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IRON, PHOSPHORUS AND LEAD RELATIONSHIPS IN SUSPENDED SEDIMENTS FROM LAKE ST. CLAIR AND THE DETROIT RIVER

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ABSTRACT

The results of ^{57}Fe Mössbauer spectral and phosphorus fractionation studies of suspended sediments retrieved from Lake St. Clair and from the Detroit River have shown that Lake St. Clair sediments have [NAIP] = 0.026 ± 0.003 [Fe^{3+}] – 0.011 ± 0.003 [Fe^{2+}], where NAIP represents nonapatite inorganic phosphorus and [ ] represents concentrations. Suspended sediments on the Canadian side of the Detroit River conform closely to this equation, whereas significant sources of phosphorus on the United States side cause marked elevation in the NAIP and organic P contents of the sediments. Much of this elevated NAIP is probably readily bioavailable. Lead–iron relationships have not been satisfactorily defined. Nevertheless, the Pb contents of suspended sediments on the Canadian side of the Detroit River are similar to those of sediments from Lake St. Clair. Significant sources of lead occur on the U.S. shore.

Keywords: iron, phosphorus, lead, sediments, Lake St. Clair, Detroit River, Ontario, Michigan.

SOMMAIRE

Une analyse des spectres de Mössbauer ^{57}Fe et du fractionnement du phosphore dans les sédiments en suspension prélevés du lac St-Clair et de la rivière Détroit démontre que les sédiments lacustres contiennent une teneur en phosphore inorganique non lié à l'apatite de 0.026 ± 0.003 [Fe^{3+}] – 0.011 ± 0.003 [Fe^{2+}]. Les sédiments en suspension du côté canadien de la rivière Détroit respectent cette relation, tandis que des concentrations élevées de phosphore du côté américain sont à l'origine des teneurs élevées tant en phosphore inorganique non lié à l'apatite qu'en phosphore organique. Une grande partie de cette fraction inorganique serait bio-disponible. Les relations régissant le fer et le plomb n'ont pas encore été définies convenablement. La quantité de plomb dans les sédiments en suspension du côté canadien de la rivière Détroit ressemble à celle des sédiments du lac St-Clair. Il y a une contamination importante en plomb en abord de la rivière du côté américain.

(Traduit par la Rédaction)

Mots-clés: fer, phosphore, plomb, sédiments, lac St-Clair, rivière Détroit, Ontario, Michigan.

INTRODUCTION

The Detroit River is a commercial shipping and recreational waterway connecting Lake St. Clair, its source, and the western basin of Lake Erie (Fig. 1). Excessive phosphorus loadings to Lake Erie in the 1960s and 1970s were considered responsible for the marked deterioration in water quality, as evident from massive algal blooms, the fouling of beaches by matts of decaying algae, and intense anoxia in the hypolimnion of the Central Basin (Burns & Ross 1972). In 1970, the Detroit River was the main source of phosphorus to Lake Erie (Great Lakes Water Quality Board 1981), contributing 26,000 tonnes. As a result of phosphorus control measures instituted in the early 1970s, the Detroit River in 1981 contributed 3,550 tonnes out of a total load of 10,500 tonnes (Great Lakes Water Quality Board 1983, Fraser & Willson 1981). Significant decreases in total phosphorus and chlorophyll concentrations in Lake Erie were measured between 1970 and 1982 (Rathke & Edwards 1985).

Inputs of iron, phosphorus and trace metals to the river are greater on the United States shore than on the Canadian (Lum & Gammon 1985, Thornley & Hamdy 1984, Fallon & Horvath 1983), reflecting the greater density of population and of industry (steel, automobile, and sewage-treatment plants). The Detroit sewage-treatment plant and a steel complex are located on the Rouge River (Fig. 1). The reactions of nonapatite inorganic phosphorus (NAIP) in aquatic systems are mainly controlled by iron and manganese hydrated oxides (Williams *et al.* 1976, Sholkovitz & Copland 1982); these oxides also adsorb and transport trace-metal ions (Gibbs 1973, Balistrieri & Murray 1982). NAIP is the main source of bioavailable phosphorus in sediments (Williams *et al.* 1980, Sagher *et al.* 1975). Lum & Gammon (1985) concluded that concentrations of 1N HCl-extractable iron and phosphorus are well correlated in suspended sediments of the Detroit River, as are also those of iron and lead. They considered that hydrochloric acid extracts most of the ferric oxides and adsorbed ions.

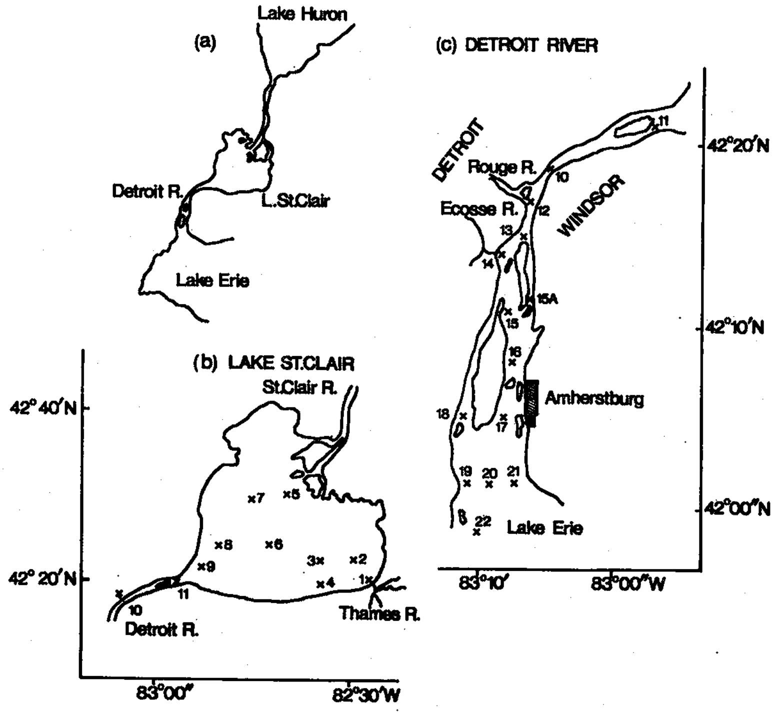

FIG. 1. Diagram showing (a) the Lake St. Clair - Detroit River system, (b) sampling locations in Lake St. Clair and (c) sampling locations in the Detroit River.

In this work, the forms of iron and phosphorus have been determined in suspended sediments retrieved from Lake St. Clair and from the Detroit River. Most of the flow into Lake St. Clair is derived from the relatively weakly polluted waters of Lake Huron (*via* the St. Clair River), hence Lake St. Clair sediments afford a basis on which to better evaluate iron–phosphorus relationships in the Detroit River.

Lake St. Clair is shallow (depth 6 m), and the water is well mixed and well oxygenated. A thin transient layer of recent sediment covers most of the glaciolustrine clay bottom. The Detroit River is fast flowing, and the bottom, for the most part, is well scoured. Sediment accumulation does occur in nearshore areas, but the sand component is usually high (Thornley & Hamdy 1984).

Iron-57 Mössbauer spectrometry and chemical fractionation of phosphorus have been used to (a) define the main forms of iron and phosphorus and the manner of association of their ions in suspended particulates, and (b) determine the importance of industrial iron compounds in the Detroit River relative to the natural background. Iron–lead relationships are also reported on, although in lesser detail.

EXPERIMENTAL DETAILS

Suspended sediments were retrieved from mid-depth at 22 stations in Lake St. Clair and in the Detroit River (Fig. 1) using a Westphalia centrifuge. Six hundred L of water were centrifuged, yielding 2 to 4 g of dry sediment. The sediments were frozen immediately and freeze-dried within two weeks of retrieval. The dry sediments were bottled and stored at 4°C. Mössbauer spectra of the freeze-dried residuals were recorded at room temperature on a 512-channel microprocessor-based spectrometer (Cryophysics Ltd. MS103) calibrated against iron foil. The source was 10 mCi ^{57}Fe in a rhodium matrix. The spectra were computed using Stone's (1967) programs on a Control Data Corporation CYBER 180/830 mainframe computer. Peak positions and half-widths within a quadrupole doublet were constrained to be equal. Two-doublet (one Fe^{2+}, one Fe^{3+}) and three-doublet (two Fe^{2+}, one Fe^{3+}) schemes were invoked. Both gave very similar Fe^{3+}:Fe^{2+} ratios; consequently, the simpler two-doublet computations are considered here. (Chlorite has two layers of octahedrally coordinated ions.)

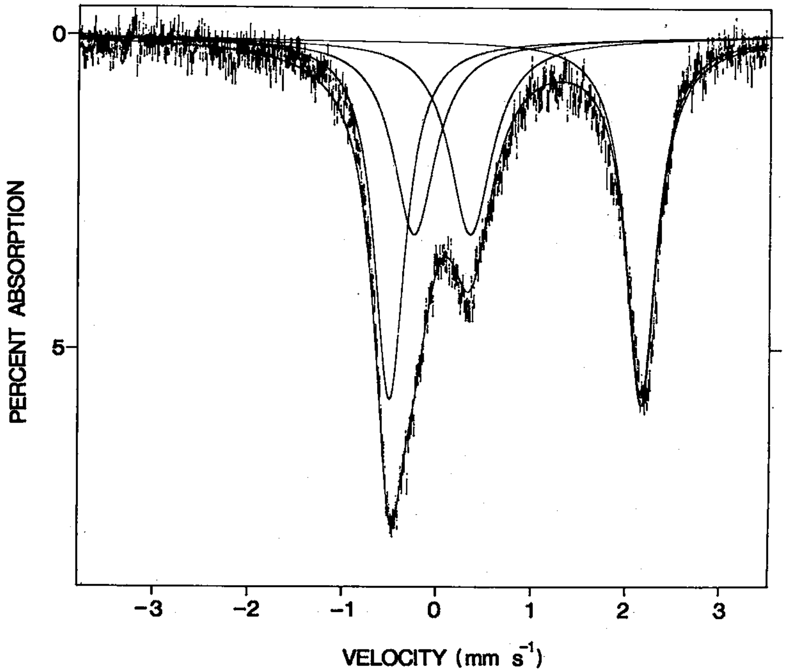

FIG. 2. Representative Mössbauer spectrum of Detroit River and Lake St. Clair suspended particulate. In this case, the sediment is from station 9–86. Chi-squared is 572 with 494 degrees of freedom.

Values of chi-squared and visual examinations of the computer fit were used as criteria for goodness of fit. Ferric:ferrous ratios were estimated to within ± 1% from the ratios of areas beneath the respective doublets. Mössbauer spectrometry, using the ^{57}Fe source, is well suited to the measurement of industrially derived ferric iron, hematite (α-Fe_2O_3) and wüstite in sediments (Manning *et al.* 1980). Some spectra were run at high velocity in order to detect the stronger outer hematite peaks.

Concentrations of NAIP, apatite P and, in some cases, organically bound P were measured following the scheme of Williams *et al.* (1976). The dithionite–citrate–bicarbonate (DCB) reagent extracts readily exchangeable ions and ferric and manganese oxides and their adsorbed ions (Lucotte & d'Anglejan 1985). The method yields reproducible values of NAIP (± 5%). Apatite P is detrital and is inert on the time-scale considered here (Williams *et al.* 1976). Organically bound P is largely unavailable (Williams *et al.* 1980).

Concentrations of total iron in the dry sediments were determined by alkaline fusion using a NaOH flux. The sediment:flux ratio was 1:8. The melted solid cake was dissolved in concentrated HCl and analyzed by atomic absorption spectroscopy using suitable standards. Ferric and ferrous iron concentrations were calculated from the total iron values and the Fe^{3+}:Fe^{2+} areal ratios. The estimated error in Fe^{2+} and Fe^{3+} concentrations is ± 6%.

Concentrations of lead were measured by digestion in a HNO_3–$HClO_4$ mixture and by atomic absorption spectroscopy. Values are good to ± 10%.

RESULTS AND DISCUSSION

Mössbauer spectral assignments

All spectra can be adequately fitted on the assumption of two doublets (Fig. 2). The outer doublet has Mössbauer parameters of isomer shift (IS) = 1.14 ± 0.02 mm s^{-1}, quadrupole splitting (QS) = 2.62 ± 0.03 mm s^{-1} and half-width (HW) = 0.39 ± 0.02 mm s^{-1}. This doublet undoudtedly marks octahedrally bonded Fe^{2+} ions in chlorite and clay structures (Coey *et al.* 1974, Readman *et al.* 1976). Chlorite was detected by X-ray diffractometry. Illite is the principal clay mineral in the Great Lakes (Thomas *et al.* 1972). The broader inner doublet, with IS = 0.38 ± 0.02 mm s^{-1}, QS = 0.61 ± 0.02 mm s^{-1} and HW = 0.55 ± 0.03 mm s^{-1}, marks ferric ions in hydrated

TABLE 1. CONCENTRATIONS OF IRON, PHOSPHORUS AND LEAD IN LAKE ST. CLAIR (STATIONS 1 to 9) AND DETROIT RIVER SUSPENDED SEDIMENTS

Date	Station	Fe_{tot} wt %	Fe^{2+} wt %	Fe^{3+} wt %	NAIP µg g^{-1}	Pb_{tot} µg g^{-1}	$Fe^{3+}:Fe^{2+}$
Oct 85	1	3.80	1.69	2.11	270	50	1.25
Oct 85	2	3.61	1.78	1.83	331	107	1.03
Oct 85	3	3.54	1.68	1.86	319	90	1.11
Sept 86	3-86A	3.19	1.45	1.74	400	nm	1.20
Oct 86	3-86B	3.19	1.38	1.81	377	nm	1.31
Oct 86	3-86C	3.19	1.40	1.79	322	nm	1.27
Oct 85	4	3.69	1.56	2.13	396	74	1.37
Oct 85	5	3.25	1.69	1.56	206	97	0.92
Oct 85	6-85	3.57	1.95	1.62	209	nm	0.83
May 86	6-86	3.00	1.11	1.89	366	65	1.70
Sept 86	6-86A	3.45	1.91	1.54	275	nm	0.81
Oct 86	6-86B	3.45	1.98	1.47	200	nm	0.74
Oct 86	6-86C	3.45	1.93	1.52	227	nm	0.79
Oct 85	7	3.32	1.80	1.52	220	nm	0.84
Oct 85	8	4.07	2.24	1.83	97	114	0.82
Oct 85	9-85	3.92	2.24	1.68	173	72	0.75
May 86	9-86	3.04	1.59	1.45	233	133	0.91
May 86	10A	3.02	1.47	1.55	219	97	1.05
Oct 85	10B-85	4.05	1.77	2.28	365	101	1.29
May 86	10B-86	3.66	1.66	2.00	164	63	1.20
May 86	11	3.56	1.59	1.97	204	66	1.24
May 86	12	3.84	1.59	2.25	735	176	1.42
May 86	13	3.28	1.54	1.74	224	85	1.13
May 86	14	3.48	1.56	1.92	930	119	1.23
May 86	15	3.00	1.56	1.44	309	85	0.92
May 86	15A	3.34	1.55	1.79	207	80	1.15
May 86	16	2.84	1.50	1.34	280	85	0.89
May 86	17	3.02	1.58	1.44	288	94	0.91
May 86	18	3.76	1.58	2.18	1370	166	1.38
May 86	19	3.36	1.63	1.73	1250	159	1.06
May 86	20	2.94	1.58	1.36	234	125	0.86
May 86	21	3.36	1.33	2.03	352	87	1.53
May 86	22	3.60	1.70	1.90	780	176	1.12

Concentrations of apatite P are 270 ± 50 µg g^{-1}. Concentrations of organic P are ~500 µg g^{-1} except for stations 13 (1100 µg g^{-1}), 15 (1160 µg g^{-1}) and 18 (2750 µg g^{-1}) on the lower U.S. side of the Detroit River. Concentrations of total filtered phosphorus are 3 to 6 µg L^{-1} except for stations 12, 18 and 19 (9 to 11 µg L^{-1}).

oxides and in clay structures (Coey *et al.* 1974, Readman *et al.* 1976). The diagenesis of chlorite and clays is unlikely to be significant in suspended and surficial bottom sediments, which has justified past uses of aluminum and ferrous ions as conservative elements (Kemp *et al.* 1976, Kemp & Thomas 1976, Manning *et al.* 1984). The wide range in values of the $Fe^{3+}:Fe^{2+}$ ratio (Table 1) reflects the different sources of particulates, namely resuspension within Lake St. Clair, inputs from the Thames and St. Clair Rivers, inputs from marshlands (northeastern Lake St. Clair), and industrial inputs, *e.g.*, Rouge River (Fig. 1). Ferric ions, hematite (α-Fe_2O_3) and wüstite ($Fe_{1-x}O$) are significant contaminants in the sediments of Hamilton Harbour, Ontario (Manning *et al.* 1980). The recording of spectra of sediment from stations 12 (mouth of the Rouge River) and 18, at high velocity, revealed weak outer peaks of hematite (at -8.0, -4.3, +5.2 and +8.5 mm s^{-1}); computation showed that 5 to 10% of the total Fe (~0.25 wt. % Fe^{3+}) is in hematite. The spectra of sediments from stations 6 (Lake St. Clair) and 15A (mid-channel Detroit River) show barely discernible hematite peaks, accounting for ~3% of total iron. The amount of steel-mill-derived hematite is, therefore, insignificant relative to the iron background, bearing in mind that most of the flow in the Detroit River is through the central shipping lanes. Crystalline hematite is probably not an efficient adsorber of phosphate and lead ions. No wüstite was detected, reflecting its low concentration (< 5% by weight) and the associated difficulty of resolving its doublet within the strong central absorptions (Manning *et al.* 1980). The slightly elevated values of the ferric:ferrous ratio at stations 12, 14, 18, and 22 on the U.S. side of the river (Table 1) suggest that industrially produced ferric iron accounts for ~10% of total Fe^{3+} at those stations.

For Lake St. Clair stations, concentrations of NAIP show a strong inverse correlation with Fe^{2+} iron ($r = -0.82$), but only a fair correlation with Fe^{3+} iron ($r = 0.50$) (Figs. 3a,b). The strongest correlation is between the concentration ratios NAIP:Fe^{2+} and $Fe^{3+}:Fe^{2+}$ (Fig. 4). The significance of this latter correlation is understood in terms of

$$[\mathrm{NAIP}] = k_1 [\mathrm{Fe}^{3+}] + k_2 [\mathrm{Fe}^{2+}] \qquad (1)$$

$$\text{or} \quad \frac{[\mathrm{NAIP}]}{[\mathrm{Fe}^{2+}]} = k_1 \frac{[\mathrm{Fe}^{3+}]}{[\mathrm{Fe}^{2+}]} + k_2 \qquad (2)$$

where [ ] represents concentrations, and k_1 and k_2 are constants. The plot of [NAIP]/[Fe^{2+}] against [Fe^{3+}]/[Fe^{2+}] yields k_1 (slope) = 0.026 ± 0.003 and k_2 (intercept) = -0.011 ± 0.003; the regression coefficient is a strong 0.91 (Fig. 4). If Detroit River stations are included, with the exception of the five outlier points (Fig. 4), the fit is not so good ($r = 0.77$), which probably reflects small inputs of iron and phosphorus along the river.

Concentrations of NAIP and Fe^{3+} iron are significantly higher in suspended sediments of the eastern side of Lake St. Clair than of the central and southern regions (Table 1, Fig. 1). Sediments of the eastern side may reflect the particulate load of the Thames River, whereas sediments of the rest of the lake are influenced more by the St. Clair River and by the weedy northwestern region. The sediment retrieved at station 6-86 (Table 1) may indicate a strong westerly advance of the Thames River sediment plume under the influence of wind and current. If the point for 6-86 is considered to be part of the normal variation in St. Clair River input, then the analysis, based on equation 2, is valid; if not, the points in the NAIP/Fe^{2+} against Fe^{3+}/Fe^{2+} plot comprise two populations that may not be related by one geochemical relationship. Linear regression analysis of points corresponding to stations 1 to 4 and 6-86 (Fig. 4, Table 1) yields values for the intercept (at $Fe^{3+}/Fe^{2+} = 0$) of -40 ™ 10^{-4} and for the slope of 220 × 10^{-4}; this line, on extrapolation, is straddled by points for the other stations in Lake St. Clair (remaining points in Fig. 4). The regression coefficient ($r = 0.77$) is significant at better than the 5% level of significance. Moreover, Mössbauer and

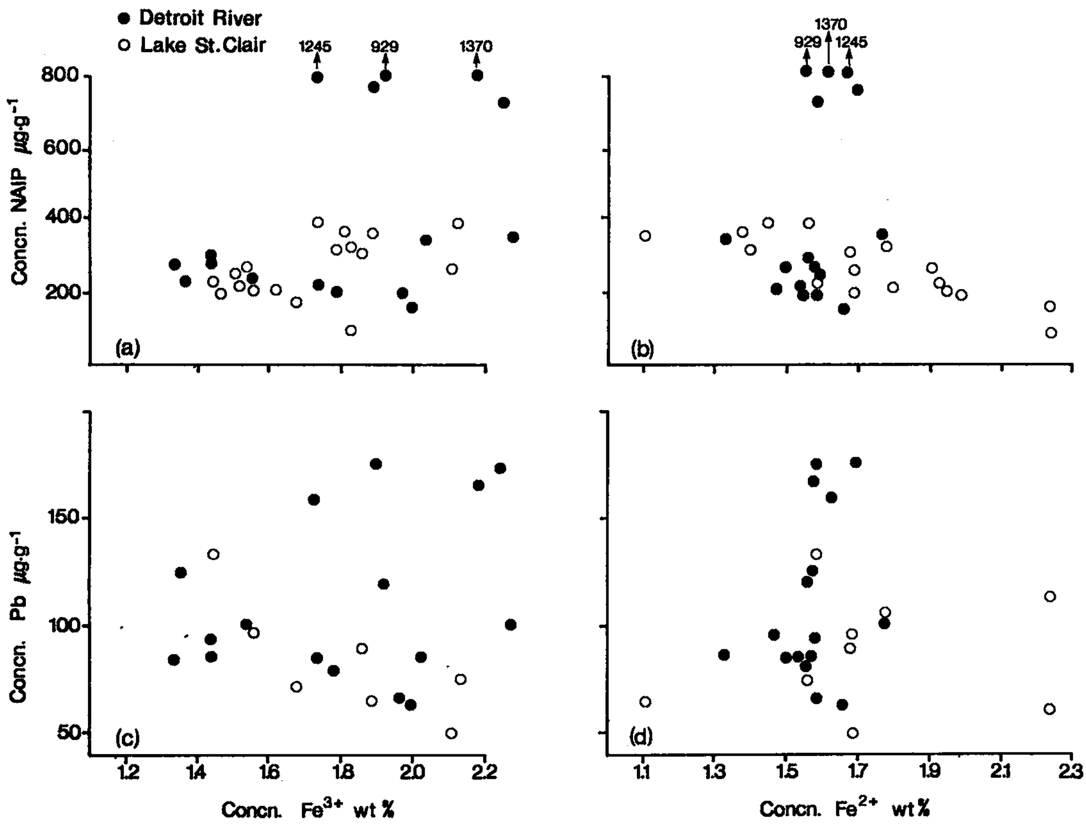

FIG. 3. Concentrations of NAIP as functions of (a) Fe^{3+} and (b) Fe^{2+} and of Pb as functions of (c) Fe^{3+} and (d) Fe^{2+}. Linear regression coefficients for Lake St. Clair sediments (open circles) are: NAIP–Fe^{3+} 0.50 (17 points), NAIP–Fe^{2+} −0.82, Pb–Fe^{3+} −0.69, and Pb–Fe^{2+} 0.24. If Detroit River data (filled circles) are included (excepting the 4 and 5 outlier points marking stations 12, 14, 18, 19 and 22), the regression coefficients are: NAIP–Fe^{3+} 0.33 (28 points), NAIP–Fe^{2+} −0.62, Pb–Fe^{3+} −0.41, and Pb–Fe^{2+} 0.15.

phosphorus analyses for suspended sediment retrieved from the Humber River, Lake Ontario, yield values for Fe^{3+}/Fe^{2+} of 1.44 and for NAIP/Fe^{2+} of 350×10^{-4}, which plot in good agreement with the regression line.

The sewage treatment plants of London, Stratford and Chatham introduce ~80 tonnes of phosphorus annually to the Thames River (Kalinauskas & Gruchalla 1984), which is small compared to the total phosphorus load carried by the river (~800 tonnes annually). The St. Clair River has a larger flow-rate and a lower population on its shore than the Thames, hence most of the phosphorus is derived naturally from Lake Huron and from soil erosion. Phosphorus applied agriculturally equilibrates rapidly with soil iron oxides before being washed into rivers. Consequently the application of equation 2 to cover all Lake St. Clair sediments (Table 1, Fig. 4) seems reasonable geochemically.

Lead-iron interactions

The total lead concentrations of the Detroit River sediment (Table 1) are in reasonable agreement with those of Lum & Gammon (1985), excluding their stations within the Rouge River. For Lake St. Clair, concentrations of Pb are poorly correlated with Fe^{2+} ($r = 0.24$, Fig. 3d) and are negatively correlated with Fe^{3+} ions ($r = -0.69$, Fig. 3c). For nine points, $r = 0.63$ at the 5% level of significance. If Detroit River sediments are included (with the exception of outlier points marking stations 12, 18, 19, and 22, Table 1), the correlations are poorer (Figs. 3c, 3d). The nega-

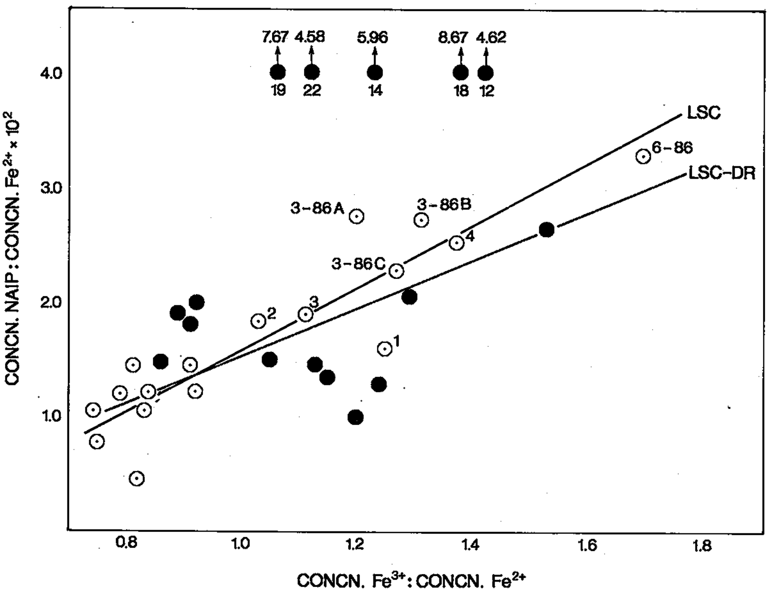

FIG. 4. A plot of the concentration ratios NAIP/Fe^{2+} against Fe^{3+}/Fe^{2+} for Lake St. Clair (open circles) and Detroit River (filled circles) stations. The numbered stations 1–6 are on the eastern side of Lake St. Clair and 12, 14, 18, 19 and 22 are on the U.S. side of the Detroit River (Fig. 1). Regression coefficients are 0.91 for all Lake St. Clair stations (17 points) and 0.77 if Detroit River stations are included (28 points, excepting the five outlier points).

tive correlation between Pb and Fe^{3+} is difficult to interpret geochemically. However, the concentration ratios Pb/Fe^{2+} and Fe^{3+}/Fe^{2+} are very poorly correlated for Lake St. Clair (r = –0.01) and for Lake St. Clair plus Detroit River sediment (r = –0.06).

GENERAL DISCUSSION

Apart from the stretch of water on the United States side from the Rouge River to Lake Erie, concentrations of lead, NAIP and organic P in the Detroit River are not greatly different from those in Lake St. Clair (Figs. 3, 4, Table 1). The iron-phosphorus relationships (Figs. 3a, 4) further confirm that the sources of phosphorus on the Canadian side of the River do not cause a marked deviation from equation 2, *i.e.*, from the "natural" Lake St. Clair background. Sediments retrieved from the U.S. side between the Rouge River and Lake Erie show considerably higher concentrations of NAIP (and organic P), which are not matched by corresponding increased concentrations of ferric iron (Table 1). Small but measurable amounts of industrial iron are released to the Detroit River; the hematite plays a very minor role in the binding of phosphate ion, whereas the ferric iron, introduced mainly as amorphous hydrated ferric oxide, is probably beneficial in adsorbing phosphate. The Fe^{3+}– NAIP relationship described by equation 1 would reflect strong chemisorption in which phosphate ions displace surface hydroxyl groups of ferric ion (Ryden *et al.* 1977). The NAIP ions introduced to the Detroit River on the lower U.S. side are weakly, more physically and nonspecifically bonded to a modified ferric hydroxide surface already loaded with phosphate (Ryden *et al.* 1977).

The most readily available form of phosphate is soluble orthophosphate ion (Sonzogni *et al.* 1982). Concentrations of total filtered phosphorus at stations 6, 10, 20 and 21 (Fig. 1) were ~4.5 μg L^{-1} which compare with ~3 μg L^{-1} carried on suspended particulates. At stations 12, 18 and 19, concentrations of total filtered phosphorus were ~10 μg L^{-1}, consistent with the elevated inputs of NAIP and organic P on the lower U.S. side of the Detroit River. The waters of Lake St. Clair and the Detroit River are well oxygenated at all times. The availability of chemisorbed particulate NAIP, *i.e.*, the NAIP conforming to equation 1, is dependent on the reduction and dissolution of the Fe^{3+}–NAIP–Fe^{2+} complex. Equation 1 probably describes a "natural" system. In contrast, the heavy NAIP inputs on the U.S. side of the Detroit River reflect nonspecifically bound P, which is readily available on depletion of soluble phosphate (Sonzogni *et al.* 1982). Consistent with these general trends, Lake St. Clair is mesotrophic with but a minor eutrophic zone off the Thames River estuary and in the northwestern corner (Great Lakes Water Quality Board 1981). A balanced macrobenthic community structure, reflecting satisfactory water quality, occurs along the whole Canadian shoreline of the Detroit River (Thornley & Hamdy 1984), whereas macrobenthos populations along the U.S. shore are seriously disrupted by pollution.

The relationships between Fe^{3+}, Fe^{2+} and NAIP described by equations 1 and 2 have not been proposed previously. NAIP and iron are strongly restricted to the clay- and clay–silt-sized fractions of Lake Erie bottom sediments (Williams *et al.* 1976), which in no way negates the negative correlation measured here between Fe^{2+} (clay) and NAIP. The surfaces of illite (the principal clay mineral in Great Lakes sediments (Thomas *et al.* 1972), chlorite, and phosphate are negatively charged, whereas hydrated ferric oxides carry positive charges (Lewis 1966). Illite and chlorite are coated, on weathering, with ferric oxides (Carroll 1958). Organic anions are normally repelled from the surfaces of negatively charged clay particles (Greenland 1965). In the presence of a binding cation, *e.g.*, Al or Fe^{3+} ions or their hydroxides, humic acids and clay particles bind through a central cation bridge (Greenland 1971, Buffle & Altmann 1987). Competition between humic and phosphate ions for adsorption sites on hydrous ferric oxides has been observed under simulated freshwater conditions by Tipping (1981). Hence, the competition between phosphate ions and clay particles (this work) is a further example of the competition between negatively charged "anions" for adsorption sites on ferric hydroxides. The NAIP–Fe^{3+}–Fe^{2+} correlation (equation 2) suggests that clays and NAIP ions compete for adsorption sites on hydrated iron oxides.

Approximately equal amounts of ferrous and ferric ions are carried into and persist in the anoxic bottom sediments of the Central Basin of Lake Erie (Manning *et al.* 1984). This finding suggests that the clay – ferric oxide association is persistent under all but strongly reducing conditions, *e.g.*, in the presence of sulfide ion (Manning *et al.* 1979). The clay – ferric oxide association may have been formed in soils.

A layer of sediment up to 10 cm thick covers the glaciolacustrine clay bottom of most of Lake St. Clair. The shallowness of the lake and wave action ensure that sediment resuspension is particularly active. The absence of a thick permanent layer of sediment prevents the development of the anoxic conditions required for reduction and dissolution of ferric phosphate complexes. The top centimeter of the bottom sediments of the Central Basin of Lake Erie and the Niagara Basin of Lake Ontario contains elevated concentrations of ferric iron and NAIP (Fe^{3+}:Fe^{2+} ~1.4, ~900 μg P g^{-1}; Manning *et al.* 1984) which are derived mainly from the precipitation of pore-water ferrous and phosphate ions diffusing into the oxidized surface-layer. The regeneration of phosphorus is a major difference between rivers and lakes; in this respect, Lake St. Clair could be considered a river.

The present study differs from that of Lum & Gammon (1985) in several ways: (a) Lake St. Clair sediments are used as a basis for comparison with Detroit River sediments; (b) 1N HCl extracts ~25% of total iron (Lum & Gammon 1985), which is significantly less than the ~50% Fe^{3+} (of total Fe) measured by Mössbauer methods (Table 1). The HCl treatment also extracts some Al, indicating partial breakdown of clays. The methods are not directly comparable in their estimation of ferric iron. Mössbauer analysis and phosphorus fractionation do provide consistent results, which relate to identifiable species (Lucotte & d'Anglejan 1985); (c) the binding capacity of ferric ions for phosphate in Lake St. Clair (k_1 = 2.6% by weight, equation 1) differs hugely from that of Lum & Gammon (20% by weight) for Detroit River and Rouge River sediments. Clearly, iron–phosphorus interactions in the Detroit and Rouge Rivers cannot be described by one formula or relationship. In particular, the mechanisms of adsorption or precipitation (or both) of iron and phosphorus are not known in highly polluted areas such as the Rouge River, on the shores of which are located sewage treatment plants and steel mills. The plots of Lum & Gammon (1985) are heavily influenced by the few points marking heavily polluted sites, *e.g.*, the Rouge River. If three points (out of 20) are excluded from their plots of HCl-extractable Pb against Fe (their Fig. 2c), regression analysis yields a new line with slope 0.047% by weight *versus* their value of 1.7%. Moreover, the regression coefficient indicates a better fit with the exclusion of the three points. Much effort has been expended in this paper to justify one Fe–P relationship for both populations of Lake St. Clair points (text above), in which the degree of pollution (and the range of values) are considerably lower.

Insufficient data were available for Lake St. Clair sediments to permit an unambiguous definition of Pb–Fe relationships. There are no major sources of lead on the Canadian shore (Table 2), whereas the U.S. shore shows major contamination. The lead introduced to the Detroit River on the U.S. side may, as with phosphate, be more easily leached from the particulates and hence be more available. This lead could be an environmental problem locally, but its mobility will be considerably reduced on deposition to the oxic sediment layer in Lake Erie, where porewater ferrous iron is oxidized and reprecipitated.

The iron–phosphorus relationships described here for suspended sediments of Lake St. Clair and most of the Detroit River indicate satisfactory water quality. Further improvement requires better control of shoreline erosion (agricultural P) and reduction in P and metal loadings on the U.S. side of the Detroit River.

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