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Bioavailability of Riverine, Sewage Plant, and Sediment  
Phosphorus in the Bay of Quinte, Lake Ontario

By:

P.G. Manning

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

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**ABSTRACT**

The summer loadings of bioavailable nonapatite inorganic phosphorus to the eutrophic Upper Bay of Quinte, Lake Ontario, are reported on for rivers, sewage treatment plants, and in-place sediments. All three sources have a highly seasonal component. Increasingly over the summer, diffusional reflux from the in-place sediments becomes the dominant source of bioavailable phosphorus. Most of the load of riverine inorganic phosphate ion, incorporated into hydrated ferric oxides, is not deposited to the organic sediments within Upper Bay; it is considered to be weakly bioavailable as it transits the Bay in oxic suspension. Remedial action to control eutrophication hinges on reducing the rate of accumulation of nonapatite inorganic phosphorus in the bottom sediments. This means severe controls on the loadings of riverine particulate matter to the Bay of Quinte.

## MANAGEMENT PERSPECTIVE

Cultural eutrophication is highly advanced in the Bay of Quinte, Lake Ontario, such that water usage, recreational, municipal and industrial, is severely impaired. The Bay receives significant inputs of bioavailable phosphorus from three sources: the sewage treatment plants, the rivers, and the in-place bottom sediments. We have determined a budget for bioavailable phosphorus for each of these sources in Upper Bay (on which the major population centres of Trenton and Belleville are located) covering the summer months when the effects of eutrophication are at their worst. This budget indicates that the diffusional reflux of readily bioavailable phosphorus from the in-place sediments becomes increasingly dominant over the summer, such that by late summer reflux accounts for approx. 60 to 70% of the available phosphorus entering Upper Bay.

The budget demonstrates that the expensive controls of the past 20 years on phosphorus loadings to the Bay have been partially successful in that concentrations of total phosphorus and chlorophyll a are significantly lower. Improvement in water clarity over the last <sup>10</sup> years has been minor. Further remedial actions are recommended that would lead to a reduction in the pool of phosphorus in the in-place sediments: a massive reduction in the inputs of riverine particulate matter supported by further reduction in sewage inputs. OK  
The former action is predicated on lower rates of soil erosion in the watershed: specific actions would include a change in agricultural practice (to one of no-tillage) and, e.g. the planting of trees on riverbanks.

## 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 the phosphorus inputs of the sewage treatment plants (Table 1), instituted in the 1970s, had led by the mid-1980s to significantly lower levels of chlorophyll *a* (Millard & Johnson 1986, Robinson 1986). Since then, improvement has been minimal. The Trent River and the smaller Moira River are the major sources of 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 difusional reflux from the in-place sediments (Minns *et al.* 1986). Sewage treatment plants on Upper Bay are located at the major centres 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 and 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 are strongly reducing (Damiani & Thomas 1974). The Bay flushes approximately eight times in the spring and once over the rest of the year; Upper Bay in summer is essentially a warm shallow visibly-green 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 (Robinson 1986, Sonzogni *et al.* 1982) is clearly indicated.

Here, the summer inputs of bioavailable phosphorus, i.e., inorganic phosphate ion, to the Upper Bay of Quinte from sewage treatment plants, from riverine particulate matter, and from the in-place sediments are compared in order to provide a firmer basis for further remedial action to control the degree of eutrophication. 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). NAIP in suspension in the Trent River is strongly incorporated (i.e. adsorbed and coprecipitated) into poorly crystalline hydrated ferric oxides (Manning & Wang 1994); binding capacities are comparable (at 18 percent by weight of ferric iron in oxide) to those measured in waters of the Great Lakes heavily polluted by effluent from steel mills and sewage plants (Lum and Gammon 1985, Mayer and Manning 1991). Lum & Gammon (1985) proposed that 18% represented the maximum assimilative capacity in natural systems. Hence, riverine particulate matter represents a potentially rich source of inorganic phosphorus to the Bay. The ferric oxides are probably redox-sensitive and would likely be reduced on deposition to bottom sediments rich in organic matter (Damiani & Thomas 1974, Manning & Wang 1994). A budget based on inputs of nonapatite inorganic phosphate ion would be more insightful than one based on concentrations of total

phosphorus.

### 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. Two cores from station 863, one sectioned under nitrogen and the other in air, gave very similar iron and phosphorus profiles; consequently, all other cores were sectioned rapidly in air and frozen immediately. Measured Eh values of the surface sediments were  $0 \pm 50$  mV (also Damiani & Thomas 1974).

Additional cores were collected from stations 891, 878, 863 (on two occasions), and 892 and submitted for  $^{210}\text{Pb}$  chronology (Turner 1991a, 1991b, Turner & Delorme 1989). On the basis of the four sites sampled, sedimentation over most of Upper Bay has been continuous and undisturbed for at least 100 years. Fine-grained 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 in the lee of land on the west side of Big Bay, e.g. at station 878 (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.

Approximately 4 g of suspended particulate matter were collected from the Trent and Moira Rivers and from Upper Bay by the continuous-flow centrifuging 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  $0.45 \mu\text{m}$  cellulose acetate filters); these samples were digested in a persulfate /  $\text{H}_2\text{SO}_4$  mixture at  $120 \text{ C}$  and analyzed photometrically using colour development in the phosphomolybdate complex. Approximately 80% of total phosphorus is in particulate matter.

Mössbauer spectra of bottom sediments (Fig. 2) and of riverine particulate matter were recorded at room temperature and resolved using the programs of Stone (1967). Lorentzian line shapes were assumed and areas and halfwidths of the two peaks within a quadrupole doublet were constrained to be equal. Values of chi-squared, a consistency of resolution from sample to sample, and the visual examination of the computed fits were used as criteria of goodness of fit. The spectrometer was calibrated against iron foil.

The Mössbauer spectra of all samples were computed on the same basis as for riverine particulate matter, i.e. using three doublets ( $\text{Fe}^{2+}_a$ ,  $\text{Fe}^{2+}_b$ , and  $\text{Fe}^{3+}$ ) (Manning and Gracey 1991); the presence of ferrous ions in at least two different sites is indicated by a strong absorption (centred at  $2.4 \text{ mm s}^{-1}$ ) and shoulder (at  $2.0 \text{ mm s}^{-1}$ ) (Fig. 2). Other weaker ferrous doublets may be present but, for consistency and convenience, two only are invoked here. The broad central doublet (at approximately  $0.0 \text{ mm s}^{-1}$  and  $0.8 \text{ mm s}^{-1}$ ) marks ferric ions in a number of positions of approximately octahedral coordination (Coe *et al.* 1974).

The spectra were also resolved, by suitably constraining peak positions and halfwidths, with the addition of a pyrite doublet (Manning *et al.* 1979). All computations converged, yielding minor concentrations of pyrite of  $3 \pm 3\%$  of total iron. Optical

microscopy of the bottom sediments revealed relatively few opaque framboids of pyrite. Pyrite is thus a minor iron phase in Upper Bay sediments; consequently, all iron abundances are reported in terms of the above three doublet fits. Measured values of isomer shift (relative to iron foil), quadrupole splitting, and halfwidth are, respectively, in  $\text{mm s}^{-1}$ , for  $\text{Fe}^{2+}_a$   $1.11 \pm 0.02$ ,  $2.64 \pm 0.02$  and  $0.36 \pm 0.02$ ; for  $\text{Fe}^{2+}_b$   $1.07 \pm 0.05$ ,  $2.15 \pm 0.07$  and  $0.35$ (constrained); and for  $\text{Fe}^{3+}$   $0.41 \pm 0.02$ ,  $0.65 \pm 0.02$  and  $0.63 \pm 0.03$ . The parameters for ferrous ions are consistent with their presence in structural positions in clay minerals and chlorite (Coey *et al.* 1974); illite is the principal clay mineral in Bay of Quinte sediments (Damiani & Thomas 1974). The presence of chlorite was confirmed in current samples by X-ray diffraction methods. The  $\text{Fe}^{2+}_a$  :  $\text{Fe}^{2+}_b$  ratio of concentrations is approximately 4.

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. Replicate analysis was provided for by the insertion of two plates in the June sampling at station 878, one at the station and the other approximately 200 m to the east. The separation (200 m) ensured that sediment at the second site was not disturbed by sampling activity at station 878. The chambers were earlier covered with a  $0.45 \mu\text{m}$  cellulose acetate dialysis membrane under nitrogen-bubbled distilled water. 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 1 cm 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 colorimetric methods based on cadmium reduction, phenol hypochlorite, and phosphomolybdate, respectively. 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 increased rapidly from zero at the sediment-water interface to  $8 \text{ mg L}^{-1}$  at 10 cm depth (Fig. 3). Hence, the in-place sediments of Upper Bay are reducing within a few mm of the sediment-water interface.

Rates of diffusional reflux of phosphate ion from the bottom sediments were calculated from Fick's First Law of random diffusion using the formulations of Krom & Berner (1980), namely  $J = P.D_t.dc/dx + wc$ , where  $J$  is the flux,  $P$  is the sediment porosity,  $D_t$  is the apparent diffusion random mixing coefficient,  $dc/dx$  is the measured concentration gradient over the top 6-7 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). Replicate measurements of reflux (at station 878) were good to  $\pm 5\%$ . Measured rates of reflux of phosphate ion (Table 2) increase strongly over the summer months, consistent with rising water temperatures and with the general trend measured for reflux from similar sediments underlying eutrophic Severn Sound, Ontario: there, rates were four times higher in summer than in winter months (Vieira & Rosa 1992).

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 (Table 3) 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 (Table 3) 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 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 semiautomatic Leco system with iodometric titration.

## RESULTS AND DISCUSSION

### Forms of iron and of phosphorus

Ferric iron is the dominant form of iron in suspended particulates and in bottom sediments (Fig. 2, Table 3). The Mossbauer parameters are consistent with the presence of ferric ions in a mixture of poorly crystalline hydrated oxides and in clay minerals: approximately 45% of riverine particulate input of ferric iron is magnetically ordered at 4K (Manning & Gracey 1991, Manning & Wang 1994). No crystalline ferric oxides were detected by X-ray diffraction methods. The ferric iron profiles in the bottom sediments show

little change with depth of burial (Fig. 4), demonstrating 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.

Approximately 80% of the phosphorus in the waters of Upper Bay and of the Trent River is in the particulate phase (Manning & Gracey 1991). In view of the severe eutrophy of the waters, most of the soluble P is probably organically bound (Stumm & Morgan 1981); concentrations of free phosphate ion in solution in summer are probably minor (Dobson 1984). Hence, the availability of riverine phosphorus mainly depends on the fate and availability of particulate NAIP: this further depends on whether riverine particulate matter is deposited to the anoxic sediments or remains in oxic suspension.

During high river flows of April, NAIP is the dominant form of particulate phosphorus (Table 3), whereas from May to October organically bound phosphorus is predominant. These trends reflect, respectively, the heavy erosion of inorganic materials from soils during spring snow-melt and run-off and, in summer, the uptake of inorganic phosphorus by phytoplankton and incorporation into tissue. Significantly, 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 particularly in the suspended particles of Upper Bay (Table 3). These trends are consistent with the physical sorting of particulates 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 is less efficiently sedimented in Upper Bay than is apatite.

### Normalizing elements

Clay minerals are structurally and compositionally relatively inert while in suspension as particulate matter and also in the surficial layers of bottom sediments of the Great Lakes (Kemp *et al.* 1976, Kemp & Thomas 1976). Ferrous and aluminum ions are therefore possible normalizing elements, although the use of Al is compromised by its coprecipitation with ferric iron and manganese as amorphous oxide. Interferences from possible vivianite in the spectral determination of ferrous ion are probably minor, as vivianite would be easily identified by sharply defined peaks in the Mossbauer spectra (Manning *et al.* 1991). Ferrous ion would appear to be a suitable normalizing element.

### Ferric/ferrous and NAIP/ferrous ratios

Ferric/ferrous and NAIP/ferrous ratios are significantly larger in riverborne suspended particulates than in the top cm of Upper Bay sediments (Table 3). The use of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{NAIP}/\text{Fe}^{2+}$  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). The average  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios of 3.1 for riverine particulate matter and 2.0 for the top cm of bottom sediments indicate that approximately 33% of riverine  $\text{Fe}^{3+}$  is not incorporated into the sediments. Significantly, the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio within the clay mineral structure in riverine particulate matter is

approximately 2 (Manning & Wang 1994). The ferric/ferrous ratios (approximately 5) for suspended particulate matter in Upper Bay strongly suggest that this "missing" ferric iron, probably hydrous oxide, remains in suspension. The source of iron and of manganese for the precipitation of ferromanganese nodules in nearshore areas of Upper Bay has been attributed to iron release from reducing offshore sediments (Damiani & Thomas 1974).

A comparison of NAIP/Fe<sup>2+</sup> ratios for riverine particulate matter ( $0.16 \pm 0.04$ , Table 3) and for bottom sediments ( $0.037 \pm 0.010$ ) indicates that, relative to clay mineral, approximately 80% of riverine NAIP is not incorporated into the bottom sediments. Much of the particulate matter is probably swept through Upper Bay, to possibly settle downstream in Middle and Lower Bays (Fig. 1). The elevated value of the ratio for suspended particulate matter within Upper Bay ( $0.9 \pm 0.3$ ) is consistent with riverine NAIP being retained in suspension, and supported by the reprecipitation in the water column of phosphate ion released by reflux from the bulk sediments. Lower values of the ratios of concentrations organic P/Fe<sup>2+</sup> for the bottom sediments confirm that minor amounts of riverine phosphorus are retained within the surficial sediments. Importantly, 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 that (following) summer. Consequently, the release of sediment phosphorus, in bioavailable form, is best measured as long-term diffusional reflux; it is dependent on microbial activity within the sediment column.

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 Fe<sup>3+</sup>-O<sub>2</sub>PO<sub>2</sub> bonds, in which

the orthophosphate ion is probably bidentate (Parfitt *et al.* 1977, Ryden *et al.* 1977). Ferric chloride is used to precipitate phosphate ion as a means of 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, i.e. riverine particulate NAIP is the least available of the major sources in Upper Bay.

### Forms of carbon and sulfur

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 Lakes and Ontario (Kemp & Thomas 1976), reflecting the eutrophy of the Bay of Quinte. The concentrations of organic carbon (13 to 15 wt%) show little change with depth of burial (Fig. 4). The ratios of concentrations organic C/Fe<sup>2+</sup> are considerably lower for the sediments ( $\approx 12$ , Fig. 4) than for the river particulate matter ( $\approx 28$ , Manning & Wang 1994), consistent with the flushing through Upper Bay of a fine-grained riverine phosphate-oxide-organic matter assemblage.

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 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.

### General discussion

The phosphorus loadings from the sewage treatment plants are reduced in April and over the summer months, from winter loads of 31 kg P day<sup>-1</sup> to 19 kg P day<sup>-1</sup>. 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 10<sup>7</sup> m<sup>3</sup> day<sup>-1</sup>, 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 in particulate matter; for the Trent River in June this amounts to 0.8 X 10<sup>7</sup> m<sup>3</sup> day<sup>-1</sup> X 6 g m<sup>-3</sup> X 0.073%, or 35 kg P day<sup>-1</sup> (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 km<sup>2</sup>. 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 phosphate ion is not known. Nevertheless, riverine particulate matter may strongly 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  $1.34 \text{ mg m}^{-2} \text{ day}^{-1}$  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  $1050 \text{ g m}^{-2} \text{ yr}^{-1}$ , at 0.030 wt% NAIP, equates to a rate of sedimentation of  $315 \text{ mg NAIP m}^{-2} \text{ yr}^{-1}$ . Against this, an assumed rate of reflux of  $1.34 \text{ mg P m}^{-2} \text{ day}^{-1}$  covering July, August and September, and one of  $0.66 \text{ mg}$



$\text{P m}^{-2} \text{ day}^{-1}$  covering May, June and October, amounts to a total reflux of approximately  $200 \text{ mg P m}^{-2}$ . 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 then  $64 \text{ mg P m}^{-2}$ . The cumulative annual reflux is therefore approximately  $260 \text{ mg P m}^{-2}$ , indicating that, within experimental error ( $\pm 30\%$ ), the rate of sedimentation of NAIP may still exceed the rate of reflux, i.e., the pool of NAIP is not diminishing.

Remedial action to control loadings of available phosphorus to Upper Bay over the important summer months requires definition of the origin of the phosphorus contained within the sedimentary pool. Thus, does this pool comprise the NAIP incorporated in the more refractory fraction of riverine particulate matter or is it sewage effluent phosphorus that is later adsorbed onto particulate matter and sedimented out? 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 the severe controls on loadings of sewage treatment plants and of but minor change in agricultural practice in the watershed, that a portion of the pool of sediment NAIP is derived from sewage effluent. Alternatively, lower rates of reflux may have been aided by higher redox potentials within the sediment column following lower rates of deposition of metabolizable organic matter to the sediments. However, the mineral phase of riverine particulate matter may well be saturated with respect to the incorporation of NAIP (see Introduction), and since the rivers are the dominant source of total inorganic phosphorus to the Bay, it is only logical to

suggest that most of the pool of sedimentary NAIP in Upper Bay is derived from riverine particulate NAIP. Calculation shows that the annual load of sewage plant phosphorus (9000 kg) to Upper Bay is comparable in amount to the NAIP contained within the top centimeter of bottom sediment (over an area of 50 km<sup>2</sup>). It is unlikely that sewage P only (and all of it) ends up as NAIP in the bottom sediment, particularly since available forms of phosphorus are rapidly taken up by algae.

Although the eutrophy of summer is driven directly by the sediment reflux of phosphorus, the ultimate driver is riverine particulate matter, functioning in the main as the carrier of NAIP to the bottom sediments. 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<sup>-1</sup>, Table 1). These insights confirm that past expense incurred in controlling sewage effluent is well justified but that the value of additional expensive controls be carefully examined.

The slow progress in the past ten years in controlling eutrophication may thus be due to the lack of emphasis placed on reducing river inputs.

On the basis of this work, remedial actions should be aimed at reducing riverine inputs of phosphorus and particulate matter to Upper Bay and, hence, at reducing the rate at which phosphorus is deposited to the bottom sediments. Such action is predicated on the basis that riverine particulate matter is the main carrier of phosphate ion (some of which may be from sewage effluent) to the bottom sediments. As a supportive measure, 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<sup>-1</sup> in summer, a loading equivalent to

the technically feasible effluent concentration of  $0.3 \text{ mg P L}^{-1}$ . However, the main action should be a significant reduction in the riverine loading of particulate matter; in effect this means a reduction in erosional forces in the watersheds of the Trent and Moira Rivers. Erosion of soil is heavily dependent on agricultural practice along the Trent and Moira rivers. To this end, practices such as no-tillage agriculture, the retention of wilderness, and tree planting along riverbanks should be encouraged. Nutrient discharge from the increasing waterfront residential development should also be examined.

How rapidly will trophic conditions in Upper Bay respond (as defined, say, by lower concentrations of chlorophyll *a* and by visual improvement in water clarity, i.e. the depth of disappearance of a Secchi disk) to lower rates of sedimentation of riverine particulate matter and of phosphorus? Any significant reduction in the rate of reflux of phosphorus, say of 25-50%, may take 10 to 20 years to develop following institution of these concerted actions. This time scale is based on the deposition of approximately ten centimeters of new sediment of lower contaminant level. Of more immediate benefit would be an increase in the flushing rate in summer, to be accomplished by the pumping of cleaner (oligotrophic) Lake Ontario water, containing approximately  $10 \mu\text{g P L}^{-1}$ , into the extreme western end of Upper Bay. Note that even with a 50% decrease in the rate of reflux, a summer concentration of  $20 \mu\text{g L}^{-1}$  of available phosphorus in a warm water column would still render Upper Bay eutrophic. However, a decline in the rate of reflux may exceed that due simply to a decrease in the rate of sedimentation of phosphorus: a parallel decrease in the rate of sedimentation of readily metabolized organic matter could lead to higher redox potentials in the sediment and to lower rates of dissolution of iron and of phosphate ion to

the porewaters.

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## CAPTIONS FOR FIGURES

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 and Lower Bays.

FIG. 2. A representative room temperature Mössbauer spectrum of Upper Bay bottom sediment, here that of the 1-2 cm section of sediment core from station 873. This core was sectioned under nitrogen. Chi-squared is 647 for 494 degrees of freedom.

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.

FIG. 4. Elemental concentration profiles 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.

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**TABLE 1. Input of available phosphorus (mainly  $\text{HPO}_4$ ) in Upper Bay of Quinte. Units  $\text{kg P day}^{-1}$**

Sources	Sewage plants		In-place seds phosphate reflux	Riverine NAIP	
	pre-1972	1991		Fe-particle	soluble
Availability	high	high	100%	slow	<100%
June	170	19	$36 \pm 11$	$47 \pm 7$	<6
August	170	19	72 (est.)	$19 \pm 3$	<3
September	170	19	$72 \pm 22$	$29 \pm 4$	<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.

**TABLE 2. Rates of sedimentation and of reflux of phosphorus in Upper Bay**

Rate of sedimentation $\text{kg m}^{-2} \text{yr}^{-1}$ ( $\text{cm yr}^{-1}$ )					
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	

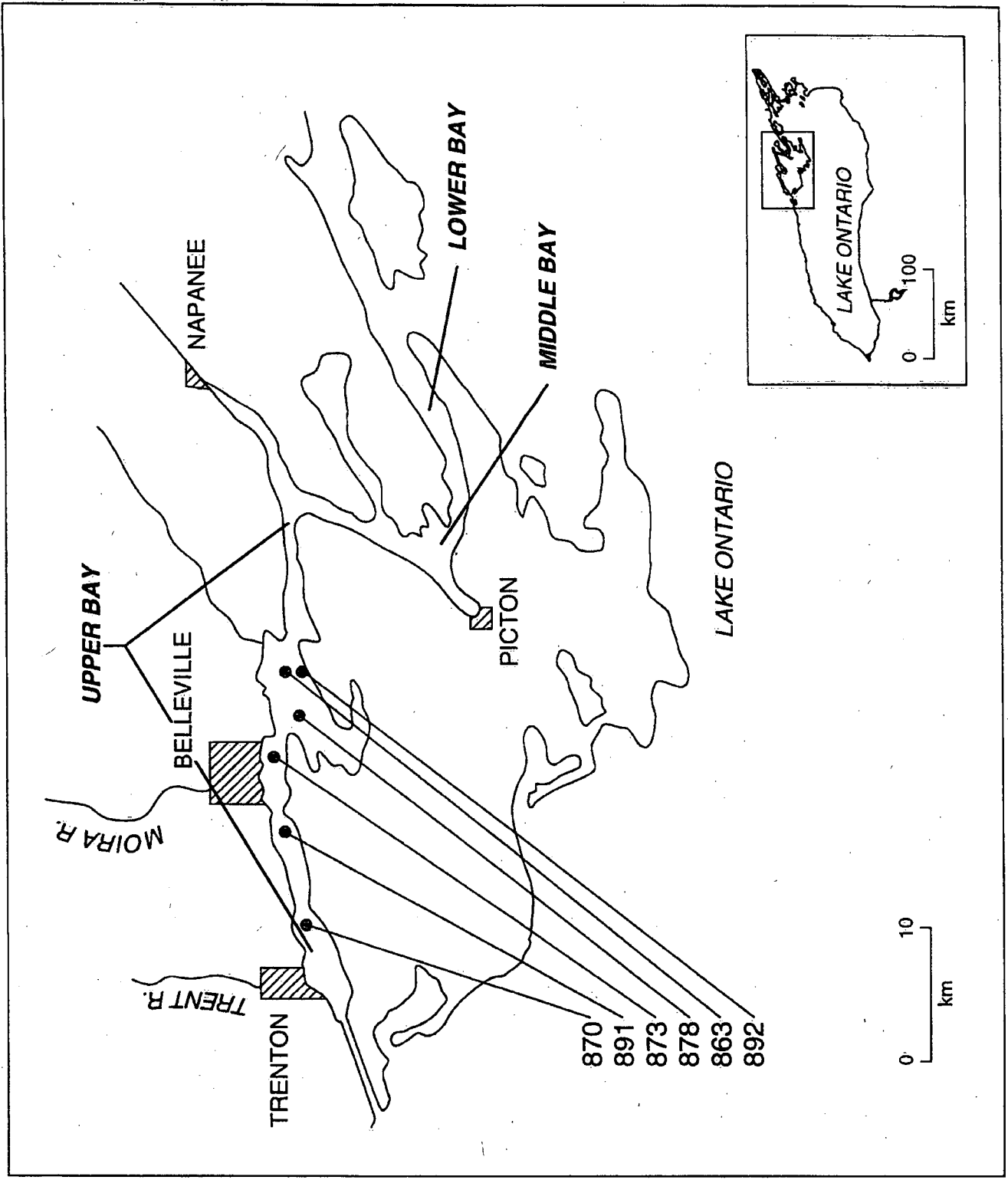
\*Sampled April 1991. \*\*Sampled October 1990.

\*\*\*Represents the average of replicate samples,  $\pm 5\%$ .

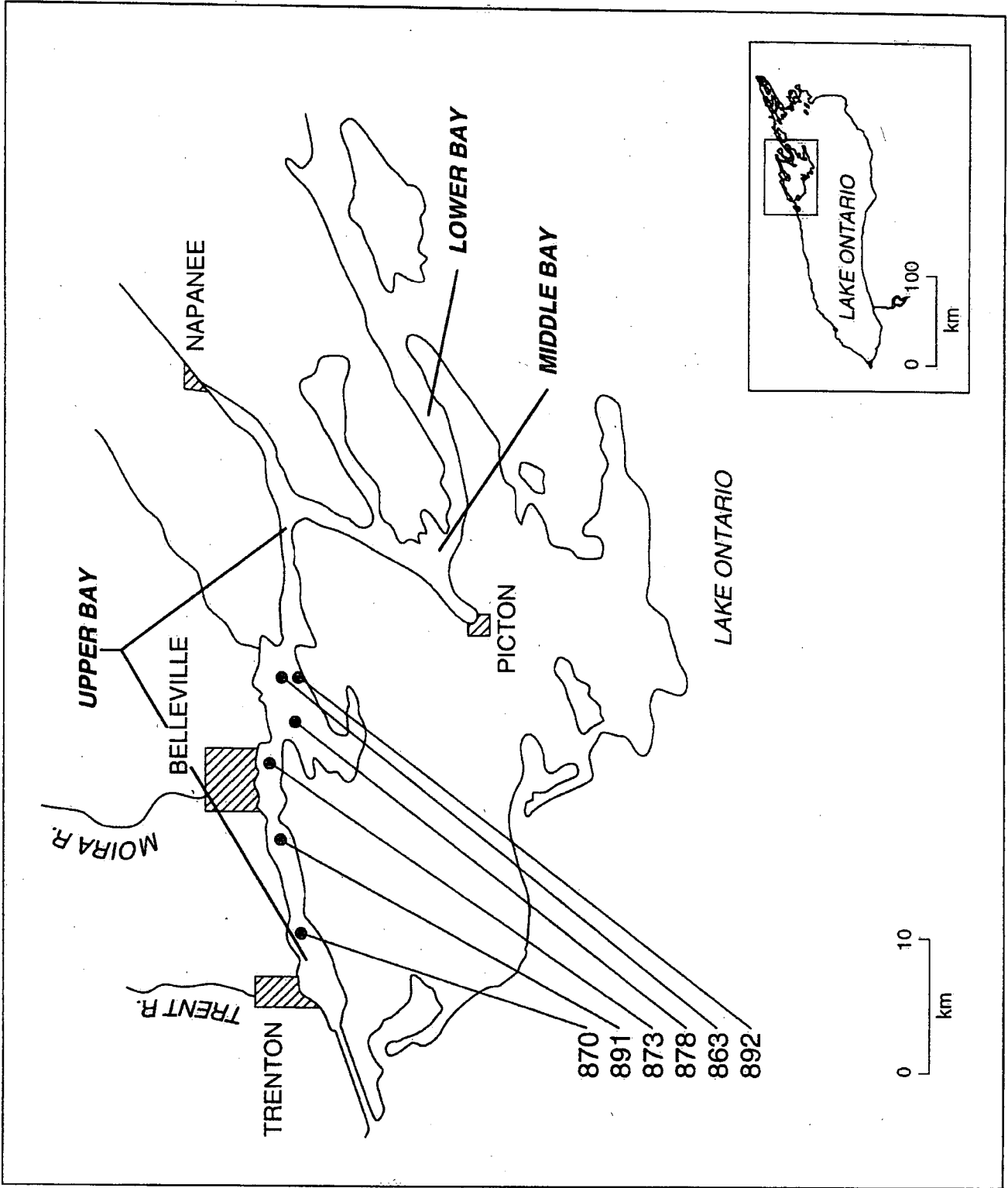
TABLE 3. Elemental concentrations (wt % dry sediment) and some ratios for suspended matter and sediments

Station, date	Fe <sup>2+</sup>	Fe <sup>3+</sup>	NAIP	ApP	OrgP	Fe <sup>3+</sup> /Fe <sup>2+</sup>	NAIP/Fe <sup>2+</sup>
<b>River particulate matter</b>							
MR Apr89	1.10	3.94	0.209	0.034	0.085	3.6	0.19
MR Apr90	0.56	2.15	0.121	0.027	0.077	3.8	0.22
TR Apr89	1.00	2.71	0.145	0.041	0.063	2.6	0.15
TR June89	0.58	1.75	<u>0.073</u>	0.024	<u>0.098</u>	3.0	0.13
TR Oct89	0.52	1.40	<u>0.066</u>	0.028	<u>0.130</u>	2.8	0.13
TR Apr90	0.53	1.67	<u>0.094</u>	0.033	<u>0.088</u>	3.2	0.18
TR May90	0.71	2.04	<u>0.087</u>	0.021	<u>0.129</u>	2.9	0.12
TR Oct90	0.49	1.32	0.080	0.029	n.m	2.7	0.16
<b>Suspended particulate matter in Upper Bay</b>							
870 Sep88	0.18	0.70	0.161	0.015	0.200	4.2	0.89
870 May89	0.16	0.80	0.123	0.006	0.116	5.0	0.77
878 Sep88	0.20	0.65	0.103	0.015	0.207	3.3	0.52
878 May89	0.17	0.80	0.324	0.006	0.138	4.6	1.91
873 Sep88	0.30	0.97	0.123	0.019	0.156	3.2	0.41
873 May89	0.15	0.80	0.141	0.005	0.126	5.1	0.94
892 Sep89	0.20	0.68	0.192	0.012	0.134	3.3	0.96
<b>Top centimeter bottom sediments of Upper Bay</b>							
870 Sep88	1.36	2.39	0.035	0.055	0.060	1.8	0.026
891 Apr91	0.86	2.29	0.044	0.047	0.051	2.2	0.055
878 Sep88	1.26	2.49	0.040	0.050	0.076	2.0	0.030
873 Sep87	1.20	2.55	0.032	0.044	0.066	2.1	0.026
873 Sep88	1.32	2.43	0.060	0.063	0.056	1.8	0.045

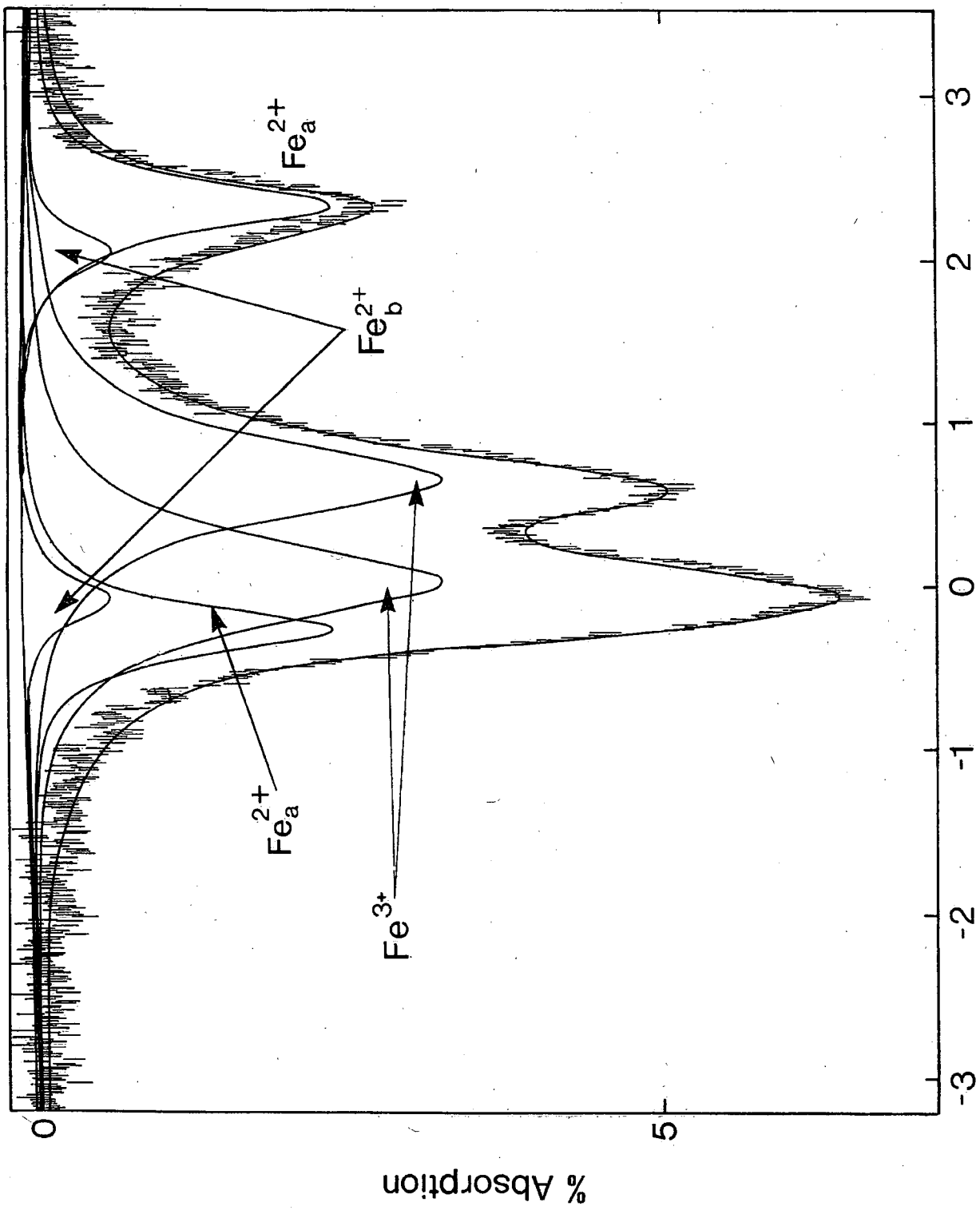
MR and TR represent the Moira and Trent Rivers. Riverine particulate matter was sampled at the estuaries. ApP is apatite phosphorus; its high insolubility renders it biologically unavailable. In all sediment cores, concentrations of NAIP decrease to  $0.035 \pm 0.005$  wt% P at 6 cm burial and to 0.030 wt% at 25 cm burial. n.m is 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.

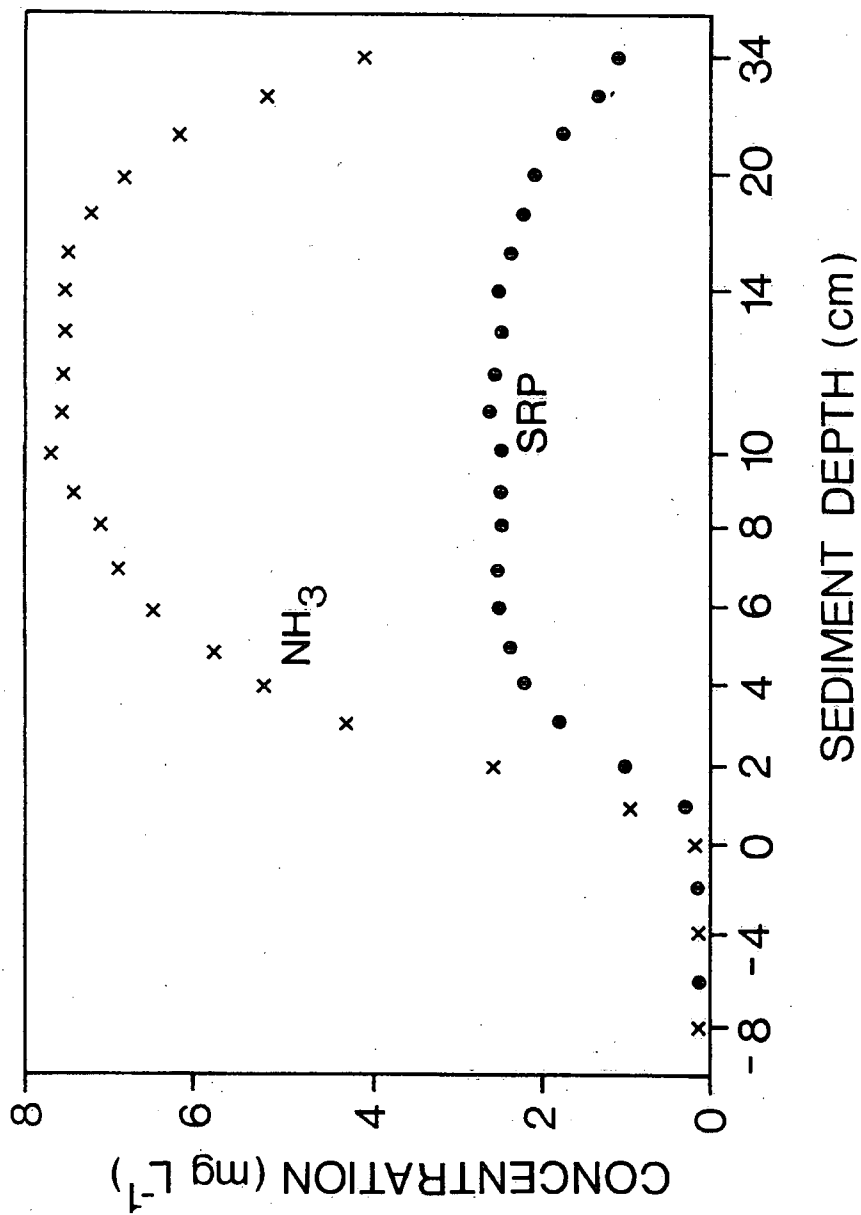


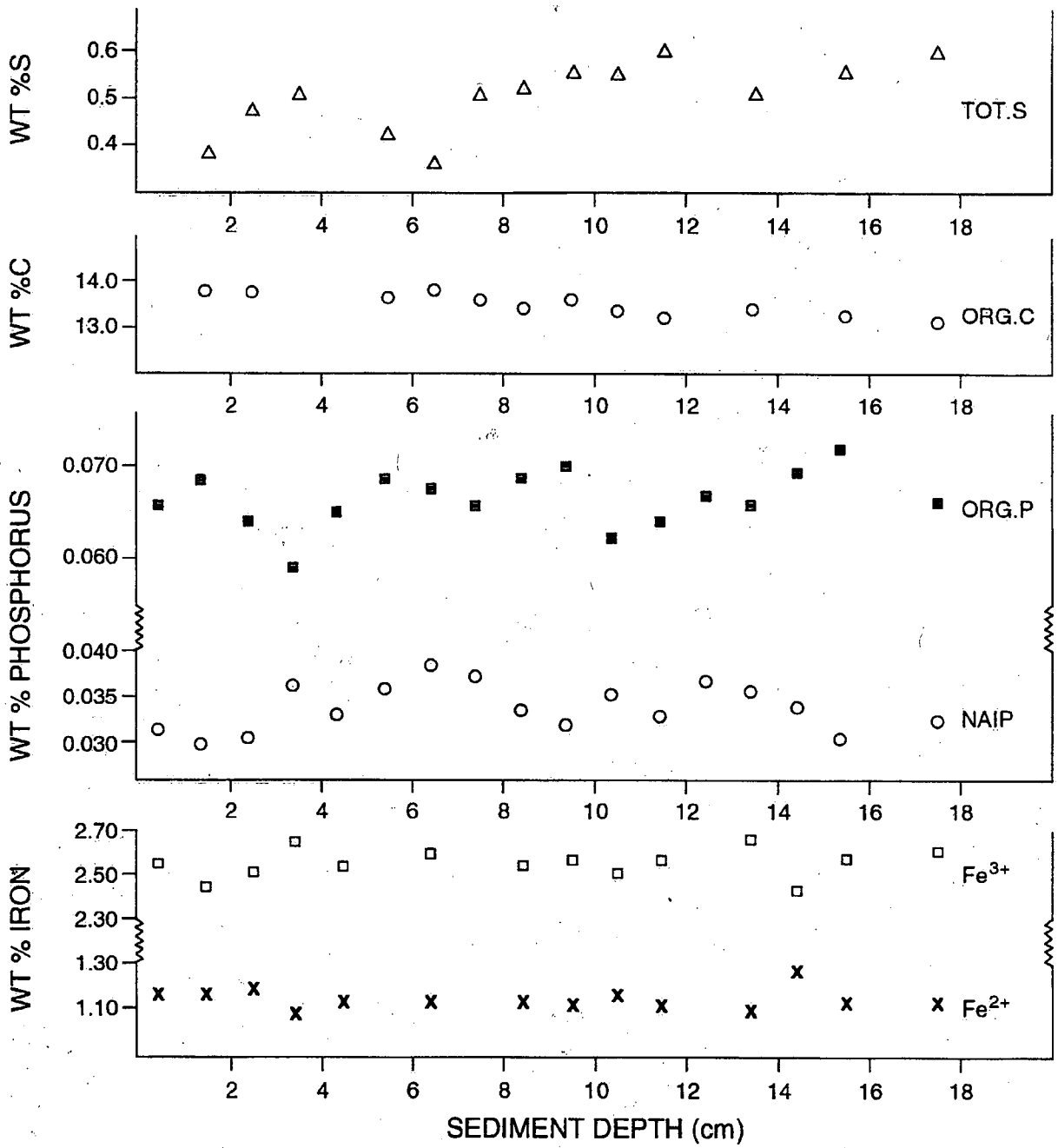
MANNING FIG. 1











MANNING  
FIG. 4.

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