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FORM AND AVAILABILITY OF INORGANIC PHOSPHORUS IN SUSPENDED PARTICULATES OF THE TRENT–SEVERN WATERWAY, ONTARIO

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ABSTRACT

Concentrations ([ ]) of nonapatite inorganic phosphorus [NAIP], ferric iron and ferrous iron, measured for suspended particulates collected from 17 of 22 stations in the Trent–Severn Waterway, Ontario, are strongly related by [NAIP] = 0.22 ± 0.02 [Fe^{3+}] - 0.46 ± 0.07 [Fe^{2+}], where Fe^{3+} is present in hydrated oxide and in clay minerals, and Fe^{2+} is in structural positions in clay minerals. The expression indicates that most of the NAIP transported to the eutrophic Bay of Quinte, Lake Ontario, is bonded to ferric iron and is in the form of a phosphate – ferric oxide – clay assemblage. The phosphate ion contained within this assemblage is not readily available for algal growth under oxic conditions. However, much of the NAIP is probably released in soluble reactive form on deposition to the reducing bottom sediments of the eutrophic Bay of Quinte.

Keywords: phosphorus, availability, iron, clay, Trent–Severn Waterway, Bay of Quinte, Lake Ontario.

SOMMAIRE

Nous avons mesuré les concentrations ([ ]) de phosphore inorganique non lié à l'apatite [NAIP], de fer ferrique et de fer ferreux dans les particules en suspension récupérées à 17 des 22 sites d'échantillonnage dans le réseau des rivières Trent et Severn, en Ontario. Ces variables obéissent à la relation [NAIP] = 0.22 ± 0.02 [Fe^{3+}] - 0.46 ± 0.07 [Fe^{2+}]. Le Fe^{3+} se présente sous forme d'oxyde hydraté et d'argiles, tandis que le Fe^{2+} occupe une position structurale dans les argiles. La relation montre que la plus grande partie du NAIP transporté vers la baie de Quinte, qui est eutrophique, dans le lac Ontario, est lié au Fe^{3+} sous forme d'un assemblage phosphate – oxyde ferrique – argile. L'ion phosphate dans cet assemblage n'est pas facilement disponible pour la croissance des algues en milieu oxygéné. Toutefois, la plus grande partie du NAIP est probablement libérée dans une forme soluble et réactive une fois déposée dans le milieu réducteur des sédiments de fond de la baie de Quinte.

(Traduit par la Rédaction)

Mots-clés: phosphore, disponibilité, fer, argile, réseau des rivières Trent et Severn, baie de Quinte, lac Ontario.

INTRODUCTION

Phosphorus is an important and often the limiting nutrient in freshwater systems (Vollenweider 1968, Imboden 1974). The most biologically available form is dissolved inorganic phosphate ion (Sagher *et al.* 1975, Sonzogni *et al.* 1982). The replenishment of this limited pool is mainly dependent on the desorption of phosphate ions from the surface of the hydrated oxides of ferric iron and manganese (Williams *et al.* 1976, 1980, Bortleson & Lee 1974). Phosphate ion adsorbed on these oxides constitutes most of the readily measurable fraction of nonapatite inorganic phosphorus [NAIP] in bottom sediments and suspended particulates (Lucotte & d'Anglejan 1985, Williams *et al.* 1976). The rate of dissolution depends on kinetic and thermodynamic factors (Stumm & Morgan 1981), but is dramatically increased on development of seasonal anoxia (Burns & Ross 1972, Mortimer 1941, Nurnberg 1988). Adsorption capacities are dependent on pH (Lijklema 1980), reflecting competition between OH^- and phosphate ions, and significant seasonal differences in pH occur in productive waters. The improved definition of the forms of phosphorus encompassed by the NAIP fraction is important to an understanding of the processes controlling phosphorus availability and, therefore, eutrophication.

Here, we report on measured correlations between concentrations of ferrous ions, ferric ions, aluminum and phosphorus in suspended particulates collected from several stations in the economically important Trent–Severn Waterway, Ontario (Fig. 1) and, for purposes of comparison, from one station in the Moira River, which drains an adjacent watershed. The Trent River, which represents that portion of the waterway downstream of Rice Lake, is the main source of water entering the highly eutrophic Bay of Quinte, Lake Ontario (Fig. 1). The Trent River is fast-flowing, falling 110 m over a distance of 80 km; it has 18 locks and waterfalls (Canadian Hydrographic Service 1987). Water usage in the Bay, municipal, industrial and recreational, is often

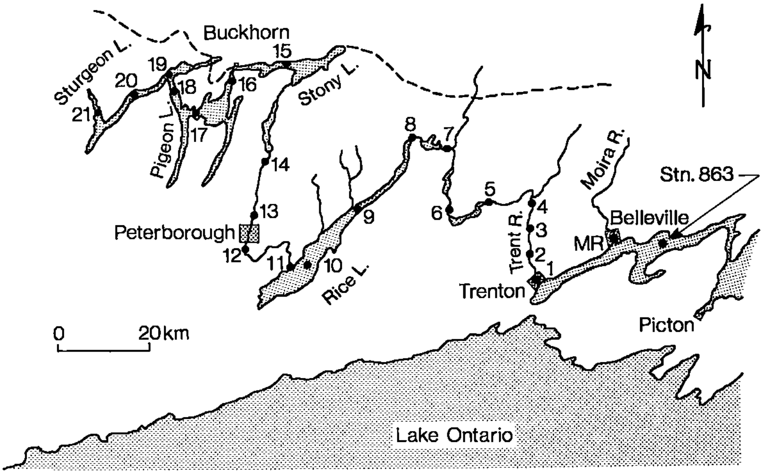

FIG. 1. Diagram showing the 22 sampling stations in the Trent–Severn Waterway, one in the Moira River and the one in the Bay of Quinte, Ontario. Dashed line separates area of igneous bedrock of the Precambrian Shield (north of line) and limestone bedrock. Station 1A is ~ 600 m upstream of station 1.

severely impaired. Earlier correlations between concentrations of ferrous iron, ferric iron and NAIP in the suspended particulates of Lake St. Clair indicate that NAIP ions and clays compete for adsorption sites on hydrated ferric oxides (Manning 1989). Although statistically significant correlation-coefficients do not provide direct evidence of a structurally and compositionally discrete species, they nevertheless provide a useful basis for the estimation of the fraction of inorganic phosphate ion not bonded within a ferric oxide – clay assemblage. The aim of this work is to determine the main inorganic forms of iron and phosphorus in the Trent River input to the Bay of Quinte.

The upper reaches of the Trent–Severn Waterway border on igneous rocks of the Precambrian Shield, whereas the lower reaches are entirely in a till plain on limestone bedrock. Rivers draining the Shield are well buffered by deposits of Precambrian dolomite. Seasonal differences in pH outweigh the smaller spatial differences (between one station and another), the higher pH values in summer (8.0 to 8.5 against 7 in winter) reflecting CO_2 uptake by algae and warmer summer temperatures (Ontario Ministry of the Environment 1989). The seasonal pH trends are reasonably parallel at all stations. At stations currently under study, pH values in early June show no obvious trend spatially and range from 7.9 to 8.4 (all values ± 0.1 pH units).

EXPERIMENTAL DETAILS

Suspended particulates were collected at 21 stations in the Trent–Severn Waterway on one field trip in May – June 1989 (Fig. 1). Particulates also were collected from station 1 in April and October 1989, from nearby station 1A in October, and from the mouth of the Moira River (Station MR) and one station (number 863) in the Bay of Quinte in April. Approximately 600 L of water were centrifuged (Westphalia continuous flow) to yield ~0.7 g of dried particulates at the upper stations and ~4.5 g at the lower stations (1-3); yields decreased steadily with increasing station number, *i.e.*, on moving upstream. The efficiency of recovery of particulate matter is not known, but it probably exceeds 70%. Bottom sediment cores were retrieved from Rice Lake (4 m depth of water) and from Pigeon Lake (station 18, 6 m). The cores were sectioned immediately into 1-cm slices from 0 to 20 cm, and thereafter into 1-cm slices every 5 cm to 40 cm depth. All samples were frozen immediately and freeze-dried on return to the laboratory. Temperature profiles showed that the water column is unstratified at all stations except 16, at which the particulates were collected from 2 m and 5 m beneath the surface of the water. The other stations were sampled 2 m beneath the surface or at mid-depth in shallower stations. Sampling continued over 10 days (May–June 1989), moving progressively upstream.

Water samples were collected at all stations, preserved in 1M H_2SO_4 and analyzed for concentrations of total phosphorus and total filtered phosphorus (0.45 μm filter) using ammonium molybdate photometry.

Stations were selected so as to include local

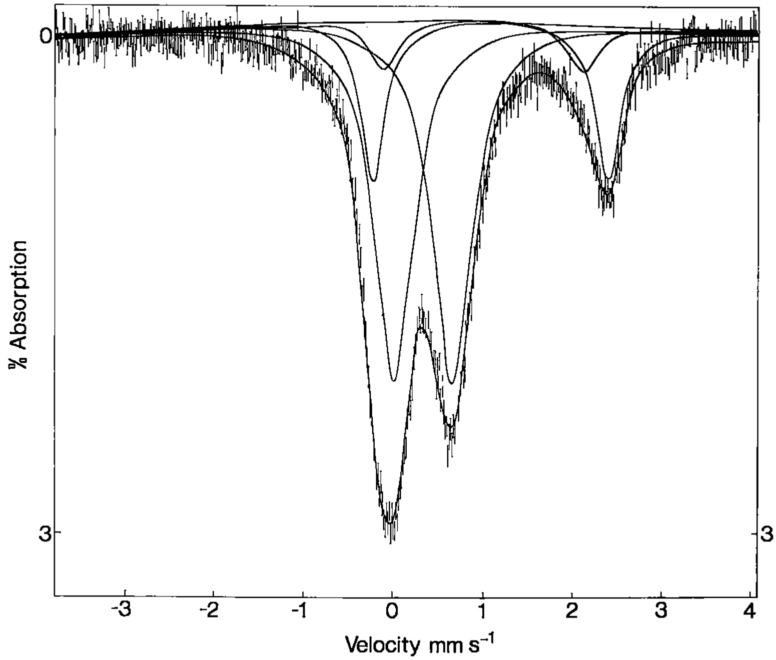

FIG. 2. Representative room-temperature Mössbauer spectrum of Trent–Severn particulates, in this case of particulates collected at station 1, April 1989. Chi-squared is 552 for 493 degrees of freedom.

(point) sources (*e.g.*, the urban centers of Trenton and Peterborough), and also two lake stations (Rice and Pigeon) at which phosphorus release from anoxic bottom sediments is possible. Generally, stations are located in deeper water.

The Mössbauer spectra of the freeze-dried particulates were recorded at room temperature on a 512-channel constant-acceleration spectrometer (Cryophysics Ltd., MS103) calibrated against iron foil. The spectra of particulates from stations 2 and 9 were also recorded at 4.2 K and over a wider velocity scale in order to determine magnetically ordered oxides. The spectra were resolved using the programs of Stone (1967). Values of chi-squared and the visual examination of the computed fits were used as criteria of goodness of fit. Although the presence of two doublets only is obvious from the visual examination of the room-temperature spectra (Fig. 2), the ferrous absorption is clearly asymmetrical. Computation proceeded on the basis of two (one Fe^{3+}, one Fe^{2+}), three (Fe^{3+}, two Fe^{2+}) and four (Fe^{3+}, two Fe^{2+}, FeS_2) doublets. Relative to the two-doublet scheme, the three-doublet scheme yielded an improved visual fit and a lower value of chi-squared. The inclusion of the pyrite doublet, with peak positions and half-widths constrained (Manning *et al.* 1979), produced inconsistent resolutions and, in most computations, pyrite concentrations of less than 3% of total iron, *i.e.*, pyrite is not present in significant amounts. The Mössbauer spectra of the surface (0 to 10 cm depth) sediments of eutrophic Rice Lake and Pigeon Lake showed minor amounts only of FeS_2 (0 to 10% of total iron); at 10 cm sediment depth, FeS_2 concentrations become significant (~20% of total iron), hence wind-driven resuspension of bottom sediment is unlikely to introduce significant amounts of pyrite to the suspended particulates. Optical microscopic examination of the freeze-dried particulates confirmed that pyrite is a very minor phase. Pyrite framboids are considerably more abundant in deeper sections (> 10 cm) of Rice Lake sediments. Hence, the spectra of the particulates are resolved on the basis of three doublets (Fe^{3+}, Fe^{2+}_A and Fe^{2+}_B), and for spectra of the Rice Lake sediments, assuming four doublets (including pyrite). The low concentrations of ferrous iron necessitated the constraining of the half-width (0.34 mm s^{-1}) of the weaker Fe^{2+}_B doublet. All computer resolutions converged successfully. Repetitive analyses are good to ± 2% for Fe^{3+} and ± 5% for Fe^{2+}_{A+B}.

The 4.2 K spectra of samples from stations 2 and 9 display a six-line pattern, characteristic of magnetically ordered ferric oxides (Murad 1988, Murad & Johnston 1987), superimposed on the paramagnetic doublets of ferrous and clay-bound ferric iron. The spectra were found to be difficult to fit; however, the best computed fit indicates a broad magnetic component with H equal to 470–500 KOe, which accounts for 40–60% of the total absorption. The broad spectra suggest that one component becomes magnetic at 4.2 K, but a range of particle sizes exists, giving a broad distribution of hyperfine fields. Hence, hydrated ferric oxides are major components of the iron in Trent River particulates. The specific oxides are not readily identified from these data (Murad & Johnston 1987), although the field gradient is similar to that of ferrihydrite (Murad 1988).

Concentrations of total iron, manganese and aluminum in the dried sediments were measured by alkaline fusion followed by dissolution in concentrated hydrochloric acid and analysis by atomic absorption spectrometry, using suitable standards. Concentrations of Fe^{2+}_{A}, Fe^{2+}_{B} and Fe^{3+} ions were calculated from the total iron values and the area ratios of the doublets from Mössbauer spectrometry. The standard errors in the concentrations Fe^{2+}_{A+B} and Fe^{3+} are ± 11% and ± 7%, respectively; much of this error is reproducible from one sample to another.

Concentrations of NAIP, apatite P and organically bound P were measured by chemical fractionation methods (Williams *et al.* 1976). The dithionite–citrate–bicarbonate reagent extracts most of the poorly crystallized ferric and manganese oxides, with good reproducibility (Lucotte & d'Anglejan 1985). Values of NAIP are good to ±5%.

RESULTS AND DISCUSSION

Mössbauer spectral assignments

All spectra were adequately and consistently resolved using two ferrous iron doublets (Fe^{2+}_{A} and Fe^{2+}_{B}) and a broad intense ferric doublet (Fig. 2). Measured values of isomer shift (IS, relative to iron foil), quadrupole splitting (QS) and half-width (HW) are, respectively: for Fe^{2+}_{A}, 1.12 ± 0.02 mm s^{-1}, 2.63 ± 0.02 mm s^{-1} and 0.33 ± 0.03 mm s^{-1}; for Fe^{2+}_{B}, 1.10 ± 0.05 mm s^{-1}, 2.14 ± 0.07 mm s^{-1} and 0.34 mm s^{-1} (constrained); for Fe^{3+}, 0.35 ± 0.02 mm s^{-1}, 0.68 ± 0.02 mm s^{-1} and 0.52 ± 0.03 mm s^{-1}. The Fe^{2+}_{A}: Fe^{2+}_{B} concentration ratio is ~2.5 : 1.

The three sets of parameters are consistent with the assignment of ferrous ions to two different structural positions in clay minerals and chlorite and of ferric iron to a mixture of hydrated oxides and clay minerals (Coey *et al.* 1974). The dominant clay mineral in the Bay of Quinte is illite (Damiani & Thomas 1974); chlorite was weakly indicated by X-ray-diffraction methods. Aluminum has been considered an inert element in the study of element mobility in sediments (Kemp *et al.* 1976, Kemp & Thomas 1976) on grounds that Al is bonded within the clay structure. The inert behavior of Al is strongly confirmed by the excellent correlation between ferrous ion and Al (r = 0.98, 25 points, Fig. 3a) for all Trent River and Moira River samples. Concentrations of ferric and ferrous ions are less well correlated (r = 0.78, Fig. 3b): a moderate correlation is expected on the grounds that illite and ferric oxide are both products of the weathering of rocks. The Fe^{3+}:Fe^{2+} ratios for stations 17, 19 and 21 are distinct outliers (Fig. 3b) and indicate the presence of a relatively intense source of ferric iron nearby, probably located within the Precambrian Shield. This source of ferric iron manifests itself also in the outlier properties of other measured parameters involving ferric iron and NAIP (Fig. 4, see below).

Forms of phosphorus

Most of the phosphorus at all stations is in particulate matter (Table 1). The soluble fraction probably contains significant amounts of organic P (Stumm & Morgan 1981). NAIP and organic P are the main forms of phosphorus in all particulates (Table 1), with the organic form dominating in most of the upper station samples. As expected for an inert element, the concentration ratio apatite P:Fe^{2+} is reasonably constant (~0.05) for all particulates, except for those with relatively low apatite concentrations (stations 14, 15, 18 and 19, Table 1), for which the experimental error is large.

The concentrations of the element pairs NAIP and total Fe, NAIP and Fe^{3+}, and NAIP and Fe^{2+} are modestly (r = 0.58, 0.57 and 0.46, respectively, 23 points) but inversely correlated, excluding the two outlier points for the April samplings of the Trent River and the Moira River (Figs. 4a, b). The correlations are poorer if the two outlier points are included in the regression analysis (r = -0.14 for the NAIP–Fe_T pair). The high iron and phosphorus concentrations measured for these April samplings reflect heavy erosion during snow-melt runoff. The inverse correlations are in contrast to the strongly positive correlations measured for NAIP and total iron in depositional sediments of the Great Lakes (Williams *et al.* 1976), for HCl-extractable P and Fe in surficial sediments of the Detroit River (Lum & Gammon 1985), and for NAIP and Fe_T in several Wisconsin lakes (Bortleson & Lee 1974). Lake St. Clair particulates yielded a strong negative correlation between NAIP and Fe^{2+} (Manning 1989).

However, the concentration ratios of NAIP:Fe^{2+}

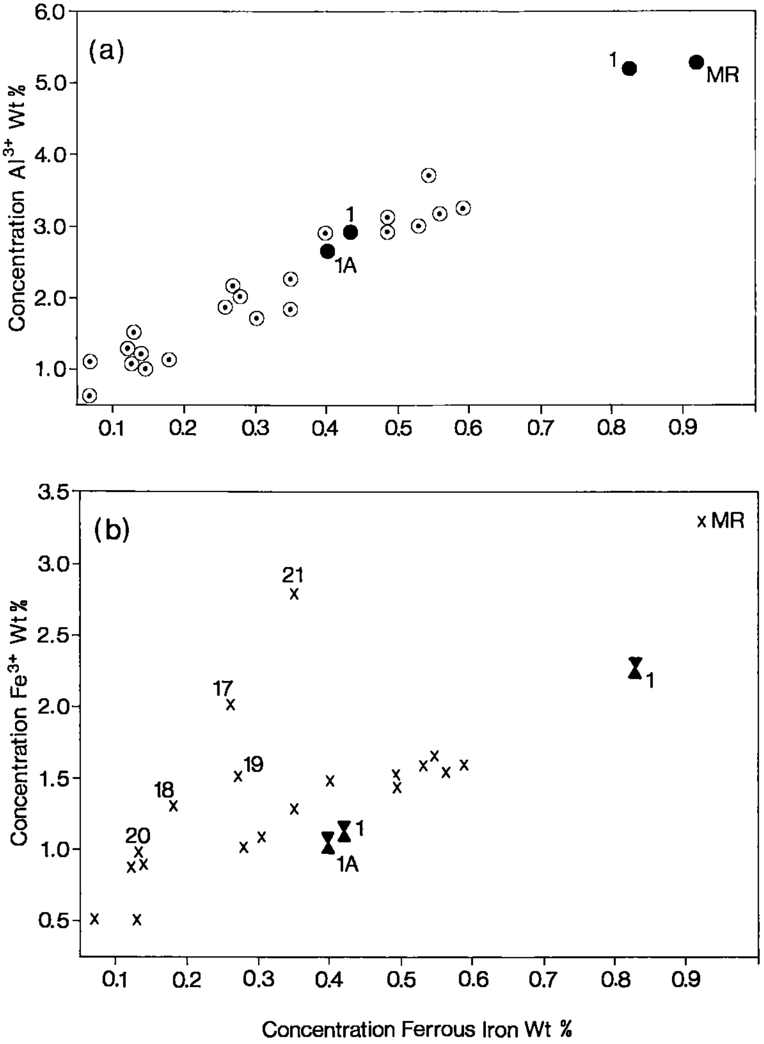

FIG. 3. Plots of concentrations of (a) aluminum and (b) ferric iron against ferrous iron for Trent-Severn particulates. Some station numbers are included in the Fe^{3+}-Fe^{2+} plot. MR represents the Moira River, and filled circles and crosses, the April and October samplings, respectively.

and Fe^{3+}:Fe^{2+} are strongly and positively correlated for 17 of 22 stations in the Trent-Severn system ($r = 0.96$, 19 points). The best straight line yields a slope of 0.22 ± 0.02 and intercept -0.46 ± 0.07 (Fig. 4c); it describes the relationship (*cf.* Manning 1989)

$$[\mathrm{NAIP}] = 0.22\,[\mathrm{Fe}^{3+}] - 0.46\,[\mathrm{Fe}^{2+}] \qquad (1)$$

where brackets represent concentrations. The negative factor for ferrous iron indicates that either clay mineral surfaces compete with NAIP ions for adsorption sites on hydrated iron oxides or that a significant proportion of the ferric iron is unavailable for binding NAIP. In the latter case, the concentration of NAIP-binding ferric oxide is equal to $[\mathrm{Fe}^{3+}{}_{\mathrm{total}}]$ minus $[\mathrm{Fe}^{3+}{}_{\mathrm{clay}}]$, and further the $[\mathrm{Fe}^{3+}{}_{\mathrm{clay}}]$:$[\mathrm{Fe}^{2+}{}_{\mathrm{clay}}]$ ratio can reasonably be assumed to be a constant for a clay in a given watershed. At the pH values of ~8, pertinent to the Trent-Severn system (Ontario Ministry of the Environment 1989), the surfaces of clays are negatively charged, and hydrated ferric oxides are positively charged (Carroll 1958, Lewis 1966, Greenland 1971). Note that equation 1 also covers the data point for the Moira River (Fig. 4c), indicating that

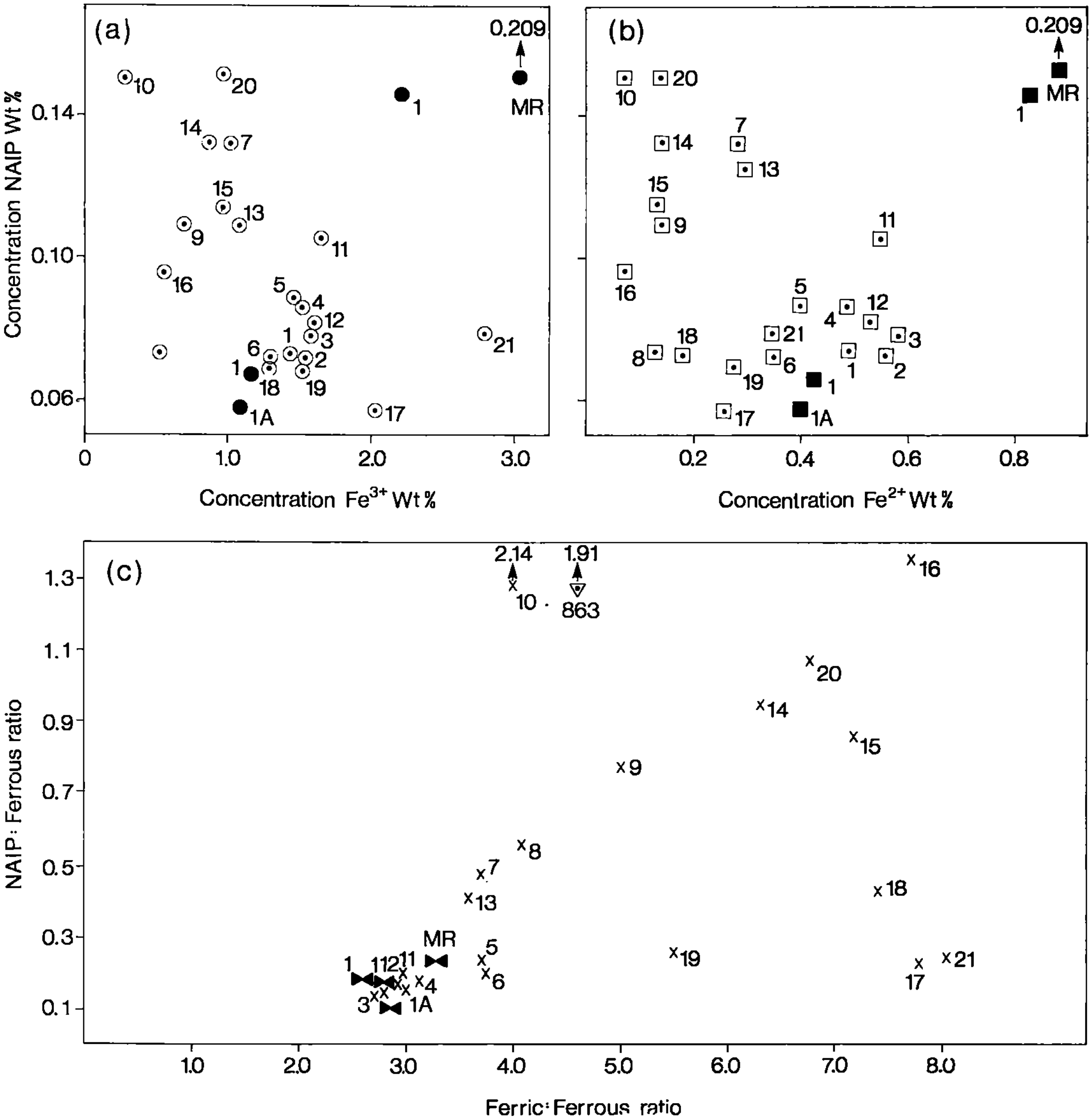

FIG. 4. Plots of concentrations of NAIP against (a) ferric iron and (b) ferrous iron, for which the coefficients of regression are -0.57 and -0.46, respectively (excluding data points for April samplings, which are marked by filled circles and squares; MR is the Moira River). Plot (c) shows the good correlation between the concentration ratios NAIP:Fe^{2+} and Fe^{3+}:Fe^{2+} for 17 of the Trent–Severn stations (19 data points, r = 0.96). Station 10 is in Rice Lake, 863 is in the Bay of Quinte, and stations 17, 18, 19 and 21 are in a small area near the Precambrian Shield and near a source of ferric iron (see text). Filled crosses mark April and October samplings of Trent River stations 1 and 1A and the Moira River station.

similar NAIP–iron complexes present in both rivers.

The points determined for particulates from stations 10, 17, 18, 19 and 21 clearly do not fit the straight line described in Figure 4c. Station 10 is in the middle of Rice Lake; the elevated NAIP:Fe^{2+} ratio probably reflects heavy phosphorus regeneration (as phosphate ion) from the anoxic bottom sediments and precipitation on suspended particulates. Measured values of NAIP:Fe^{2+} (= 0.03) and Fe^{3+}:Fe^{2+} (2.5) for the top cm of bottom sediment indicate significant loss of NAIP on deposition (Table 1, Fig. 4). Rice Lake is highly eutrophic, and the bottom sediments are sufficiently anoxic

TABLE 1. CONCENTRATION OF Fe, Al, Mn, P and C IN TRENT RIVER PARTICULATES

Stn.	Depth m	Fe Tot	Fe^{2+}	Fe^{3+}	Al	Mn	NAIP	Ap P	Org P	Org C	Tot P(U)	Tot P(F)
		weight percent dry sediment									µg L^{-1}	
1 Apr	4	3.09	0.83	2.26	5.15	0.22	0.145	0.041	0.063	12.2	42	12
1	4	1.94	0.49	1.46	3.13	0.32	0.073	0.024	0.098	16.8	30	10
1 Oct	4	1.60	0.43	1.17	2.81	0.24	0.066	0.028	0.130	21.6	30	11
1AOct*	4	1.51	0.40	1.11	2.59	0.23	0.057	0.026	0.134	22.8	29	10
2	4	2.10	0.56	1.54	3.17	0.34	0.072	0.028	0.072	15.6	28	7
3	4	2.18	0.59	1.59	3.26	0.35	0.078	0.026	0.035	16.2	25	7
4	3	2.00	0.49	1.51	2.98	0.40	0.086	0.024	0.111	16.8	27	7
5	5	1.88	0.40	1.48	2.92	0.47	0.086	0.017	0.028	18.0	24	7
6	6	1.64	0.35	1.29	2.28	0.40	0.072	0.020	0.050	18.7	25	7
7	3	1.30	0.28	1.02	2.02	0.29	0.131	0.013	0	19.6	24	7
8	3	0.65	0.13	0.52	1.49	0.22	0.073	0.008	0.151	18.7	23	7
9	5	0.84	0.14	0.70	1.06	0.23	0.109	0.005	0.006	22.9	21	6
10	4	0.35	0.07	0.28	1.11	0.34	0.150	0.006	0	23.0	18	5
11	4	2.18	0.54	1.64	3.71	0.33	0.105	0.030	0.053	13.8	23	6
12	3	2.10	0.53	1.57	3.04	0.39	0.081	0.030	0.121	13.7	20	7
13	2	1.39	0.30	1.09	1.73	0.81	0.125	0.010	0.096	21.4	15	6
14	4	1.02	0.14	0.88	1.19	0.77	0.132	0.006	0.123	23.4	14	5
15	3	1.10	0.13	0.97	1.09	0.98	0.114	0.004	0.161	21.6	12	4
16(2m)	3	0.47	n.d.	n.d	0.78	0.44	0.110	0.004	0.158	28.4	11	4
16(5m)		0.62	0.07	0.55	0.58	0.42	0.096	0.001	0.111	26.6	11	4
17	5	2.28	0.26	2.02	1.89	0.81	0.057	0.014	0.144	20.5	13	4
18	6	1.48	0.18	1.30	1.13	0.31	0.072	0.006	0.181	21.3	9	5
19	3	1.78	0.27	1.51	2.03	0.26	0.069	0.007	0.196	21.0	10	4
20	8	1.10	0.14	0.96	1.29	0.09	0.151	0.009	0.097	20.6	9	5
21	3	3.14	0.35	2.79	1.86	0.63	0.079	0.018	0.149	23.4	12	5
MR Apr	1	4.19	0.92	3.28	5.30	0.63	0.209	0.034	0.085	13.2	45	19
Rice Lake	sd	2.80	0.80	2.00	4.20	0.10	0.026	0.049		14.6		

* Sampled at second bridge ~600 m upstream of station 1. MR represents the Moira River which drains similar terrain. Apr is April, Oct is October, n.d. is not determined due to insufficeint sample. Tot P(U) and Tot P(F) are total phosphorus concentrations in umfiltered and filtered (0.45 micron) water samples, respectively. Samples collected on May/June cruise except for April and October samplings. sd refers to top cm of bottom sediment in Rice Lake (Station 10).

to produce pyrite, FeS_2. Although the City of Peterborough discharges sewage treatment effluent into the Trent River, the points for stations 11 and 12, which are located between Peterborough and Rice Lake (Fig. 1), fit the straight-line plot in Figure 4c. Peterborough makes a negligible contribution to the concentration of non-iron-associated phosphorus a few km downstream. The four remaining outlier points (Fig. 4c) mark stations (17, 18, 19 and 21), located within a narrowly defined area of the waterway, suggesting that the deviations of the points from the straight line are systematic. This area is adjacent to igneous rock of the Precambrian Shield; waterfront cottage development and low agricultural fertilizer usage probably indicate low phosphorus inputs to the water (Government of Ontario 1969).

The experimental points used in calculating the straight lines in Figure 4c are heavily grouped at low values of NAIP:Fe^{2+} and Fe^{3+}:Fe^{2+}. This grouping arises because stations 1 to 6 are located in a geologically uniform area and in a fast-flowing section of the river (the Trent River drops 45 m in a distance of 20 km). Furthermore, station 1 is sampled on three occasions (four, if the nearby station lA is included). Ferric:ferrous ratios change greatly in the upper reaches of the study area, which border on the Precambrian Shield, as a probable consequence of changing soil and rock compositions. Note that the points for stations 11 and 12 coincide with those for stations 1 to 4, whereas the points for stations 7 to 14 are well disposed along the straight line (Fig. 4c).

Forms of aluminum and manganese

The excellent correlation between concentrations of total aluminum and ferrous iron ($r = 0.98$, 25 points) is consistent with most of the aluminum being in structural positions in clay minerals and chlorite (Kemp *et al.* 1976, Kemp & Thomas 1976). However, small amounts of hydrated aluminum oxide, possibly coprecipitated with hydrated ferric oxide, also may bind phosphate ions. Freshly precipitated amorphous aluminum oxide binds phosphate efficiently at pH values 7 to 8 (Lijklema 1980). Concentrations of total aluminum and ferric iron are well correlated ($r = 0.74$, 25 points), but this may be a consequence of the good correlation ($r = 0.78$) between ferrous and ferric iron (see above). Hence the relationships postulated here between Fe^{3+}, Fe^{2+} and NAIP will be followed by those between total aluminum, Fe^{2+} and NAIP. However, 18 of the points, marking widely separated stations and encompassed by Al:Fe^{2+} values between 5.3 and 7.4, and by NAIP:Fe^{2+} values between 0.13 and 0.47 (Table 1), are very poorly correlated ($r = 0.27$, 18 points). It is probable, therefore, that hydrated aluminum oxides play a relatively minor role in the binding of phosphate ion.

Manganese may be present as the 2+ ion in clay minerals or as the 4+ ion in hydrated oxides. Concentrations of total manganese are poorly correlated with both ferrous iron (r = 0.2, 25 points) and with ferric iron (r = 0.21). Manganese concentrations are elevated in particulates collected at stations 13, 14, 15 and 17, suggestive of a source of manganese, possibly in the form of Mn^{4+} hydrated oxide, in this area. If data points for these four stations are excluded from the regression analysis, manganese and ferrous iron remain poorly correlated (r = 0.37, 21 points), whereas Mn and Fe^{3+} are moderately correlated (r = 0.62, 21 points). However, the smaller and more highly charged Mn^{4+} ions are more readily hydrolyzed than are ferric ions (Stumm & Morgan 1981), the increased competition from OH^- reducing the binding capacity for phosphate. The strong correlation between Mn and phosphorus in reducing sediments has been attributed to the association of Mn with iron (Bortleson & Lee 1974). In Lake Ontario sediments, NAIP is strongly concentrated in the brown ferric oxide layer rather than in the black MnO_2 layer (Manning *et al.* 1982). Hence, manganese oxides probably play a minor role in the binding of NAIP.

General discussion

The quantitative relationship defined by equation 1 implies stoichiometry and bonding involving ferric oxides, phosphate ion and clay surfaces. This further indicates that the NAIP fraction in suspended particulates of the Trent–Severn Waterway is mainly in the form of a mixed-anion assemblage of clay - ferric oxide - phosphate, in which phosphate ion is specifically bonded to the central ferric ion, displacing hydroxyl ions (Ryden *et al.* 1977, Stumm & Morgan 1981). The relationship $[NAIP] = 0.22 \pm 0.02\,[Fe^{3+}] - 0.46 \pm 0.07\,[Fe^{2+}]$ has the same form as that derived for Lake St. Clair particulates, *i.e.*, $[NAIP] = 0.027\,[Fe^{3+}] - 0.011\,[Fe^{2+}]$ (Manning 1989). The higher phosphate binding capacity of ferric iron in the Trent–Severn particulates (0.22 against 0.027) may be related to the higher Fe^{3+}:Fe^{2+} ratio (2.6 to 8.1 against ~1). A lessened interaction with clay surface-groups could promote the "polymerization" of the hydrated ferric oxide to form "crystallites" of higher phosphate-binding capacity. Furthermore, the conditions under which the ferric oxide precipitated in the Trent–Severn system may be different from the conditions in Lake St. Clair; freshly precipitated hydrated ferric oxide is particularly efficient in binding phosphate (Lijklema 1980).

How valid, in chemical terms, is the linear plot (of NAIP:Fe^{2+} against Fe^{3+}:Fe^{2+}) in Figure 4c, and how does equation 1 relate to phosphorus bioavailability? The weak negative correlations between concentrations of NAIP and Fe^{2+} and between NAIP and Fe^{3+} argue against a simple dependence of NAIP on iron. The concentrations of NAIP, Fe^{2+} and Fe^{3+} measured for April samplings of Trent River station 1 and the Moira River, when plotted as NAIP against Fe^{3+} and as NAIP against Fe^{2+}, yield distinct outliers (Figs. 4a, b); however, when plotted as NAIP:Fe^{2+} against Fe^{3+}:Fe^{2+}, these same data yield parameters that are consistent with the general trend of the straight line in Figure 4c and with the values of parameters measured for the May and October samplings of stations 1 and 1A. Furthermore, linear regression analysis of data points (NAIP:Fe^{2+} and Fe^{3+}:Fe^{2+}) for stations 7 to 9, 11 to 16 and 20 (10 points, r = 0.95) yields, on extrapolation to Fe^{3+}:Fe^{2+} = 2.80, a NAIP:Fe^{2+} value of 0.20, in reasonable agreement with the measured values (~0.15, Fig. 4c) for stations 1 to 4. The excellent consistency in values of the ratios NAIP:Fe^{2+} and Fe^{3+}:Fe^{2+} for the three samplings of station 1 (four, if 1A is included) indicates that the relative proportions of NAIP, Fe^{2+} and Fe^{3+} in the Trent River particulate input are reasonably constant over the productive summer season in the Bay of Quinte.

The low-temperature spectra indicate that hydrated ferric oxides are a major fraction of the iron input to the Bay. These oxides may act as a cation bridge in binding humic acids and clay particles (Buffle & Altman 1987, Greenland 1971). Competition between negatively charged anions and adsorption sites on iron oxides has been described in many systems, *e.g.*, between humate–sulfate and phosphate on goethite (Hawke *et al.* 1989), arsenate–selenite and phosphate on goethite (Hingston *et al.* 1971), selenite–silicate and phosphate on amorphous hydrated oxide (Balistrieri & Chao 1990), and humate and phosphate on goethite and X-ray-amorphous ferric gel (Tipping 1981). Phosphate, selenite and silicate are considered to form inner-sphere complexes with iron oxides (Balistrieri & Chao 1990), displacing water molecules and binding directly to the central iron. Phosphate probably binds as a bidentate ligand (Parfitt & Russell 1977). Moreover, mixed-ligand complexes of the form phosphate–metal^{n+}–carboxylate are extremely stable in solution (Manning & Ramamoorthy 1972). In these Trent–Severn particulates, therefore, it is possible that phosphate and clay "anions" form stoichiometric inner-sphere mixed-ligand complexes with the central ferric ion. In particulates collected at stations 17, 18, 19 and 21, the low concentrations of NAIP suggest that humate ions assume the available adsorption sites (Fig. 4c); many of the upper lakes are relatively shallow and highly colored with humic compounds.

The dissolution of phosphate, in response to the depletion of the pool of dissolved inorganic phosphate under oxic conditions, requires the breaking of Fe^{3+} - PO_4 bonds in which two atoms of oxygen of a phosphate ion bind to a ferric ion (Parfitt & Russell 1977, Stumm & Morgan 1981). X-ray-diffraction patterns provide no evidence for a discrete ferric phosphate compound (*e.g.*, strengite), and in the absence of such compounds, the NAIP contained within the clay - ferric oxide - phosphate "complex" may be considered as available on a long-term basis only. Lake St. Clair is mesotrophic, and here also concentrations of NAIP may be quantified in terms of equation 1, although with different values of k_1 and k_2 (Manning 1989). Most of this contained NAIP will be released only under conditions of bottom sediment anoxia, *e.g.*, in Rice Lake or the Bay of Quinte.

During the spring snow-melt, the rates of flow of the Trent and Moira rivers and the NAIP concentrations in the suspended particulates are extremely high (Sly 1986; Table 1). The relatively steep gradient of the Trent River, which necessitates the numerous locks and waterfalls along its ~80 km length, ensures that the suspended particulates are not exposed to an anoxic or a severely oxygen-deficient environment. Consequently, in early summer, the top ~1 cm of Bay of Quinte sediment may be considered a mixture of freshly deposited NAIP-enriched river-borne particulates and sediment deposited the previous year. With the rapid increase in water temperatures in early summer, microbial decomposition of organic matter will generate reducing conditions and the reduction and release of iron and NAIP ions. Phosphorus release from the strongly reducing bottom sediments of Rice Lake and reprecipitation on suspended particulates are indicated by the graphical point for station 10 in Figure 4. Moreover, particulate phosphorus in excess of that defined by equation 1 also is measured (Fig. 4c) for station 863 in the Bay of Quinte (Fig. 1). Heavy regeneration of phosphorus from the organic-matter-rich bottom sediments of the Bay of Quinte has been modeled by Minns *et al.* (1986). This excess NAIP is weakly bonded to particulates because the primary binding sites on the iron oxides are already saturated. The river-borne loads of phosphorus may contribute substantially to eutrophication in the Bay of Quinte.

Because clay minerals (illite) and chlorite undergo minor compositional change in the absence of strong sulfide production, Fe^{2+} may be used as an inert element in estimating the loss of phosphate ion from the particulate assemblage on deposition to reducing sediments. The release of ferric iron (as ferrous ion under reducing conditions) and of phosphorus may then be followed by smaller Fe^{3+}:Fe^{2+} and NAIP:Fe^{2+} ratios in the bottom sediments. The strong association between ferric iron and the two oxygen-binding "anions", clay and phosphate, may well explain the ferromanganese coatings on near-shore sands and gravels in eutrophic embayments (Damiani *et al.* 1973, Rossmann & Callender 1968); iron released from the bottom sediments and oxidized in the near-shore zone will bind to an available silicate surface, *e.g.*, glaciolacustrine clays.

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