

Element Budgets in three Bohemian Forest lakes and their watersheds in the 2000 hydrological year: I. Čertovo Lake

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Abstract

Fluxes of major ions and nutrients and seasonal variations in their concentrations were measured within watershed-lake ecosystems of Čertovo, Černé, and Plešné Lakes from November 1999 to November 2000. This part provides results on Čertovo Lake. 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 577 days and evaporation was 18% of precipitation height (1625 mm). The Čertovo watershed was a net source of SO_4^{2-} , NO_3^- , H^+ , Ca^{2+} , Mg^{2+} , Na^+ , Si, Al, and Fe and a net sink for NH_4^+ , K^+ , DOC, TON, and TP compared to their deposition on the forest floor. Net terrestrial production of acidity was dominated by SO_4^{2-} release from soils ($89 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$) and high watershed export of NO_3^- ($122 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$). Ionic composition of tributaries showed seasonal variations with the most pronounced changes in NO_3^- , base cations and Al concentrations. Compared to the composition of tributaries, the lake output was affected by (1) direct atmospheric deposition on the lake surface, (2) chemical and biological in-lake processes, and (3) sedimentation and/or element release from sediments. Internal alkalinity generating processes neutralized ~50% of the total (terrestrial and atmospheric) H^+ input into the lake. Denitrification, sulfate 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 the dominant in-lake H^+ generating process. The net nutrient retention (carbon, phosphorus, nitrogen, and silica) and removal (carbon and nitrogen) in the lake varied between 24% and 37% of their input.

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

INTRODUCTION

Extremely high emissions of sulfur and nitrogen compounds in Central Europe (both ~280 $\text{mmol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$) have declined by ~70% and ~35%, respectively, during the last decade (KOPÁČEK & al., in press). Parallel decreases in deposition rates of SO_4^{2-} , NO_3^- , and NH_4^+ have resulted in a rapid improvement of water quality in acidified mountain lakes in the adjacent areas (e.g., VESELY & al. 1998a, b, KOPÁČEK & al. 1998a, STODDARD & al. 1999).

Artificial recovery experiments based on exclusion of acid precipitation by the means of roofs (e.g. WRIGHT & al. 1993, HULTBERG & al. 1998, GUNDERSEN & al. 1998) have shown that recovery process may occur in two stages: (1) Relatively rapid improvement of waters in the first years after reduction in acid deposition and (2) longer and slower recovery of waters associated with soil recovery. Similarly to the 1st stage, recent changes in water chemistry of the Bohemian Forest lakes have corresponded closely to changes in S and N deposition (KO-

PÁČEK & al. 1998a). However, these changes have been more or less delayed to changes in S and N deposition (KOPÁČEK & al., in press). Besides the reduction in deposition of acidifying pollutants, recovery of atmospherically acidified regions depends on watershed processes like sulfate desorption, organic S cycling in soils (WRIGHT & HAUHS 1991, NOVÁK & al. 1996, TORSSANDER & MÖRTH 1998), and factors affecting N cycling in watershed (e.g., DISE & WRIGHT 1995). Consequently, the extent and rapidity of the ongoing recovery of the Bohemian Forest lakes will depend on the fate of S deposited in soils and factors affecting terrestrial N cycling. A quantification of these processes deserves studies of element fluxes within the whole watershed-lake ecosystem.

The first mass balance of a watershed-lake ecosystem in the Bohemian Forest was performed in the 1998 hydrological year (Čertovo Lake; KOPÁČEK & al. 2000a). This study quantified fluxes of ions to estimate the major sources and sinks of protons within the ecosystem. The aim of this study is to quantify the major terrestrial and aquatic sources and sinks of water constituents in three Bohemian Forest watershed-lake ecosystems differing in acidity, phosphorus loading, and ability to assimilate nitrogen. Using annual fluxes of major elements in precipitation, throughfall, tributaries, and output from the lake we calculate here mass balances for major ions and nutrients to quantify their sinks and sources within the watershed and lake during their transport throughout the ecosystem. In this part (I) we provide data on Čertovo Lake in the 2000 hydrological year and compare them to similar datasets from Černé Lake (part II; KOPÁČEK & al. 2001a) and Plešné Lake (part III; KOPÁČEK & al. 2001b).

MATERIALS AND METHODS

Study site description

Čertovo Lake (CT), situated at 49°10' N, 13°12' E, and at the altitude of 1028 m a.s.l., is a dimictic, oligotrophic lake with the following morphological characteristics: area, 10.5 ha; volume, 1.852×10^6 m³; maximum depth, 36 m; mean depth, 17.9 m; watershed area including lake, 87.5 ha (ŠVAMBERA 1939); and theoretical water residence time, ~570 days (KOPÁČEK & al. 2000a). The lake is surrounded by steep forested rocky slopes with the maximum local relief of 315 m. The bedrock is made up of mica-schist (muscovitic gneiss), quartzite, and small amounts of pegmatite (VESELÝ 1994). Soils are acidic podzols in different stage of development and/or cambisol (average depth of ~0.6 m) with unsaturated sorption complex (VESELÝ & al. 1993, J. KOPÁČEK – unpubl.). Norway spruce (80–140 years old) dominates the watershed vegetation. Details on land use history of CT watershed and lake water chemistry and biology are given in VESELÝ & al. (1993), FOTT & al. (1994), VESELÝ (1994), VRBA & al. (1996), and KOPÁČEK & al. (2000a).

The lake has seven surface tributaries (CT–I to CT–VII; KOPÁČEK & al. 2000a); CT–V was temporal and the others were perennial in 2000. CT–II was the major tributary, representing 43–71% of the total water input by surface tributaries.

Sampling and analyses

Atmospheric deposition was collected at three sites (for their location see HRUŠKA & al. 2000 or KOPÁČEK & al. 2000a). Two sites were situated in the forest (throughfall, 9 samplers each) at altitudes of 1045 m a.s.l. (TF–1) and 1330 m a.s.l. (TF–2), and one site was in the open area without trees (precipitation, 2 samplers, altitude of 1175 m a.s.l.). Samples were taken from 11 November 1999 to 14 November 2000. Rain was sampled in two-week intervals, and snow in three to five-week intervals. All samples from each site were combined to obtain an integrated sample.

Samples from tributaries and outlet were taken monthly and biweekly, respectively, between 11 October 1999 and 11 December 2000. Discharges of tributaries were estimated using a method of stop-watch and bucket. Samples were immediately filtered through a 40- μm polyamide sieve to remove coarse particles. Each sample was analyzed separately and chemical inputs to the lake were calculated from volume-weighted mean concentrations for the seven tributaries. A discharge of outlet was measured with a recording gauge situated ~ 150 m downstream of the lake outflow. Samples of lake water were taken monthly at the deepest part of the lake from the surface (0.5 m) and bottom (~ 33 m; 0.5 m above sediment). Unfavorable conditions (~ 2 -cm thin ice) did not allow us to sample deep water layers in November 1999. Instead, water column profile (0.5, 10, 20, 28, and 33 m) was sampled on 12 January 2000 and before end of the study on 16 October 2000. 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 organic matter, and dissolved Al, Fe, and P and organic N forms. 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, Schimadzu), ANC (Gran titration), pH, dissolved reactive P (DRP, molybdate method, MURPHY & RILEY 1962), NH_4^+ (rubazoic acid method; KOPÁČEK & 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 KOPÁČEK & HEJZLAR (1993), but larger amounts of sample were evaporated to obtain a detection limit of P ~ 0.5 $\mu\text{g}\cdot\text{l}^{-1}$. Total and dissolved organic N (TON and DON; Kjeldahl digestion according to PROCHÁZKOVÁ 1960) and dissolved reactive silica (Si; molybdate method) were determined within one week after sampling. 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. Particulate organic carbon (PC) was analyzed with a TOC 5000A analyzer (Schimadzu) by combustion of the glass-fibre filter (MN-5; pore size of 0.4 μm ; Macherey Nagel) with the retained particulate organic matter.

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 concentrations of total Fe (Fe_T), dissolved Fe (Fe_D), and organically bound Fe (Fe_O) were analyzed by the thiocyanate colorimetric method after sample evaporation and digestion with perchloric acid (HEJZLAR & KOPÁČEK 1998). Fe_O was analyzed after the ion-exchange procedure in the subsamples used for Al_O determination. The concentration of ionic Fe (Fe_I) was the difference between Fe_D and Fe_O . Equivalent concentrations of Al_I and Fe_I (Al_I^{n+} and Fe_I^{m+}) 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 hydroxocomplexes, respectively, at the sample pH (KOPÁČEK & al. 2000b).

The reliability of analytical methods was checked by means of a standard sample (frozen subsamples of water mixed from all CT tributaries) which was assayed with each series of samples. Mean \pm standard deviations of 17 replications were: pH, 4.35 ± 0.06 ; Ca^{2+} , 0.51 ± 0.05 $\text{mg}\cdot\text{l}^{-1}$; Mg^{2+} , 0.46 ± 0.04 $\text{mg}\cdot\text{l}^{-1}$; Na^+ , 1.10 ± 0.08 $\text{mg}\cdot\text{l}^{-1}$; K^+ , 0.32 ± 0.07 $\text{mg}\cdot\text{l}^{-1}$; $\text{NH}_4\text{-N}$, 35 ± 2 $\mu\text{g}\cdot\text{l}^{-1}$; $\text{NO}_3\text{-N}$, 0.60 ± 0.03 $\text{mg}\cdot\text{l}^{-1}$; SO_4^{2-} , 5.62 ± 0.15 $\text{mg}\cdot\text{l}^{-1}$; Cl^- , 0.82 ± 0.03 $\text{mg}\cdot\text{l}^{-1}$; F^- ,

0.03±0.01 mg.l⁻¹; DOC, 3.50±0.12 mg.l⁻¹; TP, 2.88±0.06 µg.l⁻¹; Si, 2.14±0.02 mg.l⁻¹; DON, 0.43±0.02 mg.l⁻¹; Al_p, 0.48±0.03 mg.l⁻¹; and Fe_p, 0.08±0.01 mg.l⁻¹. Moreover, the correctness of analyses was checked using ionic balance control. The concentrations of organic acid anions (R⁻, µeq.l⁻¹) in the balance were obtained independently of the other ions. The R⁻ concentrations in tributaries were estimated according to KOPÁČEK & al. (2000b). The OLIVER & al. (1983) model and a coefficient of 3 and 4 µeq per mg DOC were used to estimate R⁻ concentrations in the lake output and in precipitation (and throughfall), respectively (KOPÁČEK & al. 2000a). 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 5% for precipitation and <±3% for TF-1, TF-2, tributaries, output, and lake water.

Mass balances

Mass balance of chemical constituents in the watershed and lake was calculated according to the equation (1) and the equation (2), respectively:

$$Q_{DEP}C_{DEP} + P_W = Q_{IN}C_{IN} \quad (1)$$

$$Q_{IN}C_{IN} + Q_P C_P + P_L = Q_{OUT} + \Delta M_L \quad (2)$$

Where Q_{DEP} , Q_{IN} , Q_P , and Q_{OUT} (all in m³.yr⁻¹) are total atmospheric deposition of water on the forest floor, water input into the lake from its watershed, direct atmospheric deposition on lake surface, and total water output from the lake, respectively. C_{DEP} , C_{IN} , C_P , and C_{OUT} (all in kg.m⁻³) are annual volume weighted mean (VWM) concentrations of a constituent in the atmospheric deposition on the forest floor, in tributaries, in direct atmospheric deposition on the lake surface, and in the lake output, respectively. P_W and P_L (both in kg.yr⁻¹) are the net mass production (when positive) or retention (when negative) of a constituent in the watershed and lake, respectively. ΔM_L (kg.yr⁻¹) is change in storage of a constituent in the lake. An analogous change in storage of a constituent in watershed was assumed to be negligible in a one-year balance and was neglected in equation (1). ΔM_L was obtained as the difference between element amounts in the lake on 16 October and 12 January 2000, which were calculated by linking concentration data for the individual water layers of the lake with their corresponding volumes.

Water balance was determined from the annual heights of precipitation and throughfall and the budget for Cl⁻ assuming that (1) Cl⁻ behaved conservatively with no net retention or production within the whole ecosystem, (2) 20% and 80% of watershed area received atmospheric deposition in the form of precipitation and throughfall, respectively, and (3) 30% and 70% of throughfall deposition were comparable to that at sites TF-1 and TF-2, respectively. The total water input into the lake was the sum of Q_{IN} and Q_P . Q_{IN} was calculated from equation (1) and VWM concentrations of Cl⁻ in the atmospheric deposition and tributaries and neglecting P_W of Cl⁻. Q_{OUT} was calculated from equation (2) using the annual VWM concentrations of Cl⁻ in tributaries, precipitation, lake outflow, change in storage of Cl⁻ in the lake during mass budget period, and neglecting P_L of Cl⁻. The VWM concentrations of Cl⁻ (and also other elements) were calculated as follows: (1) Annual volume- and period-weighted mean composition of tributaries was determined using the compositions and discharges of all tributaries and lengths of periods between the individual samplings. (2) The annual VWM composition of water output from the lake was calculated by linking continuously monitored discharge data of the outlet with the corresponding biweekly concentration data by the method of period-weighted mean. (3) The annual VWM composition of the atmospheric deposition on the forest floor was calculated from the heights and VWM compositions of precipitation and throughfall.

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 on mass budget calculations, see KOPÁČEK & al. (2000a).

The annual accumulation rate of C, P, N, Ca, Mg, Al, and Fe in sediments was estimated from mass accumulation rate ($53 \text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$; VESELY & al. 1993) and their concentrations in the uppermost 1-cm layer. The deepest sediments of the lake were collected using a gravity corer in October 1996 and November 1998 and were analyzed as described by KOPÁČEK & al. (2000c).

RESULTS AND DISCUSSION

Chemical composition of atmospheric deposition, tributaries, and lake output

Annual precipitation height measured at open area was 1625 mm in CT watershed in the 2000 hydrological year (Table 1). The amount of throughfall was ~10% higher in the upper part of the watershed (TF-2) and ~20% lower at the lake elevation (TF-1). This difference is in concordance with the data from previous years (HRUŠKA & al. 2000), suggesting higher horizontal deposition in the upper part of watershed and loss of water due to evaporation from canopies at throughfall sites. The annual VWM compositions of TF-1 and TF-2 were well comparable but differed importantly from precipitation (Table 1). The annual VWM concentration of ions in precipitation was $150 \mu\text{eq}\cdot\text{l}^{-1}$ with the following average equivalent composition: base cations (BC = sum of Ca^{2+} , Mg^{2+} , Na^{+} and K^{+}), 23%; H^{+} , 8%; NH_4^{+} , 19%; SO_4^{2-} , 21%; NO_3^{-} , 19%; Cl^{-} , 6%; and R^{-} , 3%. In contrast, the average ionic concentrations in throughfall was nearly twofold higher ($275 \mu\text{eq}\cdot\text{l}^{-1}$) and differed in relative composition (BC, 30%; H^{+} , 8%; NH_4^{+} , 12%; SO_4^{2-} , 17%; NO_3^{-} , 17%; Cl^{-} , 6%; and R^{-} , 9%). The concentrations of conservative ions with negligible exchange in canopies (Na^{+} , Cl^{-} , and SO_4^{2-}) were ~1.8 to 1.9 fold higher in throughfall than in precipitation. However, the throughfall concentrations of Mg^{2+} and K^{+} were increased by canopy leaching and were 3–4 fold higher. In contrast, the NH_4^{+} and NO_3^{-} concentrations were negatively affected by canopy interactions, being only 1.2 and 1.5 fold higher, respectively, in throughfall than in precipitation. The involved canopy processes and their consequence for throughfall composition have been discussed e.g. by LOVETT (1992), DISE & al. (1998) and KOPÁČEK & al. (2000a).

The canopy interactions affected also nutrient concentrations in atmospheric deposition. The throughfall concentrations of TP and organic N were twofold, the concentrations of Si fourfold, and DOC even sevenfold higher than in precipitation (Table 1). On the other hand, the VWM concentrations of DRP were comparable ($\sim 7 \mu\text{g}\cdot\text{l}^{-1}$) in both precipitation and throughfall.

The average discharge of CT tributaries varied from 0.8 to $14 \text{ l}\cdot\text{s}^{-1}$ and the average surface input was $27 \text{ l}\cdot\text{s}^{-1}$ (Table 1). The annual VWM concentration of ions in CT input via all tributaries was $408 \mu\text{eq}\cdot\text{l}^{-1}$ with the following average equivalent composition: BC, 25%; H^{+} , 13%; $\text{Al}_1^{\text{p}+}$, 11%; SO_4^{2-} , 24%; NO_3^{-} , 18%; Cl^{-} , 4%; and R^{-} , 4%. Compared to the throughfall, relative contribution of $\text{Al}_1^{\text{p}+}$, H^{+} , and SO_4^{2-} to the total ionic pool of CT input increased, while NH_4^{+} was retained in soils. All tributaries were more acidic than throughfall with the annual VWM pH between 4.15 and 4.51 and had higher concentrations of SO_4^{2-} and NO_3^{-} (Table 1). All tributaries had lower concentrations of DOC, TP, and TON than throughfall and DRP was always below the detection limit of $1 \mu\text{g}\cdot\text{l}^{-1}$.

Table 1. – The VWM concentrations of the major constituents of atmospheric deposition (precipitation, Precip.; throughfall, TF–1 and TF–2), tributaries (CT–1 to CT–VII), terrestrial transport (lake input via tributaries, CT_{IN}), lake output (CT_{OUT}) and lake water at the start (CT_{START}; 12 January 2000) and end (CT_{END}; 16 October 2000) of the Certovo 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 PRITZER (1999) as the sum of molar concentrations of all dissolved mineral constituents. Data on TON in TF–1 and TF–2 are based on 0.4- μ m filtered samples.

	Precip.	TF–1	TF–2	CT–1	CT–II	CT–III	CT–IV	CT–V	CT–VI	CT–VII	CT _{IN}	CT _{OUT}	CT _{START}	CT _{END}
n	17	17	17	13	13	13	13	10	13	13	13	36	1	1
Height	mm	1300	1749	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Q	l.s ⁻¹	NA	NA	0.8	14.0	1.7	3.8	0.9	2.7	3.2	27.0	38.3	NA	NA
pH	mg.l ⁻¹	4.89	4.69	4.32	4.29	4.15	4.18	4.21	4.51	4.51	4.27	4.42	4.62	4.69
Ca ²⁺	mg.l ⁻¹	0.28	0.55	0.54	0.49	0.43	0.43	0.45	0.71	0.69	0.53	0.49	0.50	0.51
Mg ²⁺	mg.l ⁻¹	0.04	0.13	0.13	0.37	0.33	0.32	0.35	0.50	0.43	0.38	0.33	0.35	0.34
Na ⁺	mg.l ⁻¹	0.26	0.33	0.46	0.83	0.78	0.68	0.69	1.04	1.01	0.81	0.75	0.70	0.70
K ⁺	mg.l ⁻¹	0.25	1.09	1.05	0.35	0.33	0.29	0.32	0.35	0.41	0.35	0.36	0.29	0.39
NH ₄ -N	mg.l ⁻¹	0.40	0.41	0.47	0.03	0.02	0.03	0.03	0.02	0.03	0.03	0.05	0.10	0.12
NO ₃ -N	mg.l ⁻¹	0.44	0.65	0.65	0.69	1.10	1.07	1.09	1.01	0.92	1.05	0.78	0.47	0.45
SO ₄ ²⁻	mg.l ⁻¹	1.34	1.98	2.40	5.01	4.59	5.34	4.84	5.80	4.65	4.83	4.72	5.11	4.84
Cl ⁻	mg.l ⁻¹	0.33	0.54	0.64	0.56	0.49	0.45	0.51	0.62	0.59	0.55	0.58	0.58	0.62
F ⁻	mg.l ⁻¹	0.003	0.01	0.01	0.04	0.02	0.02	0.02	0.03	0.02	0.02	0.03	0.02	0.05
DOC	mg.l ⁻¹	1.0	5.9	6.6	3.8	4.7	5.6	5.8	1.8	2.3	4.3	3.0	2.5	2.4
TON	mg.l ⁻¹	0.15	0.30	0.33	0.20	0.26	0.31	0.27	0.13	0.17	0.23	0.23	0.23	0.23
Si	mg.l ⁻¹	0.01	0.04	0.05	2.06	1.90	1.81	1.53	2.32	2.45	1.95	1.59	1.62	1.59
TP	μ g.l ⁻¹	15.0	30.1	30.8	4.1	3.0	3.3	2.6	2.1	2.6	2.8	3.5	2.6	2.6
Al _T	μ g.l ⁻¹	7	8	11	351	655	692	661	711	642	624	553	553	524
Al _I	μ g.l ⁻¹	ND	ND	ND	242	494	480	454	547	560	472	459	455	439
Al ₀	μ g.l ⁻¹	ND	ND	ND	111	165	204	164	71	89	152	74	44	44
Fe _T	μ g.l ⁻¹	ND	ND	ND	151	133	130	147	103	33	113	122	139	230
Fe _I	μ g.l ⁻¹	ND	ND	ND	<5	27	<5	<5	<5	<5	55	51	36	36
Fe ₀	μ g.l ⁻¹	ND	ND	ND	82	60	72	48	12	21	54	48	44	127
ANC	μ eq.l ⁻¹	-12	-20	-26	-60	-64	-68	-68	-35	-36	-58	-47	-27	-21
TDS	μ mol.l ⁻¹	110	175	191	277	302	291	275	349	324	305	268	251	252

Discharge of CT outlet varied between 4.5 l.s⁻¹ in summer (second half of June) and 277 l.s⁻¹ during snowmelt (22 April 2000) with the annual average of 38 l.s⁻¹. The annual VWM concentration of ions in CT output was 360 µeq.l⁻¹ (BC, 26%; H⁺, 11%; Al_i³⁺, 13%; SO₄²⁻, 27%; NO₃⁻, 16%; Cl⁻, 5%; and R⁻, 1.5%). Compared to the input, the VWM composition of output had lower concentrations of total dissolved solids, H⁺, NO₃⁻, SO₄²⁻, Al forms, and Si but higher concentrations of NH₄⁺, TP, and ANC (Table 1). These differences were in part the reason of (1) mixing of water from tributaries with water from direct atmospheric deposition on the lake surface (precipitation), (2) in-lake (assimilatory and dissimilatory) processes, and (3) transport across the sediment-water interface. The importance of these processes was estimated using the mass budgets for individual water constituents and is discussed later in the text.

Seasonal variations in chemical composition of tributaries and lake water

Temperature stratification of the lake developed characteristically for a dimictic temperate lake but both the autumn and spring overturns (in November and April, respectively) were not complete and bottom layers below ~25 m were not mixed (Fig. 1). The reason was a very a short lake water cooling period in autumn and heating in spring. The water temperature of outflow decreased from 5 to 3°C rapidly between 10 and 16 November (the lake mixed at

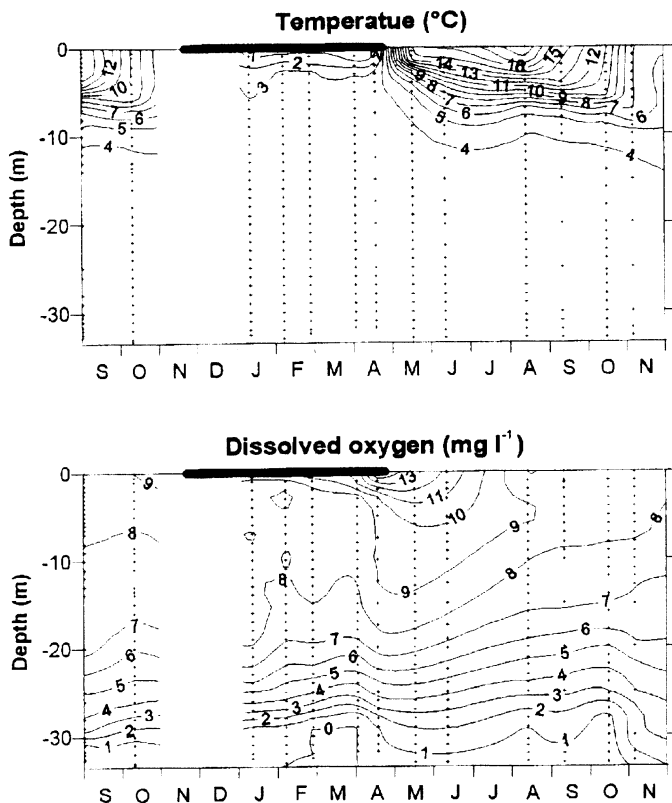


Fig. 1. – Depth-time diagrams of temperature and dissolved oxygen in Čertovo Lake in the 2000 hydrological year. Thick lines represent ice-cover.

3.6–3.8°C), and the ice cover was formed between 20 and 24 November 1999. The ice cover lasted to 23–26 April 2000, and temperature of outflow was already 6°C four days later (30 April). Again, the lake mixed at ~3.7°C. Temperature of input water was higher than that of the surface layer of the lake water in winter and lower in summer (Fig. 2). The differences in water temperature significantly influenced the quality of the lake output especially in winter, when the surface layer of cold lake water (<3°C) was only 3–4 m deep (Fig. 1). The inlet water had a temperature between 1 and 2°C and had a lower density than the lake water below 3 m. Consequently, the most of the inlet water entered the surface layer of CT lake and flowed under the ice. The quality of CT output in winter thus reflected variations in pH, ANC, SO_4^{2-} , BC, NO_3^- , Al_T , and Si in tributaries (Fig. 2).

The most pronounced variations were observed in NO_3^- , BC and Al_T concentrations. This pattern was consistent with lower terrestrial bio-consumption of inorganic N during the dormant period than in summer and with the positive relationships between terrestrial transport of Al_T and NO_3^- (KOPÁČEK & al. 2000d) and BC and NO_3^- (KOPÁČEK & HEJZLAR 1998) in the Bohemian Forest streams. Nitrate accumulated in soils by microbial processes in winter was an important carrier for Al_T^{nl} and BC from soils in the CT watershed. The flushing of soil solution into the surface water at the beginning of the snowmelt can serve as an essential source of nitrate (e.g., STOTTEMYER & TROENDLE 1992). In concordance, both the elevated NO_3^- concentrations and discharge of tributaries during the snowmelt resulted in the maximal fluxes of NO_3^- , BC and Al_T within the CT watershed-lake ecosystem in April (Fig. 2). However, these fluxes left the lake largely without mixing with deeper water layers due to the density/temperature stratification, and affected the lake water chemistry only for a short period.

Most of solutes accumulated in snow packs is released during a relatively short period at the beginning of the thaw (e.g. JOHANNESSEN & HENRIKSEN 1978). In contrast to NO_3^- , which was supplied by soils, concentrations of other ions rapidly decreased by dilution and the chemical composition of CT input and output dramatically changed towards the end of snowmelt with a sharp decrease in SO_4^{2-} , BC, and Al_T concentrations and pH (Fig. 2). Apparently, the continuing elevated terrestrial transport of NO_3^- was in part compensated for by higher H^+ concentrations during this period (Fig. 2).

A pronounced seasonal variation in Si concentrations in tributaries was inversely correlated to discharge ($P < 0.05$). The variations in TP concentrations in CT outlet were associated with ice-free periods (Fig. 2) when the direct atmospheric deposition of P importantly contributed to the total P supply of the lake (Table 1). In winter, when precipitation was accumulated on the ice, tributaries were a dominant TP source for the lake.

Permanently low NH_4^+ concentrations in tributaries (even during periods of snowmelt or heavy rains) suggested very rapid retention of NH_4^+ in soils (Fig. 2). The different pattern of NH_4^+ concentrations in CT output had two reasons: (1) direct atmospheric deposition of NH_4^+ on the lake surface (Table 1) and (2) internal NH_4^+ generation by dissimilatory processes in the CT hypolimnion (see later). Under oxic conditions, NH_4^+ is usually rapidly nitrified in the water column (WETZEL 1983). However, nitrification has probably ceased in Čertovo Lake due to its acidification as described for North American lakes by RUDD & al. (1988).

Seasonal variation in chemical composition of lake water essentially affected the internal alkalinity generation and vice versa. Depleted concentrations of dissolved oxygen (< 1 mg.l⁻¹; Fig. 1) resulted in low redox potentials above the bottom and in dissimilatory reductions of NO_3^- and SO_4^{2-} and in the increase in NH_4^+ and Fe_i^{m} concentrations. The development of lake water chemistry along the vertical profile during winter and summer temperature stratification is given in Fig. 3 and seasonal variations in the epilimnion and hypolimnion are given in Fig. 4. The redox changes led to the increase in the hypolimnetic

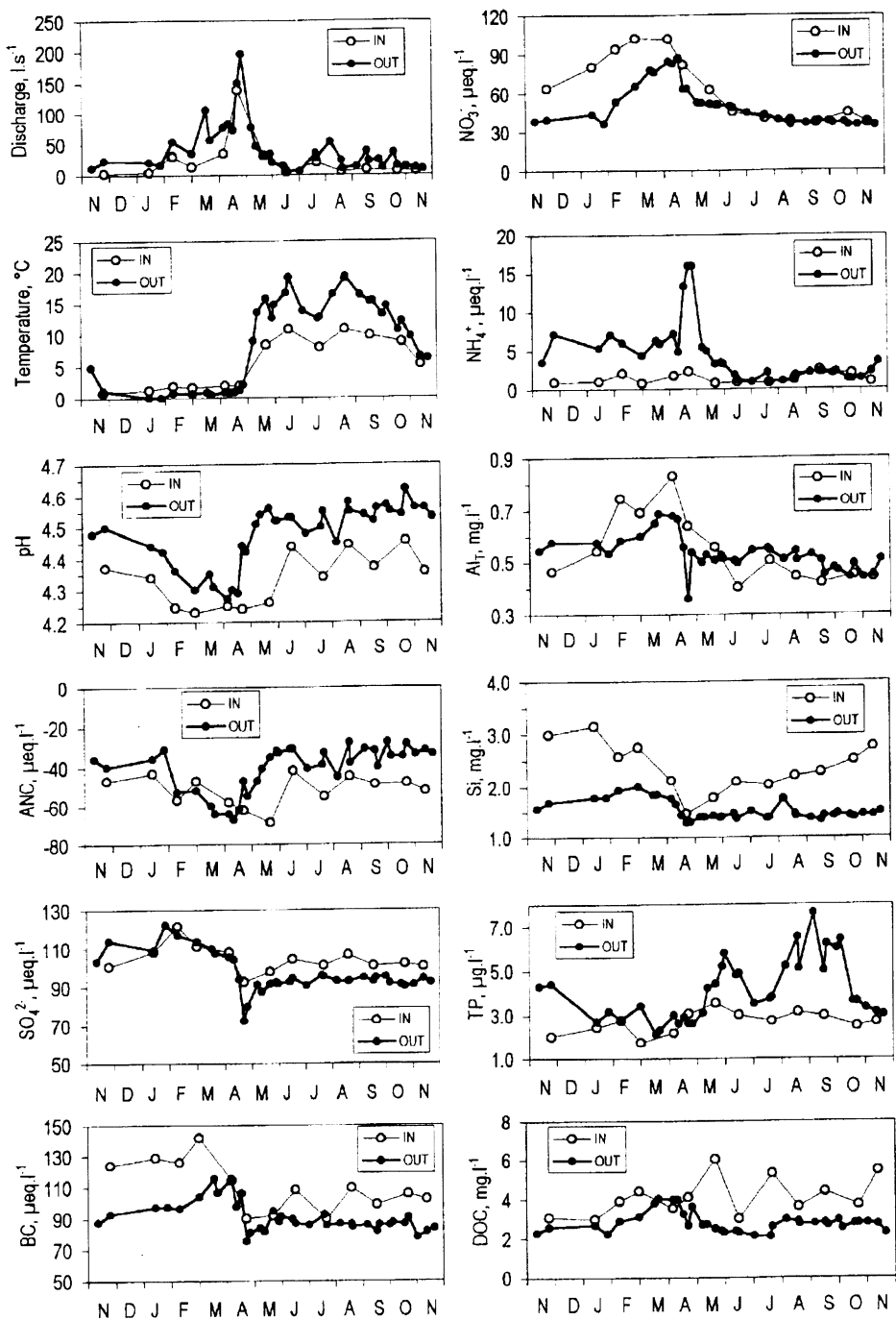


Fig. 2. – Seasonal patterns of discharge, temperature, pH and concentrations of major ions and nutrients in the Čertovo Lake tributaries (open circles; volume-weighted means for all surface tributaries; IN) and the outlet (full circles; OUT) in the 2000 hydrological year.

pH and ANC, while the release of base cations from the sediments was less important (Fig. 3, 4), except for K^+ . The release of K^+ from sedimenting material and/or sediments increased its concentration above the bottom compared to the epilimnion throughout summer, similarly as in 1998 (KOPACEK & al. 2000a).

Dissimilatory decomposition of sedimenting seston was also a primary source of the hypolimnetic NH_4^+ . The high NH_4^+ concentrations in the CT output in April (Fig. 2) thus resulted in part from this NH_4^+ source (Fig. 3) and from snow accumulated on the ice. Because the water overturn was incomplete, the permanently high NH_4^+ concentrations above CT bottom were reduced only partly by mixing with upper water layers (Fig. 4).

With the pH increase towards neutrality (5–6) above the bottom, ionic Al species hydrolyzed and formed Al_{PART} (mostly colloidal Al hydroxides) with large specific surfaces and

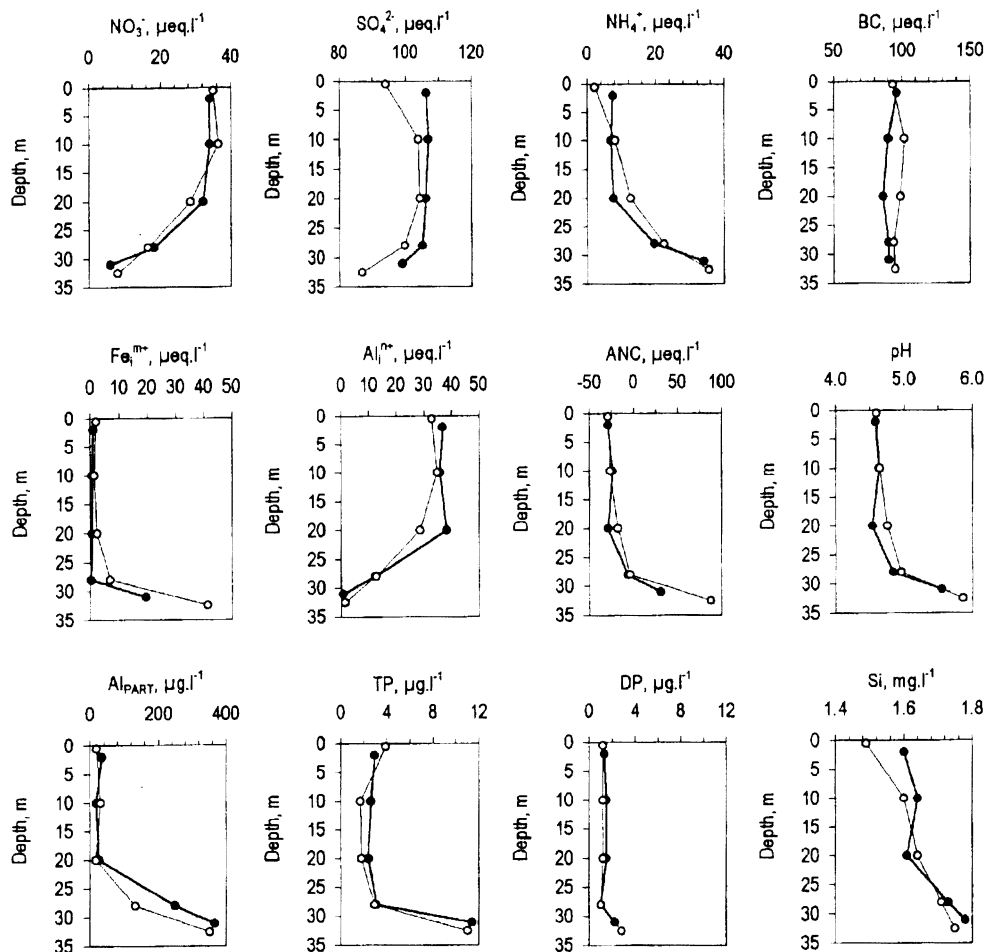


Fig. 3. – Water column profiles of major chemical parameters (BC, base cations; ANC, acid neutralizing capacity; TP, total P; and DP, dissolved P) in Čertovo Lake during winter and summer temperature stratification. Full circles, 12 January 2000; open circles, 16 October 2000.

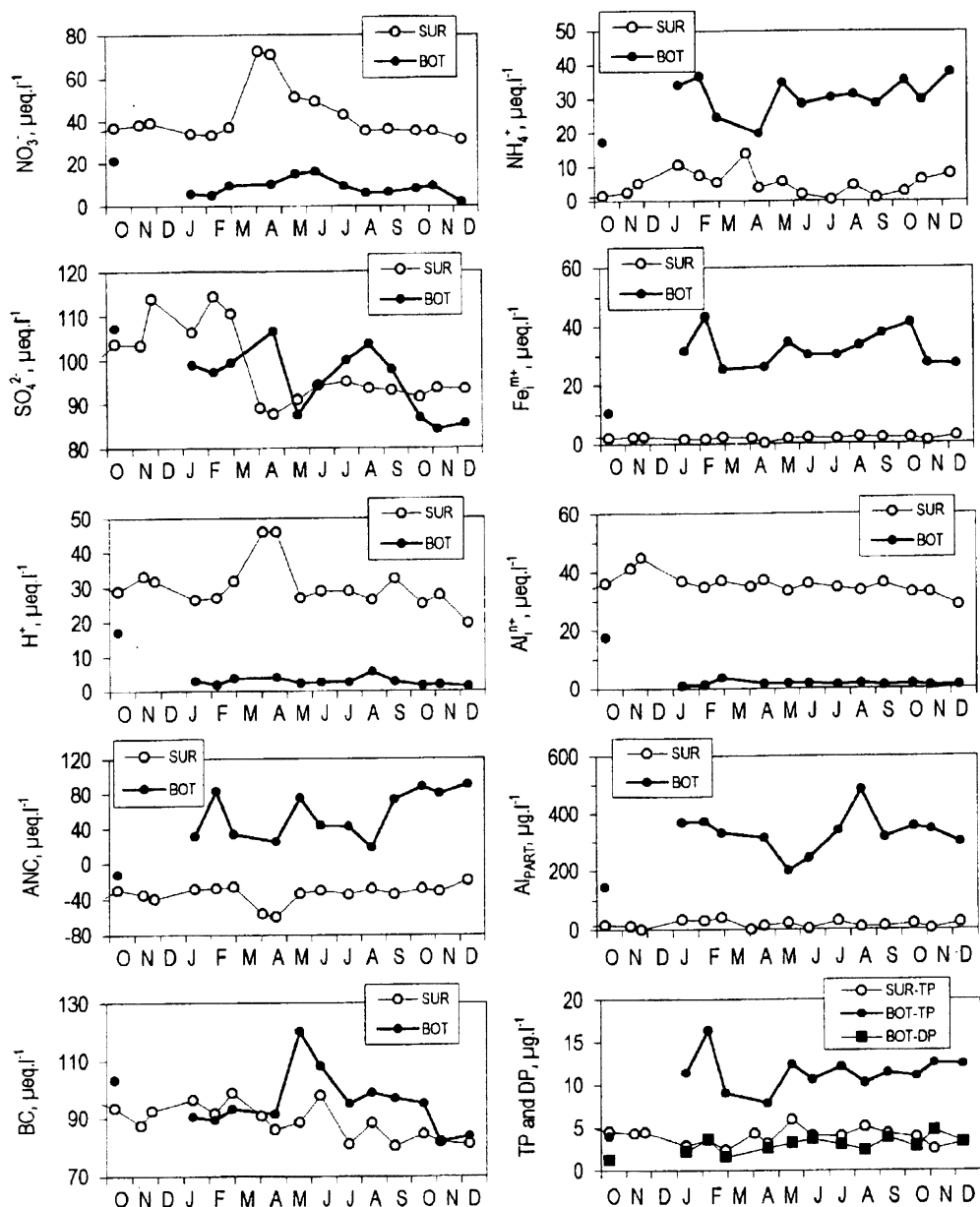


Fig. 4. – Seasonal patterns of surface (0.5 m below the surface; open circles; SUR) and bottom (0.5 m above sediment; full circles; BOT) concentrations of major ions and P at the deepest part of Čertovo Lake in the 2000 hydrological year. Abbreviations refer to: BC, base cations; ANC, acid neutralizing capacity; TP, total P; and DP, dissolved P.

strong ability to bind orthophosphate from the liquid phase. Thus, orthophosphate liberated from the sedimenting organic matter by dissimilatory processes was removed from the liquid phase (KOPÁČEK & al. 2000c). This process explains the low concentrations of Al₃₊⁺ and DP

(concentrations of DRP were $<2 \mu\text{g}\cdot\text{l}^{-1}$) and the increased concentrations of Al_{PART} and TP above the bottom of CT lake (Fig. 3) throughout the study (Fig. 4).

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

Water input (deposition) into the ecosystem was $1.42 \times 10^6 \text{ m}^3 \cdot \text{yr}^{-1}$ ($1.25 \times 10^6 \text{ m}^3 \cdot \text{yr}^{-1}$ on the forest floor and $0.17 \times 10^6 \text{ m}^3 \cdot \text{yr}^{-1}$ on the lake surface). The other water fluxes within the CT watershed-lake ecosystem were estimated from the Cl⁻ budgets: Water outputs from the watershed and lake were 1.23×10^6 and $1.17 \times 10^6 \text{ m}^3 \cdot \text{yr}^{-1}$, respectively. The evaporation from the whole ecosystem was 18% of precipitation. The resulting average water residence time in CT was 577 days. The independently measured water output from the ecosystem ($1.21 \times 10^6 \text{ m}^3 \cdot \text{yr}^{-1}$) was in a relatively good concordance with the water output estimated from the Cl⁻ budget.

The mass fluxes of the major ions and nutrients in CT watershed, calculated from equation (1), are given in Table 2. The terrestrial exports of SO_4^{2-} , NO_3^- , H^+ , Ca^{2+} , Mg^{2+} , Na^+ , Si, and Al and Fe species were higher than their deposition on the forest floor. In contrast, the depositions of NH_4^+ , K^+ , DOC, TON and TP on the forest floor were higher than their export from the watershed into the lake.

The net terrestrial production of elements is operationally defined in this study as the difference between their transport from the watershed via tributaries and their deposition on the forest floor. However, for non-conservative elements, deposition on the forest floor does not represent their total input into the ecosystem (e.g. JOHNSON 1992, LOVETT 1992). For example, the real input of NH_4^+ and NO_3^- into CT ecosystem was probably higher due to their adsorption on vegetation and assimilation within canopies. On the other hand, the deposition of Ca^{2+} , Mg^{2+} , K^+ , P, and C on the forest floor overestimated their real atmospheric input, partly involving their terrestrial cycling (canopy leaching). However, net terrestrial production of elements in Table 2 provides a useful tool to assess the ability of CT watershed to release or retain elements, especially when comparing with other Bohemian Forest lakes (KOPÁČEK & al. 2000a,b) or with previous results on CT from the 1998 (KOPÁČEK & al. 2000a) and 1999 (J. KOPÁČEK – unpubl. data) hydrological years.

Watershed of CT was a net source of acidity with H^+ production of $52 \text{ meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, which was ~50% more than in 1998 and 1999. This difference was associated in part with higher release of SO_4^{2-} and less retention of dissolved inorganic nitrogen ($\text{DIN} = \text{NO}_3^- + \text{NH}_4^+$) than in 1998. The terrestrial export of SO_4^{2-} was 2.3 times higher than deposition flux in 2000 and net terrestrial SO_4^{2-} production was $89 \text{ meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ (i.e., ~30% and ~15% more than in 1998 and 1999, respectively). In contrast to 1998 and 1999, when ~40% and 11% of DIN deposition on the forest floor, respectively, was retained in the watershed, CT soils became a net source of DIN in 2000. The terrestrial production of NO_3^- exceeded NH_4^+ retention (Table 2) and watershed export of DIN ($122 \text{ meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, mostly as NO_3^-) slightly exceeded DIN deposition on the forest floor ($121 \text{ meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$).

The elevated terrestrial export of strong acid anions was compensated for by the higher terrestrial production of Ca^{2+} , Mg^{2+} , Na^+ ($65 \text{ meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) and Al_i ($72 \text{ meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$). A complete budget for terrestrial H^+ consuming and generating processes is given in Table 2.

The mass fluxes of major ions and nutrients in the lake, calculated from equation (2), are given in Table 3. The total input of H^+ into the lake from atmospheric deposition and tributaries was $68 \text{ keq}\cdot\text{yr}^{-1}$, H^+ output was $45 \text{ keq}\cdot\text{yr}^{-1}$ and the in-lake storage of H^+ decreased by $7 \text{ keq}\cdot\text{yr}^{-1}$ (pH increased from 4.62 to 4.69) during the study (Table 1 and 3). The net in-lake H^+ reduction was $30 \text{ keq}\cdot\text{yr}^{-1}$. Reductions in NO_3^- , SO_4^{2-} , and R^- concentrations were the dominant alkalinity generating processes, while Al_i^{net} hydrolysis was the major in-lake source of

Table 2. – Mass balance of the major ions and nutrients and net production of protons in Čertovo 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 ⁺	25	0.03	66	0.09	40	0.05		
Ca ²⁺	611	0.79	646	0.84	35	0.05		2
Mg ²⁺	139	0.18	466	0.60	327	0.42		27
Na ⁺	496	0.64	995	1.29	499	0.65		22
K ⁺	1117	1.45	424	0.55	-693	-0.90	18	
NH ₄ -N	552	0.72	29	0.04	-523	-0.68	37	
NO ₃ -N	755	0.98	1292	1.67	537	0.70	38	
SO ₄ ²⁻	2623	3.40	5936	7.69	3314	4.29	69	
Cl ⁻	700	0.91	700	0.91	NA	NA		
F ⁻	12	0.01	27	0.04	16	0.02	1	
DOC	6615	8.57	5275	6.84	-1340	-1.74		14
TON	349	0.45	282	0.37	-67	-0.09		
Si	50	0.06	2395	3.10	2345	3.04		
TP	34	0.04	3	0.00	-31	-0.04		
Al _f	12	0.02	766	0.99	754	0.98		56
Fe _f	ND	ND	138	0.18	138	0.18		1

H⁺ (Table 3). In-lake reduction of NO₃⁻ and SO₄²⁻ can be modeled as a first-order reaction (KELLY & al. 1987) and increases with their loading. In concordance, the in-lake reduction in NO₃⁻ and SO₄²⁻ (333 and 149 meq.m⁻².yr⁻¹, respectively) was more pronounced in 2000 than in 1998 and 1999 (KOPÁČEK & al. 2000a).

The photochemical and microbial degradation of allochthonous organic matter (e.g. LINDELL & al. 1995, WETZEL & al. 1995) and co-precipitation with Al_{PART} (e.g. KOPÁČEK & al. 2000c) were the most probable explanation for the in-lake reduction in organic carbon concentrations. The annual in-lake reduction in DOC and R⁻ was 19.3 g.m⁻².yr⁻¹ and 72 meq.m⁻².yr⁻¹, respectively, which provides 3.7 meq of charge per mg of the removed DOC. This charge density is in good concordance with values obtained empirically for DOC in waters of Bohemian Forest lakes (3–4 meq.mg⁻¹; KOPÁČEK & al. 2000a). The internal consumption of R⁻ was ~50% less in 2000 than in 1998 probably due to ~30% lower DOC input into the lake. Similarly, a comparison of the results on other Bohemian Forest lakes (KOPÁČEK & al. 2001a, b) suggests a positive correlation between in-lake reduction in R⁻ concentrations and terrestrial DOC loading. The photochemical degradation of allochthonous recalcitrant organic matter has also important consequences for the microbial productivity of lakes. Partial photochemical degradation of allochthonous DOC produces biologically available compounds for bacterial growth (WETZEL & al. 1995) and can explain higher productivity of heterotrophic microbial biomass than the phytoplankton biomass observed in CT by VRBA & al. (2000).

The accumulation rate of Ca and Mg in sediments calculated from the sediment composition and mass accumulation rate was 9 and 11 kg.yr⁻¹, which was substantially less than their in-lake retention calculated from the mass balance (Table 3). Surprisingly high in-lake reten-

Table 3. – Mass balance of the major ions and nutrients and net production of protons in Čertovo Lake 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; 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 ⁺	2	68	-7	45	-30	-0.3		
Ca ²⁺	47	693	67	571	-56	-0.5	3	
Mg ²⁺	7	474	-12	383	-102	-1.0	8	
Na ⁺	44	1039	9	880	-150	-1.4	7	
K ⁺	43	467	182	423	137	1.3		4
NH ₄ -N	67	96	33	60	-3	0.0	0	
NO ₃ -N	74	1367	-32	917	-482	-4.7		34
SO ₄ ²⁻	224	6161	-111	5531	-741	-7.2		15
Cl	55	755	78	677	NA	NA		
F ⁻	0.6	28	0.0	30	1.6	0.0		0
DOC	161	5436	-128	3567	-1996	-19.3		7
TON	25	307	-5	270	-42	-0.4		
Si	2	2397	-44	1861	-580	-5.6		
TP	2.5	6.0	-0.1	4.1	-2.0	-0.02		
Al _T	1	767	-54	648	-174	-1.7		
Al _I	ND	579	-29	538	-71	-0.7	15	
Al _u	ND	187	0	86	-100	-1.0		
Fe _T	ND	138	168	143	173	1.7		
Fe _I	ND	68	152	60	145	1.4		3
Fe _u	ND	67	-1	56	-12	-0.1		

tion was also observed for Na⁺, which is a conservative ion. The probable explanation for this disproportion is a direct input of the atmospheric deposition with low concentrations of base cations (Table 1) into the lake. Such overflow occurs during snowmelt and during heavy rains and can dilute the output. This pattern could explain why the biggest differences between BC concentrations in tributaries and outflow were observed in winter (Fig. 2). In the 1998 hydrological year, when the snow cover in CT watershed was extremely low, the mass fluxes of BC were roughly balanced (KOPÁČEK & al. 2000a). Hence, sampling of overflow during snowmelt is needed to confirm this hypothesis.

The lake was a net sink for all nutrients, removing 33% of TP, 30% of total N (TN), 37% of DOC, and 24% of Si inputs (Table 3). In-lake removal was substantially higher than the average accumulation in sediments for N (527 vs. 163 kg.yr⁻¹), slightly higher for organic C (1996 vs. 1670 kg.yr⁻¹), while substantially lower for TP (2 vs. 10 kg.yr⁻¹). The difference between the in-lake removal of N and N burial in sediments was a rough estimation of net denitrification rate (250 mmol.m⁻².yr⁻¹) and was comparable to the two other Bohemian Forest lakes in this study (KOPÁČEK & al. 2001a, b). The data on the Bohemian Forest lakes are higher than measured rates of denitrification in North American and Scandinavian lakes (97–220 mmol.m⁻².yr⁻¹; KELLY & al. 1987), probably due to higher terrestrial transport and hence, higher NO₃⁻ loading of the Bohemian Forest lakes.

The annual TP retention in the lake (1.5 and $3 \text{ kg} \cdot \text{yr}^{-1}$) in the 1998 and 1999 hydrological years was similar to this study. The higher average burial of TP in sediments than the in-lake retention of TP suggests another source of P for the lake. We hypothesize that this disproportion can be explained in part by a "shore effect" and by the filtration of water during sampling. In most cases of sampling there was no litter retained on $40\text{-}\mu\text{m}$ sieve. However, there was some coarse material retained during increased discharges. Similarly, overflow can represent another source of coarse particles, which were not included in the estimation of this study. Recycling of fine dust particles along the shore by wind and deposition of coarse particles (e.g. leaves and needles) can also represent a significant portion of nutrient input to the littoral zone (PSENNER 1984, KOPÁČEK & al. 1998b). Despite the fact that amount of this nutrient input decreases sharply with the distance from the bank and may be neglected beyond $\sim 10 \text{ m}$ offshore (PSENNER 1984) it may be important for the small Bohemian Forest lakes with relatively high ratio of shore line to lake area. If the "shore effect" covers the difference between the measured in-lake TP retention and the average TP burial in sediment, it would represent a dominant P source for the lake and would roughly equal to the sum of TP supplied by atmospheric deposition and tributaries (Table 3). However, the major portion of TP in tributaries ($\sim 60\%$) was in dissolved form and DRP formed $>40\%$ of TP in precipitation, suggesting so that these two sources have a dominant impact on the lake supply with easily available P for primary production.

The lake was a net source of Fe ($173 \text{ kg} \cdot \text{yr}^{-1}$; Table 3), which was apparently mobilized from sediments in anoxia (Fig. 2). However, sediment analysis showed that the average burial of Fe in sediments was $182 \text{ kg} \cdot \text{yr}^{-1}$. This disproportion can be also explained by an additional non-sampled Fe supply from terrestrial sources, probably the same as in the case of P.

More than 99% of Al_T entering the lake was in the dissolved form (Al_i , 75% ; Al_o , 25% ; Table 3). In contrast, proportion of Al_i in the pool of Al_T increased to 83% in the lake output, while proportion of Al_o decreased to 13% , and 4% of Al_T were in the form of Al_{PART} . In-lake retention of Al_T was $174 \text{ kg} \cdot \text{yr}^{-1}$ and was well comparable with the average accumulation rate of Al in sediments ($244 \text{ kg} \cdot \text{yr}^{-1}$). The changes in the Al speciation in the lake can be explained by two major processes: (1) the photochemical degradation of allochthonous DOC, which liberated organically bound Al_o and increased the pool of Al_i (KOPÁČEK & al. 2000a) and (2) hydrolysis of Al_i at higher pH than in tributaries and formation and sedimentation of Al_{PART} (e.g. KOPÁČEK & al. 2000c). The in-lake reduction in Al_o fluxes (and liberation of Al_i) ranged between 15 and $100 \text{ kg} \cdot \text{yr}^{-1}$ in the 1998–2000 period, which represented $3\text{--}17\%$ of the external input of Al_i . The terrestrial input of Al_i depends on leaching of strong acid anions and has decreased substantially during the reversal of CT ecosystem from atmospheric acidification (VESELÝ & al. 1998b). In contrast, the terrestrial input of Al_o is positively correlated with DOC (KOPÁČEK & al. 2000b). Consequently, the relative importance of the photochemical liberation of Al_i from Al_o will probably increase with the ecosystem reversal from acidification and the expected reduction in the terrestrial Al_i transport.

The annual removal of Si in CT lake varied from $2.5\text{--}5.6 \text{ g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ in the 1998–2000 period (Table 3 and J. KOPÁČEK – unpubl.) and was comparable to Černé Lake but lower than in more productive Plešné Lake (KOPÁČEK & al. 2001a, b). The concentrations of Si exhibited a negative heterograde curve against depth (Fig. 3). Such pattern is typical for oligotrophic lakes, where reduction in dissolved Si is mostly associated with intensive Si assimilation by diatoms, which sediment and bury Si in sediments (WETZEL 1983). However, diatoms are absent in CT lake (NEDBALOVÁ & VRTIŠKA 2000). In contrast, Chrysophyceae form an important portion of phytoplankton biomass there (NEDBALOVÁ & VRTIŠKA 2000) and the sedimentation of chrysophycean cysts and scales could be the most probable mechanism decreasing Si concentrations in the water column of the Bohemian Forest lakes (J. VRBA – pers. comm.).

CONCLUSIONS

The total atmospheric input of H^+ into CT watershed-lake ecosystem was 28 keq.yr^{-1} in the 2000 hydrological year which was $\sim 35\%$ less than in 1998. However, CT watershed was $\sim 50\%$ more pronounced net source of H^+ ($52 \text{ meq.m}^{-2}.\text{yr}^{-1}$) than in 1998, predominantly due to a higher sulfate release from soils and less terrestrial assimilation of DIN (CT watershed was a net source of DIN in 2000). The lake received 68 keq.yr^{-1} of H^+ and was a net sink of 30 keq.yr^{-1} H^+ ($291 \text{ meq.m}^{-2}.\text{yr}^{-1}$) with assimilation and denitrification of NO_3^- ($333 \text{ meq.m}^{-2}.\text{yr}^{-1}$), sulfate reduction ($150 \text{ meq.m}^{-2}.\text{yr}^{-1}$), and photochemical and microbial decomposition of allochthonous organic matter ($72 \text{ meq.m}^{-2}.\text{yr}^{-1}$) being the most important aquatic proton-consuming processes. The hydrolysis of Al_i^{n+} was a dominant aquatic source of H^+ ($144 \text{ meq.m}^{-2}.\text{yr}^{-1}$). Output of H^+ from the ecosystem (lake outflow) was 45 keq.yr^{-1} . Consequently, the CT watershed-lake ecosystem was more pronounced net annual source of protons ($\sim 17 \text{ keq.yr}^{-1}$) than in 1998.

Terrestrial sources mostly dominated the total input of NO_3^- , TON, DOC, and Si into the lake, while direct atmospheric deposition on the lake surface was a major allochthonous source of NH_4^+ and DRP. Tributaries and precipitation were comparable TP sources for the lake. The lake was a net sink for all nutrients, removing 33% of TP, 30% of TN, 37% of DOC, and 24% of Si supplied by both terrestrial and atmospheric sources.

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