

Determination of sediment phosphorus concentrations in St. Albans Bay, Lake Champlain: Assessment of internal loading and seasonal variations of phosphorus sediment-water column cycling

Final Report

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SECTION 1 – EXECUTIVE SUMMARY

This study was undertaken to determine the current quantity of phosphorus in the sediments of St. Albans Bay, Vermont, USA, and to address the role of seasonal variations related to changing redox conditions and mineralization on phosphorus cycling and mobility in those sediments.

43 separate cores were collected in the first week of August, 2004 with the assistance of the Vermont Department of Environmental Conservation to assess the overall concentration and spatial distribution of phosphorus, iron, and manganese in the sediments of St. Albans Bay. These cores were sectioned into 0-1, 1-2, 2-3, 3-4, 4-5, 5-8, and 8-12 cm aliquots and their porosity, organic content, soluble reactive phosphorus (NH₄Cl extracted), mineralizable phosphorus (NaOH extracted), residual inorganic phosphorus (HCl extracted), acid-extractable iron and manganese (HCl extracted), amorphous Fe and manganese (ascorbic acid extracted), reactive phosphorus (ascorbic acid extracted), and total iron, manganese, and phosphorus (aqua regia extracted) determined. Statistical analysis of the data indicates that the mobility of phosphorus is tied to the mobility of iron and manganese, especially in the top 2 cm of sediment. The total amount of phosphorus tied up in the bay is significant; in the top 10 cm there are approximately 1200 tons of phosphorus associated with amorphous iron and manganese oxyhydroxide minerals, and over 4000 tons of total phosphorus. An original purpose of the study was to compare phosphorus concentrations in cores collected during 2004 with cores sampled by previous studies in 1982 and 1992. However, comparison to previous studies in a direct, quantitative fashion was determined to be inappropriate due to problems with how sampling results would be influenced by redox front positions and to potential mobility of phosphorus collected by the various studies at different points in time during the summer season, potential problems with analytical procedures in older reports not comparable to newer, more accurate methods employed here, spatial heterogeneities in the system, and indeterminate sedimentation rates for different parts of the bay.

A total of 10 separate sampling excursions were undertaken between late May and early October of 2004 in order to gather data to determine the seasonal changes in redox chemistry within the top few centimeters of sediments using *in situ* electrochemical methods to investigate porewater iron, manganese, sulfur, and oxygen chemistry. Sediment core samples were additionally sectioned and analyzed to determine the distribution of iron, manganese and phosphorus for a comparative study looking at the relative mobility of these elements over this time period. It is well known that Fe and Mn oxyhydroxide minerals strongly sorb phosphorus to their surfaces (Shenker et al., 2005; van der Zee et al., 2003; Roden and Edmonds, 1997).

When these minerals are reduced due to conditions in the sediments becoming more anoxic, the sorbed phosphorus can be released into adjacent porewaters where it may diffuse and potentially reach the overlying water column - where it would serve as a nutrient source, potentially driving algal activity. Electrochemical results show that the comparatively colder and windier conditions of summer 2004 kept iron oxyhydroxide minerals in surficial sediments of the inner bay from being reduced, but that manganese oxyhydroxide minerals were completely reduced up to the sediment-water interface and soluble Mn was observed in the water column. This observation is coupled with statistical analysis of the sediment core chemistry from our seasonal site which suggests that phosphorus mobility is strongly correlated with changes in iron and manganese mineralization. While manganese minerals can release significant Mn into the porewater and overlying water columns, the continued presence of oxidized iron oxyhydroxides through the summer should have effectively contained any significant phosphorus released from manganese oxyhydroxide minerals. However, in summers where conditions may select for more reducing conditions to drive iron reduction (generally higher temperatures, less turbulence from wind shear, and greater photosynthetic activity), or in parts of the bay where conditions select for greater anoxia, the redox front may move well into the water column, transform a more significant proportion of oxidized iron and manganese oxyhydroxide minerals, and release substantial phosphorus into the overlying water column.

In summary, the results of this study indicate that there remains a substantial reservoir of phosphorus in the sediments of St. Albans Bay which is mobile within the sediment column due to changing redox front positions and associated changes in iron and manganese mineralization. This sediment reservoir has the potential to contribute phosphorus to the water in the bay for a long period of time into the future; flux of sediment into the overlying water column will be at least partly based on highly reducing events which may vary considerably in space and time.

2. INTRODUCTION

2.1. Problem description: St. Albans Bay: Sediment-bound phosphorus of St. Albans Bay has been a problematic source of phosphorus driving seasonal algal blooms and eutrophication of an important water body for many years (Smeltzer, 2003). This internal load of phosphorus in the sediments has been the subject of several studies attempting to characterize the total amounts held in the sediments as well as the rate and mechanism(s) of release to the water column (Ackerly, 1983; Martin et al., 1994; Smeltzer et al., 1994; Cornwell and Owens, 1999). Martin et al. (1994) used the results of their field work, compared to those done 12 years prior by Ackerly, to develop a predictive model for the rate at which phosphorus would naturally be removed from the sediments through a combination of exchange out of the sediment and mass transport into the larger Lake Champlain system. This projected self-cleaning effect has not proven to be accurate, in that phosphorus concentrations in the bays and the occurrence of algal blooms has not decreased as projected (Smeltzer, 2003). In light of this, we have undertaken this study to both assess current P levels in the sediments of St. Albans Bay and to investigate seasonal variations in redox properties and P levels in those sediments to better understand the driving forces behind P mobility in this environment.

2.2. Phosphorus mobility associated with redox processes and mineralogy changes. The competition between O₂ entrainment into the water column (a function of both photosynthesis and wind creating turbulence and increased O₂ mixing of the water column; Langmuir, 1997) and depletion as a result of primary productivity and interaction with reduced species governs where the redox front in the sediment will be at any particular time (Figure 1). This redox front describes where there is a transition from oxic conditions (presence of significant O₂) to anoxic conditions (no O₂ and the presence of reduced forms of iron, manganese, and/or sulfur).

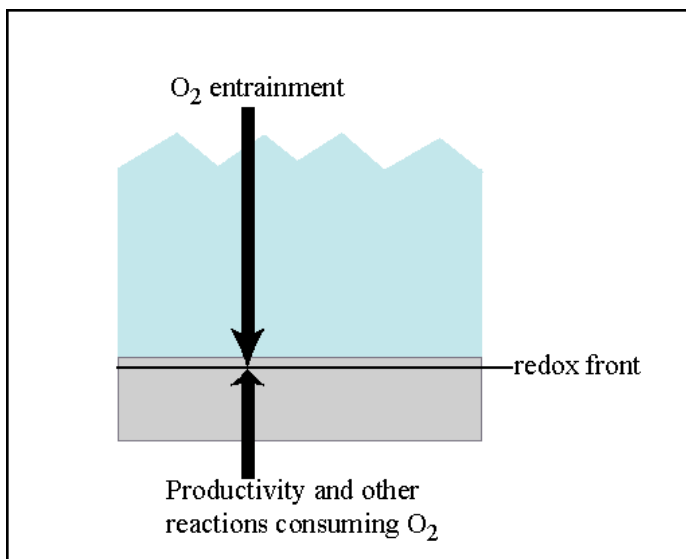


Figure 1 - Depiction of processes governing oxygen penetration into sediments

It has been shown, at Rehoboth Bay in southern Delaware, that seasonal variations in redox character of sediments can promote substantial P release from sediments into the overlying water column (Rozan et al., 2002). This release was shown to depend on the reduction of ferric oxyhydroxide minerals which display a strong affinity for phosphorus (Krom and Berner, 1981; Rozan et al., 2002). Ackerly (1983) specifically noted that a significant fraction of phosphorus species are most likely sorbed to iron oxyhydroxide minerals in the sediments of St. Albans Bay. The redox changes associated with the transformation of iron-bearing minerals in sediments is thought to be driven by microbial activity and the consumption of organic matter to drive anoxia (Kostka and Luther, 1995). While this may be associated with increased senescence in some environments (Rozan et al., 2002), the presence of excess organic material is all that is required to drive heterotrophic microbial activity (Brock and Madigan, 1991). Increased temperature may substantially increase the rate at which microorganisms are able to utilize organic material as a metabolic substrate coupled to oxygen reduction, thereby increasing the level of anoxia. In an environment with no lack of organic material, the temperature alone may thus be a critical factor in driving significant changes of iron mineralogy which then may drive P release from the sediment to the overlying water column. Seasonal algal bloom activity thus may suggest a seasonal influence of phosphorus input

to the St. Albans Bay watershed tied to changing redox front positions through the summer season.

Observation of these changing redox states in water and sediments requires careful consideration of the tools and techniques used in assessing speciation changes for oxygen, iron, sulfur, and manganese in the sediments and overlying water. It is commonly accepted that redox disequilibrium is commonplace and results in erroneous measurements of redox state with platinum ORP electrodes (Grenthe et al., 1992). Oxygen probes are only sensitive to dissolved oxygen and do not work well in suboxic environments or in sediments. Microelectrodes have been developed which are able to measure O_2 , H_2O_2 , Fe^{3+} , Fe^{2+} , H_2S , HS^- , $S_2O_3^{2-}$, Mn^{2+} , Cu^{2+} , and many other species *in situ* and in real time (Brendel and Luther, 1995; Luther et al., 1999; Luther et al., 2003; Druschel et al., 2003). These tools have been used in Lake Champlain to assess the dynamics of redox speciation and their effect on porewater pH and pCO_2 concentrations (Cai et al., 2002). Rozan et al. (2002) combined the use of Au-amalgam microelectrodes with sediment sampling and porewater extraction techniques to correlate the spatial changes in Fe porewater speciation with changing sediment and porewater P concentrations over time in Rehoboth Bay, Delaware.

2.3. Summary of previous work done in St. Albans Bay: The eutrophic conditions and flux of nutrients into St. Albans Bay has seen considerable attention in the past 25 years. Ackerly's 1983 M.S. thesis was among the first reports on the phosphorus load contained in the sediments of the bay. Ackerly found that increased phosphorus loading was reflected in profiled gradients controlled by a combination of anthropogenic loading and "microzone retention". He hypothesized that the iron oxide fraction in the sediment did not reflect trends with respect to HCl-extracted P, but did note several relationships of P extracted other ways (NH_4Cl and NaOH extracted) that suggest absorption to mineral grains, including iron-rich organic muds. Ackerly's report was followed up with the 1994 report from Martin et al., which repeated Ackerly's sampling locations and extraction methods. Martin et al. found that there was substantially less phosphorus in the sediments of St. Albans Bay measured in 1992 than there was in 1982. This conclusion noted that P loading to the bay had dropped off significantly with upgrades to

the St. Albans Waste Water Treatment Facility (WWTF) and the closure of the Hood Dairy facility in 1986 and 1983, respectively. The response of the bay sediments was subsequently modeled and the results extrapolated to predict that mean P levels in the water column would drop to beneath the water quality goal of 17 $\mu\text{g/l}$ by 1995. A report by Smeltzer et al. (1994) looked more closely at modeling the loading and cycling of P in the sediments of St. Albans Bay and modeled definitive links between sediment P release and redox processes affected by temperature and wind. Cornwall and Owens (1999 and HydroQual, Inc. 1999) next did a detailed study of a number of areas in Lake Champlain, including St. Albans Bay, to look at processes of eutrophication and sediment P cycling. Field studies (Cornwell and Owens 1999) noted higher rates of soluble P release rates from the sediments associated with both microbial metabolic activity (noting specifically metal oxide reduction leading to high soluble Fe and Mn concentrations). Modeling exercises (HydroQual, Inc. 1999) were able to reproduce P dynamics in many areas of the lake except in low oxygen environments such as St. Albans Bay. A lay monitoring program at St. Albans Bay (Picotte 2002) and the monitoring program supported by the Lake Champlain Basin program (DEC report 2004) have helped to create a database of water column P concentrations

3. STUDY DESCRIPTION

3.1 Goals of this study: The goals of this study were twofold:

- a. Assess the amount of phosphorus which is currently present in the sediments of St. Albans Bay, and compare current amounts with levels measured during previous studies conducted in 1982 and 1992, if appropriate.
- b. Investigate seasonal changes in redox properties (the position of the redox front, Figure 1) and determine if they may be linked to possible ways in which phosphorus in the sediments may be made available to organisms in the water column.

Comparison with previous studies (Ackerly, 1983 and Martin et al., 1994) is only possible and appropriate if the overall amount of seasonal variation is negligible; i.e., if there is any reason to think that P levels in the sediment may be variable due to

conditions that are not repeatable (like weather) then determining changes in P content of the bay is not possible with any accuracy. Assessment of the phosphorus concentrations present in the bay sediments combined with advances in understanding how phosphorus may behave in the system will be of greater use to the community.

3.2. Description of Study Sites: 43 study sites in the inner, middle, and outer regions of St. Albans Bay and the Stevens Brook wetland area were sampled in the first week of August, 2004 (Figure 2 for map, Table 1 for specific locations catalogued by Global Positioning System).

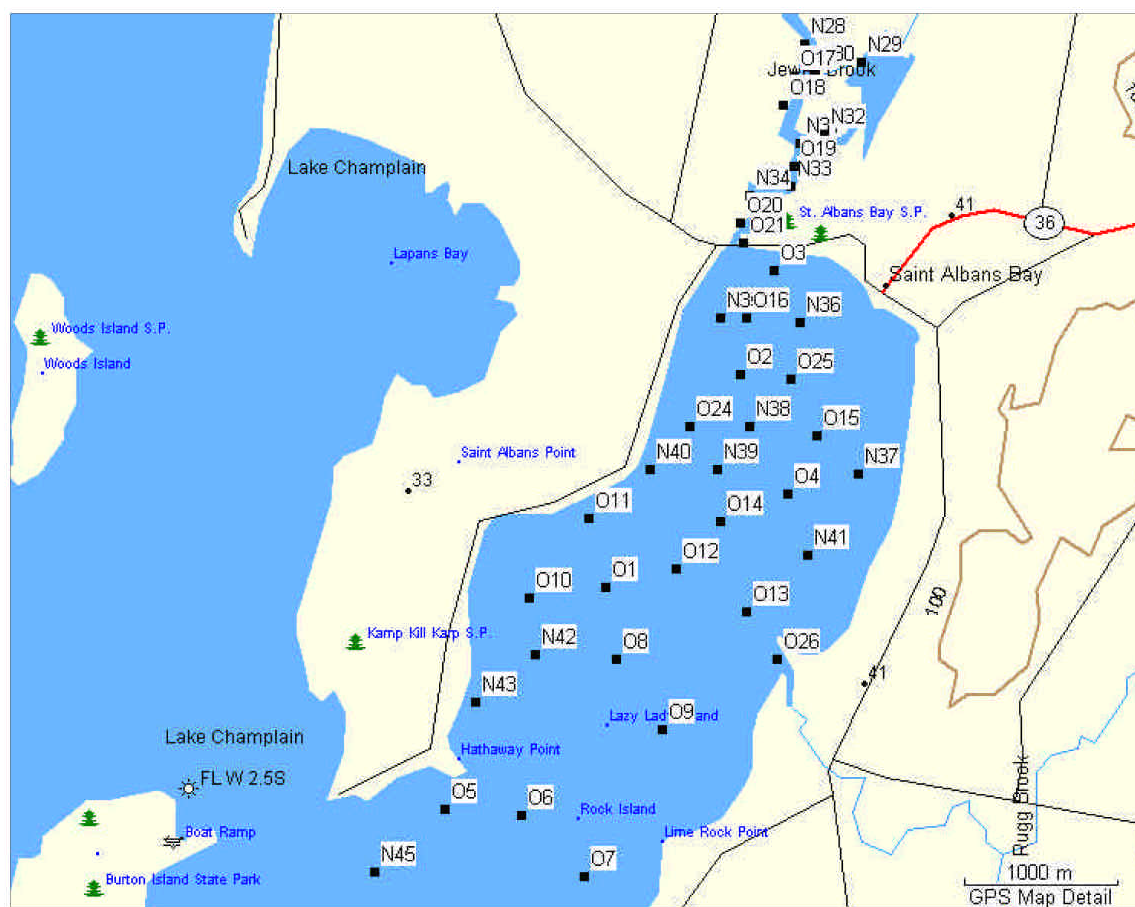


Figure 2 - Map showing study sites sampled in August 2004

Table 1 - GPS located positions of study sites sampled in August 2004

Site	Latitude	Longitude	Site	Latitude	Longitude
1	N44 47.400	W73 09.733	24	N44 47.967	W73 09.317
2	N44 48.150	W73 09.067	25	N44 48.133	W73 08.817
3	N44 48.517	W73 08.900	26	N44 47.150	W73 08.883
4	N44 47.733	W73 08.833	27	N44 46.100	W73 10.683
5	N44 46.621	W73 10.535	28	N44 49.317	W73 08.750
6	N44 46.598	W73 10.155	29	N44 49.250	W73 08.467
7	N44 46.386	W73 09.837	30	N44 49.217	W73 08.700
8	N44 47.150	W73 09.683	31	N44 48.967	W73 08.767
9	N44 46.900	W73 09.450	32	N44 49.000	W73 08.650
10	N44 47.367	W73 10.117	33	N44 48.817	W73 08.817
11	N44 47.647	W73 09.820	34	N44 48.783	W73 09.017
12	N44 47.467	W73 09.383	35	N44 48.350	W73 09.167
13	N44 47.317	W73 09.033	36	N44 48.333	W73 08.767
14	N44 47.633	W73 09.167	37	N44 47.800	W73 08.483
15	N44 47.933	W73 08.683	38	N44 47.967	W73 09.017
16	N44 48.350	W73 09.033	39	N44 47.817	W73 09.183
17	N44 49.200	W73 08.800	40	N44 47.817	W73 09.517
18	N44 49.100	W73 08.850	41	N44 47.517	W73 08.733
19	N44 48.883	W73 08.800	42	N44 47.167	W73 10.083
20	N44 48.683	W73 09.067	43	N44 47.000	W73 10.383
21	N44 48.617	W73 09.050	44	N44 46.233	W73 10.083
			45	N44 46.400	W73 10.883

The study sites were reached using Vermont Department of Environmental Conservation boats and the assistance of Pete Stangel during this sampling period. A seasonal site was chosen close to site 16 and sampled over the course of the summer (between 06/23/04 and 10/07/04), accessed using a University of Vermont Department of Geology canoe outfitted with an outrigger system. At least 2 duplicate cores were taken for each trip to the seasonal site. The seasonal site was selected as a site whose position and depth were likely to be strongly affected by the competing processes which govern the position of the redox front (see Figure 1).

3.3. Description of analytical techniques:

Core Sampling. Sediment cores were collected in positions described above with a KB3 type (or Glew) gravity core sampler using a plastic liner tube 2.5" in diameter. The

sampler was rigged to take cores in water up to 100 ft depth, using a brass messenger to trigger the seal and lead weights to drive the coring device into the sediment. Following collection, the ends of the core tube were sealed with end caps and stored upright in a cooler at approximate ambient bottom temperatures. The seasonal cores were brought back to the lab and extruded under Ultra High Purity (UHP) Nitrogen flow using a piston assembly attached to a stationary frame and sectioned as the cores emerge from the top at 0-1, 1-2, 2-3, 3-4, 4-5, 5-8, and 8-12 cm intervals using a PTFE coated spatula. The 43 sediment cores collected in August were extruded immediately after collection on site (either on the boat or on shore) using identical techniques but without applied UHP nitrogen. Sediment sections were collected in screw-top plastic tubes and stored for analyses.

In situ electrochemistry. For the 2 seasonal sites we utilized Au-amalgam microelectrodes prepared after the methods outlined in Brendel and Luther (1995) and Luther et al. (2003). Briefly, 100 μm diameter gold wire was soldered to a shielded cable and encased inside a drawn glass tube filled with WestMarine epoxy. The tip was polished with a succession of diamond grits and plated with a thin film of mercury, which was then amalgamated by applying a 9V potential vs. a platinum wire in 1 N NaOH. The electrode was calibrated for O_2 , Fe^{2+} , Mn^{2+} , and H_2S in the lab. A Pt counter electrode and Ag/AgCl reference electrode are used in conjunction with the Au-amalgam working electrode, which is lowered through the water and sediment in the sampled core using an automated micromanipulator system (DLK-MAN1) integrated with the potentiostat (DLK-60) and computer controller which drives the electrochemical analyses. Voltammetric assessment of O_2 , H_2O_2 , Fe^{2+} , Fe^{3+} , $\text{FeS}_{(\text{aq})}$, H_2S , HS^- , $\text{S}_x\text{O}_y^{n-}$, Mn^{2+} was accomplished over 100 μm increments through the sediment-water interface and extending through the top 3-4 cm of sediment, depending on the physical limitations of driving the electrode through variably compacted sediment and the complete detection of the redox properties which define the redox front. Measurements were made in real time, using cyclic voltammetry measurements starting with an initial potential of -0.1V held for 2 seconds, then scanned between -0.1V and -1.8V vs. Ag/AgCl at a rate of 1V/second.

Sediment Extractions. Sectioned sediment samples were processed and P extracted using techniques identical to those used by Martin et al. (1994), except for total P extractions for reasons described below. In summary, each sample sediment fraction was weighed wet, dried at 105°C for at least 48 hours, cooled in a dessicator and reweighed, then ground with a ceramic mortar and pestle, sieved through a #140 sieve, and repartitioned into fractions for extraction. Another aliquot of the sediment was ashed at 380°C to determine total organic content. Each dried sample was split into 0.25-0.5 g sections and placed in 15ml tubes. One set up samples went through a sequential extraction, first reacting on a rotator for at least 30 minutes with 1 N ammonium chloride (NH₄Cl), the supernatant collected and stored for analysis, and the solid then rinsed with 0.1 M KCl. The same solid sample was then reacted with 1 M sodium hydroxide (NaOH) for at least 18 hours (again kept agitated by placing a sealed tube on a rotator), the supernatant collected and stored for analysis, and the solid then rinsed with 0.1 M KCl. The same solid sample was then reacted with 0.5 M HCl for at least 8 hours (again kept agitated by placing a sealed tube on a rotator), the supernatant collected and stored for analysis, and the solid then rinsed with 0.1 M KCl. This sequential extraction scheme ideally extracts the soluble reactive P with the NH₄Cl, mineralizable P with NaOH, and finally residual P with HCl. The Fe and Mn will be very minimally extracted using the NH₄Cl or NaOH extractions, and acid-soluble fractions will be extracted with HCl. Another aliquot of dried sediment was reacted with an Ascorbic Acid solution (made using 10 g sodium citrate and 10 g sodium bicarbonate in 200 ml nitrogen-purged water, to which 4 g of ascorbic acid is slowly added) for at least 24 hours (kept agitated by placing a sealed tube on a rotator) before the supernatant was collected and stored for analysis. The ascorbic acid extraction liberates reactive phosphorus in addition to amorphous iron and manganese. A final aliquot of dried sediment samples underwent an aqua regia digestion at 85°C for at least 1 hour to dissolve all fractions containing P, Fe, and Mn. Aqua Regia recovers total phosphorous, iron, and Manganese in sediment samples. This method was tested for P, Fe, and Mn analysis against perchloric acid (85%), HCl-HNO₃-H₂O₂ (Aqua regia with 1% H₂O₂ addition), and nitric acid (18 M) digestion methods (both hot and

cold) and showed the greatest recovery and linearity of additions corresponding to the range of values for these sediments. Table 2 summarizes the sediment extraction techniques that were employed for both the large single sampling and the seasonal samples. We did not use perchloric acid digestion for total P per the Martin et al. (1994) study because in developing extraction and analytical procedures, we had better recovery and fewer sample matrix interference effects using Aqua Regia extractions analyzed by ICP-OES when compared to perchloric and nitric acid extractions. While these differences in extraction methods may well be cause for some differences between the past and previous studies, analytical techniques that were different likely contribute more significantly to any differences between samples taken in 1992 or 1982 (as described in extractant analysis section below). These extraction and analytical differences are likely a small component of why there might be differences between samples collected in different years (1982, 1992, 2004).

Parameter	Extraction Method	Reference
Total P	HNO ₃ - HCl digestion at 85°C	EPA 3050B
Soluble reactive P	1 N NH ₄ Cl	Williams et al. (1967)
Mineralizable P	1 N NaOH	Jackson (1970)
Residual inorganic P	0.5 N HCl	Williams et al. (1967)
Organic Matter	Ignition at 380°C	Ackerly (1983)
Reactive P ¹ Amorphous Fe ²	Ascorbic acid	Anschutz et al. (1998)
Total Fe	HNO ₃ - HCl digestion at 85°C	EPA 3050B
Total Mn	HNO ₃ - HCl digestion at 85°C	EPA 3050B
Acid-extractable Fe and Mn	0.5 N HCl	Williams et al. (1967)

Table 2 – Sediment extraction methods and appropriate references

¹ – Martin et al. (1994), called this P in extracts and digests

² – Applied to seasonal samples and selected subset of other samples.

Extractant Analyses: Original plans to analyze phosphorus using ion chromatography and colorimetric methods proved unfeasible due to the high concentrations of Fe in these sediments which serve to interfere with the flow of eluent in ion chromatography and interfere with color development in colorimetric methods. Phosphorus, iron, and manganese for extractant samples were measured with Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) using a HY-Joriba Optima 2C ICP-OES housed in the Department of Geology at the University of Vermont. Methods were developed as part of this work to analyze these elements in aqua regia, ascorbic acid, and HCl matrices, and P in NH₄Cl and NaOH matrices. The samples were generally diluted by 1:10 to 1:20 in water or matrix solution and placed in 15 ml falcon tubes in an autosampler rack. The samples were aspirated into the plasma flame (at 10,000°C) where they are completely ionized, and the emission spectra collected using a monochromator high resolution spectrophotometer. Emission lines were selected from a battery of different possibilities for appropriate detection limit, linear response range, and minimal interferences; lines used were: Fe 259.940, Mn 257.610, and P at 178.610 or 178.229. Each analysis was done in triplicate with a check standard run every 10 samples to assess instrument drift and determine baseline for quality control. Sample concentrations were always insured to be within the linear, constrained ranges of the standards employed, and the mixed standards were matrix matched to ensure accurate determinations of each element. All check standards were checked to be within 5% of their calibrated value, any deviation from this and samples were re-run after calibration and a check of all optics.

SECTION 4 - SEASONAL MEASUREMENTS OF PHOSPHORUS, IRON, MANGANESE

4.1 Seasonal sampling results: Seasonal samples of St. Albans Bay sediments from our selected study site were analyzed by voltammetry and the redox front position was observed to change over the course of the summer (Figure 3). The data points for each of

the points in each profile represented in figure 3 is determined from the voltammetry analyses. Each profile depicts the concentration of oxygen, manganese (in Mn^{2+} form), iron (as ferrous, Fe^{2+} , or ferric, Fe^{3+} forms of iron), and iron sulfide clusters (which are the predominantly observed chemical form of soluble reduced sulfur in these sediments) as a measurement in nA, the current associated with each chemical species which reacts at the electrode which is directly proportional to concentration. Profiles depict oxygen (O_2) depletion near the sediment/water interface (marked as 0 depth on these profiles), a consequence of primarily biological activity which utilizes oxygen as an electron acceptor and the copious organic matter in the sediments as substrate. When this oxygen is consumed, bacterial species which can utilize alternate electron acceptors (essentially breathing oxidized forms of manganese, iron, and sulfur for example) with organic matter (as food) for metabolic energy are likely active in these sediments. The presence of reduced manganese, iron, and sulfur in the sediments (seen as the increase of reduced Fe, Mn, or FeS with greater depth in Fig. 3 profiles) indicates the presence and activity of these organisms. The abiotic reactions which could generate these chemical species at conditions similar to St. Albans Bay sediments are very slow. Note that these reactions directly, or at least indirectly, cause dissolution or transformation of iron or manganese oxyhydroxide minerals in these types of systems, and that where oxyhydroxide mineral transformation is going on at any time is defined by the position of redox fronts in the sediment profiles such as those presented in Figure 3.

Analyses indicate that even in the first electrochemically measured core on 06-23-04, the sediments were anoxic very close to the sediment-water interface. Following this, manganese reduction became more prevalent, with manganese reduction going through the top of the sediment water interface in the samples from 07-26-04. While iron and sulfate reduction were observed to occur in the porewaters from these sediments, notably getting as high as 9 mm from the sediment-water interface in mid-August, at no time in our sampling did either process breach the sediment-water interface. The apparent role of manganese reduction in the sediments observed in the course of the summer caused us to alter some of the original analysis plans to focus more on Mn relationships with respect to phosphate levels as opposed to evaluating the role of iron sulfide mineralization.

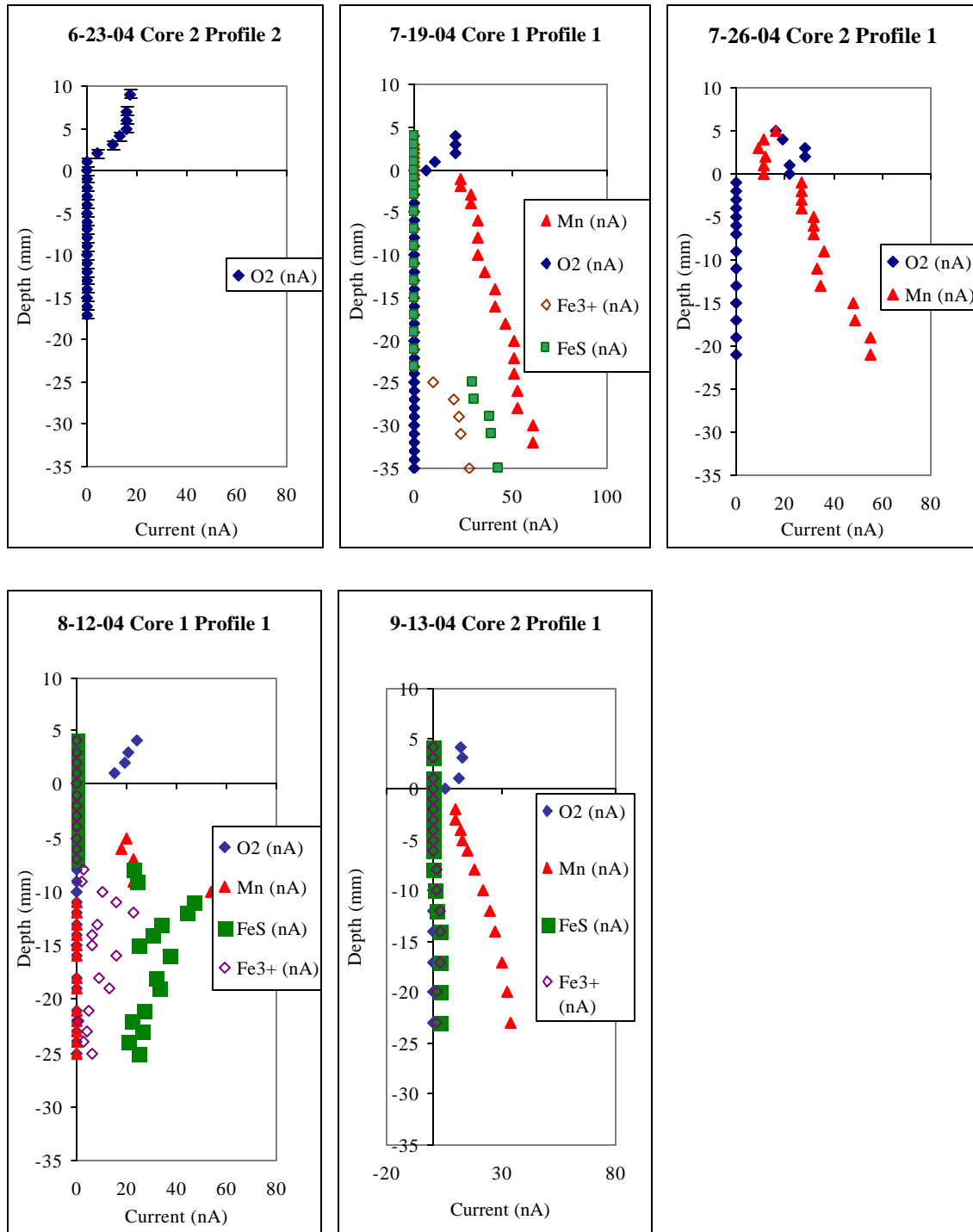


Figure 3 - Profiles of porewater chemistry from voltammetric analysis of selected seasonal cores

4.2. *Weather data:* Given the potential importance of wind and temperature on the positioning of the redox fronts in these systems (Figure 1) we have compiled weather

data from the closest monitoring station available (Burlington Airport). Data from summer 2004, over the time span we sampled sites in Saint Albans Bay, are graphed in Figure 4. Average and maximum daily temperatures are plotted as well as average daily windspeeds. The summer was generally colder and had a greater number of windy days than average, conditions that would affect the redox front in a manner which would keep more of the sediment oxic as opposed to anoxic (refer to Figure 1).

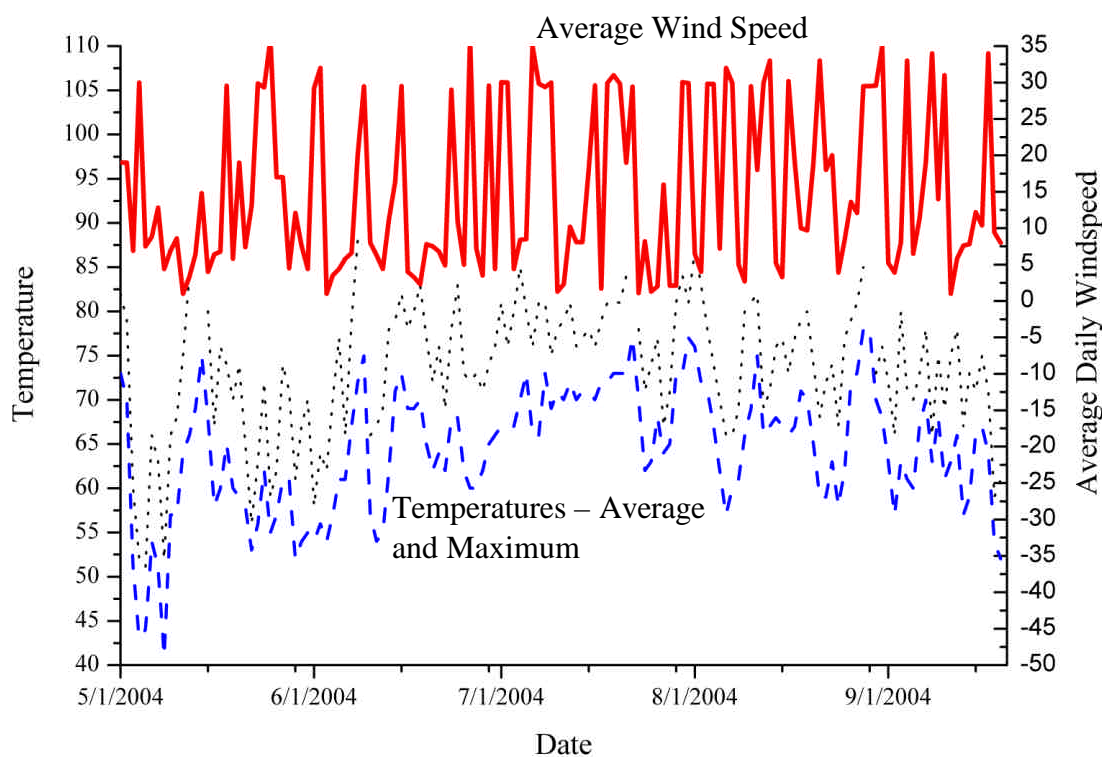


Figure 4 – Graph of weather data collected May 1 through September 30, 2004 at Burlington International Airport. Temperature is in degrees Fahrenheit and windspeed is in miles per hour.

4.3. Overlying water chemistry data. Water samples collected through the course of the summer by Pete Stangel (VT DEC) at the approximate location of the seasonal site are tabulated in Table 3. Table 4 shows a comparison of the averaged monthly data from 2004 with the averages from the period 1992-2004 (data from the VT DEC long-term monitoring program). Figure 5 plots the total phosphorous from this location and the total P data collected and analyzed by the VT DEC at Station 40, part of the long-term monitoring program database

(http://www.anr.state.vt.us/dec/waterq/cfm/champlain/lp_longterm-lakes.cfm), for the 2004 season. The apparent disconnect between significant shifts in sediment redox front positions and overlying water chemistry at station 40 is likely due to a combination of undefined P fluxes from the sediment and possibly that activity in the sediment below station 40 may be different from the seasonal spot where the sediments were collected for this study. A seeming spike in total P concentrations measured at the seasonal station which is above the averages for station 40 suggests that the flux of P from sediments may have significant spatial and temporal constraints, i.e., different locations at different times may exhibit very different P flux out of the sediment. These points require detailed study of the specific flux of P out of the sediment in different locations, which was not a topic specifically covered by the experiments or data in this study.

	07/19/04	07/26/04	09/16/04	09/30/04	10/19/04
DO	7.5	8.4		8.7	9.8
TN	0.37	0.44	0.53	0.4	0.39
TP (mg/l)	30	43	51	30	30
Ca	16.7	19.1	20.9	18	19.1
Fe	0.12	0.115	0.244	0.181	0.126
K	1.63	1.97	2.2	1.86	1.85
Mg	3.65	4.15	4.38	3.96	4.02
Na	6.3	8.2	8.01	7.03	7.41

Table 3 - Water column data for seasonal site from VT DEC (Pete Stangel, pers. comm.), concentrations are in mg/l except as noted for total phosphorus (TP).

Month	Mean TP (mg/l)	
	1992-2003	2004
Apr	0.019	
May	0.023	0.023
Jun	0.027	0.029
Jul	0.028	0.029
Aug	0.030	0.027
Sep	0.031	0.034
Oct	0.024	0.024

Table 4 – Compilation of average values for St.Albans Bay waters (VT DEC Station 40) showing no significant differences for 2004 compared to the past years since 1992.

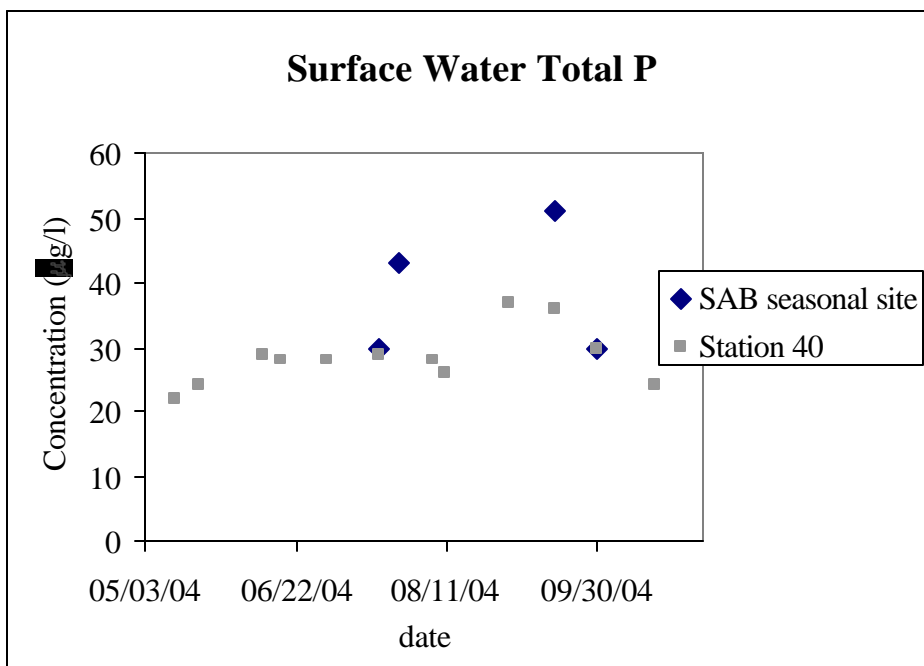


Figure 5 – Water column phosphorus at Station 40 and selected samples also taken above the seasonal sampling site used in this study. (Data from Pete Stangel, VT DEC, pers. Comm.)

4.4 Sediment extraction data, seasonal: Sediment sections from seasonal samples taken 5/27/04, 06/23/04, 7/7/04, 07-19-04, 07/26/04, 08/05/04, 08/12/04, 08/18/04, 09/13/04, and 10/07/04 were extracted with sequential HCl-NaOH and Ascorbic acid. Tabulated analytical results for each of these extractions are in Appendix A. Summary plots of these datasets in time are found in Figures 6-9. Replicate cores were fully analyzed for a number of these dates; while internal check standards and triplicate measurements of each sample indicate little error in the measurements, there is substantial heterogeneity in different cores collected the same day at locations no more than 10 meters apart (Figure 7). Appendix A-2 tabulates the seasonal extraction data by section, averages for these depths across the season are in Table 5. Plotted as profiles, Figures 10 and 11, relationships between phosphorus concentrations and the Fe and Mn becomes clear, especially for the samples extracted with Ascorbic Acid, which should selectively solubilize the Fe and Mn oxyhydroxide minerals in the sediment and any P that may be associated with it.

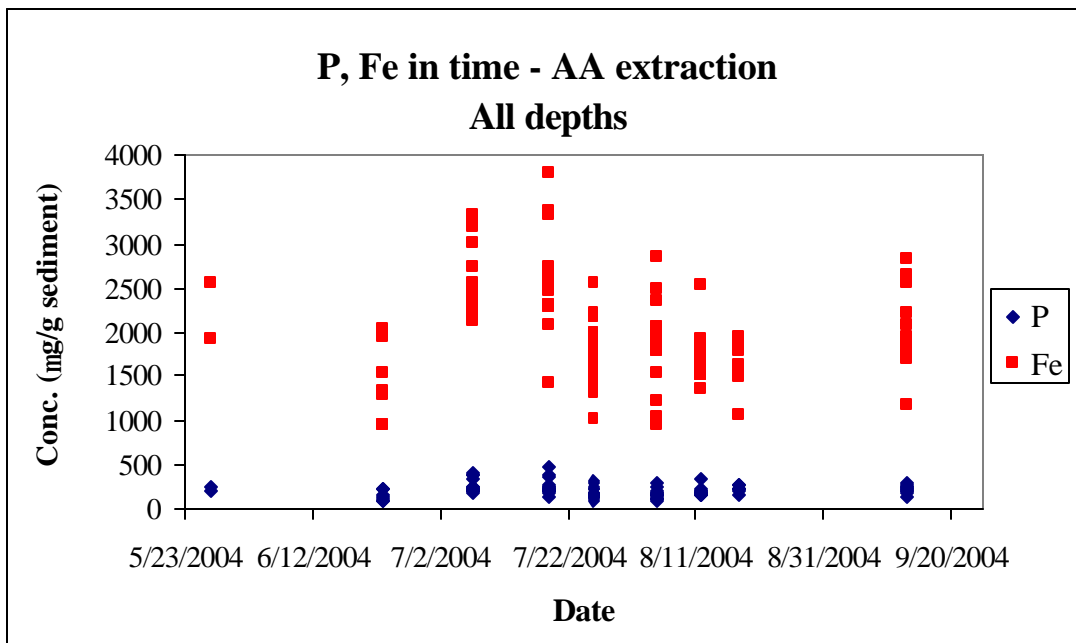


Figure 6- Ascorbic Acid extraction results for seasonal samples

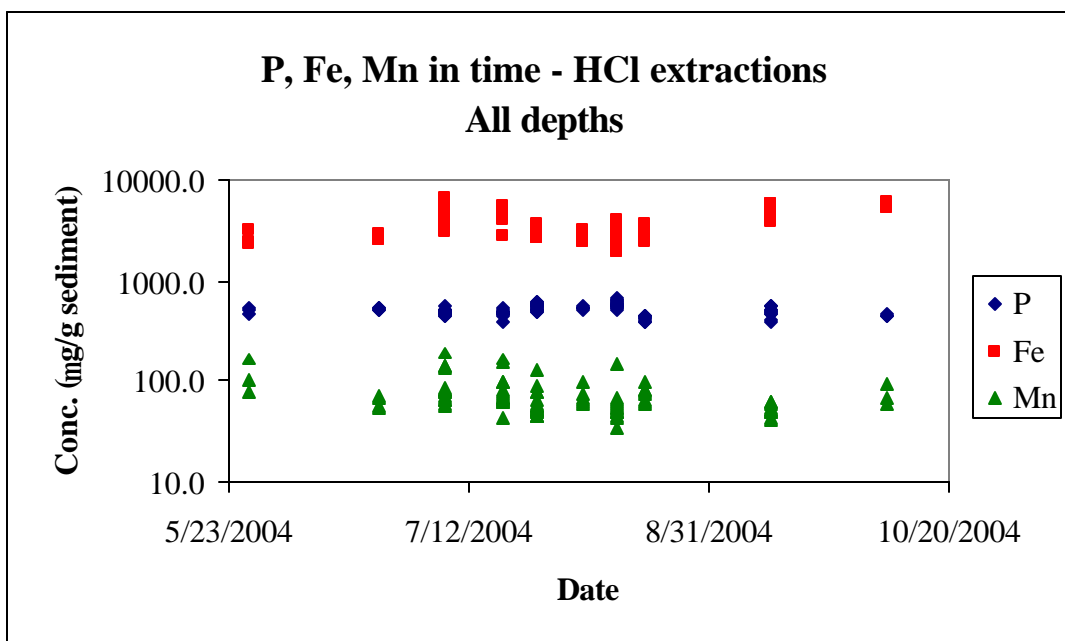


Figure 7 - HCl extracted results for seasonal samples

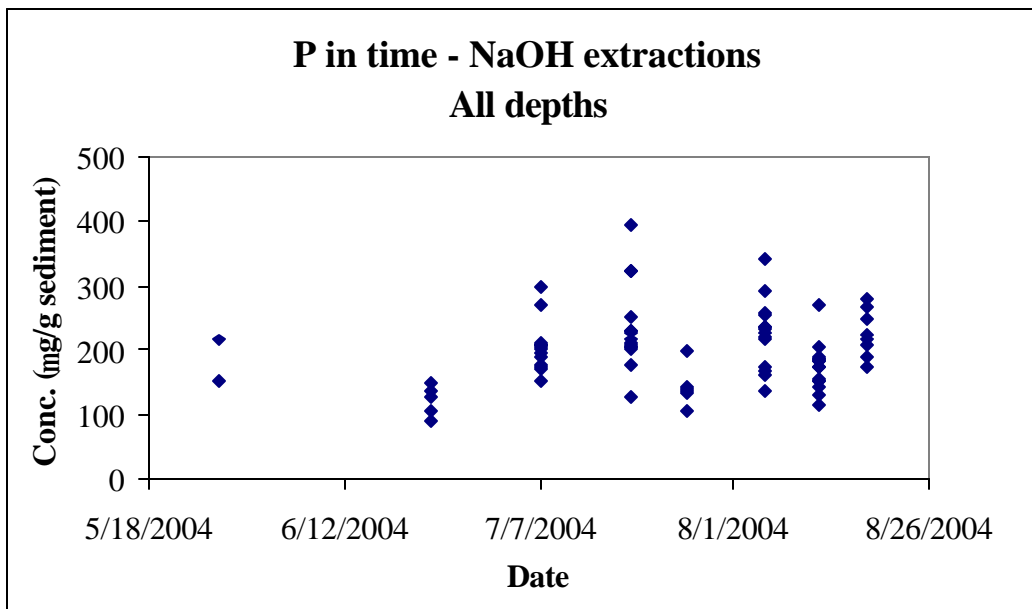


Figure 8 - NaOH extracted results for seasonal samples

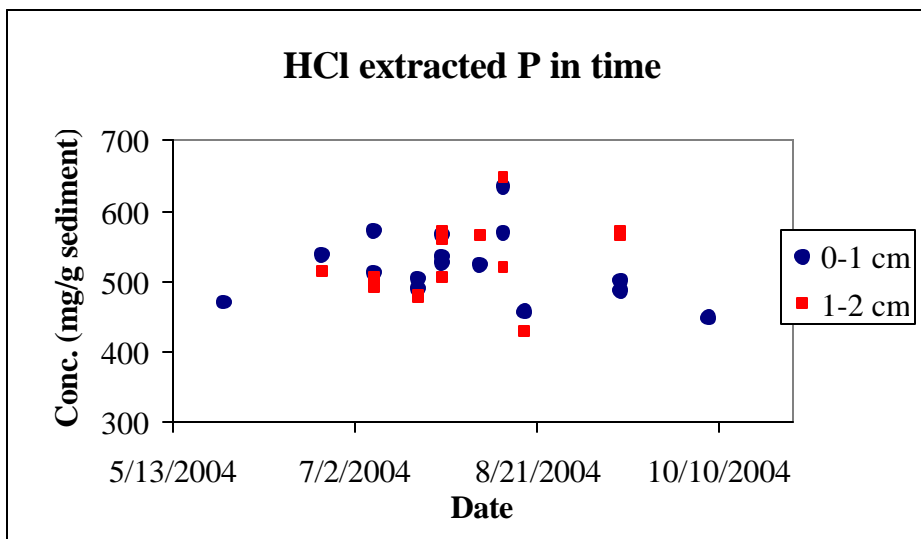


Figure 9 - HCl extracted results for seasonal samples in top 2 cm sections

depth	HCl extractions			NaOH	Ascorbic Acid extractions		
	$\mu\text{g/g sed}$	$\mu\text{g/g sed}$	$\mu\text{g/g sed}$	$\mu\text{g/g sed}$	$\mu\text{g/g sed}$	$\mu\text{g/g sed}$	$\mu\text{g/g sed}$
	Fe	Mn	P	P	Fe	Mn	P
0-1 cm	4081	111	519	269	2517	211	296
1-2 cm	3906	77	528	219	2242	139	237
2-3 cm	3633	62	519	210	1995	106	196
3-4 cm	3737	61	506	201	2029	102	192
4-5 cm	3563	61	520	196	1859	93	179
5-6 cm	3285	61	531	181	1907	99	178
6-8 cm	3475	63	536	178	1679	85	167
8-10 cm	3335	55	508	157	1573	79	156

Table 5 – Averaged values for Fe, Mn, and P extracted from 10 seasonal cores.

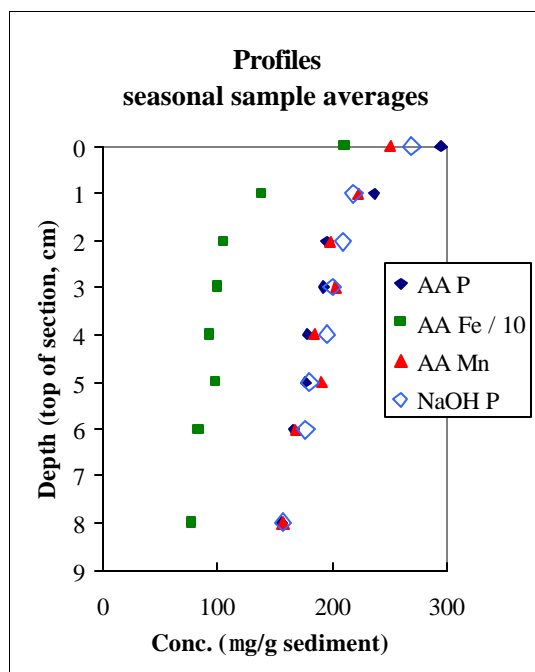


Figure 10 – Profile of averages for seasonal site from ascorbic acid extractions

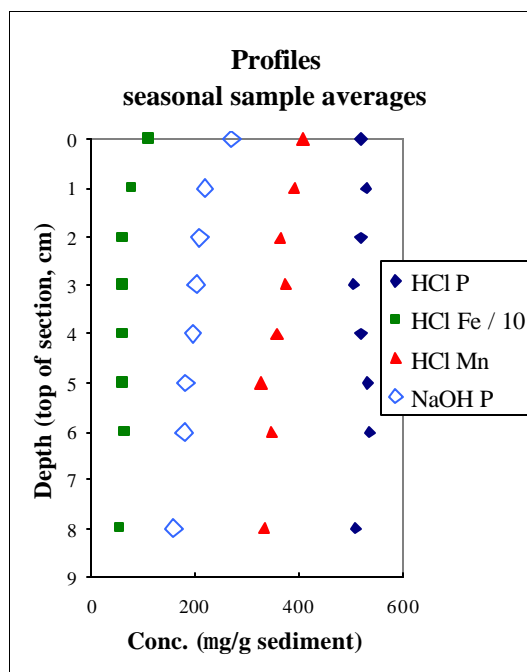


Figure 11 – Profile of averages for seasonal site from hydrochloric acid extractions

Comparing how iron, manganese, and phosphorus concentrations in the top of the sediment column changes over time, compared to how chlorophyll-A (which generally correlates with algal densities) in the water column changes over time may be another test of whether there were any discernible links between P mobilized from the sediments and algal densities in summer 2004. Direct statistical comparison of these datasets is not appropriate, however, as the degree of heterogeneity in the sediments would be quite different from any spatial heterogeneity in the water column. We can estimate any trends only in the broadest sense, and plots of these data for Fe and Mn extracted from the top centimeter can be found in Figures 12 and 13. While there appears to be some inverse relationships between Chlorophyll-A and Mn, little relationship exists between Chlorophyll-A and Fe. We concentrate on the top of the sediment column because the activity of oxides at the top will be critical to the release of potentially bioavailable phosphorus into the water column. This trend reflects the importance of Mn redox changes through the course of summer 2004, changes which were observed to occur in the pore water analyses (Section 4.1).

4.5. Statistical analysis of seasonal data: One of the primary questions this study seeks to address regards the driving forces which may affect phosphorus mobility in the sediments of St. Albans Bay. Particularly the role of FeOOH and MnOOH minerals and their ability to sorb orthophosphate ions from solution will be impacted by the position of the redox front which may thus have significant impacts on P mobility due to the reduction and dissolution of those minerals. The correlation between P and Mn and/ or Fe is therefore critical in starting to determine if this process may be an important factor in the remobilization and essential cycling of phosphorus between the sediment and overlying water column. Appendix A-3 contains a tabulation relating Mn, Fe, and P for samples extracted with ascorbic acid or hydrochloric acid. The tables present Pearson correlation coefficients (a number between 0 and 1 indicates none to perfect correlation, respectively while a number between 0 to -1 indicates none to perfect inverse correlation) and P-values (which is a statistical test of the significance of the correlation, if the P-value is less than 0.050, the correlation is significant; if the P-value is greater than 0.050, there is insufficient proof to statistically support the relationship). Table 6 lists Pearson correlation coefficients between reactive phosphorus and amorphous manganese or iron for depth intervals measured on seasonal samples through the 2004 sampling season. All P-values for these samples were below 0.050, indicating a statistically significant and strong correlation between these elements in time. Similar data for hydrochloric acid extracted P, Mn, and Fe have P-values in excess of 0.050, indicating that there is no statistically significant correlation to be made between those elements when extracted with HCl.

Depth	Ascorbic Acid	
	P-Fe	P-Mn
0-1 cm	0.863	0.894
1-2 cm	0.933	0.921
2-3 cm	0.829	0.567
3-4 cm	0.604	0.559
4-5 cm	0.732	0.777
5-6 cm	0.889	0.895
6-8 cm	0.866	0.804
8-10 cm	0.894	0.876

Table 6 – Pearson correlation coefficients for ascorbic acid extracted reactive phosphorus with amorphous iron and manganese.

The statistical analysis of seasonal sediment samples indicates that the mobility of phosphorus within the sediment is closely tied to both iron and manganese. Significant differences in how P is related to Fe and Mn depending on how the elements were extracted further suggest that the mobility of P is tied to forms of manganese and iron that are specifically solubilized by Ascorbic acid, namely iron and manganese oxyhydroxide minerals. Combined with the electrochemistry data showing that redox fronts in this system do change over time, these results show that changes in the iron and manganese oxyhydroxide minerals are an important driving force in the mobility of phosphorus within the sediments of St. Albans Bay.

Phosphorus Mobility: The arguments above show definitely that seasonal phosphorus mobility is at least partly governed by changes in iron and manganese oxyhydroxide mineralization within the sediment. This study does not specifically address the release of phosphorus from the sediment into the overlying water column, though establishing the mechanism by which phosphorus may be mobilized is a necessary step in properly determining the flux of P in and out of the sediments of St. Albans Bay. In light of this finding, it is likely that any release of phosphorus into the overlying water column would require that mineral transformation should consume all available sites where any mobilized phosphorus could stick on its way out of the sediment and into the water column. Put another way, because reduction of iron and manganese occurs lower in the sediment (see profiles, figure 3) the last oxyhydroxide minerals to be dissolved would be at the top, nearest the sediment/water interface. As phosphorus released lower in the sediment column diffuses upwards, if it encounters an iron and manganese oxyhydroxide mineral which has spare space for another phosphorus ion, it will stick there. Only when that phosphorus can diffuse through the top sediments to the overlying water column without encountering an iron and manganese oxyhydroxide mineral WITH available sorption sites (i.e., there can be iron and manganese oxyhydroxide minerals present but if they are 'full' of P and no more can stick, the free P won't be affected) will that phosphorus continue to diffuse into the water column. This scenario may result in significant flux of P over short time frames, an episodic event when the sediment is most reduced (where the balance of oxygen penetration and oxygen consumption is pushed

well into the water column, after Figure 1). The only P flux measurements taken for St. Albans Bay (Cornwell and Owens, 1999) did not take this into account and thus are not representative of how significant reservoirs of P may be mobilized into the water column in St. Albans Bay (a point which the authors were cognizant to point out in Cornwell and Owens, 1999).

SECTION 5 – ST. ALBANS BAY SEDIMENT SAMPLING AND ASSESSMENT OF PHOSPHORUS LOAD

5.1. Bay-wide samples sediment extraction: Results of the analysis of extractions from the 43 core samples collected in early August are tabulated in Appendix B-1. Sample concentrations in general vary over 3 orders of magnitude bay-wide and can display significant heterogeneity mineralogically and chemically over short intervals. Soluble reactive phosphorus (NH₄Cl extracted) has a minimum measured value of 0.2 µg/g sediment to a maximum of 177 µg/g sediment and an average of 14 µg/g sediment. Mineralizable phosphorus (NaOH extracted) averages 363 µg/ g sediment, with a minimum of 2 µg/ g sediment, and a maximum of 2292 µg/ g sediment. Residual phosphorus (HCl extracted) averages 358 µg/ g sediment, with a minimum of 2 µg/ g sediment, and a maximum of 2413 µg/ g sediment. Reactive phosphorus (ascorbic acid extracted) averages 372 µg/ g sediment, with a minimum of 9 µg/ g sediment, and a maximum of 1880 µg/ g sediment. Total phosphorus (Aqua Regia extracted) averages 3400 µg/ g sediment, with a minimum of 493 µg/ g sediment, and a maximum of 4432 µg/ g sediment. When normalized to the sediment mass in each sampled section, the average phosphorus is 3000 µg/ g sediment. Table 7 gives averages with minimum/maximum values broken down by region of the bay: Inner Bay (IB), Middle Bay (MB), Outer Bay (OB), and the Stevens Brook Wetland area (SBW). The Stevens Brook wetland area contains the highest total, reactive, and mineralizable phosphorus values in the area on average.

		Porosity	Organic Content	Totals			Sequential Extraction →						Ascorbic Acid		
				Aqua Regia Extraction			NH ₄ Cl	NaOH	HCl						
				Fe	Mn	P	P	P	Fe	Mn	P	Fe	Mn	P	
average	IB	55%	4.2	32883	794	1394	13	280	5066	83	400	3435	207	272	
	MB	60%	4.1	39689	845	1474	10	263	5421	126	337	3620	288	263	
	OB	65%	4.3	52864	2394	2058	18	567	8586	302	221	8188	1238	717	
	SBW	52%	7.8	31343	797	2293	29	950	3044	46	213	2684	132	907	
maximum	IB	75%	35	63438	2445	3195	177	627	37361	440	2413	7303	565	579	
	MB	77%	7.6	81945	3017	2868	23	751	11945	641	617	9171	1049	719	
	OB	76%	6.6	68526	7654	3881	32	835	10783	920	291	12873	3605	1713	
	SBW	75%	26	52515	2438	4432	69	2292	8461	122	416	5232	211	1880	
minimum	IB	15%	0.2	5497	48	493	2.8	18	534	15	134	372	20	23	
	MB	21%	0.7	7487	16	525	0.2	36	481	9	126	207	18	9	
	OB	21%	1.0	35096	628	1101	4	247	5442	118	143	4520	444	344	
	SBW	24%	2.5	10681	130	667	8	229	118	7	2	881	47	274	

Table 7 - Tabulated averages, minimums, and maximum values for each region of St. Albans Bay; IB=Inner Bay, MB=Middle Bay, OB=Outer Bay, SBW=Stevens Brook Wetland.

5.2. *Potentially bioavailable inorganic phosphorus*: Considering the area of the bay, the total amount of reactive phosphorus that may be bioavailable is dependent on how much of the sediment is potentially exchangeable with the overlying water column. From the electrochemical data (Figure 3) collected in summer 2004 (this study), the top few cm are certainly active with respect to potential P mobilization and escape as soluble phosphorus into the water column. There are a number of ideas concerning what forms phosphorus would be present in that may be bioavailable (Martin et al., 1994 expressed bioavailable phosphorus as the total of NH₄Cl and NaOH extracted phosphorus for instance). Given that we are thinking about phosphorus that may be mobilized/immobilized by redox processes governing iron oxyhydroxide minerals, the most appropriate data to use may be the ascorbic acid extracted fraction. To determine how much phosphorus may potentially be released through remineralization in the sediments due to anoxia we must make some inferences from the available electrochemical data about how much sediment may be potentially vulnerable to recycling into the water column through the action of changing redox front position in time. We must keep in mind when looking at the electrochemical data from summer 2004 (Figure 3) that while porewater fluctuations in Mn, Fe, and S speciation were observed at 3-4 cm depth, this summer was a cooler and windier summer (Figure 4) – summers prior or in the future will produce different mineralization

conditions, governed by the balance of processes that determines redox front position at any time (Figure 1).

If we assume that the top 4 cm of sediment are potentially active with respect to redox changes and potential remineralization which would release phosphorus, that the porosity of that material is, on average, 60%, there are approximately 300 metric tons of phosphorus in the bay which may be reworked and at least partially released into the overlying water column as a result of increased anoxia in the sediments, and 1000 tons of total phosphorus (Table 8). This amount of phosphorus increases to over 700 tons of reactive P and 2400 tons of total P if we assume the reactive depth is 10 cm, as Cornwell and Owens modeled (1999). Considering that current estimates of phosphorus loading into the bay (from both point and nonpoint sources) is approximately 8 metric tons per year (from the Lake Champlain Phosphorus TMDL, VT DEC and NYS DEC 2002), and sedimentation rates are approximately 0.15 cm per year (Cornwell and Owens, 1999) the top 4 cm should have accumulated approximately 200 tons of total phosphorus (in the past 27 years, though this number is likely low as it does not span the time before significant improvements were made to the waste treatment facility, but it also assumes that the majority of sediment discharge stays in the bay). Sedimentation rates likely do not account for the high porosity in the top few centimeters and are likely off by as much as 50% given compaction seen even in only the top 12 cm of these materials. Another P component which would affect the total P amounts would be derived from any naturally occurring phosphorus that would be contained in the sediment as different mineralized, sorbed, or organic forms associated with the sediment's geologic origin. Assessment of this 'background' P for these materials was outside the scope of this study, and would require much deeper cores to look at a significant record which would include pre-industrial or settlement activity samples. Outside of this geologic reservoir, the phosphorus currently in the system likely also represents an historical reservoir of anthropogenically loaded P which has been reworked and mobilized through redox processes to be concentrated towards the water interface.

	Reactive P, mg/ g sediment	Area, m ²	reactive depth, m	volume sediment, m ³	volume sediment, cm ³	mass sediment, g	mass sediment, dry	Reactive P, mg	Reactive P, tons
IB	272	2.59E+06	0.04	1.03E+05	1.0E+11	2.6E+11	1.0E+11	2.81E+13	28
MB	263	4.33E+06	0.04	1.73E+05	1.7E+11	4.3E+11	1.7E+11	4.56E+13	46
OB	717	7.03E+06	0.04	2.81E+05	2.8E+11	7.0E+11	2.8E+11	2.02E+14	202
SBW	907	1.78E+05	0.04	7.10E+03	7.1E+09	1.8E+10	7.1E+09	6.44E+12	6
density = 2.5 g/cm ³ n= 0.4								reactive P, bay-wide	282

	Total P, mg/ g sediment	Area, m ²	depth, m	volume sediment, m ³	volume sediment, cm ³	mass sediment, g	mass sediment, dry	Total P, ug	Total P, tons
IB	1394	2.59E+06	0.04	1.03E+05	1.0E+11	2.6E+11	1.0E+11	1.44E+14	144
MB	1474	4.33E+06	0.04	1.73E+05	1.7E+11	4.3E+11	1.7E+11	2.55E+14	255
OB	2058	7.03E+06	0.04	2.81E+05	2.8E+11	7.0E+11	2.8E+11	5.79E+14	579
SBW	2293	1.78E+05	0.04	7.10E+03	7.1E+09	1.8E+10	7.1E+09	1.63E+13	16
density = 2.5 g/cm ³ n= 0.4								total P, bay-wide	994

Table 8 - Calculations for determining total amount of P potentially available through remineralization of Fe and Mn minerals. Where n is the sediment fraction and corresponds to a porosity of 60%.

5.3. *Statistical analysis of bay-wide samples:* Differences between P, Fe, and Mn for samples collected at the same time, but varying in sample position provide a picture of the spatial distribution of P, and an indication of whether any of the processes seen to affect seasonal distribution within sediment profile translate to any lateral diffusion of P across the bay. Correlation of Fe, Mn, and P for samples taken only in early August 2004 show a different trend with respect to the ascorbic acid extracted samples as compared to samples taken as part of the seasonal study. Table 9 shows Pearson Correlation Coefficients and P-values for both the aqua regia digested total Fe, Mn, and P concentrations and for the reactive P - amorphous Fe and Mn

Depth	Aqua Regia		Ascorbic Acid	
	P-Fe	P-Mn	P-Fe	P-Mn
0-1 cm	0.603/0.000	0.418/0.007	0.801/0.000	0.767/0.000
1-2 cm	0.726/0.000	0.482/0.002	0.427/0.033	0.363/0.074
2-3 cm	0.495/0.001	0.303/0.057	0.351/0.093	0.317/0.131
3-4 cm	0.642/0.000	0.382/0.016	0.177/0.408	0.184/0.390
4-5 cm	0.657/0.000	0.601/0.000	0.350/0.086	0.366/0.072
5-8 cm	0.644/0.000	0.492/0.001	0.224/0.305	0.321/0.135
8-12 cm	0.508/0.001	0.201/0.220	0.254/0.254	0.322/0.143
ALL	0.580/0.000	0.445/0.000	0.428/0.000	0.451/0.000

Table 9 - Person Correlation coefficients / P-values for basin samples 1-43 (Aqua Regia) and 1-27 (Ascorbic Acid). Values that are statistically valid are in bold, note that P-values greater than 0.050 indicate no statistically supported relationship between elements.

concentrations from ascorbic acid digestions. The differences between these correlations and those for the seasonal sampling are especially noticeable for Fe, Mn, and P extracted with ascorbic acid. Bay-wide differences across the bay and wetlands area are not generally due to changes associated with Fe and Mn minerals EXCEPT in the top 1 or 2 cm, where there is good correlation. This may indicate that reactive phosphorus in the system is constrained to the top 2 cm, afterwards phosphorus sorption to other materials or as precipitation of a distinct mineral phase may be a more important control on the overall. Spatial distribution of these materials across the bay is controlled by processes which are distinctly different from processes which were shown to control the P mobility seasonally. While seasonal variations in P positions tracked very well with changes in iron and manganese oxyhydroxide minerals, variable P concentrations across the bay are likely affected by a number of physical characteristics related to sediment provenance (origin), and reworking associated with sediment transport.

Historical profile information: The spatial distribution of total phosphorus in the bay is imprinted by the seasonal redox processes discussed above, which has resulted in the redistribution of sediment-bound phosphorus (Figure 14). If one considers that sediment loading rates in the bay have been estimated at approximately 0.15 cm of sediment per year (Cornwell and Owens, 1999), then a 10 cm sediment profiles should represent approximately 65 years of sediment. This would include time well before and after large changes in the overall phosphorus loading to the St. Albans Bay system due to upgrades to the waste treatment facility, closure of a large dairy, and continued significant

improvements to public education and community involvement in reducing P input into the bay. If phosphorus was deposited with sediment over time and there was no mobilization of that P with seasonal change, one may expect a profile such as the one depicted in Figure 15. None of the profiles in this study (see data in appendices as well as representative profiles in Figures 10, 11, and 14), regardless of spatial position, time of sampling, or extraction method, show this type of profile. This strongly suggests that significant, persistent, and seasonally active changes in redox fronts have induced reworking of phosphorus to effectively smear out the historical (past ~65 year history from this study) component. This effectively means that while significant improvement has been made to limit P loading into St. Albans Bay, the historical legacy of high phosphorus loading into the bay remains a significant component of near-surface sediment chemistry.

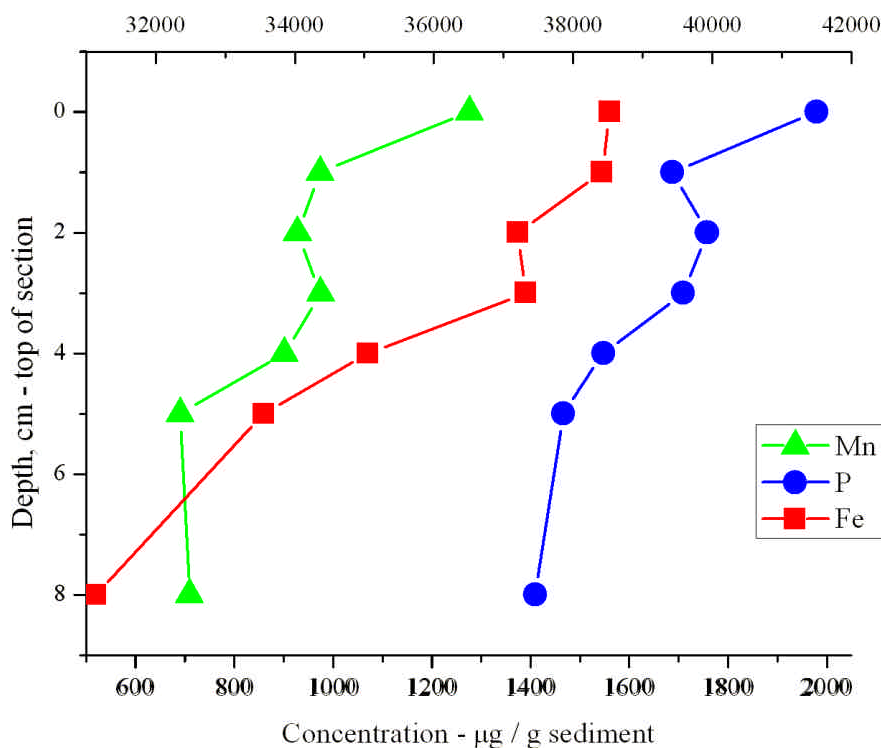


Figure 14 – Profile plot of averaged aqua regia extraction data from all cores at specified depths (marked at top of core sections) collected in St. Albans Bay, August 2004. Iron (Fe) data corresponds to the top x-axis, while phosphorus (P) and Manganese (Mn) correspond to the bottom y-axis.

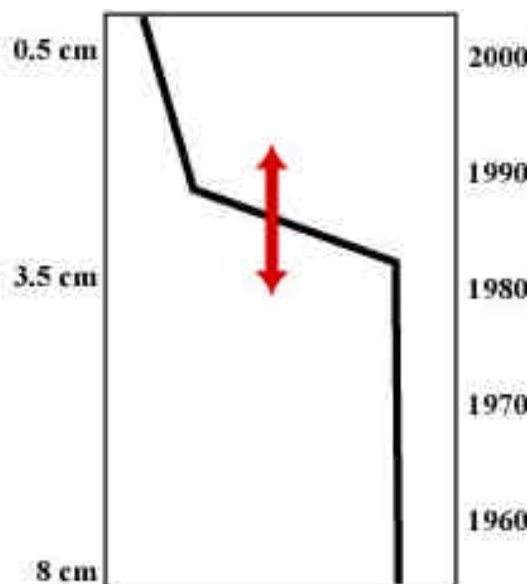


Figure 15 – Generalized diagram of a sediment P profile that should be observed given significant decreases in P loading to St. Albans Bay.

5.4. Historical comparison of bay-wide samples: One of the original goals of this study was to assess how the phosphorus levels may have changed from the time of the first detailed study of sediment phosphorus concentrations in St. Albans Bay by Ackerly (1983), followed by Martin et al. (1994). Appendix C lists all of the common sample sites and depth intervals between this study, Ackerly (1983; samples collected 1982), and Martin et al. (1994; samples collected 1992). While there can now be observed significant differences between all of the study databases, the following points must be made as potential difficulties in making a direct, quantitative comparison:

1. We have now shown that P is mobile in these sediments in large part due to transformation of iron and manganese oxyhydroxide minerals, and the position of redox fronts which would determine where this activity is actively occurring changes on very short timescales and may additionally be variable depending on spatial location. There is no constraint to base a comparison at times when the redox chemistry in the sediment profile would have been at comparable conditions, or even to base the sampling period on some combination of weather conditions which would affect redox front positions.

2. The flux rate of phosphorus from sediments into the overlying water column is almost completely unknown for sediments of St. Albans Bay, and given these results, fluxes may differ significantly and in a very episodic fashion. There is significant lack of constraint as to the flux of phosphorus from/to the sediment into the overlying water column (and subsequent incorporation into algal biomass) between these studies and no way to determine if significant P may have been tied up as a suspended algal fraction when the sediments were sampled.
3. Chemical and physical heterogeneities seen on several scales in this study and others, in addition to the significant effect of bioturbation due to bivalve activity observed by Cornwell and Owens (1999), suggest that taking a core from the exact same type of location 12 or 22 years later is most likely impossible.
4. Ackerly (1983) and Martin et al. (1994) used a colorimetric procedure for analysis of their extraction solutions. The high amount of iron present in samples processed for total P (aqua regia or perchloric acid extractions), HCl-extracted P, or ascorbic acid extractions would serve as an analytical interference which would yield lower P measurements due to competition between the Fe^{3+} and colorimetric complex for the ascorbic acid. After experiencing problems with our matrix-matched, mixed standard (standards containing not only P, but also Fe and Mn) with the same colorimetric complex, we developed specific methods for ICP-OES which do not suffer from this potential analytical difficulty. Repeating the procedure to back-calculate what the Fe interference is not possible.
5. Sedimentation rates for St. Albans Bay are not well constrained, but Cornwell and Owens (1999) give rates of 0.13 and 0.18 cm per annum, determined from ^{210}Pb dating of a core from two locations in St. Albans Bay from the 1996 sampling by Horn Point Environmental Laboratories. Comparing levels of cores collected 22 and 12 years prior is an offset of approximately 3-4 and 1.5-2 cm, respectively, a calculation which further assumes a sedimentation rate that is constant, something that is almost certainly not the case in a small shallow basin with multiple inputs and unresolved current transport. Observed differences in sediment compaction (seen in this study as variation in porosity; Table 6) additionally support the idea

that sediment transport, deposition, and reworking is significantly heterogeneous over the St. Albans Bay sediment surface.

While making any sort of direct comparison between samples from specific locations is inappropriate for these reasons, there is certainly significant phosphorus contained in the sediments of St. Albans Bay. On average, Ackerly found 1400 μg total P / g sediment, Martin found 1100 μg total P / g sediment, and this study found 1800 μg total P / g sediment in the bay. For reference to direct comparison of each sample, which as pointed out above is not strictly appropriate, refer to Figures 16, 17, and 18. We DO NOT contend that these numbers necessarily indicate an increase in the overall amount of phosphorus contained in these sediments over time. A significant part could be due to different sampling times when more P could have been mobilized from the sediment into an algal fraction in the water column and a significant part could be due to analytical differences. How much P could be liberated into an algal fraction which may exist in the water column is impossible to determine from available data in 1982 and 1992, and there is little indication from any trend of phosphorus gradients with depth at those sampling times to suggest this may or may not have been an important process. There is also significant Fe and Mn in these sediments, and significant indication that the presence, reductive dissolution and transport followed by oxidation and reprecipitation of FeOOH and MnOOH minerals plays a significant role in P mobility and bioavailability to the overlying water column.

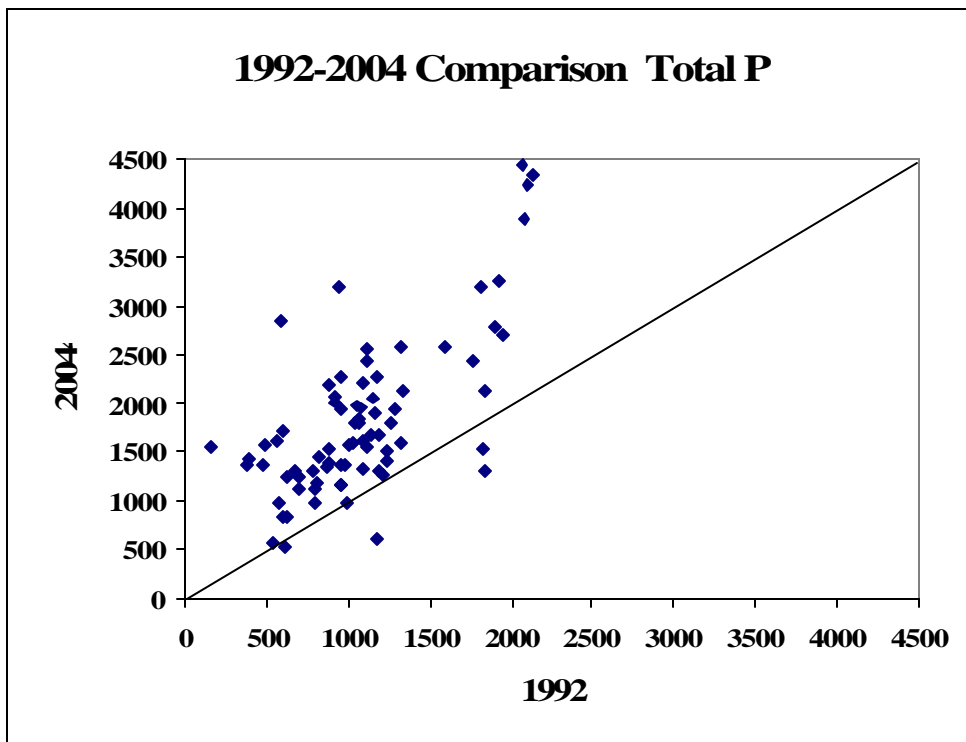


Figure 16 – Scatter plot comparing total P concentrations for each common site and spatial intervals 0-1, 1-2, 4-5, and 8-12 between 1992 and 2004 studies.

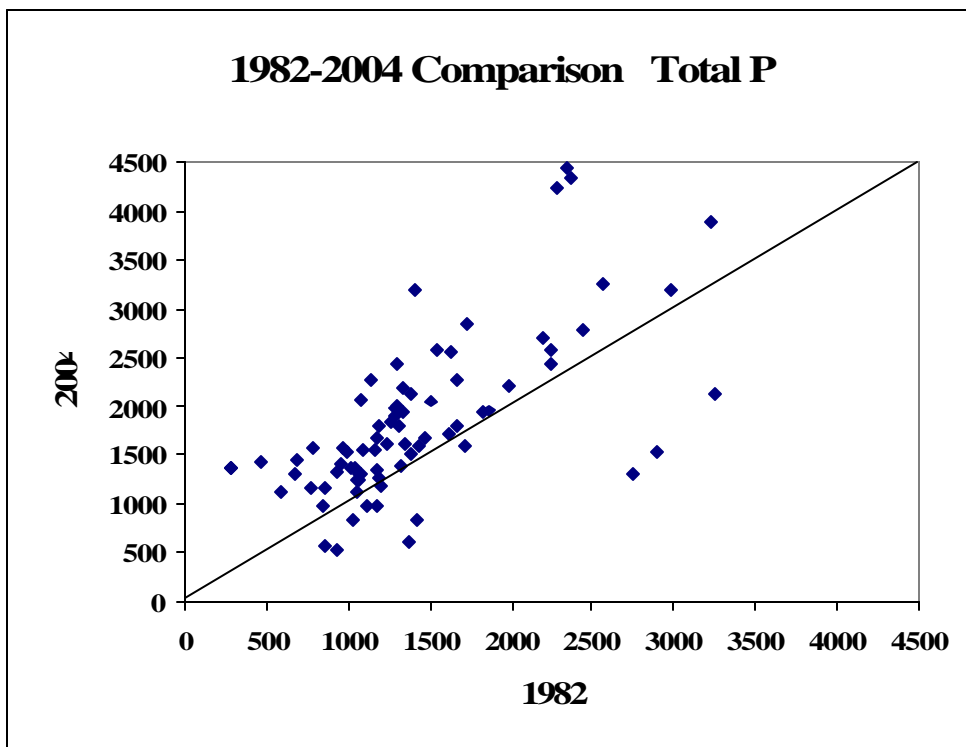


Figure 17 – Scatter plot comparing total P concentrations for each common site and spatial intervals 0-1, 1-2, 4-5, and 8-12 between 1982 and 2004 studies.

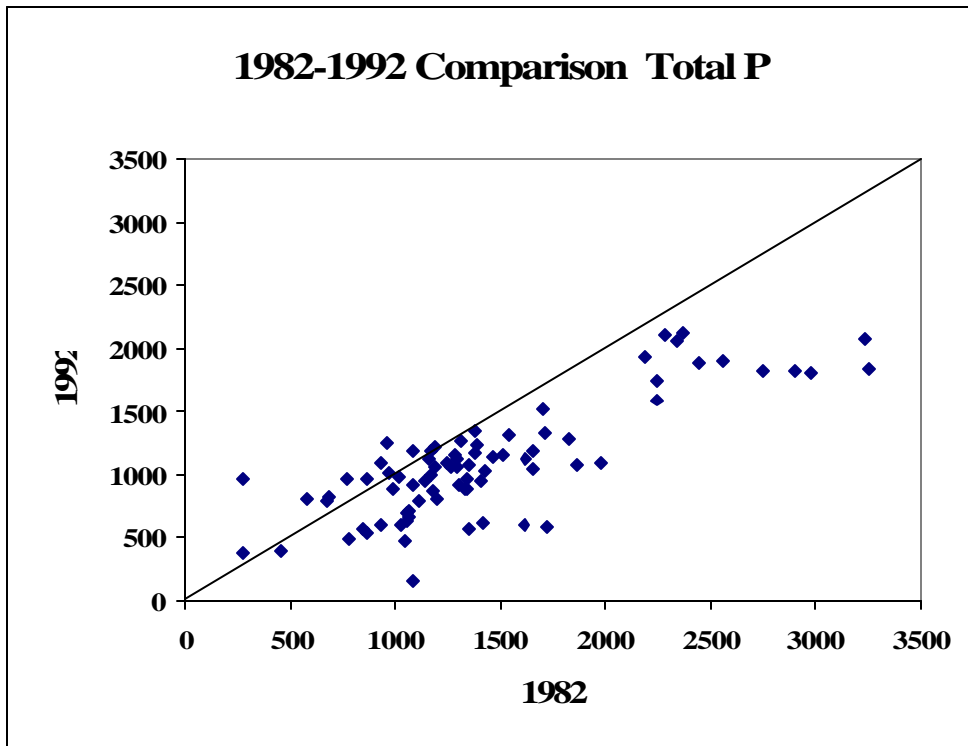


Figure 18 – Scatter plot comparing total P concentrations for each common site and spatial intervals 0-1, 1-2, 4-5, and 8-12 between 1982 and 1992 studies.

SECTION 6 – SUMMARY AND CONCLUSIONS

In this study, it was determined that there are significant amounts of phosphorus retained in St. Albans Bay sediments, and that the mobility of phosphorus in those sediments is at least partially controlled by changes in manganese and iron oxyhydroxide minerals. The seasonal component of these redox changes, analytical differences, and a strong spatial heterogeneity in these sediments make any direct comparison between this study and the studies of Ackerly (1983) or Martin et al. (1994) inappropriate. It is of considerable interest and importance to the St. Albans Bay community to assess whether the phosphorus content in the sediments of the bay is at all decreasing with time, as had been suggested would happen (Martin et al., 1994). It is reasonable to state from this data that

any net loss of phosphorus through exchange with the main lake is not occurring at the rates which had been previously predicted and that the amount of phosphorus which is currently in the sediments will likely persist for some time. Additionally, remobilization of the phosphorus through the column as redox fronts move up and down through the seasons may keep a significant fraction of the historical phosphorus load nearer the top of the sediment column.

6.2. Recommendations for future study: A more thorough understanding of how phosphorus may be released and made bioavailable as a function of the dissolution of iron and manganese oxyhydroxides in the bay would be necessary in order to determine the potential role that sediment recycling of phosphorus plays on overall algal activity of the bay. Critical to this point is the flux of phosphorus out of the sediment into the water column and how that phosphorus persists in the water column and potentially diffuses out of the bay into the main lake. Another related question relates to whether there are specific chemical conditions (especially affecting N:P ratios which are thought to be an important factor in selecting algae species; M. Watzin, pers. Comm.) which may develop in the bay which selects for blue-green algae over other varieties, and if those conditions are selected by any process involving nutrient cycling in the sediments. Finally, what the overall sorption capacity of the iron and manganese oxyhydroxides is would be critical for understanding how they may or may not limit the amount of phosphorus that could escape from the sediment column into the water column. An investigation of phosphorus levels through a deeper section of sediments may give a better indication of phosphorus loading changes in time and the potential role of phosphorus remobilization along changing redox fronts. Any treatment option must also assess how the effects of seasonal redox cycling will be affected by chemical or physical perturbation.

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Appendix A-1 – Seasonal data by date

				HCl extractions			NaOH	Ascorbic Acid extractions		
				µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed
Sample Date	Core #	Interval	Porosity (%)	Fe	Mn	P	P	Fe	Mn	P
5/27/2004	1	0-1cm	59	3151	168	470	216	2571	279	249
5/27/2004	1	1-2cm	64							
5/27/2004	1	2-3cm	68	2353	77	525		1925	136	194
6/23/2004	1	0-1cm	74	2987	69	536		2042	129	233
6/23/2004	1	1-2cm	71	2841	68	513		1949	125	218
6/23/2004	1	2-3cm	67	2558	55	556	127	1328	82	137
6/23/2004	1	3-4cm	67	2514	53	532	148	1519	89	153
6/23/2004	1	4-5cm	62				88	948	62	92
6/23/2004	1	5-6cm	62				105	937	64	93
6/23/2004	1	6-8cm	65				136	1275	82	122
7/7/2004	1	0-1cm	81	4651	194	569		3297	307	378
7/7/2004	1	1-2cm	79	4200	138	505	271	3323	274	397
7/7/2004	1	2-3cm	77	3499	71	526	208	2136	100	213
7/7/2004	1	3-4cm	76	3110	59	452	172	2415	107	219
7/7/2004	1	4-5cm	76	3470	63	533	152	2210	98	187
7/7/2004	1	5-6cm	75	3303	57	497	171	2204	108	210
7/7/2004	1	6-8cm	74	3370	67	495	205	2310	120	240
7/7/2004	1	8-10cm	71	3418	65	527	199	2195	116	249
7/7/2004	2	0-1cm	82	6167	136	511		3015	228	327
7/7/2004	2	1-2cm	79	6693	137	493	299	3188	195	379
7/7/2004	2	2-3cm	77	5416	78	486	206	2231	101	216
7/7/2004	2	3-4cm		5802	80	481	187	2748	107	211
7/7/2004	2	4-5cm	75	5406	81	483	206	2407	113	213
7/7/2004	2	5-6cm	71	5542	79	491	175	2552	120	226
7/7/2004	2	6-8cm	72	5653	85	493	211	2374	117	230
7/7/2004	2	8-10cm	72	5158	77	453	193	2485	122	230
7/19/2004	1	0-1cm		5227	169	489	394	3793	430	472
7/19/2004	1	1-2cm		5101	97	476	323	3381	264	361
7/19/2004	1	2-3cm		4337	69	480	231	2577	150	252
7/19/2004	1	3-4cm		4139	61	491	201	2314	115	221
7/19/2004	1	4-5cm		4034	61	494	204	2481	116	206
7/19/2004	1	5-6cm		4145	64	472	203	2727	133	232
7/19/2004	1	6-8cm		4267	66	510	208	2293	112	200
7/19/2004	1	8-10cm		2836	42	390	127	1417	69	130
7/19/2004	2	0-1cm	79	5473	156	503	325	3324	320	382
7/19/2004	2	1-2cm	77	5091	97	480				
7/19/2004	2	2-3cm	75	4442	68	478	216	2319	118	202
7/19/2004	2	3-4cm	75	4827	77	460	231	2733	140	253

				HCl extractions			NaOH	Ascorbic Acid extractions		
				µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed
Sample Date	Core #	Interval	Porosity (%)	Fe	Mn	P	P	Fe	Mn	P
7/19/2004	2	4-5cm	75	5119	80	470	254	2705	139	260
7/19/2004	2	5-6cm	58	4502	66	496	228	2524	122	220
7/19/2004	2	6-8cm	71	4820	74	543	209	2282	113	196
7/19/2004	2	8-10cm	68	4224	64	487	177	2091	100	182
7/26/2004	1	0-1cm	75	3691	128	527		2225	221	288
7/26/2004	1	1-2cm	70	3465	78	559		2185	162	238
7/26/2004	1	2-3cm	69	3331	65	503	197	2186	133	224
7/26/2004	1	3-4cm	66	2856	52	563	136	1597	96	160
7/26/2004	1	4-5cm	63	2876	52	524	132	1709	94	162
7/26/2004	1	5-6cm	62	2819	52	587	138	1582	87	146
7/26/2004	1	6-8cm	62	2867	55	585	141	1571	86	146
7/26/2004	1	8-10cm	56	2741	54	585	104	1296	67	121
7/26/2004	2	0-1cm	74	3538	90	534		2567	203	312
7/26/2004	2	1-2cm	69	3099	59	505		1854	109	179
7/26/2004	2	2-3cm	67	2750	48	631		1813	91	152
7/26/2004	2	3-4cm	66	3053	57	529		2006	102	176
7/26/2004	2	4-5cm	66	2990	57	553		1905	98	170
7/26/2004	2	5-6cm	64	2722	44	577		1666	86	149
7/26/2004	2	6-8cm	61					1363	70	125
7/26/2004	2	8-10cm	62	2674	44	523		1020	53	96
7/26/2004	3	0-1cm	74	3152	77	565		2005	147	221
7/26/2004	3	1-2cm	66	2763	51	571		1478	79	142
7/26/2004	3	2-3cm	67	2910	48	612		1635	81	128
7/26/2004	3	3-4cm	65	2669	46	595		1801	90	139
7/26/2004	3	4-5cm	63	2925	53	578		1712	85	137
8/5/2004	1	0-1cm	72				259	2502	179	254
8/5/2004	1	1-2cm	71				172	2067	108	169
8/5/2004	1	2-3cm	71				255	2061	104	195
8/5/2004	1	3-4cm	74				294	2359	112	176
8/5/2004	1	4-5cm	69				238	1968	96	147
8/5/2004	1	5-6cm	59				167	1533	72	116
8/5/2004	1	6-8cm	55				162	1217	58	104
8/5/2004	1	8-10cm	53				134	1023	56	84
8/5/2004	2	0-1cm	76	3139	96	521	344	2852	219	295
8/5/2004	2	1-2cm	71	2578	63	565	238	1813	102	155
8/5/2004	2	2-3cm	66	2556	59	548	228	1775	84	138
8/5/2004	2	3-4cm	60	2491	66	546	216	1966	97	155
8/5/2004	2	4-5cm	62	2539	66	554	236	1873	102	164

				HCl extractions			NaOH	Ascorbic Acid extractions		
				$\mu\text{g/g sed}$	$\mu\text{g/g sed}$	$\mu\text{g/g sed}$	$\mu\text{g/g sed}$	$\mu\text{g/g sed}$	$\mu\text{g/g sed}$	$\mu\text{g/g sed}$
Sample Date	Core #	Interval	Porosity (%)	Fe	Mn	P	P	Fe	Mn	P
8/5/2004	2	5-6cm	61	2406	73	549	222	1764	93	151
8/5/2004	2	6-8cm	54					950	45	107
8/12/2004	1	0-1cm	73	2333	67	633	153	1615	115	233
8/12/2004	1	1-2cm	70	2291	43	647	130	1514	66	175
8/12/2004	1	2-3cm	70	2397	49	557	186			
8/12/2004	1	3-4cm	70	3296	61	584	204	1756	94	203
8/12/2004	1	4-5cm	65	2413	53	675	181	1509	70	170
8/12/2004	1	5-6cm	64	2886	63	601	186	1927	109	185
8/12/2004	1	6-8cm	61	1967	49	629	151			
8/12/2004	1	8-10cm	56	2196	35	658	115			
8/12/2004	2	0-1cm	76	3959	144	567	272	2540	252	337
8/12/2004	2	1-2cm	72	2435	58	520	150	1855	106	183
8/12/2004	2	2-3cm	69	2322	49	573	187	1672	89	158
8/12/2004	2	3-4cm	67	3015	56	556	174	1638	85	160
8/12/2004	2	4-5cm	66	2651	53	562	181	1630	84	184
8/12/2004	2	5-6cm	63	2096	52	591	171	1507	77	193
8/12/2004	2	6-8cm	60	1919	44	582	143	1345	60	148
8/18/2004	1	0-1cm	73	2913	96	455	188	1617	134	279
8/18/2004	1	1-2cm	72	3607	80	427	171	1562	99	220
8/18/2004	1	2-3cm	74	3252	76	398	268	1767	160	234
8/18/2004	1	3-4cm	72	3294	75	397	250	1846	131	228
8/18/2004	1	4-5cm	76	3371	82	418	280	1821	118	260
8/18/2004	1	5-6cm	65	2428	63	449	227	1964	121	211
8/18/2004	1	6-8cm	64	2939	65	455	215	1486	70	214
8/18/2004	1	8-10cm	60	3437	58	444	208	1059	46	159
9/13/2004	1	0-1cm		4871	58	499		2080	99	215
9/13/2004	1	1-2cm		5711	61	571		2662	128	252
9/13/2004	1	2-3cm		4944	54	495		1674	60	203
9/13/2004	1	3-4cm		4762	52	517		1959	85	223
9/13/2004	1	4-5cm		4596	49	515		1840	76	185
9/13/2004	2	0-1cm		4053	41	485		2229	118	262
9/13/2004	2	1-2cm		4804	51	564		2554	124	254
9/13/2004	2	2-3cm		5704	63	476		2826	104	289
9/13/2004	2	3-4cm		4868	48	411		1785	75	210
9/13/2004	2	4-5cm		3931	43	400		1171	46	146
10/7/2004	1	0-1cm		5987	92	448				
10/7/2004	1	2-3cm		5357	59	456				
10/7/2004	1	3-4cm		5362	66	475				

Appendix A-2 – Seasonal data grouped by depth

0-1 cm sections					HCl extractions			NaOH	Ascorbic Acid extractions		
					µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed
Interval	Sample Date	Core #	Interval	Porosity (%)	Fe	Mn	P	P	Fe	Mn	P
0-1cm	5/27/2004	1	0-1cm	59	3151	168	470	216	2571	279	249
0-1cm	6/23/2004	1	0-1cm	74	2987	69	536		2042	129	233
0-1cm	7/7/2004	1	0-1cm	81	4651	194	569		3297	307	378
0-1cm	7/7/2004	2	0-1cm	82	6167	136	511		3015	228	327
0-1cm	7/19/2004	1	0-1cm		5227	169	489	394	3793	430	472
0-1cm	7/19/2004	2	0-1cm	79	5473	156	503	325	3324	320	382
0-1cm	7/26/2004	1	0-1cm	75	3691	128	527		2225	221	288
0-1cm	7/26/2004	2	0-1cm	74	3538	90	534		2567	203	312
0-1cm	7/26/2004	3	0-1cm	74	3152	77	565		2005	147	221
0-1cm	8/5/2004	1	0-1cm	72				259	2502	179	254
0-1cm	8/5/2004	2	0-1cm	76	3139	96	521	344	2852	219	295
0-1cm	8/12/2004	1	0-1cm	73	2333	67	633	153	1615	115	233
0-1cm	8/12/2004	2	0-1cm	76	3959	144	567	272	2540	252	337
0-1cm	8/18/2004	1	0-1cm	73	2913	96	455	188	1617	134	279
0-1cm	9/13/2004	1	0-1cm		4871	58	499		2080	99	215
0-1cm	9/13/2004	2	0-1cm		4053	41	485		2229	118	262
0-1cm	10/7/2004	1	0-1cm		5987	92	448				

1-2 cm sections					HCl extractions			NaOH	Ascorbic Acid extractions		
					µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed
Interval	Sample Date	Core #	Interval	Porosity (%)	Fe	Mn	P	P	Fe	Mn	P
1-2cm	5/27/2004	1	1-2cm	64							
1-2cm	6/23/2004	1	1-2cm	71	2841	68	513		1949	125	218
1-2cm	7/7/2004	1	1-2cm	79	4200	138	505	271	3323	274	397
1-2cm	7/7/2004	2	1-2cm	79	6693	137	493	299	3188	195	379
1-2cm	7/19/2004	1	1-2cm		5101	97	476	323	3381	264	361
1-2cm	7/19/2004	2	1-2cm	77	5091	97	480				
1-2cm	7/26/2004	1	1-2cm	70	3465	78	559		2185	162	238
1-2cm	7/26/2004	2	1-2cm	69	3099	59	505		1854	109	179
1-2cm	7/26/2004	3	1-2cm	66	2763	51	571		1478	79	142
1-2cm	8/5/2004	1	1-2cm	71				172	2067	108	169
1-2cm	8/5/2004	2	1-2cm	71	2578	63	565	238	1813	102	155
1-2cm	8/12/2004	1	1-2cm	70	2291	43	647	130	1514	66	175
1-2cm	8/12/2004	2	1-2cm	72	2435	58	520	150	1855	106	183
1-2cm	8/18/2004	1	1-2cm	72	3607	80	427	171	1562	99	220
1-2cm	9/13/2004	1	1-2cm		5711	61	571		2662	128	252
1-2cm	9/13/2004	2	1-2cm		4804	51	564		2554	124	254

2-3 cm sections					HCl extractions			NaOH	Ascorbic Acid extractions		
					µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed
Interval	Sample Date	Core #	Interval	Porosity (%)	Fe	Mn	P	P	Fe	Mn	P
2-3cm	5/27/2004	1	2-3cm	68	2353	77	525		1925	136	194
2-3cm	6/23/2004	1	2-3cm	67	2558	55	556	127	1328	82	137
2-3cm	7/7/2004	1	2-3cm	77	3499	71	526	208	2136	100	213
2-3cm	7/7/2004	2	2-3cm	77	5416	78	486	206	2231	101	216
2-3cm	7/19/2004	1	2-3cm		4337	69	480	231	2577	150	252
2-3cm	7/19/2004	2	2-3cm	75	4442	68	478	216	2319	118	202
2-3cm	7/26/2004	1	2-3cm	69	3331	65	503	197	2186	133	224
2-3cm	7/26/2004	2	2-3cm	67	2750	48	631		1813	91	152
2-3cm	7/26/2004	3	2-3cm	67	2910	48	612		1635	81	128
2-3cm	8/5/2004	1	2-3cm	71				255	2061	104	195
2-3cm	8/5/2004	2	2-3cm	66	2556	59	548	228	1775	84	138
2-3cm	8/12/2004	1	2-3cm	70	2397	49	557	186			
2-3cm	8/12/2004	2	2-3cm	69	2322	49	573	187	1672	89	158
2-3cm	8/18/2004	1	2-3cm	74	3252	76	398	268	1767	160	234
2-3cm	9/13/2004	1	2-3cm		4944	54	495		1674	60	203
2-3cm	9/13/2004	2	2-3cm		5704	63	476		2826	104	289
2-3cm	10/7/2004	1	2-3cm		5357	59	456				

3-4 cm sections					HCl extractions			NaOH	Ascorbic Acid extractions		
					µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed
Interval	Sample Date	Core #	Interval	Porosity (%)	Fe	Mn	P	P	Fe	Mn	P
3-4cm	6/23/2004	1	3-4cm	67	2514	53	532	148	1519	89	153
3-4cm	7/7/2004	1	3-4cm	76	3110	59	452	172	2415	107	219
3-4cm	7/7/2004	2	3-4cm		5802	80	481	187	2748	107	211
3-4cm	7/19/2004	1	3-4cm		4139	61	491	201	2314	115	221
3-4cm	7/19/2004	2	3-4cm	75	4827	77	460	231	2733	140	253
3-4cm	7/26/2004	1	3-4cm	66	2856	52	563	136	1597	96	160
3-4cm	7/26/2004	2	3-4cm	66	3053	57	529		2006	102	176
3-4cm	7/26/2004	3	3-4cm	65	2669	46	595		1801	90	139
3-4cm	8/5/2004	1	3-4cm	74				294	2359	112	176
3-4cm	8/5/2004	2	3-4cm	60	2491	66	546	216	1966	97	155
3-4cm	8/12/2004	1	3-4cm	70	3296	61	584	204	1756	94	203
3-4cm	8/12/2004	2	3-4cm	67	3015	56	556	174	1638	85	160
3-4cm	8/18/2004	1	3-4cm	72	3294	75	397	250	1846	131	228
3-4cm	9/13/2004	1	3-4cm		4762	52	517		1959	85	223
3-4cm	9/13/2004	2	3-4cm		4868	48	411		1785	75	210
3-4cm	10/7/2004	1	3-4cm		5362	66	475				

4-5 cm sections					HCl extractions			NaOH	Ascorbic Acid extractions		
					µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed
Interval	Sample Date	Core #	Interval	Porosity (%)	Fe	Mn	P	P	Fe	Mn	P
4-5cm	6/23/2004	1	4-5cm	62				88	948	62	92
4-5cm	7/7/2004	1	4-5cm	76	3470	63	533	152	2210	98	187
4-5cm	7/7/2004	2	4-5cm	75	5406	81	483	206	2407	113	213
4-5cm	7/19/2004	1	4-5cm		4034	61	494	204	2481	116	206
4-5cm	7/19/2004	2	4-5cm	75	5119	80	470	254	2705	139	260
4-5cm	7/26/2004	1	4-5cm	63	2876	52	524	132	1709	94	162
4-5cm	7/26/2004	2	4-5cm	66	2990	57	553		1905	98	170
4-5cm	7/26/2004	3	4-5cm	63	2925	53	578		1712	85	137
4-5cm	8/5/2004	1	4-5cm	69				238	1968	96	147
4-5cm	8/5/2004	2	4-5cm	62	2539	66	554	236	1873	102	164
4-5cm	8/12/2004	1	4-5cm	65	2413	53	675	181	1509	70	170
4-5cm	8/12/2004	2	4-5cm	66	2651	53	562	181	1630	84	184
4-5cm	8/18/2004	1	4-5cm	76	3371	82	418	280	1821	118	260
4-5cm	9/13/2004	1	4-5cm		4596	49	515		1840	76	185
4-5cm	9/13/2004	2	4-5cm		3931	43	400		1171	46	146

5-6 cm sections					HCl extractions			NaOH	Ascorbic Acid extractions		
					µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed
Interval	Sample Date	Core #	Interval	Porosity (%)	Fe	Mn	P	P	Fe	Mn	P
5-6cm	6/23/2004	1	5-6cm	62				105	937	64	93
5-6cm	7/7/2004	1	5-6cm	75	3303	57	497	171	2204	108	210
5-6cm	7/7/2004	2	5-6cm	71	5542	79	491	175	2552	120	226
5-6cm	7/19/2004	1	5-6cm		4145	64	472	203	2727	133	232
5-6cm	7/19/2004	2	5-6cm	58	4502	66	496	228	2524	122	220
5-6cm	7/26/2004	1	5-6cm	62	2819	52	587	138	1582	87	146
5-6cm	7/26/2004	2	5-6cm	64	2722	44	577		1666	86	149
5-6cm	8/5/2004	1	5-6cm	59				167	1533	72	116
5-6cm	8/5/2004	2	5-6cm	61	2406	73	549	222	1764	93	151
5-6cm	8/12/2004	1	5-6cm	64	2886	63	601	186	1927	109	185
5-6cm	8/12/2004	2	5-6cm	63	2096	52	591	171	1507	77	193
5-6cm	8/18/2004	1	5-6cm	65	2428	63	449	227	1964	121	211

6-8 cm sections					HCl extractions			NaOH	Ascorbic Acid extractions		
					µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed
Interval	Sample Date	Core #	Interval	Porosity (%)	Fe	Mn	P	P	Fe	Mn	P
6-8cm	6/23/2004	1	6-8cm	65				136	1275	82	122
6-8cm	7/7/2004	1	6-8cm	74	3370	67	495	205	2310	120	240
6-8cm	7/7/2004	2	6-8cm	72	5653	85	493	211	2374	117	230
6-8cm	7/19/2004	1	6-8cm		4267	66	510	208	2293	112	200
6-8cm	7/19/2004	2	6-8cm	71	4820	74	543	209	2282	113	196
6-8cm	7/26/2004	1	6-8cm	62	2867	55	585	141	1571	86	146
6-8cm	7/26/2004	2	6-8cm	61					1363	70	125
6-8cm	8/5/2004	1	6-8cm	55				162	1217	58	104
6-8cm	8/5/2004	2	6-8cm	54					950	45	107
6-8cm	8/12/2004	1	6-8cm	61	1967	49	629	151			
6-8cm	8/12/2004	2	6-8cm	60	1919	44	582	143	1345	60	148
6-8cm	8/18/2004	1	6-8cm	64	2939	65	455	215	1486	70	214

8-10 cm sections					HCl extractions			NaOH	Ascorbic Acid extractions		
					µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed	µg/g sed
Interval	Sample Date	Core #	Interval	Porosity (%)	Fe	Mn	P	P	Fe	Mn	P
8-10cm	7/7/2004	1	8-10cm	71	3418	65	527	199	2195	116	249
8-10cm	7/7/2004	2	8-10cm	72	5158	77	453	193	2485	122	230
8-10cm	7/19/2004	1	8-10cm		2836	42	390	127	1417	69	130
8-10cm	7/19/2004	2	8-10cm	68	4224	64	487	177	2091	100	182
8-10cm	7/26/2004	1	8-10cm	56	2741	54	585	104	1296	67	121
8-10cm	7/26/2004	2	8-10cm	62	2674	44	523		1020	53	96
8-10cm	8/5/2004	1	8-10cm	53				134	1023	56	84
8-10cm	8/12/2004	1	8-10cm	56	2196	35	658	115			
8-10cm	8/18/2004	1	8-10cm	60	3437	58	444	208	1059	46	159

Appendix A-3 – Statistical Correlation matrices (P, Mn, Fe) for seasonal samples calculated with Minitab v13.32.

Pearson Correlation Coefficient			P-Values		
AA - 0-1	Fe	Mn	AA - 0-1	Fe	Mn
Mn	0.9		Mn	0.000	
P	0.863	0.894	P	0.000	0.000
HCl - 0-1	Fe	Mn	HCl - 0-1	Fe	Mn
Mn	0.355		Mn	0.178	
P	-0.414	-0.045	P	0.11	0.869
AA - 1-2	Fe	Mn	AA - 1-2	Fe	Mn
Mn	0.915		Mn	0.000	
P	0.933	0.921	P	0.000	0.000
HCl - 1-2	Fe	Mn	HCl - 1-2	Fe	Mn
Mn	0.618		Mn	0.019	
P	-0.346	-0.573	P	0.225	0.032
AA - 2-3	Fe	Mn	AA - 2-3	Fe	Mn
Mn	0.449		Mn	0.093	
P	0.829	0.567	P	0	0.027
HCl - 2-3	Fe	Mn	HCl - 2-3	Fe	Mn
Mn	0.333		Mn	0.207	
P	-0.608	-0.697	P	0.013	0.003
AA - 3-4	Fe	Mn	AA - 3-4	Fe	Mn
Mn	0.644		Mn	0.01	
P	0.604	0.559	P	0.017	0.03
HCl - 3-4	Fe	Mn	HCl - 3-4	Fe	Mn
Mn	0.444		Mn	0.097	
P	-0.521	-0.44	P	0.047	0.101
AA - 4-5	Fe	Mn	AA - 4-5	Fe	Mn
Mn	0.883		Mn	0.000	
P	0.732	0.777	P	0.002	0.001
HCl - 4-5	Fe	Mn	HCl - 4-5	Fe	Mn
Mn	0.449		Mn	0.124	
P	-0.591	-0.326	P	0.034	0.277
AA - 5-6	Fe	Mn	AA - 5-6	Fe	Mn
Mn	0.932		Mn	0.000	
P	0.889	0.895	P	0.000	0.000
HCl - 5-6	Fe	Mn	HCl - 5-6	Fe	Mn
Mn	0.595		Mn	0.069	
P	-0.506	-0.491	P	0.136	0.149
AA - 6-8	Fe	Mn	AA - 6-8	Fe	Mn
Mn	0.965		Mn	0.000	
P	0.866	0.804	P	0.001	0.003
HCl - 6-8	Fe	Mn	HCl - 6-8	Fe	Mn
Mn	0.955		Mn	0	
P	-0.543	-0.697	P	0.165	0.055
AA - 8-10	Fe	Mn	AA - 8-10	Fe	Mn
Mn	0.989		Mn	0	
P	0.894	0.876	P	0.003	0.004
HCl - 8-10	Fe	Mn	HCl - 8-10	Fe	Mn
Mn	0.927		Mn	0.001	
P	-0.51	-0.387	P	0.197	0.344

All Concentrations in $\mu\text{g/g}$ sediment					Totals			Sequential Extraction -----> ----->							
					Aqua Regia Extraction			NH ₄ Cl	NaOH	HCl			Ascorbic Acid		
sample #	cm	Location	porosity (%)	organic content (%)	Fe	Mn	P	P	P	Fe	Mn	P	Fe	Mn	P
1	0-1	MB	69%	4.3	60642	1409	2214	13.4	354	9802	186	355	4939	438	429
1	1-2	MB	72%	4.5	59436	1542	1954	14.1	424	11438	261	355	4284	216	365
1	2-3	MB	75%	1.5	60725	1078	2214	14.9	490	6880	84	239	6843	365	449
1	3-4	MB	72%	4.8	81945	1473	2564	15.2	309	10343	174	319	1416	69	137
1	4-5	MB	72%	4.6	55165	916	1745	17.3	290	9061	138	335	3704	202	281
1	5-8	MB	68%	5.1	63286	1069	1983	11.9	244	8079	108	343	3504	195	252
1	8-12	MB	67%	5.0	57503	940	1678	13.3	367	7441	100	358	3488	222	279
2	0-1	IB	64%	3.5	63438	1722	3195	19.4	365	5419	176	451	4659	403	579
2	1-2	IB	72%	2.7	48056	895	2203	17.6	451	2416	39	235	4495	319	391
2	1-2	IB	66%	3.4	47338	1070	1778	29.6	254	4528	91	202	3088	187	289
2	2-3	IB	63%	4.3	44708	764	2016	18.5	320	3503	59	286	3161	173	290
2	3-4	IB	63%	4.2	44570	749	2018	13.0	372	4000	57	289	3556	193	347
2	4-5	IB	64%	3.8	32066	509	1374	15.9	333	3297	50	278	3716	164	364
2	5-8	IB	64%	3.9	52869	809	2252	17.7	108	2485	33	276	3325	168	323
2	8-12	IB	55%	3.5	16980	260	1190	13.9	74	2906	29	333	2282	101	221
3	0-1	IB	46%	2.1	13310	304	973	13.2	175	2115	45	546	1900	149	211
3	1-2	IB	46%	2.4	29498	532	2277	6.0	127	3773	111	2413	2096	341	135
3	2-3	IB	46%	2.0	16259	287	1159	12.1	192	1994	29	544	1945	98	190
3	3-4	IB	40%	2.4	15646	289	1354	7.3	276	4803	45	235	2260	112	168
3	4-5	IB	38%	2.1	14332	277	1060	10.5	147	2060	31	462	941	53	74
3	5-8	IB	32%	1.8	14163	206	1072	4.5	164	2210	22	429	1815	57	155
3	8-12	IB	28%	1.7	19111	181	1305	3.9	128				3005	43	117
4	0-1	IB	75%	4.5	44440	73	1541	21.7	392	11245	231	395	5898	415	484
4	1-2	IB	74%	5.6	47451	56	1565	10.2	346	6305	98	248	5522	360	415

All Concentrations in $\mu\text{g/g}$ sediment					Totals			Sequential Extraction -----> ----->							
					Aqua Regia Extraction			NH ₄ Cl	NaOH	HCl			Ascorbic Acid		
sample #	cm	Location	porosity (%)	organic content (%)	Fe	Mn	P	P	P	Fe	Mn	P	Fe	Mn	P
4	2-3	IB	72%	4.8	41786	48	1242	9.4		6381	82	257	5377	291	348
4	3-4	IB	71%	11.8	42763	63	1319	4.8	252				5292	299	384
4	4-5	IB	67%	5.4	45728	58	1370	8.2	292				6361	358	412
4	5-8	IB	69%	5.1	40013	54	1120	176.8	221	37361	440	1959	5279	297	370
4	8-12	IB	67%	5.1	39228	48	1163	13.7	203	4931	57	233	3151	208	212
5	0-1	MB	70%	5.3	37627	48	1566	4.9	168	3646	138	181	4891	673	373
5	1-2	MB	71%	5.4	44218	22	1422	4.1	302	7033	81	316	1579	60	75
5	2-3	MB	65%	5.4	52861	1294	2868	8.4	294	8321	77	308	9171	395	540
5	3-4	MB	58%	4.7	32393	31	1356	7.6	181	3946	65	314	2913	286	213
5	4-5	MB	45%	3.1	27348	25	1241	2.9	159	3449	42	255	3046	200	213
5	5-8	MB	27%	2.9	18182	16	869	0.8	93	1533	22	126	2683	170	155
5	8-12	MB	23%	1.8	26091	407	1364	15.0	143	2942	32	350	2825	101	160
6	0-1	MB	71%	4.3	36676	2653	1841	20.0	569	6398	641	318	4726	1049	459
6	1-2	MB	73%	4.4	39889	69	1481	11.7		6887	354	287	5055	881	480
6	2-3	MB	71%	7.6	40299	57	1530	22.8					5008	728	493
6	3-4	MB	64%	3.9	32096	51	1214	4.9	280	4601	252	297	4313	578	442
6	4-5	MB	56%	3.1	22482	28	865	1.5	141	3291	57	289	2587	250	199
6	5-8	MB	41%	2.4	20470	30	770	7.4	161	3937	130	321	4251	310	188
7	0-1	MB	61%	2.7	16151	602	1163	5.1	84	1993	125	349	4503	213	149
7	1-2	MB	44%	1.7	16043	353	1115	1.7	43	2402	40	457	1032	92	52
7	2-3	MB	28%	1.1	18630	303	1114	1.2	49	2425	37	521	1422	79	62
7	3-4	MB	21%	0.7	37358	579	1307	0.5	97	1600	24	617	785	54	9
7	4-5	MB	25%	1.1	55455	767	1448	0.2		4507	59	427	1578	97	28
8	0-1	MB	74%	3.1	59565	1646	2436	18.3	693	8939	417	366	6350	803	641

All Concentrations in $\mu\text{g/g}$ sediment					Totals			Sequential Extraction -----> ----->							
					Aqua Regia Extraction			NH ₄ Cl	NaOH	HCl			Ascorbic Acid		
sample #	cm	Location	porosity (%)	organic content (%)	Fe	Mn	P	P	P	Fe	Mn	P	Fe	Mn	P
8	1-2	MB	77%	4.6	33627	896	1181	13.6	541	8153	261	314	6172	476	527
8	2-3	MB	76%		59232	1425	2087	16.8	751	9698	251	548	5772	507	423
8	3-4	MB	74%	3.3	63397	1148	1797	19.4	210	3900	66	233	3244	262	258
8	4-5	MB	70%	5.0	38267	655	1531	12.0	260	5316	123	321	3745	329	240
8	5-8	MB	72%	4.3				17.3	498	5109	77	384	3000	242	227
8	8-12	MB	59%	4.7				10.0	192	6645	96	416	2062	141	146
9	0-1	MB	44%	1.2	10030	223	827	15.7	54	997	18	487	973	70	96
9	1-2	MB	35%	0.0	7487	109	525	6.7	40				365	24	26
9	2-3	MB	31%	1.4	8932	148	583	4.3	107	481	10	311	207	18	16
9	3-4	MB	31%	2.0	10614	151	579	2.1	36	552	9	303	1115	35	49
9	4-5	MB	40%	2.9	19725	202	662	6.9	177	2429	31	501	605	62	48
9	5-8	MB	42%	3.6	30850	345	987	4.2	65	1903	43	379	687	102	42
10	0-1	MB	72%	4.1	67104	1623	1942	17.1	373	11926	257	347	6407	485	429
10	1-2	MB	74%	3.2	58904	1280	1594	14.9	259	6473	111	238	5338	370	320
10	2-3	MB	74%	3.2	60706	1634	2154	18.6	459	7294	137	191	6368	521	555
10	3-4	MB	73%	4.6	74125	1756	2583	13.9	509	11591	222	319	5675	378	473
10	4-5	MB	71%	4.2	70845	1607	2320	16.2	398	11945	227	333	5401	341	455
10	5-8	MB	68%	4.1	63949	1740	2040	11.5		10666	289	299	7494	567	529
10	8-12	MB	71%	4.4	65241	1356	1944	13.2	396	8268	137	297	5458	335	360
11	0-1	MB	75%	5.0	57537	3017	2857	16.3	513	6948	419	260	6434	953	719
11	2-3	MB	73%	5.2	47279	959	1701	10.4	219	5030	62	255	3708	192	208
11	3-4	MB	69%	4.7	44252	898	1616	8.1	187	4405	39	189	4874	233	245
11	4-5	MB	63%	4.4	35095	689	1397	5.4	231	3591	44	364	6756	288	504
11	5-8	MB	50%	3.2	23791	468	1372	6.1	122	1854	31	312	1292	85	97

All Concentrations in $\mu\text{g/g}$ sediment					Totals			Sequential Extraction -----> ----->							
					Aqua Regia Extraction			NH ₄ Cl	NaOH	HCl			Ascorbic Acid		
sample #	cm	Location	porosity (%)	organic content (%)	Fe	Mn	P	P	P	Fe	Mn	P	Fe	Mn	P
12	0-1	MB	74%	5.1	60254	1941	2277	9.8	374	6620	252	297	6144	586	482
12	1-2	MB	72%	5.0	8014	128	619	7.9	532				5338	345	367
12	2-3	MB	70%	5.1	50945	1038	1881	7.3	419	5014	103	273	0	0	0
12	3-4	MB	69%	4.6	58301	1167	1970	16.8	311	4180	79	237	5663	387	369
12	4-5	MB	71%	4.6	53752	1021	2046	9.1	389	5598	89	255	5703	296	510
12	5-8	MB	71%	5.0	44807	886	1550	5.7	251	6832	168	407	4184	268	299
12	8-12	MB	57%	4.6	36397	626	1377	5.8	164	2857	44	279	2472	164	151
13	0-1	MB	54%	2.8	23777	519	1237	6.8	85	4220	74	516	1587	128	105
13	1-2	MB	34%	3.4	23216	497	1244	6.9	81	3497	57	350	2824	173	128
13	2-3	MB		2.8	18388	337	1145		149	2846	30	451	1865	100	81
13	3-4	MB	34%	2.4	11414	212	841	4.2	75				1700	104	72
13	4-5	MB	34%	1.8	15439	228	784	7.1	248	3136	43	461	822	36	38
13	5-8	MB	28%	1.2	19626	247	1103	3.2	79	1564	15	374	1631	42	48
13	8-12	MB	27%	3.6	20526	231	1169	2.3	60	2822	21	289	1690	55	86
14	0-1	IB	74%	4.9	59200	1558	2196	13.9	371	5025	147	253	4868	431	420
14	1-2	IB	74%	5.5	51727	1206	2047	12.7	531	5380	141	181	7303	426	518
14	2-3	IB	74%	7.0	53303	915	1942	0.0	627	7137	124	269	1790	112	137
14	3-4	IB	73%	5.5	50255	879	1690	11.7	353	7317	120	336	5359	270	334
14	4-5	IB	71%	5.6	52045	1020	1759	8.7	476	5050	94	255	4180	246	248
14	5-8	IB	71%	5.7	46923	856	1509	9.1	538	7685	117	394	4976	276	310
14	8-12	IB	64%	4.9	42102	795	1448	12.1	339	2719	57	234	3199	274	332
15	0-1	IB	72%	3.7	46643	1106	1677	14.6	353	5012	93	256	4660	338	377
15	1-2	IB	72%	4.9	42928	769	1514	12.2	355	10903	170	435	4135	238	305
15	2-3	IB	73%	5.5	46254	732	1679	11.6	374	11578	168	440	5026	208	355

All Concentrations in $\mu\text{g/g}$ sediment					Totals			Sequential Extraction -----> ----->							
					Aqua Regia Extraction			NH ₄ Cl	NaOH	HCl			Ascorbic Acid		
sample #	cm	Location	porosity (%)	organic content (%)	Fe	Mn	P	P	P	Fe	Mn	P	Fe	Mn	P
15	3-4	IB	70%	5.7	51525	944	1799	9.9	144	7078	107	271	6118	285	370
15	4-5	IB	63%	5.1	40315	621	1399	12.9	237	7282	85	289	4471	197	302
15	5-8	IB	69%	5.8	41420	673	1352	13.2	313	10760	135	479	3842	211	259
15	8-12	IB	63%	5.3	47979	764	1891	18.0	335	12248	228	689			
16	0-1	IB	46%	3.7	15011	241	1272	6.2	211	4932	70	574	1556	88	185
16	2-3	IB	45%	4.0	20849	336	1306	8.5	148	2016	23	271	1528	82	154
16	3-4	IB	43%	4.4				5.4	185						
16	4-5	IB	39%	2.9	12709	188	987	5.9	169	1510	20	337	1320	60	126
16	5-8	IB	37%	2.9				2.8	117	1924	23	391	1656	89	111
16	8-12	IB	38%	3.4	15467	190	1112	3.9	171	2205	22	543	2021	86	159
17	0-1	SBW	65%	8.4	46766	602	4327	40.2	1124	4042	64	251	5232	193	927
17	1-2	SBW	70%	22.0				24.5	800	1179	29	85	2043	140	1492
17	2-3	SBW	73%	22.3	21314	402	4245	19.6	2292	1455	45	100	1752	144	1641
17	3-4	SBW	74%	26.5	15898	384	4432	23.9	1993	901	31	53	1400	140	1880
17	4-5	SBW	72%	16.3	13127	646	2581	69.1	909	511	15	37	1771	211	1471
17	5-8	SBW	71%	13.4	16164	737	2140	44.0	1430	879	29	54	881	99	1387
17	8-12	SBW	75%	22.9	11949	524	2711	30.1	1447	1083	57	51	1059	143	1096
19	0-1	SBW	52%	4.9	33707	438	2144	20.2	619				1667	81	389
19	1-2	SBW	54%	5.2	48278	623	3206	28.2	923	118	7	2	2054	81	571
19	2-3	SBW	48%	5.2					411	3185	54	383			
19	3-4	SBW	49%	4.6	24405	274	1525		229	2958	42	307	1504	52	346
19	4-5	SBW	42%	5.7	26742	320	1642	12.9	470	2801	40	270	2052	67	428
19	5-8	SBW	38%	6.0	20958	237	1335	10.6		2366	36	290	1847	62	327
19	8-12	SBW	28%	3.0	22190	271	1295	7.7					1561	47	274

All Concentrations in $\mu\text{g/g}$ sediment					Totals			Sequential Extraction -----> ----->							
sample #	cm	Location	porosity (%)	organic content (%)	Aqua Regia Extraction			NH ₄ Cl	NaOH	HCl			Ascorbic Acid		
					Fe	Mn	P	P	P	Fe	Mn	P	Fe	Mn	P
20	0-1	SBW	69%	4.2	42315	667	3253	41.0	572	2465	40	167	4367	193	919
20	1-2	SBW	70%	7.4				32.4	674	4351	52	260	4503	189	864
20	2-3	SBW	70%	8.6	39926	584	2797	31.7	796	5092	53	294	4493	167	842
20	3-4	SBW	71%	9.4	36206	496	2437	31.1	904	8461	122	393	3673	161	809
20	4-5	SBW	67%	6.5				32.4	972	5523	56	293	4250	163	859
20	5-8	SBW	67%	9.9				26.4	896	6116	57	416			
20	8-12	SBW	57%	8.5	28257	373	2134	24.1	592	4358	48	339	4880	171	704
21	0-1	IB	21%		5540	107	658	6.6	69	1974	46	415	825	64	70
21	1-2	IB	21%	0.4	6551	100	765	3.5		852	18	515	531	29	39
21	2-3	IB	19%	0.3	5497	85	679	3.5		654	15	394	401	20	28
21	3-4	IB	19%	0.2	7157	106	828	3.9	37	1141	24	393	406	23	34
21	4-5	IB	32%	0.3	6207	101	556	3.4		534	16	223	372	24	23
21	5-8	IB	19%	0.4	7376	111	650	4.3	42	1281	25	314	2057	125	125
21	8-12	IB	18%	0.6	6635	111	493	3.1	18	1343	28	244	658	40	80
24	0-1	IB	70%	4.9	39276	1297	1800	11.8	496	6720	232	277	5690	565	520
24	1-2	IB	71%	4.2				16.0	213	7004	150	301	5012	423	473
24	2-3	IB	67%	4.8				9.9	213	2713	41	155	3997	270	298
24	3-4	IB	64%	4.1	48100	949	1801	8.4	341	2982	46	139	4211	269	333
24	4-5	IB	63%	4.7	48167	986	1861	10.0	330	3296	68	134	4591	318	453
24	5-8	IB	59%	4.6				8.1	326	6300	79	428			
24	8-12	IB	46%	3.4	47126	662	2165	8.9	350	3741	43	429	1943	100	123
25	0-1	IB	68%	4.1	34357	808	1602	16.8	347	4704	114	310	4871	355	486
25	1-2	IB	70%	4.9	48600	806	1838	13.5	466	4501	50	240	4082	183	295
25	2-3	IB	63%	4.4	51324	829	2187	13.2		1429	22	327	5706	202	407

All Concentrations in $\mu\text{g/g}$ sediment					Totals			Sequential Extraction -----> ----->							
					Aqua Regia Extraction			NH_4Cl	NaOH	HCl			Ascorbic Acid		
sample #	cm	Location	porosity (%)	organic content (%)	Fe	Mn	P	P	P	Fe	Mn	P	Fe	Mn	P
25	3-4	IB	53%	4.7	36490	634	1540	13.4	367	4734	52	263	3721	209	275
25	4-5	IB	61%	4.3	38997	710	1642	16.8	541	4521	69	318	3522	212	315
25	5-8	IB	59%	4.8	36536	533	1460	11.9	280	4444	59	322	3746	151	221
25	8-12	IB	49%	4.1	32596	493	1406	0.0	260	4532	50	482	2630	142	219
27	0-1	OB	74%	1.0	68526	7654	3881	31.6	835	8316	920	160	12873	3605	1713
27	1-2	OB	75%	2.9	68178	3558	2576	27.5					8852	1354	861
27	2-3	OB	74%	2.3	65365	2524	2147	21.5	247	5442	118	143	7703	821	500
27	3-4	OB	73%	4.3	64492	3033	2055	3.9	431	10783	251	232	9612	1089	443
27	4-5	OB	71%	4.3	64461	2156	2367	18.5	512	8677	129	224	6858	594	539
27	5-8	OB	72%	5.0	59259	2250	2165	13.4	810	9779	221	280	6900	761	620
27	8-12	OB	60%	3.3	49298	1455	1593	9.1		8518	174	291	4520	444	344

All Concentrations in $\mu\text{g/g}$ sediment					Totals		
					Aqua Regia Extraction		
sample #	cm interval	Location	porosity (%)	organic content (%)	Fe	Mn	P
28	3-4	SBW	53%	7.3	44177	2142	2181
28	4-5	SBW	59%	8.9	36074	1766	1748
28	5-8	SBW	48%	6.7	38588	1909	1840
28	8-12	SBW	59%	9.9	37806	1788	1516
29	0-1	SBW	44%	3.3	10681	489	667
29	1-2	SBW	35%	3.2	15661	696	929
29	2-3	SBW	29%	2.5	14062	173	988
30	0-1	SBW	37%	4.8	32963	586	3018
30	2-3	SBW	31%	4.5	28181	347	2139
30	3-4	SBW	24%	4.5	33198	1653	2248
30	4-5	SBW	27%	3.9	38374	1859	2535
30	5-8	SBW	30%	3.0	29160	1391	1651
30	8-12	SBW	28%	3.4	13946	236	823
31	0-1	SBW	55%	4.5	28263	363	2090
31	1-2	SBW	38%	4.7	26450	392	2009
31	2-3	SBW	39%	5.6	26416	364	1967
31	3-4	SBW	42%	5.6	32174	439	2500
31	5-8	SBW	36%	4.5	30248	396	2379
31	8-12	SBW	26%	3.1	15556	179	1126
32	0-1	SBW	60%	10.8	36605	452	2736
32	1-2	SBW	68%	12.3	43400	444	2551
32	2-3	SBW	68%	13.1	35940	381	2534
32	3-4	SBW	68%	12.2	52515	2438	3057
32	4-5	SBW	63%	12.8	11926	130	951
32	5-8	SBW	66%	12.7	43950	473	2652

All Concentrations in $\mu\text{g/g}$ sediment					Totals		
					Aqua Regia Extraction		
sample #	cm interval	Location	porosity (%)	organic content (%)	Fe	Mn	P
33	1-2	SBW	43%	4.8	29355	336	1945
33	2-3	SBW	47%	5.1	39220	1914	2486
33	3-4	SBW	47%	4.8	30360	334	2192
33	4-5	SBW	43%	5.2	28551	343	2122
33	5-8	SBW	34%	5.2	37021	461	2677
33	8-12	SBW	41%	5.5	33429	435	2392
34	0-1	SBW	59%	6.4	37657	461	2520
34	1-2	SBW	59%	5.2	49518	2430	2972
34	2-3	SBW	60%	6.2	44115	2172	2838
34	3-4	SBW	58%	5.3	42451	2029	2789
34	4-5	SBW	57%	5.5	44944	2197	2856
34	5-8	SBW	48%	5.0	35261	418	2517
34	8-12	SBW	51%	6.5	36096	447	2475
35	0-1	IB	68%	4.9	41294	2011	1663
35	1-2	IB	65%	5.0	40414	1989	1438
35	2-3	IB	62%	4.4	35355	1739	1306
35	3-4	IB	62%	4.3	36643	1771	1416
35	4-5	IB	58%	3.5	41408	1993	1627
35	5-8	IB	57%	4.9	36510	1705	1352
35	8-12	IB	56%	4.4	32672	1623	1239
36	0-1	IB	43%	1.8	13638	620	970
36	1-2	IB	42%	1.8	12555	583	943
36	2-3	IB	35%	1.5	11702	546	944
36	3-4	IB	30%	1.4	11180	533	839
36	4-5	IB	31%	0.9	9340	417	759

All Concentrations in $\mu\text{g/g}$ sediment					Totals		
					Aqua Regia Extraction		
sample #	cm interval	Location	porosity (%)	organic content (%)	Fe	Mn	P
36	5-8	IB	25%	1.0	10282	467	962
36	8-12	IB	22%	0.6	9547	401	504
37	0-1	IB	70%	4.4	48953	2417	2016
37	1-2	IB	63%	4.2	36505	654	1408
37	2-3	IB	65%	5.2	26262	442	1119
37	3-4	IB	60%	5.4	44431	537	1218
37	4-5	IB	60%	5.1	34652	557	1286
37	5-8	IB	54%	4.9	29518	422	1081
37	8-12	IB	44%	3.5	29550	1432	1239
38	0-1	IB	69%	4.6	48218	2445	1874
38	1-2	IB	63%	5.1	44847	2125	1540
38	2-3	IB	69%	5.2	45846	2216	1470
38	3-4	IB	69%	6.3	42852	2102	1443
38	4-5	IB	61%	5.8	48651	2394	1763
38	5-8	IB	62%	4.6	35176	514	1123
38	8-12	IB	48%	4.0	28329	1382	1176
39	1-2	IB	69%	100.0	40311	758	1464
39	2-3	IB	68%	5.3	49939	939	1794
39	5-8	IB	63%	5.0	42783	677	1398
40	0-1	IB	62%	35.2	28613	1438	1380
40	1-2	IB	53%	4.1	21764	670	997
40	2-3	IB		3.1	19639	937	905
40	3-4	IB	37%	2.3	13433	663	746
40	4-5	IB	27%	1.5	10038	436	776
40	5-8	IB	15%	1.1	11317	467	783

All Concentrations in $\mu\text{g/g}$ sediment					Totals		
					Aqua Regia Extraction		
sample #	cm interval	Location	porosity (%)	organic content (%)	Fe	Mn	P
40	8-12	IB	22%	1.5	15641	709	818
41	0-1	MB	69%	5.0	32822	794	1319
41	1-2	MB	68%	5.2	47583	901	1575
41	2-3	MB	69%	6.0	37396	638	1451
41	3-4	MB	67%	5.8	32591	482	1111
41	4-5	MB	68%	6.4	35331	513	1150
41	5-8	MB	67%	6.1	17235	232	550
41	8-12	MB	64%	5.2	39454	1936	1110
42	0-1	MB	72%	4.6	47753	1906	1734
42	1-2	MB	70%	4.8	42503	1262	1452
42	2-3	MB	73%	6.0	57547	1356	1849
42	3-4	MB	67%	5.4	45622	1325	1440
42	4-5	MB	67%	4.6	60358	2939	1810
42	5-8	MB	67%	5.7	43928	1307	1527
42	8-12	MB	57%	5.2	47808	724	1567
43	0-1	MB	74%	5.7	41378	1150	1478
43	1-2	MB	71%	5.3	38916	790	1105
43	2-3	MB	70%	5.9	34749	859	1239
43	3-4	MB	67%	5.7	38804	823	1302
43	4-5	MB	67%	5.5	27075	591	843
43	5-8	MB	44%	3.4	27874	387	949
43	8-12	MB	35%	3.0	29108	396	925
44	0-1	OB	75%	3.7	54837	2833	2617
44	1-2	OB	74%	4.1	55051	3595	2317
44	2-3	OB	76%	5.8	57113	3040	1848

All Concentrations in $\mu\text{g/g}$ sediment					Totals		
					Aqua Regia Extraction		
sample #	cm interval	Location	porosity (%)	organic content (%)	Fe	Mn	P
44	3-4	OB	73%	5.2	50720	2593	1498
44	4-5	OB	76%	6.6	49531	2447	1533
44	5-8	OB	66%	4.4	43547	1630	2176
44	8-12	OB	44%	3.9	47753	2316	1900
45	0-1	OB	74%	4.8	47616	1445	1680
45	1-2	OB	70%	5.9	49159	1747	2199
45	2-3	OB	68%	6.2	51368	1951	2144
45	3-4	OB	57%	4.3	47024	1671	1745
45	4-5	OB	39%	4.8	44382	1093	2347
45	5-8	OB	21%	3.8	37366	666	1325
45	8-12	OB	46%	3.5	35096	628	1101

Appendix C - Historical Comparison

Core Number Depth		Total Phosphorus ($\mu\text{g/g}$)			Total Iron ($\mu\text{g/g}$)			D P -	D P -	D Fe -	D Fe -
		1982	1992	2004	1982	1992	2004	1982	1992	1982	1992
1	1	1984	1090	2214	34520	35856	60642	230	1124	26122	24786
1	2	1864	1077	1954	30235	35986	59436	90	877	29201	23450
1	4	1625	1115	2564	30164	35961	81945	939	1449	51781	45984
1	8	1168	1183	1678	28259	35081	57503	510	495	29244	22422
2	1	1407	944	3195	27296	28051	63438	1788	2251	36142	35387
2	2	1338	877	2203	23745	25326	48056	865	1326	24311	22730
2	4	1299	914	2018	23407	25922	44570	719	1104	21163	18648
2	8	1194	801	1190	25736	25770	16980	-4	389	-8756	-8790
3	1	1171	995	973	16883	12376	13310	-198	-22	-3573	934
3	2	1141	948	2277	13605	11674	29498	1136	1329	15893	17824
3	4	1176	868	1354	14586	9794	15656	178	486	1070	5862
3	8	1063	669	1305	10998	9612	19111	242	636	8113	9499
4	1	1086	158	1541	30382	33430	44440	455	1383	14058	11010
4	2	972	1002	1565	27480	35140	47451	593	563	19971	12311
4	4	931	1087	1319	26187	33968	41786	388	232	15599	7818
4	8	859	954	1163	24109	30542	39228	304	209	15119	8686
5	1	779	495	1566	13217	8632	37627	787	1071	24410	28995
5	2	460	397	1422	9158	6883	44218	962	1025	35060	37335
5	4	276	382	1356	6484	4626	32393	1080	974	25909	27767
5	8	276	955	1364				1088	409		
7	1	766	955	1163	9270	14928	16151	397	208	6881	1223
7	2	581	798	1115	9068	11347	16043	534	317	6975	4696
7	4	671	784	1307	9170	39457	37358	636	523	28188	-2099
7	8	683	824	1448	33353	44328	55454	765	624	22101	11126
8	1	1707	1518		29933	30702					
8	2	1292	1115	2436	26923	27349	59565	1144	1321	32642	32216
8	4	1082	915	2087	26118	26988	59232	1005	1172	33114	32244
8	8	988	881	1531	20970	20886	38267	543	650	17297	17381
9	1	1418	619	827	14526	6710	10030	-591	208	-4496	3320
9	2	930	606	525	20010	6139	7487	-405	-81	-12523	1348
9	4	862	542	579	25314	6663	10614	-283	37	-14700	3951
9	8	846	571	987	12807	17528	30580	141	416	17773	13052
10	1	1828	1283	1942			67104	114	659		
10	2	1716	1321	1594	35961	37671	58904	-122	273	22943	21233
10	4	1541	1316	2583	28489	37301	70845	1042	1267	42356	33544
10	8	1337	958	1944	33198	34518	65241	607	986	32043	30723
11	1	1726	588	2857	21306	13053	57537	1131	2269	36231	44484
11	2	1615	603	1701	24062	14629	47279	86	1098	23217	32650
11	4	1346	566	1616	35278	15029	44252	270	1050	8974	29223
11	8	1039	479	1372	58459	14287	23721	333	893	-34738	9434

Core Number	Depth	Total Phosphorus ($\mu\text{g/g}$)			Total Iron ($\mu\text{g/g}$)			D P -	D P -	DFe -	DFe -
		1982	1992	2004	1982	1992	2004	1982	1992	1982	1992
12	1	1660	1176	2277	33689	34845	60254	617	1101	26565	25409
12	2	1373	1174	619	33224	44264	8014	-754	-555	-25210	-36250
12	4	1287	1057	1970	33051	31969	58301	683	913	25250	26332
12	8	1325	877	1377	30812	27214	36397	52	500	5585	9183
13	1	1061	702	1237	1663	14223	23216	176	535	21553	8993
13	2	1051	624	1244	23439	16516	18388	193	620	-5051	1872
13	4	1028	595	841	23355	18117	11414	-187	246	-11941	-6703
15	1	1465	1132	1677				212	545		
15	2	1381	1229	1514				133	285		
15	4	1305	1255	1799				494	544		
15	8	1281	1156	1891				610	735		
16	1	1185	1210	1272				87	62		
16	2	1081	1187	1306				225	119		
16	4	1109	790	987				-122	197		
16	8	1057	696	1112				55	416		
17	1	2370	2136	4327	23742	30578	46766	1957	2191	23024	16188
17	2	2288	2108	4245	23885	28241	21314	1957	2137	-2571	-6927
17	4	2344	2067	4432				2088	2365		
17	8	2195	1941	2711				516	770		
19	1	3255	1838	2144	24481	24040	33707	-1111	306	9226	9667
19	2	2982	1809	3206	23775	22391	48278	224	1397	24503	25887
19	4	2898	1826	1525	24353	22392	24405	-1373	-301	52	2013
19	8	2752	1834	1295	22794	22986	22190	-1457	-539	-604	-796
20	1	2565	1914	3253	24591	30204	42318	688	1339	17727	12114
20	2	2444	1894	2797	16657	29889	39926	353	903	23269	10037
20	4	2248	1757	2437	23981	27339		189	680		
20	8	1378	1337	2134	19053	18947	28257	756	797	9204	9310
24	1	1658	1040	1800	29264	29798	39276	142	760	10012	9478
24	2	1349	1070		28360	28478	48100			19740	19622
24	4	1185	1064	1801	26235	26939	48167	616	737	21932	21228
24	8	1013	977	1363	22185	23774	37823	350	386	15638	14049
25	1	1238	1083	1602	20985	26181	34357	364	519	13372	8176
25	2	1265	1058	1838	22384	24679	48600	573	780	26216	23921
25	4	1160	1116	1540	20110	23340	36490	380	424	16380	13150
25	8	957	1238	1406	13677	24255	32596	449	168	18919	8341
27	1	3234	2080	3881	48893	42759	68526	647	1801	19633	25767
27	2	2248	1587	2576	38174	37685	68178	328	989	30004	30493
27	4	1507	1146	2055	34329	34553	64492	548	909	30163	29939
27	8	1427	1023	1593	33160	34287	49298	166	570	16138	15011
AVERAGES		1433	1099	1832	24073	24515	39911	399	733	15838	15396

Appendix D

Raw data files are available on an excel spreadsheet.

Note that all ICP analyses presented are the result of triplicate analyses, analytical errors presented are from deviations in analysis.