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Phosphorus inactivation by aluminum in the water column and sediments: Lowering of in-lake phosphorus availability in an acidified watershed-lake ecosystem

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Abstract

Acid precipitation has been shown to reduce phosphorus (P) outputs from terrestrial sources. We present field evidence that the in-lake P cycle may also be disrupted in atmospherically acidified watershed-lake ecosystems. Plešné Lake in the Bohemian Forest is an acidified forest lake with epilimnetic pH of 4.5–4.9, total P concentration of ∼10 μg L^{-1}, and pronounced anoxia above the bottom during winter and summer stratification periods. The water chemistry of the anoxic zone develops in a predictable way: After depletion of dissolved oxygen, concentrations of nitrate and sulfate decrease while concentrations of ammonium, iron, alkalinity, and pH increase; the only exception to the general pattern is a permanently low concentration of dissolved reactive P (<1 μg L^{-1}) above the sediment.

This in-lake P inactivation can be explained by the acidification of soils in the watershed and subsequent precipitation of Al in the lake. The suggested mechanism is as follows: atmospheric deposition of strong acids has resulted in strong acidification and nitrogen saturation of soils in the Plešné Lake watershed and, consequently, in high terrestrial losses of Al (0.78–1.04 mg L^{-1}), SO_4^{2-} (4.5–7.7 mg L^{-1}), and NO_3^- (0.48–1.15 mg L^{-1} NO_3-N) to the lake. Biological removal of NO_3^- and SO_4^{2-} by both assimilatory and dissimilatory reduction contributes greatly to the total in-lake alkalinity generation and to the increase in water pH. Under higher pH, ionic Al species hydrolyze and form colloidal Al hydroxides (Al_{part}), which coagulate dissolved organic carbon and adsorb orthophosphate in the water column. The Al hydroxides settle and increase the P sorption capacity of the sediment. The elevated content of fresh Al oxyhydroxides in the surface sediment reduces P release to the water column after orthophosphate liberation from ferric oxyhydroxides during anoxia, because Al_{part} complexes are not sensitive to redox changes. The example of Plešné Lake shows that atmospheric acidification of a watershed-lake ecosystem may provide the natural conditions for in-lake P inactivation similar to the lake restoration technique based on the artificial addition of Al salt to the water column.

Acidification of a watershed-lake ecosystem is a complex process that changes the original lake water chemistry and biology in several ways (Schindler 1988*a,* 1994). Many of the involved processes are well understood (e.g., Kelly 1994; Psenner and Catalan 1994), but the impact of acidification on the phosphorus (P) cycle remains questionable. Productivity of soft-water lakes is generally limited by the availability of P (Schindler 1977). Any reduction in P loading from internal or external sources, as well as decreasing P availability to phytoplankton, could further reduce the productivity of these lakes. This process, called ‘‘oligotrophication,’’ has been reported by several authors (e.g., Almer et al. 1978; Broberg 1984; Jansson et al. 1986). Their experimental and empirical data suggest a possible effect of soil and water acidification on the P cycle due to the increased P retention in soils and formation of particulate P-aluminum and P-iron compounds in the water column. On the basis of laboratory experiments, Dickson (1978) has predicted the oligotrophication of fresh waters within pH range of 5–6 due to P precipitation by aluminum, the concentration of which generally increases in acidic waters. In concordance with this prediction, Vyhnálek et al. (1994) and Fott et al. (1994) have reported an extremely low content of chlorophyll and the extinction of planktonic crustacea in the High Tatra Mountains lakes with pH values between ∼5 and ∼6. Concentrations of P and organic matter were lower in these lakes than in lakes less or more acidified (Kopáček et al. 1995). In contrast, the experimental acidification of lakes did not affect their original P levels and/or extent of primary production (Schindler et al. 1985; Brezonik et al. 1993). In their review on oligotrophication, Olsson and Pettersson (1993) concluded that the oligotrophication hypothesis was questionable and had not yet been validated.

The purpose of our study is to show that acidification may influence the in-lake P cycle, at least in a strongly acidified watershed-lake ecosystem. We provide here the example of the atmospherically acidified Plešné Lake in the Bohemian Forest, where increased Al inputs from terrestrial sources and internal alkalinity generation are responsible for P inactivation at the water-sediment interface and for the elevated ability of sediment to bind P.

Materials and methods

Description of study sites—Plešné Lake is situated in the Bohemian Forest (the Šumava Mountains; 48°47′N, 13°52′E; ∼150 km south of Prague) at an altitude of 1,090 m above sea level. The lake is of glacial origin and small

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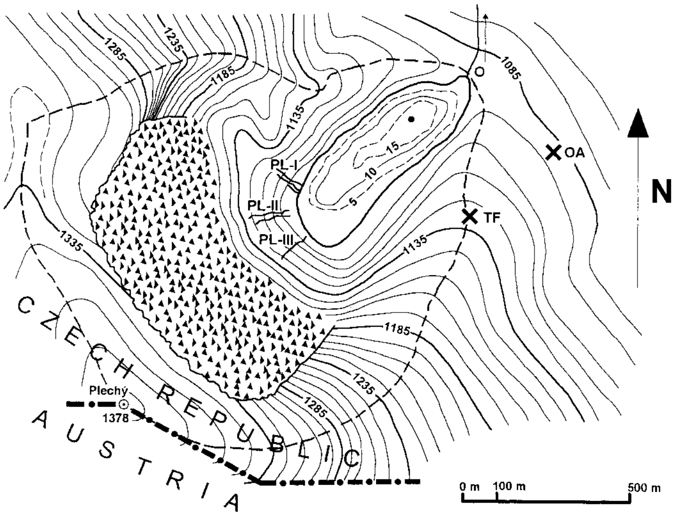

Fig. 1. Map of the Plešné Lake watershed (solid dashed line) with the locations of sampling sites: (1) lake water and sediment, full circle at the maximum depth in the bathymetric map of the lake; (2) tributaries, PL-I, PL-II, and PL-III; (3) outlet (O); and (4) precipitation samplers, solid crosses (OA, open area; TF, throughfall). The area with black triangles represents the rocky, sparsely forested, steep lake wall.

(area of 7.5 ha, volume of 617,000 m^3, maximum depth of 18 m), surrounded by steep forested rocky slopes. The theoretical water residence time, calculated from the precipitation volume in 1998 (*see below*), is approximately 1 yr. The watershed of Plešné Lake is 66.6 ha, and the bedrock is made up of granites (Veselý 1994). Most of the watershed is covered with a thin layer of forest humus. Soils are iron containing acidic podzols with low levels of Ca and K and an unsaturated sorption complex; soil profiles deeper than 10 cm are sparse (Veselý 1994). Vegetation is dominated by secondary (~150 yr old) Norway spruce forest with sparse white fir and beech. The forest covers >70% of the lake watershed. Since World War II, access to the lake watershed and most kinds of land use have been restricted due to frontier protection (up to 1989) and by administrative decisions (in 1960, the Šumava Mountains became a protected area).

Plešné Lake is a dimictic, oligotrophic to mesotrophic lake with anoxia in the hypolimnion during both winter and summer stratification periods. The lake was already acidified in the early 1960s, when pH values <5.4 were determined by Procházková (pers. comm.). At present, the lake is fishless, macrozooplankton are sparse and consist of two crustacean species in low densities, and the phytoplankton community is dominated by acid-tolerant species of green algae, dinoflagellates, and cyanobacteria. The lake water is low in base cations, the carbonate buffering system is depleted, and sulfate and nitrate are the dominant anions (Hejzlar et al. 1998). The lake has three accessible tributaries (Fig. 1); two of them (PL-I and PL-II) are on the surface, while tributary PL-III is subsurface but accessible in a small cave.

Water sampling and analyses—Atmospheric deposition was collected in bulk samplers protected against light and bird perching and fitted with a 100-μm polyamide sieve to remove coarse particles. Samplers were situated within 400 m east of the lake (1) in the rocky area without trees (precipitation, two samplers, altitude ~1,090 m above sea level), and (2) in the forest (throughfall, nine samplers, altitude ~1,130 m above sea level; Fig. 1). Samples were taken from 4 November 1997 to 4 November 1998. Rain was sampled in 2-week intervals and snow in 2- to 4-week intervals. All samples from each site were combined to obtain an integrated sample. Water samples from the Plešné Lake and its tributaries were taken roughly monthly from 14 October 1997 to 4 November 1998. Tributaries were sampled near their inlets to the lake and the water discharge was estimated by means of a bucket and stopwatch. In subwatersheds containing several tributaries in close proximity (PL-I and PL-II; Fig. 1), an integrated sample was taken with sample volumes proportional to the discharge of the individual streams. Samples were immediately filtered through a 40-μm polyamide sieve to remove coarse particles. Each sample was analyzed separately, and chemical inputs to the lake were calculated from volume-weighted mean concentrations for the three tributaries.

Samples of lake water were taken at the deepest point of the lake (Fig. 1) from the following depths: 0.5, 4, 8, and 12 m, the upper layer of the anoxic zone (14–16 m), and 0.5 m above the bottom (mostly ~17 m). Temperature, dissolved oxygen, and pH were measured with the DataSonde 4 (Hydrolab) at 0.5 m intervals. On 24 February 1998 and 13 August 1998, depth profiles of dissolved oxygen and pH were measured at six additional sites along the lake. The lake outlet was sampled at 2-week intervals together with atmospheric deposition. The samples of lake water were immediately filtered through a 200-μm polyamide sieve.

In the laboratory, samples were filtered with membrane filters (pore size of 0.45 μm) for determination of ions and with glass-fiber filters (MN-5; pore size of 0.4 μm; Macherey Nagel) for the analyses of P, organic matter, and dissolved Al and Fe. The samples for pH; acid neutralizing capacity (ANC); and total P, Al, and Fe were not filtered. Dissolved and particulate organic carbon (DOC and POC) were analyzed with a LiquiTOC analyzer (Foss/Heraeus) for the filtrate and by combustion of the glass-fiber filter with the retained particulate organic matter, respectively. ANC (Gran titration), pH, dissolved reactive P (DRP, molybdate method, Murphy and Riley 1962), total P (TP), and dissolved P (DP) were analyzed within 24 h of sampling. TP and DP were determined by perchloric acid digestion according to Kopáček and Hejzlar (1993), but larger amounts of sample were evaporated to obtain a detection limit of about 0.5 μg P L^{-1}. Particulate P (PP) was the difference between TP and DP. Total and dissolved organic N (TON and DON) were determined by Kjeldahl digestion and distillation (Procházková 1960) within 1 week of sampling. Particulate organic nitrogen was the difference between TON and DON. Samples for ion determination (Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, and F^-) were frozen at −20°C and analyzed by ion chromatography (Thermo Separation Products) within a month.

Fractionation of Al was obtained as follows: total Al (T-Al), dissolved Al (D-Al), and nonlabile Al (NL-Al) were analyzed in nonfiltered samples, filtered samples, and cation exchange treated samples after their filtration, respectively. Concentration of Al in each fraction was determined with acid digestion of the sample according to Driscoll (1984) within 2 d of sampling. Ionic Al (Al_i) was the difference between D-Al and NL-Al concentrations. Particulate Al (Al_{part}) was the difference between T-Al and D-Al concentrations. Hence, D-Al represents the sum of ionic Al forms, dissolved Al-organic complexes, and colloidal Al particles <0.4 μm; NL-Al represents dissolved Al-organic complexes and colloidal Al particles <0.4 μm; Al_i represents ionic Al forms (Al^{3+} and Al complexes with hydroxide, sulfate, and fluoride); and Al_{part} represents acid-soluble Al particles >0.4 μm. Total Fe and dissolved Fe (T-Fe and D-Fe) were analyzed by the thiocyanate colorimetric method after sample evaporation and digestion with perchloric acid. This colorimetric method gave comparable results (slope of 1.02 ± 0.02, $r = 0.99$, $P < 0.001$) with inductively coupled plasma atomic emission spectrometry (ICP) for 50 samples with Fe concentrations between 0.05 and 8 mg L^{-1}.

Sediment sampling and analyses—Sediment samples were collected at the deepest point with the gravity corer according to Hruška (1986) and were immediately sectioned into 5-cm intervals. Sediments were stored wet in the dark at 5°C until analyzed. Sediment cores were collected for (1) phosphorus sorption characteristics on 22 July 1997, and (2) determination of phosphorus fractionation on 11 June 1998. All characteristics were measured within 10 d of sampling. Wet samples were homogenized by passing through a 0.2-mm nylon sieve. Sediment portions for determination of C, P, N, Ca, Al, Fe, Mn, and Zn contents were lyophilized. Sediment pH was measured directly in the wet sample. Water content of fresh sediment was determined at 105°C, loss on ignition (LOI) at 550°C. The C content was analyzed on the LiquiTOC analyzer (Foss/Heraeus); P by the nitric-perchloric acids digestion method of Kopáček and Hejzlar (1995); N by Kjeldahl combustion according to Procházková (1960); and Ca, Al, Fe, Mn, and Zn by atomic absorption spectroscopy.

Phosphorus fractionation—Five fractions of P were extracted from sediment layers of 0–5, 5–10, 10–15, 15–20, and 40–45 cm by the consecutive use of the following extraction solutions (Psenner and Puczko 1988): (1) distilled water at 20°C (20 min) to obtain P dissolved in the interstitial water and loosely bound P, (2) dithionate-bicarbonate (0.1 M $Na_2S_2O_4$, 0.1 M $NaHCO_3$) at 40°C (30 min) to release P from iron oxyhydroxides under anoxic conditions, (3) 1 M NaOH at 20°C (16 h) to remove P from the amorphous Al and Fe oxyhydroxides, (4) 0.5 M HCl at 20°C (24 h) to release P combined with carbonates and apatite, and (5) 1 M NaOH at 85°C (24 h) to remove P associated with organic matter. Concentrations of DRP, TP, and DOC in the individual fractions were analyzed with the same methods as the lake water. Al and Fe concentrations were determined by the ICP technique.

Sorption studies—Eight samples of wet sediment (containing ~15 mg of dry matter) were shaken for 24 h at ~25°C with 25 ml of artificial lake water (SO_4^{2-}, Cl^-, Na^+, K^+, Ca^{2+}, and Mg^{2+} concentrations of 5.6, 0.5, 1.0, 0.5, 1.1, and 0.2 mg L^{-1}, respectively) containing between 0 and 40 mg L^{-1} P as KH_2PO_4. Because P sorption is pH dependent (Detenbeck and Brezonik 1991), sorption experiments were conducted at the original pH values of the samples, which were maintained by adding 0.1 M HCl and/or 0.1 M NaOH solutions. During the experiments, pH was checked (and adjusted if necessary) in 2-h intervals for the first 12 h, then in 6-h intervals thereafter. However, changes in pH during these experiments were negligible. After shaking, the suspensions were centrifuged at ~1,000 g for 15 min, filtered (0.4 μm), and the orthophosphate concentrations in the supernatants were determined by the method of Murphy and Riley (1962) as DRP. The difference between DRP concentration before and after the procedure was used to calculate the quantity of P sorbed by the sediments. The sorption data were fitted to the linear form of the Langmuir equation (correlation coefficients were always >0.98), and the sorption maximum (X_m) was calculated for each sample (Barrow 1978).

The influence of pH on the P sorption equilibrium was studied in the pH range from 3 to 8. The experiments were performed as described above, but the original P concentration was 10 mg L^{-1} in each sample. In addition to DRP, supernatants were also analyzed for equilibrium concentrations of D-Al and D-Fe on the ICP analyzer, and for DOC.

Results and discussion

Chemistry of atmospheric deposition and tributaries—Precipitation measured in the open area (1,258 mm) represented the direct atmospheric deposition onto the lake surface, while throughfall (982 mm) represented atmospheric deposition onto the forest floor. Direct atmospheric deposition was an important element source for the lake due to a relatively small watershed to lake area ratio (~9). Of the total amount of water entering the lake, ~17% originated from direct atmospheric deposition and ~83% from the watershed, assuming 30% evapotranspiration from the forest.

Volume-weighted mean concentrations of TP were 20.4 and 30.3 μg L^{-1} in precipitation and throughfall, respectively (Table 1). Most of the TP was in particulate form; the average contribution of DRP to the TP pool was 25% in precipitation and 5% in throughfall. Atmospheric deposition of aluminum was low and negligible compared to the terrestrial sources (Table 1).

The chemical composition of tributaries differed from throughfall chemistry. The most pronounced difference was in the SO_4^{2-} concentrations, which were twice as high in tributaries, probably due to sulfate leaching from soils. The high rates of SO_4^{2-} leaching may reflect high historical rates of sulfate deposition; current deposition is likely lower due to the ~50% reduction in S emissions in the area during the 1990s (Kopáček et al. 1998). The terrestrial increase in concentrations of base cations was low (Table 1), and the elevated concentrations of anions in tributaries relative to deposition were compensated for by the increase in Al concentrations and decrease in pH values. On an equivalence

Table 1. Volume-weighted mean (VWM) composition of atmospheric deposition to the lake surface (precipitation) and to the forest floor (throughfall), and average composition of the individual tributaries, all tributaries (VWM concentrations for the tributaries PL-I, PL-II, and PL-III), total input (83% of tributaries and 17% of precipitation), and outlet of Plešné Lake in 1997–1998. Number of observations (*n*). Average pH values were calculated from average H^+ concentrations. ND, not determined or determined irregularly.

		Atmospheric deposition VWM concentration		Individual tributaries Average concentrations			All tributaries VWM concentration			Total input	Outlet		
		Precipitation	Throughfall	PL-I	PL-II	PL-III	Avg.	Min.	Max.	Avg.	Avg.	Min.	Max.
n		22	2	14	10	12	14	14	14	14	29	29	29
pH		4.90	4.32	4.14	4.23	4.49	4.23	4.16	4.31	4.29	4.76	4.54	4.92
ANC	μeq liter^{-1}	−3	−37	−63	−61	−34	−55	−66	−40	−46	−15	−34	−4
Ca^{2+}	mg liter^{-1}	0.19	0.84	0.68	0.78	1.19	0.83	0.63	1.02	0.72	1.01	0.71	1.24
Mg^{2+}	mg liter^{-1}	0.03	0.14	0.16	0.16	0.25	0.18	0.14	0.24	0.16	0.22	0.17	0.27
Na^+	mg liter^{-1}	0.25	0.40	1.30	1.27	1.18	1.28	0.94	1.58	1.10	1.02	0.71	1.30
K^+	mg liter^{-1}	0.35	1.69	0.29	0.33	0.39	0.32	0.23	0.42	0.33	0.40	0.25	0.52
NH_4-N	μg liter^{-1}	480	413	<10	<10	<10	<10	<10	29	85	18	<10	61
NO_3-N	μg liter^{-1}	326	764	609	730	1005	721	484	1151	654	348	223	671
SO_4^{2-}	mg liter^{-1}	1.3	3.4	6.3	5.7	6.4	6.3	4.5	7.7	5.4	5.9	4.2	6.6
Cl^-	mg liter^{-1}	0.40	0.65	0.63	0.55	0.54	0.59	0.45	0.74	0.56	0.57	0.40	0.72
DOC	mg liter^{-1}	1.3	11.5	12.5	9.9	4.3	9.6	6.1	15.0	8.2	3.0	1.6	5.5
TP	μg liter^{-1}	20.4	30.3	ND	ND	ND	ND	ND	ND	ND	10.0	4.3	21.2
DP	μg liter^{-1}	7.4	6.5	27.3	27.5	13.6	23.4	16.7	32.0	20.7	1.8	<1	3.3
DRP	μg liter^{-1}	5.0	1.5	22.8	23.9	11.7	19.8	14.6	26.1	17.3	<1	<1	2.0
T-Al	μg liter^{-1}	4	10	ND	ND	ND	ND	ND	ND	ND	566	396	699
D-Al	μg liter^{-1}	ND	ND	934	901	838	894	781	1040	740	454	249	652
NL-Al	μg liter^{-1}	ND	ND	373	323	151	308	171	433	260	73	23	170
Al_l	μg liter^{-1}	ND	ND	562	578	686	585	423	794	490	381	226	547

basis, H^+ and Al^{n+} ions dominated the cation pool in tributaries comprising on average 25 and 24%, respectively, whereas SO_4^{2-}, NO_3^-, and organic acids were prominent (55, 22, and 15%, respectively) in the anion pool.

The volume-weighted mean concentration of DP in the three tributaries was 23 μg L^{-1} on average with DRP as the dominant P fraction (~85%). The TP concentrations in tributaries and in direct atmospheric deposition were comparable; however, the watershed was the major source of DRP for Plešné Lake. Volume-weighted mean concentrations of D-Al varied from 781 to 1,040 μg L^{-1}, with a predominant contribution of Al_i (~60% in the surface tributaries and ~80% in PL-III). There were only negligible differences between concentrations of TP and DP or T-Al and D-Al, which were irregularly determined in the tributaries. Hence, the DP and D-Al concentrations given in Table 1 adequately represent the input of total P and total Al to the lake.

Lake water chemistry—The average chemical composition of the lake outlet differed from the total lake input, having lower concentrations of NO_3^- and P (by ~50%), DOC (by ~60%), and Al_i (by ~20%) and higher pH and ANC values (Table 1). The average composition of total lake input was estimated from volume-weighted mean compositions of tributaries and precipitation and the amounts of water entering the lake from watershed (83%) and direct atmospheric deposition (17%). However, the actual differences between the total input and output could be more or less pronounced due to the low proportion of sampled water in the total water input. The water input from the three accessible tributaries to the Plešné Lake was usually <42% of the outlet, indicating that about half of the total water input occurred via diffuse runoff and/or inaccessible subsurface tributaries.

The surface tributaries PL-I and PL-II had lower concentrations of Ca^{2+}, Mg^{2+}, NO_3^-, and Al_i, lower pH, and higher concentrations of DOC, DP, DRP, and NL-Al than the subsurface tributary PL-III (Table 1). The importance of the subsurface input to the lake is indicated by the lake Ca^{2+} budget. Ca^{2+} concentrations were higher in the lake outlet than in the total input, while in-lake processes were only a limited Ca^{2+} source (*see later*). Because concentrations of NO_3^- and Al_i were higher in PL-III than in the surface tributaries, their real in-lake decrease was probably somewhat higher than suggested by the data in Table 1. In contrast, the real in-lake decrease in P and DOC concentrations was probably lower.

The seasonal patterns of pH and DOC, NO_3^-, SO_4^{2-}, P, and Al concentrations in the lake outlet and tributaries are given in Fig. 2. Concentrations of NO_3^- in the tributaries were highest in winter, then decreased during the growing season, while DOC and DP concentrations followed an opposite trend. Concentrations of NO_3-N in the tributaries were ~0.5 mg L^{-1} even in the summer, indicating an advanced stage of N saturation of the watershed according to Stoddard (1994). In addition, consistently lower NO_3^- concentrations in the outlet indicated the year-round activity of N-consuming in-lake processes. The outlet SO_4^{2-} concentrations decreased only in winter and summer. Concentrations of P, DOC, and Al were consistently higher in the tributaries than in the outlet. The outlet concentrations of TP were roughly stable throughout the year except for May, when the samples were contaminated with pollen. Values of pH in the outlet were 0.4 to 0.6 units higher and showed a more pronounced seasonal pattern than in the tributaries.

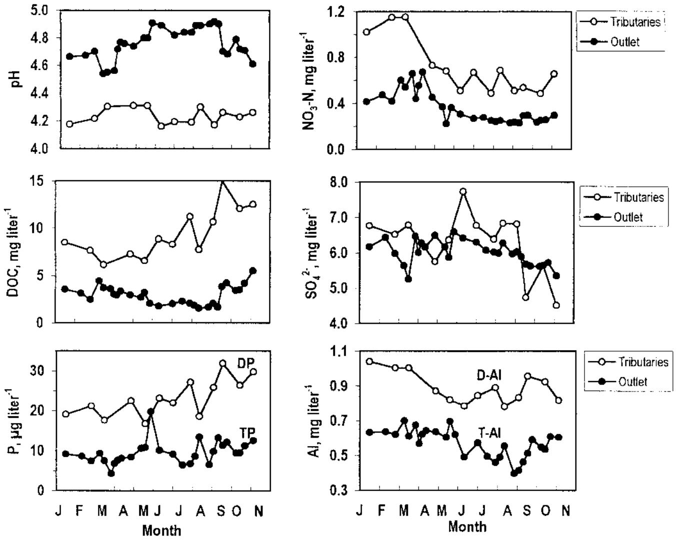

Fig. 2. Seasonal patterns of pH and concentrations of DOC, P (DP in tributaries and TP in outlet), NO_3^-, SO_4^{2-}, and Al (D-Al in tributaries and T-Al in outlet) in the Plešné Lake tributaries (volume-weighted means for the tributaries PL-I, PL-II, and PL-III) and outlet in 1998.

In-lake processes—Depth and time variations in physical and chemical parameters of lake water are shown in Fig. 3. The temperature stratification of Plešné Lake developed characteristically for a dimictic temperate lake. The autumn and spring overturns occurred in mid-November and mid-April, respectively; ice cover lasted from 20 November 1997 to 9 April 1998. The summer stratification was well developed and lasted until early November 1998. The thermocline depth was 4–5 m in summer, then it gradually deepened in autumn. Dissolved oxygen concentrations in the surface layer fluctuated around 100% saturation. Pronounced metalimnetic maxima in dissolved oxygen concentrations were characteristic for the whole summer and reached 12–13 mg L^{-1} from May to August. Hypolimnetic concentrations of dissolved oxygen decreased rapidly after the autumn and spring overturns and were depleted to values <0.1 mg L^{-1} in the bottom layer (1–2 m above the sediments) within ~6 weeks.

Dissimilatory reduction processes occurred under low redox potentials in the hypolimnion. These processes, well known from eutrophic lakes (e.g., Wetzel 1983), led to further chemical changes in the lake water composition. Concentrations of NO_3^- and SO_4^{2-} decreased, while concentrations of NH_4^+ and Fe forms increased by their release from sedimenting matter and/or sediments (Figs. 3, Fig. 4). The dissimilatory reduction processes led to alkalinity production in bottom waters as described by Schindler (1986) and Psenner and Catalan (1994). ANC was negative in the water column but close to zero or positive above the sediment, where it reached maxima of 237 and 56 μeq L^{-1} during winter and summer stratification, respectively (Fig. 3).

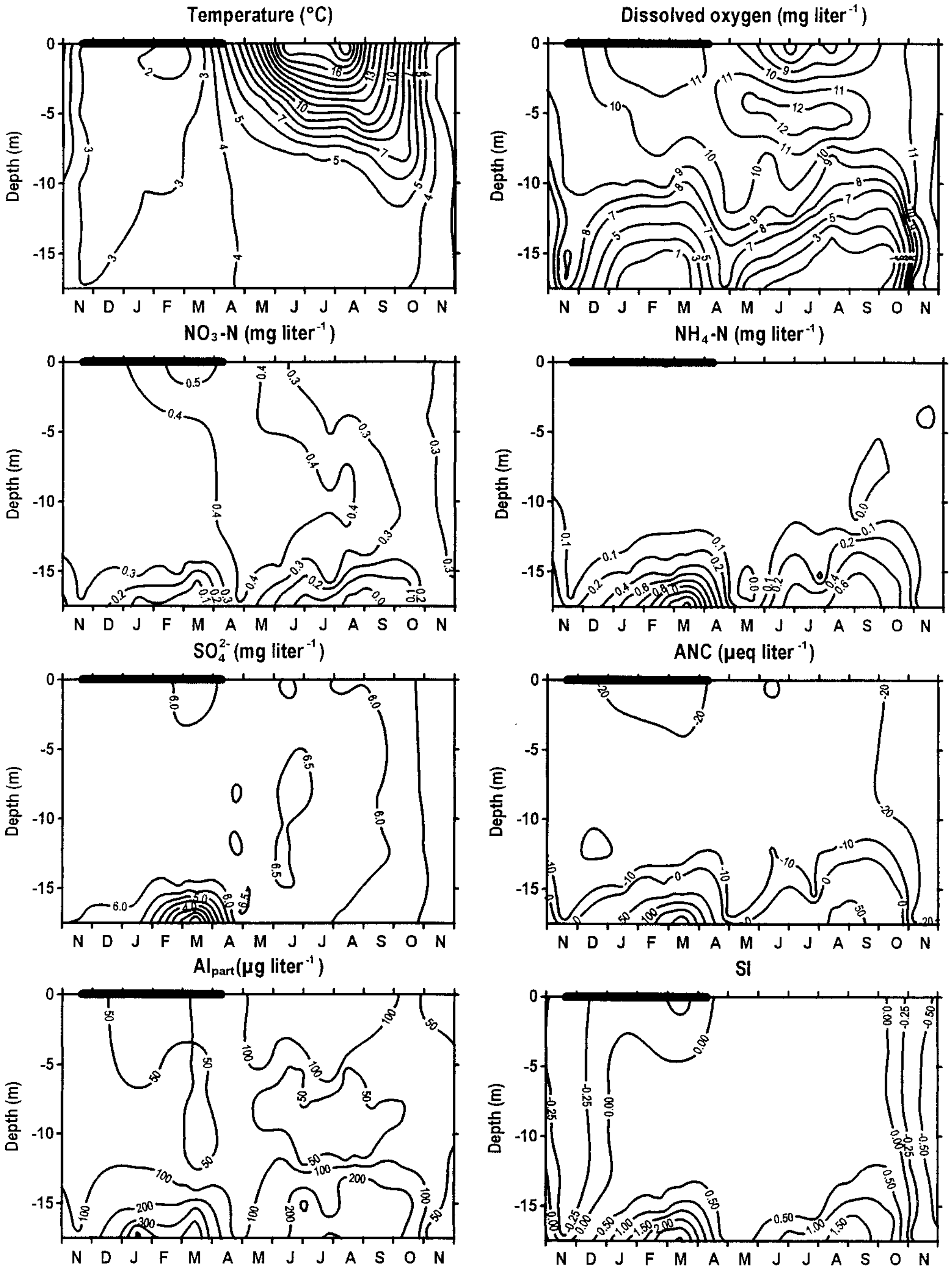

Fig. 3. Depth-time diagrams of temperature and concentrations of dissolved oxygen, NO_3^-, NH_4^+, SO_4^{2-}, ANC, Al_{part}, and saturation index (SI). SI was estimated according to Driscoll (1985) for Al_i concentrations with respect to the solubility of microcrystaline gibbsite ($pK_{SO} = 9.35$). Plešné Lake, 1997–1998. Thick lines represent ice cover.

High ANC values in winter mostly originated from the pronounced hypolimnetic reduction of sulfate and iron, while nitrate reduction was the dominant alkalinity generation process in summer. During winter anoxia, the SO_4^{2-} concentration above the sediment decreased by 4.1 mg L^{-1} compared to the autumn overturn, but only by 0.5 mg L^{-1} during summer stratification. The highest hypolimnetic concentrations of iron were found in winter. Most of the T-Fe liberated from the sediments was in the dissolved form (Fig. 4). The concentration of Fe^{2+} was not determined in 1998, but Fe^{2+} represented nearly all the D-Fe pool above the sediment during our previous study in 1994 (Kopáček and Hejzlar unpubl. data). The NO_3^- concentration was depleted above the sediment both in winter and summer (Fig 3).

The release of base cations from the sediment, which can play an important role in in-lake alkalinity generation (Psen-

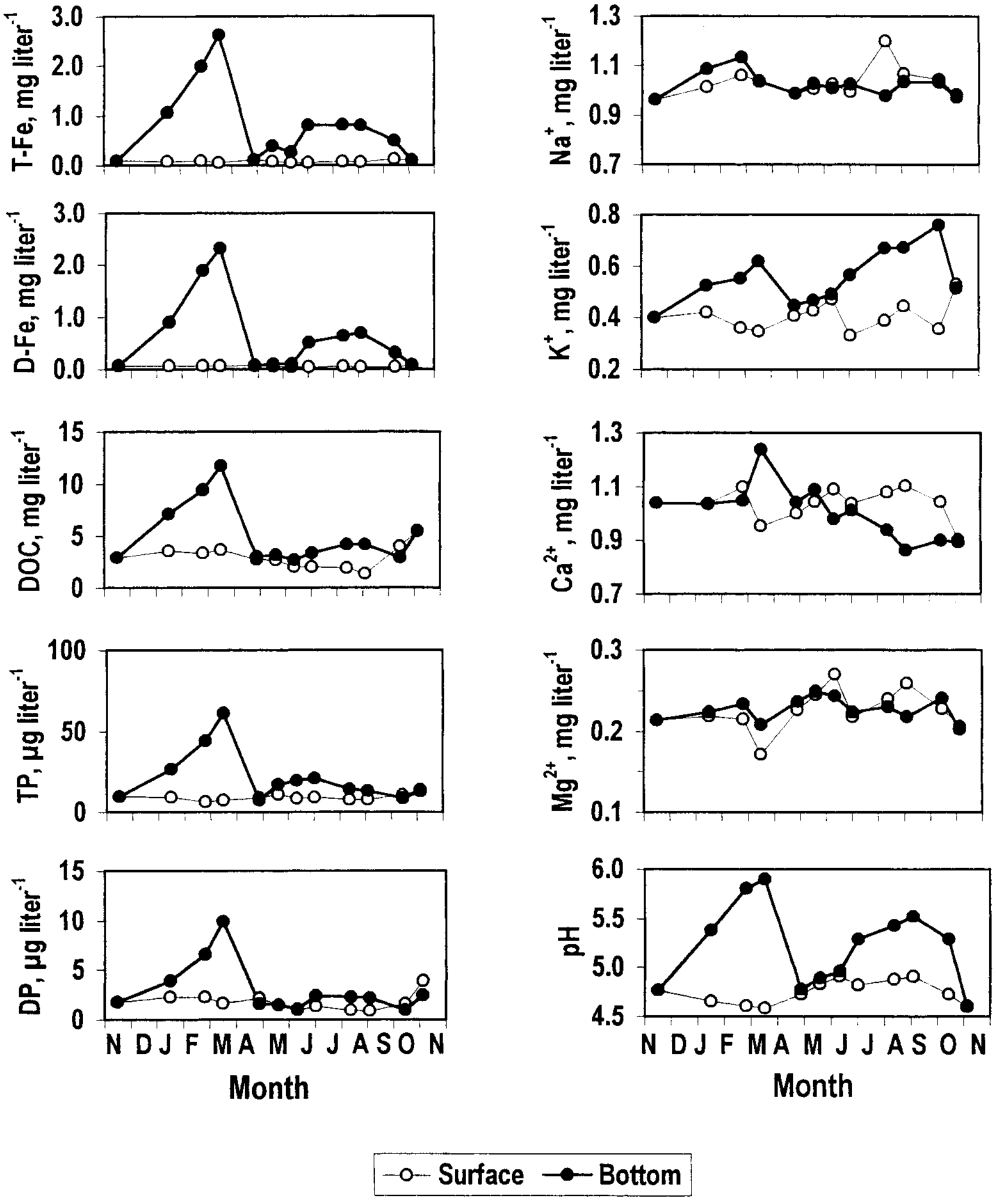

Fig. 4. Seasonal patterns of surface (0.5 m below the surface, open circles) and bottom (0.5 m above sediment, full circles) concentrations of selected constituents at the deepest part of Plešné Lake, 1997–1998. T-Fe and D-Fe, total and dissolved Fe; DOC, dissolved organic C; TP and DP, total and dissolved P.

ner 1988), contributed only slightly to the ANC increase in the Plešné Lake (Fig. 4). Concentrations of base cations were mostly stable and comparable in the surface and bottom layers throughout the year. The only exception was the hypolimnetic K^+ concentration, which was ~50% elevated in winter and twofold higher in summer compared to the epilimnetic concentration. Only a slight increase was observed in Ca^{2+} concentration in late winter (Fig. 4).

Concentrations of DOC, TP, and DP followed similar patterns as D-Fe (Fig. 4) being elevated during anoxia. The increase in DOC concentration provided a pronounced pool of organic acid anions in the water above the sediment. This is evident from changes in the ionic composition of hypolimnetic water during winter and summer anoxia given in Table 2.

Table 2 summarizes net changes in ionic composition of the water above the sediment during winter and summer stratification periods compared to the autumn and spring overturns, respectively. The measured net change in HCO_3^- concentration determined by Gran titration agreed closely with calculated net change in HCO_3^- determined from ionic balance (i.e., 237 vs. 221 μeq L^{-1} in winter, and 56 vs. 55 μeq L^{-1} in summer). When calculated according to Psenner (1988), the contribution of changes in Fe^{2+}, SO_4^{2-}, and NO_3^- concentrations to alkalinity generation was ~45%, 45%, and 5%, respectively, in winter, and ~45%, 15%, and

Table 2. Net changes in the chemistry of the Pleŝné Lake hypolimnion 0.5 m above the sediment during winter stratification (15 November 1997–17 March 1998) and summer stratification (28 April 1998–3 September 1998). Values are in μeq liter^{-1}, dissolved oxygen (O_2) in μmol liter^{-1}.

	Winter stratification			Summer stratification		
	15 Nov	17 Mar	Net change	28 Apr	3 Sep	Net change
ANC	−15	237	252	−15	56	71
HCO_3^-	0	237	237	0	56	56
O_2	284	0	−284	250	0	−250
H^+	17	1	−16	17	3	−14
NH_4^+	6	120	114	4	52	48
Na^+	42	45	3	43	45	2
K^+	10	16	6	10	17	7
Ca^{2+}	52	62	10	52	43	−9
Mg^{2+}	17	17	0	19	18	−1
Fe^{2+}	2	82	80	2	24	22
Al^{n+}	34	2	−32	34	2	−32
SO_4^{2-}	126	41	−85	130	122	−7
NO_3^-	24	2	−22	30	0	−30
Cl^-	16	16	0	17	16	−1
F^-	5	5	0	6	5	−1
A^{m-}	12	63	51	13	21	8
HCO_3^- (calc)			221			55

A^{m-} (concentration of organic acids) was calculated from DOC concentration, pH, and the average carboxyl content of organic acids (5.9 μeq per 1 mg of DOC) obtained for the Šumava lakes and their tributaries by Kopáček and Hejzlar (1998).

A^{n+} (concentration of positively charged Al species) was estimated from Al_i concentration and the average charge (n); n was estimated from the distribution of particular ionization fractions of Al hydroxocomplexes, neglecting F^- and SO_4^{2-} complexes (Kopáček and Hejzlar 1998).

HCO_3^- (calc) = $[H^+] + [NH_4^+] + [Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}] + [Fe^{2+}] + [Al^{n+}] - [SO_4^{2-}] - [NO_3^-] - [Cl^-] - [F^-] - [A^{m-}]$, where brackets represent net changes in equivalent concentrations of components.

40%, respectively, in summer. Hydrolysis of Al_i and liberation and dissociation of organic acid anions were the important alkalinity consuming processes.

An important change in the lake water chemistry was the increase in hypolimnetic pH values during stratification (Fig. 4). This is a typical pattern in lakes with a depleted carbonate buffering system, compared to nonacidified lakes, where pH above the bottom usually decreases during anoxia (e.g., Wetzel 1983). The changes in pH resulted in changes in Al speciation, particularly in the decrease in ionic Al species (Table 2). The depth variation of T-Al concentration was usually low, except for its increase above the sediment during winter stratification. In contrast, the in-lake concentrations of Al_i and Al_{part} varied both with depth and time (Fig. 3).

Values of the mineral saturation index (SI) given in Fig. 3 suggest when the in-lake formation of Al_{part} was favored thermodynamically with respect to formation of mineral phases of microcrystalline gibbsite ($Al(OH)_3$). The SI values were estimated according to Driscoll (1985) as $\log(Q_p/K_p)$, where Q_p is the ion activity product of the solution (we used Al_i concentrations for a rough estimation) and K_p is the thermodynamic solubility of the microcrystaline gibbsite ($pK_{SO} = 9.35$). An SI value >0 suggests oversaturation with respect to the solubility of the mineral phase, SI $= 0$ indicates equilibrium, and SI < 0 represents undersaturation. Positive SI values corresponded well with the elevated Al_{part} concentrations and low Al_i values in the water column of Plešné Lake.

Precipitation of Al occurred in the epilimnion as well as the hypolimnion during summer temperature stratification (Fig. 3). The input entering the epilimnion was more acidic and thus higher in Al_i than the epilimnetic water resulting in the formation of Al_{part} as the input mixed with surface lake water. The lowest and most stable concentrations of Al_{part} were found between 5 and 12 m depth in Plešné Lake, while higher values were found both in the epilimnion and above the sediment. The inverse pattern was observed for Al_i.

Concentrations of P were elevated just above the bottom, and most of the P was associated with particles >0.4 μm (note different scales for TP and DP in Fig. 4). In contrast, the concentration of DRP was always below the detection limit of the method ($\sim$1 μg L^{-1}) throughout the water column. This fact was surprising, because the reduction and dissolution of ferric oxyhydroxides in sediments is commonly associated with the liberation and release of iron-bound inorganic P to the water column (e.g., Wetzel 1983; Cooke et al. 1993). Because DRP concentrations were generally undetectable, the increase in hypolimnetic concentrations of DP was probably associated either with dissolved organic matter liberated from Al hydroxide floc at the elevated pH (*see later*) or with particles and/or colloids <0.4 μm that passed through the filter during filtration.

Phosphorus inactivation in the water—In-lake alkalinity generation increases water pH, which shifts the equilibrium concentrations of ionic Al forms toward particulate forms. The ionic Al species supplied from terrestrial sources hydrolyze in the lake and form Al oxyhydroxides under conditions of oversaturation with respect to the solubility of microcrystalline gibbsite. The colloidal Al oxyhydroxides coagulate dissolved organic matter and strongly adsorb orthophosphate (e.g., Dickson 1978; Lijklema 1980; Driscoll 1985). Above the bottom, orthophosphate liberated from the sedimenting organic matter by dissimilatory processes is removed from the liquid phase by adsorption onto the colloidal Al oxyhydroxides. This process can explain the elevated hypolimnetic TP concentrations but undetectable DRP during anoxic conditions.

The orthophosphate sorption by colloidal Al oxyhydroxides probably occurs even in the epilimnion under conditions of elevated Al_{part} concentrations. This P inactivation would explain the high P limitation of primary production in Plešné Lake indicated by high activities of extracellular phosphatases despite relatively high TP concentrations of ~10 μg L^{-1} (Vrba and Bittl pers. comm.; Hejzlar et al. 1998).

The allochthonous dissolved organic matter entering Plešné Lake had high C : P and N : P ratios. The average molar ratios of DOC to DOP (dissolved organic P, DOP = DP − DRP) and DON to DOP in tributaries were ~6,700 and ~200, respectively. The particulate C : P and N : P molar ratios of temperate lakes are mostly higher than Redfield ratios with averages of 306 and 24, respectively (Hecky et al. 1993). However, the average molar POC : PP and PON : PP ratios in the seston of the Plešné Lake epilimnion were substantially higher (960 and 80, respectively) than the above averages, suggesting that allochthonous organic matter is a significant component of the lake particulate material. Dissolved allochthonous organic matter was probably coagulated and precipitated by Al in the water column as described, e.g., by Dickson (1978). The high particulate C : P and N : P ratios in the Plešné Lake epilimnion decreased during sedimentation. While the CO_2 and NH_4^+ liberated from the sedimenting organic matter by dissimilatory processes remained dissolved in the hypolimnion water, orthophosphate was probably adsorbed on Al oxyhydroxide floc (Lijklema 1980) and returned to the particulate form. The lower molar C : P and N : P ratios of 360 and 26, respectively, in the uppermost sediment layer reflected this P enrichment of sedimenting matter.

The increase in lake water pH due to internal alkalinity generation was the most important process controlling solubility of Al in the Plešné Lake water column. The highest pH values were observed in the anoxic hypolimnion (Fig. 4). However, we measured pH changes in the deepest part of the lake, which did not allow us to assess the extent of a potential formation of Al_{part} in shallower parts where oxic conditions prevailed. Some alkalinity generation processes, like sulfate and nitrate reduction in the sediment and water, are known to be important even under oxic conditions in the water column (Kelly and Rudd 1984; Schindler 1988*b*; Kelly 1994). We determined longitudinal profiles of pH and dissolved oxygen concentrations in Plešné Lake to estimate the spatial pattern of internal alkalinity generation during both winter and summer stratification. Concentrations of dissolved oxygen were <1 mg L^{-1} only in the deepest part of the lake (below 15 m) both in winter and summer, while the pH values were elevated over a wider area (Fig. 5). In addition, pH values were also slightly elevated in the epilimnion during the summer (Fig. 4). Thus, conditions for formation of Al oxyhydroxides and adsorption of orthophosphate were not only associated with the deepest part of the lake but also might occur in a substantially bigger volume of Plešné Lake.

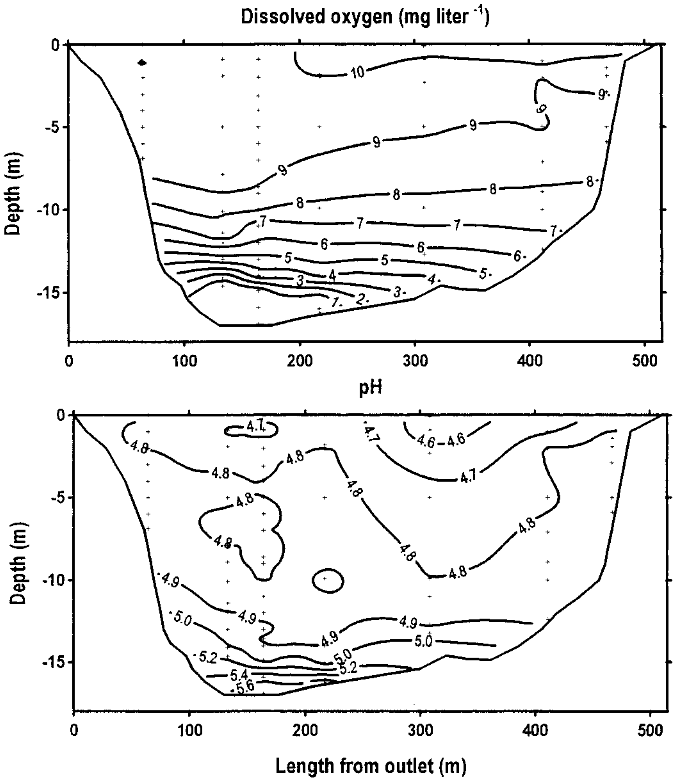

Fig. 5. Longitudinal-depth diagrams of dissolved oxygen concentration and pH in Plešné Lake during winter temperature stratification (24 February 1998).

Sediments—The sediment of Plešné Lake is rich in organic matter (Table 3). Loss on ignition varied between 68 and 75% and C content varied from 340 to 450 g kg^{-1}. Both parameters were higher in the upper layers. Other constituents also showed vertical differences. Values of pH ranged between 6.2 and 5.7, decreasing from older to younger layers. Relatively stable Al and Zn contents between 15- and 50-cm depth in the core sharply increased in the upper 15 cm. In contrast, P and Ca contents dropped by ~50% in the layers from 0 to 15 cm compared to the deeper sediment. The core was not dated; however, the onset of acidification is probably reflected in the sharp increases in Al and Zn above 10-cm depth (Table 3). This is supported by the occurrence of spheroidal carbonaceous particles, originating from high-temperature combustion of fossil fuel, in the upper 0–15 cm of the Plešné Lake sediment sampled by Schmidt (pers. comm.) in 1990. On the basis of these results, we can assume that the sediment layers below 15 cm are not affected by anthropogenic acidification, the 10–15-cm layer is a transition zone, and the layers between 0 and 10 cm reflect acidification-derived changes in the watershed-lake ecosystem. The small decline in Al and Zn in the uppermost sediment layer compared with the 5–10-cm layer may reflect ecosystem recovery from acidification in the 1990s due to

Table 3. Chemical composition of Plešné Lake sediment (sampled on 22 July 1997) and P sorption maximum (X_m) calculated using Langmuir equations from P sorption experiments. ND, not determined.

	Fresh sediment		Dry matter								
Layer (cm)	pH	Water (%)	LOI (%)	C (g kg^{-1})	N (g kg^{-1})	P (g kg^{-1})	Ca (g kg^{-1})	Al (g kg^{-1})	Fe (g kg^{-1})	Mn (mg kg^{-1})	Zn (mg kg^{-1})	X_m (g kg^{-1})
0–5	5.7	97	75	450	37	3.2	3.6	43	8.8	71	460	13.8
5–10	5.8	96	68	380	29	3.1	4.0	48	8.7	81	490	9.8
10–15	6.0	93	67	370	23	3.6	3.9	35	8.8	62	180	6.5
15–20	6.1	93	68	340	23	5.3	6.6	33	8.8	51	120	5.6
20–25	6.1	93	72	340	25	5.7	7.9	34	7.3	60	110	4.8
25–30	6.1	92	70	350	26	5.7	7.7	32	7.4	53	100	5.1
30–35	6.1	92	70	350	27	6.3	7.7	28	7.2	33	100	3.7
35–40	6.1	91	68	380	24	6.4	7.9	28	7.3	40	85	ND
40–45	6.2	91	68	390	23	6.9	6.6	32	6.9	38	55	4.2
45–50	6.2	91	68	390	22	7.2	9.6	38	8.0	34	95	ND

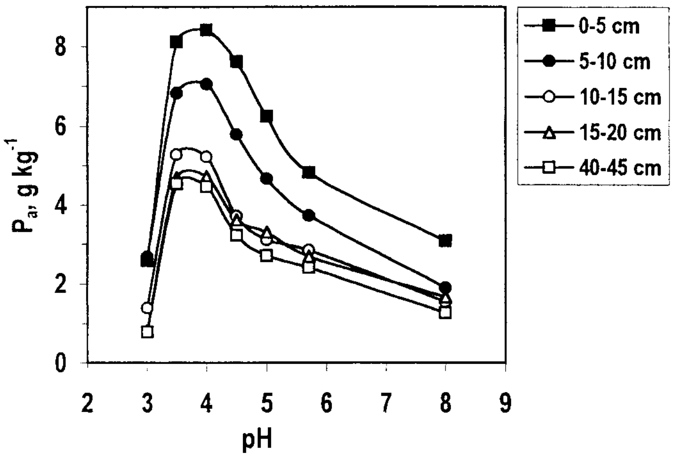

Fig. 6. The ability of the Plešné Lake sediment (22 July 1997) to bind P at different pH values with a starting PO_4-P concentration of 10 mg L^{-1}. P_a is the amount of P (g) sorbed per 1 kg of sediment (dry matter). Legend denotes particular sediment layers. Filled points represent two upper sediment layers affected by acidification.

Central European reductions in the atmospheric emissions of S and N compounds (Kopáček et al. 1998). Concentrations of Al and trace metals in the water column of Plešné Lake substantially decreased during this period (Veselý et al. 1998).

Although there were only negligible differences in the sediment ability to sorb P in the layers below 15-cm depth (X_m values), the layers above 10 cm adsorbed considerably more P (Table 3). The ability of sediment to sorb P decreased slightly at pH values higher than the original pH (~6), but increased with decreasing pH. The maximum ability of each sediment layer to sorb P was at pH ~ 4 and decreased sharply at pH < 3.5 (Fig. 6). The sorption ability of the two upper layers was substantially higher than that for the sediment below 10 cm over the entire pH range. Similarities in the P sorption-pH curves for layers below 15 cm further support the conclusion that the sorption ability of the sediment below 15 cm is similar. The equilibrium concentrations of P, Al, Fe, and DOC in water associated with 0–5-cm sediment were lowest at pH ~ 4 (Fig. 7). Equilibrium concentrations of DOC and DRP were substantially higher at both lower and higher pH values, whereas equilibrium concentrations of Al and Fe were only slightly higher than their minima at pH > 4, but sharply increased at pH < 4.

The pH-derived changes in the sediment ability to adsorb P are well known from numerous soil and sediment studies. The P-binding capacity of noncalcareous sediments increases with acidity due to the protonation of surface Al and Fe functional groups in Al and Fe oxyhydroxides (e.g., Edzwald et al. 1976; Detenbeck and Brezonik 1991). After reaching a maximum at pH ~ 4, the sharp decline in P sorption capacity of the sediment and the increase in Al and Fe concentrations in supernatant suggest dissolution of Al and Fe oxyhydroxides in the sediment at pH values <4. This process also liberated organic matter combined with Al and/or Fe oxyhydroxides resulting in increase in DOC concentrations. Equilibrium concentrations of DOC also increased

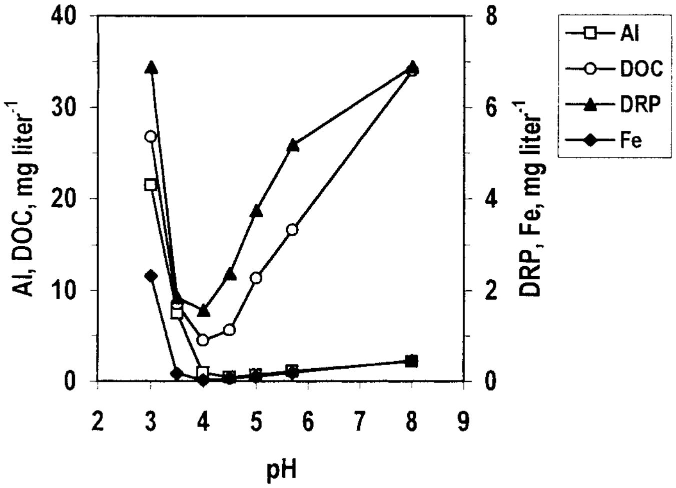

Fig. 7. Equilibrium concentrations of DRP, DOC, Al, and Fe in the supernatants from the sorption experiment shown in Fig. 6. Layer 0–5 cm of sediment sampled on 22 July 1997.

sharply when the supernatant pH increased over the range 4.5–8 (Fig. 7). A similar effect could explain the elevated DOC concentrations above the bottom of Plešné Lake during anoxia (Fig. 4). Sedimenting particulate matter probably contained coagulated organic substances combined with Al_{part}. These particles were formed in the water column at a lower pH than that which occurred in the hypolimnion during the presence of anoxic conditions. The increase in pH could then have resulted in conditions favorable for DOC liberation from the particulate matter.

Phosphorus fractionation in the sediment—Chemical characteristics and their vertical variations in a sediment core, which was used for P fractionation, were similar to the data given in Table 3. Total extractable P, Al, Fe, and DOC, determined as the sums of the amounts extracted by the individual fractionation steps according to Psenner and Pucsko (1988) (Table 4), were on average 107, 103, 100, and 63%, respectively, of their total contents in the sediment samples.

The dominant fraction of sediment P was associated with metal oxyhydroxides (NaOH extraction at 20°C). This extraction step liberated 89–94% of TP and 86–94% of DRP from the individual sediment layers (Table 5). Only 2–5% of TP and 2–6% of DRP were extracted by dithionate-bicarbonate and 1–4% of both TP and DRP were water extractable. The NaOH extraction at 20°C liberated 90–94% of total Al and 38–67% of C (i.e., 86–94% of the total extractable DOC). Most of the sediment Fe (42–52%) was also liberated by NaOH extraction at 20°C (Fig. 8), while the dithionate-bicarbonate and HCl fractions contributed 24–35% and 19–24%, respectively. Total P and DRP extracted by NaOH at 20°C increased with sediment depth, and Al and Fe extracted by NaOH at 20°C were highest in the upper layers (Fig. 8).

Table 4. Total-extractable (TE) amount of Al, Fe, TP, DRP, and DOC liberated from Plešné Lake sediment (sampled on 11 June 1998). Values are sums of all extraction steps of the fractionation method according to Psenner and Pucsko (1988). P_{TBC} is total P binding capacity of the sediment, $P_{TBC} = X_m$ + TE-DRP. For X_m see Table 3. Units are g per kg of dry matter.

	Sediment layer (cm)				
	0–5	5–10	10–15	15–20	40–45
TE-DOC	270	207	222	184	174
TE-Al	45.8	48.5	41.6	26.8	30.0
TE-Fe	6.8	7.7	7.7	6.4	6.0
TE-TP	3.6	3.3	4.3	4.3	5.1
TE-DRP	1.0	1.4	2.2	2.5	3.5
P_{TBC}	14.8	11.2	8.7	8.1	7.7

Phosphorus inactivation in the sediment—The average molar ratios of total Al to total Fe were 11 for the individual sediment layers and 24 for the NaOH (20°C) extracts, which extracted most of the P from the sediment samples. These results imply a dominant role for Al oxyhydroxides in the P sorption capacity of Plešné Lake sediment. The importance of Al was also suggested by the tight correlation ($P < 0.001$) between X_m and Al content in the sediment layers between 5- and 45-cm depth in the core (Fig. 9). The P sorption capacity of the uppermost layer was substantially higher than that predicted from total Al in deeper layers.

We suggest that the reason for higher P sorption in the upper sediment layer was the presence of fresh colloidal Al hydroxide floc originating in the water column. Such fine-grained particulate matter has a large surface area (Detenbeck and Brezonik 1991), and freshly prepared Al gel sorbs 1 to 2 orders of magnitude more P than gibbsite (McLaughlin et al. 1981). When the Al hydroxide floc settles onto the sediment surface, it may effectively retain P liberated deeper in the sediment. The sorbed P is stable under both oxic and reducing conditions because Al hydroxides are not sensitive to redox changes. This P-inactivation mechanism has been used in lake restoration (Cooke at al. 1993). Dissolved P concentrations are reduced by adding an Al salt (aluminum sulfate or sodium aluminate) to the water column to form aluminum phosphate and a colloidal aluminum hydroxide floc to which certain P fractions sorb.

Only 2–5% of P in the Plešné Lake sediment was associated with ferric oxyhydroxides, which are potentially sol-

Table 5. Percentage proportion of the individual extraction steps in the total extractable Al, Fe, TP, DRP, and DOC amounts given in Table 4. Data are averages for sediment layers of 0–5, 5–10, 10–15, 15–20, and 40–45 cm depths. The abbreviations refer to the following extraction steps by Psenner and Pucsko (1988): H_2O, distilled water, DB, dithionate-bicarbonate, NaOH-20, NaOH at 20°C; HCl; and NaOH-85, NaOH at 85°C.

	Extraction step				
	H_2O	DB	NaOH-20	HCl	NaOH-85
Al	1	1	91	1	6
Fe	1	28	45	21	5
TP	2	3	92	1	2
DRP	2	3	91	3	1
DOC	3	5	83	1	8

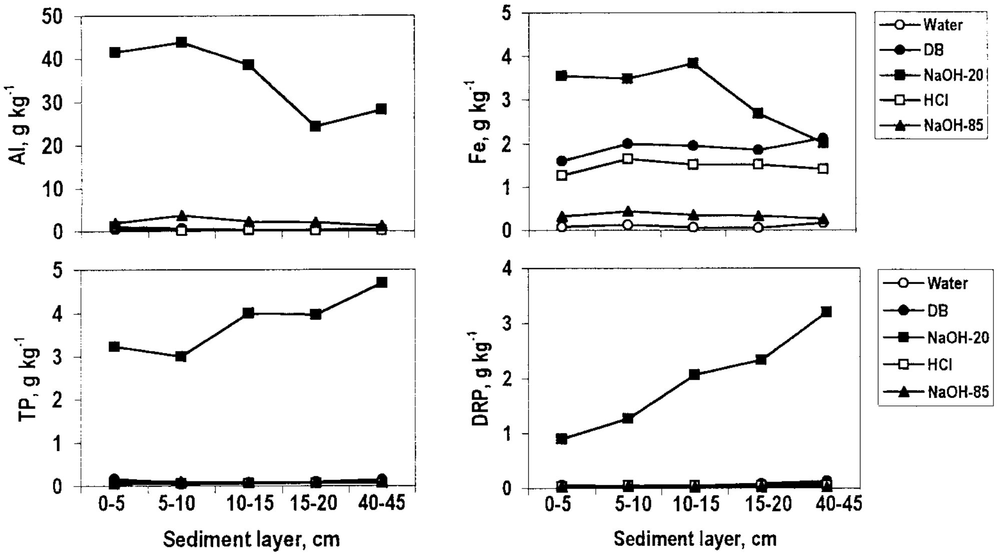

Fig. 8. The amounts of Al, Fe, TP, and DRP extracted by the individual fractionation steps according to Psenner and Pucsko (1988) from the 0–5-, 5–10-, 10–15-, 15–20-, and 40–45-cm layers of Plešné Lake sediment (11 June 1998). The abbreviations in the legend refer to the particular extraction steps: H_2O, distilled water; DB, dithionate-bicarbonate; NaOH-20, NaOH at 20°C; HCl; and NaOH-85, NaOH at 85°C.

uble during anoxia. This implies that hypolimnetic changes in redox potential had only a limited effect on P liberation from the sediment. Moreover, the release of the liberated P from the sediment was further limited by the high adsorption capacity of Al oxyhydroxides. Thus, increases in DRP have never been observed above the Plešné Lake sediment during anoxia (Hejzlar et al. 1998; this study).

High Al contents, even in the preacidification layers of the sediment, suggest that the Plešné Lake sediments have always functioned as an efficient P sink. The P sorption maximum was highest in the uppermost 0–10 cm of the sediment (Table 3) along with the elevated Al content. Despite a higher X_m value, total extractable DRP was substantially lower in the upper 0–10 cm than in deeper layers (Fig 8). We estimated the total capacity of the sediment to bind P by both sorption and chemical bonds (P_{TBC} = P total binding capacity) to determine whether the lower X_m values of the deeper sediment layers might be caused by higher amounts of originally bound P. The P_{TBC} value was calculated as the sum of total extractable DRP and X_m. Results given in Table 4 show that P_{TBC} was 7–8 g kg^{-1} in sediment layers below 10 cm, 11 g kg^{-1} in the 5–10-cm layer, and 15 g kg^{-1} in the uppermost layer. Thus, the acidification-derived increase in Al inputs from the watershed to the lake increased considerably the ability of the Plešné Lake sediment to bind P.

At present we are not able to explain why P content decreases as X_m values increase within the upper 0–15-cm layers of the Plešné Lake sediment (Table 3). This pattern could be caused by the decreasing P inputs from the watershed. We can only hypothesize whether this decline reflected the elevated atmospheric deposition of strong acids in the industrial era or a change in forest composition. The original mixed forest (Norway spruce, white fir, and beech) was replaced by the present spruce forest in the last few centuries. Both influences might lead to changes in (1) the base cation content of the soil, (2) soil acidification, and (3) Al concentrations in the soil solution. In podzol soils, P fixation to Al complexes may act to reduce terrestrial P export when the soils are acidified (Jansson et al. 1986).

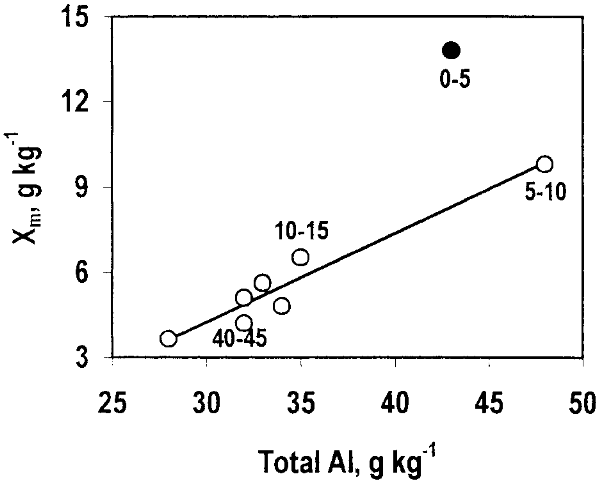

Fig. 9. Relationship between P sorption maximum (X_m) and total content of Al in Plešné Lake sediment (22 July 1997). Values are in g per 1 kg dry weight of sediment. Open circles, sediment layers between 5 and 45 cm; full circle, the uppermost 0–5-cm layer. Numbers at points refer to the depth of the sediment layer (cm). Solid line represents linear regression $X_m = 0.31 \times \text{Al} - 5$ ($r = 0.97$; $P < 0.001$) calculated for the layers below 5-cm depth in the sediment core.

Conclusions

In-lake P inactivation by Al in Plešné Lake is a process resulting from atmospheric acidification of the whole watershed-lake ecosystem and may be also applicable to lakes in other acidified areas. High rates of acid deposition and nitrogen saturation of Plešné Lake watershed result in elevated terrestrial inputs of Al, SO_4^{2-}, and NO_3^- to the lake. Biological reduction of NO_3^- and SO_4^{2-} in the water column and sediment contributes to the in-lake alkalinity generation and an increase in pH values, especially in the hypolimnion. The amount of alkalinity generated in the lake increases with the increase in the loads of SO_4^{2-} and NO_3^-. The greater the in-lake alkalinity generation, the higher the pH of the lake water compared to the input and, consequently, the greater the potential for formation of colloidal Al hydroxides in the water column. The precipitation of Al has several potential effects on in-lake P availability. First, Al content increases in the uppermost sediment layer (compared to the deeper preacidification layers), increasing its P-adsorption capacity and preventing P release from sediment at low redox potentials. Second, elevated concentration of Al colloids above the sediment binds orthophosphate liberated from the sedimenting seston and retains it in the sediment. Finally, the formation of Al colloids in the epilimnion may reduce P availability for the phyptoplankton there as well.

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