

Chemistry of Prášílské Lake and its tributaries during the 1998 summer temperature stratification

Chemismus Prášílského jezera a jeho přítoků během letní teplotní stratifikace v roce 1998

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Abstract

Water composition in the watershed-lake ecosystem of Prášílské Lake has been strongly affected by atmospheric acidification and forest decline. In 1998, all surface tributaries were acidic (pH from 3.75 to 4.87) with SO_4^{2-} and NO_3^- the major anions (17–41% and 1–69%, respectively) of the anion pool. Organic acid anions significantly contributed to the acidity of tributaries, constituting 2–41% of the anion pool in the individual tributaries. The tributaries draining sub-watersheds with damaged forest had increased NO_3^- concentrations (up to $2.4 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$) and the elevated losses of base cations. In-lake biochemical processes significantly influenced lake water chemistry. During the summer temperature stratification, pH, acid neutralizing capacity, K^+ , NH_4^+ , DOC, particulate Al, TP, and Fe forms were elevated, while NO_3^- and ionic Al were lowered. Dissimilatory processes liberated CO_2 , NH_4^+ , and phosphate from sedimenting seston. Biological nitrate removal and reduction of ferric oxyhydroxides resulted in alkalinity generation and in pH increase in the hypolimnion. Under conditions of increased pH, inorganic Al species hydrolyzed and formed particulate Al hydroxides, which adsorbed orthophosphate. This process resulted in elevated concentrations of total P (but undetectable dissolved reactive P) above the bottom and in lowered concentrations of ionic Al forms.

Key words: Nitrogen, sulfur, aluminum, organic carbon, phosphorus, atmospheric deposition.

Introduction

The first chemical analyses of Prášílské Lake (e.g. pH of 5.3–5.7, $\text{NO}_3\text{-N}$ of 0.08–0.24 mg l^{-1} , and SO_4^{2-} of 1.3–3.0 mg l^{-1}) come from the early 1960s (PROCHÁZKOVÁ & BLAŽKA, 1999). Their data on other Bohemian Forest lakes already suggested the impact of atmospheric acidification on lake water composition, predominantly lower pH values and increased NO_3^- and SO_4^{2-} concentrations compared to the 1930s (JÍROVEC & JÍROVCOVÁ 1937). Lake water acidification of Prášílské Lake progressed until 1986–1987, when pH was ~4.4 and $\text{NO}_3\text{-N}$ and SO_4^{2-} reached 0.52–0.67 and ~6.2 mg l^{-1} , respectively (VESELY 1996, VESELY & al. 1998a). A continuous decline in SO_4^{2-} concentrations has occurred since the second half of the 1980s, while NO_3^- concentrations have slightly increased in the 1990s (VESELY & al. 1998a). This phenomenon was untypical compared to other Bohemian Forest lakes, where both SO_4^{2-} and NO_3^- concentrations have declined due to the reduction in Central European S and N emissions (KOPÁČEK & al. 1998a). The increase in NO_3^- concentrations in Prášílské Lake has been associated

with elevated nitrate leaching from terrestrial sources due to forest reduction in its watershed (VESELY 1996).

FOTT & al. (1994) have reported on the survival of planktonic crustacea in Prášílské Lake even during the late 1980s when these zooplankton species became extinct in other Bohemian Forest lakes with comparable pH levels. Their survival in Prášílské Lake was explained by lower Al concentrations than in other Bohemian Forest lakes. Lower concentrations of Al in Prášílské Lake have resulted in lower levels of potentially toxic Al hydroxocomplexes and a high proportion of inorganic Al was complexed with F⁻ (KOPÁČEK & HEJZLAR 1998; VESELY & al. 1998b). The historically lower Al concentrations in Prášílské Lake are probably associated with low SO₄²⁻ concentrations (KOPÁČEK & HEJZLAR 1998).

The chemistry of Prášílské Lake has been intensively studied in the 1990s. VRBA & al. (1996) have reported on the nutrient and microbial status of Prášílské lake. SCHMIDT & al. (1993) and HRUŠKA & al. (1999) have provided palaeolimnological records of the Prášílské lake sediment. SCHMIDT & al. (1993) and KOPÁČEK & HEJZLAR (1998) have reported on the chemical and nutrient composition of the Prášílské tributaries. However, the published data are based on a limited number of samplings (usually ≤ 4 per year) and on the chemical composition of epilimnetic water. This paper provides a more detailed study on the depth and time variations in the chemistry of Prášílské Lake during the summer temperature stratification in 1998 in view of the following aspects: (1) composition of atmospheric deposition, (2) chemistry of all surface tributaries (terrestrial characteristics), and (3) biochemical in-lake processes.

Materials and methods

Description of study sites

Prášílské Lake (PR, German name – Stubenbachsee) is situated in the Bohemian Forest (13° 24' E, 49° 04' N) at an altitude of 1079 m a. s. l. The lake is of glacial origin. Its surface area is 3.7 ha, maximum depth is 15 m, volume is 274,000 m³, and watershed area is 52.4 ha. All morphological data come from ŠVAMBERA (1939). The lake is surrounded by steep slopes in the western part and by moderate slopes in the southern part of the watershed. A narrow moraine forms the northern and eastern parts of the watershed (Fig. 1). Most tributaries are situated along the western bank (tributary PR-I, PR-II, PR-III, and PR-IV), while tributary PR-V (the major surface water input) and PR-VI enter the lake from the south. The bedrock of the Prášílské watershed consists of granites in the northern part and of mica-schist in the southern part (VESELY 1994).

The forest surrounding Prášílské Lake was not intensively exploited in the Middle Ages and predominantly consisted of 200–300 year-old spruce in 1812; however, it was seriously damaged by gales in 1868 and 1870 (VESELY 1994). Since 1985, the approximately 150-year forest (predominantly Norway spruce) has been drastically reduced (from ~80% to < 30% of the watershed area) by gales and insects (VESELY 1996). A part of the damaged forest area has recovered in the southern part of the watershed along tributaries PR-V and PR-VI.

Sampling and analyses

Water samples from Prášílské Lake and its tributaries were taken 7 times (roughly monthly) from May 25, 1998 to October 12, 1998. Tributaries were sampled near their inlets to the lake and the water discharge was estimated by means of bucket and stop-watch. Samples were immediately filtered through a 40-µm polyamide sieve to remove coarse particles. Each sample was analyzed separately and the average element concentration in the total input to the lake by all tributaries was calculated as volume-weighted mean concentration.

Samples of lake water were taken at the deepest point of the lake (Fig. 1) from the following depths: 0.5 m, 4 m, 8 m, 10–12 m, the upper layer of the anoxic zone (12–14 m), and 0.5 above the bottom (~14.5 m). The samples were immediately filtered through a 200- μm polyamide sieve to remove zooplankton. Temperature and dissolved oxygen were measured with the DataSonde 4 (Hydrolab, USA) at 0.5 m intervals.

In the laboratory, samples were filtered with membrane filters (pore size of 0.45 μm) for determination of ions and with glass-fibre filters (pore size of 0.4 μm ; MN-5, Macherey Nagel, Germany) for the analyses of P, organic matter, and dissolved Al and Fe. The samples for pH, alkalinity (acid neutralizing capacity, ANC), and total P, Al, and Fe were not filtered. Dissolved and particulate organic carbon (DOC and POC) and total inorganic C (TIC) were analyzed with a LiquiTOC analyzer (Foss/Heracus, Germany). Absorbance at 254 nm (A_{254}), pH, ANC (Gran titration), dissolved reactive P (DRP, molybdate method, MURPHY & RILEY 1962), total P (TP) and dissolved P (DP) were analyzed within 24 hours after sampling. TP and DP were determined by perchloric acid digestion according to KOPÁČEK & HEJZLAR (1993), but larger amounts of sample were evaporated to obtain a detection limit of P $\sim 0.5 \mu\text{g l}^{-1}$. Particulate P (PP) was the difference between TP and DP. Molar absorptivities of dissolved organic matter at 254 nm ($A_{254}:\text{DOC}$, $\text{m}^2 \text{mol}^{-1}$) were calculated as ratios of A_{254} (absorption path of 1 m) to DOC concentrations (mol m^{-3}). Total and dissolved organic N (TON and DON) were determined by Kjeldahl digestion and distillation (PROCHÁZKOVÁ 1960) within one week after sampling. 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, USA) within a month. Fractionations of Al and Fe were obtained as follows: Total reactive Al and total Fe (TR-Al; T-Fe), dissolved reactive Al and dissolved Fe (DR-Al; D-Fe), and organically bound Al and Fe (Al_o ; Fe_o) were analyzed in non-filtered samples, filtered samples, and filtered and cation exchange treated samples, respectively. Concentration of Al in each fraction was determined with acid digestion of the sample according to DRISCOLL (1984) within two days after sampling. Concentration of Fe was analyzed by the thiocyanate colorimetric method after sample evaporation and digestion with perchloric acid (HEJZLAR & KOPÁČEK, 1998). Particulate Al (Al_{part}) was the difference between TR-Al and DR-Al concentrations. Ionic forms of Al and Fe (Al_i ; Fe_i) were the differences between DR-Al and Al_o , and D-Fe and Fe_o concentrations, respectively. Equivalent concentrations of Al_i and Fe_i ($\mu\text{eq l}^{-1}$) were calculated by multiplying the molar Al_i and Fe_i concentrations ($\mu\text{mol l}^{-1}$) by average charges of Al hydroxocomplexes (n) and 2, respectively. The n value was estimated from the theoretical distribution of ionization fractions of aqueous Al (KOPÁČEK & HEJZLAR 1998). Concentrations of organic acid anions (R^- ; $\mu\text{eq l}^{-1}$) were estimated according to the OLIVER & al. (1983) model as described by KOPÁČEK & HEJZLAR (1998).

Atmospheric deposition was not measured directly in the PR watershed, but we operated 5 sampling sites in other parts of the Bohemian Forest from November 4, 1997 to November 4, 1998. Two sites were situated at Plešné Lake: (1) in an open rocky area without trees at 1090 m a.s.l., and (2) in the forest at 1130 m a.s.l. Three sites were situated at Čertovo Lake: (1) in an open area without trees at 1175 m a.s.l., (2) and (3) in the forest at 1045 and 1330 m a.s.l., respectively. The open area (precipitation) and forest area (throughfall) sites were equipped with 2 and 9 samplers, respectively. All samples from each site were combined to obtain one integrated sample for the site. Rain was sampled in two-week intervals and snow was sampled in two- to four-week intervals depending on the precipitation amount. Analytical methods used for the atmospheric deposition analyses were the same as for the lake water.

Results and discussion

General

Volume weighted mean (VWM) concentrations of atmospheric deposition are given in Table 1. Atmospheric deposition in the open area and in throughfall represent averages of two and three, respectively, sites operated in the watersheds of Plešné and Čertovo Lakes. The average atmospheric deposition given for the Prášílské watershed was obtained from the above values with respect to the present forest cover. In the calculation we assumed that (1) 70 % of the Prášílské watershed has been deforested (VESELY 1996) and received atmospheric deposition close to that obtained in the open areas and (2) 30 % of atmospheric deposition was through-fall. Concentrations of the individual constituents in the atmospheric deposition at Plešné and Čertovo Lakes mostly differed by less than 20 %. As the Prášílské watershed is situated between the above sites and at comparable elevation, we assume that the calculated average atmospheric deposition into this area represents a realistic estimation.

The amount of atmospheric deposition and Cl⁻ concentrations in the atmospheric deposition and lake were used to calculate the water balance of the Prášílské watershed-lake ecosystem (assuming chloride to be a conservative ion). The estimated annual averages were as follows: precipitation, 1350 mm; evapotranspiration, ~400 mm (~30 % of atmospheric deposition); and water outflow, ~950 mm. The last value represents an annual outflow of ~5.3 10⁵ m³ and the average water residence time in the Prášílské Lake of ~0.5 year in the 1997–1998 hydrological year.

Water discharge in the individual tributaries varied from < 0.1 to ~30 l s⁻¹. During our study, tributaries PR-I, PR-III, and PR-V were perennial, while tributaries PR-II and PR-IV were without water once and four times, respectively, and tributary PR-VI had water (~1.0 l s⁻¹) only in October. The PR-V was the major tributary, representing 75–93 % of the total surface water input to Prášílské Lake.

Tributaries and atmospheric deposition

The average chemical composition of the individual tributaries and total surface water input to the lake are given in Table 1. All tributaries were strongly acidic, with a depleted carbonate buffering system, and pH values ranging from 3.75 to 4.87. On an equivalence basis, base cations (sum of Ca²⁺, Mg²⁺, Na⁺, and K⁺) dominated the cation pool with average contributions of 39–90 % in the individual tributaries. Contributions of H⁺ and Al³⁺ ions were quantitatively less important than the sum of base cations, comprising 6–42 % and 3–17 %, respectively. In the anion pool, SO₄²⁻ was most prominent (17–41 %), whereas NO₃⁻ and R⁻ contributed between 1–69 % and 3–53 %, respectively. The contribution of Cl⁻ ions ranged from 9 to 14 %. The VWM relative composition of the total surface water input to Prášílské Lake was as follows: (1) Cations: Na⁺, 29 %; Ca²⁺, 23 %; Mg²⁺, 23 %; H⁺, 16 %; Al³⁺, 4 %; K⁺, 3 %; and Fe³⁺, 2 %. (2) Anions: SO₄²⁻, 39 %; NO₃⁻, 25 %; R⁻, 21 %; Cl⁻, 14 %; and F⁻, 1 %.

Chemical composition of tributaries substantially differed from the average atmospheric deposition. Concentrations of Ca²⁺, Mg²⁺, and Na⁺ were two to six times higher, while the K⁺ concentration was on average ~4 times lower in tributaries than in atmospheric deposition. Compared to the average atmospheric deposition, pH was lower in tributaries PR-III, PR-IV, and PR-VI. PR-IV was the most acidic of all tributaries and had the highest concentrations of SO₄²⁻, Al³⁺, and elevated DOC and DP. In contrast, tributary PR-I was the least acidic (pH between 4.8–4.9), with the lowest SO₄²⁻ concentrations (1.6–2.1 mg l⁻¹) but the highest concentrations of base cations and NO₃⁻ (1.9–2.4 mg l⁻¹ NO₃-N). These NO₃-N concentrations were ~3 times higher than the concentration of total inorganic nitrogen (TIN = NO₃-N + NH₄-N) in

atmospheric deposition (Table 1). The elevated concentrations of $\text{NO}_3\text{-N}$ in tributaries PR-I, PR-II, PR-III, and PR-IV, compared to TIN in atmospheric deposition, probably occurred due to lower bioconsumption of N and higher mineralization of soil organic matter (VITOUSEK & al. 1979) reflecting the recent forest damage in their sub-watersheds. Substantially lower $\text{NO}_3\text{-N}$ concentrations ($0.02\text{--}0.56 \text{ mg l}^{-1}$) than in atmospheric deposition were observed in tributaries PR-V and PR-VI, which drain areas with young, rapidly growing forest.

The average atmospheric input of SO_4^{2-} to the Prášílské watershed was substantially lower than to the nearly completely forested watersheds of other Bohemian Forest lakes. The reason behind this was lower dry and horizontal deposition of S compounds due to the smaller specific adsorption surface of the deforested area. Dry and horizontal deposition represented $\sim 50\%$ of total S deposition in the Bohemian Forest during our study; compare SO_4^{2-} concentrations in throughfall and in precipitation in open area (Table 1). Concentrations of SO_4^{2-} in Prášílské tributaries (2.5 mg l^{-1}) were only slightly elevated compared to the average sulfate concentration in atmospheric deposition (1.8 mg l^{-1}). If we assume a 30% increase in SO_4^{2-} concentration in atmospheric deposition due to the 30% evapotranspiration, the theoretical average SO_4^{2-} concentration in the tributaries would be 2.4 mg l^{-1} . The comparability of the theoretical and observed SO_4^{2-} concentrations in tributaries suggests that the sorption and desorption of SO_4^{2-} in soils of Prášílské watershed were closer to an equilibrium than in the watersheds of the Plešné and Čertovo Lakes. Concentrations of SO_4^{2-} in tributaries of Plešné and Čertovo Lakes were ~ 2 times higher than in throughfall, suggesting pronounced sulfate desorption from soils (KOPÁČEK & al. in press and unpubl. data).

Generally, we may assume that precipitation in open areas is roughly equivalent to direct atmospheric input to lakes (KOPÁČEK & al. 1998b). From this point of view, atmospheric deposition was an important source of P for Prášílské lake ($\sim 0.9 \text{ kg y}^{-1}$), being $\sim 30\%$ of the terrestrial P load ($\sim 2.7 \text{ kg y}^{-1}$). The terrestrial P input was estimated from the average VWM concentration of DP in tributaries (Table 1) and the annual water outflow. The total annual P input of 3.6 kg represented a specific load of 0.1 g of P per m^2 of the lake per year.

Tributaries PR-III, PR-IV, PR-V, and PR-VI had substantially higher DOC concentrations ($6\text{--}16 \text{ mg l}^{-1}$) and concentrations of organic acids anions ($26\text{--}72 \text{ } \mu\text{eq l}^{-1}$) than other tributaries and atmospheric deposition (Table 1), suggesting an important contribution of soil-derived dissolved organic matter to their acidity. Molar absorptivities of DOC were also higher there ($47\text{--}50 \text{ m}^2 \text{ mol}^{-1}$) than in tributaries PR-I and PR-II ($36\text{--}37 \text{ m}^2 \text{ mol}^{-1}$). Molar absorptivities were measured at the original pHs. The real values of molar absorptivity (at $\text{pH} = 7$) would be higher because absorptivity of organic matter increases with pH. Consequently, the molar absorptivities of samples with the highest DOC concentrations (e.g., tributaries PR-IV and PR-VI) are probably most underestimated (compared to the $\text{pH} = 7$ level) due to their lowest pH values (Table 1). Thus, the high values of molar absorptivity in the Prášílské Lake tributaries with higher DOC concentrations imply that a relative proportion of unsaturated carbon bonds in the total pool of dissolved organic matter increases with increasing DOC concentrations. This might be a result of the more frequent occurrence of more acidic organic and peaty soils in the drainage areas of these tributaries.

Compared to atmospheric deposition, Al concentrations were elevated in all tributaries. However, all but the most acidic tributary PR-IV had concentrations of DR-Al lower than the tributaries of other Bohemian Forest lakes (KOPÁČEK & HEJZLAR 1998). The VWM concentrations of DR-Al in the total surface input of Prášílské Lake varied from 114 to 326 mg l^{-1} with $\sim 60\%$ contribution of Al_0 .

Relationships among the chemical constituents in the individual Prášílské tributaries followed several general patterns (Fig. 2). Concentrations of H^+ were closely correlated to SO_4^{2-} ($r=0.81$, $P<0.001$) and DOC ($r=0.74$, $P<0.001$) concentrations suggesting that both atmospher-

ic acidification and organic acids contributed to the acidity of Prášílské tributaries (Fig. 2A). In contrast, H^+ was not correlated to NO_3^- ($r=0.12$, $P>0.1$). Concentrations of Al_i and Fe_i were tightly associated with SO_4^{2-} ($P<0.001$; Fig. 2B), partly associated with R^- ($r=0.31$, $P<0.05$), but not with NO_3^- ($r=0.14$, $P>0.1$). Base cations were positively correlated with nitrate ($P<0.001$; Fig. 2C) while their correlation to SO_4^{2-} and R^- was negative ($r=0.44$, $P<0.01$ and $r=0.78$, $P<0.001$, respectively). A tight negative correlation was found between R^- and NO_3^- ($r=0.66$, $P<0.001$). This pattern has been discussed in KOPÁČEK & HEJZLAR (1998). Dissolved organic matter in tributaries was an important source of organically bound Al and Fe (Fig. 2D), dissolved phosphorus (Fig. 2E) and organic nitrogen (Fig. 2F).

Lake water

The average chemical composition of the epilimnetic water differed from the VWM composition of tributaries in lower concentrations of NO_3^- (by ~15 %), DOC (by 38 %), Al_o (by 47 %), Fe_o (by ~70 %) and in higher pH and ACN values (Table 1). The decrease in Al_o and Fe_o concentrations was probably associated with photochemical decomposition of allochthonous organic matter; this process together with coprecipitation with metals also participated in the DOC decrease (HEJZLAR & KOPÁČEK, unpubl. data).

Substantial differences occurred between the chemistry of epilimnetic and hypolimnetic waters during the summer temperature stratification (Table 1). The elevated pH and concentrations of ANC, K^+ , NH_4^+ , DOC, Al_{part} , TP, and Fe and lowered concentrations of NO_3^- and Al_i were the most pronounced changes above the lake bottom. Biochemical in-lake processes can explain all of the above mentioned changes.

In-lake processes

Depth and time variations of the physical and chemical parameters of the lake water are shown in Fig. 3. The summer stratification of Prášílské Lake was well developed during the study from May to October (autumn overturn occurred on November 3, 1998). The thermocline depth was 3–5 m. Epilimnetic concentrations of dissolved oxygen (DO) were 8–10 $mg\ l^{-1}$, while hypolimnetic DO concentrations continuously decreased and were depleted to values $< 1\ mg\ l^{-1}$ in the bottom layer (1 m above the sediment) from July to the autumn overturn.

The bulk of dissimilatory 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^- decreased due to denitrification above the bottom. In contrast, concentrations of NH_4^+ and Fe forms increased by their release from the sedimenting matter and sediments, respectively (Fig. 3). Redox conditions above the sediment were not low enough for SO_4^{2-} to be reduced. This fact was surprising with respect to our previous studies on Prášílské Lake in the first half of the 1990s, when we usually observed decreased SO_4^{2-} concentrations and the presence of H_2S in the hypolimnion during summer temperature stratification (e.g., VRBA & al. 1996).

Denitrification and reduction of Fe oxyhydroxides are the H^+ consuming processes and lead to alkalinity production (e.g. SCHINDLER 1986 and 1988, PSENNER & CATALAN 1994). Consequently, the negative ANC values in the water column increased above zero in the bottom layer of Prášílské Lake (Fig. 3). The other in-lake alkalinity generating processes, such as the release of base cations from the sediment (PSENNER 1988) contributed only slightly to the ANC increase in the Prášílské Lake. Concentrations of base cations were mostly stable and comparable in the surface and bottom layers throughout the summer (for average values see Table 1). The only exception was the hypolimnetic concentration of K^+ , which was ~50% elevated compared to the epilimnetic values.

The reduction and dissolution of ferric oxyhydroxides in sediments is commonly associat-

ed with the liberation and release of iron-bound inorganic P to the water column (e.g., WETZEL 1983, COOKE & al. 1993). Dissimilation of sedimenting matter is another source of the hypolimnetic P (e.g., PSENNER 1988). However, the DP and DRP concentrations were ~ 3 and $< 1 \mu\text{g l}^{-1}$, respectively, in the whole water column within the study (see epilimnetic and hypolimnetic P concentrations in Table 1). In contrast to DP and DRP, the TP concentrations were elevated above the bottom (Fig. 3), showing that all the increase in TP concentrations was associated with particles $> 0.4 \mu\text{m}$. This phenomenon has been explained by pH-derived changes in the water chemistry of acidified lakes during their temperature stratification (KOPÁČEK & al. in press). The processes involved can be explained as follows:

Denitrification and reduction of Fe oxyhydroxides increased the hypolimnetic pH values (Fig. 4). Such an increase is a typical pattern in lakes with a depleted carbonate buffering system in contrast to non-acidified productive lakes, where the pH above bottom decreases due to CO_2 release from sedimenting organic matter and sediments during the temperature stratification (e.g. WETZEL 1983). The increase in pH induced changes in Al speciation. While the depth variation of TR-Al concentration was usually low, the Al_i and Al_{part} concentrations varied both in depth and time (Fig. 4).

The temporal and spatial pattern of the in-lake Al_{part} formation is given in Fig. 4. The mineral saturation index (SI) indicates conditions when the formation of Al_{part} in the form of mineral phases of microcrystalline gibbsite ($\text{Al}(\text{OH})_3$) was favored thermodynamically. 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 microcrystalline gibbsite ($\text{p}K_{\text{SO}} = 9.35$). An SI value > 0 suggests oversaturation with respect to the solubility of the mineral phase, $SI = 0$ indicates equilibrium, and $SI < 0$ represents undersaturation. The area of positive SI values corresponded with the elevated Al_{part} concentrations and lowered Al_i values in the water column of Prášílské Lake. Under the conditions of oversaturation with respect to the solubility of microcrystalline gibbsite, the pH increase shifts the equilibrium concentrations of Al_i toward Al_{part} forms (Al oxyhydroxides). The colloidal Al oxyhydroxides strongly adsorb orthophosphate (e.g. LIJKLEMA 1980, DRISCOLL 1985). The phosphate liberated from the sedimenting organic matter and sediments by dissimilatory processes is removed from the liquid phase by adsorption onto the particulate Al oxyhydroxides. This process explains the elevated hypolimnetic TP concentrations but undetectable DRP even under anoxic conditions.

The proportion of P sources (i.e. sedimenting matter and sediment) in the hypolimnetic pool of TP in Prášílské Lake was roughly equal. This estimation was based on the analysis of changes in C:N:P ratios of allochthonous and autochthonous organic matter as follows: The average molar POC:PP and PON:PP ratios in the epilimnetic particulate matter of Prášílské Lake were 715 ± 220 and 56 ± 42 , respectively (Table 2). These values are substantially higher than C:N:P ratios of marine plankton (106:16:1, REDFIELD 1958), which have been inferred to be indicative of nutrient-sufficient status of plankton, but they are also ~ 2 times higher than the particulate C:P and N:P ratios of temperate lakes with severely P limited growth of plankton (HECKY & al. 1993). Thus, the high epilimnetic ratios of POC:PP and PON:PP suggest another source of particulate organic matter in the Prášílské Lake seston. While the composition of airborne particulates in atmospheric deposition was close to the Redfield ratio (Table 2), the allochthonous dissolved organic matter entering Prášílské Lake via tributaries had substantially higher C:N:P ratios. The average molar ratios of DOC to DON, DOC to DOP (dissolved organic P, $\text{DOP} = \text{DP} - \text{DRP}$), and DON to DOP in tributaries were 33, ~ 3800 and 117, respectively (Table 2). Consequently, a possible explanation of the high C:P and N:P ratios of sedimenting matter in Prášílské Lake is that a part of dissolved allochthonous organic matter was coagulated and precipitated by Al in the water column.

The molar C:P and N:P ratios of the uppermost sediment layer (367 and 28, respectively) were ~2 times lower than in the epilimnetic particulate matter, indicating a change in its composition during sedimentation. This relative P-enrichment of sedimenting matter can be explained by dissimilatory processes, which liberate CO_2 , NH_4^+ , and phosphate from the sedimenting seston in the hypolimnion (e.g., PSENNER 1988). However, while the liberated CO_2 and NH_4^+ remained dissolved in the water, phosphate was adsorbed on Al oxyhydroxide floc and was recovered to particulate form. If the increase in hypolimnetic TP concentration had been associated only with the dissimilation of sedimenting matter, it should have been equal to the increase in CO_2 and NH_4^+ concentrations. In a strongly acidic lake with depleted carbonate buffering system, TIC is approximately equal to the concentration of CO_2 . In this case the hypolimnetic TIC: NH_4^+ ratio represents the ratio between CO_2 and NH_4^+ liberated from sedimenting matter. The average molar ratio TIC: NH_4^+ (15 ± 5) above the bottom of Prášilské Lake was comparable to the average POC:PON molar ratio of the epilimnetic particulate matter (15 ± 9). In contrast, the hypolimnetic TIC:TP and NH_4^+ :TP ratios were ~40% lower than the sestonic POC:PP and PON:PP ratios (Table 2). This pattern suggests that the TP concentrations above the bottom originated both from the sedimenting organic matter and sediment.

The Al hydroxides settle from the water column and increase the P sorption capacity of the sediment (COOKE & al. 1993). The elevated content of fresh Al oxyhydroxides in the surface sediment reduces P release to the water column after phosphate liberation from ferric oxyhydroxides during anoxia, since P-Al complexes are not sensitive to redox changes (COOKE & al. 1993). Such a mechanism also prevents P liberation from sediment in Plešné Lake (KOPÁČEK & al., in press). However, the molar Al:Fe ratio of the Plešné sediment is ~11, while it is only 5 and 3 in the uppermost (0–1 cm) and lower layers, respectively, of the Prášilské sediment (KOPÁČEK, unpubl. data). Lower input of Al from terrestrial sources of Prášilské Lake thus resulted in lower sedimentation rate of Al oxyhydroxides and in less effective immobilization of P in the sediment compared to Plešné Lake. We conclude, that sediment of Prášilské Lake could be a limited source of P under the hypolimnetic anoxia. However, the liberated P was adsorbed by Al oxyhydroxides, which were formed above the bottom at elevated pH, and settled back to the sediment.

Conclusion

All tributaries of Prášilské Lake were strongly acidic (pH from 3.75 to 4.87) during the summer temperature stratification in 1998. On the equivalence basis, base cations dominated the cation pool (78 %) and SO_4^{2-} the anion pool (39 %) of the total surface input to the lake. The average SO_4^{2-} concentration in tributaries (2.5 mg l^{-1}) was comparable to atmospheric deposition, suggesting no pronounced release or adsorption of SO_4^{2-} in soils. Concentrations of Al_i were tightly ($P < 0.001$) associated with SO_4^{2-} and were lower than in the tributaries of other Bohemian Forest lakes (KOPÁČEK & HEJZLAR, 1998). The average proportion of organic acid anions in the anion pool was 21 %, suggesting that both strong acid and organic acid anions contributed in an important way to the acidity of the Prášilské Lake tributaries. The average proportion of NO_3^- in the anion pool was 25 %. The elevated concentrations of NO_3^- in tributaries PR-I, PR-II, PR-III, and PR-IV (up to $2.4 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$) resulted from the forest damage in their sub-watersheds. However, the $\text{NO}_3\text{-N}$ concentrations varied between 0.02 and 0.56 mg l^{-1} even in tributaries PR-V and PR-VI, which drained areas with young recovering forest, indicating some signs of N-saturation (STODDARD 1994) of their sub-watershed. The terrestrial losses of base cations were positively correlated ($P < 0.001$) with the elevated nitrate leaching and were not associated with SO_4^{2-} and R⁺ leaching.

In-lake biochemical processes influenced lake water chemistry as follows: pH, ANC, K^+ ,

NH_4^+ , DOC, Al_{part} , TP, and Fe were elevated, while NO_3^- and Al_i were lowered in comparison with tributaries and atmospheric deposition. Dissimilatory processes liberated CO_2 , NH_4^+ , and phosphate from the sedimenting seston, which increased their concentrations in the water above sediment. Biological removal of nitrate and reduction of ferric oxyhydroxides resulted in alkalinity generation and the increase in pH values in the hypolimnion. Under these conditions of increased pH, Al_i species hydrolyzed and formed particulate Al hydroxides, which adsorbed orthophosphate. Phosphate liberated from the sedimenting organic matter and sediments by dissimilatory processes was removed from the liquid phase by adsorption onto the colloidal Al oxyhydroxides. The settling of Al oxyhydroxide floc to the sediment further limited the release of inorganic P from the sediment to the water column at low redox potentials. Thus, the pH-derived changes in the distribution of Al fractions reduced the return of dissolved P from the hypolimnion into the productive zone. Changes in the distribution of Al fractions probably also reduced potential toxicity of Al_i to zooplankton, converting it to Al_{part} .

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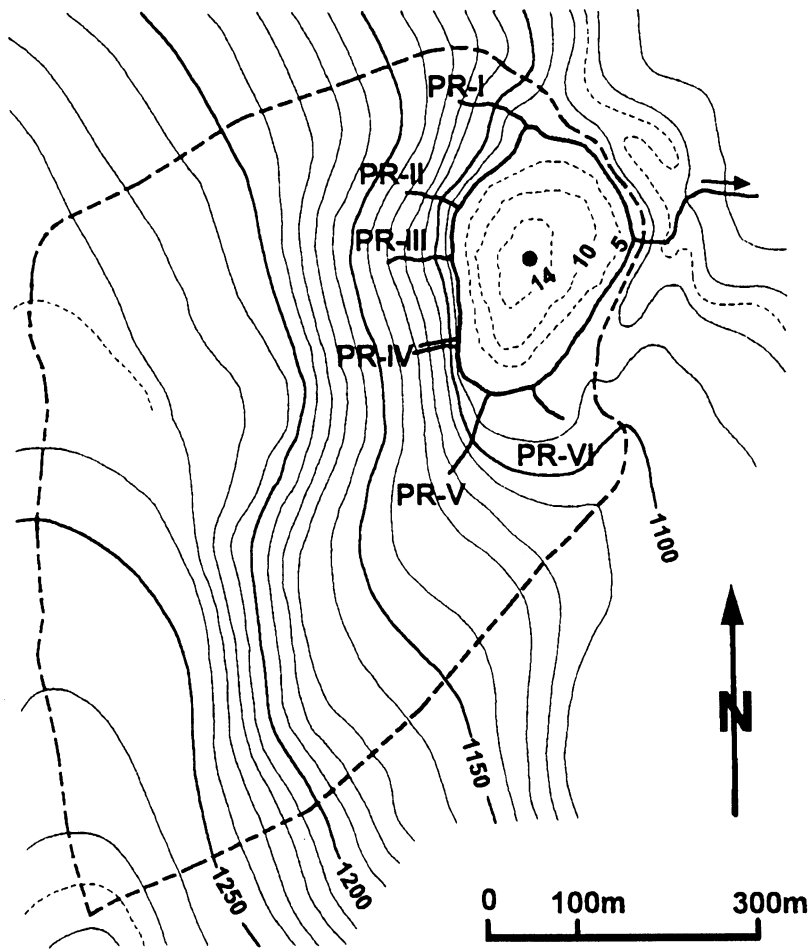


Fig. 1. – Map of the Prášílské Lake watershed (solid dashed line) with the location of sampling site (full circle at the maximum depth in the bathymetric map of the lake), tributaries (PR-I, PR-II, PR-III, PR-IV, PR-V, and PR-VI), and outflow.

Table 1. – Average atmospheric deposition at Plešné and Čertovo lakes (OA, open area; TF, throughfall) and calculated average deposition at Prášilské watershed (PR); average composition of the individual surface tributaries and volume weighted mean (VWM) composition of the total surface water input into Prášilské Lake; and the average (avg.), minimum (min.), and maximum (max.) concentrations of elements in the epilimnetic (0.5 m below surface) and hypolimnetic (0.5 m above bottom) waters of Prášilské Lake. Notes: *PR-VI was sampled only in October, ND means not determined.

	Atmospheric depos.				Individual tributaries						Total surface input			Epilimnion			Hypolimnion		
	OA	TF	PR	PR	PR-I	PR-II	PR-III	PR-IV	PR-V	PR-VI*	avg.	min.	max.	avg.	min.	max.	avg.	min.	max.
pH	4.77	4.40	4.64	4.64	4.87	4.68	4.39	3.95	4.74	4.34	4.69	4.36	4.89	4.90	4.68	4.98	5.33	5.05	5.63
ANC	-9	-32	-15	-13	-13	-22	-45	-65	-21	-52	-23	-47	-9	-12	-20	-7	27	0	66
Ca ²⁺	0.18	0.69	0.31	1.47	1.29	0.73	0.59	0.53	0.63	0.63	0.59	0.49	0.72	0.65	0.56	0.81	0.51	0.42	0.62
Mg ²⁺	0.04	0.14	0.06	0.61	0.54	0.37	0.30	0.35	0.31	0.36	0.36	0.32	0.40	0.36	0.29	0.43	0.40	0.37	0.42
Na ⁺	0.22	0.38	0.26	1.41	1.09	0.85	0.60	0.85	0.44	0.87	0.73	0.96	0.76	0.71	0.81	0.75	0.73	0.73	0.79
K ⁺	0.32	1.41	0.61	0.54	0.48	0.31	0.89	0.12	0.11	0.16	0.06	0.36	0.37	0.27	0.45	0.61	0.46	0.46	0.87
NH ₄ -N	451	508	466	11	8	8	14	2	0	3	0	18	20	10	36	377	238	483	483
NO ₃ -N	342	652	424	2134	1502	847	1519	341	17	469	360	630	397	309	548	142	10	329	329
SO ₄ ²⁻	1.33	3.15	1.81	1.78	3.03	2.78	4.42	2.48	2.35	2.50	1.87	3.16	2.66	2.11	3.00	3.06	3.00	3.13	3.13
Cl ⁻	0.36	0.68	0.45	0.86	0.72	0.65	0.69	0.63	0.45	0.64	0.50	0.75	0.63	0.54	0.71	0.70	0.65	0.74	0.74
F ⁻	0.01	0.02	0.01	0.03	0.03	0.03	0.03	0.02	0.03	0.03	0.01	0.04	0.03	0.02	0.04	0.04	0.03	0.03	0.04
DOC	1.32	9.96	3.62	1.14	2.85	6.38	11.9	6.38	15.9	6.21	3.45	10.0	3.88	2.88	5.51	4.26	3.53	6.26	6.26
A ₃₅₄ /DOC	24	20	22	36	37	49	50	49	47	48	49	43	45	51	49	45	49	45	54
TON	318	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	318	255	390	ND	ND	ND
DON	209	467	278	74	175	272	493	220	347	221	179	303	254	190	305	217	60	362	362
TP	16.8	25.1	19	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	6.4	3.9	9.0	27.9	12.1	58.3
DP	6.1	9.9	7.1	1.7	2.3	3.5	7.2	5.3	12.3	5.1	3.0	6.1	2.9	1.8	4.2	2.9	2.1	3.6	3.6
DRP	3.7	5.4	4.2	0.4	0.5	0.6	1.5	0.9	3.0	0.9	0.0	2.3	0.2	0.0	0.6	0.5	0.0	2.0	2.0
DR-Si	ND	ND	ND	3.1	2.4	1.9	2.2	2.1	1.9	2.1	1.9	2.3	1.5	1.5	1.7	2.0	1.7	2.1	2.1
TR-Al	5	11	7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	193	168	249	371	234	526
DR-Al	ND	ND	ND	160	260	351	749	174	500	194	114	326	145	94	242	153	92	229	229
Al ₀	ND	ND	ND	30	85	191	320	126	386	129	67	191	68	44	119	100	60	190	190
T-Fe	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	87	54	141	1299	346	2433
D-Fe	ND	ND	ND	11	12	101	250	205	476	189	124	236	52	25	117	510	86	1492	1492
Fe ₀	ND	ND	ND	7	11	56	179	130	434	118	23	180	36	6	128	153	83	283	283
R	µeq l ⁻¹	ND	ND	ND	6	13	26	42	31	72	29	15	54	21	17	27	22	15	29
Al ₁	µeq l ⁻¹	ND	ND	ND	7.2	12.3	14.4	45.2	3.4	10.5	4.8	1.8	12.4	4.3	2.2	8.5	1.8	0.9	4.0
Fe ₁	µeq l ⁻¹	ND	ND	ND	0.1	0.1	1.6	2.5	2.7	1.5	2.5	1.6	6.4	0.6	0.0	1.3	14.2	0.0	43.2

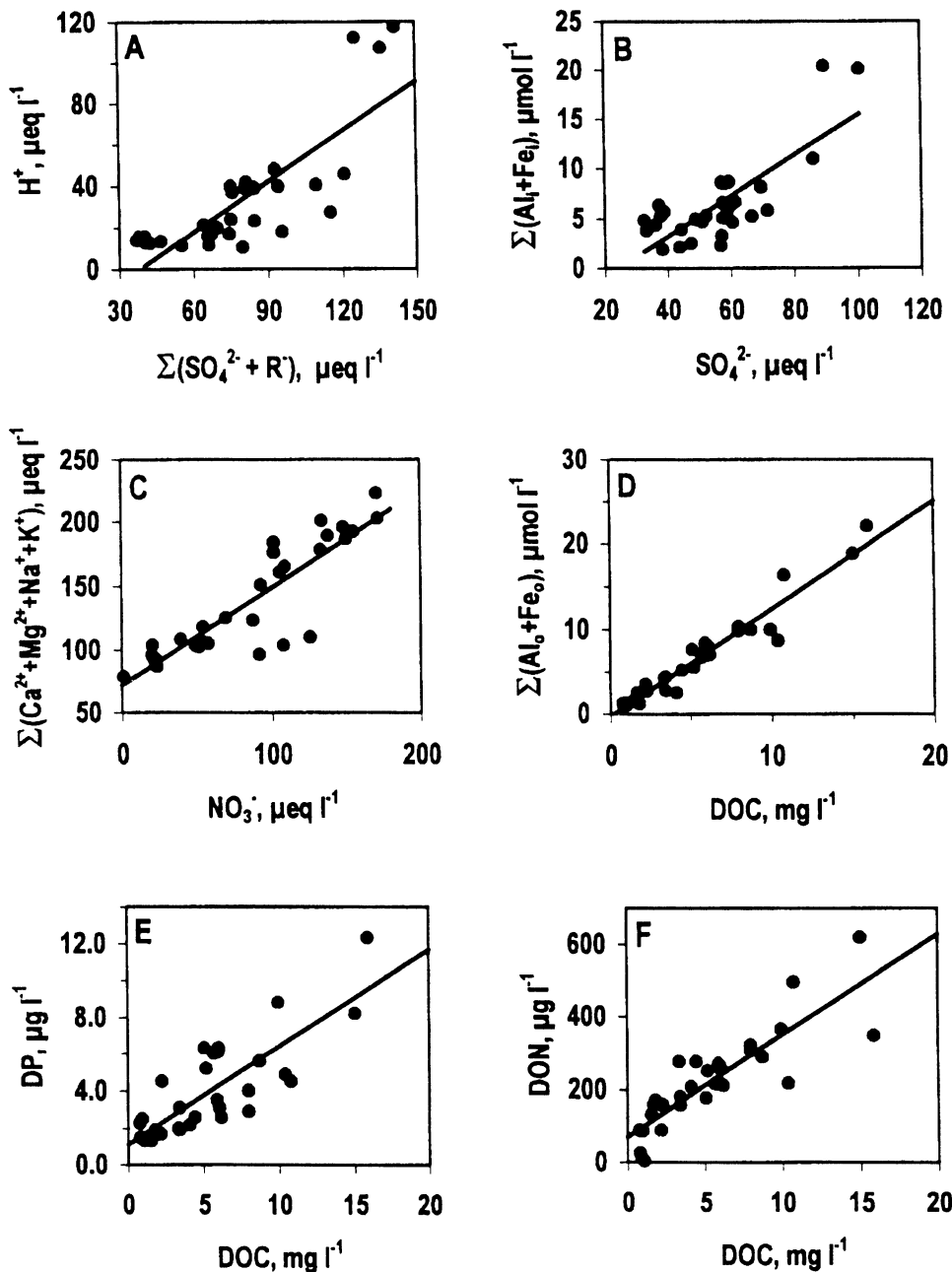


Fig. 2. – Relationships in the water composition of surface tributaries into Prášílské Lake (May-October, 1998). Solid lines represent linear regressions between individual chemical constituents: A, $y = -31 + 0.81x$ ($r = 0.81$); B, $y = -5 + 0.20x$ ($r = 0.78$); C, $y = 71 + 0.77x$ ($r = 0.89$); D, $y = -0.3 + 1.3x$ ($r = 0.97$); E, $y = 1.1 + 0.53x$ ($r = 0.82$); F, $y = 71 + 28x$ ($r = 0.86$). In all regressions $P < 0.001$.

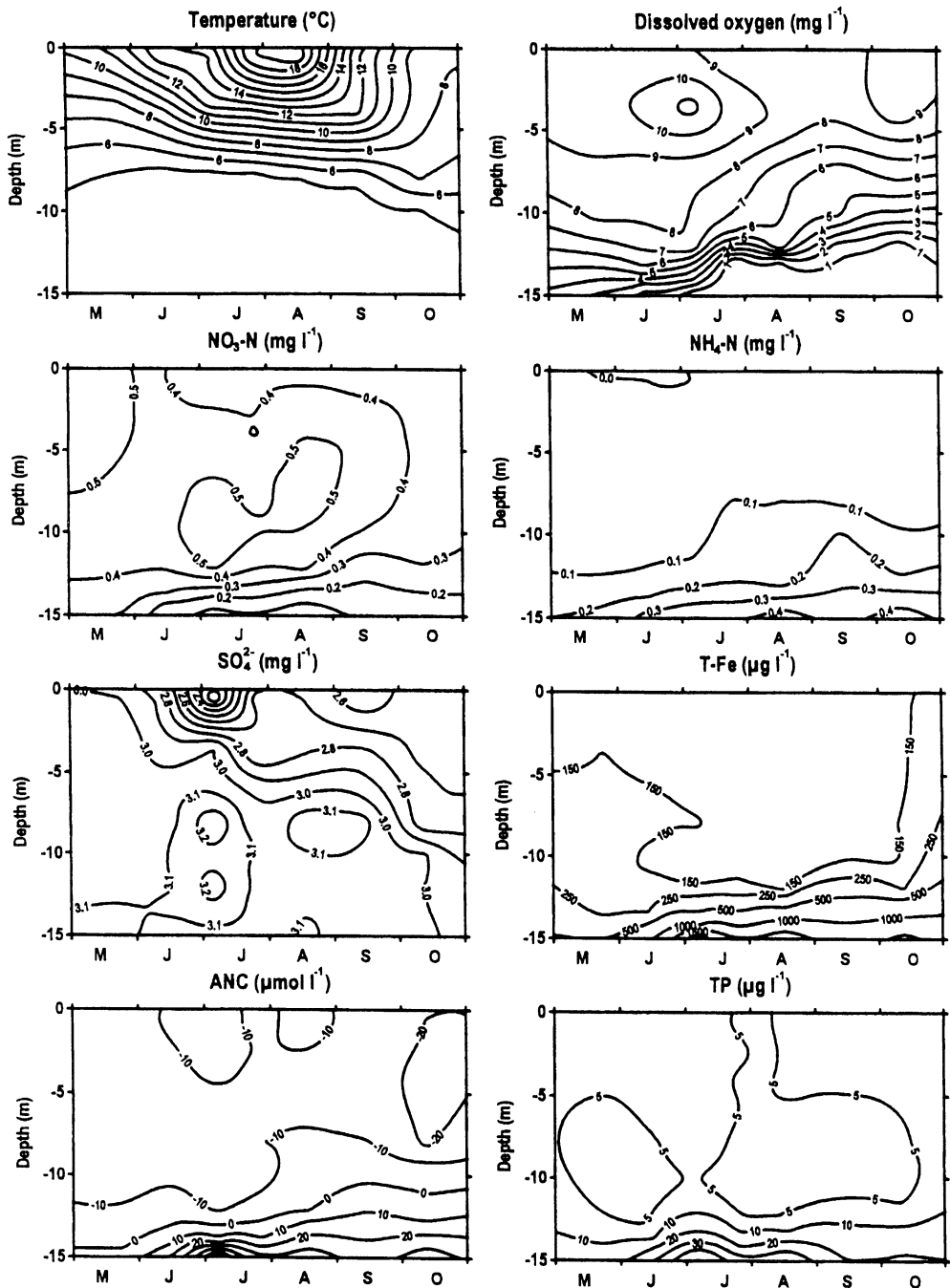


Fig. 3. – Depth-time diagrams of temperature and concentrations of dissolved oxygen, NO_3^- , NH_4^+ , SO_4^{2-} , T-Fe, ANC, and TP in Prášilské Lake during the summer temperature stratification in 1998.

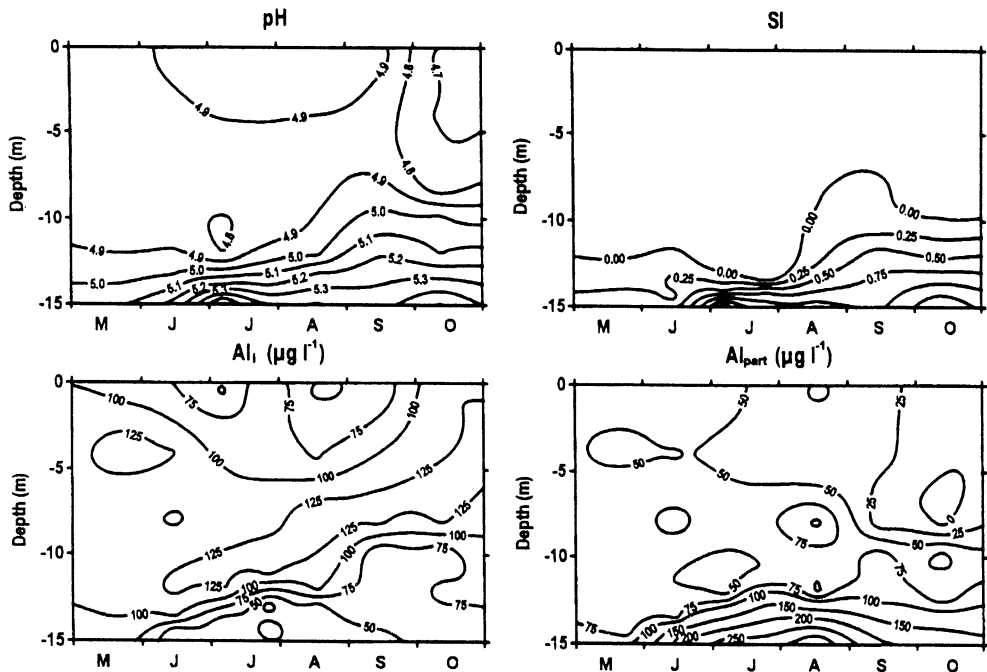


Fig. 4. – Depth-time diagrams of pH, concentrations of Al_i and Al_{part} , and saturation index (SI) in Prášílské Lake during the summer temperature stratification in 1998. SI was estimated according to DRISCOLL (1985) for Al_i concentrations with respect to the solubility of microcrystalline gibbsite ($pK_{s0}=9.35$).

Table 2. – Comparison of C:N:P molar ratios in dissolved and particulate organic matter and sediments of the Prášílské Lake and its inputs compared to the average composition of marine plankton (REDFIELD 1958) and particulate matter of lakes (HECKY & al. 1993).

Substance	Note	C:N	C:P	N:P
Marine plankton	REDFIELD (1958)	7	106	16
Particulate matter of lakes	HECKY & al. (1993)	13	306	24
Allochthonous input via atmospheric deposition	Average atmosph. deposition in the open area at Plešné and Čertovo Lakes	POC:PON	POC:PP	PON:PP
		9	195	23
		DOC:DON	DOC:DOP	DON:DOP
Allochthonous input via surface tributaries into Prášílské Lake	Average for year 1997 ¹⁾ 1998	7	1435	195
		DOC:DON	DOC:DOP	DON:DOP
		38	4400	120
Particulate organic matter in the epilimnion of Prášílské Lake	Average for year 1998	33	3820	117
		POC:PON	POC:PP	PON:PP
Prášílské Lake hypolimnion (0.5 m above sediment)	Average for year 1998	15±9	715±220	56±42
		TIC:NH ₄ ⁺	TIC:TP	NH ₄ ⁺ :TP
Sediment ²⁾ of Prášílské Lake	Layer (cm) 0-1	15±5	430±200	31±10
		C:N	C:P	N:P
		13	367	28

¹⁾ KOPÁČEK & HEJZLAR (1998)

²⁾ Sediment was sampled on 8. October 1996 in the deepest part of the lake and analyzed as described by (KOPÁČEK & al., in press).