Element budgets in three Bohemian Forest lakes and their watersheds in the 2000 hydrological year: III. Plešné Lake

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Abstract
Fluxes of major ions and nutrients and seasonal variations in their concentrations were measured within the watershed-lake ecosystem of Plešné Lake from November 1999 to November 2000. Water balance in the ecosystem was estimated from precipitation and throughfall amounts and Cl^- balance assuming Cl^- to be a conservative ion. Resulting water residence time was 267 days and evaporation was 24% of precipitation height (1655 mm). Soils in watershed of Plešné Lake were a net source of acidity (H^+ production of 29 meq.m^{-2}.yr^{-1}). Net terrestrial production of acidity was dominated by SO_4^{2-} release from soils (85 meq.m^{-2}.yr^{-1}), NH_4^+ retention in soils (40 meq.m^{-2}.yr^{-1}), and NO_3^- release from soils N (22 meq.m^{-2}.yr^{-1}). The release of Ca^{2+}, Mg^{2+}, and Na^+ (85 meq.m^{-2}.yr^{-1}) and ionic Al forms (56 meq.m^{-2}.yr^{-1}) were major terrestrial H^+ sinks. Ionic composition of tributaries showed seasonal variations with most pronounced changes in NO_3^-, base cations, and Al concentrations. In-lake alkalinity generating processes neutralized ~58% of the total (terrestrial and atmospheric) H^+ input into the lake. Assimilation and denitrification of NO_3^-, SO_4^{2-} reduction, and photochemical and microbial decomposition of allochthonous organic matter were the most important aquatic proton-consuming processes, while hydrolysis of inorganic Al species was a dominant in-lake H^+ generating process. Nutrient loading of Plešné Lake (TP, 0.13 g.m^{-2}.yr^{-1}; Si, 14 g.m^{-2}.yr^{-1}; DOC, 86 g.m^{-2}.yr^{-1}) was three to fivefold higher than nutrient loading of Čertovo and Černé Lakes. Net in-lake removal of carbon, phosphorus, nitrogen, and silica in Plešné Lake varied between 34% and 51% of their input.

Key words: Acidification, nitrogen, sulfur, aluminum, base cations, pH, organic carbon, silica, phosphorus

INTRODUCTION

The limnological research of Plešné Lake (PL) was performed on a less frequent basis compare to the research of the two largest Bohemian Forest lakes, Černé (CN) and Čertovo (CT) before the 1980s. Except for the first limnological study by FRIČ (1873) and four samplings of water and biota by the HRBÁČEK's group in the 1959–1961 period (PROCHÁZKOVÁ & BLAŽKA 1999), there was only very limited information on PL composition, fauna, and flora available either in the form of published or unpublished data or personal communications. These data were first summarized by VESELÝ (1994) and recently amended by HEJZLAR & al. (1998).

Regular monitoring of PL chemistry started in 1984 (e.g. VESELÝ & al. 1998a, b). Results on irregular monitoring of PL zooplankton (mostly J. FOTT – pers. comm.) and phytoplankton are given by SCHMIDT & al. (1993) and summarized by VRBA & al. (1996, 2000). Bottom sediments of PL were first investigated by VESELÝ (1988) a then by SCHMIDT & al. (1993) for chemical composition (loss on ignition, metals), siliceous scales and cysts, and carbonaceous particles.

The rapid reversal of Central European lakes from acidification in the 1990s (e.g. Kopáček & al. 1998a) and higher nutrient concentrations in PL compared to other Bohemian Forest lakes (e.g. Vrba & al. 2000) has rapidly increased the scientific interest in PL and research of PL watershed-lake ecosystem has intensified. Hejzlar & al. (1998) performed the first detail limnological study of PL lake including water and sediment chemistry and biota. Kopáček & al. (2000a) have published the first coherent data on chemistry of atmospheric deposition, tributaries, and lake water and water-sediment interactions in the PL ecosystem. The spatial and temporal variability in chemistry of PL tributaries was studied by Kopáček & Hejzlar (1998) and Kopáček & al. (2000b). Nedbalová & Vrtiška (2000) studied the recent phytoplankton composition in PL and Bittl & al. (2001) and Vrba & al. (submitted) evaluated causes and effects of aluminum-induced phosphorus limitation of plankton on the structure of pelagic food webs. Borovec (2000) and Kopáček & al. (2000a) analyzed PL sediments for C, N, and P contents, estimated their phosphorus sorption characteristics, and determined individual P fractions. Anderson & al. (2000) have reported on the nutrient composition of terrestrial vegetation and soil N-cycling, and Veselý (1994) and Kopáček & al. (1998b) provided first data on bedrock and soil composition of PL watershed.

The aim of this paper is to quantify major fluxes of ions and nutrients within the PL watershed-lake ecosystem in the 2000 hydrological year and compare them to the fluxes within the CT and CN ecosystems (Kopáček & al. 2001a, b).

MATERIALS AND METHODS

Study site description

Plešné Lake is situated at 48°47' N, 13°52' E, and at an altitude of 1090 m a.s.l. The lake is of glacial origin, dimictic, and oligo- to mesotrophic, with anoxia in the hypolimnion during both winter and summer stratification periods. The lake area is 7.5 ha, volume of 6.17×10^5 m^3, and maximum depth of 18 m (Švambera 1939). The average water residence time is ~1 year (Kopáček & al. 2000a). The area of PL watershed is 66.6 ha (including lake) and is steep with the maximum local relief of 288 m. The bedrock is made up of granites and most of the watershed is covered with a thin layer of forest humus and iron containing acidic podzols (Veselý 1994, Kopáček & al. 1998b). Norway spruce (~150 years old) dominates the watershed vegetation and the forest covers >70% of the lake watershed. Details on land use history of the PL watershed and lake water chemistry and biology are given by Veselý (1994), Vrba & al. (1996), Hejzlar & al. (1998), and Kopáček & al. (2000a).

The lake was already acidified in the early 1960s, when pH values <5.4 were measured by Procházková & Blažka (1999). At present, the lake is fishless, macrozooplankton are sparse and consist of two crustacean species low in density, and the phytoplankton community is dominated by acid-tolerant species of green algae, dinoflagellates, and cyanobacteria (Hejzlar & al. 1998, Nedbalová & Vrtiška 2000). The lake water is low in base cations, the carbonate buffering system is depleted, and sulfate and nitrate are dominant anions (Veselý & al. 1998a, Hejzlar & al. 1998).

The lake has two surface tributaries (PL–I and PL–II). Tributary PL–III is subsurface but accessible in a small cave. Since the reconstruction of a dam in autumn 1999, the water level has slightly decreased compared to previous years and PL–III can be sampled at its inlet. Another subsurface tributary (PL–IV) was discovered in January 2000 and is accessible in a small artificial (0.5 m deep) well at present (Fig. 1). A calibrated weir was build ~15 m downstream from the lake outlet in October 1999 and the water discharge and temperature have been continuously monitored using a gauge-recorder (a part of an automatic weather station MS16; J. Fiedler, České Budějovice; readings in 15-minute intervals) since 24 July 2000.

Sampling and analyses

Atmospheric deposition was collected in bulk samplers protected against light and bird perching, and fitted with a 100-μm polyamide sieve to remove coarse particles. Samplers were situated within 400 m east of the lake (1) in the rocky area without trees (precipitation, 2 samplers, altitude ~1090 m a.s.l.), and (2) in the forest (throughfall, 9 samplers, altitude ~1130 m a.s.l.; Fig. 1). Samples were taken from 2 November 1999 to 31 October 2000. Rain was sampled in two-week intervals, and snow in two to three-week intervals. All samples from each site were combined to obtain an integrated sample.

Water samples from tributaries were taken in approximately monthly periods. Tributaries PL–I to III were sampled from 14 October 1999 to 30 November 2000, while sampling of PL–IV started on 27 January 2000. 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 subwatersheds containing several tributaries in close proximity (PL–I and PL–II; Fig. 1), an integrated sample was taken with sample volumes proportional to the discharge of the individual streams. Samples were immediately filtered through a 40-μm polyamide sieve to remove coarse particles.

Samples from the outlet were taken biweekly (weekly during snowmelt) between 11 October 1999 and 29 November 2000. The discharge from the lake was measured manually in 1 to 6-day intervals between 1 November 1999 and 24 July 2000 at a calibrated weir and then automatically in 15-minute intervals with the recording gauge. Water column profile (0.5, 5, 10, 13, and 17.5 m) was sampled at the deepest part of the lake on 6 September 1999 and 9 October 2000. The samples of lake water were immediately filtered through a 200-μm polyamide sieve.

Concentrations of acid neutralizing capacity (ANC), dissolved organic carbon (DOC) dissolved reactive P (DRP), total and dissolved P (TP and DP), total and dissolved organic N (TON and DON), dissolved reactive silica (Si), Ca^{2+}, Mg^{2+}, Na^+, K^+, NO_3^-, SO_4^{2-}, Cl^-, F^-, total Al (Al_T), organically bound Al (Al_o), ionic Al (Al_i), total Fe (Fe_T), organically bound Fe (Fe_o), and ionic Fe (Fe_i), pH, equivalent concentrations of Al_i and Fe_i (Al_i^{n+} and Fe_i^{m+}) and organic acid anions (R^-, $\mu eq.l^{-1}$) were obtained as described by KOPÁČEK & al. (2001a).

The reliability of analytical methods was checked by means of ionic balance control approach and the same standard sample as described by KOPÁČEK & al. (2001a). The average differences between the sum of the cations and the sum of the anions calculated for annual volume (or discharge) weighted means according to MOSELLO & al. (1995) were $<\pm 5\%$.

Mass balances

Mass balance of chemical constituents in the PL watershed and lake was calculated analogously to CT (KOPÁČEK & al. 2001a) with the following exceptions:

(1) Water level of PL varied only negligibly during the 2000 hydrological year and changes in its volume were neglected. Lake water composition at the beginning and end of the study was based on water composition on 6 September 1999 and 9 October 2000, respectively.

(2) Water balance was determined from annual heights of precipitation and throughfall and the budget for Cl^-. In this calculations we assumed that 30% and 70% of watershed area received atmospheric deposition in the form of precipitation and throughfall, 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 terrestrial export of elements to the lake was calculated from concentrations in the four tributaries as follows. First, the average composition of surface input was obtained as the VWM for tributaries PL–I and PL–II and the average composition of subsurface input was obtained as the arithmetical mean for tributaries PL–III and PL–IV. Second, the proportion of surface (r) and subsurface ($1\text{-}r$) tributaries in the total terrestrial water export to the lake was estimated from the balance for Ca^{2+} ions (equation 1) using the difference in Ca^{2+} concentrations in the subsurface and surface PL tributaries (see later):

$$rQ_{IN}C_{SUBSUR}+(1-r)Q_{IN}C_{SUR}+Q_PC_P+P_L=Q_{OUT}C_{OUT}+\Delta M_L \qquad (1)$$

Where Q_{IN}, Q_P, and Q_{OUT} (all in $m^3.yr^{-1}$) are water input into the lake from the watershed, direct atmospheric deposition on the lake surface (precipitation), and total water output from the lake, respectively. C_{SUBSUR}, C_{SUR}, C_P, and C_{OUT} (all in $kg.m^{-3}$) are concentrations of Ca^{2+} in subsurface and surface tributaries, precipitation, and in the lake output, respectively. P_L ($kg.yr^{-1}$) is a net retention of a Ca^{2+} in the lake sediments and ΔM_L ($kg.yr^{-1}$) is change in storage of Ca^{2+} in the lake during the mass balance period. The net retention of Ca^{2+} in sediment (20 $kg.yr^{-1}$) was estimated from the average mass accumulation rate in PL (85 $g.m^{-2}.yr^{-1}$) and the average concentration of Ca^{2+} in the uppermost sediment layer (3.1 $mg.g^{-1}$ of dry weight). The average mass accumulation rate was calculated from the average accumulation rate of sediment (5.3 $mm.yr^{-1}$) and the water content of the uppermost sediment layer (98.4%) in PL (SCHMIDT & al. 1993). The r value, obtained from equation (1), was 0.3, suggesting that ~30% of the terrestrial water export entered the lake via the subsurface tributaries.

Net terrestrial and aquatic production (or consumption) of protons and the contributions of individual constituents to these processes were estimated from budgets for ions, using the equation of electroneutrality. According to this approach, any increase in concentration of cations or decrease in concentration of anions are proton consuming processes. In contrast, any decrease in concentration of cations or increase in concentration of anions are proton producing reactions. For details see KOPÁČEK & al. (2000c).

The annual accumulation rate of C, P, N, Al, and Mg in sediments was estimated analogously to Ca.

RESULTS AND DISCUSSION

Chemical composition of atmospheric deposition, tributaries, and lake output

Annual precipitation level, measured at open area, was 1655 mm and throughfall amount was 22% lower in PL watershed in the 2000 hydrological year (Table 1). The annual volume weighted mean (VWM) concentration of ions in PL precipitation (122 $\mu eq.l^{-1}$) was 19% lower than in CT watershed (KOPÁČEK & al. 2001a) but with comparable average equivalent composition as follows: base cations (BC = sum of Ca^{2+}, Mg^{2+}, Na^+, and K^+) of 21%; H^+, 10%; NH_4^+, 19%; SO_4^{2-}, 18%; NO_3^-, 20%; Cl^-, 8%; and R^-, 3%). VWM concentration of ions in PL throughfall (304 $\mu eq.l^{-1}$) was 10% higher than in the CT watershed. The relative ionic composition of PL throughfall (BC, 30%; H^+, 9%; NH_4^+, 11%; SO_4^{2-}, 14%; NO_3^-, 19%; Cl^-, 5%; and R^-, 12%) differed from the composition of precipitation in a similar way as in the CT watershed. Horizontal deposition and canopy interactions were the dominant processes affecting the throughfall composition and are discussed in a more detail by KOPÁČEK & al. (2000c and 2001a). The canopy interactions affected also nutrient concentrations in atmospheric deposition. Throughfall concentrations of TP and organic N were threefold and concentrations of DOC and Si even one order of magnitude higher than in precipitation (Table 1). On the other hand, VWM concentrations of DRP were comparable (3 and 4 $\mu g.l^{-1}$) in precipitation and throughfall, respectively.

Table 1. – The VWM concentrations of the major constituents of atmospheric deposition (precipitation, Precip.; and throufgfall, TF), tributaries (PL–I to PL–IV), terrestrial transport (lake input via tributaries, PL_{IN}), lake output (PL_{OUT}) and lake water at the start (CT_{START}; 6 September 2000) and end (CT_{END}; 9 October 2000) of the study in the Plešné watershed-lake ecosystem. Number of observations, n; not determined, ND; not applicable, NA; pH averages were calculated from the average H^+ concentrations. Total dissolved solids (TDS) were calculated according to PITTER (1999) as the sum of molar concentrations of all dissolved mineral constituents. Data on TON in TF are based on 0.4-µm filtered samples.

		Precip.	TF	PL–I	PL–II	PL–III	PL–IV	PL_{IN}	PL_{OUT}	PL_{START}	PL_{END}
n		23	23	13	9	12	9	13	31	1	1
Height	mm	1655	1290	NA	NA	NA	NA	NA	NA	NA	NA
Q	l.s^{-1}	NA	NA	1.3	1.0	ND	ND	ND	22.9	NA	NA
pH		4.91	4.59	4.25	4.34	4.62	4.79	4.46	4.70	4.91	5.02
Ca^{2+}	mg.l^{-1}	0.18	0.63	0.62	0.58	1.23	1.60	0.90	0.83	0.83	0.80
Mg^{2+}	mg.l^{-1}	0.03	0.14	0.14	0.13	0.24	0.34	0.19	0.18	0.18	0.17
Na^+	mg.l^{-1}	0.22	0.38	1.19	1.06	1.25	1.26	1.16	0.94	1.05	1.06
K^+	mg.l^{-1}	0.17	1.26	0.34	0.29	0.41	0.44	0.35	0.34	0.35	0.34
NH_4–N	mg.l^{-1}	0.34	0.49	0.04	0.04	0.03	0.03	0.04	0.08	0.11	0.13
NO_3–N	mg.l^{-1}	0.34	0.79	0.74	0.72	1.14	1.21	0.89	0.44	0.23	0.17
SO_4^{2-}	mg.l^{-1}	1.05	2.10	4.41	3.89	5.34	6.67	4.81	4.49	4.74	4.24
Cl^-	mg.l^{-1}	0.32	0.50	0.48	0.39	0.45	0.45	0.44	0.45	0.40	0.43
F^-	mg.l^{-1}	0.004	0.012	0.03	0.04	0.07	0.11	0.06	0.06	0.08	0.09
DOC	mg.l^{-1}	0.8	9.0	11.1	8.8	3.6	1.5	7.0	3.9	3.9	3.7
TON	mg.l^{-1}	0.15	0.37	0.35	0.31	0.19	0.14	0.26	0.17	0.20	0.21
Si	mg.l^{-1}	0.002	0.07	4.05	3.61	4.19	4.05	3.88	2.49	2.65	2.71
TP	µg.l^{-1}	11.5	29.4	29.2	29.1	13.8	5.6	21.1	11.7	9.0	11.8
Al_T	µg.l^{-1}	6	15	822	742	770	720	756	518	451	475
Al_i	µg.l^{-1}	ND	ND	433	406	609	634	490	280	252	170
Al_o	µg.l^{-1}	ND	ND	390	333	142	56	256	124	95	125
Fe_T	µg.l^{-1}	ND	ND	141	102	46	13	86	83	109	134
Fe_i	µg.l^{-1}	ND	ND	47	42	20	0	30	22	42	53
Fe_o	µg.l^{-1}	ND	ND	92	58	22	10	52	34	37	33
ANC	µeq.l^{-1}	–12	–31	–66	–59	–26	–10	–44	–25	–22	4
TDS	µmol.l^{-1}	88	199	360	326	434	465	379	277	277	268

Chemical composition of tributaries differed from atmospheric deposition, having in general higher concentrations of Na^+, SO_4^{2-}, Si, and forms of Al and Fe. Concentrations of other water constituents in PL tributaries reflected their type. Surface tributaries had substantially higher concentrations of DOC, TON, TP (mostly DRP), Al_o and all Fe forms, while lower pH and concentrations of Ca^{2+}, Mg^{2+}, NO_3^-, SO_4^{2-}, Al_i, and ACN than subsurface tributaries (Table 1). The estimated VWM composition of terrestrial input into PL via all tributaries was 407 µeq.l^{-1} with the following average equivalent composition: BC, 29%; H^+, 10%; Al_i^{n+}, 11%; SO_4^{2-}, 24%; NO_3^-, 15%; Cl^-, 3%; and R^-, 7%. Contributions of NH_4^+ and F^- were <1%.

In contrast to other Bohemian Forest lakes, PL tributaries have one order of magnitude higher concentrations of TP and ~2-fold higher Si concentrations (VRBA & al. 2000) due primarily to its different bedrock composition (KOPÁČEK & al. 1998b). DRP represented ~80%

of TP in PL–I to III and ~55% in PL–IV. Moreover, significant relationship was observed between DRP and DOC concentrations in tributaries PL–I (P<0.05), PL–II (P<0.05) and PL–III (P<0.001). Similarly to tributaries of other Bohemian Forest lakes (KOPÁČEK & HEJZLAR 1998, KOPÁČEK & al. 2000b), concentrations of Al_o and Fe_o in tributaries PL–I to PL–III were correlated with DOC (P<0.01).

Water output from PL varied between <1.0 $l.s^{-1}$ (beginning of November 1999 and middle June 2000) and 256 $l.s^{-1}$ on 23 April, with the annual average of 19.4 $l.s^{-1}$. The annual VWM concentration of ions in PL output was 302 $\mu eq.l^{-1}$ (BC, 35%; H^+, 7%; Al_i^{n+}, 6%; NH_4^+, 2%; SO_4^{2-}, 31%; NO_3^-, 10%; Cl^-, 4%; and R^-, 4%). Compared to the input via tributaries, VWM composition of output had lower concentrations of total dissolved solids, H^+, NO_3^-, SO_4^{2-}, Al forms, TP, and Si but higher concentrations of NH_4^+ and ANC (Table 1). These differences were in part the result of (1) mixing of water from tributaries with precipitation, (2) in-lake assimilatory and dissimilatory processes, and (3) sedimentation. The importance of these processes was estimated using the mass budgets for individual water constituents and is discussed later in the text.
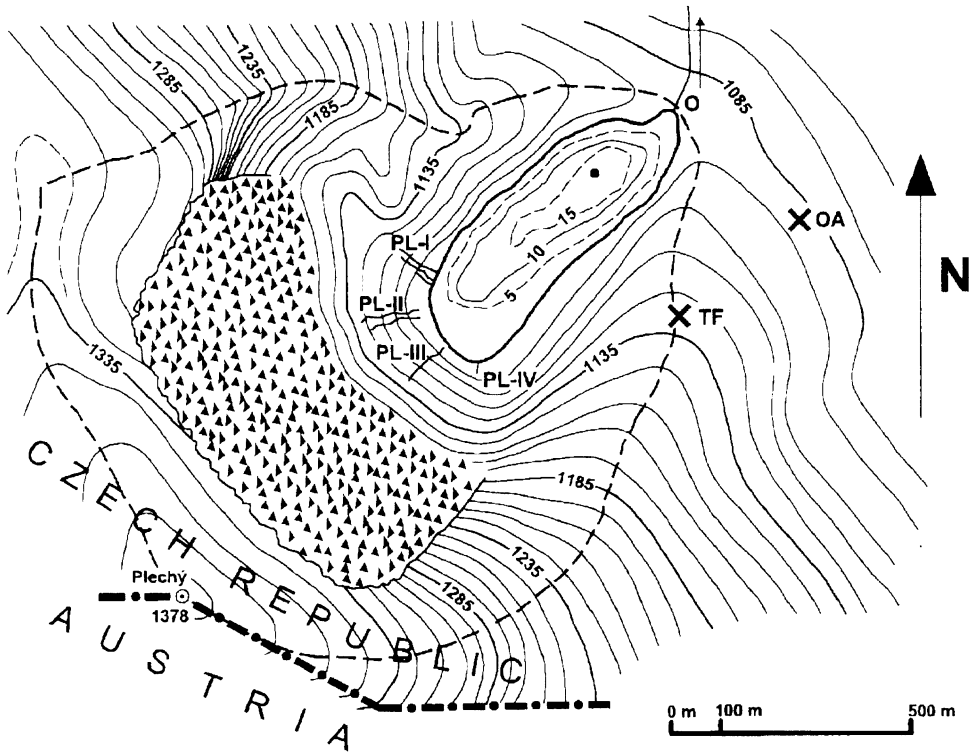

Fig. 1. – The map of the Plešné Lake watershed (solid dashed line) with the locations of sampling sites: (1) lake water, full circle at the maximum depth in the bathymetric map of the lake; (2) tributaries, PL–I to PL–IV, (3) outlet (O), and (4) precipitation samplers, solid crosses (OA, open area; TF,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

Seasonal variations in chemical composition of tributaries and lake water

Seasonal variations in physical and chemical variables are given in Fig. 2. Because the chemical composition of PL–I and PL–II was similar, only data on PL–I are shown. The chemistry of subsurface tributaries was similar for some water constituents and differed for others. In the former case, Fig. 2 shows only data on PL–III, while both data on PL–III and PL–IV are given in the later case.

Temperature of surface tributaries varied between 0.2 and 9.5°C, while temperature of subsurface tributaries was more stable (1–6°C in PL–III and 3–4.5°C in PL–IV). The temperature stratification of PL was not regularly measured during this study but probably developed characteristically for a dimictic temperate lake with the autumn and spring overturns as in the previous years (HEJZLAR & al. 1998, KOPÁČEK & al. 2000a). The autumn overturn probably occurred between 16 and 19 November, when temperature of the lake outlet decreased from 5.4 to 3.8°C (Fig. 2). Ice cover started to form on 19 November 1999 and lasted until 30 April 2000. Then, the temperature of lake outlet sharply increased and the lake mixed probably between 20 and 29 April 2000 (Fig. 2).

The chemical compositions of PL tributaries showed pronounced seasonal variations, with the most significant seasonal cycles in NO_3^-, Al_T, and Si concentrations. Higher NO_3^- concentrations during the dormant period resulted from lower terrestrial bio-consumption of inorganic N. This elevation of concentrations of strong acid anions in soil solutions led to the elevated Al leaching. The NO_3^- concentrations sharply decreased in summer, but still they were >300 μeq.l^{-1} and >800 μeq.l^{-1} in surface and subsurface tributaries, respectively, throughout the whole vegetation period (Fig. 2), suggesting a progressed stage of N-saturation of PL watershed according to STODDARD (1994). The seasonal variation in Si concentrations in tributaries PL–I and PL–II was inversely correlated with discharge (P<0.01). Similar relationships were characteristic also for CT and CN tributaries (KOPÁČEK & al. 2001a, b) and can be also expected in the PL subsurface tributaries (Fig. 2), the exact discharges of which are unknown. A sharp decrease in SO_4^{2-} and BC concentrations was observed in all tributaries in the early May during the final stage of snowmelt in the watershed. Most solutes in snow packs were already washed out during the beginning of snowmelt (JOHANNESSEN & HENRIKSEN 1978). The continuing melt of snow with depleted solutes resulted in dilution of baseflow and the lowering of ionic concentrations in tributaries (Fig. 2).

Similarly to CT and CN (KOPÁČEK & 2001a, b), the water composition of PL output was affected during snowmelt, when concentrations of SO_4^{2-}, BC, Al_T, and Si sharply decreased, as well as ANC and pH (Fig. 2). In contrast, concentrations of NH_4^+ in PL output peaked, due primarily to the release of NH_4^+ accumulated in snow on the ice-cover. Water output was highest during this period and, consequently, the elevated NH_4^+ output from the lake during snowmelt affected NH_4^+ balance in the lake, which was (similarly to CN, KOPÁČEK & al. 2001b) a net source of ammonium (see later).

The VWM concentration of ANC and pH in the PL output (–25 μeq.l^{-1} and 4.70, respectively) was lower than that of the CN output (–15 μeq.l^{-1} and 4.77, respectively). However, their seasonal variations were higher in PL. In summer, pH increased over 5 and ANC was positive in PL (Fig. 2). The higher alkalinity in PL output was probably associated with epilimnetic processes. Higher pH and ANC concentrations in the PL epilimnion compared to the upper hypolimnion are typical for the PL chemistry (e.g. HEJZLAR & al. 1998, KOPÁČEK & al. 2000a) and are associated with in-lake alkalinity generation in the euphotic zone due to high productivity and photochemical and microbial decomposition of allochthonous DOC (see later). Consequently, pH and ANC increased in the PL epilimnion in summer more than in the other two lakes studied. The positive ANC values in PL outlet during the most of sum-
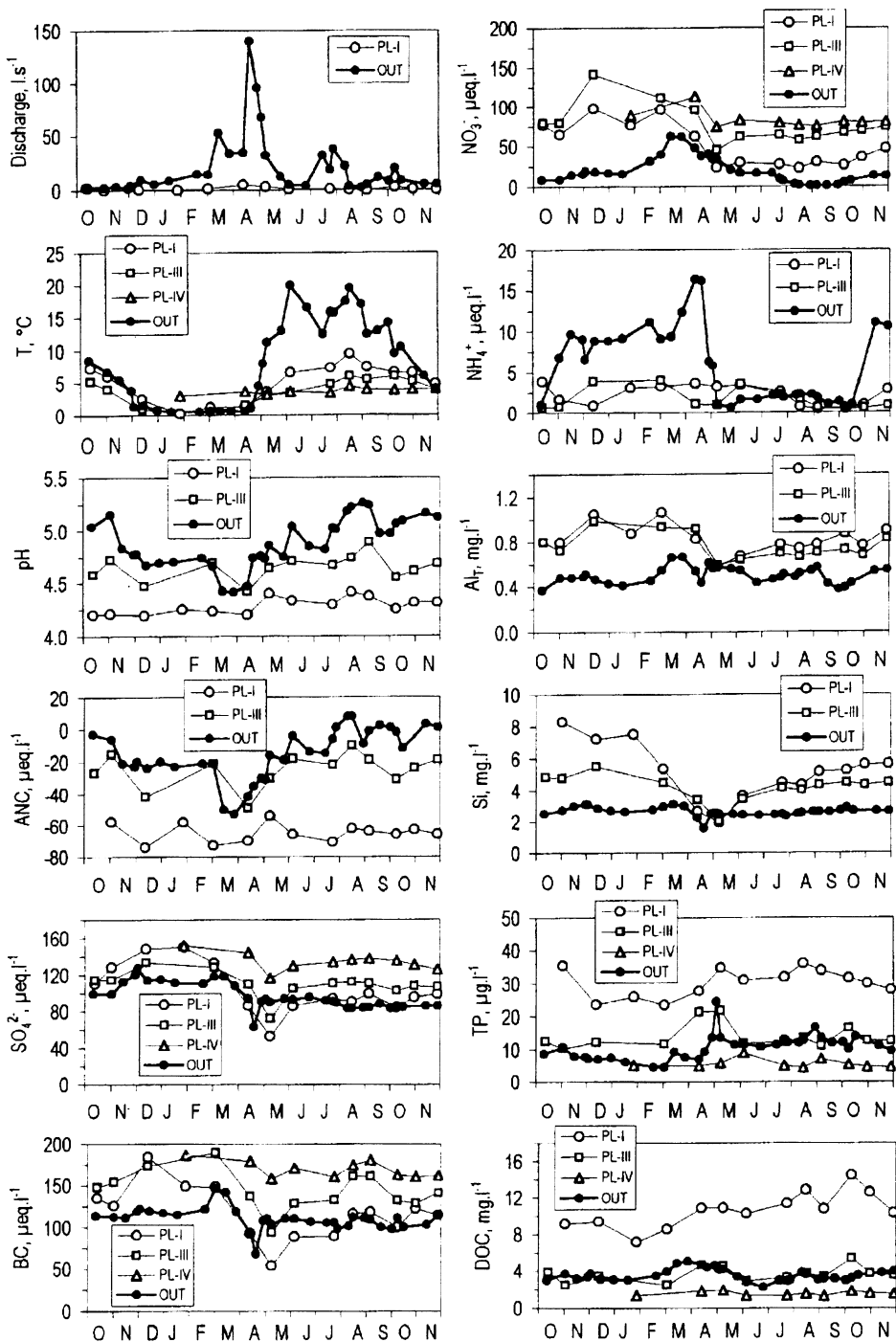
Fig. 2. – Seasonal patterns of discharge, temperature, pH and concentrations of major ions and nutrients in the Plešné Lake tributaries and the output in the 2000 hydrological year.

mer 2000 (Fig. 2) has been the first documented recovery of alkalinity in the strongly acidi-fied Bohemian Forest lakes after several decades of a depleted carbonate buffering system in their waters. This recovery was, however, primarily enabled by a reversal of chemistry of PL from atmospheric acidification due to a rapid decline in deposition of strong acid anions in the 1990s (VESELÝ & al. 1998a).

The variations in TP concentrations in PL outlet were associated (similarly to CT and CN; KOPÁČEK & al. 2001a, b) with ice-free periods (Fig. 2) when the direct atmospheric deposi-tion of P contributed to the total P supply of the lake (Table 1). However, this variation was less pronounced than in the other two lakes due to higher TP concentrations in PL tributaries.

A small peak in DOC concentrations in the PL output, which occurred in the late winter (Fig. 2) and was accompanied with elevated Al_o and Fe_o concentrations, was typical for all the lakes studied, and resulted probably from flushing of soils at the beginning of snowmelt (KOPÁČEK & al. 2001b).

Water, ionic, and nutrient fluxes within the Plešné watershed-lake ecosystem

Water input (deposition) into the ecosystem was 9.51×10^5 $m^3.yr^{-1}$ (8.27×10^5 $m^3.yr^{-1}$ on the forest floor and 1.24×10^5 $m^3.yr^{-1}$ on the lake surface). The other water fluxes within the PL watershed-lake ecosystem were estimated from the Cl^- budgets: Water outputs from the wa-tershed and lake were 8.14×10^5 and 8.42×10^5 $m^3.yr^{-1}$, respectively. Evaporation from the whole ecosystem was 24% of precipitation. Resulting average water residence time in PL was 267 days. The independently measured water output from the ecosystem at the calibrated weir was 25–30% lower than the water output estimated from the Cl^- budget. However, the dis-charge of the outlet had not been measured continuously until July, and occasional readings before that time could cause a significant underestimate of the real water flux, especially du-ring snowmelt.

The mass fluxes of major ions and nutrients in PL watershed are given in Table 2. Terres-trial exports of SO_4^{2-}, NO_3^-, H^+, Ca^{2+}, Mg^{2+}, Na^+, F^-, Si, DOC, and species of Al and Fe were higher than their deposition on the forest floor and only the depositions of NH_4^+ and K^+ were higher than their transport from the watershed soils. The total atmospheric input of H^+ into the PL watershed-lake ecosystem was 19 $keq.yr^{-1}$ (17 $keq.yr^{-1}$ on the forest floor and 2 $keq.yr^{-1}$ on the lake surface). The terrestrial production and consumption of protons were 103 and 84 $keq.yr^{-1}$, respectively. There were the following two major terrestrial sources of protons: (1) SO_4^{2-} release from soil (49%; 85 $meq.m^{-2}.yr^{-1}$) and (2) NH_4^+ assimilation and/or nitrification and NO_3^- release from the soil (37%; 62 $meq.m^{-2}.yr^{-1}$). In contrast, the release of Ca^{2+}, Mg^{2+}, and Na^+ (60%; 85 $meq.m^{-2}.yr^{-1}$) and Al_i^{n+} (39%; 56 $meq.m^{-2}.yr^{-1}$) were major ter-restrial proton sinks. The net release of H^+ from the terrestrial sources ranged between 17 $keq.yr^{-1}$ (29 $meq.m^{-2}.yr^{-1}$) as estimated from the budget for H^+ (based on pH measu-rements), and 19 $keq.yr^{-1}$, as calculated from the terrestrial sources and sinks of protons (Ta-ble 2).

Among the three watersheds studied in 2000, the PL watershed produced the least amount of protons and Al (KOPÁČEK & al. 2001a, b) due primarily to the following reasons: First, the PL watershed more effectively immobilized N and was a more pronounced net sink of dis-solved inorganic nitrogen (DIN = NO_3^- + NH_4^+). The PL soils retained nearly all NH_4^+ depo-sited on the forest floor (Table 2). The net terrestrial production of NO_3^- (22 $meq.m^{-2}.yr^{-1}$) rep-resented ~50% of the NH_4^+ retention and was ~2-fold and 4-fold lower than in the CT and CN watersheds, respectively (KOPÁČEK & al. 2001a, b). Consequently, the terrestrial export of NO_3^- (85 $meq.m^{-2}.yr^{-1}$) was lower than in the other two watersheds. At the comparable terres-trial export of SO_4^{2-}, the PL watershed was a significantly lower source of strong acid anions.

Table 2. – Mass balance of major ions and nutrients and net production of protons in Plešné watershed in the 2000 hydrological year. Release of cations and removal of anions are proton-consuming processes, while removal of cations and release of anions are proton-producing reactions. Negative values of production indicate net removal. Abbreviations: NA, not applicable; ND, not determined.

	Deposition on the forest floor		Watershed export		Net terrestrial production		H^+ source	H^+ sink
	$kg.yr^{-1}$	$g.m^{-2}.yr^{-1}$	$kg.yr^{-1}$	$g.m^{-2}.yr^{-1}$	$kg.yr^{-1}$	$g.m^{-2}.yr^{-1}$	$keq.yr^{-1}$	$keq.yr^{-1}$
H^+	17	0.03	34	0.06	17	0.03		
Ca^{2+}	391	0.66	689	1.17	298	0.50		15
Mg^{2+}	82	0.14	147	0.25	65	0.11		5
Na^+	265	0.45	953	1.61	688	1.16		30
K^+	721	1.22	286	0.48	−435	−0.74	11	
NH_4–N	360	0.61	31	0.05	−329	−0.56	24	
NO_3–N	519	0.88	704	1.19	185	0.31	13	
SO_4^{2-}	1429	2.42	3852	6.52	2423	4.10	50	
Cl	362	0.61	362	0.61	NA	NA		
F	7.6	0.01	42	0.07	35	0.06	2	
DOC	5068	8.57	6374	10.8	1306	2.21	2	
TON	222	0.38	229	0.39	7	0.01		
Si	36	0.06	3205	5.42	3170	5.36		
TP	19	0.03	19	0.03	0	0.00		
Al_T	10	0.02	631	1.07	621	1.05		33
Fe_T	ND	ND	78	0.13	78	0.13		1

Second, the watersheds differed in production of BC. The terrestrial production of Ca^{2+} in the PL watershed (25 $meq.m^{-2}.yr^{-1}$) was ~10-fold and 2-fold higher than that in CT and CN watersheds, respectively, and Na^+ production (51 $meq.m^{-2}.yr^{-1}$) was ~2-fold higher. In contrast, Mg^{2+} production (9 $meq.m^{-2}.yr^{-1}$) was ~4-fold lower in the PL watershed. These differences were in good concordance with the differences in the bedrock composition of the watersheds (KOPÁČEK & al. 1998b), as well as in the chemical composition of surface waters (KOPÁČEK & HEJZLAR 1998). The terrestrial retention of K^+ (originating mostly from canopy leaching; e.g. KOPÁČEK & al. 2001a) was comparable in all watersheds studied (19–23 $meq.m^{-2}.yr^{-1}$). Altogether, a net production of BC was higher in the PL than in CN and CT watersheds (66, 63, and 42 $meq.m^{-2}.yr^{-1}$, respectively).

Plešné Lake was a net sink of H^+, BC, NO_3^-, SO_4^{2-}, DOC, TP, Si, and Al and a net source of NH_4^+, TON, and Fe (Table 3). Total H^+ input into the lake (the sum of terrestrial export and direct atmospheric deposition on the lake surface) was 36 $keq.yr^{-1}$. The H^+ output from the lake was 17 $keq.yr^{-1}$ and the in-lake storage of H^+ decreased by 2 $keq.yr^{-1}$ (pH increased from 4.91 to 5.02) during the study (Table 1 and 3). The net in-lake H^+ reduction was 21 $keq.yr^{-1}$. Reductions in NO_3^-, SO_4^{2-}, and R^- concentrations were dominant alkalinity generating processes, accounting for 53%, 19%, and 26%, respectively, while the Al_i^{n+} hydrolysis was a major (63%) in-lake source of H^+ (Table 3).

Plešné Lake was a net sink for all nutrients, removing 48% of TP, 38% of TN, 51% of DOC, and 34% of Si inputs (Table 3). In-lake removal was higher than the average accumulation in sediments for N (400 vs. 220 $kg.yr^{-1}$), organic C (3307 vs. 2280 $kg.yr^{-1}$), and Mg (8 vs. 5 $kg.yr^{-1}$), while lower for TP (10 vs. 21 $kg.yr^{-1}$) and Al (181 vs. 252 $kg.yr^{-1}$). The dif-

Table 3. – Mass balance of major ions and nutrients and net production of protons in Plešné Lake in the 2000 hydrological year. The release of cations and removal of anions are proton-consuming processes, while the removal of cations and release of anions are proton-producing reactions. Negative values of production indicate a net removal. Abbreviations: NA, not applicable; ND, not determined; DAD, direct atmospheric deposition on the lake surface (precipitation). Total input into the lake is the sum of DAD and watershed export (Table 2).

	DAD	Total input	Change in storage	Output	Net production		H^+ source	H^+ sink
	$kg.yr^{-1}$	$kg.yr^{-1}$	$kg.yr^{-1}$	$kg.yr^{-1}$	$kg.yr^{-1}$	$g.m^{-2}.yr^{-1}$	$keq.yr^{-1}$	$keq.yr^{-1}$
H^+	1.5	36	−1.7	17	−21	−0.3		
Ca^{2+}	23	712	−19	698	NA	NA	1[1]	
Mg^{2+}	4	151	−8	151	−8	−0.1	1	
Na^+	27	981	7	793	−181	−2.4	8	
K^+	22	308	−6	290	−23	−0.3	1	
NH_4-N	42	73	14	67	8	0.1		1
NO_3-N	42	746	−38	368	−415	−5.5		30
SO_4^{2-}	131	3983	−312	3781	−514	−6.9		11
Cl	40	402	22	380	NA	NA		
F	0.5	43	0.0	54	11	0.1	1	
DOC	104	6477	−146	3316	−3307	−44.1		14
TON	14	243	−17	266	6	0.1		
Si	0.2	3206	35	2093	−1077	−14.4		
TP	1.4	20	1.7	9	−10	−0.1		
Al_t	0.8	632	15	436	−181	−2.4		
Al_i	ND	392	−50	236	−206	−2.8	20	
Al_o	ND	232	18	105	−109	−1.5		
Fe_t	ND	78	15	70	7	0.1		
Fe_i	ND	28	7	18	−2	−0.03		−0.1
Fe_o	ND	48	−3	28	−22	−0.30		

[1]Estimated from a net retention of Ca^{2+} in sediment.

ference between the in-lake removal of N and N burial in sediments was a rough estimate of net denitrification rate (170 mmol.m^{-2}.yr^{-1}), which was ~30% lower than in the two other Bohemian Forest lakes in this study (KOPÁČEK & al. 2001a, b). The average burial of TP in sediments was lower than the in-lake TP retention by 11 kg.yr^{-1}. This difference was similar to CT and CN (KOPÁČEK & al. 2001a, b) and suggested the same additional TP sources for the Bohemian Forest lakes (needles, dust, overflow), which are discussed in a more detail in part I of this study (KOPÁČEK & al. 2001a).

Among the lakes studied, PL was the most effective sink for nutrients supplied by terrestrial sources and precipitation. The PL retained nearly one order of magnitude more TP (0.13 g.m^{-2}.yr^{-1}) and ~3-fold more Si (14 g.m^{-2}.yr^{-1}) than CT and CN. These differences were due primarily to the higher productivity of PL (VRBA & al. 1996, 2000), resulting from ~5-fold higher P loading from terrestrial and atmospheric sources compared to the two other lakes (0.27 vs. ~0.05–0.06 g.m^{-2}.yr^{-1}). However, in-lake reduction in NO_3 (396 meq.m^{-2}.yr^{-1}) was only ~15% higher in PL than in CT and CN and the SO_4^{2-} reduction (143 meq.m^{-2}.yr^{-1}) was even lower there than in CT and CN (KOPÁČEK & al. 2001a, b). This disproportion can prob-

ably be explained by a lower NO_3^- loading of PL compared to CT and CN (710 vs. 940–960 meq.m^{-2}.yr^{-1}) and by the formation of anoxia in the PL hypolimnion. The hypolimnetic anoxia was shown to lead to a pronounced dissimilatory reduction of NO_3^- and SO_4^{2-} and to a significant decline in their concentrations above the PL bottom (HEJZLAR & al. 1998, KOPÁČEK & al. 2000a). The low concentrations of NO_3^- and SO_4^{2-} represent a low concentration gradient across the water-sediment interface, and, consequently, a lower diffusion flux and reduction in the sediments (KELLY & al. 1987). Thus, the internal alkalinity generation, resulting from the dissimilatory reduction of strong acid anions in the water column and sediments, was surprisingly comparable in all three lakes studied (480–550 meq.m^{-2}.yr^{-1}) despite differences in their nutrient loading, water residence times, and a different intensity of epilimnetic processes.

On the other hand, the in-lake alkalinity generation by the photochemical and microbial decomposition of allochthonous organic matter was by far the highest in PL out of all the lakes studied. The reason behind that was the higher DOC loading. The highest and lowest in-lake reduction in R$^-$ flux (190 and 56 meq.m^{-2}.yr^{-1}) was in PL and CN, respectively, with DOC loading of 86 and 35 g.m^{-2}.yr^{-1}.

CONCLUSIONS

The total atmospheric input of H$^+$ into PL watershed-lake ecosystem was 19 keq.yr^{-1} in the 2000 hydrological year. The output of H$^+$ from the lake was 17 keq.yr^{-1}. Thus, the watershed-lake ecosystem was a net sink of ~2 keq.yr^{-1} of H$^+$. The watershed was a net source of H$^+$ (29 meq.m^{-2}.yr^{-1}) with NH_4^+ retention and NO_3^- and SO_4^{2-} release from soils as the most pronounced terrestrial proton-generating process and with BC and Al_i^{n+} leaching as the principal proton consuming processes. The lake was a net sink of H$^+$ (21 keq.yr^{-1}; 278 meq.m^{-2}.yr^{-1}), with assimilation and denitrification of NO_3^- (396 meq.m^{-2}.yr^{-1}), photochemical and microbial decomposition of allochthonous organic matter (190 meq.m^{-2}.yr^{-1}) and reduction of SO_4^{2-} (143 meq.m^{-2}.yr^{-1}) being the most important aquatic proton-consuming processes. Hydrolysis of Al_i^{n+} was a dominant aquatic source of H$^+$ (273 meq.m^{-2}.yr^{-1}).

Terrestrial sources dominated a total input of NO_3^-, TON, DOC, TP, DRP, and Si into the lake, while direct atmospheric deposition on the lake surface was a major allochthonous source of NH_4^+. The lake was a net sink for all nutrients, removing 48% of TP, 38% of TN, 51% of DOC, and 34% of Si supplied by both terrestrial and atmospheric sources.

The watershed of PL produced more BC and less Al_i^{n+} per square meter of its area than the CT and CN watersheds. Plešné Lake had the highest loading of TP, DOC, and Si and the highest in-lake retention of TP, NO_3^-, DOC, and Si per its area among the three lakes studied.

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