added were calibrated by titration of a 0.01639 N Na_2CO_3 standard solution prior to each series of titrations. pH was measured with an Orion semi-micro gel-filled combination electrode (calibrated as described above). Results were converted to mg/L HCO_3^-.

Samples from a core in Lake Superior were tested to determine whether alkalinity measured in air was affected by iron oxidation (which can consume alkalinity). One sample was collected from the oxidized zone, one from the redox horizon, and one from the reduced zone, all under N_2. Alkalinity was determined immediately in a nitrogen-filled glove bag. Samples were then removed and exposed to air, and alkalinity measured again on a second aliquot of the sample. These same samples were then allowed to sit, open to the atmosphere, for 7 hours; alkalinity was measured once more, using a third aliquot. The results of this test are shown in Figure A1-2. Although there seems to be a slight reduction alkalinity with time, this may be within the error of

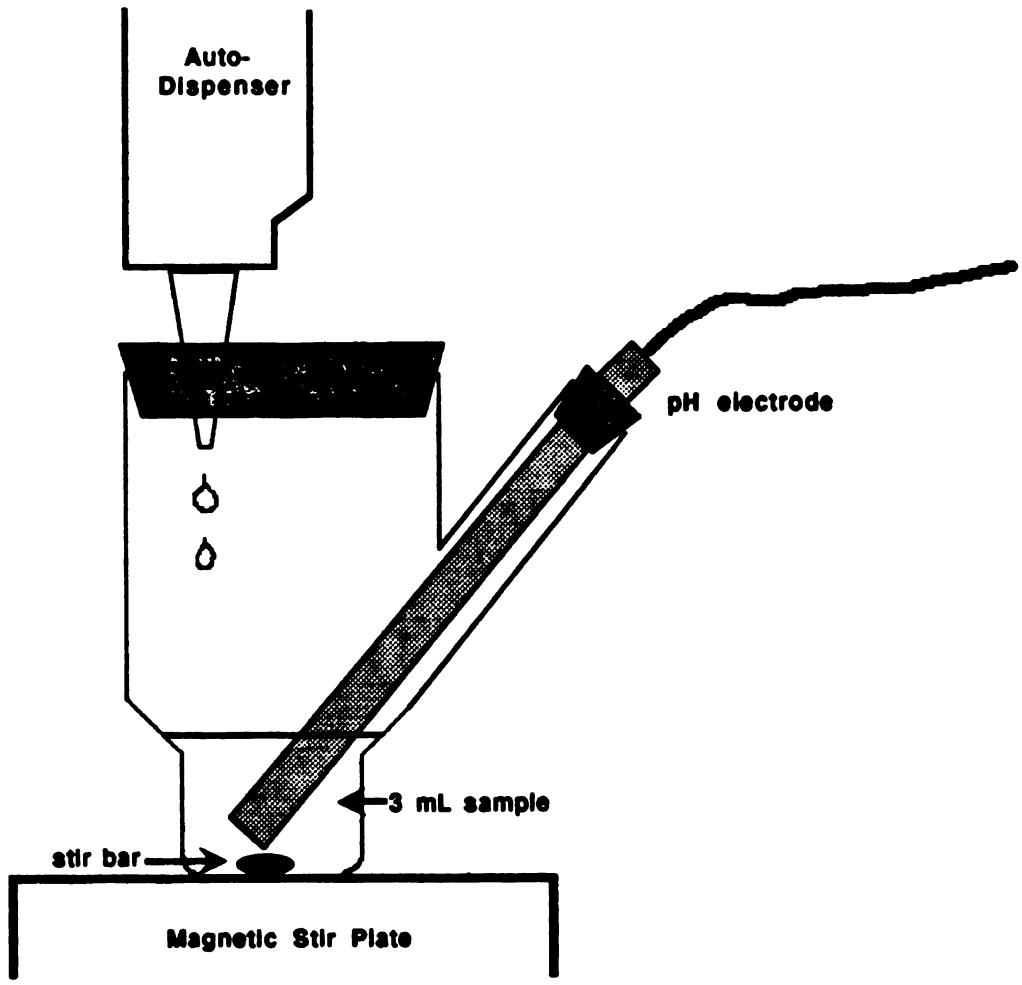


Figure A1-1. Alkalinity measurement apparatus for small-volume samples.

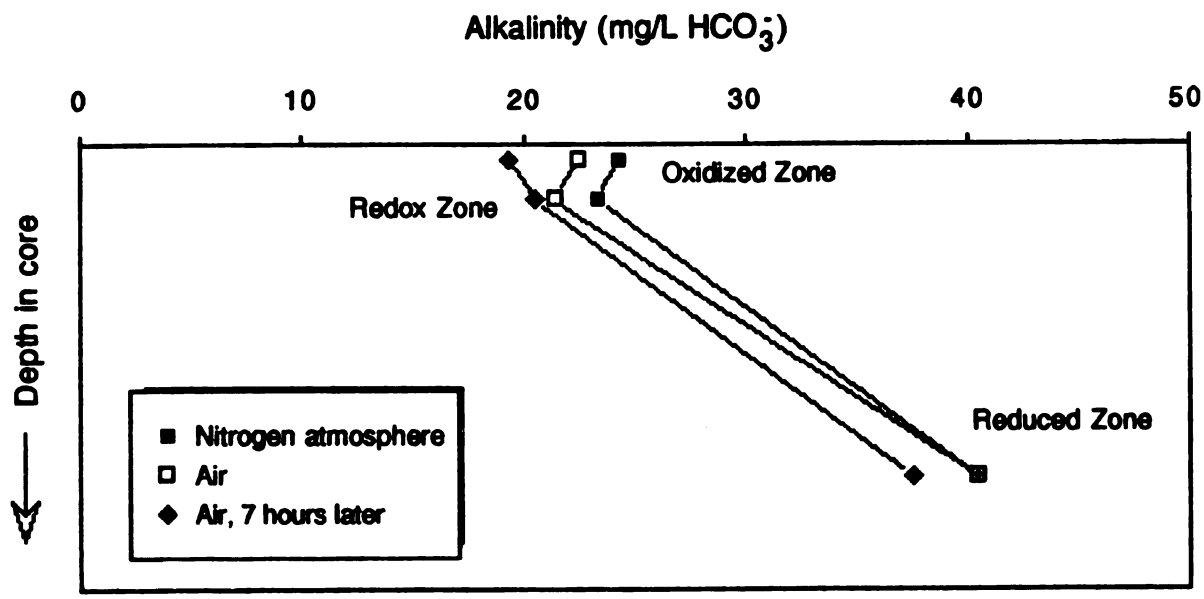


Figure A1-2. Results of alkalinity measurement in air vs. nitrogen atmosphere test.

the method. The least amount of variation is seen in the sample from the reduced zone, where effects of iron oxidation would be seen. In this sample, there is no difference between alkalinity measured in N_2 and that in air soon afterward. This suggests that the effects of iron oxidation are insignificant at porewater iron levels encountered, and alkalinities determined in air are valid.

Sequential Chemical Extractions

ARSENIC

Arsenic was extracted from sediment samples following the procedures developed by McKee et al. (1989) from the methods of Gephart (1982), Gupta and Chen (1975), and Tessier et al. (1979). Steady-state analysis was performed to verify that these procedures and reaction times were suitable for arsenic (see Figure A1-3). All processing steps that involved opening sample containers were done in an inert atmosphere (N_2 bag), until the final oxidizing step. Following each extraction step, leachate was separated form sediment by centrifuging at 15,000 rpm for 20 min. Between extractions, the sediment was washed by adding 10 mL of distilled deionized water (DDW). This was mixed into the sediment with a vortex mixer, then samples were centrifuged to separate the water, which was removed by pipetting. Sediment samples were then treated with the subsequent extraction procedure, either immediately or following overnight storage in a refrigerator.

Samples were thawed in a refrigerator for 3-7 days. In a N_2-filled glove bag, sample tubes were opened and a portion transferred to acid-cleaned, pre-weighed labelled centrifuge tubes. An additional portion was transferred to small plastic bottle for determination of the dry/wet weight ratio. Centrifuge tubes containing sediment subsamples for extractions were then re-weighed to determine the weight of the wet sediment; this was later converted to dry weight equivalent using the dry/wet weight ratios.

1. Exchangeable fraction (EX) 10 mL of 1.0 M magnesium chloride (at 7 pH) were added to each sample. Sample tubes were placed on a wrist-action shaker for 1 hour, then centrifuged. Leachate was transferred into acid-cleaned plastic bottles, and sediment was rinsed.

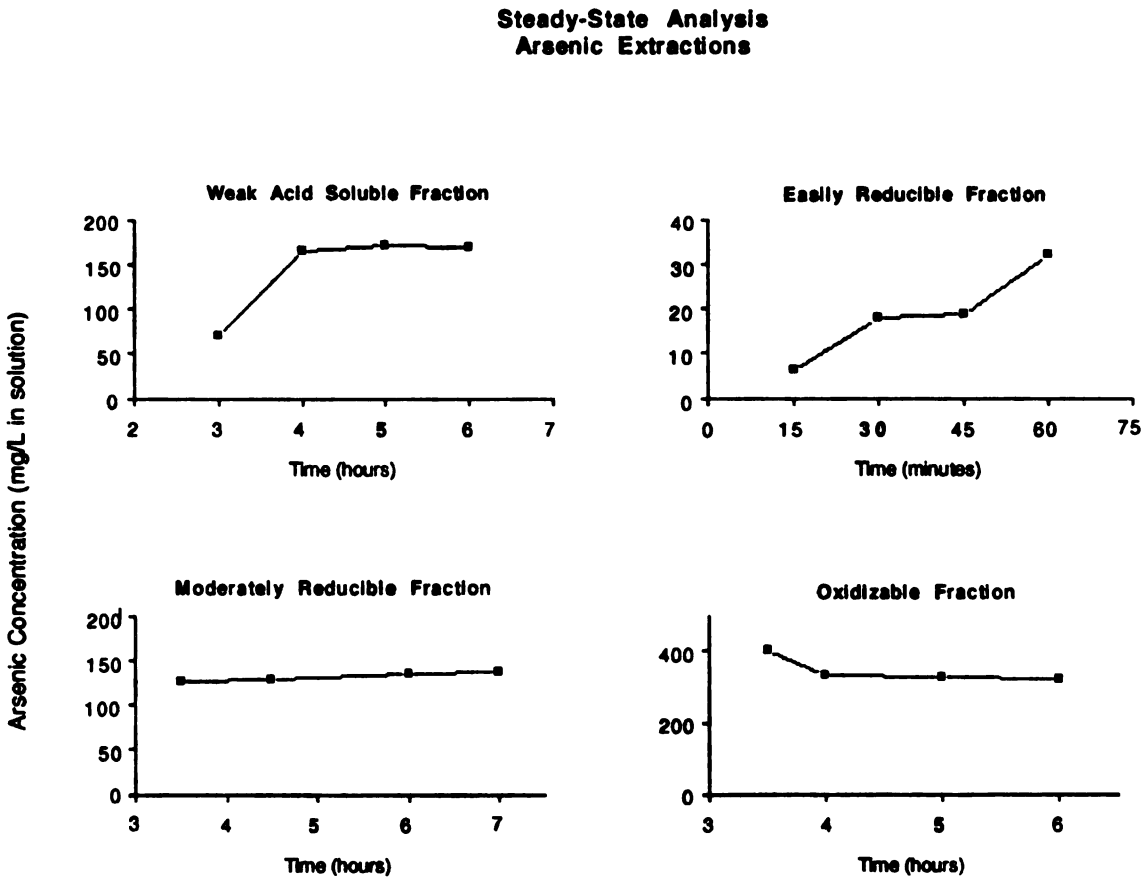


Figure A1-3. Results of steady-state analysis for arsenic extractions.

2. Weak-acid soluble fraction (WAS) 10 mL of 1.0 M sodium acetate (pH adjusted to 5.0 with acetic acid) was added to each sample. Tubes were placed on the shaker for 5 hours, then centrifuged. Leachate was transferred into acid-cleaned plastic bottles and sediment was rinsed.

3. Easily reducible fraction (ER) 25 mL of 0.10 M $NH_2OH{\cdot}HCL$ in 0.010 M HNO_3 was added to each sample, which was placed on the shaker for 30 min, then centrifuged. Leachate was transferred into acid-cleaned plastic bottles and sediment was rinsed.

4. Moderately reducible fraction (MR): 20 mL of 0.040 M hydroxylamine hydrochloride in 25% (v/v) acetic acid was added to each sample. Samples were placed in a water bath maintained at 90°C for 5 hours. Samples were agitated approximately every 30 min. Samples were centrifuged, leachate was transferred into acid-cleaned plastic bottles, and sediment was rinsed.

5. Oxidizable fraction (OX): 3 mL of 0.020 M HNO_3 was added to each sample, then a total of 8 mL of 30% H_2O_2 (with pH adjusted to 2 using HNO_3) was added. The peroxide was added in 500 µL aliquots to prevent bubbling-over of samples. Samples were placed in a water bath maintained at 85°C for 5 hours and were agitated approximately every 30 min. During this step, samples were exposed to the atmosphere since bottle caps had to be left unscrewed during heating. After 5 hours, samples were placed on the shaker to cool, then 5 mL of 3.2 M ammonium acetate was added to each sample, and shaking continued for 1 hour. Leachates were then pipetted into 25 mL Class A volumetric flasks and diluted to 25 mL with DDW. Leachates were then transferred to acid-cleaned plastic bottles for storage. Sediment was washed.

MERCURY

Mercury was extracted from sediment samples following the sequential chemical extraction procedures developed by Strunk (1991). All processing steps that involved opening sample containers was done in an inert atmosphere (N_2 bag). Following each extraction step, leachate was separated from sediment by centrifuging at 15,000 rpm for 20 minutes. Between extractions, the sediment was washed by adding 10 mL of distilled deionized water (DDW). This was mixed into the sediment with a vortex mixer, then samples were centrifuged to separate the water, which was removed by pipetting. Sediment samples were then treated with the subsequent extraction procedure, either immediately or following overnight storage in a refrigerator.

Frozen samples were thawed in a refrigerator for 3-4 days. In a N_2-filled glove bag, sample tubes were opened and a portion transferred to acid-cleaned pre-weighed labelled centrifuge tubes. An additional portion was transferred to small plastic bottle for determination of the dry/wet weight ratio. Centrifuge tubes containing sediment subsamples for extractions were then re-weighed to determine the weight of the wet sediment; this was later converted to dry weight equivalent using the dry/wet weight ratios.

1. Exchangeable fraction (EX): 10 mL of 10% (w/v) KCl was added to each sample and samples were placed on a wrist-action shaker for 1 hour. Samples were then centrifuged. Leachate was transferred into acid-cleaned plastic sample containers and analyzed immediately (as described below). Sediment was rinsed as described above.

2. Base Soluble fraction (BS): 15 mL of 0.10 N NaOH was added to each sample. Samples were placed on the shaker for 30 hours, then centrifuged. Leachate was transferred into acid-cleaned plastic sample containers and analyzed immediately. Sediment was rinsed.

3. Acid Soluble fraction (AS): 10 mL of 1.0 N HCl was added to each sample. Samples were placed on the shaker for 6 hours, then centrifuged. Leachate was transferred into acid-cleaned plastic sample containers and analyzed immediately. Sediment was rinsed.

4. Oxidizable fraction (OX): 2 mL of 0.020 M HNO_3 was added to each sample, then a total of 7 mL of 30% H_2O_2 (with pH adjusted to 2 using HNO_3) was added. The peroxide was added in 1 mL aliquots to prevent bubbling-over of samples. Samples were placed in a water bath maintained at 50°C for 5 hours and were agitated approximately every 30 min. During this step, samples were exposed to air since bottle caps had to be left unscrewed during heating. After 5 hours, samples were placed on the shaker to cool, then 4 mL of 2.0 M ammonium chloride in 20% HNO_3 was added to each sample, and shaking continued for 1 hour. Leachates were then pipetted into 25 mL Class A volumetric flasks and diluted to 25 mL with DDW. Leachates were then transferred to acid-cleaned plastic sample containers and analyzed. Sediment was washed.

Chemical Analysis

ARSENIC

Arsenic was analyzed in leachates and porewaters by graphite furnace atomic absorption using stabilized temperature platform furnace (STPF) conditions. This involves use of pyrolitic-coated graphite tubes, L'vov platforms, a cooldown step in the furnace program prior to atomization of the sample, maximum-power atomization, internal gas stop during atomization, fast spectrometer electronics, peak area measurement, baseline offset correction, matrix modification, and Zeeman effect background correction (Beaty, 1988). Several studies have shown this set of conditions to provide superior results (e.g. Grobenski et al., 1984; Desaulniers et al., 1985; Letourneau et al., 1987). Calibrations were performed using blanks and standards prepared in extraction solutions for the leachates or in acidified DDW for porewaters. Each of these matrices required slightly different programs for optimum results; optimum conditions were determined prior to each set of analyses. Most of the leachate solutions required dilution with DDW prior to analysis; this was done automatically by the autosampler according to defined ratios. Sample volumes (or sample + diluent volumes) were 20 µL. Nickel nitrate was used as a matrix modifier and was added automatically by the autosampler (5 µL of 0.068 M $Ni(NO_3)_2$ solution, to give 0.02 mg Ni per 20 µL sample). Temperature programs and dilution factors are summarized on Table A1-1.

MERCURY

Mercury was analyzed in leachates by flow-injection / hydride-generation technique using the Perkin-Elmer *Zeeman-5100* atomic absorption (AA) spectrometer with *MHS / FIAS 200* system. This method utilizes flow injection technology to determine mercury concentrations in small-volume samples. Peristaltic pumps transport sample to a mixing manifold where it reacts with sodium borohydride. Mercury is reduced to elemental mercury vapor, which is transferred by argon gas to a heated quartz cell in the AA light path, where absorbance is read. This method uses less concentrated reagents than other hydride reduction methods, reducing potential contamination. The carrier solution was 1.0 % (v/v) HCl prepared using Optima™ HCl and

DDW. Reduction solution was 0.2 % (w/v) $NaBH_4$ prepared with Aldrich reagent-grade $NaBH_4$ in 0.05 % (w/v) NaOH and DDW. Samples were also acidified to 1 % HCl with Optima™ HCl.

Mercury in porewater samples was analyzed by FIAS-MHS with the addition of the Perkin-Elmer Amalgam System attachment which amalgamates mercury from samples onto a gold-platinum gauze, allowing lower concentrations of mercury to be detected. Mercury vapor generated in the mixing manifold is transferred to the gold in the Amalgam. Upon heating, mercury is released at once, whereupon it is carried by argon gas to the heated quartz cell in the AA light path, where absorbance is read. Conditions for analysis of mercury in waters and sediment leachates are summarized in Table A1-2.

Organic Carbon Determinations

The organic carbon content was measured in splits of the core samples used for chemical extraction for arsenic, using the modified Walkley-Black procedure of Gaudette et al. (1974). Samples were dried at 60°C, ground with a mortar and pestle, dried again, and 0.2 to 0.5 g was weighed out. The sample was oxidized with potassium dichromate (1.0 N) and sulfuric acid (concentrated) for 30 minutes. Phosphoric acid (85%) and sodium fluoride were added. The dichromate remaining after oxidation of the organic matter was titrated with ferrous ammonium sulfate (0.5 N), using diphenylamine as an indicator. The percent organic carbon in each sample was calculated as:

$$\% \text{ OC} = 10\ (1\text{-}T/S)\ [(1.0)\ (0.003)/W]\ 100$$

where 10 = the volume of $K_2Cr_2O_7$ added
T = the volume of $Fe(NH_4)_2(SO_4)_2$ required to titrate the sample
S = the volume of $Fe(NH_4)_2(SO_4)_2$ required to titrate the blank
1.0 = the normality of the $K_2Cr_2O_7$
.003 = the mass (g) of 1 meq of carbon
W = the mass of the sample, and
100 is to convert to percent.

Samples were run in batches of 6, with a blank prepared for each batch.

Table A1-1. Graphite furnace conditions for arsenic analyses.

Fraction:		Porewater	EX	WAS	ER	MR	OX
Dilution		none	1 to 3	1 to 1	none	1 to 1	1 to 1
Dry Step	Temp	120	130	130	130	130	130
	Ramp	1	1	1	1	1	1
	Time	60	85	70	90	75	75
Thermal Pretreatment	Temp	1400	900	1500	1500	900	1200
	Ramp	1	1	5	4	1	1
	Time	40	30	25	35	20	10
Cool Down	Temp	20	20	20	20	20	20
	Ramp	1	1	1	1	1	1
	Time	15	15	15	15	15	15
Atomization	Temp	2600	2500	2400	2300	2600	2500
	Ramp	0	0	0	0	0	0
	Time	5	5	5	5	5	5
Clean Out	Temp	2600	2600	2600	2600	2600	2600
	Ramp	1	1	1	1	1	1
	Time	5	5	7	7	5	5

Dilution indicates sample to diluent ratio; diluent is DDW
Temperatures in °C Ramp and hold Times in seconds
Sample (or sample + diluent) volume = 20 µL
NiNO3 matrix modifier added (0.02 mg Ni per 20 µL sample)

Table A1-2. FIAS-200 conditions for mercury analyses.

	Porewater	EX	BS	AS	OX
Method	amalgam	normal	amalgam	normal	normal
Dilution	-	-	1/10	-	-
Acid added	3% HCl	3% HCl	3% HCl*	-†	-†

* add acid immediately before analysis †solution sufficiently acidic

Amalgam Program

	time (sec)	speed (rpm) pump 1	speed (rpm) pump 2	valve position	other events
Steps:					
prefill	15	100	40	fill	-
fill	15	100	40	fill	air, argon
inject	25	0	120	inject	argon
flush	10	0	40	fill	argon
heat	15	0	40	fill	heat, read
cool	10	0	40	fill	air, argon
return	1	0	0	fill	-

Run using short reaction coil, and with glass fiber only in drying tube.
Cell temperature 100°C Sample volume 1000 µL

FIAS Program

	time (sec)	speed (rpm) pump 1	speed (rpm) pump 2	valve position	other events
Steps:					
prefill	20	100	120	fill	-
fill	15	100	120	fill	-
inject	20	0	120	inject	read
return	1	0	120	fill	-

Argon flow 50 mL/min Run using long reaction coil
Cell temperature 150°C Sample volume 500 µL

APPENDIX 2

SAMPLE DATA

Table A2-1 presents shipboard core descriptions. Cores are listed in order by core number, from 1988gc1 through 1989gc8. Locations and water depths are also given for each core. SBL sample locations and water depths appear at the end of the table.

Table A2-2 presents data for the sediment sub-samples used for the chemical extractions and those for determination of wet/dry weight ratios. Core and SBL sample data for arsenic analysis appear first, followed by core and SBL sample data for mercury analysis.

Table A2-1 Shipboard Core Descriptions

Core	Sample	Depth cm	Description
1988gc1		*pH, Alkalinity*	44° 46.19' N, 86° 43.37' W, depth = 242 m (792 ft)
	1	0 - 1	light brown flocculent sediment
	2	1 - 2	...same, turning slightly greyer
	3	2 - 3	dark grey, somewhat firmer
	4	3 - 4	dark grey with black streaks and light brown streaks
	5	4 - 5	black bands (1 mm thick top & bottom) in pale grey
	6	5 - 6	...same
	7	6 - 7	top 1/2 cm grey, bottom 1/2 cm black, odor sulfide?
	8	7 - 8	...same
	9	8 - 9	...same
	10	9 - 10	...same, distinctly banded, bottom very dark
	11	10 - 11	darker, 3 black bands with grey/brown between; drier
	12	11 - 13	sulfide odor, organic matter
		13 - 19	alternating dark grey/black and light grey bands
	13	19 - 21	light grey with one 3 mm black band
		21 - 31	top 5 cm banded then 5 cm grey clay
	14	31 - 33	banded dark/grey
		33 - 43	4 dark bands ~2 mm thick a few cm apart
	15	43 - 45	streaky < 1 mm black bands in light grey/tan mud
		45 - 55	top 4.5 cm tan, 2 cm banded, 3.5 cm tan
	16	55 - 57	light tan/grey with one ~1 mm thick black streak
		57 - 67	patchy rather than banded (black on tan)
	17	67 - 69	...same
		69 - 79	~2 cm dark, 4 cm tan, 1.5 cm dark, rest tan with streaks
	18	79 - 81	~1 cm thick black band at top, tan below, quite solid
		81 - 91	alternating black & tan layers ~2 cm thick; sulfide odor
	19	91 - 93	very firm with thin bands of black in tan
	20	93 - 96	mostly dark; seems fairly dry
1988gc2		*Mercury*	44° 46.19' N, 86° 43.37' W, depth = 242 m (792 ft)
	1	0 - 1	light greenish brown flocculent sediment
	2	1 - 2	same color, somewhat firmer
	3	2 - 3	...same
	4	3 - 4	somewhat greyer; worm (?)
	5	4 - 5	...same, firmer
	6	5 - 6	...same, with ~1 mm thick black band
	7	6 - 7	lighter ~2 mm with dark streaks; dry area at bottom
	8	7 - 8	seems more solid, but gets weeter again at bottom
	9	8 - 9	grey color, no dark streaks/layers
	10	9 - 10	same appearance, slightly firmer; wetter at bottom
	11	10 - 11	same color with small black streak; middle firmer
	12	11 - 12	...same. firmer at base

Table A2-1 Continued

Core	Sample	Depth (cm)	Description
1988gc2			
		12 - 14	grey with dark grey streaks
	13	14 - 16	top: darker grey streaks, base: lighter with black band
		16 - 24	top 3 cm dark grey, 3,5 cm tan/grey, 1.5 cm dark grey
	14	24 - 26	light with dark streaks; ~2 mm black layer in center
		26 - 34	alternating layers dark grey and light tan/grey w/ black
	15	34 - 36	tan/grey with black band at top, dark streaks at bottom
		36 - 44	alternating 2-3 cm layers tan/grey and dark grey/black
	16	44 - 46	light tan/grey
		46 - 54	...same, with some mottling, sand at botom
	17	54 - 56	light tan/grey firm clay w/ black streaks; pocket of sand
		56 - 64	very dry, firm layers dark gray; water oozes from cracks
	18	64 - 66	color slightly lighter, no dark streaks
		66 - 74	...same
	19	74 - 76	...same
	20	76 - 78	...same
1988gc3		*Arsenic*	44° 45.98' N, 86° 42.94' W, depth = 254 m (832 ft)
	1	0 - 1	Flocculant, dark brown, very soupy
	2	1 - 2.5	Soupy, tan becoming grey below
	3	2.5-3.5	Dark grey, drier
	4	3.5-4.5	Dark grey, moist (wetter than above)
	5	4.5-5.5	Dark grey becoming tan
	6	5.5-6.5	Tan & grey
	7	6.5-7.5	Tan & black layers, becoming drier
	8	7.5-8.5	Tan with many black streaks
	9	8.5-9.5	Tan with black streaks, 1-2 mm top black band
	10	9.5-10.5	Tan with black streaks
	11	10.5-11.5	Tan with black streaks, drier
	12	16.5-18.5	Homogeneous tan & grey, few black streaks, moist
	13	23.5-25.5	Tan & grey with few black streaks
	14	30.5-32.5	Tan & grey with black streaks
	15	37.5-39.5	Tan & grey with black streaks
	16	44.5-46.5	Tan & grey with black streaks, moist
	17	51.5-53.5	Tan & grey with black streaks
	18	58.5-60.5	Tan with dark streaks which are chunky
1988gc4		*Iron*	44° 45.98' N, 86° 42.94' W, depth = 254 m (832 ft)
	1	0 - 1	flocculent sediment with some overlying water
	2	1 - 2	fairly solid (for top of core)
	3	2 - 3	grey mud
	4	3 - 3.3	hard dry layer ~3 mm (not like redox), soupy below

Table A2-1 Continued

Core	Sample	Depth (cm)	Description
1988gc4			
	5	3.3 - 4.3	soupy clay
	6	4.3 - 5.3	...same
	7	5.3 - 6.3	tan with darker (organic?) layers
	8	6.3 - 7.3	...same
	9	7.3 - 8.8	...same
	10	8.8 - 10.1	...same
	11	10.1 - 11.1	...same, becoming firmer
	12	11.1 - 12.1	...same
		12.1 - 22	...same
	13	22 - 24	...same
		24 - 34	...same
	14	34 - 36	...same
		36 - 46	..same, with hair-like things
	15	46 - 48	thick black streaks
		48 - 74	
	16	74 - 76	quite cohesive clay, mostly tan, some darker clay
1988gc7	*pH & Alkalinity*		44° 28.42' N, 86° 45.07' W, depth = 275 m (900 ft)
	1	0 - 1	tan/grey goo with some overlying water
	2	1 - 2	tan soupy mud
	3	2 - 3	...same
	4	3 - 4	becoming grey
	5	4 - 5	dark grey, very dark at bottom
	6	5 - 6	dark grey becoming black
	7	6 - 7	thin layer of dark on top, mostly tan clay
	8	7 - 8	tan with black specks, thin streaks
	9	8 - 9	...same
	10	9 - 10	tan mud, still moist
	11	10 - 11	tan with a few grey streaks, becoming firmer
	12	11 - 12	...same
		12 - 17	...same
	13	17 - 19	...same
		19 - 24	...same
	14	24 - 26	...same
		26 - 30	...same
	15	30 - 32	...same
		32 - 36	...same
	16	36 - 38	...same
		38 - 42	...same
	17	42 - 44	...same
		44 - 48	same with darker streaks near bottom
	18	48 - 50	same with very faint dark streaks

Table A2-1 Continued

Core	Sample	Depth (cm)	Description
1988gc7			
		50 - 54	same with black layer at base
	19	54 - 56	alternating grey/tan bands
		56 - 60	alternating grey/black bands
	20	60 - 62	grey with diffuse black bands
		62 - 66	...same
	21	66 - 68	grey with few black bands
		68 - 72	grey with ~2 cm black band at ~70 cm
	22	72 - 74	...same
		74 - 78	several black bands ~0.5 cm thick
	23	78 - 80	...same
		80 - 84	...same
	24	84 - 86	...same, a little drier
		86 - 90	...same
	25	90 - 92	grey & tan with black streaks
		92 - 96	...same
	26	96 - 98	...same
1988gc9		*Mercury*	44° 28.42' N, 86° 45.07' W, depth = 275 m (900 ft)
	4	0 -1	Greenish-tan flocculant material with overlying water
	2	1 - 2	Same, becoming greyer at base
	3	2 - 3	Grey-tan, a little firmer (but still soupy)
	4	3 - 4	... same
	5	4 - 5	...same, but with dark grey/blak at bottom ~1/2 cm
	6	5 - 6	dark grey with discontinuous black streaks (~1 mm)
	7	6 - 7	... same
	8	7 - 8	... same, with a pebble; lighter grey/tan at bottom
	9	8 - 9	light grey/tan with dark grey streaks
	10	9 - 10	... same
	11	10 - 11	light grey/tan with small black, things (~.5 cm x 1 mm)
	12	11 - 12	... same, without black things
	13	12 - 14	light tan/grey with few fmall dark streaks
	14	18 - 20	light tan/grey with few small discontinuous black streaks
	15	24 - 26	light tan/grey with dark streaks
	16	30 - 32	... same, dark streaks rare
	17	36 - 38	... same
	18	42 - 44	... same
	19	48 - 50	... same, maybe more dark streaks
	20	54 - 56	... same, dark streaks rare
	21	60 - 62	... same
	22	66 - 68	light tan/grey with ~ 5 mm thick dark streaks
	23	72 - 74	alternating tan bands and dark/black
	24	78 - 80	... same, more dark than light

Table A2-1 Continued

Core	Sample	Depth (cm)	Description
1988gc10		*Iron*	44° 28.42' N, 86° 45.07' W, depth = 275 m (900 ft)
	1	0 - 1	
	2	1 - 2	
	3	2 - 3	
	4	3 - 4	
	5	4 - 5	
	6	5 - 7	
	7	7 - 9	
	8	9 - 11	See core 1988gc9 for description.
	9	11 - 13	
	10	13 - 15	
	11	15 - 17	
	12	27 - 29	
	13	39 - 41	
	14	51 - 53	
	15	63 - 65	
	16	75 - 77	
1988gc11		*Arsenic*	44° 28.42' N, 86° 45.07' W, depth = 275 m (900 ft)
	1	0 - 1	
	2	1 - 2	
	3	2 - 3	See core 1988gc9 for description.
	4	3 - 4	
	5	4 - 5	
	6	5 - 6	
	7	6 - 7	
	8	7 - 8	
	9	8 - 9	
	10	9 - 10	
	11	10 - 11	
	12	11 - 13	
	13	17 - 19	
	14	23 - 25	
	15	29 - 31	
	16	35 - 37	
	17	41 - 43	
	18	47 - 49	
	19	53 - 55	
	20	59 - 61	
	21	65 - 67	
	22	71 - 73	
	23	77 - 79	
	24	83 - 85	

Table A2-1 Continued

Core	Sample	Depth (cm)	Description
1988gc12		*pH & Alkalinity*	46° 44.84' N, 84°46.96' W, depth = 122 m (400 ft)
	1	0 - 1	light brown flocculent mud
	2	1 - 2	top same, less soupy; orange, cake-like redox at base
	3	2 - 2.5	solid cake-like material with sand. greyer mud at base
	4	2.5 - 3.25	alternating tan/brown mud, some sand
	5	3.25 - 4.25	top firm cakelike redox; below grey mud, sulfide odor
	6	4.25 - 5.25	top soft mud with black streaks, then tan, sandy mud
	7	5.25 - 6.25	alternating dark/black and light tan layers with sand
	8	6.25 - 7.25	similar, tan with 1 black band near top
	9	7.25 - 8.25	tan with thin black streaks
	10	8.25 - 10	...same
	11	10 - 12	...same
	12	12 - 14	...same
	13	14 - 16	...same
		16 - 20	...same
	14	20 - 22	...same
		22 - 26	...same, becoming slightly more cohesive
	15	26 - 28	...same
		28 - 32	...same, contains a pebble ~ 1 cm diameter
	16	32 - 24	...same
		34 - 38	...same
	17	38 - 40	...same
		40 - 44	...same
	18	44 - 46	...same
		46 - 50	...same
	19	50 - 52	...same
		52 - 56	...same
	20	56 - 58	...same
		58 - 62	...same
	21	62 - 64	...same
		64 - 68	...same
	22	68 - 70	...same
1988gc15		*Arsenic*	46° 44.84' N, 84°46.96' W, depth = 122 m (400 ft)
	1	0 - 1	Tan flocculent clay
	2	1 - 2	Redox layer
	3	2 - 3	Grey clay
	4	3 - 4	Dry tan clay
	5	4 - 5	Grey on top, changing to tan
	6	5 - 6	Tan clay
	7	6 - 8	... same
	8	8 - 10	... same
	9	10 - 12	... same
	10	12 - 14	... same
	11	14 - 16	... same
	12	16 - 18	... same
	13	28 - 30	... same
	14	40 - 42	... same

Table A2-1 Continued

Core	Sample	Depth (cm)	Description
1988gc15			
	15	52 - 64	... same
	16	74 - 76	... same
1988gc17		*Mercury*	46° 45.15' N, 84°47.02'W, depth = 122 m (400 ft)
	1	0 - 1	brown flocculent mud; redox at base
	2	1 - 2	redox, becoming grey-brown at base
	3	2 - 3	grey, some redox near center of core
	4	3 - 4	grey becoming tan with black layers
	5	4 - 5	tan with black layers, changing to tan, less firm
	6	5 - 6	tan
	7	6 - 7	tan with dark grey streaks
	8	7 - 8	tan with a little grey
	9	8 - 9	tan
	10	9 - 10	tan
	11	10 - 11	tan
	12	11 - 12	tan with black streaks near base
	13	12 - 14	tan
	14	14 - 16	tan with dark
	15	16 - 18	tan with occassional thin dark streaks
	16	18 - 20	...same
		20 - 25	...same
	17	25 - 27	...same
		27 - 32	...same
	18	32 - 34	...same
		34 - 39	...same
	19	39 - 41	...same
		41 - 46	...same
	20	46 - 48	...same
		48 - 53	...same
	21	53 - 55	...same
		55 - 60	...same
	22	60 - 62	...same
		62 - 67	...same
	23	67 - 69	...same
		69 - 74	...same
	24	74 - 76	...same; ~1 mm thick sand layer in middle
1988gc19		*pH & Alkalinity*	47° 22.26' N, 86° 58.03' W, depth = 330 m (1082 ft)
	1	0 - 1	brown flocculent mud
	2	1 - 2	same, changing to tan firmer clay
	3	2 - 3	tan clay
	4	3 - 4	...same
	5	4 - 5	...same
	6	5 - 6	...same
	7	6 - 7	...same with lighter colored blotches
	8	7 - 8	...same
	9	8 - 9	...same
	10	9 - 10	...same
	11	10 - 11	tan changing to lighter orange-tan

Table A2-1 Continued

Core	Sample	Depth (cm)	Description
1988gc19			
	12	11 - 12	hard orange redox layer ~4 mm, tan w/ red streaks below
	13	12 - 13	tan clay with small reddish streaks and light tan blotches
	14	13 - 14	...same
	15	14 - 15.5	...same
	16	15.5 - 16.5	...same
	17	16.5 - 18	...same, red streaks larger
	18	19 - 20	...same, with thin discontinuous redox bands
	19	20 - 22	...same; redox discrete layers ≤ 1 mm thick
	20	22 - 24	same with firmer clay streaked with grey
	21	24 - 26	...same, changing to greyer clay
		26 - 31	...same, greyer, wetter at base
	22	31 - 33	grey clay with small black streaks
		33 - 38	...same
	23	38 - 40	...same
		40 - 45	...same
	24	45 - 57	...same
		57 - 52	...same
	25	52 - 54	...same
		54 - 59	...same
	26	59 - 61	...same
		61 - 66	...same
	27	66 - 68	...same
		68 - 73	...same
	28	73 - 75	...same
1988gc22		*Mercury*	47° 22.26' N, 86° 58.03' W, depth = 330 m (1082 ft)
	1	0 - 1	brown flocculent on top; lighter brown clay beneath
	2	1 - 2	tan clay
	3	2 - 3	...same
	4	3 - 4	...same, start to see red streaks at bottom
	5	4 - 5	...same
	6	5 - 6	...same, number of red streaks/blotches increasing
	7	6 - 7	...same with orange redox layer ~2 mm thick in center
	8	7 - 8	top ~ 1 mm = tan clay with v. thin redox; grey clay below
	9	8 - 9	grey clay
	10	9 - 10	...same
	11	10 - 11	...same
	12	11 - 12	...same
	13	12 - 14	...same
	14	14 - 16	...same
	15	16 - 18	...same, with some tan spots
	16	189 - 20	...same
		20 - 25	...same
	17	25 - 27	...same
		27 - 32	...same, tan spots disappear toward bottom
	18	32 - 34	plain grey clay
		34 - 49	
	19	39 - 41	...same
		41 - 46	...same
	20	46 - 48	...same
		48 - 53	...same

Table A2-1 Continued

Core	Sample	Depth (cm)	Description
1988gc22			
	21	53 - 55	...same
		55 - 60	...same
	22	60 - 62	...same
		62 - 67	...same
	23	67 - 69	...same
		69 - 74	...same
	24	74 - 76	...same
1988gc25		*Arsenic*	47° 21.96' N, 86° 58.01' W, depth = 305 m (1000 ft)
	1	0 - 1	Dark brown flocculent mud on top, then tan soupy clay
	2	1 - 2	Tan clay, with some flocculent material
	3	2 - 3	Tan
	4	3 - 4	Tan clay
	5	4 - 5	... same
	6	5 - 6	... same
	7	6 - 8	... same
	8	8 - 10	... same
	9	10 - 12	Tan, becoming mottled with lighter clay
	10	12 - 13	Tan
	11	13 - 14	Tan with dark streaks
	12	14 - 15	Tan with dark streaks
	13	15 - 16	Tan with darker streak
	14	16 - 17	Darker tan with orange areas
	15	17 - 18	Tan, seems to be getting darker
	16	18 - 19	... same
	17	19 - 20	... same
	18	20 - 21	Mottled dark/light tan
	19	21 - 22	Darker tan with light tan mottling
	20	22 - 24	... same
	21	24 - 26	Top cm = solid, dry dark tan, then wet grey clay below
	22	31 - 33	Wet grey clay
	23	38 - 40	... same
	24	45 - 47	Lighter colored, very wet grey clay
1989gc3		*Arsenic*	42° 26.53' N, 69° 45.97' W, depth = 284 m (930 ft)
	1	0 - 1	Light brown flocculent
	2	1 - 2	... same
	3	2 - 3	Light brown with darker streaks
	4	3 - 4	... same
	5	4 - 5	Light brown, slightly firmer
	6	5 - 6	... same
	7	6 - 7	Light brown, pudding-like, still burrows
	8	7 - 8	Light brown, burrowed
	9	8 - 9	...same

Table A2-1 Continued

Core	Sample	Depth (cm)	Description
1989gc3			
	10	9 - 10	... same
	11	10 - 11	... same
	12	11 - 13	... same
	13	13 - 15	Same, without burrows
	14	15 - 17	... same
	15	17 - 19	Same, firmer clay
	16	19 - 21	... same
	17	21 - 23	... same
	18	23 - 25	... same
	19	25 - 28	... same
	20	28 - 31	... same
	21	31 - 34	... same
	22	34 - 39	... same
	23	39 - 44	... same
	24	44 - 49	... same
1989gc5	*pH & Alkalinity*		42° 26.48' N, 69° 46.29' W, depth = 284 m (930 ft)
	1	0 - 1	rusty brown
	2	1 - 2	brown
	3	2 - 3	somewhat greyer
	4	3 - 4	...same
	5	4 - 5	...same
	6	5 - 6	...same
	7	6 - 7	...same with dark spots
	8	7 - 8	...same
	9	8 - 9	olive clay
	10	9 - 10	...same
	11	10 - 11	...same
	12	11 - 13	...same
	13	13 - 15	...same
	14	15 - 17	...same
	15	17 - 19	...same
	16	19 - 21	...same, becoming very sticky
	17	21 - 23	...same
	18	23 - 25	...same
	19	25 - 38	...same
	20	28 - 31	...same
	21	31 - 34	...same
	22	34 - 37	...same
	23	37 - 40	...same
	24	40 - 43	...same

Table A2-1 Continued

Core	Sample	Depth (cm)	Description
1989gc6		*Iron*	42° 26.50' N, 69° 46.29' W, depth = 284 m (930 ft)
	1	0 - 1	
	2	1 - 2	
	3	2 - 3	Squeezer core; similar to 1988 gc5
	4	3 - 4	
	5	4 - 5	
	6	5 - 6	
	7	6 - 7	
	8	7 - 8	
	9	8 - 9	
	10	9 - 10	
	11	10 - 12	
	12	12 - 14	
	13	14 - 16	
	14	16 - 18	
	15	18 - 20	
	16	20 - 22	
	17	22 - 24	
	18	24 - 26	
	19	26 - 30	
	20	30 - 34	
1989gc8		*Mercury*	42° 26.50' N, 69° 46.29' W, depth = 284 m (930 ft)
	1	0 - 1	wet brown mud
	2	1 - 2	brown mud, becoming somewhat greyer; worm
	3	2 - 3	...same
	4	3 - 4	...same
	5	4 - 5	...same
	6	5 - 6	...same, with burrow
	7	6 - 7	...same
	8	7 - 8	...same, with burrows
	9	8 - 9	...same
	10	9 - 10	...same, becoming sticky
	11	10 - 11	...same
	12	11 - 13	...same, with creature: ~0.5 cm long, hard
	13	13 - 15	...same, becoming stickier
	14	15 - 17	...same
	15	17 - 19	...same
	16	19 - 21	...same, with black wormy thing
	17	21 - 23	...same
	18	23 - 25	...same
	19	25 - 28	...same
	20	28 - 31	...same
	21	31 - 34	...same
	22	34 -37	...same

Table A2-2 Sediment Sample Data

Core #		Core Samples		Wet/Dry Determination			Extraction Samples	
		Depth interval	Mean depth	wet weight	dry weight	dry/wet	wet weight	~ dry weight
	Sample	cm	cm	grams	grams	weight ratio	grams	grams
Arsenic								
1988gc3								
	1	0 - 1	0.5	1.51289	0.55679	0.36803	1.24791	0.45927
	2	1 - 2.5	1.8	1.21263	0.48834	0.40271	1.34151	0.54024
	3	2.5-3.5	3.0	1.77804	0.73838	0.41528	1.72833	0.71774
	4	3.5-4.5	4.0	1.24884	0.55137	0.44151	1.49908	0.66185
	5	4.5-5.5	5.0	2.02556	0.91233	0.45041	2.07150	0.93302
	6	5.5-6.5	6.0	1.41100	0.64832	0.45948	1.83553	0.84338
	7	6.5-7.5	7.0	2.05233	0.95372	0.46470	1.77911	0.82675
	8	7.5-8.5	8.0	2.08065	0.95907	0.46095	1.49323	0.68830
	9	8.5-9.5	9.0	1.64574	0.77784	0.47264	1.31570	0.62185
	10	9.5-10.5	10.0	1.98097	0.99239	0.50096	1.69555	0.84941
	11	10.5-11.5	11.0	2.71278	1.28165	0.47245	1.42070	0.67121
	12	16.5-18.5	17.5	2.08058	1.03332	0.49665	1.53222	0.76098
	13	23.5-25.5	24.5	2.19701	1.10886	0.50471	2.23549	1.12828
	14	30.5-32.5	31.5	1.96470	0.94041	0.47865	1.81123	0.86695
	15	37.5-39.5	38.5	1.92341	0.97087	0.50476	1.77534	0.89613
	16	44.5-46.5	45.5	2.71523	1.39003	0.51194	1.60184	0.82004
	17	51.5-53.5	52.5	1.97922	1.06140	0.53627	2.19354	1.17633
	18	58.5-60.5	59.5	2.61789	1.33931	0.51160	2.98531	1.52728
1988gc11								
	1	0 - 1	0.5	0.75637	0.29558	0.39079	2.56585	1.00270
	2	1 - 2	1.5	1.26585	0.50292	0.39730	3.37624	1.34137
	3	2 - 3	2.5	1.09362	0.49005	0.44810	3.46879	1.55436
	4	3 - 4	3.5	1.62051	0.77437	0.47786	2.57502	1.23049
	5	4 - 5	4.5	1.44922	0.69695	0.48091	2.91062	1.39976
	6	5 - 6	5.5	1.46045	0.66858	0.45779	3.55113	1.62567
	7	6 - 7	6.5	1.48942	0.70611	0.47408	2.97563	1.41070

Table A2-2 continued

Core #	Core Samples		Wet/Dry Determination			Extraction Samples	
	Depth interval	Mean depth	wet weight	dry weight	dry/wet	wet weight	~ dry weight
Sample	cm	cm	grams	grams	weight ratio	grams	grams
1988gc11							
8	7 - 8	7.5	1.55081	0.72684	0.46868	3.10997	1.45759
9	8 - 9	8.5	2.47678	1.13170	0.45692	2.78264	1.27145
10	9 - 10	9.5	2.05148	0.98509	0.48019	4.00611	1.92367
11	10 - 11	10.5	1.84375	0.90675	0.49180	3.17578	1.56184
12	11 - 13	12.0	2.97855	1.24960	0.41953	3.02482	1.26901
13	17 - 19	18.0	1.99147	0.90219	0.45303	3.09231	1.40090
14	23 - 25	24.0	2.22299	0.98635	0.44370	3.51464	1.55946
15	29 - 31	30.0	2.24775	1.09933	0.48908	3.01430	1.47423
16	35 - 37	36.0	2.94395	1.41683	0.48127	2.94238	1.41607
17	41 - 43	42.0	1.66466	0.82089	0.49313	2.86805	1.41431
18	47 - 49	48.0	2.77137	1.36214	0.49150	2.35928	1.15960
19	53 - 55	54.0	2.70766	1.25746	0.46441	3.65772	1.69868
20	59 - 61	60.0	3.47083	1.63881	0.47217	3.31304	1.56431
21	65 - 67	66.0	2.70467	1.35683	0.50166	4.37770	2.19613
22	71 - 73	72.0	2.83860	1.34705	0.47455	4.62449	2.19454
23	77 - 79	78.0	2.10578	1.05684	0.50188	5.11606	2.56763
24	83 - 85	84.0	2.69196	1.42957	0.53105	4.16398	2.21129
1988gc15							
1	0 - 1	0.5	0.93778	0.52155	0.55615	2.65019	1.47391
2	1 - 2	1.5	1.07100	0.61715	0.57624	4.42414	2.54935
3	2 - 3	2.5	1.91073	1.15740	0.60574	4.94289	2.99409
4	3 - 4	3.5	1.39655	0.94480	0.67652	4.49445	3.04060
5	4 - 5	4.5	1.97863	1.38164	0.69828	6.13306	4.28260
6	5 - 6	5.5	2.36580	1.48494	0.62767	5.34189	3.35294
7	6 - 8	7.0	1.77032	1.13092	0.63882	4.94390	3.15827
8	8 - 10	9.0	2.11118	1.30469	0.61799	4.94099	3.05349
9	10 - 12	11.0	1.88163	1.25739	0.66825	6.65387	4.44642

Table A2-2 continued

Core #		Core Samples		Wet/Dry Determination			Extraction Samples	
		Depth interval	Mean depth	wet weight	dry weight	dry/wet	wet weight	~ dry wt
	Sample	cm	cm	grams	grams	weight ratio	grams	grams
1988gc15								
	10	12 - 14	13.0	2.78028	1.62015	0.58273	5.13483	2.99221
	11	14 - 16	15.0	2.87739	1.76830	0.61455	6.23434	3.83131
	12	16 - 18	17.0	3.28405	1.71053	0.52086	6.41117	3.33932
	13	28 - 30	29.0	3.12921	1.75206	0.55990	6.68382	3.74230
	14	40 - 42	41.0	3.33362	1.72877	0.51859	5.14800	2.66968
	15	52 - 64	53.0	2.10027	1.11749	0.53207	6.18694	3.29188
	16	74 - 76	75.0	3.16955	1.76761	0.55768	6.17221	3.44215
1988gc25								
	1	0 - 1	0.5	0.58211	0.24903	0.42781	2.21933	0.94944
	2	1 - 2	1.5	1.16563	0.47850	0.41051	2.53967	1.04255
	3	2 - 3	2.5	1.04397	0.52670	0.50452	1.85848	0.93763
	4	3 - 4	3.5	0.99784	0.49626	0.49733	2.86449	1.42461
	5	4 - 5	4.5	1.58805	0.79189	0.49866	4.06165	2.02536
	6	5 - 6	5.5	1.46332	0.75193	0.51385	3.72410	1.91364
	7	6 - 8	7.0	2.35517	1.21819	0.51724	2.74709	1.42091
	8	8 - 10	9.0	2.04568	1.03025	0.50362	3.81373	1.92068
	9	10 - 12	11.0	2.45402	1.30515	0.53184	2.75447	1.46494
	10	12 - 13	12.5	2.07095	1.06334	0.51346	3.09829	1.59083
	11	13 - 14	13.5	1.98685	1.04754	0.52724	2.87596	1.51631
	12	14 - 15	14.5	2.46789	1.27517	0.51670	4.92171	2.54307
	13	15 - 16	15.5	2.26129	1.10553	0.48889	4.87075	2.38128
	14	16 - 17	16.5	1.76939	0.92107	0.52056	3.39613	1.76788
	15	17 - 18	17.5	2.33754	1.14823	0.49121	4.49821	2.20958
	16	18 - 19	18.5	2.42445	1.22366	0.50472	4.92246	2.48445
	17	19 - 20	19.5	2.40150	1.18717	0.49435	3.19474	1.57930
	18	20 - 21	20.5	2.70228	1.24690	0.46143	4.03132	1.86015
	19	21 - 22	21.5	2.68601	1.26488	0.47091	4.77298	2.24766

Table A2-2 continued

Core #	Core Samples			Wet/Dry Determination			Extraction Samples	
	Depth interval	Mean depth	wet weight	dry weight	dry/wet	wet weight	~ dry wt
Sample	cm	cm	grams	grams	weight ratio	grams	grams
1988gc25							
20	22 - 24	23.0	3.17895	1.42878	0.44945	3.72964	1.67629
21	24 - 26	25.0	2.05399	1.05548	0.51387	3.62971	1.86519
22	31 - 33	32.0	2.20932	1.14827	0.51974	3.09829	1.61030
23	38 - 40	39.0	1.72175	0.79538	0.46196	2.82891	1.30684
24	45 - 47	46.0	2.30610	1.31221	0.56902	5.73629	3.26405
1989gc3							
1	0 - 1	0.5	0.87412	0.40115	0.45892	2.83023	1.29885
2	1 - 2	1.5	0.87285	0.78595	0.90044	3.79384	3.41613
3	2 - 3	2.5	1.57583	0.71979	0.45677	3.59196	1.64070
4	3 - 4	3.5	1.96229	0.91164	0.46458	4.02493	1.86990
5	4 - 5	4.5	1.68903	0.40304	0.23862	5.12181	1.22218
6	5 - 6	5.5	2.74275	1.28111	0.46709	5.61109	2.62088
7	6 - 7	6.5	2.30236	1.08009	0.46912	2.63014	1.23386
8	7 - 8	7.5	2.40351	1.11810	0.46519	5.55932	2.58617
9	8 - 9	8.5	1.57828	0.74855	0.47428	3.62502	1.71928
10	9 - 10	9.5	1.73204	0.83877	0.48427	3.57476	1.73114
11	10 - 11	10.5	2.45509	1.17645	0.47919	5.00188	2.39684
12	11 - 13	12.0	2.26928	1.10387	0.48644	4.64321	2.25865
13	13 - 15	14.0	2.59938	1.25016	0.48095	3.36753	1.61960
14	15 - 17	16.0	1.92568	0.93780	0.48700	3.88616	1.89255
15	17 - 19	18.0	2.17240	1.02770	0.47307	3.87986	1.83545
16	19 - 21	20.0	2.84232	1.36902	0.48166	5.96126	2.87128
17	21 - 23	22.0	2.88252	1.45782	0.50574	4.66267	2.35812
18	23 - 25	24.0	2.44582	1.21434	0.49650	4.75580	2.36124
19	25 - 28	26.5	1.78754	0.90051	0.50377	5.01539	2.52661
20	28 - 31	29.5	2.04331	1.03888	0.50843	3.73724	1.90012
21	31 - 34	32.5	2.29837	1.18156	0.51409	5.09152	2.61748

Table A2-2 continued

Core # / Sample	Core Samples: Depth interval cm	Core Samples: Mean depth cm	Wet/Dry Determination: wet weight grams	Wet/Dry Determination: dry weight grams	Wet/Dry Determination: dry/wet weight ratio	Extraction Samples: wet weight grams	Extraction Samples: ~ dry wt grams
1989gc3							
22	34 - 39	36.5	2.58865	1.30681	0.50482	5.47232	2.76255
23	39 - 44	41.5	2.95407	1.50178	0.50838	5.58648	2.84004
24	44 - 49	46.5	3.09290	1.56550	0.50616	6.65030	3.36611
Fluff site 1595		0.0	0.52764	0.24706	0.46824	1.66725	0.78067
Fluff site 1601		0.0	0.67818	0.25572	0.37707	2.24051	0.84482
Fluff site 1607		0.0	0.76530	0.34557	0.45155	2.33041	1.05229
Fluff site 1615		0.0	0.64110	0.27359	0.42675	2.63046	1.12255
Mercury							
1988gc2							
1	0 - 1	0.5	1.27092	0.49702	0.39107	2.77325	1.08454
2	1 - 2	1.5	1.71086	0.70708	0.41329	1.71725	0.70972
3	2 - 3	2.5	1.27274	0.57707	0.45341	2.49960	1.13334
4	3 - 4	3.5	1.36145	0.62657	0.46022	2.91234	1.34032
5	4 - 5	4.5	1.70057	0.71815	0.42230	2.61512	1.10436
6	5 - 6	5.5	2.15723	0.96866	0.44903	3.32542	1.49321
7	6 - 7	6.5	1.34508	0.59772	0.44438	3.12207	1.38737
8	7 - 8	7.5	1.86094	0.91480	0.49158	3.87272	1.90375
9	8 - 9	8.5	1.66810	0.80955	0.48531	2.40464	1.16700
10	9 - 10	9.5	1.61264	0.75169	0.46612	3.02299	1.40909
11	10 - 11	10.5	2.04977	0.94340	0.46025	3.00588	1.38345
12	11 - 12	11.5	1.97977	0.99121	0.50067	3.11332	1.55874
13	14 - 16	15.0	2.28400	1.04202	0.45623	2.64637	1.20734
14	24 - 26	25.0	2.68479	1.25168	0.46621	3.79222	1.76798
15	34 - 36	35.0	2.11426	1.03857	0.49122	3.98021	1.95516
16	44 - 46	45.0	2.12947	1.07901	0.50670	3.02419	1.53237
17	54 - 56	55.0	2.34542	1.35706	0.57860	3.00664	1.73964

Table A2-2 continued

Core #	Core Samples		Wet/Dry Determination			Extraction Samples	
	Depth interval	Mean depth	wet weight	dry weight	dry/wet	wet weight	~ dry wt
Sample	cm	cm	grams	grams	weight ratio	grams	grams
18	64 - 66	65.0	1.69964	1.00457	0.59105	3.54533	2.09546
19	74 - 76	75.0	2.06049	1.24460	0.60403	3.16945	1.91445
20	76 - 78	77.0	2.10962	1.26898	0.60152	2.78020	1.67235
1988gc9							
1	0 - 1	0.5	1.15851	0.46772	0.40373	2.18171	0.88081
2	1 - 2	1.5	1.76590	0.67755	0.38369	2.58690	0.99256
3	2 - 3	2.5	0.89634	0.38131	0.42541	2.97161	1.26415
4	3 - 4	3.5	1.65064	0.64613	0.39144	2.62897	1.02909
5	4 - 5	4.5	1.12565	0.45349	0.40287	3.30669	1.33216
6	5 - 6	5.5	1.62410	0.69844	0.43005	3.53841	1.52168
7	6 - 7	6.5	1.81952	0.85612	0.47052	3.53743	1.66443
8	7 - 8	7.5	1.38284	0.68973	0.49878	3.68366	1.83733
9	8 - 9	8.5	1.77254	0.83831	0.47294	3.27370	1.54827
10	9 - 10	9.5	1.84891	0.88554	0.47895	4.11746	1.97207
11	10 - 11	10.5	1.82320	0.88447	0.48512	3.21045	1.55745
12	11 - 12	11.5	1.34700	0.61844	0.45912	2.76571	1.26980
13	12 - 14	13.0	1.93792	0.93590	0.48294	3.62117	1.74881
14	18 - 20	19.0	1.45465	0.64452	0.44308	2.48375	1.10049
15	24 - 26	25.0	2.14654	1.11114	0.51764	2.87119	1.48625
16	30 - 32	31.0	3.13922	1.57805	0.50269	3.00192	1.50903
17	36 - 38	37.0	2.64609	1.27224	0.48080	3.58980	1.72598
18	42 - 44	43.0	2.16600	0.99958	0.46149	3.80581	1.75633
19	48 - 50	49.0	2.41639	1.13681	0.47046	3.26246	1.53485
20	54 - 56	55.0	2.22397	1.13759	0.51151	4.76683	2.43830
21	60 - 62	61.0	2.46091	1.20618	0.49014	4.53988	2.22516
22	66 - 68	67.0	2.30572	1.16164	0.50381	3.88706	1.95833
23	72 - 74	73.0	1.83600	0.91306	0.49731	4.00106	1.98976
24	78 - 80	79.0	2.19773	1.07516	0.48921	3.72297	1.82133

Table A2-2 continued

Core #		Core Samples		Wet/Dry Determination			Extraction Samples	
		Depth interval	Mean depth	wet weight	dry weight	dry/wet	wet weight	~ dry wt
	Sample	cm	cm	grams	grams	weight ratio	grams	grams
1988gc17								
	1	0 - 1	0.5	1.81180	0.85244	0.47049	1.79836	0.84612
	2	1 - 2	1.5	1.88236	1.02664	0.54540	2.65988	1.45070
	3	2 - 3	2.5	2.20178	1.30817	0.59414	2.67938	1.59193
	4	3 - 4	3.5	2.63558	1.63835	0.62163	2.36405	1.46956
	5	4 - 5	4.5	1.95858	1.32584	0.67694	3.23079	2.18705
	6	5 - 6	5.5	2.00794	1.30693	0.65088	2.01443	1.31115
	7	6 - 7	6.5	2.44360	1.46895	0.60114	2.43909	1.46624
	8	7 - 8	7.5	2.79585	1.93020	0.69038	3.81394	2.63307
	9	8 - 9	8.5	1.58147	0.91990	0.58167	2.47279	1.43836
	10	9 - 10	9.5	1.62049	0.99936	0.61670	2.61783	1.61442
	11	10 - 11	10.5	1.80795	0.98590	0.54531	3.15238	1.71904
	12	11 - 12	11.5	1.64575	0.91672	0.55702	3.22836	1.79827
	13	12 - 14	13.0	2.23299	1.28255	0.57436	3.22048	1.84973
	14	14 - 16	15.0	2.58247	1.24843	0.48342	2.78728	1.34744
	15	16 - 18	17.0	2.10646	1.10553	0.52483	3.60927	1.89425
	16	18 - 20	19.0	2.44542	1.15066	0.47054	3.58705	1.68784
	17	25 - 27	26.0	2.04698	1.07546	0.52539	2.83773	1.49091
	18	32 - 34	33.0	2.53835	1.25804	0.49561	3.65928	1.81359
	19	39 - 41	40.0	3.02659	1.56589	0.51738	3.66538	1.89639
	20	46 - 48	47.0	2.55180	1.42591	0.55879	3.08365	1.72310
	21	53 - 55	54.0	2.61470	1.36917	0.52364	2.41241	1.26324
	22	60 - 62	61.0	1.90204	1.02956	0.54129	3.84929	2.08359
	23	67 - 69	68.0	2.16568	1.14957	0.53081	5.30206	2.81440
	24	74 - 76	75.0	2.30864	1.26764	0.54909	2.86326	1.57217
1988gc22								
	1	0 - 1	0.5	1.35804	0.63733	0.46930	4.11989	1.93347
	2	1 - 2	1.5	1.56372	0.77454	0.49532	3.16780	1.56907

Table A2-2 continued

Core #		Core Samples		Wet/Dry Determination			Extraction Samples	
		Depth interval	Mean depth	wet weight	dry weight	dry/wet	wet weight	~ dry wt
	Sample	cm	cm	grams	grams	weight ratio	grams	grams
1988gc22								
	3	2 - 3	2.5	2.03613	0.97176	0.47726	3.95277	1.88649
	4	3 - 4	3.5	1.71620	0.87767	0.51140	3.72754	1.90628
	5	4 - 5	4.5	1.35713	0.69670	0.51336	4.58145	2.35195
	6	5 - 6	5.5	1.53424	0.74590	0.48617	3.32868	1.61830
	7	6 - 7	6.5	1.92503	0.80976	0.42065	3.24383	1.36451
	8	7 - 8	7.5	1.44057	0.70003	0.48594	3.42102	1.66241
	9	8 - 9	8.5	2.59679	1.34720	0.51879	3.36067	1.74350
	10	9 - 10	9.5	2.31409	1.09206	0.47192	3.70141	1.74676
	11	10 - 11	10.5	2.70243	1.36781	0.50614	3.98262	2.01577
	12	11 - 12	11.5	1.86968	0.92078	0.49248	3.68274	1.81368
	13	12 - 14	13.0	1.86238	0.89979	0.48314	3.60165	1.74010
	14	14 - 16	15.0	1.93331	0.96436	0.49881	2.89968	1.44640
	15	16 - 18	17.0	1.50212	0.72388	0.48191	3.78784	1.82538
	16	18 - 20	19.0	2.07999	1.02839	0.49442	5.27540	2.60827
	17	25 - 27	26.0	1.85160	0.91242	0.49277	3.61703	1.78238
	18	32 -34	33.0	2.76643	1.40601	0.50824	4.20378	2.13653
	19	39 - 41	40.0	1.77612	0.94015	0.52933	4.02726	2.13174
	20	46 - 48	47.0	2.12862	1.03731	0.48732	3.56107	1.73537
	21	53 - 55	54.0	1.88315	0.98722	0.52424	3.74926	1.96551
	22	60 - 62	61.0	2.06616	1.03191	0.49943	4.99164	2.49299
	23	67 - 69	68.0	2.15511	1.19313	0.55363	2.89384	1.60211
	24	74 - 76	75.0	2.37589	1.23540	0.51997	3.84780	2.00075
89GC8								
	1	0 - 1	0.5	1.25563	0.56340	0.44870	2.00296	0.89873
	2	1 - 2	1.5	1.07859	0.51442	0.47694	2.02042	0.96361
	3	2 - 3	2.5	1.28632	0.62289	0.48424	2.25069	1.08988
	4	3 - 4	3.5	1.35043	0.64495	0.47759	2.43011	1.16059

Table A2-2 continued

Core #	Core Samples		Wet/Dry Determination			Extraction Samples	
	Depth interval	Mean depth	wet weight	dry weight	dry/wet	wet weight	~ dry wt
Sample	cm	cm	grams	grams	weight ratio	grams	grams
89GC8							
5	4 - 5	4.5	2.40897	1.09779	0.45571	1.94760	0.88754
6	5 - 6	5.5	2.52538	1.18587	0.46958	2.30064	1.08034
7	6 - 7	6.5	2.21545	1.06894	0.48249	3.64111	1.75681
8	7 - 8	7.5	2.21621	1.02984	0.46469	2.55978	1.18949
9	8 - 9	8.5	2.88055	1.36967	0.47549	2.55672	1.21569
10	9 - 10	9.5	2.27791	1.10803	0.48642	1.61037	0.78332
11	10 - 11	10.5	2.32274	1.14232	0.49180	2.13179	1.04841
12	11 - 13	12.0	2.51958	1.21993	0.48418	3.34065	1.61748
13	13 - 15	14.0	2.59653	1.29776	0.49981	3.73755	1.86805
14	15 - 17	16.0	2.82979	1.36299	0.48166	2.91268	1.40291
15	17 - 19	18.0	2.99679	1.46540	0.48899	3.55038	1.73610
16	19 - 21	20.0	2.83456	1.38307	0.48793	2.67569	1.30555
17	21 - 23	22.0	2.54408	1.22791	0.48265	3.57149	1.72379
18	23 - 25	24.0	2.18263	1.11442	0.51059	3.37421	1.72282
19	25 - 28	26.5	2.81461	1.40393	0.49880	3.03417	1.51345
20	28 - 31	29.5	2.49371	1.75632	0.70430	4.14225	2.91739
21	31 - 34	32.5	3.82467	1.91552	0.50083	3.78560	1.89595
22	34 - 37	35.5	3.02081	1.51325	0.50094	5.02759	2.51853
SBL samples							
site 1595		0.0	0.97758	0.42867	0.43850	1.87612	0.82268
site 1601		0.0	1.36209	0.51712	0.37965	2.00687	0.76191
site 1607		0.0	1.66125	0.78651	0.47344	2.42264	1.14699
site 1615		0.0	2.44514	0.95462	0.39042	3.06737	1.19755

APPENDIX 3

ANALYTICAL DATA

Results of chemical analyses of arsenic extraction solutions are presented in Table A3-1. Corresponding sediment concentrations are also presented. These were calculated from solution concentrations and dry/wet sediment ratios (see Appendix 2) according to the following formula:

$$\text{sediment concentration } (\mu g/g) = \frac{\text{solution concentration } (\mu g/L) \times \text{solution volume (L)}}{\text{wet sample mass (g)} \times \text{dry/wet mass ratio}}$$

Total extractable arsenic is calculated as the sum of the sediment concentrations for all of the extracted phases. Data appears in core number order, with SBL data at the end.

Results of chemical analyses of mercury extraction solutions are presented in Table A3-2. Sediment concentrations were determined in the same manner as for arsenic concentrations. Data appears in core number order, with SBL data at the end.

Results of porewater analyses are reported in Table A3-3. These include arsenic and mercury concentrations, ferrous iron concentrations, and values of pH and alkalinity. Data appears in site order, with all data for a given site on the same page.

Organic carbon contents of sediment samples are reported in Table A3-4. Data is presented in site order.

Table A3-1 Extractable Arsenic Data

Sol'n indicates concentration detected in leachate solutions, µg/L
Sed indicates concentration in µg/g in sediment (dry weight basis)
n.d. indicates not detected

Core # sample	Depth cm	EX sol'n µg/L	EX sed µg/g	WAS sol'n µg/L	WAS sed µg/g	ER sol'n µg/L	ER sed µg/g	MR sol'n µg/L	MR sed µg/g	OX sol'n µg/L	OX sed µg/g	TOTAL As µg/g
1988gc3												
1	0.5	9.30	0.202	47.5	1.034	60.9	3.315	220.9	9.620	162.8	8.86	22.83
2	1.8	8.80	0.163	36.0	0.666	19.5	0.902	130.6	4.835	127.5	5.90	12.30
3	3.0	9.10	0.127	85.2	1.187	44.0	1.533	145.9	4.066	74.8	2.61	9.39
4	4.0	4.70	0.071	45.6	0.689	48.6	1.836	49.2	1.487	49.4	1.87	5.88
5	5.0	n.d.	n.d.	28.0	0.300	19.2	0.514	42.6	0.913	34.6	0.93	2.65
6	6.0	n.d.	n.d.	20.7	0.245	18.9	0.560	30.0	0.711	26.9	0.80	2.31
7	7.0	n.d.	n.d.	23.4	0.283	21.9	0.662	35.2	0.852	18.6	0.56	2.36
8	8.0	n.d.	n.d.	15.4	0.224	19.6	0.712	25.8	0.750	21.2	0.77	2.46
9	9.0	n.d.	n.d.	34.6	0.556	60.0	2.412	28.6	0.920	67.6	2.72	6.61
10	10.0	n.d.	n.d.	28.0	0.330	45.1	1.327	35.8	0.843	58.2	1.71	4.21
11	11.0	n.d.	n.d.	23.2	0.346	16.2	0.603	27.7	0.825	32.8	1.22	3.00
12	17.5	n.d.	n.d.	23.6	0.310	49.1	1.613	29.3	0.770	43.2	1.42	4.11
13	24.5	n.d.	n.d.	34.1	0.302	21.0	0.465	73.5	1.303	81.4	1.80	3.87
14	31.5	n.d.	n.d.	31.2	0.360	37.4	1.078	52.2	1.204	90.0	2.60	5.24
15	38.5	n.d.	n.d.	36.5	0.407	27.4	0.764	73.2	1.634	112.2	3.13	5.94
16	45.5	n.d.	n.d.	22.9	0.279	18.6	0.567	42.3	1.032	48.2	1.47	3.35
17	52.5	n.d.	n.d.	26.6	0.226	9.7	0.206	65.7	1.117	29.6	0.63	2.18
18	59.5	n.d.	n.d.	37.4	0.245	10.4	0.170	82.9	1.086	37.6	0.62	2.12
1988gc11												
1	0.5	9.40	0.094	36.8	0.367	21.4	0.534	304.6	6.076	180.0	4.49	11.46
2	1.5	n.d.	n.d.	26.6	0.198	18.5	0.345	148.2	2.210	166.4	3.10	5.85
3	2.5	n.d.	n.d.	71.6	0.461	35.7	0.574	88.4	1.137	99.0	1.59	3.76
4	3.5	n.d.	n.d.	30.9	0.251	18.1	0.368	33.7	0.548	27.9	0.57	1.73
5	4.5	n.d.	n.d.	16.5	0.118	3.3	0.059	27.5	0.393	35.7	0.64	1.21
6	5.5	n.d.	n.d.	23.6	0.145	6.3	0.097	43.8	0.539	49.7	0.76	1.55
7	6.5	n.d.	n.d.	32.4	0.230	8.2	0.145	45.0	0.638	50.7	0.90	1.91
8	7.5	n.d.	n.d.	48.9	0.335	35.8	0.614	73.0	1.002	75.7	1.30	3.25

Table A3-1 (cont'd).

Core # sample	Depth cm	EX sol'n µg/L	EX sed µg/g	WAS sol'n µg/L	WAS sed µg/g	ER sol'n µg/L	ER sed µg/g	MR sol'n µg/L	MR sed µg/g	OX sol'n µg/L	OX sed µg/g	TOTAL As µg/g
1988gc11												
9	8.5	n.d.	n.d.	43.8	0.344	23.5	0.462	63.0	0.991	57.3	1.13	2.92
10	9.5	n.d.	n.d.	44.9	0.233	53.5	0.695	96.6	1.004	144.0	1.87	3.80
11	10.5	n.d.	n.d.	41.6	0.266	34.5	0.552	102.8	1.316	159.5	2.55	4.69
12	12.0	11.00	0.087	55.1	0.434	68.3	1.346	57.4	0.905	120.1	2.37	5.05
13	18.0	n.d.	n.d.	51.5	0.368	61.5	1.098	80.3	1.146	100.4	1.79	4.40
14	24.0	12.90	0.083	72.5	0.465	38.5	0.617	109.8	1.408	139.6	2.24	4.73
15	30.0	n.d.	n.d.	48.7	0.330	43.4	0.736	68.3	0.927	52.4	0.89	2.88
16	36.0	13.10	0.093	42.3	0.299	61.9	1.093	144.4	2.039	151.4	2.67	6.10
17	42.0	13.10	0.093	40.2	0.284	47.7	0.843	78.7	1.113	86.7	1.53	3.77
18	48.0	n.d.	n.d.	26.8	0.231	29.6	0.638	56.5	0.974	40.3	0.87	2.71
19	54.0	n.d.	n.d.	37.4	0.220	36.7	0.540	110.0	1.295	107.9	1.59	3.64
20	60.0	n.d.	n.d.	32.5	0.208	25.3	0.404	61.5	0.786	43.0	0.69	2.09
21	66.0	n.d.	n.d.	31.5	0.143	28.1	0.320	91.2	0.831	100.7	1.15	2.44
22	72.0	n.d.	n.d.	22.2	0.101	53.8	0.613	85.4	0.778	78.0	0.89	2.38
23	78.0	n.d.	n.d.	31.5	0.123	37.7	0.367	114.9	0.895	118.6	1.15	2.54
24	84.0	n.d.	n.d.	44.4	0.201	29.7	0.336	91.3	0.826	97.5	1.10	2.46
1988gc15												
1	0.5	n.d.	n.d.	13.4	0.091	18.5	0.314	446.0	6.052	58.3	0.99	7.45
2	1.5	n.d.	n.d.	7.3	0.029	9.1	0.089	50.0	0.392	3.1	0.03	0.54
3	2.5	n.d.	n.d.	49.0	0.164	63.1	0.527	231.2	1.544	7.7	0.06	2.30
4	3.5	n.d.	n.d.	58.0	0.191	163.1	1.341	183.0	1.204	4.6	0.04	2.77
5	4.5	n.d.	n.d.	41.2	0.096	16.6	0.097	99.7	0.466	26.0	0.15	0.81
6	5.5	n.d.	n.d.	42.5	0.127	23.8	0.177	53.8	0.321	12.7	0.09	0.72
7	7.0	n.d.	n.d.	41.0	0.130	40.9	0.324	68.7	0.435	18.8	0.15	1.04
8	9.0	n.d.	n.d.	37.1	0.122	21.6	0.177	50.4	0.330	11.9	0.10	0.73
9	11.0	n.d.	n.d.	55.1	0.124	47.0	0.264	64.4	0.290	33.7	0.19	0.87
10	13.0	n.d.	n.d.	35.9	0.120	62.5	0.522	62.9	0.420	7.5	0.06	1.13
11	15.0	n.d.	n.d.	64.1	0.167	71.2	0.465	83.8	0.437	23.0	0.15	1.22
12	17.0	n.d.	n.d.	67.7	0.203	119.5	0.895	83.9	0.502	13.3	0.10	1.70
13	29.0	n.d.	n.d.	49.9	0.133	47.7	0.319	71.7	0.383	21.2	0.14	0.98

Table A3-1 (cont'd).

Core # sample	Depth cm	EX sol'n µg/L	EX sed µg/g	WAS sol'n µg/L	WAS sed µg/g	ER sol'n µg/L	ER sed µg/g	MR sol'n µg/L	MR sed µg/g	OX sol'n µg/L	OX sed µg/g	TOTAL As µg/g
1988gc15												
14	41.0	n.d.	n.d.	49.3	0.185	47.3	0.443	72.0	0.539	15.2	0.14	1.31
15	53.0	n.d.	n.d.	43.4	0.132	61.1	0.464	82.1	0.499	21.5	0.16	1.26
16	75.0	n.d.	n.d.	52.3	0.152	40.8	0.296	74.8	0.435	22.4	0.16	1.05
1988gc25												
1	0.5	n.d.	n.d.	10.9	0.115	7.5	0.197	60.0	1.264	28.1	0.74	2.32
2	1.5	n.d.	n.d.	9.9	0.095	15.9	0.381	47.1	0.904	20.5	0.49	1.87
3	2.5	n.d.	n.d.	8.7	0.093	6.7	0.179	29.4	0.627	10.7	0.29	1.18
4	3.5	n.d.	n.d.	5.3	0.037	5.2	0.091	25.8	0.362	11.1	0.19	0.69
5	4.5	n.d.	n.d.	3.3	0.016	2.4	0.030	22.9	0.226	10.2	0.13	0.40
6	5.5	n.d.	n.d.	4.4	0.023	3.8	0.050	19.7	0.206	7.7	0.10	0.38
7	7.0	n.d.	n.d.	4.1	0.029	2.9	0.051	18.3	0.258	5.4	0.10	0.43
8	9.0	n.d.	n.d.	3.2	0.017	2.9	0.038	20.1	0.209	7.8	0.10	0.37
9	11.0	n.d.	n.d.	3.3	0.023	4.2	0.072	22.1	0.302	8.1	0.14	0.53
10	12.5	n.d.	n.d.	3.9	0.025	4.2	0.066	25.3	0.318	8.9	0.14	0.55
11	13.5	n.d.	n.d.	3.8	0.025	3.3	0.054	22.3	0.294	7.8	0.13	0.50
12	14.5	n.d.	n.d.	5.2	0.020	5.1	0.050	23.6	0.186	7.6	0.07	0.33
13	15.5	n.d.	n.d.	6.9	0.029	4.1	0.043	25.9	0.218	7.3	0.08	0.37
14	16.5	n.d.	n.d.	6.3	0.036	3.6	0.051	34.5	0.390	8.1	0.11	0.59
15	17.5	n.d.	n.d.	6.8	0.031	3.9	0.044	20.0	0.181	6.8	0.08	0.33
16	18.5	n.d.	n.d.	8.6	0.035	6.6	0.066	21.3	0.171	11.7	0.12	0.39
17	19.5	n.d.	n.d.	8.5	0.054	7.3	0.116	35.3	0.447	7.9	0.13	0.74
18	20.5	n.d.	n.d.	10.5	0.056	11.9	0.160	34.4	0.370	10.6	0.14	0.73
19	21.5	n.d.	n.d.	11.2	0.050	7.1	0.079	43.5	0.387	19.1	0.21	0.73
20	23.0	n.d.	n.d.	9.9	0.059	15.7	0.234	142.9	1.705	21.3	0.32	2.32
21	25.0	n.d.	n.d.	9.8	0.053	7.6	0.102	54.5	0.584	15.5	0.21	0.95
22	32.0	n.d.	n.d.	29.6	0.184	26.4	0.410	24.5	0.304	20.3	0.32	1.21
23	39.0	n.d.	n.d.	43.4	0.332	27.6	0.528	76.5	1.171	15.7	0.30	2.33
24	46.0	n.d.	n.d.	0.4	0.001	31.1	0.238	23.7	0.145	15.5	0.12	0.50

Table A3-1 (cont'd).

Core # sample	Depth cm	EX sol'n µg/L	EX sed µg/g	WAS sol'n µg/L	WAS sed µg/g	ER sol'n µg/L	ER sed µg/g	MR sol'n µg/L	MR sed µg/g	OX sol'n µg/L	OX sed µg/g	TOTAL As µg/g
1989gc3												
1	0.5	15.05	0.116	33.1	0.255	15.9	0.306	47.9	0.738	13.4	0.26	1.56
2	1.5	9.05	0.026	38.2	0.112	19.7	0.144	44.5	0.261	14.4	0.11	0.62
3	2.5	11.55	0.070	35.7	0.218	21.8	0.332	62.5	0.762	18.2	0.28	1.59
4	3.5	13.90	0.074	38.1	0.204	36.4	0.487	69.0	0.738	17.9	0.24	1.67
5	4.5	12.20	0.100	25.0	0.205	4.9	0.100	49.1	0.803	20.0	0.41	1.52
6	5.5	13.95	0.053	25.4	0.097	8.2	0.078	27.5	0.210	16.0	0.15	0.54
7	6.5	2.00	0.016	27.0	0.219	6.7	0.136	14.6	0.237	6.8	0.14	0.73
8	7.5	1.00	0.004	29.2	0.113	3.9	0.038	29.3	0.227	20.1	0.19	0.57
9	8.5	1.00	0.006	21.5	0.125	5.6	0.081	17.5	0.204	11.6	0.17	0.58
10	9.5	16.90	0.098	26.8	0.155	4.7	0.068	16.2	0.187	10.6	0.15	0.56
11	10.5	21.35	0.089	25.2	0.105	2.9	0.030	26.1	0.218	18.3	0.19	0.54
12	12.0	29.90	0.132	40.6	0.180	10.4	0.115	20.4	0.181	15.1	0.17	0.64
13	14.0	35.80	0.221	54.6	0.337	7.6	0.117	15.0	0.185	12.6	0.19	0.83
14	16.0	36.30	0.192	60.1	0.318	10.8	0.143	15.5	0.164	12.4	0.16	0.79
15	18.0	56.10	0.306	58.5	0.319	8.3	0.113	16.5	0.180	12.0	0.16	0.78
16	20.0	71.40	0.249	85.2	0.297	22.9	0.199	24.1	0.168	21.0	0.18	0.85
17	22.0	49.20	0.209	52.6	0.223	9.7	0.103	27.4	0.232	14.3	0.15	0.71
18	24.0	64.20	0.272	61.9	0.262	8.9	0.094	20.5	0.174	12.3	0.13	0.66
19	26.5	44.70	0.177	42.4	0.168	7.5	0.074	25.9	0.205	15.1	0.15	0.60
20	29.5	49.70	0.262	53.9	0.284	13.2	0.174	18.0	0.189	10.3	0.14	0.78
21	32.5	48.50	0.185	38.9	0.149	10.1	0.096	32.7	0.250	13.8	0.13	0.63
22	36.5	45.10	0.163	47.8	0.173	19.4	0.176	32.5	0.235	15.6	0.14	0.73
23	41.5	62.90	0.221	38.9	0.137	11.5	0.101	33.2	0.234	18.5	0.16	0.63
24	46.5	77.40	0.230	56.9	0.169	12.7	0.094	44.8	0.266	21.5	0.16	0.69
SBL samples												
site 1595	0.0	12.20	0.156	20.1	0.257	10.9	0.349	165.3	4.235	161.9	5.18	10.18
site 1601	0.0	22.70	0.269	30.4	0.360	11.0	0.326	209.2	4.953	200.0	5.92	11.82
site 1607	0.0	24.30	0.231	26.1	0.248	7.8	0.185	324.4	6.166	197.0	4.68	11.51
site 1615	0.0	8.50	0.076	29.9	0.266	10.0	0.223	57.0	1.016	147.0	3.27	4.85

Table A3-2 Extractable Mercury Data

Sol'n indicates concentration detected in leachate solutions, µg/L
Sed indicates concentration in ng/g in sediment (dry weight basis)
n.d. indicates not detected

Core #	sample	Depth cm	BS sol'n µg/L	BS sed ng/g	AS sol'n µg/L	AS sed ng/g	OX sol'n µg/L	OX sed µg/g	TOTAL Hg ng/g
1988gc2									
	1	0.5	3.09	42.74	4.83	44.54	1.37	31.58	118.85
	2	1.5	2.14	45.23	2.63	37.06	1.09	38.40	120.68
	3	2.5	0.89	11.78	2.61	23.03	2.52	55.59	90.40
	4	3.5	0.62	6.94	1.76	13.13	3.20	59.69	79.76
	5	4.5	0.52	7.06	1.19	10.78	2.67	60.44	78.28
	6	5.5	0.17	1.71	0.15	1.00	3.30	55.25	57.96
	7	6.5	n.d.	n.d.	0.20	1.44	1.35	24.33	25.77
	8	7.5	n.d.	n.d.	0.26	1.37	0.76	9.98	11.35
	9	8.5	n.d.	n.d.	0.06	0.51	0.15	3.21	3.73
	10	9.5	n.d.	n.d.	0.13	0.92	0.32	5.68	6.60
	11	10.5	0.08	0.87	0.23	1.66	0.25	4.52	7.05
	12	11.5	0.02	0.19	0.11	0.71	0.27	4.33	5.23
	13	15.0	0.05	0.62	0.06	0.50	0.51	10.56	11.68
	14	25.0	n.d.	n.d.	0.04	0.23	0.49	6.93	7.16
	15	35.0	n.d.	n.d.	0.36	1.84	2.62	33.50	35.34
	16	45.0	0.11	1.08	0.10	0.65	1.10	17.95	19.68
	17	55.0	n.d.	n.d.	n.d.	n.d.	0.94	13.51	13.51
	18	65.0	n.d.	n.d.	n.d.	n.d.	0.68	8.11	8.11
	19	75.0	n.d.	n.d.	n.d.	n.d.	1.88	24.55	24.55
	20	77.0	n.d.	n.d.	0.05	0.30	0.70	10.46	10.76
1988gc9									
	1	0.5	0.87	14.82	4.01	45.53	1.22	34.63	94.97
	2	1.5	0.80	12.09	4.40	44.33	1.19	29.97	86.39
	3	2.5	0.41	4.86	1.88	14.87	2.26	44.69	64.43

Table A3-2 (cont'd).

Core #	sample	Depth cm	BS sol'n µg/L	BS sed ng/g	AS sol'n µg/L	AS sed ng/g	OX sol'n µg/L	OX sed ng/g	TOTAL Hg ng/g
1988gc9									
	4	3.5	n.d.	n.d.	0.96	9.33	2.91	70.69	80.02
	5	4.5	n.d.	n.d.	0.37	2.78	4.06	76.19	78.97
	6	5.5	n.d.	n.d.	0.05	0.33	6.38	104.82	105.15
	7	6.5	n.d.	n.d.	0.07	0.42	5.48	82.31	82.73
	8	7.5	n.d.	n.d.	0.01	0.05	1.96	26.67	26.72
	9	8.5	n.d.	n.d.	0.01	0.06	0.82	13.24	13.31
	10	9.5	n.d.	n.d.	0.01	0.05	0.97	12.30	12.35
	11	10.5	n.d.	n.d.	0.02	0.13	0.86	13.80	13.93
	12	11.5	n.d.	n.d.	0.07	0.55	0.64	12.60	13.15
	13	13.0	n.d.	n.d.	0.01	0.06	1.58	22.59	22.64
	14	19.0	n.d.	n.d.	0.05	0.45	0.95	21.58	22.04
	15	25.0	n.d.	n.d.	0.06	0.40	0.75	12.62	13.02
	16	31.0	n.d.	n.d.	0.01	0.07	0.75	12.43	12.49
	17	37.0	n.d.	n.d.	0.01	0.06	0.74	10.72	10.78
	18	43.0	n.d.	n.d.	0.01	0.06	0.95	13.52	13.58
	19	49.0	n.d.	n.d.	0.02	0.13	0.66	10.75	10.88
	20	55.0	n.d.	n.d.	0.01	0.04	0.76	7.79	7.83
	21	61.0	n.d.	n.d.	0.05	0.22	0.68	7.64	7.86
	22	67.0	n.d.	n.d.	0.07	0.36	0.63	8.04	8.40
	23	73.0	n.d.	n.d.	0.01	0.05	0.60	7.54	7.59
	24	79.0	n.d.	n.d.	0.03	0.16	0.46	6.31	6.48
1988gc17									
	1	0.5	6.66	118.07	2.48	36.64	0.46	13.59	168.30
	2	1.5	3.84	39.70	2.65	22.83	1.01	17.41	79.94
	3	2.5	2.16	20.35	1.33	10.86	0.84	13.19	44.41
	4	3.5	0.98	10.00	0.63	5.44	0.39	6.63	22.08

Table A3-2 (cont'd).

Core #	sample	Depth cm	BS sol'n µg/L	BS sed ng/g	AS sol'n µg/L	AS sed ng/g	OX sol'n µg/L	OX sed ng/g	TOTAL Hg ng/g
1988gc17									
	5	4.5	0.25	1.71	0.05	0.32	0.42	4.80	6.84
	6	5.5	0.02	0.23	0.09	0.88	0.34	6.48	7.59
	7	6.5	n.d.	n.d.	0.01	0.09	0.43	7.33	7.42
	8	7.5	n.d.	n.d.	0.21	0.99	0.52	4.94	5.93
	9	8.5	n.d.	n.d.	0.07	0.61	0.32	5.56	6.18
	10	9.5	n.d.	n.d.	0.02	0.15	0.52	8.05	8.21
	11	10.5	n.d.	n.d.	0.15	1.15	0.44	6.40	7.55
	12	11.5	n.d.	n.d.	0.17	1.15	0.47	6.53	7.69
	13	13.0	n.d.	n.d.	0.05	0.33	1.00	13.52	13.85
	14	15.0	n.d.	n.d.	0.04	0.34	0.67	12.43	12.77
	15	17.0	n.d.	n.d.	0.12	0.79	0.79	10.43	11.22
	16	19.0	n.d.	n.d.	0.07	0.51	0.59	8.74	9.25
	17	26.0	n.d.	n.d.	n.d.	n.d.	0.49	8.22	8.22
	18	33.0	n.d.	n.d.	0.05	0.33	0.65	8.96	9.29
	19	40.0	n.d.	n.d.	0.01	0.06	0.81	10.68	10.74
	20	47.0	n.d.	n.d.	0.05	0.32	0.54	7.83	8.16
	21	54.0	n.d.	n.d.	0.04	0.35	0.43	8.51	8.86
	22	61.0	n.d.	n.d.	n.d.	n.d.	0.80	9.60	9.60
	23	68.0	n.d.	n.d.	n.d.	n.d.	0.84	7.46	7.46
	24	75.0	n.d.	n.d.	0.01	0.07	0.75	11.93	12.00
1988gc22									
	1	0.5	2.84	22.03	2.34	13.80	4.34	56.12	91.95
	2	1.5	0.85	8.13	0.84	6.05	1.47	23.42	37.60
	3	2.5	0.35	2.78	1.09	6.70	1.35	17.89	27.38
	4	3.5	0.43	3.38	0.83	5.14	1.13	14.82	23.34
	5	4.5	n.d.	n.d.	0.89	4.54	1.38	14.67	19.21

Table A3-2 (cont'd).

Core #	sample	Depth cm	BS sol'n µg/L	BS sed ng/g	AS sol'n µg/L	AS sed ng/g	OX sol'n µg/L	OX sed ng/g	TOTAL Hg ng/g
1988gc22									
	6	5.5	n.d.	n.d.	1.14	8.10	1.05	16.22	24.32
	7	7.0	n.d.	n.d.	1.01	8.51	1.03	18.87	27.38
	8	9.0	n.d.	n.d.	0.07	0.48	1.50	22.56	23.04
	9	11.0	n.d.	n.d.	0.08	0.53	1.33	19.07	19.60
	10	12.5	n.d.	n.d.	n.d.	n.d.	1.34	19.18	19.18
	11	13.5	n.d.	n.d.	0.03	0.17	1.53	18.98	19.15
	12	14.5	n.d.	n.d.	0.01	0.06	1.39	19.16	19.22
	13	15.5	n.d.	n.d.	0.06	0.41	2.73	39.22	39.63
	14	16.5	n.d.	n.d.	n.d.	n.d.	1.88	32.49	32.49
	15	17.5	n.d.	n.d.	n.d.	n.d.	1.67	22.87	22.87
	16	18.5	n.d.	n.d.	0.01	0.05	2.08	19.94	19.98
	17	19.5	n.d.	n.d.	n.d.	n.d.	1.14	15.99	15.99
	18	20.5	n.d.	n.d.	n.d.	n.d.	1.21	14.16	14.16
	19	21.5	n.d.	n.d.	0.06	0.29	1.13	13.25	13.54
	20	23.0	n.d.	n.d.	0.07	0.44	1.16	16.71	17.15
	21	25.0	n.d.	n.d.	0.08	0.43	1.04	13.23	13.66
	22	32.0	n.d.	n.d.	n.d.	n.d.	1.12	11.23	11.23
	23	39.0	n.d.	n.d.	n.d.	n.d.	0.95	14.82	14.82
	24	46.0	n.d.	n.d.	0.12	0.64	6.03	75.35	75.98
1989gc8									
	1	0.5	1.13	18.86	1.53	17.53	1.26	35.05	71.44
	2	1.5	0.16	2.49	0.82	8.85	0.76	19.72	31.06
	3	2.5	0.32	4.40	0.37	3.50	0.75	17.20	25.10
	4	3.5	n.d.	n.d.	0.32	2.87	0.92	19.82	22.68
	5	4.5	n.d.	n.d.	0.17	2.01	0.75	21.13	23.14
	6	5.5	n.d.	n.d.	0.26	2.58	0.83	19.21	21.78

Table A3-2 (cont'd).

Core #	sample	Depth cm	BS sol'n µg/L	BS sed ng/g	AS sol'n µg/L	AS sed ng/g	OX sol'n µg/L	OX sed ng/g	TOTAL Hg ng/g
1989gc8									
	7	6.5	n.d.	n.d.	0.09	0.58	1.22	17.36	17.94
	8	7.5	n.d.	n.d.	0.23	2.09	0.79	16.60	18.69
	9	8.5	n.d.	n.d.	0.14	1.31	0.91	18.71	20.03
	10	9.5	n.d.	n.d.	0.10	1.40	0.59	18.83	20.23
	11	10.5	n.d.	n.d.	0.12	1.28	0.72	17.17	18.45
	12	12.0	n.d.	n.d.	0.17	1.17	1.03	15.92	17.09
	13	14.0	n.d.	n.d.	0.08	0.46	1.28	17.13	17.59
	14	16.0	n.d.	n.d.	0.16	1.20	0.97	17.29	18.48
	15	18.0	n.d.	n.d.	0.15	0.96	1.10	15.84	16.80
	16	20.0	n.d.	n.d.	0.07	0.60	1.07	20.49	21.08
	17	22.0	n.d.	n.d.	0.02	0.13	1.09	15.81	15.93
	18	24.0	n.d.	n.d.	0.10	0.62	1.06	15.38	16.00
	19	26.5	n.d.	n.d.	0.10	0.73	1.04	17.18	17.91
	20	29.5	n.d.	n.d.	n.d.	n.d.	0.95	8.14	8.14
	21	32.5	n.d.	n.d.	n.d.	n.d.	0.92	12.13	12.13
	22	36.5	n.d.	n.d.	n.d.	n.d.	1.28	12.71	12.71
SBL samples									
site	1595	0.0	0.54	9.85	3.10	41.45	0.95	28.87	80.16
site	1601	0.0	1.55	30.52	3.49	49.93	1.00	32.81	113.26
site	1607	0.0	1.11	14.52	3.37	32.03	0.82	17.87	64.41
site	1615	0.0	1.13	14.15	1.83	17.27	1.30	27.14	58.56

Table A3-3. Porewater Data

n.d. = not detectable

Arsenic			Mercury			Ferrous Iron			pH & Alkalinity			
Core # Sample	Depth cm	As µg/L	Core # Sample	Depth cm	Hg µg/L	Core # Sample	Depth cm	Fe(II) mg/L	Core # Sample	Depth cm	pH	Alkalinity mg/L HCO3
Lake Michigan North Basin - 1												
88gc3			88gc2			88gc4			88gc1			
1	0.5	2.1	1	0.5	0.02	1	0.5	n.d.	1	0.5	6.35	153
2	1.8	4.7	2	1.5	0.12	2	1.5	0.29	2	1.5	7.00	153
3	3.0	6.3	3	2.5	0.09	3	2.5	0.99	3	2.5	7.25	167
4	4.0	9.6	4	3.5	0.04	4	3.8	1.52	4	3.5	7.45	160
5	5.0	9.4	5	4.5	0.06	5	4.8	1.70	5	4.5	7.50	167
6	6.0	8.8	6	5.5	0.11	6	5.8	0.88	6	5.5	7.55	175
7	7.0	8.4	7	6.5	0.14	7	6.8	1.02	7	6.5	7.60	165
8	8.0	8.1	8	7.5	0.11	8	8.1	0.96	8	7.5	7.55	184
9	9.0	8.5	9	8.5	0.04	9	9.5	1.16	9	8.5	7.50	179
10	10.0	9.5	10	9.5	0.05	10	10.6	0.89	10	9.5	7.45	175
11	11.0	8.0	11	10.5	0.07	11	11.6	0.96	11	10.5	7.50	169
12	17.5	8.6	12	11.5	n.d.	12	23.0	1.96	12	12.0	7.55	180
13	24.5	7.6	13	15.0	0.01	13	35.0	2.82	13	20.0	7.40	189
14	31.5	6.5	14	25.0	0.01	14	47.0	2.55	14	32.0	7.40	189
15	38.5	7.1	15	35.0	0.07				15	44.0	7.20	204
16	45.5	7.0	16	45.0	0.20				16	56.0	7.20	189
17	52.5	6.9	17	55.0	0.15				17	68.0	7.20	198
18	59.5		18	65.0	0.21				18	80.0	7.10	204
			19	75.0	0.11				19	92.0	7.10	204
			20	77.0	0.12				20	94.0	7.25	192

Table A3-3 (cont'd).

Arsenic			Mercury			Ferrous Iron			pH & Alkalinity			
Core # Sample	Depth cm	As µg/L	Core # Sample	Depth cm	Hg µg/L	Core # Sample	Depth cm	Fe(II) mg/L	Core # Sample	Depth cm	pH	Alkalinity mg/L HCO3
Lake Michigan North Basin - 2												
88gc11			**88gc9**			**88gc10**			**88gc7**			
1	0.5	2.0	1	0.5	0.05	1	0.5	n.d.	1	0.5	5.80	135
2	1.5	3.0	2	1.5	0.08	2	1.5	n.d.	2	1.5	7.00	159
3	2.5	3.5	3	2.5	0.08	3	2.5	n.d.	3	2.5	7.05	173
4	3.5	4.5	4	3.5	0.06	4	3.5	0.33	4	3.5	7.25	168
5	4.5	4.3	5	4.5	0.03	5	4.5	0.15	5	4.5	7.00	178
6	5.5	3.7	6	5.5	0.06	6	6.0	0.33	6	5.5	7.05	173
7	6.5	2.9	7	6.5	0.02	7	8.0	0.37	7	6.5	7.10	178
8	7.5	5.4	8	7.5	0.02	8	10.0	0.80	8	8.5	7.00	173
9	8.5	5.3	9	8.5	n.d.	9	12.0	0.63	9	9.5	7.05	183
10	9.5	4.2	10	9.5	0.02	10	14.0	0.80	10	11.5	7.15	178
11	10.5	5.9	11	10.5	n.d.	11	16.0	0.80	11	12.5	7.30	183
12	12.0	5.2	12	11.5	0.01	12	28.0	0.93	12	19.0	7.20	178
13	18.0	7.1	13	13.0	n.d.	13	40.0	1.00	13	26.0	7.15	178
14	24.0	8.8	14	19.0	n.d.	14	52.0	0.73	14	28.0	7.05	183
15	30.0	5.3	15	25.0	n.d.	15	64.0	1.20	15	34.0	7.20	183
16	36.0	15.3	16	31.0	0.01	16	76.0	1.20	16	38.0	7.05	178
17	42.0	7.1	17	37.0	0.10				17	46.0	7.10	197
18	48.0	5.1	18	43.0	0.10				18	52.0	7.00	188
19	54.0	7.8	19	49.0	0.11				19	58.0	7.10	202
20	60.0	5.6	20	55.0	0.12				20	64.0	7.00	182
21	66.0	7.0	21	61.0	0.11				21	70.0	7.00	203
22	72.0	6.3	22	67.0	0.05				22	76.0	7.00	203
23	78.0	7.0	23	73.0	0.08				23	82.0	7.00	200
24	84.0	6.8	24	79.0	0.10				24	88.0	7.00	197
									25	96.0	7.00	207

Table A3-3 (cont'd).

Arsenic			Mercury			Ferrous Iron			pH & Alkalinity			
Core # Sample	Depth cm	As µg/L	Core # Sample	Depth cm	Hg µg/L	Core # Sample	Depth cm	Fe(II) mg/L	Core # Sample	Depth cm	pH	Alkalinity mg/L HCO3
Lake Superior - Ile Parisienne												
88gc15			**88gc17**			**88gc15**			**88gc12**			
1	0.5	1.9	1	0.5	0.10	1	0.5	n.d.	1	0.5	6.40	45.4
2	1.5	2.3	2	1.5	0.18	2	1.5	n.d.	2	1.5	6.90	44.5
3	2.5	7.0	3	2.5	0.14	3	2.5	2.10	3	2.3	6.95	31.8
4	3.5	2.6	4	3.5	0.17	4	3.5	2.40	4	2.9	7.20	31.8
5	4.5	7.5	5	4.5	0.14	5	4.5	2.25	5	3.8	7.20	28.1
6	5.5	8.4	6	5.5	0.08	6	5.5	2.30	6	4.8	7.30	29.3
7	7.0	4.9	7	6.5	0.15	7	7.0	4.30	7	5.8	6.90	46.8
8	9.0	7.9	8	7.5	n.d.	8	9.0	2.70	8	6.8	7.10	48.3
9	11.0	10.3	9	8.5	0.15	9	11.0	2.40	9	7.8	6.90	48.3
10	13.0	7.9	10	9.5	0.14	10	13.0	4.15	10	9.1	6.75	61.0
11	15.0	12.0	11	10.5	0.04	11	15.0	4.35	11	11.0	6.65	61.0
12	17.0	10.1	12	11.5	0.04	12	17.0	5.05	12	13.0	7.20	73.7
13	29.0	8.2	13	13.0	0.01	13	29.0	2.85	13	15.0	7.10	66.1
14	41.0	5.8	14	15.0	0.02	14	41.0	2.65	14	21.0	6.80	73.7
15	53.0	6.1	15	17.0	0.03	15	53.0	3.20	15	27.0	6.65	83.9
16	75.0	8.1	16	19.0	0.01	16	65.0	5.40	16	33.0	6.80	68.6
			17	26.0	0.07				17	39.0	6.90	91.5
			18	33.0	0.50				18	45.0	6.85	96.6
			19	40.0	n.d.				19	51.0	6.80	107
			20	47.0	n.d.				20	55.0	6.55	117
			21	54.0	0.30				21	63.0	6.60	117
			22	61.0	n.d.				22	69.0	6.50	120
			23	68.0	0.09							
			24	75.0	n.d.							

Table A3-3 (cont'd).

Arsenic			Mercury			Ferrous Iron			pH & Alkalinity			
Core # Sample	Depth cm	As µg/L	Core # Sample	Depth cm	Hg µg/L	Core # Sample	Depth cm	Fe(II) mg/L	Core # Sample	Depth cm	pH	Alkalinity mg/L HCO3
Lake Superior - Caribou Basin												
88gc25			**88gc22**			**88gc25**			**88gc19**			
1	0.5	0.9	1	0.5	0.21	1	0.5	n.d.	1	0.5	7.00	44.9
2	1.5	0.6	2	1.5	0.29	2	1.5	n.d.	2	1.5	6.90	38.9
3	2.5	0.8	3	2.5	0.29	3	2.5	n.d.	3	2.5	7.70	43.1
4	3.5	0.4	4	3.5	0.35	4	3.5	n.d.	4	3.5	7.70	44.9
5	4.5	0.3	5	4.5	0.14	5	4.5	n.d.	5	4.5	7.70	41.9
6	5.5	0.2	6	5.5	0.27	6	5.5	n.d.	6	5.5	7.60	41.9
7	7.0	0.1	7	6.5	0.23	7	7.0	n.d.	7	6.5	7.60	43.1
8	9.0	0.4	8	7.5	0.28	8	9.0	n.d.	8	7.5	7.40	45.5
9	11.0	0.2	9	8.5	0.18	9	11.0	n.d.	9	8.5	6.80	44.9
10	12.5	0.4	10	9.5	0.14	10	12.5	n.d.	10	9.5	7.30	44.9
11	13.5	1.2	11	10.5	0.16	11	13.5	n.d.	11	10.5	7.30	48.5
12	14.5	0.9	12	11.5	0.07	12	14.5	n.d.	12	11.5	7.30	49.1
13	15.5	1.5	13	13.0	0.15	13	15.5	n.d.	13	12.5	7.30	50.9
14	16.5	n.m.	14	15.0	0.20	14	16.5	n.d.	14	13.5	7.30	50.9
15	17.5	1.8	15	17.0	0.23	15	17.5	n.d.	15	14.8	7.40	49.7
16	18.5	2.0	16	19.0	0.54	16	18.5	0.10	16	16.0	7.30	49.7
17	19.5	3.5	17	26.0	0.77	17	19.5	0.20	17	17.3	7.00	53.9
18	20.5	n.m.	18	33.0	0.27	18	20.5	0.13	18	19.0	7.20	55.7
19	21.5	3.5	19	40.0	0.24	19	21.5	0.18	19	21.0	7.30	57.5
20	23.0	2.5	20	47.0	0.21	20	23.0	0.13	20	23.0	7.30	62.9
21	25.0	n.m.	21	54.0	0.28	21	25.0	0.05	21	25.0	7.30	64.1
22	32.0	7.0	22	61.0	0.20	22	32.0	0.45	22	32.0	7.40	76.6
23	39.0	13.3	23	68.0	0.24	23	39.0	0.58	23	39.0	7.30	83.8
24	46.0	8.9	24	75.0	0.22	24	46.0	0.25	24	46.0	7.40	100
n.m. = not measured						25	53.0	0.58	25	53.0	7.50	101

Table A3-3 (cont'd).

Arsenic			Mercury			Ferrous Iron			pH & Alkalinity			
Core # Sample	Depth cm	As µg/L	Core # Sample	Depth cm	Hg µg/L	Core # Sample	Depth cm	Fe(II) mg/L	Core # Sample	Depth cm	pH	Alkalinity mg/L HCO3
Gulf of Maine - Murray Basin												
89gc3			**89gc8**			**89gc6**			**89gc5**			
1	0.5	5.2	1	0.5	0.02	1	0.5	0.021	1	0.5	7.53	138
2	1.5	6.5	2	1.5	n.d.	2	1.5	0.017	2	1.5	7.40	120
3	2.5	7.3	3	2.5	0.04	3	2.5	0.025	3	2.5	7.39	138
4	3.5	7.9	4	3.5	n.d.	4	3.5	0.019	4	3.5	7.30	103
5	4.5	8.8	5	4.5	0.04	5	4.5	0.015	5	4.5	7.29	106
6	5.5	5.2	6	5.5	0.04	6	5.5	0.023	6	5.5	7.29	155
7	6.5	4.0	7	6.5	0.02	7	6.5	0.019	7	6.5	7.30	189
8	7.5	4.3	8	7.5	0.05	8	7.5	0.056	8	7.5	7.31	182
9	8.5	5.7	9	8.5	0.02	9	8.5	0.015	9	8.5	7.32	196
10	9.5	7.1	10	9.5	0.07	10	9.5	0.047	10	9.5	7.47	103
11	10.5	5.7	11	10.5	n.d.	11	11.0	0.499	11	10.5	7.33	151
12	12.0	13.8	12	12.0	0.06	12	13.0	0.663	12	12.0	7.34	148
13	14.0	17.5	13	14.0	0.06	13	15.0	0.713	13	14.0	7.38	196
14	16.0	21.3	14	16.0	0.02	14	17.0	0.495	14	16.0	7.43	168
15	18.0	11.0	15	18.0	0.05	15	19.0	0.234	15	18.0	7.42	261
16	20.0	16.4	16	20.0	0.02	16	21.0	0.170	16	20.0	7.44	203
17	22.0	17.0	17	22.0	0.05	17	23.0	0.062	17	22.0	7.46	203
18	24.0	17.0	18	24.0	n.d.	18	25.0	0.071	18	24.0	7.39	244
19	26.5	22.1	19	26.5	n.d.	19	28.0	0.030	19	26.5	7.26	299
20	29.5	18.9	20	29.5	0.03				20	29.5	7.27	330
21	32.5	25.5	21		n.d.				21	32.5	7.27	381
22	36.5	11.9	22		n.d.				22	35.5	7.36	433
23	41.5	30.4							23	38.5	7.34	330
24	46.5	43.0							24	41.5	7.25	328

Table A3-4. Organic Carbon Data

Site	Core #	% OC	Depth (cm)	Site	Core #	% OC	Depth (cm)
Lake	LMNB-1-SBL	2.55	0.0	LMNB-2	88gc11-9	2.42	8.5
Michigan	1988gc3-1	3.21	0.5		10	2.42	9.5
North	2	3.13	1.8		11	2.77	10.5
Basin - 1	3	2.91	3.0		12	2.69	12.0
	4	2.66	4.0		13	2.60	18.0
	5	2.38	5.0		14	2.98	24.0
	6	2.39	6.0		15	2.69	30.0
	7	2.24	7.0		16	2.74	36.0
	8	2.26	8.0		17	2.74	42.0
	9	2.29	9.0		18	2.49	48.0
	10	2.11	10.0		19	2.47	54.0
	11	3.19	11.0		20	2.10	60.0
	12	1.85	17.5		21	2.18	66.0
	13	2.45	24.5		22	2.14	72.0
	14	2.36	31.5		23	2.13	78.0
	15	2.49	38.5		24	2.05	84.0
	16	2.11	45.5				
	17	1.99	52.5	Lake	LSIP-SBL	2.76	0.0
	18	2.05	59.5	Superior	1988gc15-1	1.44	0.5
				Ile	2	1.00	1.5
Lake	LMNB-2-SBL	3.22	0.0	Parisienne	3	0.98	2.5
Michigan	1988gc11-1	3.17	0.5		4	0.46	3.5
North	2	3.30	1.5		5	0.59	4.5
Basin - 2	3	3.02	2.5		6	0.99	5.5
	4		3.5		7	0.84	7.0
	5	2.69	4.5		8	0.94	9.0
	6	2.61	5.5		9	0.78	11.0
	7	2.57	6.5		10	1.09	13.0
	8	3.04	7.5		11	1.23	15.0

Table A3-4 (cont'd).

Site	Core #	% OC	Depth (cm)	Site	Core #	% OC	Depth (cm)
LSIP	88gc15-12	1.62	17.0	LSCB	88gc25-22	1.64	32.0
	13	1.51	29.0		23	1.66	39.0
	14	1.53	41.0		24	0.43	46.0
	15	1.67	53.0				
	16	1.37	75.0		1989gc3-1	1.58	0.5
				Gulf of	2	1.13	1.5
Lake	LSCB-SBL	3.96	0.0	Maine	3	1.81	2.5
Superior	1988gc25-1	3.29	0.5	Murray	4	1.71	3.5
Caribou	2	3.24	1.5	Basin	5	1.76	4.5
Basin	3	2.70	2.5		6	1.66	5.5
	4	2.38	3.5		7	1.66	6.5
	5	2.29	4.5		8	1.69	7.5
	6	2.02	5.5		9	1.80	8.5
	7	1.95	7.0		10	1.66	9.5
	8	1.90	9.0		11	1.61	10.5
	9	1.80	11.0		12	1.81	12.0
	10	1.53	12.5		13	1.89	14.0
	11	1.63	13.5		14	1.85	16.0
	12	1.70	14.5		15	1.88	18.0
	13	1.31	15.5		16	1.84	20.0
	14	1.24	16.5		17	1.73	22.0
	15	1.71	17.5		18	1.71	24.0
	16	2.24	18.5		19	1.25	26.5
	17	1.79	19.5		20	1.74	29.5
	18	2.26	20.5		21	1.67	32.5
	19	1.29	21.5		22	1.89	36.5
	20	1.27	23.0		23	1.75	41.5
	21	1.51	25.0		24	1.89	46.5

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