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FERRIC OXIDE AND THE BINDING OF PHOSPHORUS, LEAD AND CARBON IN RIVER PARTICULATE MATTER

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ABSTRACT

The concentrations ([ ]) of nonapatite inorganic phosphorus (NAIP) and of iron in suspended particulate matter collected from 23 stations in the Trent – Severn Waterway, Ontario, over two field years, are best related by $[\mathrm{NAIP}] = 0.18 \pm 0.01\ [\mathrm{Fe}^{3+}_{\mathrm{T}}] - 0.35 \pm 0.04\ [\mathrm{Fe}^{2+}_{\mathrm{CL}}]$, where the subscripts T and CL represent total and clay, respectively. The form of the equation arises from the distribution of ferric iron between relatively surface-active hydrated oxides ($\mathrm{Fe}^{3+}_{\mathrm{OX}}$) and surface-inactive clay. The equation reduces to $[\mathrm{NAIP}] \approx 0.18\ [\mathrm{Fe}^{3+}_{\mathrm{OX}}]$. Lead and organic carbon are governed by similar relationships; thus $[\mathrm{Pb}] \approx 0.010 \pm 0.002\ [\mathrm{Fe}^{3+}_{\mathrm{OX}}]$, and $[\mathrm{Org\ C}] \approx 39 \pm 4\ [\mathrm{Fe}^{3+}_{\mathrm{OX}}]$. These correlations are consistent with the formation, within the river, of an assemblage of composition $(\mathrm{NAIP})_{0.32}(\mathrm{Fe}^{3+}_{\mathrm{OX}})_1(\mathrm{Org\ C})_{182}\mathrm{Pb}_{0.003}$ in atomic proportions, in which the orthophosphate ion and organic C (partly as fulvate or humate ion) are specifically bonded to ferric iron, and lead, possibly to groups on the fulvate–humate ion. Deposition of the particulate matter to the bottom clay–silt sediments of the eutrophic Bay of Quinte would likely cause reduction of $\mathrm{Fe}^{3+}_{\mathrm{OX}}$ and dissolution of the NAIP in bioavailable form. Riverine inputs of NAIP greatly exceed those of the sewage-treatment plants.

Keywords: phosphorus, iron, lead, organic carbon, particulate matter, Trent – Severn Waterway, Ontario.

SOMMAIRE

Les concentrations ([ ]) de phosphore inorganique non lié à l'apatite (NAIP) et de fer dans les particules en suspension prélevées à 23 sites dans le réseau des rivières Trent et Severn, en Ontario, au cours de deux saisons d'échantillonage, répondent à l'expression $[\mathrm{NAIP}] = 0.18 \pm 0.01\ [\mathrm{Fe}^{3+}_{\mathrm{T}}] - 0.35 \pm 0.04[\mathrm{Fe}^{2+}_{\mathrm{CL}}]$, dans laquelle les symboles T et CL représentent la quantité totale et la fraction incorporée dans la structure de l'argile, respectivement. La forme de l'équation découle de la distribution du fer ferrique entre les oxydes hydratés à surface relativement active ($\mathrm{Fe}^{3+}_{\mathrm{OX}}$) et les argiles, dont la surface est inactive. Avec simplifications, l'équation devient $[\mathrm{NAIP}] \approx 0.18[\mathrm{Fe}^{3+}_{\mathrm{OX}}]$. La concentration de plomb et celle du carbone organique répondent à une relation semblable: $[\mathrm{Pb}] \approx 0.010 \pm 0.002[\mathrm{Fe}^{3+}_{\mathrm{OX}}]$, et $[\mathrm{C\ org}] \approx 39 \pm 4[\mathrm{Fe}^{3+}_{\mathrm{OX}}]$. Ces corrélations concordent avec la formation, dans la rivière, d'un assemblage de composition $\{\mathrm{NAIP})_{0.32}(\mathrm{Fe}^{3+}_{\mathrm{OX}})_1(\mathrm{C\ org})_{182}\mathrm{Pb}_{0.003}$ (proportions atomiques), dans lequel l'ion orthophosphate et le carbone organique (présent en partie sous forme d'ion fulvate ou humate) sont spécifiquement liés au fer ferrique, et le plomb, possiblement aux groupes actifs sur l'ion fulvate–humate. La déposition de tels matériaux en particules sur les sédiments argileux et silteux du fond de la baie de Quinte, eutrophique, causerait probablement une réduction du $\mathrm{Fe}^{3+}_{\mathrm{OX}}$ et une dissolution du phosphore inorganique non lié à l'apatite sous sa forme biodisponible. L'apport de tel phosphore par la rivière surpasse grandement la contribution des usines de traitement des effluents urbains.

(Traduit par la Rédaction)

Mots-clés: phosphore, fer, plomb, carbone organique, matériau en particules, réseau des rivières Trent et Severn, Ontario.

INTRODUCTION

Hydrated ferric oxides are strongly linked to the binding and transport of natural compounds and contaminants in aquatic systems (Gibbs 1973, 1977). Ferric oxides adsorb inorganic anions (*e.g.*, phosphate; Berner 1973, Hingston *et al.* 1967, Lijklema 1980, Lum & Gammon 1985), organic anions (*e.g.*, humate and fulvate; Parfitt *et al.* 1977, Sholkovitz 1976, Tipping 1981), and heavy metal ions (Balistrieri & Murray 1982, Lum & Gammon 1985, Tessier *et al.* 1979). However, the adsorption of humic and fulvic acids modifies the adsorption capacity of hydrated ferric oxides for other ions: the binding of phosphate may be reduced through competitive reaction (Tipping 1981), and metal ions may bind selectively to specific groups on the humate and fulvate molecules (Bunzl 1974, Stevenson 1979). At pH values of 6 to 8, humate and fulvate ions enhance the adsorption of lead and other metal ions onto hydrated oxides (Laxen 1983).

The adsorption of phosphate and metal ions onto insoluble hydrated oxides and humic or fulvic compounds reduces their bioavailability (Livens 1991, de Wit *et al.* 1990). The formation of soluble complexes with fulvate and humate molecules, in some cases through cation reduction (Ephraim & Marinsky 1990, Hem 1960), increases metal mobility. Under oxic conditions, contaminant availability depends on the thermodynamic and kinetic factors controlling the desorption of ions to yield the free hydrated ion (Sonzogni *et al.* 1982). Freshly precipitated ferric oxides effectively remove phosphate ions from circulation (Manning *et al.* 1991). Phosphate and humate probably function as multidentate ligands (Ryden *et al.* 1977, Parfitt & Russell 1977). The eventual deposition of riverine particulate matter to the anoxic bottom sediments of lakes would cause reduction of hydrated ferric oxides, with consequent release of phosphate and other contaminants (Burns & Ross 1972, Mortimer 1941). The Trent River, with its high load of particulate phosphorus (Minns *et al.* 1986), is the major source of water and of total phosphorus to the highly eutrophic Bay of Quinte, Lake Ontario. The Bay is a designated environmental "Area of Concern" in the Great Lakes. Ferric iron is the main binder of NAIP in the Trent River particulate matter (Manning & Gracey 1991).

Here the concentrations of organic carbon, nonapatite inorganic phosphorus (NAIP) and lead are collated with the concentrations of ferric and ferrous iron in suspended particulate matter collected over two field seasons from 23 stations in the recreationally and economically important Trent – Severn Waterway, Ontario. The aim of the work is to better define the form and composition of the particulate assemblage carrying NAIP to the Bay of Quinte and to relate this form to a process by which NAIP can be released to stimulate algal growth. NAIP represents the main pool of bioavailable phosphorus in sediments and suspended particulate matter (Williams *et al.* 1976, 1980). However, the need to demonstrate reproducibility in particulate chemistry from year to year is an important prerequisite to planning remedial action in the Bay of Quinte.

EXPERIMENTAL DETAILS

Suspended particulate matter was collected by centrifuging 600 L to 1000 L of water from mid-depth at 21 stations in the Trent – Severn Waterway (Fig. 1)

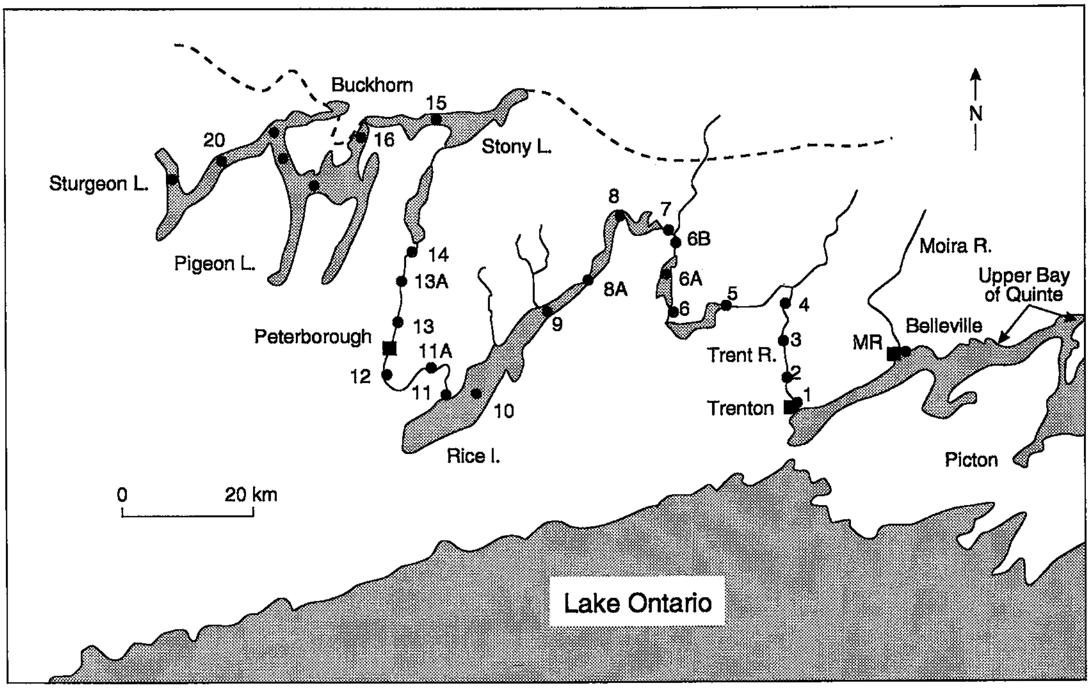

FIG. 1. Diagram showing sampling stations along the Trent – Severn Waterway, May–June 1990. Most stations also were sampled in May–June 1989 (Manning & Gracey 1991). Station 1A is ~600 m upstream of station 1. The Waterway becomes the Trent River downstream of Rice Lake. Bedrock is fractured limestone south of the dashed line and igneous rocks of Precambrian age north of the line. The populations of Peterborough and Trenton are 61,000 and 16,000, respectively.

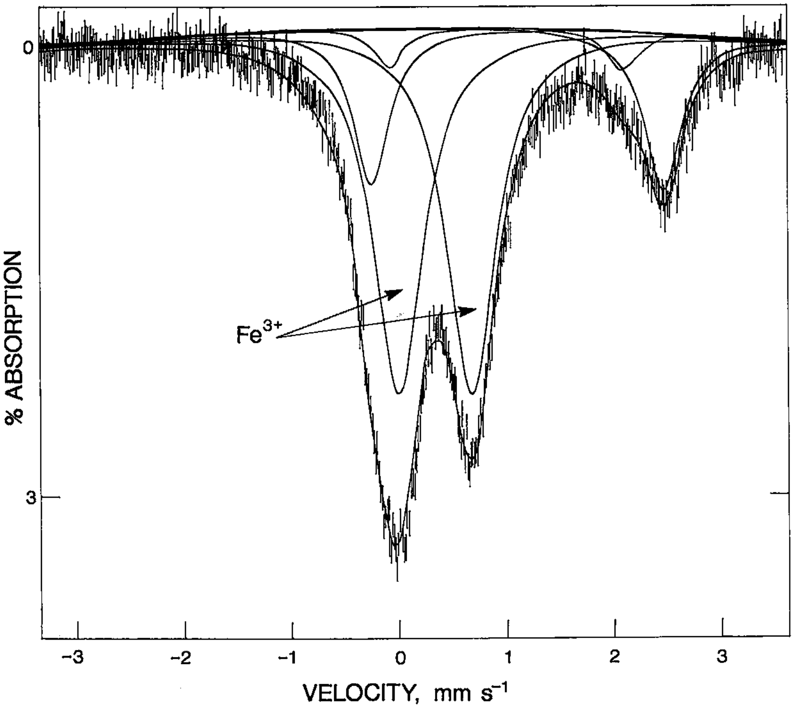

FIG. 2. Room-temperature Mössbauer spectrum of Trent River particulate matter, station 2, May–June 1990. Chi-squared is 545 for 494 degrees of freedom.

on one field-trip in May–June 1990. Particulate matter also was collected from stations 1 and 1A in April and October 1990. All samples were frozen immediately following collection and later freeze-dried. Approximately 4 g of dry particulate matter were collected per 600 L of water at the lower stations (1–4), and 1 g at the higher stations. Water temperatures were 17.1 ± 0.6°C. Water was collected from mid-depth. Many of the stations also were sampled in 1989 (Manning & Gracey 1991).

The Mössbauer spectra of all samples of particulate matter (Fig. 2) were recorded at room temperature on a spectrometer calibrated against iron foil (Manning & Gracey 1991). Spectra were resolved using the programs of Stone (1967). Values of chi-squared and visual examination of the computed fit were used as criteria of goodness of fit. Spectra were computed on the basis of three doublets (Fig. 2), two marking ferrous ions in two different octahedrally coordinated positions in clay minerals and chlorite (Coey *et al.* 1974, Manning & Gracey 1991). Ferrous iron may be distributed over a larger number of sites, but on the basis of obvious inflections, two doublets only are invoked. The third doublet, broadened and the most intense, marks ferric ions in a wide range of octahedra of slightly differing symmetry; simply, ferric ions are mainly located in the structures of clay minerals (mainly illite) and in amorphous or poorly crystallized hydrated oxides (Coey *et al.* 1974, Manning & Gracey 1991). Consistent with these assignments, measured values of isomer shift (relative to iron foil), quadrupole splitting, and half width are (in mm s^{-1}): for Fe$^{2+}_{A}$, 1.12 ± 0.02, 2.63 ± 0.03 and 0.34 ± 0.03; for Fe$^{2+}_{B}$, 1.10 ± 0.04, 2.10 ± 0.06 and 0.34 (constrained); for Fe^{3+}, 0.34 ± 0.02, 0.68 ± 0.02 and 0.53 ± 0.04. The ratio of Fe$^{2+}_{A}$and Fe$^{2+}_{B}$concentrations is approximately 3:1.

The Mössbauer spectra of particulate matter collected from stations 1 and 9 in May–June 1990 were recorded at 4 K in order to determine the concentrations of superparamagnetic hydrated ferric oxides (Fig. 3) (Murad 1988, Murad & Johnston 1987); such oxides are considered to be the prime surfaces for adsorption of phosphate and other anions (Lijklema 1980, Ryden *et al.* 1977). The 4 K spectra display the well-developed patterns of magnetically ordered ferric oxides, with a field gradient (470 to 500 kOe) consistent with that for ferrihydrite (Murad 1988). Based on area ratios, the 4 K spectra show that 40% of the iron in the particulate matter is in hydrated oxide at station 1, and 50% at station 9.

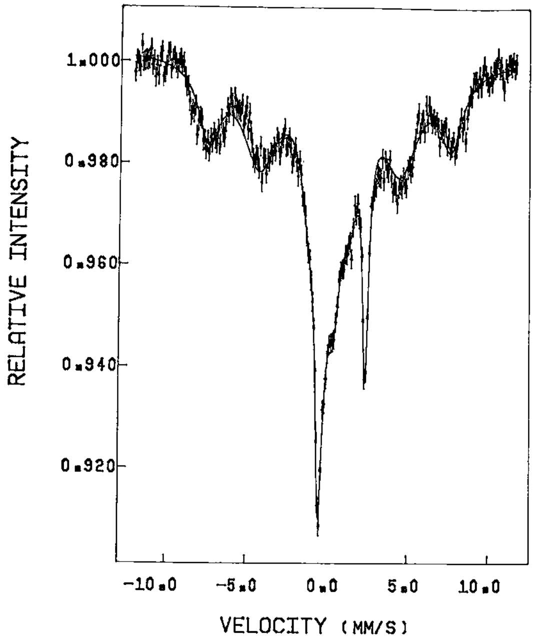

FIG. 3. Mössbauer spectrum (at 4 K) of Trent River particulate matter from station 9, May–June 1989, showing development of magnetic hyperfine pattern.

Particulate matter from stations 2 and 7 was leached with dithionite solution in order to remove preferentially the poorly crystallized iron oxides. Mössbauer spectrometry of the leached particles, after drying, yielded a Fe^{3+}:Fe^{2+} ratio of 1.30 for the sample from station 2, and 1.43 for that from station 7, which values compare with 2.75 and 3.64 for the unleached particulate matter, respectively. Approximately 50 to 60% of the ferric iron is extracted, indicating that iron oxides represent a significant fraction of the total ferric iron. However, the degree to which iron is extracted from within the structures of clay minerals by the dithionite solution is not known.

Concentrations of NAIP, organically bonded phosphorus and apatite phosphorus were measured by wet-chemical fractionation (Williams *et al.* 1976). Concentrations of NAIP are reproducible to ±5%. The specificity of extraction is good (Lucotte & d'Anglejan 1985). In aquatic systems, NAIP is strongly associated with the hydrated oxides of iron and manganese (Williams *et al.* 1976, Bortleson & Lee 1974). Concentrations of total iron, total lead, Al, and Mn were determined by dissolution of the samples in aqua regia and subsequent atomic absorption spectrometry using suitable controls and standards. Concentrations of organic carbon were measured using a Leco induction furnace (Kemp 1971). All concentrations are presented as weight percent of dry sediment.

RESULTS AND DISCUSSION

Relationships between iron and phosphorus

Concentrations of the pairs of elements NAIP–Fe^{2+} and NAIP–Fe^{3+} are poorly and negatively correlated (Fig. 4). By way of contrast, the concentration ratios NAIP:Fe^{2+} and Fe^{3+}:Fe^{2+} are strongly and positively correlated for all 1989 and 1990 data (Fig. 4). The plot described in Figure 4 translates to

$$[\mathrm{NAIP}] = 0.18 \pm 0.02\,[\mathrm{Fe}^{3+}_{\mathrm{T}}] - 0.35 \pm 0.04\,[\mathrm{Fe}^{2+}_{\mathrm{CL}}], \tag{1}$$

where brackets represent concentrations, $\mathrm{Fe}^{3+}_{\mathrm{T}}$ is total ferric iron, and $\mathrm{Fe}^{2+}_{\mathrm{CL}}$ is ferrous iron in the sheet silicates illite and chlorite (Damiani & Thomas 1974). The form of the plot had been attributed earlier [Manning (1989) for Lake St. Clair particulate matter, Manning & Gracey (1991) for Trent River 1989 data] to competition between clay minerals and phosphate ions for binding sites on the surfaces of hydrated ferric oxides. This explanation ignores the likelihood that clay minerals, rather than occupying surface sites on the ferric oxides, may be tying up ferric ion within their structures.

Although statistically and geochemically significant, equation (1) does not define directly the relationship between NAIP and surface-active ferric iron (*i.e.*, hydrated ferric oxides). Significant concentrations of ferric iron occur in structural positions in the layer of octahedra in illite (Deer *et al.* 1962). The increasing Fe^{3+}:Fe^{2+} ratios with generally higher station number (Table 1) more likely reflect increasing $\mathrm{Fe}^{3+}_{\mathrm{OX}}$:$\mathrm{Fe}^{2+}_{\mathrm{CL}}$ ratios rather than changes in $\mathrm{Fe}^{3+}_{\mathrm{CL}}$:$\mathrm{Fe}^{2+}_{\mathrm{CL}}$ ratio. These changing oxide:clay ratios represent differences in soil chemistry between the upper reaches of the watershed, which drain the Precambrian Shield, and the lower reaches, which drain more productive soils overlying limestone bedrock. The binding of NAIP is probably more sensitive to changes in the concentration of $\mathrm{Fe}^{3+}_{\mathrm{OX}}$ than of $\mathrm{Fe}^{3+}_{\mathrm{CL}}$ because of the diluting effect of substitution of ferric iron into the structures of clay minerals.

Therefore, in attempting to reproduce the form of equation (1), allowance must be made for the presence, within the structures of clay minerals, of a form of ferric iron that is relatively inert toward NAIP, Pb, and organic matter. If it is assumed that the Fe^{2+} content of the clay minerals is constant along the 150 km stretch of river and that hydrated ferric oxides ($\mathrm{Fe}^{3+}_{\mathrm{OX}}$) and clay minerals adsorb NAIP independently of each other, then

$$[\mathrm{NAIP}] = k_1[\mathrm{Fe}^{3+}_{\mathrm{OX}}] + k_2[\mathrm{Fe}^{2+}_{\mathrm{CL}}], \tag{2}$$

where k_1 and k_2 are constants. Because the Mössbauer spectrometer at room temperature cannot distinguish

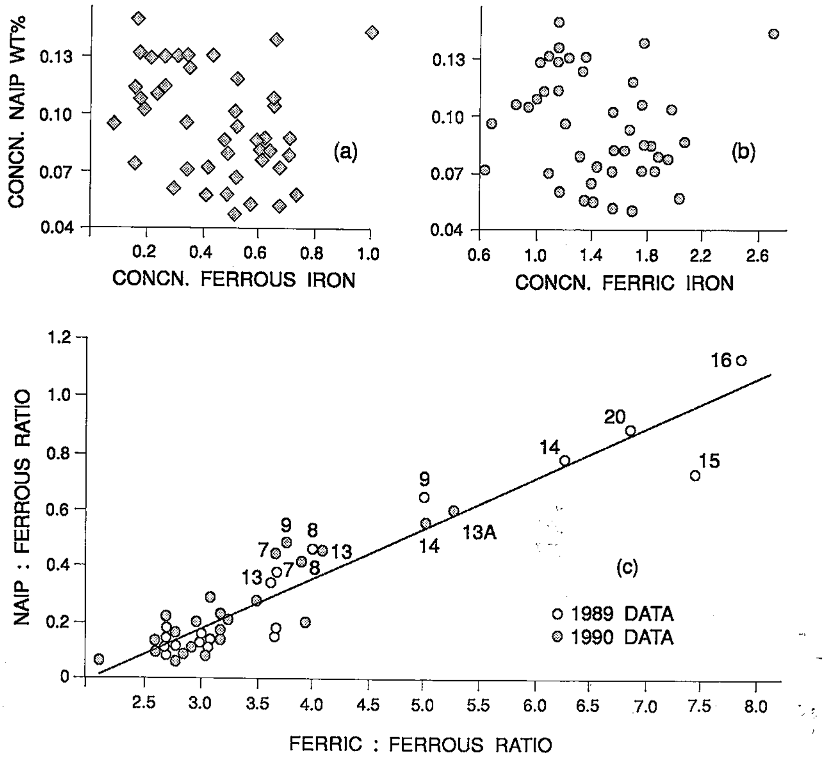

FIG. 4. Plots describing relationships between concentrations of (a) NAIP and Fe^{2+}_{CL}, for which the regression coefficient is –0.28, (b) NAIP and Fe^{3+}_{T}, $r = -0.13$, and between (c) NAIP:Fe^{2+}_{CL} and Fe^{3+}_{T}:Fe^{2+}_{CL}, $r = 0.94$, 43 points. The straight line in (c) corresponds to [NAIP] = 0.18 ± 0.01 [Fe^{3+}_{T}] – 0.35 ± 0.04 [Fe^{2+}_{CL}], or [NAIP] ≈ 0.18 [Fe^{3+}_{OX}].

between Fe^{3+}_{OX} and Fe^{3+}_{CL} (*i.e.*, it measures their sum only), equation 2 transcribes to [NAIP] = $k_1[Fe^{3+}_{T} - Fe^{3+}_{CL}] + k_2[Fe^{2+}_{CL}]$, = $k_1[Fe^{3+}_{T}] - k_1[Fe^{3+}_{CL}] + k_2[Fe^{2+}_{CL}]$, whence

$$\frac{[NAIP]}{[Fe^{2+}_{CL}]} = k_1 \frac{[Fe^{3+}_{T}]}{[Fe^{2+}_{CL}]} - k_1 \frac{[Fe^{3+}_{CL}]}{[Fe^{2+}_{CL}]} + k_2. \qquad (3)$$

For a short stretch of river flowing through a single geological province it can be assumed, to a first approximation, that $[Fe^{3+}{}_{CL}]:[Fe^{2+}{}_{CL}]$ is a constant, n. Hence

$$\frac{[NAIP]}{[Fe^{2+}_{CL}]} = k_1 \frac{[Fe^{3+}_{T}]}{[Fe^{2+}_{CL}]} - nk_1 + k_2, \qquad (4)$$

which has the same form as that of the plot in Figure 4. Consequently, $k_1 = 0.18 \pm 0.01$ and $nk_1 - k_2 = 0.35 \pm 0.04$. A linear relationship also was measured for suspended particulate matter in Lake St. Clair (Manning 1989), for which $k_1 = 0.027$ and $nk_1 - k_2 = 0.011$. The values of n and k_2 are unknown, and equation (4) cannot be solved unambiguously, since the waters of Lake St. Clair and the Trent River drain different watersheds with possibly different compositions of the clay minerals.

At pH values of 7 to 8, the surfaces of hydrated ferric oxides are positively charged, those of clays are negatively charged (Carroll 1958, Lewis 1966), and phosphate is an anion. If the binding of phosphate ion to a clay surface is much weaker than to an oxide surface, then it can be assumed that $k_1 \gg k_2$ or $k_2 \approx 0$, whence $n = 1.95 \pm 0.65$. A Fe^{3+}_{CL}:Fe^{2+}_{CL} ratio of ~2 is not unreasonable for illite, because the degree of substitution of a divalent cation into an octahedrally coordinated (Al^{3+}, Fe^{3+}) layer is likely to be limited (Deer *et al.* 1962). The plot in Figure 4 would then reduce to

$$[NAIP] \approx 0.18\,[Fe^{3+}_{OX}], \qquad (5)$$

i.e., ferric iron (in hydrated oxide) binds 18% of its weight of NAIP.

Calculated concentrations of Fe^{3+}_{OX}, based on equation (5) and measured values of NAIP, indicate that

TABLE 1. CONCENTRATIONS OF Fe, NAIP, Pb AND Org C, AND SOME RATIOS AGAINST STATION NUMBER IN TRENT RIVER PARTICULATES

Station (1990)	Fe^{2+}_{CL}	Fe^{3+}_{T}	NAIP	Pb	Org C	Mg	Al	Fe^{3+}_{T}:Fe^{2+}_{CL}	NAIP:Fe^{2+}_{CL}	Pb:Fe^{2+}_{CL}	Org C:Fe^{2+}_{CL}
	weight percent										
1 Apr	0.53	1.67	0.094	0.0073	17.0	0.60	2.47	3.16	0.18	0.0138	32.1
1A Apr	0.53	1.67	0.119	0.0053	16.0	0.60	2.59	3.16	0.22	0.0100	30.2
1 May	0.71	2.04	0.087	0.0148	16.5	1.50	4.29	2.87	0.12	0.0208	23.2
2 May	0.60	1.58	0.083	0.0067	15.8	1.00	3.40	2.62	0.14	0.0111	26.2
3 May	0.62	1.64	0.083	0.0126	16.3	1.70	3.38	2.63	0.13	0.0203	26.2
4 May	0.56	1.58	0.053	0.0177	17.8	1.20	3.28	2.82	0.095	0.0316	31.8
5 May	0.54	1.69	0.051	0.0039	16.6	1.60	3.30	3.11	0.093	0.0072	30.6
6 May	0.41	1.40	0.056	0.0094	19.7	1.30	2.70	3.41	0.14	0.0229	48.0
6A May	0.44	1.35	0.132	0.0102	20.2	1.40	2.72	3.07	0.30	0.0232	45.9
6B May	0.30	1.18	0.060	0.0067	21.8	1.20	2.18	3.93	0.20	0.0223	72.7
7 May	0.31	1.14	0.136	0.0076	22.8	1.00	2.40	3.68	0.44	0.0245	73.5
8 May	0.27	1.04	0.113	0.0079	24.3	1.10	2.18	3.85	0.42	0.0298	90.0
8A May	0.34	1.20	0.097	0.0072	22.8	1.20	2.60	3.53	0.29	0.0212	67.1
9 May	0.27	1.01	0.130	0.0061	25.5	0.80	2.10	3.74	0.48	0.0226	94.4
10 May	0.34	1.09	0.070	0.0053	25.9	1.50	2.38	3.21	0.21	0.0156	76.2
11 May	0.66	1.78	0.141	0.0077	16.9	1.60	3.78	2.70	0.21	0.0117	25.6
11A May	0.74	2.02	0.058	0.0106	15.3	2.00	4.30	2.73	0.078	0.0143	20.7
12 May	0.65	1.76	0.107	0.0059	18.3	1.80	3.26	2.71	0.16	0.0091	28.2
13 May	0.24	1.00	0.110	0.0039	23.0	0.90	1.80	4.10	0.45	0.0160	94.7
13A May	0.22	1.16	0.130	0.0106	25.4	0.90	1.62	5.27	0.59	0.0482	115.5
14 May	0.19	0.94	0.105	0.0080	24.3	0.90	1.38	5.01	0.56	0.0426	129.3
15 May	0.52	1.55	0.102	0.0086	24.7	1.50	3.12	2.98	0.20	0.0165	47.5
1 Oct	0.49	1.32	0.080	0.0054	18.0	1.10	3.00	2.73	0.16	0.0111	36.7
1A Oct	0.69	1.43	0.051	0.0112	19.2	1.30	4.10	2.09	0.074	0.0163	27.9

The corresponding data for 1989 samplings, except for Pb and organic C, are presented in Manning & Gracey (1991).
Station 1A, not shown in Figure 1, is ~ 600 m upstream of station 1. Concentrations of Mn are in the range 0.2 to 0.6 wt%.

~32% of Fe^{3+}_T is available ferric oxide at station 1 and ~70% at station 9. The dithionite reagent extracts ~50% of the total ferric iron in samples from station 2 and ~60% from station 7; the specificity of extraction is not known, but hydrated oxides are clearly important forms of iron in the particulate matter. The 4 K Mössbauer determinations show that magnetic oxides account for ~40% of the particulate iron at station 1, and ~50% at station 9. Note that assigning significant values to k_2 leads to larger values of n, lower calculated values of available ferric oxide, and poorer agreement with the dithionite and 4 K Mössbauer determinations of oxides. The consistency in the concentrations of hydrated ferric oxides measured by the different methods suggests that the premises underlying equations 1 to 5 are reasonable and valid. These equations represent a geochemical basis for determining the bioavailability of riverine phosphorus: contaminants adsorbed on the surfaces of small (10 to 50 mm) particles of superparamagnetic oxide (Murad 1988) are probably released on reduction of the oxide in the reducing sediments underlying eutrophic lakes.

Relationships between iron and organic carbon

Concentrations of the pairs of elements organic carbon – Fe^{2+} and organic carbon – Fe^{3+} are strongly and negatively correlated (Fig. 5) for particulate matter collected in 1990. However, the concentration ratios carbon:Fe^{2+} and Fe^{3+}:Fe^{2+} are strongly and positively correlated (Fig. 5), the linear regression yielding [org C] = 39 ± 4 [Fe^{3+}_T] – 76 ± 12 [Fe^{2+}_{CL}]. Equation (4) is readily adapted to organic carbon – iron interaction, whence $k_{1C} = 39$, $nk_{1C} - k_{2C} = 76$, and $n = 1.95 \pm 0.50$, in good agreement with the value of n derived from iron-phosphorus relationships. The value of n defines the amount of unavailable (clay-bound) ferric iron.

Organic carbon probably binds to ferric iron *via* carboxyl or salicylate groups of organic molecules: the structures of humic and fulvic acids contain numerous such groupings (Bunzl 1974, Livens 1991, Stevenson 1982). The large value of k_{1C} (= 39) reflects the high average molecular weight (4000) of large organic molecules, values not inconsistent with the binding of a humic or fulvic acid molecule. However, humic and

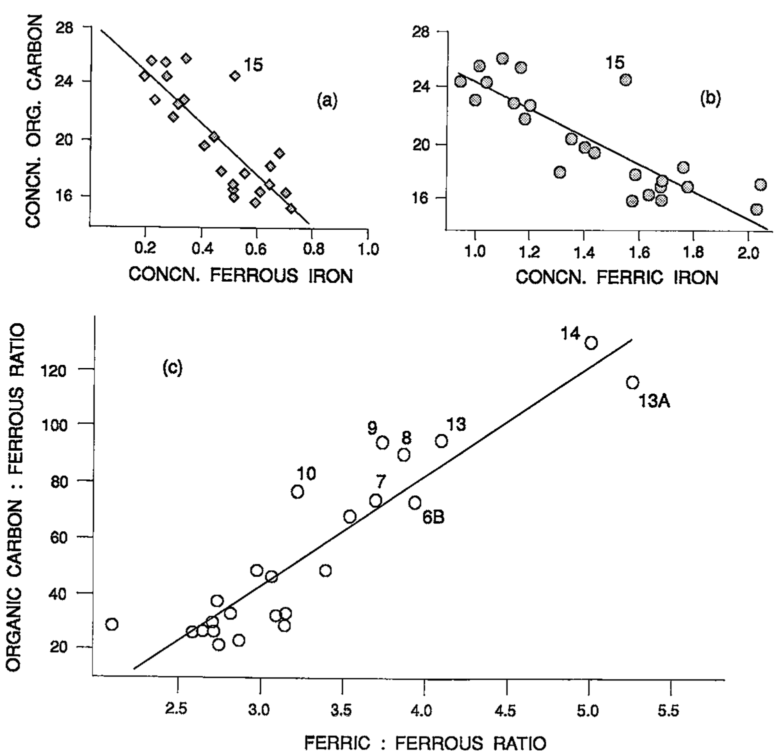

FIG. 5. Plots describing relationships between concentrations of (a) organic carbon and Fe^{2+}_{CL}, for which $r = -0.84$, (b) organic carbon and Fe^{3+}_{T}, $r = -0.85$, and (c) organic carbon:Fe^{2+}_{CL}, and Fe^{3+}_{T}:Fe^{2+}_{CL}, $r = 0.92$, 24 points. The slope of the line is 39 ± 4 and corresponds to [organic C] ≈39 [Fe^{3+}_{OX}].

fulvic acids cannot account for all of the particulate carbon; algae and their decaying remnants contribute significantly. Anions such as phosphate and fulvate are unlikely to bind strongly to each other at pH values of 7–8, but such anions will bind through a central bridging cation (Ramamoorthy & Manning 1974).

Although ferric oxides and organic matter interact strongly in aquatic systems, the significance of the correlation reported here, in terms of the chemical bonding, is not obvious. Whereas iron oxides control the transport and availability of the phosphate ion, it may be that organic matter controls ferric oxide. The correlation between ferric iron and organic carbon could be a consequence of a similar origin. However, the growth and decay of algae within the river make this unlikely. The chemistry underlying the reaction between ferric oxide and organic matter requires further study.

Relationships between iron and lead

Concentrations of lead are significantly lower than those in the surface sediments of the Great Lakes (Kemp & Thomas 1976). Concentrations of the pairs of elements Pb–Fe^{2+} and Pb–Fe^{3+} are weakly correlated, in marked contrast to the good correlation between the concentration ratios Pb:Fe^{2+} and Fe^{3+}:Fe^{2+} (Fig. 6). Linear regression analysis of the ratio plot yields a slope (= k_{1Pb}) of 0.010 ± 0.002 and an intercept ($-nk_{1Pb} + k_{2Pb}$) of −0.0132 ± 0.0063, from which n = 1.3 ± 0.9, in fair agreement with the value of n derived from the data on NAIP and organic carbon. The negatively valued intercepts and the calculated values of n, within experimental error, point to the same binding agent for NAIP, organic carbon and lead, namely hydrated ferric oxides.

Cluster analysis

Generally, cluster analysis confirms the associations of elements determined by linear regression analysis (Fig. 7). Particular attention is drawn to the close association or grouping of the ratios NAIP:Fe^{2+}, Fe^{3+}:Fe^{2+} and Org C:Fe^{2+}, and the poor grouping of NAIP with any significant metal.

General discussion

Nonapatite inorganic phosphorus is transported in the Trent River mainly in the form of a NAIP–Fe^{3+}-

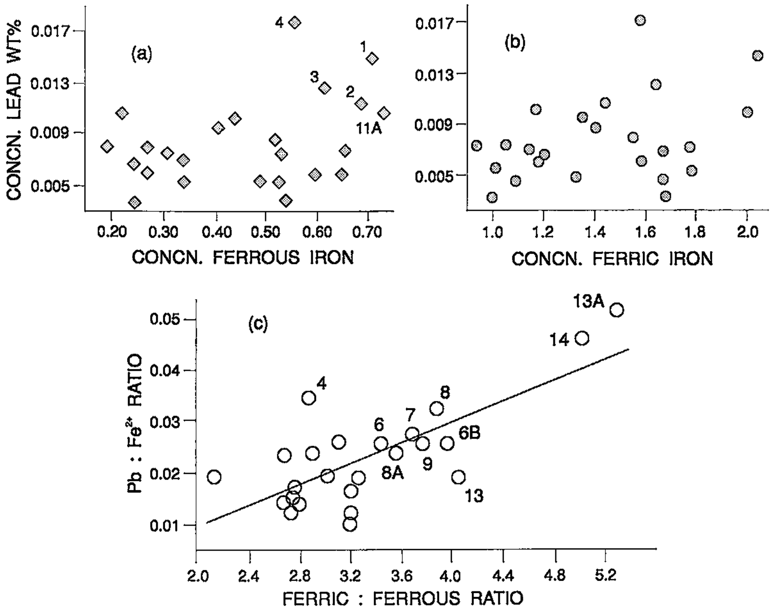

FIG. 6. Plots describing relationships between concentrations of (a) lead and Fe^{2+}_{CL}, for which $r = 0.36$, (b) Pb and Fe^{3+}_{T}, $r = 0.36$, and (c) Pb:Fe^{2+}_{CL} and Fe^{3+}_{T}:Fe^{2+}_{CL}, $r = 0.75$, 24 points. Straight line corresponds to [Pb] ≈ 0.010 [Fe^{3+}_{OX}].

carboxylate mixed-ligand assemblage of approximate composition $(NAIP)_{0.18}Fe^{3+}_{OX}$ (organic $C)_{39}Pb_{0.01}$ by weight, and $(NAIP)_{0.32}Fe^{3+}_{OX}$ (organic $C)_{182}Pb_{0.003}$ in atomic proportion, in which the organic C is partly in the form of a large molecule such as humate or fulvate. Other heavy-metal ions, besides lead, also are adsorbed onto the assemblage. The flocculation of non-silicate iron, humate and phosphate ion has been described by Price & Calvert (1973). The assemblage is probably loosely associated with the surfaces of clay minerals (Buffle & Altman 1987).

Mixed-ligand inner-sphere complexes of the type orthophosphate – M^{n+} – carboxylate (*e.g.*, fulvate) are of enhanced stability in solution (Ramamoorthy & Manning 1974). Although statistically significant correlations do not confirm direct (inner sphere) bonding between ferric iron and fulvate or phosphate ion, it is nevertheless likely, in the solid state also, that the anions function as multidentate ligands and displace hydroxyl ions from the central ferric ion, and that the binding of NAIP promotes the binding of the large humate and fulvate ions (Ramamoorthy & Manning 1974). In the same sense, it is then likely that, if significant inner-sphere bonding did occur between ferric oxide and clay, the binding of phosphate to a central ferric ion would promote the additional binding of oxide–ion-based clay surfaces. The formation of a mixed-ligand complex would argue against a competitive process between the phosphate ion and clay minerals for ferric oxide sites.

The degree of binding between ferric oxide and clay mineral is of importance because the availability of riverine particulate NAIP within the Bay of Quinte is related to the efficiency of sedimentation of the ferric-iron-centered compound. The physical sorting of oxide and clay may be an important process in the turbulent waters of Upper Bay. Strongly reducing clay–silt sediments are deposited over much of the bottom of Upper Bay (Damiani & Thomas 1974). The lower redox potentials of Bay sediments, relative to those of a river environment, provide the necessary conditions under which riverine particulate NAIP is rendered available in the Bay of Quinte. NAIP adsorbed on Fe^{3+}_{OX}, passing through Upper Bay in suspension in well-oxygenated water, is probably weakly available.

The weak interaction between ferric oxides and clay surfaces in river particulate matter, in the presence of abundant phosphate and fulvate or humate ions, may be consistent with the presence of ferromanganese nodules and coated sands in nearshore areas of the Bay of Quinte (Damiani *et al.* 1973) and Lake Ontario near-shore (Cronan & Thomas 1972). These high-energy nearshore areas are marked by low rates of deposition of organic matter on exposed beds of glaciolacustrine clays and sands, conditions that are more favorable to the binding of hydrated ferric oxides to a silicate surface. Soils and sediments are significant reservoirs of inorganic phosphate and organic matter.

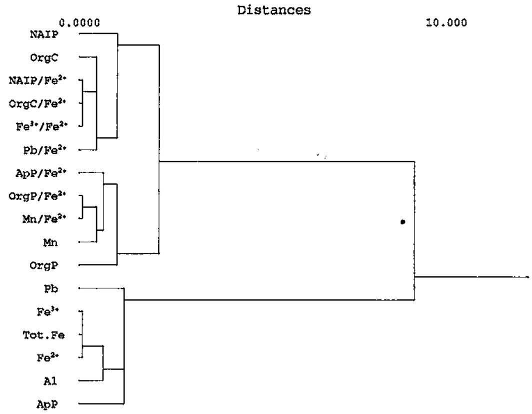

FIG. 7. Illustration of the major groupings of elements in Trent River particulate matter (1990 data) based on a minimum of variance method. Similar groupings are generated for 1989 to 1990 data, except that the 1989 samples were not analyzed for lead. Distance is a measure of the degree of association.

The magnitude of the riverine inputs of potentially available NAIP is readily described, particularly in the spring and early summer months, when river flows are heavy, when the inputs of the sewage-treatment plants are reduced (inputs from the major centers of Belleville and Trenton are 31 kg day^{-1} P from November to April and 19 kg day^{-1} from May to October), and when algal biomass is increasing. Thus the mean flow of the Trent River in May, averaged over a 25-year period, is 1.7 × 10^7 m^3 day^{-1} (Ontario Ministry of the Environment 1989). The concentration of particulate matter at Trenton (station 1) in May 1990 was ~6 g m^{-3}, yielding a mean particulate input of 1 × 10^5 kg day^{-1} and a mean NAIP input (at 0.087 wt%) of 87 kg day^{-1}. The flow of the Moira River at Belleville (Fig. 1) is approximately one-third that of the Trent (Ontario Ministry of the Environment 1989) and, based on similar concentrations of particulate NAIP (Manning & Gracey 1991), the total river load is then ~115 kg day^{-1} NAIP, greatly in excess of the inputs of the sewage treatment plants (19 kg day^{-1}). In April, when river flows are extremely high, the riverine load is greater than 300 kg day^{-1}; the June load is approximately 45 kg day^{-1}. If made available, these massive amounts of phosphorus would kick-start the summer's algal growth in Upper Bay.

The relationship derived for particulate matter in Lake St. Clair (Manning 1989), [NAIP] = 0.026 [$\mathrm{Fe^{3+}_{T}}$] – 0.011 [$\mathrm{Fe^{2+}_{CL}}$], describes a lower capacity for adsorption for NAIP (2.6 wt%) and a value of n of 0.42 (compare with equations (1) to (4) above): 50–60% of [$\mathrm{Fe^{3+}_{T}}$] is $\mathrm{Fe^{3+}_{OX}}$. The "HCl-extractable" data of Lum & Gammon (1985) yield an adsorption capacity of 20 wt% for phosphorus on iron, in good agreement with the Trent River value (18%). This agreement may be fortuitous; the slopes of the plots provided by Lum & Gammon (1985) are heavily influenced by points for local grossly polluted areas, and the specificity of extraction by HCl is not known. The Trent River and Lake St. Clair – Detroit River drain different watersheds. Bedrock geology in the lower reaches for the Trent is carbonate, whereas that of the Lake St. Clair – Detroit River system is shale.

Lead ions, in particulate matter, are transported in the Trent River on the phosphate – $\mathrm{Fe^{3+}_{OX}}$ – humate or fulvate complex. The $\mathrm{Fe^{3+}_{OX}}$:Pb weight ratio is ~100:1 (Fig. 6), *i.e.*, an adsorption capacity of 1.0 wt%. The mode of binding is not answered, but it may be through specific groups on the humate–fulvate ion (Bunzl 1974, Stevenson 1979). Based on the HCl extraction of particulate matter in the Detroit River (Lum & Gammon 1985), the adsorption capacity of extractable iron for lead is 1.7 wt%. Their plots are strongly influenced by values for particulate matter from channels with heavily industrialized shorelines; a re-analysis of their data suggests that within the main channel of the Detroit River, the adsorption capacity is ~0.5 wt% (Manning 1989).

Sequential wet-chemical fractionation (Tessier *et al.* 1979) confirmed the strong association between iron and Cu, Pb and Zn in stream sediments, but a poor correlation between the metals and organic carbon. Metal ions adsorbed on iron oxides are extracted in their Fraction 3 ($\mathrm{NH_2OH{\cdot}HCl}$ + acetic acid extractant), whereas organically associated metals would be extracted in their Fraction 4. Conceivably, the reduction and dissolution of iron oxides in Fraction 3 could also displace Pb ions from the humate–fulvate ion, either through competitive reaction or through a change in charge distribution within the humate–fulvate molecule.

Although rivers dominate the load of total phosphorus to the Bay of Quinte (Minns *et al.* 1986), their contribution to available phosphorus and to eutrophication has been largely ignored, partly because of a lack of appreciation of a mechanism for phosphorus release. The different redox regimes of a river and the bottom sediments of the Bay provide the necessary conditions, particularly in light of the abundance, in the riverine particulate matter, of hydrated ferric oxides of small particle size and high P-adsorption capacity. The bottom sediments of Upper Bay are strongly reducing (Damiani & Thomas 1974), phosphorus release being promoted by a well-oxygenated and warm (~25°C in summer) water column. Hence, the environmental significance of this work lies in the isolation of the main adsorbing cation ($\mathrm{Fe^{3+}_{OX}}$) and, in general terms, in the quantitative geochemical basis it provides for determining the amount of inorganic phosphorus (and other contaminants) available for release on particulate deposition to anoxic sediments.

The relatively inert behavior of clay, in terms of the adsorption of P and of structural and compositional stability, makes clay (Fe^{2+}) a useful agent for normalizing concentrations of contaminants between riverine particulate matter and bottom sediments. Concentrations of ferric iron and NAIP are strongly associated with the clay-sized fraction of Great Lakes sediments (Williams *et al.* 1976). Iron release from the bottom sediments is the likely source of metal ions for the ferromanganese nodules and coated sands in the nearshore areas of the Bay of Quinte (Damiani *et al.* 1973).

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