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The Binding OF Metal and Phosphate lons in the Contaminated Waters Of Hamilton Harbour, Ontario

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

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ABSTRACT

Heavy loadings of contaminant metal ions to Hamilton Harbour, Lake Ontario, are largely incorporated into hydrated ferric oxides that are also of industrial origin. Over most of the Harbour, contaminant concentrations in suspended particulate matter are covered by the statistically-significant relationship [contaminant] = $[Fe_T^{3+}] - (n_{CL}k_1 - k_2)$ [Fe_{CL}^{2+}] + i, where [] represents concentration, Fe_T^{3+} is total ferric iron, k_1 and k_2 are constants, n_{CL} is the ratio of ferric/ferrous iron in inert clay mineral, CL, and i is the background concentration. The relationship breaks down for particulate matter collected from an anoxic hypolimnion and from a surface water plume; the deviations arise in the first instance from the sedimentary release of iron (and Mn) and in the second from nonequilibration with Harbour water. The poorly-crystalline ferric oxides are beneficial in binding, and thus reducing the bioavailabilities of, contaminant ions; on the other hand, these 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: Pb 1.4, Zn 7, Mn 55, Cú 0.3, Ni 0.3, andCd 0.03. Concentrations of nonapatite inorganic phosphorus are not correlated with ferric and ferrous iron. Phosphorus is not released from the sediments during hypolimnion anoxia.

NWRI Cont # 98-257

Management Perspective

P G. Manning and X. Wang

98-257

National Water Research Institute Aquatic Ecosystem Restoration Branch

Title

Authors:

NWRI Publication #:

Citation:

EC Priority Issue

Conserving Ecosystems, Great Lakes 2000, RAPs

The binding of metal and phosphate ions in the

contaminated waters of Hamilton Harbour Ontario

Current Status

Hamilton Harbour is contaminated by effluents from steel mills and sewage treatment plants. Sediment toxicity due to metals seems to be less than predicted by total metal analyses. We now have evidence that the anthropogenic iron compounds have a high capacity for binding zinc and other toxic metals. The metals are removed from solution and thus rendered less bioavailable. Toxic metals are not greatly released from sediment during summer anoxia. Contrary to previous assumptions, phosphorus is not associated with anthropogenic iron in Hamilton Harbour. Algae seem to out compete iron compounds for available phosphate ion. This explains why the phosphorus/algae relationship for the Harbour is similar to those found elsewhere. This is more evidence that the Harbour will respond normally to nutrient load reductions recommended by the Remedial Action Plan

The lead author has retired. The importance of the work will be communicated to the RAP process.

Next Steps:

INTRODUCTION

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

$[\text{contaminant}] = [\text{Fe}_{T}^{3+}] - (n_{\text{CL}}k_1 - k_2) [\text{Fe}_{\text{CL}}^{2+}] + i \quad (1)$

where brackets represent concentrations, Fe^{3+} 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), and i is the background concentration. The ratio n_{cL} is a measure of the concentration of unavailable ferric iron (Manning & Wang 1994, 1995). A basic assumption is that $[Fe_{0x}^{3+}] = [Fe_{T}^{3+}] - [Fe_{CL}^{3+}]$, where OX represents hydrated oxide. The validity of this equation has yet to be applied to the study of iron-contaminant interaction in bodies of water heavily contaminated with iron and toxic metals. Hamilton Harbour is a polluted embayment of area 25 km² 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. Consequently, 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 precipitates in the harbour as poorly crystalline hydrated oxide. These oxides provide adsorption sites for phosphate and metal ions (Berner 1973, Lum & Gammon 1985, Laxen 1983, Ryden et al. 1977, Parfitt & Russell 1977).

The Harbour is strongly stratified in summer. The bottom sediments are enriched in organic matter and are strongly reducing (Mayer & Manning 1990). Incursions of cleaner oxygenated water from Lake Ontario into the bottom waters ensure that hypolimnetic anoxia is occasionally interrupted (Harris *et al.* 1980). A plot of [NAIP]/[Fe_{Cl}²⁺] against [Fe_T³⁺]/[Fe_{Cl}²⁺] is linear (Mayer & Manning 1991), but some points corresponding to particulate matter collected from certain stations within the Harbour, including the anoxic hypolimnion of the "deep hole", deviate from the line to such an extent that important events are possibly implicated . Here, the utility of equation (1) in describing ferric oxide - contaminant binding in Hamilton Harbour is assessed through a reexamination of previously published data (Mayer & Manning 1990, 1991) and supported by analyses for recently recovered particulate matter. The aims of this work are to determine (a) the potential benefit of industrially produced ferric iron in binding, and therefore reducing the bioavailability of, phosphate and metal contaminants, and (b) the extent of contaminant release from the bottom sediments during seasonal anoxia.

EXPERIMENTAL DETAILS

Approximately 5 g of suspended particulate matter was 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 laboratry. Water samples were collected at the same time.

The particulate matter was analysed for the different forms of iron (ferrous, ferric, hematite, and wustite (Fig. 2) by Mossbauer spectrometry at room temperature following the methods described earlier (Mayer & Manning 1990). Measured values of isomer shift (relative to iron foil), quadrupole splitting, and halfwidth are, respectively: for Fe²⁺ 1.13 mm s⁻¹, 2.59 mm s⁻¹, 0.42 mm s⁻¹, all \pm 0.03 mm s⁻¹; for Fe³⁺ 0.38 mm s⁻¹, 0.72 mm s⁻¹, and 0.55mm s⁻¹, all \pm 0.03; for wustite 0.95 \pm 0.05 mm s⁻¹, 0.75 \pm 0.05 mm s⁻¹, and 0.48 mm s⁻¹ (constrained); and for hematite the isomer shift is 0.43 \pm 0.03 mm s⁻¹. These values are consistent with the ferrous and ferric iron being mainly in clay mineral and hydrated oxide, respectively (Coey *et al.* 1974, Mayer & Manning 1990).

The 4 K Mössbauer spectrum of sample B4 displayed an intense but poorly defined magnetic pattern consistent with the presence of ferric iron in poorly crystalline oxides (Murad 1988). Approximately 60% of the iron was contained within the magnetically ordered oxide. That ferric iron is an important contaminant in Harbour particulate matter has been demonstrated by Mayer & Manning (1990).

The different forms of phosphorus (NAIP, apatite, and organically bound) in particulate matter were measured by chemical fractionation (Williams *et al.* 1976). NAIP represents the major pool of bioavailable phosphorus (Williams *et al.* 1980). NAIP values are reproducible to $\pm 5\%$, but the unknown specificity of the citrate/dithionite/bicarbonate extractant makes the accuracy difficult to assess. However, most of the NAIP is phosphate ion bonded to the hydrated oxides of iron and manganese (Lucotte & d'Anglejan 1985). Water samples were collected; analysis based on color development in the phosphomolybdate complex showed that approximately 85% of the NAIP is in the particulate phase.

The concentrations of total metals (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 $\pm 5\%$ 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 Fe³⁺_T and Fe²⁺_{CL} are good to $\pm 10\%$.

RESULTS AND 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 .[Fe³⁺_{OX}] + k_2 .[Fe²⁺_{CL}] +i, where Fe³⁺_{OX} is ferric iron in hydrated oxide, and Fe²⁺_{CL} proxies for clay mineral (Manning & Wang 1994). The factor k_1 represents a coefficient of incorporation of contaminant into hydrated oxide. 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 n_{CL} = intercept/k₁. For contaminant ions binding to the same ferric iron fraction, values of n should be similar. However, local sources of contaminants, e.g. industrial and sewage outfalls and anoxic sediments, may be marked by significant deviations from equation (1). Note that whereas phosphate ion is specifically bonded to the ferric ion (in oxide), metal ions must of necessity be bonded via an intervening anion, possibly an OH⁻ or O²⁻ 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.

Manganese - iron relationships

Concentrations of Mn are negatively correlated with ferrous iron and poorly correlated with ferric iron (Fig. 3a, b). Multiple regression analysis, for 26 of 29 points, demonstrates a strong correlation between manganese ions and ferric iron (Fig. 3c), however, a plot of the residuals against Mn concentration (Fig. 3d) shows a significant deviation between predicted and measured concentrations. One point, that for a predicted Mn concentration of 0.00 wt%, corresponding to station 4 and adjacent to a point source (Fig. 1), is not representative of Mn - Fe relationships within the harbour. Omission of this point from the regression analysis yields r = 0.59 for 25 of 29 points in Figure 3c, and r = 0.29 in Figure 3d. Concentrations of Mn and ferric iron are definitely correlated.

Measured concentrations of manganese (5.94 wt%) greatly exceed predicted concentrations (2.25 wt %) in anoxic water (station 2-21m, September sampling). Hence, manganese ions are released from the sediments during hypolimnion anoxia (Fig. 3c) in relatively greater amounts than are ferrous ions. Within the surface plume, concentrations of manganese are considerably lower than predicted (Fig. 3c). Consequently, the steel mills are not a significant source of manganese.

Trace metal - iron relationships

Concentrations of the metals Pb, Zn, and Ni are poorly correlated with concentrations of ferrous iron (Fig. 4) for 26 of 29 points. Concentrations of Pb and Ni are well correlated with those of ferric iron (Fig 4; r = 0.50 and 0.39 at the 1% and 5% levels of significance, respectively), whereas Zn and Fe³⁺ (r = 0.37, Fig. 4) are marginally correlated.

Multiple regression on 26 of 29 points confirms the srong association between the pairs Pb, Zn, and Ni and Fe³⁺ (Fig. 5; r = 0.50 at the 1% level of significance). Concentrations of Pb, Zn, and Ni ions in the anoxic hypolimnion waters (station 2-21m September sampling) are lower than predicted on the basis of ferric iron concentrations (equation 1), i.e., there is little or no release of these trace metal ions from the sediments during bottom anoxia. Within the surface water plume (station 3), concentrations of Pb and Zn are at or near predicted levels (Fig. 5), and the steel mills are also sources of these metals. Zinc may be released during the recycling of scrap galvanized iron. Nickel is not released in significant amounts from the steel mills (Fig. 5). Fe³⁺_{OX}, for example, binds 1.4% by weight of Pb (Table 2).

Copper ions (Fig. 6c, d) are well correlated with Fe_{0x}^{3+} . Cd is not released from the sediments during hypolimnion anoxia (Fig. 6c).

Inorganic phosphorus - iron relationships

Concentrations of NAIP are marginally correlated with concentrations of ferrous iron (Fig. 7; r = 0.39 at the 5% level of significance for 26 of 29 points), but are poorly correlated with ferric iron (Fig 7b). Multiple regression analysis (Fig. 7c) yields values of $k_1 = 0.0012 \pm 0.027$, $-nk_1 + k_2 = 0.052 \pm 0.035$, and intercept = 0.174 ± 0.043 wt%. The fit is good at the 5% level of significance (Fig. 7c, d). The value of k_1 is not significant and indicates that NAIP is probably not associated with ferric iron in Hamilton Harbour particulate matter. Ferric iron does not control the availability of phosphate ion.

Organic carbon - iron relationships

Concentrations of organic carbon are strongly and negatively correlated (Fig. 8a, b) with ferrous iron (r = -0.83) and with ferric iron (r = -0.89). Multiple regression analysis, based on equation (1), yields the relationship [organic C] = -1.61 ± 1.15 [Fe³⁺] - 5.92 ± 1.47 [Fe²⁺] + 24.1 ± 1.89, for which r = 0.85 (Fig. 8c, d; Table 2). Concentrations of organic carbon are relatively low at shallow nearshore stations HH1 and HH4, where turbidity and iron concentrations are high (Mayer & Manning 1990).

General discussion

The concentrations of manganese, lead, zinc, and probably Cu and nickel in particulate matter in Hamilton Harbour are strongly correlated with the concentrations of one fraction of ferric iron. The consistent value of n_{CL} equal to 1-2 measured for Pb, Zn, and Mn is indicative of binding to one and the same fraction of ferric iron, namely hydrated oxide. For particulate matter in the Trent River, values of n_{CL} (of 1 to 2, Table 2, Fig. 9) measured for several metals are in reasonable agreement (Manning & Wang 1995).

The model and the associated plots as described in Figures 3-6 clearly highlight point source inputs of contaminants; hence, 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; in contrast, Pb, Zn, 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 ferric fraction of the industrially produced iron is clearly beneficial in removing large quantities of trace metal ions from solution, through adsorption and/or coprecipitation. The bioavailability of metals is, thus, reduced through their incorporation into particulate matter. Bioavailability is then dependent on kinetic constraints placed on the rate of desorption and of dissolution of metal ions. A more important process might be photochemically activation, in which the absorption of light by cations, such as ferric, manganese and chromium, leads to the reduction of the absorbing metal ion and the oxidation of organic matter (Miles & Brezonick 1981, Morel 1983). Such processes are likely to be highly efficient in Hamilton Harbour, because of the high concentrations of ferric iron and organic matter. The importance of the photochemically stimulated

break-up of the assemblage is further heightened by the high binding capacity for Pb 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.

The weak association between ferric iron and phosphate ion suggests that in Hamilton Harbour ferric iron plays a minor role in the binding of phosphate ion. Algae would seem to outcompete ferric iron for phosphate ion. Additional reductions in phosphorus inputs to the harbour from sewage tratment plants are indicated. However, 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. The negative correlation between iron and organic carbon arises in part from the low concentrations of organic carbon in particulate matter at station 4 and often at stations 1 and 6 (Mayer & Manning 1990) and relatively high values in offshore surface waters.

Initially, improvements to water quality in Hamilton Harbour could be based on additional reductions in the loadings of phosphorus from the sewage plants so as to increase the margin in assimilative capacity. Following this, reductions in the loadings of iron could be stressed.

ACKNOWLEDGEMENTS

The authors thank Technical Operations staff for field support and Dr. O. El Kei for the plasma emission spectroscopic analyses. Discussions with M.N. Charlton and T. Mayer are also acknowledged.

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).

FIG. 2. Room temperature Mössbauer spectrum of suspended particulate matter collected from middepth station B4 in 1993. Chi-squared is 544 for 490 degrees of freedom. Symbology is: Fe^{3+} is mainly hydrated ferric oxide, Fe^{2+} is ferrous iron in the clay structure.

FIG. 3. Plots describing, for 26 of 29 points, (a) a negative correlation between concentrations of Mn and Fe^{2+} , hence Mn is mainly anthropogenic, (b) a weak correlation between Mn and Fe^{3+} , (c) a good agreement between predicted concentrations of Mn, based on multiple regression analysis (Table 2), and (d) a drift in the residuals. One point in (d), at a predicted concentration of 0.00 wt% Mn, influences the curve; omission of this point yields r = 0.29, i.e. any dfift is not significant.

FIG. 4. Plots describing the poor correlations between concentrations of Pb, Zn, and Ni and ferrous iron, and the good correlations between Pb and Ni and ferric iron. The Zn-Fe³⁺ correlation is marginal (r = 0.37).

FIG. 5. Plots describing the good correlation between predicted and measured concentrations of Pb, Zn, and Ni based on multiple regression analysis (Table 2), for 26 of 29 points.

FIG. 6. Plots describing the good agreement between predicted and measured concentrations of (a) and (b) Cu, and (c) and (d) Cd, for 26 0f 29 points. The elemental pairs Cu-Fe²⁺, Cu-Fe³⁺, Cd-Fe²⁺, and Cd-Fe³⁺ are poorly correlated, with r values.

FIG. 7. Plots describing, for 26 of 29 points, (a) a positive correlation between concentrations of NAIP and ferrous iron (r = 0.39 at the 5% level of significance), and (b) a weak correlation between NAIP and ferric iron. Predicted (on the basis of multiple regrecssion analysis) and measured concentrations of NAIP are correlated (c) and (d) at the 5% level of significance. The value of k_1 (0.001 ± 0.027, Table 2) confirms the weak dependence of NAIP on Fe³⁺.

FIG. 8. Plots describing a strong inverse correlation between organic carbon and iron.

FIG. 9. Plots describing multiple regression analysis for zinc in Trent River particulate matter. Points cover several field trips conducted over three years.

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Station	Fe ³⁺	Fe ²⁺	Pb	Zn	Cu	Ni	Cd	NAIP			
weight per cent											
B1	1.702	0,769	0.012	0.073	0.006	0.003	0.00038	0.292			
B2	1.771	0.796	0.011	0.072	0.005	0.002	0.00037	0.215			
B3	1.632	0.790	0.095	0.069	0.005	0.002	0.00042	0.174			
B4	2.162	0.934	0.016	0.099	0.006	0.003	0.00047	0.178			
B5	3.181	1.639	0.038	0.295	0.010	0.002	0.00091	0.344			

TABLE 1. Elementary concentrations in Hamilton Harbour particulate matter

Contamina nt	k _i	-nk ₁ +k ₂	Intercept wt%	n	[deep sed] wt%						
Mn	0.55±0.06	-0.67±0.12	-0.46±0.14	0.8	0.150						
Pb	0.014±0.0039	-0.007±0.006	0.0043±0.006	2.0	0.0025						
Zn	0.074±0.026	-0.065±0.034	0.064±0.041	1.0	0.011						
Ni	0.0026±0.00077	-0.00092±0.00099	0.00025±0.0012		0.010						
Cu	0.0032±0.0013	-0.0041±0.0017	0.00013±0.00021	0.8	0.0005						
Cd	0.00029±0.000007	-0.00005±0.00009	0.000005	<u></u>	0.0001						
Org Ć	-1.61±1.15	-5.9±1.5	24.1±1.9								
NAIP	-0.0012±0.027	-0.051±0.035	0.1736±0.043	、	0.03						
Trent River particulate matter											
Mn	0.86±0.13	1.93±0.33	0.048±0.32	2							
Pb ·	0.0054±0.0007	0.0094±0.0019	0.0017±0.0017	2							
Zn	0.0096±0.0011	0.011±0.0028	0.0013±0.0020	1							
Cu	0.010±0.0012	0.0058±0.0030	0.00028±0.0022	. 1							

TABLE 2. Measured parameters for Hamilton Harbour particulate matter

Mössbauer measurements yield Fe^{3+} : Fe^{2+} ratios of 0.8 to 1.0 for deeper precolonial sediments of western Lake Ontario, in reasonable agreement with n. The concentrations of metal contaminants in deeper (reducing) water sediments may reflect concentration of non-labile (background) metal ions.







a 0



FIG:3

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FIGH



F16.5









FIG.7.





FIG. 8



FIG. 9



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