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A PALEOLIMNOLOGICAL ASSESSMENT OF THREE OLIGOTROPHIC WATERSHEDS IN MAINE

By

Tiffany Ann Wilson

B.A. University of Maine, 1995

A THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

(in Ecology and Environmental Science)

The Graduate School

The University of Maine

May, 2008

Advisory Committee:

Dr. Stephen A. Norton, Professor of Earth Sciences, Advisor

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A PALEOLIMNOLOGICAL ASSESSMENT OF THREE OLIGOTROPHIC WATERSHEDS IN MAINE

By Tiffany A. Wilson

Thesis Advisor: Dr. Stephen A. Norton

An Abstract of the Thesis Presented
In Partial Fulfillment of the Requirements for the
Degree of Master of Science
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Phosphorus (P) is a limiting nutrient in aquatic ecosystems. Its bioavailability determines the trophic status of lakes. The biogeochemistry of P in surface waters can be controlled by a combination of abiotic and biotic factors. Dissolved inorganic aluminum (Al) and iron (Fe) hydrolyze in streams and lakes to produce $Al(OH)_3$ and $Fe(OH)_3$ in the water column. These hydroxides may also form through photo-oxidation of complexes with DOC, liberation of inorganic metal species, and precipitation, followed by sedimentation. These solid phases readily adsorb P from the water column, reducing the amount that is available for biological nutrition (Kopáček et al. 2000; Huser & Rydin 2005). Microorganisms play a role in the aquatic P cycle through facultative uptake and release of P, which is governed by seasonal oxygen stress (Gächter et al. 1988). Some combination of abiotic (mainly Al and Fe) and biotic (DOC complexation and microbial) factors ultimately controls the transport to, mobility within, and fate of P in a lake. Oligotrophic surface waters are characterized by low primary productivity, mainly due to

low concentrations of bioavailable P, a consequence of insignificant internal loading of P from sediment.

Lake sediment cores provide a geochemical record of concentrations of Al and Fe hydroxides and associated P that have been deposited over time, and thus an assessment of the stability of the processes controlling P. I dissolved sediments from cores from Little Long Pond, Upper Hadlock Pond, and Mud Pond, Maine using a chemical extraction (Psenner et al. 1988) that sequentially separates the reducible (mainly Fe(III)) and base-soluble (mainly Al) metal hydroxides and associated P. Using ^{210}Pb activity to determine dates of sediment downcore, I constructed a historical profile of the Al-Fe-P geochemistry for each lake. Cores show that P is mainly associated with $Al(OH)_3$ throughout the entire period of record, exceeding the last 300 years. There was very little P associated with reducible Fe, indicating low potential for P release during seasonal anoxic conditions. High extractable Al concentrations relative to Fe and P are the result of chronically acidic conditions and/or high preferential export of Al from soils in these catchments. Evidence of anthropogenic impacts includes increased rates of sedimentation likely due to land disturbances (mainly logging) and erosion within the catchments. Strong correlation of Al and P, and diatom species abundance data, throughout the cores indicate that all three ponds have maintained a stable acidic, oligotrophic status over the last several centuries.

Mineralization of sediment organic P was modeled by fitting organic-P and Al-P downcore concentrations to reversible or irreversible first-order transformation models. The calculated $t_{½}$ of organic P for the three lakes ranges from 24 to 546 years, generally

10 to 100s of times longer than $t_{1/2}$ of high-P (eutrophic) lakes (Reitzel et al. 2007; Ahlgren et al. 2005; Penn et al. 1995; and others).

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My gratitude is limitless for the help, support, advice and encouragement of my advisory committee. Dr. Norton's enthusiasm for ecosystem-level geochemistry truly convinced me to pursue this degree with the care and thoroughness that he exemplifies. I thank Dr. Amirbahman for helping me analyze my data and explaining environmental chemistry processes the way an engineer does. I thank Dr. Fernandez for advice with procedures and useful data interpretation from the eyes of a "soils guy." Indeed, I acknowledge the entire dynamic "Al-P Group" for being the brains and workforce behind a great collaborative project of which this thesis is a small part.

The National Science Foundation Grant # DEB-0415348 funded the collection and analysis of samples for this project as well as my participation in the 2006 BIOGEOMON conference in Santa Cruz, CA. The US National Park Service allowed us permission to take sediment samples from Upper Hadlock Pond in Acadia National Park. Dave Manski and Bill Gawley of the NPS provided helpful information about the site and pertinent water chemistry data.

I am grateful to the staff and students at the Sawyer Environmental Chemistry Research Laboratory for allowing me time and equipment for processing my samples. I'm especially indebted to John Cangelosi for invaluable expertise in operating the piston corer, and his willingness to carry more than a fair share of the field gear. I also thank Heather Goss, Mollie Laird, and Dr. Norton for field assistance in crisp but sunny weather. Throughout my research, I have encountered several folks who consistently spark academically productive discussions, namely Ed Lindsey, Bjorn Lake, Sharon

Sneed, Mike Handley, and Mike SanClements. Jiri Kopáček has been an important resource to my work with his vast knowledge of and literature pertaining to geochemistry of acidified catchments.

The University of Maine has many great scientific resources and I particularly acknowledge Dennis Anderson who prepared and counted the diatoms in my sediment samples and helped me to interpret the species abundance data. I thank Dr. Charles Hess and Vincent Guisseppe in the Department of Physics and Astronomy for analyzing ^{210}Pb and clarifying the processes involved in accurate dating of sediment.

Finally, I thank my family and friends for a lifetime of pure encouragement and support.

TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

SEDIMENT GEOCHEMISTRY OF AL, FE, AND P FOR TWO HISTORICALLY ACIDIC, OLIGOTROPHIC MAINE LAKES

Abstract

Phosphorus (P) may be liberated from lake sediments by reductive dissolution of $Fe(OH)_{3(S)}$ during periods of hypolimnetic anoxia. P, however, remains adsorbed to $Al(OH)_{3(S)}$ regardless of redox conditions. During chronic or episodic acidification of a catchment, ionic Al is mobilized from soils to receiving waters. A fraction of the mobilized Al may precipitate as a consequence of higher pH of the receiving waters. We hypothesized that phosphorus retention in lake sediments is directly related to the magnitude of Al loading in response to low pH in the watershed. We studied cores representing over 200 years of sediment accumulation in historically acidic Mud Pond and Little Long Pond in eastern Maine, USA. Sequential chemical extractions of sediment were used to assess the history of Al, Fe, and P interactions. Mud Pond is a first-order pond with a pH of ~4.7, having acidified slightly in response to anthropogenic acidification from ~1930. The inlet stream to Mud Pond has dissolved Al concentrations often exceeding 500 μg/L, of which more than half is organically-bound. Mud Pond drains into Little Long Pond, a second-order pond with a historical pH of <6, and which has shown little pH or alkalinity response to increases or decreases in atmospheric SO_4^{2-} input.

Sequential extractions show that Al and P are predominantly in the 0.1 M NaOH-extractable fraction in the sediments from both ponds throughout the cores. The concentration of the likely biogenic and non-reactive P within the NaOH fraction increases up core from <30% to ~60%. Extractable Fe (<20% of extractable Al) is mainly in the 0.1 M NaOH-extractable fraction, except for the top few cm, which are predominantly in the bicarbonate-dithionite reducible fraction. Accumulation rates of sediment, Al, Fe, and P in both ponds have increased in the last 50-60 yr, but fractions remain in the same proportion. Throughout both sediment cores the molar ratio of specific Al:P fractions greatly exceeds 25, and molar ratio of specific Al:Fe fractions greatly exceeds 3, the thresholds proposed by Kopáček et al. (2005) for P release during anoxia. The data illustrate a continuous association of P with Al in both ponds during the last two centuries, likely due to the persistent natural acidity of the catchments.

Introduction

Chronic and episodic acidification greatly impacts the chemistry of freshwater catchments and may have an effect on nutrient cycling in lakes (Steinberg and Wright 1994). Phosphorus (P) concentrations and bioavailability are well-studied for surface waters because P is typically the limiting nutrient for primary productivity, and therefore, controls the trophic status of a lake (Schindler 1977). P is transported to lakes by catchment drainage, generally associated with solid phases of iron (Fe), aluminum (Al), calcium (Ca), and humic substances (Ulrich and Pöthig 2000a). Lakes that develop hypolimnetic anoxia during summer stratification may experience P release from bottom sediments due to reductive dissolution of Fe(III) and associated P (Amirbahman et al.

2003), and/or possible release of stored polyphosphate from bacteria under anaerobic conditions (Hupfer and Gächter 1995). Lakes with elevated inputs of Al due to acidification are likely to precipitate Al as $Al(OH)_3$, because alkalinity production in the lake and/or mixing of waters results in an increase in pH and a decrease in the solubility of $Al(OH)_3$, which may result in the removal of P from the water column (Kopáček et al. 2000). Precipitated Al may also originate from photo-oxidation of dissolved organically-bound Al (Kopáček et al. 2006). Precipitation of Al and associated P is pH-dependent but not redox-dependent. Therefore, Al immobilizes P even during anoxia, whereas Fe does not (Ulrich and Pöthig 2000b).

There are limited data that describe the effect of acid deposition on P concentrations in surface waters. Ogburn and Brezonik (1986) explained the oligotrophication hypothesis (low P in the water column of acidic lakes) as being due to an optimum P sorption by sediment at pH 4.0-5.5. Huser and Rydin (2005) describe an example of acido-oligotrophication resulting from increased P immobilization by complexation and precipitation of Al-P in the sediment of Lake Gårdsjön, Sweden, from sediment dated 1950 to 2001, where the increased P immobilization corresponded to a decrease in lake pH and increase in Al input. Ulrich and Pöthig (2000a) similarly found that sediment P in reservoirs with acidified catchments was mainly associated with Al. Kopáček et al. (2005) developed an empirical relationship from 43 lake sediment studies, which sets a threshold for release of sediment P based on ratios of operationally-defined molar fractions of Al, Fe, and P. The fractions are characterized by their solubility during a sequential chemical extraction procedure based on that of Psenner et al. (1988), shown in Figure 1.1. The ratios, [NaOH25-Al]:[BD-Fe] >3 or [NaOH25-Al]:[NH_4Cl-P+BD-P]

>25, define the thresholds above which P is unlikely to be released from sediment during hypolimnetic anoxia (Kopáček et al. 2005). Recently, Lake et al. (2007) demonstrated the validity of the proposed model by Kopáček et al. (2005) in the field.

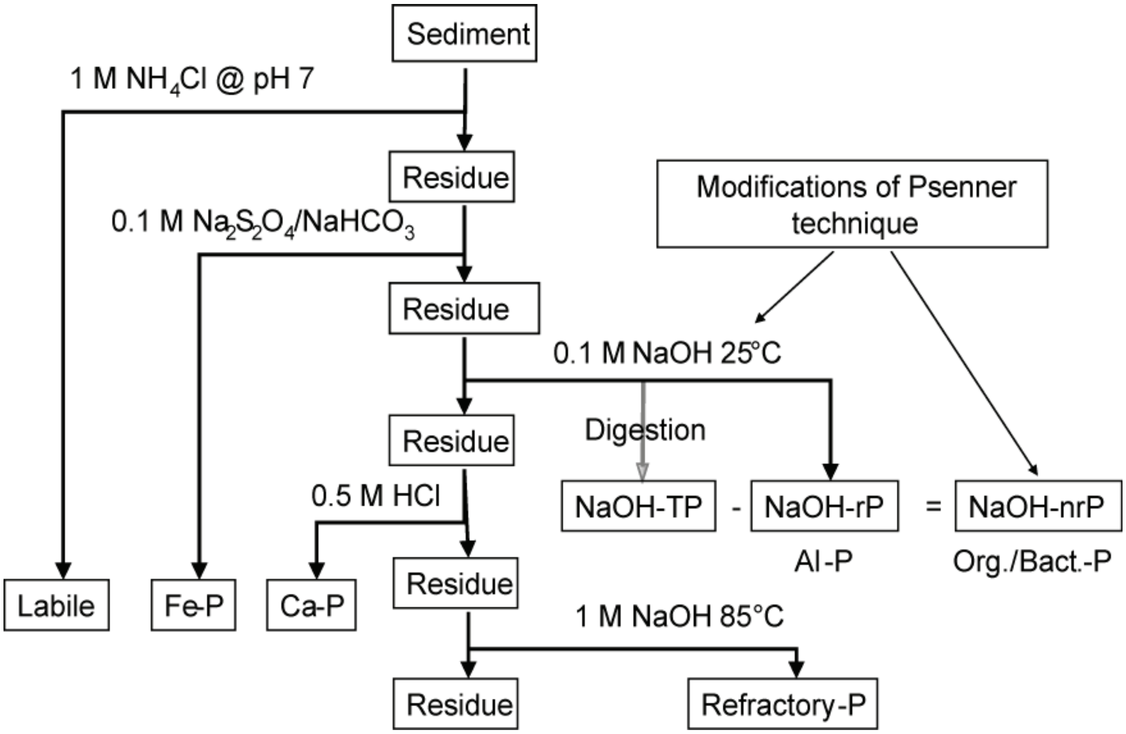

Figure 1.1 Sequential extraction method for lake sediment based on Psenner et al. (1988) and Hieltjes and Lijklema (1980)

Materials and Methods

Site Description

Sediment cores were collected in March 2005 from Mud Pond (MP) and downstream Little Long Pond (LLP), in eastern Maine, USA (Figure 1.2). MP (N44.634°, W68.088°, elevation 102 m) is a 1.6 ha, first-order pond with a total catchment drainage area of 0.65 km^2. LLP (N44.638°, W68.080°, elevation 72 m) is a

24.3 ha, second-order pond with a total catchment drainage area of 2.36 km^2, including drainage from MP. Both catchments are currently forested (spruce, fir, and red oak) and undeveloped, though there are records of logging and forest fire prior to 1905 (Davis et al., 1994). MP is 16.2 m deep and has a residence time of ca. 1 month. LLP is 25.3 m. deep and has a residence time of ca. 1 year (Maine DEP 2006). Water residence time is pond volume divided by the average annual rainfall on the catchment, including the lake surface. Both ponds develop anoxic hypolimnia during summer and winter density stratification, and are typically ice-covered from December to April. Both catchments contain steep slopes with coarse, shallow, organic-rich soils overlying thin granitic till and some exposed granitic bedrock. Thus surface waters are poorly buffered and acid-sensitive.

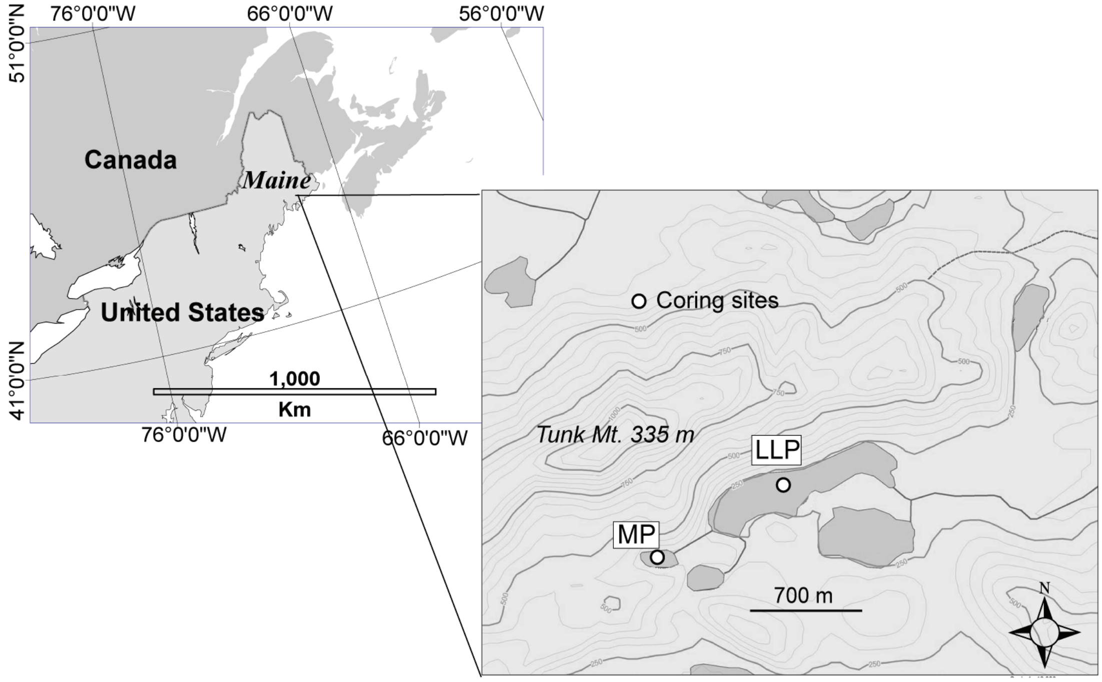

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Figure 1.2 Little Long Pond and Mud Pond site locations.

Chemistry for MP and LLP and the analytical methods are in Table 1.1. Only intermittent data exist on the chemistry and hydrology of the inlets and outlets. MP is an oligo-mesotrophic, naturally acidic, and fishless lake, with a pH <5. The low pH is caused primarily by organic acids (up to 8 mg/L dissolved organic carbon, DOC) from catchment drainage, and secondarily by excess SO_4^{2-} from atmospheric deposition (Davis et al. 1994). Al is mobilized by low pH catchment inputs, largely complexed with organic acids, and reaches concentrations up to 500 μg/L in the water column of MP. Total P (TP) is typically <10 μg/L in the summer epilimnion and up to 18 μg/L in the hypolimnion. During late summer anoxia, substantial Fe and SO_4^{2-} reduction generates alkalinity in the hypolimnion, though the effect on pH is minimal perhaps due to buffering by the dissolved organic matter. LLP is oligotrophic and naturally acidic with a pH ~6, and has lower DOC than MP. LLP has shown little to no pH response to anthropogenic atmospheric input. Al concentrations in the water column are historically <100 μg/L in both the epilimnion and hypolimnion, though the major inlet concentration is in the hundreds of μg/L; TP is <5 μg/L in the epilimnion and inlets, and up to 12 μg/L in the hypolimnion of LLP. Hypolimnetic anoxia in LLP results in little Fe or SO_4^{2-} reduction, and no significant alkalinity or pH change.

Table 1.1 Ranges of annual mean values (1983-2005) for selected water chemistry parameters of Little Long (LLP) and Mud (MP) ponds. Methods included gran titration for ANC (acid neutralizing capacity); ion chromatography for SO_4^{2-}; DOC (dissolved organic carbon) by IR; Al and Fe (total dissolved) by ICP-AES or graphite furnace atomic absorption (pre-1999); P (total) by persulfate digestion/molybdate-blue colorimetry. Fe values were only measured in 2005 (Maine DEP 2006).

	LLP (epilimnion)	**LLP (hypolimnion)**	**MP (epilimnion)**	**MP (hypolimnion)**
pH	5.47 - 6.04	5.19 - 5.61	4.61 - 4.87	4.61 - 5.08
ANC, µeq/L	1.1 - 16.9	7.9 - 20.3	(-27.2) - (-8.2)	(-29.8) - 20.3
SO_4^{2-}, µeq/L	59 - 80	62 - 79	72 - 105	56 - 110
DOC, mg/L	0.8 - 2.4	0.8 - 3.1	2.9 - 5.8	3.4 - 6.3
Al, µg/L	10 - 71	46 - 84	235 - 433	310 - 439
P, µg/L	1 - 4	5 - 12	4 - 8	7 - 17
Fe, µg/L	4	29	33	514

Sediment Collection and Processing

Sediment was obtained at points 13 m deep in MP and 24 m deep in LLP during ice-cover (March 2005), using a 10 cm diameter, stationary piston corer with an acrylic core tube (Davis and Doyle 1967). Cores were taken near but not at the deepest points of the ponds in order to avoid sampling previously disturbed sites, e.g., those of Davis et al. (1994). Sediment cores were sectioned at the lakes using stainless steel and plastic ware. Sediment was sectioned in the field in 0.5 cm intervals from 0 to 10 cm, in 1 cm intervals from 10 to 30 cm, and in 2 cm intervals from 30+ cm. Samples were placed directly into Whirlpack™ bags and stored at 4°C in the dark.

At the laboratory, 0.5 g wet sediment aliquots were taken from several intervals for diatom analysis, and 10 to 20 g aliquots were dried at 100°C in ceramic crucibles for percent water determination. The remaining sediment was frozen at -20°C until processed for further analysis. Dried sediment aliquots were homogenized with ceramic mortar and pestle and percent loss on ignition (%LOI) was determined by heating ~0.5 g of dried sediment at 550°C for 4 hr. Dry sediment was dated by analyzing the gamma activity of ^{210}Pb. The constant rate of supply (CRS) model of Appleby and Oldfield (1978) was used to calculate the age of the midpoints (Figure 1.3) of the sediment increments based on determination of supported and unsupported ^{210}Pb activities.

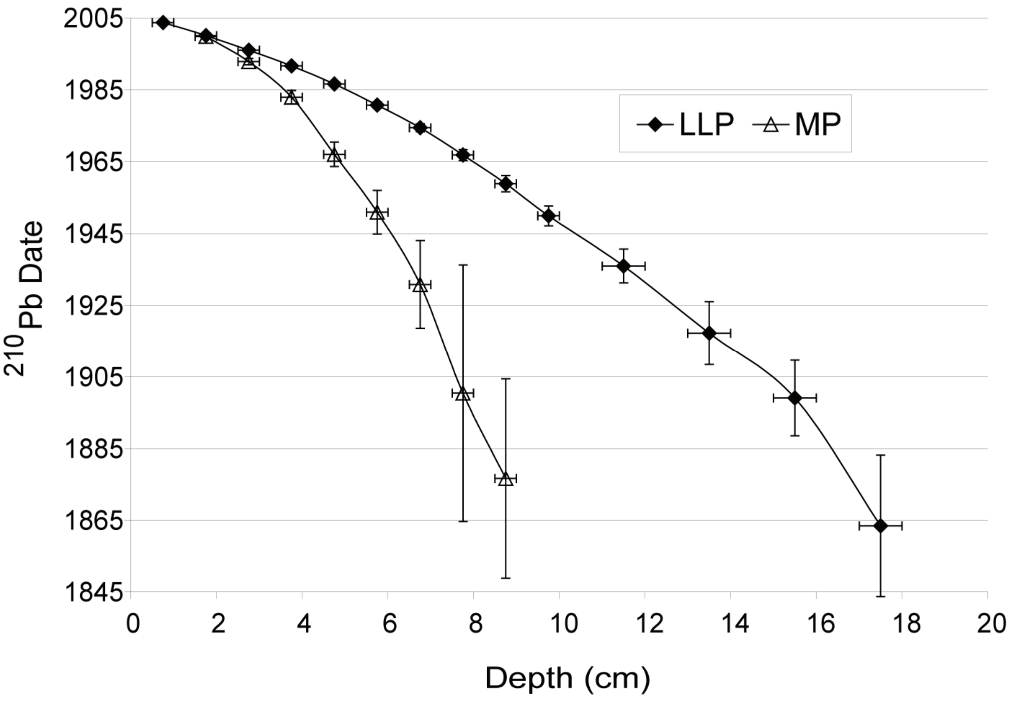

Figure 1.3 ^{210}Pb dating profiles for Little Long (LLP) and Mud (MP) Ponds, Maine. Vertical bars are ^{210}Pb counting errors. Horizontal bars represent the thickness of the sediment increment.

Sediment chemistry

Sequential extraction (Figure 1.1) was performed on 1 to 2 g of wet sediment to determine operationally-defined fractions of Al, Fe, and P: A) 1M NH_4Cl, pH 7, at 25°C for 1 hr to obtain the exchangeable fraction, B) 0.11M bicarbonate-dithionite (BD) at 40°C for 30 min to release the reducible portion that is primarily Fe and Mn (oxyhydr)oxides and associated P, C) 0.1M NaOH at 25°C for 16 hr to dissolve Al and Fe(III) hydroxides and oxyhydroxides and associated P, as well as organic-P, D) 0.5M HCl at 25°C for 16 hr to dissolve acid-soluble minerals, and E) 1M NaOH at 85°C for $\geq$24 hr to solubilize residual material. The procedure by Psenner et al. (1988) has been utilized in several similar studies (e.g. Huser and Rydin 2005; Coolidge 2004; Kopáček et al. 2000) using 1 M NaOH. We found that 0.1 M NaOH, based on comparable procedures of Hieltjes and Lijklema (1980), Ahlgren et al. (2005), and others, has a sufficiently high pH to accomplish the third fractionation step. Total extractable concentrations are the sum of concentrations from the five sequential extractions.

Extractions were performed on 21 sediment core increments from LLP and 22 from MP, with higher frequency in the top 10 cm of the core. Batches of 16 samples were extracted together and each batch contained a duplicate sample and a reagent blank. For each step, the extraction solution was added to the wet sediment in a 50 mL plastic centrifuge tube, capped and shaken in a water bath at the desired temperature and for the appropriate duration, and centrifuged at ~3000 rpm for 15 min. The supernatant was collected into a polypropylene bottle. The same sediment was then rinsed with extraction solution, centrifuged, decanted and mixed with the supernatant collected previously.

Concentrations of Al and Fe in the extracts were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES; Perkin-Elmer model 3300XL).

Total P (TP) was analyzed by ICP-AES (for the BD, NaOH25, HCl, and NaOH85 solutions) and by the molybdate-blue spectrophotometric method (Murphy and Riley 1962) (for the NH_4Cl extraction). The NaOH25 fraction was also analyzed using the molybdate-blue method for reactive P (NaOH25-rP), which is the P in solution as orthophosphate and is assumed to be mainly associated with sediment Al. The difference between NaOH25-TP and NaOH25-rP is NaOH25-nrP (non-reactive P) (Psenner et al. 1988). NaOH25-nrP is likely the organic-P and bacteria-incorporated P fraction (Ahlgren et al. 2005).

Results

Using ^{210}Pb dating (Figure 1.3) we calculated sediment mass accumulation rates in LLP and MP during the last ~100 yr. Lack of precision of ^{210}Pb dates in older sediment requires us to assume a constant (baseline) accumulation rate prior to this time period, based on the lower part of the dated record. Accumulation rate is higher in LLP than in MP as described previously by Norton et al. (1992) that integrated unsupported ^{210}Pb and stable anthropogenic Pb in MP are both about 0.1 of that of LLP, suggesting substantial bypassing of sediment in MP. Both ponds exhibit increasing sedimentation rates since the1950s (Figure 1.4). Total extractable Al, Fe, and P also increase in accumulation rate over this time period, but when normalized for mass accumulation rate, the resulting flux of these elements shows a much less pronounced increase, if any (Figure 1.5). LOI is higher in MP than in LLP, with an average of 52% and 41% in the two lakes, respectively. LOI quantifies the loss of organic matter and water from dehydration of Fe and Al hydroxides in the sediment. LOI is relatively constant throughout both cores, excluding a few deeper intervals (24-26 cm) of MP, where the LOI is distinctly lower.

The ^{210}Pb dates of these intervals were extrapolated to be earlier than 1600. Those same intervals also have lower water content than surrounding intervals.

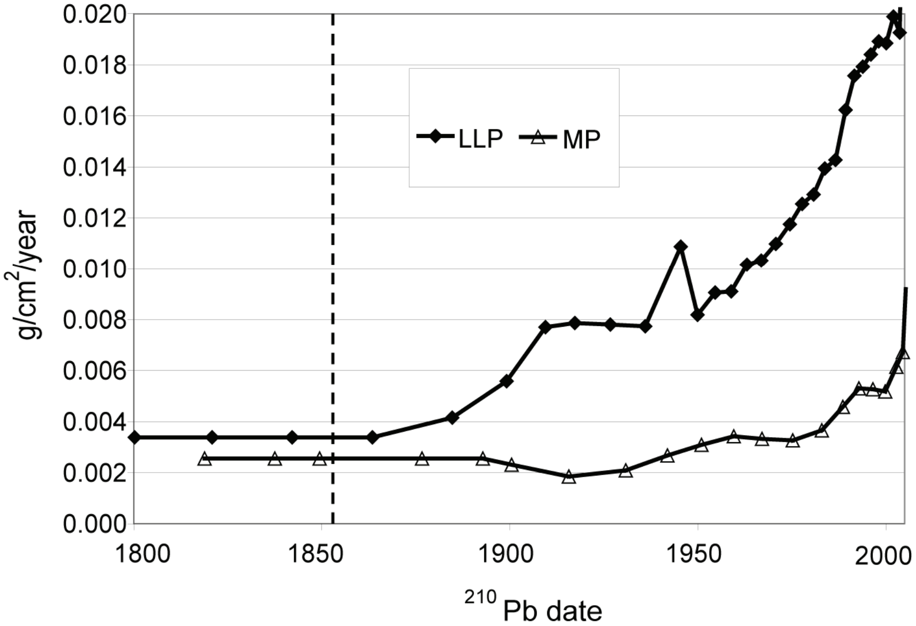

Figure 1.4 Sedimentation rate (g/cm^2/year) in Little Long (LLP) and Mud (MP) Ponds, Maine, calculated using ^{210}Pb dating. Sedimentation rates are considered to be constant ~pre-1900. The dashed line indicates the extent of ^{210}Pb dating; dates prior to ~1850 are extrapolated. Symbols represent data points.

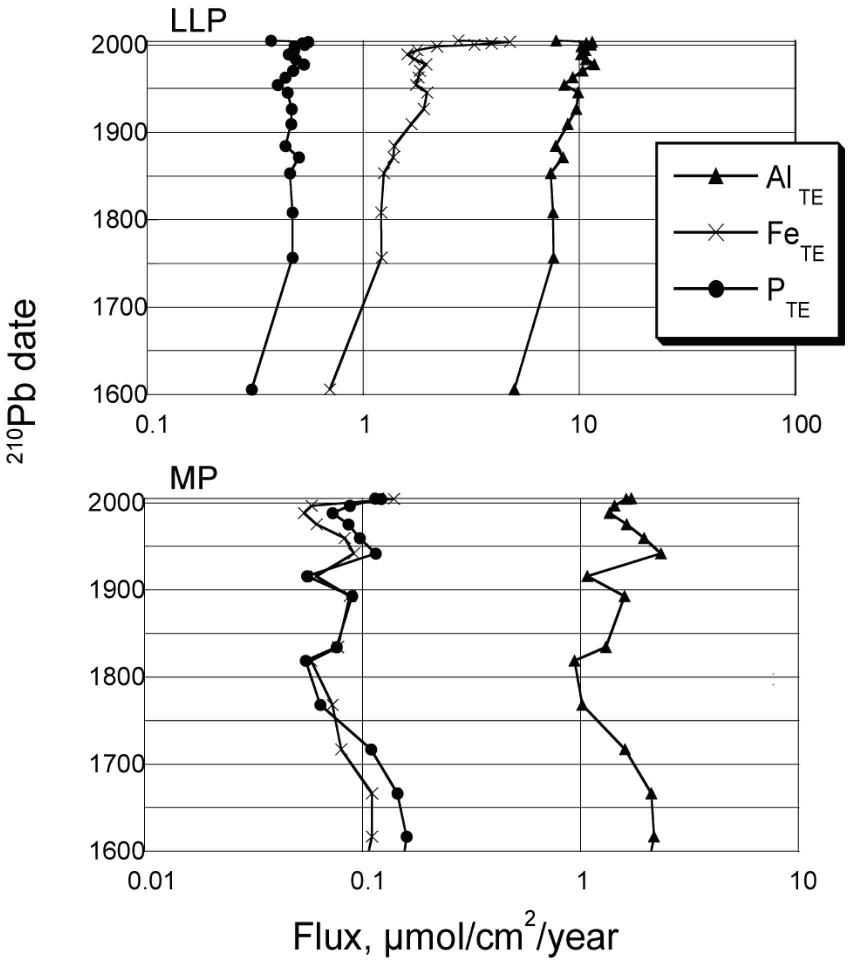

Figure 1.5 Flux, normalized to sedimentation rate, of total extractable Al, Fe and P in Little Long Pond (LLP) and Mud Pond (MP) based on sequential extraction chemistry from sediment cores collected in March of 2005.

In both cores, the highest percentage of extractable Al and P are in the NaOH25 fraction. Table 1.2 summarizes the proportions of total extractable Al, Fe, P (fractionated into rP and nrP) in each sequential extraction fraction. LLP and MP exhibit similar fractionation patterns with approximately 80% of Al and ≥ 95% of P in the NaOH25 fraction. The remaining ~20% of Al is nearly evenly divided between the mineral (HCl soluble) and the recalcitrant (NaOH85) fractions. A negligible proportion of P is found in the other fractions, notably, P associated with the BD fraction that is released under anoxic conditions (Coolidge 2004; Kopáček et al. 2005). Both the rP and nrP fractions are significant in the NaOH25 extract. In both LLP and MP cores, the proportion of nrP decreases and rP increases with increasing sediment age (Figure 1.6). Reducible Fe (BD-soluble) is highest in the top few cm of sediment. In deeper sediment, most Fe occurs in the NaOH25 fraction. Reducible Fe is likely a transient that occurs at the sediment-water interface. Compared to MP, the flux of total extractable elements to LLP sediment is higher for Al (2-5 times), Fe (10 times), and P (3-4 times). The molar ratio of Al as Al (oxy)hydroxides (NaOH25-Al) to labile and reducible P (NH_4Cl-P+BD-P) in the sediment exceeds 25 throughout the cores from both ponds (Figure 1.7). There is a 30-50% decline in that ratio in sediment younger than 1970.

Table 1.2 Percent of total extractable Al, Fe, TP and rP in the individual extraction steps, averaged for all sediment increments. Numbers in parentheses are ranges of %TE from bottom interval to top interval. ND = no data.

Little Long Pond

	NH_4Cl	**BD**	**NaOH25**	**HCl**	**NaOH85**
Al	<1	1	80 *(87-83)*	12 *(7-9)*	7 *(6-7)*
Fe	<1	37 *(32-57)*	48 *(50-35)*	9 *(13-5)*	6 *(5-2)*
TP	<1	0	97	1	2
rP	ND	ND	41 *(58-25)*	ND	ND

Mud Pond

	NH_4Cl	**BD**	**NaOH25**	**HCl**	**NaOH85**
Al	<1	2 *(0.5-6)*	79 *(76-80)*	7 *(2-9)*	12 *(14-12)*
Fe	<1	32 *(37-33)*	31 *(26-34)*	21 *(21-19)*	15 *(16-13)*
TP	<1	3	95 *(96-91)*	1	1
rP	ND	ND	35 *(61-12)*	ND	ND

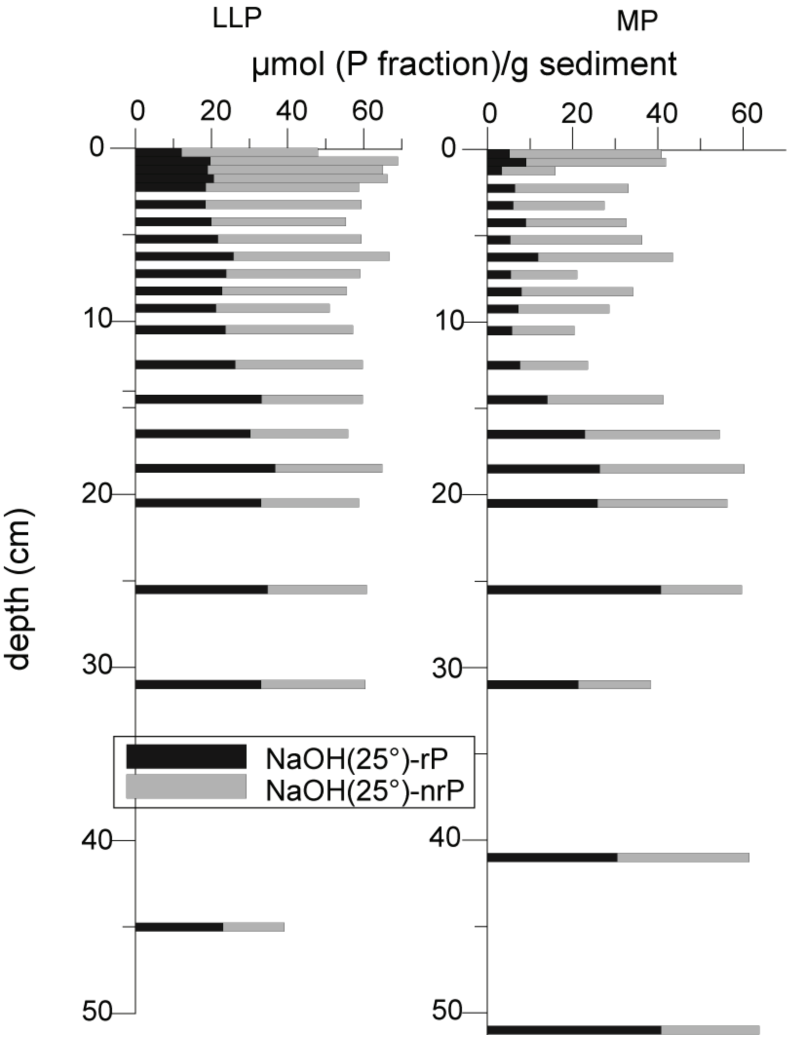

Figure 1.6 Sediment phosphorus from Little Long (LLP) and Mud (MP) Ponds extracted by 0.1M NaOH at 25°C as the third step of a sequential extraction based on Psenner et al. (1988) and Hieltjes and Lijklema (1980). The reactive portion (NaOH25-rP) is ortho-P that is potentially complexed with Al as Al-P. The non-reactive portion (NaOH25-nrP) is biogenic-P. In both Mud (MP) and Little Long (LLP) ponds, the proportion of P as Al-P is lower in younger sediment than in older sediment.

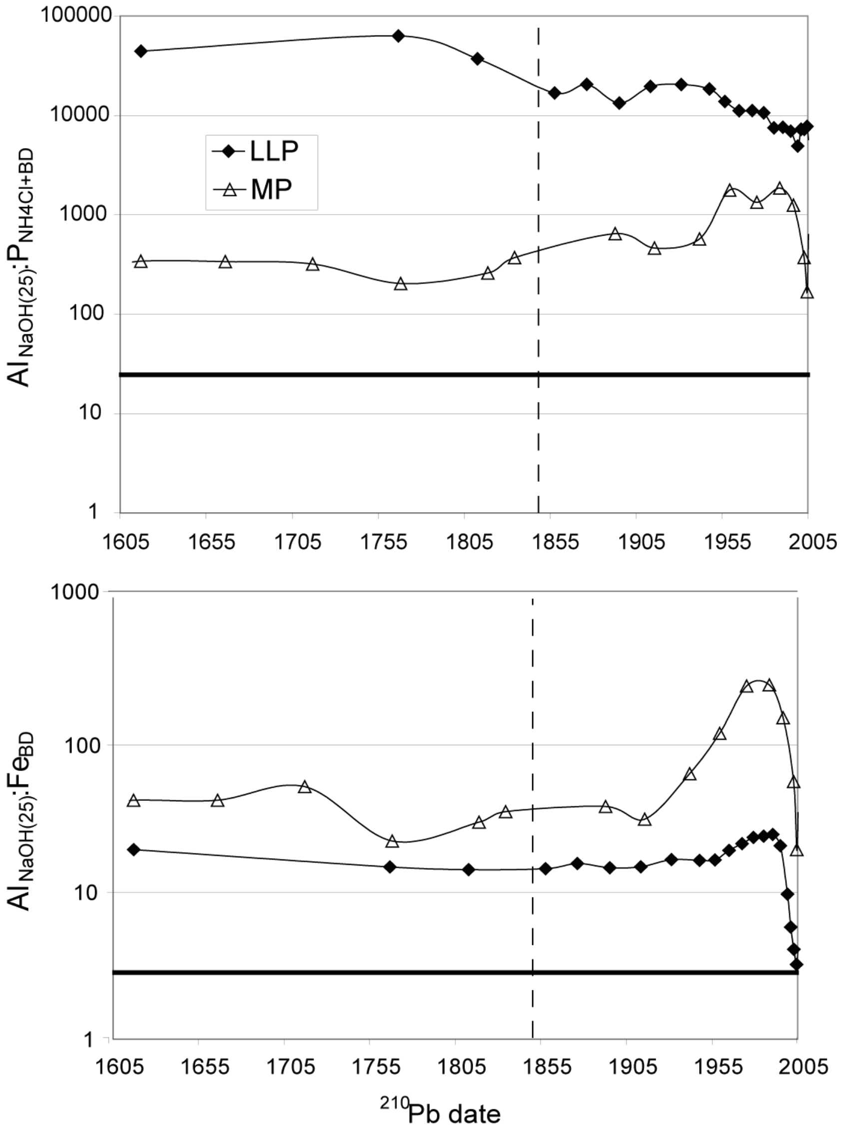

Figure 1.7 Molar ratio (dry weight basis) of NaOH25-Al to NH_4Cl-P+BD-P (upper graph) and NaOH25-Al to BD-Fe (lower graph) extracted from dated sediment intervals from Little Long (LLP) and Mud (MP) Ponds. The estimated minimum threshold ratios for P retention by sediment during anoxia are 25 and 3, respectively (Kopáček, et al. 2005) and are indicated by the heavy horizontal lines. These oligotrophic systems exceed that minimum ratio through time. The dashed line indicates the extent of ^{210}Pb dating, and dates prior to ~1850 are extrapolated.

Discussion

The chronic historical acidity of the Mud and Little Long Pond catchments proposed by Davis et al. (1994) has maintained conditions for high Al mobility throughout the period of time examined in our cores. Despite some recovery from atmospheric SO_4^{2-} input since the Davis study, both ponds remain at a low pH. Historically small loads of P to these ponds make it difficult to assess any changes in P flux to the ponds related to acidification. We focus on the chemical associations of Al, Fe, and P deposited to the sediment over the last two centuries.

Both ponds show a clear historical relationship between sediment Al and P as indicated by concentrations of the two elements in the operationally-defined extraction method. The data support the oligotrophication hypothesis mentioned earlier. The flux of Al to the profundal sediments of both ponds is several times higher than those of Fe and P, suggesting that removal of P from the water column and storage in sediment may be dominated by Al. The pH of the two ponds differs, but the mechanisms of P removal, retention, and burial by $Al(OH)_3$ seem to be similar. Mud Pond has a pH <5, but has a greater input of inorganic Al which may precipitate as $Al(OH)_3$ and remove orthophosphate from the water column (Porcal et al. in review, this volume; Kopáček et al. 2006). Although LLP has lower input concentrations of inorganic Al, the hypolimnetic pH of 5 to 6 is likely to precipitate Al as $Al(OH)_3$ and remove orthophosphate. Allochthonous and autochthonous sources of P to both ponds are historically low, suggesting that the small pool of biologically available P is readily controllable by Al.

The increase in sedimentation rates (Figure 1.4) was not expected because the catchments have remained relatively undisturbed by humans for a century. A nonanthropogenic disturbance such as the beaver dam at the major outlet of MP would increase the water residence time and affect sedimentation but this explanation does not apply to LLP. A systematic bias of ^{210}Pb activity could skew the results but the bias would have to apply to both cores. We do not have a satisfactory explanation for the increasing mass accumulation rates.

Reduction and oxidation of Fe occurs in the seasonal hypolimnia of these ponds and is likely involved with a higher proportion of P release than of P capture. LLP sediment almost reaches the threshold for P release because of significant amounts of reducible Fe in the uppermost layers. However, any P that is mobilized with Fe(III) reduction is likely adsorbed by abundant Al. The top few cms of sediment become Fe-enriched with oxidative precipitation of previously mobilized Fe(II), after the lake turnover.

Declines in the [NaOH25-Al]:[NH_4Cl-P+BD-P] ratios (Figure 1.7) suggest a decrease in inorganic Al, and/or an increase in labile P from the catchment during the past ~20 yr. Early 20th century land disturbances (fire and logging) and subsequent years or decades of catchment response may be factors that have affected the mobilization of Al by altering the proportion of inorganic Al to Al-organic complexes. Changes in Al and P fluxes are masked by the increase in sedimentation rates. $Al(OH)_3$ concentrations in the sediment are high enough relative to P that a small decrease of Al input would not change the mechanisms controlling P release.

The increase in the proportion of biogenic P (NaOH25-nrP used as a proxy) compared to orthophosphate (NaOH25-rP) in younger sediments (Figure 1.6) suggests a higher input of organic-P in recent sediments or diagenetic mineralization of P, increasing with age (depth). The half life of these biogenic-P compounds is in the range of 10 to 20+ years (Ahlgren et al. 2005).

Conclusions

Sediments from MP and LLP contain higher concentrations of extractable Al than Fe and P throughout the period of time represented by the cores. After normalization with respect to the sedimentation rate, Al flux has increased in LLP but shows no decrease in the SO_4^{2-} recovery period (post-1970s). In MP, the normalized Al flux to the sediment shows no obvious trend with respect to historic pH perturbations, but is highest in ~1940. Normalized P and Fe fluxes to the sediment remain fairly constant throughout the cores with the exception of surface enrichment of Fe in the top few cm. We can not speculate about the effects of recovery from acidification on P loading, because these sites are inherently acidic and remain so to the present day. However, the data from these oligotrophic systems suggest that Al may be the predominant abiotic control of sediment P retention.

Acknowledgements

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CHAPTER 2

A PALEOLIMNOLOGICAL ASSESSMENT OF PHOSPHORUS DYNAMICS IN UPPER HADLOCK POND CATCHMENT, ACADIA NATIONAL PARK, MAINE

Introduction

Oligotrophic freshwater lakes are those which have low nutrient phosphorus (P) and are characterized by low primary productivity, high water clarity, and high dissolved oxygen concentrations, all favorable characteristics in the definition of lake water quality. Conversely, eutrophic lakes are those that have high P concentrations and poor water quality, commonly induced by point or non-point sources of P from human activities or by internal loading from lake sediments. Because there is a common interest in maintaining oligotrophy and reversing eutrophication in impacted lakes, P is a commonly-studied element in freshwater systems.

The classical model (Mortimer 1941) of P recycling in lakes is based on the flux of P and ferrous iron (Fe(II)) from sediment during hypolimnetic anoxic conditions which favor the reductive dissolution of ferric hydroxide ($Fe(III)(OH)_3$). Oxic conditions reverse this process, resulting in precipitation of $Fe(III)(OH)_3$ which sorbs PO_4^{3-} in the water column and settles back to the sediment. Termed the “ferrous wheel,” this redox-sensitive cycle can play an important role in sediment-water P flux, yet it is not the dominant control in some systems. Recent studies by Amirbahman et al. (2003), Coolidge (2004), and Kopáček et al. (2005a) demonstrate that P loading due to the ferrous wheel is likely interrupted if there is sufficient aluminum hydroxide ($Al(OH)_3$) in the lake-bottom sediment. $Al(OH)_3$ solubility is redox-insensitive with a pH-dependent minimum solubility at pH 6.7. Under conditions where the dissolved inorganic Al (Al_i) concentration exceeds the solubility of $Al(OH)_3$ at the lake pH, amorphous $Al(OH)_3$ precipitates, readily binding inorganic P, and settles out of the water column to the sediment. Dissolved inorganic Al inputs are elevated in some lakes as a result of anthropogenic or episodic catchment acidification, and/or from photooxidation of organically-bound Al releasing inorganic Al (Kopáček et al. 2006). Generally, pH increases along the hydrologic surface flow path of an acidified catchment because of carbon dioxide degassing, input of groundwater with higher pH, and/or alkalinity-generating processes. A lake is typically the point along the hydrologic flow path where pH is highest and $Al(OH)_3$ is likely to precipitate, scavenge PO_4 from the water column, and permanently remove it from the dissolved P pool to the sediment, regardless of hypolimnetic anoxia.

This study employs paleolimnological methods to investigate the above-mentioned interactions of Al, Fe, and P in acidic, oligotrophic Upper Hadlock Pond, Maine over the past ~200 years. The research focuses on the following hypotheses:

1. *Lakes that have undergone catchment acidification and a resulting increase in Al input will accumulate Al-richer sediments which retain P (acido-oligotrophication).*
2. *Most sediment P will be associated with $Al(OH)_3$ throughout the acidification period.*

3. *A decrease of biologically-available P during acidification will affect phytoplankton (diatom) species composition and abundance.*
4. *Acido-oligotrophication may be reversing with reduction of sulfur emissions and deposition, which leads to recovery from catchment acidification, reduced Al flux to the lake, and decreased accumulation of P by precipitating Al.*

The goal of this research was to gain a better understanding of historical pH conditions and associated P dynamics by studying the Upper Hadlock Pond sediment record that spans several centuries. This analysis is part of a larger study exploring various catchment processes relating to abiotic controls on the trophic status of oligotrophic water (Norton et al. 2006). This work supplements concurrent studies of soil and stream geochemical processes related to aluminum mobilization and consequent oligotrophy as a result of catchment acidification (Goss and Norton in press, Huntress et al. 2007, Laird 2006). This study also augments research on lake sediment Al, Fe and P dynamics by Pearce (2000), Coolidge (2003), and Kopáček et al. (2005a), among others.

Literature Review

Phosphorus in lakes

The trophic status of a freshwater lake or pond typically depends on the concentration of phosphorus (P) in the water column that is available as a nutrient for phytoplankton uptake and growth, in other words, its biological productivity. In lake ecosystems, P is the limiting nutrient and an increase in bio-available P can lead to eutrophication (high productivity). Conversely, low concentrations of available P limit lake productivity and are associated with oligotrophy (Wetzel 2001). Eutrophy is generally considered to be an unfavorable condition of lake water quality and is associated with algal blooms, low water clarity, oxygen depletion, loss of fish species, and an increase of macrophytes. For this reason, the control of lake P is a well-studied topic and there are many prevention and remediation techniques aimed at limiting P input to and/or removing P from lake water columns. Phosphorus in lakes comes from several sources: external (allochthonous) sources such as atmospheric deposition, transport from inlet streams, non-point runoff from catchment soils and direct groundwater input, and from internal (autochthonous) sources such as the lake bottom sediment.

The relative contribution to lake P directly from atmospheric deposition and groundwater influx is quite small. The majority of allochthonous P is mobilized into soil solutions, transported to streams, and then to lakes (Pettersson et al. 1988). The bio-available form of P is PO_4 and it can be transported as dissolved PO_4, as particulate inorganic P (Reinhardt et al. 2004, Roy et al. 1999), or as organically associated P. The inorganic particulate forms are those that are adsorbed to a solid phase such as Fe-hydroxide, Al-hydroxide, or humic substance (Ulrich and Pöthig 2000b). Fe-hydroxide formation depends on redox conditions in the water. The solubility of $Fe(OH)_3$ is extremely low under normal pH conditions and in oxygenated water, encouraging precipitation of $Fe(OH)_3$ and adsorption of P in oxic stream waters. Al-hydroxide precipitation, which is Eh independent, will occur if dissolved inorganic Al concentrations exceed saturation in solution with respect to solid phase Al-hydroxide at a given pH. The solubility of Al-hydroxide decreases to a minimum close to pH = 6 (Drever 1997). Therefore, if acidic streams carrying relatively high concentrations of inorganic Al discharge into higher pH lakes, precipitation of Al-hydroxide is likely to occur and with it, the removal of dissolved PO_4 from the water column (Kopáček et al. 2000). Ionic Al and Fe concentrations in lakes may become high enough to precipitate hydroxides after photochemical liberation of organically-bound Al and Fe by solar radiation (Kopáček et al. 2006). The hydroxides subsequently bind and remove P from the water column. Conversely, when these carrier phases are dissolved by lower Eh (for Fe) or pH (for Al) they may release the adsorbed P as PO_4.

The major autochthonous P source in lakes is lake-bottom sediment. Sediment contains P in various forms. The internal loading of P to the water column is dependent on how it is bound in the sediment (Boström 1984). Mobilization of P from sediment to porewater can happen by desorption, dissolution, ligand exchange, mineralization, cellular metabolism, and/or autolysis of cells (Boström et al. 1988). The composition of organic matter and/or solid phases with which P is associated in the sediment, as well as the chemistry of the pore water, determine the dynamic exchange of P at the sediment-water interface. Freshly-deposited surface sediments contain more potentially mobile P whereas in deeper, older sediments (typically 5-10 cm or more) the P is more refractory (Rydin 2000). Temporal changes in P dynamics of surface sediments are influenced by changes within the lake, including input of organic matter, flux of electron acceptors, temperature, oxygen, and, and variation of groundwater input. Concurrently, changes in microbial and other biological activity in the lake and sediments promote P uptake and release (Enell and Lofgren 1988).

Internal loading or recycling of P can occur in dimictic lakes during thermal stratification and the consequent development of anoxic hypolimnia. The low Eh environment of the hypolimnion, especially at the sediment-water interface, induces P release from dissolution of iron (Fe)-III solid phases (Mortimer 1941) and from sediment microbes (Hupfer and Gächter 1995). However, because Al-hydroxide formation/dissolution is independent of Eh, it can scavenge PO_4 regardless of anoxia, (Huser and Rydin 2005, Kopáček et al. 2005a). Simulation studies show that PO_4 adsorption to Al-hydroxide is favored over adsorption to Fe-hydroxide if both solid phases are present in equal concentration (Ulrich and Pöthig 2000a). Several studies support this mechanism of Al control on P internal loading (Berkowitz et al. 2006, Huser and Rydin 2005, Kopáček et al. 2000, Reitzel et al. 2006) in lakes with catchments that export relatively high concentrations of Al.

Aluminum mobilization

Aluminum is least soluble under circumneutral conditions (pH 6 to 7); its solubility increases at pH values outside that range. Circumstances under which pH is reduced in surface water catchments will likely enhance Al dissolution, and that Al will be mobilized from soils to soil solutions and eventually transported to streams, rivers and lakes via hydrologic flow paths. Decreased pH in catchments can be caused by deposition of anthropogenic sulfate and nitrate (acid rain) or by natural episodic acidification during high hydrologic discharge (Seip et al. 1989, Sullivan et al. 1986) caused by major rain storms and/or rapid snowmelt. The "salt effect" may play a role in episodic acidification, especially in areas of marine-influenced dry and wet deposition (Heath et al. 1992, Hindar et al. 1995). Landscape factors including elevation, slope, land cover (vegetation), and proportion of wetlands influence the susceptibility of a catchment to acidification and subsequent Al mobilization (Cory et al. 2006).

Along with mineral acidity from SO_4 and NO_3 deposition, organic acidity also suppresses pH and mobilizes Al to surface waters. Aluminum is solubilized and forms both weak and strong complexes with organic acids (Al-DOC) that are released by terrestrial plants and microorganisms. These organic ligands mobilize Al from soil minerals and keep Al in solution while making it less toxic to organisms than inorganic Al species (Gensemer and Playle 1999). Molot and Dillon (2003) identified Al mass transfer as a function of both DOC and pH in a set of lakes in Ontario, Canada. These Al-DOC complexes are subject to photochemical transformation by solar radiation, which liberates a significant amount of inorganic Al in lake waters that can rapidly hydrolyze under circumneutral pH (Kopáček et al. 2006). The $Al(OH)_3$ precipitate can contribute significantly to lake sediment Al concentrations (Kopáček et al. 2005b).

Elevated concentrations of Al have been documented in acid-sensitive surface waters in several northern, temperate, forested ecosystems in western and northern Europe, eastern Canada, southeastern China, and the northeastern United States (Cronan and Schofield 1979, Schindler 1988, Xue et al. 2003). These acid-sensitive regions are characterized by thin, poorly-buffered soils, with low base saturation (Cronan and Schofield 1990, Reuss et al. 1987). Commonly in forested catchments, Al-DOC comprises a significant portion of the total Al and contributes to potential $Al(OH)_3$-P sorption mechanisms (Driscoll et al. 1996, Tipping et al. 1988). The role of Al in controlling internal P loading in lakes may be enhanced in these types of systems where Al and/or Al-DOC inputs to lakes are relatively high.

Anthropogenic acidification caused by industrialization has affected several lake ecosystems and their catchments in Maine, USA along with many other regions in the northern hemisphere. Acadia National Park (ANP), Maine is in the pathway of, and intercepts, pollutant-transporting westerly air masses; hence, the park landscape is well suited to studies of environmental effects of atmospheric contaminants that contribute to surface water acidification. This research focuses on Upper Hadlock Pond (Figure 2.1) in ANP, Maine, which has been monitored for water quality by the National Park Service for ~20 years. Upper Hadlock Pond is oligotrophic, maintains a pH below seven, and receives waters from an acid-sensitive catchment that receives relatively high wet and dry deposition of sulfate (Kahl et al. 2007).

Iron mobilization

Iron (Fe) is the fourth most abundant element in the earth's crust, and is ubiquitous in the environment. It is mobilized to surface waters primarily from low pH, low redox, high DOC forest soil solutions (Borg 1986). Like Al, Fe export increases during high discharge events both as particulate and dissolved Fe, though its mobilization is controlled more by DOC concentration than by pH (Molot and Dillon 2003, Reinhardt et al. 2004). Dissolved organic acids, represented by DOC, have a high affinity for binding Fe, keeping Fe in solution yet rendering it biologically unavailable to aquatic organisms (Maranger et al. 2006). Fe-DOC complexes (organically-bound Fe or Fe_o) commonly constitute the majority of total Fe in surface waters of acidic forested catchments (Kopáček et al. 2006, Laird 2006). Molot and Dillon (2003) showed that export rates of DOC and Fe are highly correlated in several lakes in Ontario, Canada, and Fe mass transfer is mainly a function of DOC concentration.

In-lake processes have a significant effect on the Fe budget. Microbially-catalyzed reductive dissolution of Fe(III) hydroxide from lake bottom sediments is a consequence of seasonal stratification and the development of an anoxic hypolimnion that releases Fe(II) to the water column and may also release adsorbed PO_4 (Amirbahman et al. 2003). Another in-lake source of ionic Fe is photochemical liberation of Fe from organically-bound Fe by solar radiation (Kopáček et al. 2006). Some ionic Fe may remain in the water column, though formation of $Fe(OH)_3$ is favored under circumneutral, oxic conditions. Fresh amorphous $Fe(OH)_3$ precipitate easily sorbs PO_4 and removes it from the water column to the bottom sediment where the floc is subject to the seasonal anoxic dissolution described above. Thus, the internal Fe cycle in dimictic lakes is governed by season and the total dissolved, ionic Fe concentrations in the water and surface sediment vary accordingly.

Sediment chemistry

Because P exists in various fractions in the lake sediment matrix and they have different mobility, it is important to be able to determine the fractions of interest. Many phosphorus fractionation schemes have been developed for soils and sediment, each using different chemical extraction sequences to dissolve P from the matrix (Table 2.1).

Unfortunately, it is difficult to quantitatively separate specific P compounds, and operational definitions of element fractions differ. Pettersson et al. (1988) compared several P fractionation methods and summarized the operational definitions and shortcomings of each (Table 2.1). My study utilizes a sequential chemical extraction procedure for lake sediment that separates Al, Fe, P and Ca fractions of interest such that the data are comparable to other relevant lake sediment studies. The procedure is based on that of Psenner et al. (1988), with two chemical modifications and one additional analytical step. The element fractions of interest are outlined in Table 2.2. The major shortcoming of this procedure is potential resorption of extracted P by calcium carbonates, which is avoided because the Upper Hadlock watershed and lake sediments have low dissolved Ca and no solid phase $CaCO_3$.

Table 2.1 Comparison of different soil and sediment extraction methods for fractionation of phosphorus, from Pettersson et al. 1988.

	Extraction	Proposed fraction	Shortcomings
1. Chang and Jackson (1957)	a. NH_4Cl 1mol/l b. NH_4F 0.5 mol/l pH 8.2 c. NaOH 0.1 mol/l d. HCl 0.5 mol/l e. CDB f. NaOH	labile P Al-bound P Fe-bound P Ca-bound P reductant-soluble P refractory P	extraction of Fe-P by NH_4F resorption by CaF_2 precipitation of phosphate with iron
2. Williams et al. (1971)	a. NaOH/NaCl 0.1/1.0 mol/l b. CDB 85°C c. HCl 0.5 mol/l	non-occluded Fe-, Al-P reductant-soluble P apatite P	resorption by carbonates in calcareous sediments Ca-P and org-P released by CDB
3. Williams et al. (1976)	a. CDB 0.22/1.0g/0.1M b. NaOH 1 mol/l c. HCl 0.5 mol/l	non-apatite P apatite P	resorption by carbonates in calcareous sediments Ca-P and org-P released by CDB
4. Hieltjes and Lijklema (1980)	a. NH_4Cl 1mol/l pH7 b. NaOH 0.1 mol/l c. HCl 0.5 mol/l	labile P Fe- and Al-bound P Ca-bound P	dissolution of small amounts of Fe-P and Al-P by NH_4Cl
5. Psenner et al. (1985)	a. H_2O b. DB 0.11 mol/l 40°C c. NaOH 1 mol/l d. HCl 0.5 mol/l e. NaOH 1 mol/l 85°C	water-soluble P reductant-soluble P Fe- and Al-bound P Ca-bound P refractory P	resorption by carbonates in calcareous sediments

Table 2.2 Chemical extraction sequence for fractionation of elements of interest in lake sediment. Organic P in step 3 refers to humic-P and biogenic P. The method is based on Psenner et al. (1988) and Hieltjes and Lijklema (1980).

Extraction step	Type of extraction	Result
1	1M NH_4Cl @pH 7	ion-exchangeable Al, Fe, P, and Ca
2	0.11M $NaHCO_3$-$Na_2S_2O_4$	reducible metal hydroxides (Fe, Mn, P)
3	0.1M NaOH @25°C	Al- and Fe- hydroxides and oxyhydroxides; Al-P, Fe-P, organic P*
4	0.5M HCl	crystalline Al, Fe, P, and Ca
5	1M NaOH @85°C	residual (non-labile) Al, Fe, P , and Ca
Sum		total extractable Al, Fe, P, and Ca

Diatoms as indicators

Fossil biota can be useful representatives of past ecological and environmental conditions. Diatoms are aquatic single-cell algae whose cell walls (tests) are silica. Different taxa have morphologically unique tests and resistant to degradation over time. Individual species may have narrow ranges of tolerance and optima for specific environmental conditions, including the water quality parameters of pH, alkalinity, and epilimnetic total P concentrations and dissolved organic carbon (DOC) (Dixit et al. 1999, Dixit et al. 1992). Calibration models based on fossil diatom species abundance have been developed from large sets of corresponding lake surface sediment and modern water chemistry data from several different lake research programs in northeastern North America (Ginn et al. 2007). These models are used to infer past environmental conditions in lakes and applied to track historical changes such as those induced by human impact, including acidification and cultural eutrophication.

Materials and Methods

Site Description

Upper Hadlock Pond (UHP) is in Acadia National Park, coastal Maine, USA (Figure 2.1.). UHP (N44°19.253', W68°17.240', elevation 70 m.) is 15.4 hectares, with a total catchment drainage area of 340 hectares. The entire catchment is above the post-Wisconsinan marine limit. Soils are primarily acidic Spodosols, a stony Schoodic-rock outcrop-Lyman complex derived from granite and phyllite-bearing tills, with shallow depth to homogeneous Cadillac Granite bedrock. The catchment has a 21% slope, and is 70% spruce and fir forest with summit shrubland and bogs at higher elevations. Bedrock exposure is common in the upper 10% of the catchment.

Paleoecological evidence indicates that vegetation in the Hadlock Brook catchment has not been substantially disturbed by fire or clear-cutting during the last several centuries, and the spruce-fir canopy there has remained largely intact (Schauffler et al. 2004). Route 198, a major paved road, skirts the west side of the pond. The three carriage road stone bridges (two separate roads) that cross Upper Hadlock inlet streams were built in 1925-1926.

UHP is 13.5 m. deep with a water residence time of about three months, develops a seasonal anoxic hypolimnion, and is typically ice-covered in winter. UHP is a soft water, low Ca pond with a pH of ca. 5.5-6.5. It receives input of more acidic waters via Hadlock Brook and its tributaries and Parkman Stream from the north/northeast. UHP is mesotrophic, with total phosphorus (TP) typically <10 μg/L in the water column and low potential for internal P loading from bottom sediments (Maine DEP, 2006). DOC concentrations range from 3 to 5 mg/L. Al concentrations in the water column are generally <150 µg/L based on data from National Park Service monitoring studies since the 1980s. More than 20 years of select water chemistry data from UHP are presented in Table 2.4.

Surface water inputs to UHP via Hadlock Brook and Parkman Stream vary seasonally as the chemistry and hydrology of the streams are sensitive to heavy precipitation and snowmelt. During three high discharge events at Hadlock Brook in 2005 and 2006 (Huntress et al. 2007, Laird 2006) total and dissolved Al and Fe, total P, and DOC concentrations were positively correlated with discharge. Most dissolved Al and Fe during high flow was organically complexed. The importance of DOC for mobilization of these metals is evident, particularly for Fe which is not soluble under soil water and stream oxic conditions. Particulate Al and Fe had similar patterns and were strongly correlated, evidence for mobilization of either dissolved or particulate Al and Fe hydroxide from upper soil horizons during high discharge acidic events (Laird 2006). The maximum measured stream concentrations during these three events are shown in Table 2.3. Considering the volume of UHP is 5.3×10^{8} liters, and a rain event such as the one monitored at Hadlock Brook on Feb 5, 2006 discharged up to 10^{6} liters/hour from the portion of the UHP catchment drained by Hadlock Brook, we can assume that such high volume episodic inputs are the main source of Al, Fe, P and DOC to UHP. Typical baseflow of Hadlock Brook, which has lower concentrations of these elements, only discharges about 10^{5} liters/day, a much smaller contribution to the pond. Given that volume-weighted inputs of Al, Fe and DOC from Hadlock Brook (and likely Parkman Stream) are higher than typical epilimnetic concentrations in UHP (Table 2.3), we can presume that the pond is a sink for these elements. Aluminum and Fe are retained as precipitated solid phases in the pond sediments and/or as dissolved species in the meta- or hypolimnion during seasonal stratification. DOC is broken down by photochemical processes, mineralized by biological processes, and/or settles out as particulate organic matter to the pond sediment.

Table 2.3 Comparison of Al, Fe, P and DOC concentrations to Upper Hadlock Pond (UHP) from Hadlock Brook as compared to concentrations in the epilimnion (as a proxy for pond outlet concentrations). The subscript "max" denotes the maximum concentration which occurred during peak discharge. Epilimnetic concentrations are the average of four sample dates in June, July, August and October 2005. Chemical data from Laird (2006), Huntress (2008), and B. Lake (unpublished).

Hadlock Brook high discharge events					
	discharge_{max}	Al_{max}	Fe_{max}	P_{max}	DOC_{max}
	Liters/hour x 10^6	µg/L			mg/L
10 Nov 2005	0.34	277	25	1.2	4.1
5 Feb 2006	1.0	326	23	0.5	4.1
8 June 2006	1.2	458	62	3.5	8.7
UHP epilimnion 2005					
	n/a	41	25	3.9	4.2

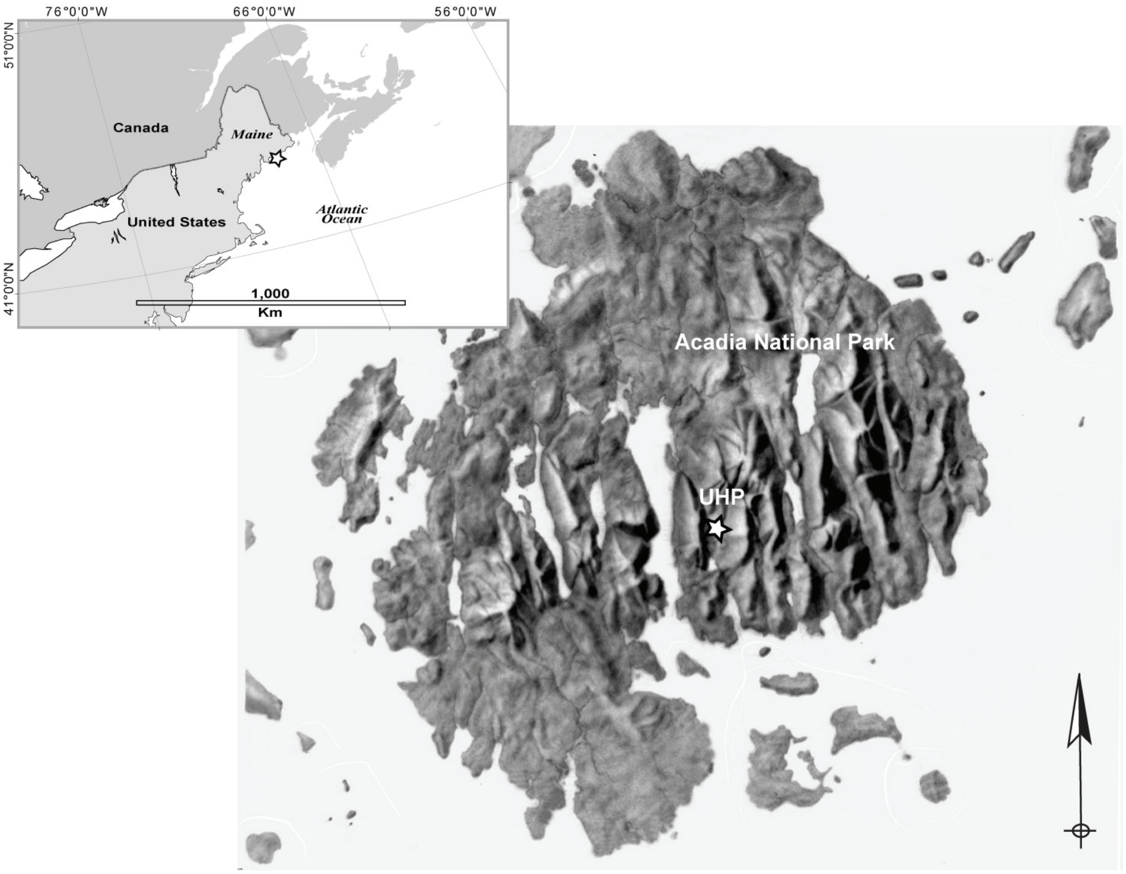

Figure 2.1 Location of Upper Hadlock Pond (UHP), Acadia National Park, USA.

Table 2.4 Annual averages (± standard deviation) of epilimnetic chemistry data for Upper Hadlock Pond. Unpublished data from Maine DEP, Maine VLMP and ANP (1983 through 2004) and B. Lake (2005, unpublished). ND = no data; n = number of samples.

Year	n	pH	ANC μeq/L	SO_4 μeq/L	DOC mg/L	Dissolved Al μg/L	Total P μg/L
1982	2	6.43 (± 0.03)	51.5 (± 9.8)	96 (± 9.2)	ND	75 (± 23)	ND
1983	6	6.06 (± 0.41)	24.0 (± 14.0)	101 (± 7.8)	ND	106 (± 59)	ND
1984	6	5.92 (± 0.44)	22.1 (± 16.7)	90 (± 6.4)	3.1	95 (± 36)	2.2
1986	1	6.60	62.0	ND	ND	ND	ND
1988	3	ND	62.6 (± 8.3)	ND	ND	ND	ND
1989	2	6.17	51.3 (± 16.1)	108	4.5	90	ND
1994	8	6.35 (± 0.25)	ND	ND	ND	ND	ND
1995	8	6.13 (± 0.22)	66.7 (± 22.6)	73	4.2	16	11.0 (± 1.4)
1996	5	5.94 (± 0.27)	50.7 (± 3.1)	71	ND	ND	5.2
1997	2	6.50 (± 0.13)	ND	ND	ND	ND	ND
1998	2	6.18 (± 0.08)	39.4	93	3.9 (± 0.4)	74	4.9
2000	2	6.15 (± 0.43)	ND	ND	ND	ND	ND
2001	3	6.49 (± 0.08)	47.2 (± 4.6)	ND	3.2	ND	12.0
2002	3	6.23 (± 0.30)	55.2 (± 13.9)	ND	ND	ND	ND
2003	4	6.56 (± 0.44)	41.8 (± 18.5)	ND	3.1	ND	4.0
2004	2	6.46 (± 0.06)	71.4 (± 38.9)	ND	3.5	ND	4.1
2005	4	6.38 (± 0.17)	50.0 (± 14.6)	65 (± 2.2)	4.2 (± 0.1)	41 (± 43)	3.9 (± 1.2)

Paleolimnology

Sediment collection and processing

A sediment core was obtained at a point 11 m deep at UHP (N44°19.253', W68°17.240') during ice cover in March 2005 using a 10 cm diameter, stationary piston corer with an acrylic core tube (Davis and Doyle 1969). Sediment cores were sectioned at the lake using stainless steel and plastic ware. Sediment was sectioned in 0.5 cm intervals from 0 to 10 cm, in 1 cm intervals from 10 to 30 cm, and in 2 cm intervals below 30 cm. Samples were placed directly into Whirlpack™ bags and stored at 4°C in the dark.

At the laboratory, 0.5 g wet sediment aliquots were taken from several intervals for diatom analysis, and 10 to 20 g aliquots were dried at 100°C in ceramic crucibles for percent water (percent solids) determination. The remaining sediment was frozen at -20°C until processed for further analysis. Dried sediment aliquots were homogenized with ceramic mortar and pestle and percent loss–on-ignition (%LOI) was determined by heating ~0.5 g. of dried sediment at 550°C for 4 hours. Dry sediment was dated by analyzing gamma activity of ^{210}Pb. The constant rate of supply (CRS) model of Appleby and Oldfield (1978) was used to calculate the age of the midpoints of the sediment increments based on determination of supported and unsupported ^{210}Pb activities.

Accumulation rates of sediment mass for each interval were calculated using the following set of algorithms:

$$DM = \frac{[\rho_S \times (100 - VW) \times Z]}{100} \tag{2.1}$$

$$VW = \frac{\%H_2O}{\left[\%H_2O + \dfrac{(100 - \%H_2O)}{\rho_S}\right]} \times 100 \tag{2.2}$$

$$\rho_S = \frac{[\rho_O \times OM + \rho_I \times IM]}{100} \tag{2.3}$$

$$MAR = \frac{DM}{y_i} \tag{2.4}$$

where DM = dry mass per area (g/cm^2)

VW = volume % water in one cm^3 of sediment

ρ_S = solid density (g/cm^3)

ρ_O = density of organic matter (assumed 1.6 g/cm^3)

ρ_I = density of inorganic matter (assumed 2.5 g/cm^3)

OM = % organic matter on a dry weight basis (%LOI)

IM = % inorganic matter (100 – OM)

MAR = mass accumulation rate of sediment (g/cm^2/year)

y_i = number of years represented by the sediment interval

Sediment chemistry

The following sequential extraction (Figure 2.2) was performed on 1 to 2 g subsamples of wet sediment (previously frozen) to determine operationally-defined fractions of Al, Fe, P, and Ca at several depth intervals through the core: A) 8 mL of 1M NH_4Cl, pH 7, at 25°C for 1 hr to obtain the exchangeable fraction, B) 25 mL of 0.11M Na bicarbonate-Na dithionite (BD) at 40°C for 30 min to release the reducible portion--primarily Fe and Mn oxyhydroxides and associated P, C) 25 mL of 0.1M NaOH at 25°C for 16 hr. to dissolve Al and Fe hydroxides and oxyhydroxides and associated P, as well as organic-P, D) 25 mL of 0.5M HCl at 25°C for 16 hr. to dissolve acid-soluble minerals, and E) 25 mL of 1M NaOH at 85°C for ≥24 hr to solubilize residual material. The procedure (Psenner et al. 1988) has been utilized in several similar studies (Coolidge 2004, Huser and Rydin 2005, Kopáček et al. 2000), but using 1M NaOH rather than 0.1M NaOH for Step C. We modified the strength of NaOH for our study based on the procedure of Hieltjes and Lijklema (1980). Total extractable (TE) concentrations are defined as the sum of concentrations from the five sequential extractions.

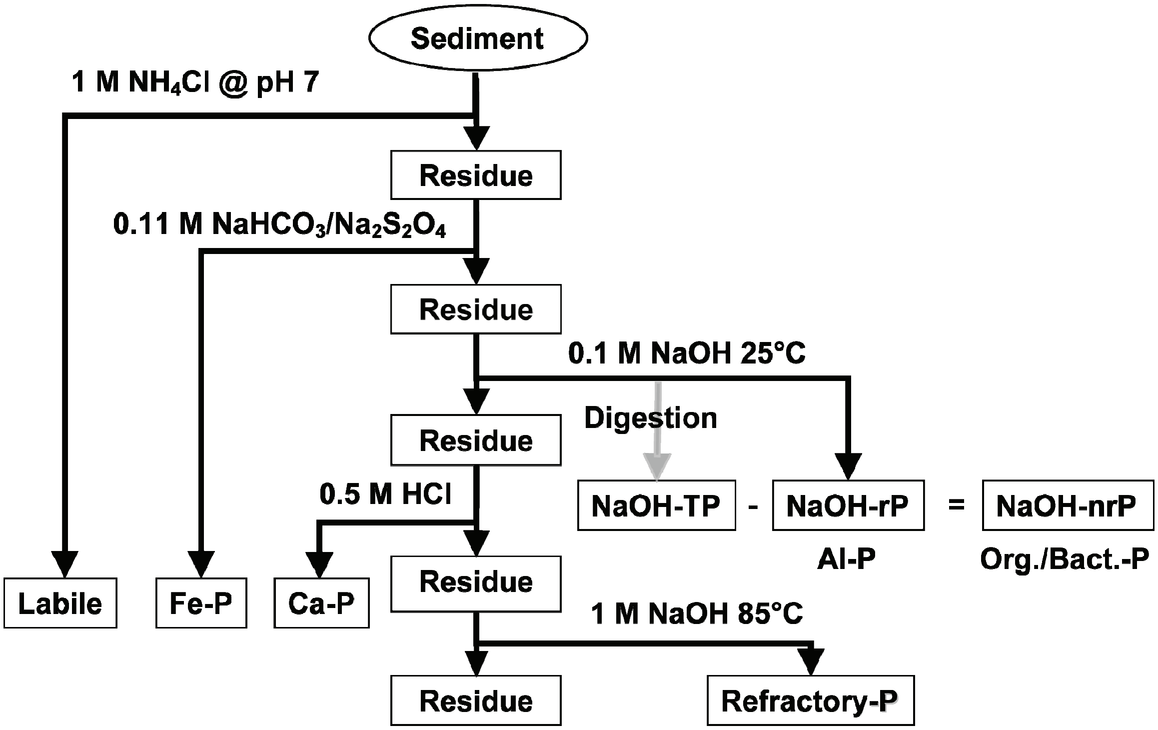

Figure 2.2 Sequential extraction method for phosphorus and associated elements in Upper Hadlock Pond sediments. The procedure is based on Psenner et al. (1988) and Hieltjes and Lijklema (1980).

Extractions were performed on 19 sediment core sections from UHP, with higher frequency in the top 10 cm of the core. Batches of 16 samples were extracted together and each batch included a duplicate sample and a reagent blank. For each step, the appropriate volume of extraction solution was added to an aliquot of wet sediment in a 50 mL plastic centrifuge tube, capped and shaken in a water bath at temperature for the appropriate amount of time, and centrifuged at ~3000 rpm for 15 min. The supernatant was collected and the sediment rinsed with the same volume of extraction solution as the first time, centrifuged and decanted a second time.

Concentrations of Al and Fe in the extracts were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES; Perkin-Elmer model 3300XL).

The NH_4Cl, BD, and NaOH solutions were diluted 1:10 for ICP-AES analysis. Total P (TP) was analyzed by either ICP-AES (for the BD, NaOH25, HCl, and NaOH85 solutions) or by the molybdate-blue spectrophotometric method (Murphy and Riley 1962)(for the NH_4Cl solution). The NaOH25 fraction was also analyzed using the molybdate-blue method for reactive P (NaOH25-rP), which is the P in solution as PO_4 and is assumed to be associated with Al in the sediment. The difference between NaOH25-TP and NaOH25-rP is NaOH25-nrP (non-reactive P) (Psenner et al. 1988). NaOH25-nrP is likely the organic-P and bacteria-incorporated P fraction (Ahlgren et al. 2005).

Element concentrations were measured in the supernatant solutions as µg/L and converted to µmol per gram of dry sediment using the following equation:

$$(2.5)\quad C_{sed} = \frac{C_e \times V_e}{m_{wet} \times MW \times \%solid}$$

where C_{sed} = concentration of element in dry sediment (µmol/g)

C_e = concentration of element in extractant solution (µg/L)

V_e = volume of solution used for extraction, including rinse solutions (L)

m_{wet} = mass of wet sediment subjected to extraction (g)

MW = molecular weight of element (µg/µmol)

% solid = proportion of wet sediment that is solid material (1 - %moisture)

Accumulation rate (*AR*) of elements of interest (µmol/cm^2/year) in the sediment were calculated using equation (2.6):

$$(2.6)\quad AR = MAR \times C_{sed}$$

where AR = accumulation rate of element of interest (µmol/cm^2/year)

C_{sed} = concentration of element in sediment interval (µmol/g dry sediment)

MAR= mass accumulation rate (g/cm^2/year) from equation (2.4)

These element accumulation rates were then normalized to account for sediment mass accumulation. Normalized accumulation rate, NAR, gives a sense of the rate at which the flux of some element differs relative to the changing sedimentation rate.

$$(2.7) \qquad NAR = \frac{AR}{MAR_i \big/ MAR_{base}}$$

In this equation $MAR_i \big/ MAR_{base}$ is the ratio of the sediment accumulation rate of the interval of interest to a baseline mass accumulation rate from a deep, steady-state interval. Thus, NAR may not increase if an increase in AR is matched by an increase in MAR.

Laboratory quality control

Spectroscopic analyses (both ICP-AES and molybdate-blue spectrophotometric methods) of samples followed several quality control criteria: laboratory reagent blank (LRB) analysis, laboratory replicate sample (LRS) analysis, and calibration verification sample (CVS) analysis. One LRB and one LRS sample for each reagent used in the sequential extraction procedure was processed and analyzed with every sample batch. Analytical calibrations for each element were verified for accuracy using a mid-range CVS made from a different source than the calibration standards. This CVS was analyzed once for every ten samples analyzed, with acceptability requirements of ±15% of the known concentration. Final sample concentrations of the sediment extraction supernatants were determined using equation (2.5) (above) after subtraction of the batch LRB measured concentration.

Diatom enumeration

We used diatom species abundances in the sediment to reconstruct lake chemical changes through time. Inferred lake water pH and alkalinity are based on previous calibrations developed by Dixit et al. (1999). Diatom assemblages may also reflect historical changes in Al concentrations and bioavailable P in the water column. This study includes enumeration of fossil diatom assemblages in 14 intervals from UHP. We chose to characterize diatoms from deeper/older sediment (19 cm, dated as pre-1800) up to the top, with greater frequency in the top 10 cm.

Approximately 0.5 cm^3 subsamples were processed for each sediment interval. Each subsample was boiled in chromic acid for two hours to oxidize the organic matter, rinsed with distilled water four times, and brought to a constant volume of 10 ml. A portion of this solution was settled onto cover slips by the method of Battarbee (1973) and mounted on glass slides in Cargille Meltmount^{TM} for observation at 600-1250 magnification using oil immersion with phase contrast optics. At least 500 valves were identified and counted per sediment interval. The most useful taxonomic reference for this flora is *Diatoms of Low-Alkalinity Lakes in the Northeastern United States* (Camburn and Charles 2000). Other iconographic references include Camburn et al. (1984-1986), Krammer and Lange-Bertalot (1986), Patrick and Reimer (1966a, b). Historical pH and total P concentrations were reconstructed using the maximum likelihood (ML) model of Ginn et al. (2007). This model is based on a wide-range calibration set of 494 lakes in northeastern North America.

Statistical Analysis

Regression analysis was performed using R: Copyright 2006, The R Foundation for Statistical Computing, version 2.3.1 (2006-06-01), ISBN 3-900051-07-0. Significant correlations between measured sediment variables (Al, Fe, P and Ca fractions, LOI, depth) were computed for the sediment core data in order to explain historical and current sediment chemistry trends and dynamics. Assumptions of normality and constant variance were tested, and statistical outliers were removed from the statistical analyses.

Results and discussion

Moisture content and loss on ignition

Water content was highest in the top sediments of the UHP sediment core and declined irregularly downward (Figure 2.3). Loss-on-ignition (LOI) varied slightly with depth (Figure 2.3); the average throughout the UHP core is 35%. LOI is a parameter that is interpreted as the amount of organic matter in sediment but may also include water lost from $Al(OH)_3$ and $Fe(OH)_3$ phases that is not removed during 100°C drying. In these sediments, the LOI may consist of up to 5% (of 100%) from $Al(OH)_3$ dehydration, based on Al concentrations. Table 2.5 presents the values for percent moisture and LOI in the intervals that also underwent the sequential extraction.

Chronostratigraphy

The rate of decay of ^{210}Pb (half life of 23 years) makes it a useful radionuclide for dating lake sediment, but to an age limit of only about 100-150 years. The depth of accurately dateable sediment will vary depending on the activity of supported and unsupported ^{210}Pb, both of which are affected by the rate of sediment accumulation in a particular lake. We calculated sediment ages using two models, CRS and CIC, which are based on a constant rate of supply and a constant initial concentration of unsupported ^{210}Pb, respectively (Figure 2.4). Assuming that peak deposition of ^{137}Cs should be at approximately 1963, when the atmospheric load and consequent fallout of that radionuclide was elevated from atmospheric testing of nuclear bombs, the best model fit is the CRS. The unsupported ^{210}Pb activity was measurable in UHP to a depth of 18 cm, which corresponds to ~150 year old sediment. ^{210}Pb values for uncounted intervals were interpolated as were the ages of intervals. Sediment ages older than ~150 years (deeper intervals) are extrapolated based on the assumption of a constant rate of sediment accumulation and supported ^{210}Pb in the older sediments (MAR_{base} from eq. (2.7) above).

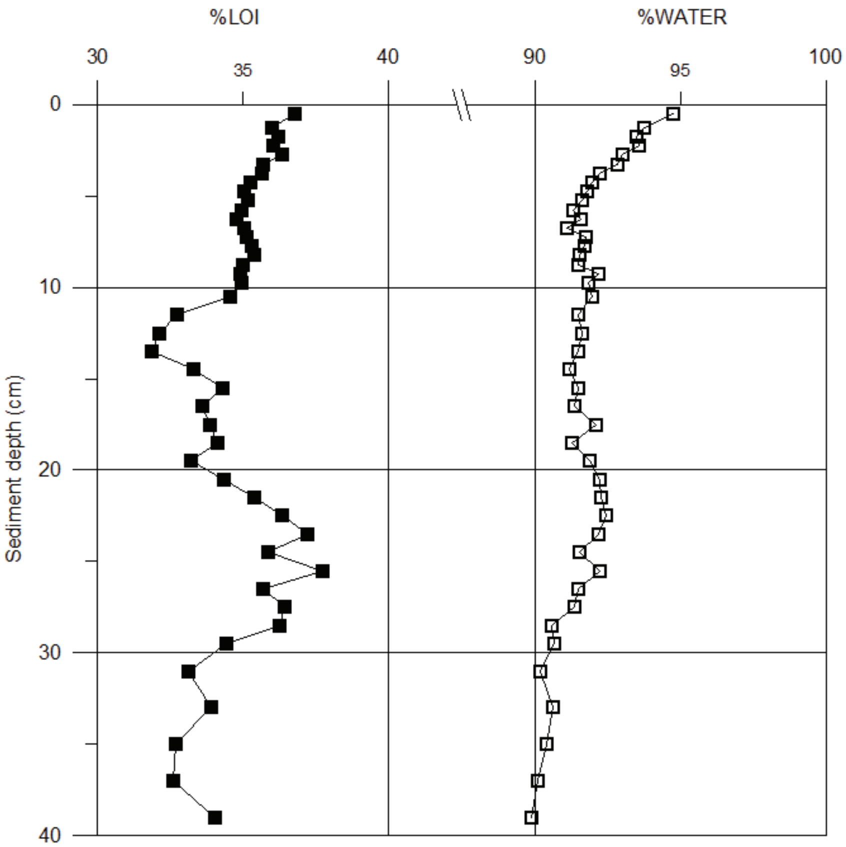

Figure 2.3 Loss-on-ignition and moisture in sediment core intervals from Upper Hadlock Pond, Acadia National Park, Maine (sampled in March, 2005).

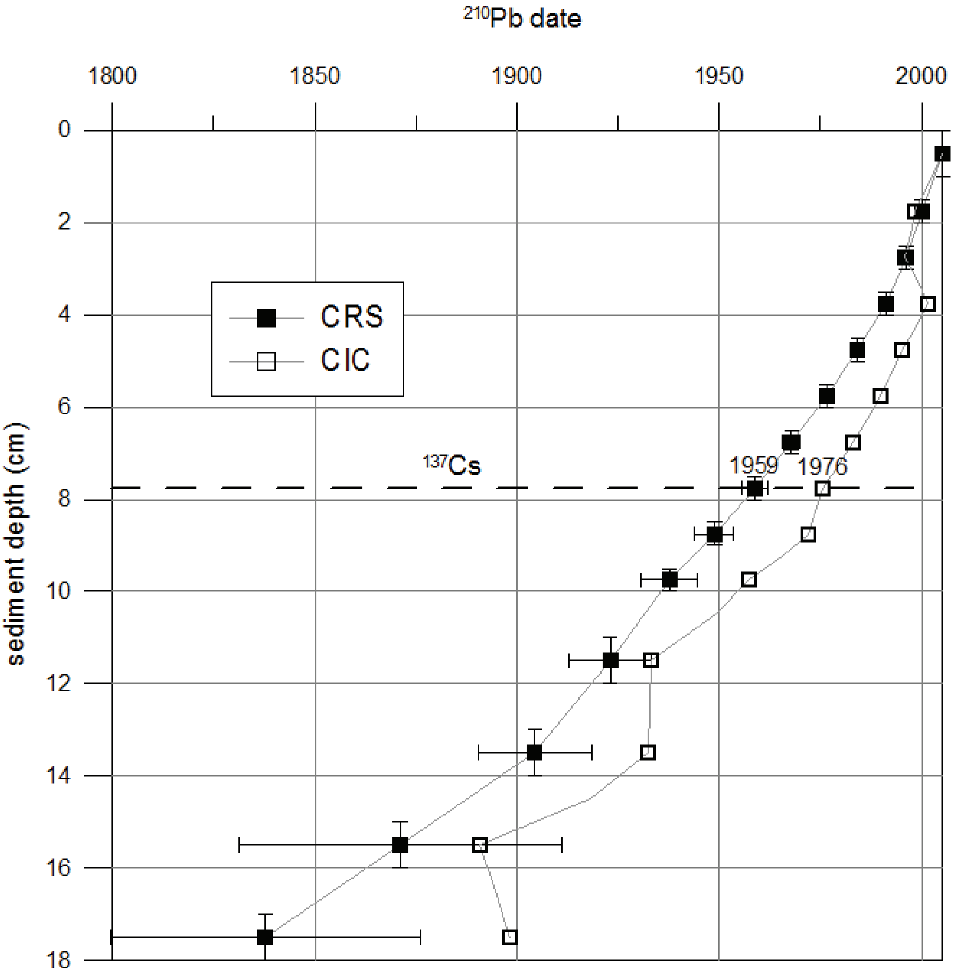

Figure 2.4 ^{210}Pb dating profiles for the sediment core from Upper Hadlock Pond, Acadia National Park, Maine, USA retrieved in March of 2005. Models are based on constant rate of supply (CRS) and constant initial concentration (CIC) of unsupported ^{210}Pb to the sediment. Horizontal bars are ^{210}Pb counting errors. Vertical bars represent the thickness of the sediment increment. The dashed line is the depth at which ^{137}Cs activity was highest.

Using CRS ^{210}Pb dates, we calculated sediment mass accumulation rates in UHP for the last ~150 years. Lack of precision of ^{210}Pb dates in older sediment requires us to assume a constant (baseline) accumulation rate prior to ~100 years ago. Figure 2.5 illustrates the rate of the last 200 years of mass accumulation (*MAR*), calculated using equations (2.1)-(2.4) and using a MAR_{base} of 0.0055 g/cm^2/year. UHP has an increasing sedimentation rate in the last 30 to 50 years, along with a pronounced temporary increase in the early part of the 1900s.

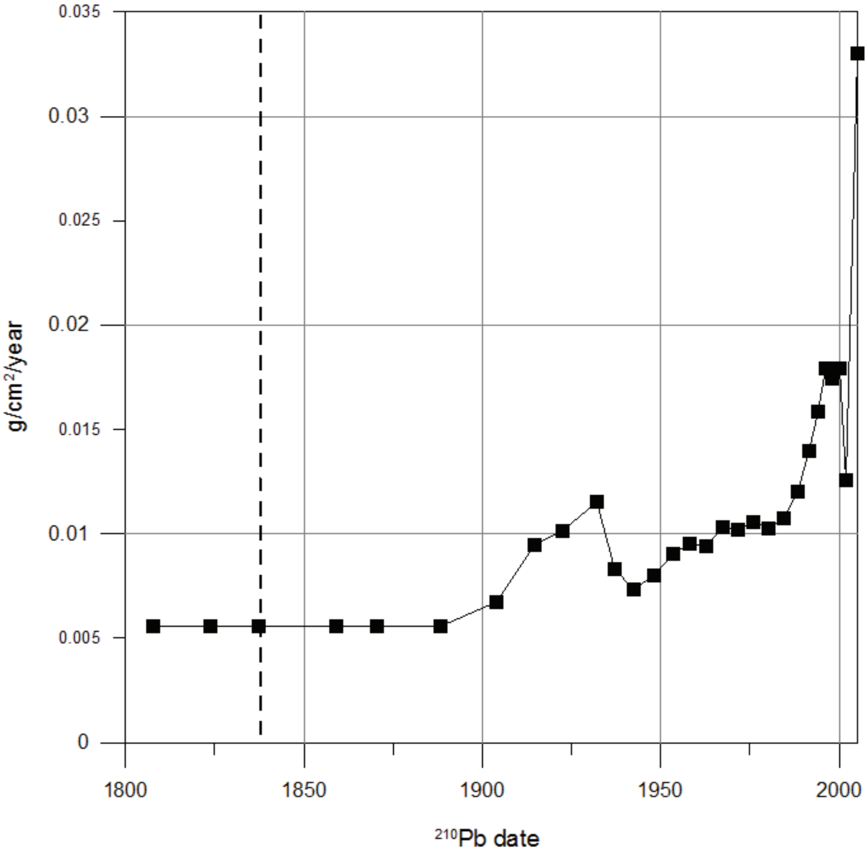

Figure 2.5 Profundal sediment accumulation rate (g/cm^2/year) of Upper Hadlock Pond, Acadia National Park, Maine, calculated using ^{210}Pb dating. The rate is assumed to be constant ~pre-1900. The dashed line indicates the extent of ^{210}Pb dating; dates prior to 1837 are extrapolated.

Sequential extraction results

Tables 2.5 and 2.6 summarize results for analyses of Upper Hadlock Pond sediments. Figures 2.6-2.9 and the following text sections present a more detailed assessment of Al, Fe, P, and Ca fractionation for these sediments.

Table 2.5 Interval depth, ^{210}Pb date, moisture, loss on ignition (LOI), and total extractable (TE) concentrations of Al, Fe, and P for Upper Hadlock Pond, Maine (UHP) sediment. TE concentrations are on a dry weight basis and are the sum of concentrations from a sequence of five extractions. Dates in italics are extrapolated.

Sediment interval	^{210}Pb date of midpoint	Moisture %	LOI %	TE-Al µmol/g	TE-Fe µmol/g	TE-P µmol/g	TE-Ca µmol/g
0-1 cm	2005	94.8	36.8	1223	418	51.3	65.0
1.5-2 cm	2000	93.5	36.2	1414	277	55.2	107.5
2.5-3 cm	1996	93.0	36.3	1017	175	38.8	76.7
3.5-4 cm	1992	92.2	35.6	1342	221	51.4	93.9
4.5-5 cm	1985	91.8	35.0	1277	178	49.8	87.2
5.5-6 cm	1976	91.3	34.9	1468	212	52.4	87.0
6.5-7 cm	1967	91.1	35.0	1335	194	48.8	80.5
7.5-8 cm	1958	91.7	35.3	1540	226	57.3	95.0
8.5-9 cm	1948	91.5	35.0	1351	199	49.6	76.6
9.5-10 cm	1937	91.8	34.9	1402	196	50.4	79.6
11-12 cm	1923	91.5	32.7	1117	158	38.7	60.9
13-14 cm	1904	91.5	31.9	990	147	33.2	57.0
15-16 cm	1871	91.5	34.3	867	114	36.8	56.3
17-18 cm	*1837*	92.1	33.8	1241	154	54.9	93.0
19-20 cm	*1808*	91.9	33.2	1252	160	52.4	95.0
21-22 cm	*1778*	92.3	35.4	1028	135	43.7	80.8
23-24 cm	*1749*	92.2	37.2	1253	144	56.0	98.5
28-29 cm	*1670*	90.6	36.3	1301	122	61.1	104.5
36-38 cm	*1514*	90.1	32.6	732	69	31.2	54.2

Aluminum fractionation

The average total extractable Al (TE-Al) throughout the depth of sediment from UHP is 1218 μmol/g dry sediment (Table 2.5). Figure 2.6 displays the proportions of Al fractions, as defined by the sequential extraction, in the sediment core from UHP. The highest percentage of extractable Al is in the NaOH25 fraction, mainly Al hydroxides and oxyhydroxides. The average percentage of TE-Al of this fraction through the depth of each core is 80% and proportions vary little with depth. The remaining ~20% of TE-Al is more or less evenly divided between the mineral (HCl soluble) and recalcitrant (NaOH85 soluble) fractions, which are also quite consistent with depth (Table 2.6).

Iron fractionation

Specific Fe fractions from the three sediment cores are shown in Figure 2.7. On average through the UHP core, most Fe is in the NaOH25 fraction, though it varies with depth (Table 2.6). Reducible Fe (BD-soluble) is the highest fraction in the top few centimeters of sediment and is likely a transient form of Fe that is enriched at the sediment surface. The BD fraction decreases downward in absolute amount and proportion, the latter from 50% to about 20% of TE-Fe, at the expense of the NaOH25, HCl and NaOH85 fractions. Average total extractable Fe (TE-Fe) concentration is 184 μmol/g dry sediment, and TE-Fe for each extracted interval is shown in Table 2.5.

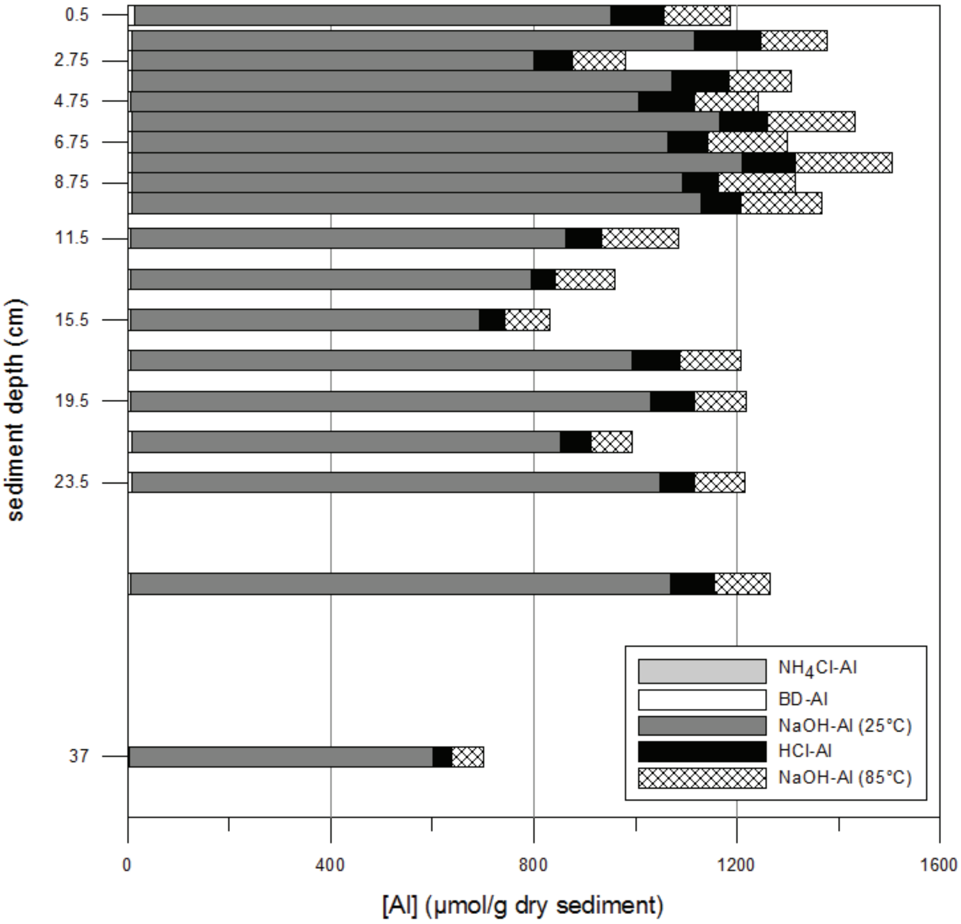

Figure 2.6 Aluminum fractionation in Upper Hadlock Pond, Maine, USA core sediments.

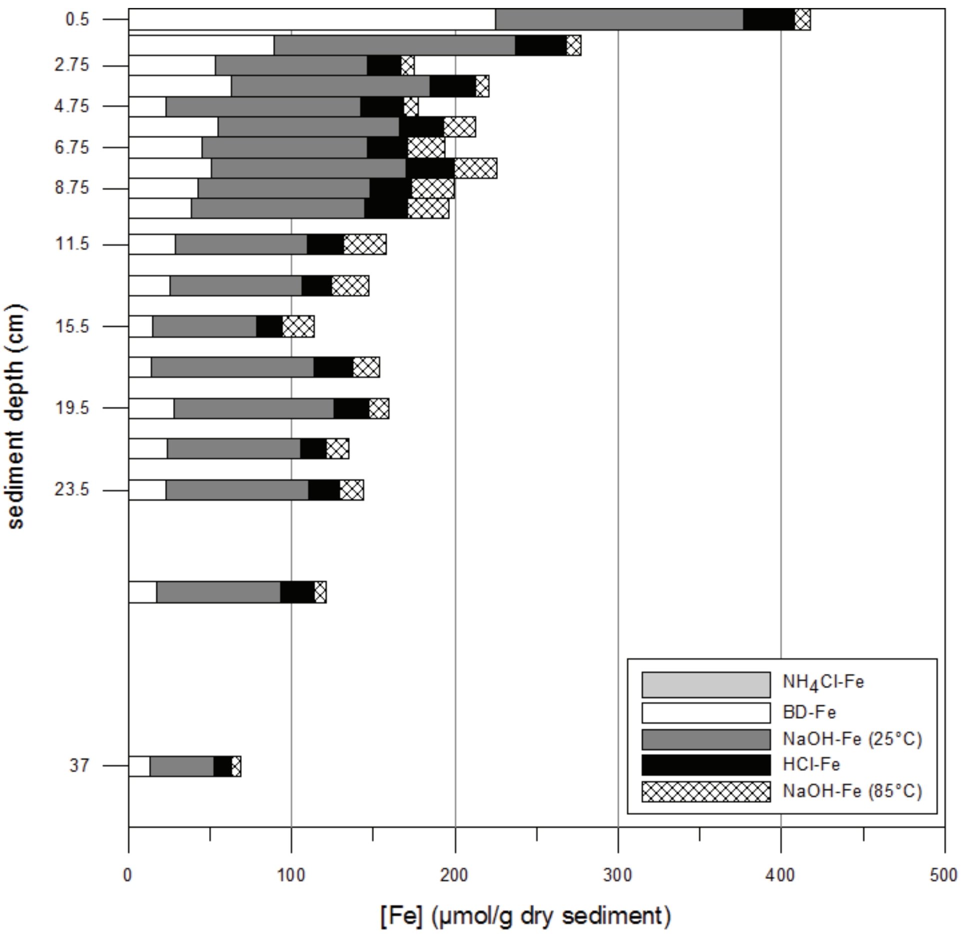

Figure 2.7 Iron fractionation in Upper Hadlock Pond, Maine core sediments.

Calcium fractionation

UHP total extractable Ca (TE-Ca), averages 82 µmol/g dry sediment through the core. About 71% of TE-Ca is the readily exchangeable portion extracted by NH_4Cl (Figure 2.8, Table 2.5).

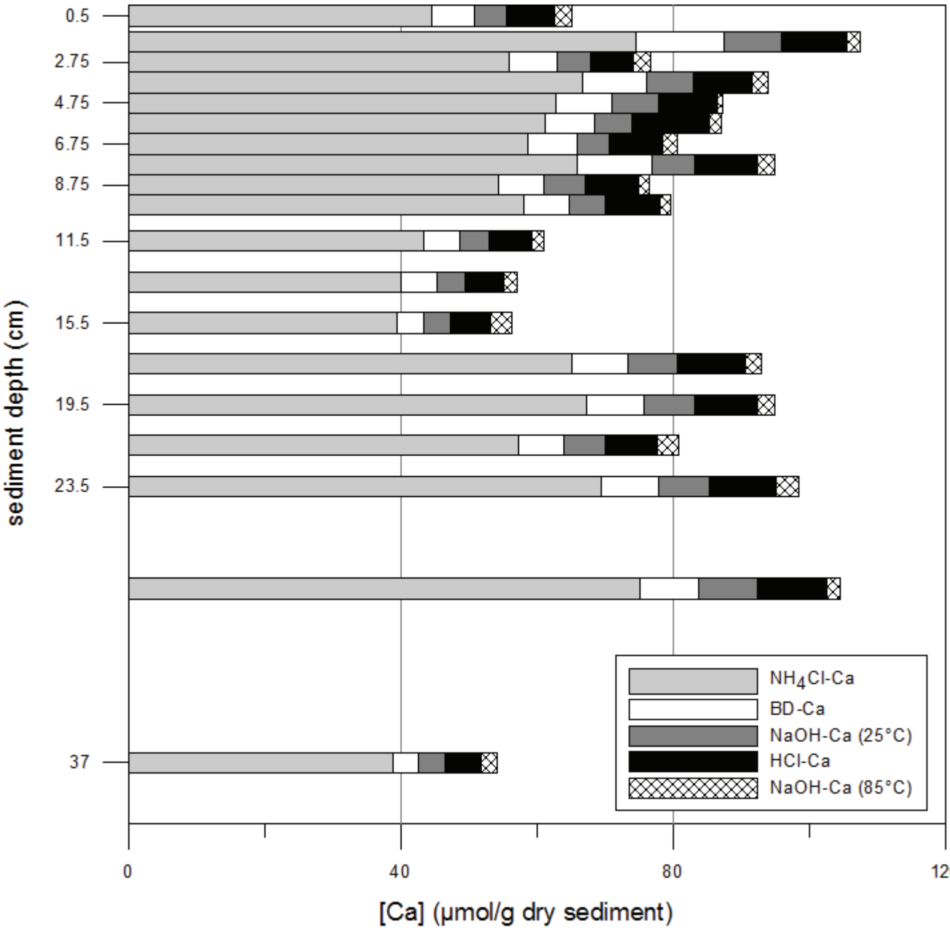

Figure 2.8 Calcium fractionation in Upper Hadlock Pond, Maine core sediments.

Phosphorus fractionation

Average total extractable P (TE-P) in UHP sediment is 51 µmol/g dry sediment. Of this, 88%, on average, of the TE-P is in the NaOH25 fraction, which is operationally defined as P associated with Al hydroxides and oxyhydroxides (Al-P), or biogenic P and organic P (org-P). A negligible amount of P occurs in the other fractions (Figure 2.9, Table 2.6). Of the P in the NaOH25 extract, there are significant amounts of both Al-P and org-P. The proportion of org-P decreases and Al-P increases with increasing sediment depth (age). This is likely due to mineralization of organic P with time, discussed further in Chapter 3.

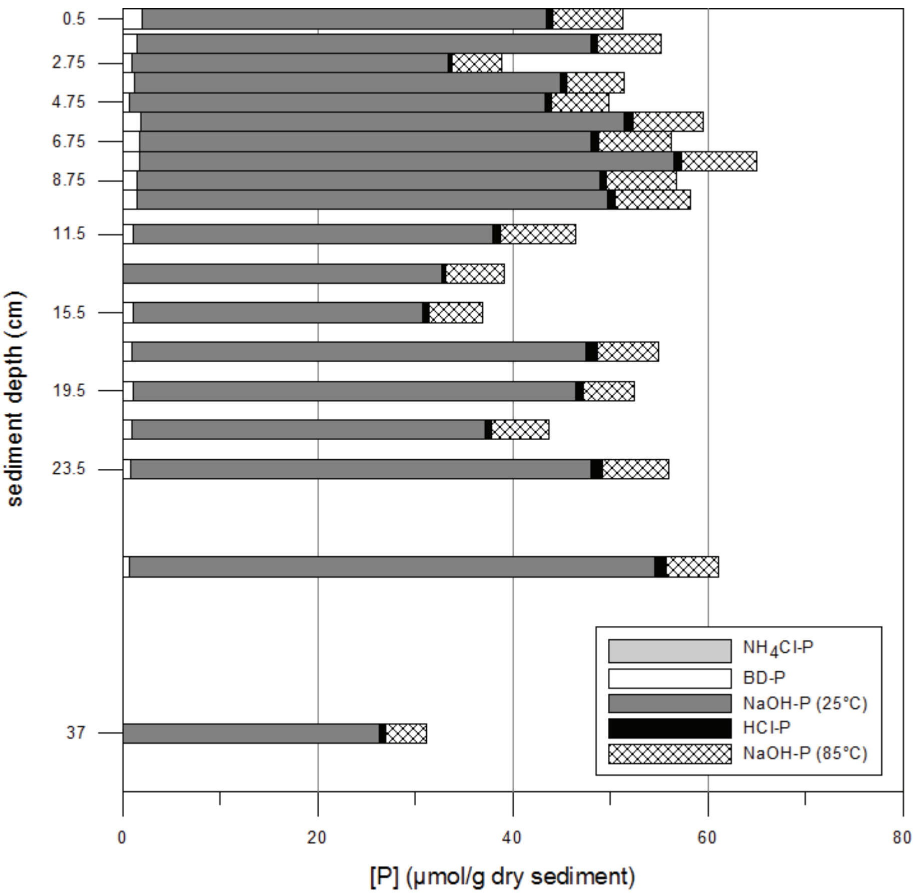

Figure 2.9 Phosphorus fractionation in Upper Hadlock Pond, Maine core sediments.

In summary, the concentrations of the four elements of interest over the period of time captured by the UHP sediment core are displayed in Figure 2.10. Table 2.6 summarizes the proportions of each fraction of Al, Fe, P and Ca throughout the sediment core.

Table 2.6 Percent of total extractable Al, Fe, TP, rP and Ca in the individual extraction steps, averaged for all Upper Hadlock Pond, Maine, USA sediment increments. Numbers in parentheses are ranges of %TE from bottom interval to top interval. ND = no data.

	NH_4Cl	**BD**	**NaOH25**	**HCl**	**NaOH85**
Al	<1	<1	80 *(82-77)*	7 *(5-9)*	10 *(8-11)*
Fe	<1	25 *(19-54)*	54 *(56-36)*	12 *(16-7)*	9 *(8-2)*
TP	<1	2 *(0-4)*	88 *(85-81)*	2	8
rP	ND	ND	40 *(41-25)*	ND	ND
Ca	71 *(72-69)*	9 *(7-10)*	7	10 *(10-11)*	3

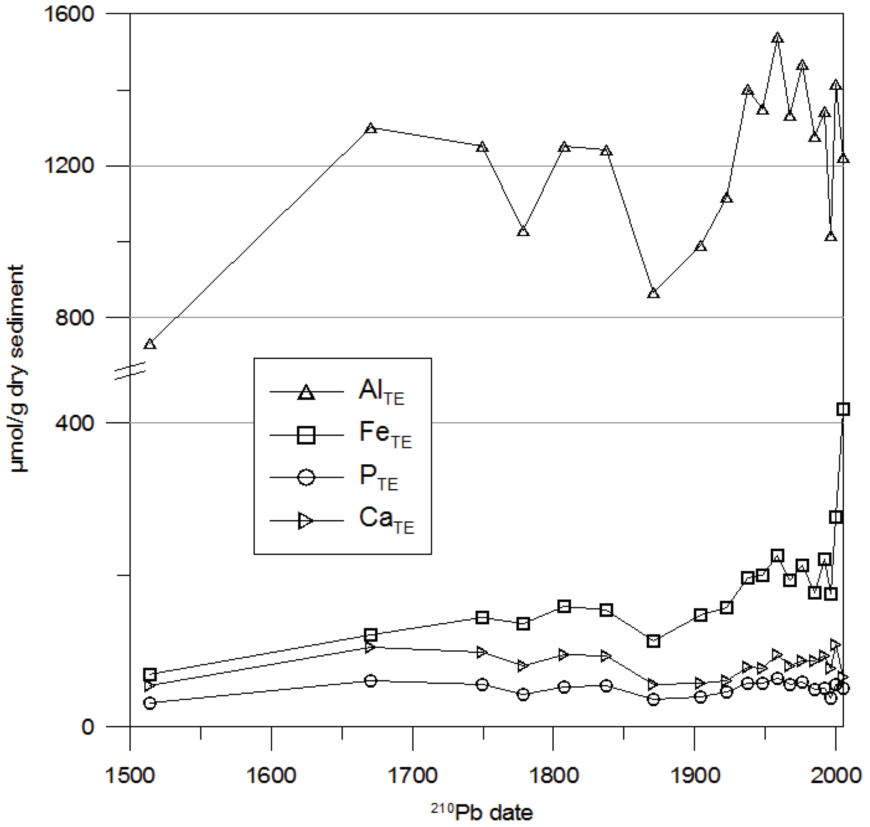

Figure 2.10 Total extractable Al, Fe, P and Ca concentrations in Upper Hadlock Pond, Maine, USA sediments. Pre-1850 dates are extrapolated.

Statistical Correlations

Table 2.7 shows the correlation coefficients and associated significance levels among measured sediment variables in UHP sediment. Most (90%) of the variation in sediment P (mainly as NaOH25-P) concentration is explained by NaOH25-Al concentration in UHP. The significant and relatively high correlation between NaOH25-Al and NaOH25-P increases our confidence in the conclusion that NaOH25-P is P associated with precipitated Al-hydroxide.

Table 2.7 Correlation coefficients of select Upper Hadlock Pond, Maine, USA sediment extraction variables. Units for variables are: LOI, %; depth, cm; element fractions, μmol/g dry sediment. *p-value<0.05; **p-value<0.01.

	Depth	LOI	NaOH25 Al	HCl-Al	BD-Fe	NaOH25 Fe	HCl-Fe	NaOH25 rP	NaOH25 nrP
LOI	0.02								
NaOH25 Al	0.02	0.11							
HCl-Al	0.25*	0.16	0.39**						
BD-Fe	0.35**	0.18	0.01	0.19					
NaOH25 Fe	0.53**	0.16	0.29*	0.70**	0.57**				
HCl-Fe	0.51**	0.08	0.49**	0.71**	0.38**	0.84**			
NaOH25 rP	0.32*	0.00	0.43**	0.02	0.22*	0.02	0.00		
NaOH25 nrP	0.14	0.24*	0.82**	0.52**	0.22*	0.55**	0.72**	0.15	
NaOH25 P	0.01	0.11	0.90**	0.29*	0.00	0.14	0.31*	0.66**	0.73**
NH_4Cl Ca	0.04	0.22*	0.51**	0.38**	0.03	0.08	0.09	0.47**	0.31*
HCl-Ca	0.01	0.01	0.61**	0.30*	0.01	0.07	0.12	0.58**	0.39**

Element flux

Combining total extractable Al, Fe, and P concentrations with mass accumulation rate as in equation (2.7) gives a value for flux of the elements to the lake bottom sediment, normalized for variation in sedimentation rate. The elements exhibit slight changes in flux over the last two centuries, noticeably, a decrease from around 1850 to the early 1900's. There is an apparent increase in Fe flux in recent years, which is attributed to surface enrichment of Fe caused by oxidative precipitation in the water column of previously mobilized Fe(II) after lake turnover, and perhaps from upward diffusion and precipitation of reductively dissolved buried $Fe(OH)_3$. The flux profiles through time for each element appear parallel, though at different values (Figure 2.11), with Al >Fe >P. From this profile we can conclude that though sedimentation rate of UHP has varied in the last 200 years, the sediment quality has remained fairly consistent.

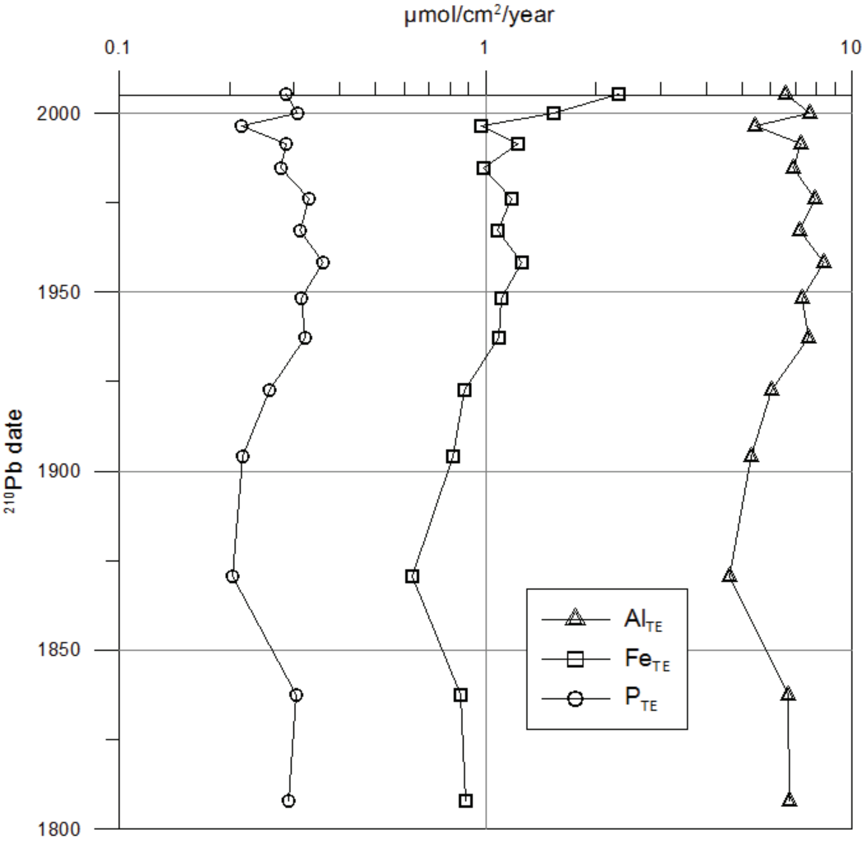

Figure 2.11 Flux of total extractable Al, Fe, and P to the profundal sediment of Upper Hadlock Pond, Maine, USA, normalized to the mass accumulation rate.

Diatom analysis and modeling

Sediment diatoms were enumerated from the UHP core and the results are described below. A graphical representation of the relative species abundances at enumerated sediment intervals is shown in Figure 2.12. Abundance weighted mean

(AWM) values, which represent optimal pH and total P (μg/l) values for the diatom species, are from Dixit et al. (1999) and are given in parentheses after the taxon's name.

Fourteen sediment intervals were analyzed, the deepest (18-18.5 cm) of which dates to ~1700. A total of 175 species (or varieties) were identified, including 33 species of *Eunotia*, 23 species of *Navicula*, and 13 species of *Fragilaria*. The most striking feature of the diatom stratigraphy is the gradual increase in relative abundance of *Cyclotella stelligera* (7.3; 7) starting at 9 cm. The increase is accompanied by a gradual decrease in *Aulacoseira distans* var. *nivalis* (6.3; 7). Also decreasing, starting at about the same time, are all *Navicula,* largely consisting *of Navicula leptostriata* (6.6; 8) and *N. subtilissima* (6.4; 10).

Relative species abundance data were used to reconstruct past pH and total P concentrations of UHP using the model of Ginn et al. (2007). The model is robust for acquiring diatom-inferred pH, but is weak for diatom-inferred total P (DI-TP). The DI parameters obtained for dated sediments using this model are in Table 2.8. The reconstruction shows a slight increase in pH starting at about 1927; the mean pre-1927 DI-pH is 6.41 and the mean post-1927 DI-pH is 6.54. DI-TP, which represents epilimnetic total P concentration, is consistently low (<3 μg/L) throughout the last 200 years, implying historic and persistent oligotrophic conditions of UHP, and in mild disagreement with water chemistry. The mean pre-1927 DI-TP is 2.25 μg/L, twice the post-1927 mean of 1.15 μg/L. This change in sediment P was likely controlled by Al because even a slight pH increase in this circumneutral range is likely to promote $Al(OH)_3$ formation which would scavenge and remove P from the water column. Alternatively, an increase in DOC would be accompanied by increased organically-bound metals, increased production of hydroxide phase in the water column through photo-oxidation, and increased scavenging of PO_4. Indeed there is a subtle increase in both Al and P flux to the sediment in the early part of the 20th century (Figure 2.11) which corroborates these diatom reconstruction data.

Table 2.8 Diatom-inferred pH (DI-pH) and total phosphorus (DI-TP) values for Upper Hadlock Pond sediments. The inferred values are based on a diatom reconstruction model of Ginn et al. (2007).

Interval depth	Sediment boundary dates		Diatom-inferred (Ginn)	
cm	top	bottom	DI-pH	DI-TP (μg/L)
1-1.5	2003	2001	6.56	1.05
2-2.5	1999	1997	6.57	0.80
3-3.5	1995	1993	6.53	1.10
4-4.5	1990	1986	6.59	0.74
5-5.5	1983	1978	6.43	0.94
6-6.5	1974	1970	6.67	1.05
7-7.5	1965	1960	6.54	1.10
8-8.5	1956	1951	6.52	1.27
9-9.5	1945	1940	6.51	1.53
10-11	1935	1927	6.48	1.89
12-13	1919	1909	6.31	1.99
14-15	1896	1879	6.48	1.94
16-17	1863	1847	6.45	2.63
18-19	1832	1815	6.41	2.42

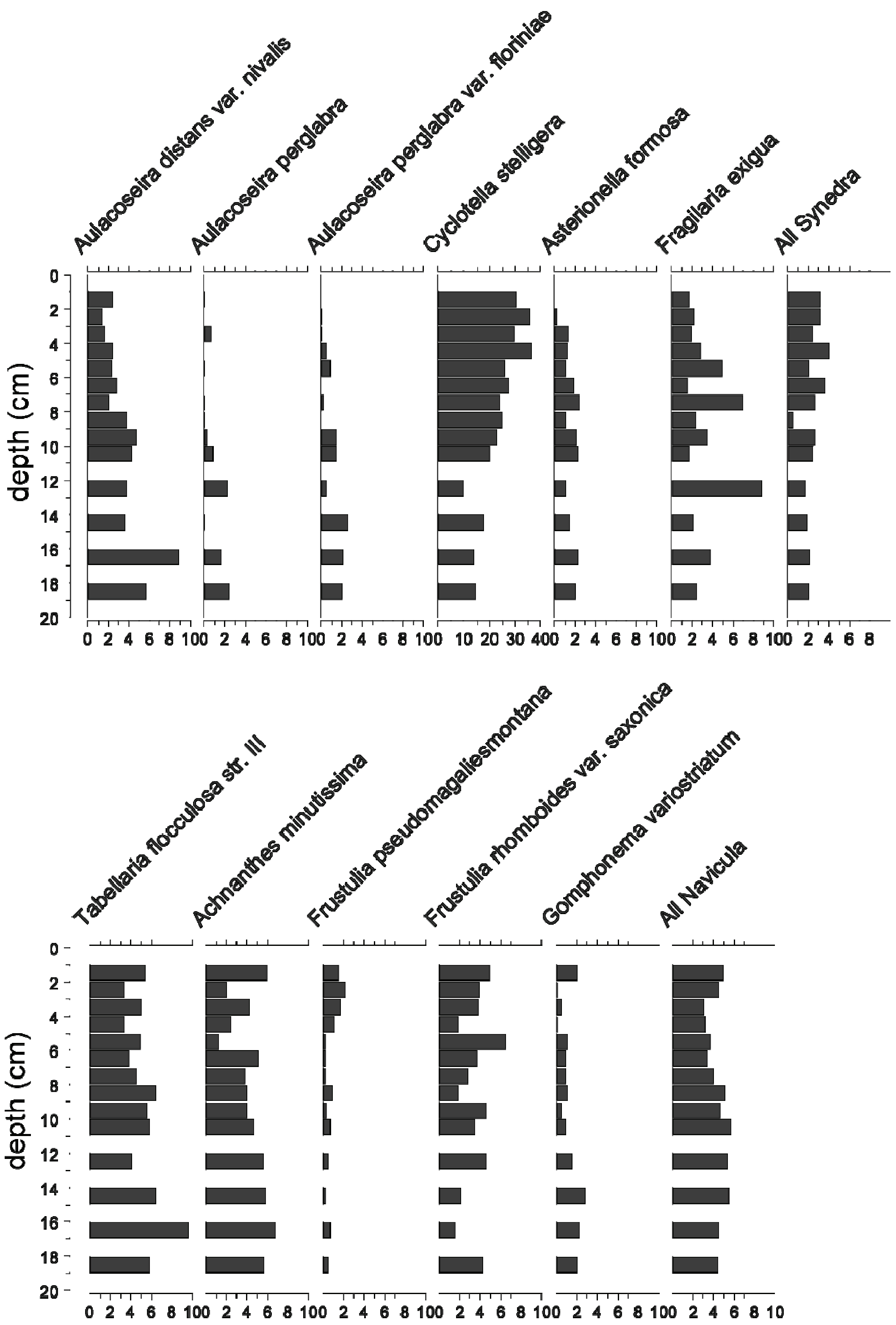

Figure 2.12 Relative abundances (% total) of diatom taxa from 14 sediment intervals of a core from Upper Hadlock Pond, Maine, USA (2005).

Conclusions

Conclusions related to research hypotheses

1. Lakes that have undergone catchment acidification and a resulting increase in Al input will accumulate more Al-rich sediments which retain P (acido-oligotrophication).

The molar concentration of extractable Al in sediment is much greater than that of Fe, Ca, and P for UHP throughout the period represented by the core. UHP (Figure 2.10) exhibits an increase in total Al concentration, most of which is Al-hydroxide, of about 400 μmol/g dry sediment (a 40% increase) between the late 1800s and the late 1900s. The Al concentration data suggest that some mechanism caused an increase in sediment Al in UHP over the past century. Changes in the quality of catchment soils as a consequence of disturbances may have enhanced the export of DOC and organically bound Al to UHP during that time period. Increasing DOC production resulting from spruce-fir forest development in the catchment (Lawrence et al. 1986), a decrease in mineral acid deposition, and/or climate warming (Evans et al. 2005) may promote export of organic Al. An increase in the number and/or magnitude of storm events during this time period is another potential explanation because Al export from the catchment is directly related to stream hydrology.

2. Most sediment P will be associated with $Al(OH)_3$ throughout the acidification period.

This hypothesis is clearly supported, based on the assumption that NaOH25-P is P associated with $Al(OH)_3$. In UHP, this P fraction was by far largest fraction throughout the core. However, dividing this base-soluble portion into reactive (Al-P) and non-reactive (org-P) sub-fractions leads us to a slightly different conclusion. The org-P sub-fraction dominates in shallower (younger) sediments and the Al-P sub-fraction dominates in deeper (older) sediments, likely due to mineralization of organic and biogenic P over time. From this we conclude that initially-sedimented P from the water column is org-P as well as $Al(OH)_3$-sequestered P, and over time much of the org-P becomes liberated by mineralization and re-sequestered as Al-P. Chapter 3 discusses the rates and implications of these P dynamics in more detail.

3. A decrease of biologically-available P during acidification will affect phytoplankton (diatom) species composition and abundance.

The sediment chemistry and diatom analyses show that the pond has been historically slightly acidic and pH has not been significantly affected by acid deposition in the 20th century. The significant (50%) decrease in DI-TP, potentially caused by an increase in pH after about 1927, may have decreased total phytoplankton but not necessarily relative species abundances. The profile of UHP sediment consistently shows evidence of P retention through time. This and consistently low DI-TP values lead us to conclude that P that reaches the sediment is permanently sequestered there, rendered unavailable to biota. Historical effects on diatom species and abundance are likely due to the subtle changes in pH, favoring $Al(OH)_3$ formation and consequent scavenging of already limited bioavailable P from the water column.

4. Acido-oligotrophication may be reversing with reduction of sulfur emissions, which leads to recovery from catchment acidification, and reduced Al flux.

The sulfate (SO_4^{2-}) concentration in precipitation at McFarland Hill, Acadia National Park has declined since monitoring began in 1981 (NADP/NTN 2006) from >30 μeq/L to <20 μeq/L (Figure 2.13), likely in response to industrial emission reductions litigated by the EPA Clean Air Act of 1970 and its amendments in 1990. Nevertheless, the acidity of UHP appears to be relatively unaffected by these changes in atmospheric SO_4^{2-} deposition, as lake pH (Table 2.4) exhibits no identifiable trend since 1982 and DI-pH shows little change between the late 1800s to and the 1970s), and recovery (post-1980). Diatom interpretations do not support significant anthropogenic acidification. We conclude that extractable Al flux has remained high, relative to extractable Fe, P, and Ca throughout the period represented by the core, and likely plays a dominant role in the maintenance of the oligotrophic state of UHP. The changes in Al and P flux to the sediment are very subtle in this system, though the association between them is supported by both diatom reconstruction and sediment extraction chemistry.

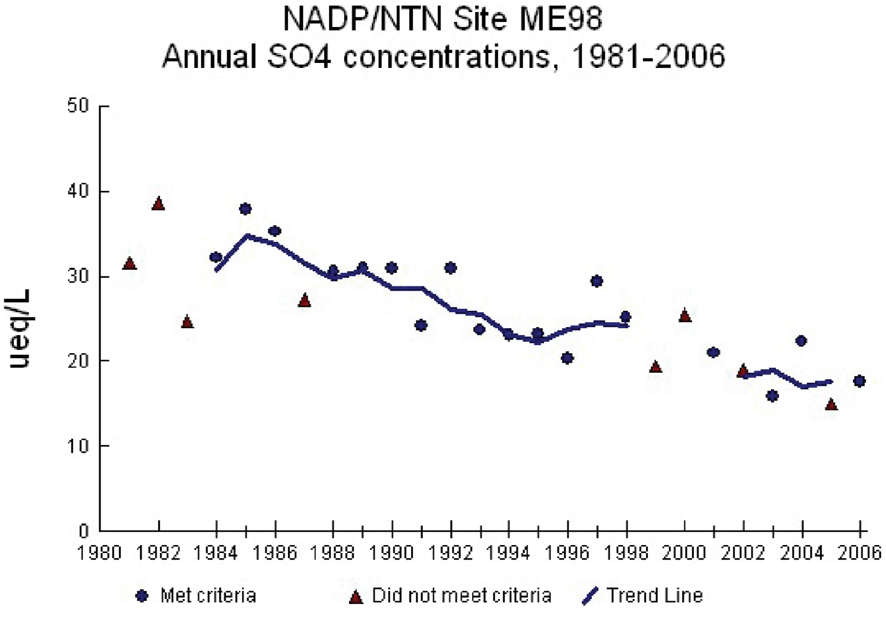

Figure 2.13 Sulfate (SO_4^{2-}) concentration in precipitation at McFarland Hill (Site ME98), Acadia National Park, Maine from 1981-2006). Plot is from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) data set (http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=ME98).

Conclusions

Sediments from UHP comply with conditions for P retention as determined empirically by Kopáček et al. (2005a). The molar ratio of Al as Al (oxy)hydroxides (NaOH25-Al) to labile and reducible P (NH_4Cl-P + BD-P) in the sediment far exceeds 25 throughout the period of time represented by the sediment core (Figure 2.14). The molar ratio of NaOH25-Al to reducible Fe (BD-Fe) exceeds three throughout the same time period, though decreases near the sediment surface occur due to cyclical precipitation of Fe from the water column and precipitation of upward diffusing Fe in the sediment. There is no surface enrichment of sediment P as there is with Fe, so we can assume that P does not cycle to and from the water column as readily as Fe does. Based on this empirical model, along with the DI-TP model evidence, we conclude that UHP has been historically oligotrophic because of sediment phosphorus retention, dominantly by Al hydroxide.

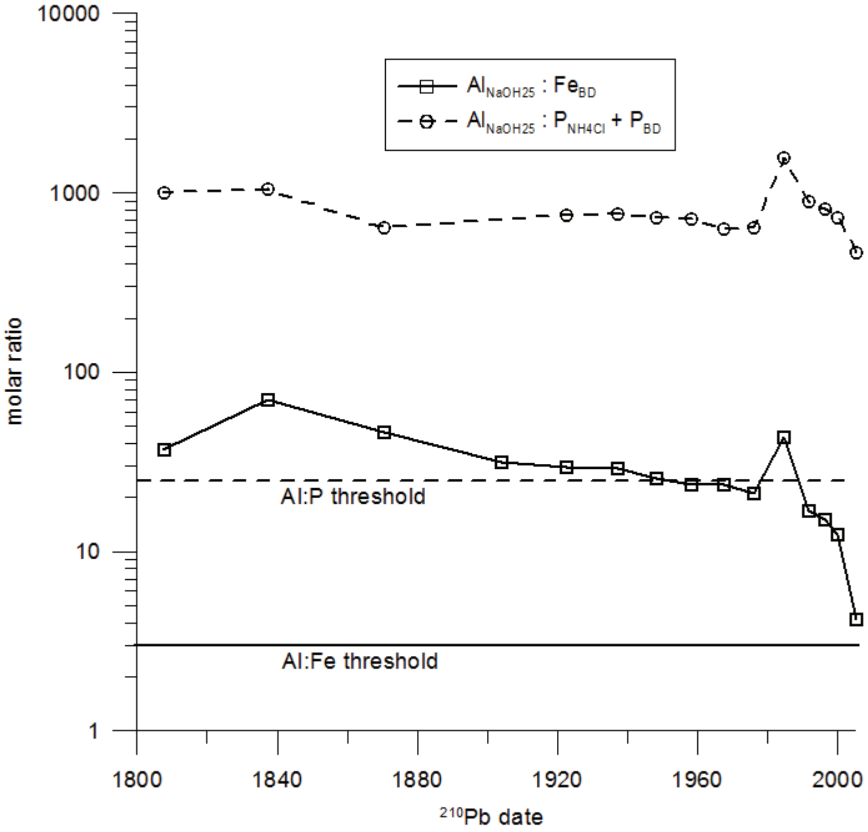

Figure 2.14 Molar ratio (dry weight basis) of NaOH25-Al to NH4Cl-P+BD-P and NaOH25-Al to BD-Fe extracted from dated sediment intervals from Upper Hadlock Pond, Maine, USA. The estimated minimum threshold ratios for P retention by sediment during anoxia are 25 and 3, respectively (Kopáček et al. 2005) as indicated by the horizontal lines.

Though acid deposition does not appear to have a noticeable effect on the geochemistry of UHP, we do see conjectural evidence of other anthropogenic impacts on the catchment. Patterns represented by diatom-inferred pH and slight changes in element flux suggest catchment disturbance(s) in the early 20th century. This could be a signal derived from carriage road construction over Hadlock and Parkman streams in the 1920’s which likely had some impact on sedimentation and chemical inputs to the pond. During that same era (early 1900’s) there was man-powered ice harvest from UHP (Ice Harvesting Sampler, 1991), which may have disrupted the natural biogeochemical winter cycle of the pond and/or the chemical budgets of elements of interest. Pre-1820 construction of route 198 likely temporarily increased sedimentation into UHP.

Climate variability also influences catchment hydrology and temperature, and therefore plays a major role in the transport and fate of biogeochemical signals such as the ones we studied. Precipitation data from the National Climatic Data Center, (http://www.ncdc.noaa.gov/oa/ncdc.html) for coastal Rockland, Maine (about 75 km from UHP) reveal a significant increase in the number of storms (>0.1” precipitation) per year and storm intensities from the period 1949-1999 (Figure 2.15.). Such an intensification of hydrology over this 50 year span likely affected geochemistry of the UHP catchment and may be reflected in the pond sediment, though the extent of the effect is not clear in this study because of the low time resolution represented by our core. Because Al-DOC increases with discharge, changing hydrology may have counterbalanced the decrease in acid deposition in the last 20 years as a factor in mobilizing Al from the catchment to UHP.

In the absence of a complete local climate history, watershed history, and additional chemical analyses, interpretations of the combined anthropogenic influences on Upper Hadlock Pond must remain speculative. Overall, the system appears to be quite stable, and trophic status of the pond has not been affected by local perturbations in the catchment at least in the last two centuries.

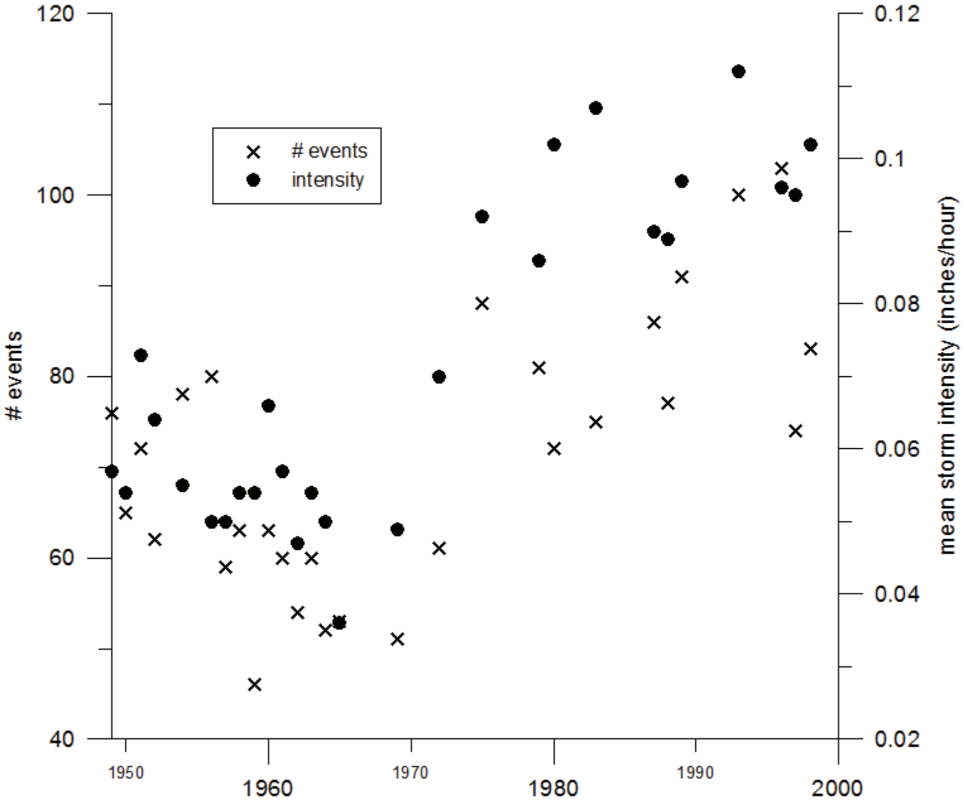

Figure 2.15 Precipitation data for Rockland, Maine from the NOAA National Climatic Data Center (NCDC) online data set. This 50 year record of hydrologic events at a coastal Maine site shows an increasing trend in the number of annual storms and their magnitude.

CHAPTER 3

SEDIMENTARY PHOSPHORUS DYNAMICS IN OLIGOTROPHIC LAKES

Abstract

Sediment cores from three oligotrophic, chronically acidic (pH <6.5) lakes in Maine, USA, were used to study historical lake phosphorus (P). Long-term oligotrophy in these lakes is consistent with high aluminum (Al) hydroxide concentrations in the lake sediments. Aluminum can inhibit internal P loading, even during periods of hypolimnetic anoxia, when P can be liberated from dissolution of sediment iron (Fe) hydroxide. Fractionated P profiles were determined using a sequential chemical extraction technique. Sediments were extracted with NH_4Cl, Na bicarbonate-dithionite (BD), 0.1M NaOH at 25°C, HCl, and 1M NaOH at 85°C. All three lakes meet the criteria for sediment P retention based on threshold sediment concentrations of [NH_4Cl-Al+BD-Al+NaOH25-Al]:[NH_4Cl-Fe+BD-Fe] ratio > 3 and [NaOH25-Al]:[NH_4Cl-P+BD-P] ratio > 25 determined by (Kopáček et al. 2005). The 0.1M NaOH soluble fraction was analyzed for total P (TP) and molybdate-reactive P (rP), the difference being non-reactive P (nrP); rP represents the P associated with $Al(OH)_3$ (Al-P) and nrP represents the organic and biogenic P. Even though TP showed no decrease with sediment depth, as is typically observed in eutrophic lakes, the nrP:TP ratio decreased and the rP:TP ratio increased with depth to a constant value indicating conservation of mineralized organic P. Two models were developed for each lake based on normalized concentrations of nrP and rP through the depth of the cores. The first model assumes a first-order decay of nrP, with the rate

coefficient being a function of time, as freshly deposited nrP is mineralized faster than the more recalcitrant, older nrP of deeper sediments. This model represents irreversible organic P mineralization, where the mineralized inorganic P is permanently sequestered by the sediment. It is likely that any permanent burial of mineralized P in these systems is controlled by sediment $Al(OH)_3$. Alternatively, the data can be modeled with a simple first-order reversible transformation reaction between nrP and rP representing biotic mineralization of organic P followed by incorporation of the inorganic P into microbial biomass. The presence of microbes in the sediment was shown using DNA analysis. In both models, TP is preserved with no loss to the overlying water. The rate coefficients determined by both models are not consistent among the three study lakes. This can be explained by variable quality of allochthonous and autochthonous P and organic matter contributions to, as well as the microbial communities within, the sediments of each lake.

Introduction

Phosphorus (P) concentrations and bioavailability are well-studied for surface waters because P is the limiting nutrient for primary productivity, and therefore controls the trophic status of a lake. Phosphorus is transported to lakes by catchment drainage, and is generally associated with solids of iron (Fe), aluminum (Al), calcium (Ca) and humic substances (Ulrich and Pöthig 2000). Lakes that develop hypolimnetic anoxia during summer or winter stratification may experience P release from the sediment to the water column. Redox values and pH are abiotic factors known to regulate this internal P cycle within lakes, along with biotic factors such as sediment microorganisms (Gächter et al. 1988).

The classic model of P release from lake bottom sediments involves reductive dissolution of Fe(III) following the onset of hypolimnetic anoxia (Einsele 1936; Mortimer 1941). Solid $Fe(OH)_3$ readily adsorbs available orthophosphate (PO_4), removing it from the water column and sequestering it in the sediment. Microbially-catalyzed Fe(III) reduction in the sediment promotes the dissolution of these complexes and the subsequent release of Fe(II) and PO_4.

Microbes may also be directly involved in hypolimnetic P release. Redox-controlled metabolism of stored inorganic polyphosphate (poly-P) by sediment bacteria is another recognized P release mechanism (Hupfer et al. 2004). Poly-P has been measured by nuclear magnetic resonance (^{31}P NMR) spectroscopy in surficial lake sediments, where microbes accumulate it during oxic conditions (Hupfer and Gächter 1995). Poly-P is potentially released from sediment microbes during anoxia and early diagenesis, contributing to its relatively short half-life in sediment (Ahlgren et al. 2005; Reitzel et al. 2006).

Allochthonous and autochthonous organic matter contribute to the sediment P pool and are subject to transformation in the water column and diagenesis after settling. Golterman et al. (1998) attribute mineralization of phytate (inositol hexaphosphate, humic-P from plant material) as a significant source of P release from sediment during anoxia. Because primary production is limited in oligotrophic surface waters, the main sources of nutrients (P, nitrogen, carbon) to lake sediments are likely allochthonous rather than autochthonous. The subsequent fate of sedimented P is highly dependent on chemical gradients between sediment, lake bottom waters, porewater, and biological activity of the benthos.

Amirbahman et al. (2003) found that hypolimnetic P and Fe(II) fluxes from lake sediments do not always correlate with each other. In such cases, elevated concentrations of Al, common in low pH surface waters in Europe and northeastern North America, may control the release of dissolved P from sediment. Solid phase $Al(OH)_3$ forms as a hydrolysis product of dissolved inorganic Al in the pH range of 5 to 7. Because it has a high sorptive capacity for PO_4, $Al(OH)_3$ removes P from the water column despite the low redox potential (Kopáček et al. 2000; Ulrich & Pothig 2000). Photochemical liberation of inorganic Al from organically-bound Al contributes to this pool of precipitating $Al(OH)_3$ (Kopáček et al. 2006).

Based on sediment chemistry data from 43 lakes, Kopáček et al. (2005) proposed a model to define a threshold for release of sediment P based on ratios of operationally-defined soluble fractions (Psenner et al. 1988) of Al, Fe, and P. They used a sequential extraction method involving: (1) Distilled water (H_2O) for loosely-bound and pore-water-soluble Al, Fe and P, (2) 0.1 M sodium bicarbonate-buffered sodium dithionite solution (BD) at 40°C for soluble P associated with reducible Fe-(oxy)hydroxides, (3) 1 M sodium hydroxide at 25°C (NaOH25) for $Al(OH)_3$, remaining Fe(III)-(oxy)hydroxides and associated P, (4) 0.5 M hydrochloric acid (HCl) for acid-soluble minerals such as calcite and apatite, and (5) 1 M NaOH at 85°C (NaOH85) for more recalcitrant mineral and organic Al, Fe and P fractions not extracted in previous steps. The molar ratios of [H_2O–Al+BD–Al+NaOH25–Al]:[H_2O–Fe+BD–Fe+NaOH25–Fe] >3 and [NaOH25–Al]:[H_2O–P+BD–P]>25 are defined as operational targets for estimating the potential for sedimentary P retention in lake sediments. This relationship was later corroborated by Lake et al. (2007) for a set of lakes of varying trophic status in Maine, USA.

More detailed characterization of sediment P separates the NaOH-soluble fraction into non-reactive (nrP) and reactive (rP) components, based on reactivity of PO_4 with molybdenum in a colorimetric method (Murphy and Riley 1962). Measured rP is mainly aluminum-bound P while organic and biogenic P compounds (e.g. poly-P, pyrophosphates, monoesters and diesters) make up the nrP fraction (Ahlgren et al. 2005; Reitzel et al. 2007). Thus nrP concentrations tend to correlate with bacterial biomass in sediment (Goedkoop and Pettersson 2000). Ahlgren et al. (2005) showed that TP and nrP in the Swedish mesotrophic Lake Erken sediments decreased with depth, reflecting mineralization and liberation of dissolved P over time. Using ^{31}P NMR, they distinguished individual components of nrP and found that mono- and diester-P compounds persist for several decades in sediment, whereas pyrophosphates (an inorganic product of cellular ATP hydrolysis) diminished much more quickly. In this case, nrP was considered the primary source of sediment P to be recycled to the water column, due in part to the lack of solid phases (e.g. $Al(OH)_3$) available for adsorption of generated PO_4.

In this study we focus on three lakes in Maine, USA, in order to assess sediment characteristics that contribute to P retention and their stable oligotrophic status. The sediment profiles of these lakes show relatively steady concentrations of total P with depth, even though fractions of TP, namely rP and nrP, change with depth. In contrast, some eutrophic lake sediments exhibit a decrease of TP with depth (Ahlgren et al. 2006; Ahlgren et al. 2005; Carignan and Lean 1991; Hupfer et al. 2004; Malmaeus and Rydin 2006; Penn et al. 1995; Rydin 2000) largely because they consistently release dissolved P, from mineralization, to the water column. We performed sequential chemical extraction of sediments spanning more than a century of deposition to determine whether they meet the Al, Fe and P concentration criteria for P retention as defined by Kopáček et al. (2005). We evaluated the rate of mineralization of nrP with depth (time) using two different models.

Materials and Methods

Site Descriptions

Sediment cores were collected in March 2005 from Mud Pond (MP), Little Long Pond (LLP), and Upper Hadlock Pond (UHP) in eastern Maine, USA (Figure 3.1). MP (N44.634°, W68.088°) drains into LLP (N44.638°, W68.080°); their catchments are currently forested (red spruce, balsam fir, and red oak) and undeveloped, though there are records of both logging and forest fire in the past 150 years (Davis et al. 1994). UHP (N44°19.253', W68°17.240') is located in Acadia National Park, coastal Maine, USA, with a forested and somewhat-developed catchment (paved road and gravel carriage roads). All catchments are well drained, with thin, stony soil and some exposed granite bedrock, maintaining characteristically low acid neutralizing capacity (ANC), acid-sensitive surface waters.

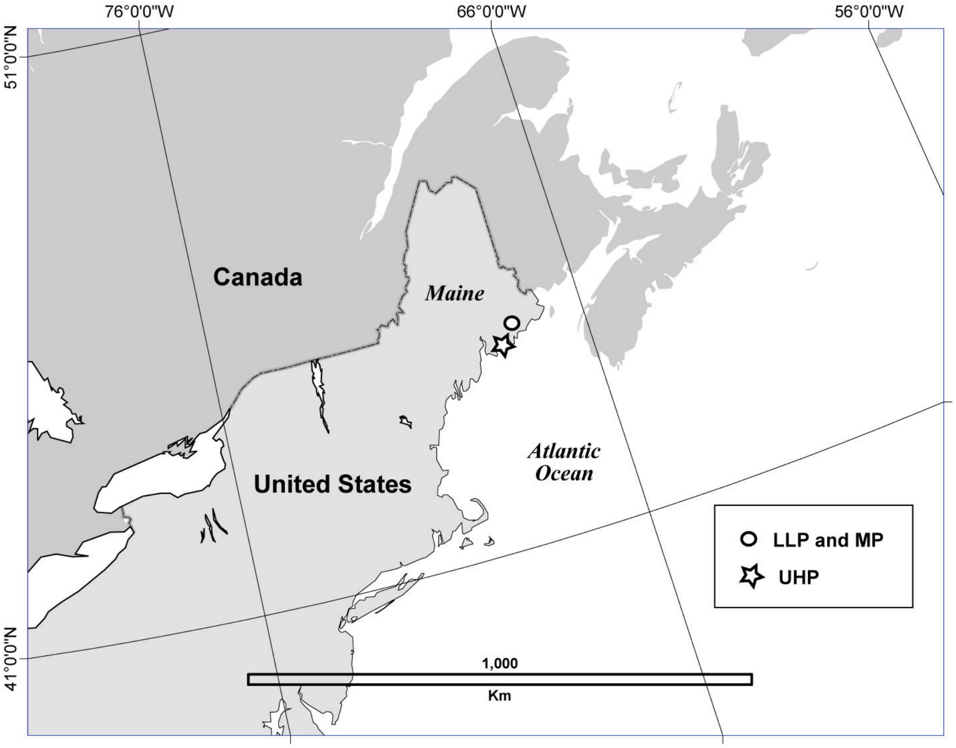

Figure 3.1 Location of study sites. LLP = Little Long Pond; MP = Mud Pond; UHP = Upper Hadlock Pond.

All three ponds are acidic and develop anoxic hypolimnia during seasonal stratification. MP, UHP and to a lesser extent LLP release dissolved reducible metals (Fe and Mn) to their hypolimnia, yet they release little P. Of the three study ponds, MP has the highest dissolved Al concentrations (>200 ug/L) and the lowest pH and ANC. The pH, ANC, and Al concentrations of LLP are lower than those of UHP. Table 3.1 highlights the morphologic and relevant chemical characteristics of each pond.

Table 3.1 Morphological and chemical characteristics of Little Long, Mud, and Upper Hadlock Ponds from Maine DEP, 2006. Chemistry data are ranges of annual mean values (1983-2005) for selected parameters. Analytical methods included gran titration for ANC (acid neutralizing capacity); ion chromatography for SO_4^{2-}; DOC (dissolved organic carbon) by IR; Al, Fe and Mn (total dissolved) by ICP-AES or graphite furnace atomic absorption (pre-1999); P (total) by persulfate digestion/molybdate-blue colorimetry. Fe and Mn values were only measured in 2005.

		Little Long	**Mud**	**Upper Hadlock**
Area (ha)		24.3	1.6	15.4
Drainage area (ha)		236	82	339
Depth$_{max}$ (m)		25.3	16.2	11.3
Elevation (m)		72	102	70
Water residence time (yr)		0.97	0.11	0.24
pH	Epi	5.47 - 6.04	4.61 - 4.87	5.92 – 6.60
	Hypo	5.19 - 5.61	4.61 - 5.08	5.68 – 6.05
ANC µeq/L	Epi	1.1 - 16.9	(-27.2) - (-8.2)	22.1 – 71.4
	Hypo	7.9 - 20.3	(-29.8) - 20.3	18.0 – 88.9
SO_4^{2-} µeq/L	Epi	59 - 80	72 - 105	65 - 108
	Hypo	62 - 79	56 - 110	61 - 102
DOC mg/L	Epi	0.8 - 2.4	2.9 - 5.8	3.1 – 4.5
	Hypo	0.8 - 3.1	3.4 - 6.3	4.5
Al µg/L	Epi	10 - 71	235 - 433	16 - 106
	Hypo	46 - 84	310 - 439	108 - 195
P µg/L	Epi	1 - 4	4 - 8	2 - 11
	Hypo	5 - 12	7 - 17	7 - 12
Fe µg/L	Epi	4	33	25
	Hypo	29	514	532
Mn µg/L	Epi	18	8	11
	Hypo	22	16	303

Sediment collection and processing

Sediment was obtained during ice-cover (March 2005) at near-profundal depths of 24, 13, and 11 m for LLP, MP, and UHP, respectively, using a 10 cm diameter, stationary piston corer with an acrylic core tube (Davis and Doyle 1969). Sediment cores were sectioned at the lake using stainless steel and plastic ware. Sediment was sectioned in 0.5 cm intervals from 0 to 10 cm, in 1 cm intervals from 10 to 30 cm, and in 2 cm intervals from 30+ cm. Samples were placed directly into Whirlpack™ bags and stored at 4°C in the dark.

At the laboratory, wet sediment aliquots were dried at 100°C in ceramic crucibles for percent water determination. The remaining sediment was frozen at -20°C until processed for further analysis. Dried sediment aliquots were homogenized with ceramic mortar and pestle and percent loss on ignition (%LOI) was determined by heating ~0.5 g of dried sediment to 550°C for 4 hr. Carbon (C) and nitrogen (N) were measured by combustion (LECO CN-2000 analyzer). DNA concentration was determined in wet sediments, and we determined specific functional groups (detailed methods below) with quantitative polymerase chain reaction (qPCR). Dry sediment was dated by quantifying gamma activity of ^{210}Pb. The constant rate of supply (CRS) model of Appleby and Oldfield (1978) was used to calculate sediment age based on determination of supported and unsupported ^{210}Pb activities.

Sediment chemistry

Operationally-defined fractions of Al, Fe, and P were determined based on a sequential extraction procedure of Psenner et al. (1988). We modified the first step by using NH_4Cl instead of distilled water (Tessier et al. 1979) and the third step by using 0.1M NaOH in place of 1M NaOH (Hieltjes and Lijklema 1980). The sequence was performed on 1 g or more of wet sediment using the following steps: A) 1M NH_4Cl, pH 7, at 25°C for 1 hr to obtain the loosely sorbed, exchangeable, and porewater fractions, B)

0.11M Na bicarbonate-dithionite (BD) at 40°C for 30 min to release the reducible fractions, primarily Fe and Mn (oxy)hydroxides and associated P, C) 0.1M NaOH at 25°C for 16 hr to dissolve some Al and Fe (oxy)hydroxides and associated P, as well as some organic and biogenic P, D) 0.5M HCl at 25°C for 16 hr to dissolve acid soluble minerals, and E) 1M NaOH at 85°C for ≥24 hr to solubilize residual material. Total extractable (TE) concentrations are the sum of concentrations from the five sequential extractions. Extractions were performed on 21 sediment core sections from LLP, 22 from MP, and 19 from UHP, with higher frequency in the top 10 cm of each core. Batches of 16 samples were extracted together and each batch contained a duplicate sample and a reagent blank. For each step, the extraction solution was added to an aliquot of wet sediment in a 50 mL plastic centrifuge tube, capped and shaken in a water bath at temperature for the appropriate amount of time, and centrifuged at ~3000 rpm for 15 min. The supernatant was collected and the sediment rinsed with extraction solution, centrifuged and decanted a second time.

Concentrations of Al and Fe in the extracts were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES; Perkin-Elmer model 3300XL). TP was analyzed by either ICP-AES (for the BD, NaOH25, HCl, and NaOH85 solutions) or by the molybdate-blue spectrophotometric method with persulfate oxidation, based on Murphy and Riley (1962) (for the NH_4Cl solution). The NaOH25 fraction was also analyzed using the molybdate-blue method for reactive P (NaOH25-rP), which is the P in solution as PO_4 and is assumed to be associated with Al in the sediment. The difference between NaOH25-TP and NaOH25-rP is NaOH25-nrP (non-reactive P) (Furumai and

Ohgaki 1982; Psenner et al. 1988). NaOH25-nrP is likely the organic-P and bacteria-incorporated P fraction (Ahlgren et al. 2005).

DNA extraction and quantitative PCR

DNA was extracted from approximately 1 g of sediment according to manufacturer's instructions using the Ultraclean Soil DNA Kit (MoBio Laboratories, Inc., Carlsbad, CA). DNA was quantified in a Stratagene MX3000P using the Quant-it picogreen dsDNA assay kit (Molecular Probes, Eugene, OR). Real-time quantitative PCR reactions were then performed in a Stratagene MX3000P to assess the abundance of denitrifiers, *Geobacter*, sulfate-reducing bacteria, and methanogens using the primer sets indicated in Table 3.2. Reactions were performed using the Quantitect SYBR green PCR kit (Qiagen, Valencia, CA) and 0.6 μM final primer concentration, with melting curves performed at the end of each reaction to ensure product integrity. Forty cycles were performed at the recommended temperatures and times with one modification. The fluorescence reading was taken after extension, followed by a post-extension heating step at the temperature indicated in Table 3.2. Plasmids containing the gene of interest were used as quantitation standards, and were prepared by cloning PCR products into the pcR2.1 plasmid using the Topo TA cloning kit (Invitrogen, Carlsbad, CA). Concentrations were normalized to dry weight of sediment.

Table 3.2 Parameters for qPCR analyses of sediments from Little Long, Mud, and Upper Hadlock Ponds. *Geobacter* quantification is a proxy for Fe-reducers.

Functional group	Target gene	Primer	Anneal Temp (°C)	Read Temp (°C)	Primer Reference
Denitrifiers	*nir*S *nir*K	Flacd, R4cd Flacu, R3cu	55	84	Hallin & Lindgren (1999)
Geobacter	*16s rRNA*	Geo494f, Geo825R	53	83	Anderson et al. (1998) Holmes et al. (2002)
Sulfate-reducing bacteria	*dsr*B	dsrp2060f, dsr4r	55	82	Geets et al. (2006) Wagner et al. (1998)
Methanogens	*mcr*A	mcrAf, mcraR	56	82	Luton et al. (2002)

Results

Sediment Chemistry

Sediment LOI, and C and N concentrations varied among the three study ponds (Figure 3.2). MP had the highest mean LOI, C and N, followed by LLP then UHP. The mean C:N ratio was lowest in UHP (12.96), followed by LLP (13.45), and MP (14.7), and was most variable in MP. In all cores, the average total extractable Al (Al-TE) was at least 14 times higher than P-TE and at least four times higher than Fe-TE. Only in MP is P-TE greater than Fe-TE (Table 3.3). The highest percentages of extractable Al and P are in the NaOH25 fraction, whereas Fe occurs roughly equally in the BD and NaOH25 fractions. The Al, Fe and P concentrations resulting from the sequential extraction are in Figure 3.3.

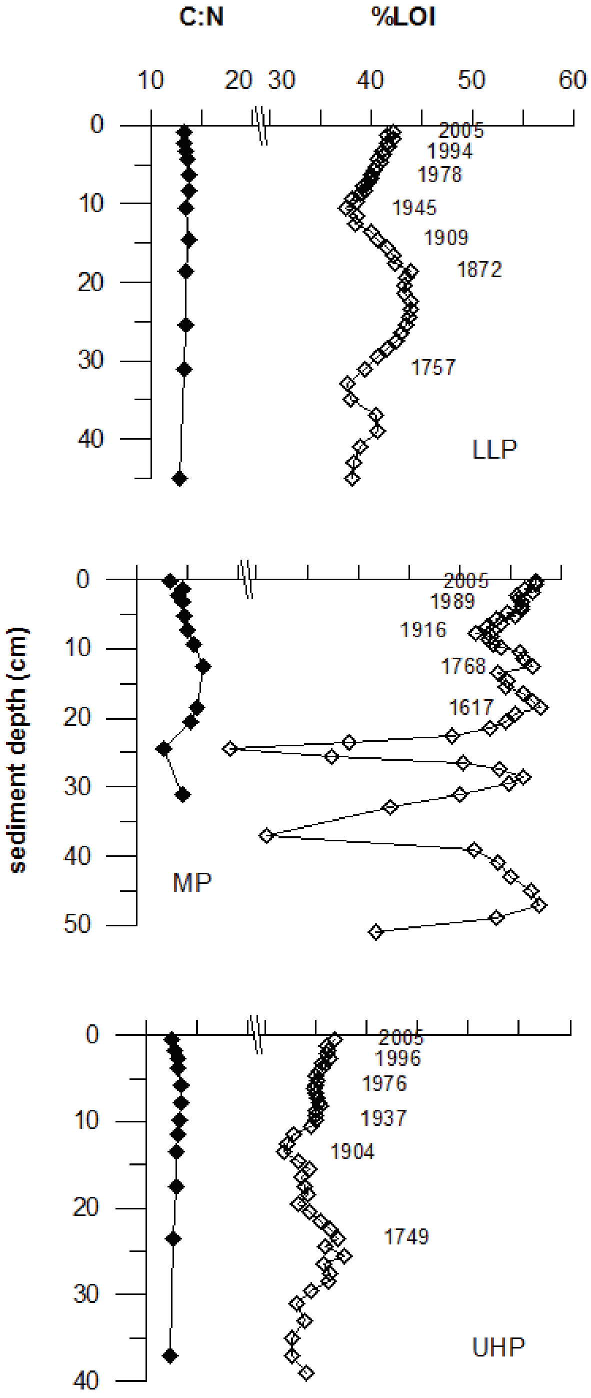

Figure 3.2 Carbon/nitrogen ratio (C:N, filled diamonds) and percent loss on ignition (%LOI, open diamonds) of sediment through the depth of profundal cores taken from Little Long (LLP), Mud (MP), and Upper Hadlock (UHP) Ponds. Select ^{210}Pb dates (those older than ~150 years are extrapolated) are displayed for reference.

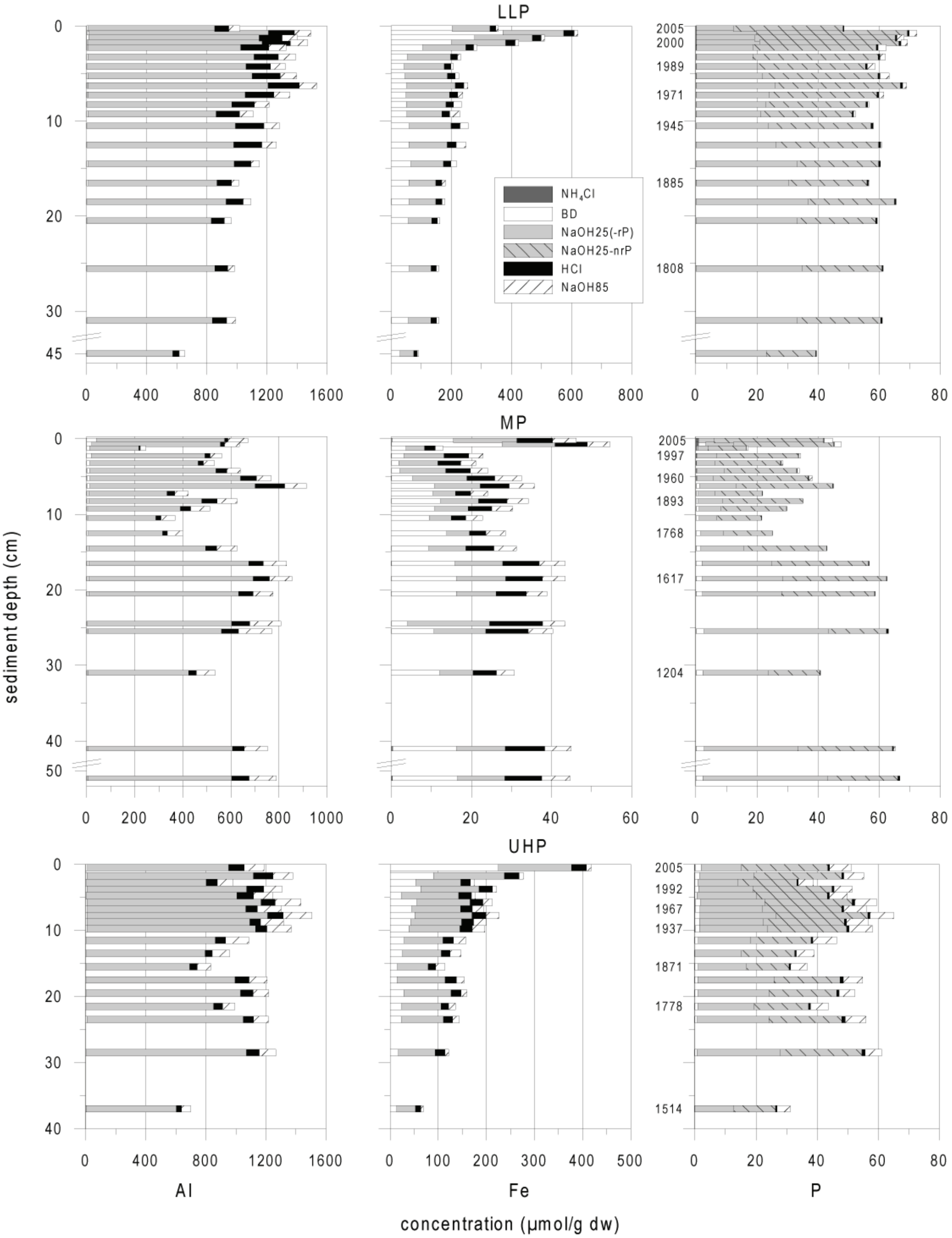

Figure 3.3 Results from sequential extraction of sediments from Little Long Pond (LLP), Mud Pond (MP) and Upper Hadlock Pond (UHP). Corresponding years of deposition, determined by ^{210}Pb dating, and extrapolated dates are shown on the P graph for each pond.

Table 3.3 Mean concentration ± standard deviation of % loss on ignition (LOI) and total extractable elements per gram of dry sediment from all sequentially-extracted intervals of Little Long Pond (LLP), Mud Pond (MP), and Upper Hadlock Pond (UHP) cores.

	LOI	Al-TE	Fe-TE	P-TE
	%	---------------µmol/g dry sed--------------		
LLP	41 ± 1.9	1210 ± 222	260 ± 125	60 ± 7.3
MP	52 ± 8.7	638 ± 176	34 ± 10	43 ± 16
UHP	35 ± 1.5	1218 ± 210	184 ± 74	51 ± 9.1

Of the P in the NaOH25 extract, there is a consistent decrease in the nrP and increase in the rP fractions with increasing sediment age (Figure 3.3). P-TE does not change significantly with depth. This suggests that there is a transformation of nrP to rP that takes place without any significant release of P from the sediment. We developed two models of sedimentary P dynamics that describe this transformation (Figures 3.4 and 3.5). These models assume a constant sediment deposition rate and a negligible loss of P from the sediment to the overlying water.

Model A: Variable rate coefficient in the transformation of nrP (the irreversible model)

The basis for this model is that sediment nrP is subject to first-order mineralization with time (depth), and that its corresponding rate coefficient is a function of time (Figure 3.4). According to this model, the more labile nrP is mineralized faster initially, and with time, the more recalcitrant nrP is mineralized at a slower rate, and mineralization is an irreversible process.

$$\frac{d[\mathrm{nrP}]}{dt} = -k(t)[\mathrm{nrP}] \tag{3.1}$$

The data fit an exponentially-decaying rate coefficient as follows:

$$k(t) = ae^{-bt} \tag{3.2}$$

where *a* is the initial rate coefficient and *b* is the rate constant for the decay of the rate coefficient *k(t)*. The analytical solution to equation (3.1) is

$$[\mathrm{nrP}] = [\mathrm{nrP}]_{\circ} \exp\left(\frac{a}{b}\left(e^{-bt} - 1\right)\right) \tag{3.3}$$

The constants *a* and *b* were fitted using non-linear least squares technique and are shown in Table 3.4 for each lake. Model simulations for sediment rP are based on mass balance (conservation of total NaOH25-P) with respect to sediment nrP. Simulated sediment rP is calculated as follows:

$$[\mathrm{rP}] = [\mathrm{nrP}]_{\circ} + [\mathrm{rP}]_{\circ} - [\mathrm{nrP}] \tag{3.4}$$

According to this model, the mineralization rates (*k(t)*) of sediment nrP depend on the age of the sediment. The order of increasing *k(t)* in younger sediments (t = 10 y) is MP<UHP<LLP. In older sediments (t = 100 y), the sequence changes to UHP<MP<LLP.

Table 3.4 Calculated constants for the transformation of nrP to rP in sediments of three oligotrophic lakes in Maine, USA. The constants are based on an irreversible model (Model A) with a variable rate coefficient and a reversible reaction model (Model B).

	Model A		**Model B**		
	***a* (yr^{-1})**	***b* (yr^{-1})**	**k_f (yr^{-1})**	**k_r (yr^{-1})**	**K (= k_f/k_r)**
Little Long Pond	9.34×10^{-3}	1.52×10^{-2}	1.14×10^{-2}	9.26×10^{-3}	1.23
Mud Pond	1.27×10^{-3}	1.40×10^{-3}	7.01×10^{-3}	2.13×10^{-2}	0.33
Upper Hadlock Pond	8.76×10^{-3}	2.52×10^{-2}	2.91×10^{-2}	3.09×10^{-2}	0.94

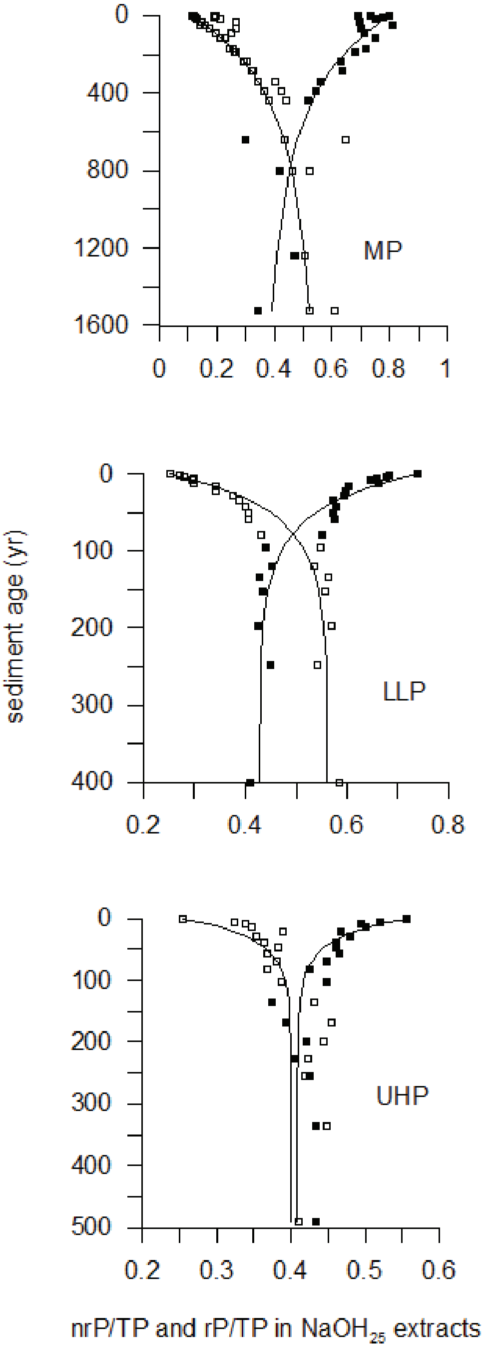

Figure 3.4 Variable rate coefficient model (solid lines) fitted to data from the three study ponds. Solid points are nrP/TP and hollow points are rP/TP from the NaOH (25°) extraction. The model implies that the rate of transformation of nrP (non-reactive phosphorus) to rP (reactive phosphorus) is a function of time.

Model B: Reversible reaction between nrP and rP (the reversible model)

The basis for the model is a simple first-order reversible transformation reaction between nrP and rP (Figure 3.5). Surface sediments initially carry a higher amount of nrP than rP and with time, nrP is transformed to rP. However, the steady-state ratio of the two implies that the transformation may also be a reversible process:

$$\mathrm{nrP} \underset{k_r}{\overset{k_f}{\rightleftarrows}} \mathrm{rP} \tag{3.5}$$

that leads to

$$r_{\mathrm{nrP}} = -k_f[\mathrm{nrP}] + k_r[\mathrm{rP}] \tag{3.6}$$

$$r_{\mathrm{rP}} = k_f[\mathrm{nrP}] - k_r[\mathrm{rP}] \tag{3.7}$$

where r_{nrP} and r_{rP} are the transformation rates for nrP (mineralization) and rP (incorporation into microbial cells), respectively, and k_f and k_r are the forward and reverse transformation rate constants, respectively. Equations (3.6) and (3.7) were approximated using the finite difference method, and the best fits to the rate constants were provided using the non-linear least squares technique. Calculated rate constants are in Table 3.4. According to this model, the k_f and k_r values for the study ponds are in the order MP<LLP<UHP and LLP<MP<UHP, respectively.

We used the forward transformation rates, k_f or $k(t)$, derived from each model to calculate the half-life ($t_{1/2} = -\frac{\ln(0.5)}{k_f}$) of sediment P in each of these three oligotrophic ponds for comparison with other published values.

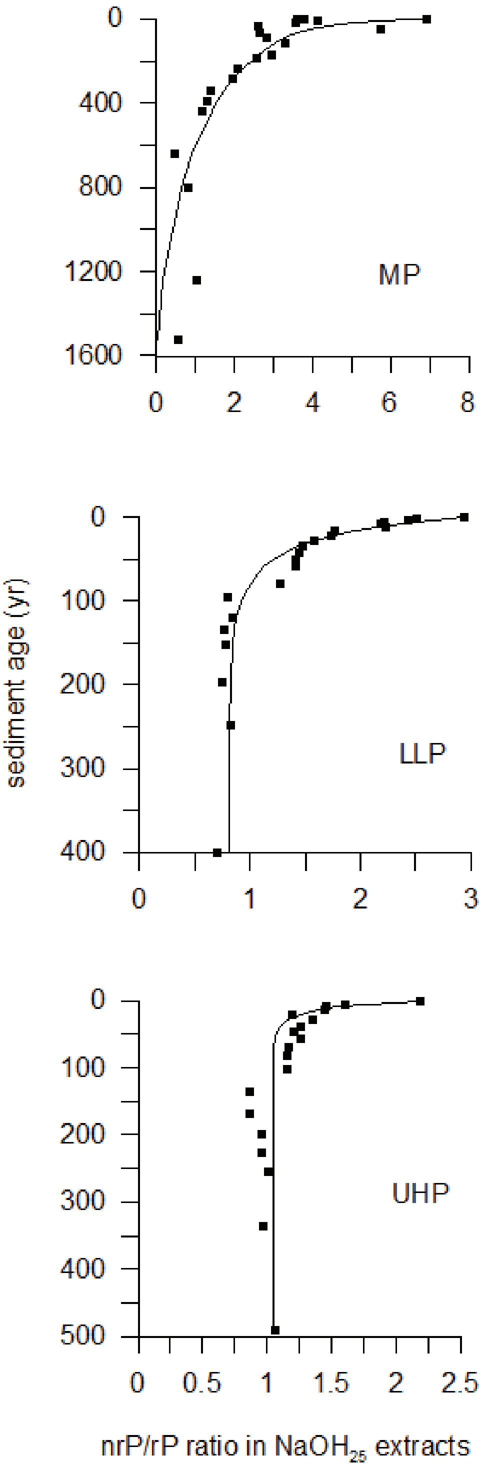

Figure 3.5 Reversible reaction model (solid line) fitted to data points from the three study ponds. The models imply a first-order reversible transformation of nrP (non-reactive phosphorus) to rP (reactive phosphorus) that reaches a steady state with age (depth).

Microbial analysis

Total sediment DNA concentration differed among the three lakes as did the number of organisms from each functional group (Table 3.5). Figure 3.6 shows DNA concentration and the abundance of organisms per gram of dry sediment for each functional group through the depth of each core. Dsr (sulfate reducers) were the most abundant functional group in all cores throughout the depth of each, followed by Geo (proxy for Fe-reducers). In MP, there is a significant linear correlation between nrP/rP and DNA concentration (Figure 3.7) as both decrease with depth (age) in the core. This relationship does not appear in LLP or UHP sediment.

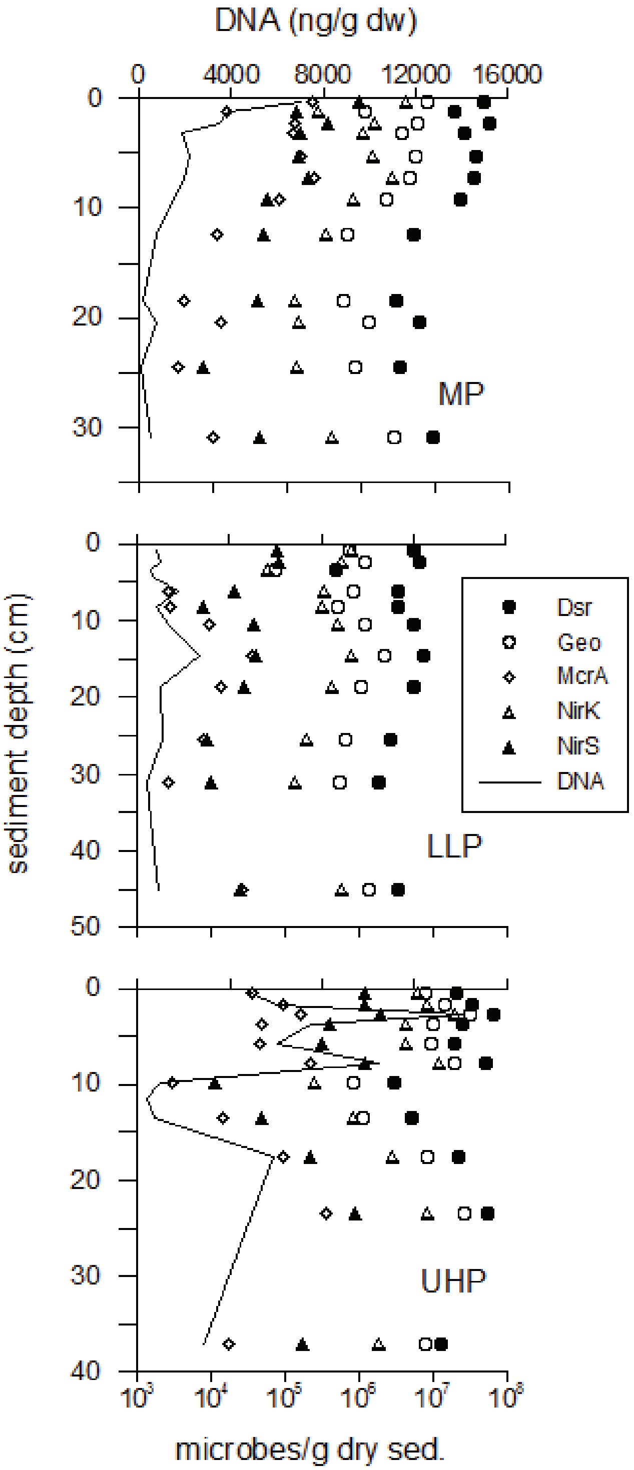

Figure 3.6 DNA concentration (ng/g) and quantities of microbial functional groups through depth of sediment cores from the study sites. Geo = *Geobacter*; Dsr = sulfate reducers; McrA = methanogens; NirK and NirS = denitrifier groups.

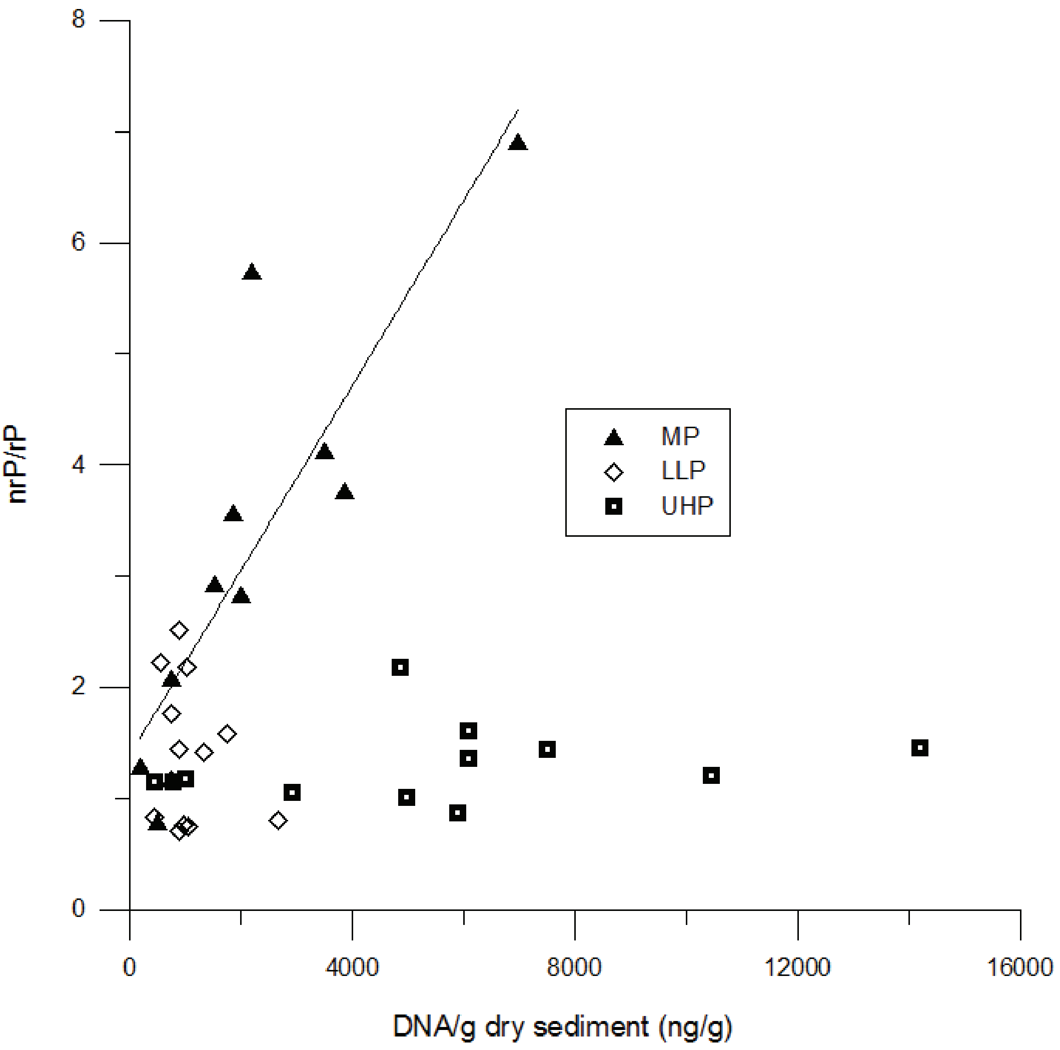

Figure 3.7 Relationship of nrP/rP to DNA concentration in sediment from the three study ponds. The solid line is a linear fit ($r^2 = 0.74$) for MP data, the only pond that exhibits a significant correlation.

Table 3.5 Half-life ($t_{1/2}$) values calculated for sediment P fractions and their sources from this and previous studies.

Diagenetic material		$t_{1/2}$ (yr)	Reference
Lake sediment P, fast fraction		0.14	(Penn et al. 1995)
Lake sediment P, slow fraction		6.3	
Water column P; model		0.09 – 0.63	
Aged algae; experimental		0.11	
Organic sediment P; model		0.02	
Exchangeable sediment P; models		9.9	
		3.9	
		2.4 – 17.3	
		1.9	
Marine sediment P; model		2.3	
Lake sediment; model		0.04 – 0.08	(Schauser et al. 2004)
Lake sediment; biogenic P fractions		13 - 23	(Ahlgren et al. 2005)
Lake sediment; biogenic P fractions	NaOH-soluble humic	6 – 88	(Reitzel et al. 2006)
	NaOH-soluble non-humic	1 – 29	
Lake sediment; biogenic P fractions		0.8 – 7.1	(Reitzel et al. 2007)
Marine sediment; biogenic P fractions		3--16	(Ahlgren et al. 2006)
Lake sediment; reversible model	LLP	61	This study
	MP	99	
	UHP	24	
Lake sediment; irreversible model	LLP	74	
	MP	546	
	UHP	79	

Discussion

In eutrophic and mesotrophic lakes, the input of P over time is typically larger than the amount finally stored in the sediment (Rydin 2000). Several studies of the mesotrophic Lake Erken, Sweden (Ahlgren et al. 2005; Reitzel et al. 2007; Rydin 2000) and hypertrophic Lake Onandaga, New York (Penn et al. 1995) describe a net loss of P from sediment over time by characterizing the concentrations of P fractions in lake sediment profiles using the same chemical extraction sequence employed in this study. Biogenic P (NaOH25-nrP) from Lake Erken sediments was further characterized by Ahlgren et al. (2005) using ^{31}P NMR spectroscopy, quantifying rates of degradation (Table 3.6) of various P compounds that contribute to the mobile P pool. Malmaeus and Rydin (2006) and Ahlgren et al. (2006) attribute net loss of sediment total P to mineralization and upward diffusion of dissolved P to the water column in Lake Erken and in a eutrophic area of the Baltic Sea. Hupfer et al. (2004) found that most lake surficial sediments (0-0.5 cm depth) have higher total P, BD-P, NaOH25-rP, and NaOH25-nrP than deeper sediments (4-5 cm depth), likely due to mobilization of diagenetically-altered solid P with time. In their comparison of six European lakes, one oligotrophic lake and one mesotrophic lake with intensive sediment bioturbation did not have this P gradient.

The lakes in our study are oligotrophic and do not release appreciable dissolved P from their bottom sediments, despite the seasonal development of stable anoxia and release of dissolved Fe(II) (MP and UHP) and Mn(II) (UHP) (Table 3.1). Additionally, the profundal sediment total P does not decrease with depth in any of the study lakes, lending evidence to their long-term P retention capacity. The decrease in nrP and increase in rP with depth suggest that P mineralization occurs with time but there is no upward diffusion of dissolved P. Instead, we propose two possible explanations backed by the models presented above: a) Mineralized nrP becomes sequestered by redox-insensitive $Al(OH)_3$ in the sediment, as Al is dominant throughout depth in all three cores, as shown by model A (Figure 3.3); b) Sediment nrP is mineralized to rP by the resident microbes, and then incorporated into the microbial biomass as nrP, as shown by model B. The presence of microbes at depth in these sediments is shown in Figure 3.6.

Table 3.6 Mean values and ranges (in parentheses) of DNA concentration, numbers of microbes of various functional groups (see Table 2 for definitions), and carbon to nitrogen ratio (mass:mass) in sediment cores from the three study ponds.

	DNA µg/g	Geo	Dsr	McrA	NirK + NirS	C:N
		------------------organisms/g x 10^6------------------				
LLP	1.09 (0.44 – 2.66)	0.95 (0.076 – 2.2)	4.1 (1.9 – 7.4)	0.013 (0.003 – 0.035)	0.46 (0.06 – 0.89)	13.45 (12.87 – 13.82)
MP	2.00 (0.12 – 6.98)	3.1 (0.59 – 8.1)	22.4 (3.0 – 54.7)	0.083 (0.004 – 0.24)	1.3 (0.15 – 5.2)	14.70 (12.66 – 16.50)
UHP	5.42 (0.43 – 14.2)	12.6 (0.86 - 31.8)	28.9 (2.9 – 67.8)	0.10 (0.003 – 0.36)	6.9 (0.25 – 21.0)	12.96 (12.29 – 13.50)

Role of aluminum in lake trophic state

All ponds meet the requirements for sediment P retention as defined by Kopáček et al. (2005) and supported by Lake et al. (2007), based on molar ratios of Al, Fe and P fractions, throughout the periods of time represented by the cores (approximately 400, 1500, and 500 years for LLP, MP and UHP, respectively). In LLP, MP and UHP the ratio of [NH_4Cl–Al+BD–Al+NaOH25–Al] to [NH_4Cl–Fe+BD–Fe] ranges from 3.3 to 24.8, 20.1 to 255, and 4.2 to 69.9, respectively. The ratios of [NaOH25–Al] to [NH_4Cl–P+BD–P] throughout each core exceed 5000, 150, and 450 in LLP, MP and UHP, respectively. In all sediment intervals the Al:Fe ratio is > 3 and Al:P is > 25 (Figure 3.8), thus exceeding the threshold for P-retention by the sediment $Al(OH)_3$.

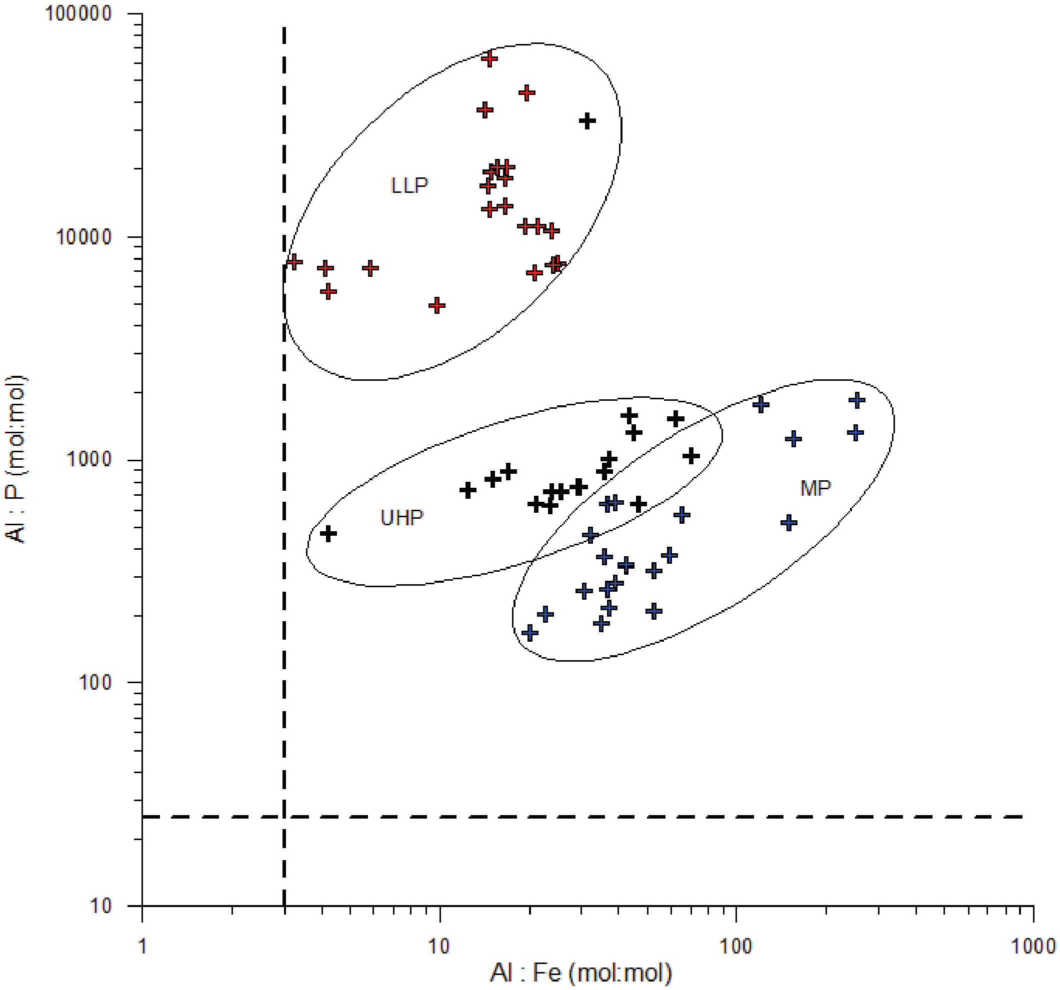

Figure 3.8 Ratio of NaOH25-Al to NH_4Cl-P+BD-P (Al:P) versus the ratio of NH_4Cl-Al+BD-Al+NaOH25-Al to NH_4Cl-Fe+BD- Fe (Al:Fe) for Little Long Pond (LLP), Mud Pond (MP) and Upper Hadlock Pond (UHP) sediments. The dashed lines represent the thresholds of Al:Fe and Al:P for P retention in lake sediments as defined by Kopáček et al. (2005).

Transformation models

The relatively good correspondence between rP data and simulated rP in both transformation models A and B suggests that, as nrP is mineralized, it is incorporated into the rP fraction, and that any P release into the water column following nrP mineralization is negligible. However, the nature of rP fraction at depth is not clear. The irreversible model (Model A) suggests that the ultimate fate of rP is adsorption to metal hydroxides that precipitate from the water column and age indefinitely in the sediment. This rP fraction may include primarily P associated with $Al(OH)_3$, but may also include P associated with vivianite ($Fe_3(PO_4)_2$). Because high concentrations of $Al(OH)_3$ increase the P sorption capacity of lake sediments (Kopáček et al. 2000), the elevated sediment Al found in LLP, MP and UHP sediments could lead to permanent burial of rP following its mineralization, with insignificant diffusion of dissolved P to overlying water.

Alternatively, Model B implies a sedimentary mechanism that transforms a portion of rP back to nrP. Biotic uptake of available rP (primarily PO_4), released via mineralization of organic P, would drive the reverse reaction. The plausibility of this model is supported by the fact that microbes exist throughout the depth of the cores (Figure 3.6). The relative consistency with depth of microbial biomass based on DNA and PCR analyses suggests benthic biotic activity may reach steady-state, perhaps due to acidic, nutrient-limited conditions within the ponds and bottom sediment.

The calculated $t_{½}$ of sediment nrP according to our models varies among ponds and also changes with sediment age in the reversible model. Compared to similar studies (referenced in Table 3.6), the $t_{½}$ values calculated from our models are quite high, especially in MP. It is likely that sedimented and buried nrP in these systems is generally more recalcitrant than in more eutrophic lakes. Allochthonous organic matter, especially humic material, may be the main source of P to these oligotrophic systems, as this portion is more recalcitrant, with a longer $t_{½}$ (Reitzel et al. 2007). Supporting this idea also is the relatively high C:N ratios in the sediments, suggesting a terrestrial origin of organic matter in the lake bottom sediments (Kaushal and Binford 1999; Wolfe et al. 2002). Fractions of sediment P with short $t_{½}$, such as those associated with algae and facultative microbes, are likely not abundant in these sediments. This is consistent with the P-limited condition of the lakes, which inhibits the growth of phytoplankton and luxury uptake and storage of P by microbes.

Conclusions

The dynamics of sediment P in lakes vary depending on the trophic status and other biogeochemical conditions. Much of the work devoted to lake sediment P has focused on factors that contribute to internal loading of eutrophic systems and explanation of biogeochemical processes that regulate the flux of dissolved P to the water column. This study complements the work done on eutrophic lakes as it uses comparable techniques to quantify factors that limit or even permanently disrupt internal loading in oligotrophic lakes. The models presented here quantify mineralization of nrP in the sediment as a function of time (depth), and the net rates are typically slower than those reported for eutrophic systems. It is likely that in all lakes, regardless of their trophic status, organic P is mineralized in the sediment and the sorption capacity of the sediment controls the extent to which dissolved P is removed from the water. Permanent sorption and burial occur in sediments that have excess $Al(OH)_3$ as compared to reducible Fe hydroxides, which release P with the onset of anoxia.

By determining concentrations of Al, Fe, and P fractions, the presence and quantity of microbes, and mineralization rates of P in these historically oligotrophic lakes, we have gained insight on sediment characteristics that prevent internal loading. These attributes may help to determine target doses for water treatment in problematic eutrophic waters. Speciation studies help define historical trophic conditions and help evaluate potential impacts related to nutrient loading from anthropogenic disturbances.

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APPENDICES

APPENDIX A

SEQUENTIAL EXTRACTION DATA

Measured concentrations of elements of interest in all sediment intervals for all study sites. LLP= Little Long Pond; MP=Mud Pond; UHP=Upper Hadlock Pond.

Table A.1 Aluminum concentrations

Lake	**Midpoint depth (cm)**	**NH_4Cl-Al**	**BD-Al**	**NaOH-Al (25°C)**	**HCl-Al**	**NaOH-Al (85°C)**	**Al_{TE}**
		------------------------------µmol/g dry sediment----------------------------					
LLP	0.25	0.2	9.9	842	93	74	1019
	0.75	0.7	13.4	1195	174	109	1492
	1.25	0.4	12.8	1134	154	102	1403
	1.75	0.6	9.8	1156	190	114	1471
	2.25	0.8	7.4	1016	187	116	1328
	3.25	0.4	7.1	1105	163	115	1391
	4.25	0.2	6.2	1053	164	99	1322
	5.25	0.3	6.5	1094	188	108	1396
	6.25	0.5	7.2	1199	209	115	1530
	7.25	0.4	6.2	1048	191	106	1351
	8.25	0.2	6.1	960	151	98	1214
	9.25	0.3	6.4	855	157	89	1108
	10.5	0.2	6.0	983	190	105	1284
	12.5	0.2	6.1	971	188	97	1263
	14.5	0.1	8.2	972	113	57	1150
	16.5	0.2	8.6	857	98	48	1012
	18.5	0.2	5.9	921	114	52	1093
	20.5	0.2	4.6	824	87	46	962
	25.5	0.0	5.5	847	87	46	985
	31	0.0	4.1	832	96	58	990
	45	0.1	3.8	569	43	37	652
MP	0.25	0.2	40.4	533	14	82	670
	0.75	0.0	20.9	535	17	62	635
	1.25	0.0	12.3	205	6	24	246
	2.25	0.0	19.3	472	22	48	562
	3.25	0.1	13.4	449	22	47	532
	4.25	0.7	11.6	525	45	56	639
	5.25	0.9	12.0	626	67	62	768
	6.25	0.7	12.6	687	123	91	915
	7.25	0.4	7.5	325	33	55	422
	8.25	0.3	8.4	470	64	83	625
	9.25	0.3	6.8	382	44	80	512
	10.5	0.2	5.5	282	22	59	368
	12.5	0.2	6.7	309	20	65	400

Lake	Midpoint depth (cm)	NH_4Cl-Al	BD-Al	NaOH-Al (25°C)	HCl-Al	NaOH-Al (85°C)	Al_{TE}
		------------------------------	-------------	μmol/g dry sediment	-------------	------------------------------	
	14.5	0.3	7.6	486	47	86	627
	16.5	0.4	8.5	665	60	95	830
MP	18.5	0.3	7.5	684	68	94	854
	20.5	0.4	7.1	624	61	82	775
	24.5	0.1	1.6	601	75	130	808
	25.5	0.5	3.6	556	72	139	771
	31	0.3	4.4	419	33	78	534
	41	0.4	5.1	601	49	96	752
	51	0.3	3.9	599	73	114	790
UHP	0.5	0.1	12.7	939	104	131	1223
	1.75	0.0	8.4	1108	130	131	1414
	2.75	0.0	7.0	794	75	104	1017
	3.75	0.0	7.5	1063	114	121	1342
	4.75	0.0	5.1	1001	112	125	1277
	5.75	0.2	8.2	1158	94	173	1468
	6.75	0.2	8.7	1056	77	158	1335
	7.75	0.2	8.1	1202	104	190	1540
	8.75	0.2	7.5	1085	72	152	1351
	9.75	0.2	7.5	1123	76	161	1402
	11.5	0.2	6.2	856	69	153	1117
	13.5	0.2	5.2	790	48	116	990
	15.5	0.1	5.2	687	50	90	867
	17.5	0.2	6.7	986	95	119	1241
	19.5	0.2	6.2	1023	86	104	1252
	21.5	0.1	6.9	845	60	81	1028
	23.5	0.2	7.0	1041	69	99	1253
	28.5	0.0	5.3	1064	86	110	1301
	37	0.0	2.3	600	36	61	732

Table A.2 Iron concentrations

Lake	**Midpoint depth (cm)**	**NH_4Cl-Fe**	**BD-Fe**	**NaOH-Fe (25°C)**	**HCl-Fe**	**NaOH-Fe (85°C)**	**Fe_{TE}**
		---------------------------µmol/g dry sediment---------------------------					
LLP	0.25	0.0	202.4	126.1	19.3	8.9	357
	0.75	0.1	370.9	202.6	35.1	11.5	620
	1.25	0.0	277.9	191.0	30.1	10.8	510
	1.75	0.1	200.0	180.1	32.1	11.7	424
	2.25	0.0	104.9	142.8	26.1	11.4	285
	3.25	0.0	53.5	143.6	23.2	11.2	231
	4.25	0.0	42.6	133.3	22.5	9.0	208
	5.25	0.0	45.5	141.3	26.1	11.5	224
	6.25	0.0	50.9	161.6	29.1	13.2	255
	7.25	0.0	49.1	144.3	27.8	16.8	238
	8.25	0.0	49.9	131.7	25.0	27.0	234
	9.25	0.0	51.6	116.7	26.1	33.4	228
	10.5	0.0	59.8	138.6	30.2	28.0	257
	12.5	0.1	58.4	127.5	29.6	32.4	248
	14.5	0.2	65.3	107.9	24.8	19.1	217
	16.5	0.1	58.6	89.3	20.1	12.5	181
	18.5	0.3	58.9	88.6	21.4	9.6	179
	20.5	0.1	57.0	77.5	18.8	8.8	162
	25.5	0.1	59.6	72.7	17.8	7.6	158
	31	0.7	56.2	75.0	18.9	7.9	159
	45	0.1	29.2	45.3	11.8	4.8	91
MP	0.25	0.2	15.4	15.8	8.9	5.9	46.1
	0.75	0.1	27.5	13.2	8.1	5.7	54.6
	1.25	0.1	3.6	4.6	2.7	1.9	12.9
	2.25	0.1	3.1	10.0	6.2	3.6	22.9
	3.25	0.1	1.8	9.8	5.7	3.8	21.1
	4.25	0.1	2.1	11.4	6.2	4.4	24.1
	5.25	0.1	5.2	13.5	7.0	6.7	32.5
	6.25	0.0	10.7	11.5	7.2	6.3	35.7
	7.25	0.0	10.4	5.6	3.8	4.2	24.0
	8.25	0.0	12.3	9.5	7.2	5.3	34.3
	9.25	0.0	10.8	8.3	5.9	5.2	30.3
	10.5	0.0	9.4	5.5	3.6	4.2	22.8
	12.5	0.0	13.9	5.6	4.2	5.0	28.6
	14.5	0.0	9.3	9.3	7.0	5.6	31.2
	16.5	0.1	15.8	11.9	9.2	6.5	43.4
	18.5	0.0	16.2	12.3	9.2	5.7	43.4
	20.5	0.1	16.1	9.9	7.5	5.1	38.8
	24.5	0.0	4.0	20.4	13.3	5.6	43.3
	25.5	0.0	10.6	12.9	10.6	6.2	40.3
	31	0.0	12.1	8.3	5.8	4.5	30.7
	41	0.4	15.9	12.1	9.9	6.6	44.9
	51	0.3	16.3	11.8	9.2	7.1	44.6

Lake	**Midpoint depth (cm)**	**NH_4Cl-Fe**	**BD-Fe**	**NaOH-Fe (25°C)**	**HCl-Fe**	**NaOH-Fe (85°C)**	**Fe_{TE}**
		---------------------------µmol/g dry sediment---------------------------					
UHP	0.5	0.0	225	152	31	10.0	418
	1.75	0.0	90	147	31	8.9	277
	2.75	0.0	53	94	20	8.3	175
	3.75	0.0	63	121	28	8.1	221
	4.75	0.0	23	119	27	8.7	177
	5.75	0.0	55	111	27	19.4	212
	6.75	0.0	45	101	25	23.0	194
	7.75	0.0	51	119	30	26.4	226
	8.75	0.0	42	106	25	26.1	199
	9.75	0.0	39	106	26	25.5	196
	11.5	0.0	29	80	22	26.4	158
	13.5	0.0	25	81	18	22.7	147
	15.5	0.0	15	64	16	19.2	114
	17.5	0.1	14	100	24	16.1	154
	19.5	0.0	28	98	21	12.1	159
	21.5	0.0	24	82	16	14.1	135
	23.5	0.0	23	87	19	14.4	144
	28.5	0.0	17	76	21	7.8	121
	37	0.0	13	39	11	5.4	69

Table A.3 Phosphorus concentrations

Lake	**Midpoint depth**	**NH_4Cl-P**	**BD-P**	**NaOH-rP (25°C) Al-P**	**NaOH-nrP (25°C) Org-P**	**HCl-P**	**NaOH-P (85°C)**	**P_{TE}**
	(cm)	**---------------------------µmol/g dry sediment---------------------------**						
LLP	0.25	0.15	0.0	12.2	35.8	0.38	0.0	48.5
	0.75	0.15	0.0	19.7	49.4	0.60	2.5	72.3
	1.25	0.16	0.0	19.0	46.1	0.57	2.3	68.1
	1.75	0.16	0.0	20.6	45.6	0.67	2.1	69.2
	2.25	0.21	0.0	18.5	40.3	0.61	2.7	62.3
	3.25	0.16	0.0	18.4	41.0	0.61	1.8	62.0
	4.25	0.14	0.0	20.0	35.3	0.58	2.6	58.7
	5.25	0.15	0.0	21.7	37.8	0.68	2.9	63.2
	6.25	0.11	0.0	25.8	41.0	0.75	1.3	68.9
	7.25	0.09	0.0	23.9	35.2	0.68	1.6	61.5
	8.25	0.09	0.0	22.8	32.8	0.58	0.5	56.7
	9.25	0.06	0.0	21.2	29.8	0.53	0.6	52.2
	10.5	0.05	0.0	23.7	33.5	0.67	0.2	58.2
	12.5	0.05	0.0	26.2	33.5	0.67	0.3	60.7
	14.5	0.05	0.0	33.1	26.6	0.58	0.0	60.4
	16.5	0.06	0.0	30.2	25.7	0.46	0.2	56.6
	18.5	0.04	0.0	36.8	28.1	0.55	0.0	65.5
	20.5	0.05	0.0	33.0	25.7	0.45	0.1	59.4
	25.5	0.02	0.0	34.8	26.1	0.41	0.0	61.3
	31	0.01	0.0	33.0	27.5	0.49	0.0	61.0
	45	0.01	0.0	23.0	16.2	0.25	0.0	39.5
MP	0.25	0.84	0.0	5.2	35.7	0.20	2.8	44.7
	0.75	0.87	2.3	9.1	32.8	0.21	2.3	47.6
	1.25	0.29	0.3	3.3	12.6	0.08	0.6	17.2
	2.25	0.27	0.1	6.5	26.6	0.18	0.7	34.3
	3.25	0.24	0.0	6.0	21.5	0.19	0.6	28.5
	4.25	0.14	0.3	9.0	23.6	0.20	0.7	33.9
	5.25	0.17	0.2	5.4	30.9	0.28	1.1	38.1
	6.25	0.09	1.1	11.9	31.6	0.31	0.0	45.0
	7.25	0.06	0.6	5.5	15.6	0.12	0.0	21.9
	8.25	0.05	0.7	8.0	26.2	0.14	0.0	35.1
	9.25	0.08	1.0	7.3	21.3	0.15	0.0	29.8
	10.5	0.03	1.1	5.8	14.6	0.08	0.0	21.6
	12.5	0.02	1.5	7.6	15.9	0.09	0.0	25.1
	14.5	0.07	1.5	14.1	27.2	0.14	0.0	42.9
	16.5	0.03	1.9	22.8	31.6	0.25	0.0	56.7
	18.5	0.10	1.9	26.4	34.0	0.23	0.0	62.5
	20.5	0.08	2.1	25.8	30.4	0.22	0.0	58.7
	24.5	0.02	1.1	60.8*		1.12	2.7	65.7
	25.5	0.08	2.6	40.7	19.0	0.69	0.0	63.1
	31	0.07	2.2	21.3	17.0	0.18	0.0	40.7
	41	0.11	2.7	30.5	31.0	0.46	0.5	65.2
	51	0.03	2.2	40.8	23.0	0.69	0.0	66.8

* Sample was not measured for NaOH-rP; value is for NaOH-P (NaOH-rP + NaOH-nrP)

Lake	Midpoint depth	NH_4Cl-P	BD-P	NaOH-rP (25°C) Al-P	NaOH-nrP (25°C) Org-P	HCl-P	NaOH-P (85°C)	P_{TE}
	(cm)	---------------------------µmol/g dry sediment---------------------------						
UHP	0.5	0.06	2.0	13.0	28.4	0.58	7.2	51.3
	1.75	0.05	1.5	17.9	28.7	0.67	6.5	55.2
	2.75	0.04	0.9	13.2	19.2	0.45	5.0	38.8
	3.75	0.03	1.2	17.9	25.8	0.66	5.9	51.4
	4.75	0.03	0.6	19.4	23.3	0.70	5.8	49.8
	5.75	0.06	1.8	21.1	28.6	0.90	7.2	59.5
	6.75	0.06	1.6	20.4	25.9	0.72	7.4	56.2
	7.75	0.04	1.6	24.9	30.0	0.80	7.7	65.0
	8.75	0.04	1.5	21.0	26.4	0.72	7.2	56.8
	9.75	0.06	1.4	22.2	26.0	0.77	7.7	58.2
	11.5	0.03	1.1	17.1	19.7	0.67	7.8	46.5
	13.5	0.02	0.0	15.1	17.5	0.50	5.9	39.1
	15.5	0.02	1.1	15.9	13.8	0.59	5.5	36.8
	17.5	0.02	0.9	24.9	21.6	1.15	6.3	54.9
	19.5	0.03	1.0	23.3	22.1	0.85	5.2	52.4
	21.5	0.01	0.9	18.5	17.7	0.68	5.9	43.7
	23.5	0.02	0.8	23.4	23.8	1.23	6.8	56.0
	28.5	0.04	0.7	27.3	26.5	1.12	5.4	61.1
	37	0.00	0.0	12.8	13.5	0.62	4.2	31.2

Table A.4 Calcium concentrations

Lake	Midpoint depth (cm)	NH_4Cl-Ca	BD-Ca	NaOH-Ca (25°C)	HCl-Ca	NaOH-Ca (85°C)	Ca_{TE}
		-----------------------------	------------	μmol/g dry	sediment	------------	-----------------------------
LLP	0.25	17.7	3.7	3.4	3.4	0.3	28.5
	0.75	27.6	5.5	5.7	4.8	0.3	44.0
	1.25	24.9	5.7	6.0	4.5	0.8	42.0
	1.75	28.4	6.0	6.4	5.1	0.1	46.0
	2.25	29.1	5.8	6.4	5.0	0.2	46.5
	3.25	30.7	5.6	6.6	5.2	0.2	48.2
	4.25	34.1	6.1	6.6	5.1	0.4	52.3
	5.25	40.0	6.0	7.3	5.7	0.4	59.3
	6.25	42.6	7.1	8.8	6.3	0.0	64.8
	7.25	39.2	6.7	7.4	5.8	0.0	59.1
	8.25	36.6	5.4	6.2	5.4	0.0	53.7
	9.25	36.4	5.6	7.0	5.5	0.0	54.5
	10.5	45.4	7.0	7.1	6.8	0.0	66.4
	12.5	53.7	9.4	7.7	7.8	0.0	78.5
	14.5	52.3	7.3	5.5	7.4	0.7	73.2
	16.5	47.6	5.7	5.5	6.2	1.2	66.3
	18.5	57.2	7.2	5.8	7.0	1.4	78.6
	20.5	51.3	6.9	4.2	6.6	1.3	70.3
	25.5	52.1	6.1	4.5	6.4	1.1	70.2
	31	53.2	7.0	4.4	6.6	1.0	72.3
	45	35.5	4.4	3.3	4.4	1.2	48.8
MP	0.25	20.3	2.7	0.0	5.0	7.0	35.0
	0.75	17.3	1.3	3.0	4.0	5.2	30.8
	1.25	9.2	0.0	0.6	1.6	2.2	13.5
	2.25	16.3	0.4	0.8	3.0	2.7	23.2
	3.25	14.7	0.8	1.4	2.6	1.7	21.2
	4.25	15.2	0.0	1.3	3.0	1.7	21.1
	5.25	17.8	0.6	1.5	3.6	0.9	24.5
	6.25	27.7	3.2	4.2	3.6	2.3	41.0
	7.25	15.5	2.5	2.2	1.9	1.5	23.5
	8.25	27.6	2.9	3.5	3.1	1.1	38.3
	9.25	26.4	2.2	2.2	2.4	1.1	34.3
	10.5	34.7	1.2	2.4	1.5	2.3	42.1
	12.5	25.0	2.8	1.7	1.8	0.4	31.8
	14.5	33.0	1.7	2.8	3.1	1.7	42.3
	16.5	43.0	4.6	3.5	4.1	1.9	57.1
	18.5	45.1	4.5	3.8	4.0	1.1	58.6
	20.5	39.2	3.4	2.9	3.8	1.7	51.0
	24.5	12.9	1.7	4.2	5.3	0.1	24.2
	25.5	22.9	2.7	3.5	4.3	0.0	33.4
	31	21.2	2.0	2.9	2.1	0.3	28.5
	41	45.1	4.0	3.8	3.7	2.5	59.1
	51	35.3	2.9	4.1	3.5	0.9	46.8

Lake	**Midpoint depth (cm)**	**NH_4Cl-Ca**	**BD-Ca**	**NaOH-Ca (25°C)**	**HCl-Ca**	**NaOH-Ca (85°C)**	**Ca_{TE}**
		----------------------------µmol/g dry sediment----------------------------					
UHP	0.5	44.6	6.2	4.8	6.9	2.5	65.0
	1.75	74.5	12.9	8.6	9.4	2.0	107.5
	2.75	56.0	7.0	4.8	6.3	2.5	76.7
	3.75	66.6	9.6	6.8	8.6	2.2	93.9
	4.75	62.7	8.3	6.9	8.5	0.8	87.2
	5.75	61.2	7.3	5.5	11.4	1.6	87.0
	6.75	58.6	7.3	4.7	7.9	2.1	80.5
	7.75	65.9	11.0	6.4	9.2	2.6	95.0
	8.75	54.3	6.7	6.2	7.8	1.6	76.6
	9.75	58.1	6.7	5.3	8.0	1.5	79.6
	11.5	43.4	5.3	4.3	6.3	1.6	60.9
	13.5	40.1	5.2	4.2	5.7	1.8	57.0
	15.5	39.4	3.8	4.0	5.8	3.1	56.3
	17.5	65.2	8.2	7.2	10.0	2.5	93.0
	19.5	67.3	8.4	7.4	9.2	2.6	95.0
	21.5	57.2	6.7	6.1	7.7	3.1	80.8
	23.5	69.4	8.3	7.5	9.8	3.4	98.5
	28.5	*75.1*	8.7	8.5	10.3	1.9	104.5
	37	*38.8*	3.7	3.9	5.4	2.4	54.2

Table A.5 Manganese concentrations

Lake	Midpoint depth (cm)	NH_4Cl-Mn	BD-Mn	NaOH-Mn (25°C)	HCl-Mn	NaOH-Mn (85°C)	Mn_{TE}
		---------------------------μmol/g dry sediment---------------------------					
LLP	0.25	0.16	<1.82	<1.82	0.14	<1.27	0.31
	0.75	0.30	<1.82	<1.82	0.22	<1.27	0.52
	1.25	0.27	<1.82	<1.82	0.19	<1.27	0.46
	1.75	0.32	<1.82	<1.82	0.21	<1.27	0.53
	2.25	0.31	<1.82	<1.82	0.19	<1.27	0.50
	3.25	0.25	<1.82	<1.82	0.19	<1.27	0.44
	4.25	0.31	<1.82	<1.82	0.18	<1.27	0.49
	5.25	0.42	<1.82	<1.82	0.21	<1.27	0.63
	6.25	0.57	<1.82	<1.82	0.22	<1.27	0.78
	7.25	0.62	<1.82	<1.82	0.21	<1.27	0.82
	8.25	0.64	<1.82	<1.82	0.19	<1.27	0.83
	9.25	0.71	<1.82	<1.82	0.20	<1.27	0.91
	10.5	0.97	<1.82	<1.82	0.22	<1.27	1.19
	12.5	1.32	<1.82	<1.82	0.24	<1.27	1.56
	14.5	1.53	<1.82	<1.82	0.24	<1.27	1.78
	16.5	1.51	<1.82	<1.82	0.20	<1.27	1.71
	18.5	1.97	<1.82	<1.82	0.22	<1.27	2.19
	20.5	1.69	<1.82	<1.82	0.21	<1.27	1.89
	25.5	1.96	<1.82	<1.82	0.21	<1.27	2.17
	31	2.47	<1.82	<1.82	0.28	<1.27	2.74
	45	1.30	<1.82	<1.82	0.18	<1.27	1.48
MP	0.25	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	0.75	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	1.25	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	2.25	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	3.25	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	4.25	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	5.25	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	6.25	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	7.25	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	8.25	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	9.25	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	10.5	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	12.5	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	14.5	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	16.5	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	18.5	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	20.5	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	24.5	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	25.5	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	31	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	41	<0.58	<1.82	<1.82	<0.18	<1.27	<DL
	51	<0.58	<1.82	<1.82	<0.18	<1.27	<DL

Lake	Midpoint depth (cm)	NH_4Cl-Mn	BD-Mn	NaOH-Mn (25°C)	HCl-Mn	NaOH-Mn (85°C)	Mn_{TE}
		---------------------------μmol/g dry sediment---------------------------					
UHP	0.5	0.74	19.90	1.62	0.75	<1.27	23.01
	1.75	0.52	4.09	0.99	0.57	<1.27	6.17
	2.75	0.62	2.67	0.58	0.38	<1.27	4.26
	3.75	1.15	3.55	0.80	0.53	<1.27	6.03
	4.75	1.30	3.01	0.85	0.49	<1.27	5.64
	5.75	1.33	3.29	0.79	0.46	<1.27	5.87
	6.75	1.15	2.76	0.66	0.40	<1.27	4.96
	7.75	1.12	3.17	0.79	0.47	<1.27	5.55
	8.75	0.69	2.68	0.69	0.37	<1.27	4.43
	9.75	0.83	2.52	0.68	0.39	<1.27	4.41
	11.5	0.74	1.65	0.50	0.32	<1.27	3.21
	13.5	0.54	1.64	0.50	0.26	<1.27	2.95
	15.5	0.64	1.26	0.40	0.23	<1.27	2.53
	17.5	0.96	2.08	0.68	0.36	<1.27	4.08
	19.5	1.00	1.95	0.67	0.32	<1.27	3.95
	21.5	0.87	1.62	0.54	0.24	<1.27	3.27
	23.5	1.23	1.78	0.58	0.29	<1.27	3.88
	28.5	1.87	1.08	0.56	0.30	<1.27	3.82
	37	0.92	0.43	0.25	0.16	<1.27	1.77

Table A.6 Lead concentrations

Lake	Midpoint depth (cm)	NH_4Cl-Pb	BD-Pb	NaOH-Pb (25°C)	HCl-Pb	NaOH-Pb (85°C)	Pb_{TE}
		----------------------------µmol/g dry sediment----------------------------					
LLP	0.25	<0.031	<0.097	<0.097	0.132	<0.068	0.132
	0.75	<0.031	<0.097	<0.097	0.176	<0.068	0.176
	1.25	<0.031	<0.097	<0.097	0.162	<0.068	0.162
	1.75	<0.031	<0.097	<0.097	0.187	<0.068	0.187
	2.25	<0.031	<0.097	<0.097	0.193	<0.068	0.193
	3.25	<0.031	<0.097	<0.097	0.212	<0.068	0.212
	4.25	<0.031	<0.097	<0.097	0.237	<0.068	0.237
	5.25	<0.031	<0.097	<0.097	0.270	<0.068	0.270
	6.25	<0.031	<0.097	<0.097	0.283	<0.068	0.283
	7.25	<0.031	<0.097	<0.097	0.256	<0.068	0.256
	8.25	<0.031	<0.097	<0.097	0.261	<0.068	0.261
	9.25	<0.031	<0.097	<0.097	0.226	<0.068	0.226
	10.5	<0.031	<0.097	<0.097	0.231	<0.068	0.231
	12.5	<0.031	<0.097	<0.097	0.163	<0.068	0.163
	14.5	<0.031	<0.097	<0.097	0.085	<0.068	0.085
	16.5	<0.031	<0.097	<0.097	0.052	<0.068	0.052
	18.5	<0.031	<0.097	<0.097	0.044	<0.068	0.044
	20.5	<0.031	<0.097	<0.097	0.036	<0.068	0.036
	25.5	<0.031	<0.097	<0.097	0.035	<0.068	0.035
	31	<0.031	<0.097	<0.097	0.023	<0.068	0.023
	45	<0.031	<0.097	<0.097	0.016	<0.068	0.016
MP	0.25	<0.031	<0.097	<0.097	0.070	<0.068	0.070
	0.75	<0.031	<0.097	<0.097	0.080	<0.068	0.080
	1.25	<0.031	<0.097	<0.097	0.028	<0.068	0.028
	2.25	<0.031	<0.097	<0.097	0.083	<0.068	0.083
	3.25	<0.031	<0.097	<0.097	0.091	<0.068	0.091
	4.25	<0.031	<0.097	<0.097	0.129	<0.068	0.129
	5.25	<0.031	<0.097	<0.097	0.159	<0.068	0.159
	6.25	<0.031	<0.097	<0.097	0.131	<0.068	0.131
	7.25	<0.031	<0.097	<0.097	0.075	<0.068	0.075
	8.25	<0.031	<0.097	<0.097	0.073	<0.068	0.073
	9.25	<0.031	<0.097	<0.097	0.041	<0.068	0.041
	10.5	<0.031	<0.097	<0.097	0.029	<0.068	0.029
	12.5	<0.031	<0.097	<0.097	0.030	<0.068	0.030
	14.5	<0.031	<0.097	<0.097	0.039	<0.068	0.039
	16.5	<0.031	<0.097	<0.097	0.048	<0.068	0.048
	18.5	<0.031	<0.097	<0.097	0.025	<0.068	0.025
	20.5	<0.031	<0.097	<0.097	0.033	<0.068	0.033
	24.5	<0.031	<0.097	<0.097	0.056	<0.068	0.056
	25.5	<0.031	<0.097	<0.097	0.048	<0.068	0.048
	31	<0.031	<0.097	<0.097	0.046	<0.068	0.046
	41	<0.031	<0.097	<0.097	0.041	<0.068	0.041
	51	<0.031	<0.097	<0.097	0.043	<0.068	0.043

Lake	**Midpoint depth (cm)**	**NH_4Cl-Pb**	**BD-Pb**	**NaOH-Pb (25°C)**	**HCl-Pb**	**NaOH-Pb (85°C)**	**Pb_{TE}**
		---------------------------µmol/g dry sediment---------------------------					
UHP	0.5	<0.031	<0.097	0.269	0.144	<0.068	0.413
	1.75	<0.031	<0.097	0.342	0.229	<0.068	0.571
	2.75	<0.031	<0.097	0.244	0.182	<0.068	0.426
	3.75	<0.031	<0.097	0.329	0.272	<0.068	0.601
	4.75	<0.031	<0.097	0.339	0.240	<0.068	0.579
	5.75	<0.031	<0.097	0.283	0.267	<0.068	0.550
	6.75	<0.031	<0.097	0.248	0.225	<0.068	0.473
	7.75	<0.031	<0.097	0.315	0.237	<0.068	0.552
	8.75	<0.031	<0.097	0.234	0.203	<0.068	0.437
	9.75	<0.031	<0.097	0.217	0.187	<0.068	0.405
	11.5	<0.031	<0.097	0.111	0.112	<0.068	0.223
	13.5	<0.031	<0.097	0.051	0.080	<0.068	0.131
	15.5	<0.031	<0.097	0.071	0.080	<0.068	0.150
	17.5	<0.031	<0.097	0.077	0.076	<0.068	0.153
	19.5	<0.031	<0.097	0.064	0.060	<0.068	0.123
	21.5	<0.031	<0.097	0.028	0.039	<0.068	0.067
	23.5	<0.031	<0.097	0.034	0.040	<0.068	0.074
	28.5	<0.031	<0.097	0.025	0.039	<0.068	0.064
	37	<0.031	<0.097	0.012	0.014	<0.068	0.027

Table A.7 Silicon concentrations

Lake	**Midpoint depth (cm)**	**NH_4Cl-Si**	**BD-Si**	**NaOH-Si (25°C)**	**HCl-Si**	**NaOH-Si (85°C)**	**Si_{TE}**
		----------------------------		**µmol/g dry sediment**		**----------------------------**	
LLP	0.25	<5.7	<17.8	678	72	5426	6176
	0.75	<5.7	<17.8	764	103	8808	9675
	1.25	<5.7	<17.8	743	94	8004	8842
	1.75	<5.7	<17.8	634	101	8791	9526
	2.25	<5.7	<17.8	512	87	9036	9635
	3.25	<5.7	<17.8	601	101	8951	9652
	4.25	<5.7	<17.8	572	99	7724	8395
	5.25	<5.7	<17.8	604	112	8631	9348
	6.25	<5.7	<17.8	653	104	9325	10081
	7.25	<5.7	<17.8	608	97	8560	9266
	8.25	<5.7	<17.8	694	100	7871	8665
	9.25	<5.7	<17.8	610	119	7454	8183
	10.5	<5.7	<17.8	696	120	8863	9679
	12.5	<5.7	<17.8	708	145	8978	9832
	14.5	<5.7	<17.8	1048	146	6887	8081
	16.5	<5.7	<17.8	919	153	5569	6641
	18.5	<5.7	<17.8	936	178	6342	7456
	20.5	<5.7	<17.8	918	168	5662	6748
	25.5	<5.7	<17.8	1002	176	5372	6550
	31	<5.7	<17.8	891	113	6630	7635
	45	<5.7	<17.8	749	81	3707	4537
MP	0.25	<5.7	<17.8	1772	109	2063	3944
	0.75	<5.7	<17.8	1721	110	2037	3868
	1.25	<5.7	<17.8	725	49	767	1540
	2.25	<5.7	<17.8	1431	126	2078	3635
	3.25	<5.7	<17.8	1180	80	1858	3118
	4.25	<5.7	<17.8	1101	123	2411	3635
	5.25	<5.7	<17.8	1124	120	3072	4317
	6.25	<5.7	<17.8	933	158	4373	5464
	7.25	<5.7	<17.8	593	86	2015	2694
	8.25	<5.7	<17.8	585	99	3275	3959
	9.25	<5.7	<17.8	508	88	2590	3186
	10.5	<5.7	<17.8	380	57	1741	2178
	12.5	<5.7	<17.8	342	53	1829	2224
	14.5	<5.7	<17.8	382	89	3110	3580
	16.5	<5.7	<17.8	410	108	3590	4108
	18.5	<5.7	<17.8	387	114	3712	4213
	20.5	<5.7	<17.8	487	110	3479	4075
	24.5	<5.7	<17.8	323	53	1988	2364
	25.5	<5.7	<17.8	374	82	2634	3090
	31	<5.7	<17.8	409	57	1777	2244
	41	<5.7	<17.8	292	56	3191	3539
	51	<5.7	<17.8	329	64	2820	3212

Lake	**Midpoint depth (cm)**	**NH_4Cl-Si**	**BD-Si**	**NaOH-Pb (25°C)**	**HCl-Si**	**NaOH-Si (85°C)**	**Si$_{TE}$**
		---------------------------µmol/g dry sediment---------------------------					
UHP	0.5	<5.7	<17.8	736	91	4436	5263
	1.75	<5.7	<17.8	660	93	4911	5665
	2.75	<5.7	<17.8	604	70	3349	4024
	3.75	<5.7	<17.8	717	95	4585	5397
	4.75	<5.7	<17.8	630	*75*	4576	5281
	5.75	<5.7	<17.8	847	98	4391	5336
	6.75	<5.7	<17.8	799	86	4115	5000
	7.75	<5.7	<17.8	795	127	4942	5864
	8.75	<5.7	<17.8	792	131	3891	4813
	9.75	<5.7	<17.8	770	102	3988	4860
	11.5	<5.7	<17.8	572	60	3494	4126
	13.5	<5.7	<17.8	618	70	3376	4065
	15.5	<5.7	<17.8	467	40	2822	3329
	17.5	<5.7	<17.8	545	65	4918	5528
	19.5	<5.7	<17.8	534	59	5432	6025
	21.5	<5.7	<17.8	481	44	4257	4782
	23.5	<5.7	<17.8	536	51	4501	5088
	28.5	<5.7	<17.8	447	46	4849	5342
	37	<5.7	<17.8	298	28	2312	2638

Table A.8 Zinc concentrations

Lake	**Midpoint depth (cm)**	**NH_4Cl-Zn**	**BD-Zn**	**NaOH-Zn (25°C)**	**HCl-Zn**	**NaOH-Zn (85°C)**	**Zn_{TE}**
		----------------------------μmol/g dry sediment----------------------------					
LLP	0.25	<0.25	<0.77	0.52	0.25	<0.54	0.76
	0.75	<0.25	<0.77	0.73	0.32	<0.54	1.06
	1.25	<0.25	<0.77	0.66	0.27	<0.54	0.94
	1.75	<0.25	<0.77	0.73	0.36	<0.54	1.09
	2.25	<0.25	<0.77	0.77	0.43	<0.54	1.20
	3.25	<0.25	<0.77	0.78	0.76	<0.54	1.54
	4.25	<0.25	<0.77	0.73	1.49	<0.54	2.22
	5.25	<0.25	<0.77	0.74	2.56	<0.54	3.30
	6.25	<0.25	<0.77	0.85	2.58	<0.54	3.43
	7.25	<0.25	<0.77	0.77	2.22	<0.54	3.00
	8.25	<0.25	<0.77	0.70	2.06	<0.54	2.77
	9.25	<0.25	<0.77	0.61	1.95	<0.54	2.56
	10.5	<0.25	<0.77	0.66	2.16	<0.54	2.82
	12.5	<0.25	<0.77	0.50	2.00	<0.54	2.50
	14.5	<0.25	<0.77	0.39	1.16	<0.54	1.55
	16.5	<0.25	<0.77	0.29	0.68	<0.54	0.97
	18.5	<0.25	<0.77	0.39	0.50	<0.54	0.90
	20.5	<0.25	<0.77	0.27	0.40	<0.54	0.66
	25.5	<0.25	<0.77	0.27	0.37	<0.54	0.64
	31	<0.25	<0.77	0.30	0.51	<0.54	0.81
	45	<0.25	<0.77	0.20	0.69	<0.54	0.90
MP	0.25	<0.25	<0.77	<0.77	0.57	<0.54	0.57
	0.75	<0.25	<0.77	<0.77	0.48	<0.54	0.48
	1.25	<0.25	<0.77	<0.77	0.20	<0.54	0.20
	2.25	<0.25	<0.77	<0.77	0.59	<0.54	0.59
	3.25	<0.25	<0.77	<0.77	0.71	<0.54	0.71
	4.25	<0.25	<0.77	<0.77	1.10	<0.54	1.10
	5.25	<0.25	<0.77	<0.77	1.79	<0.54	1.79
	6.25	<0.25	<0.77	<0.77	2.79	<0.54	2.79
	7.25	<0.25	<0.77	<0.77	1.16	<0.54	1.16
	8.25	<0.25	<0.77	<0.77	0.94	<0.54	0.94
	9.25	<0.25	<0.77	<0.77	0.36	<0.54	0.36
	10.5	<0.25	<0.77	<0.77	0.16	<0.54	0.16
	12.5	<0.25	<0.77	<0.77	0.14	<0.54	0.14
	14.5	<0.25	<0.77	<0.77	0.17	<0.54	0.17
	16.5	<0.25	<0.77	<0.77	0.36	<0.54	0.36
	18.5	<0.25	<0.77	<0.77	0.22	<0.54	0.22
	20.5	<0.25	<0.77	<0.77	0.15	<0.54	0.15
	24.5	<0.25	<0.77	<0.77	0.89	<0.54	0.89
	25.5	<0.25	<0.77	<0.77	0.95	<0.54	0.95
	31	<0.25	<0.77	<0.77	0.43	<0.54	0.43
	41	<0.25	<0.77	<0.77	0.33	<0.54	0.33
	51	<0.25	<0.77	<0.77	1.05	<0.54	1.05

Lake	**Midpoint depth (cm)**	**NH_4Cl-Zn**	**BD-Zn**	**NaOH-Zn (25°C)**	**HCl-Zn**	**NaOH-Zn (85°C)**	**Zn_{TE}**
		--------------------------µmol/g dry sediment--------------------------					
UHP	0.5	<0.25	<0.77	1.19	0.50	<0.54	1.95
	1.75	<0.25	<0.77	1.52	0.73	<0.54	2.45
	2.75	<0.25	<0.77	1.28	0.86	<0.54	2.31
	3.75	<0.25	<0.77	1.80	1.80	<0.54	3.81
	4.75	<0.25	<0.77	1.83	2.25	<0.54	4.28
	5.75	<0.25	<0.77	1.60	2.10	<0.54	3.93
	6.75	<0.25	<0.77	1.50	1.73	<0.54	3.41
	7.75	<0.25	<0.77	1.53	1.98	<0.54	3.78
	8.75	<0.25	<0.77	1.47	1.39	<0.54	3.02
	9.75	<0.25	<0.77	1.31	1.28	<0.54	2.75
	11.5	<0.25	<0.77	0.89	1.44	<0.54	2.44
	13.5	<0.25	<0.77	0.93	0.84	<0.54	2.04
	15.5	<0.25	<0.77	0.68	0.84	<0.54	1.64
	17.5	<0.25	<0.77	0.83	1.21	<0.54	2.19
	19.5	<0.25	<0.77	0.85	1.35	<0.54	2.36
	21.5	<0.25	<0.77	<0.77	0.96	<0.54	1.69
	23.5	<0.25	<0.77	<0.77	0.94	<0.54	1.70
	28.5	<0.25	<0.77	<0.77	1.42	<0.54	2.09
	37	<0.25	<0.77	<0.77	0.58	<0.54	0.93

APPENDIX B

STATISTICAL CORRELATIONS

Correlation coefficients of variables measured in the study sediments. The values for Upper Hadlock Pond are included in Chapter 2. Units for variables are: LOI, %; depth, cm; element fractions, µmol/g dry sediment. *p-value<0.05; **p-value<0.01.

Table B.1 Little Long Pond correlation coefficients.

	Depth	LOI	$NaOH_{25}$ Al	HCl-Al	BD-Fe	$NaOH_{25}$ Fe	HCl-Fe	$NaOH_{25}$ rP	$NaOH_{25}$ nrP
LOI	0.00								
$NaOH_{25}$ Al	0.49**	0.01							
HCl-Al	0.42**	0.27*	0.62**						
BD-Fe	0.25*	0.11	0.18	0.01					
$NaOH_{25}$ Fe	0.74**	0.02	0.79**	0.57**	0.44**				
HCl-Fe	0.39**	0.13	0.62**	0.67**	0.26*	0.76**			
$NaOH_{25}$ rP	0.79**	0.04	0.21*	0.26*	0.21*	0.52**	0.19		
$NaOH_{25}$ nrP	0.67**	0.00	0.76**	0.47**	0.49**	0.91**	0.57**	0.53**	
$NaOH_{25}$ P	0.00	0.08	0.41**	0.09	0.15	0.17	0.25*	0.07	0.22*

Table B.2 Mud Pond correlation coefficients.

	Depth	LOI	$NaOH_{25}$ Al	HCl-Al	BD-Fe	$NaOH_{25}$ Fe	HCl-Fe	$NaOH_{25}$ rP	$NaOH_{25}$ nrP
LOI	0.44**								
$NaOH_{25}$ Al	0.09	0.01							
HCl-Al	0.10	0.13	0.51**						
BD-Fe	0.12	0.00	0.12	0.01					
$NaOH_{25}$ Fe	0.01	0.00	0.70**	0.12	0.12				
HCl-Fe	0.21*	0.01	0.77**	0.22*	0.31*	0.75**			
$NaOH_{25}$ rP	0.83**	0.26*	0.32**	0.20*	0.21*	0.09	0.44**		
$NaOH_{25}$ nrP	0.00	0.06	0.77**	0.20*	0.19	0.82**	0.75**	0.09	
$NaOH_{25}$ P	0.45**	0.07	0.73**	0.31*	0.31*	0.45**	0.84**	0.77**	0.51**
NH_4Cl-Ca	0.41**	0.00	0.27*	0.23*	0.24*	0.05	0.36**	0.55**	0.16
HCl-Ca	0.01	0.01	0.75**	0.15	0.23*	0.89**	0.82**	0.15	0.92**

APPENDIX C

DIATOM SPECIES ABUNDANCE DATA

Graphs showing abundance of diatom species in enumerated sediment intervals from Little Long Pond and Mud Pond. The graph for Upper Hadlock Pond is included in Chapter 2.

Figure C.1 Little Long Pond diatom species abundances.

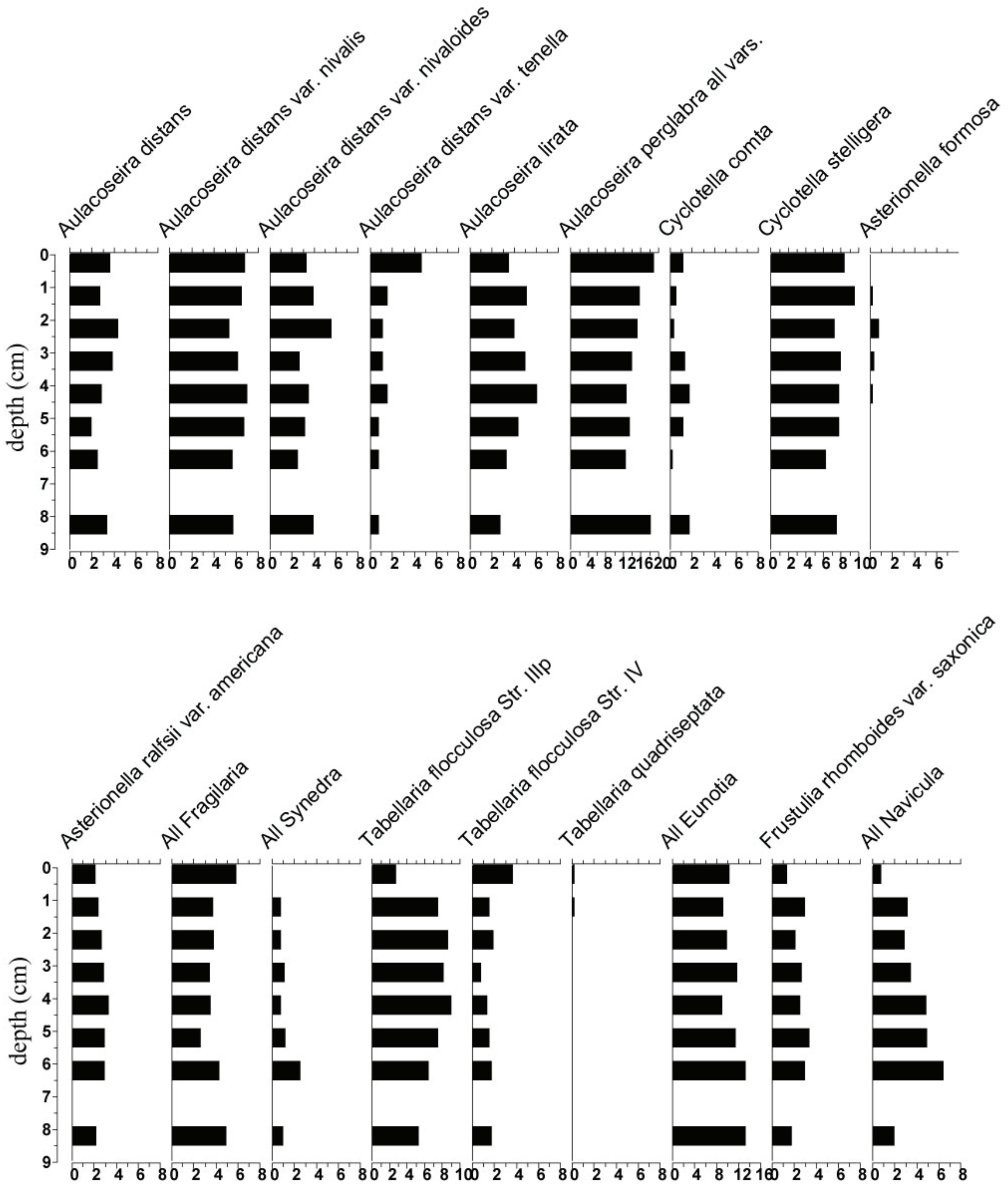
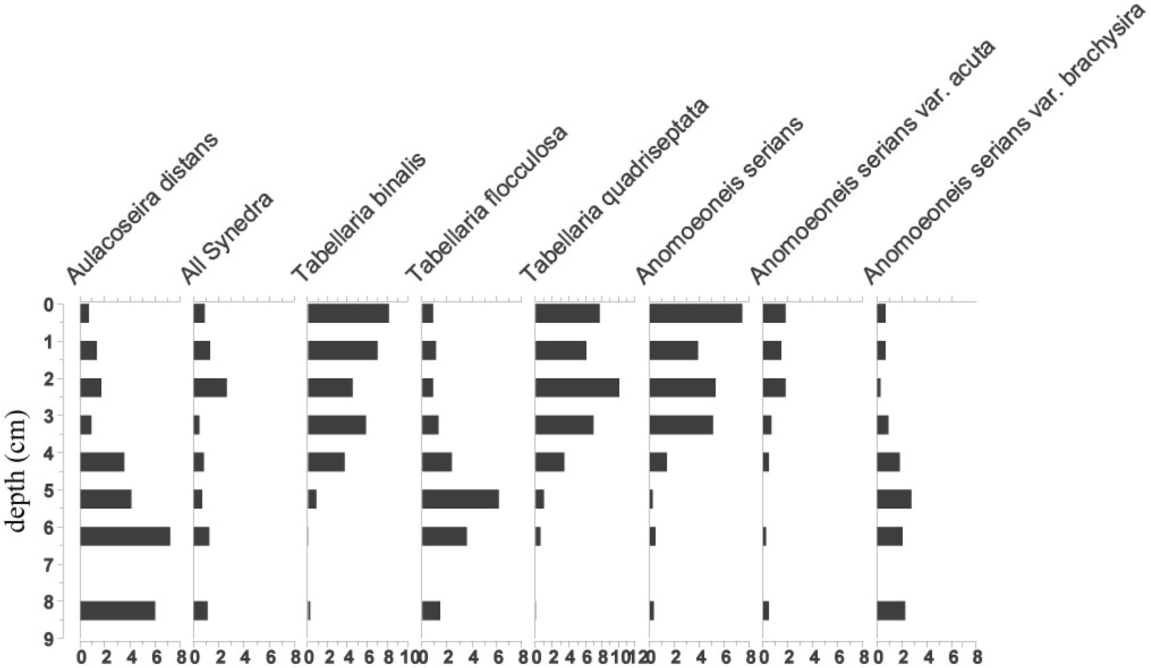
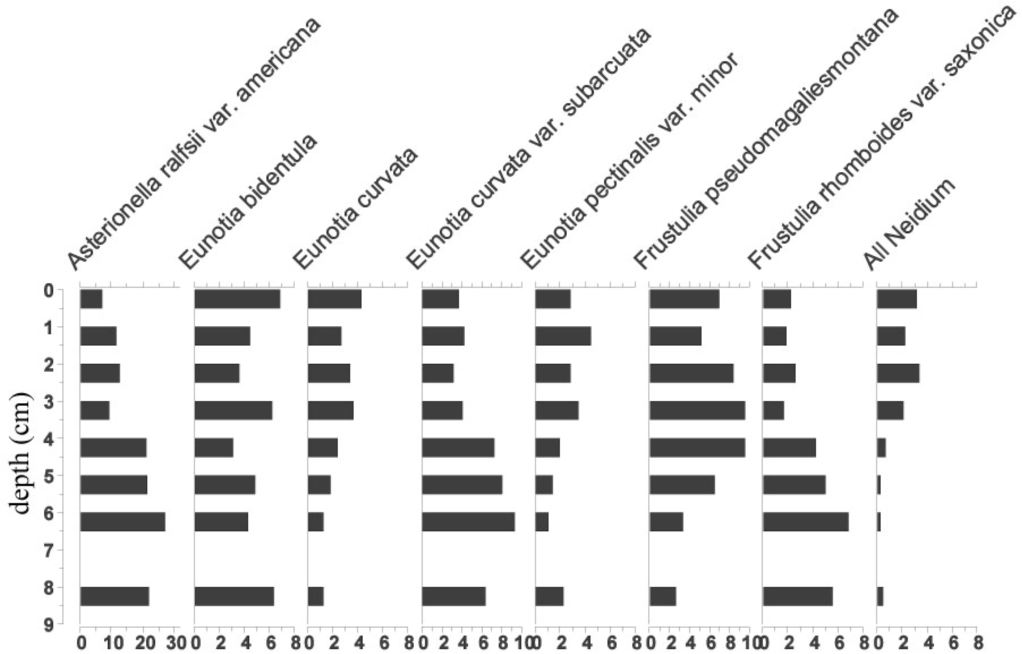


Figure C.2 Mud Pond diatom species abundances.





APPENDIX D

DIATOM – INFERRED VALUES

Diatom-inferred pH (DI-pH) and total phosphorus (DI-TP) values for Little Long Pond and Mud Pond sediments. The inferred values are based on a diatom reconstruction model of Ginn et al. (2007). The table for Upper Hadlock Pond is included in Chapter 2.

Table D.1 Little Long Pond diatom-inferred values.

Interval depth	Sediment boundary dates		Diatom-inferred (Ginn)	
cm	top	bottom	DI-pH	DI-TP (µg/L)
0-0.5	2005	2005	6.00	4.16
1-1.5	2003	2001	6.05	4.06
2-2.5	1999	1997	6.05	4.55
3-3.5	1995	1993	6.01	4.22
4-4.5	1991	1988	6.02	4.15
5-5.5	1986	1982	6.00	4.27
6-6.5	1980	1976	5.97	4.51
8-8.5	1965	1961	5.97	3.97

Table D.2 Mud Pond diatom-inferred values.

Interval depth	Sediment boundary dates		Diatom-inferred (Ginn)	
cm	top	bottom	DI-pH	DI-TP (µg/L)
0-0.5	2005	2005	4.69	3.59
1-1.5	2004	2001	4.73	3.94
2-2.5	1999	1995	4.82	4.11
3-3.5	1991	1986	4.68	3.79
4-4.5	1979	1971	4.76	4.33
5-5.5	1964	1955	4.80	4.75
6-6.5	1947	1937	4.79	5.44
8-8.5	1897	1885	4.77	5.38

BIOGRAPHY OF THE AUTHOR

Tiffany Ann Wilson was born in 1974 in Bangor, Maine, grew up in Dixmont, Maine and graduated from Nokomis Regional High School in Newport, Maine in 1991. She attended the University of Maine at Orono, Maine and completed a B.A. in zoology in 1995.

Tiffany spent one year living in Tempe, Arizona working at a blood screening laboratory then returned to Maine in 1996 and began employment at the University of Maine Environmental Chemistry Laboratory. She currently is laboratory manager in the Department of Civil and Environmental Engineering at the same institution. During her years of employment she acquired an interest in ecological monitoring and worked on several academic projects related to human impacts on the environment. This work led to the pursuit of a graduate degree in environmental studies. She is a candidate for the Master of Science degree in Ecology and Environmental Science from the University of Maine in May, 2008.