SIMULATED MOBILIZATION OF METALS FROM SEDIMENTS IN RESPONSE TO LAKE ACIDIFICATION

By

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MANAGEMENT PERSPECTIVE

The most recent layers of lake sediments in many parts of Canada show highly elevated levels of metals which can be related to the increased contributions from anthropogenic sources. Some of these lakes which are sensitive to acid rain have shown a marked drop in their pH values in recent years. There has therefore been some concern that the increasing acidification of the lakes will liberate the toxic metals from the sediments and consequently will adversely affect the quality of the overlying lake water. The objectives of this study are two-fold: a) using different chemical extractants, to determine the leachable fractions of metals in highly contaminated lake sediments; and b) to evaluate the mobilization of the available metals in the sediments,a function of pH during an extended period of time. Previous studies of metal release from soils and sediments have generally been of short-term duration.

The study shows that a large percentage of the pollutant metals are mobile as determined by chemical extraction technique. The release of each metal increases exponentially below a threshold pH value, which is about 4.0 for Cu, Ni, Zn and Cd and about 3.5 for Fe. The data suggest that a decrease in pH alone is unlikely to be the controlling variable in any release of pollutant metals from most lake sediments.

PERSPECTIVE-GESTION

Dans plusieurs lacs du Canada, les couches sédimentaires les plus récentes renferment des niveaux très élevés de métaux que l'on peut attribuer à certains lacs qui sont particulièrement susceptibles aux pluies acides ont connu une chute marquée de leur pH au cours des dernières années. On craint par conséquent que l'acidification progressive des lacs ne libère les métaux toxiques mêlés aux sédiments et n'altère la qualité des eaux des lacs. Cette étude a pour but premièrement, de déterminer la fraction lessivable des métaux présents dans les sédiments lourdement contaminés au moyen d'agents d'extraction et deuxièmement, d'évaluer la mobilisation des métaux en présence dans les sédiments, une fonction qui se fait du pH sur une période prolongée. Des études preabables sur le transfert de metaux des sols et sediments, ont été generalement de durée à court terme.

L,étude révéle qu'un grand pourcentage de metaux polluants sont mobiles, comme les techniques d'extraction chimique l'a demontré. En deca d'une certaine valeur du pH, qui est de l'ordre de 4,0 pour le cuivre, le nickel, le zinc et al cadmium et de 3,5 pour le fer, la libération des composés métalliques suit une courbe exponentielle. D'après les données, il semble peu probable qu'une chute du pH soit la variable déterminante dans la diffusion des polluants métalliques issus des sédiments lacustres.

RESUME

Les formes de métaux polluants qui peuvent se détacher des sédiments au fond des lacs sont mesurées de facon estimative au moyen d'agents extracteurs. On étudie également dans un microcosme en laboratoire les effets de l'acidification des lacs sur la mobilisation des composés metalliques. En deca d'une certaine valeur et de 3, 5 pour le fer, la libéeration des composés métalliques suit une courbe exponentielle. D'après les données, il semble peu probable qu'une chute du pH soit la variable déterminante dans la diffusion des polluants métalliques issus des sédiments lacustres.

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ABSTRACT

The regenerable forms of pollutant metals in lake sediments are estimated using different chemical extractants and the effects of lake acidification on the mobilization of such metal fractions studied in laboratory microcosm. The release of each metal is found to increase exponentially below a threshold pH value, which is about 4.0 for Cu, Ni, Zn and Cd and about 3.5 for Fe. The data suggest that a decrease in pH alone is unlikely to be the controlling variable in any release of pollutant metals from most lake sediments.

INTRODUCTION

The most recent layers of lake sediments in many parts of Canada show highly elevated levels of metals which can be related to the incresed contributions from anthropogenic sources. Some of these lakes which are sensitive to acid rain have shown a marked drop in their pH values in recent years (e.g., refs. 1-3). There has therefore been some concern that the increasing acidification of the lakes will liberate the toxic metals from the sediments and consequently will adversely affect the quality of the overlying lake water.

The objectives of this study are two-fold: (a) using different chemical extractants, to determine the leachable fractions of metals in highly contaminated lake sediments; and (b) to evaluate the mobilization of the available metals in the sediments a function of pH during an extended period of time. Previous studies of metal release from soils and sediments have generally been of short-term duration (see refs. 4-6).

METHODOLOGY

The highly contaminated lake sediments used in the study were obtained from Ramsey Lake (45°25'N, 81°00'W) which is located about 8 km from the tall smelter stack at Sudbury, Ontario. The lake receives

no mine tailings and is fed by runoff and underground springs. The metal input comes mostly from the atmosphere so that the chemical composition of metal-bearing aerosols falling into the lake is, presumably, similar to that falling into many lakes in Ontario (11); Sudbury has some of the largest point sources of airborne metals in the province. The pH of the lake water was 6.8, an important consideration in a study aimed at understanding the potential effects of acid stress on lake sediments.

Representative sediment samples were collected using Birge-Eckman grab sampler at Station G (Figure 1) which has a water depth of 9 m. The oxidized surficial sediments (top 3 cm layer) were carefully sectioned off using a plastic knife. The procedure was repeated until a large composite sample was obtained. In the laboratory, about 30 litres of the homogenized wet sediments were put into each of two identical polyethylene containers measuring 60x60x75 cm. To the sediment which covered a depth of about 10 cm, 110 litres of distilled water was added (forming a layer of about 30 cm) and then the mixture was allowed to settle. A steady stream of air was passed through the water column to provide mixing and aerobic conditions without disturbing the sediment-water interface. The tanks were maintained at the temperature of 22+2°C.

When the system stabilized, the starting pH value (6.2) was recorded and the acidification with conc. H_2SO_4 commenced. After the first acid spike, the pH of the water dropped to about 5.5 but was

back up to 6.2 after 24 hours. More acid was added and the procedure repeated over several days until a pH reading was obtained which remained unchanged for one week. The water sample was then taken from the mid-point of the water column. Proceeding in this manner, the pH of the system was gradually lowered to a final value of 2.8 over a period of 12 months.

Three sediment cores were also collected using a Benthos gravity corer at locations marked in Figure 1. Core W2 was located at the deepest point (20 m) in the lake while W1 and E1 were obtained from 8 m of water. Each core was quickly sliced into 2 cm sections, placed in self-sealing plastic bags and then frozen. Subsequently, the samples were freeze-dried and ground to 200 mesh size. An aliquot (2.0 g) of each sample was leached with dithionate-citrate-bicarbonate (DCB) mixture while another aliquot (1.0 g) was treated with 20 ml of 0.5 N H_2SO_4. The sample extraction was done in plastic tubes which were shaken gently for 24 hours and the leachate was then removed by high speed centrifugation.

Total metal concentration in each sediment sample was determined following repeated digestion with hydrofluoric nitric and perchloric acid according to the method of Agemian and Chau (1977). Organic carbon in the sediments was determined by dry combustion in a Leco furnace after removing the carbonate carbon with sulfurous acid (8).

The Fe, Cu, Zn, Ni, Cd, Mn and Al in water samples (from metal release experiments) and sediment leachates were determined by atomic absorption spectrometry according to the Analytical Methods Manual (9).

RESULTS AND DISCUSSION

The total metal concentrations in Ramsey Lake sediments are given in Table 1. The marked enrichment of Cu, Pb, Ni and Fe in the surficial sediments (the 0-3 cm layer employed in the metal release experiments) is not unexpected considering the closeness of the lake to major point sources of the metals. The eastern basin (Stn E1) sediments generally show slightly higher levels of metals in the most recent layers. This feature conceivably is related to the particular redox regime responsible for the high accumulation of iron and manganese oxyhydroxides. The sharp decrease in metal concentrations with depth is a common feature of lake sediments in the Sudbury basin (10-12). From the sediment accumulation rate of 0.9 mm/yr (185 g/m^2yr) in the western basin (Stns W1 and W2), the onset of accelerated metal deposition (7-9 cm below sediment-water interface) can be dated to the beginning of mining and smelting operations in Sudbury around 1890 (11).

Various chemical extractants have been used to assess the capacity of sediments and soils to liberate their trace metal burden. In spite of the large volume of literature on the subject (see refs. 4, 13, 14) no single extractant has been shown to remove diagnostically the available forms of any of the trace metals. A variety of extractants have therefore been tried, ranging in severity from dilute solutions of inorganic and organic salts and acids to

strong oxidizing or reducing agents. Two such extractants in common use have been employed in the present study: the dithionate-citrate-bicarbonate (DCB) mixture which removes mostly the reducible phases and 0.5N H_2SO_4 which extracts the readily soluble components in the sediments. The amount of each metal leached out by these two reagents are summarized in Figures 2 and 3. Basically, the regression line for each metal was compared with the regression line obtained for the duplicate which was then tested for slope equality (15). Duplicate slopes were compared to determine if they could be pooled. Once the test of the hypothesis indicated similarity of slopes, the data were pooled and statistically treated to form the new regression lines shown in two figures.

In general, the profiles of DCB extractable metals tend to parallel those of total metals with marked enrichment of this phase in the surficial sediments. This implies that the smelters at Sudbury are a major contributor of DCB extractable metals in the lake sediments. It is generally believed that the DCB treatment liberates metals adsorbed or coprecipitated with oxides and hydroxides of Fe and Mn and some of the Al present as coatings on clays and other sediment particles (16-18). A comparison of Figure 2 and Table 1 shows that DCB treatment releases 40-50% of the total Fe in the surficial aerobic sediments at W1 and E1 but only 25% of the total Fe at the more reduced Station W2. A build-up of Fe in the surficial sediments can be attributed to (a) the fact that Fe input from anthropogenic sources

may be more mobile or (b) the precipitation of labile Fe derived diagenetically from the older sediments. The liberation of significant amounts of Al by DCB is generally noteworthy.

It is generally accepted that extraction with reducing DCB reagent (pH, about 7) gives a rough estimate of that portion of trace metals bound to metal oxides. A comparison of data in Table 1 and Figure 2 shows that 25-35% of the total Ni, 1-4% of the Cu, 25-30 of the Zn and 10-20% of the total Cr in the surficial sediments are associated with metal oxides. The values for lead are in the range of 15 to 30%. These levels of tracemetal association with the reducible oxide phases are comparable to what have been reported for polluted sediments in other areas (4, 13, 14). The Ni-DCB, Cu-DCB and Pb-DCB (not shown) are strongly enriched in the surficial sediments, and decrease sharply with depth in the sediment (Figure 2). Because of their generic association with oxides, a significant fraction of the trace metals released by the smelters ultimately reach the lake sediments in DCB extractable form. It should, however, be noted that Zn-DCB has an inexplicably noisy profile.

The profiles of metals extracted using dilue H_2SO_4 are shown in Figure 3. For Fe, this reagent extracts about 80-90% of the Fe-DCB in the surficial sediments. By contrast, the dilute acid extracts considerably (2- to 3-fold) more Al than DCB (compare Figures 2 and 3). A remarkable thing, however, is that the acid treatment liberates 45-55% of the total Ni and 70-80% of the total Cu in the surficial

sediments (compare Fig. 3 and Table 1). The implication with reference to Figure 2 is that less than 10% and 55-70% of the potentially mobile Cu and Ni in the surficial sediments are tied up with the oxyhydroxides. Copper has a marked affinity for organic matter in lacustrine sediments (13, 19, 20). It would thus appear that the acid treatment has resulted in the release of organically bound Cu which apparently accounts for about 50-60% of the total burden of this metal in the sediments. The dissolution of metal sulfides can be discounted in the aerobic surficial sediments used in the present experiments.

A number of studies have shown that a significant fraction of the trace metals in freshwater sediments can be bound to the carbonate phases (13, 21). Ramsey Lake sediments contain less than 1.0% of carbonate carbon. The organic carbon, however, is 3-5% at the sediment-water interface and declines to 1-3% in the deeper sediments (Figure 4). The role of the organic matter as a primary matrix for Cu in these sediments has already been noted.

The preceding discussion has deliberately dwelt on the most recent sediments which were employed in the long-term release experiment. These sediments show the highest levels of toxic metal pollution and are the ones exposed to acidic lake waters. The preceding data on trace metal associations in the sediments are therefore critical to the understanding of how much of the available metal can be liberated in response to lake acidification.

The long-term, pH-induced release of metals from the sediments to the overlying water is depicted in Figure 5. Without exception, the release of each metal increases exponentially with a decrease in pH below a threshold value. For Cu, Ni, Zn and Cd, the threshold value is about 4.0 and for Fe about 3.5. Before the breakthrough pH is reached, there is only a gradual increase in metal mobilization as the pH is lowered. The actual amount of metals liberted from the sediments is significant. At the pH of 2.8, it is estimated that 120 ug/cm^2 of Ni, 110 ug/m^2 of Cu and 18 ug/m^2 of Zn are expelled by the sediments. Assuming that the 10 m water depth at the sampling station is completely mixed, such an acid stress would be expected to add 120 ug/l Ni, 110 ug/l Cu and 18 ug/l Zn to the overlying water. Such potential contributions from sediments may be compared with the current Ni, Cu and Zn concentrations in the water of 220, 16 and 8.0 ug/l, respectively (11).

The breakthrough pH values for metals in sediments (Figure 5) are lower than those for sewage sludge which have been reported to be about 5.5 for Ni and Zn and 4.5 for Cu (22). There is some evidence that the release of metals from anaerobic sediments, in particular, begins at pH values higher than those of the experimental microcosms. David _et al_. (5) and Galloway _et al_. (3) found that Zn is mobilized at pH below 5.5 and Pb at pH of less than 3.5 from sediments of Adirondack lakes, northeastern United States. Schindler _et al_. (23) observed a significant release of Al, Mn, Zn and Fe at pH of 5-6 from

sediments of a eutrophic lake which was being subjected to artificial acidification. The reduction in Zn, Cd and Pb concentrations in the most recent sediments of Gardsjon Lake (Sweden) has been attributed to the leaching out of labile metals by the acidic (pH, 4.7) lake waters (24). A similar interpretation has also been proposed for the reduced metal burdens in surficial sediments of some lakes in the Sudbury basin (11, 12).

It should be emphasized that the present study was designed to test specifically the role of pH alone on the release of metals under static aerobic conditions. Extrapolation of the results to field situations must be done in a circumspect manner. For example, the resuspension and bioturbation of sediments can markedly affect the amount of metals released (25). Furthermore, a reduction in Eh of the sediments can have a dramatic effect on the rate of metal release as documented by the DCB extraction and by field observations already referred to.

Ramsey Lake is probably typical of many oligotrophic lakes where an oxidized surficial layer overlies the generally reduced sediments (26, 27). As the redox boundary is diagenetically moved upward with sediment accretion, some of the trace metals may be expected to be mobilized. This raises the possibility that the metal enrichment in the oxidized surficial sediments of some oligotrophic lakes could be diagenetically mediated. The function of the oxidized layer as a barrier in the transfer of mobilized metals to the overlying water has certainly not received the attention it deserves.

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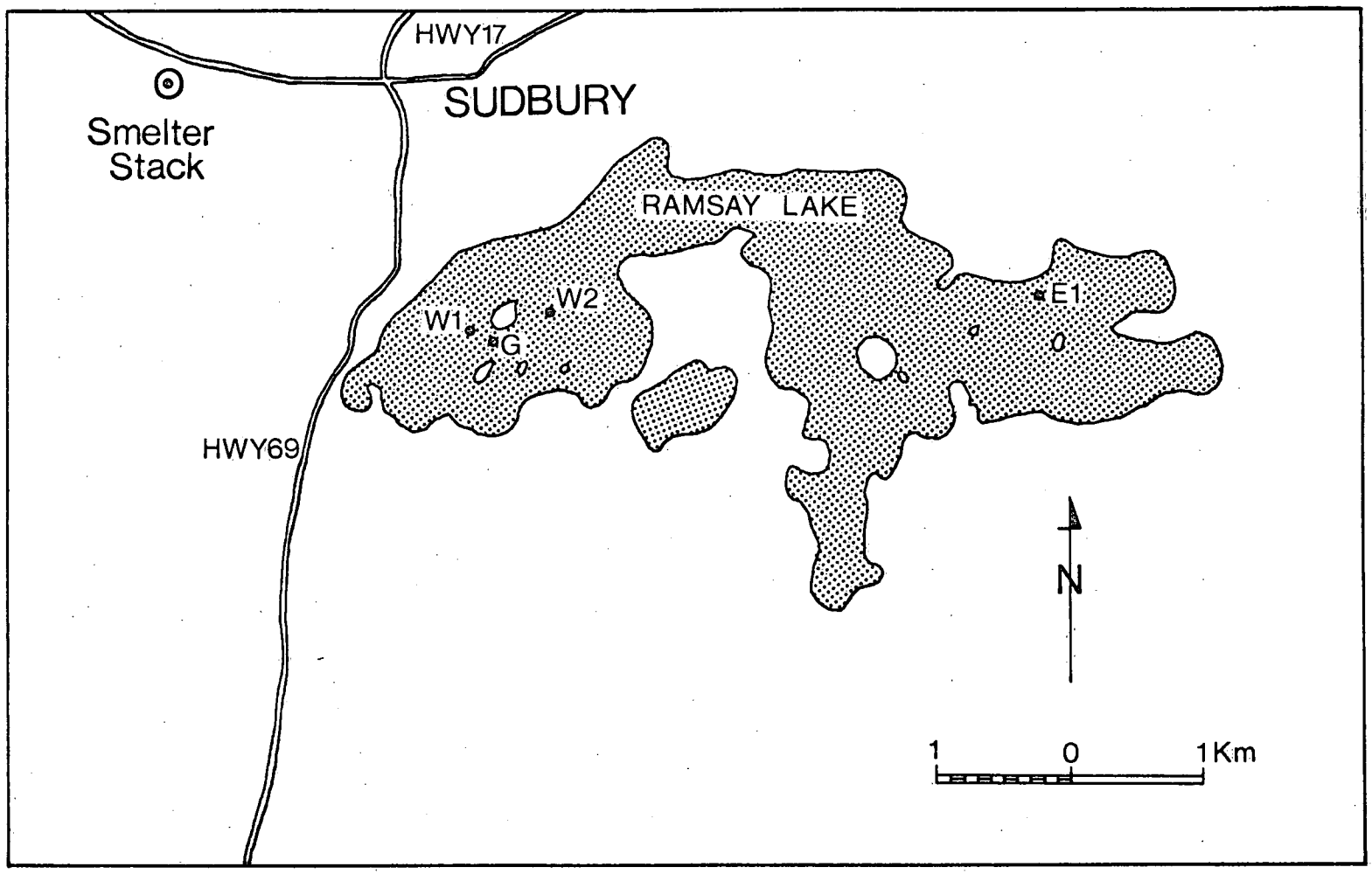
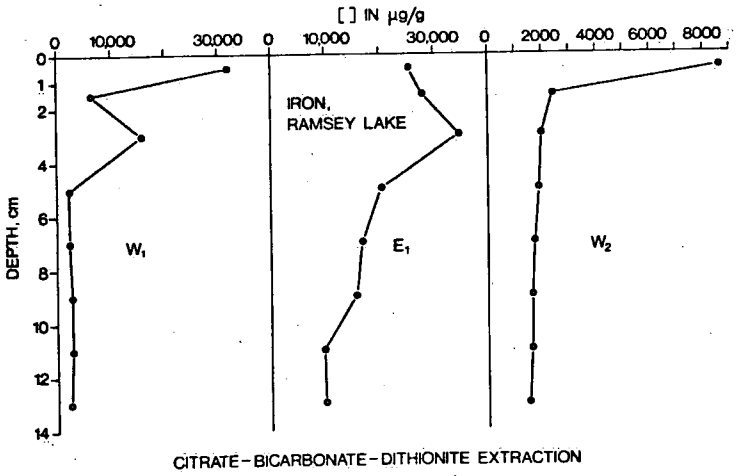
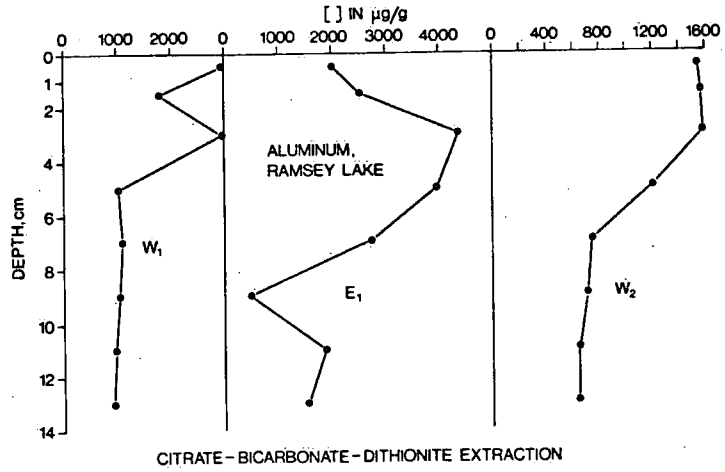
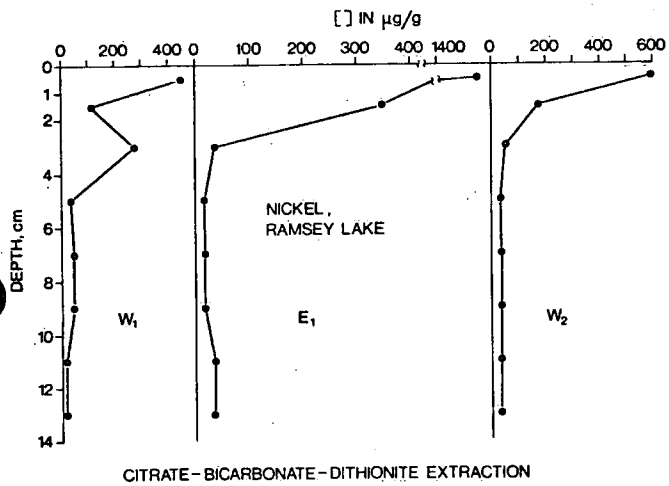
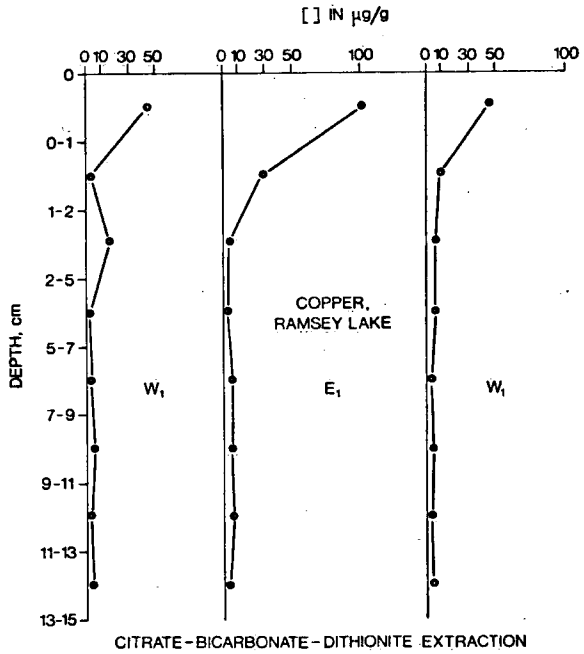

HWY17
SUDBURY
Smelter
Stack
RAMSAY LAKE
W1
W2
G
E1
HWY69
N
1
0
1 Km

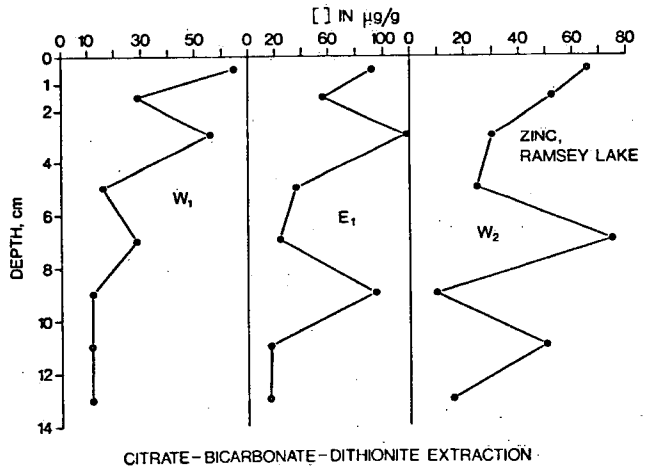
FIG. 1


[ ] IN µg/g
IRON,
RAMSEY LAKE
DEPTH, cm
W1
E1
W2
CITRATE-BICARBONATE-DITHIONITE EXTRACTION


[ ] IN µg/g
ALUMINUM,
RAMSEY LAKE
DEPTH, cm
W1
E1
W2
CITRATE-BICARBONATE-DITHIONITE EXTRACTION


[ ] IN µg/g
NICKEL,
RAMSEY LAKE
DEPTH, cm
W1
E1
W2
CITRATE-BICARBONATE-DITHIONITE EXTRACTION


[ ] IN µg/g
COPPER,
RAMSEY LAKE
DEPTH, cm
W1
E1
W1
CITRATE-BICARBONATE-DITHIONITE EXTRACTION


[ ] IN µg/g
ZINC,
RAMSEY LAKE
DEPTH, cm
W1
E1
W2
CITRATE-BICARBONATE-DITHIONITE EXTRACTION

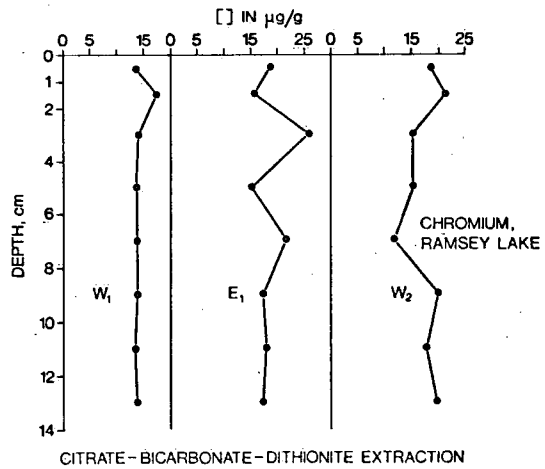
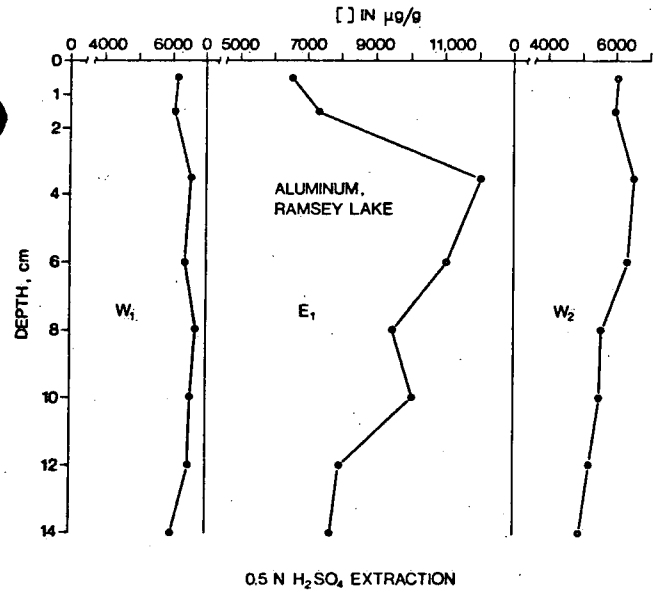
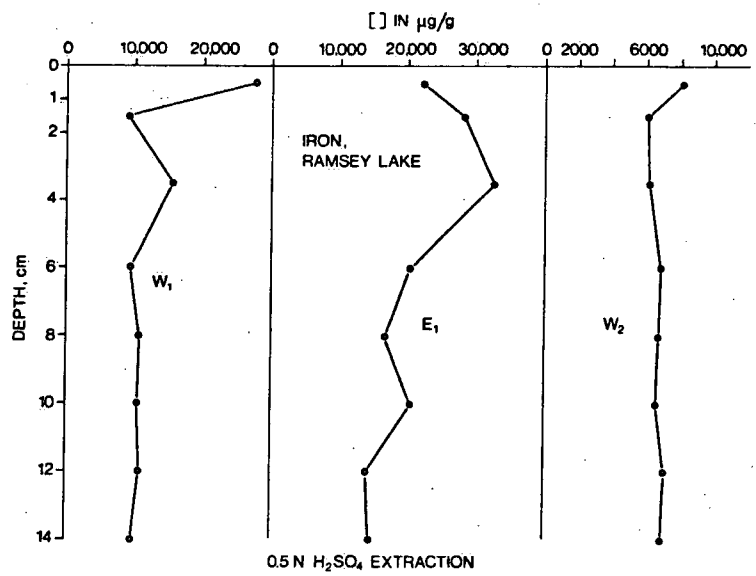
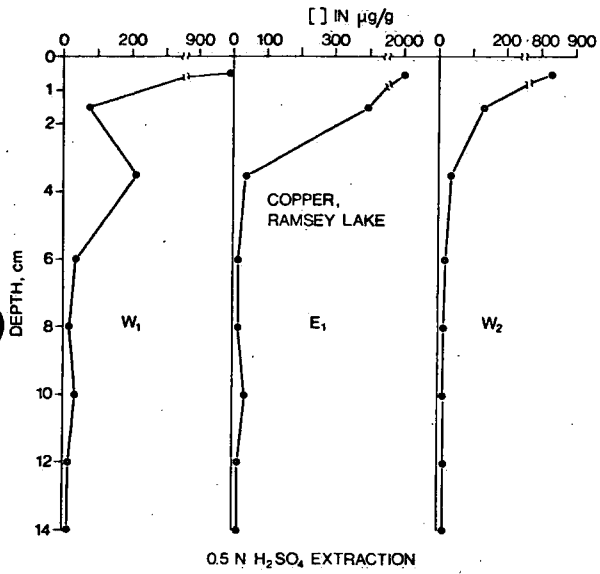
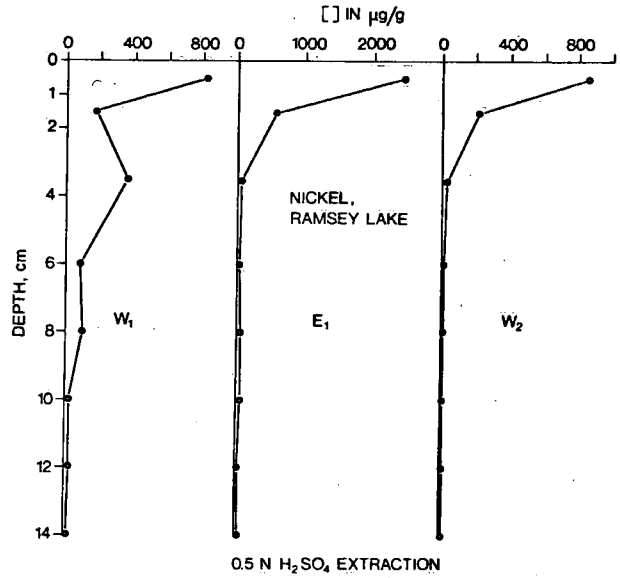

[ ] IN µg/g
CHROMIUM,
RAMSEY LAKE
DEPTH, cm
W1
E1
W2
CITRATE-BICARBONATE-DITHIONITE EXTRACTION

FIG. 2


[ ] IN µg/g
ALUMINUM,
RAMSEY LAKE
DEPTH, cm
W1
E1
W2
0.5 N H2SO4 EXTRACTION


[ ] IN µg/g
IRON,
RAMSEY LAKE
DEPTH, cm
W1
E1
W2
0.5 N H2SO4 EXTRACTION


[ ] IN µg/g
COPPER,
RAMSEY LAKE
DEPTH, cm
W1
E1
W2
0.5 N H2SO4 EXTRACTION


[ ] IN µg/g
NICKEL,
RAMSEY LAKE
DEPTH, cm
W1
E1
W2
0.5 N H2SO4 EXTRACTION

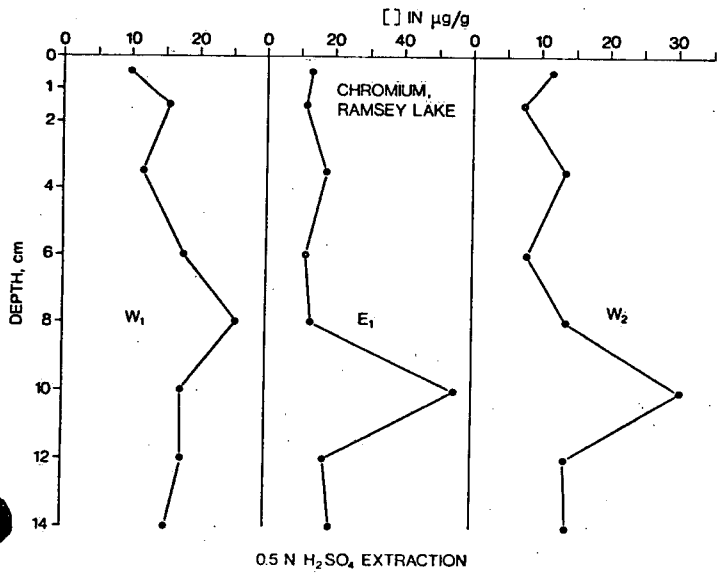
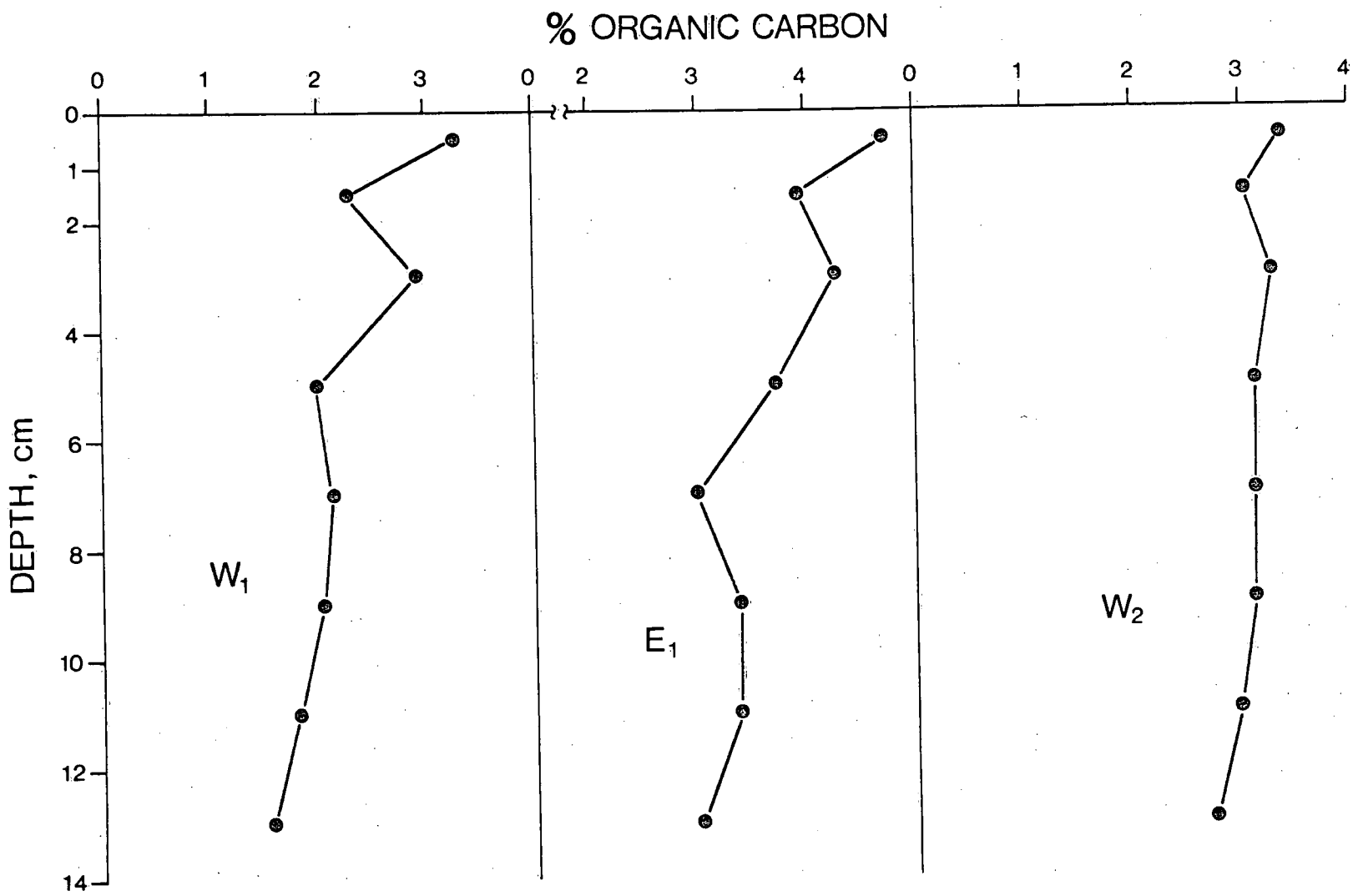

[ ] IN µg/g
CHROMIUM,
RAMSEY LAKE
DEPTH, cm
W1
E1
W2
0.5 N H2SO4 EXTRACTION

FIG. 3.



ORGANIC CARBON,
RAMSEY LAKE

FIG. 4

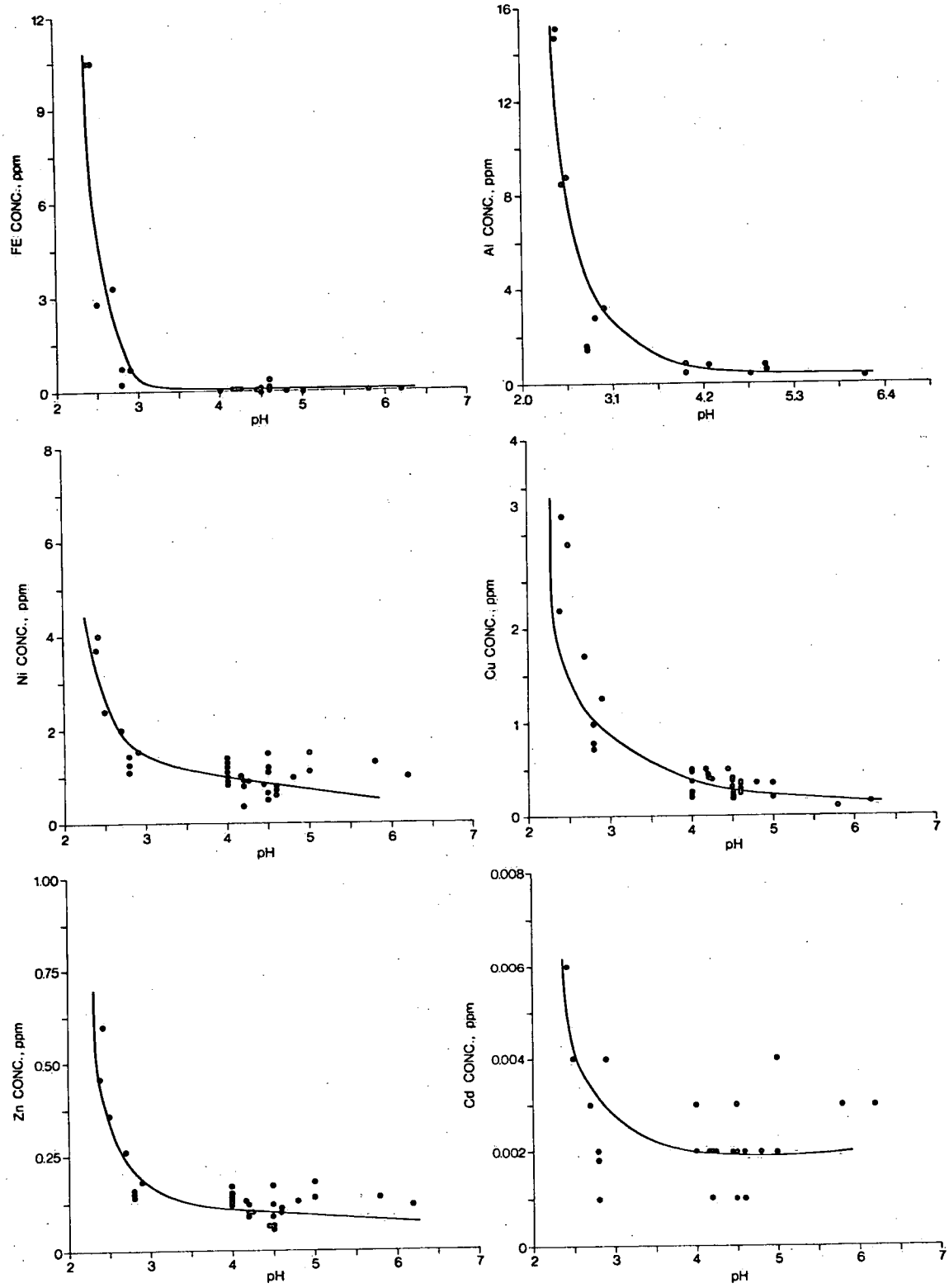

FE CONC., ppm
pH
Al CONC., ppm
pH
Ni CONC., ppm
pH
Cu CONC., ppm
pH
Zn CONC., ppm
pH
Cd CONC., ppm
pH

FIG. 5

TABLE 1. Total metal concentrations in Ramsey Lake sediments. µg/g

Depth	Fe	Ni	Cu	Zn	Pb	Cr
Station W1						
0 - 2	61200.	1880.	1320.	198.	122.0	132.
2 - 3	30600.	370.	130.	139.	18.5	139.
3 - 5	37900.	656.	236.	174.	35.9	133.
5 - 7	29500.	114.	40.	114.	16.2	114.
Station W2						
0 - 2	60600.	4340.0	2930.	384.	253.0	131.
2 - 3	54400.	989.0	593.	198.	98.9	109.
3 - 5	59900.	118.0	56.	138.	31.4	128.
5 - 7	44600.	78.5	32.	136.	24.2	145.
Station E1						
0 - 2	35700.	1740.0	1060.0	212.	81.0	82.0
2 - 3	26500.	397.0	204.0	122.	50.9	77.4
3 - 5	25700.	119.0	40.3	110.	12.8	101.0
5 - 7	26900.	76.7	27.9	120.	12.0	88.6