

Mass balance of nutrients and major solutes in the Plešné watershed-lake ecosystem in the 2001 hydrological year

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Abstract

Fluxes of major ions and nutrients were evaluated in Plešné Lake and its watershed in the 2001 hydrological year. The mass balance of nutrients was based on allochthonous fluxes (terrestrial export via tributaries and atmospheric deposition), sedimentation, and output. Major results of the study are as follows. (1) The net terrestrial H^+ production (15 keq.yr^{-1}) resulted predominantly from net SO_4^{2-} and NO_3^- release from soils, and NH_4^+ assimilation. The net in-lake H^+ consumption (22 keq.yr^{-1}) was mostly associated with reduction in NO_3^- (55%), organic acid anions concentrations (24%), and SO_4^{2-} (13%). (2) Hydrolysis of ionic Al (Al_i) was the dominant in-lake source of H^+ . The external input of Al_i (348 kg.yr^{-1}) was increased by 113 kg.yr^{-1} in the lake due to photochemical liberation of Al_i from organically bound Al. Of the total Al_i pool, 49% was completely hydrolyzed and produced particulate Al. (3) The external inputs of total organic C, total N, total P, and dissolved Si were 6520, 908, 19.9, and 3158 kg.yr^{-1} (87, 12, 0.27, and $42 \text{ g.m}^{-2}.\text{yr}^{-1}$), and their net in-lake removals were 10%, 24%, 54%, and 28%, respectively. Sedimentation fluxes of C, N, and P from the epilimnion were 1990, 211, and 8.9 kg.yr^{-1} , and their average accumulations in the sediments were 1585, 151, and 13.4 kg.yr^{-1} , respectively. (4) NO_3^- -N (total input of 602 kg.yr^{-1}) was the dominant in-lake form of N. The net in-lake removal of NO_3^- -N was 340 kg.yr^{-1} , of which ~75% was assimilated by plankton and 25% denitrified. The absence of nitrification due to long-lasting water acidification led to a situation in which the lake became a net source of NH_4^+ -N (78 kg.yr^{-1}), resulting because dissimilative liberation of NH_4^+ -N exceeded its assimilation.

Key words: Nitrogen, phosphorus, carbon, silica, sulfur, aluminum, acidification, forest lake

INTRODUCTION

Former mass budget studies on three Bohemian Forest lakes showed that the total inputs of P, silica (Si) and dissolved organic carbon (DOC) were three to fivefold higher into Plešné Lake than into Čertovo or Černé Lakes (KOPÁČEK et al. 2001a,b,c). The net in-lake removals of C, P, N, and Si in Plešné Lake varied between 34% and 51% of their inputs (KOPÁČEK et al. 2001c). Such a rough estimation is usually sufficient for elements with a sedimentary cycle (P), because their in-lake removal equals their storage in sediments (WETZEL 2001). In contrast, the net in-lake removal of N does not allow distinguishing between their sedimentation and other in-lake sinks. Nitrogen can be removed from the water column by assimilation and sedimentation of seston, as well as by denitrification in the anoxic hypolimnion or sediments (KELLY et al. 1987, WETZEL 2001). Most of these fluxes can be estimated on the basis of mass balance of individual N species in the lake and/or their proportional changes to P (denitrifica-

tion; MOLOT & DILLON 1993). However, the desirable description of in-lake nutrient fluxes requires a more precise estimation of their sedimentation rate, recycling by microbial decomposition of seston, and storage in sediments.

The mass budget of elements in the Plešné watershed–lake ecosystem had the highest uncertainty among the three lakes in the 2000 hydrological year, due to unmeasured atmospheric deposition at higher watershed elevations (KOPÁČEK et al. 2001a,b,c). The difference between amounts and compositions of deposition at two (low and high elevation) throughfall plots in the Čertovo Lake watershed (KOPÁČEK et al. 2001a) showed that measurements from only one plot cannot be simply applied to the whole watershed with the great terrain relief.

To avoid the above shortcomings in the element mass balance within the Plešné watershed–lake ecosystem in the 2001 hydrological year, we (1) established a new plot for the sampling of throughfall deposition in the upper part of the watershed, and (2) extended the in-lake mass budget study for measurement of C, N, P, and Al sedimentation rates. This paper summarizes results of the 2001 mass budget study, and quantifies major fluxes of ions and nutrients within the Plešné watershed–lake ecosystem with particular interest paid to the in-lake transformations of N, P, and Al.

MATERIALS AND METHODS

Study site description

Plešné Lake (48°47'N; 13°52'E; 1090 m above sea level, a.s.l.) is a dimictic, mesotrophic lake with an area of 7.5 ha, volume of $6.17 \times 10^5 \text{ m}^3$, maximum depth of 18 m (ŠVAMBERA 1939), and theoretical water residence time of <1 year. The lake has four accessible tributaries; two of them (PL-I and PL-II) are on the surface, while PL-III and PL-IV are subsurface. The lake was atmospherically acidified already in the early 1960s, when pH values <5.4 were measured by PROCHÁZKOVÁ & BLAŽKA (1999). Acidification progressed until the middle 1980s, when pH ranged between 4.4 and 4.65 (VESELY et al. 1998a). At present, the lake is in a stage of chemical reversal from acidification with pH approaching ~5, but still with a depleted carbonate buffering system and sulphate (SO_4^{2-}) being the dominant anion (KOPÁČEK et al. 2001c). Plešné Lake is fishless, submersed littoral macrophytes are sparse (~0.02 ha), zooplankton are present in low densities (<1% of the total plankton biomass, mainly represented by *Heterocope saliens* and pelagic rotifers), and the phytoplankton community is dominated by acid-tolerant species of green algae, dinoflagellates, and filamentous cyanobacteria (HEJZLAR et al. 1998, NEDBALOVÁ & VRTISKA 2000, VRBA et al. 1996, 2003).

The watershed of the lake (66.6 ha including the lake) is steep, with a maximum local relief of 288 m. Wetland and bare rock covers 1% and 5% of the watershed, respectively. Soil cover is dominated by acid lithosol, podzol, and spodo-dystric cambisol with low (15%) base saturation (KOPÁČEK et al. 2002b). The bedrock is made up of granites (VESELY 1994, KOPÁČEK et al. 2002b). The forest (99% is Norway spruce) covers ~90% of the watershed and is on average 160 years old.

Sampling and analyses

Atmospheric deposition was collected in bulk samplers situated at three plots within 0.5 km of Plešné Lake. Precipitation was sampled in the open rocky area without trees (2 samplers) at an altitude of ~1090 m a.s.l. Throughfall was sampled at two forest plots (9 samplers each) at altitudes of ~1130 m a.s.l. (TF_I) and ~1330 m a.s.l. (TF_{II}). Samples were taken from 31 October 2000 to 5 November 2001. Rain was sampled in two-week intervals and snow in two to three-week intervals, and all samples from each site were always combined to obtain an integrated sample.

Water samples from tributaries were taken in approximately month periods (in three-week intervals during snowmelt) from 9 October 2000 to 5 November 2001. Surface tributaries were sampled near their inlets to the lake and the water discharge value was estimated using a bucket and stop-watch; discharges of PL-III and PL-IV were not measured. In sub-watersheds containing several tributaries in close proximity (PL-I and PL-II), 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.

Samples from the outlet were taken biweekly between 2 October 2000 and 19 November 2001. The discharge from the lake was continuously monitored using a gauge-recorder (part of the automatic weather station MS16; J. Fiedler, České Budějovice; readings in 15-minute intervals) at a calibrated weir. A water column profile (0.5, 4, 9, 14, and 17 m) was sampled at the deepest part of the lake between 9 October 2000 and 5 November 2001. Temperature and dissolved oxygen were measured with the DataSonde 4 (Hydrolab, USA) at 1-m intervals. The samples of lake water were immediately filtered through a 200- μm polyamide sieve.

In the laboratory, samples were filtered with membrane filters (A45/25; pore size of 0.45 μm ; Macherey Nagel) for determination of ions and silica, or with glass-fiber filters (MN-5; pore size of 0.4 μm ; Macherey Nagel) for the analyses of dissolved organic matter, Al, Fe, P, and organic N. The samples for pH, acid neutralizing capacity (ANC), total Al, Fe, phosphorus and organic N were not filtered. Dissolved organic carbon (DOC; TOC 5000A analyzer, Shimadzu), ANC (Gran titration), pH, dissolved reactive P (DRP; molybdate method by MURPHY & RILEY 1962), NH_4^+ (rubazotic acid method; KOPACEK & PROCHÁZKOVÁ 1993), and total and dissolved P (TP and DP) were analyzed within 24 hours after sampling. TP and DP were determined by perchloric acid digestion according to KOPACEK & HEJZLAR (1993), but samples were fourfold concentrated by evaporation to obtain a detection limit of P $\sim 0.5 \mu\text{g.l}^{-1}$. Total and dissolved organic N (TON and DON; Kjeldahl digestion; PROCHÁZKOVÁ 1960) and dissolved reactive silica (Si; molybdate method; GOLTERMAN & CLYMO 1969) were determined within one week after sampling. Particulate P (P_{part}) and/or particulate N (N_{part}) were the difference between TP and DP, and/or TON and DON. Particulate organic carbon (C_{part}) in lake water was analyzed with the TOC 5000A analyzer (Shimadzu) by combustion of the glass-fibre filter (MN-5; pore size of 0.4 μm ; Macherey Nagel) with the retained particulate organic matter. In precipitation and tributaries, C_{part} was estimated on the basis of chemical oxygen demand determinations (HEJZLAR & KOPACEK 1990) of non-filtered (COD) samples and filtrate (COD_f) assuming that $(\text{COD} - \text{COD}_f) : \text{C}_{\text{part}}$ and $\text{COD}_f : \text{DOC}$ ratios are comparable (with an average of 3.4). Concentration of chlorophyll *a* was determined spectrophotometrically on Whatman GF/C filters after acetone extraction (LORENZEN 1967); values were not corrected for phaeopigments.

Samples for ion determination (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NO_3^- , SO_4^{2-} , Cl^- , and F^-) were frozen at -20°C and analyzed by ion chromatography (Dionex IC25, USA) within a month.

Fractionation of aluminum according to DRISCOLL (1984), i.e. total Al (Al_t), dissolved Al (Al_d), and organically bound Al (Al_o), were analyzed in non-filtered samples, filtered samples, and cation exchange treated samples after their filtration, respectively, using the method by DOUGAN & WILSON (1974). The concentration of ionic Al (Al_i) was the difference between Al_d and Al_o . The concentration of particulate Al (Al_{part}) was the difference between Al_t and Al_d . The respective Fe fractions were obtained analogously to Al, and their concentrations were determined by the thiocyanate colorimetric method after sample evaporation and digestion with perchloric acid (HEJZLAR & KOPACEK 1998). Equivalent concentrations of Al_i and Fe_i (Al_i^{m+} and Fe_i^{n+}) were obtained from their molar concentrations and the average charges of Al hydroxocomplexes (n) and Fe hydroxocomplexes (m), respectively. The n and m values were estimated from the theoretical distribution of ionization fractions of aqueous Al and Fe hyd-

roxocomplexes, respectively, at the sample pH (KOPÁČEK et al. 2000a). Concentrations of organic acid anions (R^- , $\mu\text{eq.l}^{-1}$) were obtained independently of ionic composition, from concentrations of DOC, Al^{3+} , Fe^{3+} , and pH as described by KOPÁČEK et al. (2000a).

The reliability of analytical methods was checked by means of an ionic balance control approach (KOPÁČEK et al. 2000a). The differences between the sum of the cations and the sum of the anions represented between -2.8% to 3.9% of the total ionic content in the annual volume (or discharge) weighted mean composition of precipitation, throughfall, tributaries, lake water, and output.

Sedimentation rate and sediments

Sedimentation rate was measured at the deepest part of the lake by means of sediment traps situated between two buoys at 9-m (the chemically most stable water layer; see below) and 16-m (1 m above the bottom) depths. The traps consisted of two Plexiglas tubes, 300 mm long and 50 mm in diameter, and were exposed for two and one-month intervals in winter and ice-free periods, respectively. Because the first samples (November–December 2000) were lost, this study was performed until 8 January 2002. Suspended material from the traps was homogenized by shaking and analyzed for dry weight (DW, 105°C), ash (after 2 hours at 550°C), and total concentrations of P, Al, and Fe after nitric and perchloric acid digestion (KOPÁČEK et al. 2001d). Concentrations of C_{part} (on filters) and N_{part} (in suspension) were determined as described for water samples. The average sedimentation rate ($\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$) was calculated for each sampling interval from the retained amount and the interval length. The annual in-lake sedimentation rate ($\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) was the sum of amounts retained in the 9-m depth from 4 January 2001 to 8 January 2002. This value was used to calculate the total amount ($\text{kg}\cdot\text{yr}^{-1}$) of sedimenting elements. In this calculation we assumed that (1) the sediment deposition on the bottom was negligible in the epilimnion and littoral zone due to intensive water mixing and sediment re-suspension, and (2) all allochthonous and autochthonous particulate material was stored uniformly under the thermocline. The average thermocline depth was ~ 4 m (see below). The lake area at the 4-m depth is 5.2 ha (ŠVAMBERA 1939).

Concentrations of C, N, and P in the Plešné Lake sediment were obtained as averages of available data on surface sediments in 7 cores sampled at the deepest part between 1994 and 1998 (HEJZLAR et al. 1998, KOPÁČEK et al. 2000b, BOROVEC 2000, and J. BOROVEC – pers. comm.). The average mass accumulation rate in Plešné Lake ($85 \text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) was estimated from the average accumulation rate of sediment ($5\text{--}6 \text{ mm}\cdot\text{yr}^{-1}$; SCHMIDT et al. 1993, KOPÁČEK – unpubl. data) and the water content of the uppermost sediment layer (98.4%). This estimation was close to the values observed by J. VESELY (pers. comm.; $\sim 60 \text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$). The total mass accumulation in the sediment ($4461 \text{ kg}\cdot\text{yr}^{-1}$) was estimated from the average mass accumulation rate and the lake area at the 4-m depth.

Dissimilation of sedimenting seston in the hypolimnion

Hypolimnetic production of P, NH_4^+ and TIC (as CO_2) by biological decomposition of both sedimenting seston and sediment was estimated using changes in their concentrations below the 9-m depth during periods of lake stratification. In this calculation, the element concentrations at 9, 14, and 17 m were assumed to be representative for water layers between the 9-m and 12-m depths (89840 m^3), the 12-m and 15-m depths (54560 m^3), and the 15-m depth and bottom (15920 m^3), respectively. Data on the volumes come from ŠVAMBERA (1939). The hypolimnetic element amounts on 4 December 2000 and 9 April 2001 were used to characterize the winter stratification period. Analogously, data on 2 May 2001 and 1 October 2001 were used for the summer stratification period. An element's production was the difference between its hypolimnetic amounts at the end and beginning of the period, recalculated proportionally

for the whole November–April and May–October periods for winter and summer, respectively. The annual hypolimnetic production of elements was the sum for both periods.

Mass balances

Water balance in the Plešné watershed-lake ecosystem was determined from the annual heights of precipitation and throughfall and the budget for Cl⁻ assuming that Cl⁻ behaved conservatively with no net retention or production within the whole ecosystem. Mass balance of chemical constituents was calculated according to KOPÁČEK et al. (2001a) with the following exceptions:

(1) We assumed that 10% and 90% of watershed received atmospheric deposition in the form of precipitation and throughfall, respectively, and throughfall deposition was the average of that at the TF_L and TF_H sites.

(2) Water level of Plešné Lake varied during the 2001 hydrological year. The water level was 30 cm lower in September 2001 due to an artificial manipulation. The original water level was reached in early November 2001. Consequently, the change in water storage in the lake was negligible in the annual water balance. In-lake storage of elements at the beginning and end of the study was based on water composition on 9 October 2000 and 5 November 2001, respectively.

(3) The annual volume weighted mean (VWM) composition of water output from the lake was calculated by linking discharge data for the outlet with the corresponding biweekly concentration data by the method of period-weighted mean.

(4) The average composition of surface input was obtained as the VWM for tributaries PL-I and PL-II. The average composition of subsurface input was obtained as the arithmetical mean for tributaries PL-III and PL-IV. The average proportion of surface and subsurface tributaries (70% and 30%, respectively) in the total terrestrial water export to Plešné Lake was estimated on the basis of Ca²⁺ balance. Here we used differing Ca²⁺ concentrations in the subsurface and surface tributaries and the net annual Ca retention in sediments that was calculated from the sediment composition and average mass accumulation rate (KOPÁČEK et al. 2001c).

RESULTS

Chemical composition of atmospheric deposition, tributaries, and lake output

Annual precipitation height and throughfall deposition (TF_L) were 1408 and 1067 mm, respectively, in the lower part of the Plešné watershed in the 2001 hydrological year. Throughfall deposition in the upper watershed area (TF_H) was 1602 mm. The difference between TF_H and TF_L represented a pronounced gradient of water deposition on the forest floor, increasing 2.7 mm per 1 m of elevation, and was almost two times higher than the gradient for the Čertovo Lake watershed (1.4 mm.m⁻¹ in the same period; KOPÁČEK – unpubl. data). Concentrations of most constituents were higher in TF_L than in TF_H (Table 1) due to higher evaporation at lower altitude.

The concentrations of conservative ions with negligible exchange in canopies (Na⁺, Cl⁻, and SO₄²⁻) were ~1.6 to 1.8 fold higher in throughfall than in precipitation (Table 1). The throughfall concentrations of Mg²⁺ and K⁺ were increased by canopy leaching and were 3–9 fold higher. In contrast, the NH₄⁺ concentrations were negatively affected by canopy interactions, being only 1.2 fold higher in throughfall than in precipitation. Such an impact of canopy processes on the throughfall composition is in concordance with other forest sites (e.g., LOVETT 1992, DISE et al. 1998).

Table 1. The VWM concentrations of the major constituents of atmospheric deposition (precipitation, Precip.; and throughfall at low and high elevation, TF_l and TF_h, respectively), tributaries (PL-I to PL-IV), terrestrial transport (lake input via tributaries, PL_{IN}), and lake output (PL_{OUT}) in the Plešné watershed-lake ecosystem in the 2001 hydrological year. Number of observations, n: not determined. ND: not applicable. NA: pH averages were calculated from the average H⁺ concentrations.

		Precip.	TF _l	TF _h	PL-I	PL-II	PL-III	PL-IV	PL _{IN}	PL _{OUT}
n		24	24	24	13	13	13	13	13	29
Height	mm	1408	1067	1602	NA	NA	NA	NA	NA	NA
pH		4.94	4.67	4.76	4.31	4.39	4.66	4.80	4.43	4.93
Ca ²⁺	mg.l ⁻¹	0.17	0.50	0.42	0.61	0.63	1.12	1.45	0.82	0.70
Mg ²⁺	mg.l ⁻¹	0.04	0.11	0.09	0.12	0.11	0.22	0.30	0.16	0.15
Na ⁺	mg.l ⁻¹	0.17	0.26	0.24	0.98	0.93	1.12	1.25	1.03	0.85
K ⁺	mg.l ⁻¹	0.12	1.11	0.78	0.28	0.27	0.41	0.45	0.32	0.32
NH ₄ ⁺ -N	µg.l ⁻¹	367	432	412	10	10	8.5	7.0	9.3	80
NO ₃ ⁻ -N	µg.l ⁻¹	326	603	504	543	619	961	1114	715	310
SO ₄ ²⁻	mg.l ⁻¹	1.01	1.68	1.51	3.73	3.59	4.62	5.53	4.09	3.55
Cl	mg.l ⁻¹	0.25	0.46	0.43	0.45	0.45	0.39	0.44	0.44	0.36
F	mg.l ⁻¹	0.004	0.020	0.009	0.07	0.06	0.13	0.15	0.09	0.07
DOC	mg.l ⁻¹	0.9	8.1	5.6	11.3	8.4	3.4	1.5	7.7	3.5
C _{part}	mg.l ⁻¹	0.48	ND	ND	0.20	0.30	0.47	0.47	0.31	2.68
TON	µg.l ⁻¹	212	ND	ND	374	321	214	156	301	374
DON	µg.l ⁻¹	115	396	352	360	321	214	115	289	181
Si	mg.l ⁻¹	<0.01	0.07	<0.01	4.08	3.70	4.14	4.16	3.98	2.44
TP	µg.l ⁻¹	20.0	20.7	20.0	27.7	28.8	12.6	5.2	22.4	10.5
DP	µg.l ⁻¹	13.4	6.2	6.2	27.1	27.5	10.9	4.1	21.4	2.3
DRP	µg.l ⁻¹	12.5	2.3	1.8	22.0	24.7	9.6	3.2	18.2	1.0
Al _l	µg.l ⁻¹	4	ND	ND	783	716	718	691	739	457
Al _u	µg.l ⁻¹	ND	ND	ND	375	388	555	597	439	229
Al _v	µg.l ⁻¹	ND	ND	ND	400	313	141	54	282	101
Fe _l	µg.l ⁻¹	19	ND	ND	145	101	48	11	97	83
Fe _u	µg.l ⁻¹	ND	ND	ND	34	33	14	-2	25	25
Fe _v	µg.l ⁻¹	ND	ND	ND	104	71	25	13	68	26
ANC	µeq.l ⁻¹	-13	-24	-18	-65	-52	-21	-10	-46	-8

The VWM concentrations of most solutes (especially Na⁺, H⁺, SO₄²⁻, NO₃⁻, Si, Al, and Fe) were generally higher in tributaries than in precipitation and throughfall, while NH₄⁺ and K⁺ concentrations were lower (Table 1). The chemical composition of tributaries reflected their origin. Surface tributaries had substantially higher concentrations of DOC, TON, TP (mostly in the form of DRP), Al_u and Fe_u, while lower pH and concentrations of Ca²⁺, Mg²⁺, NO₃⁻, SO₄²⁻, and Al_l than subsurface tributaries (Table 1).

Water output from Plešné Lake was 5–20 l s⁻¹ in winter and reached 86 l s⁻¹ during snowmelt. Compared to the input via tributaries, VWM composition of the output had lower concentrations of H⁺, NO₃⁻, SO₄²⁻, Al forms, TP, and Si but higher concentrations of NH₄⁺ and ANC (Table 1). Most TP (81%), TON (57%), and a significant part of organic C (43%) left the lake in the particulate form (Table 1).

Seasonal variations in physical variables and nutrient concentrations in the Plešné Lake

Table 2. Mass balance of major ions and nutrients in Plešné watershed-lake ecosystem in the 2001 hydrological year. Negative values of net production (Net prod.) indicate a net removal. Abbreviations: ADFP, atmospheric deposition on the forest floor (precipitation and throughfall); DAD, direct atmospheric deposition on the lake surface (precipitation); NA, not applicable; ND, not determined. The balance includes only external element sources, primary production of DOC and C_{part} are not included. All fluxes are in $kg \cdot yr^{-1}$.

	Watershed				Lake			
	ADFF	Net prod.	Export	DAD	Total input	Change in storage	Output	Net prod.
H ⁺	14	15	30	1	31	-1	10	-22
Ca ²⁺	334	316	650	18	668	14	619	-36
Mg ²⁺	73	51	124	4	128	12	131	15
Na ⁺	193	593	786	18	804	34	747	-24
K ⁺	659	-404	255	13	268	-7	280	6
NH ₄ -N	329	-321	7	39	46	7	70	32
NO ₃ -N	413	154	567	34	602	-12	274	-340
SO ₄ ²⁻	1202	2041	3243	106	3349	-70	3135	-285
Cl ⁻	337	NA	337	27	364	49	315	NA
F ⁻	10	62	72	0.4	72	0.0	63	-10
DOC	4754	1371	6124	98	6222	370	3124	-2728
C _{part}	ND	ND	247	51	298	1	2365	2068
TON	272	-43	229	22	261	17	330	87
DON	272	-43	229	12	241	12	160	-69
Si	20	3138	3158	0.2	3158	114	2155	-890
TP	16.1	1.7	17.8	2.1	19.9	-0.1	9.2	-10.7
DP	5.5	11.4	16.9	1.4	18.3	0.2	2.0	-16.1
DRP	2.5	11.9	14.4	1.3	15.7	-0.4	0.9	-15.2
Al _f	0.3	585	586	0.4	586	10	404	-173
Al _l	ND	348	348	ND	348	31	202	-115
Al _t	ND	224	224	ND	224	22	89	-113
Fe _l	1.6	75.1	76.7	2.0	79	8	73	2
Fe _t	ND	20.2	20.2	ND	20	-3	22	-1
Fe _o	ND	54.2	54.2	ND	54	12	23	-19

tributaries and outlet are given in Fig. 1. Because the chemical composition of PL-I and PL-II was similar (Table 1), only data on PL-I are shown. The chemical composition of subsurface tributaries was stable. In contrast, the chemistry of surface tributaries showed pronounced seasonal variations, with the most significant seasonal cycles for NO₃⁻, Si, and TP concentrations. Higher NO₃⁻ concentrations during the dormant period resulted from the lower terrestrial bio-consumption of inorganic N. Most seasonal variability in concentrations of strong acid anions was associated with NO₃⁻, because concentrations of SO₄²⁻ and Cl⁻ were relatively stable throughout the year, except for dilution during snowmelt. Consequently, concentrations of base cations (BC = sum of Ca²⁺, Mg²⁺, Na⁺, and K⁺) and Al_l in the Plešné Lake tributaries were tightly correlated with NO₃⁻ (P<0.001; linear regression) and exhibited similar seasonal trends (Fig. 1). The seasonal variation in Si concentrations in tributaries PL-I and PL-II was inversely correlated with discharge (P<0.01; linear regression).

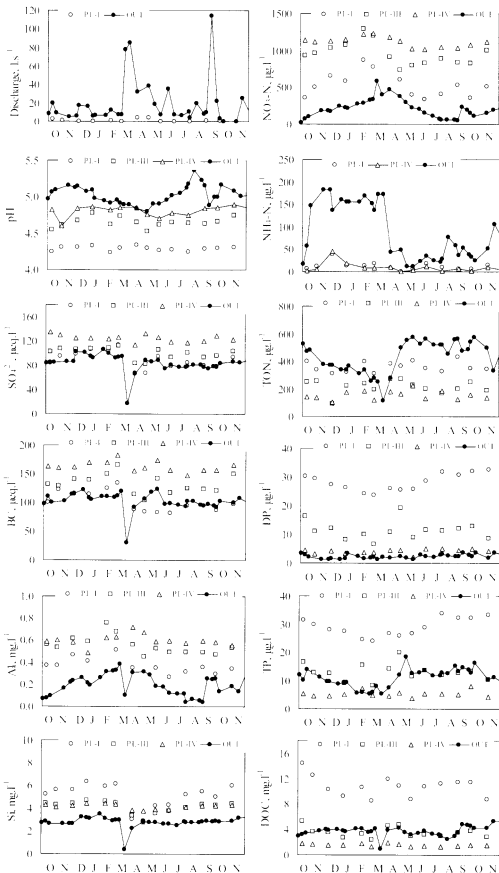


Fig. 1. Seasonal patterns of discharge, pH and concentrations of selected ions and nutrients in the Plešné Lake tributaries (PL-I, PL-III, and PL-IV) and the output (OUT) in the 2001 hydrological year. Abbreviations: Base cations (BC), ionic Al (Al), dissolved silica (Si), total organic nitrogen (TON), dissolved and total phosphorus (DP, TP), and dissolved organic carbon (DOC).

The water composition in Plešné Lake output was most significantly affected during snow-melt, when concentrations of DOC, Si, TN and most ions sharply decreased. Only NO_3^- concentrations exhibited an increase due to their maximum terrestrial export in this period (Fig. 1). The NH_4^+ concentrations in the output exceeded their levels in tributaries throughout the year and peaked in winter. In contrast, the elevated TP and TON concentrations were associated with the elevated primary production in the ice-free period. Concentrations of DP were stable ($1.3\text{--}3.7 \mu\text{g.l}^{-1}$) in Plešné Lake output throughout the year (Fig. 1) and DRP was mostly $<1 \mu\text{g.l}^{-1}$, with the exception of the maximum outflow period in the middle of June, when DRP reached $2.9 \mu\text{g.l}^{-1}$.

Element balance in the Plešné watershed–lake ecosystem

Water input into the whole ecosystem (deposition on the forest floor and lake surface) was $9.37 \times 10^5 \text{ m}^3.\text{yr}^{-1}$ and water output from the lake was $8.82 \times 10^5 \text{ m}^3.\text{yr}^{-1}$ (based on the Cl^- balance). The resulting average water residence time in Plešné Lake was 255 days. A relatively low value of water evaporation (6%) from the ecosystem resulted from the calculation of water input into the ecosystem, which was based on the real water deposition on the forest floor (i.e., throughfall). The water deposited by throughfall represented precipitation minus evaporation from canopies. For example, throughfall deposition of water at site TF_1 was on average 24% lower than precipitation at a comparable altitude (Table 1). This means that the total water evaporation from ecosystem (the difference between precipitation and output) was ~30%.

The mass fluxes of major ions and nutrients in the Plešné watershed–lake ecosystem are given in Table 2. Terrestrial export of ions was higher than their deposition on the forest floor, except for NH_4^+ and K^+ , which were effectively decreased by soil processes.

The total external input of total organic C, TN, TP, and Si into Plešné Lake was, respectively, 6520, 908, 19.9, and 3158 kg.yr^{-1} (87, 12, 0.27, and $42 \text{ g.m}^{-2}.\text{yr}^{-1}$), and their net in-lake removal was 10%, 24%, 54%, and 28% (Table 2). The removal of dissolved nutrient forms was even higher (88%, 57%, and 44% for DP, NO_3^- -N, and DOC, respectively). In contrast, the lake was a net source of particulate forms of nutrients (2068, 156, and 5.3 kg.yr^{-1} of C_{part} , N_{part} , and P_{part} , respectively). As in the previous year (KOPÁČEK et al. 2001c), the lake was a net source of NH_4^+ -N (32 kg.yr^{-1}).

Depth–time variations in physical parameters and chemistry of the water column

Depth and time variations in physical and chemical parameters of lake water are shown in Figs. 2 and 3. The autumn and spring overturns occurred at the end of November and at the beginning of May, respectively. The spring overturn, however, was not complete and the water layer below 14 m was not completely mixed (Fig. 2). Ice cover lasted from early December to the end of April.

The chemical composition of the water column was more stable in winter than in the ice-free period. Major changes in the epilimnion composition were associated with the period of maximum phytoplankton growth from July to October, when chlorophyll *a* and C_{part} concentrations varied within $25\text{--}49 \mu\text{g.l}^{-1}$ (Fig. 2) and $3.0\text{--}3.9 \text{ mg.l}^{-1}$ (Fig. 3), respectively. The increased assimilation of nutrients led to a significant reduction in the epilimnetic NH_4^+ -N, NO_3^- -N, and TIC concentrations (Fig. 3), and an increase in pH. At the elevated pH, Al_3^+ hydrolyzed and formed Al_{part} (Fig. 2). The annual average (\pm standard deviation) concentrations of C_{part} , N_{part} , and P_{part} in the Plešné epilimnion were 2620 ± 840 , 249 ± 87 , and $8.1 \pm 1.8 \mu\text{g.l}^{-1}$, respectively.

Hypolimnetic concentrations of dissolved oxygen were depleted to values $<1 \text{ mg.l}^{-1}$ in the bottom layer (1–4 m above the sediments) during both the winter and summer stratification periods, and also during the uncompleted spring overturn. At the low redox potentials, dissimilatory reduction processes occurred, decreasing NO_3^- (and also SO_4^{2-}) concentrations and

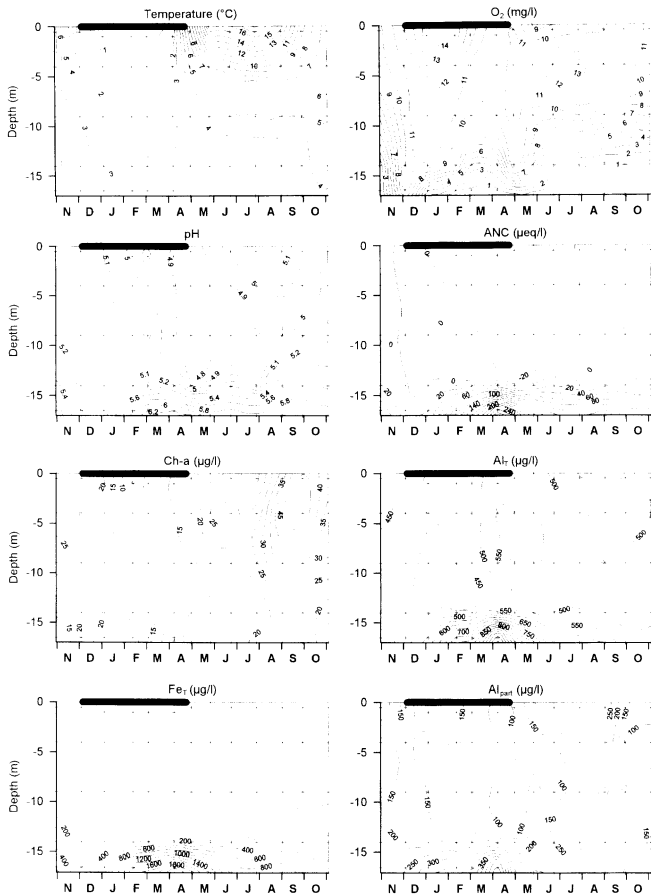


Fig. 2. Depth-time diagrams of temperature, pH, and concentrations of dissolved oxygen (O₂), acid neutralizing capacity (ANC: Gran titration), chlorophyll *a* (Ch-*a*), total and particulate Al (Al_t, Al_{part}) and total Fe (Fe_t) in Plešné Lake in the 2001 hydrological year. Thick lines represent ice-cover.

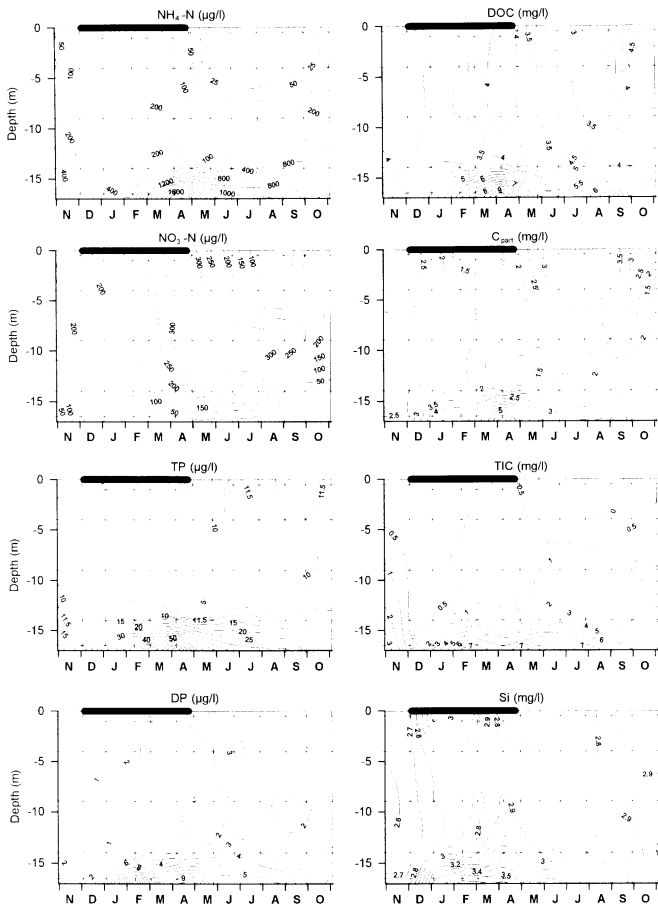


Fig. 3. Depth-time diagrams of NH₄-N, NO₃-N, total and dissolved phosphorus (TP, DP), dissolved organic, particulate and total inorganic carbon (DOC, C_{part}, TIC), and dissolved silica (Si) concentrations in Plešné Lake in the 2001 hydrological year. Thick lines represent ice-cover.

increasing concentrations of Fe forms (Figs. 2, 3). The associated alkalinity production led to an increase in the hypolimnetic pH and ANC values, and a re-establishment of the carbonate buffering system below ~14-m depth (Fig. 2). Similarly as in the epilimnion, the hypolimnetic concentrations of Al_{part} increased along with the increasing pH gradient due to Al_i hydrolysis. These changes were least pronounced in the most chemically stable water layer between 8–12 m, with the lowest Al_{part} and highest NO_3^-N concentrations in the whole water column.

Concentrations of TIC, NH_4^+-N , and TP liberated by biological decomposition from the sedimenting seston and/or sediments were elevated above the bottom throughout the study. They increased rapidly after the autumn overturn, reached the maximum in March and April, slightly decreased during the uncompleted spring overturn in May, and then steadily increased until October (Figs. 2 and 3). The estimated hypolimnetic productions of TIC, NH_4^+-N , and TP were 1021, 81, and 2.4 $kg \cdot yr^{-1}$, respectively. While these results reasonably represent NH_4^+-N and TP liberation due to seston and sediment dissimilation, the hypolimnetic TIC production included both CO_2 produced by bacterial decomposition of DOC and liberated by C_{part} dissimilation.

Sediment composition and sedimentation rate of particulates

Element concentrations in the surface layers of the Plešné Lake sediment varied within the following ranges: 327–452 $g \cdot kg^{-1}$ (mean of 355 $g \cdot kg^{-1}$) for C, 29–44 $g \cdot kg^{-1}$ (34 $g \cdot kg^{-1}$) for N, 2.6–3.5 $g \cdot kg^{-1}$ (3.0 $g \cdot kg^{-1}$) for P, and 29–45 $g \cdot kg^{-1}$ (37 $g \cdot kg^{-1}$) for Al. All the above data are relative to dry weight of the sediment. The average LOI was 72%. The average accumulation rates of these elements and their annual accumulation in the sediment below the 4-m depth are given in Table 3.

Annual cycles of the sedimentation rate of DW, ash, major nutrients and Al are given in Fig. 4. The results obtained for the 9-m and 16-m depths significantly differed. Sedimentation rates measured in the 9-m depth were more or less comparable to the accumulation rates, while the rates measured above the bottom were significantly higher (Table 3). The higher sedimentation rate above the bottom than in the 9-m depth can be explained by accumulation

Table 3. Annual average sedimentation rate of particulate matter (dry weight (DW) and ash content), major nutrients, and Al in Plešné Lake. ND, not determined.

	Unit	DW	Ash	C	P	N	Al
Sedimentation rate (9 m) ¹⁾	$g \cdot m^{-2} \cdot yr^{-1}$	94	14	38	0.17	4.0	2.4
Sedimentation rate (16 m) ¹⁾	$g \cdot m^{-2} \cdot yr^{-1}$	195	36	72	0.51	8.2	5.6
Accumulation rate in sediment ²⁾	$g \cdot m^{-2} \cdot yr^{-1}$	85	23	30	0.25	2.9	3.1
Sedimentation flux ³⁾	$kg \cdot yr^{-1}$	4936	746	1990	8.9	211	125
Storage in sediments ⁴⁾	$kg \cdot yr^{-1}$	ND	ND	ND	10.7	133	173
Accumulation in sediment ⁵⁾	$kg \cdot yr^{-1}$	4461	1231	1585	13.4	151	163

¹⁾ Sedimentation rates in 9-m and 16-m depths were measured using sedimentation traps.

²⁾ Average accumulation rate in the sediment was estimated from the average sediment (0–10 cm) composition and average mass accumulation rate.

³⁾ Sedimentation flux was estimated from sedimentation rate in the 9-m depth and lake area in the 4-m depth.

⁴⁾ The N storage in sediments was the difference between N sedimentation flux in the 9-m depth and dissimilative NH_4^+-N production below this depth. The P and Al storage in sediments was set equal to their net in-lake retention.

⁵⁾ Accumulation in sediment was estimated for the lake area in the 4-m depth, using the accumulation rate in sediment.

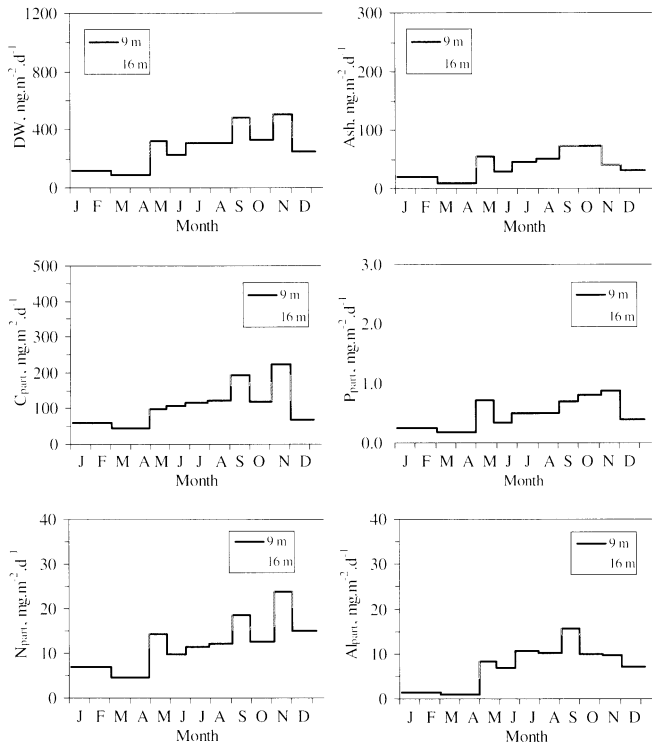


Fig. 4. Annual cycles of sedimentation rate of particulate matter (dry weight, DW; and ash), particulate nutrients (C_{part} , N_{part} , and P_{part}) and aluminum (Al_{part}) in the 9-m and 16-m depths in Plešné Lake between 4 January 2001 and 8 January 2002.

of particulates in the deepest part of the lake (the so called funneling effect). However, the reason for the elevated sedimentation rate above the bottom in the early summer is unclear, and may be associated with the formation of a nepheloid layer above the bottom due to thermocline motions and internal seiches (KALFF 2002). This occurred 2 months after the maximum concentrations of particulate matter in the bottom water (see concentrations of Al_{part} , C_{part} , and TP in Figs. 2 and 3 in the March–April period). The disproportion cannot be explai-

ned by the re-suspension of sediments during the incomplete spring overturn, either. As the observed sedimentation rates above the bottom are not fully understood, we use only the results from the 9-m depth in the further mass fluxes evaluations. Using these data and lake area below the 4-m depth, the sedimentation fluxes of C, N, P, and Al in Plešné Lake were 1990, 211, 8.9, and 125 kg.yr⁻¹, respectively. The sedimentation flux of N was higher than N storage in sediments due to the partial liberation of NH₄-N by dissimilation of sedimenting seston. For P and Al, the sedimentation fluxes were lower than their storage in sediments because the sedimentation flux did not include the formation of particulate matter below the 9-m depth.

DISCUSSION

Compared to the input via tributaries, the VWM composition of Plešné Lake output had lower concentrations of most water constituents, except for NH₄⁺ and particulate element forms (Table 1). These differences were a net result of (1) atmospheric deposition on the lake surface, (2) in-lake assimilatory and dissimilatory processes, (3) metal hydrolysis at elevated pH, and (4) sedimentation. The importance of individual processes was estimated using the mass budgets for individual elements as follows.

The in-lake nitrogen cycle

On an annual basis, Plešné Lake removed 222 kg.yr⁻¹ of TN input, being a net sink of NO₃-N (340 kg.yr⁻¹), and a net source of TON and NH₄-N (87 and 32 kg.yr⁻¹, respectively) (Table 2). The major fluxes and in-lake transformations of N forms are summarized in Table 4.

Assimilation and denitrification were the dominant in-lake sinks of NO₃-N. We assume that the total in-lake production of TON originated from NH₄-N and NO₃-N assimilation, and that N₂ fixation was negligible. Nitrogen fixation was not measured, but cyanobacteria (*Pseudanabaena* sp. and *Limnospira* sp.) represented <15% of the phytoplankton biomass in Plešné Lake (NEDBALOVÁ & VRTIŠKA 2000, VRBA et al. 2003), and epilimnetic NH₄-N and NO₃-N were reduced (but not depleted) for only a relatively short period (Fig. 3). Under such conditions, the N limitation of phytoplankton growth is unlikely and N₂ fixation can be neglected (KALFF 2002).

The total in-lake production of TON can be estimated as the sum of its net production (86 kg.yr⁻¹) and sedimentation flux of N (211 kg.yr⁻¹), resulting in 297 kg.yr⁻¹. NH₄-N is usually the primary N source for phytoplankton (PROCHÁZKOVÁ et al. 1970; WETZEL 2001). So, we assumed that all NH₄-N entering the lake (46 kg.yr⁻¹; Table 2) was assimilated, and that the NO₃-N assimilation was 251 kg.yr⁻¹ (i.e., 297 minus 46 kg.yr⁻¹). The difference between the net NO₃-N retention in the lake and its assimilation gave 89 kg.yr⁻¹ of NO₃-N, which was de-

Table 4. Major fluxes and transformations of nitrogen forms in Plešné Lake in the 2001 hydrological year. All fluxes are in kg.yr⁻¹.

	Input	Assimilation	Denitrification	Nitrification	Dissimilation	Sedimentation	In-lake change in storage	Output
NH ₄ -N	46	-46	0	0	+78	0	+7	70
NO ₃ -N	602	-251	-89	0	0	0	-12	274
TON	261	+297	0	0	-78	-133 ^a	+17	330

^aN₂ storage in sediments

nitrified. A comparable result ($100 \text{ kg} \cdot \text{yr}^{-1}$) on the denitrification rate was obtained using a N : P ratio method, based on changes in the N : P ratios of the net TN and TP retention in the lake and of the N and P concentrations in the surface sediments (MOLOT & DILLON 1993).

The high $\text{NH}_4\text{-N}$ concentrations are typical for the Bohemian Forest lakes (RUŽICKA et al. 1981). For example, their annual weighted mean concentrations varied between 50 and $120 \mu\text{g} \cdot \text{l}^{-1}$ in outputs from Čertovo, Černé, and Plešné Lakes in 2000, while their concentrations in lake tributaries were one order of magnitude lower (KOPÁČEK et al. 2001a,b,c). Such a situation is uncommon because $\text{NH}_4\text{-N}$ is assimilated by the phytoplankton and usually also rapidly nitrified by bacteria under oxic conditions so that its epilimnetic concentrations are commonly low in most lakes (WETZEL 2001). The additional $\text{NH}_4\text{-N}$ input by atmospheric deposition can in part explain the elevated $\text{NH}_4\text{-N}$ concentrations in the outputs from the Bohemian Forest lakes but not the net production of $\text{NH}_4\text{-N}$ in these lakes (Table 2; KOPÁČEK et al. 2001b,c).

While both $\text{NH}_4\text{-N}$ and a part of $\text{NO}_3\text{-N}$ are assimilated by the phytoplankton, the dissimilatory decomposition of sedimenting seston and sediment liberates N entirely as $\text{NH}_4\text{-N}$. The assimilation and dissimilation occur also in acid waters, but nitrification ceased in the Bohemian Forest lakes due to their long-term acidification ($\text{pH} < 5$ for several decades), as has been described for acidified lakes (RUDD et al. 1988). Because $\text{NH}_4\text{-N}$ is not removed from the water column by nitrification, its concentration increases even in the oxic hypolimnetic layers during the stratification periods (Figs. 2 and 3) and, during winter, also in the output from the lake (Fig. 1). If we assume that all $\text{NH}_4\text{-N}$ entering the lake was assimilated and the lake was the net source of $32 \text{ kg} \cdot \text{yr}^{-1}$ of $\text{NH}_4\text{-N}$ (Table 2), the total dissimilative $\text{NH}_4\text{-N}$ production was $78 \text{ kg} \cdot \text{yr}^{-1}$. This result, based on a mass balance approach, corresponds well with the hypolimnetic $\text{NH}_4\text{-N}$ production ($81 \text{ kg} \cdot \text{yr}^{-1}$). The results show that the internal $\text{NH}_4\text{-N}$ source can exceed its sinks in the acidified lakes with a significant assimilation of $\text{NO}_3\text{-N}$.

The measured sedimentation flux of N_{part} was $211 \text{ kg} \cdot \text{yr}^{-1}$ (in the 9-m depth) but this amount was further reduced by $78 \text{ kg} \cdot \text{yr}^{-1}$ due to the dissimilative $\text{NH}_4\text{-N}$ production. The resulting amount of N_{part} finally stored in the sediments was $133 \text{ kg} \cdot \text{yr}^{-1}$. This N storage in the sediments was probably underestimated because the N_{part} production below the 9-m depth was not measured. Still, the estimated N_{part} storage in the sediments was relatively well comparable with the long-term average N accumulation in the Plešné Lake sediment ($151 \text{ kg} \cdot \text{yr}^{-1}$).

The in-lake phosphorus cycle

The total in-lake input of TP was $19.9 \text{ kg} \cdot \text{yr}^{-1}$, of which $2.1 \text{ kg} \cdot \text{yr}^{-1}$ was supplied by precipitation (Table 2). Most TP (92%) was in the dissolved form and 79% in the form of DRP, due primarily to the high DRP concentrations in surface tributaries (Table 1). On an annual basis, Plešné Lake was a net sink of 88% of DP ($16.1 \text{ kg} \cdot \text{yr}^{-1}$) which was converted to P_{part} . Biomass production and P immobilization by Al_{part} were two major processes responsible for this change in P forms.

The net TP retention in the lake was $10.7 \text{ kg} \cdot \text{yr}^{-1}$, representing the P_{part} portion stored in the sediments. The annual P_{part} output was $7.2 \text{ kg} \cdot \text{yr}^{-1}$ and P_{part} storage in the lake decreased by $0.3 \text{ kg} \cdot \text{yr}^{-1}$ during the study. The sum of these fluxes ($17.6 \text{ kg} \cdot \text{yr}^{-1}$) represented the total annual flux of P_{part} in Plešné Lake. Of this P_{part} flux, $1.5 \text{ kg} \cdot \text{yr}^{-1}$ originated from external sources and the rest ($16.1 \text{ kg} \cdot \text{yr}^{-1}$) from the in-lake processes (biotic and abiotic DP transformation into a particulate form).

The measured sedimentation flux of P_{part} in the 9-m depth was $8.9 \text{ kg} \cdot \text{yr}^{-1}$, being in good agreement with the net TP retention in the lake ($10.7 \text{ kg} \cdot \text{yr}^{-1}$), assuming formation of P_{part} also below this depth. The average P accumulation in the Plešné Lake sediment ($13.4 \text{ kg} \cdot \text{yr}^{-1}$),

however, was higher than the above two independent estimations and suggests an additional P source for the lake. An underestimated input of coarse particles into the lake could explain this disproportion. We did not include the input of particles $>40\ \mu\text{m}$ in tributaries, which was indeed negligible during all samplings but could be a significant source of particulate organic matter during high-flow episodes. The deposition of needles and leaves can represent another significant nutrient input to the littoral zone of forest lakes (PSENNER 1984). Such an additional input of organic material would be a relatively more significant P than N source for the sediments, due to the different fate of ammonia and orthophosphate, liberated from the settling material during its biological decomposition, in the strongly acidified Plešné Lake. While ammonia remains dissolved in water, orthophosphate is removed from the liquid phase by the colloidal Al, converted to a particulate form, and settles (KOPÁČEK et al. 2000b).

Proton balance in the watershed and lake

The total atmospheric input of H^+ was $14.5\ \text{keq}\cdot\text{yr}^{-1}$ on the forest floor, while its export reached $29.5\ \text{keq}\cdot\text{yr}^{-1}$. The net terrestrial H^+ production of $15\ \text{keq}\cdot\text{yr}^{-1}$ resulted predominantly from the net SO_4^{2-} and NO_3^- release from soils (and NH_4^+ assimilation), which was not fully compensated for by the release of Ca^{2+} , Mg^{2+} , Na^+ , and Al^{3+} (Table 5).

The lake was a net sink of H^+ in contrast to its watershed. Total H^+ input into the lake (the sum of terrestrial export and direct atmospheric deposition on the lake surface) was $31\ \text{keq}\cdot\text{yr}^{-1}$. The H^+ output from the lake was $10\ \text{keq}\cdot\text{yr}^{-1}$ and the in-lake storage of H^+ decreased by $1\ \text{keq}\cdot\text{yr}^{-1}$ (pH increased from 5.02 to 5.10) during the study. The net in-lake H^+ reduction was $22\ \text{keq}\cdot\text{yr}^{-1}$. Reductions in NO_3^- , R^- , and SO_4^{2-} concentrations were the dominant alkalinity generating processes, accounting for 55%, 24%, and 13% of the H^+ neutralization, respectively (Table 5). The individual processes involved in both terrestrial and aquatic proton balances and the differences between Plešné and other Bohemian Forest watershed-lake ecosystems were discussed in more detail by KOPÁČEK et al. (2001a,b,c)

Table 5. Net production of protons in Plešné Lake and its watershed in the 2001 hydrological year based on mass balance of major ions (H^+ calculated) and pH measurements (H^+ measured). Release of cations and removal of anions are proton-consuming processes, while removal of cations and release of anions are proton-producing reactions (for ionic fluxes in the ecosystem see Table 2). Negative values of production indicate net removal. Chloride was assumed to be a conservative ion with neither production nor consumption within the ecosystem and was excluded from the balance. BC, base cations. Data are expressed in $\mu\text{eq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, given on a watershed and/or lake area basis.

	H^+ source	
	Watershed	Lake
BC	-53	20
$\text{NH}_4^+\text{-N}$	34	-30
$\text{NO}_3^-\text{-N}$	17	-324
SO_4^{2-}	64	-79
F	5	0
DOC	3	-142
Al^{3+}	-43	231
Fe^{3+}	-1	1
H^+ calculated	26	-324
H^+ measured	23	-288

The in-lake aluminum cycle

Despite ~50% reduction in aluminum inputs into Plešné Lake during the last decade (VESELY et al. 1998b) its concentration was still high during this study (Table 1). With the pH increasing towards neutrality, Al_i hydrolyzed with an equivalent production of H^+ and formed colloidal Al_{part} (STUMM & MORGAN 1981), which accumulated above the bottom, increasing Al_T concentrations (Fig. 2). The Al_i hydrolysis was the dominant in-lake H^+ producing process, significantly reducing net in-lake alkalinity production due to the NO_3^- , R^- , SO_4^{2-} reduction (Table 5).

However, the amount of alkalinity consumed by Al_i hydrolysis cannot be simply estimated on the basis of Al_i budgets because the in-lake concentrations of individual Al forms change. The in-lake pool of Al_i increases while that of Al_o decreases due to the photochemical liberation of aluminum from organic complexes (KOPÁČEK et al. 2003). Moreover, the charge of Al_i changes inversely to pH, being lower in the lake output than in the tributaries. Consequently, alkalinity budgets associated with Al chemistry must be based on the Al_i^{++} fluxes.

The major changes in Al speciation in the lakes studied are summarized in Table 6. The external input of Al_i ($348 \text{ kg}\cdot\text{yr}^{-1}$) was increased by $113 \text{ kg}\cdot\text{yr}^{-1}$ due to photochemical liberation of Al_i from Al_o in the lake. Of the total in-lake pool of Al_i ($461 \text{ kg}\cdot\text{yr}^{-1}$), 49% was completely hydrolyzed and resulted in the production of Al_{part} . A major part of Al_{part} ($173 \text{ kg}\cdot\text{yr}^{-1}$) was removed from the water column by sedimentation. This Al storage in sediments corresponded well with the long-term Al accumulation in sediments (Table 3).

The net in-lake H^+ production (alkalinity consumption) associated with the Al transformations was $17.3 \text{ keq}\cdot\text{yr}^{-1}$ ($231 \mu\text{eq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) and dominated (~90%) the total internal H^+ source (Table 5). Despite strong water acidification in Plešné Lake (Fig. 2), pH of the surface sediments is relatively high (~5.7, KOPÁČEK et al. 2000b), limiting possible dissolution of Al oxyhydroxides (STUMM & MORGAN 1981). Because the oxyhydroxides are insensitive to redox changes, the Al_{part} buried in the bottom represent a stable alkalinity sink in the ecosystem.

In the Al balance (Table 6), we neglected sedimentation of Al_o , which can potentially occur due to organic matter coagulation (DRISCOLL & POSTEK 1995). The mass Al_o to DOC ratio in the lake input was 0.037 (Table 1). If the whole sedimentation flux of C_{part} (Table 3) had originated from coagulation, the related Al_o sedimentation would have been $\sim 70 \text{ kg}\cdot\text{yr}^{-1}$. But, primary production in Plešné Lake was the dominant source of C_{part} as suggested by high concentrations of chlorophyll *a* (Fig. 2) and high assimilation of N (Table 4). Consequently, we hypothesize that the Al_o sedimentation played a far less important role in the in-lake Al_o removal than did photochemical liberation.

Table 6. Major fluxes and transformations of aluminum forms in Plešné Lake in the 2001 hydrological year. ND, not determined. All fluxes are in $\text{kg}\cdot\text{yr}^{-1}$.

	Input	Photo-liberation	Hydrolysis	Sedimentation	In-lake change in storage	Output
Al_o	224	-113	0	ND ^{a)}	22	89
Al_i	348	+113	-228	0	31	202
Al_{part}	14	0	+228	-173 ^{b)}	-43	112

^{a)} Al_o potentially removed from water column by coagulation of organic matter.

^{b)} Al_{part} storage in sediments.

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REFERENCES

- BOROVEC J., 2000: Chemical composition and phosphorus fractionation of sediments in the Bohemian Forest lakes. *Silva Gabreta*, 4: 179–184.
- DISE N.B., MATZER E. & GUNDERSEN P., 1998: Synthesis of nitrogen pools and fluxes from European forest ecosystems. *Water Air and Soil Pollution*, 105: 143–154.
- DOUGAN W.K. & WILSON A.L., 1974: The absorptiometric determination of aluminium in water. A comparison of some chromogenic reagents and the development of an improved method. *Analyst*, 99: 413–430.
- DRISCOLL C.T., 1984: A procedure for the fractionation of aqueous aluminum in dilute acidic waters. *International Journal of Environmental Analytical Chemistry*, 16: 267–284.
- DRISCOLL C.T. & POSTEK K.M., 1995: The chemistry of aluminum in surface waters. In: *The environmental chemistry of aluminum*. SPOSITO G. (ed.), Lewis Publishers, Chelsea, pp. 363–418.
- GOLTERMAN H.L. & CLYMO R.S., 1969: *Methods for chemical analysis of fresh waters*. Blackwell, Oxford, 172 pp.
- HEJZLAR J. & KOPACEK J., 1990: Determination of low chemical oxygen demand values in water by the dichromate semi-micro method. *Analyst*, 115: 1463–1467.
- HEJZLAR J. & KOPACEK J., 1998: Zkumakové metody pro stanovení celkového manganu a železa ve vodách [Test tube methods for determination of total Mn and Fe in waters]. *Hydrochémie '98*, VÚVH, Bratislava, pp. 89–96.
- HEJZLAR J., KOPACEK J., VRBA J., ČIZKOVA R., KOMARCOVA J. & ŠIMEK K., 1998: Limnological study of Plešné Lake in 1994–1995. *Silva Gabreta*, 2: 155–174.
- KALFF J., 2002: *Limnology: inland water ecosystems*. Prentice-Hall, Upper Saddle River, NJ, 592 pp.
- KELLY C.A., RUDD J.W.M., HESSLEIN R.H., SCHINDLER D.W., DILLON P.J., DRISCOLL C.T., GHERINI S.A. & HECKY R.E., 1987: Prediction of biological acid neutralization in acid-sensitive lakes. *Biogeochemistry*, 3: 129–140.
- KOPACEK J. & HEJZLAR J., 1993: Semi-micro determination of total phosphorus in fresh waters with perchloric acid digestion. *International Journal of Environmental Analytical Chemistry*, 53: 173–183.
- KOPACEK J. & PROCHAZKOVA L., 1993: Semi-micro determination of ammonia in water by the rubazoic acid method. *International Journal of Environmental Analytical Chemistry*, 53: 243–248.
- KOPACEK J., HEJZLAR J. & MOSELLO R., 2000a: Estimation of organic acid anion concentrations and evaluation of charge balance in atmospherically acidified colored waters. *Water Research*, 34: 3598–3606.
- KOPACEK J., HEJZLAR J., BOROVEC J., PORCAL P. & KOTEROVA L., 2000b: Phosphorus inactivation by aluminum in the water column and sediments: A process lowering in-lake phosphorus availability in an acidified watershed-lake ecosystem. *Limnology and Oceanography*, 45: 212–225.
- KOPACEK J., HEJZLAR J., KANA J. & PORCAL P., 2001a: Element budgets in three Bohemian Forest lakes and their watersheds in the 2000 hydrological year: I. Certovo Lake. *Silva Gabreta*, 6: 35–52.
- KOPACEK J., HEJZLAR J., KANA J., PORCAL P. & PSENAKOVA P., 2001b: Element budgets in three Bohemian Forest lakes and their watersheds in the 2000 hydrological year: II. Černé Lake. *Silva Gabreta*, 6: 53–72.
- KOPACEK J., HEJZLAR J., KANA J. & PORCAL P., 2001c: Element budgets in three Bohemian Forest lakes and their watersheds in the 2000 hydrological year: III. Plešné Lake. *Silva Gabreta*, 6: 73–86.
- KOPACEK J., BOROVEC J., HEJZLAR J. & PORCAL P., 2001d: Parallel spectrophotometric determinations of iron, aluminum, and phosphorus in soil and sediment extracts. *Communications in Soil Science and Plant Analysis*, 32: 1431–1443.
- KOPACEK J., KANA J., ŠANTRUCKOVA H., PORCAL P., HEJZLAR J., PICEK T. & VESELY J., 2002: Physical, chemical, and biochemical characteristics of soils in watersheds of the Bohemian Forest lakes: I. Plešné Lake. *Silva Gabreta*, 8: 43–62.
- KOPACEK J., HEJZLAR J., KANA J., PORCAL P. & KLEMENTOVA S., 2003: Photochemical, chemical, and biological transformations of dissolved organic carbon and its impact on alkalinity production in acidified lakes. *Limnology and Oceanography*, 48: 106–117.
- LORENZEN C.J., 1967: Determination of chlorophyll and phaeopigments: spectrophotometric equations. *Limnology and Oceanography*, 12: 2243–246.
- LOVETT G.M., 1992: Atmospheric deposition and canopy interactions of nitrogen. In: *Atmospheric Deposition and Forest Nutrient Cycling*. JOHNSON D.W. & LINDBERG S.E. (eds) *Ecological Studies*, 91: 152–166. Springer-Verlag, New York.

- MOLOI L.A. & DILLON P.J., 1993. Nitrogen mass balances and denitrification rates in central Ontario Lakes. *Bio-geochemistry*, 20: 195–212.
- MURPHY J. & RILEY J.P., 1962: A modified single-solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*, 27: 31–36.
- NEDBALOVA L. & VRIŠKA O., 2000: Distribution of phytoplankton of Bohemian Forest lakes. *Silva Gabreta*, 4: 213–221.
- PROCHÁZKOVÁ L., 1960: Einfluss der Nitrate und Nitrite auf die Bestimmung des organischen Stickstoffs und Ammoniums im Wasser. *Archiv für Hydrobiologie*, 56: 179–185.
- PROCHÁZKOVÁ L., BLÁŽKA P. & KRÁLOVÁ M., 1970: Chemical changes involving nitrogen metabolism in water and particulate matter during primary production experiments. *Limnology and Oceanography*, 15: 797–807.
- PROCHÁZKOVÁ L. & BLÁŽKA P., 1999: Chemistry and biology of the Bohemian Forest lakes in the early 1960s. *Silva Gabreta*, 3: 65–72.
- PSENNER R., 1984: The proportion of empenuston and total atmospheric inputs of carbon, nitrogen, and phosphorus in the nutrient budget of small mesotrophic lake (Piburger See, Austria). *Internationale Revue der gesamten Hydrobiologie*, 69: 23–39.
- RUDD J.W.M., KELLY C.A., SCHINDLER D.W. & TURNER M.A., 1988: Disruption of the nitrogen cycle in acidified lakes. *Science*, 240: 1515–1517.
- RUZICKÁ L., STUCHLIK E. & VRBA J., 1981: Limnologický výzkum Černého jezera na Šumavě [Limnological research of Černé Lake in the Bohemian Forest]. Ms, Institute of Parasitology and Hydrobiology, Faculty of Sciences, Charles University, Prague, 44 pp. (in Czech).
- SCHMIDT R., ARZET K., FACHER E., FOIT J., IRIWECK K., REHÁKOVÁ Z., ROSE N., STRASKRABOVÁ V. & VESELY J., 1993: Acidification of Bohemian Lakes. Recent trends and historical development. Bundesministerium für Wissenschaft und Forschung [GZ 45.168/1-27b (91)], Institut für Limnologie der Ö.A.W., Mondsee, 158 pp.
- STUMM W. & MORGAN J.J., 1981: *Aquatic Chemistry*. Wiley, New York, 780 pp.
- ŠVAMBERA V., 1939: Jezera na České straně Šumavy [Lakes in the Czech part of the Bohemian Forest]. *Shorník české společnosti zeměpisné*, 45: 15–23.
- VESELY J., 1994: Investigation of the nature of the Šumava lakes: a review. *Časopis Národního Muzea, Praha, Řada přírodovědná*, 163: 103–120.
- VESELY J., HRUSKA J., NORTON S.A. & JOHNSON C.E., 1998a: Trends in water chemistry of acidified Bohemian lakes from 1984 to 1995: I. Major solutes. *Water Air and Soil Pollution*, 108: 107–127.
- VESELY J., HRUSKA J. & NORTON S.A., 1998b: Trends in water chemistry of acidified Bohemian lakes from 1984 to 1995: II. Trace elements and aluminum. *Water Air and Soil Pollution*, 108: 425–443.
- VRBA J., KOPÁČEK J., STRASKRABOVÁ V., HEJZLAR J. & ŠIMEK K., 1996: Limnological research of acidified lakes in Šumava Mountains (Bohemia): trophic status and dominance of microbial food webs. *Silva Gabreta*, 1: 151–164.
- VRBA J., KOPÁČEK J., FOIT J., KOHOÚT L., NEDBALOVÁ L., PRAZÁKOVÁ M., SOLDAN T. & SCHAUMBERG J., 2003: Long-term studies (1871–2000) on acidification and recovery of lakes in the Bohemian Forest (Central Europe). *The Science of the Total Environment*, 310: 73–85.
- WEITZEL R.G., 2001: *Limnology*, 3rd Ed., Academic Press, New York, 1006 pp.