

# FORMS OF IRON, PHOSPHORUS AND SULFUR IN THE SEDIMENTS OF THE EUTROPHIC BAY OF QUINTE, LAKE ONTARIO

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#### MANAGEMENT PERSPECTIVE

The Bay of Quinte, Lake Ontario, has been identified by the International Joint Commission (IJC) as an Area of Concern. The many municipal, industrial and recreational uses have been severely impaired for many years. Cultural eutrophication since the early 1800s has been Here, chronologically-dated sections of sediment severe. core collected from the Bay of Quinte describe the decline in water quality from the oligotrophy of precolonial times to the hypereutrophy of today. Increased inputs of phosphorus and sulfur have combined to generate sulfide ion in the anoxic sediments, the action of which is to mobilize Most of the available phosphorus is contained phosphorus. within the top 6 cm of the sediment column; depletion of this pool of available P will take at least 10 years even if no more phosphorus enters the Bay.

#### PERSPECTIVE DE GESTION

La baie de Quinte, sur le lac Ontario, a été désignée comme étant un secteur préoccupant par la Commission mixte internation-Son utilisation par les municipalités, par l'industrie et à ale. des fins récréatives est sérieusement compromise depuis plusieurs années. Depuis le début du XIX<sup>e</sup> siècle, l'eutrophisation y est très La datation de carottes de sédiments de la baie de prononcée. Quinte illustre la détérioration de la qualité de l'eau, soit le passage des eaux oligotrophes des temps précoloniaux aux eaux hypereutrophes d'aujourd'hui. Les déversements élevés de phosphore et de soufre ont engendré la présence d'ions sulfure dans les sédiments anoxiques, dont l'effet est de mobiliser le phosphore. La presque totalité du phosphore disponible est contenue dans les six centimètres supérieurs de l'échantillon cylindrique; l'épuisement de tout le phosphore disponible pourrait exiger au moins dix ans, même en l'absence de tout apport additionnel de phosphore dans la baie.

Increased inputs of phosphate and sulfate ions to the Bay of Quinte, Lake Ontario, since European settlement have generated significant concentrations of pyrite in the bottom sediments. The active layer of sediment in which phosphate ions are entrained and are continuously regenerated over the medium term (a few years) is confined to the -8 cm between the sediment-water interface and the sulfate-reducing horizon. Beneath this horizon, the sediments are not great sinks for nonapatite inorganic phosphorus, the main source of bioavailable phosphorus. Sulfide ions probably cause the desorption of phosphate ions from the surfaces of iron-bearing clays and oxides.

**KEYWORDS:** Iron, phosphorus, sulfur, sediments, eutrophication, Bay of Quinte.

#### ABRÉGÉ

Les déversements d'ions phosphate et d'ions sulfure dans la baie de Quinte, située sur le lac Ontario, depuis les débuts de la colonisation européenne, ont engendré des concentrations significatives de pyrite dans les dépôts de fond. La couche active des sédiments, d'où sont entraînés et où sont regénérés les ions phosphate à moyen terme (quelques années), correspond aux quelque huit centimètres supérieurs de la couche se situant entre l'interface eau-sédiments et la frontière sulfato-réductrice. Au-delà de cette frontière, les sédiments ne présentent pas d'accumulation significative de phosphate inorganique autre que l'apatite, la principale source de phosphore biodisponible. Les ions sulfure sont probablement responsables de la désorption d'ions phosphate de la surface d'argile ferreuse ou d'oxydes ferreux.

MOTS CLÉS : Fer, phosphore, soufre, sédiments, eutrophisation, baie de Quinte.

### INTRODUCTION

The Bay of Quinte is a highly eutrophic elongated Z-shaped embayment on the northern shore of Lake Ontario The impact of European colonial settlement on (Fig. 1). water quality in the Bay has been severe. The three main periods of migration were the arrival of approximately two thousand United Empire Loyalists in the Adolphus Reach area in 1771, the advent of the timber trade in ~1810, and the heavy voluntary migration of 1838-1850. The fossil chironomid (midge larval) succession in sections of sediment core retrieved from Adolphus Reach (Fig. 1) follows the decline in trophic status (Warwick 1980), from the oligotrophic of times to the currently highly eutrophic. precolonial Improved sewage treatment plant operation since 1975 and the reduction of phosphorus concentrations in household detergents in 1972 have led to reduced phosphorus and chlorophyll concentrations in the water (Robinson 1986). However, municipal and recreational usage of the water is severely impaired.

The bottom sediments of the Bay of Quinte are rich in organic carbon (Damiani & Thomas 1974), reflecting the high productivity in the nutrient enriched waters. The bottom waters from Middle Bay to Adolphus Reach are depleted in oxygen in summer (Minns & Johnson 1986). A knowledge of the forms and concentrations of iron, phosphorus and sulfur is important to an understanding of phosphorus regeneration in eutrophic systems. Here, the forms of these elements are determined in sections of a sediment core retrieved from Adolphus Reach (station 861A, 44°02'33"N 77°01'12"W, in 22 m water) and from within an estimated 100 m of Warwick's station (Warwick 1980). The aims of the work are (a) to relate the improved resolution of forms of iron, phosphorus and sulfur in the bottom sediments to cultural development and (b) to determine the depth of the active sediment layer and the pool of available phosphorus. Supportive data are presented for sediment cores from two other stations (Fig. 1) in the Bay, one nearby in Adolphus Reach (station AR2, 44°02'33"N 77°02'00"W, in 22 m water) and the other in Middle Bay (station 862, 44°05'39"N 77°04'27"W, in 8 m water).

# EXPERIMENTAL

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A 60-cm long core was retrieved from station 861A using a gravity corer in September 1988, care being taken to lower the corer gently into the sediment so as to minimize disturbance of the surface layer. The core was sectioned into 1-cm slices from 0 to 20 cm and into 2-cm slices from 20 to 60 cm. The sections were frozen immediately and freeze-dried on return to the laboratory. All sections were an olive-grey with no visual indication of a significant brown oxidized surface layer. The core from station AR2 was sectioned into 1-cm slices from 0 to 14 cm and that from station 862 into 1-cm slices from 0 to 15 cm and every 5 cm thereafter. All sediments were of a silty-clay composition (Damiani & Thomas 1974).

Suspended sediments were collected from the overlying water at, or near, these stations in August and October 1987, using a continuous-flow Westphalia centrifuge. The samples were frozen immediately and freeze-dried in the laboratory.

Mossbauer spectra were recorded at room temperature on a 512-channel spectrometer (Cryophysics MS103) calibrated against iron foil. Approximately  $10^6$  counts per channel were collected. The spectra were resolved assuming Lorentzian line shapes. Four doublets were invoked, two marking ferrous ions in two different octahedrally coordinated sites in clay and chlorite lattices, one marking ferric ions in clays and amorphous hydrated oxides, and a fourth marking pyrite, FeS<sub>2</sub>. The presence of pyrite was confirmed by optical microscopy (several sections contained abundant opaque framboids) and by X-ray diffraction. Peak areas and half-widths within a quadrupole doublet were constrained to be equal. Because the ferric iron and pyrite doublets are superimposable, the peak positions and halfwidths of the pyrite doublet were constrained in all computations using parameters determined for crystalline pyrite, i.e., isomer shift = 0.31 mm s<sup>-1</sup>, quadrupole splitting = 0.60 mm s<sup>-1</sup>, and half-width = 0.30 mm s<sup>-1</sup> (Manning et al. 1979). Values of chi-squared and visual examination of the computed fit were used as criteria of goodness of fit.

Concentrations of nonapatite inorganic phosphorus (NAIP), apatite-P and organically-bound phosphorus were determined after Williams et al. (1976). NAIP is an important source of bioavailable phosphorus (Williams et al. 1980); depletion of the pool of soluble reactive phosphorus causes desorption of phosphate ion from the surfaces of ferric (and other) metal oxides. Concentrations of organic carbon, inorganic carbon and total sulfur were measured using a Leco induction furnace (Kemp 1971). Concentrations of total iron were determined by bomb digestion and atomic absorption spectrometry (Agemian & Chau 1975). All concentrations are given as weight percent of dry sediment.

The Ambrosia (ragweed) pollen horizon, calibrated to ~1850 in south-eastern Ontario (McAndrews et al. 1973), was determined following Faegri & Iverson (1964). From the initial rise in pollen count (Table 1), the ~1850 horizon is placed at ~34 cm depth. Warwick (1980) placed the Ambrosia horizon in his cores at 37 cm. The pollen count is strongly diluted by the heavy mineral sediment load in the few years following major land clearance (Warwick 1980).

### RESULTS AND DISCUSSION

# Mossbauer spectral assignments

The Mossbauer spectra at first glance comprise two doublets at energies characteristic of ferrous and ferric ions in octahedral coordination (Fig. 2) (Coey et al. 1974). However, the high-energy ferrous absorption has, in all spectra, an obvious shoulder, hence all computations included a second weaker ferrous doublet. Further, significant misfits to the central absorption envelope in the spectra of sediments from 12 to 15 cm depth prompted the inclusion of a pyrite doublet (Manning et al. 1979, 1988); all computations converged successfully. The outer doublets with measured Mossbauer parameters of isomer shift (IS) = 1.12  $\pm$  0.01 mm s<sup>-1</sup>, quadrupole splitting (QS) = 2.69  $\pm$  $0.02 \text{ mm s}^{-1}$ , and half-width (HW) =  $0.38 \pm 0.02 \text{ mm s}^{-1}$ , and secondly, IS =  $1.05 \pm 0.05 \text{ mm s}^{-1}$ , QS =  $2.20 \pm 0.06 \text{ mm s}^{-1}$ , and HW (constrained) =  $0.38 \text{ mm s}^{-1}$ , clearly mark ferrous ions in two different lattice sites in clays and chlorite (Coey et al. 1974, Manning et al. 1984); the ratio of their respective intensities is ~5:1. The broad relatively intense central doublet with IS, QS, and HW values of 0.39  $\pm$  0.01 mm s<sup>-1</sup>, 0.68  $\pm$  0.01 mm s<sup>-1</sup>, and 0.61  $\pm$  0.02 mm s<sup>-1</sup>, respectively, marks ferric ions in clay minerals and amorphous hydrated oxides (Coey et al. 1974).

The inclusion of pyrite in the four-doublet scheme is supported on several grounds: (i) optical microscopy and X-ray diffraction patterns confirm the abundance of pyrite framboids in the 14 to 15-cm section and their scarcity in deeper sections of core; (ii) the visual fit on the highenergy limb of the main envelope is considerably improved; (iii) values of chi-squared are significantly lower for the four-doublet fit relative to the three-doublet, i.e., 478 versus 603 for the 13 to 14-cm section and 516 versus 673 for the 14 to 15-cm section; (iv) measured half-widths for the central "ferric" doublet in a three-doublet fit were considerably smaller for the 12 to 13-cm, 13 to 14-cm, and 14 to 15-cm sections (0.45 mm s<sup>-1</sup> versus the 0.62 mm s<sup>-1</sup> for the low-pyrite deeper sections), reflecting the relatively small half-widths of the pyrite absorptions; inclusion of the pyrite doublet removed this inconsistency; (v) the measured pyrite profile is very similar to that of total sulfur (Fig. 3). The Mossbauer spectra remained unchanged after treatment with 0.2 M HCl, suggesting that FeS compounds are present in negligible amounts.

The iron profiles for core 861A (Fig. 3) can be divided into four ranges, as a function of sediment depth (and, hence, of time), based on significant differences in the distributions of the iron compounds and on human activities around the Bay. Also, these changes in the iron distributions coincide well with changes in the distributions

of phosphorus and sulfur. The ranges are: (a) from 0 to 8-cm depth (from the present to ~1960). Small amounts of ferric iron are reduced, but redox potentials are insufficiently low to reduce large amounts of sulfate, consequently pyrite production is weak. Phosphate ion is heavily regenerated from deeper sections within this range (Fig. 4). (b) from 8 to 26 cm-depth (from 1960 to ~1880). Pyrite production is very significant, reflecting reduction of ferric and sulfate ions under conditions of steadily increasing (with real time) concentrations of organic carbon and sulfur (Fig. 4). Concentrations of ferrous ions (in clay minerals and chlorite) remain constant, consistent with the conservative (inert) behaviour of the minerals (Kemp & Thomas 1976, Kemp et al. 1976). Concentrations of NAIP are remarkably low due to massive regeneration in the top 8 cm (Fig. 4). (c) from 26 to 40-cm depth (~1880 to ~1820). Attention is drawn to the inverse relationship between  $Fe^{2+}$ and Fe<sup>3+</sup> ions marked by the significant "blip" at 34 to 36-cm depth (Fig. 3). It is unlikely that this is due to the reduction of ferric ions and precipitation of the ferrous ions, but rather to a shift in the clay:ferric oxide ratio in suspended particulates entering the Bay. This sharply-defined ferrous peak (Fig. 3) is nearly coincident with the Ambrosia horizon, which marks the major episode of The accelerated runoff of snowmelt and land clearance. heavy rains, following destruction of the forests, would lead to increased erosion of clay from river banks, whereas

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ferric oxides in sub-surface soil horizons would remain relatively undisturbed. Significantly, the fairly steady organic carbon profile of precolonial times (Fig. 4) shows an initial drop at 34 to 36-cm depth. (d) from 40 to 60 cm (~1820 to ~1760). Ferrous:ferric ratios gradually decrease with real time (except for the sharp Fe<sup>3+</sup>-NAIP discontinuity at 48 to 50 cm, Figs. 3, 4), reflecting increasing inputs of ferric iron to the Bay and to the sediments. This may be related to early settlement on the Bay. The Mossbauer spectra show no significant indication of the ferromanganese nodules observed by Warwick (1980) at ~40 cm depth (Fig. 3). Minor amounts of iron are therefore present in nodules. Pyrite concentrations are very low, consistent with low production of organic matter in precolonial times (Warwick 1980).

The pyrite profile in core 861A is clearly reproduced in the cores from stations AR2 and 862: pyrite forms at the expense of ferric iron (Table 2). The three cores define a large area of Bay of Quinte sediment in which sulfide generation is an important diagenetic process. The initial rise in pyrite production, at ~30 cm depth in 861A, at ~14 cm in AR2, and at ~40 cm in 862, is probably a reasonable indicator of the relative rates of sedimentation at the three sites. Oxygen concentrations in the bottom waters are severely depleted in summer (Minns & Johnson 1986).

The total phosphorus concentration profile (Fig. 4) is very similar to that of Warwick (1980) but shows more structure in the 26 to 46 cm range. Most of the structure in the total phosphorus profile is due to NAIP (Fig. 4). The sharp phosphorus peak at 48 to 50 cm coincides reasonably in position, but not in intensity, with Warwick's (1980) 51.5 cm peak. The organic phosphorus profile (Fig. 4) reflects the gradual increasing productivity with time in the Bay; the minimum at 34 to 36 cm depth is consistent with Warwick's suggestion that productivity decreased due to heavy mineral suspension in the water column following major land clearance. The organic phosphorus and apatite phosphorus fractions are relatively unavailable (Williams et al. 1980), due to incorporation into organic esters and phospholipids and to the high insolubility of apatite.

The NAIP contained within the top 8 cm of sediment represents a significant pool of potentially available phosphorus. The phosphate ion is probably adsorbed on the surfaces of clay minerals, hydrated ferric oxides and calcium carbonates, the whole further bonded to organic matter via carboxyl groups (Buffle & Altman 1987). The surfaces of iron-bearing clays and ferric oxides are probably readily "poisoned" by sulfide ions, causing reduction of iron and

dissolution of phosphate ions. The source of the NAIP lies in the combination of deposition in falling detritus, significant medium-term (a few years) regeneration from deeper sections of the 0 to 8-cm fraction and minor long-term regeneration from deeper sections of the core. (Short-term regeneration is that phosphorus released within days or weeks of deposition of fresh organic matter.) NAIP is severely depleted in the 8 to 20-cm section of core (Fig. 4) in which sulfide production is high. The 0 to 8-cm fraction therefore represents the active layer, in terms of phosphorus regeneration, in the sediments around station 861A. In support of this, our total phosphorus profile (Fig. 4), is not displaced to 4 cm greater depth relative to the total phosphorus profile of Warwick (1980); 4 cm corresponds to 16 years time difference in coring (1972 versus 1988) and a sedimentation rate of ~2.5 mm yr<sup>-1</sup>. Further, the phosphorus profiles show no response to decreased phosphorus loadings to the Bay (nor to lower water concentration of phosphorus) since 1975 (equivalent to 3 cm deposition). The organic phosphorus component seems refractory with respect to sulfide generation (Fig. 4).

Based on the depths of their respective sulfatereducing horizons, similar thicknesses of active surface layers of ~8 cm are inferred for stations 862 and AR2 (Table 2). The total sulfur profile (Fig. 3), as a function of sediment depth, is similar to profiles measured for several lakes in the northern United States (Mitchell et al. 1988). From reasonably constant precolonial values of ~0.25% S and 3% of total iron, concentrations of total sulfur and of pyrite increase rapidly to a maximum at ~14 cm burial (Fig. 3). For the 13 to 14-cm section, based on 27% of total iron being in pyrite and a total iron content of 3.3 wt%, the concentration of pyrite-S is ~1.0 wt%, or ~50% of total sulfur. Most of the remaining suflur is probably organically bound (Landers & Mitchell 1988, Mitchell et al. 1988). Treatment with 0.2 M HCl showed that FeS compounds are minor phases.

Preliminary porewater data collected by us indicate the absence of nitrate ion ( $0.3 \text{ mg L}^{-1}$ ) but abundant ammonia (-2 mg L<sup>-1</sup>) in surficial sediments from a nearby location in Middle Bay, confirming the strongly reducing properties of the bottom sediments. Redox potentials are sufficiently low, after 6 cm burial, that sulfate reduction becomes significant (Fig. 3). The increases in concentrations of total sulfur and of pyrite, relative to the precolonial background, arise from anthropogenic influences on the Bay, firstly from the increased deposition of sulfate ion to the waters of the Bay of Quinte and, secondly, from

the more strongly reducing conditions generated in the buried sediments by the heavier deposition of metabolizable carbon compounds (Berner 1984). Sulfate concentrations in Lake Ontario have risen from 10 mg  $L^{-1}$  to 27 mg  $L^{-1}$  since 1900 (Dobson 1984) and a commensurate increase has undoubtedly occurred in the Bay of Quinte, largely as a consequence of the burning of fossil fuels. The Moira River drains an area of extensive sulfide mineralization (Mudroch & Capobianco 1980). Increased nutrient loadings to the Bay stimulated the growth of aquatic plants and the increased deposition of metabolizable organic matter to the bottom sediments; this organic matter was removed more rapidly from the oxic zone under higher rates of sedimentation (Warwick Bottom sediments of similar age in the eutrophic 1980). Kingston Basin of Lake Ontario and in the mesotrophic Central Basin of Lake Erie (Manning et al. 1984, Kemp et al. 1976) contain negligible amounts of pyrite, even though the hypolimnion waters are severely depleted of oxygen in summer (Burns & Ross 1972, Dobson 1984). Pyrite formation is extensive in the sediments of two highly eutrophic lakes (Manning et al. 1979, 1988). The waters of the Bay of Quinte were probably eutrophic in ~1880 (30 cm burial).

Concentrations of inorganic carbon decline from 0.70 wt% in the 0 to 1-cm section to -0.2% in the 19 to 20-cm section and to -0.1% at 30 cm depth; most of the carbon is therefore organic (Fig. 4). Beneath the Ambrosia

horizon (depths 33 cm), the fairly uniform organic carbon concentrations clearly mark precolonial deposition (Fig. 4). The significant break at 34 to 36 cm coincides with the minimum in organic phosphorus concentrations (Fig. 4) and is consistent with Warwick's (1980) suggestion that heavy mineral suspension in the water column reduced productivity. The organic carbon 'break', the organic phosphorus minimum and the sharp  $Fe^{2+}$  peak (Fig. 3) all indicate that the 34 to 36-cm section best marks the ~1850 horizon.

# General discussion

Chronologically, from the major European settlement of 1838 to 1850, the following sequence of human activities and sedimentary horizons is presented. With the clearing of the forest, the rate of runoff of snowmelt and of heavy precipitation increased, causing swollen rivers and increased erosion of surface soils and river banks. On the other hand, the subsurface (~30 cm deep) Podzol iron horizon remained relatively uneroded. This differential erosion is marked by the temporary  $Fe^{2+}$  (clay) peak at the 34 to 36-cm depth (Fig. 3). At this time also, the concentrations of organic carbon and organic phosphorus in the detritus on the bottom of the Bay changed (Fig. 4). With increasing nutrient load and with the initial erosional pulse considerably reduced, productivity in the Bay increased leading to higher concentrations of NAIP and of organic phosphorus in the bottom sediments (34 to 20 cm burial). Concentrations of metabolizable organic carbon in the falling detritus were also increasing and sulfide was being generated in increasing concentrations in the bottom sediments (after ~8 cm burial), as a consequence of which NAIP in the sediments decreased (30 to 20 cm burial). As eutrophication and increasing inputs of sulfate became firmly established, the generation of sulfide became the dominant diagenetic process in the bottom sediments, leading to the almost complete regeneration and removal of NAIP from the sediment column (20 to 8 cm burial). The released phosphate ion migrated upward and was reprecipitated near the sediment-water inter-The maximum pyrite concentration (at ~13 to 14 cm face. burial) bears no direct relation to any given human activburial of the near-surface sediments to ~14 cm will ity: produce equally high or possibly higher values of pyrite.

The sharply defined NAIP peak at 48 to 50 cm depth and the broader peak centred at 42 to 44 cm depth (Fig. 4) may mark earlier settlement, notably the 1771 arrival of Empire Loyalists in the Adolphus Reach area and the ~1810 advent of the timber trade. In general, the maxima and minima in concentrations of NAIP and of  $Fe^{3+}$  are coincident (Figs. 3, 4), even in the pre-1850 era, e.g., the 48 to 50 cm peaks. The refractory nature of the ~0.025% NAIP carried to 60 cm depth in the precolonial sediments and to 20 cm depth in the more recent sulfide-rich sediments (Fig. 4) suggests that this NAIP fraction, ultimately derived from soils, was not readily available for algal growth in the oxygenated water column.

The net binding capacity of bottom sediments in the vicinity of station 861A is ~0.025% NAIP (Fig. 4), this being the amount of NAIP carried to depth. Release of phosphate ion to the porewaters from this refractory fraction may be considered long-term. The concentration of NAIP in the top 3 cm of bottom sediment is 0.12% (Fig. 4). The concentration of NAIP in the suspended sediment collection from several stations in Adolphus Reach and Middle Bay (station 862) is also ~0.12%. The current annual rate of sedimentation at station 861A is ~200 g m<sup>-2</sup> (Warwick 1980), equivalent to ~240 mg NAIP m<sup>-2</sup>. Approximately 80% of this is regenerated over the top 8 cm of sediment, yielding an average medium-term rate of release of ~200 mg NAIP  $m^{-2}$  yr<sup>-1</sup>, or ~0.55 mg NAIP  $m^{-2}$  day<sup>-1</sup>. An assumed loss of  $1 \text{ mg m}^{-2} \text{ day}^{-1}$  from long-term release from deeper sediment is equivalent to the annual loss of a 1 cm section containing 0.035 wt% NAIP; this is not sustainable, particularly if much of the deeply buried NAIP is relatively refractory, e.g., adsorbed on better crystallized ferric oxides of soil origin. The annual average rate of release is unlikely to greatly exceed 0.55 mg NAIP  $m^{-2}$  day<sup>-1</sup>, however the rate of release will be greater in the warmer water of summer. This

rate of release is not inconsistent with other calculated values of 0 to 14 mg P m<sup>-2</sup> day (Minns et al. 1986), based on modelling methods.

A positive aspect of sulfide generation is that the deposited NAIP is mainly regenerated over the medium term, i.e., over ~30 years: beneath 8 cm sediment depth, the concentration of NAIP is lower than that in Great Lakes sediment. Regeneration from these deeper sediments is unlikely to be excessive, particularly because the ~0.02% NAIP may represent the refractory residue of soil ferric oxide-NAIP compounds; this residue is also unavailable in the suspended sediment of river and the Bay. Sulfide production will still occur as the current surface sediments are buried to a depth of 8 cm, however, a significant reduction in future phosphorus loading would lead to lower inputs of organic carbon and to lower levels of sulfide production. Drastic reductions of available phosphorus inputs to the Bay, say through diversion of sewage and agricultural phosphorus to Lake Ontario, would not be immediately followed by equally significant reductions in regenerated phosphorus; the time lag in response would be equivalent to the time required for the elimination of NAIP from the current 8 cm-thick active layer, probably 10 to 30 years.

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- FIG. 1. Diagram showing sampling sites 861A and AR2 in Adolphus Reach and 862 in Middle Bay.
- FIG. 2. Representative Mossbauer spectrum of Bay of Quinte sediment, in this case section 14 to 15 cm from station 861A. Chi-squared = 516 for 491 degrees of freedom.
- FIG. 3. Plots of concentrations of  $FeS_2$ ,  $Fe^{3+}$  and  $Fe^{2+}$  and total sulfur as functions of sediment depth for core 861a. Total iron concentration is 4.2 ± 0.2 wt% averaged for several sections.
- FIG. 4. Plots of concentrations of total phosphorus, NAIP, organic P and organic C as functions of sediment depth. Concentrations of inorganic carbon are minor relative to organic carbon. Concentrations of apatite are ~0.0450% P between 0 and 40 cm and ~0.060% P in the precolonial sediments.

TABLE 1. AMBROSIA POLLEN COUNT AND COUNT PER GRAM (x10<sup>-3</sup>) As a function of depth in core 861A

55	2 2 9
19- 16	44-0.
18-19	40-42
210	4
62	1.2
17-18	38-40
192	3
58	1.3
16-17	36-38
150	5
49	1.5
15-16	34-36
188	2
62	0.6
14-15	32-34
174	13
77	2.9
13-14	30-32
116	34
44	5.4
12-13	28-30
196	54
77	9.5
11-12	26-28
138	100
44	27
10-11	24-26
141	75
47	14
9-10	22-24
79	151
50	45
8-9	20-22
101	152
50	49
gm-1	gm-1
cm	cm
count	count
count	count
Depth.	Depth.
Pollen	Pollen
Pollen	Pollen

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Station AR2				Station 862					
Depth cm	Fe <sup>2+</sup>	Fe <sup>3+</sup> wt%	Fe(S <sub>2</sub> )	PŢ	Depth cm	Fe <sup>2+</sup>	Fe <sup>3+</sup> wt%	Fe(S <sub>2</sub> )	SŢ
0-1 4-5 5-6 6-7 8-9 9-10 10-11 11-12 12-13 13-14	26.5 27.2 26.9 25.6 26.1 25.7 25.9 24.6 25.6 26.4	68.8 60.8 60.7 63.8 55.2 53.6 56.6 61.0 63.8 66.3	4.7 12.1 12.4 10.7 18.7 20.7 17.5 13.5 10.7 7.4	0.27 0.17 0.05 0.03 0.03	0-1 10-11 11-12 13-14 14-15 19-20 24-25* 29-30 30-40	27.7 27.2 25.9 27.8 26.8 24.9 25.0 26.0 26.0 26.7	68.3 68.6 66.6 65.1 59.0 57.2 53.9 56.9 60.9	4.0 4.2 7.5 7.2 14.2 14.9 21.2 17.1 12.5	0.7 0.9 1.0 1.7

TABLE 2. CONCENTRATIONS OF IRON AND PHOSPHORUS IN BAY OF QUINTE SEDIMENTS

AR2 sediments contain 3.4 wt% Fe and 862 contain 3.15 wt% Fe. \*Approximately 40% of  $S_T$  is in FeS<sub>2</sub>.





NOITAROSAA %

F12,2



SEDIMENT DEPTH cm

F16.3



SEDIMENT DEPTH cm

1G.4





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