

BIOAVAILABILITY OF RIVERINE, SEWAGE PLANT, AND SEDIMENT PHOSPHORUS IN THE BAY OF QUINTE, LAKE ONTARIO

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ABSTRACT

The loadings of bioavailable nonapatite inorganic phosphorus in riverine suspended solids, sewage effluent and bottom sediments to the eutrophic Upper Bay of Quinte, Lake Ontario, are reported. The form and magnitude of all three sources are seasonally dependent. Increasingly over the summer, diffusional reflux from in-place sediments becomes the dominant source of bioavailable phosphorus. Values of the ratio phosphorus:ferrous iron show that most of the load of riverine inorganic phosphate ion is not deposited in the organic sediments within Upper Bay. It is considered to be weakly bioavailable, as it is transported through the Bay in oxic suspension. Remedial action to control eutrophication hinges on reduction of the rate of accumulation of nonapatite inorganic phosphorus in the bottom sediments. This means additional controls on sewage effluent, and a reduced loading of riverine phosphorus.

Keywords: bioavailable phosphorus, sources, remedial action, Bay of Quinte, Lake Ontario.

SOMMAIRE

Les ajouts de phosphore biodisponible d'origine inorganique et non liée à l'apatite dans la fraction solide en suspension dans les rivières, dans l'effluent urbain et dans les sédiments de fonds à Upper Bay, dans la baie de Quinte, eutrophique, du lac Ontario, sont ici décrits. La forme et l'ordre de grandeur de ces trois sources sont saisonniers. Au cours de l'été, le reflux diffusional des sédiments en place devient la source de plus en plus importante de phosphore biodisponible. Les valeurs du rapport de phosphore à fer ferreux montrent que la plupart de la masse d'ions phosphate d'origine inorganique transportée par les rivières n'est pas déposée dans les sédiments organiques de Upper Bay. Cette fraction serait faiblement biodisponible, étant transportée dans la baie en suspension oxygénée. Pour remédier à l'eutrophication, il faudra réduire le taux d'accumulation du phosphore inorganique non incorporé à l'apatite dans les sédiments lacustres. Ceci impose un contrôle additionnel des effluents urbains, et une réduction dans l'apport de phosphore par les rivières.

(Traduit par la Rédaction)

Mots-clés: phosphore biodisponible, sources, solution pro-active, baie de Quinte, lac Ontario.

INTRODUCTION

Cultural eutrophication is highly advanced in the industrially and recreationally important Bay of Quinte, Lake Ontario (Fig. 1). Algal blooms are massive, and water usage is severely impaired (Johnson & Hurley 1986). Controls on phosphorus inputs from the sewage treatment plants (Table 1), instituted in the 1970s, resulted in a reduction of chlorophyll *a* by the mid-1980s (Millard & Johnson 1986, Robinson 1986). Since then, improvement has been minimal. The Trent River and the smaller Moira River are the major sources of particulate matter and nonapatite inorganic phosphate ion (NAIP) to the Bay of Quinte (Manning & Gracey 1991, Manning & Wang 1994). Modeling exercises, based almost entirely on seasonal variations in concentrations of total

phosphorus, suggest that the phosphorus budgets within Upper Bay are dominated by diffusional reflux from the in-place sediments (Minns *et al.* 1986). Sewage treatment plants on Upper Bay are located at the major centers of Trenton (population 16,000) and Belleville (37,000).

The long axis of Upper Bay lies along the direction of the prevailing southwesterly winds (Fig. 1); consequently, the waters remain well-mixed and oxic all summer. Resuspension of bottom sediment, particularly at the eastern end of Big Bay, is heavy. Mean depth of water is 3 m, and maximum depth, 5 m. The bottom sediments are rich in organic matter and strongly reducing (Damiani & Thomas 1974). The Bay flushes approximately eight times in the spring and once over the rest of the year. The Upper Bay in summer is essentially a warm, shallow, visibly green

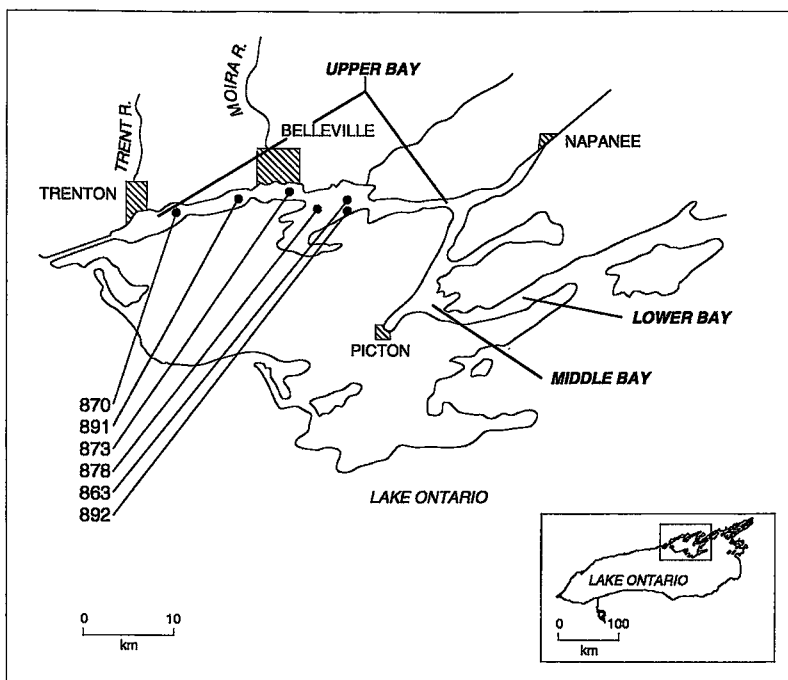


FIG. 1. Diagram depicting sampling stations in the Upper Bay of Quinte. The sewage treatment plants of Trenton and Belleville are close to the estuaries of the Trent and Moira rivers, respectively. Also shown are the downstream Middle Bay and Lower Bay.

lake. Seasonal trends in the concentrations of total phosphorus (annual means of $30 \mu\text{g P L}^{-1}$ rise to summer means of $70 \mu\text{g P L}^{-1}$) are matched by similar trends in chlorophyll *a* (Millard 1986, Nicholls *et al.* 1986, Robinson 1986). A summer source of soluble reactive phosphate ion is clearly indicated (Robinson 1986, Sonzogni *et al.* 1982). High summer temperatures, low levels of oxygen, and high values of pH are all factors that promote the release of phosphate ion from bottom sediments (Redshaw *et al.* 1990). A

long residence-time in the water column prior to sedimentation also favors availability (Boström *et al.* 1988).

Most of the bioavailable phosphorus in riverine particulate matter and in lacustrine sediments of the Great Lakes basin is contained within the nonapatite inorganic phosphorus (NAIP) fraction, which in turn is strongly associated with ferric iron and with the clay-sized fraction (Williams *et al.* 1976, 1980, Stone & English 1993, DePinto *et al.* 1981). Fine-grained sediment constitutes a potentially rich source of phosphorus to Lake Erie in spring and autumn (Logan 1987). NAIP in suspension in the Trent River is strongly incorporated (*i.e.*, adsorbed and coprecipitated) into poorly crystalline hydrated ferric oxides (Manning & Wang 1994). The ferric oxides would be reduced on deposition to bottom sediments rich in organic matter (Damiani & Thomas 1974). A budget based on inputs of nonapatite inorganic phosphate ion would yield more insight than one based on concentrations of total phosphorus. Hence, the summer loadings of bioavailable phosphorus, *i.e.*, inorganic phosphate ion, to the Upper Bay of Quinte in sewage treatment plants, riverine particulate matter, and in-place sediments are compared in order to focus remedial measures to control eutrophication.

TABLE 1. INPUT OF AVAILABLE ORTHOPHOSPHATE ION IN UPPER BAY OF QUINTE

Sources	Sewage plants		In-place sediment phosphate reflux	Riverine NAIP	
	pre-1972	1991		solids	soluble
Availability	high	high	100%**	slow	<100%
June	170	19	36 ± 11	47 ± 6	<6
August	170	19	72(est.)	19 ± 3	<8
September	170	19	72 ± 22	29 ± 4	<5

* Riverine soluble P is <15% of total P. River flow is at a minimum in August. est is estimated on the assumption that rates of reflux are unlikely to be lower than in September. ** Nürnberg (1985). Units: kg P day⁻¹.

EXPERIMENTAL DETAILS

Gravity cores of bottom sediments were collected from six stations (870, 891, 873, 878, 863, and 892) in Upper Bay (Fig. 1). The dark grey cores of clay-silt sediment were extruded and sectioned into 1-cm slices immediately on retrieval. All sections were frozen and later freeze-dried. Although freeze-drying may change the size of particles, it is unlikely to change valence states of iron significantly. Two cores from station 863, one sectioned under nitrogen and the other in air, gave very similar profiles of iron and phosphorus; consequently, all other cores were sectioned rapidly in air and frozen immediately. Measured values of Eh of the surface sediments, 0 ± 50 mV, are in agreement with those of Damiani & Thomas (1974). Additional cores were collected from stations 891, 878, 863 (on two occasions) and 892, and submitted for ^{210}Pb chronology (Turner 1991a, b, Turner & Delorme 1989).

Approximately 4 g of suspended particulate matter was collected in the Trent and Moira rivers and the Upper Bay by continuous-flow centrifugation of 600 L of water at mid-depth. The greenish brown particulate matter was frozen on collection and later freeze-dried. Concurrently, water samples were collected and preserved in sulfuric acid for the determination of total phosphorus and total filtered phosphorus (through 0.45- μm cellulose acetate filters); these samples were digested in a persulfate/ H_2SO_4 mixture at 120°C and analyzed photometrically using color development in the phosphomolybdate complex. The distribution of solids among sand, silt and clay in several samples of riverine particulate matter was determined by sedimentological methods. Sand-sized particles were separated from silt and clay by sieving.

The Mössbauer spectra of bottom sediments and suspended particulate matter were recorded at room temperature and resolved following procedures described earlier (Manning & Wang 1994). Two ferrous doublets are used, for consistency and convenience. A broad central doublet, at approximately 0.0 mm s^{-1} and 0.8 mm s^{-1} (Manning & Wang 1994), marks ferric ions in a number of positions of approximately octahedral coordination (Coe *et al.* 1974).

Samples of porewater were collected from station 863 in September 1988 and June 1989, and from station 878 in June 1989 and September 1989, by the manual (diver-assisted) insertion of clear acrylic plates (with 5-mL chambers recessed at 1-cm intervals) into the sediment. The chambers were earlier covered with a 0.45- μm cellulose acetate dialysis membrane under nitrogen-bubbled distilled water. Replicate analysis was provided for by the insertion of two plates in the June sampling at station 878. The chamber coincident with the sediment-water interface was noted visually by the diver on retrieval 14 days later; this chamber

was also marked by a horizontal surface stain of brown ferric "hydroxide". The main redox boundary is within one centimeter of the sediment-water interface. Each chamber was sampled by syringe immediately on retrieval. Concentrations of nitrate, nitrite, ammonium, and phosphate ions were measured, after suitable dilution, using standard methods. Rates of diffusional reflux of phosphate ion (J , $\text{mg m}^{-2} \text{ day}^{-1}$) from the bottom sediments were calculated from Fick's First Law of random diffusion $J = P \cdot D_t \cdot dc/dx + wc$, where P is the sediment porosity, D_t is the apparent diffusion random-mixing coefficient, dc/dx is the concentration gradient over the top 5–7 cm of sediment, and wc is an advective component. For soluble reactive phosphate ion, D_t is equal to $3.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (Krom & Berner 1980).

Concentrations of total iron and total aluminum in the dried sediments were determined by dissolution in aqua regia and by atomic absorption spectrometry using suitable standards. Concentrations of ferric and ferrous iron were then calculated from the total iron values and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ spectral area ratios. Replicate analyses indicate a standard error in total iron and aluminum values of $\pm 5\%$ and in ferric:ferrous ratios of $\pm 2\%$.

Concentrations of NAIP, apatite phosphorus, and organically bound phosphorus were measured by chemical fractionation (Williams *et al.* 1976). Strong correlations between the concentrations of ferric iron and NAIP in lake sediments and river particulate matter (Williams *et al.* 1976, Manning & Wang 1994) confirm that the dithionite – citrate – bicarbonate reagent extracts ions mainly associated with the hydrated oxides of iron and manganese (Lucotte & d'Anglejan 1985). The method yields reproducible concentrations of NAIP ($\pm 5\%$). Concentrations of organically bound carbon were measured using a Leco induction furnace following the method of Kemp (1971). Concentrations of total sulfur were determined by a semi-automatic Leco system with iodometric titration.

RESULTS

On the basis of the four sites sampled, sedimentation over most of Upper Bay has been continuous and undisturbed for at least 100 years. Silty clay sediment covers approximately 40% of the bottom (Damiani & Thomas 1974). Rates of sedimentation (Table 2) and the thickness of the sediment layer (>80 cm) are particularly high at station 878, in the lee of land on the west side of Big Bay (Fig. 1). In contrast, the sediment layer is approximately 40 cm thick over much of the eastern end of Big Bay, where the wind fetch is long and sediment resuspension events are relatively intense.

Values of isomer shift (relative to iron foil), quadrupole splitting, and halfwidth are similar to those

TABLE 2. RATES OF SEDIMENTATION AND OF REFLUX OF PHOSPHORUS IN UPPER BAY

Rate of sedimentation $\text{kg m}^{-2} \text{yr}^{-1}$ (cm yr^{-1})					
Station	891	878	863*	863**	892**
Mass rate	0.22	1.05	0.37	0.54	0.46
Thickness	(0.28)	(2.06)	(0.32)	(0.84)	(1.21)
NAIP $\times 10^4$	0.66	3.2	1.1	1.6	1.4
Rate of reflux of soluble inorganic P $\text{mg m}^{-2} \text{day}^{-1}$					
Station	878	878	863	863	
Date	June 89	Sept 89	Sept 88	June 89	
Rate	0.66	1.34***	1.42	0.52	

* Sampled April 1991. ** Sampled October 1990. *** Represents the average of replicate analyses, $\pm 5\%$.

reported by Manning & Wang (1994). Ferrous ions are assigned to structural positions in clay minerals and chlorite (Coe *et al.* 1974); illite is the principal clay mineral in Bay of Quinte sediments (Damiani & Thomas 1974). Chlorite was confirmed in current samples by X-ray diffraction.

Ferric ions are present in a mixture of poorly crystalline hydrated oxides and in clay minerals (Coe *et al.* 1974). Approximately 45% of riverine particulate ferric iron is magnetically ordered at 4 K (Manning & Gracey 1991, Manning & Wang 1994). No crystalline ferric oxides were detected by X-ray diffraction. The ferric iron profiles in the bottom sediments show little change with depth of burial (Fig. 2), which demonstrates the absence of any significant oxidizing horizon at the sediment-water interface; consequently, ferrous ions diffusing upward in the porewaters are released to the overlying water. Spectral resolution with the inclusion of a pyrite doublet (Manning *et al.* 1979) and optical microscopy indicated that pyrite is a minor phase in the bottom sediments.

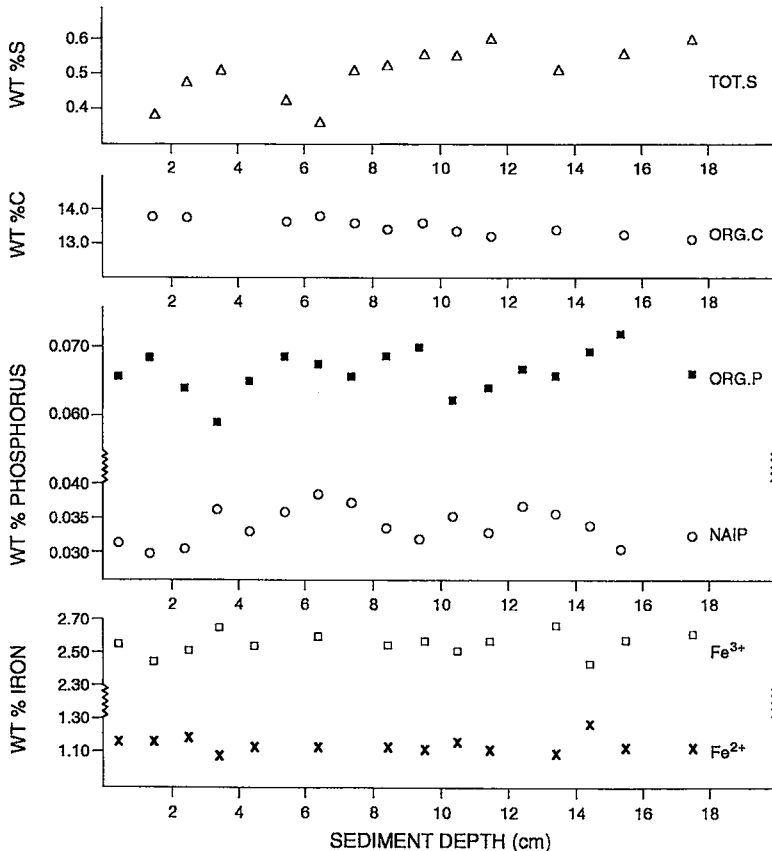


FIG. 2. Profiles of elemental concentration for forms of iron and phosphorus and for total sulfur and organic carbon in a core from station 873. Sediment-core profiles show minor differences from station to station within Upper Bay.

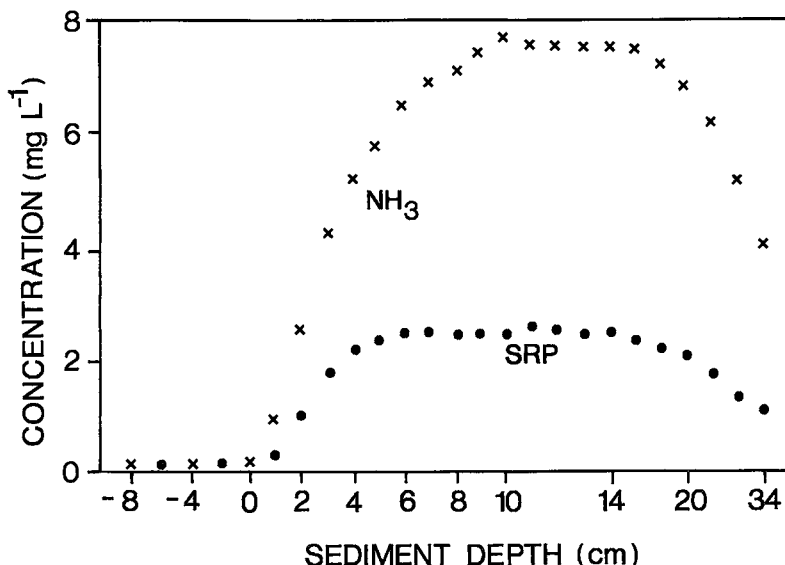


FIG. 3. Concentration of soluble phosphate ion and ammonium ion in porewater as a function of depth beneath the sediment-water interface. Sampled in June 1989 at station 878.

Concentrations of nitrate and nitrite ion are below the levels of detection ($<5 \text{ mg L}^{-1}$) within 1 cm of the sediment-water interface; concentrations of ammonia increase rapidly from zero at the sediment-water interface to 8 mg L^{-1} at 10 cm depth (Fig. 3). Hence, the in-place sediments of Upper Bay are reducing within a few millimeters of the sediment-water interface. Replicate values of reflux (at station 878) are good to $\pm 5\%$. Rates of reflux of phosphate ion (Table 2) increase strongly over the summer months, in a way consistent with rising water temperatures and with the general trend calculated for reflux from similar sediments underlying eutrophic Severn Sound, Ontario: there, rates of reflux were found to be four times higher in summer than in winter (Vieira & Rosa 1992).

Approximately 80% of the phosphorus in the waters of Upper Bay and of the Trent River is in the particulate phase (Manning & Gracey 1991). Sand-sized particles make up $<5\%$ of total riverine solids, and contain less than 0.02 wt% NAIP. The silty clay fraction contains $>0.07 \text{ wt}\%$ NAIP, confirming the dominant role of fine-grained solids in the riverine transport of NAIP (DePinto *et al.* 1981, Williams *et al.* 1980). In view of the severe eutrophy of the waters, most of the soluble P is probably organically bound (Stumm & Morgan 1981). Concentrations of soluble phosphate ion in summer are minor (Dobson 1984). Hence, the availability of riverine phosphorus mainly depends on the fate and availability of fine-grained particulate NAIP. This further depends on whether

riverine particulate matter is deposited in the anoxic sediments or remains in oxic suspension.

During the high rate of flow in the river in April, NAIP is the dominant form of particulate phosphorus (Table 3), whereas from May to October, organically bound phosphorus is predominant. These trends reflect the erosion of inorganic materials from soils during spring run-off and, in summer, the uptake of inorganic phosphorus by phytoplankton. Concentrations of NAIP greatly exceed those of apatite in all samples of riverine particulate matter, in marked contrast to their relative values in the bottom sediments and suspended particles of Upper Bay (Table 3). These trends are consistent with the physical sorting of particulate matter based on particle size. Apatite is concentrated in the silt-sized fraction of Great Lakes sediments, whereas ferric oxides and NAIP are in the finer clay fraction (Williams *et al.* 1976). Consequently, NAIP associated with fine-grained solids will remain suspended in the water column of the Upper Bay longer than coarser-grained solids.

Concentrations of organic carbon in the bottom sediments of Upper Bay are lower than those in riverine particulate matter collected at Trenton, but greatly exceed those of the sediments underlying the open waters of Lake Ontario (Kemp & Thomas 1976). The concentrations of organic carbon (13 to 15 wt%) show little change with depth of burial (Fig. 2).

Concentrations of total sulfur in all cores are approximately 0.5 wt% and show minor change with depth of burial (Fig. 4). The flat profile confirms the

TABLE 3. ELEMENTAL CONCENTRATIONS AND SOME RATIOS FOR SUSPENDED MATTER AND SEDIMENTS

Station, date	Fe ³⁺	Fe ²⁺	NAIP	ApP	OrgP	Fe ³⁺ / Fe ²⁺	NAIP/ Fe ²⁺
River particulate matter							
MR Apr89	1.1	3.9	0.209	0.03	0.09	3.6	0.19
MR Apr90	0.6	2.2	0.121	0.03	0.08	3.8	0.22
TR Apr89	1	2.7	0.145	0.04	0.06	2.6	0.15
TR June89	0.6	1.8	0.073	0.02	0.1	3.0	0.13
TR Oct89	0.5	1.4	0.066	0.03	0.13	2.8	0.13
TR Apr90	0.5	1.7	0.094	0.03	0.09	3.2	0.18
TR May90	0.7	2	0.087	0.02	0.13	2.9	0.12
TR Oct90	0.5	1.3	0.08	0.03	n.m.	2.7	0.16
Suspended particulate matter in Upper Bay							
870 Sep88	0.2	0.7	0.161	0.02	0.2	4.2	0.89
870 May89	0.2	0.8	0.123	0.01	0.12	5.0	0.77
878 Sep88	0.2	0.7	0.103	0.02	0.21	3.3	0.52
878 May89	0.2	0.8	0.324	0.01	0.14	4.6	1.91
873 Sep88	0.3	1	0.123	0.02	0.16	3.2	0.41
873 May89	0.2	0.8	0.141	0.01	0.13	5.1	0.94
892 Sep89	0.2	0.7	0.192	0.01	0.13	3.3	0.96
Top centimeter bottom sediments of Upper Bay							
870 Sep88	1.4	2.4	0.035	0.06	0.06	1.8	0.026
891 Apr91	0.9	2.3	0.044	0.05	0.05	2.2	0.055
878 Sep88	1.3	2.5	0.04	0.05	0.08	2.0	0.030
873 Sep87	1.2	2.6	0.032	0.04	0.07	2.1	0.026
873 Sep88	1.3	2.4	0.06	0.06	0.06	1.8	0.045

MR and TR represent the Moira and Trent rivers. Riverine particulate matter was sampled at the estuaries. ApP is apatite phosphorus; its high insolubility renders it biologically unavailable. In all sediment cores, concentrations of NAIP decrease to 0.035 ± 0.005 wt% P at 6 cm burial and to 0.030 wt% at 25 cm burial. n.m.: not measured. Coring in April was aimed at collecting, via the top cm of sediments, a sample of the massive loading of particulate matter from the spring run-off. Wt% dry sediment.

absence of a subsurface sulfate-reducing horizon. Pyrite is, thus, a minor phase in Upper Bay sediments. Most of the sulfur is probably organically bound.

DISCUSSION

Ferric/ferrous and NAIP/ferrous ratios

Clay minerals remain structurally and compositionally unchanged while in suspension and in surficial layers of bottom sediments of the Great Lakes (Kemp *et al.* 1976, Kemp & Thomas 1976). None of the sharply defined peaks of vivianite (Manning *et al.* 1991) is present in the Mössbauer spectra. The use of Fe³⁺/Fe²⁺ and NAIP/Fe²⁺ ratios as measures of the non-sedimentation or release of ferric iron and NAIP is justified on grounds that (a) the inorganic component

of bottom sediments is mainly derived from the inputs of the Trent and Moira rivers, (b) the ratios, as determined at the mouth of the rivers, are reasonably independent of season and year (Table 3), and (c) the top cm of sediment corresponds, at stations 878 and 892, to less than one year of sediment accumulation (Turner & Delorme 1989, Turner 1991b). Hence, ferrous ion is a suitable normalizing element for purposes of comparison.

Ferric iron is the dominant form of iron in suspended particulate matter and in bottom sediments (Table 3). The ferric/ferrous ratio is significantly larger in riverborne particulate matter than in the top cm of Upper Bay sediments (Table 3); hence, ferric iron compounds are less efficiently deposited than are silty clay materials. The values of the ferric/ferrous ratio (approximately 5) for suspended particulate matter in Upper Bay strongly suggest that this "missing" ferric iron, as hydrous oxide, remains in suspension. The source of iron and of manganese for the precipitation of ferromanganese nodules in nearshore areas of Upper Bay (Table 3) has been attributed to iron release from reducing offshore sediments (Damiani & Thomas 1974).

A comparison of NAIP/Fe²⁺ ratios for riverine particulate matter (0.16 ± 0.04) and for bottom sediments (0.037 ± 0.010) indicates that, relative to clay mineral, at least 80% of riverine NAIP is not incorporated into the bottom sediments (Table 3). One possible explanation is that the fine-grained particulate matter is transported through the Upper Bay and deposited downstream in the Middle and Lower bays (Fig. 1). The elevated value of the ratio for suspended particulate matter within Upper Bay (0.9 ± 0.3) is consistent with riverine NAIP being retained in suspension, and is supported by the reprecipitation in the water column of phosphate ion released by reflux from the bulk sediments. Lower organic P/Fe²⁺ values for bottom sediments suggest that minor amounts of riverine phosphorus are retained within the surficial sediments. Therefore, minor amounts of the massive spring load of riverine NAIP ($300 \text{ kg P day}^{-1}$ in April) are retained in the top one or two centimeters of bottom sediment for short-term release in the summer. The release of sediment phosphorus, in bioavailable form, is best measured as long-term diffusional reflux.

The ratios of concentrations organic C/Fe²⁺ are considerably lower for the sediments (≈ 12 , Fig. 2) than for the river particulate matter (≈ 28 , Manning & Wang 1994). This is consistent with the flushing through Upper Bay of a fine-grained assemblage of phosphate - oxide - organic matter.

Loading of phosphorus

The bioavailability of particulate NAIP in suspension in the oxic waters of Upper Bay is reduced by the kinetic constraints placed on the breaking of

$\text{Fe}^{3+}\text{-O}_2\text{PO}_2$ bonds, in which the orthophosphate ion is probably bidentate (Parfitt & Russell 1977, Ryden *et al.* 1977). Ferric chloride is used to precipitate phosphate ion in controlling the growth of algae (Boers *et al.* 1994). Furthermore, the desorption of NAIP from riverine particulate matter is suppressed by the inputs of free phosphate ion from the sewage plants and from sediment reflux. Riverine particulate NAIP is the least available of the major sources in Upper Bay.

The phosphorus loadings from the sewage treatment plants are reduced in April and over the summer from winter loads of 31 kg P day⁻¹ to 19 kg P day⁻¹. The immediate contribution of riverine particulate NAIP to the nutrient budget declines with decreasing river flow over the summer months (mean 25-year flows in the Trent River from April to October are, in units of 10⁷ m³ day⁻¹, 2.9, 1.7, 0.8, 0.5, 0.35, 0.5, and 0.8, respectively; Ontario Ministry of the Environment 1989). The mean flow of the Moira River is approximately one-third that of the Trent, and iron-NAIP interactions and concentrations are similar in both rivers (Manning & Gracey 1991). Daily loadings of riverine particulate NAIP to the Bay are calculated from the flow rates times the concentration of NAIP; for the Trent River in June this amounts to $0.8 \times 10^7 \text{ m}^3 \text{ day}^{-1} \times 6 \text{ g m}^{-3} \times 0.073\%$, or 35 kg P day⁻¹ (Table 3). In contrast, the diffusional reflux of phosphate ion from the in-place sediments increases markedly over the summer (Table 1), following the trend in rising water temperatures and increasing microbial activity. The September porewater samplings occurred less than three weeks after maximum water temperatures. Fine-grained sediment covers approximately 40% of the bottom of Upper Bay, from Trenton to the east end of Big Bay (Fig. 1), *i.e.*, an area of approximately 54 km². Assuming that the rates of reflux for stations 878 and 863 (Table 2) are valid for all of Upper Bay, then the diffusional reflux of phosphorus becomes the dominant source of available phosphorus budget over most of the summer (Table 1), regardless of the degree of availability of riverine particulate NAIP.

Photochemically initiated reduction-oxidation reactions at the surfaces of particulate matter will undoubtedly lead to the dissolution of phosphate ion. Ferric and manganese ions efficiently catalyze such reactions, their reduction promoting the oxidation and decomposition of organic matter (Miles & Brezonick 1981, Morel 1983). The riverine NAIP - $\text{Fe}^{3+}_{\text{OX}}$ - organic anion assemblage, with its intimate association of ferric ion and organic ion, is clearly susceptible to photochemical reduction-oxidation and to dissolution. The rate of dissolution of the phosphate ion is not known. Nevertheless, riverine particulate matter may support sediment reflux in stimulating eutrophication. Particulate NAIP is, therefore, potentially bioavailable subject to kinetic restraints. Organic anions released during the decay of algae in Upper Bay are more likely to displace other organic anions, possibly fulvate or

humate ions from the riverine NAIP - $\text{Fe}^{3+}_{\text{OX}}$ - organic anion assemblage (Ramamoorthy & Manning 1974).

The errors in the measured inputs are unlikely to be sufficiently large so as to seriously compromise the relative magnitudes of the different sources of available phosphorus (Table 1). Sewage plant inputs are known to $\pm 5\%$, and river loads, to $\pm 15\%$. The rate of reflux of 1.34 mg m⁻² day⁻¹ measured in September (Table 2) yields, over 100 days of release and a mean depth of water of 3.0 m, an equivalent elevation in phosphorus concentration in Upper Bay of 40 $\mu\text{g L}^{-1}$, a value that is consistent with the mean summer maximum in the concentrations of total phosphorus of 70 $\mu\text{g P L}^{-1}$ (Robinson 1986), *i.e.*, the refluxed 40 $\mu\text{g P L}^{-1}$ plus the mean annual concentration of 30 $\mu\text{g P L}^{-1}$. Hence, the rates of reflux are probably good to $\pm 30\%$.

The mass rate of sedimentation at station 878 of 1050 g m⁻² yr⁻¹, at 0.030 wt% NAIP, equates to a rate of sedimentation of 315 mg NAIP m⁻² yr⁻¹. Comparable amounts of organic P are also deposited in the bottom sediments (Table 3), providing through mineralization an additional source of NAIP ions to the porewaters. Against this, an assumed rate of reflux of 1.34 mg P m⁻² day⁻¹ covering July, August and September, and one of 0.66 mg P m⁻² day⁻¹ covering May, June and October, amounts to a total reflux of approximately 200 mg P m⁻². In the compositionally similar sediments of eutrophic Severn Sound, Ontario, rates of reflux in winter are 25% those of summer (Vieira & Rosa 1992). Translated to Upper Bay of Quinte, the expected winter release is 64 mg P m⁻². The cumulative annual reflux is therefore approximately 260 mg P m⁻². Hence, the rate of sedimentation of NAIP exceeds the rate of reflux, *i.e.*, the pool of NAIP is not diminishing. Nürnberg (1991) calculated that the external load to the Upper Bay is three times the "threshold external load", *i.e.*, the load at which the flux downward equals the flux upward from anoxic sediments. She stated that recovery is possible only where the threshold load exceeds the external load. However, it is unlikely that all of the sedimented NAIP and organic P is ultimately available.

Basis for remedial action

Remedial action to control available phosphorus in the Upper Bay requires definition of the origin of the phosphorus pool contained within the sediments. Does this pool comprise the NAIP incorporated into the more refractory fraction of riverine particulate matter or is it NAIP, of sewage and sedimentary (reflux) origin, that is taken up by algae and deposited within an organic matrix? A significant trend of the last 20 years has been the decrease in the mean summer concentration of total phosphorus (from 90 $\mu\text{g P L}^{-1}$ to 70 $\mu\text{g P L}^{-1}$) and the consequent inference from modeling exercises of lower rates of reflux (Minns

et al. 1986). This trend suggests, in light of recent controls on sewage inputs and of but minor change in agricultural practice in the watershed, that a significant portion of the pool of sediment NAIP has in past years been derived from sewage effluent. Under the conditions low flow during the summer, suspended particles, enriched in organic material, settle out of the water column more efficiently. Internal cycling is an important process in the Upper Bay. The sedimentation of refractory riverine phosphorus may also contribute to the sediment pool of NAIP: clay materials are coated with iron "hydroxides", which incorporate inorganic phosphorus. The rivers are the dominant source of NAIP to the Bay. The rate at which phosphorus (NAIP and organic forms) is sedimented out to the bottom is clearly key to remedial action.

Although the eutrophy of summer is driven directly by the sediment reflux of phosphorus, the ultimate drivers are the sewage treatment plants and the rivers. Riverine matter may also contribute directly from the desorption of phosphate ion off current inputs of suspended matter. Prior to controls, sewage phosphorus completely dominated all other sources in summer (170 kg P day⁻¹, Table 1). These insights confirm that past expense incurred in controlling sewage effluent is well justified, and that additional controls are in order.

The Upper Bay is too large a body of water to treat chemically, as proposed for an English reservoir (Redshaw *et al.* 1990). Remedial action should be based on reduction of the efficiency of internal cycling of phosphorus in the Upper Bay, *i.e.*, on reducing the rate at which phosphorus is deposited in the bottom sediments. Over the short term, the loadings of the sewage treatment plants could be further reduced, by heavier additions of ferric chloride at relatively little cost, to 12 kg P day⁻¹, a loading equivalent to the technically feasible effluent concentration of 0.3 mg P L⁻¹. Medium-term erosional forces in the watersheds of the Trent and Moira rivers need to be controlled, not only on account of the high loading of available phosphorus, but also on account of a high degree of incorporation of NAIP into particulate matter (Lum & Gammon 1985). Erosion is heavily dependent on agricultural practice.

Any significant reduction in the rate of reflux of phosphorus, and, hence, any improvement in trophic condition, may take 10 to 20 years to develop following these concerted actions. This time scale is based on the deposition of approximately 10 centimeters of sediment of lower contaminant level. These actions would be strongly enhanced by the pumping of cleaner Lake Ontario water, containing 10 µg P L⁻¹, into the Upper Bay *via* the canal at its western end. A pumping rate commensurate with the mean flow of the river during the summer, 60 m³ s⁻¹, would effectively double the rate at which suspended particulate matter is flushed out of the Upper Bay.

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