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Sediment Phosphorus Cycling in a Managed System Irondequoit Bay, N.Y.

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Sediment phosphorus cycling in a managed system

Irondequoit Bay, N.Y.

A Thesis

Presented to the Graduate Faculty

of the Department of Biological Sciences

at the State University of New York College at Brockport in

Partial Fulfillment for the degree of Master of Science

by

Daniel J. White

December 2006

THESIS DEFENSE

Daniel White

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Abstract

The current status of internal phosphorus loading was evaluated in Irondequoit Bay, NY, an embayment of Lake Ontario. Sediment core incubation experiments and phosphorus water column profiles were used to quantify the release rate of phosphorus from the deep-water sediments of Irondequoit Bay during summer periods of low hypolimnetic oxygen. The top 25 cm of sediment cores collected monthly from May 2004 through September 2004 were analyzed for total phosphorus, total manganese, total iron, and total aluminum. Phosphorus fractionation of the sediment cores was determined through sequential extraction. Phosphorus water column data collected during the summer of 2003 and 2004 yielded an average release rate of 8.15 mg P/m²/day. Sediment core incubation experiments yielded an average release rate of 2.89 mg P/m²/day. Predictive models yielded estimates of phosphorus release rates ranging from 0.11 to 31.56 mg P/m²/day. Total phosphorus concentrations in the sediment averaged 1.389 ± 0.150 g P/kg dry wt. Sequential extraction of phosphorus fractions from the top 25 cm of deep-water sediment revealed that approximately 25% of phosphorus was stored in a redox-sensitive form, most likely sorbed onto iron and manganese oxyhydroxides. Iron and manganese profiles from the water column indicated that manganese from the sediment was cycling with phosphorus into the overlying waters, while iron did not demonstrate evidence of cycling. Iron was kept out of solution by low concentrations of oxygen that had been maintained in the hypolimnion through a summer oxygen supplementation program on Irondequoit Bay.

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Introduction

Phosphorus is generally recognized as the limiting nutrient controlling algal growth in most freshwater systems (Wetzel, 2001). A common goal of many lake restoration efforts is the reduction of phosphorus concentrations in the water column. Lowering phosphorus concentrations in the water column can reduce algal growth, thereby lowering productivity and the trophic status of the lake and result in a successful lake restoration (Ostrofsky *et al.*, 1989).

Phosphorus reduction programs often target sources of phosphorus that are external to the lake; however, some lakes have been slow to respond to these reductions in their external phosphorus load (e.g. Boström *et al.*, 1988; Ostrofsky *et al.*, 1989). The persistence of high phosphorus concentrations within lakes with reduced external loading might be the result of phosphorus released from the lake's sediments. Lake sediments are generally sinks for phosphorus (Baldwin *et al.*, 2002; Boström *et al.*, 1988; Larsen *et al.*, 1981). In fact, some lake sediments may retain 90% or more of the lake's annual incoming phosphorus load, although 20-50% is more common (Larsen *et al.*, 1981). Differences in sediment phosphorus retention between lakes result from differences in lake morphometry, water renewal rates, history of external loading, and edaphic characteristics of the drainage basin (Boström *et al.*, 1988).

Besides being a sink for phosphorus, sediments may also act as a source of phosphorus to the water column through a group of processes collectively known as internal phosphorus loading. In lakes with recently reduced external phosphorus loads, internal phosphorus

loading can become the lake's dominant source of phosphorus and thereby control average lake water phosphorus concentrations (Nürnberg, 1984; Pettersson, 1998). In this way, phosphorus "recycled" from the sediments may support the lake's trophic status (Rydin, 2000).

There exists no single theory that can explain all phosphorus exchanges between sediment and the water column (Boström *et al.*, 1988). The release of phosphorus from the sediment may occur through several biotic and abiotic mechanisms (Ostrofsky *et al.*, 1989; Baldwin *et al.*, 2002; Boström *et al.*, 1988; Khoshmanesh *et al.*, 2002). Lakes most likely to have high rates of internal loading are eutrophic and alkaline with high concentrations of iron-bound phosphorus and low organic content in their sediments (Ostrofsky *et al.*, 1989). The extent to which phosphorus is released is partially dependent upon how it is bound to the sediment, which depends upon the pathway from which it was incorporated into the sediment (Baldwin *et al.*, 2002).

Irondequoit Bay and phosphorus pollution

Irondequoit Bay, adjacent to Rochester in northeastern Monroe County, New York, is one of the larger embayments along the southern coast of Lake Ontario (Fig. 1) and has a long history of human use and settlement. Degraded water quality, foul odors, and floating mats of algae and vegetation were first reported in the early 1900s (Environmental Health Laboratory, 2001; Bannister and Bubeck, 1978). Excessive phosphorus loading was believed to be the cause of degraded conditions in the bay, and restoration efforts have focused on the reduction of external and internal phosphorus loading (Bannister and Bubeck, 1978). Phosphorus loading to the Bay via Irondequoit

Creek was significantly reduced by the diversion of wastewater effluents to the Frank E. Van Lare Sewage Treatment Plant (Environmental Health Laboratory, 2001). In another effort to reduce phosphorus inputs to the Bay, all Combined Sewer Overflows (CSOs) were eliminated from the Rochester system by 1986 (Environmental Health Laboratory, 2001). Despite these efforts to reduce the external loading of phosphorus, Irondequoit Bay remained in a hyper-eutrophic state.

The Irondequoit Basin Framework Plan, developed in the 1980s by Monroe County, set the goal of achieving a stable mesotrophic state in Irondequoit Bay. In order to achieve this goal, nonpoint source pollution was investigated. The primary source of nonpoint pollution, urban runoff, was addressed through the Irondequoit Creek Empire Wetlands Nutrient Management Project (Environmental Health Laboratory, 2001). Another major nonpoint source of phosphorus pollution was occurring from the Bay's sediments (internal loading) (Environmental Health Laboratory, 2001). After exploring several restorative techniques aimed at controlling internal loading, sediment sealing with alum was decided upon as the most cost effective (Environmental Health Laboratory, 2001). In 1986, under the Phase II study, alum was applied to the areas of the bay where water depth was > 6 m (Environmental Health Laboratory, 2001). The alum treatment reduced phosphorus levels in the water column by 60 to 75% (Environmental Health Laboratory, 2001). Despite the initial success of the alum application, additional measures were required to limit internal loading during periods of low hypolimnetic oxygen levels.

In 1993, the Irondequoit Bay Oxygen Supplementation Project was developed to prevent oxygen depletion in Irondequoit Bay during the summer. Oxygen supplementation seeks to control phosphorus levels by both chemical and biological means (Environmental Health Laboratory, 2001). During the summer months, increasing the oxygen content of deep water areas decreased the reductive dissolution of iron oxides in the sediment. This prevented the movement of iron, and its associated phosphorus, from the sediment to the water column. Biological control of algae was achieved by maintaining higher dissolved oxygen levels in the metalimnion; this produced an environment that was more conducive to algal-grazing zooplankton (Environmental Health Laboratory, 2001).

Initially oxygen levels in the metalimnion were maintained at 4 to 5 ppm (Environmental Health Laboratory, 2001). This proved to be expensive, and it was found that a lower metalimnion oxygen level would maintain a sufficiently oxidizing environment (Environmental Health Laboratory, 2001). After 1998, oxygen levels were maintained at 0.5 to 1.5 ppm of oxygen in the metalimnion (Environmental Health Laboratory, 2001).

Maintaining relatively low levels of oxygen in the metalimnion may add a measure of biological control of phosphorus pollution by creating a *Dapina* protection zone (Environmental Health Laboratory, 2001). The *Dapina* protection zone is an area with sufficient oxygen to support large algal-grazing zooplankton, such as *Daphnia sp.*, but without sufficient oxygen to support planktivorous fish (Environmental Health Laboratory, 2001). This would create a large population of algal-grazing zooplankton that would control the growth of algae through top-down biological control. As the

zooplankton move out of the *Dapina* protection zone into the productive waters of the epilimnion, they are grazed upon by planktivorous fish. Two of the most common planktivorous fish in the open waters of the Bay are alewives (*Alosa pseudoharengus*) and emerald shiners (*Notropis atherinoides*), which migrate out of the Bay into Lake Ontario in late summer. As these fish migrate out of the Bay, they export the biomass that they have consumed and in this way transport phosphorus from the Bay to Lake Ontario (Environmental Health Laboratory, 2001).

The goal of this study is to evaluate the current effectiveness of the alum treatment applied in 1986 and the benefits of continuing oxygen supplementation. To achieve this goal, physical and chemical parameters in the water column of Irondequoit Bay were measured throughout the summer months of 2003 and 2004. I have also sought to quantify and characterize the phosphorus in the deep-water sediments of Irondequoit Bay through sequential extraction of sediment phosphorus. A better understanding of phosphorus cycling in Irondequoit Bay will allow more effective management decisions in the future.

Literature Review

Incorporation of phosphorus into sediments

Dissolved phosphate may be abiotically incorporated into the sediment through adsorption (sorption) and precipitation/coprecipitation reactions (Holtan *et al.*, 1988). Sorption reactions involve the removal of phosphate from solution to a solid and may be either physically or chemically mediated (Baldwin *et al.*, 2002). Physically mediated

sorption results in the formation of an outer sphere complex, whereas chemically mediated sorption (chemisorption) results in an inner sphere complex. Physically mediated sorption entails a much smaller decrease in energy than does chemisorption and is, therefore, more easily reversible (Baldwin *et al.*, 2002). Chemisorption is usually thought to be partly or completely irreversible (Baldwin *et al.*, 2002). Sediment surface coatings consisting of the oxides and oxyhydroxides of iron and aluminum are the most important sites for anion adsorption (Baldwin *et al.*, 2002). On sediment mineral surfaces, orthophosphate becomes covalently bound to the metal centre through ligand exchange with surface hydroxyl groups resulting in an inner sphere complex with the metal ion (Baldwin *et al.*, 2002).

Manganese minerals, which also form oxides and oxyhydroxides, may adsorb orthophosphate in the same manner as iron and aluminum (Boström *et al.*, 1988). However, due to a less negative surface charge at common ambient sediment pH values, manganese minerals have less affinity for phosphate than iron and aluminum (Baldwin *et al.*, 2002). When high phosphorus concentrations cause most of the aluminum and iron surfaces to become saturated, manganese oxides may become an important sink for phosphorus (Yao and Millero, 1996).

Another means by which phosphorus may leave the water column and enter the sediment is through precipitation reactions (Baldwin *et al.*, 2002). A precipitation reaction involves the formation of an insoluble compound by the combination of soluble ions in solution. Phosphatic minerals may form authigenically (within the sediment) through the

precipitation of phosphates with metal ions (Baldwin *et al.*, 2002). The metal ions most commonly associated with these mineral formation in natural water bodies are Ca^{2+} and Fe^{3+} , and to a lesser extent Fe^{2+} (such as forms the mineral vivianite) (Baldwin *et al.*, 2002, and references therein). Baldwin *et al.* (2002) suggested that these authigenically formed mineral phases were a small contributor to the mineral phosphate compounds found within lake sediments, which were for the most part allogenicly derived from adjacent geological deposits and surface soils. However, Baldwin *et al.* (2002) pointed out that Ruttenberg (1992) found that authigenic calcium apatite was more soluble than allogenic apatite of igneous or metamorphic origin and was more likely to be a source of bioavailable phosphorus.

Calcite, formed by the combination of calcium and carbonate ions, can sorb/co-precipitate phosphorus (Baldwin *et al.*, 2002). Calcite coprecipitation may be a substantial mechanism of phosphorus removal from highly calcareous lakes (Boström *et al.*, 1988; Baldwin *et al.*, 2002). Boström *et al.* (1988) suggested that in several calcium-rich lakes, calcium might play a more important role in the exchange of phosphorus between the sediment and water column than iron. The effect calcite precipitation had on phosphorus cycling varied among lakes depending upon different initial phosphorus concentrations, differences in dominate algal and cyanobacterial species, lake morphometry, type of precipitate, and the occurrence of interacting substances (Boström *et al.*, 1988).

Phosphorus may also be incorporated into the sediment through the deposition of organic matter. Several researchers have found that a large proportion of available sediment phosphorus is bound in bacterial biomass (Baldwin *et al.*, 2002). Direct excretion of phosphorus containing compounds, settling of dead algal cells, and deposition of plant materials from macrophytes can enrich lake sediments in phosphorus. Phosphorus containing organic compounds (organic-P compounds) found in aquatic environments includes deoxyribonucleic acids, ribonucleic acid, adenosine monophosphate, inositol hexaphosphate, and polyphosphate (Baldwin *et al.*, 2002). Orthophosphate may also be incorporated into high molecular weight humic acids (Baldwin *et al.*, 2002). Organic-P compounds may be hydrolyzed by exo-enzymes produced and released into the environment by aquatic microbiota (Baldwin *et al.*, 2002; Herbes *et al.*, 1975).

Remobilization of phosphorus from the sediments

Baldwin *et al.* (2002) outlined two processes necessary for phosphorus to remobilize from the sediments to the overlying water. The first process is the release of phosphorus from the sediment particle to the interstitial waters within the sediments. The second process involves the transfer of phosphorus from the interstitial water to the overlying water column.

Phosphorus will desorb from sediment particles under certain chemical conditions.

Phosphorus released through these equilibrium shifts is often termed readily desorbable phosphorus and may be of ecological significance (Baldwin *et al.*, 2002; Rydin 2000).

Shifts in solid phase – solution phase phosphorus equilibrium, resulting from changes in

solution chemistry, may result in phosphorus being released from sediment particles (Baldwin *et al.*, 2002). The changes in solution chemistry most often associated with these shifts are pH and phosphate concentration of the interstitial waters within the sediment (Ostrofsky *et al.*, 1989; Baldwin *et al.*, 2002).

Phosphorus associated with mineral surfaces in the sediment is in some form of equilibrium with phosphorus dissolved in the interstitial waters surrounding the sediment (Baldwin *et al.*, 2002). As phosphorus is removed from solution in the interstitial waters, the equilibrium shifts, resulting in a net release of phosphorus from the sediment (Baldwin *et al.*, 2002). At any given moment the position of the equilibrium will depend upon the thermodynamics of the reactions involved (Baldwin *et al.*, 2002). Phosphorus will desorb more readily off minerals with a high solubility constant (Baldwin *et al.*, 2002). The rate of desorption will vary with the way that phosphorus is bound to the mineral; phosphorus associated with outer sphere complexes will desorb more readily than phosphorus associated with inner sphere complexes (Baldwin *et al.*, 2002).

Several researchers have documented a positive correlation between phosphate release and pH (Boström *et al.*, 1982; Drake and Heaney, 1987). The importance of pH to sorption/desorption resulted from the net surface charge of a mineral surface. Mineral surface with a positive or neutral net surface charge had a higher affinity for anions such as phosphate (Baldwin *et al.*, 2002). The solution pH affected the surface charge of metal oxyhydroxides through protonation of the surface hydroxyl groups (Baldwin *et al.*, 2002). At high pH, ligand exchange occurred replacing phosphate at the mineral surfaces with

hydroxyl ions (Pettersson, 1998). Andersen (1975) attributed a decrease in phosphorus release at $\text{pH} > 9.5$ to precipitation of phosphorus as hydroxyapatite.

In many bodies of water the most extreme periods of phosphorus release will occur under low oxygen conditions. During thermal stratification, the hypolimnion of a lake may become depleted of oxygen. As oxygen concentration decreases toward analytical zero, there is a decrease in redox potential, resulting in a more reducing environment. Under reducing conditions, reduction of iron oxides and oxyhydroxides in sediments may cause phosphorus associated with these compounds to be released (Mortimer, 1941; Ostrofsky *et al.*, 1989; Baldwin *et al.*, 2002). Manganese oxides and oxyhydroxides function in a similar manner to iron except that they will reduce at a higher redox potential and hence at higher oxygen concentrations (Davison, 1993). The reduction of iron and manganese minerals and subsequent release of phosphorus associated with these minerals can make up a significant portion of a lake's phosphorus budget.

Living organisms may also cause phosphorus to be released from the sediment either through active excretion or cell death and subsequent mineralization (Ostrofsky *et al.*, 1989; Baldwin *et al.*, 2002; Davison 1993). Sediments are not merely inert mixtures of minerals and recalcitrant organic matter; they also contain a large number of living organisms (Baldwin *et al.*, 2002). Baldwin *et al.* (2002) estimated that 1 cubic meter of fine organic sediment would contain *c.* 500 grams of living bacteria. Phosphorus bound in the bacterial biomass may be mobilized via direct excretion, hydrolysis of organic

compounds, through autolysis after cell death, or through migration of the organisms (Baldwin *et al.*, 2002; Boström *et al.*, 1988; Pettersson, 1998).

It has long been known that under low redox condition (such as are found in anaerobic environments) part of the sediment's iron (III) pool is reduced to iron (II), causing iron (II) and associated phosphorus to go into solution (Mortimer, 1941). This was originally thought to be a purely chemical process (Boström *et al.*, 1988). More recently it has been recognized that bacteria play an important role in the release of phosphorus under low oxygen conditions. Iron reduction may be partly the result of microbial process, such as the utilization of iron (III) as an alternative electron acceptor (Boström *et al.*, 1988).

Koshmanesh *et al.* (2002) observed that some facultative anaerobic microbes were able to assimilate "remarkable" amounts of phosphorus as polyphosphate granules. Much of this stored polyphosphate was released as orthophosphate when the microbes were exposed to an anaerobic environment in the presence of acetate (a simple fatty acid present in most lake sediments) (Koshmanesh *et al.*, 2002).

The transfer of phosphorus from the interstitial waters to the overlying water column is accomplished either through molecular diffusion or through mass transfer of pore water (Baldwin *et al.*, 2002). Baldwin *et al.* (2002) argued that since molecular diffusion was such a slow process, that in most instances it would have little impact on the exchange of phosphorus from the sediment pore water to the overlying water column. However, Boström *et al.* (1988) suggested that the long duration over which phosphorus release events occurred in deep stratified lakes compensated for the slow rate of transport.

Physical disturbances of the sediment-water interface may also result in mass transfer of phosphorus from the interstitial waters to the water column (Baldwin *et al.*, 2002). Such physical disturbances may result from hydrologic events, such as high flow events that result in bed scouring; anthropogenic causes, such as dredging; physico-chemical reactions, such as the ebullition of gasses from the sediment entraining pore water; or through the actions of organisms, from physical disturbances of the sediment by bottom feeding organism or bio-irrigation of sediments by invertebrates (Baldwin *et al.*, 2002; Boström *et al.*, 1988). Phosphorus may also be transported from the sediment to the water through direct excretion of macrophytes (McRoy *et al.*, 1972).

Sequential extraction

There have been many different chemical extraction schemes designed to determine the manner and relative proportion by which phosphorus is stored in sediment or soil. These procedures usually take the form of a set of sequential extractions that move from less rigorous to more rigorous extractions at each step. The extractions are not absolutely selective for the phosphorus fraction they target and are considered to be operationally defined by the method. The first extraction in most sequential extraction schemes usually consists of a high ionic strength solution, such as a 1-molar solution of ammonium chloride or sodium chloride. This phosphorus fraction often termed “easily extractable phosphorus” or “loosely sorbed phosphorus” represents phosphorus that is either in the interstitial pore water of the sediment or phosphorus that is bound in an outer sphere complex on solid surfaces (readily desorbable phosphorus). The second extraction involves reacting the sample with a strong reducing agent such as sodium dithionite. This

phosphorus fraction often termed “redox-sensitive phosphorus” represents phosphorus bound to iron and manganese oxyhydroxides through inner sphere complexes. The third extraction involves reacting the sample with a sodium hydroxide solution. Over a relatively long period of time (16 hours), sodium hydroxide will extract phosphorus bound to aluminum hydroxides and large phosphorus containing organic complexes. Analyzing the sodium hydroxide extract for soluble reactive phosphorus will yield the “aluminum bound phosphorus”; analyzing this extract for nonreactive phosphorus yields the “organically bound phosphorus”. The final extraction involves reacting the sample with a dilute hydrochloric acid solution. This phosphorus fraction termed “calcium bound phosphorus” represents phosphorus bound to, or precipitated as, a calcium mineral phase and phosphorus sorbed onto calcite minerals. Since the manner in which phosphorus is stored in the sediment will determine how it is released, phosphorus fractionation analysis can yield important insights into the cycling of phosphorus within an aquatic ecosystem.

Methods

Field procedures

The water column and sediment of Irondequoit Bay was sampled at the North Bay site (Fig. 1, Table 1), weekly from 11 June 2003 to 5 August 2003 and monthly from 19 May 2004 to 26 October 2004. The North Bay site is the same location as the Monroe County Environmental Health Department’s Station 1 and is the deepest part of Irondequoit Bay (approximately 23 meters deep). Sediment cores were also taken from the Bridge and Middle Bay sites (Fig. 1, Table 1).

Temperature, dissolved oxygen, pH, and a water sample were taken at 1-m intervals.

Temperature, dissolved oxygen, and pH were measured with a Quanta G Hydrolab and water samples were taken with a horizontal Van Dorn water bottle. Before each use, the pH electrode on the Hydrolab was calibrated against two buffers, and the dissolved oxygen electrode was calibrated to 100% dissolved oxygen saturation over moisture saturated air. In order to increase resolution, a water sample was also taken 0.5 m above the sediment – water interface. Immediately after sampling, a sub-sample of each water sample was filtered through a MAGNA 0.45-micron nylon filter; the filtrate was retained and frozen.

During each of the monthly sampling dates in 2004, a sediment core was collected using a messenger operated gravity type KB core sampler fitted with 91×5-centimeter (36×2-inch) CAB plastic (cellulose acetate butyrate) liner tube and frozen within three hours of sampling. On 8 May 2003, two sediment cores were taken at each of the sites (North Bay, Middle Bay, and Bridge) and used in sediment core incubation experiments.

Laboratory procedures

Water samples

Unfiltered water samples were stored at ~4°C until analysis, and filtered water samples were kept frozen until the time of analysis. On five dates (23 June 2004, 29 July 2004, 24 August 2004, 30 September 2004 and 26 October 2004) water was collected from the

epilimnion, metalimnion, and hypolimnion and analyzed for alkalinity within three hours (Method 2320 B, APHA, 1999). Soluble reactive phosphorus (SRP) (using filtered water samples) and total phosphorus (TP) were analyzed by the automated ascorbic acid reduction method (Method 4500-P F, APHA, 1999) using of a Technicon autoanalyzer. For total phosphorus, unfiltered water samples were digested with persulfate and sulfuric acid prior to analysis (Method 4500-P B, 5, APHA, 1999). Water samples digested with nitric acid (USEPA SW846 Method 3050B) were analyzed for total aluminum, total iron, and total manganese with a Thermo Elemental, IRIS 1000, inductively coupled plasma atomic emission spectrophotometer (ICP AES).

Sediment samples

The sediment cores were immediately frozen and subsequently dissected into 2-cm sections from the sediment surface to 10 cm of depth, and 5-cm sections from 10 cm to 50 cm of depth. Light colored bands (approximately 1 cm in width) in the sediment cores were removed and analyzed separately (Table 2). The dissected sections were kept frozen until analysis.

After thawing, each segment of the core was homogenized and two sub-samples were taken. Moisture content of a sub-sample was determined by establishing its mass before and after drying in a pre-weighed crucible overnight at 105°C. Loss on ignition was determined from the same sub-sample after ignition in a muffle furnace at 350°C for 16 hours. Another sub-sample was digested with nitric acid (USEPA SW846 method 3050B) and analyzed for total aluminum, total iron, total manganese, and total phosphorus by ICP

AES. The third sub-sample of each dissected section was used for the sequential extraction of phosphorus.

Sequential extraction

The fractionation scheme of Rydin (2000) was modified as follows (Fig. 2). A 1-M sodium chloride solution was substituted for the ammonium chloride solution during the extraction of loosely sorbed phosphorus to prevent the “salting-out” of ammonium salts during ICP – AES analysis. Unlike Rydin (2000), an unbuffered salt solution was used in order to prevent changes to the protonation of mineral surfaces within the sediment. A single extraction with the bicarbonate dithionite reagent was found not to be sufficient to remove redox sensitive phosphorus. By performing this extraction twice, extraction efficiency was greatly improved. A 0.1-M sodium chloride wash after the redox sensitive, sodium hydroxide extractable, and hydrochloric extractable extractions removed entrained fluids and solubilized any phosphorus that may have been loosely sorbed onto mineral surfaces during the extraction process. All of the extracts were analyzed for SRP; the sodium hydroxide extract was analyzed for TP (see *Water samples* section for details of analysis). The nonreactive phosphorus concentration for the sodium hydroxide extraction was calculated by subtracting its SRP concentration from its TP concentration.

Sediment core incubation experiments

The sediment core incubation experiments were conducted in a similar manner to those described by Nürnberg (1988). The sediment cores were kept in the corer liner tubes in

which they had been sampled. Upon return to the laboratory, the cores were wrapped in aluminum foil in order to avoid exposing the sediment to light and stored at 7°C in an environmental growth chamber. The liner tubes were fitted with an airtight manifold equipped with an inflow and outflow port (Fig. 3). The inflow port allowed water to be injected into the liner tube near the top of the manifold, while the outflow port allowed the removal of water near the sediment-water interface. In order to achieve anoxic conditions, the core tubes were filled with a 10% sodium sulfite solution made with surface water from Irondequoit Bay.

Immediately after oxygen was purged from the core tubes with sodium sulfite, water from the core tubes was sampled periodically for a 24-day period. One hundred five ml of 10% sodium sulfite lake-water solution was forced through the inflow port, and a sample was collected from the outflow port. Dissolved oxygen was measured immediately with a YSI model 58 dissolved oxygen meter, and pH was measured with a Beckman meter calibrated daily using two buffers (4.01 and 9.18). All samples were analyzed for TP (see *Water samples* section for details of analysis). The samples were analyzed for total phosphorus rather than soluble reactive phosphorus to eliminate bias caused by adsorption of phosphate onto iron hydroxides that may occur during oxic filtration (Nürnberg, 1988).

Prediction of phosphorus release rates from models in the literature

Ostrofsky *et. al.* (1989) examined the relationship between phosphorus release rates and several sediment and lake characteristics from 57 lakes representing a variety of sediment

types and trophic conditions (Table 7). For the 57 lakes, Ostrofsky *et. al.* (1989) compared in-lake and sediment characteristics with rates of phosphorus release from laboratory incubation experiments on their sediments. From this comparison the authors derived a model to explain variation between release rates from the lakes:

$$\text{SLOPE} = 3.380 \ln \text{TP} + 2.274 \ln \text{Alkalinity} + 4.270 \ln \text{NaOH-P} - 0.243 \text{LOI} - 20.642$$

$$n = 57, r = 0.715, \text{SE} = 5.342$$

where SLOPE was equal to the amount of phosphorus released during incubation experiments, in units of $\mu\text{g P}/25 \text{ cm}^3$ contained sediments/day. By assuming the sediments used in the incubation experiments had a surface area of 53.56 cm^2 , we can convert these rates to $\text{mg P}/\text{m}^2/\text{day}$.

Ostrofsky *et. al.* (1989) measured only the top 2.5 cm of sediment cores collected at the deepest point in each lake. In order to be comparable with these results, the average values for the top 2 cm of five sediment cores collected monthly at the North Bay site of Irondequoit Bay from May through September of 2004 are presented in Table 7. Total phosphorus values for both Ostrofsky *et. al.* (1989) and Irondequoit Bay were from surface samples taken at the time of sediment core collection. The Irondequoit alkalinity value was the average ($n = 4$) alkalinity concentration from the epilimnion of the North Basin site from June through September of 2004. In the sequential extraction scheme used by Ostrofsky *et. al.* (1989), loosely sorbed phosphorus was extracted with ammonium chloride. The sodium hydroxide extraction ($\text{NaOH-P}_{\text{metals}}$) incorporated both redox sensitive form of phosphorus (iron bound phosphorus) and aluminum bound phosphorus, whereas in the sequential extraction scheme used for Irondequoit Bay

sediments, loosely sorbed phosphorus was extracted with sodium chloride. The sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) extraction targeted the redox sensitive phosphorus; the sodium hydroxide reactive phosphorus (NaOH-RP) extraction targeted the aluminum bound phosphorus. In order to be comparable with the results from Ostrofsky *et. al.* (1989), the sodium hydroxide phosphorus ($\text{NaOH-P}_{\text{metals}}$) value for Irondequoit Bay in Table 6 was the average of the sums of the $\text{Na}_2\text{S}_2\text{O}_4$ and NaOH-RP extractions. In Table 6, inorganic sediment phosphorus is the sum of the loosely sorbed phosphorus, $\text{NaOH-P}_{\text{metals}}$, and HCL-P fractions; organic sediment phosphorus is the difference between Total sediment phosphorus and Inorganic sediment phosphorus.

Nürnberg (1988) determined release rates of phosphorus from anoxic sediment surfaces with core tube incubations and several phosphorus fractions within the corresponding sediments for seven North American lakes representing a wide range of trophic, buffer capacity, and other chemical characteristics. Sediment characteristics examined by the author included total sediment phosphorus, redox-sensitive phosphorus (as measured with a bicarbonate dithionite extraction), percent moisture, and sediment loss on ignition. Appendix 1 lists several regressions that Nürnberg (1988) claimed can be used to predict phosphorus release rates from either total sediment phosphorus or bicarbonate dithionite extractable phosphorus. Nürnberg (1988) found that the correlations of phosphorus release rates with both total sediment phosphorus and bicarbonate dithionite extractable phosphorus can be improved by expressing phosphorus per wet sediment weight instead of dry sediment weight (Table 8). Nürnberg (1988) was able to improve the correlation of the regression for total sediment phosphorus (TP_s) based upon dry weight by adding

sediment loss on ignition (LOI) as a second variable (Appendix 1). The mean concentrations of total sediment phosphorus, bicarbonate dithionite extractable phosphorus, and sediment loss on ignition for the top 10 cm of sediment cores sampled monthly at the North Bay site on Irondequoit Bay from May through September of 2004 were averaged, and these averages were applied to the regression in Nürnberg (1988) to predict phosphorus release rates (Table 8).

Calculations

The mass of a chemical component (i.e. TP, SRP, Fe, and Mn) in the Bay at any given

time was calculated with the formula used in Larsen *et al.* (1981): $\text{Mass} = \sum_{i=1}^n C_i V_i$

where C_i was the concentration at a volume increment V_i . Volume increments for the Bay were calculated by multiplying the area of the volume increment, taken from a hypsographic curve (Fig. 4), by the vertical height of the volume increment. Masses of chemical components found in any strata of the Bay (i.e. epilimnion, metalimnion, and hypolimnion) were found by the summation of $C_i V_i$ for each volume increment in that stratum. Phosphorus release rates for the sediment were calculated by dividing the increase of phosphorus in the hypolimnion by the number of days over which the change occurred. Areal release rates (giving the amount of phosphorus lost/per unit time/per unit area) were calculated by dividing the phosphorus release rates by the area of sediment overlain by anaerobic water.

The amount of phosphorus released from the sediment in the sediment core incubation experiments was calculated by the summation of the increase in TP between subsequent

sampling dates. The increase in TP between sampling dates was calculated with the equation: $TP_{\text{increase}} = \sum M_t - M_{t-1}$ where M_t was the amount of phosphorus in the water of the core tube at sampling date t , and M_{t-1} was the amount of phosphorus in the water of the core tube on the sampling date previous to sampling date t . The amount of phosphorus in the water of each core tube was calculated by multiplying the TP concentration of the water in the core tubes by the volume of water in the core tubes and corrected for the amount of phosphorus removed during sampling on the previous date.

Results

Water column

Thermal stratification and dissolved oxygen

The water column of Irondequoit Bay was thermally stratified throughout both the 2003 and 2004 sampling periods (Fig. 5, 6). During both years similar trends of decreasing hypolimnetic oxygen levels were observed. By 17 June 2003 and by 23 June 2004 dissolved oxygen (D.O.) levels had become suboxic at 23 m. A suboxic environment has a D.O. concentration between 30×10^{-6} mol/l (0.96 mg/l) and 1×10^{-6} mol/l (0.03 mg/l), as opposed to an anoxic environment which has a dissolved oxygen concentration below 1×10^{-6} mol/l (0.03 mg/l) (Eby, 2004). This decreasing trend of hypolimnetic D.O. concentrations continued until all concentrations were below 1 mg/l by 22 July 2003 and 29 July 2004. During both years the hypolimnion remained suboxic throughout the rest of the sampling period, with only a few exceptions occurring near the metalimnion boundary in 2003 (Fig. 5, 6). Dissolved oxygen concentrations never reached anoxic

conditions, with the lowest observed concentration (0.06 mg/l) occurring on 29 July 2003, at 23 m.

Between 30 September 2004 and 26 October 2004, the top boundary of the hypolimnion decreased 5 m, from 13 m to 18 m, respectively (Fig. 6). During this same period, a decrease in the average epilimnion temperature of 6.66°C occurred while the depth of the epilimnion increased (Fig. 6). These changes were due to the onset of fall mixis.

Phosphorus concentrations of the water column

On the initial sampling dates of 2003 and 2004 (11 June 2003 and 19 May 2004), total phosphorus concentrations were low and varied little throughout the water column (Fig. 7, 8). As hypolimnetic dissolved oxygen concentration decreased over the course of each season, hypolimnetic total phosphorus and soluble reactive phosphorus concentrations increased, especially at lower depths (Fig. 7, 8). During the 2003 sampling period, a maximum concentration for total phosphorus (1.34 mgP/l) was observed on 29 July 2003 at 23 m, and a maximum concentration for soluble reactive phosphorus (0.92 mgP/l) was observed on 29 July 2003 at 22.5 m (Fig. 7). During the 2004 sampling period, a maximum concentration for total phosphorus (0.92 mgP/l) was observed on 30 September at 23 m, and a maximum concentration for soluble reactive phosphorus (0.75 mgP/l) was observed on 26 October 2004 at 22 m (Fig. 8).

Phosphorus content of the basin

The total phosphorus content of the entire basin during the 2003 sampling period was at its minimum value (586 kg P) on 11 June 2003 (Fig. 9). A generally increasing trend was observed until a maximum value (1,658 kg P) was observed on 29 July 2003. There was a decrease in total phosphorus concentrations of the bottom 5 m of the water column between 29 July 2003 and 5 August 2003, causing a decrease of both the entire basin and hypolimnion total phosphorus content. This decrease in phosphorus concentrations coincided with a slight increase in hypolimnetic nitrate concentration between 29 July 2003 and 5 August 2003 (Fig. 11).

The total phosphorus content of the entire basin during the 2004 sampling period was at its minimum value (396 kg P) on 19 May 2004 (Fig. 10). A generally increasing trend was observed until a maximum value (3,376 kg P) was observed on 30 September 2003. A decrease in the phosphorus content of the entire basin occurred between 30 September 2003 and 26 October 2003 (Fig. 10). During this period, the phosphorus content of the epilimnion increased while the phosphorus content of the hypolimnion decreased (Fig. 10). This shift in the phosphorus content of the epi- and hypolimnion resulted from an expanding epilimnion and shrinking hypolimnion with the onset of fall mixis. During fall mixis, the previously low oxygen water from the meta- and hypolimnion was mixed with the well-oxygenated waters of the epilimnion. Much of the hypolimnetic phosphorus then precipitated out of solution and migrated to the sediments.

During both years, changes in the phosphorus content of the hypolimnion mirrored the changes of the phosphorus content of the entire basin, while the phosphorus content of

the epilimnion and metalimnion varied little (Fig. 9, 10). This pattern of hypolimnetic phosphorus accumulation supports the hypothesis that the sediment is the main source of phosphorus during the late summer.

Loading rates

Phosphorus accumulated in the hypolimnion of the North Basin at a rate of 10.67 kg/day from 11 June 2003 to 5 August 2003 and at a rate of 15.08 kg/day from 19 May 2004 to 30 September 2004: an average of 12.87 kg/day for 2003 and 2004 (Table 3). The areal rate for the hypolimnion of the North Basin during the 2003 sampling period was 6.75 mg of phosphorus released per square meter of the basin surface area per day (mg P/m²/day) (Table 3). During the 2004 sampling period an areal rate of 9.54 mg P/m²/day was observed, giving an average between 2003 and 2004 of 8.15 mg P/m²/day (Table 3).

Iron and manganese

There was a trend in increasing manganese in the hypolimnion throughout the 2004 sampling period (Fig. 12). We did not observe the same trend in iron concentrations (Fig. 13). All iron concentrations were under 1.0 mg/l except below 22 m on four of the dates. The samples taken near the sediment, which had high concentrations of iron, also had high amounts of suspended materials. It is likely that most of the iron in these samples was associated with suspended sediment particles and not in solution. There was little relationship between total phosphorus concentrations and iron concentrations for the same samples ($r^2=0.142$; Fig. 14). There was a strong correlation between total phosphorus concentrations and manganese concentrations ($r^2=0.924$; Fig. 15).

Alkalinity

The average alkalinity for all dates and depths measured during the 2004 sampling period was 233.7 mg CaCO₃/l (S.E. ± 5.67 mg CaCO₃/l). Alkalinity was highest in the hypolimnion and lowest in the epilimnion (Fig. 16). While there may have been a slight increase in alkalinity of the hypolimnion (from 253.2 mg CaCO₃/l on 29 July 2004 to 284.5 mg CaCO₃/l on 26 October 2004), no other temporal trends were observed during the 2004 sampling period (Fig. 16).

pH

On all dates of the 2003 sampling period, a similar spatial trend was observed. The pH was at a relatively high level in the epilimnion, with a decreasing trend beginning near the epilimnion-metalimnion border (Fig. 17). The pH of the hypolimnion remained relatively constant, with some dates later in the season (22 July 2003, 29 July 2003, and 5 August 2003) exhibiting an increase in pH a few meters above the sediment (Fig. 17). An exception to this trend occurred on 17 June 2003 and 22 July 2003 where pH suddenly decreased one half meter above the sediment. The pH of the water column during the 2004 sampling period followed a similar trend as it did in 2003, except that all dates exhibited increasing pH levels within a few meters of the sediment (Fig. 18).

Sediment

Loss on ignition and percent moisture

The average loss on ignition value of the sediment was 8.42% (S.E. \pm 0.16%) with values ranging from 7.21% to 10.84% (Table 5). The average percent moisture value of the sediment was 66.81% (S.E. \pm 1.29%) with values ranging from 51.95% to 85.60% (Table 5).

Sediment phosphorus

The average phosphorus concentration of the sediment was 1.389 ± 0.150 g P/kg dry weight (DW) with values ranging from 0.426 to 6.719 g P/kg DW (Table 5). The light colored bands (alum layer) in the sediment cores from June, July, and September were where the highest phosphorus concentrations were observed (average phosphorus concentration of 4.124 g P/kg DW (S.E. \pm 1.313 g P/kg DW). Phosphorus concentrations in the sediments demonstrated no seasonal trend in average phosphorus concentrations (Fig. 19, 20). The only phosphorus trend seen with depth was an increase in phosphorus concentrations around the alum layer (which occurs at a depth of between 18.5 cm to 24 cm) in those cores from which the alum layer was separated (Figure 21).

Sediment iron

The average iron concentration of the sediment was 24.415 g Fe/kg DW (S.E. \pm 0.760 g Fe/kg DW) with values ranging from 16.447 g Fe/kg DW to 38.807 g Fe/kg DW (Table 5). Average iron concentrations increased between June to September, especially within the top 10 cm of the sediment profiles (Fig. 19, 20). The concentration of iron in the first 2 cm below the sediment-water interface increased throughout the season from a low of 16.447 g Fe/kg DW on 19 May 2004 to 27.410 g Fe/kg DW on 30 September 2004 (Fig.

22). Sediment iron profiles from August and September demonstrated higher concentrations of iron below 10 cm of depth than did the profiles from earlier in the season (Fig. 22).

Sediment manganese

The average manganese concentration of the sediment was 1.727 ± 0.053 g Mn/kg DW with values ranging from 0.909 to 2.530 g Mn/kg DW. Average manganese concentrations showed a slight increase during the 2004 sampling period (Fig. 19 and 20). The concentration of manganese in the first 2 cm below the sediment-water interface increased throughout the season from a low of 1.292 g Mn/kg DW on 19 May 2004 to 2.293 g Mn/kg DW on 30 September 2004 (Fig. 23).

Sediment aluminum

The average aluminum concentration of the sediment was 16.544 ± 0.667 g Al/kg DW with values ranging from 10.809 to 28.154 g Al/kg DW (Fig. 24). On 23 June, 29 July, and 30 September the areas suspected of being the alum layer had significantly higher ($p = 0.003$) concentrations of aluminum than did the rest of the sediment.

Sequential extraction

The percentage of phosphorus recovered with the sodium chloride extraction ranged from 0.2% to 2.6% with an average of $1.3\% \pm 0.1\%$. The sodium chloride fraction was the smallest phosphorus fractions in all of the cores (Fig. 25). The percentage of phosphorus recovered with the sodium dithionite extraction ranged from 8.6% to 55.6% with an

average of $30.2\% \pm 1.2\%$. The sodium dithionite fraction was lowest in the areas suspected of representing the alum layer (Fig. 25). The percentage of soluble reactive phosphorus recovered with the sodium hydroxide extraction ranged from 3.9% to 59.4% with an average of $12.4\% \pm 2.1\%$. The sodium hydroxide extraction was highest in soluble reactive phosphorus in the areas suspected of representing the alum layer (Fig. 25). The percentage of non-reactive phosphorus recovered with the sodium hydroxide extraction ranged from 3.4% to 18.1% with an average of $12.3\% \pm 0.6\%$. The percentage of phosphorus recovered with the hydrochloric acid extraction ranged from 10.7% to 54.5% with an average of $38.9\% \pm 1.6\%$. The hydrochloric fraction had the highest average percentage of phosphorus recovered (Fig. 25). Though no light colored band was observed in the sediment core taken on 19 May 2004, the sequential extraction of a 5-cm section between 15 and 20 cm of depth exhibited high levels of aluminum bound phosphorus (NaOH-SRP), which is a characteristic associated with the alum layer (Fig. 25).

Sediment core incubation experiments

The core incubation experiment was run for 25 days under anoxic conditions. The amount of total phosphorus released from each of the core incubation experiments ranged from 52.98 to 94.26 mg P/m² during this period, with an average of 72.15 mg P/m² (Table 4). Dividing the amount of total phosphorus released by the duration of the experiment yielded release rates ranging from 2.12 to 3.77 mg P/m²/day, with an average release rate of 2.89 mg P/m²/day (Table 4). A higher average release rate was observed in the two core incubation experiments from the Bridge site (3.38 mg P/m²/day) than in the

core incubations from the Middle Bay site (3.04 mg P/m²/day) and the North Bay site (2.24 mg P/m²/day) (Table 4, Fig. 1).

Prediction of phosphorus release rates from models in the literature

Table 7 compares sediment chemistry from the seven North American lakes that Nürnberg (1988) sampled and Irondequoit Bay. Percent moisture and loss on ignition average values from Irondequoit Bay (66.4% and 8.8%, respectively) were much lower than values published in Nürnberg (1988) (93.8% and 38.2%, respectively). Total sediment phosphorus and bicarbonate dithionite extractable phosphorus concentrations based upon dry sediment weight from Irondequoit Bay were similar to the lakes sampled by Nürnberg (1988) (Table 7). Nürnberg (1988) did not report concentration of phosphorus in wet sediment weights.

Predictions of release rates derived from the predictive regressions given in Nürnberg (1988) are presented in Table 8. Release rates calculated from phosphorus concentration expressed as wet weights were significantly higher than release rates calculated from phosphorus concentration expressed as dry weights (Table 8). Release rates calculated from total sediment phosphorus were lower than release rates calculated from bicarbonate dithionite extractable phosphorus (Table 8). The release rate calculated from total sediment phosphorus with loss on ignition as a second variable was higher than the other two release rates based on dry sediment weight phosphorus concentrations (Table 8).

Discussion

Sediment phosphorus

Table 5 reports the average concentrations of various parameters in the top 25 cm of Irondequoit Bay sediment cores from this study. Of the various phosphorus fractions, loosely sorbed phosphorus contributed the smallest amount to total sediment phosphorus (1.1%) and was not a significant source of phosphorus to the overlying water column. Constituting 30.9% of the total sediment phosphorus, calcium bound phosphorus (Ca-P) was the largest pool of phosphorus within the sediment (Table 5). However, calcium bound phosphorus is relatively inert and did not likely contribute much phosphorus to the water column. Aluminum bound phosphorus (Al-P) and organically bound phosphorus (Org-P) constituted 19.9% and 10.9% of the total sediment phosphorus, respectively (Table 5). The aluminum bound phosphorus represented another stable sink for phosphorus within the sediment. Though organically bound phosphorus may release some phosphorus through mineralization, due to the small size of this fraction and its slower rate of release, it is unlikely to have a significant impact on the water column.

Due to both its size (24.3% of total sediment phosphorus) and its mobility under reducing conditions, the bicarbonate dithionite extractable phosphorus (BD-P) fraction was the most significant fraction with regards to the cycling of phosphorus into the overlying water column. The BD-P fraction is composed of phosphorus sorbed onto the surfaces of or co-precipitated with iron and manganese oxyhydroxides. Due to the greater concentration of iron than manganese in the sediment (24.415 g Fe/kg DW versus 1.727 g Mn/kg DW) and iron's greater affinity for sorbing phosphates, most of the phosphate in

the BD-P fraction should be sorbed to iron oxyhydroxides (Baldwin *et al.*, 2002). Under anoxic conditions in the hypolimnion, the amount of phosphorus being released from the dissolution of iron oxyhydroxides in the sediment would be far greater than the release of phosphorus from sedimentary manganese (Baldwin *et al.*, 2002). However, manganese reduces at a higher redox potential, and hence at higher oxygen concentrations, than does iron (Davison, 1993). If suboxic levels of oxygen were maintained in the hypolimnion, it would be expected that the phosphorus associated with iron would remain immobile within the sediment while the phosphorus associated with manganese would be released.

In Tables 6 and 7, sediment characteristics from Ostrofsky *et al.* (1989) and Nürnberg (1988) were compared to sediment characteristics from Irondequoit Bay. In order to be comparable to these published works, the average values for Irondequoit Bay sediments in Table 6 were taken from the top 2 cm of sediment only, and the average values for Irondequoit Bay sediments in Table 7 were taken from the top 10 cm of sediment only.

Irondequoit Bay's lake water total phosphorus and inorganic sediment phosphorus and the various extracted fractions of phosphorus (NaOH -P metals, HCL-P, loosely sorbed P) were within the range of and similar to average values reported by Ostrofsky *et al.* (1989) for 57 eastern North American lakes (Table 6). However, total sediment phosphorus for Irondequoit Bay was slightly lower than for other lakes (1.224 for Irondequoit Bay versus 1.342 g P/kg DW) because organic sediment P was lower by ~0.2 g P/kg DW in Irondequoit Bay than in the other lakes. Similarly, sediment iron and loss on ignition were below the average and at the extreme low end of values reported from

other lakes (Table 6). Only alkalinity of water was high in Irondequoit Bay compared to the lakes reported by Ostrofsky *et al.* (1989) (202.8 versus 107 mg CaCO₃/L). This high alkalinity resulted from carbonate bedrock in the geology of the drainage basin (Bannister and Bubeck, 1978). Sediments of this managed urban bay were low in iron, low in organic matter and low in P associated with organic matter. The low organic matter content was surprising as Irondequoit Bay was the recipient of treated and untreated human sewage until the late 1970s when all wastewater effluents were diverted to the Frank E. Van Lare Sewage Treatment Plant (Environmental Health Laboratory, 2001).

Sediments in Irondequoit Bay were lower in concentrations of total sediment phosphorus, percent moisture and loss on ignition than in the seven lakes examined by Nürnberg (1988) (Table 7). However, concentrations of bicarbonate dithionite extractable phosphorus (BD-P) were higher in Irondequoit Bay than the average reported by Nürnberg (1988). Since the BD-P fraction was redox sensitive, this would suggest that Irondequoit Bay's sediments were more susceptible to phosphorus release under low redox conditions, and therefore, have a high phosphorus release rate potential.

Ostrofsky *et al.* (1989) found that lakes that are eutrophic, alkaline, with high concentrations of iron-bound phosphorus, and low organic content in their sediments are most likely to have high rates of internal phosphorus loading. When compared to the lakes reviewed in Ostrofsky *et al.* (1989) and Nürnberg (1988), Irondequoit Bay had relatively high concentration of iron and manganese bound phosphorus (as measured by BD-P and NaOH-P_{metals}) and low organic content (as measured by loss on ignition) in its

sediments, so that we should expect high rates of internal phosphorus loading. However, Irondequoit Bay is a managed system and may behave differently than expected.

Vertical distribution of sediment phosphorus

Tangorra (1996) profiled sediments in Irondequoit Bay in 1994 - a period 15 years prior to our samples. Tangorra (1996) collected two side by side core samples in approximately the same location as our North Bay site. One of the cores was used for chronological dating and the other for chemical analysis. The cores were dissected into 1 - cm intervals to approximately 1 m of sediment depth. The total phosphorus values in Tangorra's (1996) sediment ranged from 0.78 to 3.34 g P/kg DW (mean = 1.66 ± 0.09 g P/kg DW). These values agreed well with the total phosphorus values from our analysis (range = 0.426 to 6.719 g P/kg DW; mean = 1.389 ± 0.150 g P/kg DW). Tangorra (1996) observed a slight increase in sediment phosphorus from the deepest part of the core until a sharp peak occurred in the sediment corresponding to the turn of the century (approximately 0.82 m of sediment depth). Concentrations of sediment phosphorus remained stable, with limited fluctuations, until another sharp peak was observed in 1960 (at approximately 0.41 m of sediment depth). In the sediments corresponding to 1977 to 1994 (an approximate sediment depth of 0.28 m to the top of the core), Tangorra (1996) observed a decrease in sediment phosphorus, with two large peaks occurring in 1986 and 1991. In the recent sediments of Irondequoit Bay, the phosphorus levels measured in this study were consistently around 1 g/kg dry weight (mean = 1.10 ± 0.04 g P/kg DW) to a depth of 15 cm (Fig. 21). Our sediment phosphorus concentrations compared well with the most recent sediments described by Tangorra (1996). The large phosphorus peak from

1986 that Tangorra (1996) found was most likely the alum layer that we identified in some of our cores.

The peak (6.719 g P/kg DW) in total sediment phosphorus occurred in the 18 to 21 cm range. This appeared to be a very thin layer as phosphorus concentrations in samples taken at 25 and 17 cm in different cores were relatively low (Fig. 21) Aluminum levels peaked at 19 to 21cm (Fig. 24). We believe this was the remnants of the alum treatment in 1986, when alum was applied to areas of the lake greater than 6 - m deep to control phosphorus cycling from the sediments. Phosphorus peaks within the sediment near the alum layer have been observed in other lakes (Lewandowski *et al.*, 2003; Rydin *et al.*, 2000), whereas in lakes without alum treatments these phosphorus peaks were not observed (Dillon and Evans, 1993; Holtan *et al.*, 1988).

Lewandowski *et al.* (2003) identified an alum layer in the sediments of Lake Süsser See (Germany) by observing a peak in the sediments profile of total sediment phosphorus, sodium hydroxide extractable soluble reactive phosphorus (NaOH-SRP), and aluminum extracted with sodium hydroxide (EA1). In a similar manner the light-colored bands that we dissected out of some of the sediment cores demonstrated the highest concentrations of total sediment phosphorus and NaOH-SRP (Fig. 21 and 25). Lewandowski *et al.* (2003) argued against using total aluminum concentrations to identify an alum layer, due to high concentrations of background aluminum found in many lake sediments. Instead, Lewandowski *et al.* (2003) used EA1 analysis to delineate the alum layer in their sediment profile, since EA1 analysis extracts autochthonous aluminum salts while

leaving behind the more stable allochthonous aluminum minerals. However, in Irondequoit Bay sediment profiles, peaks were observed in total aluminum corresponding to the area where the alum layer was suspected to exist (Fig. 24).

From peaks observed in total sediment phosphorus, NaOH-SRP, and total aluminum profiles of the sediment, it can be concluded that the light-colored bands observed in some sediment cores were the remnants of the alum layer. The depth of these bands demonstrated that at least 18.5 cm of fresh sediment have been deposited on top of the alum layer since it was applied in 1986.

Phosphorus release rates

The average Irondequoit Bay phosphorus release rate from the sediment incubation experiments (2.89 mg P/m²/day, Table 4) compared well with the calculated rate from the Ostrofsky *et al.* (1989) model (2.98 mg P/m²/day). Since the Ostrofsky *et al.* (1989) regression model is based on lakes not treated with alum, the result was surprising. As a managed system treated with alum, we expected our estimates of release rates to be much lower than those from the regression model. That the model and the sediment incubation experiment results agreed so closely suggests that the alum layer is no longer inhibiting phosphorus release from the sediments.

The various regression models published in Nürnberg (1988) gave a wide range of phosphorus release rates (range = 0.11 to 31.56 mg P/m²/day, Table 8). The release rates predicted from dry sediment concentrations (range = 0.11 to 6.35 mg P/m²/day, Table 8)

were similar to the release rates derived from sediment core incubation (2.89 mg P/m²/day, Table 4) and loading rates from the hypolimnion (8.15 mg P/m²/day, Table 3).

The dry sediment regressions from Nürnberg (1988) were based on three predictors: total sediment phosphorus (TP_s), bicarbonate dithionite extractable phosphorus (BD-P) and total sediment phosphorus with loss on ignition as a second variable (TP_s-LOI) (Appendix 1). The dry sediment TP_s as a predictor provided a very low release rate for Irondequoit Bay (0.11 mg P/m²/day, Table 8). Nürnberg (1988) found that adding loss on ignition as a second variable improved the predictive power of the regression. By using the dry sediment TP_s-LOI regression model, the estimate for Irondequoit Bay increased to 6.35 mg P/m²/day (Table 8) and was comparable in the same order of magnitude as the 2.89 mg P/m²/day estimate from our sediment core incubation experiments.

Interestingly, the Irondequoit Bay phosphorus release rate estimated from increased hypolimnetic phosphorus during the summer (8.15 mg/m²/day, Table 3) was more similar to the Nürnberg TP-LOI model.

The wet sediment regressions from Nürnberg (1988) were based on two predictors: total sediment phosphorus (TP_s) and bicarbonate dithionite extractable phosphorus (BD-P). Both wet sediment regressions yielded extremely high phosphorus release rates (23.82 and 31.56 mg P/m²/day, Table 8). This result was an artifact of Irondequoit Bay sediment having a much lower percent moisture ratio than the sediment Nürnberg (1988) used to construct the regressions (Table 7). Since freezing sediment may force excess moisture out of the sediment, the lower moisture content of Irondequoit Bay cores likely resulted

from freezing the sediment cores before analysis. For this reason, the release rates derived from the wet sediment regressions were not reasonable estimates for internal loading in Irondequoit Bay.

Internal phosphorus loading rates from both the sediment incubation experiments and field observations ranged from 2.24 to 9.54 mg P/m²/day (Tables 3 and 4). The average phosphorus release rate from field observations (8.15 mg P/m²/day, Table 3) was within the range of other release rates calculated in a similar manner from lakes reported by Nürnberg (1984) (Table 9). The average release rate derived from the sediment core incubation experiments (2.89 mg P/m²/day, Table 4) was also within the range of other release rates calculated in a similar manner from lakes reported by Nürnberg (1984) (Table 10).

In general, the sediment core incubation experiments provided smaller internal phosphorus loading rates than did the field observations. Phosphorus loading rates determined through field observations may be overestimated through phosphorus release from settling plankton, decaying macrophytes, and oxic sediments (Nürnberg, 1987). Phosphorus loading rates derived from field observations may also be overestimated if external loads of phosphorus are not constant over the period of anoxia (Nürnberg, 1987). Another possible reason for the discrepancy between release rates estimated in the laboratory and those estimated in the field is that the sediment in laboratory experiments is not vulnerable to physical disturbances that may occur within the sediments of a lake. These physical disturbances may cause mass transfer of phosphorus from the sediment,

resulting in higher loading rates from field observations. Lastly, the use of sodium sulfite to deoxygenate water in the sediment core incubation experiments may have interfered with the mechanisms of phosphorus release either chemically (sulfate reduction) or physically (flocculation), resulting in underestimates of phosphorus release rates.

Management

Since estimates of internal phosphorus loading prior to the alum treatment in 1986 were much larger in magnitude than our highest estimate (17 versus 9.54 mg/m²/day; Environmental Health Laboratory, 2001), sediment phosphorus management has been successful and continues to limit the transfer of phosphorus from the sediment.

Phosphorus levels were reduced by 60 to 75% by the alum application in 1986 (Environmental Health Laboratory, 2001). The injection of liquid oxygen to the hypolimnion maintains suboxic conditions in the hypolimnion (Fig. 5, 6). Both practices serve to control phosphorus release from the sediment. However, there is clearly ongoing release from the sediment, and the oxygenation process is important to controlling phosphorus releases from Irondequoit Bay's sediments.

Welch and Cooke (1999) found that alum treatments of dimictic lakes had a reasonable longevity of 15 years. The alum layer still exists, and can be physically seen in most sediment cores. That a significant amount of sediment phosphorus was sequestered in the alum layer can be seen not only by high total sediment phosphorus concentrations (mean = 3.446 ± 1.150 ; Fig. 21) found at the alum layer, but also by the large amounts of aluminum bound phosphorus (mean = 1.953 ± 0.835 ; Fig. 25) found in these layers

during sequential extraction. However, sedimentation over the past twenty years has caused new sediment to be laid overtop of the alum layer. Lewandowski *et al.* (2003) found that a layer of new sediment thicker than 5 cm causes the alum layer to have hardly any effect on phosphorus release. This new sediment negates the effectiveness of the alum layer in inhibiting phosphorus release from the sediment.

As stated above, with suboxic levels of oxygen in the hypolimnion, sediment manganese would be expected to cycle with phosphorus, while iron remained in the sediment. The strong correlation between manganese and phosphorus and the lack of correlation between iron and phosphorus (Fig. 14 and 15) within the water column indicates that sediment manganese, but not sediment iron, was releasing its associated phosphorus into the hypolimnion of Irondequoit Bay.

The injection of liquid oxygen into the Bay plays a vital role in keeping iron, and its associated phosphorus, within the sediments. Sequential extraction revealed that approximately 25% of sediment phosphorus is stored in redox sensitive forms. Since phosphorus tends to fill up the binding sites of iron before manganese (Baldwin *et al.*, 2002), the majority of this fraction is most likely stored as iron bound phosphorus. Oxygen injection to the Bay is preventing this pool of iron bound phosphorus from being released. If oxygen injection ceased and the phosphorus bound to iron was allowed to cycle with the water column, a return to the hypereutrophic conditions that dominated the Bay prior to alum treatment might occur.

Works Cited

- Andersen, J.M. 1975. Influence of pH on release of phosphorus from lake sediments. *Archiv für Hydrobiologie* 76: 411-419.
- APHA. 1999. Standard Methods for the Examination of Waste and Wastewater. American Public Health Association, 17th ed. New York, N.Y.
- Baldwin, D.S., A.M. Mitchell, and J.M. Olley. 2002. 12. Pollutant-Sediment Interactions: Sorption, Reactivity and Transport of Phosphorus. Pages 265-276 in P.M. Haygarth and S.C. Jarvis, editors. *Agriculture, Hydrology, and Water Quality*. CABI pub. Wallingford, UK.
- Bannister, T.T., and R.C. Bubeck. 1978. Limnology of Irondequoit Bay, Monroe County, New York. In J.A. Bloomfield (ed). *Lakes of New York State-Volume 2*. Academic Press, New York, New York.
- Bannister, T.T., A.D. Weidemann, S. Wilke-Mounts and L. Phillips. 1982. Irondequoit Bay Report No. 11: New benthic map of the bay and revised area depth and volume-depth functions. University of Rochester.
- Boström, B., M. Jansson, and C. Forsberg. 1982. Phosphorus release from lake sediments. *Archiv für Hydrobiologie Beiheft Ergebnisse Limnologie* 18: 5-59
- Boström, B., J.M. Andersen, S. Fleischer, and M. Jansson. 1988. Exchange of phosphorus across the sediment-water interface. *Hydrobiologia* 170: 229-244
- Davison, W. 1993. Iron and manganese in lakes. *Earth-Science Reviews* 34: 119-163
- Dillon, P.J. and H.E. Evans. 1993. A comparison of phosphorus retention in lakes determined from mass balance and sediment core calculations. *Water Research* 27(4): 659-668
- Drake, J.C., and S.I. Heaney. 1987. Occurrence of phosphorus and its potential remobilization in the littoral sediments of a productive English lake. *Freshwater Biology* 17: 513-523
- Eby, G. N. 2004. Principles of Environmental Geochemistry. Brooks/Cole-Thomson Learning, Inc. Pacific Grove, CA
- Environmental Health Laboratory 2001. Irondequoit Bay Oxygen Supplementation and Monitoring. Monroe County Environmental Health Laboratory, Monroe Co., N.Y.
- Herbes, S.E., H.E. Allen, and K.H. Mancy. 1975. Enzymatic characterization of soluble organic phosphorus in lake water. *Science* 187: 432-434

- Holtan, H., L. Kamp-Nielsen, and A.O. Stuanes. 1988. Phosphorus in soil, water and sediment: an overview. *Hydrobiologia* 170: 19-34
- Khoshmanesh, A., B.T. Hart, A. Duncan, and R. Beckett. 2002. Luxury uptake of phosphorus by sediment bacteria. *Water Research* 36: 774-778
- Larsen, D.P., D.W. Schults, and K.W. Malueg. 1981. Summer internal phosphorus supplies in Shagawa Lake, Minnesota. *Limnology and Oceanography* 26(4): 740-753
- Lewandowski, J., I. Schauser, and M. Hupfer. 2003. Long term effects of phosphorus precipitations with alum in hypereutrophic Lake Süsser See (Germany). *Water Research* 37: 3194-3204
- McRoy, C.P., R.J. Barsdate, and N. Nebert. 1972. Phosphorus cycling in an eelgrass (*Zostera marina* L.) ecosystem. *Limnology and Oceanography* 17: 58-67
- Mortimer, C.H. 1941. The exchange of dissolved substances between mud and water in lakes. I. *Journal of Ecology* 29: 280-329
- Nürnberg, G.K. 1984. The prediction of internal phosphorus load in lakes with anoxic hypolimnia. *Limnology and Oceanography* 29(1): 111-124
- Nürnberg, G.K. 1987. A comparison of internal phosphorus loads in lakes with anoxic hypolimnia: Laboratory incubation versus in situ hypolimnetic phosphorus accumulation. *Limnology and Oceanography* 32(5): 1160-1164
- Nürnberg, G. 1988. Prediction of phosphorus release rates from total and reductant-soluble phosphorus in anoxic lake sediments. *Canadian Journal of Fisheries and Aquatic Sciences* 45: 453-462
- Ostrofsky, M.L., D.A. Osborne, and T.J. Zebulsk. 1989. Relationship between anaerobic sediment phosphorus release and sedimentary phosphorus species. *Canadian Journal of Fisheries and Aquatic Sciences* 46: 416-419
- Pettersson, K. 1998. Mechanisms for internal loading of phosphorus in lakes. *Hydrobiologia* 373/374: 21-25
- Ruttenberg, K. 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnology and Oceanography* 37: 1460-1482.
- Rydin, E. 2000. Potentially mobile phosphorus in Lake Erken sediment. *Water Research* 34 (7): 2037-2042
- Rydin, E., B. Huser, and E.B. Welch. 2000. Amount of phosphorus inactivated by alum treatments in Washington lakes. *Limnology and Oceanography* 45(1): 226-230

Tangorra, P.A. 1996. Sediment chemistry of Irondequoit Bay, New York. Master's Thesis. SUNY Brockport. Brockport, NY.

Welch, E.B. and G.D. Cooke. 1999. Effectiveness and longevity of phosphorus inactivation with alum. *Lake and Reservoir Management* 15(1): 5-27

Wetzel, R.G. 2001. Limnology: Lake and River Ecosystems 3rd Edition. Academic Press San Diego, Ca.

White, D., J. Makarewicz, and T. Lewis. 2002. The significance of phosphorus released from the sediment under anoxic conditions in Sodus Bay, N.Y. Technical report prepared for the Wayne County Soil and Water Conservation District.

Yao, W., and F.J. Millero. 1996. Adsorption of phosphate on manganese dioxide in seawater. *Environmental Science and Technology* 30: 536-541.

Table 1. Sampling locations in Irondequoit Bay.

Site	Depth (m)	Location
Bridge	20.5	N 43° 12.671' W 77° 32.042'
Middle Bay	22.2	N 43° 12.914' W 77° 32.095'
North Bay	23.3	N 43° 13.129' W 77° 32.114'

Table 2. Depths of light-colored bands in sediment cores from the North Basin site.

Date core was taken on	Band Begins Depth from sediment surface (centimeters)	Band Ends Depth from sediment surface (centimeters)
23 June 2004	20	21
29 July 2004	18.5	20
24 August 2004	23	24
30 September 2004	20	21

Table 3. Loading Rates for Irondequoit Bay North Basin. Bathymetric data for area and volume calculations taken from Bannister *et al.*, 1982. Change and rate represent the change in phosphorus of the North Basin. Areal release rate was calculated by dividing the rate of release (in mg/day) by the surface area of the North Basin of Irondequoit Bay.

11 June 2003 to 5 August 2003

	Change (kgP)	Rate (kgP/day)	Areal (mgP/m ² /day)
Epi	52.62	0.96	0.61
Meta	180.76	3.29	2.08
Hypo	586.64	10.67	6.75
Entire	820.01	14.91	9.44

19 May 2004 to 30 September 2004

	Change (kgP)	Rate (kgP/day)	Areal (mgP/m ² /day)
Epi	525.80	3.92	2.48
Meta	415.55	3.10	1.96
Hypo	2020.71	15.08	9.54
Entire	2979.80	22.24	14.07

North Basin Hypolimnion

Year	Change (kgP)	Rate (kgP/day)	Areal (mgP/m ² /day)
2003	586.6	10.67	6.75
2004	2020.7	15.08	9.54
	Mean	12.87	8.15

Table 4. Total phosphorus increases and release rates for sediment core incubation experiments. Release rates are derived from dividing the observed increase in total phosphorus (TP Increase) by the duration of the experiment (25 days). The mean of all TP increase values and the mean of all Release Rates are presented in the row labeled "Average", at the bottom of the table. The column labeled average gives the means for each of the locations.

Location	TP Increase (mg P/m ²)	Release Rate (mg P/m ² /day)	Average (mg P/m ² /day)
Bridge	94.26	3.77	
Bridge	74.51	2.98	3.38
Middle Bay	67.86	2.71	
Middle Bay	84.39	3.38	3.04
North Bay	58.89	2.36	
North Bay	52.98	2.12	2.24
Average	72.15	2.89	

Table 5 Summary statistics for chemical and physical parameters in the top 25 cm of Irondequoit Bay sediments. Total sediment phosphorus (TPs), sodium chloride extractable phosphorus (Loosely Sorbed P), bicarbonate dithionite extractable phosphorus (BD-P), aluminum bound phosphorus (Al-P), organically bound phosphorus (Org-P), and calcium bound phosphorus (Ca-P) are expressed in mg P/g sediment dry weight. Total sediment iron (Total Fe) and total sediment manganese (Total Mn) are expressed in mg/g sediment dry weight. Percent moisture (Moisture) is expressed in percent wet sediment weight and loss on ignition (LOI) is expressed in percent dry sediment weight.

	Mean	S.E.	Min	Max
TP _s	1.389	0.150	0.426	6.719
Loosely Sorbed P	0.016	0.002	0.003	0.058
BD-P	0.338	0.015	0.152	0.623
Al-P	0.276	0.109	0.026	4.286
Org-P	0.151	0.019	0.067	0.873
Ca-P	0.429	0.019	0.210	0.809
Total Fe	24.415	0.760	16.447	38.807
Total Mn	1.727	0.053	0.909	2.530
Moisture	66.81	1.29	51.95	85.60
LOI	8.42	0.16	7.21	10.84

Table 6. Summary statistics for lake and sediment characteristics of 57 lakes examined by Ostrofsky *et. al.* (1989) and Irondequoit Bay (this study). The values from Ostrofsky *et. al.* are from the top 2.5 cm of sediment. Irondequoit Bay values are the average of the top 2 cm of monthly sediment cores sampled at the North Bay site from May thru September 2004. Total phosphorus in $\mu\text{g/L}$, alkalinity in $\text{mg CaCO}_3/\text{L}$, all sedimentary phosphorus species in g P/kg sediment dry weight, sediment iron in g Fe/kg sediment dry weight, loss on ignition in percent of dry weight. $\text{NaOH-P}_{\text{metals}}$ includes redox sensitive and aluminum bound P; HCl-P is calcium bound P.

Parameter	Ostrofsky <i>et. al.</i>	Irondequoit Bay
	Mean (Range)	Mean \pm S.E.
Total phosphorus	22 (5 - 111)	24.2 \pm 3.5*
Alkalinity	107 (11 - 287)	202.8 \pm 8.0**
Total sediment phosphorus	2.636 (1.342 - 9.212)	1.224 \pm 0.157
Organic sediment phosphorus	1.477 (0.677 - 2.520)	0.431 \pm 0.070
Inorganic sediment phosphorus	1.158 (0.308 - 7.325)	0.920 \pm 0.114
Loosely sorbed P	0.069 (0.000 - 0.872)	0.014 \pm 0.003
$\text{NaOH-P}_{\text{metals}}$	0.832 (0.188 - 5.879)	0.514 \pm 0.034***
HCl-P	0.258 (0.075 - 0.709)	0.391 \pm 0.099
Sediment Iron	46.547 (22 - 108)	22.705 \pm 2.161
Loss on ignition	27 (10 - 54)	10.1 \pm 0.3

* mean ($n = 5$) total phosphorus concentration from the surface of the North Bay site from May through September of 2004

** mean ($n = 4$) alkalinity concentration from the epilimnion of the North Bay site from June through September of 2004

***mean ($n = 5$) of the sums of the BD-P and NaOH-SRP fractions from sequential extraction analysis of sediments of the North Bay site from May through September of 2004

Table 7. Summary statistics for sediment characteristics of seven North American lakes examined by Nürnberg (1988) and Irondequoit Bay (this study). These numbers represent average values for the top 10 cm of sediment. Irondequoit Bay values are the average of monthly sediment cores sampled at the North Bay site from May through September 2004. Percent moisture is expressed in percent wet sediment weight and loss on ignition (LOI) is expressed in percent dry sediment weight, total sediment phosphorus (TP_s) and bicarbonate dithionite extractable phosphorus (BD-P) are expressed in mg P/g sediment dry weight.

	Nürnberg (1988)	Irondequoit Bay
	Mean (Range)	Mean \pm S.E.
Moisture	93.8 (90.8 - 96.3)	66.4 \pm 1.8
LOI	38.2 (23.3 - 62.5)	8.8 \pm 0.2
TP_s	1.89 (1.19 - 3.06)	1.14 \pm 0.04
BD-P	0.27 (0.03 - 0.60)	0.34 \pm 0.01

Table 8. Phosphorus release rates (RR) resulting from applying Irondequoit Bay total sediment phosphorus (TP_s) and bicarbonate dithionite (BD-P) extractable phosphorus concentrations to the predictive regressions from Nürnberg (1988). Release rates are expressed in $mg\ P/m^2/day$. Wet Sediment refers to release rates calculated from regressions using phosphorus concentrations expressed as $\mu g\ P/g$ wet weight and Dry Sediment refers to released rates calculated from regressions using phosphorus concentration expressed as $mg\ P/g$ dry weight. The Phosphorus Fraction column refers to the phosphorus fraction utilized by the regression to predict a release rate. $TP_s - LOI$ refers to the predictive regression utilizing total sediment phosphorus with loss on ignition (LOI) as a second variable.

Phosphorus Fraction	Predicted RR Wet Sediment ($mg\ P/m^2/day$)	Predicted RR Dry Sediment ($mg\ P/m^2/day$)
TP_s	23.82	0.11
BD-P	31.56	4.22
$TP_s - LOI$	***	6.35

Table 9. Estimates of phosphorus release rates from lakes of the world with anoxic hypolimnions. Release rates are calculated by the increase of phosphorus in the hypolimnion over a period of anoxia. All data are reproduced from Nürnberg, 1984 except for the value from Sodus Bay, which is taken from White *et al.*, 2002.

Lake	Release Rate ($mg\ P/m^2/d$)
Shagawa	12.1
Mendota	10.8
West Twin	6.5
East Twin	6
Erie	7.4
White Lake	19
Barten Broad	9.6
Alderfen Broad	20
Baldeggersee	9.7
Rotsee	28
Norrviken	9.2
Bergundasjoen	24.5
Esrom	11.5
Byoesjoen	20
Magog	13.5
Sodus Bay	2.7
Mean \pm SE	13.2 \pm 1.8
Median	11.2
<i>n</i>	16

Table 10. Estimates of phosphorus release rates from lakes of the world with anoxic hypolimnions. Release rates are estimated from sediment microcosm experiments. Negative release rates indicate absorption of phosphorus by sediment. Data are reproduced from Nürnberg, 1984

Lake	Release Rate	
	Anoxic (mg/m ² /d)	Oxic (mg/m ² /d)
White	34.3	-
Ursee	11	-
Furosoe	17.3	-4.5
Esrom	12.3	-1.4
St. Gribsoe	1.2	0.2
Grand Langsoe	0.8	0.6
Bergundasjoen	34	-
Alderfen Broad	20	0
Mohegon	3	0
Glanningen	18	2
Ramsjoen	20	0.3
Ryssbysjoen	20	0.7
Charles East	31	-16
Stone	32	-
Trummen	1.5	0.3
Arungen	16	1.0
Vombsjoen	6	2.6
Byoesjoen	27	7
Norrviken	10	5
Ontario	-	0.2
Memphremagog	10	-
Mean	16	-0.01
Standard Error	2.5	1.32
Median	15	0.3
<i>n</i>	20	15

Figure 1. Map of Irondequoit Bay with sample sites labeled.



Figure 2. Sequential extraction scheme modified from Rydin 2000.

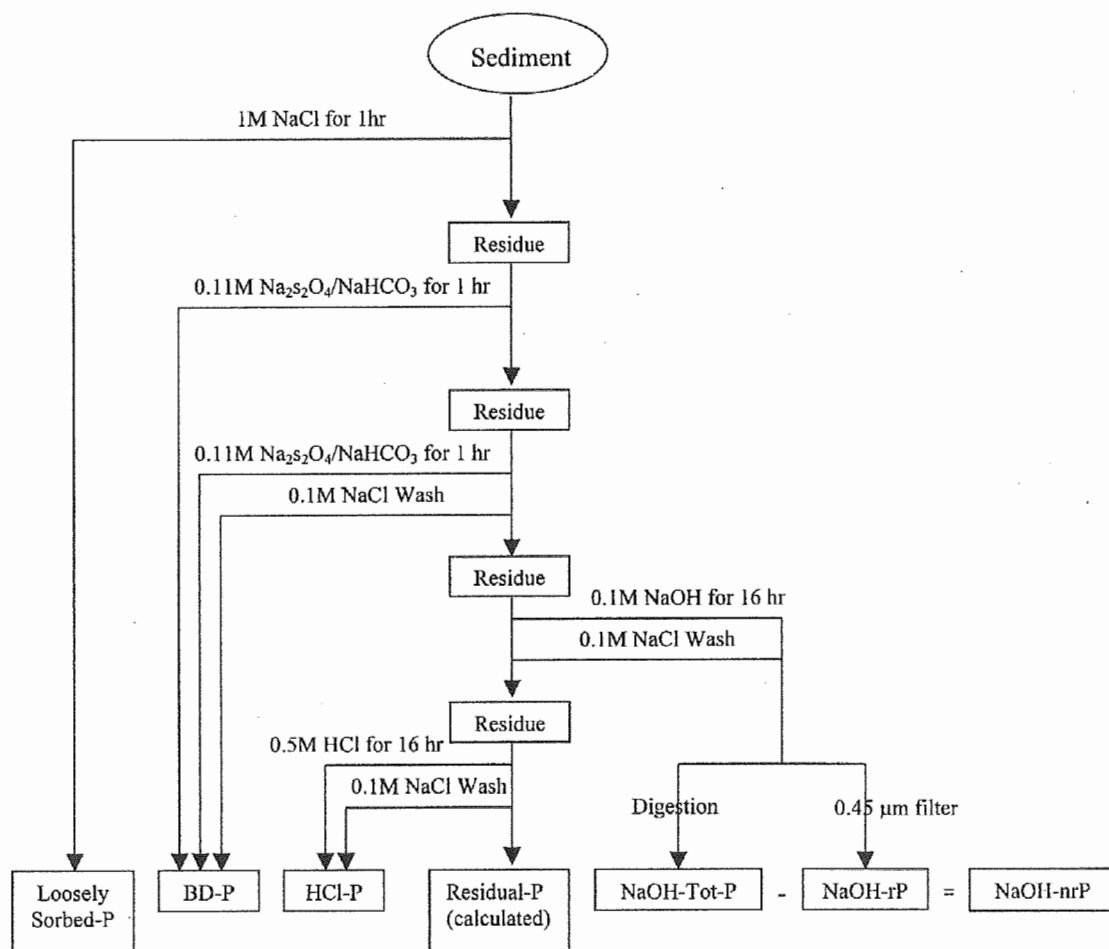


Figure 3. Sediment core incubation experiments.

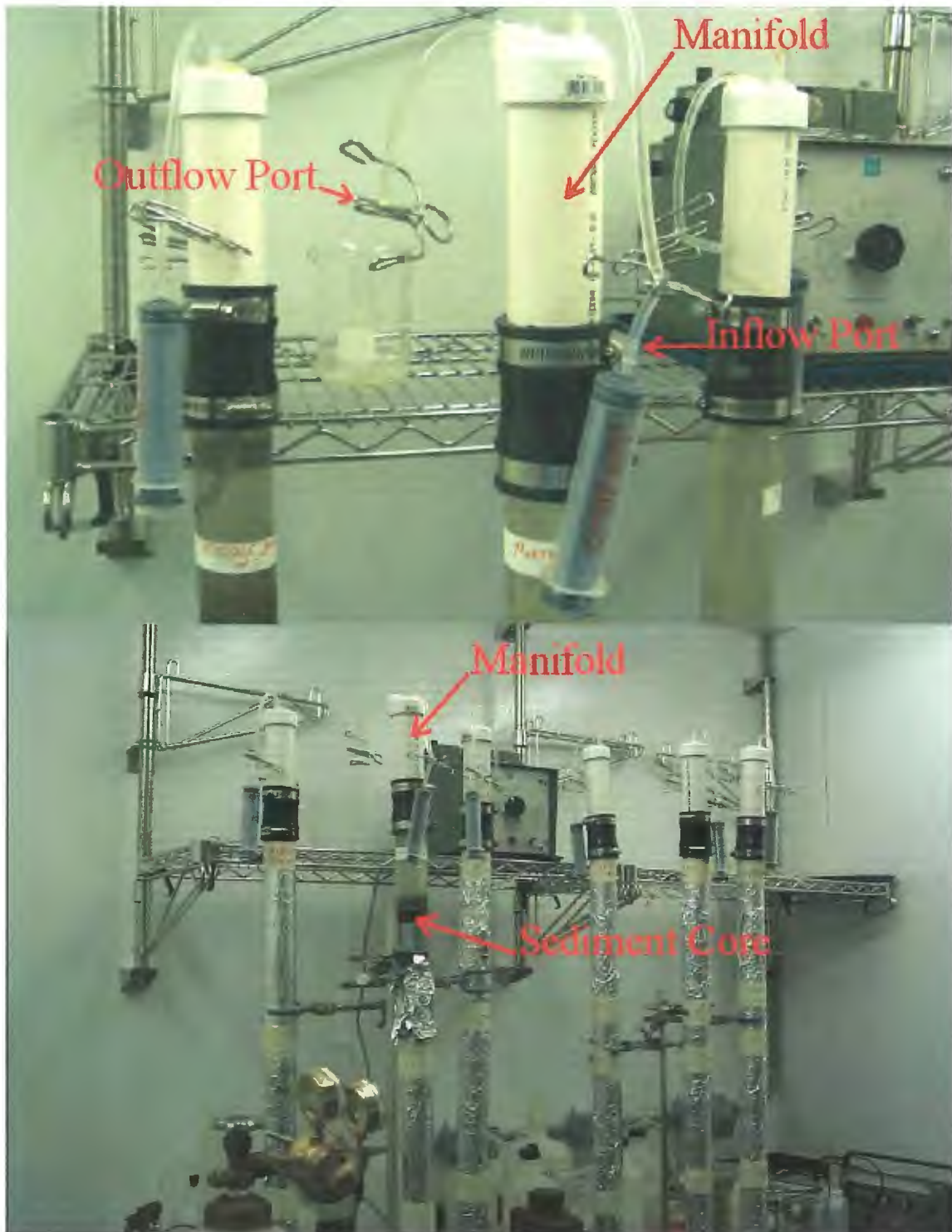


Figure 4. Hypsographic curve of Irondequoit Bay giving area of the basin at depth from the water surface. Bathymetric data taken from Bannister *et al.* (1982).

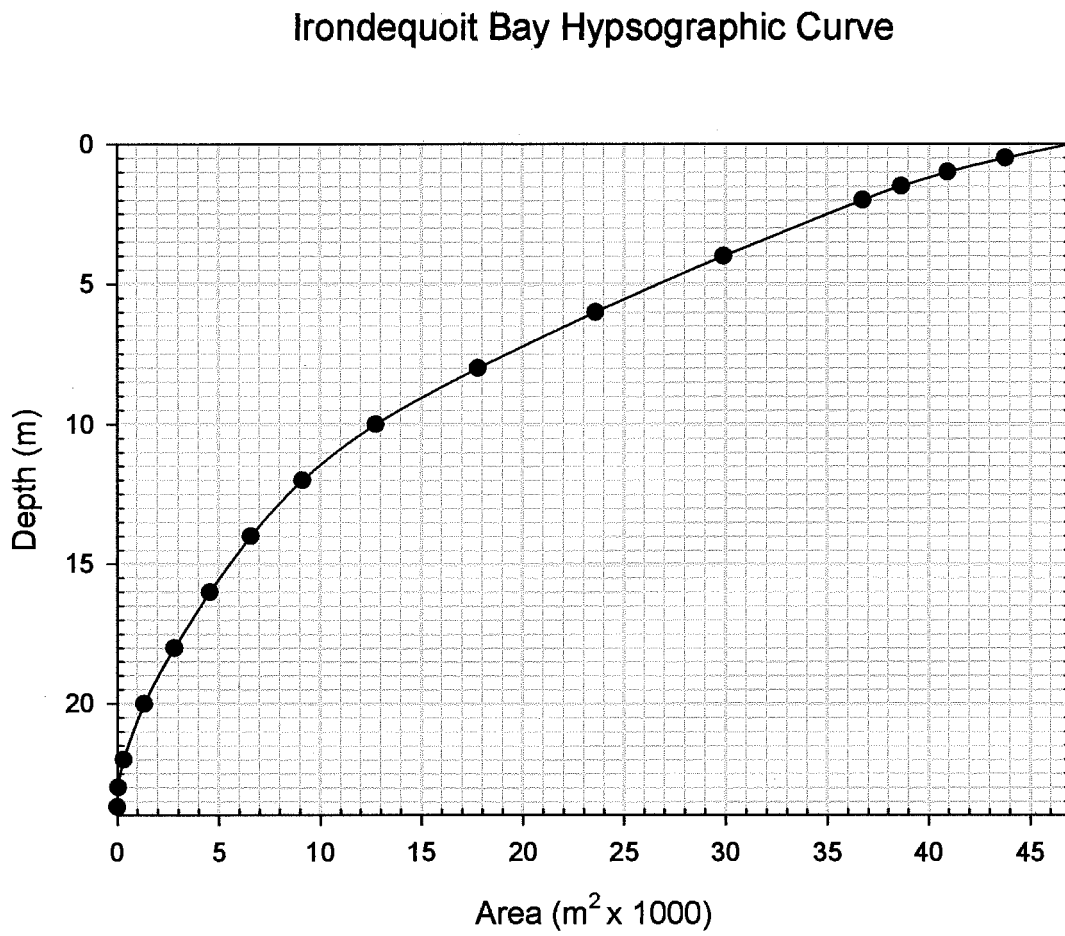


Figure 5. Dissolved oxygen (DO) and temperature (Temp) vs. depth profiles for the North Basin site of Irondequoit Bay during the 2003 sampling period.

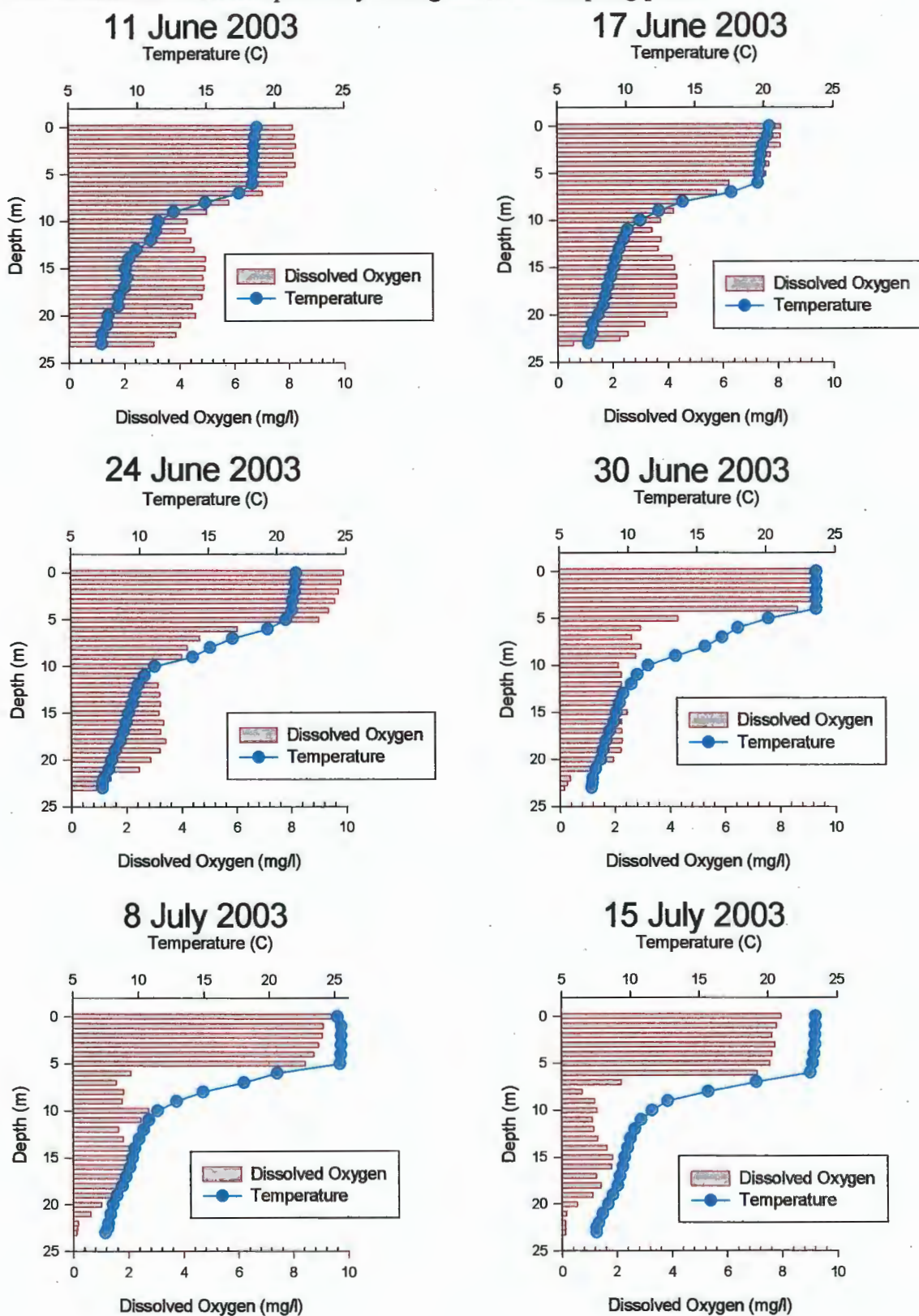


Figure 5 (continued). Dissolved oxygen (DO) and temperature (Temp) vs. depth profiles for the North Basin site of Irondequoit Bay during the 2003 sampling period.

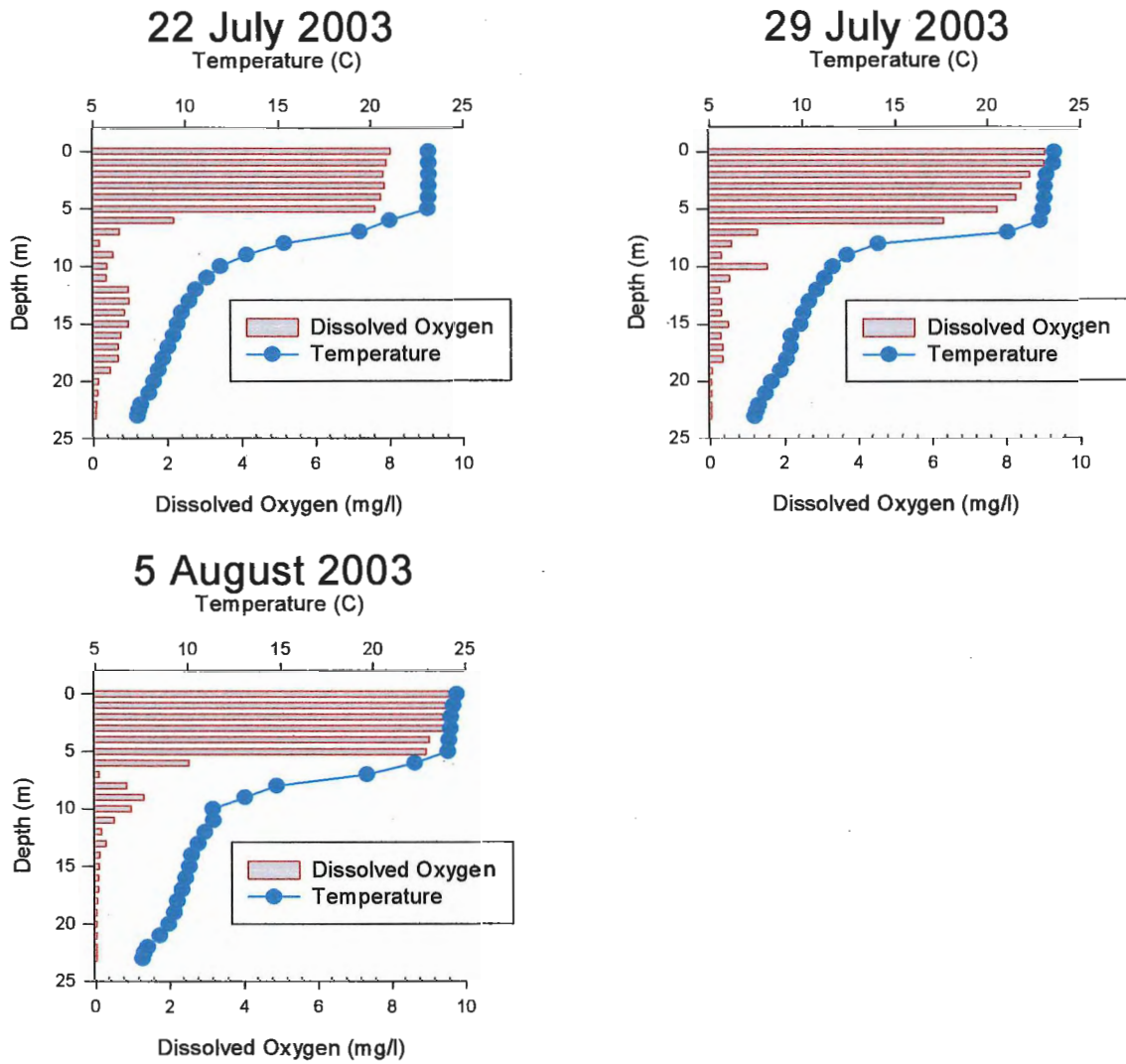


Figure 7. Total phosphorus (TP), soluble reactive phosphorus (SRP), and dissolved oxygen (DO) vs. depth profiles for the North Basin site of Irondequoit Bay during the 2003 sampling period.

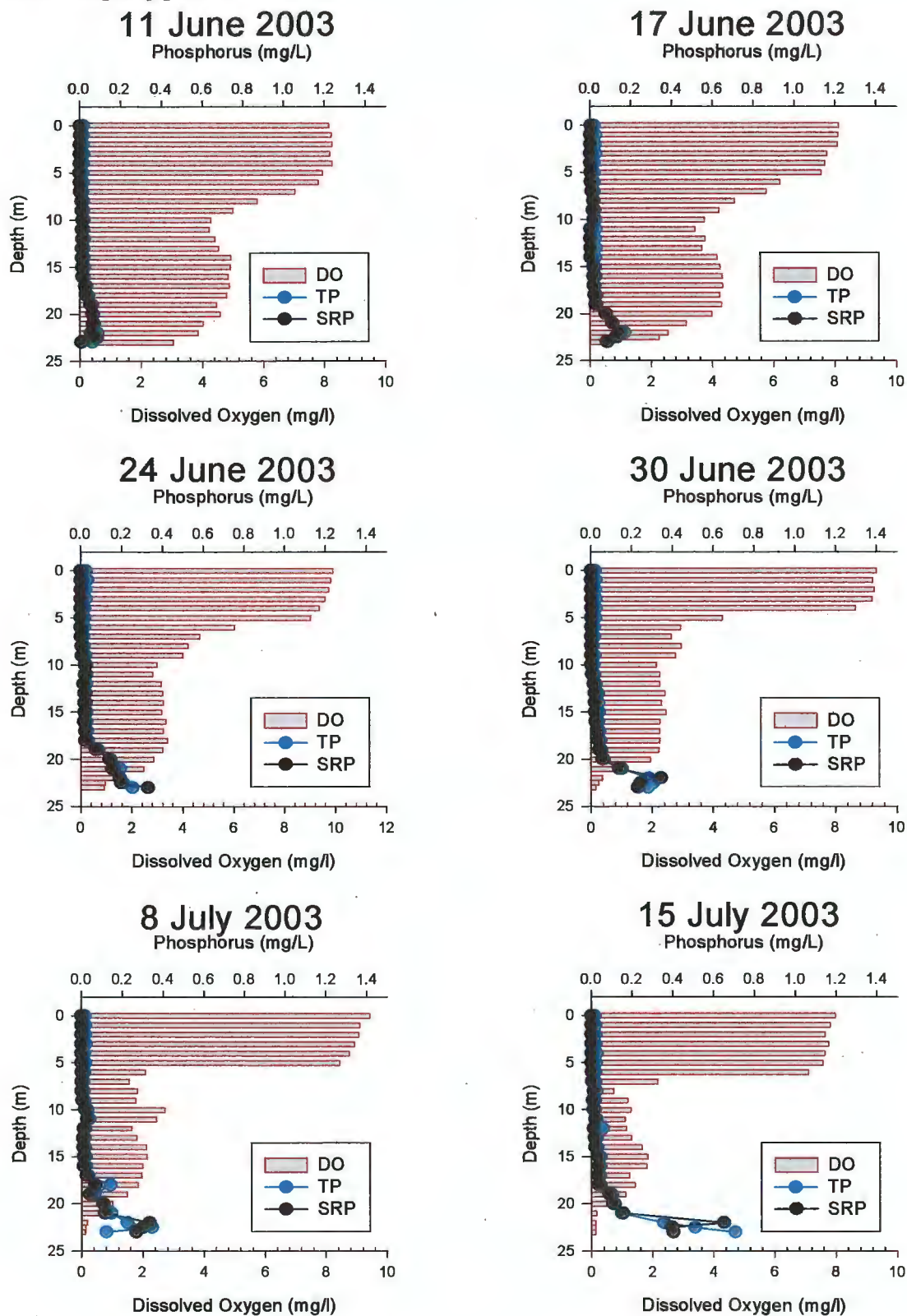


Figure 7 (continued). Total phosphorus (TP), soluble reactive phosphorus (SRP), and dissolved oxygen (DO) vs. depth profiles for the North Basin site of Irondequoit Bay during the 2003 sampling period.

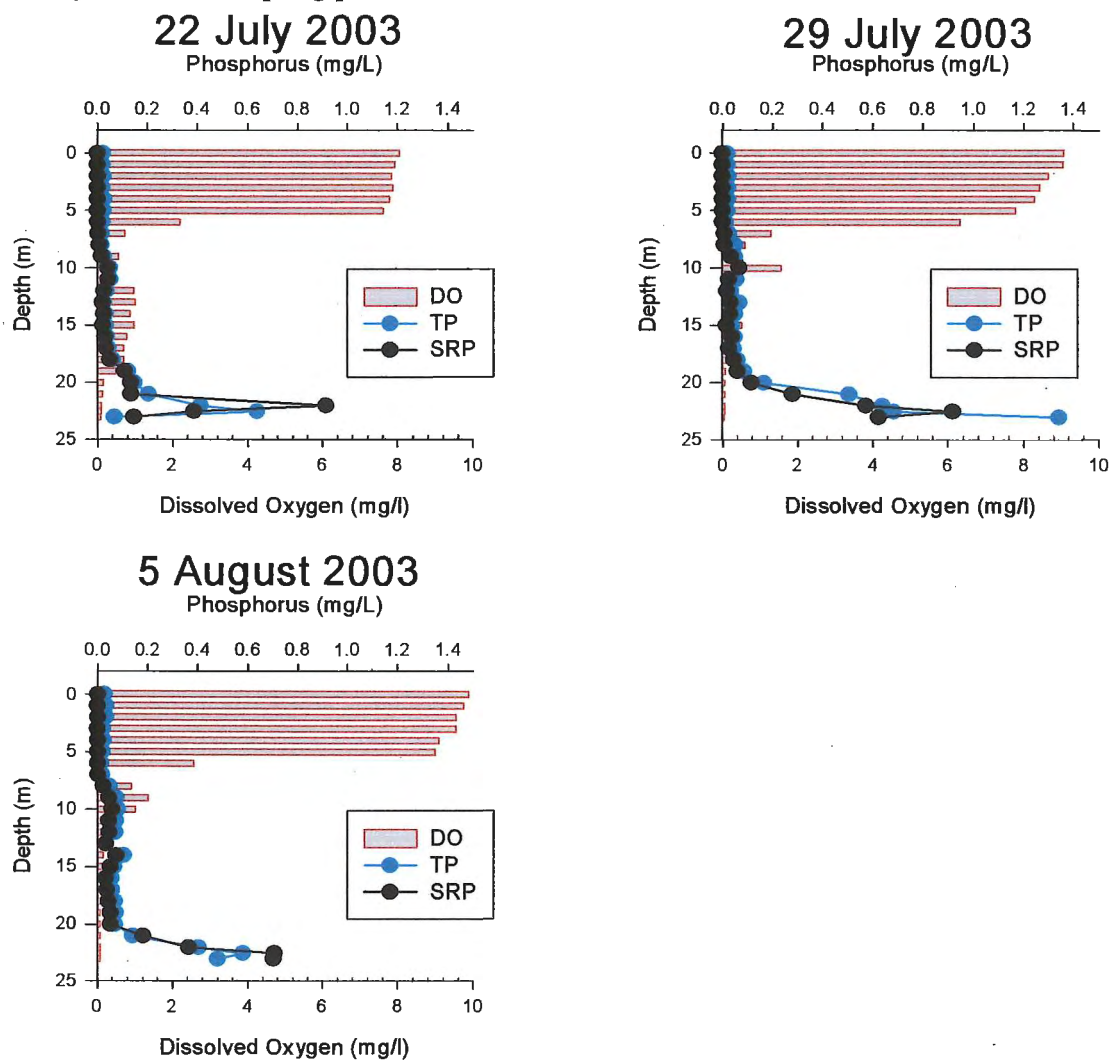


Figure 8. Total phosphorus (TP), soluble reactive phosphorus (SRP), and dissolved oxygen (DO) vs. depth profiles for the North Basin site of Irondequoit Bay during the 2004 sampling period.

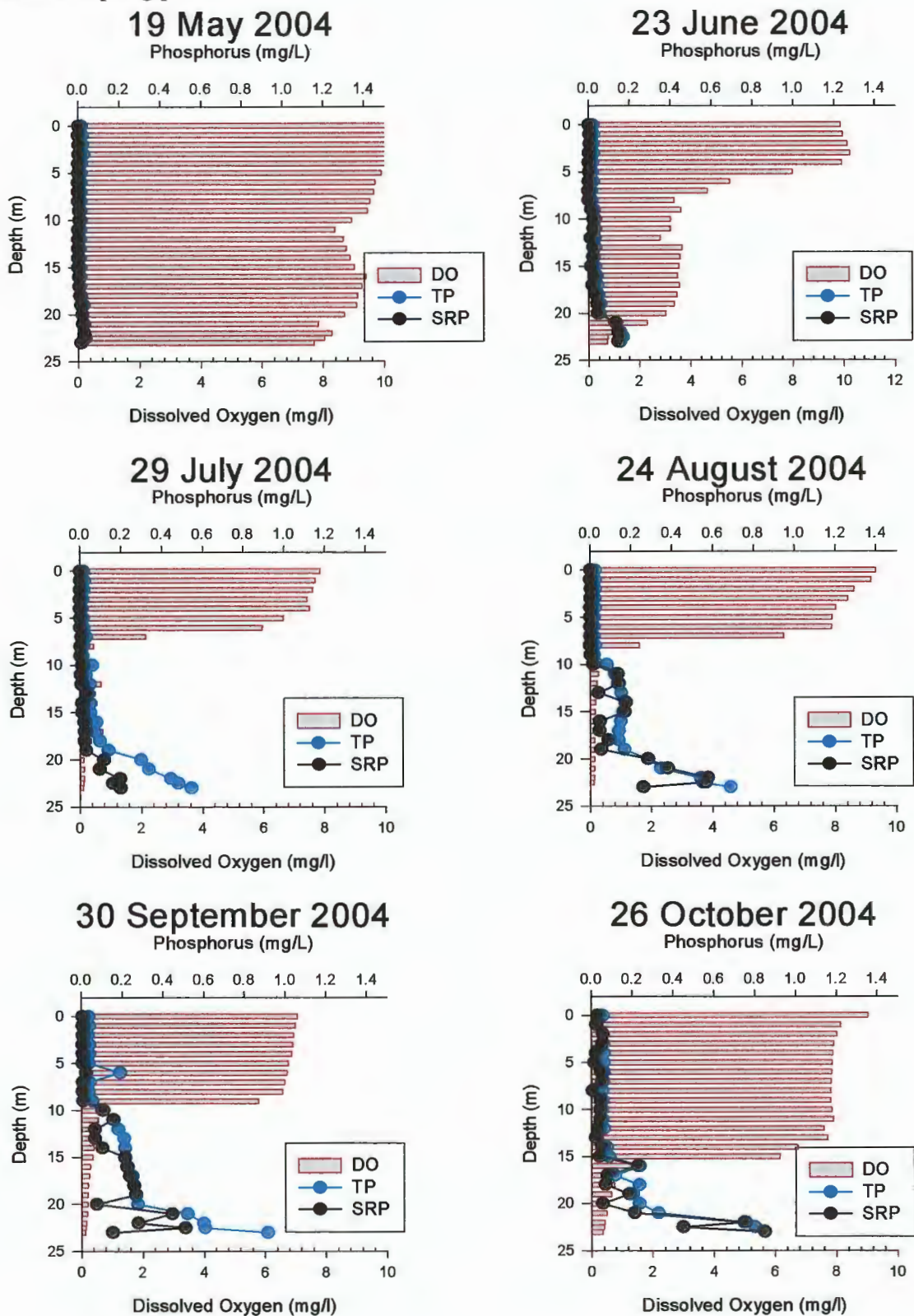


Figure 9. Total phosphorus content of the North Basin of Irondequoit Bay on sampling dates during the 2003 sampling period. Entire = The total phosphorus content of the entire North Basin, Hypo = The total phosphorus content of the hypolimnion of the North Basin, Epi = The total phosphorus content of the epilimnion of the North Basin, Meta = The total phosphorus content of the metalimnion of the North Basin.

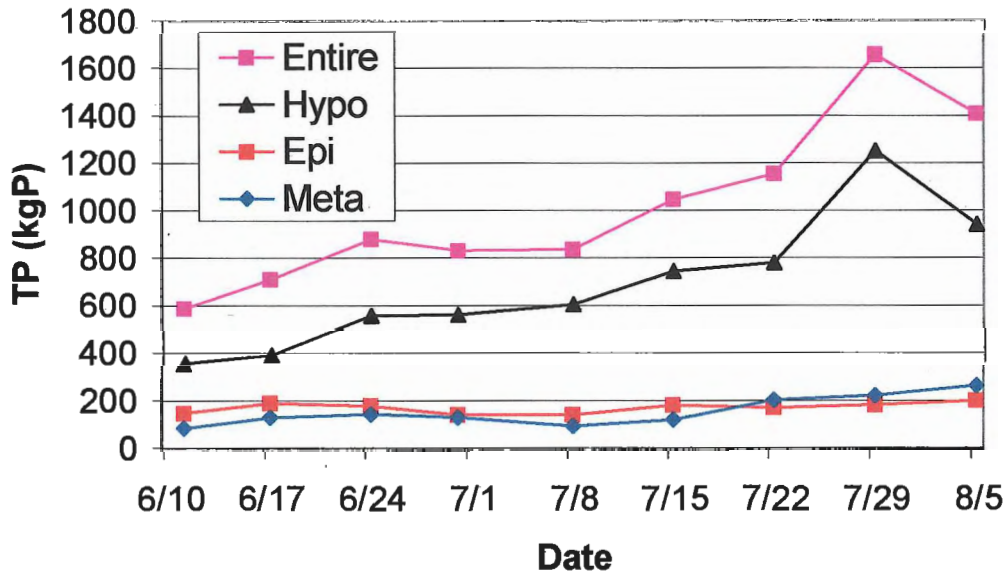


Figure 10. Total phosphorus content of the North Basin of Irondequoit Bay on sampling dates during the 2004 sampling period. Entire = The total phosphorus content of the entire North Basin, Hypo = The total phosphorus content of the hypolimnion of the North Basin, Epi = The total phosphorus content of the epilimnion of the North Basin, Meta = The total phosphorus content of the metalimnion of the North Basin.

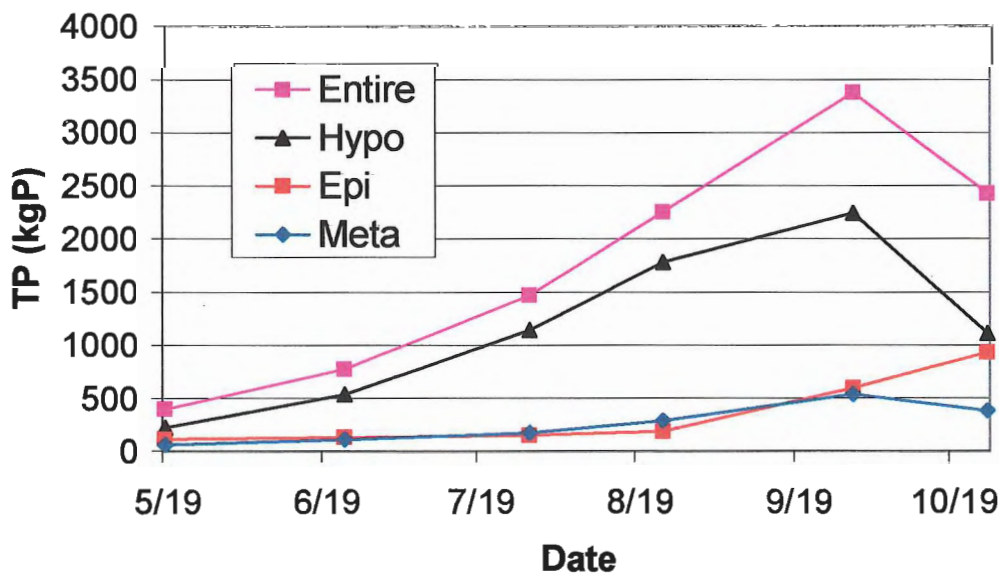


Figure 11. Nitrate + Nitrite concentrations vs. depth profiles for the North Basin site of Irondequoit Bay during the 2003 sampling period.

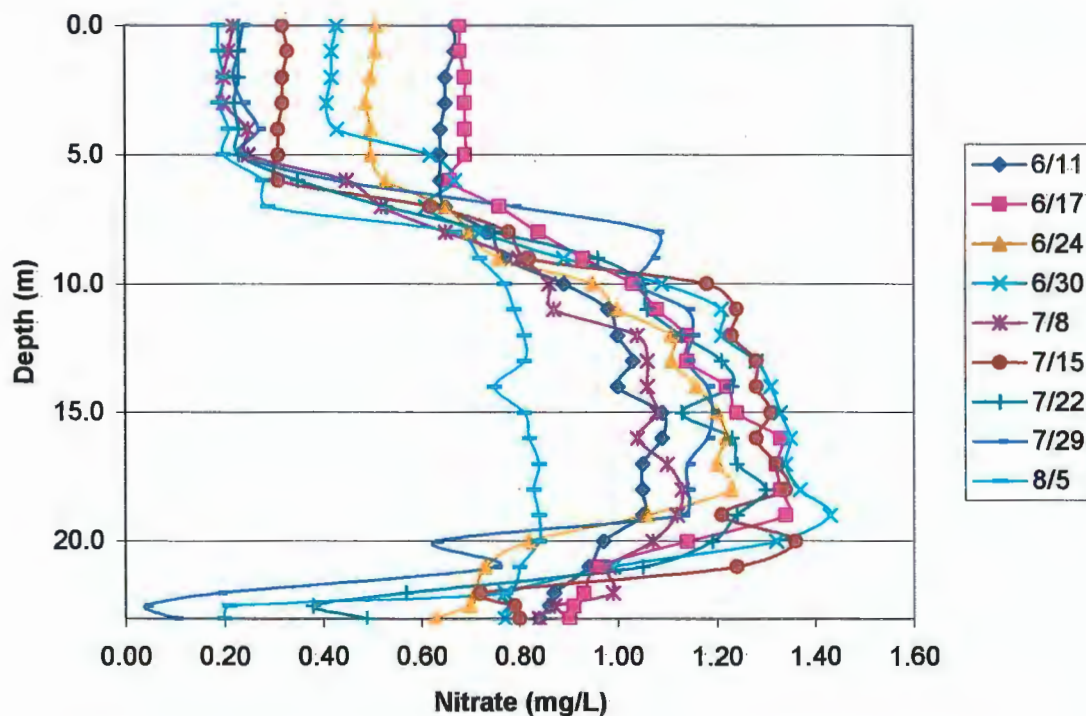


Figure 12. Manganese concentrations vs. depth profiles for the North Basin site of Irondequoit Bay during the 2004 sampling period.

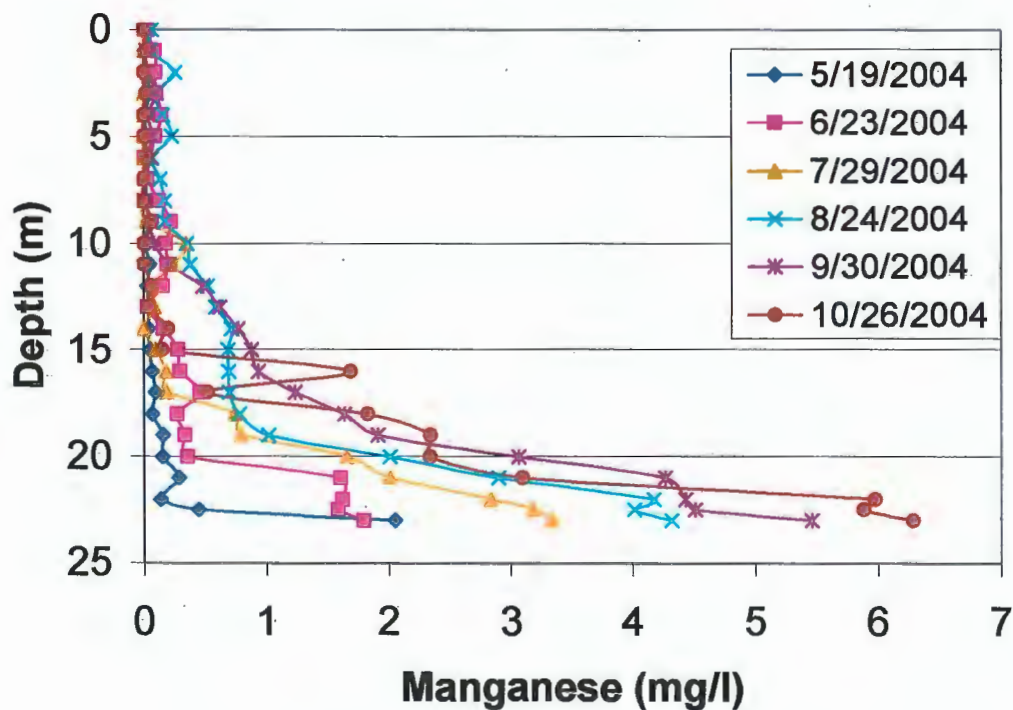


Figure 13. Iron concentrations vs. depth profiles for the North Basin site of Irondequoit Bay during the 2004 sampling period.

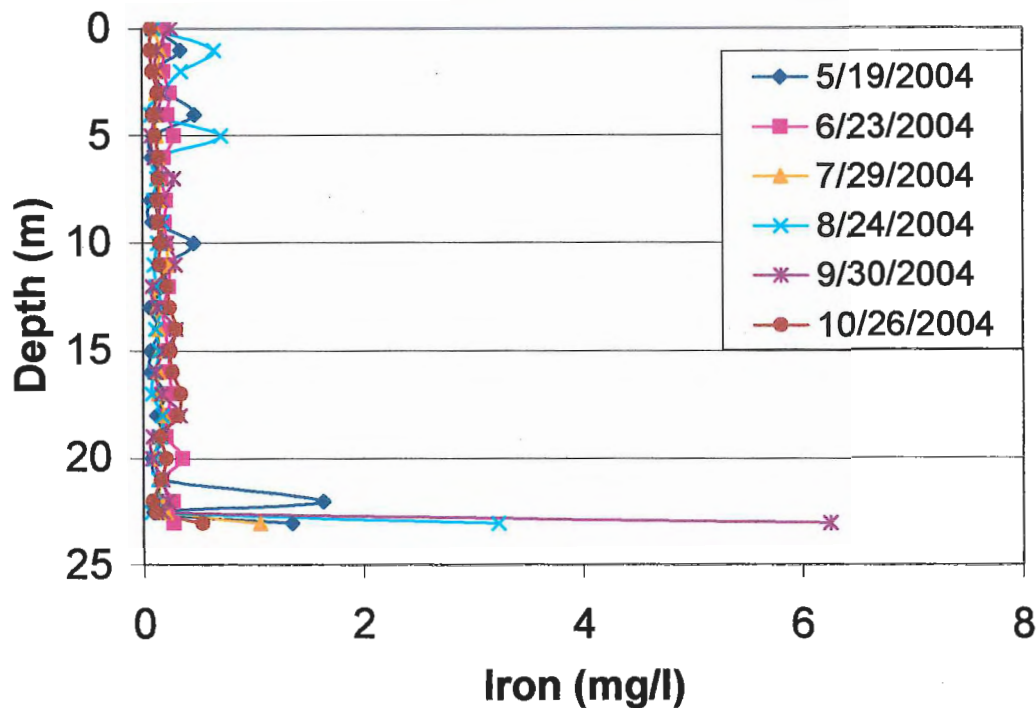


Figure 14. Iron (Fe) molar concentrations vs. total phosphorus molar concentrations of water samples taken at the North Basin of Irondequoit Bay during the 2004 sampling period.

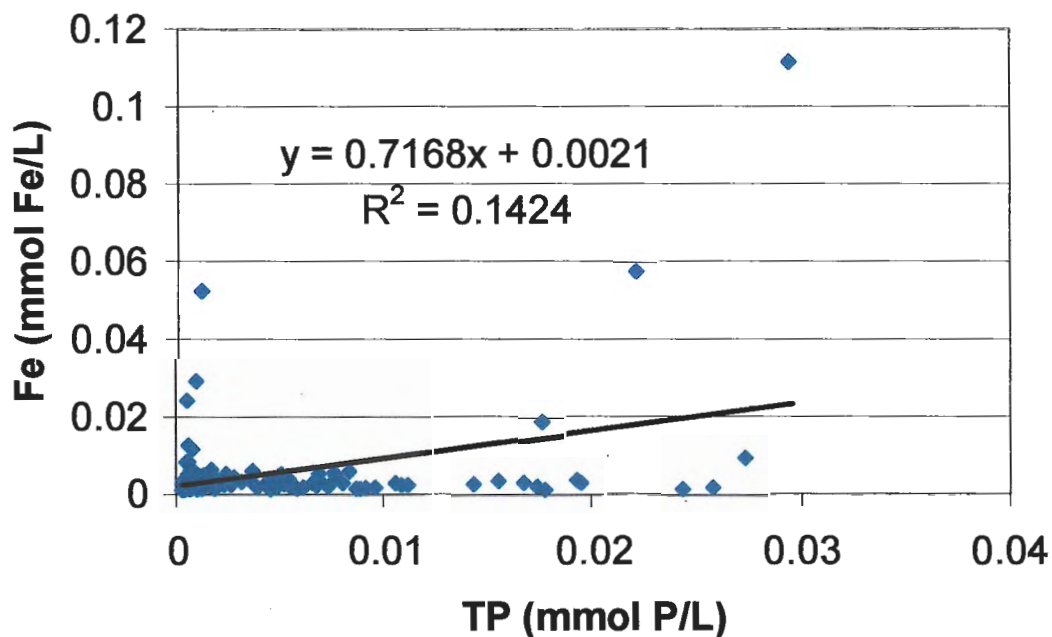


Figure 15. Manganese (Mn) molar concentrations vs. total phosphorus molar concentrations of water samples taken at the North Basin of Irondequoit Bay during the 2004 sampling period.

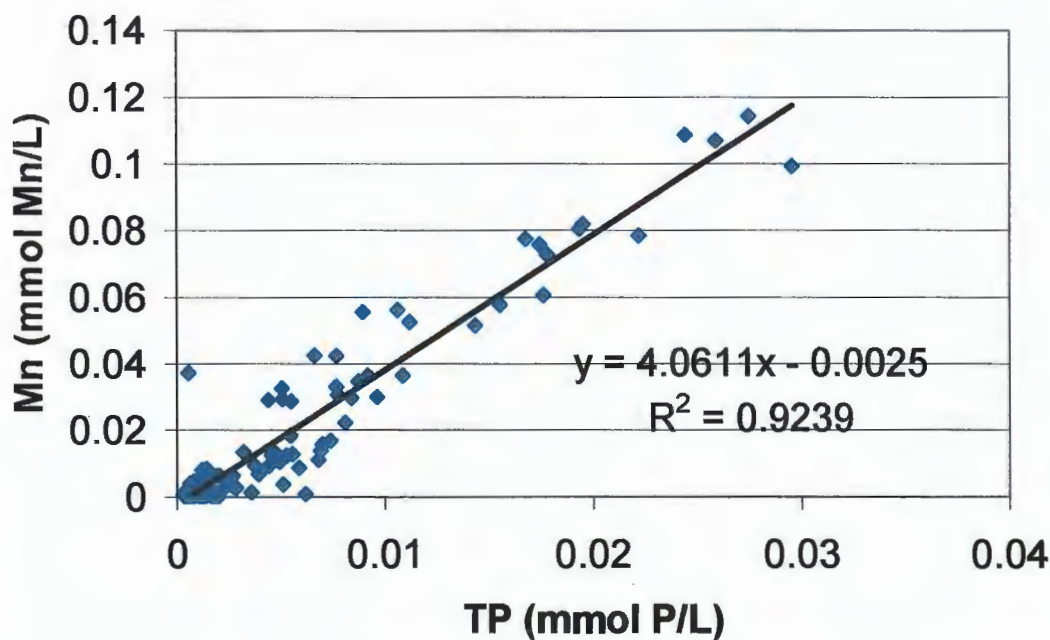


Figure 16. Alkalinity concentrations at the North Basin site of Irondequoit Bay from June 2004 to October 2004. Average = mean value of concentrations found on that sampling date, Hypo = alkalinity concentration from hypolimnion sample, Epi = alkalinity concentration from epilimnion sample, Meta = alkalinity concentration from metalimnion sample.

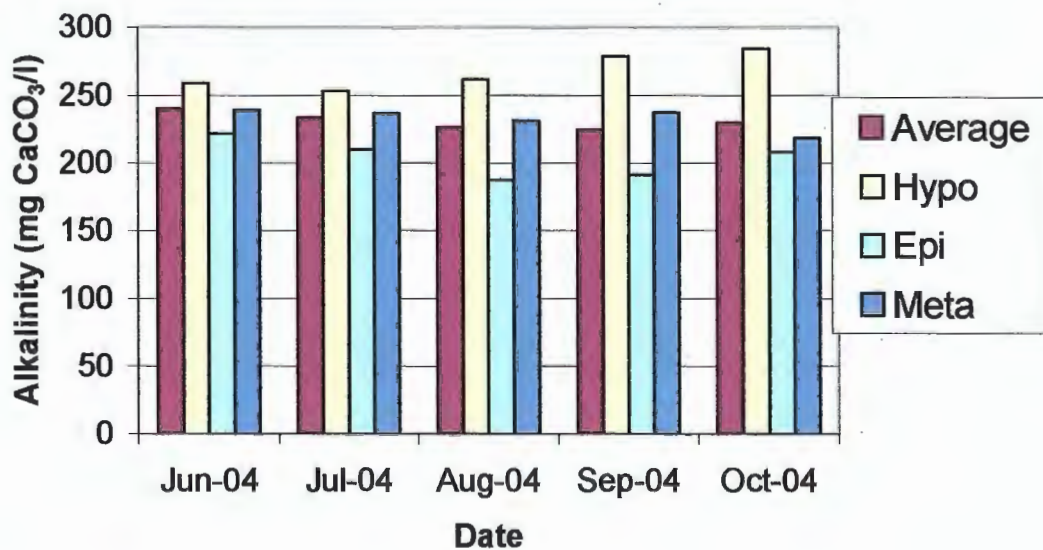


Figure 17. pH vs. depth profiles for the North Basin site of Irondequoit Bay during the 2003 sampling period.

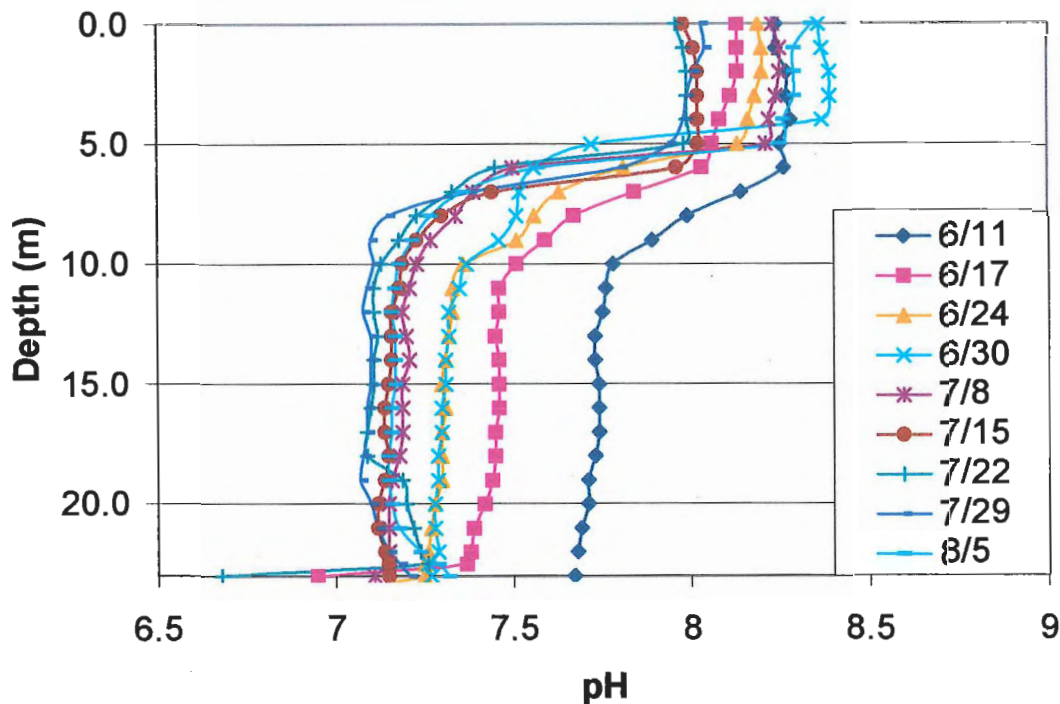


Figure 18. pH vs. depth profiles for the North Basin site of Irondequoit Bay during the 2004 sampling period.

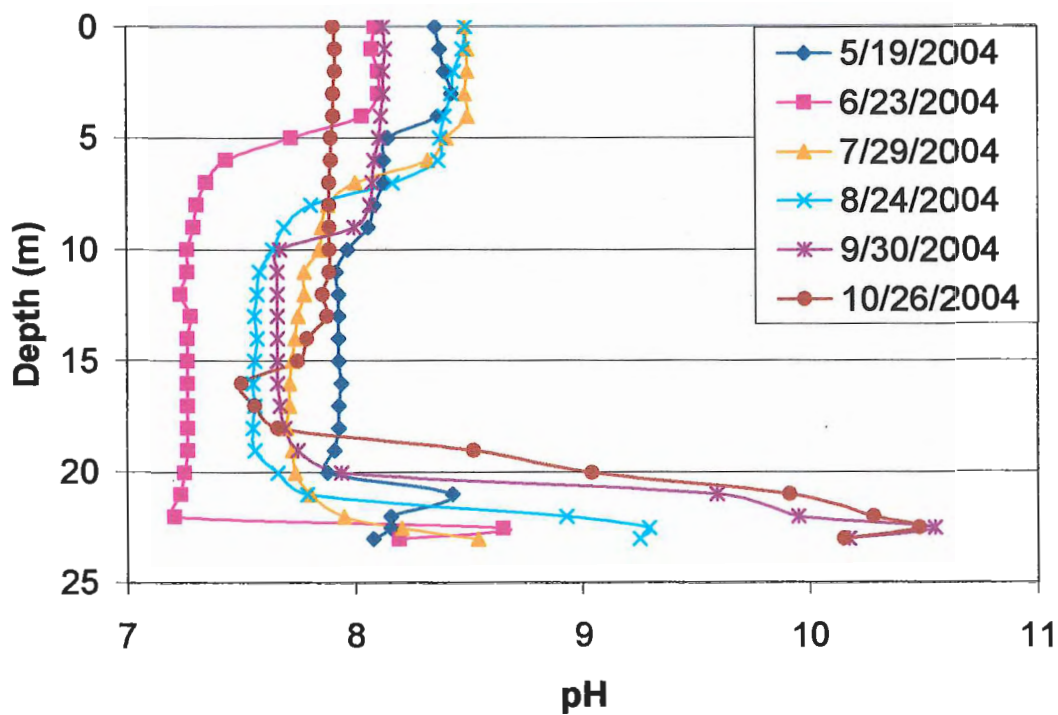


Figure 19. Iron (Fe), manganese (Mn), and phosphorus (P) mean concentrations in the top ~25 cm of sediment cores taken during the 2004 sampling period. Error bars represent \pm the standard error.

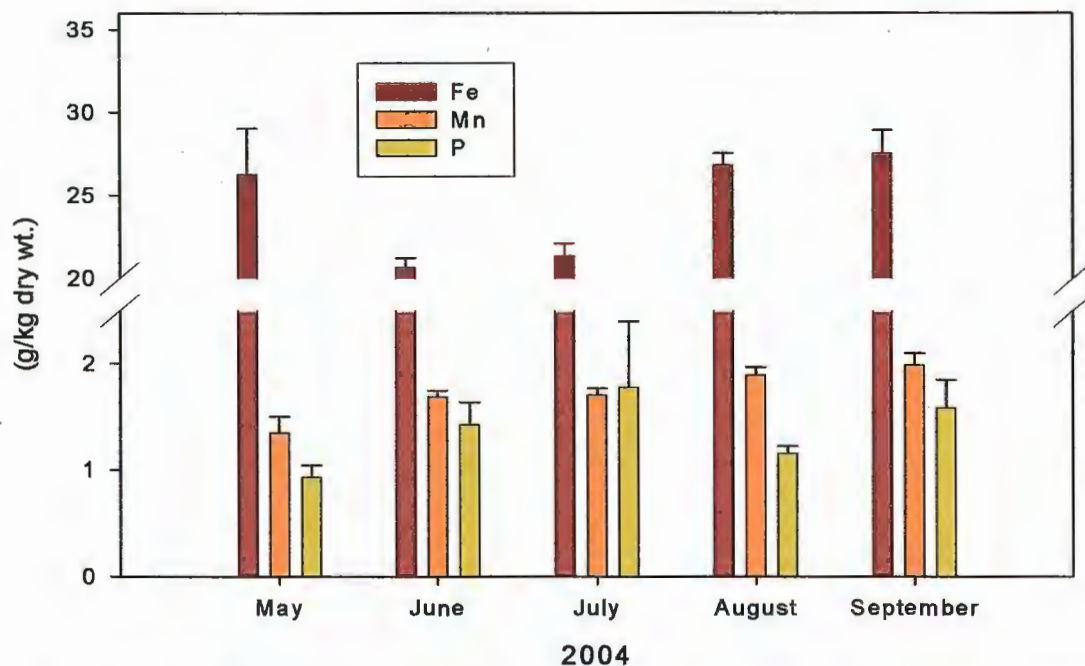


Figure 20. Iron (Fe), manganese (Mn), and phosphorus (P) mean concentrations in the top 10 cm of sediment cores taken during the 2004 sampling period. Error bars represent \pm the standard error.

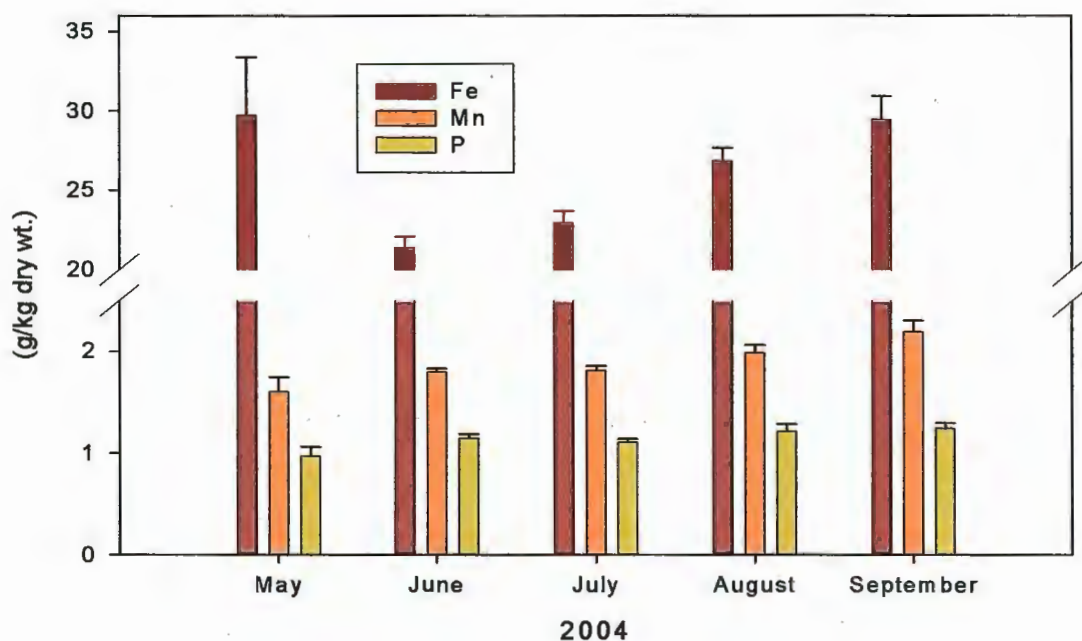


Figure 21. Sediment phosphorus profiles for sediment cores taken from the North Bay site of Irondequoit Bay during the summer of 2004.

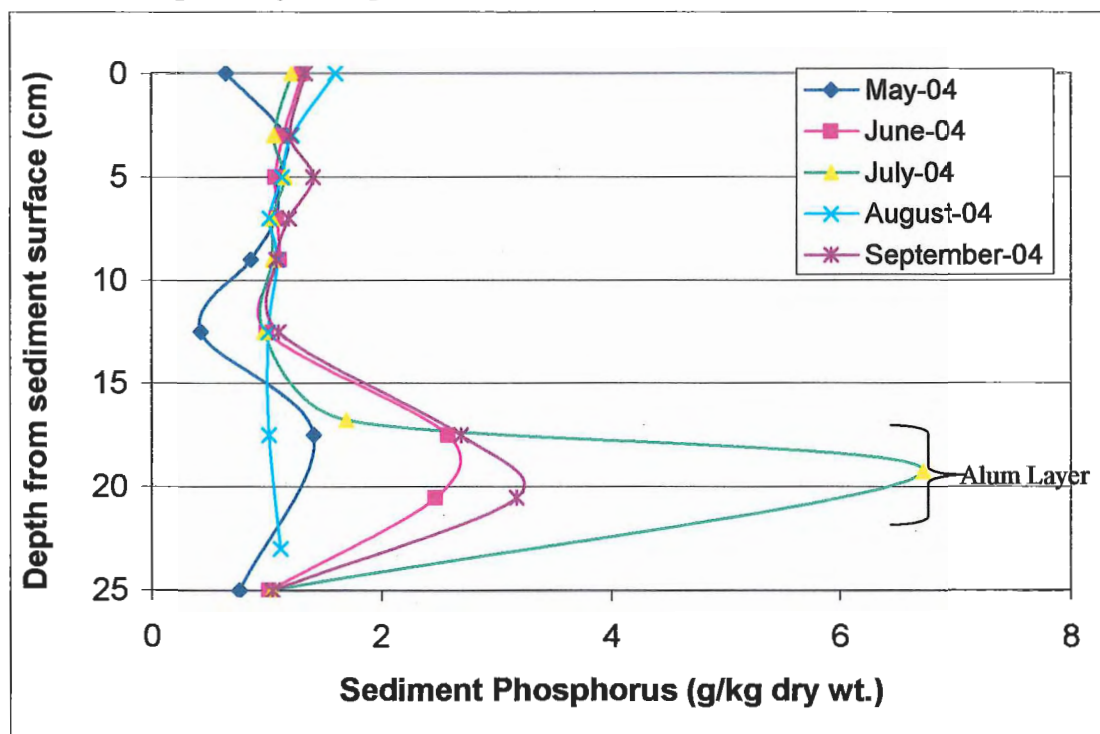


Figure 22. Sediment iron profiles for sediment cores taken from the North Bay site of Irondequoit Bay during the summer of 2004.

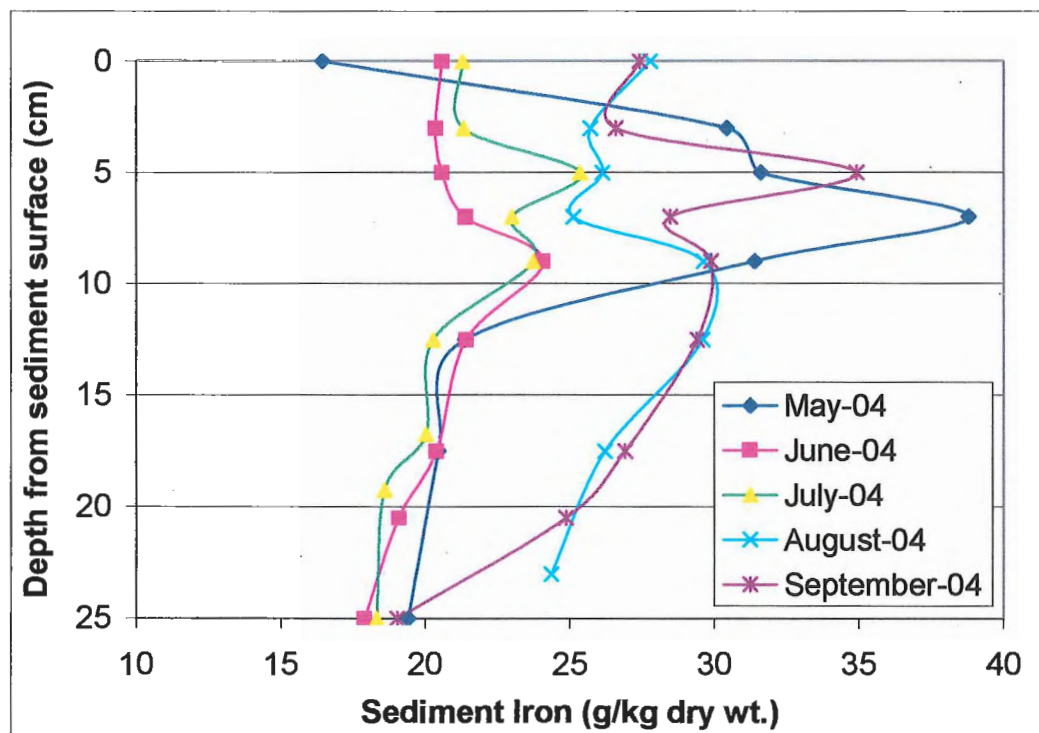


Figure 23. Sediment manganese profiles for sediment cores taken from the North Bay site of Irondequoit Bay during the summer of 2004.

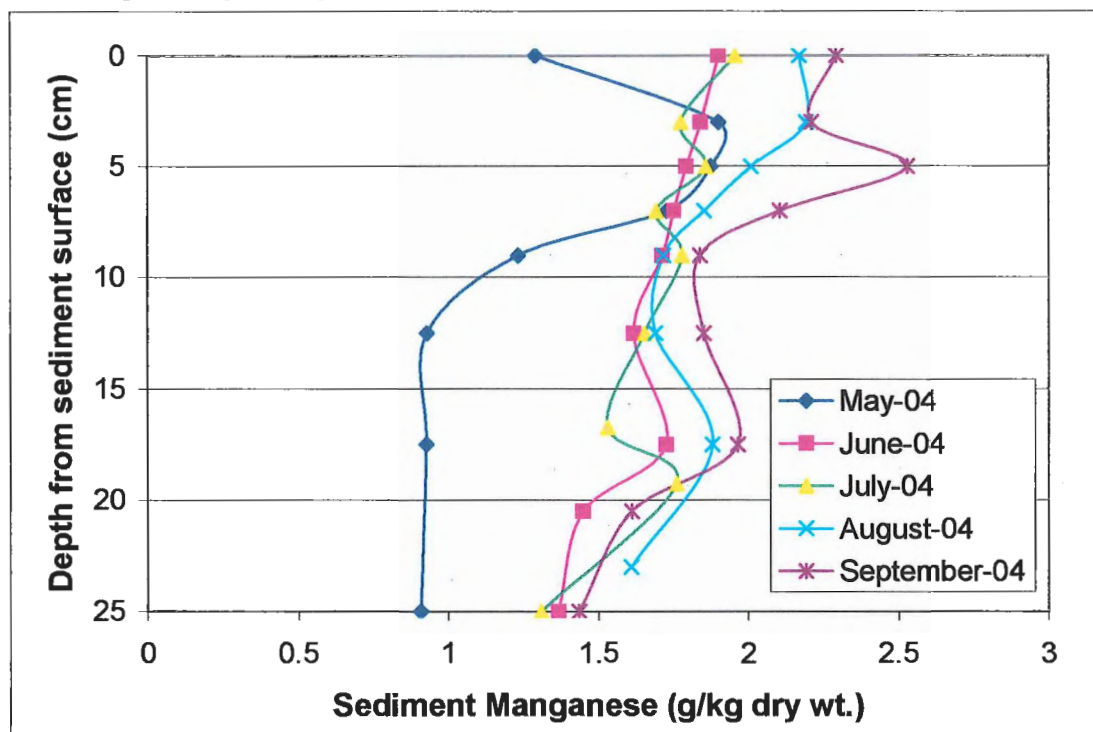


Figure 24. Sediment aluminum profiles for sediment cores taken from the North Bay site of Irondequoit Bay during the summer of 2004.

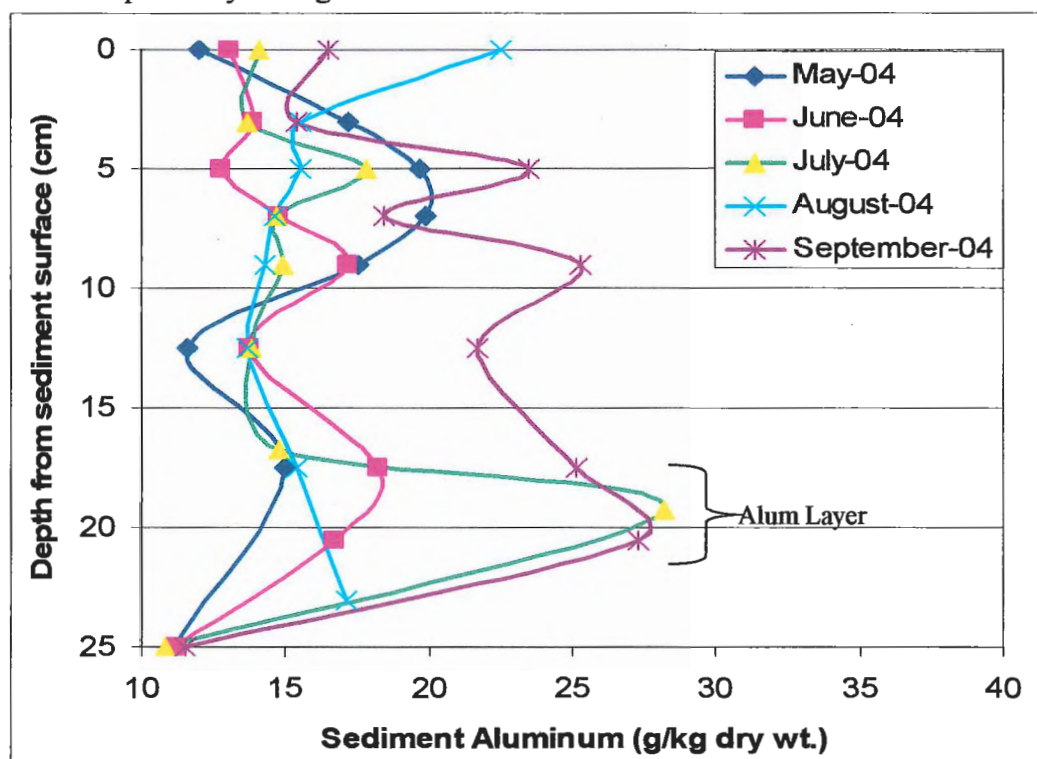
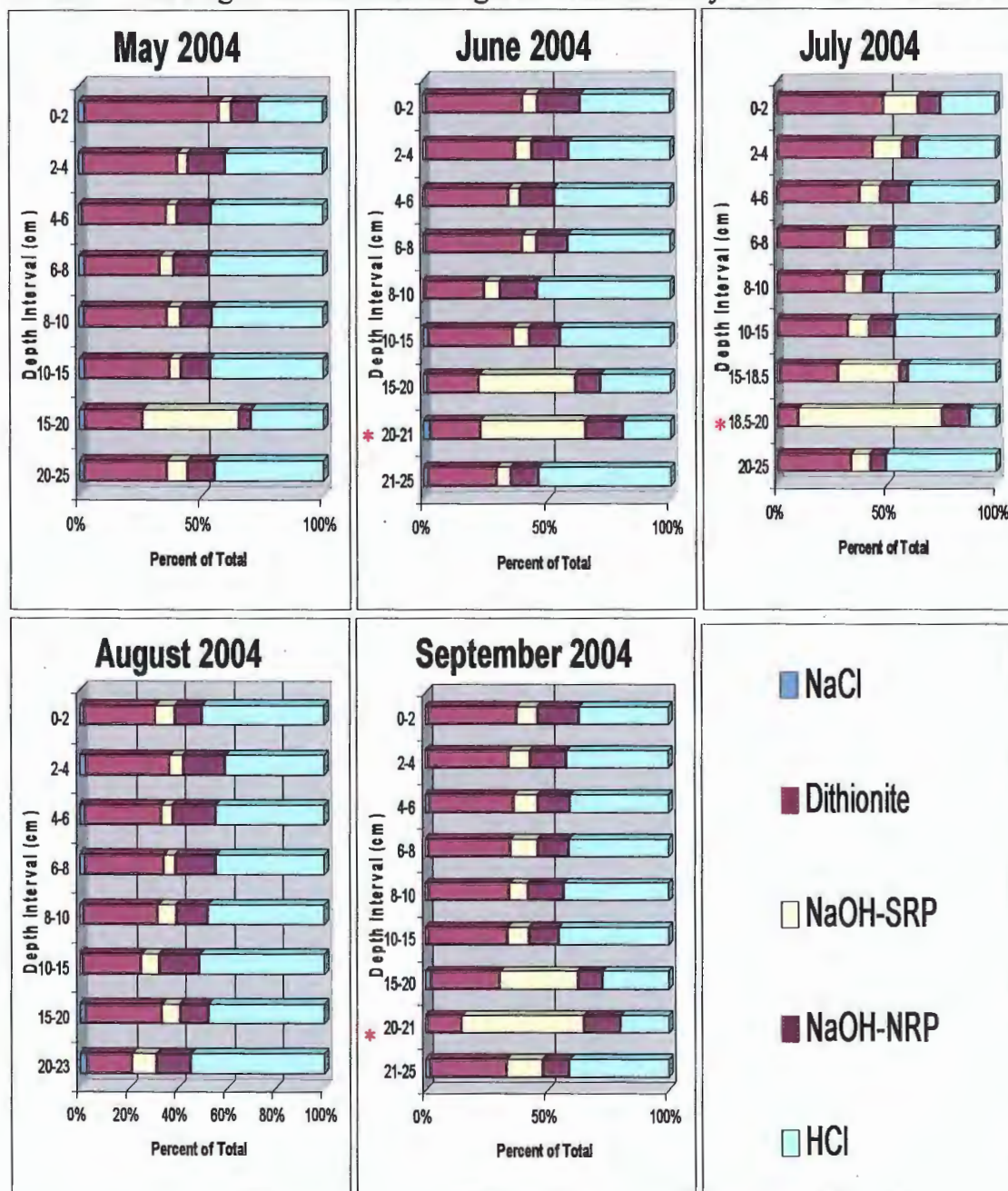


Figure 25. Sequential extraction profiles for sediment cores collected at the North Bay Site of Irondequoit Bay during the summer of 2004. The x-axis is percent each fraction makes up of the sum of all fractions. Depth intervals on the y-axis are in distance from the sediment surface. NaCl is the “loosely sorbable” fraction, Na_2SO_4 is the “redox sensitive” fraction, NaOH-SRP is the “aluminum bound” fraction, NaOH-NRP is the “organically bound” fraction, and HCL is the “calcium bound” fraction. A “*” marks the location where a light-colored band thought to be the alum layer was found in the core.



Appendix 1. Regression equations for phosphorus release rates (RR) on sediment phosphorus concentrations from seven North American lakes examined by Nürnberg (1988). Regressions were for the average concentrations of both total sediment phosphorus (TP_s) and bicarbonate dithionite extractable phosphorus (BD-P) in 0 – 10 cm of depth in anoxic sediments. Wet sediment concentrations are expressed in $\mu\text{g P/g}$ wet weight and dry sediment concentrations are expressed in mg P/g dry weight. Release rates are expressed in $\text{mg P/m}^2/\text{day}$. The third regression under Dry Sediment TP_s is the regression of phosphorus release rate and total sediment phosphorus with loss on ignition (LOI) as a second variable.

Wet Sediment TP_s	r^2	Dry Sediment TP_s	r^2
$RR = -5.59 + 0.079TP_s$	0.83	$RR = -4.30 + 3.88TP_s$	0.59
Wet Sediment BD-P	r^2	Dry Sediment BD-P	r^2
$RR = -1.38 + 0.285BD-P$	0.87	$RR = -0.47 + 13.66BD-P$	0.71
		Dry Sediment TP_s -LOI	r^2
		$RR = 4.78 + 2.75TP_s - 0.177LOI$	0.85