

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 ionic 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., Prairie 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 Fe²⁺ 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 circum-neutral 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_i) after degassing of carbon dioxide (CO₂) from soil solutions emerging to surface waters (Norton and Henriksen 1983; Roy et al. 1999) and from photochemical liberation of organically

Acknowledgments

We thank R. Schmidt from the Institute for Limnology, Mondsee, Austria, for sampling the Plešné Lake sediment. We appreciate two anonymous reviewers who significantly improved our presentation.

We are grateful to the Grant Agency of the Czech Republic (206/06/0410), the U.S. National Science Foundation (DEB-0415348), and the EC's EURO-LIMPACS (European Project to Evaluate Impacts of Global Change on Freshwater Ecosystems) project (GOCE-CT-2003-505540) for financial support. The assistance of students was supported by the MSM 6007665801 project.

bound Al (Al_0) 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 Al_i concentrations occurred in the lake by the 1950s. We expect that episodic high Al_i 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 are 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 pH_{CaCl2} 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 (Pražáková 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 of <1 mol C 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 (Pražáková et al. 2006). The uppermost Holocene sediment (0–15 cm) has been affected by acidification, particularly by elevated terrestrial Al_i 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 Pucsko (1988): (1) Distilled water (H₂O fraction) was used to obtain loosely bound and pore-water soluble P (P_{H2O}) 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 P_{BD} from Fe(OH)₃. This step dissolves most of the ferric hydroxide (Fe^{III} reduction to Fe^{II} 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 P_{NaOH~25} from the amorphous Al(OH)₃ and some Fe^{III} 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 [(Ca)₅(PO₄)₃(OH)] (P_{HCl}). (5) 1 mol L⁻¹ NaOH at 85°C (NaOH~85 fraction) removed refractory and other organically bound P (P_{NaOH~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 (SRP_{TE}), P (P_{TE}), Al (Al_{TE}), and Fe (Fe_{TE}) 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- μ m 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 \times 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 P_{TE} (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 P_{TE} and total P values, we focus on fractionation data when discussing changes in P concentrations along the seston–sediment–bedrock transect.

The P_{H₂O} and P_{NaOH~85} contributed <2% and <5%, respectively, to the P_{TE} 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 P_{BD} significantly contributed to the P_{TE} pool in the old (>350 cm) sediment (37%) and seston (13%), but was almost negligible (<4%) in the modern sediment and bedrock. The P_{NaOH~25} dominated (77% and 92%) the P_{TE} pool in the seston and modern sediment, respectively, but formed only 18% and 3% in the old sediment and bedrock, respectively. The P_{HCl} represented negligible fractions of P_{TE} 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 P_{TE} 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 Al_{NaOH~25} represented 68% and 91% of Al_{TE} in the seston and modern sediment, respectively. The higher relative efficiency of the BD extraction for the P_{BD} 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 sestonic 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 P_{BD} 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 (\pm SD) P sorption capacity of the 0–50-cm sediment layer is 324 \pm 96 mmol kg⁻¹ and is only 24% \pm 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 HCl steps. The old sediment had four-times higher concentrations of Fe_{BD} and one order of

Table 1. Average (\pm 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 mmol kg⁻¹ of dry material, except for organic C (mol kg⁻¹).

	Sedimenting seston	Sediment (0–15 cm)	Sediment (350–500 cm)	Bedrock (granite)
<i>n</i>	9	4	8	2
Organic C	34 \pm 3	28 \pm 1	0.5 \pm 0.1	ND
SRP _{H2O}	0.9 \pm 0.4	1.0 \pm 0.3	0.2 \pm 0.2	0.1
SRP _{BD}	3.0 \pm 1.3	2.8 \pm 2.7	16.6 \pm 2.3	0.7
SRP _{NaOH~25}	7.5 \pm 2.4	63 \pm 38	8.6 \pm 7.0	0.4
SRP _{HCl}	0.4 \pm 0.2	1.1 \pm 0.6	23.3 \pm 7.9	21.8
SRP _{NaOH~85}	0.9 \pm 0.3	0.7 \pm 0.2	1.6 \pm 0.7	0.2
SRP _{TE}	12.6 \pm 2.6	68 \pm 40	50 \pm 8	23.2
P _{H2O}	1.3 \pm 0.4	1.9 \pm 0.7	0.3 \pm 0.3	0.1
P _{BD}	8.0 \pm 2.5	4.7 \pm 3.1	18.9 \pm 4.9	0.4
P _{NaOH~25}	46 \pm 7	120 \pm 24	9 \pm 7	0.7
P _{HCl}	1.1 \pm 0.4	1.3 \pm 0.9	21.6 \pm 6.0	21.8
P _{NaOH~85}	3.1 \pm 1.6	2.7 \pm 1.1	1.5 \pm 0.2	0.3
P _{TE}	60 \pm 8	130 \pm 24	51 \pm 9	23
P (total)	62 \pm 8	120 \pm 27	45 \pm 9	37
Fe _{H2O}	22 \pm 20	1.1 \pm 1.0	1.0 \pm 0.6	<0.1
Fe _{BD}	174 \pm 34	42 \pm 10	142 \pm 59	4
Fe _{NaOH~25}	29 \pm 19	45 \pm 18	7 \pm 2	1
Fe _{HCl}	26 \pm 37	14 \pm 11	144 \pm 15	81
Fe _{NaOH~85}	6 \pm 5	11 \pm 9	30 \pm 7	3
Fe _{TE}	257 \pm 79	114 \pm 18	325 \pm 70	89
Fe (total)	268 \pm 109	129 \pm 8	505 \pm 50	171
Al _{H2O}	111 \pm 39	11 \pm 4	3 \pm 2	<0.1
Al _{BD}	109 \pm 37	23 \pm 11	17 \pm 9	1
Al _{NaOH~25}	588 \pm 154	1405 \pm 262	165 \pm 50	7
Al _{HCl}	12 \pm 5	13 \pm 19	178 \pm 29	84
Al _{NaOH~85}	41 \pm 27	83 \pm 37	617 \pm 197	37
Al _{TE}	861 \pm 213	1536 \pm 303	979 \pm 205	130
Al (total)	822 \pm 142	1455 \pm 205	1658 \pm 147	2815
(Ca+Mg) _{HCl}	ND	13 \pm 5	128 \pm 13	107

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 (Kopáček et al. 2001a), whereas those in bedrock were determined after dissolution with H₂SO₄, HNO₃, and HF (Kopáček et al. 2002).

magnitude lower concentrations of Al_{NaOH~25} than the modern sediment (Table 1), resulting in a very low Al(OH)₃:Fe(OH)₃ ratio of 1.2. Consequently, the role of 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 P_{HCl} and (Ca+Mg)_{HCl} (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 preacidification Holocene layers (15–270 cm) were similar to those for the modern sediment (Fig. 2). Although the P_{TE} concentrations decreased in the sediment during the Holocene (Fig. 2A), the relative proportion of individual fractions was stable, with the P_{NaOH~25} concentrations dominating (>90%) the P_{TE} pool (Fig. 2B). The modern sediment releases negligible P amounts either through BD extraction (Table 1) or during the hypolimnetic anoxia (Kopáček et al. 2004). Similarly negligible P release from the sediment was probable for the rest of the Holocene because of a similarly dominating P_{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_{TE} associated with Al(OH)₃, whereas the Late Glacial sediment has a high proportion of P associated with Fe(OH)₃. The proportion of P extractable in anoxia (P_{BD} to P_{TE} ratio) correlates positively with Fe(OH)₃ concentrations, but negatively with Al(OH)₃ concentrations and Al(OH)₃:Fe(OH)₃ ratios both for the Late Glacial and Holocene sediments (Fig. 3). The threshold Al(OH)₃:Fe(OH)₃ ratio between the sediments releasing low and high P_{BD} concentrations is ~5 (Fig. 3), higher than the ratio of 3 observed for surface sediments (Kopáček 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.

Chemical changes in the sediment—The most important change in sediment composition, associated with soil

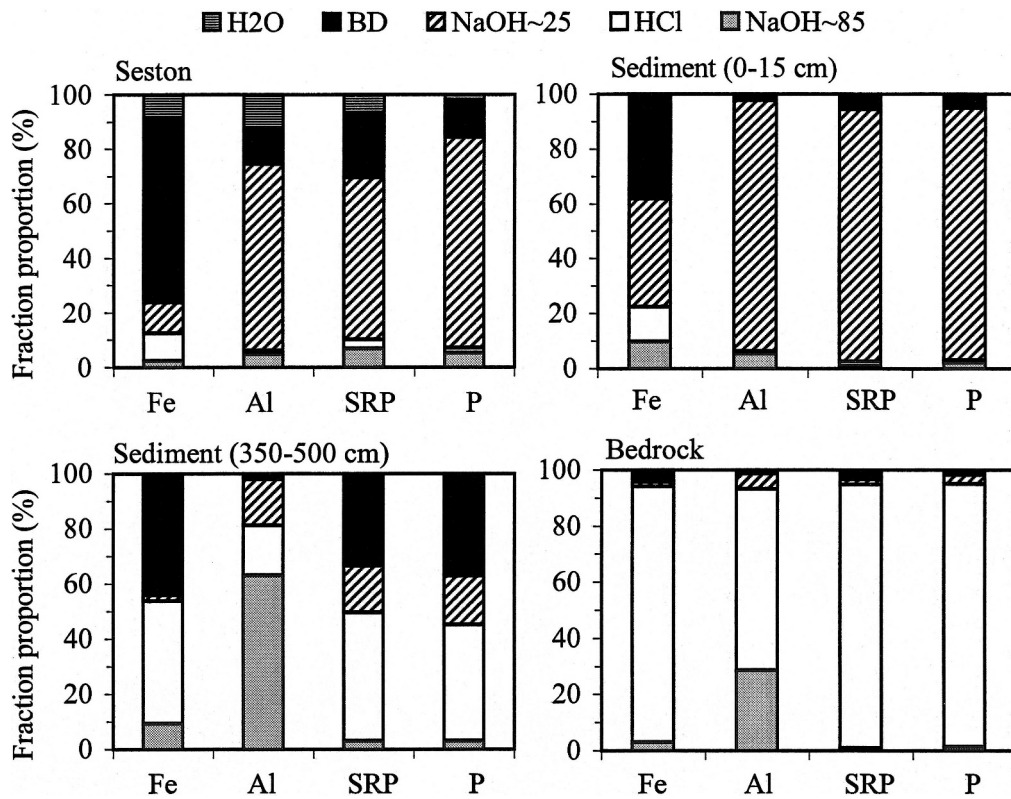


Fig. 1. The relative distribution of Fe, Al, soluble reactive P (SRP), and total (reactive + nonreactive) P from sequential extraction analyses (Psenner and Pucsko 1988) from seston, modern (0–15 cm, acidification affected) and old (350–500 cm, Late Glacial) sediments and bedrock (granite) of Plešné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

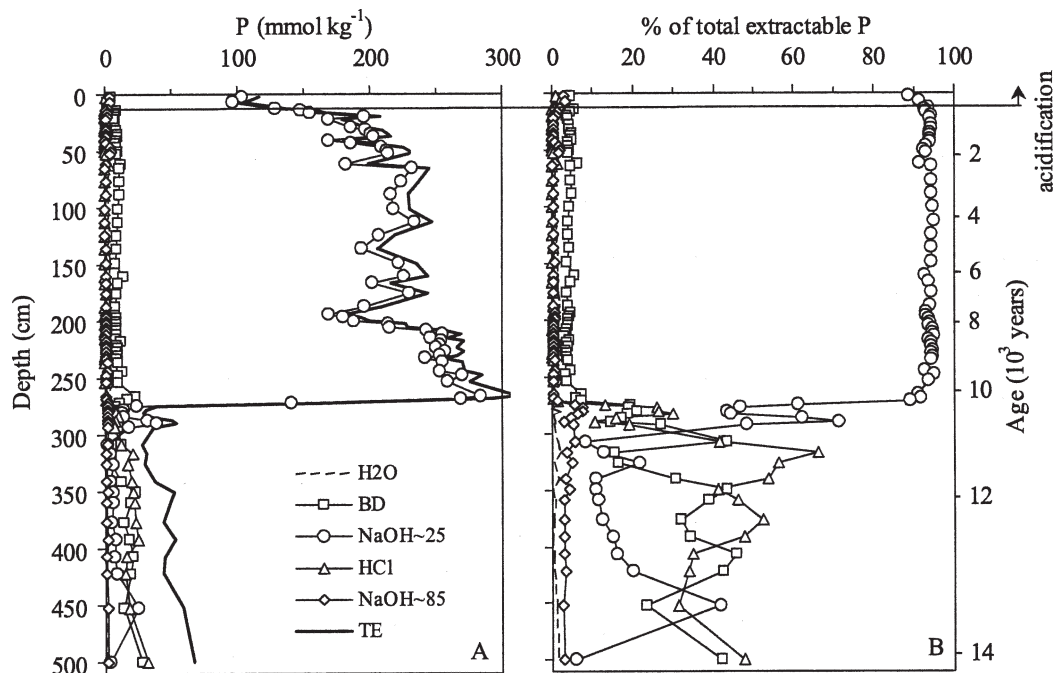


Fig. 2. (A) Concentrations of P fractions and (B) relative P fractions (Psenner and Pucsko 1988) of Plešné Lake sediments. BD, bicarbonate-dithionite; TE, total extractable. Solid horizontal line represents sediment layer affected by acidification (upper ~15 cm). Sediment age in 10³ yr BP (Pražáková et al. 2006).

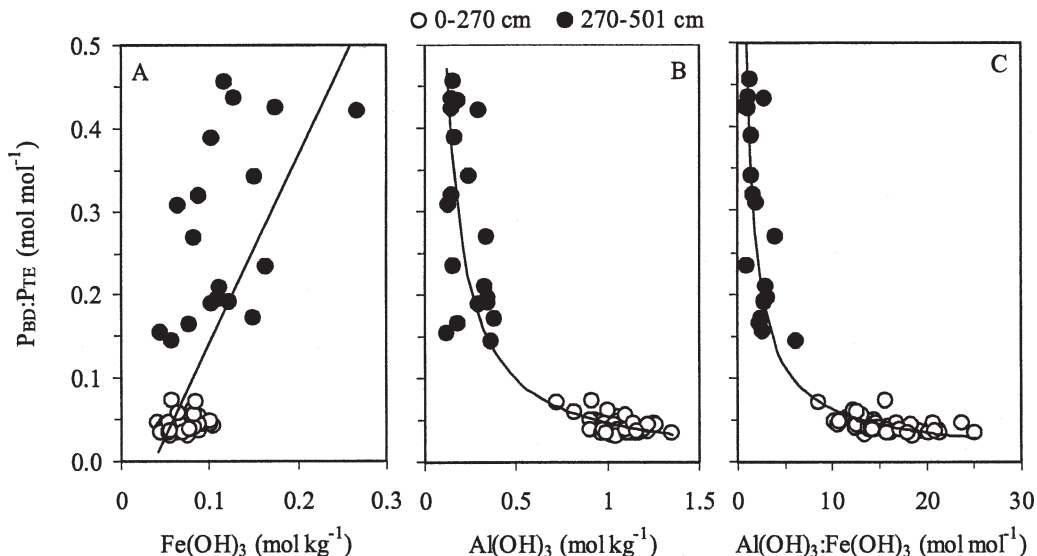


Fig. 3. Relationships between P_{BD} (bicarbonate-dithionite extractable P): P_{TE} (total extractable P) ratio and (A) $Fe(OH)_3$, (B) $Al(OH)_3$ concentrations (the sum of bicarbonate-dithionite and NaOH~25 extractable metals), and (C) $Al(OH)_3$ to $Fe(OH)_3$ ratio in the Late Glacial plus Pre-boreal (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 $p < 0.05$.

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 chydorid-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

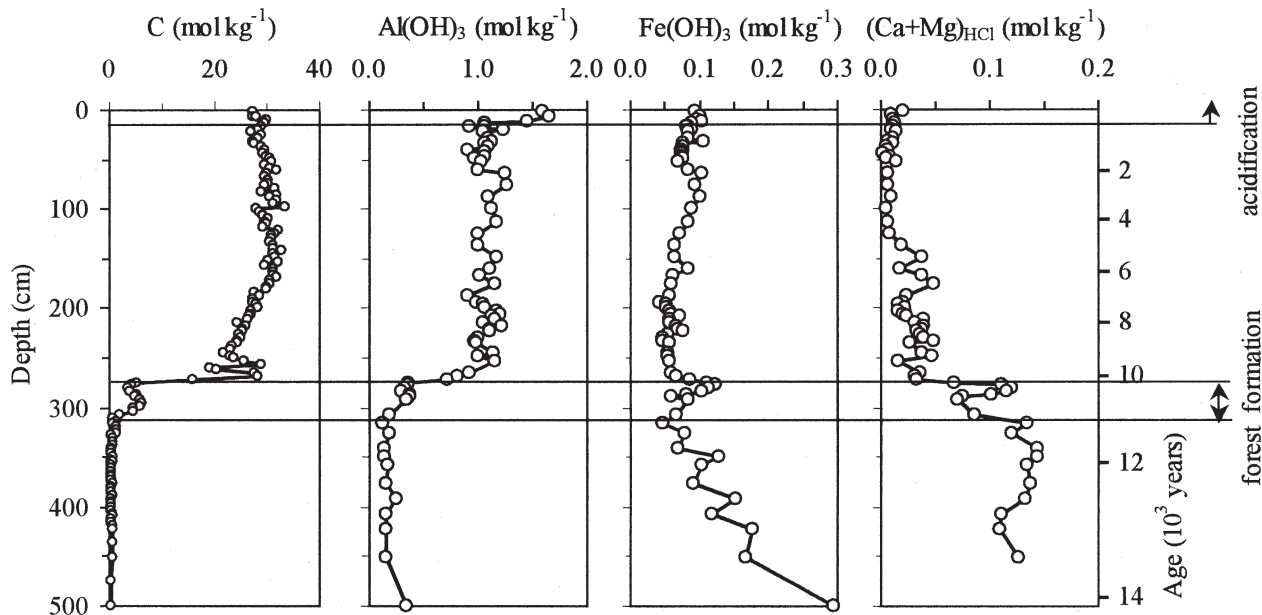


Fig. 4. Profiles of organic carbon (C), and concentrations of Al and Fe hydroxides (the sum of bicarbonate-dithionite and NaOH~25 extractable metals), and HCl-extractable Ca and Mg in the sediment of Plešné Lake. Solid horizontal lines bound sediment layers affected by acidification (upper ~15 cm) and forestation of the watershed at the beginning of Holocene (312–273 cm; Jankovská 2006). Sediment age in 10³ yr BP (Pražáková et al. 2006).

P_{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_{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_{HCl} in the Late Glacial sediment.

The $\text{Fe}(\text{OH})_3$ 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 $\text{Fe}(\text{OH})_3$ concentrations along the whole core). The $\text{Fe}(\text{OH})_3$ 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^{2+} rapidly oxidizes, hydrolyzes, and precipitates as colloidal $\text{Fe}(\text{OH})_3$ (Stumm and Morgan 1981) that is exported to the lakes by erosion. This process was likely the major $\text{Fe}(\text{OH})_3$ 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 $\text{Fe}(\text{OH})_3$ 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 $(\text{Ca}+\text{Mg})_{\text{HCl}}$, concentrations of $\text{Al}(\text{OH})_3$ 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, $\text{Al}(\text{OH})_3$ 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_i to the lake (e.g., Kopáček et al. 2001b; Huser and Rydin 2005). Elevated $\text{Al}(\text{OH})_3$ 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_i input from the watershed was low because of high-water pH and negligible soil erosion (and export of soil Al oxyhydroxides)?

*Natural photochemical source of $\text{Al}(\text{OH})_3$ 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_o to the lake. In the lake, Al was liberated (as Al_i) from the organic complexes by photo-oxidation (Kopáček et al. 2005b). At $\text{pH} > 5.5$, most of the liberated Al_i hydrolyzed, precipitated as $\text{Al}(\text{OH})_3$ (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 $\text{Al}(\text{OH})_3$ from photochemical cleaving of organic-Al complexes is similar to the average sedimentation of $26 \text{ mmol } \text{Al}(\text{OH})_3 \text{ m}^{-2} \text{ yr}^{-1}$ in the preindustrial Holocene sediment [based on the average $\text{Al}(\text{OH})_3$ 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 $\text{Al}(\text{OH})_3$ for Plešné Lake sediments throughout the Holocene, until the beginning of atmospheric acidification.

Unlike $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$ concentrations did not significantly increase in the sediment during the acidification period (Fig. 4), because the current input of Fe_i is an order of magnitude lower than that of Al_i , and Fe_i concentrations are lower than Fe_o concentrations even in the most acidified ($\text{pH} \sim 4.2$) tributary of Plešné Lake (Kopáček et al. 2005b, 2006). Photochemical liberation of Fe_i from organic complexes (Fe_o) has thus remained the dominant $\text{Fe}(\text{OH})_3$ 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_{BD}) and lower concentrations of Al, SRP_{TE} , and P_{TE} (Table 1). Seston also had the lowest proportion of SRP_{TE} in the P_{TE} pool (21%), whereas that 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_i , as well as the $\text{Al}(\text{OH})_3$ 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 overturns (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 P_{BD} 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 1.

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_i 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_{TE} was extracted in the NaOH~25 step and was associated with high Al_{NaOH~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 complexation between DOC and Al and Fe and export. The watersheds of Plešné Lake and the Maine lakes fulfill these criteria. The ratio of Al_o to Fe_o 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 Al_o liberation than for Fe_o (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_i 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 Al_o 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.

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Received: 15 September 2006

Accepted: 2 January 2007

Amended: 16 January 2007