

Element budgets in three Bohemian Forest lakes and their watersheds in the 2000 hydrological year: II. Černé 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 Černé 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 595 days and evaporation was 16% of precipitation height (1625 mm). Soils in the Černé watershed were a net source of SO₄²⁻, NO₃⁻, H⁺, Ca²⁺, Mg²⁺, Na⁺, Si, Al, and Fe and a net sink for NH₄⁺, K⁺, DOC, TON, and TP in comparison to the deposition of these compounds on the forest floor. Net terrestrial production of acidity was dominated by biochemical transformations of NH₄⁺ and NO₃⁻ production from the pool of soil organic N (129 meq.m⁻².yr⁻¹) and by SO₄²⁻ release from soil (80 meq.m⁻².yr⁻¹). Ionic composition of tributaries showed seasonal variations with the most pronounced changes in NO₃⁻, base cations, and Al concentrations. In-lake alkalinity generating processes neutralized ~68% 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 a dominant in-lake H⁺ generating process. Net nutrient retention (carbon, phosphorus, nitrogen, and silica) and removal (carbon and nitrogen) in the lake varied between 24% and 63% of their input.

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

INTRODUCTION

Černé Lake (CN) is the largest among the Bohemian Forest lakes and that is probably why it has attracted hydrobiologists for more than one century since the first Frič's survey in 1871 (FRIČ 1872). The history of CN research has been summarized by VESELÝ (1994) and VRBA & al. (2000). In short, the first reliable data on CN chemistry, e.g. pH of 6.3–7.0 and traces of NO₃-N (<0.03 mg.l⁻¹; VESELÝ & MAJER 1992) come from 1936 (JÍROVEC & JÍROVCOVÁ 1937). Despite several historical attempts to determine SO₄²⁻ concentrations in CN (summarized by VESELÝ 1994), the first reliable data (2–3 mg.l⁻¹) come from the early 1960s (PROCHÁZKOVÁ & BLÁŽKA 1999). Their data on CN already suggested the first impact of atmospheric acidification on the lake water composition, predominantly lowered pH (5.4–6.2) and increased NO₃⁻ concentrations (NO₃-N of 0.45–0.55 mg.l⁻¹) compared to the 1930s.

In comparison to Čertovo and Plešné Lakes, acidification of CN was delayed due to a small

hydroelectric power station which pumped a mixture of lake water and river water from a buffer storage reservoir on the Úhlava River (Hamerské jezírko) back into the lake between 1930 and 1975. During the 1965–1975 period, the reverse pumping was already less frequent due to technical problems and completely stopped in 1975. However, the lake water has been continuously used to supply the power station up to the present. Lake water pH decreased to ~4.5 in CN in the late 1970s (FOTT & al. 1980). These changes were accompanied by the disappearance of cladoceran species and fish (FOTT & al. 1994). Lake water acidification of CN progressed until 1986–1988, when NO_3^- -N and SO_4^{2-} concentrations reached their maxima of 1.2–1.45 and 6.5–7.3 mg.l^{-1} , respectively (VESELY & al. 1998a). A continuous decline in SO_4^{2-} and NO_3^- concentrations has occurred since the late 1980s (VESELY & al. 1998a) due to the reduction in Central European S and N emissions (KOPÁČEK & al. 1998).

The CN chemistry has been intensively studied since the early 1990s. For example, VRBA & al. (1996) have reported on the nutrient and microbial status of CN. SCHMIDT & al. (1993) and VESELY (1998) have provided palaeolimnological records of CN sediment and BOROVEC (2000) analyzed CN sediments for nutrient composition and determined individual fractions of phosphorus. SCHMIDT & al. (1993) and KOPÁČEK & HEJZLAR (1998) have reported on the chemical and nutrient composition of CN tributaries. However, the published data are based on a limited number of samplings each year and refer to the chemical composition and not to fluxes of water constituents. This paper provides the first attempt (1) to evaluate seasonal changes in chemistry of CN tributaries and the lake water and (2) to quantify the major fluxes of ions and nutrients within the watershed-lake ecosystem.

MATERIALS AND METHODS

Study site description

Černé Lake is situated at 49°11' N, 13°11' E, and at the altitude of 1008 m a.s.l. The lake is of glacial origin, dimictic, and oligotrophic with the following morphological parameters: Lake area of 18.4 ha, volume of $2.878 \times 10^6 \text{ m}^3$, and maximum depth of 40 m (ŠVAMBERA 1939). The theoretical water residence time is ~600 days (see later). The lake water is low in base cations, the carbonate buffering system is depleted, and sulfate and nitrate are dominant anions (VESELY & al. 1998a, b; KOPÁČEK & HEJZLAR 1998).

The area of the CN watershed is 129 ha (including the lake) and is steep with the maximum local relief of 335 m. The bedrock is made up of mica-schist (muscovitic gneiss) and most of the watershed is covered with shallow soils of acidic podzols in different stage of development and/or cambisol (average depth of ~0.55 m) with unsaturated sorption complex (VESELY 1994, J. KOPÁČEK – unpubl.). The forest in the CN watershed is of a secondary origin, mostly from 1820, and is dominated with Norway spruce (beech is sparse) (VESELY 1994). Details on land use history of the CN watershed and lake water chemistry and biology are given in VESELY (1994, 1998), FOTT & al. (1994), and VRBA & al. (1996).

The lake has eight surface tributaries (CN–I to CN–VIII) draining the CN watershed and one artificial tributary (CN–IX), which drains water outside the CN watershed but it is led occasionally into the lake (Fig. 1). The lake has one surface outlet, but there is usually no natural outflow because all water is used for the power station. Consequently, water level in the lake varies within ~1 m during a year due to the disproportion in the water supply and demand. The water for the power station is taken from the surface layer (0–1 m). The return water pumping was not reestablished until the end of this study.

Černé Lake

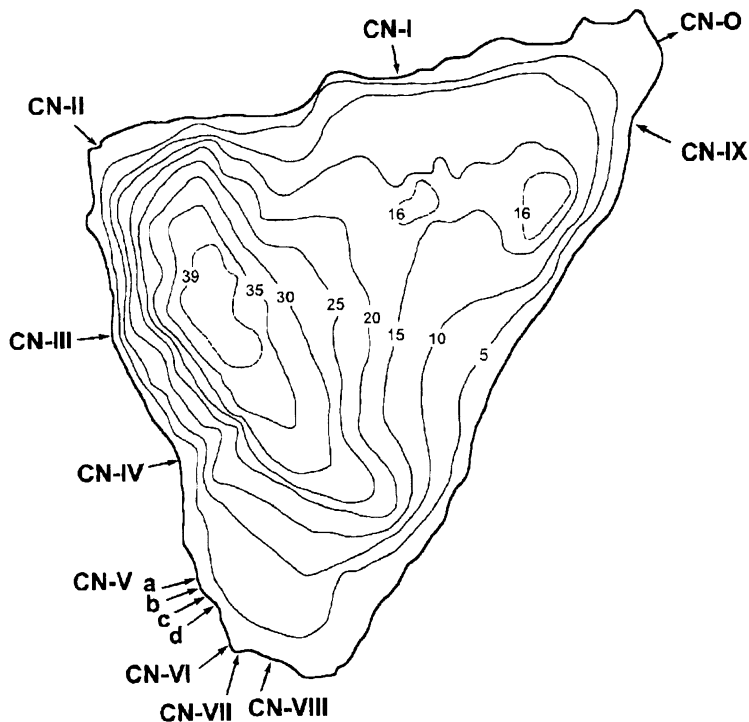


Fig. 1. – Bathymetric map of Černé Lake redrawn from ŠVAMBERA (1939) with arrows showing locations of tributaries (CN-I to CN-IX) and outflow (CN-O).

Sampling and analyses

Atmospheric deposition and throughfall at two elevations were sampled in the adjacent area (in surroundings of Čertovo Lake) and details are given in KOPÁČEK & al. (2001a). Air temperature was measured at the outlet of adjacent Čertovo Lake using an automatic weather station (MS16; J. Fiedler, České Budějovice; readings in 15-minute intervals) throughout the study. Temperatures of the major CN tributaries (CN-VII and CN-VIII) were measured continuously with temperature loggers (StowAway TidbiT –4 to 37°C, Onset, USA; readings in 1-hour intervals) between 12 January and 6 November 2000.

Samples from the tributaries and outlet (lake at the outlet, 0.5–1 m depth) were taken monthly and biweekly, respectively, between 11 October 1999 and 6 November 2000. Discharges of tributaries were estimated using the method of stop-watch and bucket. The samples were immediately filtered through a 40- μ m 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 9 tributaries. Monthly averages of discharge of outlet were calculated from the data on electric power production in the power station. Samples of lake water were taken monthly at the deepest part of the lake from the surface (0.5 m) and bottom (~38 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, a water column profile (0.5, 10, 20, 30, and 38 m) was sampled on 12 January 2000 and before the end of the study on 16 October 2000. Temperature and dissolved oxygen (O_2) were measured using the Data-Sonde 4 (Hydrolab, USA) at 1 m intervals. The samples of the lake water were immediately filtered through a 200- μ m polyamide sieve.

Concentrations of acid neutralizing capacity (ANC), dissolved and particulate organic carbon (DOC and PC), 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), particulate Al (Al_{PART}), total Fe (Fe_T), organically bound Fe (Fe_o), ionic Fe (Fe_i), equivalent concentrations of Al_i and Fe_i (Al_i^{n+} and Fe_i^{m+}), and organic acid anions (R^- , $\mu eq.l^{-1}$), and pH were obtained as described by KOPÁČEK & al. (2001a).

The reliability of chemical analyses 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 $\leq \pm 3.5\%$.

Mass balances

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

(1) The volume of CN varied during the study due to water withdrawal by the hydroelectric power station. Changes in the lake volume were calculated from changes in the water level. Change in storage of the water constituents in the lake was affected both by changes in their concentrations and the lake volume and was obtained as the difference between their amounts in the lake on 16 October 2000 and at the beginning of the study. These amounts were calculated by linking concentration data on the individual water layers of the lake with their corresponding volumes. However, the lake water composition at the beginning of the study was based on the water composition on 12 January 2000 and the lake volume on the water level in November 1999.

(2) Water balance was determined from annual heights of precipitation and throughfall and the budget for Cl. In this calculations we assumed that 20% and 80% of the watershed area received atmospheric deposition in the form of precipitation and throughfall, respectively, and 30% and 70% of throughfall deposition were comparable to that at the throughfall sites at low and high elevation, respectively.

(3) The annual volume weighted mean (VWM) composition of water output from the lake was calculated by linking monthly averaged discharge data for the outlet with the corresponding biweekly concentration data by the method of period-weighted mean. The monthly averages on water output were obtained from the hydroelectric power station and were derived from the time of energy production and average water discharge through the turbine.

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. (2000a).

The annual accumulation rate of C, P, and N in sediments was estimated from average mass accumulation rate (38 $g.m^{-2}.yr^{-1}$; J. VESELY – pers. comm.) and their average concentrations in the uppermost 1-cm layer. The deepest sediments of the lake were collected using a gravi-

ty corer in October 1996, July 1997, and November 1998 and were analyzed as described by KOPÁČEK & al. (2000b).

RESULTS AND DISCUSSION

Chemical composition of atmospheric deposition, tributaries, and lake output

Deposition on the forest floor was estimated from the data on precipitation and throughfall composition given by KOPÁČEK & al. (2001a) and the respective forested and unforested areas in the CN watershed. The annual VWM concentration of ions in deposition on the forest floor (the average deposition via precipitation and throughfall) was $249 \mu\text{eq.l}^{-1}$ with the following average equivalent composition: base cations (BC = sum of Ca^{2+} , Mg^{2+} , Na^+ and K^+), 29%; H^+ , 8%; NH_4^+ , 13%; SO_4^{2-} , 18%; NO_3^- , 17%; Cl^- , 6%; and R^- , 9%.

The average discharge of surface CN tributaries varied from 0.4 to 9 l.s^{-1} (Table 1) and the total surface water input ranged from 1.5 to 113 l.s^{-1} during the sampling days. The average water flux via surface tributaries (22 l.s^{-1}) was ~2-fold higher than the direct atmospheric deposition on the CN surface, which represented $\sim 9.5 \text{ l.s}^{-1}$. Tributaries CN-V to CN-VIII were perennial while the others temporal in 2000. CN-VII was a major tributary, representing 35–53% of the total water input by surface tributaries. The annual VWM concentration of ions in the CN tributaries was $448 \mu\text{eq.l}^{-1}$ with the following average equivalent composition: BC, 27%; H^+ , 10%; Al_i^{3+} , 13%; SO_4^{2-} , 22%; NO_3^- , 22%; Cl^- , 4%; and R^- , 3%. All tributaries were more acidic than deposition on the forest floor with the annual VWM pH between 4.04 and 4.69 and had substantially higher concentrations of SO_4^{2-} (Table 1). The lowest pH values, as well as concentrations of BC and NO_3^- were in tributaries CN-I and CN-II. Concentrations of DOC in these two inlets were the highest of all the CN tributaries and were accompanied with high levels of Al_i and Fe_o (Table 1). Moreover, CN-I and CN-II were the only tributaries in the CN watershed with elevated phosphorus content (Table 1) and represented a significant source of DRP to the lake with VWM concentrations of 6.0 and $3.2 \mu\text{g.l}^{-1}$, respectively. Otherwise, DRP was always below the detection limit of $1 \mu\text{g.l}^{-1}$ in the other CN tributaries.

The concentrations of NO_3^- in CN tributaries were higher than in tributaries of Čertovo and Plešné Lakes (KOPÁČEK & al. 2001a, b) and higher than in deposition on the forest floor (Table 1). Moreover, the VWM concentrations of dissolved inorganic nitrogen ($\text{DIN} = \text{NO}_3^- - \text{N} + \text{NH}_4^- - \text{N}$) in tributaries were (except for CN-I and CN-II) higher than in deposition and were high even in the growing season (see later), suggesting a progressive stage of N-saturation (STODDARD 1994) within the whole CN watershed.

All tributaries had lower concentrations of TP and, except for CN-I and CN-II, lower DOC and TON concentrations than deposition on the forest floor. Tributaries CN-I and CN-II drained relatively flat subwatersheds with small marshes and deeper forest soils while the other CN subwatersheds were steeper. The lower NO_3^- and high DOC concentrations in tributaries draining subwatersheds with gentle slopes were most likely due to the longer residence time of water in the soils (DISE & WRIGHT 1995). These morphological parameters importantly affected also other chemical characteristics of tributaries due to tight correlation between DP and/or DON and DOC ($P < 0.001$), and between BC and NO_3^- ($P < 0.05$) in the tributary input. Similarly to tributaries of other Bohemian Forest lakes (KOPÁČEK & HEJZLAR 1998, KOPÁČEK & al. 2000d), the concentrations of Al_i and Fe_o in CN tributary input were correlated with DOC ($P < 0.001$). Moreover, significant relationship ($P < 0.01$) was observed between the DRP and DOC concentrations in tributaries CN-I and CN-II.

The average monthly water output from CN varied between 0.9 l.s^{-1} in September and

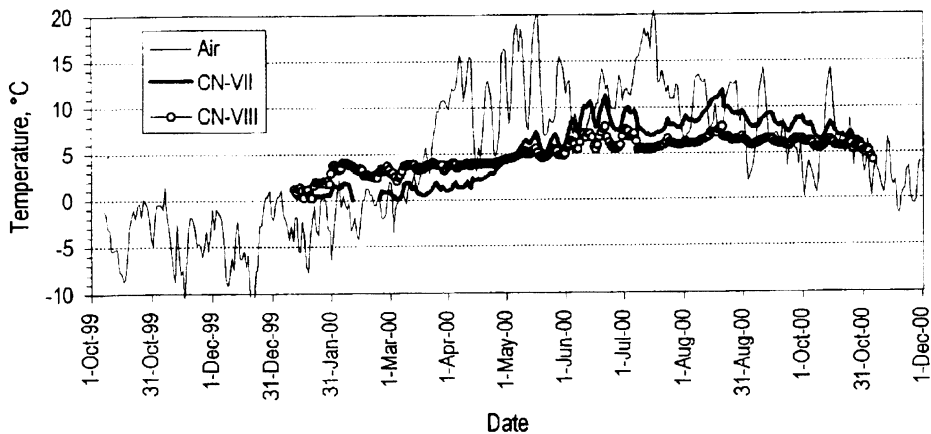


Fig. 2. – Daily average temperatures of air (at outlet from Čertovo Lake, ~1010 m a.s.l.) and the major tributaries of Černé Lake (CN-VII and CN-VIII) in the 2000 hydrological year.

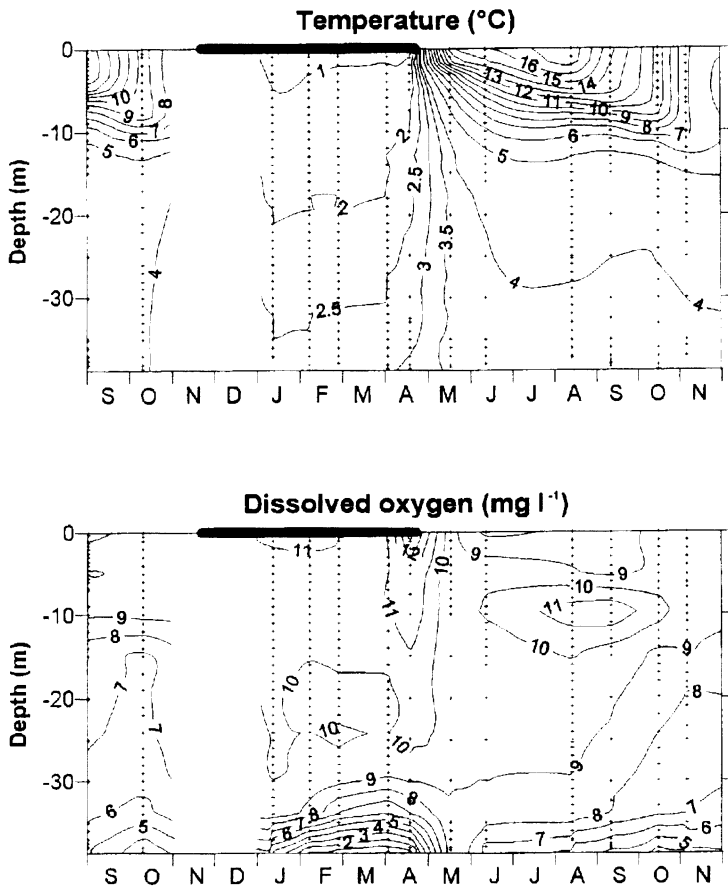


Fig. 3. – Depth-time diagrams of temperature and dissolved oxygen in Černé Lake in the 2000 hydrological year. The thick lines represent ice-cover.

124 $\text{l}\cdot\text{s}^{-1}$ in April with the annual average of 46 $\text{l}\cdot\text{s}^{-1}$. The annual VWM concentration of ions in CN output was 343 $\mu\text{eq}\cdot\text{l}^{-1}$ (BC, 37%; H^+ , 5%; Al^{3+} , 6%; NH_4^+ , 2%; SO_4^{2-} , 25%; NO_3^- , 19%; Cl^- , 5%; and R^- , 1%). Compared to the tributaries, VWM composition of output had lower concentrations of total dissolved solids, H^+ , NO_3^- , SO_4^{2-} , Al forms, and Si but higher concentrations of NH_4^+ , 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) sedimentation. 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

The temperature stratification of the lake developed typically for a dimictic temperate lake with the autumn and spring overturns. The autumn overturn occurred in November. Ice cover was formed between 20 and 24 November 1999 after ~2-week period of frost (Fig. 2). Temperature profile of the lake was not measured between October 1999 and January 2000, but the hypolimnetic temperature was 4°C in October and 2.5°C at the beginning of January (Fig. 3). Hence, we conclude that the lake was mixed and cooled until the temperature of the whole water column decreased to ~2.5°C. Ice cover lasted to 23 April 2000, then the lake mixed at 3.6°C (Fig. 3) and the temperature of lake surface sharply increased (Fig. 4).

The major tributaries CN–VII and CN–VIII drain the north-oriented lake wall and the spring of CN–VIII is close to the lake. Consequently, water temperature of CN–VIII was more stable (3–4°C in winter and 5–8°C in summer) than that of CN–VII, which was colder (0–2°C) in winter and warmer (up to 12°C) in summer (Fig. 2). Moreover, the summer temperature of CN–VII was on average ~1.5°C lower than temperature of the major tributary of Čertovo Lake (J. HEJZLAR – unpubl.), which drains the south-east-oriented lake wall.

Winter VWM temperature of tributaries was between 1.1 and 2.4°C (Fig. 4) and temperature of water column was between 0–2.5°C (Fig. 3). Consequently, tributaries had similar temperature and density as the lake water and could enter any water layer in the lake. In summer, temperature of individual tributaries varied between 5 and 13°C (with VWM values of 6.7–8.8°C; Fig. 4) while the epilimnetic temperature increased rapidly after the ice-off above 10°C (Fig. 3). Hence, density of input water was higher than that of the epilimnion and tributaries could immerse into the deeper layers of the lake.

The mixing of tributaries with deeper layers of the lake resulted in a relatively stable composition of CN output without any winter peaks associated with elevated concentrations of NO_3^- , Al_T , BC, and Si in tributaries (Fig. 4). This pattern was in contrast to the chemistry of Čertovo output, composition of which tightly reflected chemistry of tributaries due to different temperature/density conditions (KOPÁČEK & al. 2001a). Quality of CN output was affected during snowmelt, when concentrations of SO_4^{2-} , BC, and Al_T sharply decreased, as well as ANC and pH (Fig. 4). In contrast, concentrations of NH_4^+ in the CN output peaked, primarily due to the release of NH_4^+ accumulated in snow on the ice-cover and then (after the spring overturn) from the hypolimnion (Fig. 5). Water input to the lake was highest during this period and also the water amount used for the hydroelectric power station reached its maximum (Fig. 4). Consequently, NH_4^+ output from CN during snowmelt had the crucial impact on NH_4^+ balance in the lake and resulted in a “paradox” situation, when the lake became a net source of ammonium (see later).

A pronounced seasonal variation in Si concentrations in the tributaries was inversely correlated to discharge ($P < 0.01$). Variations in TP concentrations in the CN outlet were associated with ice-free periods (Fig. 4) when the direct atmospheric deposition of P importantly

Table 1. – The VWM concentrations of the major constituents of atmospheric deposition on the forest floor (ADFF), tributaries (CN-I to CN-IX), terrestrial transport (lake input via tributaries, CN_{IS}), lake output (CN_{OUT}) and lake water at the start (CN_{START}; 12 January 2000) and end (CN_{END}; 16 October 2000) of the study in the Cerné 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. Tributary CN-III had water only on 11 October 1999 and 19 April 2000 and CN-IX on 7 February 2000.

	ADFF	CN-I	CN-II	CN-III	CN-IV	CN-V	CN-VI	CN-VII	CN-VIII	CN-IX	CN _{IN}	CN _{OUT}	CN _{START}	CN _{END}
n	17	9	10	2	12	13	13	13	13	1	13	31	1	1
Q	NA	0.4	1.9	0.7	1.5	2.8	3.4	9.0	3.3	2.0	22.4	55.2	NA	NA
pH	4.69	4.04	4.17	4.41	4.18	4.28	4.30	4.46	4.69	4.06	4.37	4.77	4.97	4.93
Ca ²⁺	0.49	0.80	0.34	0.58	0.51	0.74	0.54	0.70	0.90	0.29	0.70	0.86	0.86	0.80
Mg ²⁺	0.11	0.31	0.24	0.41	0.34	0.49	0.38	0.47	0.53	0.35	0.44	0.44	0.49	0.45
Na ⁺	0.39	0.64	0.56	0.84	0.72	1.01	0.80	0.80	1.05	0.80	0.84	0.85	0.92	0.94
K ⁺	0.90	0.28	0.32	0.48	0.40	0.44	0.41	0.41	0.49	0.41	0.42	0.42	0.49	0.50
NH ₄ ⁻ N	0.44	0.02	0.04	0.02	0.03	0.04	0.05	0.02	0.04	0.03	0.03	0.12	0.06	0.09
NO ₃ ⁻ N	0.61	0.76	0.68	1.43	1.25	1.44	1.31	1.46	1.71	1.71	1.37	0.89	0.83	0.87
SO ₄ ²⁻	2.08	4.22	4.56	5.67	4.60	5.41	4.58	4.82	3.97	4.35	4.68	4.05	4.11	4.01
Cl ⁻	0.56	0.74	0.51	0.72	0.53	0.59	0.51	0.59	0.69	0.92	0.59	0.62	0.73	0.70
F ⁻	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.04	0.01	0.02	0.04	0.05	0.06
DOC	5.3	16.2	7.9	2.5	5.5	4.2	4.3	2.4	1.1	7.1	3.6	1.4	1.1	1.1
TON	0.29	0.43	0.28	0.21	0.27	0.23	0.14	0.16	0.10	0.35	0.18	0.17	0.22	0.20
Si	0.04	2.04	1.39	1.79	1.82	2.13	1.69	1.88	2.49	1.97	1.93	1.58	1.79	1.74
TP	27.5	15.3	7.5	2.8	3.2	2.4	3.7	2.0	1.9	6.0	3.0	3.5	3.2	3.1
Al _T	9.55	652	637	1063	592	735	778	827	765	1058	766	362	379	395
Al _I	ND	274	368	972	407	587	626	736	699	815	638	281	313	346
Al ₀	ND	399	264	85	183	141	154	84	43	238	121	36	18	17
Fe _T	ND	528	154	17	107	69	86	29	24	269	65	67	71	50
Fe _I	ND	39	7	<5	<5	2	<5	<5	<5	68	23	32	13	19
Fe ₀	ND	317	83	16	61	35	40	17	12	56	34	10	7	10
ANC	0.8	-66	-69	-47	-68	-64	-64	-41	-19	-69	-49	-15	-5	-12
TDS	171	272	228	364	303	372	318	351	405	365	342	289	300	301

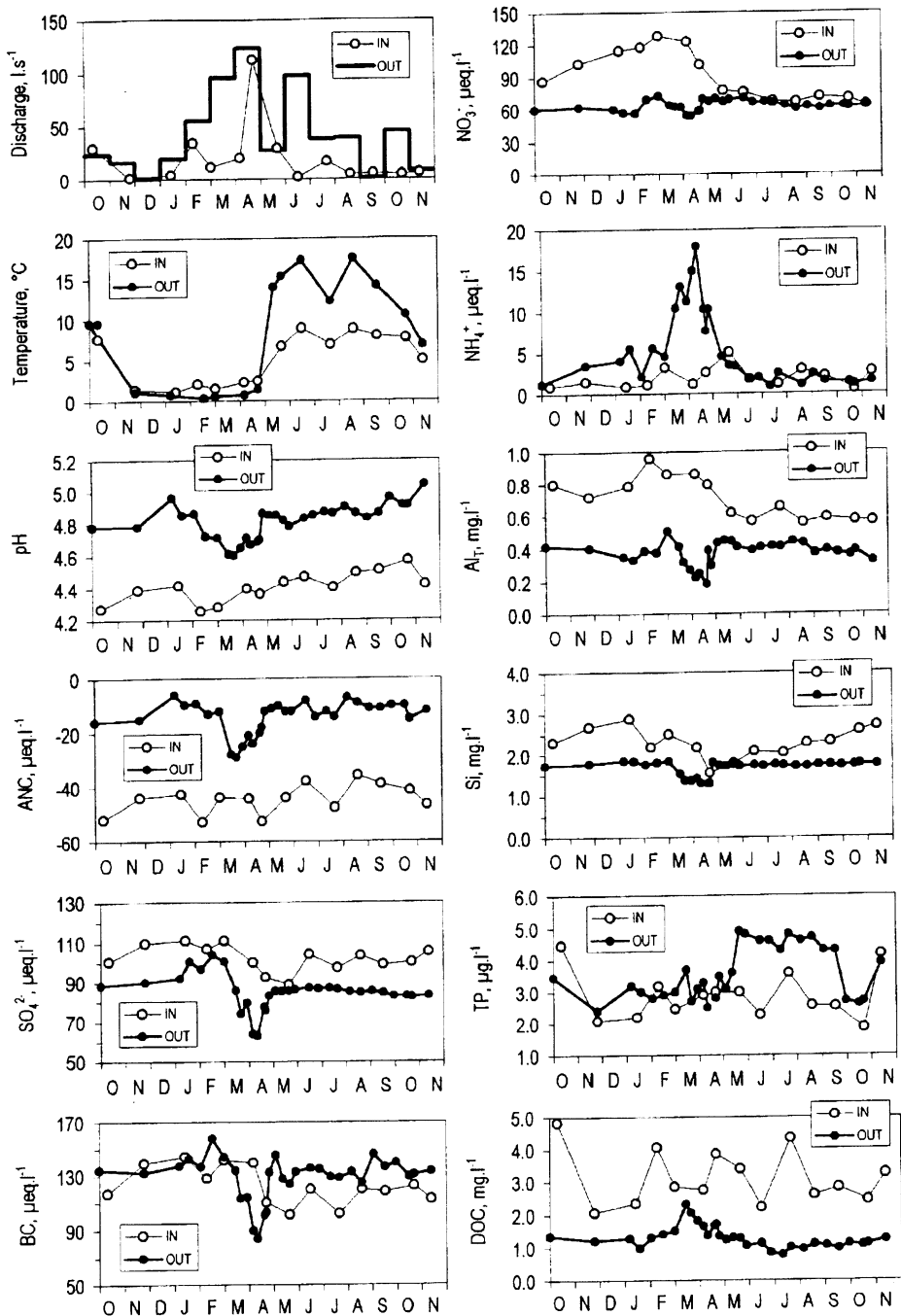


Fig. 4. – Seasonal patterns of discharge, temperature, pH and concentrations of major ions and nutrients in the Cerné Lake tributaries (open circles; volume-weighted means for all surface tributaries; IN) and the output (full circles; OUT) in the 2000 hydrological year.

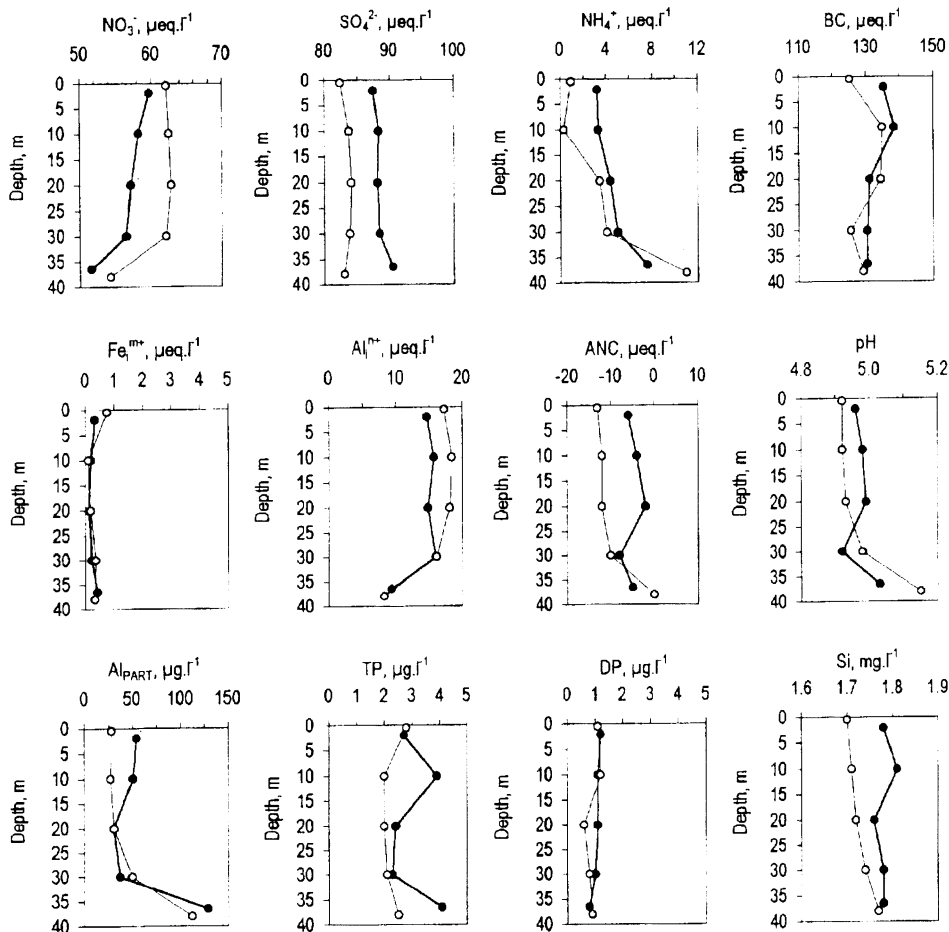


Fig. 5. – Water column profiles of major chemical parameters (BC, base cations; ANC, acid neutralizing capacity; TP, total P; and DP, dissolved P) in Černé Lake during winter and summer temperature stratification. Full circles – 12 January 2000; open circles – 16 October 2000.

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, and TP concentrations in the output were comparable with those in tributaries. The sharp increase in TP concentrations in the outlet had to be primarily associated with a liberation of TP accumulated in the snowpack. This peak was in part diluted during the spring overturn because the TP concentration in the hypolimnion was low (Fig. 5).

A small peak in DOC concentrations in the CN outlet occurred in the late winter (Fig. 4) and was accompanied with elevated Al_0 and Fe_0 concentrations, which suggested its terrestrial origin. This peak was probably associated with the beginning of snowmelt; see the increase in the air temperature in March (Fig. 2) and decreasing SO_4^{2-} concentrations at the same time (Fig. 4). Even though we have no data on DOC concentrations in the tributaries from this period, we can hypothesize that flushing of soils at the beginning of snowmelt was the DOC source as described e.g. by DENNING & al. (1991). A similar increase in in-lake DOC concen-

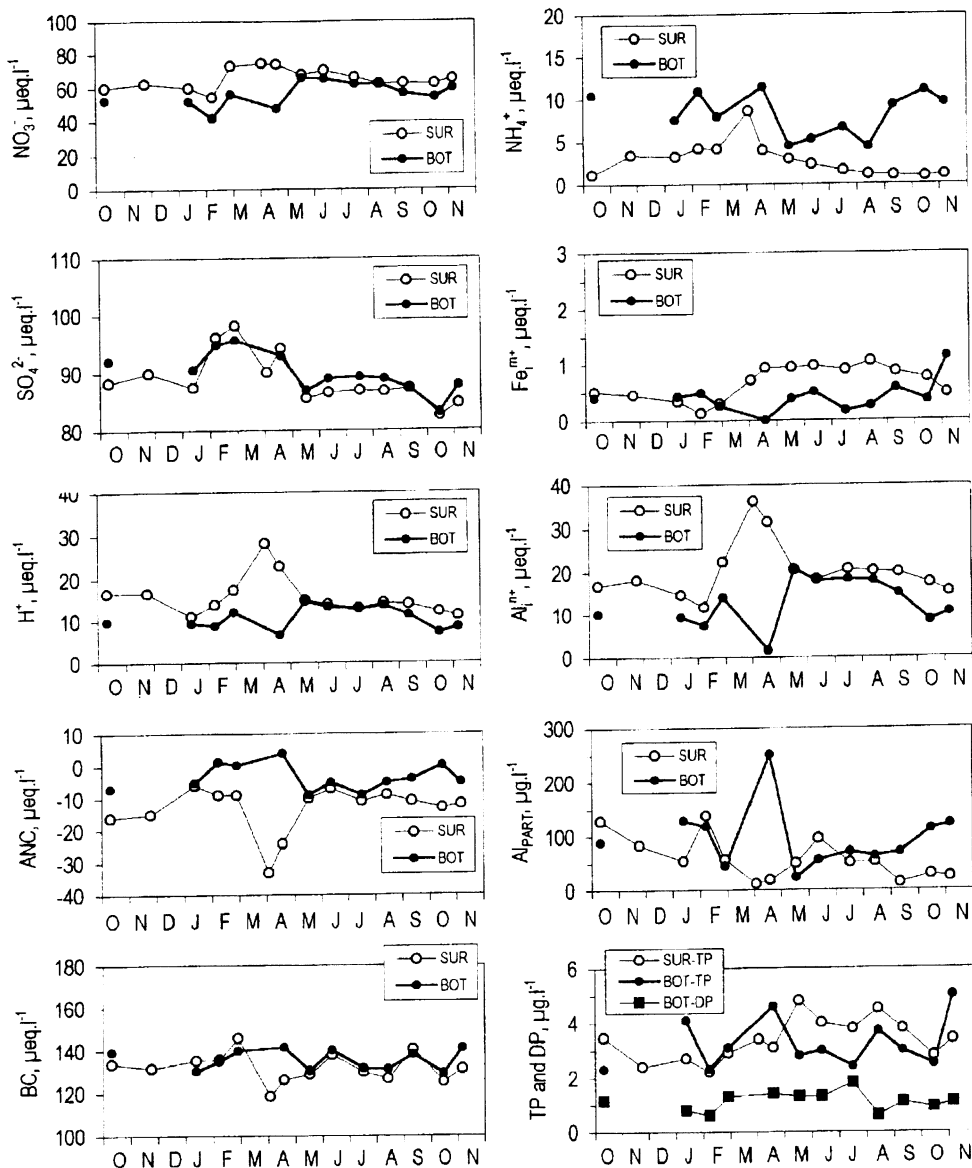


Fig. 6. – Seasonal patterns of surface (0.5 m below the surface; open circles; SUR) and bottom (0.5 m above sediment; full circles; BOT) concentrations of major ions and P at the deepest part of Černé Lake in the 2000 hydrological year. Abbreviations refer to: BC, base cations; ANC, acid neutralizing capacity; TP, total P; and DP, dissolved P.

trations during the snowmelt or just after the ice-off was observed also in Čertovo and Plešné Lakes, as well as in the Tatra lakes (KOPÁČEK & al. 2001a, b, and 1996).

In contrast to the other Bohemian Forest lakes, anoxia does not develop in the CN hypolimnion (VRBA & al. 2000). Also during this study, oxic conditions were in the whole water column even during temperature stratification periods (Fig. 3). In spite of this fact, the water

chemistry along the vertical profile of the lake significantly changed (Fig. 5). The most pronounced changes were associated with NO_3^- reduction in sediments. Sulfate and nitrate reductions in the sediment are known to be important internal alkalinity generation processes even under oxic conditions (KELLY & RUDD 1984, SCHINDLER 1988, KELLY 1994). Diffusion of NO_3^- and SO_4^{2-} into the sediment and their reduction is a first-order reaction (KELLY & al. 1987). The reaction rates of these processes depend on concentrations of NO_3^- and SO_4^{2-} above the sediment, which were high throughout the year (Fig. 6). The consequent increase in the lake water ANC and pH due to internal alkalinity generation controlled solubility of Al. The concentrations of $\text{Al}_i^{\text{D}}+$ decreased while Al_{PART} increased above the sediments (Figs. 5 and 6). The decomposition of sedimenting organic material resulted in the liberation of NH_4^+ and orthophosphate. However, while the NH_4^+ concentrations increased above the bottom, the concentrations of DRP were below the detection limit of the method ($<1 \mu\text{g}\cdot\text{l}^{-1}$) and also the DP concentrations were low due to binding of orthophosphate on Al_{PART} and contributing to the TP pool (Figs. 5 and 6).

The concentrations of BC were roughly constant along the vertical profile (Fig. 5), as well as in the epilimnion and hypolimnion (Fig. 6) and their release from the sediments probably did not significantly contribute to the internal alkalinity generation. In contrast to Čertovo and Plešné Lakes (KOPÁČEK & al. 2001a, b), there were higher O_2 concentrations and redox potential above the CN sediments and, consequently, the hypolimnetic Fe_i^{D} concentrations did not increase in CN throughout the year (Fig. 6). The concentrations of Si exhibited only a little increase along the vertical profile against depth during summer stratification, but were roughly constant along the vertical lake profile in winter (Fig. 5). In contrast, the concentrations of Si exhibited a negative heterograde curve against depth in Čertovo Lake both in summer and winter (KOPÁČEK & al. 2001a).

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

Water input (deposition) into the ecosystem was $2.09 \times 10^6 \text{ m}^3 \cdot \text{yr}^{-1}$ ($1.79 \times 10^6 \text{ m}^3 \cdot \text{yr}^{-1}$ on the forest floor and $0.30 \times 10^6 \text{ m}^3 \cdot \text{yr}^{-1}$ on the lake surface). The other water fluxes within the CN watershed-lake ecosystem were estimated from the Cl^- budgets: Water outputs from the watershed and lake were 1.71×10^6 and $1.76 \times 10^6 \text{ m}^3 \cdot \text{yr}^{-1}$, respectively. Evaporation from the whole ecosystem was 16% of precipitation. Resulting average water residence time in CN was 595 days. The water output from the ecosystem estimated in the hydroelectric power station was $1.45 \times 10^6 \text{ m}^3 \cdot \text{yr}^{-1}$, which was $\sim 18\%$ less than the water output estimated from the Cl^- budget. At present we can only speculate about the reason of such a big disproportion. There were the following three possible explanations: (1) part of the lake water leaked through the dam into the natural outlet and did not enter the power station, (2) the coefficient used for the estimation of water flow through the turbine was not correct, and (3) analyses of Cl^- concentrations and/or assumption that Cl^- behaved conservatively within the ecosystem were not correct.

The leakage of $\sim 1 \text{ l}\cdot\text{s}^{-1}$ through the dam at the outlet was often observed during sampling. However, this flux would represent only negligible difference in the water budget ($\sim 2\%$). The Cl^- analyses also seemed to be correct, having shown no errors detectable with ionic budget approach. Even if all the positive difference between the sum of cations and the sum of anions in the lake output (172 vs. $171 \mu\text{eq}\cdot\text{l}^{-1}$) was due to the underestimated Cl^- concentrations, the calculated water output would decreased only by $\sim 4\%$. However, the calculation was performed assuming Cl^- to behave conservatively in the watershed. If there had been any sink for Cl^- in the CN watershed, it would have resulted in overestimation of water fluxes. The Cl^- balances differed from zero for most of the Integrated Forest Study sites (BINKLEY 1992), as

well as for 32 North American and Scandinavian watersheds (SCHINDLER 1986). Consequently, similar non-steady state conditions in Cl⁻ budget within the CN watershed could partly explain the observed difference in the estimated water flux and water amount used for energy production. In that case, also the fluxes of other water constituents would be ~20% uncertain. However, the good concordance between the measured and Cl-induced water fluxes within the morphologically similar Čertovo ecosystem (KOPÁČEK & al. 2001a) suggests that the difference in water fluxes within the CN ecosystem may partly be due to the uncertainty in water measurement in the hydroelectric power plant. In that case, the uncertainty in the following fluxes of water constituents is <20%.

The mass fluxes of major ions and nutrients in the CN watershed are given in Table 2. The terrestrial export of SO₄²⁻, NO₃⁻, H⁺, Ca²⁺, Mg²⁺, Na⁺, F⁻, Si, and Al and Fe species were higher than their deposition on the forest floor. In contrast, deposition of NH₄⁺, K⁺, DOC, TON, and TP on the forest floor was higher than their transport from the watershed soils. The total atmospheric input of H⁺ into the CN watershed-lake ecosystem was 40 keq.yr⁻¹ (36 keq.yr⁻¹ into the watershed and 4 keq.yr⁻¹ into the lake). The terrestrial production and consumption of protons were 255 and 216 keq.yr⁻¹, respectively. There were the following two major terrestrial sources of protons: (1) NH₄⁺ assimilation and/or nitrification and production of NO₃⁻ from the soil organic N pool (56%; 129 meq.m⁻².yr⁻¹) and (2) SO₄²⁻ release from soil (35%; 80 meq.m⁻².yr⁻¹). In contrast, the release of Al_f⁺ (46%; 90 meq.m⁻².yr⁻¹) and Ca²⁺, Mg²⁺, and Na⁺ (43%; 84 meq.m⁻².yr⁻¹) were major terrestrial proton sinks. Details are given in Table 2. The net release of H⁺ from the terrestrial sources ranged between 36 keq.yr⁻¹ (33 meq.m⁻².yr⁻¹) as estimated from budget for H⁺ (based on pH measurements), and 39 keq.yr⁻¹,

Table 2. – Mass balance of major ions and nutrients and net production of protons in the Černé 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 a 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 ⁺	36	0.03	73	0.07	36	0.03		
Ca ²⁺	875	0.79	1201	1.09	325	0.29		16
Mg ²⁺	200	0.18	744	0.67	544	0.49		45
Na ⁺	711	0.64	1438	1.30	727	0.66		32
K ⁺	1602	1.45	711	0.64	-891	-0.81	23	
NH ₄ -N	791	0.72	58	0.05	-734	-0.66	52	
NO ₃ -N	1082	0.98	2342	2.12	1259	1.14	90	
SO ₄ ²⁻	3759	3.40	8006	7.24	4246	3.84	88	
Cl	1003	0.91	1003	0.91	NA	NA		
F	17	0.01	36	0.03	20	0.02	1	
DOC	9482	8.57	6088	5.50	-3394	-3.07		24
TON	501	0.45	304	0.27	-197	-0.18		
Si	72	0.06	3297	2.98	3225	2.92		
TP	49	0.04	5	0.00	-44	-0.04		
Al _f	17	0.02	1309	1.18	1292	1.17		99
Fe _f	ND	ND	111	0.10	111	0.10		1

as calculated from the terrestrial sources and sinks of protons (Table 2). The terrestrial export of H^+ was 73 keq.yr^{-1} .

Compared to the Čertovo watershed (KOPÁČEK & al. 2001a), the CN watershed was a more pronounced source of NO_3^- , BC, and Al_i^{pt} . The terrestrial production of NO_3^- was nearly twice higher than NH_4^+ retention there (Table 2) and watershed export of dissolved inorganic nitrogen ($DIN = NO_3^- + NH_4^+$; $155 \text{ meq.m}^{-2}.\text{yr}^{-1}$) exceeded by 28% the DIN_4 deposition on the forest floor. Even though the lakes are situated on the opposite sides of the same mountain at comparable elevations and in the forests of comparable nature, the concentrations of NO_3^- were higher in CN and its tributaries for more than 40 years (PROCHÁZKOVÁ & BLÁŽKA 1999; VESELY & al. 1998a). The analysis of N cycling in watershed soils (ANDERSON & al. 2000) demonstrated the highest rates of nitrification in the watershed of CN among the Bohemian Forest lakes. The reason for this difference is unclear and has recently been under a more detailed study (H. ŠANTRŮČKOVÁ – pers. comm.).

The higher terrestrial transport of NO_3^- in the CN watershed was accompanied with higher leaching of BC and Al_i^{pt} . Hence, the terrestrial production of BC and Al_i^{pt} was higher by 19 and $18 \text{ meq.m}^{-2}.\text{yr}^{-1}$, respectively, in the CN watershed than in the Čertovo watershed. Con-

Table 3. – Mass balance of the major ions and nutrients and net production of protons in Černé 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 ⁺	4	77	2	30	-45	-0.2		
Ca ²⁺	84	1285	-246	1520	-11	-0.1	1	
Mg ²⁺	13	757	-127	771	-112	-0.6	9	
Na ⁺	78	1516	-28	1492	-52	-0.3	2	
K ⁺	76	787	-3	748	-42	-0.2	1	
NH ₄ -N	118	176	89	208	121	0.7		9
NO ₃ -N	132	2474	37	1573	-864	-4.7		62
SO ₄ ²⁻	399	8405	-630	7148	-1887	-10.3		39
Cl ⁻	99	1102	0	1102	NA	NA		
F ⁻	1	37	17	70	50	0.3	3	
DOC	287	6375	-49	2387	-4037	-21.9		10
TON	44	348	-66	303	-111	-0.6		
Si	3	3300	-287	2788	-799	-4.3		
TP	4.5	9.6	-0.5	6.1	-4.0	-0.02		
Al _T	2	1311	10	639	-662	-3.6		
Al _i	ND	1090	65	499	-526	-2.9	63	
Al _o	ND	207	-4	61	-150	-0.8		
Fe _T	ND	111	-64	118	-57	-0.3		
Fe _i	ND	40	0	55	16	0.1		0
Fe _o	ND	58	9	19	-31	-0.2		

sequently, the net terrestrial export of H⁺ from the CN watershed was lower than that from the Čertovo watershed (66 and 85 meq.m⁻².yr⁻¹, respectively).

Černé Lake was a net sink for H⁺, BC, NO₃⁻, SO₄²⁻, DOC, TON, Si, Al, and Fe and a net source of NH₄⁺ (Table 3). The total H⁺ input into the lake (the sum of terrestrial export and direct atmospheric deposition on the lake surface) was 77 keq.yr⁻¹. The H⁺ output from the lake was 30 keq.yr⁻¹ and the in-lake storage of H⁺ increased by 2 keq.yr⁻¹ (pH decreased from 4.97 to 4.93) during the study (Table 1 and 3). The net in-lake H⁺ reduction was 45 keq.yr⁻¹. Reductions in NO₃⁻, SO₄²⁻, and R concentrations and in-lake production of NH₄⁺ were dominant alkalinity generating processes, accounting for 51%, 33%, 9%, and 7%, respectively, while the Al₁^{III} hydrolysis was a major (80%) in-lake source of H⁺ (Table 3).

In-lake reduction of NO₃⁻ was comparable in CN and Čertovo Lake (335 and 333 meq.m⁻².yr⁻¹, respectively) and reduction of SO₄²⁻ was even higher in CN (214 vs. 149 meq.m⁻².yr⁻¹) even though there was no anoxia in CN and consequently, only a limited reduction of these anions in the water column. This disproportion may probably be explained by higher concentrations of NO₃⁻ and SO₄²⁻ in the CN hypolimnion, a higher concentration gradient across the water-sediment interface, and, consequently, their higher diffusion flux and reduction in the sediments. In addition, we can infer somewhat larger sediment area in CN than in Čertovo Lake from bathymetry of these lakes.

Despite the higher retention of SO₄²⁻, CN was less effective sink of H⁺ than Čertovo Lake (243 and 291 meq.m⁻².yr⁻¹, respectively) primarily due to the higher proton production by hydrolysis of Al₁^{III} (340 vs. 144 meq.m⁻².yr⁻¹). Hydrolysis of Al₁^{III} was substantially higher in CN because of higher Al concentrations in tributaries and higher pH of the lake water. However, the whole CN watershed-lake ecosystem was a net sink of protons consuming 10 keq.yr⁻¹ of H⁺ while the Čertovo watershed-lake ecosystem was a net source of protons (KOPÁČEK & al. 2000a and 2001a). The major difference between the watersheds was a lower terrestrial production of protons in the CN watershed due to higher leaching of BC, predominantly Ca²⁺.

The CN was a net sink for all nutrients, removing 41% of TP, 29% of total N (TN), 63% of DOC, and 24% of Si inputs (Table 3). In-lake removal was substantially higher than the average accumulation in sediments for N (854 vs. 225 kg.yr⁻¹) and organic C (4037 vs. 2312 kg.yr⁻¹), while substantially lower for TP (4 vs. 15 kg.yr⁻¹). The difference between the in-lake removal of N and N burial in sediments was a rough estimate of net denitrification rate (244 mmol.m⁻².yr⁻¹), which was comparable to the other two Bohemian Forest lakes in this study (KOPÁČEK & al., 2001a, b). The higher average burial of TP in sediments than the in-lake retention of TP suggests another source of P for the lake. The possible TP sources are discussed in a more detail in part I of this study, as well as the factors responsible for Si retention in the lake (sedimentation of chrysophycean cysts and scales; KOPÁČEK & al. 2001a).

Why there is no anoxia in the hypolimnion of Černé Lake?

Concentrations of O₂ in the CN water column were higher than in Čertovo Lake (Fig. 3, KOPÁČEK & al. 2001a) and were significantly reduced (O₂ <1 mg.l⁻¹) in only a thin layer (<1 m) above the bottom during the winter temperature stratification period. However, anoxic layer has never been observed in the CN hypolimnion in summer (JIROVEC & JIROVCOVA 1937, FORT & al. 1980, Fig. 3). In contrast, anoxia regularly occurred in Čertovo Lake both in summer and winter stratification periods even when the lake was completely mixed during the spring and autumn overturns (e.g. in 1998, KOPÁČEK & al. 2000a).

Water transparency in CN was higher than in Čertovo Lake throughout the year with the average Secchi depths of 6.1 and 3.9 m, respectively. Historical (1982–1999) records on chlo-

rophyll *a* concentrations in CN and Čertovo Lake varied within 0.6–6.3 and 0.6–5.9 $\mu\text{g}\cdot\text{l}^{-1}$, respectively, with medians of 2.6 $\mu\text{g}\cdot\text{l}^{-1}$ in both lakes (J. FORT – pers. comm., VRBA & al. 1996, 2000). Higher transparency, lower concentrations of chlorophyll *a*, and the absence of anoxic hypolimnion in CN suggest a lower productivity of this lake. However, the total nutrient loading of CN and of Čertovo Lake by terrestrial export and direct atmospheric deposition were well comparable on the area scale (TP, 52 and 58 $\text{mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$; TN, 16 and 17 $\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$; Si, 18 and 23 $\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively), as well as on the volumetric scale (e.g. TP, 3.3 and 3.2 $\text{mg}\cdot\text{m}^{-3}\cdot\text{yr}^{-1}$, respectively), and differed only in DOC loading (35 and 53 $\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively) in 2000 (Table 3, KOPÁČEK & al. 2001a). Similarly, the in-lake retention of nutrients in CN and in Čertovo Lake were comparable (TP, 22 and 19 $\text{mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$; TN, 4.6 and 5.1 $\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$; and DOC, 22 and 19 $\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively) with the exception of Si (4.3 and 5.6 $\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively). The lower DOC input and in-lake concentration can in part explain the higher transparency in CN. However, none of the above parameters can explain why these lakes differ in oxic conditions.

Volumes of euphotic zones (twofold of Secchi depth) in CN and Čertovo Lake were 1800000 and 726000 m^3 , respectively, and the ratios of volumes of euphotic zones to the volumes of decomposition zones (water below the euphotic zone) were 1.7 and 0.6, respectively. At the comparable in-lake retention of nutrients, higher hypolimnetic concentrations of O_2 can be expected in the lake with a bigger hypolimnion (and/or with lower ratio of productive to decomposition zones) due to lower concentration of sedimenting matter (the substrate for dissimilatory decomposing processes) in the hypolimnion. The hypolimnetic nutrient loads, calculated as in-lake retention of nutrients per volume of hypolimnion (water below 5-m depth), were surprisingly higher in CN than in Čertovo Lake (TP, 1.9 and 1.4 $\text{mg}\cdot\text{m}^{-3}\cdot\text{yr}^{-1}$; DOC, 2.0 and 1.4 $\text{g}\cdot\text{m}^{-3}\cdot\text{yr}^{-1}$, respectively). Such results suggest that anoxia would preferably occur in CN and are in contrast with the observed O_2 concentrations in the lakes.

This disproportion can be probably explained by a complex of morphological and biochemical characteristics of these two lakes which can influence input of easily decomposable organic C into the CN decomposing zone and O_2 transport into the CN hypolimnion. The surprisingly high in-lake DOC removal in CN despite the lower DOC loading of this lake could result from higher amount of recalcitrant allochthonous DOC coprecipitated with Al, as well as from higher respiration of DOC in the CN epilimnion. In any case, the load of easily decomposable organic matter sedimenting into the CN hypolimnion would be lower compared to the Čertovo hypolimnion at the similar in-lake removal of DOC.

Precipitation and retention of Al were more pronounced in CN than in Čertovo Lake (3.3 and 1.7 $\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively), which might also indicate a higher Al coprecipitation with DOC. Because the molar DOC:DP ratios in the tributary input were substantially higher (5000–6000) than the sestonic molar C:P ratios in both lakes, the significant contribution of allochthonous organic matter into the total pool of seston should significantly increase the sestonic C:P ratios. Moreover, the higher input of recalcitrant organic matter into sediments should also increase their C:P ratios. However, the molar C:P ratios of seston and of the uppermost sediment layers were comparable in both lakes (700–800 in seston and ~400 in sediment), which implicate that the proportion of allochthonous DOC in seston was roughly comparable. Also, the concentrations of seston were similar in both lakes; the average concentrations (\pm standard deviations) of particulate C were 0.59 ± 0.14 and 0.57 ± 0.20 $\text{mg}\cdot\text{l}^{-1}$ in CN and Čertovo Lake, respectively, in 2000. Thus, the coprecipitation of DOC with Al cannot probably explain the observed difference in oxic conditions of the lakes.

On the other hand, the higher transparency in CN enabled the light penetration into the deeper water layers and could result in higher photochemical degradation of allochthonous recalcitrant organic matter to carbon oxides. Moreover, partial photochemical degradation of

allochthonous DOC produces biologically available compounds for bacterial growth (WETZEL & al. 1995). This mechanism can support productivity of heterotrophic microbial biomass in CN more than in Čertovo Lake. Consequently, both the higher photochemical oxidation and respiration of DOC in the CN epilimnion could result in lower loading of hypolimnion with organic C. Moreover, the lakes differ in the planktonic composition at present (e.g. VRBA & al. 2000), with almost absent zooplankton in Čertovo Lake and recovering zooplankton in CN. The zooplankton can also contribute to respiration of organic carbon in the CN water column and reduce its flux into the sediments.

Another factor, which can contribute to lower loading of the deepest water layers with sedimenting matter in CN is the lake bathymetry. Čertovo Lake has its maximum depths in the center and functions as a funnel, which can accumulate the sedimenting matter from the whole lake surface. In contrast, CN has its maximum depths in the back part (Fig. 1) and can accumulate sedimenting matter from about a half of the epilimnion. The sedimenting matter in the front half of the lake is more likely deposited and decomposed in the shallow and flat bottom of this part.

The O_2 transport and distribution in the CN hypolimnion can be more pronounced than in the Čertovo hypolimnion from at least three following reasons. First, larger CN is exposed to more intensive wind mixing. This resulted in the development of on average ~ 2 m deeper epilimnion in CN than in Čertovo Lake in 2000. The intensive water mixing in epilimnion can induce water circulation also in the hypolimnion and transport of oxygenated water into the bottom layer (e.g. WETZEL 1983). Such mechanism would explain why there is more O_2 above the CN bottom during summer stratification than during the ice-on period (Fig. 3).

Second, the higher transparency of CN enables a development of phytoplankton below the epilimnion and results in pronounced O_2 maxima in ~ 10 m depth (JIROVEC & JIROVCOVÁ 1937, FORT & al. 1980, Fig. 3). In contrast to Čertovo Lake with lower transparency and most of its primary production in epilimnion, this mechanism represents an additional O_2 source for CN hypolimnion.

Third, subsurface water inputs can also supply the CN hypolimnion with O_2 . There is a relatively large part of the CN watershed between the tributaries CN-V and CN-VII (close to the maximum depth of the lake) which supplies negligible surface water input. Although we do not know the geological structure of this subwatershed we can hypothesize that the missing water enter the lake via subsurface springs, potentially bringing O_2 below the thermocline. However, there apparently is also some subsurface input of anoxic water (VESELY 1994).

To conclude, the absence of anoxia above the bottom of CN cannot be simply explained either by differences in nutrient loading of the lake, or by somewhat lower productivity, suggested by differences in chlorophyll *a* concentrations and in-lake retention of Si. Other factors like morphological and microclimatic conditions and the intensity of respiration of organic C are more likely to explain the question asked in the subtitle of this chapter and, should be studied closely.

CONCLUSIONS

The total atmospheric input of H^+ into the CN watershed-lake ecosystem was 40 keq.yr^{-1} in the 2000 hydrological year. The output of H^+ from the lake was 30 keq.yr^{-1} . Thus, the watershed-lake ecosystem was a net sink of $\sim 10 \text{ keq.yr}^{-1}$ of H^+ . The watershed was a net source of H^+ ($33 \text{ meq.m}^{-2}\text{.yr}^{-1}$) 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^{3+} leaching as the principal proton-consuming processes. The lake was a net sink of H^+ ($243 \text{ meq.m}^{-2}\text{.yr}^{-1}$) with assimilation and denitrification of NO_3^- ($335 \text{ meq.m}^{-2}\text{.yr}^{-1}$) and reduction of SO_4^{2-} (214

meq.m⁻².yr⁻¹) being the most important aquatic proton-consuming processes. Hydrolysis of Al₃⁺ was a dominant aquatic source of H⁺ (340 meq.m⁻².yr⁻¹).

Terrestrial sources mostly dominated the total input of NO₃⁻, TON, DOC, and Si into the lake, while direct atmospheric deposition on the lake surface was a major allochthonous source of NH₄⁺ and DRP. Tributaries and precipitation were comparable TP sources for the lake. The lake was a net sink for all nutrients, removing 41% of TP, 29% of TN, 63% of DOC, and 24% of Si supplied by both terrestrial and atmospheric sources.

Neither the nutrient loading of CN nor its productivity can explain the absence of anoxia in the CN hypolimnion compared to Čertovo Lake in the 2000 hydrological year.

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