Sequential extraction of sediments [Psenner R, Pucsko R. Die Fraktionierung organischer und anorganischer Phosphorverbindungen von Sedimenten. Arch Hydrobiol/Suppl 1988. 70(1): 111–155.] from short, 210Pb-dated cores from three lakes in Maine USA demonstrates that sediment P is dominantly associated with the NaOH-extractable fraction (P-NaOH) and less with the bicarbonate-dithionite extractable fraction (P-BD). The ratios (Al-NaOH)/(Fe-BD) and (Al-NaOH)/(P-NH4Cl+P-BD) for upper sediment for two oligo-mesotrophic lakes exceeded 3 and 25, the thresholds for preventing substantial release of P from sediments during hypolimnetic anoxia [Kopáček J, Borovec J, Hejzlar J, Ulrich K-U, Norton SA, Amirbahman A. Aluminum control of phosphorus sorption by lake sediments. Environ Sci Technol 2005a;39:8784–8789.]. Hypolimnetic water chemistry verifies this effect. The third lake, currently eutrophic, has values for the ratios that are below the thresholds and this lake has substantial release of P from recent sediment. The sediment characteristics remain relatively constant over the last 150+ years, indicating that the processes responsible for P retention have operated long before atmospheric acidification of watersheds might have influenced the flux of Al and Fe to the lake. In 2002, the pH of inlets and the lakes was generally between 6 and 8. Input to the lakes had high concentrations of acid-soluble particulate and dissolved Al, Fe, and P, and dissolved Al and Fe complexed with dissolved organic carbon (DOC). Lake water column and outlet Al, Fe, and P were typically 90–95% lower than inlet concentrations over a 12 month period. Photo-oxidation of Al-DOC and Fe-DOC in the lake, liberation of inorganic Al and Fe, precipitation of Al(OH)3 and Fe(OH)3, adsorption of P by the hydroxides, and sedimentation are responsible for the changes in water quality and long-term sediment characteristics.

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1. Introduction

Phosphorus (P) is probably the most-studied element in surface waters, largely because of eutrophication of surface waters caused by increased flux of P from agriculture, industrialization, urbanization, and disposal of biological waste. Oligotrophic waters (sensu Naumann, 1919) are characterized by low primary productivity. An important question is: Why do some surface waters have low dissolved P (commonly referred to as soluble reactive phosphorus, SRP) on a sustained basis?
Phosphorus in lake water columns at any time may be derived by external loading or be recycled from bottom sediments (e.g., Bostrom and Pettersson, 1982). Internal loading may greatly affect the trophic status of a lake (Pettersson, 1998). Einsele (1936) and Mortimer (1941) first studied the release of P from lake sediments. They found good correlation between release of P and Fe from sediments during hypolimnetic anoxia. The paradigm was that iron hydroxide (Fe(OH)₃) dissolved during anoxia, releasing adsorbed PO₄³⁻. Amirbahman et al. (2003) studied five eutrophic (high P) and six oligo-mesotrophic (low to moderate P) lakes in Maine, all of which developed anoxic summer hypolimnian. Late summer hypolimnetic total P concentrations in the eutrophic lakes ranged from approximately 200 to 500 μg/L. Epilimnetic total P increased as much as 30 μg/L during summer stratification. During the same period, the oligotrophic lakes had hypolimnetic total P concentrations in the range of 5 to 20 μg/L. The distribution and change of P through time in all the hypolimnia implicated the sediment as a source. The average fluxes of total P and dissolved Fe from sediment from nine of the lakes (excluding Highland and Pennesseewassee Lakes) were strongly linearly correlated (R²=0.93). However, Highland and Pennesseewassee Lakes, both of which are oligo-mesotrophic, had Fe₃dissolved:PO₄dissolved ratios less than 10% of the predicted value based on the model developed from the other lakes (Amirbahman et al., 2003). Internal P recycling from the sediment to the hypolimnion was not restricted by the total sediment P concentration in the sediment for any of the lakes, nor was the P concentration in the water column controlled by the solubility of P-containing minerals (e.g. Caráco et al., 1991). This seemingly anomalous behavior suggested a control mechanism for P not related to Fe. We hypothesized that P chemistry in those two lakes was controlled by Al chemistry exerting a strong control on P transport to the lake, immobilization within the lake water column, and retention in the sediment during periods of anoxia for Highland and Pennesseewassee lakes (Amirbahman et al., 2003).

Dickson (1978), based on laboratory experiments, suggested that oligotrophication might result from increasing the pH of Al-rich waters, thereby precipitating Al(OH)₃ that absorbs PO₄³⁻. Liming of acidic lake water clearly causes the precipitation of Al and the lowering of dissolved P (Broberg 1984). Roy et al. (1999) and Reinhardt et al. (2004) demonstrated that acid-soluble Al(OH)₃ particulates are associated with particulate P export at high discharge from acidic watersheds. Huser and Rydin (2005) suggested that P was retained by increased Al in the recent sediment of two Swedish lakes. They argued that P was adsorbed onto Al(OH)₃ in surface or near-surface sediment. The impact of particulate Al(OH)₃ in the water column on P availability has been documented on a short-term basis for Lake Plesné in the Czech Republic (Kopáček et al., 2000) and inferred for the entire Holocene (Kopáček et al., 2007). Recent profundal sediments at Lake Plesné in the Czech Republic were enriched in acid-soluble Al(OH)₃. They argued that the lake had been a trap for Al, and that P was irreversibly sequestered in the sediment by the Al(OH)₃. They determined that the Al(OH)₃ was unsaturated with respect to adsorption of PO₄³⁻. Thus, even if there were appreciable P associated with sedimented Fe(OH)₃, it would not be released from the sediment if the hypolimnion became anoxic. Released P would merely shift from Fe(OH)₃ to Al(OH)₃. Thus, this secondary Al phase may irreversibly remove P from water and prevent cycling between the sediment and the water column of many lakes (Kopáček et al., 2001). Kopáček et al. (2005b, 2006) have demonstrated, experimentally and empirically, the importance of photo-degradation of Al-DOC complexes, followed by the release of inorganic Al (Al₃), and precipitation of Al(OH)₃. Al(OH)₃, of any origin, clearly dominates P availability in oligotrophic lakes.

We evaluated the speciation of Al, Fe, and P in 210Pb-dated sediment deposited in three lakes to test the hypothesis that Al(OH)₃ exerted a strong control on P immobilization within the lake water column, and enhanced retention in the sediment during periods of anoxia.

2. Methods

The three study lakes are dimictic with histories of summer hypolimnetic anoxia. Highland Lake and Pennesseewassee Lake are oligo-mesotrophic lakes in southern Maine USA (43°46.50’N, 70°21.58’W and 44°12.98’N, 70°34.53’W, respectively). Soils in the forested catchments are developed on till. Both lakes have high average summer hypolimnetic Fe fluxes (188 and 130 mg m⁻² day⁻¹, respectively) and low-P fluxes (<1 mg m⁻² day⁻¹). Salmon Lake in southern Maine (44°31.30’N, 69°47.09’W) is eutrophic. Till and late glacial marine clay underlie most of the watershed. Salmon Lake has an average summer hypolimnetic Fe flux of 212 mg m⁻² day⁻¹ and P flux of 13.6 mg m⁻² day⁻¹ fluxes (Amirbahman et al., 2003).

Core samples were retrieved from the deepest part of Highland, Pennesseewassee, and Salmon Lakes on August 12 and 30, and September 20, 2002, respectively, using a Davis and Doyle (1969) piston corer. The cores were sectioned in the field into Whirl-Pak™ bags in 0.5 cm intervals from 0 to 10 cm depth, 1 cm intervals from 10 to 20 cm depth, and 2 cm intervals from 20 cm to the bottom (ca. 40 cm) of the cores. The samples were kept on ice until they were returned to the laboratory where they were frozen at ~21 °C until they were dried or analyzed. Alternate intervals of each core were analyzed for moisture content (% water lost at 100 °C) and loss-on-ignition (LOI at 550 °C for 2 h).

Sediment chronology was determined by measuring 210Pb and 137Cs on selected intervals. Dried sediment intervals were capped in 1 x 4 cm polyethylene vials, equilibrated for at least three weeks, and then counted for 43,200 to 259,200 s. 210Pb gamma-ray activity was determined using the 46.52 keV emission. We used a Canberra germanium well detector (Oxford Instruments). Data were processed using GammaTrac software (Oxford Instruments). Data were analyzed by Compton continuum subtraction of the peaks. Calibration of the detector was done using U.S. EPA National Exposure Research Laboratory aqueous standards in the same geometry as the sediment samples. The 210Pb₂ (unsupported 210Pb) activity was estimated by subtracting the constant background 210Pb activity (210Pb₁), deep in the core, from total 210Pb (210Pb₂). The integrated 210Pb₂ (210Pb₂ = Bq 210Pb₂/cm²/core), necessary for dating, also assesses the amount of sediment focusing. Calculation of age of interval midpoints was based on the Constant Rate of Supply (CRS) model and
Constant Input Concentration (CIC) model (Appleby and Oldfield, 1978).

Sequential fractionation of alternate sediment intervals followed a modified version of Psenner and Pucsko (1988). The extraction sequence was: (1) 1 M NH₄Cl to remove ion-exchangeable species (NH₄Cl-extractable) (Tessier et al., 1979), (2) 0.11 M NaHCO₃ and 0.11 M NaS₂O₄ to remove reducible metal hydroxides, predominantly amorphous Fe(OH)₃, and P associated with these phases (BD-extractable), (3) 1 M NaOH at 25 °C to partially extract organic P (org-P) and P adsorbed to Al and Fe hydroxides (Al-P and Fe-P) (NaOH25-extractable), (4) 0.5 M HCl to extract mineral Al and Fe, and P associated with these minerals, as well as calcite (CaCO₃) and apatite (Ca₅(PO₄)₃(OH)) (HCl-extractable), and (5) 1 M NaOH at 85 °C to extract residual P (NaOH85-extractable).

Al, Fe, and P in each extract were measured with a Perkin Elmer 3300-XL, axial view, Inductively Coupled Plasma-Optical Emission Spectrometer. Solutions from the 1 M NaOH extraction were diluted because of the high Na concentrations. All suspensions for microwave extraction were filtered through 0.45 µm filters prior to analysis.

We calculated accumulation rates for each species (e.g., P-NaOH25) for each individual interval of sediment using the CRS chronology. Age of the mid-point of intervals corresponds with concentration data for entire intervals. Boundary ages of intervals were calculated by linear interpolation between mid-interval ages. The algorithms for accumulation rates are detailed in Norton et al. (2004). Data required are interval thickness and age, % H₂O, loss-on-ignition, concentration of species, and an assumed specific gravity of inorganic matter (2.6) and organic matter (1.6).

### 3. Results

#### 3.1. Water and loss-on-ignition (LOI)

The three cores had downward smooth decreases in % H₂O (>90% in surface sediment), reaching nearly constant values by 10 cm (Pennesseewassee >90%) and ca. 15 cm for Highland (75%) and Salmon (75%). Loss-on-ignition steadily declined downward in all three cores, reaching near-steady state by 10 cm. Pennesseewassee declined from 30% to values varying smoothly between 25 and 30%. Highland declined downward from 20 to 12 to 15%. Salmon declined from 20 to 12%. As for most temperate lakes, LOI and % H₂O covary (Coolidge, 2004). We do not know if the surface enrichment in LOI is caused only by a transient enrichment that will disappear with continued sedimentation and diagenesis, or an increased net sedimentation rate for organic matter. A small fraction of the LOI can be attributed to dehydration of secondary phases, including Al(OH)₃ and Fe(OH)₃, which account for up to 2.5% and 1%, respectively, of the LOI. However, given the constancy of the Al and Fe species (below), trends in LOI are caused dominantly by the variation in oxidizable hydrocarbon concentration.

#### 3.2. Dating of sediment

Background ²¹⁰Pb (²¹⁰Pbₗ) activities were higher than reported by Binford et al. (1993) for drainage lakes in the New England region (Table 1). The high ²¹⁰Pb suggests relatively radiogenic sediment, consistent with the granitic bedrock underlying the watersheds. The activity of ²¹⁰Pb for all lakes decreased exponentially with sediment depth. None of the profiles had substantial inflections that would suggest bioturbation or other mixing processes (Binford et al., 1993). Pennesseewassee Lake, however, had minor variation in the ²¹⁰Pb activity profile between 1 and 8 cm of the profile. The ²¹⁰Pb activity at the sediment surface (C₀), total integrated unsupported ²¹⁰Pb, and ²¹⁰Pb fluxes (F) were within or slightly higher than the ranges for New England lakes reported by Binford et al. (1993) (Table 1).

The ¹³⁷Cs peaks for the three cores are broad and occur later, based on CRS ²¹⁰Pb chronology, than the 1963/4 peak in atmospheric deposition of thermonuclear bomb fallout (Fig. 1).

### Table 1 – ²¹⁰Pb data from the study lakes

<table>
<thead>
<tr>
<th>Lake</th>
<th>²¹⁰Pbₗ Bq g⁻¹</th>
<th>C₀ Bq g⁻¹</th>
<th>∑²¹⁰Pbₗ Bq cm⁻²</th>
<th>F Bq cm⁻² yr⁻¹</th>
<th>Accumulation rate mg cm⁻² yr⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highland</td>
<td>0.097</td>
<td>1.67</td>
<td>1.035</td>
<td>0.032</td>
<td>18.3</td>
</tr>
<tr>
<td>Pennesseewassee</td>
<td>0.032</td>
<td>1.37</td>
<td>0.857</td>
<td>0.027</td>
<td>13.5</td>
</tr>
<tr>
<td>Salmon</td>
<td>0.031</td>
<td>0.75</td>
<td>0.646</td>
<td>0.020</td>
<td>35.4</td>
</tr>
<tr>
<td>New England Lakes</td>
<td>0.028–0.040</td>
<td>0.23–0.88</td>
<td>0.054–0.794</td>
<td>0.002–0.025</td>
<td>3.2–14.3</td>
</tr>
</tbody>
</table>

²¹⁰Pbₗ = supported background; C₀ = surface activity; Pbₗ = unsupported ²¹⁰Pb; F = atmospheric flux.
These peaks are broad likely because of delayed wash-in of terrestrial detritus containing $^{137}$Cs, sediment movement from shallow to deeper water, and downward molecular diffusion of $^{137}$Cs. Only the Highland $^{137}$Cs peak is in close agreement with the $^{210}$Pb chronology. Using the CIC model did not improve agreement between $^{210}$Pb and $^{137}$Cs ages. Stable Pb concentrations, which typically peak in value between 1970 and 1980 in sediment of New England lakes and in peat accumulations (Norton, 2007), have broad peaks, again suggesting wash-in of extra Pb-rich detritus. Sediment dated at 1900 A.D was reached at 11.5, 19, and 20 cm for Highland, Pennesseewassee, and Salmon, respectively.

### 3.3. Concentrations of Al, Fe, and P in sequential extracts

Total (= sum of NH$_4$Cl, B-D, NaOH$_{25}$, HCl, and NaOH$_{85}$ extractions) ext-Al, ext-Fe, and ext-P in the cores ranged from 421 to 991, 468 to 908, and 19 to 69 µmol g$^{-1}$, respectively. The two oligo-mesotrophic lakes, Highland and Pennesseewassee, had ranges for ext-Al, ext-Fe, and ext-P that are considerably higher and not overlapping with the eutrophic Salmon Lake. Highland and Pennesseewassee data were very similar so we show speciation data for only Highland and Salmon Lakes.

Al-NH$_4$Cl and Al-BD were less than 2% of ext-Al among all lakes. The average concentration of Al-NaOH$_{25}$ for Highland Lake (341±62 µmol/g, 40±7% of ext-Al; Fig. 2a) and Pennesseewassee Lake (436±50 µmol/g, 58±7% of ext-Al) was approximately twice that of Salmon Lake (191±30 µmol/g, 36±12% of ext-Al; Fig. 2b). The average concentration of Al-HCl was similar among the lakes (160±27 µmol/g [19±3% of ext-Al], 116±17 µmol/g [15±2% of ext-Al], and 144±14 µmol/g [27±10% of ext-Al]) for Highland, Pennesseewassee, and Salmon lakes, respectively, with the highest concentration of Al-HCl in Highland Lake. Highland Lake also had a higher concentration of Al-NaOH$_{85}$ (329±50 µmol/g, 39±6% of ext-Al) than Pennesseewassee (175±27 µmol/g, 23±4% of ext-Al) or Salmon Lake (183±30 µmol/g, 35±11% of ext-Al). The average concentration of ext-Al in Highland and Pennesseewassee Lakes, the low-P lakes, was 845±111 µmol/g and 746±80 µmol/g, respectively, 150% of that in the high-P Salmon Lake (530±55 µmol/g). Extractable Al in the two NaOH fractions, combined, was 60 to 83% in the three lakes (Fig. 2).

The average concentrations of Fe-NH$_4$Cl in Highland (<5% of ext-Fe; Fig. 3a) and Pennesseewassee (<2% of ext-Fe) Lakes were less than in Salmon Lake (11% of ext-Fe; Fig. 3b). The concentration of Fe-NH$_4$Cl in Salmon Lake increased toward the sediment surface, reaching a maximum of 21% of ext-Fe at the sediment–water interface. The average concentration of Fe-BD was greater for Salmon Lake sediment (24±9% of ext-Fe) than for Highland or Pennesseewassee lakes (4.5±2% and 18±2% of ext-Fe, respectively).
25% of ext-Fe, respectively). Among the lakes, the maximum concentration of Fe-BD occurred at the surface of Pennesseewassee Lake sediment (169 μmol/g, 39% of ext-Fe). The surface enrichment is likely caused by some combination of (1) SO₄ reduction in the anoxic hypolimnion and sediment, and formation of FeSₓ, (2) sedimentation of Fe(OH)₃ from the water column during oxic conditions, and (3) precipitation of Fe(OH)₃ from upwardly diffusing dissolved Fe²⁺. The Fe-NaOH₂₅ (8%, 14% and 4% of ext-Fe for Highland, Pennesseewassee and Salmon Lakes, respectively) and Fe-NaOH₈₅ (12%, 22% and 9% of ext-Fe for Highland, Pennesseewassee and Salmon Lakes, respectively) were relatively small for all lakes. The largest fraction of ext-Fe was extracted as Fe-HCl for all lakes (~72%, ~44% and ~52% for Highland, Pennesseewassee, and Salmon Lakes, respectively). The concentration of ext-Fe decreased significantly below the sediment–water interface, reaching constant concentrations within a few centimeters in all three lakes.

The concentration of P-NH₄Cl in the three lakes was <3% of ext-P at all depths. The highest concentration of P-BD in Salmon Lake was in the 0 to 2 cm interval (32% of ext-P); it decreased dramatically with increasing depth (Fig. 4a). The concentration of P-BD in Highland and Pennesseewassee was <1% of ext-P throughout the cores (Fig. 4b). Average P-NaOH₂₅ was greater for Highland (80±14% of ext-P) and Pennesseewassee (81±5% of ext-P) than for Salmon Lake (53±12% of ext-P). Salmon Lake sediments had more than twice the percentage of P-HCl (27±5%) in Highland (10±2%) and Pennesseewassee (8±2%) lakes. P-NaOH₈₅ was similar in all lakes (~10±3%, ~10±2%, and ~12±1% of ext-P for Highland, Pennesseewassee, and Salmon lakes, respectively). The average concentration of total ext-P in eutrophic Salmon Lake sediment was approximately half that of oligo-mesotrophic Highland and Pennesseewassee lake sediment. The concentration of P-BD in the surface sediment of the high-P Salmon Lake was greater than the concentration of the P-BD in the surface sediment of the other two lakes, suggesting that a smaller concentration of P in Salmon is released due to the reductive dissolution of Fe(OH)₃. It also suggests that the sediment of the low-P lakes has a greater capacity to sequester P permanently. Kopáček et al. (2000, 2001) suggested that high-P NaOH is indicative of P adsorbed to Al-hydroxides. The larger concentrations of P-NaOH₂₅ strongly correlate with the high Al-NaOH₂₅ in the low-P lake sediment supporting the hypothesis that Al-hydroxides may be responsible for natural sequestration of P in sediment (Kopáček et al., 2000, 2001). However, because NaOH₂₅ also extracts org-P, the extraction does not unequivocally allow the determination of P associated with Al (see Wilson et al., 2008).
3.4. Accumulation rates of Al, Fe, and P in sequential extracts

Mass accumulation rates for Highland and Pennesseewassee are similar (0.01 to 0.03 g/cm²/yr) but approximately half of those of Salmon. Uncertainties in dating (disagreement between 137Cs and CRS 210Pb) make it impossible to give precise values. Accumulation rates for Al, Fe, and P fractions for all three lakes vary over the last 100 years. Much of this variability is caused by the variation in the calculated sediment accumulation rates. We are unable to determine if the variability in accumulation rates is caused by dating errors or is real. If Al, Fe, and P accumulation rates are normalized to sedimentation rate, the variations in accumulation rates are substantially reduced (Figs. 5–7).

4. Discussion

Except for the top few cm of sediment, proportions of the five sequential extracts are relatively unchanged through the 210Pb-dated history represented by the cores (100 to ca. 150 years). Below that level (ca. 10–12 cm) to a depth of >40 cm (undatable by 210Pb), the speciation relationships remain nearly constant (Coolidge, 2004). Although accumulation rates of Al species vary, this is largely a function of variations in gross sedimentation rate, not changes in delivery rate of Al to sediment induced by acidification. Indeed, none of the lakes has had a pH lower than 6 at any time in the recent decades (http://pearl.maine.edu/textsearchb.asp?searchstr=LAKESSTREAMS). Extractable Fe is concentrated in the BD and HCl fractions in the three lakes, and there is no persistent trend in the proportions or flux of the fractions over the history represented by the cores except for the typical Fe enrichment in surface sediment (Fig. 3a,b). The P-NaOH$_{25}$ is more than 80% of extractable P in the two oligo-mesotrophic lakes and combined with the NaOH$_{85}$ fraction is >90% (Fig. 4). The combined P-NaOH$_{25}$ and P-NaOH$_{85}$ in these two lakes is nearly twice that of the eutrophic Salmon Lake. Thus, total accumulation rates are similar but speciation differs; more P is associated with non-NaOH fractions in Salmon sediment.

Based on sequential extraction of lake sediments, Kopáček et al. (2005a,b) suggested that if the ratios (1) (Al-NaOH$_{25}$)/(Fe-BD) and (2) (Al-NaOH$_{25}$)/(P-NH$_4$Cl+P-BD) exceed 3 and 25, respectively, then P is strongly associated with the Al(OH)$_3$ and as such, its release from sediments may be severely restricted during anoxia. For Highland Lake, these ratios are persistently in excess of 24 and 200, respectively, throughout the last 100 years. For Pennesseewassee Lake, values of ratio (2) are persistently above 1000, but in the uppermost sediment analyzed (1–1.5 cm), the (Al-NaOH$_{25}$)/(Fe-BD) ratio declines to

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**Fig. 6** – a: Accumulation rate of Fe in sediment from Highland Lake, Maine. b: Accumulation rate of Fe in sediment from Salmon Pond, Maine.

**Fig. 7** – a: Accumulation rate of P in sediment from Highland Lake, Maine. b: Accumulation rate of P in sediment from Salmon Pond, Maine.
2.4, suggesting that P may have been released from surface sediment during anoxia in recent years. Sediment from eutrophic Salmon Lake also changes in the upper few cm. Prior to about 1995, both ratios suggest that little P was released from the sediment; however, diagenesis of sediment after burial typically causes upward migration of Fe to surface sediment. Thus, older Salmon sediment (and formerly at the surface) likely had sediment characteristics more favorable for recycling of P during hypolimnetic anoxia as seen during the 1999 summer anoxia (Amirbahman et al., 2003). Thus, sediment dated to within the last decade, may be typical of surface sediment over a longer period of time. Although the P net accumulation rate is lowest for the eutrophic lake, most of the recently deposited P resides in the BD fraction and thus is released during anoxia.

These data support the hypothesis that Al(OH)_3 has been responsible for sequestering P in the sediment. The source of the Al(OH)_3 cannot be dominantly from acidification of the landscape due to acid rain. In a 2002 study (Norton et al., unpublished), tributaries, lake profiles, and outlet water of the three lakes were sampled between 10 and 14 times during the ice-free seasons and analyzed for pH, DOC, and dissolved and particulate Al, Fe, and P, among others. Tributary pHs for these lakes ranged from slightly above 5 to 8, depending on discharge and DOC concentration. Concentrations of total Al and Fe ranged from <100 to >1000 µg/L with accompanying DOC values ranging from 5 to 25 mg/L. Particulate Al and Fe were commonly major fractions of the total Al and Fe. Although dissolved Al and Fe were not specified into inorganic and organic species, it is probable that most of the dissolved Al and Fe was complexed with DOC. Lake profiles and outlet samples clearly indicate that the lake was a sink for previously dissolved and particulate Al, Fe, P, and DOC. Concentrations of Al and Fe (particulate and dissolved) were reduced between 75 and 85% from inlet values. It is probable that photo-oxidation of Al-DOC and Fe-DOC complexes transported from the catchment, release of inorganic Al and Fe in the lake, precipitation of Al(OH)_3 and Fe(OH)_3 in the lake water column, adsorption of P on these precipitates, and sedimentation of these precipitates modify incoming surface water and contribute to the sediment (Kopáček et al., 2007). Our results suggest that these processes have operated for the entire time represented by the cores (ca. 200 to 400 years) and thus were operating before any significant catchment disturbance and prior to any impact from atmospheric acidification.

5. Conclusions

Sediment cores from two oligo-mesotrophic lakes and one currently eutrophic lake indicate that extractable Al and P (Psenner and Pucsko, 1988) occur dominantly in the NaOH25 and NaOH25-extractable fractions. Extractable Fe is dominantly in the B-D and HCl fractions. The ratios (Al-NaOH25)/(Fe-BD) and (Al-NaOH25)/(P-NH4Cl + P-BD) for upper sediment for two lakes exceed 3 and 25, respectively, accurately predicting low release of P during hypolimnetic anoxia. The eutrophic lake ratios are below the thresholds. Consequently, sediment in that lake releases P during anoxia. The sediment characteristics are relatively constant over the last 100+ years, indicating that the processes responsible for sedimentation of Al(OH)_3 and net sedimentation of Fe(OH)_3 and adsorbed P have been relatively constant. None of the lakes has become acidified and thus there is little likelihood that transport of inorganic Al or Fe to the lake has increased in the last 100 years. The abundant Al and Fe hydroxide in sediment is derived from two sources: (1) Sedimentation of particulate acid-soluble Al and Fe (hydroxides) entering the lakes and (2) Photo-oxidation of abundant Al and Fe complexed with dissolved organic matter in surface inlets, followed by the release of inorganic Al and Fe, precipitation of Al and Fe hydroxide, and sedimentation. Approximately 80–90% of Al and Fe entering these lakes are removed in this manner.

Acknowledgments

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