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This Deliverable comprises two manuscripts

i) Photochemical Source of Metals for Sediments

ii) Natural inactivation of phosphorus by aluminum in pre-industrial lake sediments.
Photochemical Source of Metals for Sediments

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A mass budget study of major in-lake Al fluxes, palaeo-limnological data on a > 10 000 year old sediment record, and in situ photochemical experiments performed at Plešné Lake (Czech Republic) suggest that photochemical liberation of organically bound aluminum (Al) and iron (Fe) by solar radiation is a significant natural source of their ionic species for lakes and subsequent oxyhydroxides for sediments. The results show that photochemically induced transformation of dissolved Al and Fe to solid oxyhydroxides deposited to Plešné Lake sediment dominated (91 and 73%, respectively) their sedimentary flux throughout the preindustrial era, since soil formation initiated in the catchment. The following sequence of processes occurs: (i) soil organic acids dissolve and bind metals and export them to terrestrial to aquatic systems. (ii) Photochemical decomposition of organic–metal complexes liberates a significant portion (~50% in Plešné Lake) of organically bound Al and Fe as inorganic ions. (iii) The liberated ionic Al and Fe hydrolyze, precipitate as oxyhydroxide particles, and settle. We hypothesise that the same Al and Fe transporting process occurs in other lakes and coastal marine areas and is ecologically important because Al and Fe oxyhydroxides can bind trace metals and phosphorus.

Introduction

Pollution of surface waters with ionic, potentially toxic, aluminum species (Al) is an ecological problem related to naturally acid-sensitive areas that receive acidic precipitation (1, 2). Recent studies have identified a natural Al source for lakes that is not associated with atmospheric acidification during the industrial era: photochemical liberation of dissolved organically bound aluminum (Alorg) by solar radiation (3, 4). Similar photoliberation occurs also for organically bound iron (Feorg) in copper in lakes and seawater (3–6). The Al, and Feorg species hydrolyze, precipitate at water pH > 5 as oxyhydroxide particles (7), and settle.

Oxyhydroxides of Al and Fe (AlOX and FeOX) play an important ecological role in lake and marine sediments, binding phosphate (8–10) and trace metals (11). The in-lake AlOX and FeOX formation is important in atmospherically or naturally acidified waters receiving increased Al, and Fe, inputs from acid soils (9, 10, 12) and in lake restorations by Al-dosing (13). But, how important was their natural production for a lake ecosystem during its evolution from deglaciation until the industrial era? AlOX and FeOX in preindustrial sediments may result from (i) hydrolysis and precipitation of Al and Fe, mobilized from naturally acidic soil solutions after a pH increase due to CO2 degassing (14) or mixing with surface waters of higher pH and temperature (15), (ii) mixing of anoxic groundwater with oxygenated surface water causing Fe precipitation (12), (iii) decomposition of Al and Fe, due to changes in water chemistry between the input and the lake (16), and (iv) photochemical decomposition of organic–metal complexes (3, 4).

This paper provides hydrochemical and palaeolimnological evidence that metal transport by dissolved organic carbon (DOC) followed by photoliberation, precipitation, and deposition can be significant for the flux of Al and Fe oxyhydroxides to preindustrial lake sediments.

Materials and Methods

Site Description. An integrated study at Plešné Lake, Czech Republic, including palaeolimnological analysis, in situ photochemical experiments, and a six year mass budget on major in-lake fluxes of Al and Fe species, forms the basis of our hypotheses. Plešné Lake is a small glacial lake (tarn) at 1090 m (48°47’ N; 13°52’ E). The lake is mesotrophic, with a Secchi transparency of 1–1.5 m, thermocline depth of 4–5 m, maximum depth of 17 m, and water residence time of < 1 year. The lake is usually ice-covered from December to April, and the hypolimnetic anoxia occurs both during winter and during summer temperature stratification, with dissolved O2 concentrations < 1 mg L–1 below the 14–15 m depth (17). The catchment is fully forested with Norway Spruce and ranges in altitude up to 1378 m. Soils are developed from till, are thin and acidic, and are underlain by granite (17). Acid deposition decreased the lake water pH from background values of 6–6.5 to a minimum of ~4.5 in the middle 1980s. Since then, the pH has increased to ~5 during the ecosystem recovery from acidification (18, 19).

Sediment Sampling and Analyses. The palaeolimnological study is based on a 4 m long sediment record spanning the late Pleistocene and Holocene. Sediment was sampled with a modified Kullenberg piston corer near the deepest point of the lake by R. Schmidt in 1990 and was sectioned in 3 cm intervals. Because of a small mass in the upper three layers, we resampled and analyzed the 0–50 cm sediment layer (17) and used the data for the uppermost 15 cm. Analytical results of both sediment records were almost identical below the 15 cm depth and are combined in this study. Wet sediment was sequentially extracted by the first three processes of fractionation analysis (20): (i) distilled water, (ii) 0.1 M NaHCO3-buffered 0.1 M sodium dithionite (Na2S2O4), which dissolves Fe oxyhydroxides (Feox reduction to Fe2+) due to low redox conditions, and (iii) 1 M NaOH at 25 °C, which dissolves amorphous Al oxyhydroxides due to a high pH. Concentrations of Alox and Feox were estimated as the sum of dissolved (<0.4 µm) Al and Fe concentrations extracted by the second and third steps (10, 20). Concentrations of acid-soluble metals (Alox and Feox) and organic carbon (C) in the sediment were determined from freeze-dried subsamples after nitric-perchloric digestion (21) and analysis with a TOC5000A analyzer (Shimadzu). Loss-on-ignition was determined at 550 °C. All chemical results were calculated.
TABLE 1. Fluxes of Major Aluminum and Iron Species in Pléšné Lake, Czech Republic, for 2000–2005*  

<table>
<thead>
<tr>
<th>Flux</th>
<th>( \text{Al} )</th>
<th>( \text{Al}_p )</th>
<th>( \text{Fe} )</th>
<th>( \text{Fe}_p )</th>
<th>( \text{Fe}_o )</th>
<th>( \text{Fe}_T )</th>
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<tr>
<td><strong>input</strong></td>
<td>173±27</td>
<td>100±25</td>
<td>6.5±3</td>
<td>3.3±2.3</td>
<td>10.9±2.8</td>
<td>1.3±0.6</td>
</tr>
<tr>
<td><strong>change in storage</strong></td>
<td>-6±21</td>
<td>5±11</td>
<td>5.5±21</td>
<td>0.2±2.2</td>
<td>0.0±1.9</td>
<td>0.9±3.8</td>
</tr>
<tr>
<td><strong>output</strong></td>
<td>102±24</td>
<td>52±17</td>
<td>45±9</td>
<td>3.5±1.1</td>
<td>7.5±2.4</td>
<td>6.6±2.2</td>
</tr>
<tr>
<td><strong>photo-liberetion</strong></td>
<td>45±11</td>
<td>122±22</td>
<td>78±18</td>
<td>-3.3±5.1</td>
<td>2.9±2.3</td>
<td>1.2±1.8</td>
</tr>
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</table>

* Units: mmol m\(^{-2}\) year\(^{-1}\), on a lake area basis. Data are averages (± standard deviation) for six individual hydrological years. Species of Al and Fe: ionic (\( \text{Al}_i \), \( \text{Fe}_i \)), organically bound (\( \text{Al}_b \), \( \text{Fe}_b \)), and particulate (\( \text{Al}_p \), \( \text{Fe}_p \)), particles \( >0.4 \) \( \mu \)m. Arrows indicate changes in metal species. Change in storage in the lake water column was calculated as the average difference between in-lake inventory of metals at the end and beginning of each hydrological year. Photoliberation of ionic species was estimated as net in-lake retention of organically bound metals (input – output – change in storage, e.g., for \( \text{Al}_b: 100 – 52 = 45 \) or \( \text{Fe}_b: 55 – 21 = 34 \)); other Al and Fe removing processes (coagulation and coprecipitation with DOC) were assumed to be negligible (4). Production of particulate metals by precipitation was estimated as the net in-lake retention of their ionic species (input + photoliberation – output – change in storage, e.g., for \( \text{Al}_i: 173 + 45 = 102 \) (\( \pm 6 \)) = 122). Sedimentation flux of particulate metals was calculated as net in-lake retention of their particulate forms (input + precipitation – output – change in storage, e.g., for \( \text{Al}_p: 6.5 + 122 – 45 = 5.5 = 78 \).
The preindustrial sediment consists of two chemically distinct parts with an abrupt transition between them. Sediment below 335 cm (late Glacial period) consists of silt with concentrations of <1 mol C kg\(^{-1}\). The transition between 270 and 335 cm represents a period of soil development and stabilization in the catchment during the early Holocene (preboreal) consistent with lake evolution in deglaciated regions (27). Above 270 cm depth, there is organic-rich Holocene sediment with C concentrations between 19 and 33 mol kg\(^{-1}\) and an average loss-on-ignition of 67%. High and stable concentrations of organic C in the 0–270 cm layer suggest that erosion in the catchment and terrestrial export of mineral matter was low and constant after stabilization of soil cover and forest development. Mass accumulation rate in the sediment stabilized at an average of ~25 g m\(^{-2}\) year\(^{-1}\). The Fe\(_{ox}\) and Al\(_{ox}\) concentrations varied inversely with C concentrations in the 250–400 cm depth, with greater erosion in the late Glacial, rapidly declining after soil stabilization. The progressive natural soil acidification and DOC–metal complexation due to increasing soil organic matter (28) likely caused increased metal mobilization from the soil, causing gradually increasing Al\(_{ox}\) and Fe\(_{ox}\) concentrations (Figure 1; both \(p<0.001\)) and sedimentation rates in the 12–250 cm layer.

Both Al\(_{ox}\) and Fe\(_{ox}\) were a minor part of the Al\(_{as}\) and Fe\(_{as}\) pools in the pre-Holocene mineral-rich sediment. After the soil stabilized in the catchment, metal oxohydroxides became the dominant part of Al\(_{as}\) and Fe\(_{as}\) pools (on average 91 and 73%, respectively) during the last 10 000 years (0–250 cm, Figure 1). Concentrations of Al\(_{as}\) were low in the mineral-rich sediment below 270 cm, increased parallel to C concentrations between 270 and 250 cm, and then were stable until the onset of atmospheric acidification. In contrast to Al\(_{as}\), the Al\(_{ox}\) concentrations did not increase significantly in the 12–250 cm layer, probably due to higher variability in the data. The Fe\(_{ox}\) Concentrations decreased at the beginning of the Holocene and then increased slightly but significantly (\(p<0.001\)) from 250 cm to the surface (Figure 1).

**Mass Budget Study.** The average input of Al to the lake was dominated by Al\(_i\) and Al\(_{lo}\) while particulate Al (Al\(_{p}\)) was negligible (Table 1). The lake was, on average, a net sink of 45 mmol Al cm\(^{-2}\) year\(^{-1}\) (i.e., 45% of Al\(_i\), input). Similarly, the lake was an average net sink of 3.4 mmol of Fe\(_o\), m\(^{-2}\) year\(^{-1}\) (i.e., 31% of Fe\(_i\), input) (Table 1). Coagulation of organic C and associated Al\(_{lo}\) (2, 16) was relatively low in Plesně Lake (<10% of the Al\(_{lo}\) in-lake retention) and could not explain the observed in-lake retention of Al\(_i\) and Fe\(_i\) (4, 23). In-lake production of Al\(_{p}\) and Fe\(_{p}\), formation was thus dominantly from precipitation of their ionic forms. The average (± standard deviation) budget-based and directly measured sedimentation fluxes of Al\(_{p}\) were similar (78 ± 18 and 84 ± 9 mmol m\(^{-2}\) year\(^{-1}\), respectively), suggesting that the Al budget and Al\(_{p}\) fluxes are reasonably correct. In contrast, the average budget-based sedimentation of Fe\(_{p}\) was −3.3 ± 5.1 mmol m\(^{-2}\) year\(^{-1}\) because the lake became a net Fe source in some hydrological years due probably to underestimated terrestrial sources of particulate matter (needles from shoreline and overland flow) (23).

**Photochemical Study.** The inlet water used for in situ experiments was strongly acidic, with a pH between 4.1 and 4.3 and Al\(_o\) and Fe\(_o\) concentrations of 12–20 and 0.3–1.1 μmol L\(^{-1}\), respectively. The original DOC, Al\(_o\), and Fe\(_o\) concentrations were 720–1050, 10–15, and 1.5–2.5 μmol L\(^{-1}\), respectively. The water chemistry was significantly different after the experiment, with average decreases of ~45, 61, and 64% in DOC, Al\(_o\), and Fe\(_o\) concentrations, respectively (Table 2). Concentrations of inorganic Al and Fe increased for Al\(_o\) (see Figure 2). Because of the pH increase to 4.4–5.1 during the experiments, ionic Al\(_i\) and Fe\(_i\) hydrolyzed and partly precipitated. For example, in one of the experiments, the respective original water composition of 12 and 12 μmol L\(^{-1}\) of Al\(_i\) and Al\(_{lo}\) changed to 15, 3, and 6 μmol L\(^{-1}\) of Al\(_{lo}\), Al\(_i\), and Al\(_p\), as the pH increased from 4.2 to 4.8. The in situ experiments clearly showed that solar radiation effectively reduced the original Al\(_i\) concentrations. These results, however, did not exclude a possibility that the produced Al\(_p\) could be also formed by coagulation of organic matter, thus transforming a part of Al\(_i\) directly to Al\(_p\). But, preliminary laboratory experiments with short-time irradiation (300 nm) of water from the same inlet showed that photochemical decomposition of organic complexes was the major process responsible for the decrease in Al\(_i\) and Fe\(_i\) concentrations (3, 4). The pH and formation of particulate matter was negligible during the laboratory irradiation, while the increases in Al\(_i\) and Fe\(_i\) concentrations were reciprocal to the decrease in Al\(_o\) and Fe\(_o\) concentrations (3, 4).

The laboratory irradiation experiments caused an average reduction in concentrations of Al\(_i\) (54%) and Fe\(_i\) (70%) (4) similar to those in the in situ experiments (Table 2). But, the decrease in DOC concentrations during laboratory irradiation experiments was mostly associated with photooxidation of humic matter and was less than the DOC reduction in the in situ experiments. The partial photochemical degradation of allochthonous DOC produces numerous biologically available, low molecular weight organic acids (29, 30). Microbial decomposition is a very efficient sink for these photoproduced acidic compounds and a significant acidity-removing process (3) and likely contributed to the higher DOC removal and higher increase in pH during the in situ experiments. Several studies have indicated that direct photolysis of organic matter and secondary reactions involving reactive
oxygen species produced during photochemical processes cause significant DOC transformations (31, 32). Moreover, the degradation of DOC can be accelerated by Fe (32–34) by several pathways: (i) DOC oxidation by electron transfer from organic matter to the complexed FeIII after photon absorption (33); (ii) Fe participation in numerous types of photochemical reactions that produce radical species including peroxyl, superoxide and hydroxyl radicals (35, 36); and (iii) the heterogeneous redox reactions on the surfaces of iron oxyhydroxides (37) that form in water under oxic conditions. Thus, Fe in the inlet samples could have played an important role in the photoliberation of Al from organic complexes during our experiments.

Solar radiation decreased the original Al, and Fe concentrations in the inlet water proportionally more than DOC (Table 2). The effective complexation capacity of organic matter is approximately 0.015 ± 0.003 mol mol⁻¹ for Al and Fe in Nova Scotia lakes with pH < 5 (16). Even though these findings may not apply perfectly to Plešně Lake, the high molar (Al₆ + Fe₆)/DOC ratio in its inlet before solar irradiation (0.017 mol mol⁻¹) suggests that organic binding sites were near a high level of metal saturation. The decline in the molar (Al₆ + Fe₆)/DOC ratio to 0.011 mol mol⁻¹ during experiments (Table 2) indicates that the ability of DOC to bind metals decreased under solar radiation.

These observations suggest that photodegradation of allochthonous Al- and Fe-DOC causes decomposition of Al₆ and Fe₆. But, why does this process remove only about half of the original Al and Fe concentrations during experiments (Table 2) and on a whole lake basis (Table 1)? The binding of metals by organic ligands of natural humic substances occurs from strong bonds such as chelation associated with the carboxyl groups and weaker bonds based on electrostatic attraction and water bridges (38). We believe that the photoliberated metals originated predominantly from the weak organic–metal bonds and partly from the photo-oxidized carboxyl groups, while Al₆ and Fe₆ surviving solar radiation in complexes were associated with the surviving or newly formed carboxylic groups (39).

In-Lake Production of Metal Oxyhydroxides. Our results suggest that photochemical liberation of Al₆ and Fe₆ from terrestrial organic–metal complexes by solar radiation represents an important source of their ionic forms for surface waters. The production and transport of AlOX and FeOX to sediments occurs via the following sequence of processes: (i) soil organic acids dissolve and bind metals and export them from terrestrial to aquatic systems (38, 40). (ii) Photochemical decomposition of organic–metal complexes liberates a significant portion of organically bound Al and Fe as ions (4). (iii) The liberated ionic Al and Fe hydrolyze and precipitate as oxyhydroxide particles (7) and settle.

The annual average pH values of Plešně Lake inlets and outlets are ~4.4 and 4.9, respectively, and the hypolimnetic pH reaches values between 5 and 6 (3, 17). After release from organic bonding, Al and Fe hydrolyze along the pH gradient in the water column and precipitate as Al₆ and Fe₆ oxyhydroxides. The current proportion of Al₆ transformed to Al₇ oxyhydroxides is lower due to a lower pH than in the preindustrial times. With a preindustrial pH of 6.5 (19), Plešně Lake would be oversaturated with respect to Al(OH)₃, and ~85% of Al photoliberated from Al₆ would be transformed to Al₇ (7). The lake would have received negligible Al inputs as a consequence of the higher soil and stream pH values prior to anthropogenic acidification (19). Al₇ would have originated predominantly from photodegraded organic complexes, which were supplied in comparable amounts in the past. Provided that this assumption is correct, preindustrial sedimentation of AlOX in Plešně Lake should be close to the current production of photoliberated Al₆ corrected for lake efficiency to retain Al₆. Efficiency of Al₆ retention can be estimated on the basis of Al₆ mass budget (Table 1). In the 2000–2005 period, the water column of Plešně Lake was a net source of 122 mmol of Al₆ m⁻² year⁻¹; 45 mmol of Al₇ m⁻² year⁻¹ left the lake via outflow, and 78 mmol Al₆ m⁻² year⁻¹ was deposited in the sediment (Table 1). Thus, 64% of the in-lake Al₆ production was retained in the sediments. The Al₇ distribution between outlet and sediments is a function of lake hydrology and bathymetry. These are assumed to have not changed substantially during the Holocene. If 85% hydrolysis of the photoliberated Al₆ to Al₇ oxyhydroxide occurs, as we assume for the preindustrial lake water pH, the hypothetical Al₇ production would be ~38 mmol m⁻² year⁻¹ on a lake area basis (85% of the retained 45 mmol Al₆ m⁻² year⁻¹). Of the produced Al₇, 64% (~24 mmol Al₇ m⁻² year⁻¹) would be deposited in the sediment. Analogous calculations for Fe suggest that 1.8 mmol of Fe₆ m⁻² year⁻¹ of the retained 3.4 mmol of Fe, m⁻² year⁻¹ would become sediment. Linking the average AlOX and FeOX concentrations in the preindustrial Holocene sediments (1.06 and 0.07 mmol g⁻¹; Figure 1) to the average sediment mass accumulation rate of 25 g m⁻² year⁻¹ yields the average sedimentation of 26 mmol of AlOX and 1.7 mmol of FeOX m⁻² year⁻¹. These values are similar to the hypothetical fluxes estimated on the basis of current environmental and climatic conditions. Thus, changes in DOC terrestrial export (41, 42), associated organic–metal complexes (2, 3), and their photoreactivity (36, 43) over the last century had probably balancing effects, with little net change. These budget calculations indicate that photoliberation and hydrolysis of Al and Fe, and formation and sedimentation of particulate oxyhydroxides have significantly contributed to AlOX and FeOX in Plešně Lake sediment long before the atmospheric acidification of the area, likely since the initiation of soil formation in the catchment.

Possible Implications. The photochemical production of Al oxyhydroxides could be important in the interpretation of palaeolimnological evidence. First, trace metals and phosphorus may coprecipitate with, or adsorb to, Al and Fe oxyhydroxides (9, 11). Second, the solubility of Al oxyhydroxides is insensitive to redox change (7), and thus, AlOX concentrations in undisturbed sediments reflect the sedimentation rate of Al₇. The rate is probably influenced by climate conditions such as temperature, precipitation, and solar radiation that affect terrestrial export of DOC (42) and Al, and in-lake photoliberation and precipitation of Al₇. The positive relationship between solar radiation and temperature in preindustrial time (44) suggests higher Al₇ sedimentation during periods of higher solar activity due to more intensive Al photoliberation and lower solubility of Al oxyhydroxides at associated higher temperatures (15). Similarly, higher precipitation would increase the flux of Al to the lake but decrease the residence time of water in the lake, thereby possibly reducing the Al₇ production and sedimentation. We hypothesize that this metal transport mechanism is applicable to other lakes and coastal waters receiving terrestrial runoff from forested or peaty areas.

Acknowledgments

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Natural inactivation of phosphorus by aluminum in preindustrial lake sediments

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Abstract

Noncalcareous phosphorus (P)-rich lake sediments typically release P associated with iron hydroxide [Fe(OH)_3] during the development of hypolimnetic anoxia. High concentrations of aluminum hydroxide [Al(OH)_3] in such sediments (e.g., in aluminum [Al]-treated lakes) can prevent the P release. Here we show that sediment ability to bind P can naturally develop during lake history because of changes in the Al(OH)_3 concentration and the Al(OH)_3 to Fe(OH)_3 ratio in sediment. We reconstructed the development of sediment P-sorption characteristics through the Late Glacial and Holocene periods on the basis of sequential fractionation analysis of P, Al, iron, calcium, and magnesium in a 14,000-yr-long sediment record, fresh settling seston, and bedrock from Plešné Lake, Czech Republic. The most significant change occurred at the Late Glacial–Holocene transition (~10,000 yr before present), when the watershed became forested and soil erosion decreased. The Late Glacial sediment was rich in mineral detritus, derived from the watershed till and bedrock, had most of its P associated with Fe(OH)_3 (37%) and calcite and/or apatite (42%), and was probably able to release P during anoxia. In contrast, the Holocene sediment was highly organic, the P release during anoxia was likely negligible, and >90% of P was associated with Al(OH)_3. This Al(OH)_3 originated from photochemical liberation of Al from dissolved organically-bound Al (Al_o) exported to the lake from soils. Because the photochemical mechanism was a more efficient source for Al(OH)_3 than for Fe(OH)_3, the sediment became a P trap by the beginning of the Holocene. The ability of the sediment to immobilize P increased further during the anthropogenic acidification era because of elevated terrestrial export of Al. Similar sediment fractionation results in cores from six lakes in Maine suggest that this P-immobilizing mechanism is a general process that can occur in lakes with high Al_o inputs.

Lake and coastal marine sediments, with sorption capacities dominated by iron hydroxide [Fe(OH)_3], release phosphorus (P) associated with iron (Fe) during the development of hypolimnetic or in-sediment anoxia because of the reductive dissolution of Fe^{III} solid phases (e.g., Mortimer 1971; Jensen et al. 1995). Some studies (e.g., Praire et al. 2001; Amirbahman et al. 2003; Golterman 2004), however, show that some noncalcareous P-rich sediments may not release P during the development of anoxia, even as the hypolimnetic Fe^{2+} concentrations increase substantially. Kopáček et al. (2005a) suggested that these exceptions to Mortimer's paradigm could be associated with aluminum hydroxide [Al(OH)_3] that provides an additional redox-insensitive sorption capacity to sediments. Sediment analyses and experience with aluminum [Al]-treated lakes (e.g., Ulrich 1997; Rydin et al. 2000; Lewandowski et al. 2003) provide important insight for lakes with naturally high or elevated Al(OH)_3 concentrations in the sediment. Al(OH)_3 can prevent P release into the water column during reducing (low Eh) conditions, because it is insensitive to redox changes, and can bind the P liberated from any reductive dissolution of Fe(OH)_3. Laboratory experiments and results of chemical analyses of 52 sediments from different types of European and American lakes show that the ratio between concentrations of Al to Fe hydroxides is a reasonable predictor of the ability of the sediment to release P (Kopáček et al. 2005a). If the ratio is >3, only low amounts of P are released at low Eh conditions.

An Al(OH)_3:Fe(OH)_3 ratio >3 is typical for sediments of (1) atmospherically acidified lakes with elevated terrestrial Al export from acidic soils (because of acid dissolution of soil Al oxyhydroxides), (2) lakes treated with Al salt in the water column, and (3) alpine lakes with aluminosilicate bedrock and high soil erosion in their watersheds; sediments of these lakes contain soil detritus rich in Al oxyhydroxide (Kopáček et al. 2005a). There are, however, high Al(OH)_3:Fe(OH)_3 ratios in some circumneutral forest lakes (e.g., Norton et al. unpubl. data). Such lakes may receive abundant particulate Al(OH)_3 due to the hydrolysis and precipitation of ionic Al (Al_o) after degassing of carbon dioxide (CO_2) from soil solutions emerging to surface waters (Norton and Henriksen 1983; Roy et al. 1999) and from photochemical liberation of organically

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bound Al (Al₃) and the formation of Al(OH)₃ (Kopáček et al. 2005b, 2006). Here, we show that (1) the P sorption characteristics of sediments can significantly change during lake history because of changes in the Al(OH)₃ concentrations and Al(OH)₃ to Fe(OH)₃ ratios, and (2) natural photochemical formation of Al(OH)₃ is responsible for the change. The process has operated since the time of soil formation in a deglaciated watershed.

Materials and methods

Description of study sites—Plešné Lake is a small glacial lake (tarn) with a surface area of 0.075 km², situated in central Europe at 1,090 m (48°47′N, 13°52′E) in the mountainous area of the Bohemian Forest (the border region between the Czech Republic and Austria). The lake is mesotrophic and dimictic, with thermocline depth of 4–5 m, a maximum depth of 17 m, and a theoretical water residence time of 0.8 yr. Hypolimnetic anoxia occurs during winter and summer temperature (density) stratification, with dissolved O₂ concentrations <1 mg L⁻¹ below the 14–15-m depth (Kopáček et al. 2000). The historical records and dynamic modeling of the lake-water chemistry (Majer et al. 2003) show that the lake has been strongly atmospherically acidified since the mid-20th century. The pH values decreased from 6–6.5 in the early 1900s to <5.4 in the 1960s as the carbonate buffering system was depleted as a consequence of base cation depletion in the soil. Elevated Al₃ concentrations occurred in the lake by the 1950s. We expect that episodic high Al₃ terrestrial export could have occurred earlier, but probably not before the 1900s because of high pH and low concentrations of strong acid anions (Majer et al. 2003). Fish disappeared during acidification, and zooplankton were significantly reduced. The acidification progressed until the mid-1980s, when lake-water pH declined to ~4.5 and concentrations of dissolved Al peaked at ~30 μmol L⁻¹ (Veselý et al. 1998). Since then, pH has increased and the dissolved Al concentration has decreased during the ecosystem recovery from acidification to ~5 and 10–15 μmol L⁻¹, respectively, in 2005.

The Plešné Lake watershed (0.67 km², including the lake) is forested with Norway Spruce (>90% of the area) and ranges in altitude from 1,090 m to 1,378 m. Soils developed from till, rich in sand (~75%), and consist of ~0.2-m-deep leptosol (38%) and ~0.45-m-deep podzol (29%) or dystric cambisol (27%). The rest of the watershed has exposed granite bedrock; wetlands are negligible (~1%). Soil pHCaCl₂ is 2.5–3.1 in A-horizons and 3.2–4.4 in mineral horizons. The mean effective cation exchange capacity of the soils is dominated by exchangeable Al (57%) and H⁺ (28%); base saturation is 15% (Kopáček et al. 2002).

Sediment sampling and characteristics—A 540-cm-long sediment core, used for phosphorus and metal fractionation, was recovered with a modified Kullenberg piston corer near the deepest point of the lake by R. Schmidt in 1990 and sectioned into 3-cm intervals. Before analysis, the samples were stored in the dark at 4°C in tightly closed bottles. The previous dating and analyses of the long core showed that the sediment record spans the lake history since its deglaciation ~14,600 years ago (Prazáková et al. 2006) and consists of two chemically distinct parts with an abrupt transition between them. Sediment below 335 cm consists of silt with concentrations <1 mol kg⁻¹. The transition between 270 cm and 335 cm represents a period of soil development and stabilization in the watershed during the early Holocene (Preboreal). During the Late Glacial, the watershed of Plešné Lake was treeless, with prevailing herb vegetation and shrubs. Palynological studies indicate that a sudden vegetation change and forestation occurred because of climatic amelioration at the beginning of the Holocene (between 273 cm and 312 cm) (Jankovská 2006). Organic-rich Holocene sediment with carbon (C) concentrations between 19 mol kg⁻¹ and 33 mol kg⁻¹ occurs above 270 cm (Kopáček et al. 2006). High and stable concentrations of organic C in the 0–270-cm layer indicate that erosion in the watershed and terrestrial export of mineral detritus became slower after stabilization of the soil cover and forest development, and the mass accumulation rate in the sediment stabilized at an average of ~25 g m⁻² yr⁻¹ (Prazáková et al. 2006). The uppermost Holocene sediment (0–15 cm) has been affected by acidification, particularly by elevated terrestrial Al, export from acidified soils and its in-lake precipitation (Kopáček et al. 2000).

Sediment analyses—Wet sediment was sequentially extracted by P fractionation analysis according to Psenner and Pueckhofer (1988): (1) Distilled water (H₂O fraction) was used to obtain loosely bound and pore-water soluble P (P₁₂O₅) and (2) 0.1 mol L⁻¹ NaHCO₃-buffered 0.1 mol L⁻¹ sodium dithionite (Na₂S₂O₄) at 40°C (bicarbonate-dithionite [BD] fraction) was used to release PBD from Fe(OH)₃. This step dissolves most of the ferric hydroxide (Fe³⁺ reduction to Fe²⁺ due to low redox conditions) and some Al(OH)₃ because of a pH of ~7 at the beginning of the BD extraction. (3) Next, 1 mol L⁻¹ NaOH at 25°C (NaOH~25 fraction) extracted PNaOH~25 from the amorphous Al(OH)₃, and some Fe³⁺ hydroxide that was not dissolved in the BD step. This step dissolves amorphous Al(OH)₃ due to high pH. (4) The hydrochloric acid (HCl) fraction, 0.5 mol L⁻¹ HCl, released P associated with any calcite (CaCO₃) and apatite [(Ca₅(PO₄)₃(OH))] (P₄HCl). (5) 1 mol L⁻¹ NaOH at 85°C (NaOH~85 fraction) removed refractory and other organically bound P (PNaOH~85). All fractions were centrifuged at ~3,000 × g (except for the H₂O and BD fractions that were centrifuged at 16,000 × g) for 20 min and filtered (glass-fiber filters, pore size of 0.4 μm). In the filtrate, we determined concentrations of soluble reactive P (SRP) with the molybdate method (Murphy and Riley 1962), and concentrations of P (sum of soluble reactive and nonreactive P), Al, and Fe after nitric-perchloric acid digestion according to Kopáček et al. (2001a). Concentrations of Ca and Mg were determined by flame atomic absorption spectrometry only in the HCl extract. Total extractable SRP (SRP₄Te), P₄Te, Al₄Te, and Fe₄Te are the sums of the elements released in the five extractions. Concentrations of Al(OH)₃ and Fe(OH)₃ were estimated as the sum of metal extracted by the BD and NaOH~25 steps.
(Psenner and Pucsko 1988; Kopáček et al. 2005a). Freeze-dried aliquots were used for determination of the organic carbon (C) concentration with a TOC 5000A analyzer (Shimadzu) and for determinations of the total P, Al, and Fe concentrations (nitric-perchloric acid digestion; Kopáček et al. 2001a) in the sediment. All chemical results were corrected for reagent blanks and calculated on a dry weight sediment basis.

Because of the small mass in the upper three layers of the long core, we retrieved a second core (0–50 cm) in 1998 and analyzed the samples (Kopáček et al. 2000). Analytical results of both cores were almost identical from 50 cm to 15 cm, so we spliced the 15 cm to 0 cm data to the longer core.

Bedrock sampling and analyses—Representative samples of bedrock (granite) were taken from two places in the Plešné watershed in 1997 by the Czech Geological Survey, Prague (J. Veselý pers. comm.). The samples were crushed, and the size fractions between 0.125 mm and 0.2 mm were used for sequential P fractionation analysis (in duplicate) as described above. We report the averages for the two samples. Data on the total concentrations of P, Al, and Fe in the bedrock samples are from Kopáček et al. (2002).

Seston and water sampling and analyses—Sedimenting particulate matter was collected in sediment traps (Plexiglas tubes, 330-mm long and 60 mm in diameter; duplicates ~6 tubes each) situated at 9-m depth (chemically the most invariant water layer; Kopáček et al. 2004) at the deepest point of the lake. The samplers were deployed for 6-week intervals from 01 November 2004 to 21 November 2005. Suspended material from the traps was homogenized by passing it through a 40-μm polyethylene sieve and was analyzed for dry weight mass (105°C) and concentrations of Al, Fe, P, and organic C. Samples containing 0.1–0.2 g (dry weight) of seston were centrifuged (3,000 × g for 30 min). The supernatant was assumed to represent the first (H2O) step of the P fractionation; the results were corrected for element concentrations in the ambient lake water at the 9-m depth. The collected seston was subjected to the next four steps of sequential fractionation analysis (Psenner and Pucsko 1988). The procedure and chemical analyses were the same as described for sediment. All chemical results were calculated on a dry weight basis.

Lake water was sampled at depths of 0.5, 4, 9, 14, and 16.5 m and analyzed for pH and concentrations of total, dissolved, and organically-bound P, Al and Fe species, and O2. Details on water analyses (principally the same methods as those used for seston and fractionation extracts) are in Kopáček et al. (2004).

Results and discussion

Fractionation results—The fractionation method successfully liberated most of the total P from seston and both the modern (0–15 cm) and old (350–500 cm; Late Glacial) sediments. The concentration of PTE (sum of total P extracted by all steps) was 97–113% of total P. The fractionation was less efficient for the bedrock, but still liberated 63% of the total P in granite (Table 1). Because of the reasonable concordance between PTE and total P values, we focus on fractionation data when discussing changes in P concentrations along the seston–sediment–bedrock transect.

The PNaOH and PNaOH–85 contributed <2% and <5%, respectively, to the PTE for all samples and were negligible for the Plešné Lake ecosystem (Fig. 1). In contrast, the relative proportion of other fractions varied significantly among the samples (Fig. 1). The PBD significantly contributed to the PTE pool in the old (>350 cm) sediment (37%) and seston (13%), but was almost negligible (<4%) in the modern sediment and bedrock. The PNaOH–25 dominated (77% and 92%) the PTE pool in the seston and modern sediment, respectively, but formed only 18% and 3% in the old sediment and bedrock, respectively. The PHCl represented negligible fractions of PTE pool in seston and the modern sediment (<2%), but was significant (42%) in the old sediment and dominated (94%) in the bedrock (Fig. 1). The results show the following links between the fractionation results and composition of the samples.

1. P extracted in the first three steps (P(H2O+BD)>NaOH–25) included the majority (91% and 95% on average) of PTE in the seston and modern sediment, respectively (Fig. 1). This indicates that the P adsorption capacity of the sedimenting material and modern sediment is predominantly associated with Fe(OH)3 and Al(OH)3, which are mostly dissolved in the BD and NaOH~25 steps (Psenner and Pucsko 1988). Most P was extracted in the NaOH~25 step with Al. The AlNaOH–25 represented 68% and 91% of AlTE in the seston and modern sediment, respectively. The higher relative efficiency of the BD extraction for the PBD liberation from the seston than modern sediment (13% vs. 4%) was associated with higher concentrations of Fe and lower concentrations of Al (Table 1) and, consequently, with a lower Al(OH)3:Fe(OH)3 ratio in the seston (3.5) than in the modern sediment (15). The sesionic Al(OH)3:Fe(OH)3 ratio was close to the threshold of 3, below which high P concentrations are substantially liberated by the BD extraction (Kopáček et al. 2005a). In contrast, the high Al(OH)3:Fe(OH)3 ratio in sediments prevented PBD release during the anoxic extraction. Previous research has shown that the Plešné Lake sediment is not saturated with respect to P (Kopáček et al. 2000). The average (±SD) P sorption capacity of the 0–50-cm sediment layer is 324 ± 96 mmol kg–1 and is only 24% ± 15% saturated with P (Kopáček et al. 2000). Because most (93%) of this P sorption capacity is associated with Al(OH)3, there is a large proportion of unsaturated Al(OH)3 that can bind P that is liberated during the reductive dissolution of Fe(OH)3.

2. In contrast to the modern sediment, the old sediment had the majority of P (79%) extracted in the BD and HC1 steps. The old sediment had four times higher concentrations of FeBD and one order of
magnitudes lower concentrations of $\text{Al}_{\text{NaOH}−25}$ than the modern sediment (Table 1), resulting in a very low $\text{Al(OH)}_3: \text{Fe(OH)}_3$ ratio of 1.2. Consequently, the role of $\text{Al(OH)}_3$ in the P sorption capacity of old sediment was less important than that in the modern sediment. Moreover, high concentrations of both $\text{P}_{\text{HCl}}$ and $\text{Al(OH)}_3$ (Table 1) indicated that part of P in the old sediments was associated with apatite or calcite transported to or formed in the lake.

Fractionation results for the pre-acidification Holocene layers (15–270 cm) were similar to those for the modern sediment (Fig. 2). Although the $\text{P}_{\text{TE}}$ concentrations decreased in the sediment during the Holocene (Fig. 2A), the relative proportion of individual fractions was stable, with the $\text{P}_{\text{NaOH}−25}$ concentrations dominating (>90%) the $\text{P}_{\text{TE}}$ pool (Fig. 2B). The modern sediment releases negligible P amounts either through BD extraction (Table 1) or during the hypolimnetic anoxia (Kopaček et al. 2004). Similarly negligible P release from the sediment was probable for the rest of the Holocene because of a similarly dominating $\text{P}_{\text{NaOH}−25}$ fraction (Fig. 2B). In contrast, the sediment could be an internal P source for the lake during the Late Glacial and Pre-boreal (below 270 cm), provided anoxia developed in the hypolimnion or the upper sediment. The major difference between the Holocene and Late Glacial sediments is that the Holocene sediment has almost all P associated with $\text{Al(OH)}_3$, whereas the Late Glacial sediment has a high proportion of P associated with Fe($\text{OH})_3$. The proportion of P extractable in anoxia ($\text{P}_{\text{BD}}$ to $\text{P}_{\text{TE}}$ ratio) correlates positively with Fe($\text{OH})_3$, but negatively with $\text{Al(OH)}_3$. The threshold $\text{Al(OH)}_3$ ratio between the sediments releasing low and high P concentrations is ~5 (Fig. 3), higher than the ratio of 3 observed for surface sediments (Kopaček et al. 2005a). This difference is probably caused by sediment diagenesis and generally higher Fe concentrations in the uppermost compared to older sediments (Boyle 2001). The fractionation data in Figs. 2 and 3 suggest that Plešné Lake sediment had lost its ability to release and recycle P during anoxia and became a P trap >10,000 years ago.

Table 1. Average (±SD) element composition and results of phosphorus fractionation analyses (Psenner and Pucsko 1988) of settling seston, modern sediment (0–15 cm, acidification-affected), old sediment (350–500 cm, Late Glacial), and bedrock of Plešné Lake. Data are in nmol kg$^{-1}$ of dry material, except for organic C (mol kg$^{-1}$).

<table>
<thead>
<tr>
<th>Sedimenting seston</th>
<th>Sediment (0–15 cm)</th>
<th>Sediment (350–500 cm)</th>
<th>Bedrock (granite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>9</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Organic C</td>
<td>34±3</td>
<td>28±1</td>
<td>0.5±0.1</td>
</tr>
<tr>
<td>$\text{SRP}_{\text{H}_2\text{O}}$</td>
<td>0.9±0.4</td>
<td>1.0±0.3</td>
<td>0.2±0.2</td>
</tr>
<tr>
<td>$\text{SRP}_{\text{BD}}$</td>
<td>3.0±1.3</td>
<td>2.8±2.7</td>
<td>16.6±2.3</td>
</tr>
<tr>
<td>$\text{SRP}_{\text{NaOH}−25}$</td>
<td>7.5±2.4</td>
<td>63±38</td>
<td>8.6±7.0</td>
</tr>
<tr>
<td>$\text{SRP}_{\text{HCl}}$</td>
<td>0.4±0.2</td>
<td>1.1±0.6</td>
<td>23.3±7.9</td>
</tr>
<tr>
<td>$\text{SRP}_{\text{NaOH}−85}$</td>
<td>0.9±0.3</td>
<td>0.7±0.2</td>
<td>1.6±0.7</td>
</tr>
<tr>
<td>$\text{SRP}_{\text{TE}}$</td>
<td>12.6±2.6</td>
<td>68±40</td>
<td>50±8</td>
</tr>
<tr>
<td>$\text{P}_{\text{H}_2\text{O}}$</td>
<td>1.3±0.4</td>
<td>1.9±0.7</td>
<td>0.3±0.3</td>
</tr>
<tr>
<td>$\text{P}_{\text{BD}}$</td>
<td>8.0±2.5</td>
<td>4.7±3.1</td>
<td>18.9±4.9</td>
</tr>
<tr>
<td>$\text{P}_{\text{NaOH}−25}$</td>
<td>46±7</td>
<td>120±24</td>
<td>9±7</td>
</tr>
<tr>
<td>$\text{P}_{\text{HCl}}$</td>
<td>1.1±0.4</td>
<td>1.3±0.9</td>
<td>21.6±6.0</td>
</tr>
<tr>
<td>$\text{P}_{\text{NaOH}−85}$</td>
<td>3.1±1.6</td>
<td>2.7±1.1</td>
<td>1.5±0.2</td>
</tr>
<tr>
<td>$\text{P}_{\text{TE}}$</td>
<td>60±8</td>
<td>130±24</td>
<td>51±9</td>
</tr>
<tr>
<td>$\text{P}$ (total)</td>
<td>62±8</td>
<td>120±27</td>
<td>45±9</td>
</tr>
<tr>
<td>$\text{Fe}_{\text{H}_2\text{O}}$</td>
<td>22±20</td>
<td>1.1±1.0</td>
<td>1.0±0.6</td>
</tr>
<tr>
<td>$\text{Fe}_{\text{BD}}$</td>
<td>174±34</td>
<td>42±10</td>
<td>142±59</td>
</tr>
<tr>
<td>$\text{Fe}_{\text{NaOH}−25}$</td>
<td>29±19</td>
<td>45±18</td>
<td>7±2</td>
</tr>
<tr>
<td>$\text{Fe}_{\text{HCl}}$</td>
<td>26±37</td>
<td>14±11</td>
<td>14±15</td>
</tr>
<tr>
<td>$\text{Fe}_{\text{NaOH}−85}$</td>
<td>6±5</td>
<td>11±9</td>
<td>30±7</td>
</tr>
<tr>
<td>$\text{Fe}_{\text{TE}}$</td>
<td>257±79</td>
<td>114±18</td>
<td>325±70</td>
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<tr>
<td>$\text{Fe}$ (total)</td>
<td>268±109</td>
<td>129±8</td>
<td>505±50</td>
</tr>
<tr>
<td>$\text{Al}_{\text{H}_2\text{O}}$</td>
<td>111±39</td>
<td>11±4</td>
<td>3±2</td>
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<tr>
<td>$\text{Al}_{\text{BD}}$</td>
<td>109±37</td>
<td>23±11</td>
<td>17±9</td>
</tr>
<tr>
<td>$\text{Al}_{\text{NaOH}−25}$</td>
<td>588±154</td>
<td>1405±262</td>
<td>165±50</td>
</tr>
<tr>
<td>$\text{Al}_{\text{HCl}}$</td>
<td>12±5</td>
<td>13±19</td>
<td>178±29</td>
</tr>
<tr>
<td>$\text{Al}_{\text{NaOH}−85}$</td>
<td>41±27</td>
<td>83±37</td>
<td>617±197</td>
</tr>
<tr>
<td>$\text{Al}_{\text{TE}}$</td>
<td>861±213</td>
<td>1536±303</td>
<td>979±205</td>
</tr>
<tr>
<td>$\text{Al}_{\text{total}}$</td>
<td>822±142</td>
<td>1455±205</td>
<td>1658±147</td>
</tr>
<tr>
<td>$\text{(Ca+Mg)}_{\text{HCl}}$</td>
<td>ND</td>
<td>13±5</td>
<td>128±13</td>
</tr>
</tbody>
</table>

ND, not determined; $n$, number of samples; SRP, soluble reactive P; BD, bicarbonate-dithionite; TE, total extractable. Total concentrations of P, Al, and Fe in seston and sediment were determined after nitric-perchloric acid digestion (Kopaček et al. 2001a), whereas those in bedrock were determined after dissolution with $\text{H}_2\text{SO}_4$, $\text{HNO}_3$, and HF (Kopaček et al. 2002).
Al control of P in Holocene sediments

Fig. 1. The relative distribution of Fe, Al, soluble reactive P (SRP), and total (reactive + nonreactive) P from sequential extraction analyses (Psenner and Pucsko 1988) from seston, modern (0–15 cm, acidification affected) and old (350–500 cm, Late Glacial) sediments and bedrock (granite) of Plešné Lake. For absolute values see concentrations of total extractable Fe$_{TE}$, Al$_{TE}$, SRP$_{TE}$, and P$_{TE}$ in Table 1. BD, bicarbonate-dithionite.

Fig. 2. (A) Concentrations of P fractions and (B) relative P fractions (Psenner and Pucsko 1988) of Plešné Lake sediments. BD, bicarbonate-dithionite; TE, total extractable. Solid horizontal line represents sediment layer affected by acidification (upper ~15 cm). Sediment age in 10$^3$ yr BP (Pražaková et al. 2006).
stabilization and forestation of the watershed (Jankovská 2006) was a significant change in concentrations of P-binding phases (Fig. 4). The permanent soil cover reduced erosion and the input of mineral detritus to the lake. This reduced the dilution of sedimenting organic C, thereby increasing the concentration of organic C. Concentrations of (Ca+Mg)$_{HCl}$ decreased inversely to C either because of decreasing erosion and terrestrial export of mineral detritus (Engström and Wright, 1984), depletion of labile Ca phases in the soil (e.g., CaCO$_3$), or the sharp decrease in water pH (from $>7$ to $<6$, based on chydridd-inferred pH; Pražáková et al. 2006). The high-water pH during the Late Glacial could cause in-lake formation of calcite. Because the (Ca+Mg)$_{HCl}$ concentration extracted from the old sediments was higher than that from bedrock (Table 1), in-lake carbonate production could contribute to the (Ca+Mg)$_{HCl}$ pool. Such a process could increase the P extracted in the HCl step. Consequently, some portion of

![Fig. 3](image)

**Fig. 3.** Relationships between P$_{BD}$ (bicarbonate-dithionite extractable P): P$_{TE}$ (total extractable P) ratio and (A) Fe(OH)$_3$, (B) Al(OH)$_3$ concentrations (the sum of bicarbonate-dithionite and NaOH~25 extractable metals), and (C) Al(OH)$_3$ to Fe(OH)$_3$ ratio in the Late Glacial plus Pre-boreal (270–501 cm) and Holocene (0–270 cm) sediment of Plešné Lake. Solid lines are best fit regressions for all data: $r = 0.69$ (A), $-0.95$ (B), and $-0.96$ (C); all $p < 0.001$. Linear regressions for data on the 270–501-cm sediment layer provide: $r = 0.49$ (A), $-0.61$ (B), and $-0.50$ (C); all $p < 0.05$.

![Fig. 4](image)

**Fig. 4.** Profiles of organic carbon (C), and concentrations of Al and Fe hydroxides (the sum of bicarbonate-dithionite and NaOH~25 extractable metals), and HCl-extractable Ca and Mg in the sediment of Plešné Lake. Solid horizontal lines bound sediment layers affected by acidification (upper ~15 cm) and forestation of the watershed at the beginning of Holocene (312–273 cm; Jankovská 2006). Sediment age in 10$^3$ yr BP (Pražáková et al. 2006).
P\textsubscript{HCl} in the old sediments could originate from the P immobilized in the lake by secondary mineral phases (either P adsorption to or coprecipitation with calcite or production of biogenic apatite; Golterman 2004). The similar P\textsubscript{HCl} concentrations in the bedrock and old sediments (Table 1), however, suggest that transport of terrestrial granitic detritus (containing 0.6% of apatite) was the dominant source of P\textsubscript{HCl} in the Late Glacial sediment.

The Fe(OH)\textsubscript{3} was a minor part of the total Fe pool in the old mineral-rich sediment (Fig. 1), but became the dominant part (on average 73%, similar to the modern sediments; Fig. 1) during the last 10,000 years after soil stabilization in the watershed (see Kopáček et al. 2006 for more details on total Fe and Fe(OH)\textsubscript{3} concentrations along the whole core). The Fe(OH)\textsubscript{3} concentration decreased throughout the Late Glacial (Fig. 4), as did its proportion in the total Fe pool (from 46% at 500 cm to 10% at 315 cm). Such a decline suggests a continuously decreasing terrestrial export of secondary Fe phase (oxyhydroxides).

Weathering rates are high (as is the pH of runoff) in freshly deglaciated terrain as indicated by spatially distributed studies of soil chronosequences (Jacobson and Birks 1980) and site-specific paleolimnological studies at individual lake ecosystems (Whitehead et al. 1986). Oxidative weathering of Fe sulfides and the dissolution of readily weatherable trace minerals such as apatite and calcite would deplete the upper soils of these phases rapidly. The liberated Fe\textsuperscript{2+} rapidly oxidizes, hydrolyzes, and precipitates as colloidal Fe(OH)\textsubscript{3} (Stumm and Morgan 1981) that is exported to the lakes by erosion. This process was likely the major Fe(OH)\textsubscript{3} source for the lake sediments during the Late Glacial period, and then slowly declined as the easily weatherable minerals in the watershed became depleted. After forest establishment and soil stabilization, the Fe(OH)\textsubscript{3} concentrations increased slightly but significantly (p < 0.001) from 250 cm to the surface (Fig. 4). An increasing concentration of organic C in soils would cause reductive weathering of Fe in the parent material and a reduction of secondary Fe phases, followed by complexation of Fe with organic acids and export to the lake (Jacobson and Birks 1980).

In contrast to (Ca+Mg)\textsubscript{HCl}, concentrations of Al(OH)\textsubscript{3} were low both in the bedrock and mineral-rich sediment before soil stabilization and increased parallel to C concentrations between 312 cm and 273 cm and then sharply between 270 cm and 250 cm, after the watershed forestation (Jankovská 2006). Thereafter, Al(OH)\textsubscript{3} concentrations were stable until the onset of atmospheric acidification, during which they again increased (Fig. 4), due to the typically elevated terrestrial export of Al\textsubscript{i} to the lake (e.g., Kopáček et al. 2001b; Huser and Rydin 2005). Elevated Al(OH)\textsubscript{3} concentrations explain why the P adsorption characteristics of the Holocene sediment differed from the Late Glacial sediment throughout the >10,000-yr-long period, not just during the acidification phase (Fig. 2B). But, what was the source of inorganic Al for the lake before the acidification, when the Al\textsubscript{i} input from the watershed was low because of high-water pH and negligible soil erosion (and export of soil Al oxyhydr-oxides)?

**Natural photochemical source of Al(OH)\textsubscript{3} for sediments**—

Organic Al complexes began to form concurrently with soil formation in the watershed. The progressive natural soil acidification and dissolved organic carbon (DOC)–metal complexation due to increasing soil organic matter (Jacobson and Birks 1980) would cause increased Al mobilization. Organic acids dissolved, bound, and exported Al\textsubscript{i} to the lake. In the lake, Al was liberated (as Al\textsubscript{b}) from the organic complexes by photo-oxidation (Kopáček et al. 2005b). At pH > 5.5, most of the liberated Al\textsubscript{b} hydrolyzed, precipitated as Al(OH)\textsubscript{3} (Stumm and Morgan 1981), and was deposited as sediment (Kopáček et al. 2006). A similar mechanism affects Fe (Kopáček et al. 2005b, 2006) and other metals, such as copper (Shank et al. 2006). The estimated current sedimentation flux of Al(OH)\textsubscript{3} from photochemical cleaving of organic-Al complexes is similar to the average sedimentation of 26 mmol Al(OH)\textsubscript{3} m\textsuperscript{-2} yr\textsuperscript{-1} in the preindustrial Holocene sediment [based on the average Al(OH)\textsubscript{3} concentration and the respective average sediment mass accumulation rate; Kopáček et al. 2006]. These results suggest that the photochemical mechanism was the dominant source of Al(OH)\textsubscript{3} for Plešně Lake sediments throughout the Holocene, until the beginning of atmospheric acidification.

Unlike Al(OH)\textsubscript{3}, Fe(OH)\textsubscript{3} concentrations did not significantly increase in the sediment during the acidification period (Fig. 4), because the current input of Fe\textsubscript{i} is an order of magnitude lower than that of Al\textsubscript{i}, and Fe\textsubscript{b} concentrations are lower than Fe\textsubscript{c} concentrations even in the most acidified (pH ~4.2) tributary of Plešně Lake (Kopáček et al. 2005b, 2006). Photochemical liberation of Fe\textsubscript{i} from organic complexes (Fe\textsubscript{o}) has thus remained the dominant Fe(OH)\textsubscript{3} source for the lake sediments even during the acidification period.

**Chemical changes along the seston–sediment transect**—

Chemical composition and fractionation results of sedimenting seston differed from modern sediment, having higher concentrations of organic C and Fe (mostly Fe\textsubscript{org}) and lower concentrations of Al, SRP\textsubscript{TE}, and P\textsubscript{TE} (Table 1). Seston also had the lowest proportion of SRP\textsubscript{TE} in the P\textsubscript{TE} pool (21%), whereas in modern and old sediment represented 52% and >98%, respectively (Table 1). Whereas the lower concentrations of organic C and the higher proportion of SRP in the P pool (lower proportion of nonreactive organically bound P) in the sediment resulted from diagenesis of the settled material, the differences in metal concentrations had different origins. Respiratory depletion of organic C during diagenesis increased the sediment Al concentrations, but most of the difference between the Al concentrations in seston and modern sediment is associated with the ecosystem recovery from acidification. The recent terrestrial export of Al\textsubscript{i}, as well as the Al(OH)\textsubscript{3} flux to the sediments, has declined 50-65% during the post-acidification period, since the mid-1980s (Majer et al. 2003).

In contrast to Al and P, Fe concentrations were significantly higher in seston than in the modern sediments. This disproportion was caused by the deployment of sediment traps in the upper part of the hypolimnion. This
depth was selected to limit decomposition and chemical changes in the retained seston, because the ambient water had temperature between 3°C and 5°C and was permanently oxic, with O₂ concentrations between 5.7 mg L⁻¹ and 10.2 mg L⁻¹. The oxic conditions, however, caused an overestimation of the sedimentation flux of Fe(OH)₃ because of the following process. The hypolimnetic anoxia in the bottom layer of Plešné Lake commonly occurs for most of the year, except for short periods immediately after the spring and autumn turnovers (e.g., Kopáček et al. 2000). Fe liberated from anoxic sediments (Mortimer 1971) diffuses upward in the water column. Consequently, there were higher concentrations of total Fe in the water at the 9-m depth (1.4–2.7 μmol L⁻¹) than in the epilimnion (0.4–1.8 μmol L⁻¹). Upon reaching the oxic layers, the reduced Fe oxidizes, precipitates as Fe(OH)₃, and settles. When the settling Fe(OH)₃ reaches the anoxic zone, Fe is reduced and dissolved and continues in the cycling (the “ferrous wheel”). The Fe(OH)₃ trapped in the oxic zone in the sediment traps, however, remains stable and accumulates.

The increased Fe(OH)₃ concentration in the traps probably affected the P-fractionation results of the retained seston as compared to the modern sediment. In the lake, the seston settles to the anoxic zone, where the liberated P is mostly removed by Al(OH)₃ because of its high concentrations (Kopáček et al. 2004). In 2005, concentrations of particulate Al were two-times higher above the bottom than at the 9-m depth (9.5 mmol L⁻¹ vs. 4.9 mmol L⁻¹) due to higher pH (4.7–6.0 vs. 4.7–5.2). We assume that the relatively high concentration of PBD in the seston (compared to the modern sediment) could result from the elevated Fe(OH)₃ concentrations and the reduced Al(OH)₃:Fe(OH)₃ ratios in the traps because of the ferrous wheel. Hence, the ability of the “natural” (nontrapped) seston to liberate P during anoxia is probably lower than that suggested by the data in Table I.

Implication for other lakes—Our results show that the natural sedimentation flux of Al(OH)₃ affected the in-lake P cycle of Plešné Lake long before the acidification-induced export of Al, from the acidified soils and operated throughout the Holocene. Studies by Amirbahman et al. (2003), Wilson et al. (pers. comm.), and Norton et al. (unpubl. data) of six lakes in Maine have shown that Plešné Lake is likely not an exception. The P speciation of 50-cm (~500 yr of record) long sediment cores from Maine from acidified and nonacidified lakes and the time series of hypolimnetic chemistry indicate little release of P during anoxia (in contrast to Fe), and most of the P_TEP was extracted in the NaOH~25 step and was associated with high Al_NOHH₂O~25 concentrations, even in the preindustrial layers.

This study and previous results (Kopáček et al. 2006) suggest that the photochemical production of Al(OH)₃ in lakes with noncalcareous and Fe(OH)₃-poor sediment can significantly affect the sediment P sorption properties and could explain some exceptions from Mortimer’s paradigm. The most important prerequisite for the high input of organically-bound Al to lakes is organic soil on aluminosilicate-rich soil (e.g., shallow forest soils in glaciated areas with poorly developed adsorption horizons). In such watersheds, organic acids are in contact with mineral soil, enabling complexion between DOC and Al and Fe and export. The watersheds of Plešné Lake and the Maine lakes fulfill these criteria. The ratio of Al₆ to Fe₆ concentrations is high in these watersheds (typically 5 to 10:1 on a molar basis) (Kopáček et al. 2006; Norton unpubl. data).

Although the solar radiation is less efficient for Al₆ liberation than for Fe₆ (e.g., ~50 vs. 70% in Plešné Lake; Kopáček et al. 2005b, 2006), the process results in a higher sedimentary flux of Al(OH)₃ than Fe(OH)₃.

By extension, we hypothesize that anoxic zones in watersheds (e.g., wetlands or marshes) can alter the proportion of Al(OH)₃ and Fe(OH)₃ fluxes to lake sediment. Circum-neutral wetlands can retain Al(OH)₃ and Fe(OH)₃ formed upstream after metal photoliberation (Porcal et al. pers. comm.). Al(OH)₃, which is insensitive to redox changes, would be permanently stored in the wetland, whereas Fe would be dissolved during anoxia and exported. Such a mechanism could explain the variability of the sediment sorption characteristic in lakes situated in seemingly similar bedrock, soil, and vegetation conditions, but with wetlands along flow paths. Consequently, the watershed morphology and soil characteristics can represent important variables, predisposing the ability of lake sediment to retain P.

Under natural conditions, a sufficiently high Al(OH)₃ concentration, capable of binding P liberated from the reduced Fe(OH)₃, can occur in the sediment because of the elevated input of Al to the lake either in (1) ionic form, resulting commonly from atmospheric acidification of watershed soils, or (2) in organic form that is partly released as Al, after cleavage of organic complexes by solar radiation. Because the latter process operated throughout the Holocene, the Al-induced effect on the internal P cycling in Plešné Lake was not initiated but amplified by atmospheric acidification of the ecosystem. The terrestrial Al₆ export can be a sufficient source for the sediment Al(OH)₃ to reach the Al(OH)₃:Fe(OH)₃ ratio >3 and, consequently, for P immobilization in the sediment of other lakes with the watershed and soil characteristics similar to those of Plešné Lake.

References


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