

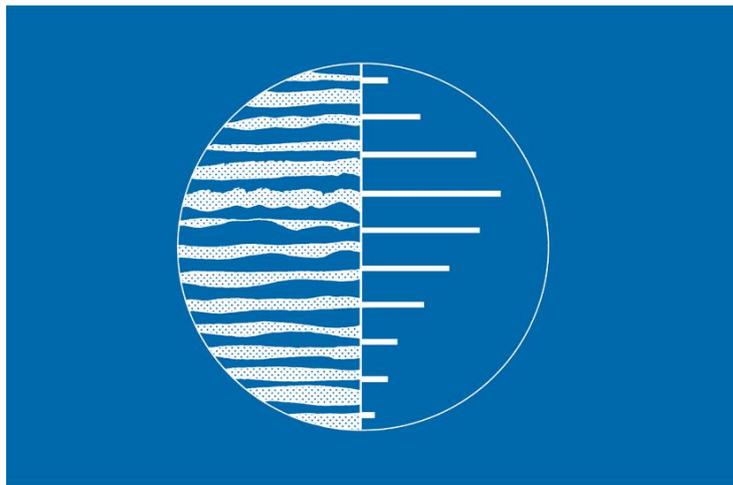
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# A record of phosphorus dynamics in oligotrophic lake sediment

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**Abstract** Historical phosphorus (P) dynamics were studied using sediment cores from three oligotrophic, acidic lakes in Maine, USA. Long-term oligotrophy of these lakes is consistent with high sediment aluminum (as  $\text{Al}(\text{OH})_3$ ) concentrations, as Al inhibits internal P loading, even under reducing conditions. The role of microbially-mediated reactions in controlling redox conditions was evaluated by estimating microbial biomass and relative abundance of specific functional groups. Sediments were fractionated using a sequential chemical extraction technique and all lakes met criteria for P retention based on threshold sediment concentrations of Al, Fe, and P fractions as determined by (Kopáček et al. (2005) *Limnol Oceanogr* 52:

1147–1155). Sediment NaOH-extractable molybdate-reactive P (rP) and non-reactive P (nrP) represent P associated with non-reducible phases, and organic matter-related P, respectively. Total P (TP) does not decrease with sediment depth, as is typical of eutrophic lake sediments; however, nrP/TP decreases and rP/TP increases for all three lakes, indicating nrP mineralization without any significant upward diffusion and release into the hypolimnion; i.e. diagenesis of P is conservative within the sediment. Two diagenetic models were developed based on nrP and rP concentrations as a function of sediment age. The first model assumes a first-order decay of nrP, the rate coefficient being a function of time, and represents irreversible nrP mineralization, where the produced  $\text{PO}_4$  is permanently sequestered by the sediment. The second model assumes a first-order reversible transformation between nrP and rP, representing biotic mineralization of organic P followed by incorporation of inorganic P into microbial biomass. Both models reflect preservation of TP with no loss to overlying water. The rate coefficients give us insight into qualities of the sediment that have affected mineralization and sequestration of phosphorus throughout the  $^{210}\text{Pb}$ -dateable history of each lake. Similar models could be constructed for other lakes to help reconstruct their trophic histories. Paleolimnological reconstruction of the sediment P record in oligotrophic lakes shows mineralization of nrP to rP, but unlike the case in eutrophic lake sediments, sediment TP is preserved in these sediments.

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## 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. In most lakes, P is transported to the lake 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. Factors known to regulate this internal P cycle within lakes include redox values and pH, abiotic factors that in part can be controlled by biotic processes, and direct biotic factors such as mineralization by sediment microorganisms (Gächter et al. 1988).

The classic model of P release from lake bottom sediments involves reductive dissolution of Fe(III) solids following the onset of hypolimnetic anoxia (Einsele 1936; Mortimer 1941). Solid Fe(OH)<sub>3</sub> readily adsorbs available orthophosphate (PO<sub>4</sub>), removing it from the water column and sequestering it in the sediment. It is now established that microbially catalyzed Fe(III) reduction in the sediment promotes the dissolution of Fe(OH)<sub>3</sub> and the subsequent release of Fe(II) and PO<sub>4</sub> (Gächter et al. 1988). The role of sulfate reduction and sulfide production, and P release in eutrophic lake sediments has been investigated (Kleeberg 1997; Mitchell and Baldwin 1998; Nurnberg 1996). The formation and precipitation of insoluble FeS species reduces the binding of P to Fe(OH)<sub>3</sub> (Kleeberg 1997; Nurnberg 1996) accompanied by release of P from the sediments may enhance the eutrophic status of lakes (Caraco et al. 1993; Smolders and Roelofs 1993; Søndergaard et al. 1996). Increases in microbially mediated sulfate reduction result in increases in P release. In addition, there is some evidence that during anaerobic nitrate-free conditions, denitrifiers can increase the dissolution of Fe(OH)<sub>3</sub> and P sorbed to it (Jansson 1987).

The conceptual model proposed by Einsele and Mortimer has been augmented to include the direct

role of microbial activity in hypolimnetic P release (Gächter and Meyer 1993; Mitchell and Baldwin 1998). Redox-controlled metabolism of stored inorganic polyphosphate (poly-P) in sediment microbes is another recognized P release mechanism (Hupfer et al. 2004). Poly-P has been measured by nuclear magnetic resonance (<sup>31</sup>P NMR) spectroscopy in surficial lake sediments, where microbes accumulate it during oxic conditions (Hupfer and Gächter 1995). Poly-P is apparently 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) attributed 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 low in oligotrophic surface waters, the main sources of nutrients (P, nitrogen, carbon) to lake sediment 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. The preservation of sedimented P, in its various forms, back through time has commonly been thought to be linked to the transient gradient in Eh at or below the sediment–water interface.

Amirbahman et al. (2003) found that hypolimnetic P and Fe(II) fluxes from lake sediments do not correlate in all lakes. In such cases, elevated concentrations of ionic Al, common in low pH surface waters in Europe and northeastern North America, may indirectly control the release of dissolved P from sediment. Solid phase Al(OH)<sub>3</sub> forms as a hydrolysis product of dissolved inorganic Al in the pH range of 5–7. Because it has a high sorptive capacity for PO<sub>4</sub>, Al(OH)<sub>3</sub> removes this species from the water column even if redox potential is low (Kopáček et al. 2000; Ulrich and Pöthig 2000). Photochemical liberation of inorganic Al from organically bound Al in the water column contributes to this pool of precipitating Al(OH)<sub>3</sub> (Kopáček et al. 2006).

Based on sediment chemistry data from 43 lakes, Kopáček et al. (2005) proposed a model defining 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 common five step sequential extraction method involving distilled water (H<sub>2</sub>O), bicarbonate-buffered sodium dithionite solution (BD), sodium hydroxide at 25°C (NaOH25), hydrochloric acid (HCl), and sodium hydroxide at 85°C (NaOH85). The molar ratios of [(H<sub>2</sub>O–Al) + (BD–Al) + (NaOH25–Al)]:[(H<sub>2</sub>O–Fe) + (BD–Fe) + (NaOH25–Fe)] >3 and [(NaOH25–Al)]:[(H<sub>2</sub>O–P) + (BD–P)] >25 are defined as thresholds for the potential for sedimentary P retention in lake sediments. Lake sediments that meet these criteria do not release significant P concentrations during the development of hypolimnetic anoxia. This relationship was corroborated by Lake et al. (2007) for a set of lakes of different trophic status in Maine, USA. The persistence of the five fractions in long sediment records has been interpreted as persistence of the P-sorbing characteristics of the sediment, and thus the trophic status of the lake (Kopáček et al. 2007).

More detailed characterization of sediment P separates the third fraction, NaOH25, following sequential extractions with H<sub>2</sub>O and BD, into non-reactive (nrP) and reactive (rP) components, based on reactivity of PO<sub>4</sub> with molybdate in a colorimetric method (Murphy and Riley 1962). Measured rP is mainly Al-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 microbial biomass in sediment (Goedkoop and Pettersson 2000). Ahlgren et al. (2005) showed that nrP and TP in the Swedish mesotrophic Lake Erken sediments decrease with increasing sediment depth, reflecting biogenic P mineralization and its release into the water column, over time. Using <sup>31</sup>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 their case, mineralized nrP was considered the primary source of sediment P to the water column, due in part to the lack of solid phases (e.g., Al(OH)<sub>3</sub>) available for adsorption of generated PO<sub>4</sub>.

In our study, we focus on short sediment cores from three lakes in Maine, USA, in order to assess the sediment characteristics that contribute to their P retention and stable oligotrophic status through time. These lakes develop anoxic hypolimnia during

summer stratification. However, the sediment profiles of these lakes show relatively steady concentrations of total P with depth, suggesting no net hypolimnetic P release into the water column, even though the rP:nrP ratios increase with depth. In contrast, some eutrophic lake sediments exhibit a decrease of TP with increasing 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 had a net release of dissolved mineralized P from the near-surface sediment to the water column. We performed sequential chemical extractions of sediments spanning more than a century of deposition to evaluate the rate of mineralization of nrP with depth (time) and examine the relationship between bacterial biomass and microbially mediated redox conditions and differences in P fractions, and to determine whether the sediments in these lakes meet the Al, Fe, and P concentration criteria for P retention as defined by Kopáček et al. (2005), as described above. Our exploration and quantification of the chemical processes affecting P diagenesis aids the paleolimnologic reconstruction of the trophic histories of these lakes. We show that the sediment P record in oligotrophic lakes, as opposed to eutrophic lakes, does not necessarily show a decrease in the TP concentration, but only mineralization of nrP to rP, followed by the latter's immobilization.

#### 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. MP (N44.634°, W68.088°) drains into LLP (N44.638°, W68.080°); their catchments are currently forested (spruce, 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 (N44.321°, W68.287°) is located in Acadia National Park, coastal Maine, USA, with a forested and lightly-developed catchment (one paved road and gravel carriage roads). All catchments are well drained, with thin, stony soil and some exposed granite bedrock, and have characteristically low acid neutralizing capacity (ANC) and acid-sensitive surface waters.

All three ponds are acidic and develop anoxic hypolimnia during seasonal stratification. MP, UHP, and LLP (to a lesser extent) release dissolved Fe and

Mn to their anoxic hypolimnia, yet they release little P. Of the three study ponds, MP has the highest dissolved Al concentrations ( $>200 \mu\text{g/L}$ ) and the lowest pH and ANC. The pH, ANC, and Al concentrations of LLP are lower than those of UHP.

## Materials and methods

Water chemistry data for these ponds were collected from 1983 to 2005 using the following analytical methods: ANC by Gran titration (Radiometer TIM 900 Autotitrator);  $\text{SO}_4^{2-}$  by ion chromatography (Dionex model DX 500); DOC (dissolved organic carbon) by a total carbon analyzer (OI Analytical model 1010); Al, Fe, and Mn (total dissolved) by ICP-AES (Perkin-Elmer model 3300XL) or graphite furnace atomic absorption (Perkin-Elmer, model 4100ZL) (pre-1999); and P (total) by persulfate digestion/molybdate-blue colorimetry. Table 1 highlights the morphologic and relevant chemical characteristics of each pond.

### Sediment collection and processing

Sediment cores were 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  $-20^\circ\text{C}$  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  $\sim 0.5$  g of dried sediment to 550°C for 4 h. Carbon (C) and nitrogen (N) were measured by combustion (LECO CN-2000 analyzer). Total DNA concentration was determined in extracts from wet sediments, and the relative abundance of specific functional groups was determined with quantitative polymerase chain reaction (qPCR).

Sediment chronology was determined by measuring  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  from selected intervals of dried sediment. Samples were equilibrated for at least 3 weeks in capped  $1 \times 4$  cm polyethylene vials.  $^{210}\text{Pb}$  gamma-ray activity was counted using 46.52 keV emission, for 43,200 to 259,200 s. We used a Canberra germanium well detector ( $1 \times 4$  cm) with 22.5% efficiency for  $^{60}\text{Co}$ . Data were processed using *GammaTrac* software (Oxford Instruments) and analyzed by Compton continuum subtraction of the peaks. The detector was calibrated with U.S. EPA National exposure research laboratory aqueous standards in the same geometry as the sediment samples. The unsupported  $^{210}\text{Pb}$  activity was estimated by subtracting the constant background  $^{210}\text{Pb}$  activity (from deep in the core), from total  $^{210}\text{Pb}$ . Ages of interval midpoints were calculated based on the Constant Rate of Supply (CRS) model of Appleby and Oldfield (1978). Sediment ages older than the limit of  $^{210}\text{Pb}$  dating, approximately 150 years, were extrapolated by assuming a constant mass accumulation rate for each lake.

### Sediment chemistry

The five operationally defined fractions of Al, Fe, and P were determined based on the sequential extraction procedure of Psenner et al. (1988). We modified the first step by using  $\text{NH}_4\text{Cl}$  instead of distilled water (Tessier et al. 1979) and the third step by using 0.1 M NaOH in place of 1 M NaOH (Hieltjes and Lijklema 1980). The sequence was performed on 1 g or more of wet sediment using the following steps: (A) 1 M  $\text{NH}_4\text{Cl}$ , pH 7, at 25°C for 1 h to obtain the loosely sorbed, exchangeable, and porewater fractions, (B) 0.1 M  $\text{NaHCO}_3$ -buffered 0.1 M  $\text{Na}_2\text{S}_2\text{O}_4$  (bicarbonate-dithionite, BD) at 40°C for 30 min to release the reducible fractions, primarily Fe and Mn (oxy)hydroxides and associated P, (C) 0.1 M NaOH at 25°C for 16 h to dissolve some Al and Fe (oxy)hydroxides and associated P, as well as some organic and biogenic P, (D) 0.5 M HCl at 25°C for 16 h to dissolve acid soluble minerals, and (E) 1 M NaOH at 85°C for 24 h 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

**Table 1** Morphological and chemical characteristics of Little Long, Mud, and Upper Hadlock ponds from Maine DEP, 2006

	Little long	Mud	Upper hadlock
Area (ha)	24.3	1.6	15.4
Drainage area (ha)	236	82	339
Depth <sub>max</sub> (m)	25.3	16.2	11.3
Elevation (m)	72	102	70
Residence time (year)	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 $\mu\text{eq/L}$			
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 <sub>4</sub> <sup>2-</sup> $\mu\text{eq/L}$			
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 $\mu\text{g/L}$			
Epi	10–71	235–433	16–106
Hypo	46–84	310–439	108–195
P $\mu\text{g/L}$			
Epi	1–4	4–8	2–11
Hypo	5–12	7–17	7–12
Fe $\mu\text{g/L}$			
Epi	4	33	25
Hypo	29	514	532
Mn $\mu\text{g/L}$			
Epi	18	8	11
Hypo	22	16	303

Chemistry data are ranges of annual mean values (1983–2005) for selected parameters. Fe and Mn values were only measured in 2005

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  $\sim 3,000$  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<sub>4</sub>Cl 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<sub>4</sub> and 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 using the Ultraclean soil DNA Kit (MoBio Laboratories, Inc., Carlsbad, CA), according to the

**Table 2** Parameters for quantitative polymerase chain reaction (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	Primer reference
Denitrifiers	<i>nirS</i>	Flacd, R4cd	55	84	Hallin and Lindgren (1999)
	<i>nirK</i>	Flacu, R3cu			
<i>Geobacter</i>	<i>16s rRNA</i>	Geo494f, Geo825R	53	83	Anderson et al. (1998) Holmes et al. (2002)
Sulfate-reducing bacteria	<i>dsrB</i>	dsrp2060f, dsr4r	55	82	Geets et al. (2006) Wagner et al. (1998)
Methanogens	<i>mcrA</i>	mcrAf, mcraR	56	82	Luton et al. (2002)

manufacturer's instructions. 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 2. Reactions were performed using the Quantitect SYBR green PCR kit (Qiagen, Valencia, CA) and 0.6  $\mu$ M 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 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.

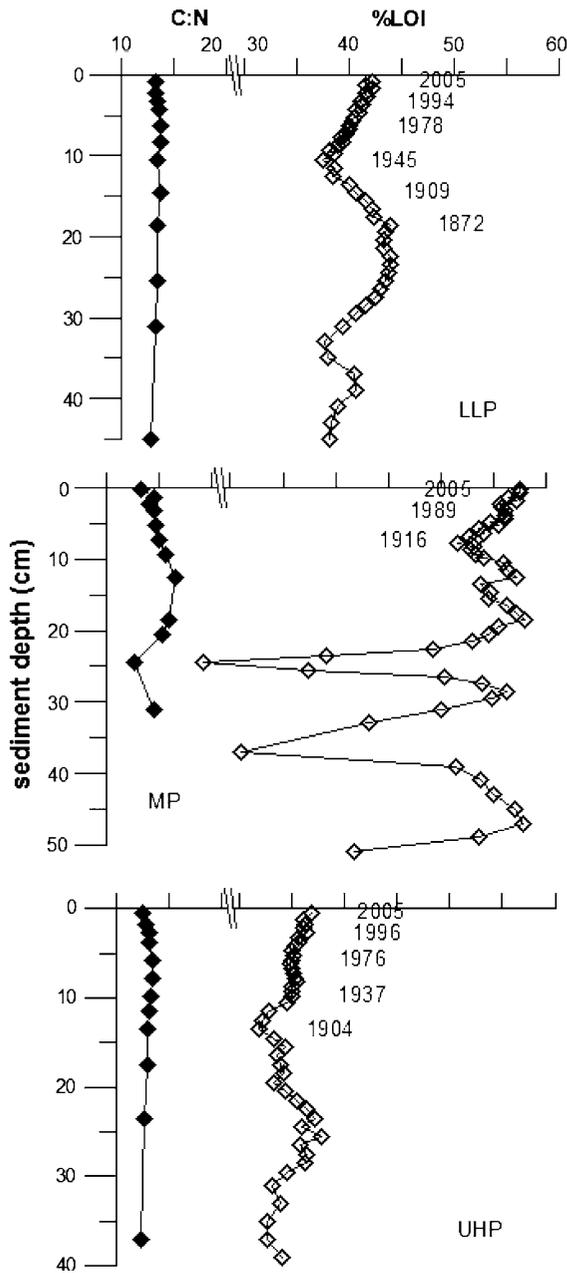
## Results

### Sediment chemistry

Sediment LOI, and C and N concentrations differed among the three study ponds (Fig. 1). MP had the highest mean LOI, C, and N, followed by LLP, then UHP. LLP and UHP LOI profiles indicate quite stable sedimentation. The LOI minima in the MP core below 20 cm (undatable by  $^{210}\text{Pb}$ ) likely are due to turbidity deposits in the steep-sided lake basin. The mean C:N ratio was lowest in UHP (13.0), followed by LLP (13.5), and MP (14.7), and was most variable

in MP. In all cores, the average total extractable Al (TAI) is at least 14 times higher than TP and at least four times higher than total extractable Fe (TFE). Only in MP is TP greater than TFE (Table 3). In all three lakes, the highest percentages of extractable Al and P are in the NaOH25 fraction, whereas Fe occurs roughly equally in the BD and NaOH25 fractions (Fig. 2). The extractable Fe in LLP and UHP is about eight times higher than in MP, and both of those cores have Fe enrichment at the sediment–water interface, corresponding to the redox cline. Interestingly, neither has a surface enrichment of P, which would be expected by the Einsele-Mortimer paradigm (Mortimer 1941).

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 for all three sediment records (Fig. 2). TP does not change significantly with depth. If one assumes a steady flux of P to the sediment, the constant TP suggests that there is a conservative transformation of nrP to rP that occurs without significant release of P from the sediment through time. We developed two models of sedimentary P dynamics that describe this diagenetic transformation (Fig. 3, 4). These models assume a constant sediment deposition rate and a negligible loss of P from the sediment to the overlying water. Because  $^{210}\text{Pb}$  measurement error increases with depth, sediment ages are most accurate in the top few centimeters. We largely ignore the dating errors when constructing our models, because most of the P transformation occurs in the top few centimeters. Sediment ages older than  $\sim 150$  years are extrapolations based on assumed constant mass accumulation rates. In MP, only the top  $\sim 8$  cm are accurately dated using  $^{210}\text{Pb}$ , due to the slow accumulation rate of sediment.



**Fig. 1** Carbon/nitrogen mass 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 Pond (LLP), Mud (MP), and Upper Hadlock (UHP) ponds. Select <sup>210</sup>Pb dates are displayed for reference

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),

**Table 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 (%)	TAI μmol g <sup>-1</sup> dry sed	TFe	TP
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

and that its corresponding rate coefficient is a function of time (Fig. 3), decreasing with increasing age. The time-dependent rate coefficient represents an initially relatively fast mineralization of the more labile nrP and the progressively slower mineralization rate of the more recalcitrant nrP. This model also assumes that mineralization is an irreversible process.

$$\frac{d[\text{nrP}]}{dt} = -k(t)[\text{nrP}] \tag{1}$$

The data fit an exponentially decaying rate coefficient as follows:

$$k(t) = ae^{-bt} \tag{2}$$

where, *a* is the initial rate coefficient and *b* is the rate constant for the decrease in the rate coefficient *k*(*t*). The analytical solution to Eq. (1) is

$$[\text{nrP}] = [\text{nrP}]_0 \exp\left(\frac{a}{b}(e^{-bt} - 1)\right) \tag{3}$$

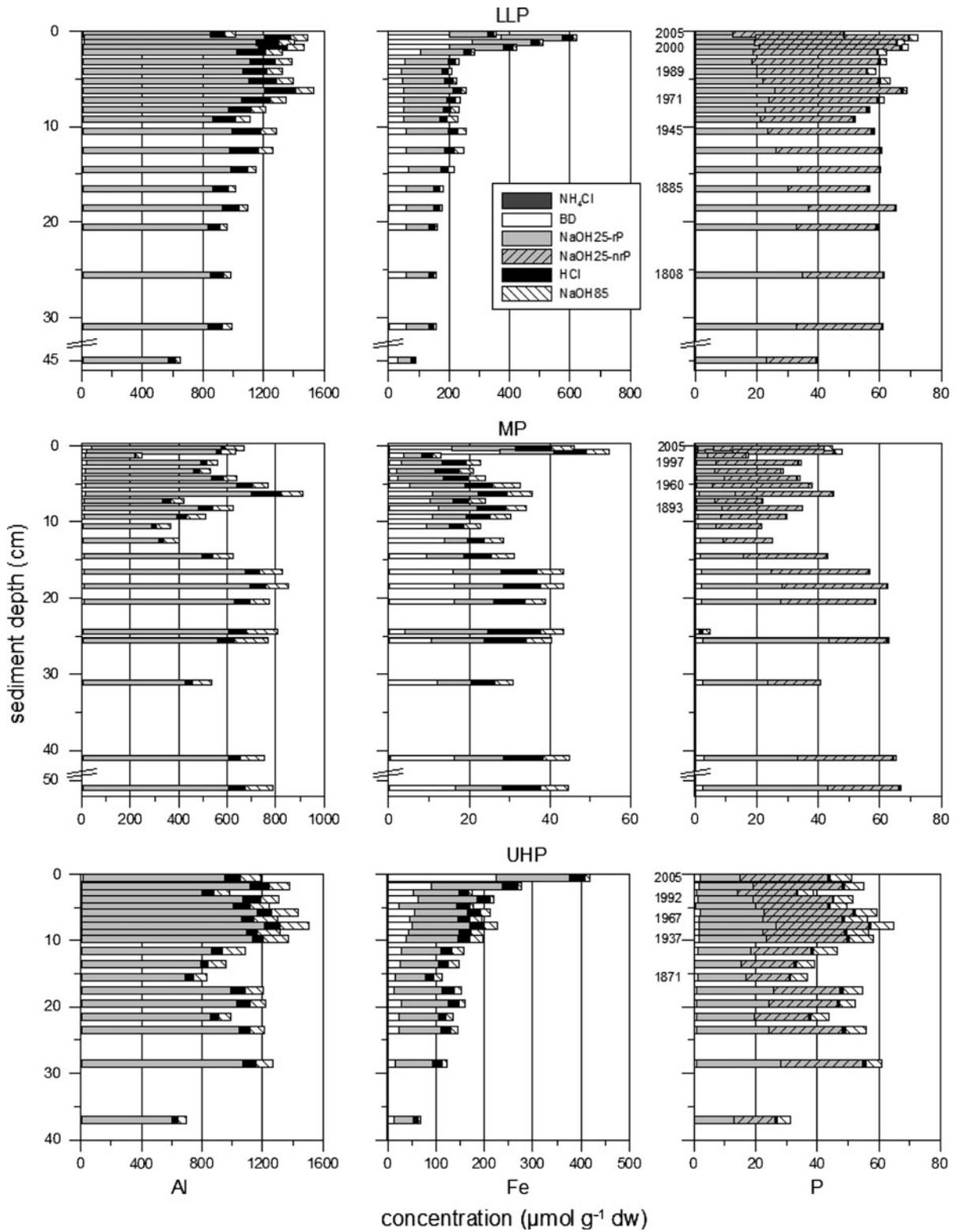
The constants *a* and *b* were fitted using non-linear least squares technique and are shown in Table 4 for each lake. Model simulations for sediment rP are based on mass balance (conservation of total NaOH25-P) with respect to sediment nrP. Simulated sediment rP is calculated as follows:

$$[\text{rP}] = [\text{nrP}]_0 + [\text{rP}]_0 - [\text{nrP}] \tag{4}$$

In Eqs. (3) and (4) [nrP]<sub>0</sub> and [rP]<sub>0</sub> are the concentrations of initially deposited nrP and rP.

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 (Fig. 4). Surface sediments initially carry a higher amount of nrP than rP and with time, nrP is



◀**Fig. 2** Results from sequential extraction of sediments from Little Long Pond (LLP), Mud Pond (MP) and Upper Hadlock Pond (UHP). Al (*left side*), Fe (*center*) and P (*right side*) concentrations are in  $\mu\text{mol/g}$  dry weight. Corresponding years of deposition, as determined by  $^{210}\text{Pb}$  dating, are shown on the P graph for each pond

transformed to rP. However, the steady-state ratio of the two implies that the transformation may also be a reversible process:



that leads to

$$r_{\text{nrP}} = -k_f[\text{nrP}] + k_r[\text{rP}] \tag{6}$$

$$r_{\text{rP}} = k_f[\text{nrP}] - k_r[\text{rP}] \tag{7}$$

where,  $r_{\text{nrP}}$  and  $r_{\text{rP}}$  are the transformation rates for nrP (mineralization) and rP (incorporation into microbial cells), respectively, and  $k_f$  and  $k_r$  are the forward (mineralization) and reverse (incorporation) rate constants, respectively. Equations 6 and 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 listed in Table 4. 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 nrP in each of these three oligotrophic ponds for comparison with other published values (Table 5).

Microbial analysis

Total sediment DNA concentration differed among the three lakes as did the number of organisms from each functional group (Table 6). Figure 5 shows DNA concentration and the abundance of organisms  $\text{g}^{-1}$  dry sediment for each functional group through the depth of each core. Sulfate reducers were the most abundant functional group in all cores throughout the depth of each, followed by *Geobacter* (a prominent phylum of iron reducers in most environments). Denitrifiers were abundant ( $>10^6 \text{ g}^{-1}$ ), and methanogen abundances were measurable but very low. In general, with the exception of methanogens, abundances were highest at the surface where electron donors are most abundant. In MP, there is a significant positive correlation between nrP/rP and

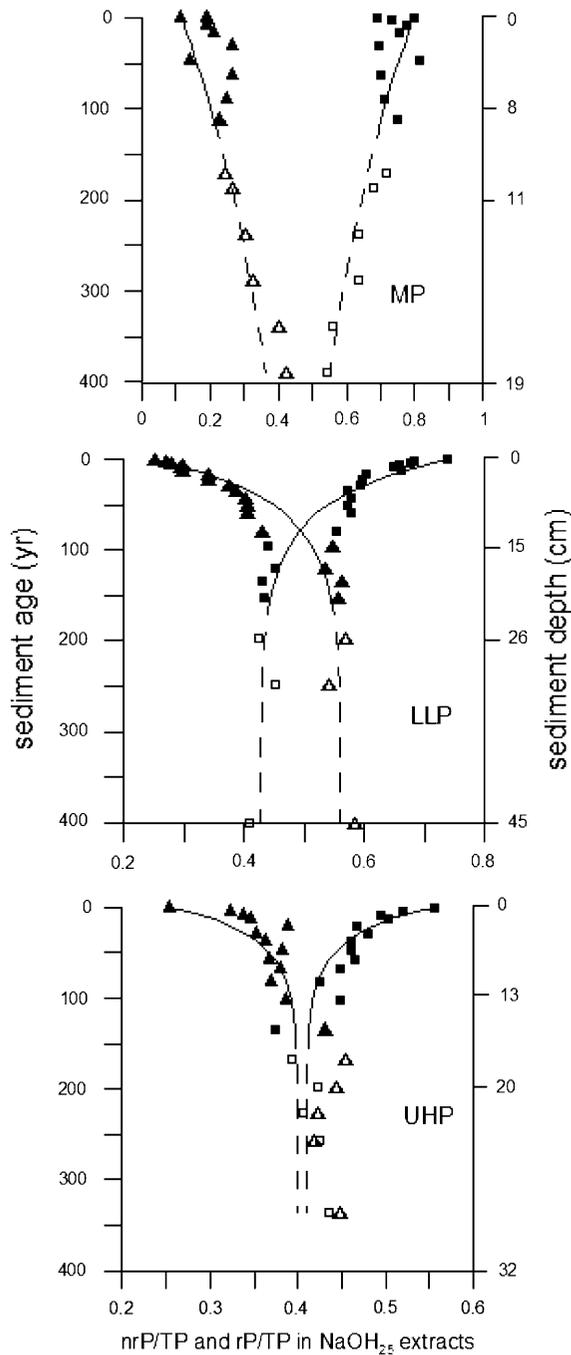
DNA ( $r^2 = 0.74$ ) as both decrease with increasing depth (age) in the core. This relationship does not appear in LLP or UHP sediment.

Discussion

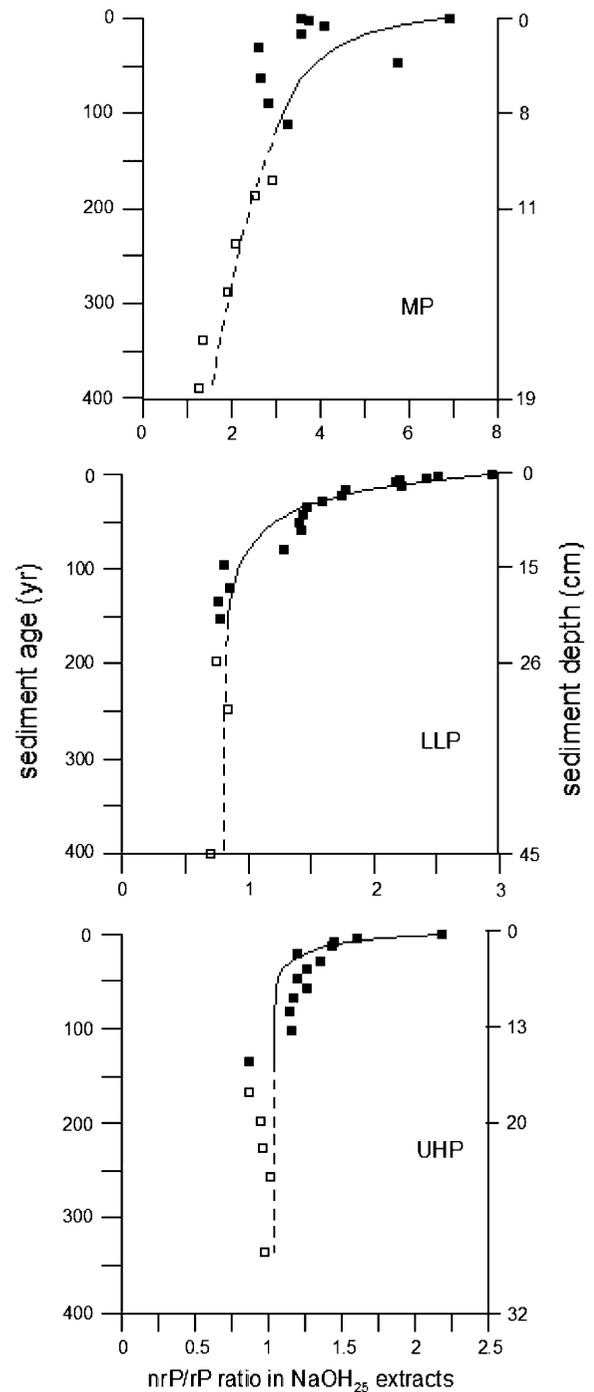
In eutrophic and mesotrophic lakes, the input of P over time is typically larger than the amount finally stored in the sediment (Rydin 2000). Several studies of the mesotrophic Lake Erken, Sweden (Ahlgren et al. 2005; Reitzel et al. 2007; Rydin 2000) and hypertrophic Lake Onandaga, New York (Penn et al. 1995), characterize the concentrations of P fractions in lake sediment profiles using the same chemical extraction sequence used in this study, and show a net loss of P from sediment over time. Biogenic P (NaOH25-nrP) from Lake Erken sediments was further characterized by Ahlgren et al. (2005) using  $^{31}\text{P}$  NMR spectroscopy, quantifying degradation rates (Table 6) of various P compounds that contribute to the mobile P pool. Malmaeus and Rydin (2006) and Ahlgren et al. (2006) attributed 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.

Cycling of P at the sediment water interface was generally believed to be an abiotic process. However, it is clear from numerous studies that bacterial activity plays an important role in P retention, burial, and flux across the sediment–water interface (Nealson 1997). Biologically-mediated storage and release of P is controlled by microbial mineralization, P incorporation into biomass, and redox-dependent processes. The contributions of biotic versus abiotic processes will vary between eutrophic and oligotrophic systems and as a function of sediment chemistry.

The lakes in our study are oligotrophic and do not release appreciable dissolved P from their bottom sediments, despite the seasonal development of



**Fig. 3** Variable rate coefficient model (*solid and dashed lines*) fitted to data from the three study ponds. Squares are nrP/TP and triangles are rP/TP from the NaOH (25°C) extraction. Data for sediment older than 150 years are plotted as open points and dashed lines, as these ages are extrapolated from the  $^{210}\text{Pb}$  datable portion. The model implies that the rate of transformation of nrP (non-reactive phosphorus) to rP (reactive phosphorus) is a function of time



**Fig. 4** Reversible reaction model (*solid line*) fitted to data points from the three study ponds. Data for sediment older than 150 years are plotted as open points and dashed lines, as these ages are extrapolated from the  $^{210}\text{Pb}$  datable portion. 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)

**Table 4** Calculated constants for the transformation of nrP to rP in sediments of three oligotrophic lakes in Maine, USA

	Model A		Model B		
	$a$ (year <sup>-1</sup> )	$b$ (year <sup>-1</sup> )	$k_f$ (year <sup>-1</sup> )	$k_r$ (year <sup>-1</sup> )	$K (= k_f/k_r)$
Little long	$9.34 \times 10^{-3}$	$1.52 \times 10^{-2}$	$1.14 \times 10^{-2}$	$9.26 \times 10^{-3}$	1.23
Mud	$1.27 \times 10^{-3}$	$1.40 \times 10^{-3}$	$7.01 \times 10^{-3}$	$2.13 \times 10^{-2}$	0.33
Upper hadlock	$8.76 \times 10^{-3}$	$2.52 \times 10^{-2}$	$2.91 \times 10^{-2}$	$3.09 \times 10^{-2}$	0.94

The constants are based on an irreversible model (Model A) with a variable rate coefficient, and a reversible reaction model (Model B)

**Table 5** Half-life ( $t_{1/2}$ ) values calculated for sediment P fractions and their sources from this and previous studies

Diagenetic material	$t_{1/2}$ (year)	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; calculated from various 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; irreversible model		This work
LLP	74	
MP	546	
UHP	79	
Lake sediment; reversible model		
LLP	61	
MP	99	
UHP	24	

anoxia and release of dissolved Fe(II) (MP and UHP) and Mn(II) (UHP) (Table 1). Additionally, similar to the observation by Hupfer et al. (2004) for oligotrophic and mesotrophic lakes, the profundal sediment TP does not decrease with increasing depth in any of the study lakes, lending evidence to their long-term P-retaining capacity. The decrease in nrP and increase in rP with depth, however, suggest that P

mineralization occurs with time but there is no upward diffusion of dissolved P.

#### Role of aluminum in lake trophic state

All lake sediment cores meet the requirements for sediment P retention as defined by Kopáček et al. (2005) and supported by Lake et al. (2007), based on molar

**Table 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 $\mu\text{g/g}$	Geo organisms $\text{g}^{-1} \times 10^6$	Dsr	McrA	NirK + NirS	C:N
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)	13.5 (12.9–13.8)
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)	14.7 (12.7–16.5)
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)	13.0 (12.3–13.5)

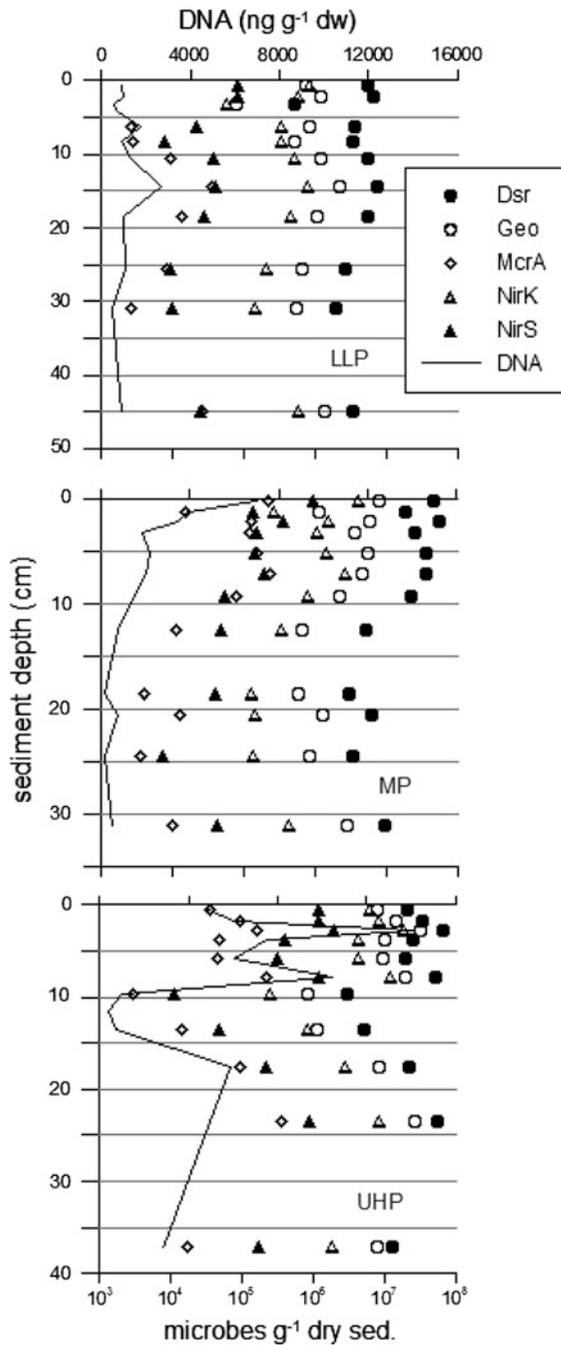
ratios of Al, Fe, and P fractions, throughout the periods of time represented by the cores (approximately 400, 1500, and 500 years for LLP, MP and UHP, respectively). In LLP, MP and UHP the  $[(\text{NH}_4\text{Cl}-\text{Al}) + (\text{BD}-\text{Al}) + (\text{NaOH}25-\text{Al})]:[(\text{NH}_4\text{Cl}-\text{Fe}) + (\text{BD}-\text{Fe})]$  ratios range from 3.3 to 24.8, 20.1 to 255, and 4.2 to 69.9, respectively. The  $[(\text{NaOH}25-\text{Al})]:[(\text{NH}_4\text{Cl}-\text{P}) + (\text{BD}-\text{P})]$  ratios 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  $>25$  (Fig. 6), thus exceeding the thresholds for P-retention by the sediment  $\text{Al}(\text{OH})_3$ .

#### 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 transformation model, model A (Fig. 3) 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  $\text{Al}(\text{OH})_3$  (Fig. 2), as evidenced by the very low concentrations of BD-P in all three lakes, but may also include P associated with vivianite ( $\text{Fe}_3(\text{PO}_4)_2$ ). The low BD-P concentration observed in this study may be due to the release of P originally bound to  $\text{Fe}(\text{OH})_3$  during the BD extraction followed by its readsorption to  $\text{Al}(\text{OH})_3$ . However, given the considerably higher concentration of NaOH25-Al than BD-Fe in all lakes, we believe that any P readsorption following BD extraction would be insignificant (Fig. 2). Further, reversing the second and third extractions on

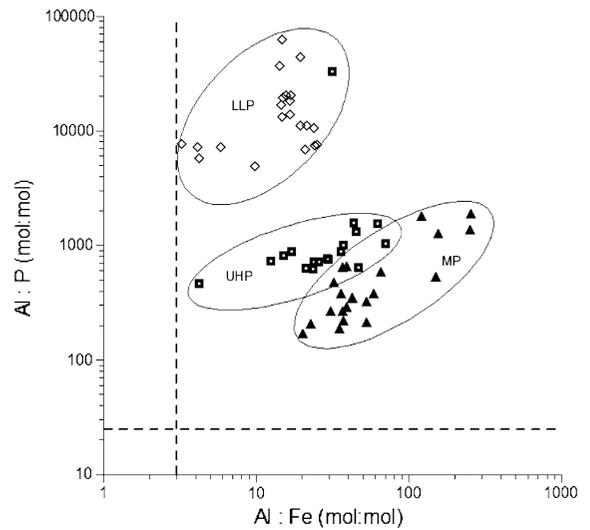
sediment from another oligotrophic lake did not produce significantly different apparent speciation of Al, Fe, and P (Norton, unpublished data). Because high concentrations of  $\text{Al}(\text{OH})_3$  increase the P sorption capacity of lake sediments (Kopáček et al. 2000), the elevated sediment Al in LLP, MP and UHP sediments should lead to permanent burial of rP following its production, with insignificant diffusion of dissolved P to overlying water. DeVicente et al. (2008) suggest that aged  $\text{Al}(\text{OH})_3$  may only have the capacity to sorb P to the point where Al:P is approximately 10:1. Navrátil et al. (2009) found that Al:P in freshly precipitated  $\text{Al}(\text{OH})_3$  may be as high as 50:1. The sediments in the three cores typically have Al:P of 20:1 in the NaOH25 fraction.

Alternatively, model B (Fig. 4) implies a more biotic sedimentary mechanism that transforms a portion of rP back to nrP, where microbial uptake of available rP (primarily  $\text{PO}_4$ ), released via mineralization of organic P, drives the reverse reaction. The plausibility of this model is supported by the observation that all total DNA concentration and the four functional groups exhibit subsurface variations in microbial biomass that correspond to variations in P mineralization rate. In LLP, there is a sharp rise in the density of all measured microbes between 10.5 and 14.5 cm depth (Fig. 5) along with a large drop in the nrP/rP ratio (Fig. 4). A similar relationship occurs in UHP at 7.75 cm and between 13.5 and 17.5 cm depth. This association of decreasing nrP/rP with increasing DNA concentration or microbe densities in these subsurface regions indicates that biota may accelerate the mineralization of nrP to rP. In MP there is a shift in nrP/rP between 5.25 and 7.25 cm depth which is not accompanied by a change in microbial densities. Instead there is an overall positive relationship between nrP/rP and microbe densities throughout the MP core. The relative consistency with depth of microbial biomass based



**Fig. 5** DNA concentration (ng g<sup>-1</sup>) 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

on DNA and PCR analyses suggests that benthic biotic activity may reach steady state, perhaps due to acidic, nutrient-limited conditions within the ponds



**Fig. 6** Ratio of NaOH25-Al to NH<sub>4</sub>Cl-P + BD-P (Al:P) versus the ratio of NH<sub>4</sub>Cl-Al + BD-Al + NaOH25-Al to NH<sub>4</sub>Cl-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)

and bottom sediment. It appears that at all three study sites, there is a combination of biotic and abiotic processes contributing to the mineralization and sequestration of P in the sediment record.

The calculated  $t_{1/2}$  of sediment nrP differs among ponds and also changes with sediment age in the reversible model. Compared to similar studies (Table 5), the  $t_{1/2}$  values calculated from our models are high, especially in MP, perhaps due to its high amount of sediment organic matter. <sup>210</sup>Pb dating errors and age approximations for the deeper sediments have a minor effect on the relative magnitudes of the  $t_{1/2}$  values for our models. It is likely that sedimented and buried nrP in these systems is generally more recalcitrant than in more eutrophic lakes. Allochthonous organic matter, especially more recalcitrant humic material, may be the main source of P to these oligotrophic systems, contributing to a longer  $t_{1/2}$  (Reitzel et al. 2007). Supporting this idea also is the relatively high sediment C:N ratios (Fig. 2), 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  $t_{1/2}$ , 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. Gächter and Meyer (1993) suggested that in oligotrophic lakes a larger fraction of the P settles with organic detritus, which is then converted to refractory organic compounds during mineralization by the in situ microbial community. In addition, P incorporated into biomass will substantially exceed depositional bioavailable P compounds.

## Conclusions

The dynamics of lake sediment P 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 released to the water. Permanent sorption and burial occur in sediments that have excess  $\text{Al}(\text{OH})_3$  as compared to reducible Fe hydroxide, which releases P with the onset of anoxia. Thus, sediment records in Al-rich systems likely preserve the net flux record of P, after initial burial of the sediment.

By determining concentrations of Al, Fe, and P fractions, the total microbial biomass, the contribution of microbes carrying out specific redox processes, and mineralization rates of P in these historically oligotrophic lakes, we have gained insight on sediment characteristics that prevent internal loading. Studies of these attributes help define historical trophic conditions and evaluate potential impacts related to nutrient loading from anthropogenic disturbances in lake systems. The techniques we used for this study are potentially

applicable to any lake with an undisturbed sediment record.

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