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15-194

THE BINDING OF METAL AND PHOSPHATE IONS IN THE CONTAMINATED WATERS OF HAMILTON HARBOUR, ONTARIO

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ABSTRACT

Industrial and municipal loadings of contaminant metal and nonapatite inorganic phosphorus ions to Hamilton Harbour, Lake Ontario, are mainly incorporated into the hydrated ferric oxide fraction of suspended particulate matter. Over most of the Harbour, contaminant concentrations in particulate matter are governed by $[\text{contaminant}]/[Fe^{2+}_{CL}] = k_1[Fe^{3+}_{T}]/[Fe^{2+}_{CL}] - n_{CL}k_1 + k_2$, where [ ] represents concentration, Fe^{3+}_{T} is total ferric iron, k_1 and k_2 are constants, and n_{CL} is the ratio of ferric/ferrous iron in inert clay mineral, CL. This linear relationship breaks down for particulate matter collected from an anoxic hypolimnion and from near an industrial outfall; thus, major sources of contaminants can be delineated. The poorly-crystalline ferric oxides, in strong association with organic matter, are beneficial in binding, and thus reducing the bioavailabilities of, contaminant ions; however, some sources of ferric oxides are also sources of metals, notably lead and zinc. Coefficients of incorporation, k_1, of contaminant ions into ferric oxides are, as weight percent of iron in oxide: P 13, Pb 2, Zn 14, Mn 60, Cd 0.036, Cu 0.38, and Ni 0.27. The high values of k_1 for phosphate and zinc ions are of concern.

MANAGEMENT PERSPECTIVE

Hamilton Harbour is an embayment of area 25 km^2 on the western end of Lake Ontario. The Harbour receives heavy inputs of phosphorus from sewage treatment plants and inputs of iron and metals from the steel mills. The waters are highly eutrophic and some metal concentrations exceed provincial guidelines. This work was designed to answer the question: Is the massive iron loading to the Harbour beneficial in binding contaminants and thus reducing their bioavailability?

We present here strong evidence to show that hydrated ferric oxides derived from industrial operations have a high capacity for binding inorganic phosphorus, zinc and other toxic metals in Hamilton Harbour. Consequently, these contaminant ions are removed from solution and retained in suspension. Industrially produced ferric iron compounds are, therefore, of benefit in reducing the availabilities of contaminant ions. On the debit side, the sources of iron are also sources of metals such as lead and particularly zinc. Improvements to water quality in Hamilton Harbour should be based on additional and simultaneous reductions in the loadings of phosphorus from the sewage plants and of iron and metals from the steel complex. It is important that the margin of assimilative capacity of ferric oxides for phosphorus and zinc be retained. The recent heavy infestation of Hamilton Harbour by zebra mussels suggests that the toxic properties of the metals is largely negated by adsorption on oxides.

INTRODUCTION

Hamilton Harbour is a polluted embayment of area 25 km^2 located at the western end of Lake Ontario (Fig. 1). The harbour receives effluent from the sewage treatment plants of Hamilton (population 320,000) and Burlington (120,000) and major inputs of metals from the steel mills on the southwest shore. The water is highly eutrophic and metal concentrations in water and sediment exceed provincial guidelines (Harris *et al.* 1980, Ontario Ministry of the Environment 1985). Besides hematite and wustite, ferric iron is a major industrial contaminant such that the ferric/ferrous ratios in suspended particulate matter greatly exceed their background values in the lake (Mayer & Manning 1990, 1991); this ferric iron is precipitated in the harbour as poorly crystalline hydrated oxide. Hypolimnetic anoxia is strongly developed in summer in deep water (Fig. 1), however incursions of oxygenated water from Lake Ontario ensure that anoxia is occasionally interrupted (Harris *et al.* 1980).

The binding of contaminant metal and nonapatite inorganic phosphate (NAIP) ions by hydrated ferric oxides (Fe^{3+}_{OX}) in riverine particulate matter is described by

$$[\text{contaminant}]/[Fe^{2+}_{CL}] = k_1[Fe^{3+}_T]/[Fe^{2+}_{CL}] - n_{CL}k_1 + k_2, \qquad (1)$$

where brackets represent concentrations, Fe^{3+}_T is total ferric iron, k_1 and k_2 are constants, and n_{CL} is the ratio of ferric/ferrous iron in unreactive clay mineral (CL). The ratio n_{CL} is a measure of the concentration of unavailable ferric iron (Manning & Wang 1994, 1995). However, the validity of equation (1) is severely compromised in waters heavily impacted by local point and nonpoint sources, e.g., the Detroit River (Manning 1989) and Hamilton Harbour (Mayer & Manning 1991).

In this work, the facility with which equation (1) describes ferric oxide-contaminant binding in Hamilton Harbour is assessed using previously published data (Mayer & Manning 1990, 1991) supported by analyses for recently recovered particulate matter. The aims are to determine (a) the potential benefit of anthropogenic ferric iron in binding phosphate and metal contaminants, and (b) how deviations from the linear relationship relate to processes and events within the Harbour.

EXPERIMENTAL DETAILS

Approximately 5 g of suspended particulate matter were collected from five stations (Fig.1) in Hamilton Harbour in November 1993 by the continuous flow centrifugation of 600 L of water at mid-depth. The water column was isothermal and the water temperature 12 C. The brown particulate matter was frozen immediately and freeze-dried on return to the laboratory. Water samples, filtered (through a 0.45 micron cellulose acetate filter) and unfiltered, were also collected.

The particulate matter was analysed for the different forms of iron (ferrous, ferric, hematite, and wustite) by Mössbauer spectrometry at room temperature (Fig. 2) following the methods of Mayer & Manning (1990). The Mössbauer spectrum of sample B4 was also recorded at 4 K in order to resolve poorly crystalline oxides. The main iron-bearing compounds in particulate matter from stations HH-1 and HH-3 were confirmed by X-ray diffraction.

Concentrations of NAIP, organic P, and apatite P in particulate matter were measured by wet chemical fractionation methods (Williams *et al.* 1976). NAIP values are reproducible to ±5%. However, the unknown specificity of the extractant, citrate/dithionite/ bicarbonate (CDB) reagent, makes the accuracy difficult to assess. Water samples were analysed using color development in the phosphomolybdate complex.

Particulate matter collected from station HH-1 in April 1986 was further extracted with CDB reagent, to remove preferentially the hydrated oxides of iron and manganese. The ferric/ferrous ratio in the residue was measured by Mössbauer spectrometry. Particulate matter from station HH-2 was washed with dilute HCl and the Mössbauer spectra again measured.

The concentrations of Fe, Pb, Zn, Mn, Cu, Cd, and Ni were determined by dissolution in aqua regia followed by inductively coupled plasma emission spectroscopy. Metal concentrations (Table 1) are accurate to ±5% relative to standard reference material. Concentrations of ferrous and ferric iron were then determined from the concentration of total iron multiplied by that proportion of the Mössbauer spectral envelope beneath the ferrous and ferric peaks, respectively; concentrations of Fe_T^{3+} and Fe_{CL}^{2+} are good to ±10%.

RESULTS

The Mössbauer spectra (Fig. 2) are identical in composition to those described earlier (Mayer & Manning 1990), showing obvious inflexions marking ferrous ions, ferric ions, hematite and wustite. The spectra were resolved as before. Measured parameters of isomer shift (relative to iron foil), quadrupole splitting, and halfwidth are, respectively: for Fe^{2+} 1.13 mm s^{-1}, 2.59 mm s^{-1}, 0.42 mm s^{-1}, all ± 0.03 mm s^{-1}; for Fe^{3+} 0.38 mm s^{-1}, 0.72 mm s^{-1}, and 0.55mm s^{-1}, all ± 0.03mms^{-1}; for wustite 0.95 ± 0.05 mm s^{-1}, 0.75 ± 0.05 mm s^{-1}, and 0.48 mm s^{-1} (constrained); and for hematite the isomer shift is 0.43 ± 0.03 mm s^{-1}. These values are in agreement with those reported earlier (Mayer & Manning 1991), and are consistent with ferrous ions being located mainly in structural sites in clay minerals and with ferric iron being in both clay minerals and hydrated oxide (Coey *et al.* 1974). The 4 K spectrum displayed an intense and broadened magnetic pattern, with an electric field gradient of 490 ± 50 kOe, marking poorly crystalline ferric oxides (Murad 1988). Approximately 60% of the iron in sample

B4 was contained within this magnetically ordered oxide; this iron represents the NAIP-binding fraction. The ferric/ferrous ratio within the clay mineral "background" is approximately 0.8.

X-ray diffraction confirmed that the main iron species were clay and chlorite, hematite, wustite and magnetite; no other crystalline ferric rion compound was identified. The ferrous iron spectral envelope remained unchanged on washing with acid, hence, vivianite, siderite, and poorly crystalline iron sulfides are minor phases only in particulate matter.

The concentrations of ferrous, ferric, NAIP and trace metal ions (Table 1) in the 1993 sampling of particulate matter are comparable to those measured earlier (Mayer & Manning 1990, 1991). Analyses of filtered and unfiltered water samples show that >85% of NAIP and metal contaminant ions are incorporated into the particulate phase.

DISCUSSION

Geochemical model

Equation (1) is derived on the assumption that the binding of NAIP and metal contaminant ions in particulate matter is governed by [contaminant] = $k_1[Fe^{3+}_{OX}] + k_2[Fe^{2+}_{CL}]$, where Fe^{3+}_{OX} is ferric iron in hydrated oxide, and Fe^{2+}_{CL} proxies for clay mineral (Manning & Wang 1994). The factor k_1 represents a coefficient of incorporation of contaminant into hydrated oxide. From equation (1), the intercept at $[Fe^{3+}_T]/[Fe^{2+}_{CL}] = 0$ is equal to $-n_{CL}.k_1 + k_2$. Assuming further that the adsorption of contaminant ions to clay surfaces is weak relative to the total binding of contaminant to oxides, through adsorption and coprecipitation, then from equation (1), n_{CL} = -intercept/k_1. The application of equation (1) to any body of water requires (a) linearity in the concentration ratio plot, (b) a negative value for the intercept at $[Fe^{3+}_T]/[Fe^{2+}_{CL}]$ equal to zero, as both n_{CL} and k_1 are positive numbers, and (c) a similar value of n_{CL} for all contaminants binding to the same fraction of ferric iron. All three criteria are satisfied in the binding of NAIP and metals to oxides in the Trent River (Manning & Wang 1994, 1995). However, massive point sources in Hamilton Harbour produce considerable scatter in the plots (Mayer & Manning 1991). Note that whereas phosphate ion is specifically bonded to the ferric ion (in oxide), metal ions must bind via an intervening anion, OH^- or O^{2-} or an organic anion such as humate or fulvate (Manning & Wang,1994). Because n_{CL} is a function of the composition of the clay minerals, its value will be different for rivers (and hence lakes) draining watersheds of different geological provinces.

Two of the assumption used in the derivation of equation (1), i.e., $[Fe^{3+}_{OX}] = [Fe^{3+}_T]$ minus $[Fe^{3+}_{CL}]$ and $[Fe^{2+}_{CL}] = [Fe^{2+}_T]$, cannot be perfectly true. However, the Mössbauer spectral signature for Fe^{2+} is reasonably "clean" and is consistent with

that expected for clay minerals and chlorite. Other ferrous compounds are undoubtedly present, but in very minor concentrations. The term CL can cover all inert forms of ferrous and ferric iron, although clay would be dominant. Values of n_{CL}, and hence of Fe^{3+}_{CL}, are confirmed by CDB extraction and sediment ratios (see below).

Interaction between NAIP ions and iron

Phosphorus is the limiting nutrient in the Great Lakes. NAIP is mainly incorporated into the hydrated oxides of iron and manganese (Lucotte & d'Anglejan 1985), and represents over the long term the main reservoir of bioavailable phosphorus (Boström *et al.* 1988, DePinto *et al.* 1981, Williams *et al.* 1976, 1980); most forms of organically-bound phosphorus require mineralization to phosphate ion (Boström *et al.* 1988). Organic P is therefore weakly available.

Concentrations of the pairs NAIP - Fe^{2+}_{CL} and NAIP - Fe^{3+}_{T} are poorly correlated (Fig. 3) with regression coefficients r of 0.39 and 0.11, respectively; for 29 points, r = 0.463 at the 1% level of significance. The concentration ratios NAIP/Fe^{2+}_{CL} and Fe^{3+}_{T}/Fe^{2+}_{CL} are well correlated for 28 of 29 points (r = 0.70; r = 0.48 at the 1% level of significance); one point, that corresponding to the April sampling of station HH-3 at 1 m depth, is excluded from all calculations (metals also) because of the large error implicit in the measurement of the low concentration of Fe^{2+}_{CL} and the correspondingly high value of the ferrous/ferric ratio (= 27, Table 4 of Mayer and Manning 1990). This ratio greatly exceeds the ratios for all other stations and, hence, would influence unduly any statistical analyses of the plots. However, two other graphical points, corresponding to the September samplings of station 2 at 21 m depth (point 2-21m, Fig. 3) and station HH-3 at 1 m (point 3-1m) are clearly outliers. Omitting further these two points, i.e., for 26 of 29 points, linear regression analysis confirms a straight line (r = 0.85; required r = 0.50 at the 1% level of significance) of slope (k_1) equal to 13% (Table 2). The large error in the intercept does not yield a significant value of n_{CL}. The linear concentration ratio plot implies bonding between phosphate ion and one fraction of the ferric ion, i.e., hydrated oxides. The phosphate ion is bidentate (Parfitt & Russell 1977, Ryden *et al.* 1977).

Points 3-1m September sampling and 2-21m September sampling lie significantly outside any line defined by the errors in slope and intercept. Station 3-1m lies within a relatively warm plume of iron-enriched effluent from the steel complex (Mayer & Manning 1991), hence, ferric ions in the plume will not have equilibrated with the NAIP released from the sewage plants. The main point source for phosphorus, the Hamilton sewage plant, is 1.5 km farther south. This plume and the associated steel mill effluent are clearly not important point sources of phosphorus. Graphical point 2-21m corresponds to seasonally anoxic

hypolimnion water, and is most likely indicative of the heavy release of iron from the bottom sediments but of minor release of phosphate ion. The formation of insoluble compounds of (Mg, K, Al, Fe^{2+}) and phosphate ion, other than vivianite, in marine sediments has been proposed by Filipek & Owen (1981).

Interaction between lead and zinc ions and iron

Concentrations of the pairs Pb - Fe^{2+}_{CL} and Pb - Fe^{3+}_{T} are poorly correlated (r values of 0.15 and 0.27, respectively, Fig. 4). The concentration ratios Pb/Fe^{2+}_{CL} and Fe^{3+}_{T}/Fe^{2+}_{CL} are well correlated; thus for 28 of 29 points, i.e., excluding the point for station 3-1m April, r = 0.75. If points corresponding to September stations 2-21m (a clear outlier) and 3-1m are also excluded, the correlation for 26 of 29 points improves significantly (r = 0.90, Fig. 4; required r = 0.50 at the 1% level of significance). The point corresponding to station 3-1m (September sampling) is consistent with this best straight line, hence the adjacent point source of iron is also a significant source of lead.

Zinc ions behave in much the same way that lead ions do. In the concentration ratio plot, the point corresponding to September station 2-21m is a significant outlier to the best straight line through 26 of 29 points; for this line r is a very significant 0.87 (Fig. 5a). The pairs Zn - Fe^{2+}_{T} and Zn - Fe^{3+}_{T} are poorly correlated (values of r = 0.20 and 0.22, respectively). The point corresponding to the plume (station 3-1m September) is consistent with the straight line (Fig. 5a), hence the point source generating the plume is a significant source of zinc. Zinc contamination is likely derived from the recycling of galvanized iron. Neither lead nor zinc is released in significant amounts from the sediments during hypolimnion anoxia, possibly because the formation of sulfide ion serves to precipitate these metals.

Measured values of k_1, i.e., linearity of ratio plots, the significantly negative values of the intercepts $-n_{CL}k_1$, and similar values of n_{CL} of 1 measured from the binding of lead and zinc (Table 2) are consistent with the criteria established above. For comparison, the Fe^{3+}/Fe^{2+} ratio in the clay structure, measured by CDB extraction, is 0.8. Moreover, Fe^{3+}/Fe^{2+} ratios in the top centimetre of bottom sediment are approximately 1 (Mayer & Manning 1990).

Interaction between manganese ions and iron

The pair Mn-Fe^{2+}_{CL} is poorly correlated (r = 0.029) whereas the pair Mn-Fe^{3+}_{T} is well correlated (r = 0.79); this association with ferric iron indicates a high proportion of Mn^{4+} ions within particulate matter. The hydrated oxides of ferric iron and manganese^{4+} are similarly redox sensitive. The concentration ratios $[Mn]/[Fe^{2+}_{CL}]$ and $[Fe^{3+}_{T}]/[Fe^{2+}_{CL}]$ are very well correlated for 26 of 29 points (r = 0.90);

graphical points corresponding to September samplings at stations 2-21m and 3-1m are significant outliers to this line (Fig. 5b). Ferric iron, as hydrated oxide, incorporates 60% of its weight of Mn. The manner of association is not defined: some manganese ion may be adsorbed but most may have coprecipitated with the ferric iron or even precipitated as a separate phase. For example, Mn is precipitated as a distinct black layer at a redox horizon in the bottom sediments of Lake Ontario (Manning *et al.* 1983); there, NAIP is strongly partitioned into the underlying reddish-brown ferric oxide layer. The plume is markedly deficient in manganese relative to ferric iron (point 3-1m, Fig. 5b), hence the plume does not represent a major source of manganese to the harbour. On the other hand, the anoxic hypolimnion waters are significantly enriched in manganese relative to ferric iron values over the harbour generally (September point 2-21m, Fig. 5b). This enrichment is consistent with the heavy release of manganese ions from the sediments on reduction of Mn^{4+} ions (in hydrous oxides) under conditions of declining redox potential. Manganese ions are mobilized sooner than Fe^{3+} ions are under conditions of declining Eh value (Burns & Nriagu 1976, Garrels & Christ 1965). The amount of manganese released from the sediments is proportionally greater than for iron (Mayer & Manning 1990). The behaviour of manganese is thus important to the understanding of aspects of the behaviour of toxic metal ions in the harbour.

The intercept in the concentration ratio plot yields a value of n_{CL} equal to 1, in agreement with values of n_{CL} measured from the interactions of lead and zinc (Table 2) and from CDB extraction.

Interaction between copper, cadmium, and nickel ions and iron

The concentration ratio plots confirm statistically significant correlations, for 26 of 29 points, between the concentration ratios M/Fe^{2+}_{CL} and Fe^{3+}_{T}/Fe^{2+}_{CL}, where M is one of Cd, Ni, and Cu (Figs. 5c, 6a,b, Table 2) in harbour particulate matter. Minor amounts of these metal ions are released during hypolimnion anoxia (Fig. 5c, 6a,b), possibly because, as with lead and zinc ions, they precipitate as their sulfides on sulfate reduction. Cadmium and nickel ions are less strongly associated with particulate ferric iron in the plume than in the harbour generally (point 3-1m in Figs.5c, 6a). Large errors in the measurement of the intercepts to the ratio plots (Table 2) render values of n_{CL} meaningless.

Although the concentration ratio plots show a strong correlation between Cu and Fe^{3+}_{ox}, the intercept is positive (Fig. 6b) and contrary to the negative intercepts measured for the other metal ions. This reflects experimental error (Table 2). Although an association between copper ions and organic matter in sediments has been noted previously (Lum & Gammon 1985), we show below that organic matter also is associated with ferric iron in the harbour particulate matter, as it is in matter suspended in the Trent River (Manning & Wang 1994).

Interaction between organic carbon, phosphorus and iron

The concentration ratios organic carbon/Fe^{2+}_{CL} and Fe^{3+}_{T}/Fe^{2+}_{CL} are well correlated for 21 of 24 points (r = 0.71, Fig. 6c), consistent with the excellent correlation measured in particulate matter from the Trent River, Ontario (Manning & Wang 1994). Concentrations of organic carbon were not measured in particulate matter collected in 1993 because of insufficient sample. Consistent with the trend established for NAIP and for some metal ions, the graphical points for stations 2-21m and 3-1m (September sampling) are distinct outliers (Fig. 6c); the relatively low value for station 2-21m is consistent with the inorganic nature of the plume effluent. Relatively minor amounts of organic matter are released to the hypolimnion during bottom anoxia.

The ratios organic P/Fe^{2+}_{CL} and Fe^{3+}_{T} / Fe^{2+}_{CL} are well correlated, r is 0.82 for 26 of 29 points. Although not shown graphically here, points 2-21m and 3-1m September sampling are distinct outliers to the best straight line, as these points are in the corresponding organic C/Fe^{2+}_{CL} against Fe^{3+}_{T} / Fe^{2+}_{CL} plot (Fig. 6c). Concentrations of organic carbon and organic P are well correlated in Lake Erie sediments (Williams *et al.* 1976). Organic forms of phosphorus are retained in the sediments during hypolimnion anoxia.

General discussion

The consistent value of n_{CL} equal to 1 measured for Pb, Zn, and Mn is indicative of binding to one and the same fraction of ferric iron, namely hydrated oxide. Thus, for sample B4, the concentration of hydrated oxide is 0.60 X 2.16 or 1.3 weight percent and the incorporated NAIP (at k_1 = 0.13) is 0.17 wt%; the measured concentration of NAIP is 0.19 wt% (Table 1). The lower value of n_{CL} measured for the binding of NAIP, indicative of a lower concentration of unavailable ferric iron, probably reflects experimental error: for particulate matter in the Trent River, values of n_{CL} (of 1.2 to 2) measured for several metals and for NAIP are in reasonable agreement (Manning & Wang 1995). Cluster analysis confirms the strong association of the elements: the strong grouping of the ratios of concentrations of elements is especially significant (Fig. 7) and is clearly superior to the simple grouping of concentrations of elements.

The model, as defined by equation (1), and the associated ratio plots (Figs. 3-6), clearly highlights sources of contaminants; generally, therefore, the plots can usefully serve as indicators of point sources of contaminants in rivers and embayments. Thus, manganese and iron are both released from the sediments during hypolimnion anoxia, manganese in relatively large amounts, whereas NAIP, Pb, Zn, Cd, Cu, and Ni are retained in the sediment. The released iron, although measured as ferric iron, is present in the hypolimnion as ferrous ion,

which is later oxidized on exposure to the atmosphere during sample processing. Lead and zinc are released together with ferric iron (rapidly hydrolyzed to hydrated oxides) in the plume emanating from the east side of the steel complex.

The role of the organic matter in binding contaminants is, however, problematic. The measured values of n_{CL} (Table 2) are not inconsistent with earlier suggestions (Manning & Wang 1994) that the organic matter and metal ions bind to the same fraction of ferric iron. In view of the wide range of organic material (from humic acids to decaying bits of algae) present in the river and in particulate matter, the anions cannot be identified. However, organic anions may control the precipitation of the ferric iron. Assuming the binding of one large organic molecule, probably as a bidentate ligand, then a k_1 value of 14 supports an approximate molocular weight of 2000 based on the product 56 X 14 X 2.5, the last factor relating C to the more representative CH_2O molecule. Large organic anions may thus function as bridging ions between the ferric ions in oxide and metal ions (Bunzl 1974, Laxen 1983, Livens 1991).

The coefficient of incorporation of NAIP into hydrated oxide, i.e. k_1 equal to 13%, is comparable to the values measured for the Trent River (k_1 = 18%, Manning & Wang 1994), for the Detroit River and tributaries (a "maximum assimilative capacity" of 18%, Lum & Gammon 1985), and at a deep-sea ridge crest (18%, Berner, 1973). Significantly, a concentration ratio plot for the eight points corresponding to stations HH-1 and HH-4 yields a straight line of slope 17%; this value approaches the "maximum assimilative capacity". In nearshore areas adjacent to sources of nutrient, this capacity may be exceeded and algal growth is stimulated. Consequently, water quality in nearshore areas of any lake will not reflect water quality lakewide. At several stations in the Detroit River, concentrations of NAIP and lead in particulate matter greatly exceed the trend in the concentration ratio plots established in upstream and offshore stations (Manning 1989). The k_1 value of 14% measured for Zn in Harbour particulate matter is of concern as it greatly exceeds the values measured in the Detroit and Trent Rivers, respectively, 2% (Lum & Gammon 1985) and 1% (Manning & Wang 1995), and may be comparable to the "maximum assimilative capacity". Some of the particulate zinc in Hamilton Harbour may be weakly bonded. Remedial action to improve water quality should be aimed at improving the margins of assimilative capacity for zinc and NAIP, i.e. reducing the values of k_1. Reductions in the loading of zinc would probably entail a lower loading of iron, which would lead to an increased availability of NAIP. Reductions in contaminant loading from the sewage plants and the steel complex should be concurrent.

The industrial ferric iron fraction is clearly beneficial in removing large quantities of inorganic phosphorus from solution, through adsorption and/or coprecipitation. Incorporation into iron oxides is the basis for the use of ferric chloride (Boers *et al.* 1994) in precipitating, and thus reducing the bioavailability of, phosphorus in lakes. Similarly, the bioavailability of metals is reduced through their incorporation into particulate matter. Bioavailability is then

dependent on kinetic constraints placed on the rate of desorption and of dissolution of phosphate ion. Most importantly, photochemical activation would lead to the reduction of ferric and manganese ions, the oxidation of organic matter (Miles & Brezonick 1981, Morel 1983), and dissolution of contaminant. Such processes are likely to be highly efficient in Hamilton Harbour, because of the high concentrations of ferric and manganese ions, the binding of organic matter within a Fe^{3+}_{ox}-NAIP-organic anion assemblage, and the high binding capacity for NAIP and Zn. Concentrations of ferrous ions in solution in the Harbour in summer may be significant, stabilised through chelation with organic ligands. The mode of interaction between hydrated ferric oxides and organic matter in natural waters is thus fundamental to an understanding of contaminant transport and bioavailability in natural waters.

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CAPTIONS FOR FIGURES

FIG. 1. Diagrammatic representation of stations in Hamilton Harbour sampled in April and September 1986 (stations HH-) and, on a smaller scale, in 1993 (stations B). HSTP and BSTP mark the outfalls of the sewage plants of Hamilton and Burlington, respectively. Surface water at station HH-3 lies within a plume from an industrial outfall.

FIG. 2. Room temperature Mössbauer spectrum of suspended particulate matter collected from mid-depth station B4 in 1993. Chi-squared is 544 for 490 degrees of freedom. Absorptions of the main iron species are identified.

FIG. 3. Plots showing the poor correlation between the pairs NAIP-Fe^{2+}_{CL} and NAIP-Fe^{3+}_{T}, and the good correlation between the concentration ratios NAIP/Fe^{2+}_{CL} and Fe^{3+}_{T}/Fe^{2+}_{CL} for 26 of 29 points ($r = 0.85$; $r = 0.50$ at the 1% level of significance). Points corresponding to stations 2-21m September, 3-1m April, and 3-1m September are not included in the regression analysis. Symbology is: circles represent April 1986 sampling, triangles September 1986, and squares November 1993. Note that the best straight line covers points corresponding to the 1986 and 1993 samplings. Ratios for 1986 sampling taken from data in Tables 1 and 4 of Mayer & Manning (1990).

FIG. 4. Plots showing poor correlations between concentrations of the pairs Pb-Fe^{2+}_{CL} and Pb-Fe^{3+}_{T}, and the good correlation between the concentration ratios Pb/Fe^{2+}_{CL} and Fe^{3+}_{T}/Fe^{2+}_{CL} for 26 of 29 points ($r = 0.50$ at the 1% level of signicance), for particulate matter collected in 1986 and 1993. Points for stations 2-21m September, 3-1m April and 3-1m September are excluded from the regression analysis and hence from the shown best straight line. Symbols are described in legend to Figure 3. Ratios for 1986 taken from data in Tables 4 and 6 of Mayer & Manning (1990).

FIG. 5. Plots describing good correlations between the concentration ratios M/Fe^{2+}_{CL} and Fe^{3+}_{T}/Fe^{2+}_{CL} for (a) Zn, (b) Mn, and (c) Cd; r is 0.50 at the 1% level of significance. Correlation coefficients for the pairs M-Fe^{2+}_{CL} and M-Fe^{3+}_{T} are: for Zn 0.20 and 0.22, Mn 0.029 and 0.79, and for Cd 0.40 and 0.35, respectively, reflecting in most instances elements that are poorly correlated. Symbols are defined in legend to Figure 3.

FIG. 6. Plots describing good correlations between the concentration ratios M/Fe^{2+}_{CL} and Fe^{3+}_{T}/Fe^{2+}_{CL} for (a) Ni, and (b) Cu, and between (c) orgC/Fe^{2+}_{T} and Fe^{3+}_{T} /Fe^{2+}_{CL}. The correlations are significantly superior to those of the pairs M(or C)-Fe^{2+}_{CL}, and M(or C)-Fe^{3+}_{T}. Symbols are defined in Figure 3.

FIG. 7. Illustration of major groupings of elements in particulate matter from Hamilton Harbour based on a minimum of variance method. Distance is an inverse function of the correlation coefficient. Data for stations 3-1m April and September samplings and 2-21m September sampling are not included in the cluster analysis (see text).

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TABLE 1. ELEMENTAL CONCENTRATIONS IN PARTICULATE MATTER FROM HAMILTON HARBOUR COLLECTED IN 1993. WEIGHT PERCENT

Contaminant	B1	B2	B3	B4	B10
NAIP	0.38	0.27	0.22	0.19	0.21
OrgP	0.32	0.22	0.24	0.21	0.18
Pb	0.0117	0.0108	0.0095	0.0161	0.0375
Zn	0.0730	0.0721	0.0668	0.0983	0.295
Mn	0.493	0.531	0.465	0.475	0.3000
Cu	0.0063	0.0054	0.0054	0.0064	0.0095
Ni	0.0026	0.0024	0.0022	0.0026	0.0205
Cd	0.00038	0.00037	0.00042	0.00047	0.00091
Fe_T	2.94	3.06	2.92	3.86	5.69
Fe^{2+}	0.77	0.79	0.79	0.93	1.64
Fe^{3+}	1.70	1.77	1.63	2.16	3.18

Concentrations of iron in wustite are in the range 0.15 to 0.3 wt%, and in hematite 0.32 to 0.6 wt%. Concentrations of apatite P are 0.01 to 0.05 wt%. The insolubility of apatite makes it unavailable.

TABLE 2. MEASURED PARAMETERS FOR THE INCORPORATION OF CONTAMINANTS INTO HYDRATED FERRIC OXIDES

Parameter	NAIP	Pb	Zn	Mn
Slope, k_1 X10^2	13±2	2.0±0.2	14±2	60±6
Intercept, X10^2	-5.0±12	-2.0±1.6	-16±12	-65±46
n_{CL}	---	1	1	1

Parameter	Cd	Ni	Cu	ORG C
Slope, k_1 X10^2	0.036±0.004	0.27±0.04	0.38±0.06	1420±290
Intercept, X10^2	-0.017±0.03	-0.11±0.3	0.23±0.47	-1290±2030
n_{CL}	---	---	---	1

k_1 is the coefficient of incorporation of contaminants into hydrated ferric oxide (wt% of Fe^{3+} in oxide)

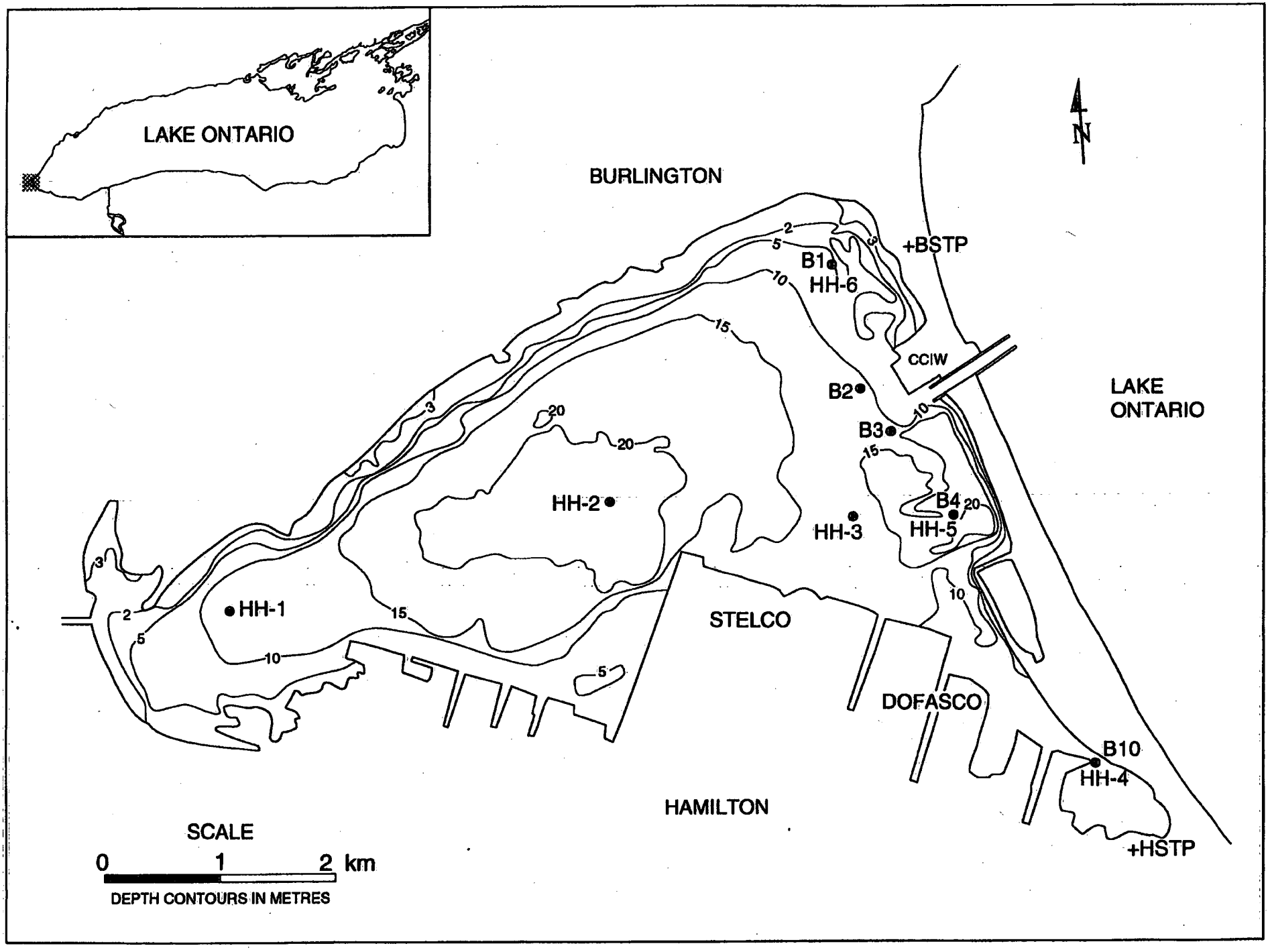
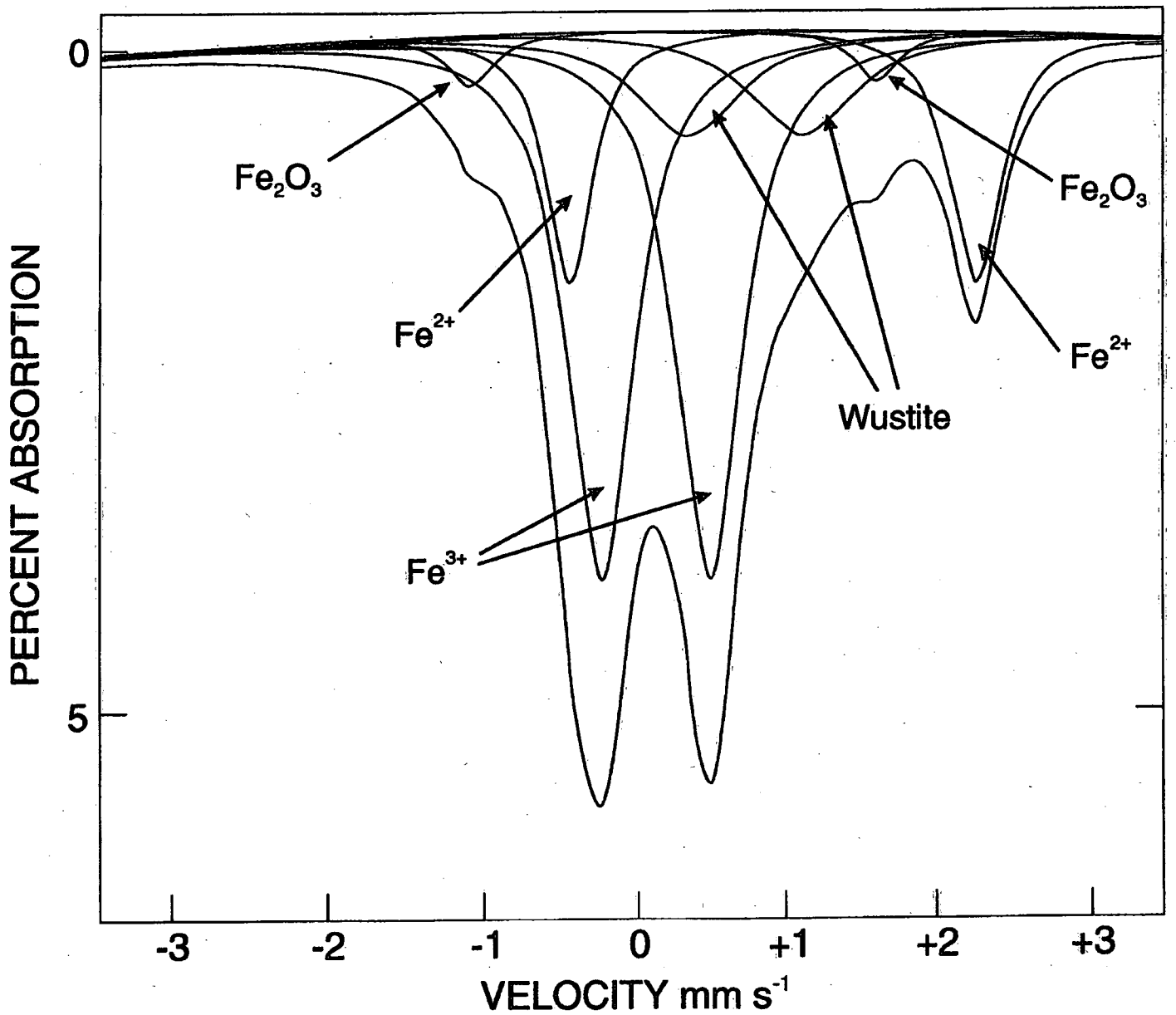
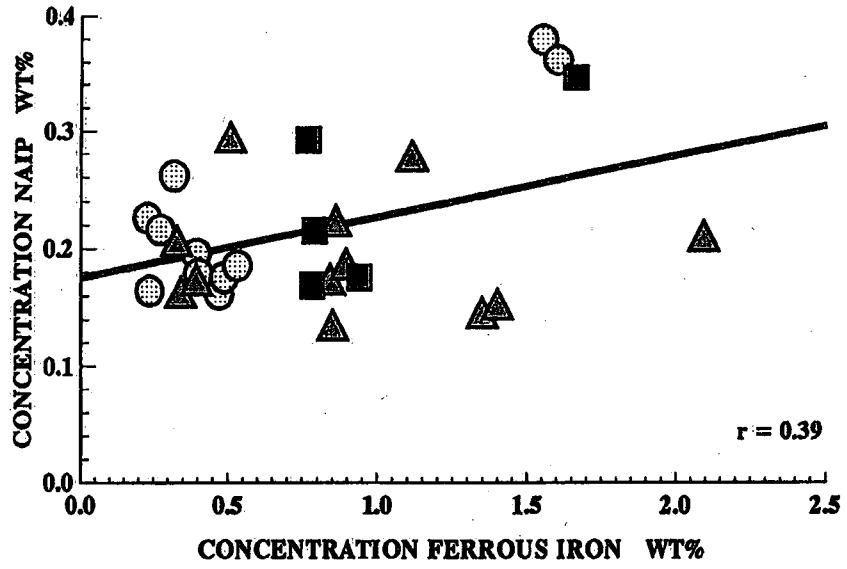
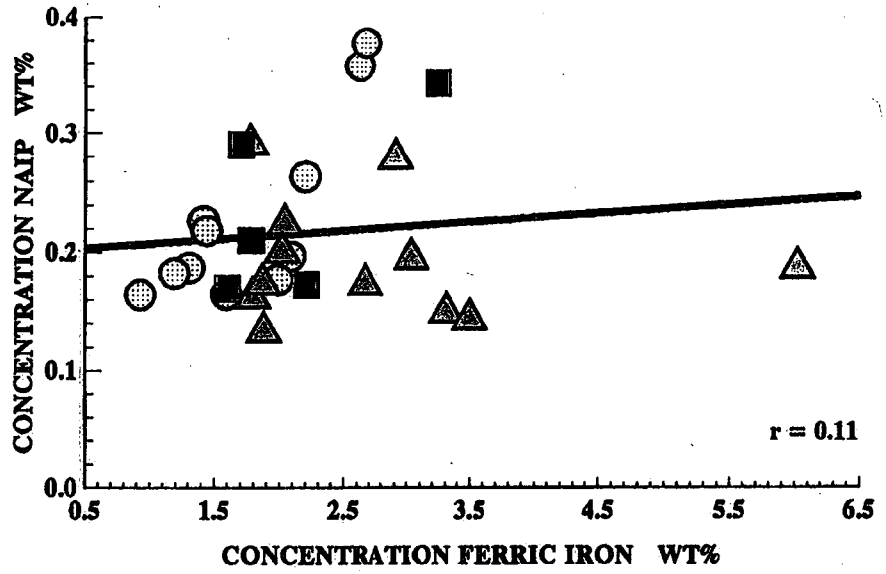

LAKE ONTARIO
BURLINGTON
N
+BSTP
B1
HH-6
CCIW
B2
B3
B4
HH-5
HH-3
HH-2
HH-1
STELCO
DOFASCO
B10
HH-4
+HSTP
HAMILTON
LAKE ONTARIO
SCALE
0 1 2 km
DEPTH CONTOURS IN METRES

FIG 1


0
5
PERCENT ABSORPTION
Fe_2O_3
Fe^{2+}
Fe^{3+}
Wustite
Fe_2O_3
Fe^{2+}
-3
-2
-1
0
+1
+2
+3
VELOCITY mm s^{-1}


CONCENTRATION NAIP WT%
0.0
0.1
0.2
0.3
0.4
0.0
0.5
1.0
1.5
2.0
2.5
CONCENTRATION FERROUS IRON WT%
r = 0.39


CONCENTRATION NAIP WT%
0.0
0.1
0.2
0.3
0.4
0.5
1.5
2.5
3.5
4.5
5.5
6.5
CONCENTRATION FERRIC IRON WT%
r = 0.11

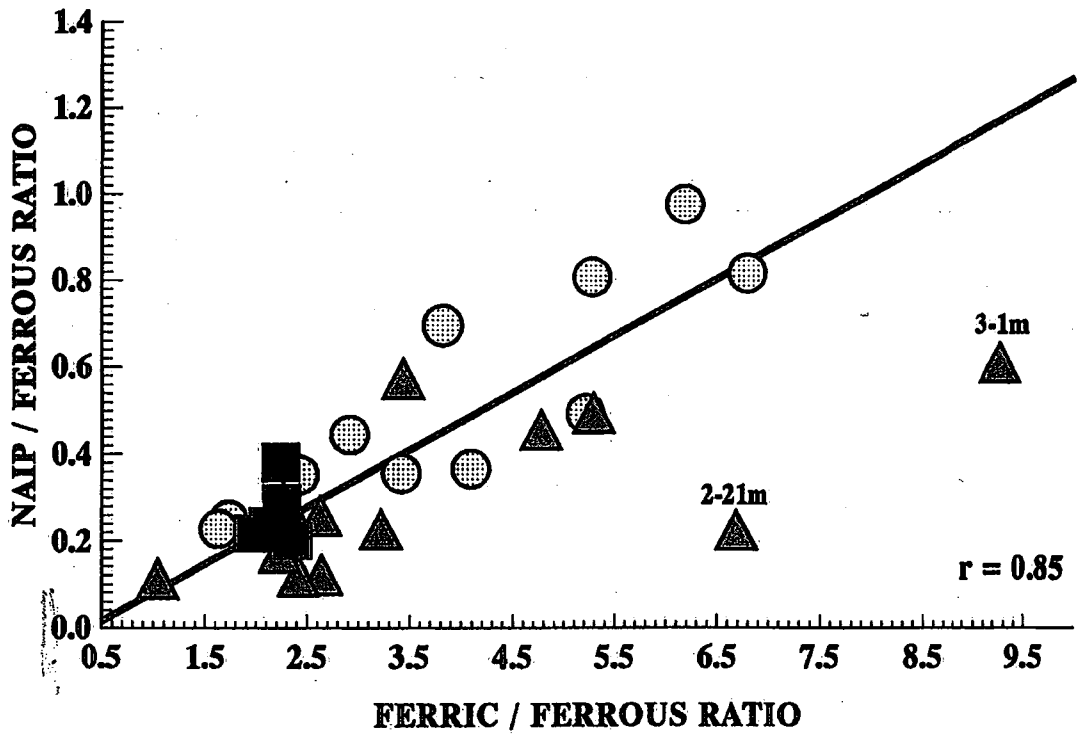
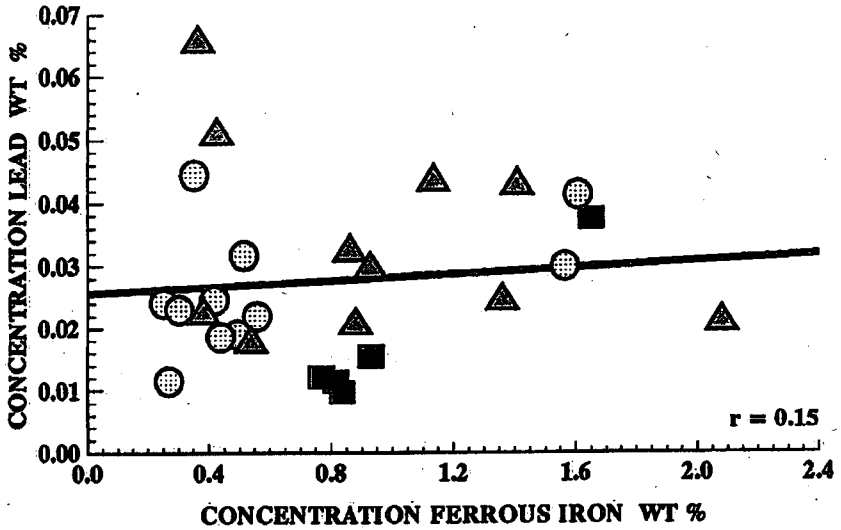
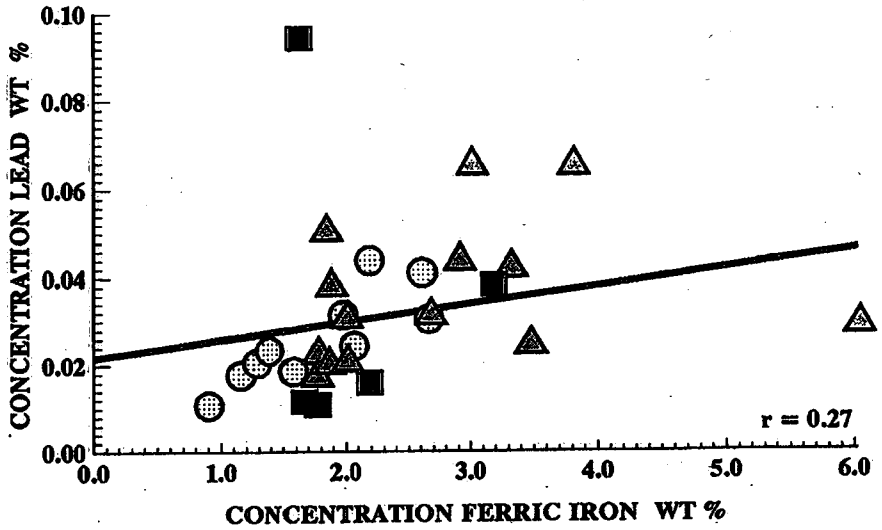

NAIP / FERROUS RATIO
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0.5
1.5
2.5
3.5
4.5
5.5
6.5
7.5
8.5
9.5
FERRIC / FERROUS RATIO
3-1m
2-21m
r = 0.85

FIG 3


CONCENTRATION LEAD WT %
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
0.0
0.4
0.8
1.2
1.6
2.0
2.4
r = 0.15
CONCENTRATION FERROUS IRON WT %


CONCENTRATION LEAD WT %
0.10
0.08
0.06
0.04
0.02
0.00
0.0
1.0
2.0
3.0
4.0
5.0
6.0
r = 0.27
CONCENTRATION FERRIC IRON WT %

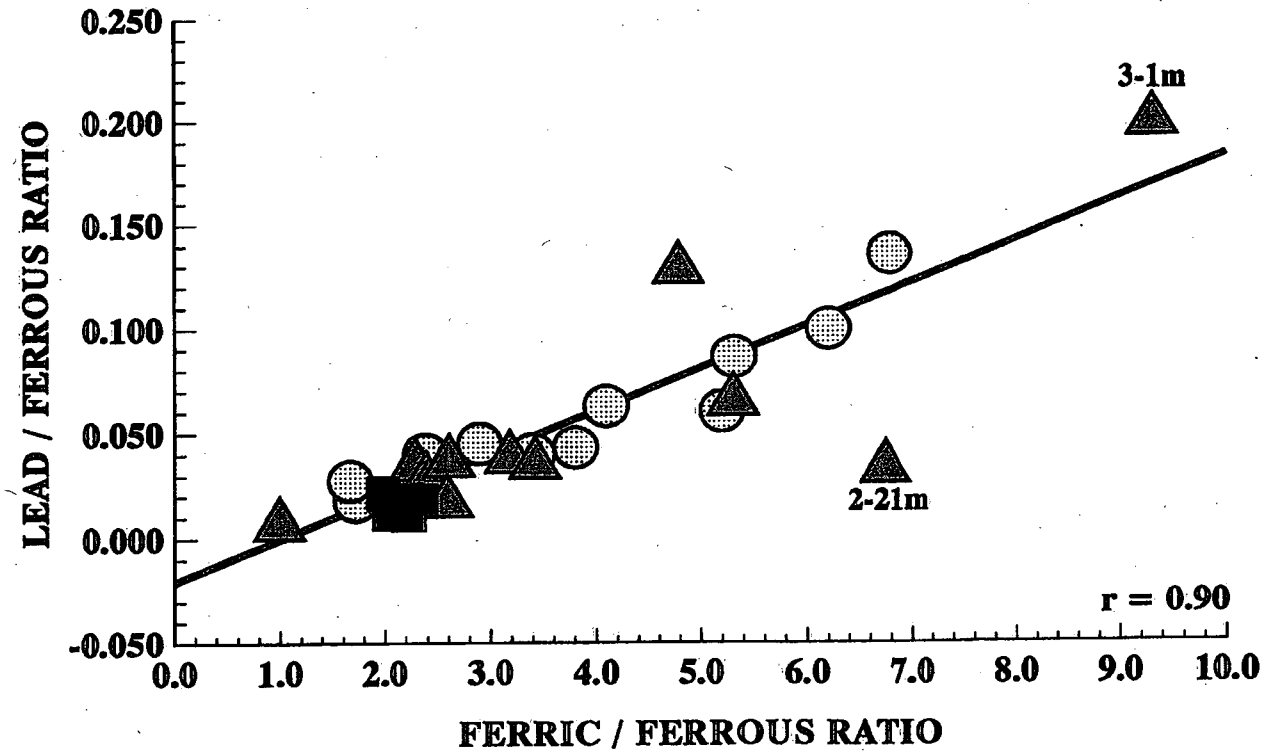

LEAD / FERROUS RATIO
0.250
0.200
0.150
0.100
0.050
0.000
-0.050
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
3-1m
2-21m
r = 0.90
FERRIC / FERROUS RATIO

FIG. 4

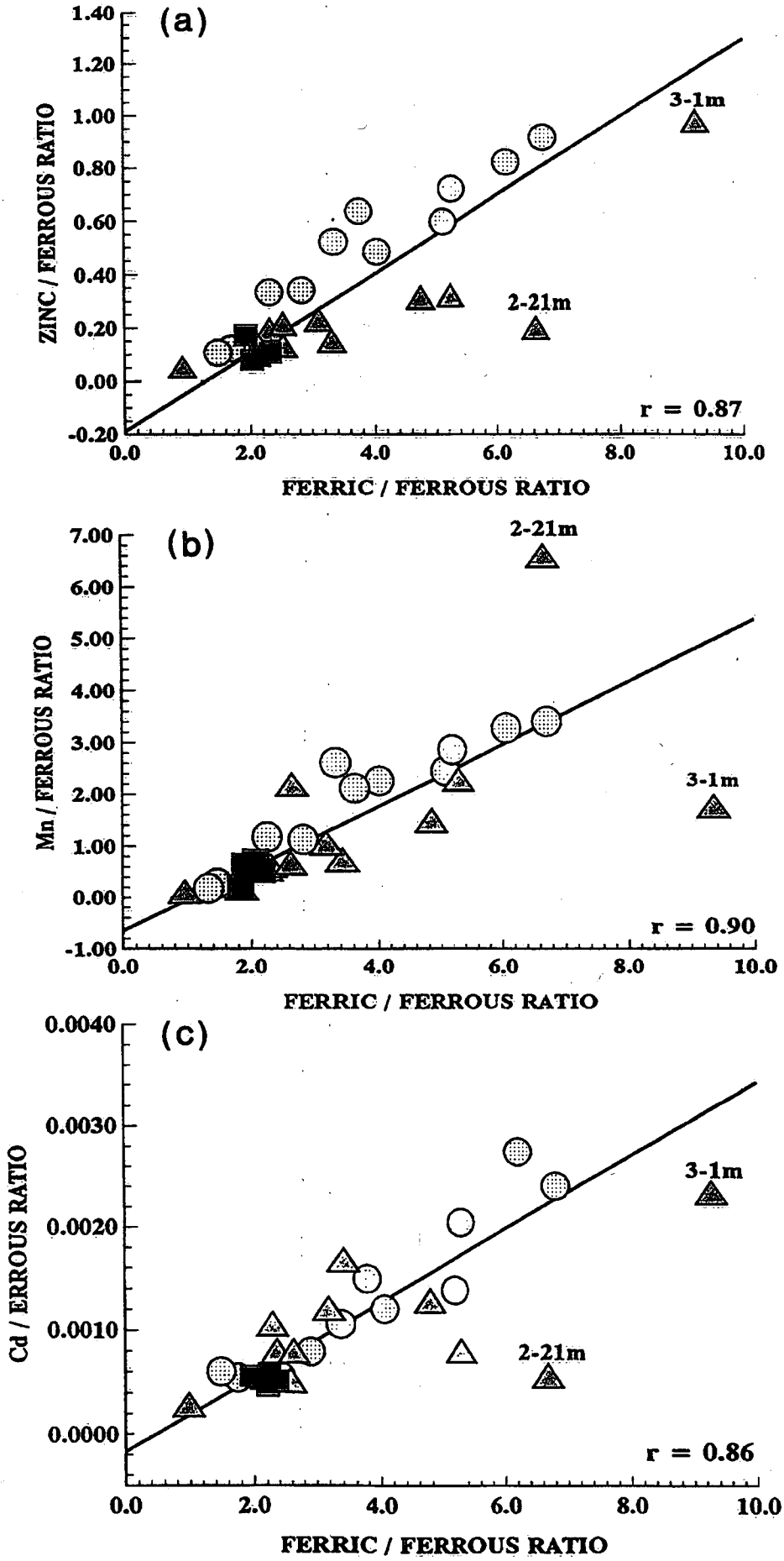

(a)
ZINC / FERROUS RATIO
FERRIC / FERROUS RATIO
3-1m
2-21m
r = 0.87
(b)
Mn / FERROUS RATIO
FERRIC / FERROUS RATIO
2-21m
3-1m
r = 0.90
(c)
Cd / FERROUS RATIO
FERRIC / FERROUS RATIO
3-1m
2-21m
r = 0.86

FIG. 5

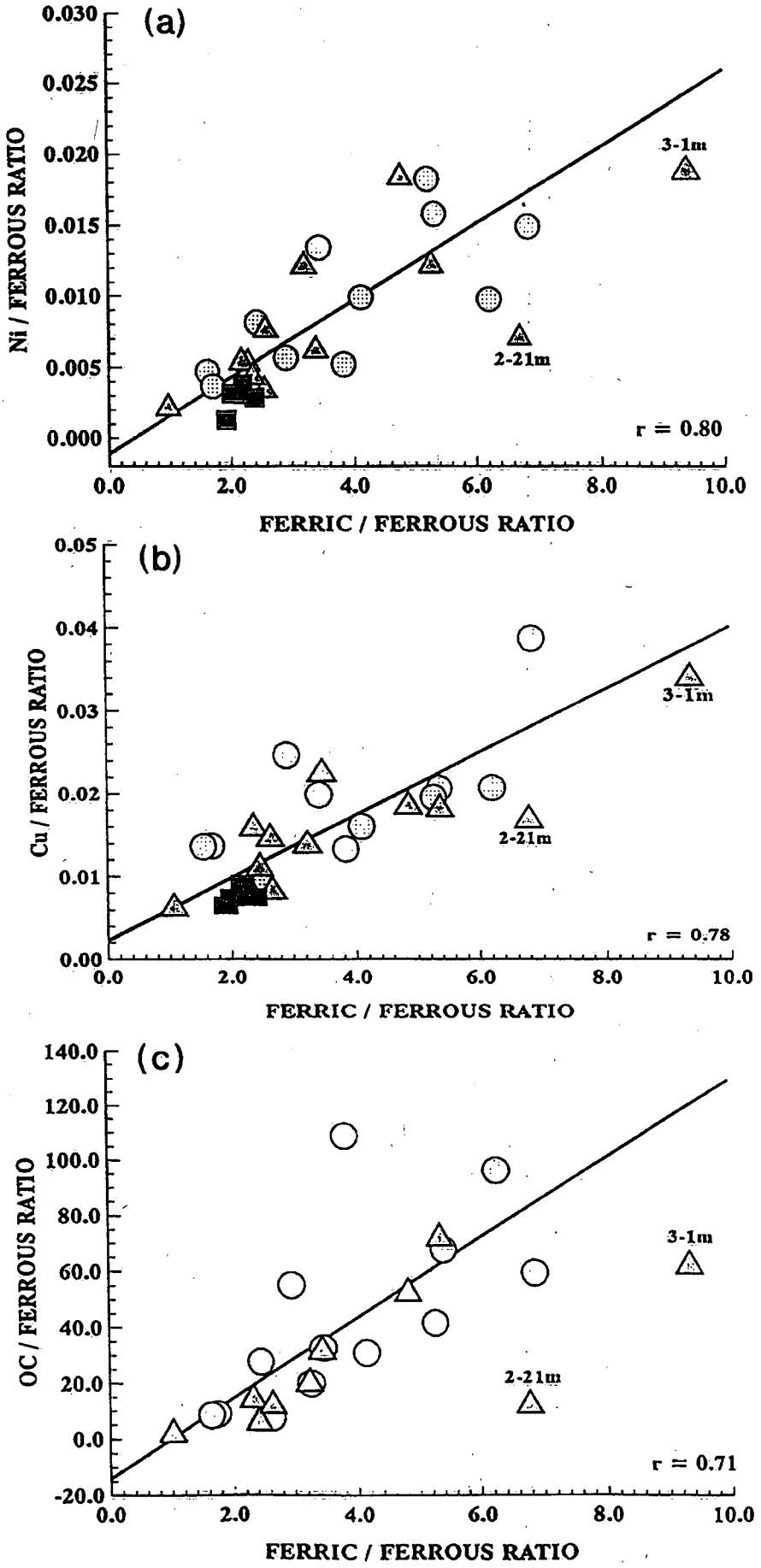

(a)
Ni / FERROUS RATIO
0.030
0.025
0.020
0.015
0.010
0.005
0.000
3-1m
2-21m
r = 0.80
0.0
2.0
4.0
6.0
8.0
10.0
FERRIC / FERROUS RATIO
(b)
Cu / FERROUS RATIO
0.05
0.04
0.03
0.02
0.01
0.00
3-1m
2-21m
r = 0.78
0.0
2.0
4.0
6.0
8.0
10.0
FERRIC / FERROUS RATIO
(c)
OC / FERROUS RATIO
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
-20.0
3-1m
2-21m
r = 0.71
0.0
2.0
4.0
6.0
8.0
10.0
FERRIC / FERROUS RATIO

FIG. 6

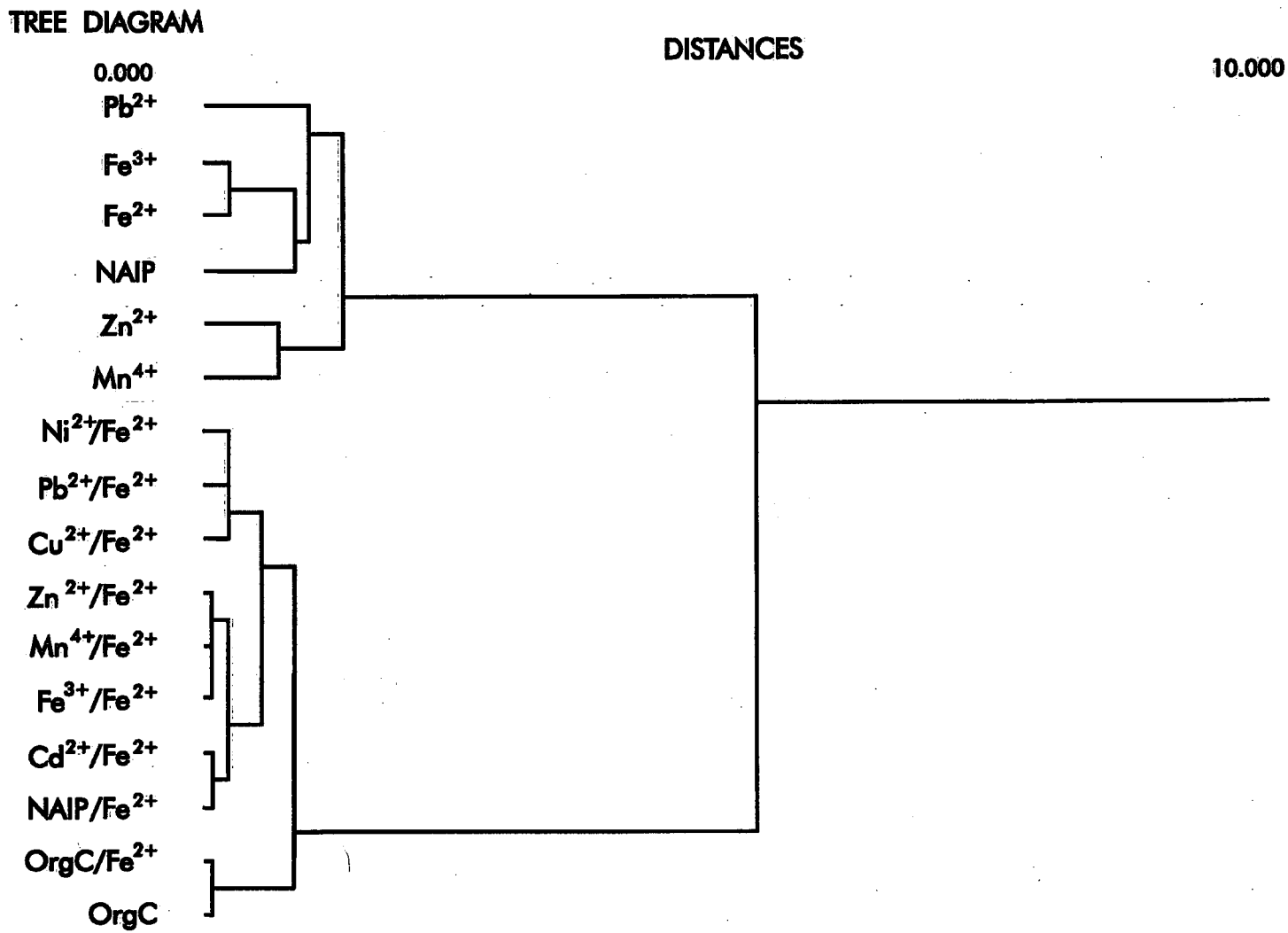

TREE DIAGRAM
DISTANCES
0.000
10.000
Pb^{2+}
Fe^{3+}
Fe^{2+}
NAIP
Zn^{2+}
Mn^{4+}
Ni^{2+}/Fe^{2+}
Pb^{2+}/Fe^{2+}
Cu^{2+}/Fe^{2+}
Zn^{2+}/Fe^{2+}
Mn^{4+}/Fe^{2+}
Fe^{3+}/Fe^{2+}
Cd^{2+}/Fe^{2+}
NAIP/Fe^{2+}
OrgC/Fe^{2+}
OrgC

FIG. 7.

Environment Canada Environnement Canada

Canada

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867 Lakeshore Road
Burlington, Ontario
L7R 4A6 Canada

National Hydrology Research Centre
11 Innovation Boulevard
Saskatoon, Saskatchewan
S7N 3H5 Canada

St. Lawrence Centre
105 McGill Street
Montreal, Quebec
H2Y 2E7 Canada

Place Vincent Massey
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Gatineau, Quebec
K1A 0H3 Canada

Centre canadien des eaux intérieures
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867, chemin Lakeshore
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L7R 4A6 Canada

Centre national de recherche en hydrologie
11, boul. Innovation
Saskatoon (Saskatchewan)
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Montréal (Québec)
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