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This is to certify that the

thesis entitled

THE EXTRACTION OF MERCURY FROM
SEDIMENT AND
THE GEOCHEMICAL PARTITIONING OF MERCURY
IN SEDIMENTS FROM LAKE SUPERIOR

presented by

Judith Lynn Strunk

has been accepted towards fulfillment
of the requirements for

M.S. degree in Geology

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Major professor

Date May 13, 1991

O-7639

THE EXTRACTION OF MERCURY FROM SEDIMENT AND THE GEOCHEMICAL PARTITIONING OF MERCURY IN SEDIMENTS FROM LAKE SUPERIOR

By

Judith Lynn Strunk

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Geology

1991

ABSTRACT

THE EXTRACTION OF MERCURY FROM SEDIMENT AND THE GEOCHEMICAL PARTITIONING OF MERCURY IN SEDIMENTS FROM LAKE SUPERIOR

By

Judith Lynn Strunk

Sequential partial extractions were performed on sediment from cores taken from Lake Superior during the summer of 1986. The cores were collected using a manned submersible. This allowed for delicate sampling of the very top layers as well as those below. The sediment was extracted, then the supernatant analyzed for mercury using cold vapor AAS, using sodium borohydride as a reductant. The phases analyzed included exchangeable, humic-fulvic acids, acid soluble, organic/sulfide phase and the residual phase. Steady state analysis was performed on sediment from a mercury contaminated lake prior to the extractions of Lake Superior sediments. The majority of the mercury is in the humic-fulvic acid and organic/sulfide phase. In general the highest level of mercury is in the top of the core. The level of mercury rapidly drops off to its lowest level at the redox zone in each core then levels off at a steady concentration.

This thesis is dedicated to my husband Larry, my daughter Laurel, the baby on the way, my parents Mr. and Mrs. Calvin Campbell and my inlaws Mr. and Mrs. Larry Strunk.

ACKNOWLEDGMENTS

I would like to thank my advisor Professor David Long for his assistance with this work. In addition I would like to thank my committee members Professors Frank D'Itri, Michael Velbel, and Duncan Sibley for all their help and suggestions. I would also like to acknowledge my husband Larry for help with the computer in preparing this thesis.

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INTRODUCTION

Problem:

Mercury levels in lakes and other fresh water systems have been intensely studied since the early 1970's. Many studies have focused on the biogeochemistry of mercury as related to organisms from algae to humans (Clarkson et al., 1984; Fimreite and Reynolds, 1973; Riisgard, 1984; Langston, 1982; Kristensen, 1982; Bjorkland et al., 1984; Glass, 1973; Evans et al., 1972; Annett et al., 1975; Annett et al., 1972; Seagran, 1970) specifically on mechanisms of methylation of mercury (Wood et al., 1968; Stary et al., 1980; Jensen and Jernelov 1969; Olsen and Cooper, 1974; Spangler et al., 1973; Clarkson et al., 1984; Verta, 1984; Tuncel et al., 1980;). Other studies have focused on desorption/adsorption phenomena (Rogers et al., 1984; Reimers and Krenkel, 1974; Ramamoorthy and Rust, 1976; MacNaughton and James, 1974; Newton et al., 1976; Farrah and Pickering, 1978; Forbes et al., 1974; Kinniburgh et al., 1978; Kudo et al., 1975 and Bothner et al., 1980), transport (Graf, 1985; Bjorkland et al., 1984; Bothner et al., 1980; Moore, 1981), relationship to particle size (Mudroch, 1983; Bartlett and Craig, 1981; Cranston, 1976), relationship to organic matter (Moore, 1981; Lindberg and Harriss, 1974; Langston, 1982; Kristensen, 1982; Crecelius et al., 1975) or organic carbon (Frimmel, et al., 1984), and the effect of atmospheric transport of acidic pollutants increasing heavy metal (Pb, Zn, Hg) concentrations (Ouellet and Jones, 1982; Jenne, 1970).

The behavior of mercury in bottom sediments is poorly understood. Most studies have considered that mercury is immobile once it is buried (Rossman, 1986; Johansen, 1983). This study examines mercury partitioning among phases of sediment to examine the hypothesis that mercury is remobilized during the early diagenesis of sediments. Other metals show remobilization during early diagenesis (McKee et al., 1988b), and desorption/adsorption studies show that mercury is associated with some of the same sediment phases that are involved in the remobilization of other trace metals. Therefore, one might expect mercury to be remobilized. Four sites in Lake Superior were chosen for this study.

Approach:

The lack of understanding of the behavior of mercury in bottom sediments is due to the fact that in previous aquatic studies sediment was analyzed for total mercury correlated with some other variable such as total organic matter, total organic carbon, sediment size and distance of transport (Table 1) (Bothner et al., 1980; Langston, 1982; Bartlett and Craig, 1981; Frenet, 1981; Lindberg et al., 1975; Riisgard, 1984; So, 1980; Tuncel et al., 1980; Baldi et al., 1983; Millward and Herbert 1981; Crecelius et al., 1975; Cranston, 1976; Eganhouse et al., 1978; Bjorkland et al., 1984; Graf, 1985; Hamdy and Post, 1985; Jenne, 1970; Mudroch, 1983; Verta, 1984; Ramamoorthy and Rust, 1976; Kristensen, 1982; Lindberg and Harriss, 1977), rather than the distribution of mercury in particular hydromorphic phases that can interact with aqueous solutions to either take up or release metals (Table 2). The hydromorphic fraction contains substrates such as clays, Fe-Mn oxides/hydroxides and organic matter. These phases are operationally defined by the chemical reaction used to extract them (exchangeable(clays), acid soluble (Fe-Mn oxides-hydroxides), base soluble (humic/fulvic acid), and oxidizable (organics/sulfides)]. Metal concentrations in these substrates are determined by sequential chemical extractions in which sediment is reacted with successively stronger chemicals (Salomons and Forstner, 1984). Metals in the detrital fraction occur in the lattice of resistant minerals and are not considered readily available to solution (Tessier et al., 1979; Forstner and Patchineelam, 1980). Because the extractions are neither totally effective in removing metals from a substrate nor totally specific for a substrate (Rendell et al., 1980; Forstner and Patchineelam,1980), results are interpreted in terms of operationally defined

Table 1: Summary of Selected Studies of Mercury in Sediments

Author/Location	**Study/Conclusion**
Langston, 1982 British Estuaries	Used selective attacks and found 64% of total extractable mercury in the organic fraction (H_2O_2), 4-32% in humic & fulvic acid phases (NaOH), and very small amounts in the oxide phase (HCl). Best correlation for mercury in sediments and total organic matter (TOM).
Cline, et al., 1973 St. Clair River	Used selective attacks. Correlation between sediment and amount of organic carbon in sediment pore water.
Chau and Saitoh, 1973 Great Lakes	Analyzed for total mercury. No apparent relationship between mercury in water and in sediments. No vertical stratification of mercury in surface vs. bottom waters. Much of the mercury is in suspended matter.
Lindberg and Harriss, 1977 Estuarine sediments	Correlation between sediment mercury and sediment organic matter, and between dissolved interstitial mercury and dissolved organic carbon.
Rae and Aston, 1981 Wyre Estuary, Irish Sea	Correlation between mercury levels and TOC and < 0.063 mm sized sediments.
Millward and Herbert, 1981 Plym Estuary	No correlation of mercury concentrations and organic carbon, clay, Fe or Mn.
Rae and Aston, 1982 Wyre Estuary, Irish Sea	Good correlation between mercury and organic carbon in the suspended solid.
Ramamoorthy and Rust, 1976 Ottawa River	Organic rich sediments have the highest mercury content. Also studied mercury adsorption/desorption, found organic rich sediment has the highest rate of adsorption.
Kristensen, 1982 stream sediment	Correlation between organic content and mercury content in the sediment.

Table 1 contiued: Summary of Selected Studies of Mercury in Sediments

Author/Location	Study/Conclusion
Crecelius et al., 1975 Pudget Sound	Used selective attacks. 82% of the mercury in the sediments is removed with H_2O_2 , 8% by a 10% NaCl solution.
Cranston, 1976 Estuary	Best correlation between mercury level and total surface area. No correlation with TOC.
Eganhouse et al., 1978 Palos Verdes sediment	Used selective chemical attacks. Most mercury found in residual and sulfide phase and small amounts with humic and fulvic acids.
Bartlett and Craig, 1981 Mersey Estuary, Britain	Correlation between mercury levels and TOC and silt sized sediment.
Kennedy et al., 1971 Southern Lake Michigan sediments	Correlation between mercury and organic carbon and mercury and total sulfur.
Phillips et al., 1987 Upper Missouri River Basin	Correlation between total mercury and deeper and, therefore, finer more highly organic sediments.

Table 2 HYDROMORPHIC PHASES AND EXTRACTIONS USED

Fraction	**Chemical Response**	**Extraction**	**Length of Extraction (hr)**
Adsorbed to Clays	Exchangeable	10% KCl	1
Humic and Fulvic Acids	Base Soluble	0.1 N NaOH	30
Fe and Mn Oxides	Acid Soluble	1 N HCl	6
Organics/Sulfides	Oxidizable	30% H_2O_2	6

phases rather than specific substrates (Forstner and Patchineelam, 1980). Even though chemical extractions are not totally efficient, results indicate metal partitioning among the hydromorphic phases are important in studying the behavior of metals in natural systems (Lion et al., 1982), particularly in terms of diagenetic processes (McKee et al., 1988a; Graybeal and Heath, 1984; Lyle et al., 1984; Skei and Paus, 1979; Fischer et al., 1986; Salomons and Forstner, 1984) and the bioavailability of metals in sediments (Langston, 1982; Pickering, 1981; Luoma and Bryan, 1981). Although a system of selective chemical extractions has been developed for trace metals, in general, there is no best single method for mercury. A variety of selective chemical extractions has been used by various scientists to desorb mercury from the sediment (Table 1). Many authors have not provided solid-solution ratios, optimum extraction temperatures, or optimum reaction times to be used. Thus, part of this study is to develop such a system of extractions. The approach is similar to Gephart (1982) and Tessier et al., (1979).

Hypothesis:

The model is that in large, deep lakes, pollutants such as dissolved forms of mercury adsorb to particulate matter in the water column and settle to lower depths in the water column eventually becoming incorporated into the bottom sediment. The suspended colloidal material in the water column above the sediment is known as the nepheloid layer. The top layer of the sediment has been termed "fluff" (McKee et al., 1988a). The fluff is the interface between the nepheloid layer and the sediment column and is easily resuspended in the water column. Mercury is adsorbed to organic material and Fe-Mn oxides. With depth in sediments redox conditions change, Fe-Mn oxides are reduced and organic material decays anaerobically. Mercury should be liberated from the sediment as it will also be reduced from the mercuric species to elemental mercury. The fate of this released mercury is not well known. It could be adsorbed onto sediments at different levels in the sediment column or be taken up by biota. This latter possibility may be indicated because the water column is relatively free of mercury, yet mercury levels in Great Lakes fish are elevated (Glass, 1973). Biomagnification of mercury could be one process causing elevated concentrations, however, the diagenetic release could be one major pathway of the mercury to biota. Biomagnification is an increase at each trophic level of the food chain of some element caused by ingestion of contaminated organisms lower in the food chain. This study is designed to determine the chemical processes important in mercury cycling in Lake Superior at the sediment-water interface and in the sediment column.

The following hypothesis has been formulated: Chemical processes occurring below the sediment-water interface cause mercury to be recycled into the overlying waters and sediments.

To test this hypothesis this study examines changes in mercury partitioning down sediment cores in selected areas of Lake Superior as a function of depth for evidence of recycling of mercury. From this the processes causing the recycling are inferred. From the above results, the sediment to water loss of mercury is calculated.

In order to accomplish this, the problems to be solved are to determine: (1) the selective chemical extraction methods suitable to selectively desorb mercury (2) the partitioning of mercury in the sediment of Lake Superior and (3) the partitioning of mercury across the sediment-water interface.

Because of the difficulty of obtaining samples from Lake Superior, experiments to determine the analytical procedures were run on sediment samples from a fresh water lake known to contain significant amounts of mercury. Deer Lake near Ishpeming in the Upper Peninsula of Michigan fits the criterion. The resulting "best methods" were then applied to samples from Lake Superior collected in the summer of 1986.

CHEMICAL PARTITIONING OF MERCURY:

Significance and Past Research:

Many studies dealing with metal ions associated with particulate matter in natural water systems report total metal concentration (Cragin and Foley, 1985; Bjorklund, et al., 1984; Hamdy and Post, 1973; Mudroch, 1983; Chau and Saitoh, 1973). However, only a few studies evaluate the partitioning of these metals, i.e. the phase they are associated with (Tessier et al., 1979). Total metal concentration of sediments does not usually provide information relative to how much is biologically or physico-chemically available, its mode of occurrence, mobilization, and transport of trace metals. To determine these parameters, hydromorphic states of the metal need to be determined (Gephart, 1982).

Bioavailability is one of the most important reasons chemical partitioning is studied. It is also one of the most difficult to define. Usually it is operationally defined, as the result of some chemical test or experiment. However there is no universally accepted method of determining bioavailability, therefore, the concept remains subject to much interpretation (Horowitz, 1985). Horowitz (1985) lists six methods for determining chemical partitioning:

1. Manual selection of phases and analysis,
2. Instrumental selection of phases and analysis,
3. Partial chemical extractions,
4. Density gradients and analysis,
5. Statistical manipulations of bulk chemical data,
6. Mathematical modeling.

Selective chemical extraction is one of the oldest and most commonly used methods to determine chemical partitioning in sediments. Much of the work was originally conducted on marine material (Goldberg and Arrhenius, 1958; Hirst and Nichols, 1958; Arrhenius and Korkish, 1959; Chester, 1965; Lynn and Bonatti, 1965; Chester and Hughes, 1966; 1967; 1969; Chester and Messiah-Hanna, 1970; Cronan and Garrett, 1973; Horowitz, 1974; Horowitz and Cronan, 1976). These early procedures usually involved two- or three- step sequential extractions, plus a total analysis. The first step of the sequential extractions typically utilizes a relatively mild chemical such as a salt solution to extract exchangeable metals, followed by successively stronger chemicals to extract more resistant fractions of the sediment. The concept of sequential extractions is based on a particular reagent being either phase specific or mechanism specific (e.g., acetic acid will only attack and dissolve carbonates)(Horowitz, 1985). After the initial work on marine sediments, further advances in chemical partitioning using sequential extractions have been made by workers in many fields (Bruland et al., 1974; Gupta and Chen, 1975; 1976; Chen et al., 1976; Luoma and Jenne, 1977; Malo, 1977; Forstner and Wittmann, 1979; Tessier et al., 1979; Nriagu and Coker, 1980; Diks and Allen, 1983). These workers attempted to differentiate between anthropogenic and natural inorganic pollutants and to try to predict or estimate bioavailability. Tessier et al.(1979) adapted an analytical procedure of soil chemical analysis to determine the partitioning of particulate trace metals (Cd, Co, Cu, Pb, Zn, Fe, and Mn) into the following five fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual. They found the standard deviation of the sequential selective extraction procedure to be better than ± 10%. "The accuracy, evaluated by comparing total trace metal concentrations to the sum of the individual fractions, proved to be satisfactory" (Tessier et al., 1979). Gupta and Chen (1975) also found the use of selective chemical attacks successful for Fe, Mn, Zn, Ni, Cr, Pb, Cd, and Cu with less than 10% deviation of mass balance for most trace metals.

The metal content in sediment can be distributed in various phases which range from fragments of the source rock (minerals, carbonates, sands) to accumulations of weathering products (hydrous oxides, clay minerals, organic matter). The mineral may be bound to the various components by a range of chemical processes e.g. ion exchange, adsorption, and compound formation (Pickering, 1981). Different types of chemical reactions may facilitate release of the heavy metals for the various fractions (Table 2). Therefore, an important aspect of sequential chemical analysis is the choice of the best reagent, one which will remove the particular phase of metal from the sediment, while leaving the structural components intact.

Several fractions have been found to bind mercury in previous studies. These include exchangeable phases such as mercury adsorbed onto surfaces of clays, sands and colloids (Cline et al., 1973), iron and manganese oxides/hydroxides (Rogers et al., 1984), oxidizable organic material (Lindberg and Harriss, 1974), and mercury associated with humic and fulvic acids (Langston, 1982; Mantoura et al., 1978; Millward and Burton, 1975).

Relatively few previous workers have examined partitioning of mercury in fresh water systems (Table 1). More marine studies of partitioning of mercury have been done but there is a problem with comparison of studies. Various researchers have used different sequential chemical extractions on different types of sediment found in different types of environments (marine, estuarine, and fresh water). This makes any comparison of data extremely difficult.

Of these 15 studies described in Table 1, only Cline et al. (1973) examined partitioning of mercury in fresh water systems and found correlation between sediment and amount of organic carbon in sediment pore water. Others were partitioning in marine environments, or correlation between total mercury and some other variable such as TOC, TOM, particle size, and/or sulfides.

The fractions most commonly considered for extraction are the ion exchangeable, the weakly adsorbed, organic bound, hydrous oxide segment and the lattice component (Pickering, 1981). For the ion exchangeable fraction the extractants used in previous studies for metals other than mercury include 0.1 M HCl, 5 M NH_4Cl, 1 M NH_4OAc, 1 M NaOAc, 0.05 M $CaCl_2$ and 1 M $MgCl_2$. Retrieval of the organic fraction has been accomplished with NaOCl or 30% H_2O_2 heated to 85° C (Tessier et al., 1979; Pickering, 1981; Rapin et al., 1983). EDTA and HCl release metal ions associated with both organic and oxide phases and, therefore, are used as extractants for determination of total metal species associated with nondetrital material (Pickering, 1981). Determination of the total lattice bound metal is usually based on the difference between total values and the sum of the various extraction values (Pickering, 1981). Total analysis may be based on either x-ray emission spectroscopy or complete dissolution of the solid sample. For dissolution method, a variety of acids have been used. Inclusion of H_2SO_4 in the mixture introduces the possibility of partial loss of those elements capable of forming sparingly soluble sulfates, while HNO_3 alone or in combination with HCl or $HClO_4$ does not completely dissolve some types of silicate minerals. For maximum recovery, HF has to be included in the mixture (Pickering, 1981).

Several problems with sequential partial extractions have recently been identified. One problem is they are not as selective as they ideally could be. Also efficiency of extraction varies according to length of treatment and sediment to extractant ratio (Forstner, 1982). Rauret et al. (1989) found the ratio of volume of extractant/weight of the sample very important while the effect of extraction time was barely noticed. Kheboian and Bauer (1987) suggest observed trends may be due to differing degrees of redistribution during extraction, influenced slightly by variations in sediment composition. Martin et al. (1987), states that the influence of matrix composition upon the amounts of the chemical extracted in each fraction means that intercomparison between different samples may be of questionable significance. Despite these limitations, sequential chemical extractions remain useful as they allow a differentiated approach in the study of interactive processes between water/biota and, though only operationally defined, solid phases (Salomons and Forstner, 1984; Martin et al., 1987). One of the advantages of sequential extractions is that they permit differentiation between samples having similar bulk chemistry. They also represent one of the few practical methods for the determination of concentration mechanisms and, therefore, provide a possible means for estimating bioavailability (Horowitz, 1985). Finally, they can provide the required chemical partitioning data needed for transport modeling (Horowitz, 1985). Selective chemical extractions also remain the only method widely available for studying partitioning of trace metals in sediments and across the sediment water interface.

Selective Chemical Extractions:

A sequential extraction procedure outlined by Tessier et al. (1979) and modified by Gephart (1982) and Tessier et al. (1985) has been shown to be useful for studying the behavior of heavy metals in natural systems (van Valin and Morse, 1982; Tessier et al., 1980; 1982; 1985; McKee et al., 1988a; 1988b). In this procedure metals in the hydromorphic fraction are sequentially extracted from clay minerals (exchangeable phase), carbonates (weakly acid soluble phase), Mn oxides (easily reducible phase), Fe oxides (moderately reducible phase), and organic matter plus sulfides (oxidizable phase). However, two of the steps in the procedure may not be appropriate for volatile elements such as mercury because they use hydroxylamine hydrochloride as a reducing agent to leach metals from iron and manganese oxides (Table 2). As a result, oxidized mercury may be reduced to its elemental form and lost from solution by volatilization. Therefore, modifications to the above extraction procedure are necessary to allow the partitioning of mercury in sediments to be determined, and to then use the modified extraction procedure to study mercury partitioning in four sediment cores from Lake Superior.

A KCl solution (Cline et al., 1973) is used to extract mercury from the exchangeable phase rather than $MgCl_2$ (Tessier et al., 1979), NaOAc or NH_4OAc (Forstner and Patchineelam, 1980; Eganhouse et al., 1978; Gibbs, 1977). Reagent grade $MgCl_2$, NaOAc, and NH_4OAc were found to be contaminated with mercury and, therefore, were not used in this study. In addition, the reaction of NH_4OAc caused severe condensation on the quartz cell during mercury analysis.

The extraction of mercury from the carbonate substrate or weakly acid-soluble phase and the hydroxylamine hydrochloride steps are eliminated, while NaOH (base soluble phase) and HCl (strongly acid soluble phase) extractions are added (Luoma and Bryan, 1981). NaOH is thought to extract metals associated with fulvic and humic acids (Pickering, 1981; Luoma and Bryan, 1981; Eganhouse et al., 1978; Jackson et al., 1982). Luoma and Bryan (1981) used HCl to extract metals associated with Fe and Mn oxides (Table 2). Unfortunately, mercury associated with Mn and Fe oxides cannot separately be differentiated by this extraction.

Langston (1982) used NaOH and HCl extractions to study mercury partitioning in selected British estuarine sediments. Reaction time was not given for the HCl extraction and is assumed to be the same as the reaction time used by Luoma and Bryan (1981). This assumption is made because Langston (1982) references Luoma and Bryan (1981) in his methods section. However, the behavior of mercury during these extractions has not been investigated as a function of reaction time with either the NaOH or HCl leach and, therefore, is determined in this study.

Tessier et al. (1979) used H_2O_2 adjusted to a pH of 2 with HNO_3 to extract metals from the oxidizable phase and this method has been used to extract mercury from sediments (Eganhouse et al., 1978). Unacidified H_2O_2 has also been used to extract metals, including mercury, from sediments (Jackson, 1958; Jackson et al., 1982; Cline et al., 1973). Langston (1982) used unacidified H_2O_2 to extract mercury from the oxidizable phase, but the details of the procedure were not given. In the present study, the procedures using unacidified H_2O_2 (Langston, 1982) and acidified H_2O_2 (Tessier et al., 1979) are compared. Reaction times appropriate for the mercury analysis are determined.

EXPERIMENTAL METHODS

Reaction-Time Experiments

The sediment for the extraction experiments was collected from Deer Lake, Ishpeming, Michigan in fall 1986. The release of mercury through the sewage treatment plant have caused the surface sediments of Deer Lake to be contaminated (MDPH, 1984). Total extractable mercury concentrations of up to 1.7 μg/g have been found (D'Itri, 1986). The Deer Lake sediments were air dried, broken up by porcelain mortar and pestle, and well mixed. Approximately 500 g were prepared for the investigation.

Total extractable mercury in the Deer Lake sample sediment was determined by reacting a 0.5 g aliquot with 4 ml 30 % H_2O_2 and 12.5 ml of concentrated H_2SO_4 (Hatch and Ott, 1968). The accuracy of the total extraction technique and mercury analysis, as described below, was checked by extracting mercury from the NBS No. 1645 river sediment standard.

To insure data quality samples were sent to the State of Michigan Department of Natural Resources (MDNR) for analysis. Sediment samples were extracted and the leachate sent to the MDNR for analysis. A subsample of the leachate was kept and analyzed in our laboratory.

Extractions were done sequentially in 50 ml polypropylene centrifuge bottles. After each extraction the sediments were rinsed with 10 ml of distilled-deionized water. Sediment was separated from the leachate by centrifuging for 20 min at 10,000 rpm in a Sorvall model SS-3 centrifuge. The leachate was then analyzed for mercury by flameless atomic absorption with a Perkin-Elmer 560 atomic absorption unit equipped with MHS-10 mercury/hydride system.

The procedure for the mercury analysis generally follows that recommended in the Perkin-Elmer Methods manual. To each 10 ml leachate sample to be analyzed for mercury (the minimum volume allowed by the hydride system), 5 drops of antifoam-A emulsion (Sigma Chemical), 2 drops of 5% $KMnO_4$ and 500 µl of concentrated HNO_3 were added. All reagents were checked for mercury contamination and the HNO_3 was purified by sub-boiling distillation. A solution of 3% $NaBH_4$ in 1 %NaOH was delivered to the sample via Ar gas causing the reduction of mercury to its elemental form which subsequently underwent volatilization. The mercury enriched vapor was passed through a quartz cell in the light path of the atomic absorption unit. An infra-red lamp was used to warm the quartz cell to control condensation.

The experiments to determine reaction times for the extractions are summarized below. The procedure is for a one gram sample. However for some of the reaction-time experiments, two grams were used and the extracting leachate doubled. This was done to increase the amount of leachate in the continuous monitoring experiments. The results from sequential chemical extraction remain the same as long as the sample/leachate ratio remains the same (McKee, 1986).

Exchangeable Fraction:

A number of salts were tried as extractants and found to be incompatible for this phase of the analysis. Among those tried were 3.2 M NH_4OAc, 1 M $MgCl_2$ reagent grade and gold label. All of these gave high absorbances for blanks indicating contamination of the chemicals. A 10% KCl solution was used as the extractant. Twenty ml of a 10% KCl solution was added to a 2 g sediment sample and reacted at room temperature (Cline et al., 1973). The leachate was sampled in 500 µl aliquots hourly over a 6 hr period and then again after 26 hr. Each 500 µl aliquot was combined with 10 ml of the KCl solution and analyzed for mercury, however, none was detected in any of the aliquots; therefore, the experiment was redesigned as follows. Approximately 10 g of the Deer Lake sediment was sieved through an 80 mesh sieve and well mixed. Seven homogenous samples one gram each were reacted with 10 % KCl at time intervals of 0.5, 1, 1.5, 2, 3, 4, 5 and 6 hr. Fifteen ml of the KCl solution was added to each sample. Mercury was measured at each monitoring time in a 10 ml aliquot from one of the samples.

Humic/Fulvic Acid Fraction:

A 0.1 N NaOH solution was used as the extractant for humic and fulvic acids. Steady state analysis was performed at intervals of 1, 2, 3, 4, 5, 6, and 7 days (Figure 1). Thirty ml of 0.1 N NaOH was added to each 2 g sediment samples at room temperature. Five hundred μl aliquots of the leachate were removed and analyzed. The peak of mercury extracted was reached between day 2 and 3, therefore, the experiment was performed again at intervals of 1, 6, 10, 20, 30, 40, and 126 hr. The aliquots were combined with 10 ml of 0.1 N NaOH and analyzed for mercury.

Acid Soluble Fraction:

HCl was used for this investigation and steady state analysis was performed. Twenty ml of 1 N HCl was added to a 2 g sample at room temperature to leach the Fe-Mn oxides (Luoma and Bryan, 1981). Removal and analysis of 500 μl aliquots diluted with 10 ml of 1 N HCl was performed and then abandoned because of very low concentrations of mercury in this phase. Homogeneous sieved samples were then used and extracted for 1, 1.5, 2, 2.5, 3, 4, 6, 8, 10 hr (Figure 2). A second 10 hour experiment was run and the mercury measured. To clearly identify the window in which steady state was reached for mercury, the same experiment was repeated for iron and manganese taking off 50 μl aliquots at time intervals of 1, 1.5, 2, 3, 4 , 6, 8, and 10 hr (Figure 2).

Organic/Sulfide Fraction:

The strongest extraction, the attack on the organic/sulfide fraction utilizes fresh 30% hydrogen peroxide. Two methods at 0^{o}, 25^{o}, 30^{o}, 40^{o}, 50^{o}, 60^{o}, 70^{o}, and 85^{o} Celsius were investigated. The first method by Langston, (1982) used 30% hydrogen peroxide. The second method, involved the addition of 0.02 M nitric acid to the sediment before the addition of the hydrogen peroxide (pH=2) (Tessier et al., 1979; Gephart, 1982). Ammonium chloride (2 M) in 20% nitric acid was added to the reaction in both Langston's and Tessier's methods one hour before analysis.

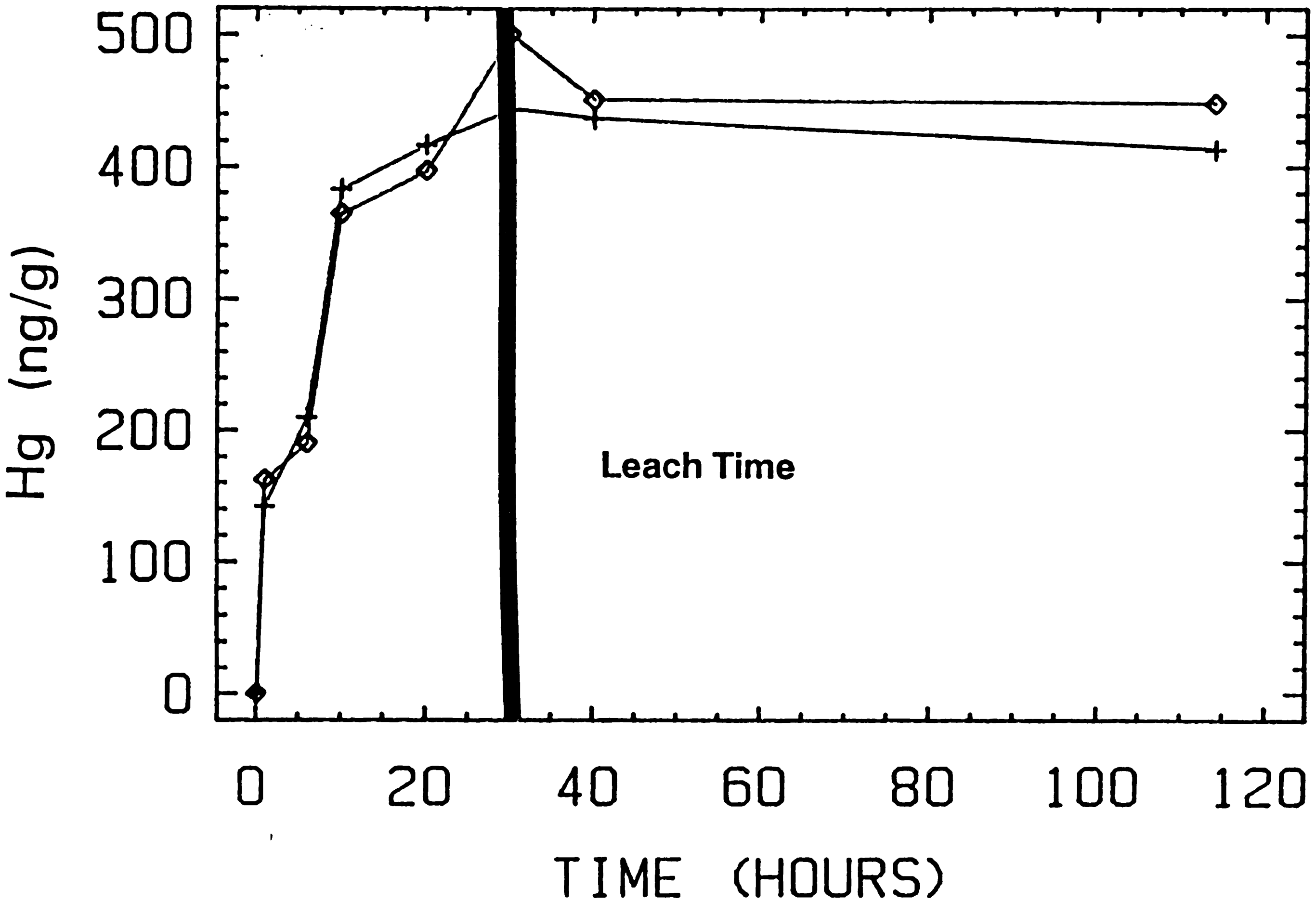

Figure 1 Base Soluble Fraction Steady State: NaOH Leach as a Function of Time

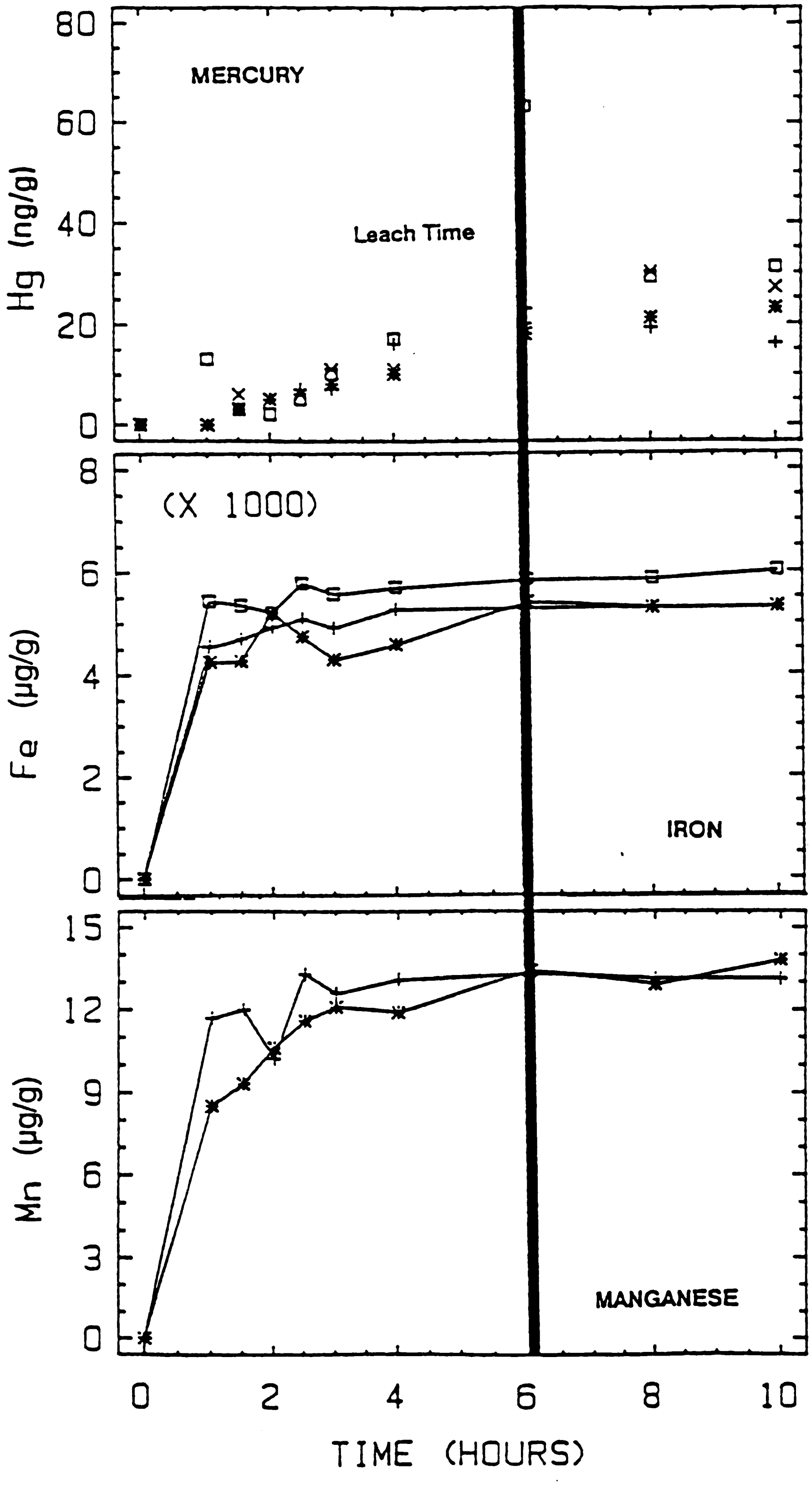

Figure 2 Acid Soluble Fraction Steady State: HCl Leach as a Function of Time

Langston's method (1982) involved slowly adding 5 ml of hydrogen peroxide to 1 g of sediment and analyzing after 2 hr, adding an additional 5 ml and analyzing after 4 and 5 hr. At 5.5 hr, after cooling to room temperature, 4 ml of ammonium chloride in 20% nitric acid was added and the supernatant analyzed after 6 hr. A 500 μl aliquot was drawn off and put in 10 ml of a blank solution consisting of the same proportions of reagents except hydrogen peroxide. Double distilled water was substituted for the hydrogen peroxide because of problems with the reaction between unreacted hydrogen peroxide and sodium borohydride used for the analysis.

The method by Tessier et al. (1979) method involved adding 2 ml of 0.02 M nitric acid and then slowly adding 4 ml hydrogen peroxide. Analysis was done at 0.5, 1.5,and 2 hr. Three additional ml of hydrogen peroxide was added and analysis was performed at 3, 4, and 5 hr. After cooling to room temperature 4 ml of 2 M ammonium chloride in 20% nitric acid was added and the supernatant analyzed after 6 hr. Aliquots of 500 μl were drawn off and analyzed for mercury. Determinations for steady state analysis was done at 0°, 25°, 60° and 85° C. (Figures 3 and 4). Additional temperature experiments without steady state were run at 0°, 25°, 30°, 40°, 50°, 60°, 70° and 85° C.

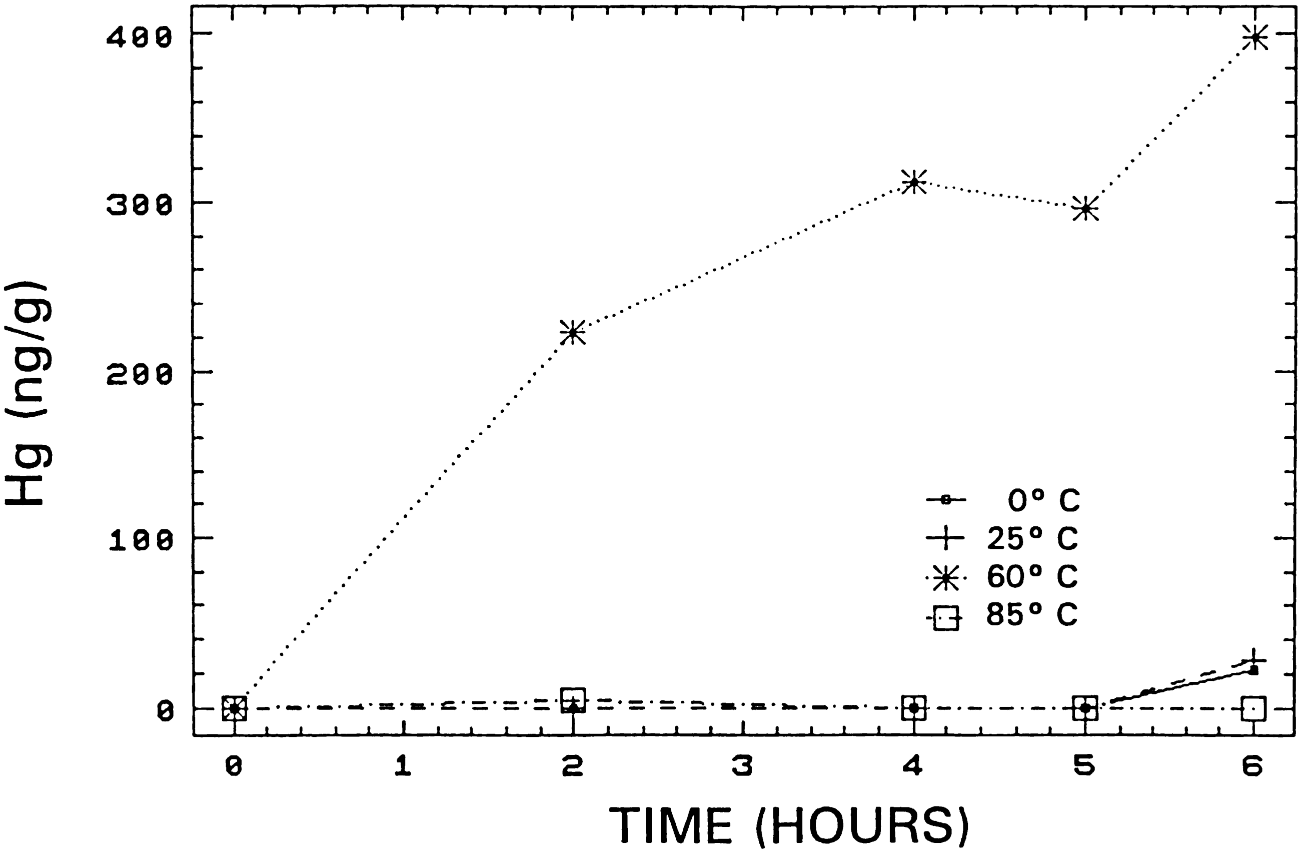

Figure 3 Oxidizable Fraction Steady State:
Langston's Method (1982) at Various Temperatures

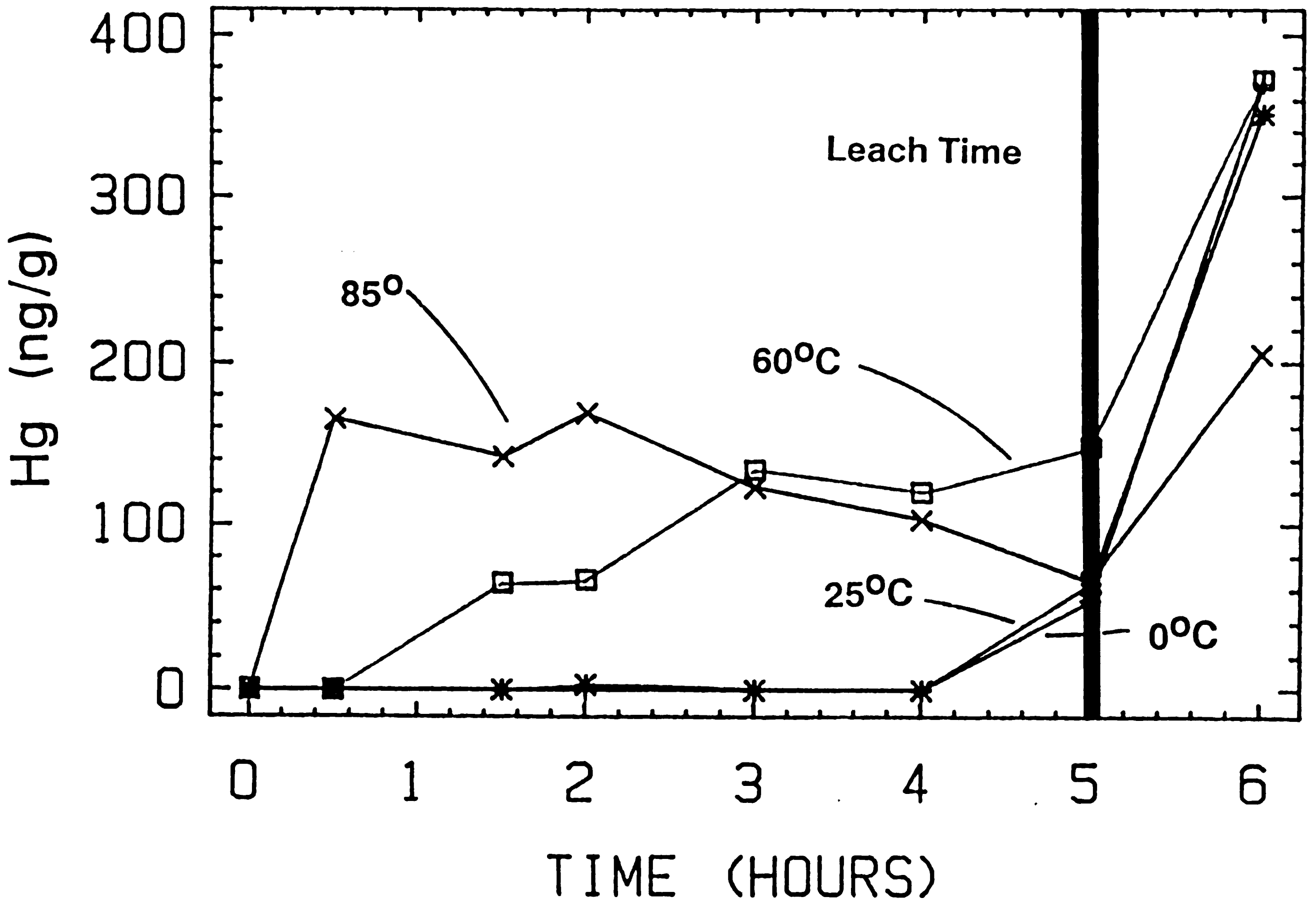

Figure 4 Oxidizable Fraction Steady State: Tessier's Method (1979) at Various Temperatures

RESULTS OF SELECTIVE CHEMICAL EXTRACTIONS:

Quality Assurance:

Total extractable mercury or that removed by selective chemical extractions, of the NBS #1645 river sediment standard was 725 ± 22 ng/g. The certified concentration of mercury in the standard is 1100 ± 50 ng/g. The mercury extracted using H_2SO_4, a method used to remove all of the mercury in one extraction, was 772 ng/g, within the range expected for the standard. In addition, results of samples sent to the MDNR laboratory agreed very well with results obtained in this study (Table 3).

Exchangeable Fraction:

As mentioned previously the exchangeable fraction experiments had to be redesigned because there wasn't enough mercury to detect when small aliquots were added to 10 ml of solution. Homogeneous sub-splits were, therefore, analyzed. The advantage of using homogeneous samples is that a larger sample can be taken at a monitoring time than when one sample-leachate mixture is repetitively sampled, allowing lower concentrations of mercury to be detected. The disadvantage of this method is that using a separate sample for each time interval can introduce variability in the reaction-time curve, because it is difficult to obtain chemically homogeneous sub-splits of a sample. Sieving the samples prior to mixing and taking the sub-splits greatly increases the chemical homogeneity of the sub-splits that are taken.

No mercury was detected in any of the seven individual samples. A 2 M KCl solution was also tried. Again, no mercury was detected in this fraction.

Humic and Fulvic Acid Fraction:

Luoma and Bryan (1981) found that trace metals and organic matter were removed slowly from this fraction and recommended one week for the time needed for this extraction to reach equilibrium. The concentration of the NaOH in the Luoma and Bryan study was chosen to maximize the extraction of copper and organic material. Langston (1982) used this extraction specifically for mercury and found a significant

Table 3 Comparison of values obtained by the Department of Natural Resources with results obtained in this study

Sample	DNR ng/g	This Study ng/g
KCl Blank	0.5	ND
KCl Deer Lake Subsplit A	0.5	ND
KCl Deer Lake Subsplit B	0.5	ND
NaOH Blank	0.5	ND
NaOH Deer Lake Subsplit A	30.0	31.0
NaOH Deer Lake Subsplit B	32.0	33.0
HCl Blank	0.5	ND
HCl Deer Lake Subsplit A	0.5	0.8
HCl Deer Lake Subsplit B	0.8	0.8
H_2O_2 Blank	0.5	ND
H_2O_2 Deer Lake Subsplit A	7.9	12.0
H_2O_2 Deer Lake Subsplit B	8.1	12.0

proportion of mercury in this fraction. Thirty hr was found to be the optimum reaction time to extract mercury from this phase (Figure 1).

Acid Soluble Fraction:

HCl (1N) was used by Langston (1982) and Luoma and Bryan (1981) to extract acid soluble metals from the sediment. Luoma and Bryan (1981) found HCl removed a greater concentration of trace metals from the sediment than other extractants. The steady state time required for the HCl extraction was not clear using just the mercury data, so iron was also measured on these samples. The iron data was not clear either, so another 10 hr experiment was run and seemed to indicate 6 hr was required before a steady state was reached. The iron and manganese experiment indicated 6 hr was needed to reach a steady state (Figure 2).

Organic/Sulfide Fraction:

The results of Langston's (1982) and Tessier et al. (1979) methods for extraction of organics/sulfides were similar. Tessier's et al. (19179) method was chosen because other trace metal experiments being run on Lake Superior sediment samples also utilized this method. Temperature was an important factor in the amount of mercury extracted. Optimum temperature for extraction was found to be between 40° and 50° C. Steady state for the experiments run at 0°, 25°, 60°, and 85° C was reached within 4 to 5 hr, but with both methods more mercury was extracted after the addition of the ammonium chloride/nitric acid reagent (Figures 3 and 4).

LAKE SUPERIOR SAMPLES

Location and Description of Core Sediments

Lake Superior is a large oligotrophic lake bordered by Michigan and Wisconsin on the south, Canada on the north, and Minnesota on the west. Lake Superior is the largest body of fresh water in the world by area and is 407 m at its deepest point. It is a glacial scour lake formed when water melted after retreat of the last continental glaciers about 11,000 years ago.

The Lake Superior core samples were obtained in August, 1986 (Tables 4-7). The cruise was part of the National Oceanic and Atmospheric Administration's (NOAA) National Undersea Research Program (NURP). The cruise took place on the R/V Seward Johnson. The locations (Figure 5) are the Caribou basin (47^{o} 22.89'N 86^{o} 57.69'W) at a depth of 335 m., the Ile Parisienne Basin (46^{o} 45.40'N 84^{o} 47.09' W), Isle Royale (47^{o} 39.24'N 87^{o} 57.98'W), and north- south trending troughs at 47^{o} 04.93'N 86^{o} 21.91'W). Sedimentation rates range from 0.12 mm/yr in the Caribou Basin to 2.29 mm/yr in the Ile Parisienne Basin (Johnson et al., 1982; Kemp et al., 1978).

Gravity cores (7.6 cm dia.) were taken from the R/V Seward Johnson. The cores were stored at 4^{o}C and sectioned within 2 hr under air. From the same site at which the core was taken, surface sediments (fluff) were also collected using the vacuum/filtration system of the manned submersible JOHNSON SEA-Link-II (McKee et al., 1988a). The fluff or the sediment boundary layer, is a layer of sediment, approximately 1 cm in depth, that separates the sediment column from the nepheloid layer. The fluff is enriched in organic matter and metals compared to the sediments

Table 4

Description of core 3 obtained offshore Isle Royale

Bottle Number	Average Depth	Thickness (cm)	Description
1	0.5	1	greenish brown wet fluff
2	1.5	1	same as bottle 1
3	2.5	1	same as bottle 1, slightly more cohesive at base, tan contact at base
4	3.25	0.5	tan, cohesive, slightly drier
5	3.75	0.5	greenish black sticky material, start of redox?
6	4.25	0.5	flaky, dry, pale,orange, fissile horizon-redox boundary
7	5.0	1	gray, wet, sticky clay, quite cohesive
8	6.0	1	same as bottle 7
9	7.5	2	gray clay as bottle 7, quite homogeneous
10	9.5	2	gray clay as bottle 7
11	11.5	2	same as bottle 7
12	13.5	2	same as bottle 7
13	16.0	3	same as bottle 7
14	19.0	3	same as bottle 7

Table 4 Continued

Description of core 3 obtained offshore Isle Royale

Bottle Number	Average Depth	Thickness (cm)	Description
15	22.5	4	more gray clay exactly as bottle 7,quite homogeneous
16	26.5	4	same as bottle 7
17	30.5	4	same as bottle7
18	34.5	4	same as bottle 7

Table 5

Description of core 7 obtained in the Caribou Basin

Bottle Number	Average Depth (cm)	Thickness (cm)	Description
1	0.5	1	top-fluff, dark greenish-gray
2	1.5	1	fluffy dark greenish-gray
3	2.5	1	tan, greenish-gray transition
4	3.5	1	tan
5	4.5	1	tan
6	5.5	1	tan, redox zone at bottom
7	6.25	0.5	thin black layer 0.5 cm., quite cohesive
8	6.30	0.1	transition zone, becoming orangish brown
9	6.55	0.5	gray clay, tan clay underneath, slight redox zone
10	6.9	0.1	tan,clay transition zone
11	7.5	1	wet, gray clay
12	8.5	1	gray clay
13	10	2	gray clay
14	12	2	gray clay
15	14	2	gray clay

Table 5 continued

Description of core 7 obtained in the Caribou Basin

Bottle Number	Average Depth (cm)	Thickness (cm)	Description
16	15.5	3	gray clay
17	18.5	6	gray clay
18	22	6	gray clay
19	27	6	gray clay
20	33	6	gray clay
21	40	8	gray clay

Table 6

Description of core 13 obtained in North-South trending troughs of Lake Superior

Bottle Number	Average Depth (cm)	Thickness (cm)	Description
1	0.5	1	chocolate brown fluff
2	1.5	1	same as 1
3	2.5	1	same as 1
4	3.5	1	dark tan, less wet, some black streaks
5	4.3	0.5	dry, brown, hard, redox layer
6	4.8	0.5	wet, gray, very smooth clay
7	5.5	1	wet, brownish gray clay, not as wet as above
8	6.5	1	no description available
9	7.5	1	moist, brownish gray clay
10	8.3	1.5	same as bottle 9, some dark streaks
11	10	2	same as bottle 10, some dark blackish streaks
12	12	2	becoming more gray but still grayish brown, very firm becoming drier
13	13	2	no description available

Table 6 continued

Description of core 13 obtained in North-South trending troughs of Lake Superior

Bottle Number	Average Depth (cm)	Thickness (cm)	Description
14	15	2	drier, brownish gray clay
15	17	2	brownish gray clay
16	19	2	brownish gray clay
17	21	2	brownish gray clay
18	22.5	1	brownish gray clay with dry interface
19	23.8	1.5	very liquid, gray clay
20	25.5	2	gray soft clay with few black streaks through it
21	27.5	2	very wet, gray clay, very fine black streaks, H_2S odor
22	29.5	2	same as bottle 21
23	31.5	2	same as bottle 21

Table 7

Description of core 21 obtained in the Ile Parisienne Basin

Bottle Number	Average Depth (cm)	Thickness (cm)	Description
1	0.5	1	no description available
2	1.5	1	no description available
3	2.5	1	very dark brown, sandy
4	3.3	0.5	black, redox layer
5	4.0	1	light red
6	5.0	1	below redox, black pieces present
7	6.0	1	gray with black horizon
8	7.5	2	same as bottle 7
9	9.5	2	same as bottle 7
10	10	1	same as botttle 7, end of black
11	12	3	light brown
12	14.5	2	light brown
13	17.0	3	light brown
14	20.5	4	light brown
15	23.0	5	light brown

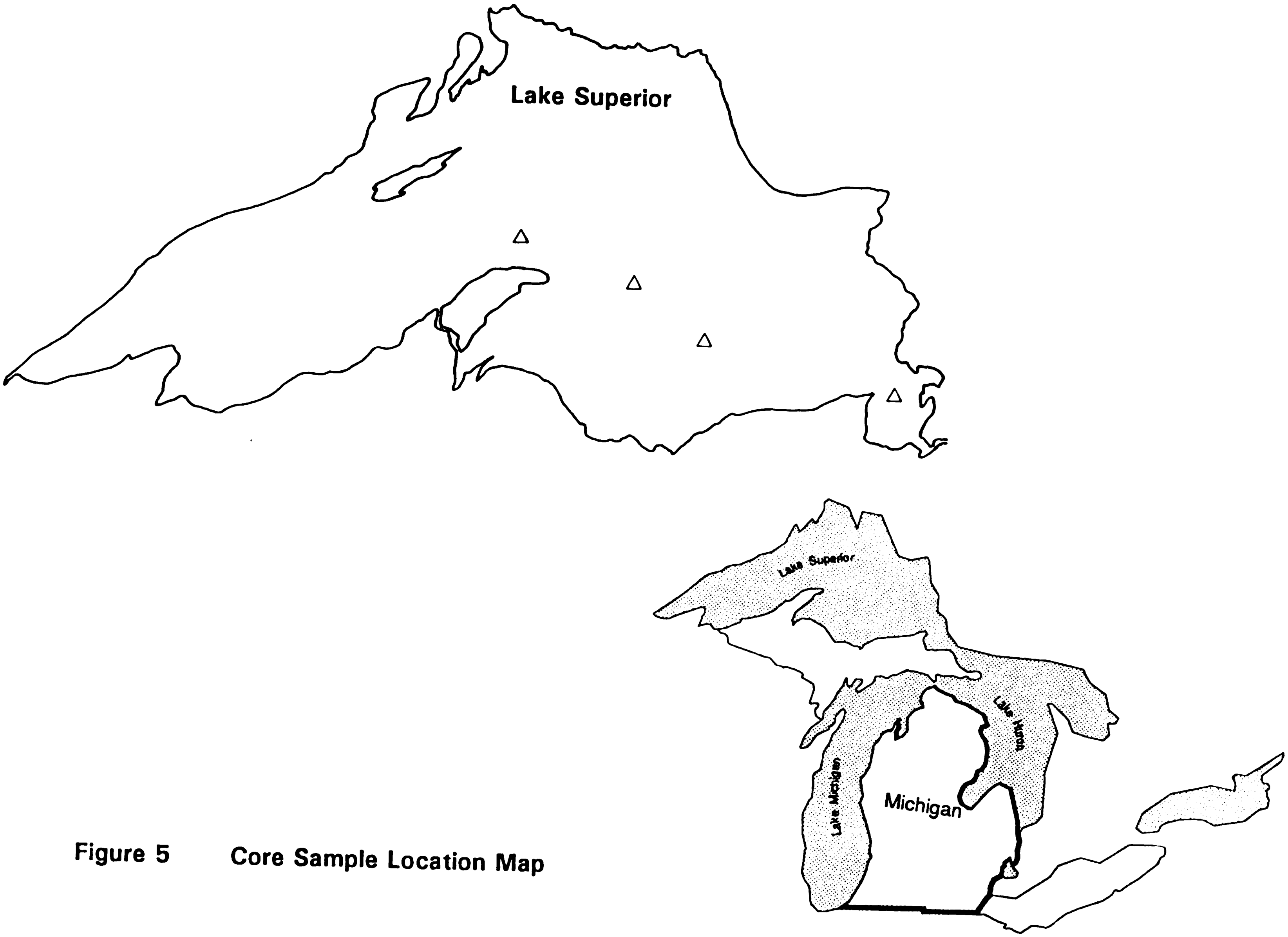

Figure 5 Core Sample Location Map

below (McKee et al., 1988a). The fluff has been observed to behave as a coherent mat when disturbed (Wilson et al., 1986). An alternative explanation for the behavior as a coherent mat is a perturbation of a density stratified layer causing an interface disturbance.

The Lake Superior sediment samples were collected under air. This was done to prevent reduction of mercury to its elemental form with subsequent loss to the atmosphere. The sediment samples (fluff and core sections) were stored frozen and then air dried for analysis. The sediment was brought to a constant weight in a desiccator if needed. All extractions were performed in the presence of air. One gram of each sample was placed in a 30 ml centrifuge tube. Mercury in the hydromorphic phases was determined by methods outlined on Table 2. Mercury was analyzed as described in the earlier methods section.

The residual phase was extracted by adding 12.5 ml of concentrated H_2SO_4 to each sample then adding 4 ml of 30% H_2O_2 and heating gently at 50° C for 2 hr. The samples were cooled to room temperature, centrifuged and the fluid removed and placed in a 100 ml volumetric flask. Double distilled deionized water was then added to bring the total volume up to 100 ml and a 25 ml aliquot was analyzed for mercury as described above.

RESULTS AND DISCUSSION

Figure 6 shows the mercury concentrations in all the hydromorphic phases in all four cores from Lake Superior. This is a log concentration plot. It shows that the base-soluble fraction and the oxidizable fraction are about equally important in sequestering mercury and both are more important than the acid soluble fraction. Mercury decreases with depth and the profiles differ between basins. The mercury concentration is at its highest level in the top few centimeters of the cores with a precipitous drop at the redox boundary (Figures 7 and 8). The redox boundary occurs between 4-4.5 cm in the Isle Royale Core (core 3), at 6 cm in the Caribou Basin Core (core 7), between 4-4.5 cm in the north-south trending troughs core (core 13) and at 3.5 cm in the Ile Parisienne Core (core 21). The values then level out below the redox boundary to between 0-20 ng/g per fraction. In the Isle Royale core (core 3) and the Ile Parisienne core (core 21) the highest concentration of mercury is found in the top sample for each fraction. In core 21 this represents the fluff layer and in core 3 it is just below the fluff, no fluff layer material was available to analyze for core 3. This observation is in disagreement with a study of sediments in Lake Superior (Rossman, 1986) in which the highest levels of mercury were found at about 3 cm and attributed to a time period between 1940 and 1970. Cores 3 and 21 show either a recent increase of mercury input or some chemical-biological process moving mercury to the surface in these sediments. Caribou Basins core profile (core 7, Figure 9) is in agreement with Rossman's profile of Lake Superior sediments and looks very much like it (Figure 10) except the top of core 7 has a higher concentration of mercury than the next sample in the core. Caribou Basins core profile shows that for the humic and fulvic acid fraction mercury peaks at 3 cm (Figures 8 and 9). In general the troughs core (core 13) exhibits a higher level of mercury at the top of the core.

The base soluble and oxidizable phases (Figure 7) show mercury to be highest

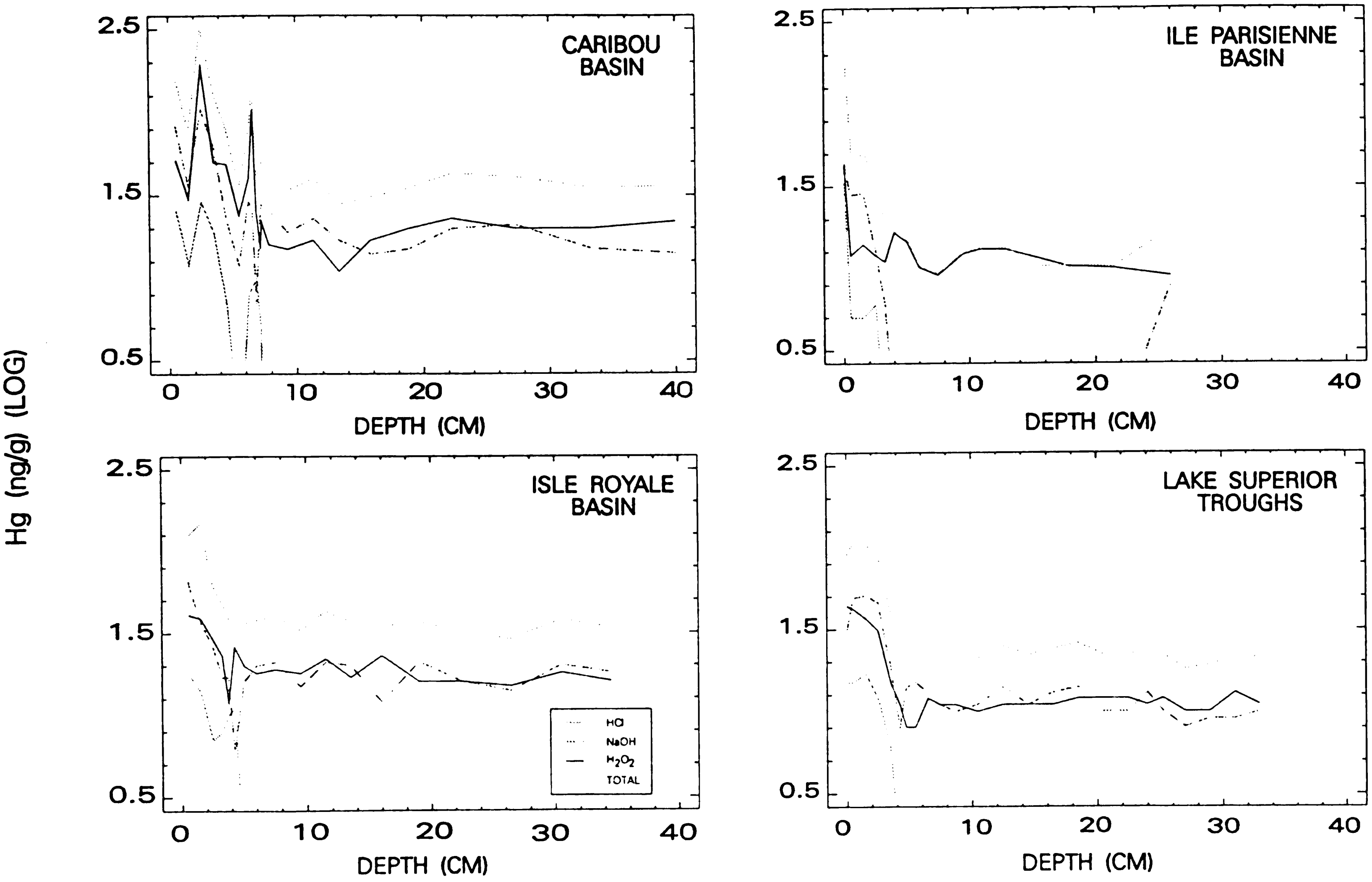

Figure 6 Mercury in the Hydromorphic Fractions (LOG)

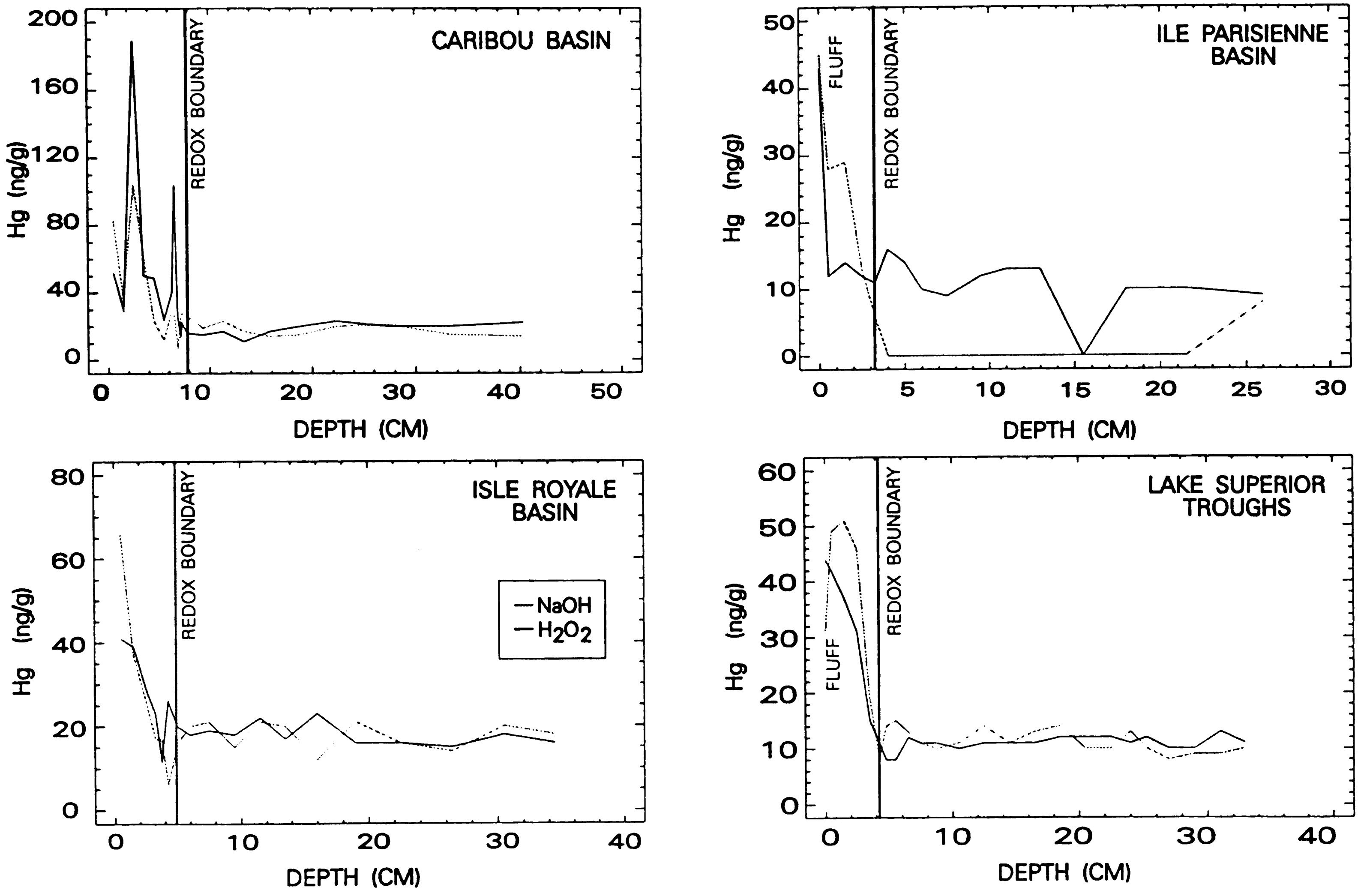

Figure 7 Mercury in the Oxidizable and Base Soluble Fractions in Cores From Lake Superior

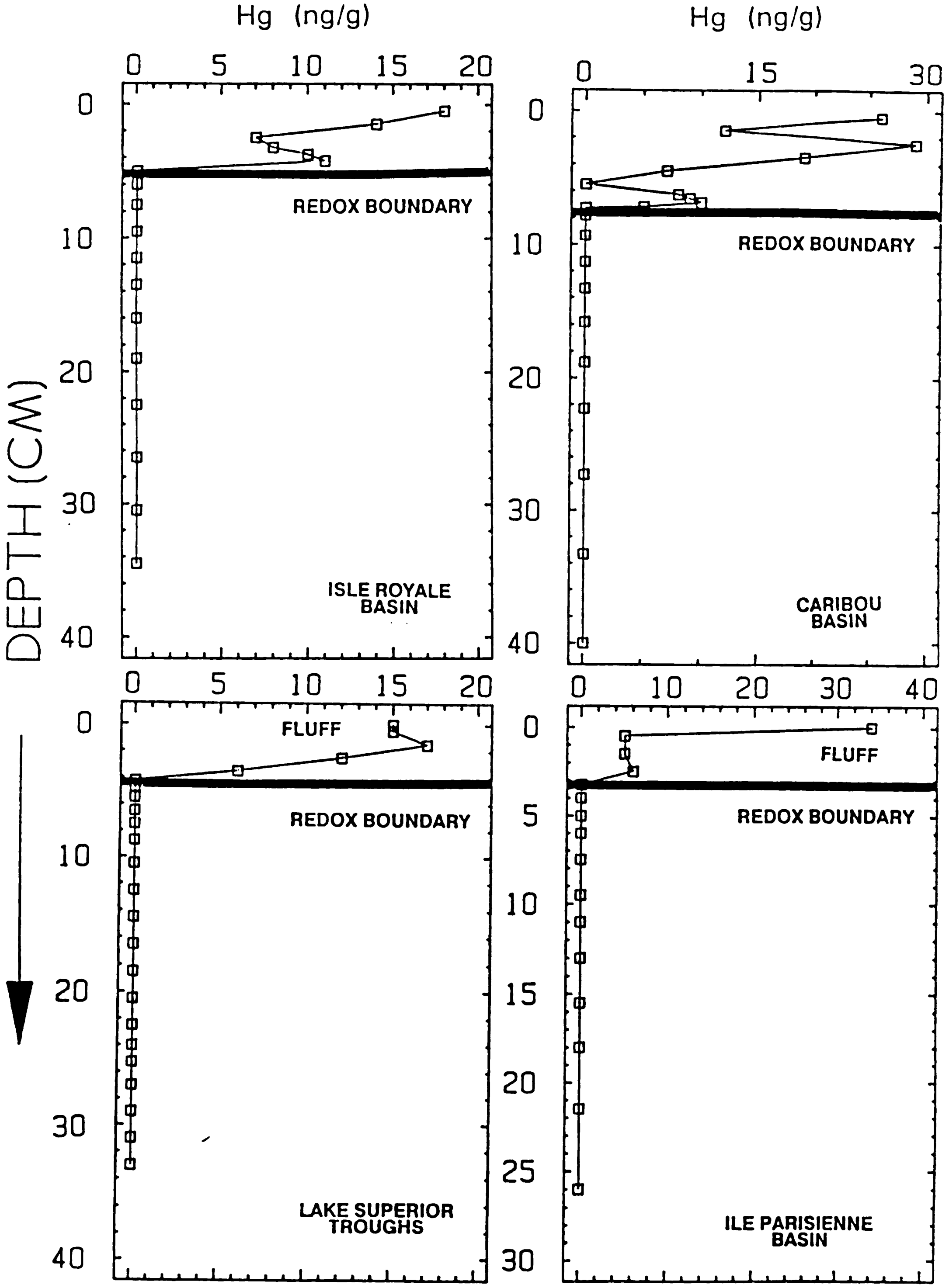

Figure 8 Acid (HCl) Soluble Fraction in Cores from Lake Superior

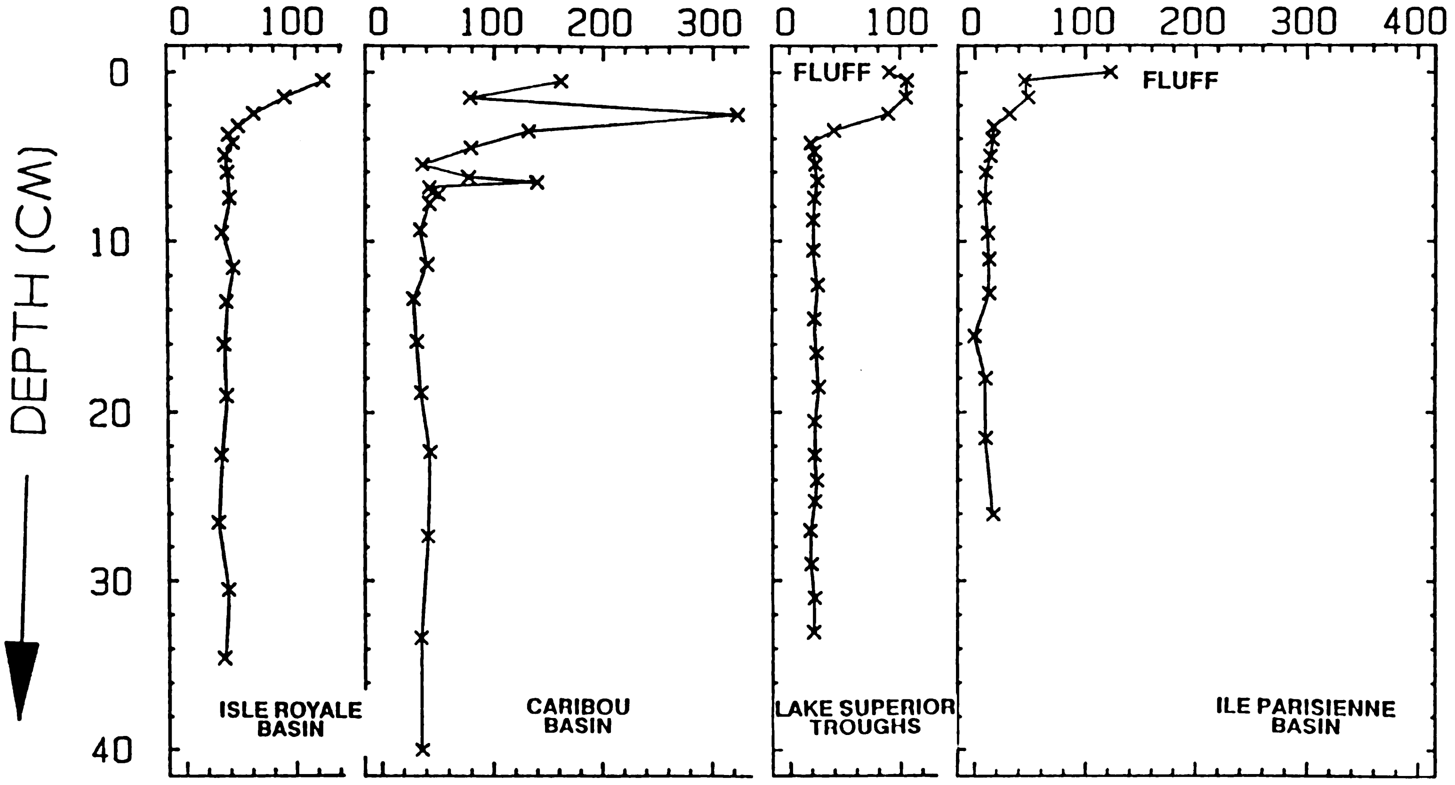

Figure 9 Total Mercury (ng/g) in Cores from Lake Superior

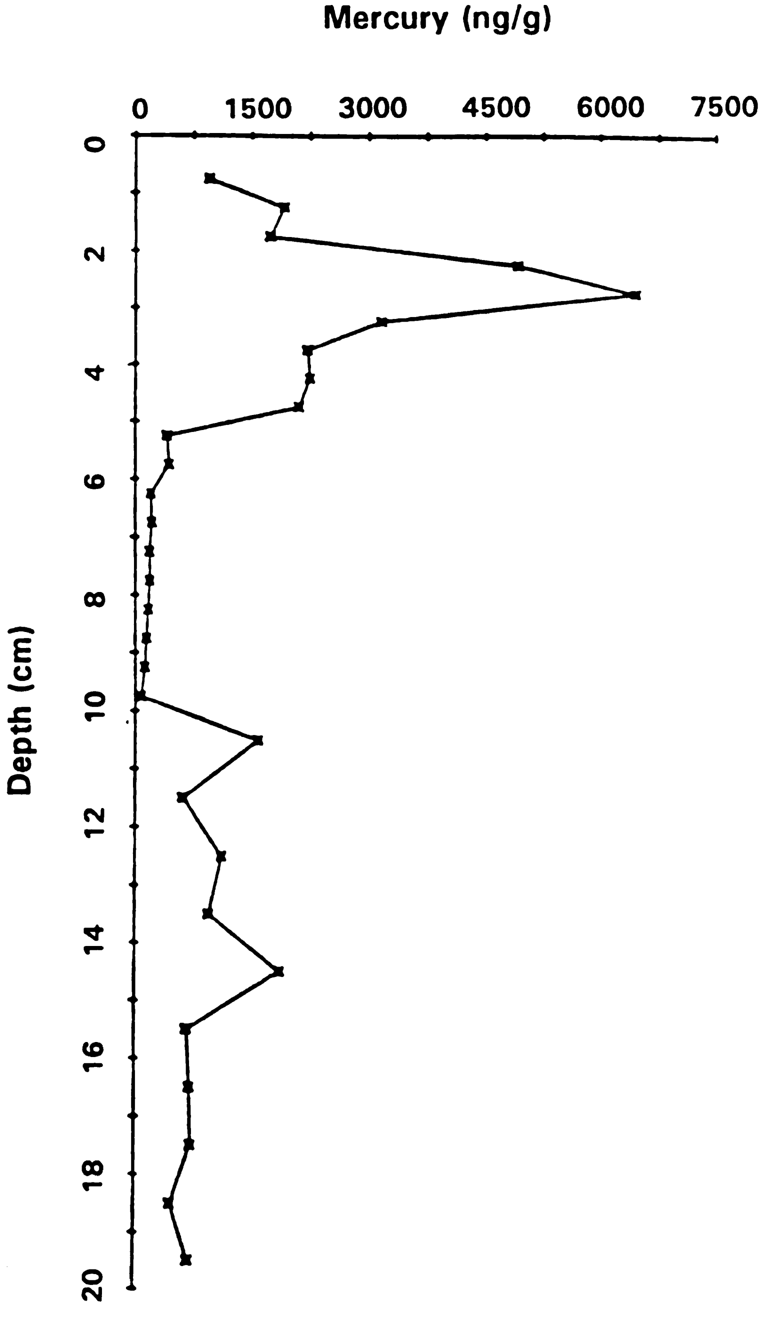

Figure 10 Vertical variation of mercury in Lake Superior sediments at station LS-83-1156A, (modified from Rossman, 1986)

above the redox boundary. The profiles are very similar to each other below the redox boundary except for the Ile Parisienne sample which shows a change in partitioning. The mercury concentrations decrease to a relatively constant baseline below the redox boundary. These results suggest that like the acid soluble fraction, mercury is being remobilized or stripped from the sediment as it is buried and undergoes reduction. It is further indicated because the depth of the redox boundary is different between the basins. Redox processes are influencing the mercury profiles.

The precipitous drop in mercury concentration at the redox horizon suggests remobilization of mercury and loss of mercury to the water by diffusion. Previously, mercury data in sediments has been interpreted as relating to time periods when mercury input was at its peak or decreased. This study suggests a dynamic process in which mercury is recycled in the sediment-water system. It would be extremely coincidental if the redox zone in these four cores all corresponded to the same time period. According to sedimentation rate estimates by Johnson et al. (1982) the sedimentation rate near Isle Royale (core 3) is 45 cm/1000 yr. The redox zone is between 4 and 4.5 cm or represents a time period of about 100 yr ago. Estimates for sedimentation rates for core 21 collected in the Ile Parisienne Basin ranges from 188 to 229 cm/1000 yr (Johnson et al., 1982; Kemp et al., 1978). The 3.5 cm redox horizon corresponds to approximately 18 yr ago or 1971. Sedimentation rate estimate for core 7 located in the Caribou Basin is approximately 0.12 mm/yr (Kemp et al., 1978). The redox zone in core 7 is located at 6 cm corresponding to 500 yr ago. The sedimentation rate for the North-South trending troughs (Core 13) is approximately 1.20 mm/yr (Kemp et al., 1978). The redox zone in core 13 is located between 4 and 4.5 cm corresponding to 33-37 yr ago. The peaks in mercury concentration occur at the top in cores 3 and 21 and at about 3 cm in cores 7 and 13. The 3 cm depth in cores 7 and 13 correspond to about 250 and 25 yr ago, respectively.

This interpretation is in disagreement with the interpretation by Johansen, (1983) and Rossman, (1984) that mercury profiles are not significantly affected by diagenesis.

Residual mercury remaining after the extractions was analyzed for these four cores. The results vary between basins (Figure 11). In the Ile Parisienne Basin mercury is present in the top 5 mm of the core but no mercury was detected in the rest of the core. The Lake Superior troughs core had no measurable remaining mercury after the hydromorphic fractions were removed. Ile Royale had mercury present in the second sample of the core but none elsewhere. The Caribou Basin core exhibited a more complicated profile than the other three cores. This profile mimics the hydromorphic fraction profiles (Figure 7 and 8) and may reflect insufficient leaching of the core. The other three cores show that most of the mercury is in the hydromorphic fraction and very little if any mercury remains after these extractions. An alternative interpretation for the mercury remaining is that the extraction used may not be complete enough.

It appears that mercury profiles in Lake Superior are not simply a record of anthropogenic input, although surface enrichment supports the indication of anthropogenic influence (Prohic and Juracic, 1989). They are also affected by diagenetic processes as well as remobilization of mercury. This means that mercury already present in the system above the redox boundary can be recycled via the pore water into the overlying water column and will not simply be buried. This is known to occur for other metals such as Mn (Robbins and Callender, 1975; Rossmann, 1984; McKee et al., 1988b), Cu and Ni (Carignan and Nriagu, 1986), and Cu and Pb (McKee et al., 1988b). Calculations of mercury loss from the redox boundary to the sediment, water, or biota above have been made using sedimentation rates reported by Kemp et al. (1978) and Johnson et al. (1982). The loss of mercury is calculated using the mass sedimentation rate in g/cm2yr, multiplied by the change in concentration of

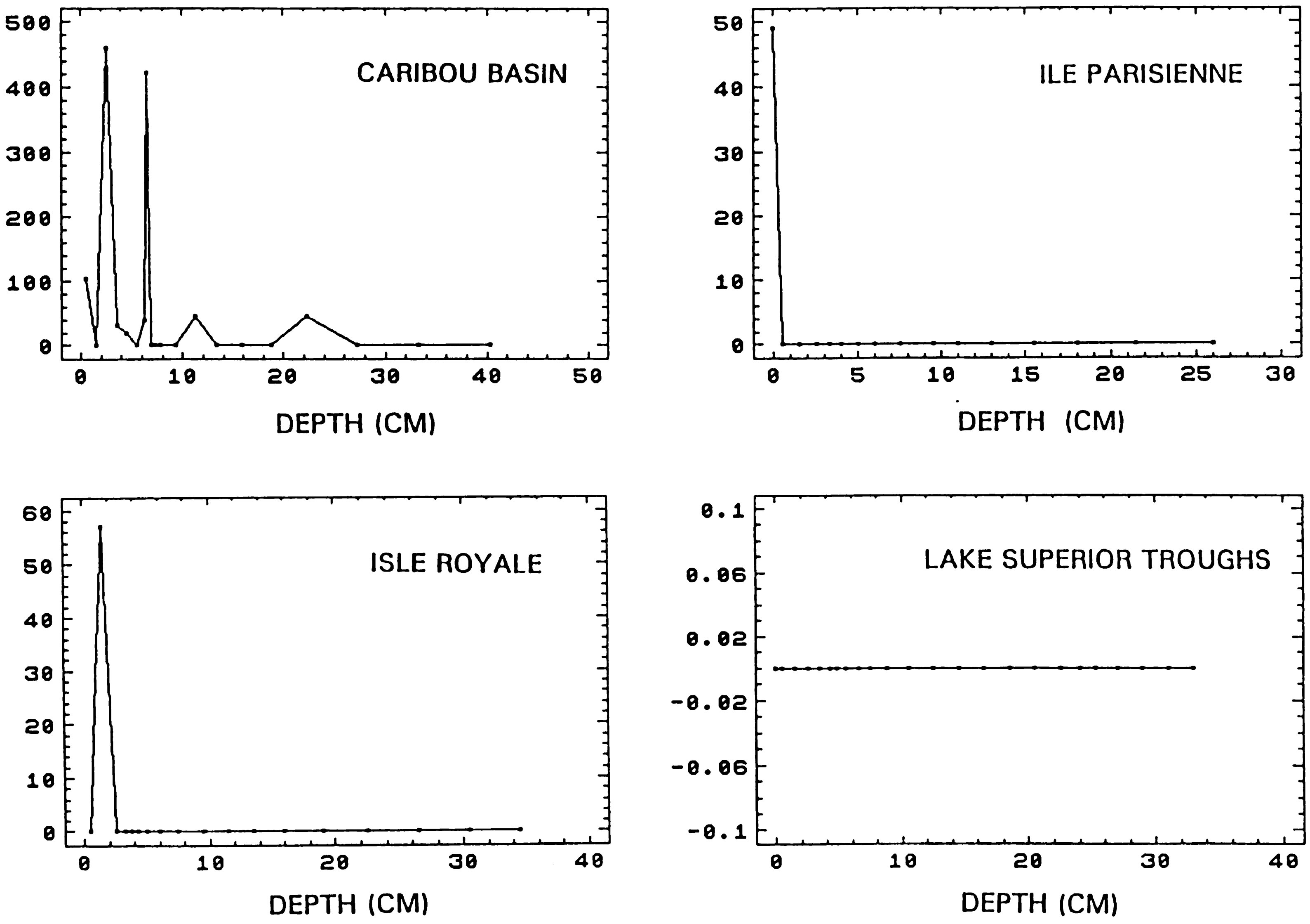

Figure 11 Residual Mercury (ng/g) in Cores from Lake Superior

mercury above the redox zone. The amount of mercury lost has been calculated for the acid soluble, base soluble and oxidizable phases (Table 8). The top table uses the difference between the highest concentration of mercury above the redox zone and the lowest concentration below the redox zone. The bottom table values were calculated using the concentration just above the redox zone and the lowest concentration below the redox zone. These values are maximum values because mercury present above the redox zone may be due to diagenesis and recycling of mercury to the sediment above. The maximum possible loss for the acid soluble phase ranges from 0.09 ng/cm^{2}yr in the Isle Royale Basin to 2.38 ng/cm^{2}yr in Ile Parisienne. The mercury remobilized from just above the redox boundary in the acid soluble phase ranged from 0.055 ng/cm^{2}yr in Isle Royale to 0.42 ng/cm^{2}yr in Ile Parisienne. The maximum possible loss of mercury in the base-soluble phase ranges from 0.24 ng/cm^{2}yr in the Isle Royale Basin to 3.15 ng/cm^{2}yr in the Ile Parisienne Basin. The mercury remobilized from just above the redox boundary for the base soluble phase ranged from undetected in Isle Royale to 0.98 ng/cm^{2}yr in the Ile Parisienne Basin. The maximum possible loss for the oxidizable phase ranges from 0.12 ng/cm^{2}yr in the Isle Royale Basin to 3.13 ng/cm^{2}yr in the Caribou Basin. The maximum possible total hydromorphic loss of mercury ranges from a low of 0.45 ng/cm^{2}yr in the Isle Royale Basin to a high of 7.77 ng/cm^{2}yr in the Caribou Basin. The mercury remobilized from just above the redox boundary ranged from 0.095 ng/cm^{2}yr in Isle Royale to 1.87 ng/cm^{2}yr in the Caribou Basin. Therefore, it appears that new additions of mercury will affect the ecosystem for years to come as will the mercury that is already present. Mercury concentrations differ in different areas of Lake Superior and in some cases there is a change in partitioning of mercury with depth. Therefore, it would be very difficult to predict mercury levels in an area of the lake without actually testing the levels. Mudroch et al. (1988) reported recent and background concentrations of selected elements in Great Lakes sediments. Lake Superior had the lowest levels of

TABLE 8

POSSIBLE MAXIMUM
MERCURY LOST FROM THE SEDIMENT (ng/cm^{2}yr)

Location	**NaOH**	**HCl**	**H_2O_2**	**Total**
Isle Royale Core 3	0.24-1.06	0.09-0.40	0.12-0.51	0.45-1.97
Caribou Basin Core 7	0.67-1.53	0.23-0.53	1.38-3.13	2.28-5.19
N/S Troughs Core 13	1.0-2.0	0.43-0.85	1.1-1.65	2.53-4.5
Ile Parisienne Core 21	2.7-3.15	2.04-2.38	1.92-2.24	6.66-7.77

MERCURY LOST FROM SEDIMENT JUST ABOVE REDOX BOUNDARY

Location	NaOH	HCl	H_2O_2	Total
Isle Royale Core 3	ND-1.06	0.05-0.24	0.04-0.18	0.10-1.48
Caribou Basin Core 7	0.05-0.11	0.08-0.18	0.70-1.58	0.83-1.87
N/S Troughs Core 13	0.2-0.4	0.15-0.3	0.1-0.2	0.45-0.90
Ile Parisienne Core 21	0.84-0.98	0.36-0.42	0.18-0.21	1.38-1.61

mercury of the Great Lakes. The other four lakes have higher levels of mercury in their sediments probably due to higher inputs reflecting the higher populations surrounding them and could face more serious problems with regards to mercury contamination of biota.

Sediment contamination represents a significant problem as an *in situ* source of pollutants (Mudroch et al., 1988). Even after elimination of external inputs, contaminants will remain in the sediments and can be released into the water column (Mudroch, 1988). Knowledge of the concentrations of contaminants in the sediments can be used for establishing the degree and spatial extent of sediment contamination, determination of sediment accumulation, investigation of historical inputs of contaminants into the lakes, estimation of present input loads, and assessing the toxicity of sediment-associated contaminants to the lake biota (Mudroch, 1988).

CONCLUSIONS

This research examined the partitioning of mercury in Lake Superior sediment cores. The technique used was selective chemical extractions. The partitioning results indicate that mercury can be extracted from the base-soluble, acid soluble and oxidizable phases. In practice, these correspond to the humic and fulvic acid, the iron-manganese and the organic sulfide phases. Mercury was not detected in the exchangeable phase (clays). The residual material after extraction does not contain significant mercury except for Caribou Basin sediments. Mercury concentrations are highest in the base-soluble and oxidizable phases. Mercury concentrations are highest above the redox boundary after which they decrease with depth to a constant value. Mercury could not be detected in the acid soluble phase below the redox boundary. Diagenetic remobilization of mercury is indicated by changes in partitioning with depth.

Concentration profiles of mercury in the cores varied in shape, with the Isle Royale (core 3) and Ile Parisienne (core 21) having the highest concentration of mercury in the top of the core and the Caribou Basin (core 7) and the North-South trending troughs (Core 13) having a peak of mercury 3 cm down in the core. The two cores with the highest concentration at the top of the core are in disagreement with past research indicating mercury input to Lake Superior has decreased in recent times. The precipitous drop in mercury concentration at the redox horizon in all four cores suggests that mercury is being remobilized by diagenesis. This is also in disagreement with past research which indicated mercury is not significantly affected by diagenesis. The driving force for mercury remobilization is reduction. Mercury is reduced as redox potential decreases. Occurring concurrently with reduction of mercury is the reduction and subsequent dissolution of Mn and Fe, and decay of organic material. Mercury concentration below the redox horizon leveled off to a fairly constant level between 20 and 40 ng/g.

APPENDIX

APPENDIX

GEOCHEMISTRY AND BIOCHEMISTRY OF MERCURY

Mercury has the atomic number 80 and atomic weight of 200.59 (Weast, 1986). Mercury can exist in three oxidation states, Hg^o, Hg^{+1}, and Hg^{+2}. The oxidation state will depend on pH, redox potential, and the type and concentration of anions which can form stable complexes with mercury (Moore and Ramamoorthy, 1984). Elemental mercury (Hg^o) occurs as a vapor, liquid, or dissolute (Jonasson and Boyle, 1972). Mercurous ion (Hg^{+1}) combines to form simple complexes such as Hg_2Cl_2. Mercuric ion (Hg^{+2}) combines to form simple complexes, oxides and sulfides. Any of these (Hg^o, Hg^{+1}, Hg^{+2}), can undergo bacterial synthesis to form organomercury compounds. Figure 12 shows the stability fields of aqueous species in a fresh water environment (36 mg/l Cl^-, 96 mg/l SO_4). In well oxygenated water with a low pH, mercuric species will predominate whereas under reducing conditions elemental mercury should prevail (Figure 12). With oxidizing conditions and a $pH > 5$ the predominant mercury species in water is Hg^o (Fleischer, 1970). The solubility of Hg^o is quite low, about 25 μg/l in lakes that are low in chloride ions. The solubility will be determined by equilibrium reaction with the solid phases [HgS; Hg^o; HgO]. In the presence of mildly reducing conditions and in the presence of sulfide ions, mercury can be precipitated as the sulfide cinnabar (Fleischer, 1970). Cinnabar is extremely insoluble with a solubility product $= 10^{-53}$ (Krauskopf, 1979). In the presence of strongly reducing conditions the mercuric ion may be converted to the free metal, therefore, increasing the solubility (Hem, 1970). Increasing the pH causes the formation of hydroxide complexes. The solubility of mercury is increased by methylation, chloride complexing and organic complexing.

The most common minerals of mercury are cinnabar and metacinnabar which contain about 86% mercury by weight (Faust and Aly, 1981). Other minerals containing mercury include tetrahedrite, sphalerite, wurtzite and other sulfides and

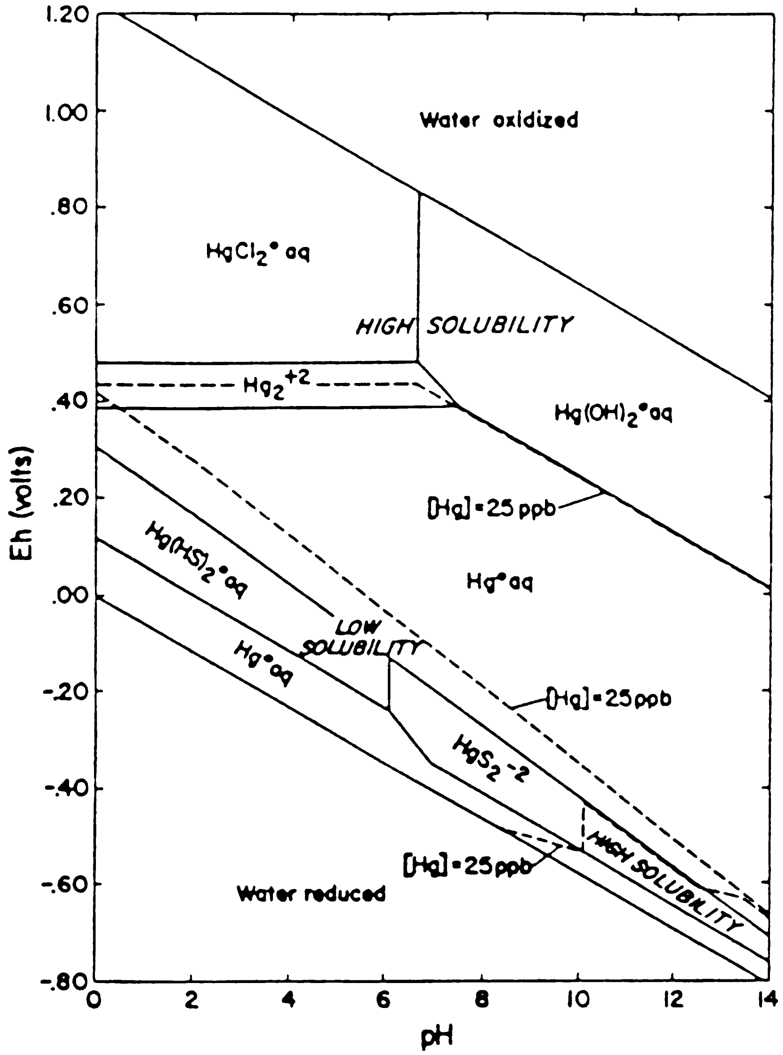

Figure 12 Stability fields for aqueous mercury at 25° C and 1 atm (Hem, 1970)

sulfosalts (Faust and Aly, 1981). Elemental mercury is volatile and is continually released to the atmosphere from ore deposits, soil surfaces and volcanic emanations (Faust and Aly, 1981). Unpolluted air generally contains between 1 and 10 ng Hg/m^3, but in areas of mercury ore, airborne levels may be as high as 20,000 ng Hg/m^3. Mercury in air is adsorbed onto particles and eventually washed out by rain to the surface of the earth, providing a natural source of mercury to the terrestrial and aquatic ecosystems. Unpolluted water contains less than 0.1 μg Hg/l, however water draining areas containing ore deposits may have levels up to 136 μg Hg/l (Faust and Aly, 1981).

Many anthropogenic sources of mercury to the environment exist. These include electrolytic preparations of chlorine and caustic soda, manufacture of batteries, silent switches, mercury vapor street lamps and fluorescent lights, fungicides, catalysts in manufacture of organic materials, pharmaceuticals, cosmetics, and dental preparations, sewage outfall from hospitals and industry, burning of fossil fuels, water based paints, and smelting of lead, zinc, and copper ores (Moore and Ramamoorthy, 1984).

Mercury forms stable covalent bonds with a variety of organic complexes. Kinetic barriers are responsible for this stability as these compounds, with the exception of methyl mercury, are thermodynamically unstable with respect to water (Faust and Aly, 1981). Cysteine, amino acids and hydroxycarboxylic acids form the strongest covalent compounds (Moore and Ramamoorthy, 1984). Mercuric and organomercuric compounds can undergo "ligand exchange reaction" with a variety of chemical species that exist in natural waters. These reactions involve the interaction of mercuric or organomercuric complexes with some chemical species, Y, to form a new complex: (Faust and Aly, 1981):

$$HgX_2 + Y = HgXY + X$$

$$HgXY + Y = HgY_2 + X$$

$$RHgX + Y = RHgY + X$$

Organomercury compounds can undergo at least three types of chemical and/or physical reactions in water. These include acid hydrolysis, demethylation, and evaporative loss of organomercurials. Acid hydrolysis occurs when the carbon-mercury bond in dialkyl or diarylmercury compounds is cleaved, or when organomercuric salts undergo this cleavage by protic acids (Faust and Aly, 1981). The general reactions are:

$$R_2Hg + HX = RHgX + RH$$

$$RHgX + HX = HgX_2 + RH$$

where R is a dialkyl or diaryl species.

Kinetic studies show these reactions to be very slow under natural conditions in the aquatic environment. Demethylation of methyl mercuric salts is very slow and has a rate constant at of 8 X 10^{-13}/sec at 25° C. It is a very rapid reaction with branched alkylmercuric salts. The general reaction is:

$$RHgX + H_2O > ROH + Hg^0 + X^-.$$

Another demethylation reaction involving the halides iodine and bromine also occurs and is dependent on being initiated in the presence of light. The reaction is:

$$2CH_3HgCl_{(aq)} + 2\,I_2 = 2CH_3I + HgI_{2(s)} + HgCl_2$$

The reaction rate with I_2 is high at pH values below 6, and decreases with increasing pH to a value of 8 or 9. Bromine rates are about 33 times slower than iodine, and no reaction was observed with chlorine saturated water. Evaporative loss of organomercury compounds from the aqueous phase may occur because many of these compounds have relatively high vapor pressures (Faust and Aly, 1981).

Mercury behaves as a Lewis acid and has a large affinity for Lewis bases such as sulfur. Mercury is quickly depleted from the water column and binds to sulfides, organic matter and clays. Partition coefficients for mercury between suspended solids and water have been calculated from field and laboratory data and range between 1.34

and 1.88 x 10^5 (Moore and Ramamoorthy, 1984). The chemical form of dissolved species of mercury determines the mode of association to suspended solids and their residence time in the water column (Moore and Ramamoorthy, 1984). Sorption/desorption phenomena and subsequent sedimentation are extremely important in determining the fate of mercury species in the water column. Processes responsible for mercury immobilization by sediment include cationic sorption, irreversible sorption by sulfide surfaces, mercury ion - organic matter (humic and fulvic complexes), covalently bonded organometallic compounds, and sorption by clays and other mineral grains (Johnsson, 1970). Organic humus in the sediment adsorbs elemental mercury which is nonpolar while ionic mercury is adsorbed to the clay portion of sediment (Reimers and Krenkel, 1974). Mercuric ion in the presence of humic acid is reduced to elemental mercury and the rate is dependent on pH, the lower the pH the faster the rate of reaction (Miller et al., 1974). Calcium and sodium can compete with Hg^{+2} for exchange sites on sediment thereby increasing mercury in water in equilibrium with sediments by 2 to 5 orders of magnitude (Feick et al., 1972). In addition, the presence of Cl^- decreases adsorption of Hg^{+2} especially at low pH. 1976). Desorption of mercury with water is negligible except at high Cl^- concentrations (Ramamoorthy and Rust, 1976; Reimers and Krenkel, 1974). Presence of organic matter in the sediment promotes sorption, and these types of sediments usually have the highest mercury content (Ramamoorthy and Rust, 1976). Mercury bound to sediments is stronger than bonding between mercury and fulvic acid regardless of the organic content of the sediment (Ramamoorthy and Rust, 1976). Fulvic and humic acids are both important fractions of organic substances and both have an affinity for trace metals. The fulvic acid fraction has a molecular weight of less than 10,000, has a higher water solubility and assumes a more important role in transporting trace metals in water than it does in incorporating them into bottom material (Fuhrer, 1986). The humic acid fraction is less soluble, has a molecular weight greater than 200,000, and is more important in trace metal transport and sorption by bottom material (Head, 1976). Mantoura et al. (1978) extracted humic materials from sea, river, and lake waters and determined stability constants for complexes with mercury and other metals. In general the stability of the metal-organic complexes followed the Irving-Williams order for the stability of chelates:

$$Mg < Ca < Cd = Mn < Co < Zn = Ni < Cu < Hg$$

This shows that mercury forms very stable complexes with natural humic materials and should compete favorably with other metals. Mantoura et al. (1978) used these stability constants in a speciation program and modeled metal speciation for fresh and marine waters. Their results showed that > 90% of copper and mercury should be bound to humic materials in fresh water environments. Millward and Burton (1975) isolated naturally occurring humic and fulvic acids and measured complexation of mercury. They found strong mercury complexation by humic acids; however, they found no such complexation by fulvic acids. Cline et al. (1973) found that the mercuric ion reacts with natural organic floc that has a specific gravity of 2.0. The floc is colloidal and can surround and bind metal ions because of a high negative surface charge (Neihof and Loeb, 1972). Therefore Cline et al. (1973) suggest mercury may be easily transported through the aquatic environment associated with organic particulate matter due to both the reactivity of mercury with organic matter and the low specific gravity of the organic floc.

The adsorptive behavior of mercury has been studied using the following substrates: silica (MacNaughton and James, 1973); goethite (Forbes et al., 1974); iron hydroxide gel (Kinniburgh and Jackson, 1978); organic material (Reimers and Krenkel, 1974; Mantoura et al., 1978); and various clay minerals (Farrah and Pickering, 1978; Hahne and Kroontje, 1973; and Newton et al., 1976). Mercury behaves similarly to other metals in that it shows an adsorption edge at pH 2-4 which is where the hydrolysis products $HgOH^+$ and $Hg(OH)_{2(aq)}$ become dominant. This behavior is only seen in the absence of ligands other than OH^- (MacNaughton and James, 1973). Mercury shows reduced adsorptive uptake, compared to other metals. At metal/oxide ratios and solution conditions where copper shows 100% adsorption onto goethite, an identical system with mercury shows a maximum of 24% adsorption (Forbes et al. 1974). This reduced uptake has been attributed to chemical and structural factors. One effect arises because the Hg-OH bond is more covalent than the other metal-OH bonds, which would tend to reduce the stability of the oxide-HO bond (Forbes et al., 1974). It is believed that the hydroxide ions act as bridges to the oxide surface and in the case of Hg-OH, the covalency causes the bridging bond to be destabilized. Another possibility for the reduced uptake of mercury is a result of the linear structure of the $Hg(OH)_{2(aq)}$ complex (Forbes et al., 1974). Other cations in solution exhibit a tetrahedral or octahedral array of water molecules or hydroxo groups. For these metals existing as this cis hydroxo species, double hydroxo-bridges can form with the oxide surface with no distortion of its structure. This bidentate bond is thought to enhance the affinity of a metal for an oxide surface (Forbes et al., 1974). The two-coordinate $Hg(OH)_2(aq)$ species, however, would have to form a distorted banana shaped complex in order for double bridging to occur. Therefore, the affinity of mercury for oxide surfaces is less than for other metals, however sorptive uptake does occur. The presence of ligand such as chloride greatly reduces and in some cases, eliminates the adsorption of mercury, especially at lower pH values. The reason for this effect probably lies in the adsorptive behavior of chloride (Forbes et al., 1974). Chloride is not specifically adsorbed, i.e. it has no attraction for a surface other than electrostatic (MacNaughton and James, 1973). This observation enhances the idea that hydroxo-bridges are important in mercury adsorption as $Hg(OH)^+$ will sorb but $HgCl^+$ will not. Three common clay minerals have been studied for their sorptive capacity for mercury: montmorillonite, illite, and kaolinite. Results of the various investigations are not consistent with each other however, several general trends can be summarized. The uptake of mercury by clays is less than that of the other trace metals (Farrah and Pickering, 1978) similar to the results of oxide studies. Secondly, each clay mineral behaves somewhat uniquely. Kaolinite shows less sorption capacity than illite or montmorillonite (Reimers and Krenkel, 1974). Illite and kaolinite show little effect of pH on sorption levels (except for illite in the study of Reimers and Krenkel, 1974), while montmorillonite shows a maximum at pH 4.5-6.0 followed by decreased uptake (Newton et al., 1976; Farrah and Pickering, 1978). Farrah and Pickering (1978) propose that this result is due to the increasing pH which allows these clays to continue to compete for mercury with aqueous $Hg(OH)_2$.

The desorption of mercury from sediment phases may be brought about by chemical changes in the system, but the efficiency of this process is not well understood. Chemical changes which may cause desorption include: the mixing of fresh and saline waters; the addition (natural or anthropogenic) of chemical components and fluctuating pH or redox conditions. The desorption reaction might be caused by a variety of processes including: competition with other metals or compounds with a higher affinity for the substrate; the formation of dissolved mercury complexes which are more stable than the sorbed species; or the dissolution of the adsorbing substrate (i.e. reduction of hydrous oxides or oxidation of organics). Mercury does not appear to readily desorb from sediment in natural environments (Rae and Aston, 1982). Because of the high stability of mercury-chloro complexes, it has been suggested by Mantoura et al., (1978) that mercury will be mobilized from fresh water sediments entering the marine environment. Several studies have addressed this problem; however, the results are inconclusive. Feick et al. (1972) showed significant desorption of mercury from sandy and organic rich sediments upon addition of calcium chloride and sodium chloride. The pH used in their experiments, however, were quite low ranging from 3.6 to 6.6. Hannan and Thompson (1977) found no detectable desorption of mercury from soil and sediments (fresh water and marine) when shaken with seawater at pH 8.1. However, the mercury was sorbed to these sediments in seawater to begin with, so desorption would not be expected. Newton et al. (1976) found the chloride solutions were very efficient desorbers for mercury sorbed onto bentonite in the absence of chloride. Lindberg and Harriss (1977) studied the effects of resuspending various mercury contaminated sediments in their corresponding surface waters (nearshore saline marsh, saline open bay, riverine, and estuarine). They measured Eh, pH, total dissolved sulfide, dissolved organic carbon, and aqueous mercury over time as they stirred the sediment. Although there was no clear correlation between aqueous mercury and any one of the other measured parameters, a distinct time-dependent pattern of desorption and readsorption did occur, regardless of whether the sediments were fresh water or marine. The release of mercury took place in two spikes, one immediately after resuspension, the other as much as three hours later. Although no direct supporting evidence was presented, the authors felt that the release of mercury came from different sediment phases with different desorption kinetics. The first spike of desorbed mercury may have been due to the release of loosely bound exchangeable mercury and/or that bound to reduced iron compounds and organic complexes. This mercury could then be reabsorbed as the reduced iron oxidizes to form a hydrous iron oxide. The second spike of mercury was explained as partial solubilization of organo-mercury complexes or the oxidation of mercuric sulfide species. Rae and Aston (1982) showed that an apparent desorption of mercury from suspended solids during the high salinity estuarine tidal cycle may have been due to physical processes rather than chemical. This further demonstrates that desorption of mercury does not readily occur. They showed that during high salinity the particle size increased and TOC decreased. Because there was a positive correlation between TOC and mercury concentration in the suspended material a decrease in the mercury concentration would be expected. These investigators further supported this hypothesis by attempting to desorb mercury from the suspended materials with solutions of

$MgCl_2$, NaCl, and H_2O_2. Only H_2O_2 was capable of desorbing a measurable amount of mercury. Ramamoorthy and Rust (1976) found no desorption of mercury from fresh water sediments when shaken in distilled water or fulvic acid solutions. This result did not depend on the organic content of the sediment because it appears that the partitioning of mercury within the sediment chemical phases determines the bioavailability of the mercury. Because of the high affinity of mercury for the various functional groups and the ubiquitous occurrence of organic material in sediments, this phase is usually considered the primary sink for mercury in sediments. Many studies have found good correlation between mercury levels and TOC; however, not all studies have demonstrated this correlation. At least one investigation has found a correlation between iron content and mercury levels (Hannan and Thompson, 1977). Sulfides have a very high affinity for mercury and thus may be an important control of mercury especially in polluted, anoxic sediments (Eganhouse et al., 1978). In summary there is no completely acceptable model for describing the uptake of mercury on sediments. The use of TOC or some other measurement of the organic fraction appears to be the best criterion for assessing the potential for the uptake of mercury by a sediment. It is clear, however, that each aqueous system has the potential for its own response to an input of mercury and general models should not be applied to specific cases.

One question this study is trying to answer is why is there a considerable elevated level of mercury in fish but low levels of mercury in the water and sediment? Methylmercury released to the overlying water, either in dissolved form or adsorbed on particulate materials is accumulated by fish with high concentration factors. Methylmercury is produced by biomethylation of mercury by bacteria. Kudo et al. (1975) found the proportion of methylmercury to the total amount of mercury in bed sediments ranged from .1-10%. B_{12} dependent synthesis of metal alkyls have been discovered for mercury, lead, thallium, palladium, platinum, gold, tin, chromium, arsenic and selenium (Wood et al., 1978; Ridley et al., 1977); Wood, 1978; Craig and

Wood, 1978). Two mechanisms have been determined for methyl transfer from methyl B_{12} to heavy metals. These mechanisms are 1) electrophilic attack by the attacking metals on the Co-C bond of methyl B_{12} and 2) methyl-radical transfer to an ion pair between the attacking metal ion and the corrin-macro cycle(Wood and Wang, 1985). Metal ions which displace the methyl group by electrophilic attack are Hg(II), Pb(IV), Tl(III), and Pd(II). Examples of free-radical transfer are Pt(II)/Pt(IV), Sn(II), Cr(II), and Au(III) (Wood and Wang, 1985).

Once methyl mercury is released from the microbial system it enters the food chain as a result of its rapid diffusion rate. In the estuarine environment the reduction of sulfate by Desulfovibrio species to produce hydrogen sulfide is quite important in reducing $CH_3Hg(II)$ concentration by S^{-2} catalyzed disproportionation to volatile $(CH_3)_2Hg$ and insoluble HgS (Wood and Wang, 1985). Fluorescence techniques and high resolution NMR show diffusion is the key to $CH_3Hg(II)$ uptake (Wood et al., 1978). Also a field study of the uptake of $CH_3Hg(II)$ by tuna fish in the Mediterranean fit perfectly the diffusion model for biota in tuna fish chains (Buffoni, 1982).

Bacteria have developed other protective mechanisms against heavy metals other than biomethylation. These include intracellular traps, binding of metal ions to cell surfaces and to extracellular ligands, and precipitation of metals by enzymes at the cell surface (Wood and Wang, 1985). Bacteria can also mediate interconversions between three inorganic forms of mercury. Aerobes can solubilize Hg^{+2} from HgS by oxidizing the sulfide through sulfite to sulfate. Once Hg^{+2} has been solubilized it can be reduced to Hg^{0} by an enzyme present in a number of bacteria (Wood, 1974). The conversion of Hg^{+2} to Hg^{0} can be regarded as a detoxification mechanism because the Hg^{0} has sufficient vapor pressure to be lost from the aqueous environment into the vapor phase (Wood, 1974).

Mercury a b-type cation (Ahrland, 1958) bonds mainly via covalent interactions and forms its strongest complexes with donors from the second and subsequent rows of the periodic table. The ligand preferences are in the sequence $N << P > As > Sb : O << S = Se = Te : F << Cl, Br < I$ with $S > N > O > F$. Whitfield and Turner (1983) plotted covalent index ΔB against electrostatic index z_i^2/r_i (Figure 13). Elements falling within the same zones on this diagram will exhibit similar solution chemistry and the stability constants of complexes formed with the three classes of ligands (hard, soft and intermediate) show clearly defined trends (Whitfield and Turner, 1983). Mercury falls in area III, along with Cu(I), Tl(I), Cd, Ag and Au(I), these are considered chloro dominated cations. Nieboer and Richardson (1980) have developed a classification of ligands encountered in biological systems (Table 9). The stability of complexes with (b) type metals increases in the sequence I < II < III. (B) type cations bind preferentially to sulfur sites and to a lesser degree, nitrogen sites. An example of a typical (b) type behavior is provided by the preference of Hg^{+2} ion for disulfide and sulphydryl groups in proteins (Vallee and Ulmer, 1972).

The complexation field (CF) diagram (Figure 13) can also predict cation toxicity. The toxic elements are confined to areas II and III and the micronutrient elements to the intermediate grouping (Whitfield and Turner, 1983). Furthermore, the toxicities of the elements for a wide range of organisms tends to increase in the sequence Area I < A-IV < Area IIA < A-IIB < AIII or a-type < borderline < b-type. Ochiai (1977), suggests that interference by extraneous elements can give rise to toxic effects by modifying their active conformation, blocking essential functional groups and displacing essential metal ions. Cations from area III and IIb bind preferentially with sulfur and to a lesser extent with nitrogen sites which are important in the functioning and conformation of proteins and enzymes (Whitfield and Turner, 1983). The bonds in which they participate are stronger than a similar z_i^2/r_i value. These cations are therefore able to participate in all three of Ochiai's toxicity mechanisms and thus will displace the micronutrient elements (Area IV, Figure 13), with the exception of the lanthanides, from the active sites in which they are involved.

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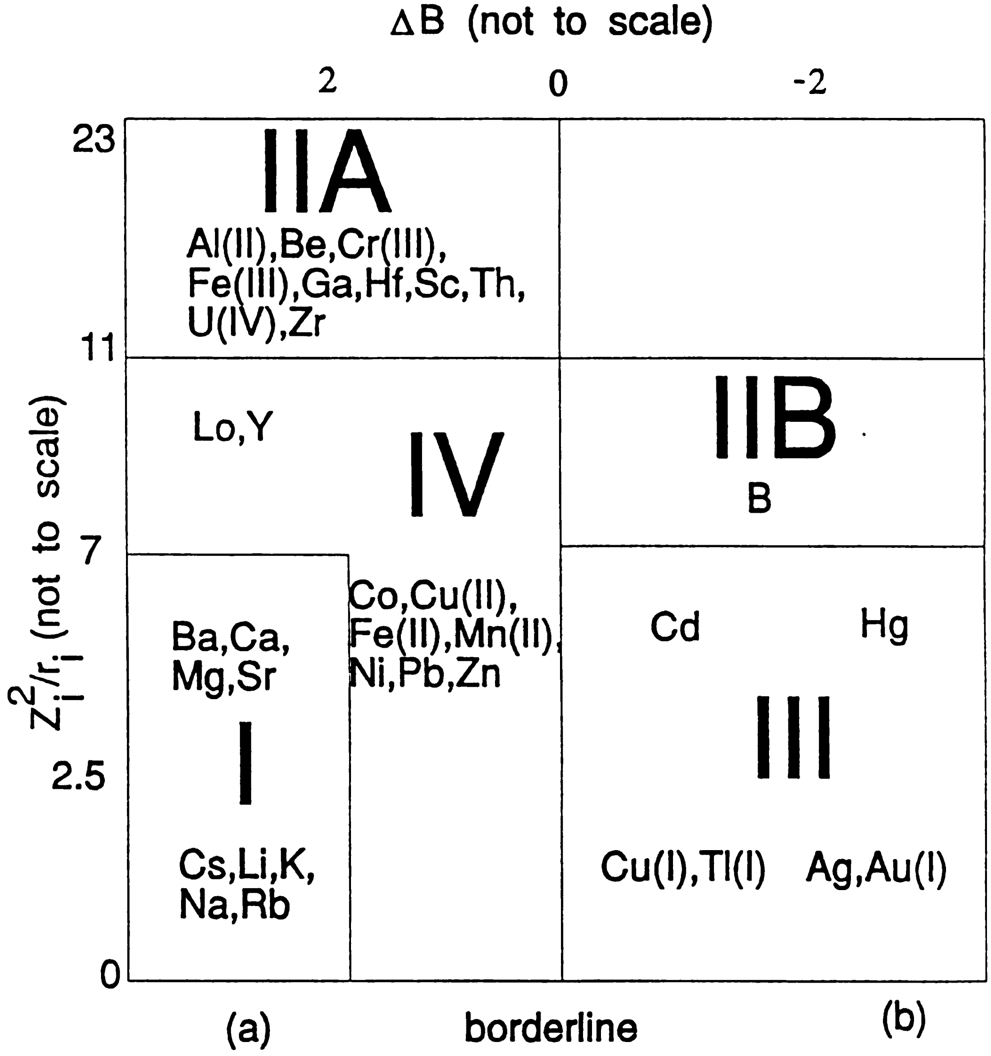

Complexation field diagram for the cationic elements. The cations are divided into four groups on the horizontal and vertical axes. I:very weakly complexed cation, II: hydrolysis-dominated cations, III: chloro-dominated cations, IV: intermediate cations.
(From Whitfield and Turner, 1983)

Figure 13 Complexation Field Diagram (Whitfield and Turner, 1983)

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