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THE BINDING OF Pb, Zn, AND OTHER METAL IONS IN SUSPENDED RIVERINE PARTICULATE MATTER

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ABSTRACT

The concentrations ([ ]) of lead, zinc, manganese, copper, and chromium ions in suspended particulate matter collected over a two-year period from the Trent – Severn Waterway, Ontario, are linearly correlated with those of ferric iron by the relationship $[M]/[\mathrm{Fe}^{2+}_{\mathrm{CL}}] = k_1 \cdot [\mathrm{Fe}^{3+}_{\mathrm{T}}]/[\mathrm{Fe}^{2+}_{\mathrm{CL}}] - n_{\mathrm{CL}} \cdot k_1 + k_2$, where k_1 and k_2 are constants, n_{CL} is the ratio of ferric iron to ferrous iron within the clay structure, M is one of Pb^{2+}, Zn^{2+}, Mn, Cu^{2+}, or Cr, and $\mathrm{Fe}^{3+}_{\mathrm{T}}$ and $\mathrm{Fe}^{2+}_{\mathrm{CL}}$ are total ferric iron and clay-bound ferrous iron, respectively. The linear relationship is predicated on the distribution of ferric iron between active hydrated oxides and relatively inactive clay minerals. Lead, zinc, manganese, copper, and chromium ions are bonded to hydrated ferric oxides *via* a bridging anion, possibly fulvate or humate ion. Coefficients of binding (k_1) are, as weight percent of ferric iron in oxide, 0.57 ± 0.04 for lead, 1.1 ± 0.1 for zinc, 90 ± 10 for manganese, 1.0 ± 0.1 for copper, and 0.5 ± 0.1 for chromium ions. These metal ions share a common carrier with phosphate ion, namely a ferric oxide – organic matter assemblage. The metals are relatively unavailable while in suspension in the river.

Keywords: lead, zinc, metals, ferric oxide, binding, particulate matter, availability, river, Trent – Severn Waterway, Ontario.

SOMMAIRE

Les concentrations ([ ]) d'ions de plomb, zinc, manganèse, cuivre, et chrome dans les particules en suspension, prélevées sur une période de deux ans du système des rivières Trent – Severn, en Ontario, montrent une corrélation linéaire avec les concentrations de fer ferrique, et répondent à la relation $[M]/[\mathrm{Fe}^{2+}_{\mathrm{CL}}] = k_1 \cdot [\mathrm{Fe}^{3+}_{\mathrm{T}}]/[\mathrm{Fe}^{2+}_{\mathrm{CL}}] - n_{\mathrm{CL}} \cdot k_1 + k_2$; dans cette expression, k_1 et k_2 sont des constantes, n_{CL} représente le rapport de fer ferrique à fer ferreux dans la structure du matériau argileux, M représente un des ions Pb^{2+}, Zn^{2+}, Mn, Cu^{2+}, ou Cr, et $\mathrm{Fe}^{3+}_{\mathrm{T}}$ et $\mathrm{Fe}^{2+}_{\mathrm{CL}}$ sont la fraction totale de fer ferrique et de fer ferreux incorporé dans la structure de l'argile, respectivement. La relation linéaire est fondée sur la distribution du fer ferrique entre oxydes hydratés, considérés actifs, et minéraux argileux, relativement inactifs. Les ions de Pb, Zn, Mn, Cu et Cr sont liés aux oxydes ferriques hydratés grâce à un anion servant de pont, peut-être un ion fulvate ou humate. Les coefficients d'attachement (k_1), exprimés en termes de pourcentage pondéral de la teneur en fer ferrique dans l'oxyde, seraient 0.57 ± 0.04 pour les ions de plomb, 1.1 ± 0.1 pour le zinc, 90 ± 10 pour le manganèse, 1.0 ± 0.1 pour le cuivre, et 0.5 ± 0.1 pour le chrome. Ces ions de métaux partagent un agent transporteur commun avec les ions phosphate, c'est-à-dire, un assemblage de fer ferrique et de matière organique. Les métaux sont donc relativement non disponibles pendant leur trajet en suspension dans la rivière.

(Traduit par la Rédaction)

Mots-clés: plomb, zinc, métaux, oxyde ferrique, attachement, matériaux en particules, disponibilité, rivière, système Trent – Severn, Ontario.

INTRODUCTION

Hydrated ferric oxides are important carriers of natural and contaminant ions in aquatic systems (Gibbs 1973, 1977, Tessier *et al.* 1979). The incorporation of phosphate and metal contaminant ions into hydrated ferric oxides beneficially reduces their bioavailability (Balistrieri & Murray 1982, Boers *et al.* 1994, Davis 1984, Manning & Wang 1994, de Wit *et al.* 1990). The adsorption of fulvic and humic acids modifies the surface activity of ferric oxides (Tipping 1981); such anions may function as bridging ions in promoting the binding of metals (Bunzl 1974, Laxen 1983, Livens 1991, Stevenson 1979). Hydrated ferric oxides have been identified as major centers of contaminant adsorption from a variety of studies, for example, bench studies using prepared oxides (Balistrieri & Murray 1982, Laxen & Sholkovitz 1981, Lijklema 1980, Tipping 1981), the statistical correlation of acid-extractable iron and contaminants (Berner 1973, Lum & Gammon 1985, Luoma & Bryan 1978), sequential wet-chemical fractionation (Tessier *et al.* 1979), and studies at the microscopic level (Fortin *et al.* 1993). Recently, the resolution of ferric iron into active (poorly crystalline hydrated oxides) and inactive (clay) forms by Mössbauer spectrometry has confirmed the role of hydrated oxides (Manning & Wang 1994) in the binding of nonapatite inorganic phosphate (NAIP) ion.

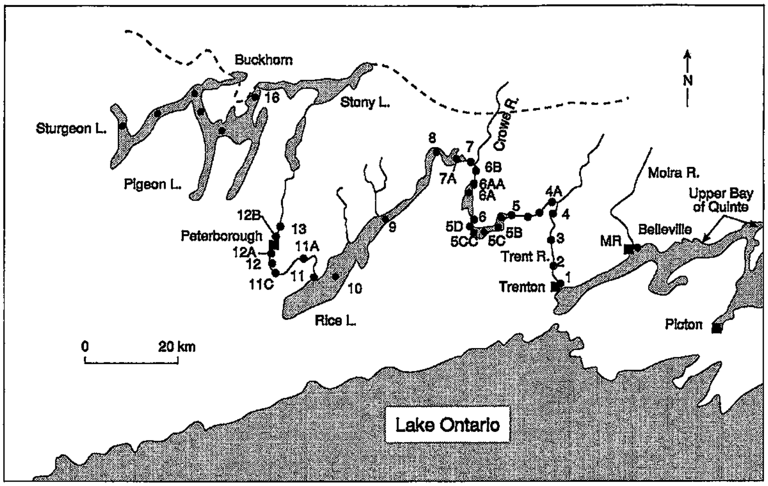

FIG. 1. Diagram showing sampling stations on the Trent – Severn Waterway, covering four field trips, in October 1991, April 1992, May 1992, and October 1992, and on the Moira River, in May 1992 (MR). Annual mean flow in the Moira River is one-third that of the Trent River. Station 1A is approximately 600 m upstream of station 1, and within the Trenton city limits. The Waterway becomes the Trent River downstream of Rice Lake. Bedrock is limestone south of the dashed line and igneous rock of Precambrian age north of the line. The populations of Peterborough, Trenton and Belleville are 61,000, 16,000, and 36,000, respectively.

The aims of this work are to determine (a) the roles of the different fractions of ferric iron in binding metal contaminant ions in particulate matter of the Trent – Severn Waterway, and in the nearby smaller Moira River, Ontario, and (b) the relative bioavailabilities of these contaminant ions in the receiving waters of the Bay of Quinte (Fig. 1). Bioavailability is discussed in terms of the processes leading to the dissolution of contaminants. Although the Waterway and the Bay of Quinte are not grossly contaminated by lead and zinc, a quantitative study of their interactions in a long river system would provide a useful basis for a reassessment of metal binding in grossly contaminated areas of the Great Lakes, such as in Hamilton Harbour (Mayer & Manning 1990, 1991).

The ecological health of the Waterway is important to the local and the provincial economy. The Waterway traverses several lakes and marshes, and its waters are highly colored by humic and fulvic acids. The bedrock underlying the river at all stations is fractured limestone. Values of pH are in the range 7.5 to 8. The Trent River is a suitable site for the study of the binding and transport of contaminants because several factors can influence ionic interactions (adsorption and coprecipitation) on different stretches of the river: agricultural development is extensive along the lower reaches, several towns of significant population occur at intervals (*e.g.*, the populations of Peterborough and Trenton are 61,000 and 21,000, respectively), and major tributaries drain into the Trent, *e.g.*, the Crowe River, which enters between stations 6B and 7 (Fig. 1) and which drains a watershed underlain mainly by igneous rocks of Precambrian age. Iron–phosphorus relationships are significantly different in waters adjacent to the Precambrian Shield (Manning & Gracey 1991). Both the rates of flow (for the Trent River, *e.g.*, the mean annual rate of flow at station 4 is 60% greater than at station 7; Ontario Ministry of the Environment 1989) and the concentrations of particulate matter in the water are greatest in the lower reaches (see below, also Manning & Wang 1994), hence the mass of contaminant flowing in the river is greatest at Trenton. Consequently, any stoichiometric relationship covering a major stretch of river (station 13 is 100 km upstream of station 1) on which the above factors have an impact indicates that equilibrium conditions are established rapidly in the river.

EXPERIMENTAL DETAILS

Suspended particulate matter was collected from mid-depth of water at 22 stations in the Trent – Severn Waterway (Fig. 1) by the continuous-flow centrifugation of approximately 1000 L of water. Two major field trips were organized, in May and October 1992, and shorter trips were held in October 1991 and April 1992. Particulate matter was also collected from the Moira River (at Belleville) in May 1992. The collation of data from several trips is necessary to confirm reproducibility over time of contaminant behavior in the river. All exposed metal surfaces in the centrifuge are made of stainless steel; care was taken to prevent friction of moving parts within the centrifuge bowls (due to imbalance) so as to reduce the risk of sample contamination, by chromium, for example. Optical and Mössbauer spectrometry showed no evidence of contamination by shards of stainless steel. All samples were frozen immediately and later freeze-dried. The approximate yield of dry particulate matter was 5 g at the lower stations and 1 g at upstream stations. Water temperature was 16 ± 1.0°C.

The room-temperature Mössbauer spectra of all samples of particulate matter were recorded and computed as described previously (Manning & Wang 1994). Three doublets are invoked, two are assigned to ferrous ions mainly in octahedral coordination in the structures of clay minerals (denoted as Fe^{2+}_{a} and Fe^{2+}_{b}, and in total by Fe^{2+}_{CL}), and the remaining broad doublet is assigned (Coey *et al.* 1974) to ferric ions mainly in sites of near-octahedral symmetry in poorly crystalline hydrated oxides (Fe^{3+}_{OX}) and in clay minerals (Fe^{3+}_{CL}). The spectral doublets of ferric ions in the different minerals are superimposed; consequently, the spectra yield ratios of concentrations of total ferric iron to total

TABLE 1. METAL CONCENTRATIONS IN TRENT RIVER PARTICULATE MATTER

Station		Fe^{2+}_{CL}	Fe^{3+}_{T}	Pb	Zn	Mn	Cr	Cu
		Weight Percent						
1	Oct 91	0.59	1.27	0.0058	0.0126	0.21	0.0052	0.0045
2A	Oct 91	0.49	1.61	0.0074	0.0092	0.39	0.0103	0.0039
2B	Oct 91	0.66	1.73	0.0061	0.0084	0.41	0.0066	0.0038
3	Oct 91	0.46	1.72	0.0069	0.0174	0.37	0.0171	0.0062
1	Apr 92	0.94	3.09	0.0112	0.0214	0.44	0.0079	0.0097
1	May 92	0.70	2.41	0.0057	0.0176	0.70	0.0075	0.0042
2	May 92	0.73	2.61	0.0067	0.0164	0.83	0.0065	0.0061
3	May 92	0.82	2.47	0.0063	0.0153	0.68	0.0075	0.0013
4	May 92	0.89	2.66	0.0062	0.0159	0.82	0.0070	0.0046
4A	May 92	0.79	2.46	0.0071	0.0164	0.74	0.0085	0.0092
4B	May 92	0.63	2.34	0.0076	0.0153	0.78	0.0110	0.0058
4C	May 92	0.78	2.72	0.0068	0.0167	0.88	0.0156	0.0038
5	May 92	0.60	2.90	0.0124	0.0184	1.22	0.0087	0.0058
5A	May 92	0.56	2.63	0.0077	0.0161	0.89	0.0075	0.0043
5B	May 92	0.52	2.50	0.0095	0.0170	0.86	0.0077	0.0077
5C	May 92	0.58	2.58	0.0153	0.0172	1.03	0.0073	0.0043
6	May 92	0.42	2.21	0.0095	0.0222	0.81	0.0108	0.0047
6A	May 92	0.47	2.22	0.0078	0.0165	0.75	0.0066	0.0048
6AA	May 92	0.44	2.04	0.0082	0.0181	0.74	0.0095	0.0207
6B	May 92	0.61	2.44	0.2566	0.0183	1.45	0.0085	0.0076
7	May 92	0.49	2.31	0.0106	0.0172	0.76	0.0084	0.0044
8	May 92	0.44	1.67	0.0057	0.0131	0.38	0.0060	0.0036
9	May 92	0.25	1.82	0.0077	0.0151	0.57	0.0013	0.0216
13	May 92	0.51	2.60	0.0136	0.0220	2.09	0.0095	0.0052
16	May 92	0.30	2.45	0.0101	0.0263	2.73	0.0096	0.0196
1	Oct 92	0.64	2.12	0.0060	0.0134	0.40	0.0054	0.0030
2	Oct 92	0.79	2.38	0.0060	0.0152	0.47	0.5561	0.0037
3	Oct 92	0.81	2.28	0.0060	0.0143	0.46	0.0067	0.0033
4	Oct 92	0.75	2.41	0.0069	0.0160	0.42	0.0071	0.0036
5	Oct 92	0.72	2.20	0.0072	0.0164	0.41	0.0083	0.0057
5A	Oct 92	0.68	2.03	0.0076	0.0153	0.44	0.0064	0.0040
5B	Oct 92	0.74	2.26	0.0087	0.0176	0.42	0.0067	0.0034
5C	Oct 92	0.61	2.03	0.0075	0.0161	0.37	0.0069	0.0047
5CC	Oct 92	0.72	2.52	0.0074	0.0163	0.49	0.0063	0.0042
5D	Oct 92	0.60	1.76	0.0056	0.0119	0.50	0.0065	0.0042
6	Oct 92	0.39	1.89	0.0069	0.0136	0.55	0.0044	0.0031
6B	Oct 92	0.48	2.05	0.0064	0.0134	0.56	0.0043	0.0042
7	Oct 92	0.39	1.57	0.0059	0.0112	0.46	0.0045	0.0036
7A	Oct 92	0.43	1.72	0.0059	0.0126	0.50	0.0045	0.0037
8	Oct 92	0.50	1.88	0.0063	0.0131	0.49	0.0047	0.0041
9	Oct 92	0.21	1.33	0.0071	0.0113	0.71	0.0049	0.0093
10	Oct 92	0.69	2.30	0.0095	0.0197	0.52	0.0064	0.0061
11	Oct 92	0.93	3.22	0.0111	0.0272	0.71	0.0091	0.0078
11CC	Oct 92	0.64	3.07	0.0148	0.0296	0.97	0.0108	0.0014
12A	Oct 92	0.50	2.62	0.0144	0.0255	1.03	0.0111	0.0065
13	Oct 92	0.32	2.12	0.0106	0.0169	1.15	0.0067	0.0083

Stations 2A and 2B Oct 91 are 0.5 km upstream and downstream of station 2 (Fig. 1), respectively.

ferrous iron, *i.e.*, Fe_T^{3+}/Fe_{CL}^{2+}. The spectra are not reproduced here because, to the eye and on computer resolution, they are very similar to those published earlier (Manning & Wang 1994). Measured values of isomer shift (measured relative to iron foil), quadrupole splitting, and half width are (in mm s^{-1}): for Fe_a^{2+} 1.13 ± 0.02, 2.62 ± 0.04 and 0.35 ± 0.02; for Fe_b^{2+} 1.11 ± 0.03, 2.15 ± 0.05 and 0.34 (constrained); for Fe^{3+} 0.34 ± 0.02, 0.66 ± 0.02 and 0.55 ± 0.03. The ratio of concentrations of Fe_a^{2+} to Fe_b^{2+} is approximately 4.

The assumption that the ferrous iron is held mainly within the structures of clay minerals is not without support. Illite and, to a lesser degree, chlorite are the principal iron-bearing compounds measured semiquantitatively by X-ray-diffraction methods in the riverine particulates and in the bottom sediments of the Bay of Quinte (Damiani & Thomas 1974). The Mössbauer hyperfine parameters are consistent with most of the ferrous iron being in clay minerals (Coey *et al.* 1974). The minerals vivianite and siderite are unstable in well-oxygenated water, and none of their well-defined spectral peaks (Manning *et al.* 1980, Nembrini *et al.* 1983) is visible in the spectra. Computation of the Mössbauer spectra with the inclusion of peaks constrained in position and halfwidth to those of vivianite and siderite confirmed that considerably less than 5% of the ferrous iron is in these minerals. Moreover, the structure of the ferrous Mössbauer absorption envelope remains unchanged on washing the particulate matter with dilute hydrochloric acid. The 4 K Mössbauer spectra of samples collected in 1989, recorded and described previously (Manning & Wang 1994), show that 40% of the particulate iron is in a hydrated oxide at station 1, and 50% at station 9. A value of 45% is similarly measured for particulate matter collected at station 1 in October 1992; the dithionite – citrate – bicarbonate reagent extracted approximately 50% of the ferric iron. This 4 K spectrum, not reproduced here as it is almost identical to the 4 K spectra of the 1989 samples (Manning & Wang 1994), shows the prominent development of a magnetic hyperfine six-line pattern marking the presence of small particles of superparamagnetic iron oxides (Murad 1988).

The concentrations of total iron, manganese, lead, zinc, and copper in dried particulate matter were measured, following sample dissolution in aqua regia, by inductively coupled plasma – emission spectroscopy using suitable controls and standards. Standards were prepared in a similar acid medium to that of the samples. Replicate analyses, based on the use of corresponding sections from two different cores, are good to ±3% for iron and ±4% for the other metals. Analyses are accurate to ±8%, relative to a standard reference material. Approximately 85% of the river load of Pb and Zn at station 1 is in the particulate phase. All concentrations are presented in Table 1 as weight percent (wt%) of dry particulate matter. The concentrations of Pb, Zn, and Cu are generally lower than in the lake bottom sediments of Lake Ontario (Kemp & Thomas 1976).

Concentrations of Fe_{CL}^{2+} and Fe_T^{3+} are then determined from the concentration of total iron (measured by plasma emission spectroscopy) and the Fe^{3+}/Fe^{2+} ratio measured from the Mössbauer spectra. Ferric/ferrous ratios are good to ±2%.

RESULTS AND DISCUSSION

Geochemical model for correlation of data

The geochemical basis for better understanding the correlations between iron and other ions lies, as demonstrated for the incorporation of NAIP, in elucidating the distribution of ferric iron between active hydrated oxides and inactive structural sites in clay minerals (Manning & Wang 1994). Thus, from the assumption that $[M] = k_1\cdot[Fe_{OX}^{3+}] + k_2\cdot[Fe_{CL}^{2+}]$, where [ ] represent concentrations, Fe_{OX}^{3+} is hydrated ferric oxide, and the constants k_1 and k_2 are coefficients of binding of metal contaminant ions on oxide and clay mineral, respectively, we get that

$$[M]/[Fe_{CL}^{2+}] = k_1\cdot[Fe_T^{3+}]/[Fe_{CL}^{2+}] - n_{CL}\cdot k_1 + k_2 \qquad (1)$$

where n_{CL} is equal to $[Fe_{CL}^{3+}]/[Fe_{CL}^{2+}]$. Hence, a plot of the concentration ratios M/Fe_{CL}^{2+} against Fe_T^{3+}/Fe_{CL}^{2+} is linear and of slope equal to k_1. The value of n_{CL} is considered to be reasonably constant for clay minerals collected along a stretch of river flowing through the same geological province. Values of n_{CL} cannot be determined unambiguously from the intercepts of the ratio plots because k_2 is an unknown. However, if it is assumed that the binding of metal ions to the surfaces of clay minerals is weaker than to those of ferric oxides, *i.e.*, $k_2 << k_1$, then n_{CL} is equal to the intercept divided by k_1. The value of n_{CL} defines the unavailable fraction of ferric iron, and hence its value should be the same within experimental error for all contaminant ions binding to the same fraction of hydrated ferric oxides. The value of the product $-n_{CL}\cdot k_1$ is of necessity negative, as both n_{CL} and k_1 are positive numbers. The value of $-n_{CL}\cdot k_1$ is dependent on the composition of clay minerals in the watershed and on the contaminant concentration in the river.

Relationships between Fe and Pb, and Fe and Zn

Concentrations of the pairs Pb – Fe_{CL}^{2+} and Zn – Fe_{CL}^{2+} are not correlated at the 5% level of significance, whereas the pairs Pb – Fe_T^{3+} and Zn – Fe_T^{3+} are well correlated (Figs. 2, 3). Clearly, lead and zinc ions are more strongly associated with hydrated ferric oxides than with clay minerals. More definitively, the elemental concentration ratios M/Fe_{CL}^{2+} and Fe_T^{3+}/Fe_{CL}^{2+}, where M is Pb^{2+} or Zn^{2+}, are extremely well and linearly correlated (Figs. 2, 3). The data presented in Figures 2 and 3 show that the criteria of negative intercepts and consistent values of n_{CL} are met for the binding of lead and zinc, and also for the phosphate ion (Manning & Wang 1994); the captions also include measured values of k_1. Using the equation $[\mathrm{Zn}^{2+}] = 0.109[\mathrm{Fe}^{3+}_{\mathrm{OX}}]$ and measured concentrations of Zn at the lower stations (Table 1), then 50–60% of $\mathrm{Fe}^{3+}_{\mathrm{T}}$ is active oxide. Our binding coefficients for lead (0.57 wt%) and zinc (1.09 wt%) agree well with the corresponding binding coefficients of 0.46% and 1.9% measured by Lum & Gammon (1985) in the highly polluted Detroit River and its tributaries. Lead–iron and zinc–iron interactions are quantitatively similar in the Moira River (Figs. 2,3; Manning & Gracey 1991).

Relationships between iron and Mn, Cr, and Cu

Concentrations of Cr and Cu are poorly correlated with the concentrations of either ferrous or ferric iron ($r = 0.12$ for the Cr – $\mathrm{Fe}^{2+}_{\mathrm{CL}}$ pair, 0.06 for Cu – $\mathrm{Fe}^{2+}_{\mathrm{CL}}$, 0.03 for Cr – $\mathrm{Fe}^{3+}_{\mathrm{T}}$ and 0.16 for Cu – $\mathrm{Fe}^{3+}_{\mathrm{T}}$); the Mn – $\mathrm{Fe}^{3+}_{\mathrm{T}}$ pair is significantly correlated ($r = 0.39$; for 46 points, r = 0.38 at 1% level of significance), whereas the Mn – $\mathrm{Fe}^{2+}_{\mathrm{CL}}$ pair is not ($r = 0.02$). Although the analytical data for Cr, Cu, and Mn are subject to more scatter than are those for Pb and Zn, plots of the ratios $\mathrm{Cr/Fe}^{2+}_{\mathrm{CL}}$, $\mathrm{Cu/Fe}^{2+}_{\mathrm{CL}}$, and $\mathrm{Mn/Fe}^{2+}_{\mathrm{CL}}$ against $\mathrm{Fe}^{3+}_{\mathrm{T}}/\mathrm{Fe}^{2+}_{\mathrm{CL}}$ (Fig. 4) point to statistically significant associations of Cr, Cu, and Mn with hydrated ferric oxides.

The plots of concentration ratio for manganese and

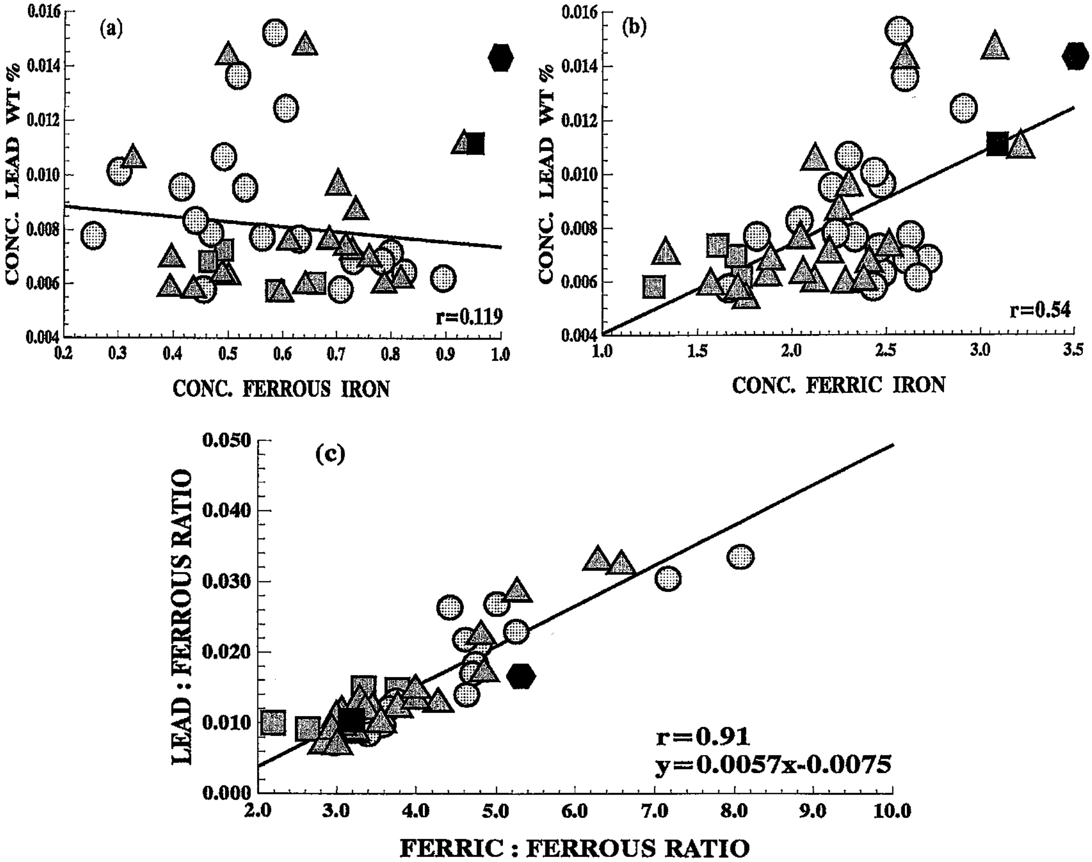

FIG. 2. Plots with regression coefficients showing relationships between a) concentrations of lead and ferrous iron, which are poorly correlated, (b) concentrations of lead and total ferric iron, which are significantly correlated ($r = 0.54$; for 45 points, $r = 0.38$ at the 1% level of significance), and (c) the ratios of concentrations $\mathrm{Pb/Fe}^{2+}_{\mathrm{CL}}$ and $\mathrm{Fe}^{3+}_{\mathrm{T}}/\mathrm{Fe}^{2+}_{\mathrm{CL}}$, which are highly and linearly correlated ($r = 0.91$, 45 points). The line corresponds to $[\mathrm{Pb}] = 0.0057 \pm 0.0004\ [\mathrm{Fe}^{3+}_{\mathrm{T}}] - 0.0075 \pm 0.0032\ [\mathrm{Fe}^{2+}_{\mathrm{CL}}]$, or $[\mathrm{Pb}] = 0.0057\ [\mathrm{Fe}^{3+}_{\mathrm{OX}}]$. The value of n_{CL}, *i.e.*, $[\mathrm{Fe}^{3+}_{\mathrm{CL}}]/[\mathrm{Fe}^{2+}_{\mathrm{CL}}]$, is 1.3 ± 0.7. One point corresponding to the May 92 sampling of station 6B is omitted; this point corresponds to values of $\mathrm{Pb/Fe}^{2+} = 0.42$ and $\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+} = 4.0$, which are incompatible by an order of magnitude with the trend of plot in (c). Symbols refer to the field trips: light square for Trent River, October 1991, dark square April 1992, circle May 1992, and triangle October 1992, and hexagon for Moira River May 1992 (Fig. 1). The point for the Moira River is not included in the regression analysis.

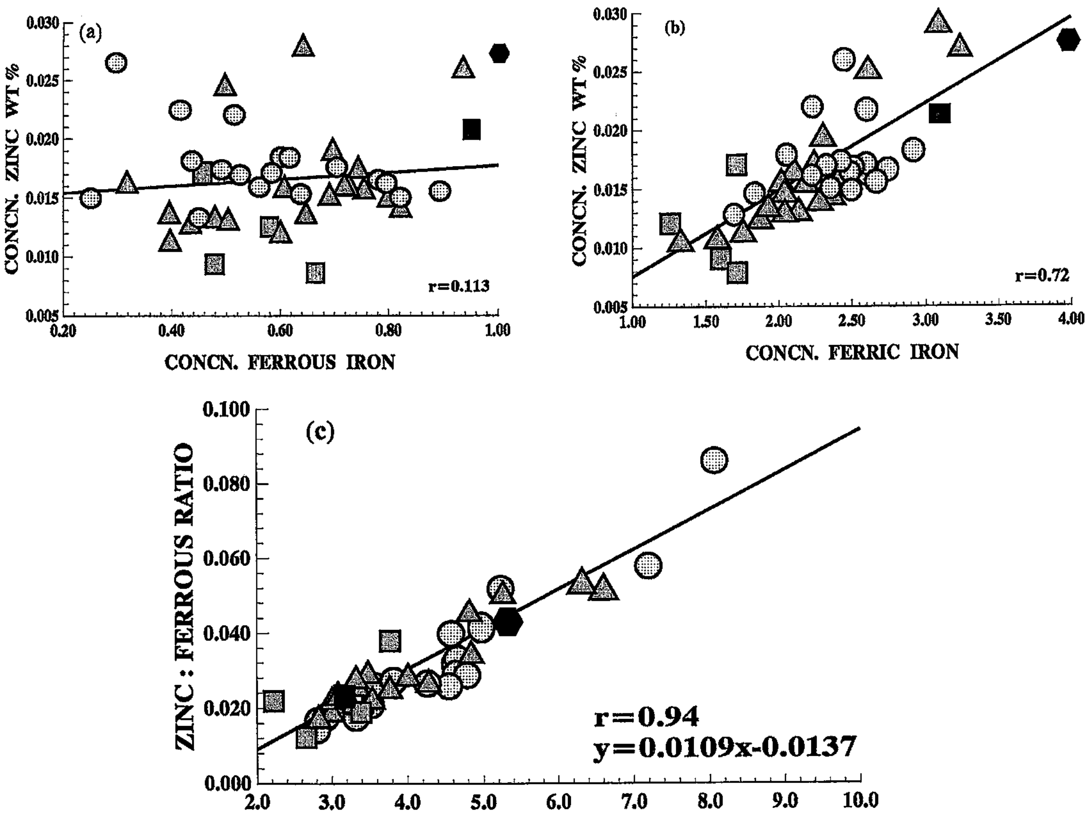

FIG. 3. Plots with regression coefficients describing relationships between (a) concentrations of zinc and ferrous iron, which are poorly correlated, (b) concentrations of zinc and total ferric iron, which are significantly correlated ($r = 0.72$; for 46 points, $r = 0.37$ at the 1% level of significance), and (c) the ratios of concentrations Zn/Fe^{2+}_{CL} and Fe^{3+}_{T}/Fe^{2+}_{CL}, which are highly and linearly correlated ($r = 0.94$, 46 points). The straight line corresponds to $[Zn] = 0.011 \pm 0.001\ [Fe^{3+}_{T}] - 0.014 \pm 0.005\ [Fe^{2+}_{CL}]$, or $[Zn] = 0.011\ [Fe^{3+}_{OX}]$. The value of n_{CL} is 1.3 ± 0.5, in agreement with those values measured for lead (1.3 ± 0.7) and phosphate ion (1.95 ± 0.5; Manning & Wang 1994). Symbols are defined in the caption to Fig. 2.

for copper ions yield significantly negative values of $-n_{CL} \cdot k_1$ (Fig. 4c), assuming that k_2 is zero. Not unexpectedly, in view of the marked similarities in the aquatic and redox chemistry of iron and manganese (Bortleson & Lee 1974, Burns & Nriagu 1976, Lum & Gammon 1985, Mortimer 1941), the association between Mn_T and Fe^{3+}_{OX} is strong ($r = 0.83$). The measured value of n_{CL} of 2.5 ± 1.0 (Fig. 4c) is reasonably consistent with the n_{CL} values measured for the binding of Pb (1.3 ± 0.7) and Zn (1.3 ± 0.5) ions.

A strong association is indicated between copper ions and ferric iron (Fig. 4b). The value of n_{CL}, 2.7 ± 1.6, is consistent with values measured for the binding of the other metals. The coadsorption of organic matter promotes the adsorption of copper ions onto ferric oxides (Laxen 1983, Luoma & Bryan 1981, Tipping & Cooke 1982). Also, copper is strongly associated with organic matter in sediments underlying the Detroit River (Lum & Gammon 1985). Hence organic matter may well play a role in the binding of metals in the Trent River.

Two of the points (3-Oct and 9-May) in the plots of concentration ratio for chromium ions (Fig. 4a) are possible "outliers". Whether or not these points are included in the regression analysis, it is clear that chromium ions are highly associated with the ferric oxide moiety (footnote to Fig. 4).

GENERAL DISCUSSION

Although the measurement of n_{CL} is prone to considerable error, the factor can, with good data, confirm the association beween several contaminant ions and one surface-active moiety within the total ferric iron fraction. Thus the values of n_{CL} measured for the incorporation of phosphate anions (1.95 ± 0.5, Manning & Wang 1994), and for the cations of Pb (1.3 ± 0.7), Zn (1.3 ± 0.5), Cu (2.7 ± 1.6), and Mn (2.5 ± 1.0) are all in

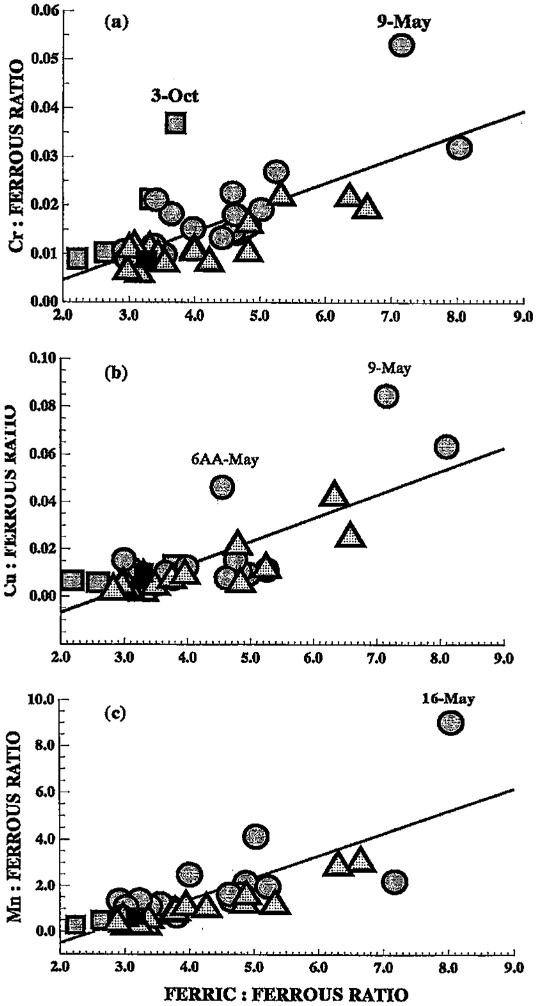

FIG. 4. Plots describing the relationships between the ratios of concentrations M/Fe$^{2+}_{CL}$ and Fe$^{3+}_{T}$/Fe$^{2+}_{CL}$ where (a) M is Cr, (b) M is Cu, and (c) M is Mn. For all 46 points, linear regression yields values of r for the respective metal ions of 0.71, 0.76, and 0.83 ($r = 0.38$ at the 1% level of significance). Linear regression yields: (a) [Cr] = 0.005 ± 0.001 [Fe$^{3+}_{T}$] − 0.005 ± 0.006 [Fe$^{2+}_{CL}$]. n_{CL} is not definitive. Omission of outliers (3-Oct and 9-May) yields values of k_1 = 0.004 ± 0.0004, and $-nk_1 + k_2$ = intercept = 0.002 ± 0.003; r is 0.80. (b) [Cu] = 0.010 ± 0.001 [Fe$^{3+}_{T}$] − 0.027 ± 0.010 [Fe$^{2+}_{CL}$], and $n_{CL} = 2.7 \pm 1.6$. (c) [Mn] = 0.95 ± 0.10 [Fe$^{3+}_{T}$] − 2.4 ± 0.8 [Fe$^{2+}_{CL}$]; n_{CL} is 2.5 ± 1.0. Symbols are defined in the caption to Fig. 2.

reasonable agreement and are bracketed by n_{CL} values of 1.5 to 2. Errors in the determination of the intercepts of the ratio plots are large. At any station, n_{CL} defines, *via* the measured concentration of Fe$^{2+}_{CL}$, the concentration of Fe$^{3+}_{CL}$ and hence the concentration of the surface-active form of ferric iron. Phosphate, Pb, Zn, Mn, Cu, and probably Cr ions are carried in water in the same particulate assemblage hosted by a Fe$^{3+}_{OX}$ – organic matter moiety (Manning & Wang 1994).

Whereas the phosphate ion is specifically coordinated to the ferric ion in hydrated oxides (Parfitt & Russell 1977, Ryden *et al.* 1977), the metal ions are necessarily indirectly bonded through an intervening (specifically bonded) anion, either hydroxyl (or oxide) or humate and fulvate. The good correlation between the concentration ratios organic carbon/ferrous iron and ferric/ferrous iron in the Trent – Severn Waterway (Manning & Wang 1994) suggests that the intervening ion is an anion of high molecular weight, such as humate or fulvate. These ions have abundant carboxylate and salicylate groups for the chelation of metals.

The plots of concentration ratio, covering the collection of particulate matter from four field trips over a two-year period, imply specific bonding between phosphate ion and ferric ions (in oxides), and between metal ions and a large organic ion that is also attached to the ferric oxide. The plots further imply a degree of stoichiometry. The bioavailability of contaminant ions incorporated into suspended particulate matter is thus heavily dependent on kinetic factors, *i.e.*, on the rates of desorption and dissolution to the free ions, HPO$^{2-}_{4}$ and MOH^{n+} (Sonzogni *et al.* 1982). The bonded ions may be considered as available over the longer term, *e.g.*, on exhaustion of the pool of the free ions through algal uptake and assimilation or as a consequence of photochemically induced reduction–oxidation reactions (Miles & Brezonick 1981, Morel 1983). These reactions are efficiently catalyzed by metal ions, particularly by the abundant ions of ferric iron and manganese, but also by contaminant ions such as chromium. The reduction of metal ions and the associated oxidation of organic matter will lead to the dissolution of the NAIP – oxide – humate assemblage. Consequently, photochemical release may play an important role in the availability of particulate contaminants in the slow-moving waters of the Bay of Quinte in summer. However, the phosphorus budget in the Bay in summer, when river flows are low, is strongly influenced by diffusional release from the bottom sediments (Minns *et al.* 1986).

At none of the river stations is the concentration of lead or zinc greatly in excess of that expected from the plots of concentration ratios (Figs. 2, 3); hence, point-source inputs of metal contaminants in concentrations greatly exceeding concentrations of ferric iron as defined by Figures 2–4, and therefore weakly bonded and bioavailable, are not a significant problem in the river. Also, most of the bottom of the river is well scoured during the spring freshet, so that the sediments, through contaminant reflux, can be but minor sources of contaminant. For several of the nearshore stations in the Detroit River (Manning 1989), plots of concentration ratios showed excessive concentrations of NAIP (and likely of lead), clearly marking point sources of contamination.

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