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Ionic fluxes in the Čertovo watershed-lake ecosystem in the 1998 hydrological year

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Abstract

Fluxes of major ions were evaluated for the watershed-lake ecosystem of Čertovo Lake in the Bohemian Forest in the 1998 hydrological year. Water balance in the watershed-lake ecosystem was estimated from precipitation and throughfall amounts and Cl^- balance, assuming Cl^- to be a conservative anion with no net release or sink in the ecosystem. Annual volume weighted mean (VWM) compositions of atmospheric deposition, tributaries, and lake output together with the water balance were used to calculate the mass balances for H^+ and major ions in the terrestrial and aquatic parts of the ecosystem. The total atmospheric input of H^+ into the Čertovo watershed-lake ecosystem was 42 keq y^{-1} (39 keq y^{-1} into the watershed and 3 keq y^{-1} into the lake). Terrestrial production and consumption of H^+ ions was 128 and 100 keq y^{-1}, respectively. There were the following terrestrial sources of protons: SO_4^{2-} release (41%), NH_4^+ assimilation and nitrification (39%), Ca^{2+} and K^+ retention (18%), and F^- release (2%). In contrast, the release of Al^{n+} (49%), Mg^{2+} (24%), Na^+ (21%), and Fe (1%) and retention of R^- (5%) were the major terrestrial sinks of protons. The net release of H^+ from the terrestrial sources was 28 keq y^{-1} (0.36 keq ha^{-1} y^{-1}). The total H^+ input into the lake, obtained as a sum of terrestrial export (66 keq y^{-1}) and direct atmospheric deposition onto the lake surface, was 69 keq y^{-1}. The H^+ output from the lake was 46 keq y^{-1} and the in-lake storage of H^+ decreased by 3 keq y^{-1}. The in-lake processes consumed 37 keq y^{-1} of H^+; decreases in R^- and NO_3^- concentrations were the dominant processes accounting for 42% and 34% of the total H^+ consumption, respectively. A probable explanation for the decrease in R^- concentration was photochemical and microbial decomposition of allochthonous organic matter, while denitrification was the most probable sink for NO_3^-. Al^{n+} hydrolysis was the major in-lake source of H^+ (88% of the total 11 keq y^{-1}). The net in-lake H^+ consumption was 26 keq y^{-1} (2.5 keq ha^{-1} y^{-1}). The whole watershed-lake ecosystem of Čertovo Lake was a net source of 4 keq H^+ in the 1998 hydrological year.

Key words: Mass balance, acidification, nitrogen, sulfur, aluminum, base cations, pH, organic acids.

Introduction

Mass-balance studies for watershed-lake ecosystems in areas sensitive to acidification show a wide variability of relative importance of terrestrial and in-lake processes in acid neutralizing capacity of the ecosystem (Schindler 1986, Stoddard 1987). Ion exchange and weathering of soils and rocks, and biological assimilation of nitrate and other anions are the dominant terrestrial sinks of protons. In contrast, nitrification or assimilation of ammonium and the net accumulation of cations in biomass are the major terrestrial sources of protons (e.g., van Breemen & al. 1984). The internal sink of protons in acid sensitive lakes is usually dominated by biochemical reduction of nitrate and sulfate (Cook & al. 1986, Rudd & al. 1986, Schindler & al. 1986, Thies 1997). Other important in-lake proton consumers are iron(III) reduction during anoxia and proton exchange for base cations in sediment (Schiff & Anderson 1986 and 1987, Psenner 1988). Nitrification, assimilation of ammonium, and

hydrolysis of ionic Al forms (Al_i) can be important in-lake proton generating processes (SCHINDLER & al. 1986, KOPÁČEK & al. 2000).

The role of terrestrial processes in proton consumption in a watershed-lake ecosystem depends on several factors like its morphology, stage of acidification, and bedrock composition. Generally, the terrestrial proton consumption prevails in non-acidified areas and its importance increases with a watershed to lake ratio. In contrast, the in-lake biochemical reduction of nitrate and sulfate becomes more important as lake acidify and concentrations of NO_3^- and SO_4^{2-} increase (SCHINDLER 1986), and is more pronounced in lakes with long water residence times (KELLY & al. 1997). In some extreme situations, the in-lake processes may become the only net sink for proton flux through the ecosystem. Such a situation was observed in some acid-sensitive areas, e.g. in Sudbury, Ontario, where the terrestrial proton sources prevailed the sinks and the water exported from watershed was more acidic than atmospheric deposition after the reduction in smelters' emissions. The reason behind it was the net loss of sulfate from soils reaching new steady state conditions after reductions in S emission (SCHINDLER 1986).

Our recent results on the composition of surface waters in the Bohemian Forrest (e.g. KOPÁČEK & al. 1999, KOPÁČEK & al. 2000) suggest similar situation to that in Sudbury area. Since 1989, the Bohemian Forest lakes have been recovered from acidification (KOPÁČEK & al. 1998a) due to ~65% and ~35% reduction in Central European emissions of S and inorganic N compounds, respectively, between the 1985–1989 and 1996–1997 periods (BERGE 1997). Recent concentrations of sulfate in some streams exceed that in throughfall by a factor of two and more and their pH values are lower than in throughfall, suggesting a depleted ability of the watersheds to neutralize acid deposition (BEUDERT & KANTOR 1999; KOPÁČEK & al. 2000).

The aim of this study is to quantify net terrestrial and aquatic sources and sinks of protons in the most acidified watershed-lake ecosystem of the Bohemian Forest (Čertovo Lake). Using fluxes of major ions in the deposition onto the forest floor, in tributaries, and in output from the lake we (1) calculate here mass balances for major ions to show which elements are released or retained in the watershed soils and vegetation and in the lake during their transport throughout the ecosystem and (2) evaluate how these changes influence concentration of protons in the water.

Materials and methods

Description of study site

Čertovo Lake is situated in the Bohemian Forest (the Šumava Mountains; 49° 10' N, 13° 12' E; ~135 km SW of Prague) at an altitude of 1028 m a. s. l. The lake is of glacial origin with the following morphological characteristics: area, 10.5 ha; volume, 1 852,000 m^3; maximum depth, 36 m; mean depth, 17.9 m; watershed area including lake, 87.5 ha (ŠVAMBERA 1939), and theoretical water residence time in the 1998 hydrological year (see later), 567 days. The lake is surrounded by steep forested rocky slopes with the maximum local relief of 315 m. The bedrock is made up of gneiss (two-mica schist), quartzite, and small amounts of pegmatite (VESELÝ & al. 1993). Most of the watershed is covered with a thin layer of forest humus. Soils are iron containing acidic podzols with low levels of Ca and K and an unsaturated sorption complex; soil profiles deeper than 10–30 cm are sparse (VESELÝ & al.1993).

Forest in the lake watershed was not probably seriously disturbed before ~1600. However, wood production is documented there in the 17th and 18th centuries and most of the original forest was clear-cut in the early 19th century (VESELÝ & al. 1993). Between 1754 and 1859, the area was used for grazing of ~100 cows. Then, this type of land use was prohi-

bited, marshy soils were drained and the watershed was reforested (VESELÝ 1994). The area has been protected as a nature park since 1911 and at present the forest (dominated with Norway spruce) is 80–140 years old (VESELÝ & al.1993).

Čertovo Lake is a dimictic, oligotrophic lake with anoxia only in the deepest part of hypolimnion during winter and late summer stratification periods. The lake has been naturally acidified for several hundreds years (VESELÝ & al.1993). Atmospheric input of strong acid anions further enhanced acidification of Čertovo Lake and PROCHÁZKOVÁ & BLAŽKA (1999) determined lake water pH of ~5.0 in the early 1960s. Atmospheric acidification of the lake progressed until the middle 1980, when pH ranged between 4.26 and 4.32, and SO_4^{2-} and NO_3^- reached 171–185 and 60–85 μeq l^{-1}, respectively (VESELÝ & al. 1993). A continuous decline in SO_4^{2-} and NO_3^- concentrations and increase in pH has occurred since the second half of the 1980s (VESELÝ & al. 1998a,b). The lake reversal of atmospheric acidification still continues, and its water composition in 1997 was as follows: pH, ~4.4; SO_4^{2-}, 123 μeq l^{-1}; and NO_3^-, 41–52 μeq l^{-1} (KOPÁČEK & HEJZLAR 1998). At present, Čertovo Lake is fishless, without any planktonic crustacea (the only zooplankton species are rotifers) and poor in number of phytoplankton species which are dominated by flagellates (FOTT & al. 1994, VRBA & al. 1996)

The lake has seven surface tributaries (Fig. 1); three of them (CT-II, CT-VI, and CT-VII) were perennial in 1997–1998, the others temporal. CT-II was the major tributary, representing 48–80% (64% on average) of the total water input by tributaries.

Sampling and analyses

Atmospheric deposition was collected at three sites (Fig. 1) using bulk samplers protected against light and bird perching, and fitted with a 100-μm polyamide sieve to remove coarse particles. 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 1175 m a. s. l.). Samples were taken from November 3, 1997 to November 4, 1998. Rain was sampled in two-week intervals, and snow in three to four-week intervals. All samples from each site were combined to obtain an integrated sample.

Samples from tributaries and outlet were taken monthly and biweekly (weekly during snowmelt), respectively. Discharges of tributaries were estimated using a stop-watches and bucket and each sample was analyzed separately. A discharge of outlet was measured with a recording gauge situated ~150m downstream of the lake outflow (Fig. 1). Samples of lake water were taken at the deepest part of the lake from the following depths: 0.5 m, the thermocline (4–6 m), 10 m, 20 m, 30 m, and 0.5 m above the bottom (~33 m). 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 mm; Macherey Nagel) for determination of ions and with glass-fibre filters (MN–5; pore size of 0.4 μm; Macherey Nagel) for the analyses of organic matter, and dissolved Al and Fe. The samples for pH, acid neutralizing capacity (ANC), and total Al and Fe were not filtered. Dissolved organic carbon (DOC) was analyzed with a LiquiTOC analyser (Foss/Heraeus). Molar absorptivity of DOC at 254 nm (A_{254}:DOC, $m^2 mol^{-1}$) was obtained as a ratio of A_{254} (absorbance at 254 nm recalculated per 1 m absorption path) to DOC concentration (mol m^{-3}). ANC (Gran titration) and pH, were analyzed within 24 hours of 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 (Thermo Separation Products) within a month. In the same sample, NH_4^+ was analyzed by the rubazoic acid method (KOPÁČEK & PROCHÁZKOVÁ 1993).

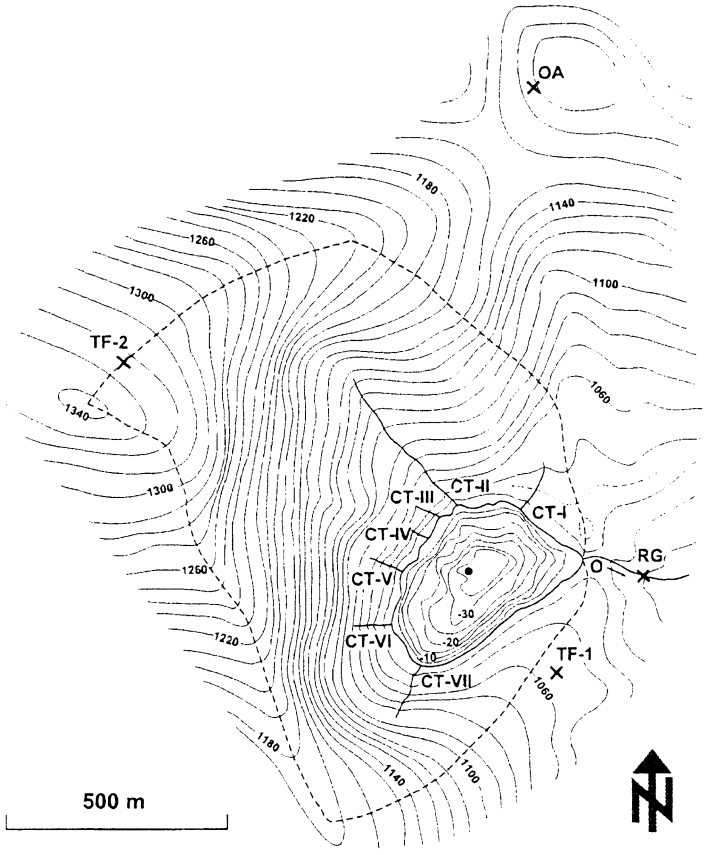

Fig. 1. – Map of the Čertovo Lake watershed (dashed line; approximate boundary) with the locations of sampling and measuring sites: (1) lake water, full circle at the maximum depth in the bathymetric map of the lake; (2) tributaries, CT-I to CT-VII, (3) outlet, O, (4) precipitation samplers, crosses (OA, open area; TF-1 and TF-2, throughfall), and (5) recording gauge, (RG).

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, with the method by DOUGAN & WILSON (1974). Concentration of ionic Al (Al_i) was the difference between Al_D and Al_o. 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. 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 hydroxocom-

plexes, respectively, at the sample pH (KOPÁČEK & al. in press). Concentrations of organic acid anions (R^-, μeq l^{-1}) in tributaries were estimated according to the OLIVER & al. (1983) model using concentrations of DOC, Al_o, Fe_o, and pH as described by KOPÁČEK & al. (in press). The OLIVER & al. (1983) model was also used to estimate R^- concentrations in the lake and its outlet. However, lower site density (3 μeq l^{-1} per mg DOC; KOPÁČEK, unpublished data) was used in the calculation due to a lower proportion of humic and fulvic acids in the total pool of organic matter in the lake compared to the tributaries. In the precipitation and throughfall, R^- concentrations were obtained by multiplying DOC concentration with a coefficient of 4 (4 μeq per mg DOC), which best fitted the charge balance control in the individual samples within pH range observed in the study (KOPÁČEK, unpublished data). As the R^- concentration was obtained independently of the other ions, its correctness could be checked in ionic balance control. The average difference between the sum of the cations and the sum of the anions calculated according to MOSELLO & al. (1995) was -0.8%, -0.9%, -2.3%, and <±1% for precipitation, TF-1, TF–2, and samples of surface water (tributaries, outlet and lake), respectively. More details on analytical methods and their precision are given in KOPÁČEK & al. (in press).

Water and mass balances

Mass balances of chemical constituents in the watershed and lake were calculated according to equations (1) and (2), respectively:

$$Q_{DEP}C_{DEP} + P_W = Q_{IN}C_{IN} \tag{1}$$

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

where Q_{DEP}, Q_{IN}, Q_P, and Q_{OUT} (all in m^3 y^{-1}) are total atmospheric deposition of water onto the forest floor, water input into the lake from its watershed, direct atmospheric deposition onto 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 concentrations of a constituent in the atmospheric deposition onto the forest floor, in tributaries, in direct atmospheric deposition onto lake surface, and in the lake output, respectively. P_W and P_L (both in kg y^{-1}) are net mass production (when positive) or retention (when negative) of a constituent in the watershed and lake, respectively. DM_L (kg y^{-1}) is change in storage of a constituent in the lake during mass budget period. 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). DM_L was obtained from equation (3):

$$\Delta M_L = V_2 C_2 - V_1 C_1 \tag{3}$$

where V_1 and V_2 (both in m^3) are lake volumes at the beginning and the end of the study, i.e., during the autumn overturns in November 1997 and November 1998, respectively. C_1 and C_2 (both in kg m^{-3}) are the respective average lake water concentrations of a constituent calculated from data on six depths between the surface and bottom.

Water balance was determined from annual heights (m y^{-1}) of precipitation and throughfall at sites 1 and 2 (H_P, H_{TF-1}, and H_{TF-2}, respectively) and the budget for Cl^-. The average atmospheric deposition of water onto the forest floor was calculated according to equation (4):

$$Q_{DEP} = (A_W - A_L)(0.2H_P + 0.8(0.3H_{TF-1} + 0.7H_{TF-2})) \tag{4}$$

where A_W and A_L (m^2) is area of the watershed (including lake) and lake, respectively. Coefficients 0.2 and 0.8 represent portions of the watershed, which were assumed to receive atmospheric deposition in the form of precipitation and throughfall, respectively. Coefficients 0.3 and 0.7 represent portions of the watershed, which were assumed to receive throughfall 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 Q_{DEP} and the annual VWM concentrations of Cl^- in the atmospheric deposition (Cl_{DEP}) and tributaries (Cl_{IN}):

$$Q_{IN} = Q_{DEP} \frac{Cl_{DEP}}{Cl_{IN}} \tag{5}$$

Q_{OUT} was calculated using Q_{IN} and Q_P, the annual VWM concentrations of Cl^- in tributaries, precipitation (Cl_P), and lake outflow (Cl_{OUT}), and the change in storage of Cl^- (ΔCl_L) in the lake during mass budget period from the rearranged equation (2):

$$Q_{OUT} = \frac{Q_{IN} Cl_{IN} + Q_P Cl_P - \Delta Cl_L}{Cl_{OUT}} \tag{6}$$

where the in-lake mass production and/or consumption of Cl^- was neglected.

All concentrations of Cl^- and other ions used in the above equations were annual volume weighted mean (VWM) averages calculated as follows. (1) Annual volume- and period-weighted mean composition of tributaries (C_{IN}) was determined using the compositions and discharges of all tributaries throughout the hydrological year. In this calculation, each flux was assumed to represent the whole period given as the sum of halves of intervals between the sampling and the previous one and between the sampling and the next one. (2) Annual VWM composition of water output from the lake (C_{OUT}) was calculated by linking continuously monitored discharge data of the outlet with the corresponding weekly to biweekly concentration data by the method of period-weighted mean. (3) Annual VWM composition of the atmospheric deposition onto the forest floor (C_{DEP}) was calculated from the heights and VWM compositions of precipitation (C_P) and throughfall at sites 1 (C_{TF-1}) and 2 (C_{TF-2}):

$$C_{DEP} = \frac{0.2 C_P H_P + 0.8(0.3 C_{TF-1} H_{TF-1} + 0.7 C_{TF-2} H_{TF-2})}{0.2 H_P + 0.8(0.3 H_{TF-1} + 0.7 H_{TF-2})} \tag{7}$$

where coefficients 0.2, 0.8, 0.3, and 0.7 are the same as in equation (4).

The net terrestrial and aquatic consumption/production of protons was calculated from mass balance budgets for H^+ (based on pH measurements). 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 with neglected concentrations of OH^-, HCO_3^-, and CO_3^{2-} (8):

$$[H^+] = [SO_4^{2-}] + [NO_3^-] + [Cl^-] + [F^-] + [R^-] - [NH_4^+] - [Na^+] - [K^+] - [Ca^{2+}] - [Mg^{2+}] - [Al^{m+}] - [Fe^{m+}] \tag{8}$$

where brackets represent equivalent concentrations of components. According to equation (8) any increase in concentration of cations or decrease in concentration of anions in an ecosystem are proton consuming processes. In contrast, any decrease in concentration of cations or increase in concentration of anions are proton producing reactions. For details and reactions involved see e.g., PSENNER (1988).

Results

The annual VWM compositions of precipitation, throughfall, tributaries and lake output, as well as chemical compositions of Čertovo Lake during the autumn overturns in 1997 and

Table 1. – VWM concentrations of the major constituents of atmospheric deposition, tributaries, lake output and lake water at the start (November 1997) and end (November 1998) of the study in the Čertovo watershed-lake ecosystem. Number of observations, n; not determined, ND; pH averages were calculated from the average H^+ concentrations.

		Precipitation	TF–1	TF–2	Tributaries	Lake output	Lake water	
							Start	End
n		17	17	17	14	37	1	1
Height	mm	1580	1020	1599				
Discharge	$l\ s^{-1}$				17.5	39.6		
pH		4.77	4.53	4.37	4.20	4.42	4.47	4.49
ANC	$\mu eq\ l^{-1}$	–14	–24	–36	–58	–41	–32	–48
Ca^{2+}	$mg\ l^{-1}$	0.17	0.66	0.56	0.49	0.50	0.53	0.49
Mg^{2+}	$mg\ l^{-1}$	0.04	0.15	0.11	0.40	0.36	0.36	0.36
Na^+	$mg\ l^{-1}$	0.20	0.34	0.38	0.83	0.71	0.69	0.71
K^+	$mg\ l^{-1}$	0.29	1.38	1.14	0.30	0.37	0.33	0.37
NH_4-N	$\mu g\ l^{-1}$	422	535	574	1	54	58	71
NO_3-N	$\mu g\ l^{-1}$	358	506	686	735	612	533	486
SO_4^{2-}	$mg\ l^{-1}$	1.46	2.96	3.29	5.55	5.46	5.60	5.28
Cl^-	$mg\ l^{-1}$	0.32	0.70	0.67	0.65	0.65	0.63	0.61
F^-	$mg\ l^{-1}$	0.01	0.02	0.02	0.05	0.045	0.06	0.04
DOC	$mg\ l^{-1}$	1.30	10.70	7.66	6.54	2.79	2.23	3.44
A_{254}:DOC	$m^2\ mol^{-1}$	12	26	26	48	39	39	40
Al_T	$\mu g\ l^{-1}$	6	10	12	665	559	587	578
Al_D	$\mu g\ l^{-1}$	ND	ND	ND	651	542	571	555
Al_o	$\mu g\ l^{-1}$	ND	ND	ND	175	71	21	65
Fe_T	$\mu g\ l^{-1}$	31*	58*	49*	164	177	160	203
Fe_D	$\mu g\ l^{-1}$	ND	ND	ND	146	125	135	115
Fe_o	$\mu g\ l^{-1}$	ND	ND	ND	100	35	20	42

*) VWM average for 1992–1996 (VESELÝ & HRUŠKA, personal communication)

1998 (the beginning and end of study, respectively) are given in Table 1. ANC and pH in the outlet was higher than in the tributaries throughout the year with the exception of melting period in March (Fig. 2). Winter concentrations of base cations, Al_T and NO_3^- were higher in the tributaries than in the outlet, while the summer K^+ and Al_T concentrations were higher in the outlet (Fig. 2). Concentrations of SO_4^{2-} were higher in the outlet than in the tributaries throughout the study, while Cl^- concentrations were comparable. Among all major water constituents of tributaries, only NO_3^-, Al_T, K^+, and DOC followed a distinctive seasonality (Fig. 2).

Depth and time variations in physical and chemical parameters of lake water are shown in Fig. 3. The temperature stratification of Čertovo Lake developed characteristically for a dimictic temperate lake. The autumn and spring overturns occurred in November and April, respectively; ice cover lasted from November 20, 1997 to April 17, 1998. Hypolimnetic concentrations of dissolved oxygen were depleted to values < 0.1 $mg\ l^{-1}$ in the bottom layer (1-2 m above the sediments) both during winter and summer stratification. At low redox potentials, dissimilatory reduction processes occurred decreasing NO_3^- and SO_4^{2-} concentrations and increasing concentrations of NH_4^+ and Fe forms. Concentrations of Fe_D varied be-

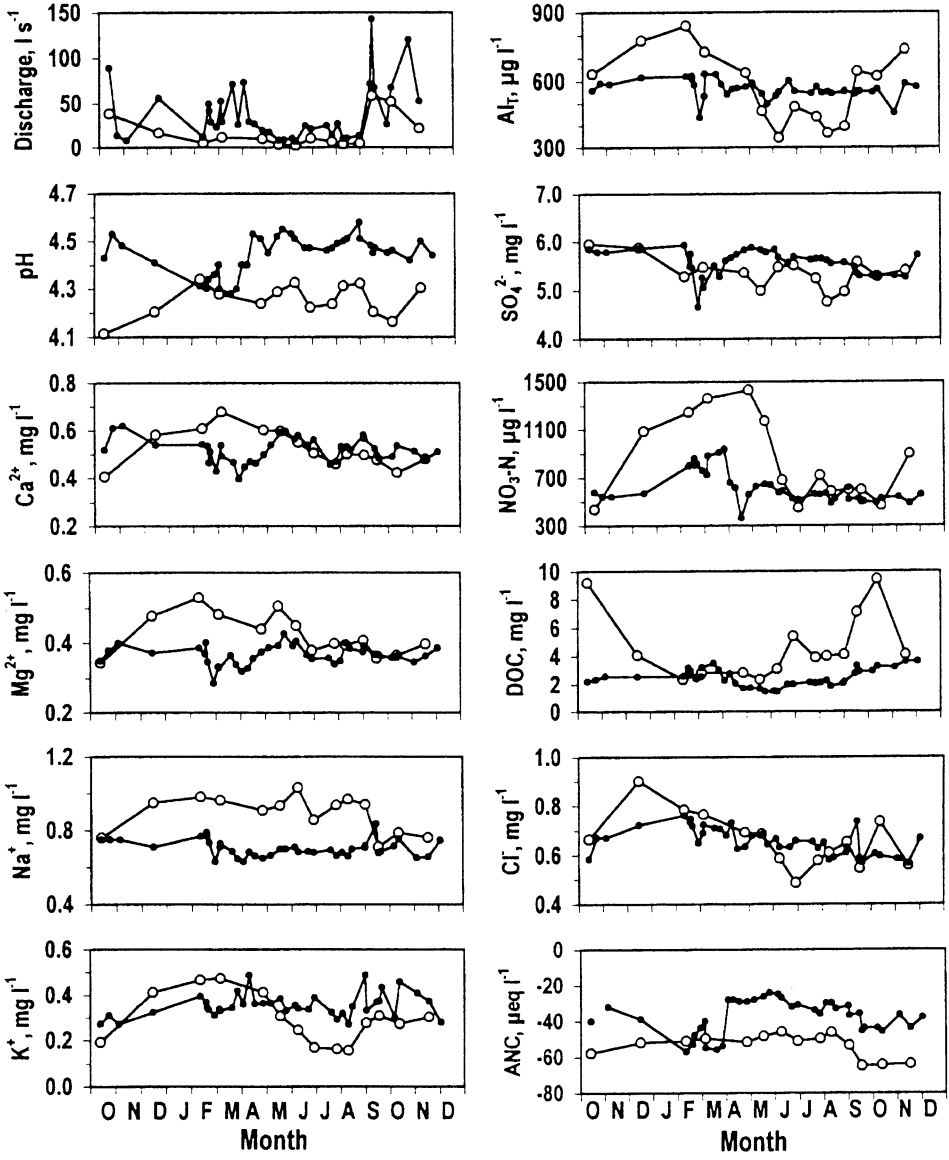

Fig. 2. – Seasonal patterns of discharge, pH and concentrations of major constituents of the Čertovo Lake tributaries (open circles, volume-weighted means for all tributaries) and the outlet (full circles) in the 1998 hydrological year.

tween 115–150 mg l^{-1} and 110–7,400 mg l^{-1} in the epilimnion and above sediments, respectively. The release of base cations from the sediments was unimportant, except for K^+, which was in summer twofold higher above the bottom compared to its epilimnetic concentration (Fig. 3). The above changes led to the increase in the hypolimnetic pH. An important change was observed in depth and time variation of molar absorptivity of DOC at 254 nm. The

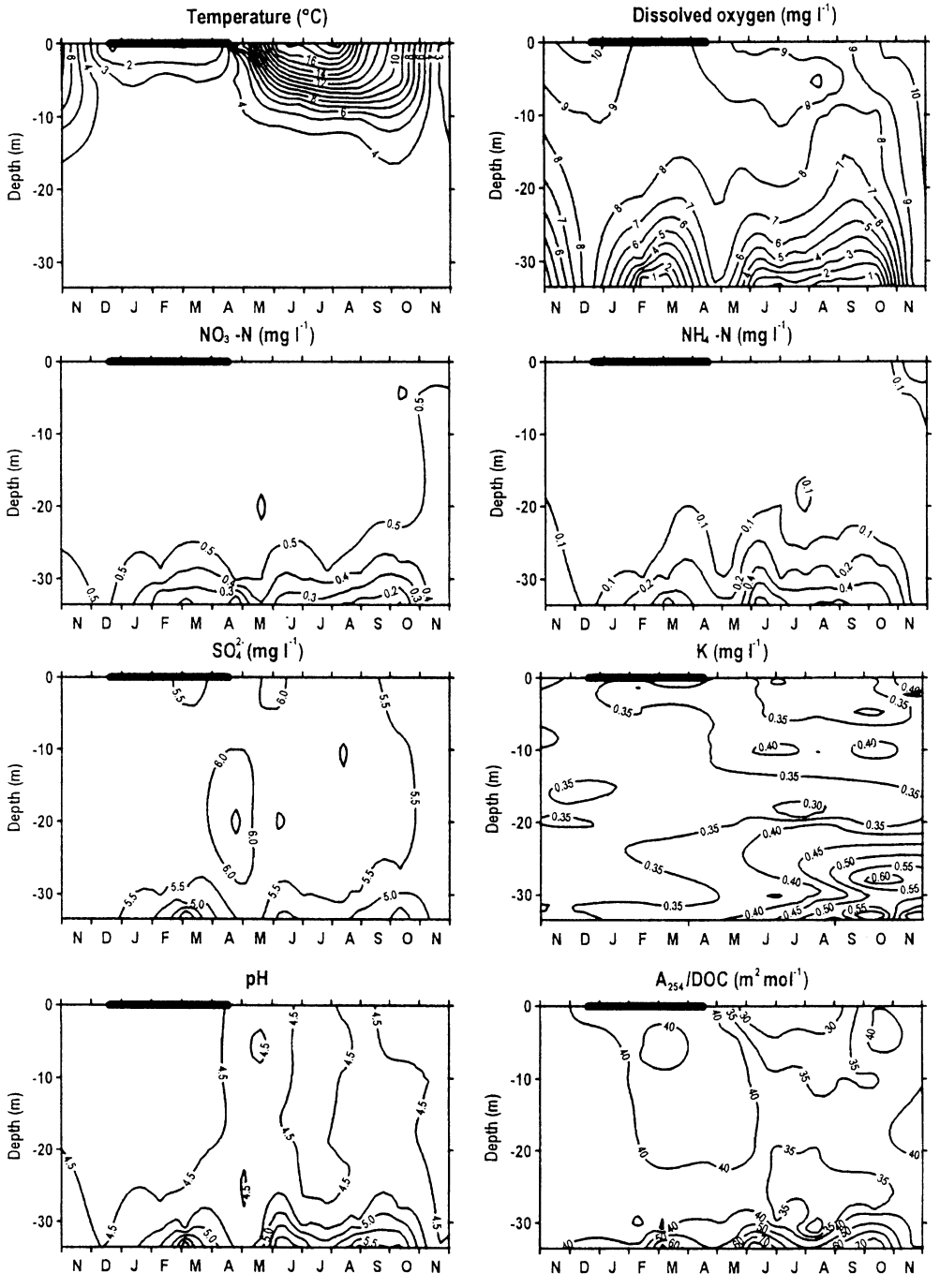

Fig. 3. – Depth-time diagrams of temperature, dissolved oxygen, NO_3-N, NH_4-N, SO_4^{2-}, K^+, pH, and molar absorptivity of DOC at 254 nm (A_{254}:DOC). Čertovo Lake in the 1998 hydrological year. Thick lines represent ice-cover.

Table 2. – Mass balance of the major water constituents in the individual parts of Čertovo watershed-lake ecosystem in the 1998 hydrological year. Negative values indicate net removal. Abbreviations: WE, watershed export (i.e. watershed output via tributaries); ND, not determined; N, not determined but negligible. Total input to the lake is the sum of direct atmospheric deposition (DAD; precipitation) on the lake surface and WE.

	WATERSHED								LAKE					
	Precipitation		Deposition onto the forest floor		WE (tributaries)		Net production		Total input (DAD+WE)		Change in storage	Output	Net production	
	kg	g m^{-2}	kg	g m^{-2}	kg	g m^{-2}	kg	g m^{-2}	kg	g m^{-2}	kg	kg	kg	g m^{-2}
H^+	21	0.03	39	0.05	66	0.09	27	0.03	69	0.66	–3	45.5	–26.4	-0.26
Ca^{2+}	206	0.27	553	0.72	509	0.66	–44	-0.06	537	5.19	–80	599	–18	-0.17
Mg^{2+}	48	0.06	118	0.15	413	0.53	295	0.38	419	4.05	–6	429	4	0.04
Na^+	242	0.31	375	0.49	854	1.11	479	0.62	886	8.57	46	846	6	0.06
K^+	351	0.45	1120	1.45	315	0.41	–805	–1.04	362	3.50	74	441	154	1.49
NH_4-N	515	0.67	601	0.78	1	0.00	–599	-0.78	70	0.68	25	65	19	0.19
NO_3-N	436	0.56	656	0.85	761	0.99	104	0.14	819	7.92	–86	729	–176	–1.70
SO_4^{2-}	1779	2.31	3187	4.13	5746	7.45	2559	3.32	5984	57.9	–593	6505	–72	-0.70
Cl^-	392	0.51	677	0.88	677	0.88	0	0.00	730	7.06	–46	776	0	0.00
F^-	0	0.00	16	0.02	47	0.06	31	0.04	47	0.45	-0.03	54	7	0.07
DOC	1586	2.06	7630	9.89	6765	8.77	–865	–1.12	6978	67.5	2226	3323	–1428	–13.8
Al_T	7	0.01	12	0.01	688	0.89	677	0.88	689	6.67	–16	666	–39	-0.38
Al_D	N	N	N	N	674	0.87	642	0.87	674	6.52	–30	645	–58	-0.56
Al_o	N	N	N	N	181	0.23	183	0.23	181	1.75	82	84	–15	-0.14
Fe_T	38	0.05	52	0.07	170	0.22	117	0.15	175	1.69	80	211	116	1.13
Fe_D	N	N	N	N	151	0.20	151	0.20	151	1.46	–37	149	–40	-0.38
Fe_o	N	N	N	N	103	0.13	103	0.13	103	1.00	41	41	–21	-0.21
H_2O[1)]	1219	1124	1035			1198		0	1190					

[1)]Water balance is in kilotons.

A_{254}:DOC ratios substantially decreased in the surface layers of the lake in summer (probably due to photobleaching), and were higher above the bottom probably due to both the elevated pH and Fe concentrations.

Individual mass fluxes in the watershed-lake ecosystem are given in Table 2. Water input (precipitation) into the ecosystem was 1.38×10^6 m^3 y^{-1} (1.22×10^6 and 0.16×10^6 m^3 y^{-1} into the watershed and lake, respectively). Water deposition onto the forest floor was 1.12×10^6 m^3 y^{-1}. Water outputs from the watershed and lake were 1.04×10^6 and 1.19×10^6 m^3 y^{-1}, respectively. Resulting average water residence time in Čertovo Lake was 567 days. The measured water output from the ecosystem was 1.25×10^6 m^3 y^{-1}, which was ~5% higher than the water output estimated from the Cl^- budget. This result indicated ~5% uncertainty in the presented water and mass budgets.

Terrestrial export (outputs from the watershed via tributaries) of SO_4^{2-}, NO_3^-, F^-, H^+, Mg^{2+}, Na^+, and Al and Fe species were higher then their deposition onto the forest floor. In contrast, depositions of NH_4^+, K^+, and Ca^{2+} onto the forest floor were higher than their losses from the watershed. The total atmospheric input of H^+ into the Čertovo watershed-lake ecosystem was 42 keq y^{-1} (39 keq y^{-1} into the watershed and 3 keq y^{-1} into the lake). The terrestrial production and consumption of H^+ ions was 128 and 100 keq y^{-1}, respectively (Table 3). There were the following major terrestrial sources of protons: SO_4^{2-} release (41%), NH_4^+ assimilation and nitrification (39%), Ca^{2+} and K^+ retention (18%), and F^- release (2%). In contrast, the release of Al^{n+} (49%), Mg^{2+} (24%), Na^+ (21%), and Fe (1%) and retention of R^- (5%) were the major terrestrial proton sinks. The net release of H^+ from the terrestrial sources

Table 3. – Net production of protons in terrestrial and aquatic parts of the Čertovo watershed-lake ecosystem in the 1998 hydrological year. Release of cations and removal of strong and organic acid anions in an ecosystem are proton consuming processes, while removal of cations and release of anions are proton producing reactions.

Ion	WATERSHED					LAKE				
	Net production of ion	Proton production				Net production of ion	Proton production			
		H^+ sink		H^+ source			H^+ sink		H^+ source	
	keq y^{-1}	keq y^{-1}	%	keq y^{-1}	%	keq y^{-1}	keq y^{-1}	%	keq y^{-1}	%
$H^{+(1)}$	27					–26				
Ca^{2+}	–2.1			2	2	-0.9		1	8	
Mg^{2+}	24	24	24			0.4	0.4	1		
Na^+	21	21	21		0.4	0.4	1			
K^+	–21			21	16	3.9	3.9	10		
Al_i^{n+}	49	49	49			–10			10	88
Fe_i^{m+}	1.0	1	1			-0.4			0.4	4
NH_4^+	–43			43	33	1.3	1.3	4		
NO_3^-	7.3			7	6	–12	12.3	34		
SO_4^{2-}	53			53	41	–1.5	1.5	4		
Cl^-	0					0				
F^-	2.0			2	2	–1.5	1.5	4		
R^-	–5.0	5	5			–15	15.3	42		
Total		*100*		*128*			*36.6*		*11.4*	

(1) Calculated from the budget for H^+ based on pH measurements.

ranged between 27 keq y^{-1} (35 meq $m^{-2} y^{-1}$), as estimated from budget for H^+ (based on pH measurements), and 28 keq y^{-1} (36 meq $m^{-2} y^{-1}$), as calculated from the terrestrial sources and sinks of protons (Table 3). The terrestrial export of H^+ was 66 keq y^{-1}.

Čertovo Lake was a net source of Fe, Mg^{2+}, NH_4^+, K^+ and a net sink for H^+, Al, NO_3^-, SO_4^{2-}, and DOC. The total H^+ input into the lake (69 keq y^{-1}) was obtained as a sum of terrestrial export and direct atmospheric deposition onto the lake surface. The H^+ output from the lake was 46 keq y^{-1} and the in-lake storage of H^+ decreased by 3 keq y^{-1} during the study (Table 2). The in-lake processes consumed 37 keq y^{-1} of H^+; decreases in R^-, NO_3^-, and SO_4^{2-} concentrations accounted for 42%, 34%, and 4%, respectively, and release of K^+, NH_4^+, and Mg^{2+} from sedimenting matter and sediments represented 15% of the total in-lake consumption of H^+ (Table 3). Al^{n+} hydrolysis was the major in-lake source of H^+ (88% of the total 11 keq y^{-1}). The net in-lake H^+ consumption was 26 keq y^{-1} (250 meq $m^{-2} y^{-1}$), as estimated both from budget for H^+ (based on pH measurements) and the in-lake sources and sinks of protons according to equation (8) (Table 3).

Discussion

Atmospheric deposition – Chemical composition of throughfall differed substantially from precipitation (Table 1). Precipitation samples were collected in bulk collectors and represented vertical wet deposition and dry deposition of particles. In addition, concentration of an element in throughfall was modified by horizontal deposition, dry deposition of gasses, canopy interactions (element exchange), and water evaporation from canopies. Deposition fluxes of conservative ions (Na^+, Cl^-) in throughfall were ~1.7 fold higher than in precipitation. Considering negligible exchange of these elements in canopies, we can assume that their total (wet, dry, and horizontal) atmospheric input into the watershed was equal to their throughfall flux. Similarly, total atmospheric input of the other elements can be roughly estimated from their precipitation fluxes, multiplied by a factor of 1.7. Comparable ratios of throughfall flux to precipitation flux (TF:P) were found for SO_4^{2-} and F^- (1.9 and 1.8, respectively), indicating negligible canopy exchange of these ions. However, throughfall fluxes of the other ions were importantly affected by canopy interactions: the TF:P ratios for Ca^{2+}, Mg^{2+}, K^+ and R^- were substantially higher than 1.7 (2.9, 2.6, 3.5, and 5.4, respectively), while the TF:P ratios for NH_4^+ and NO_3^- were lower (1.1 and 1.5, respectively). Concentration of H^+ in throughfall doubled compared to precipitation. These results implied two important conclusions. (1) Dry and horizontal deposition of strong acid anions remained an important acidity source for the ecosystem despite the substantial decline in S and N emissions in the last decade. (2) The canopy interactions importantly modified the composition of atmospheric deposition, increasing concentrations of base cations and organic acid anions and retaining inorganic nitrogen.

Net terrestrial sinks and sources of H^+ - In this study we estimated net sinks and sources of protons involved in the under-canopies terrestrial ecosystem. Namely, we calculated the differences between the deposition of elements onto the forest floor (i.e. total atmospheric deposition of elements modified by the canopy exchange) and their transport from the watershed via tributaries to the lake. Other important terrestrial sinks and sources of elements like weathering, uptake by vegetation, and litter decay were not evaluated separately but they were involved in the bulk of terrestrial processes. Consequently, our results did not provide particular element fluxes within the ecosystem but suggested which element was released or retained in soils and/or vegetation after its deposition onto the forest floor.

Reactions involving release of Al_i^{n+}, Mg^{2+}, and Na^+ were the most important terrestrial mechanisms consuming protons in the Čertovo watershed (63, 32, and 27 meq $m^{-2} y^{-1}$, respec-

tively). In contrast, the watershed exports of Ca^{2+} and K^+ were lower than their deposition onto the forest floor (Table 2), suggesting that weathering and atmospheric input were lower sources of these nutrients then their uptake by vegetation. Different patterns in the terrestrial budgets for Mg^{2+} and Ca^{2+} apparently resulted from an order of magnitude higher Mg^{2+} content in the bedrock (9.6 and 0.9 g kg^{-1}, respectively; KOPÁČEK & al. 1998b). Total atmospheric input of K^+ into the watershed, estimated as 1.7 × precipitation flux, was 20 meq m^{-2} y^{-1}. The total K^+ deposition onto the forest floor was further elevated by canopy interactions to the total of 37 meq m^{-2} y^{-1}. K^+ transport from the watershed was 10.5 meq m^{-2} y^{-1}. Hence, deposition onto the forest floor represented an important source of K^+ for the Čertovo watershed and its retention in soils significantly contributed to the terrestrial production of protons (~27 meq m^{-2} y^{-1}). Similar pattern for K^+ in that terrestrial uptake exceeded leaching was also typical for all the Integrated Forest Study sites including different forest within the Northern Hemisphere (JOHNSON 1992).

Čertovo watershed exported 1.8 times more sulfate than its received (Table 2) due to non-steady state sorption/desorption conditions in its soils after the steep reduction in S emission and weathering. The terrestrial SO_4^{2-} release (69 meq m^{-2} y^{-1}) was the most pronounced proton generating process in the watershed, producing 1.4 times more H^+ than deposition onto the forest floor (50 meq m^{-2} y^{-1}). Comparable data on the terrestrial release of SO_4^{2-} have been recently observed in the Bavarian Forest (BEUDERT & KANTOR 1999).

Deposition of total inorganic N (TIN = NH_4-N + NO_3-N) onto the forest floor was 116 meq m^{-2} y^{-1} and TIN output from the watershed was 71 meq m^{-2} y^{-1}. Total atmospheric input into the watershed was estimated as 1.7 × precipitation flux and was 155 meq m^{-2} y^{-1}. The net canopy retention of TIN (total atmospheric input minus throughfall) was 39 meq m^{-2} y^{-1}. Of the total atmospheric input of TIN into the Čertovo watershed, 25% was retained by net canopy exchange, 29% was consumed by terrestrial process and 46% was exported (tributaries). The above rough estimate of the canopy interactions in the Čertovo watershed is in concordance with results on TIN fluxes provided by the Integrated Forest Study, evaluated for European and American forest sites by LOVETT (1992). His results show that (1) total atmospheric deposition of TIN mostly exceeds its bulk deposition by a factor of 1.2–1.9 (1.5 on average), i. e. similarly to our TF:P ratio of 1.7, and (2) the net canopy retention of TIN varies between 7 and 85 meq m^{-2} y^{-1} (~35 meq m^{-2} y^{-1} on average), i.e. similarly to our estimate of 39 meq m^{-2} y^{-1}.

Atmospheric input of NH_4-N was higher than that of NO_3-N but NO_3-N prevailed in deposition onto the forest floor (Table 2) due to more effective retention of ammonium in canopies. Terrestrial processes consumed nearly all NH_4-N deposited onto the forest floor. The equivalent production of protons was 55.5 meq m^{-2} y^{-1}. Moreover, the terrestrial output of NO_3-N was 9.5 meq m^{-2} y^{-1} higher than its deposition onto the forest floor. This pattern indicated another terrestrial production of protons due to nitrification of ammonium derived from atmospheric deposition or internal mineralization of organic N. Hence, the net proton production due to the terrestrial transformations of N was 65 meq m^{-2} y^{-1}.

Aquatic sinks of H^+ - Ca^{2+} exchange, and removal of NO_3^- and SO_4^{2-} are often most important in-lake processes consuming protons (SCHINDLER 1986). The exchange capacity of sediments in Čertovo Lake had been probably depleted during the previous period of severe acidification lasting for decades, and was limited only to the K^+ release (Fig. 3), which represented proton sink of 38 meq m^{-2} y^{-1}.

In-lake removal of protons due to biological reduction of nitrate was 8–9 fold more pronounced than that of sulfate (119 and 14 meq m^{-2} y^{-1}, respectively). RUDD & al. (1986) have reported 4–5 times higher H^+ consumption by denitrification than by sulfate reduction in the sediments of non-acidified and acidified lakes. The higher importance of nitrate reduction in

Čertovo Lake was probably associated with denitrification also in water above the sediment during both summer and winter anoxia (Fig. 3). Noteworthy was the annual decline in storage of NO_3^- and SO_4^{2-} (Table 2), documenting dilution of strong acids in the lake due to its continuing reversal from atmospheric acidification.

NH_4^+ released from sedimenting matter and/or sediments during anoxia contributed to the in-lake acid removal by 13 meq m^{-2} y^{-1}. Direct atmospheric deposition and internal dissimilatory reduction processes apparently supplied more ammonium than was utilized by biological uptake. Nitrification of NH_4^+ has probably ceased in Čertovo Lake due to substantially lower pH (~4.5) than that observed (< 5.4) to disrupted this process in an artificially acidified lake (RUDD & al. 1988). Consequently, Čertovo Lake was a net source of ammonium during the study (Table 2).

SCHINDLER & al. (1986), SCHINDLER (1986), and COOK & al. (1986) have mentioned the in-lake removal of organic acids to consume some amount of protons. However, this process was negligible in their alkalinity budgets and was not included. In contrast, internal consumption of R^- was the most pronounced proton consuming process in Čertovo Lake (148 meq m^{-2} y^{-1}). The annual terrestrial export and direct atmospheric deposition of DOC into the lake were 6765 and 213 kg, respectively (Table 2). The annual change in storage of DOC in the lake and the output was 2226 kg and 3323 kg respectively. The increase in storage of DOC in lake resulted from elevated discharges of tributaries in September 1997 and higher DOC concentrations in summer and autumn compared to the winter-spring period (Fig. 2).

The in-lake composition of DOC showed two pronounced differences compared to tributaries (1) Average values of molar absorptivities were 48 mol m^{-2} in tributaries while 39 mol m^{-2} in the lake output (Table 1) and changed most rapidly in the lake epilimnion during summer (Fig. 3). (2) Average concentrations of negatively charged groups per mass of DOC were 6.2 and ~3 meq mg^{-1} in tributaries and lake output, respectively (KOPÁČEK & al. in press and unpublished data).

Sunlight have been shown to effectively reduce concentrations of dissolved aquatic humic matter, decrease its average molecular weight, and change its optical properties (e.g. photobleaching or decline in fluorescence) (LEAN 1998, ALLARD & al. 1994). Photochemical degradation of allochthonous recalcitrant organic matter can have important consequences for microbial productivity of both marine (e.g. KIEBER & al. 1989, MOPPER & al. 1991) and freshwater (e.g. LINDELL & al. 1995) ecosystems. Partial photochemical degradation of allochthonous DOC produces numerous biologically available compounds (like acetic, formic, citric, pyruvic acids, etc.; WETZEL & al. 1995) and results in the enhanced bacterial growth. In concordance with the published results and our data on the qualitative and quantitative changes in DOC we hypothesize that photochemical and microbial degradation of allochthonous organic matter was the most probable explanation for the reduction in organic carbon and R^- concentration in Čertovo Lake. Another process, which might partly decrease DOC concentrations in the water column, was its coagulation and precipitation by Al (e.g. DICKSON 1978, KOPÁČEK & al. 2000).

Reduction of SO_4^{2-} in sediments can be modeled as a first-order reaction (KELLY & al. 1987), which implies, that the rate of alkalinity generation in a lake will decrease with the decrease in the concentration of SO_4^{2-}. Similar pattern can be expected also for NO_3^- (KELLY & al. 1987, SCHINDLER 1986). Consequently, the importance of in-lake alkalinity generation due to biological reduction of sulfate and nitrate should decrease with the recent reductions in S and N emission and deposition. The importance of cation exchange capacity of sediments among in-lake alkalinity generating processes is also expected to decline when acidification lasts for a long period (SCHIFF & ANDERSON 1987). In this situation, a relative importance of in-lake removal of allochthonous organic anions within the aquatic alkalinity budget

will probably increase in forest lakes with high inputs of DOC. Moreover, the future role of organic matter in the internal alkalinity generation can increase also absolutely due to the following reasons:

(1) We can expect an increase in concentrations of organic acid anions in lake tributaries during the ecosystem reversal from atmospheric acidification as a result of the increased ionization of carboxyl groups due to declining concentrations of strong acid anions in soil solutions and increasing pH (WRIGHT & al. 1988). Then, the in-lake removal of organic matter will neutralize larger negative charge per mass unit of organic carbon. (2) The increase in soil water pH can lead to increased dissociation of acidic organic matter and, consequently, to increased leaching of DOC. Moreover, exclusion of strong acid anions from atmospheric deposition is followed by decreased concentrations of aluminum and calcium in surface waters (e.g. WRIGHT & al. 1988, KOPÁČEK & al. 1998a) which can lead to lesser precipitation of organic acids as metal humates (LYDERSEN 1998). If these processes were inverse to the acidification-derived loss of DOC from lake water (e.g., DAVIS & al. 1985, STEINBERG 1991), they could lead to increased DOC concentrations during an ecosystem reversal from acidification. However, such an increase in DOC concentrations in surface waters is hypothetical and has not been up to now confirmed by experimental reduction in strong acid deposition (e.g. WRIGHT & al. 1988). (3) The increasing intensity in UV-B radiation can increase photochemical decomposition of organic matter and penetration of UV-B radiation, which could accelerate the decomposition of DOC (SCHINDLER & al. 1996).

Aquatic sources of H^+ - Hydrolysis of Al_i and Fe_i was the most important in-lake process producing protons (97 and 4 meq m^{-2} y^{-1}, respectively). Moreover, changes in Al and Fe chemistry in Čertovo Lake provided another evidence of the importance of photochemical degradation of allochthonous organic matter. The lake was a net sink for 15 and 21 kg y^{-1} of Al_o and Fe_o, respectively (Table 2). Photochemical degradation of allochthonous DOC liberated organically bound Al and Fe, which increased Al_i and Fe_i concentrations in the lake. Hydrolysis of Al_i and formation and sedimentation of Al_{part} resulted in a net retention of Al_T in the lake (Table 2). In contrast to Al_T, the lake was a net source for Fe_T (Table 2), which released from sediments during anoxia (Fig. 3). The reduction of Fe(III) consumes ~1 mol of H^+ per mol of Fe and represents an important source of alkalinity in a lake hypolimnion (e.g. PSENNER 1988). However, the release of iron from Čertovo Lake represented a net source of protons (Table 3) due to oxidation of Fe^{2+} to Fe^{3+} and its hydrolysis in oxic layers of the lake.

According to the data given in Tables 2 and 3, the in-lake removal of Ca^{2+} was another process generating protons. However, such a result seems to be erroneous and resulting from uncertainty in budget estimation. Water budget was based on the assumption that Cl^- behaved conservatively within the watershed-lake ecosystem. However, SCHINDLER (1986) has summarized mass budgets for watersheds of 32 North American and Scandinavian lakes showing important chloride losses from 10 of them. Similarly, the Cl^- balances differed from zero for most of the Integrated Forest Study sites (BINKLEY 1992). Continuous decline in Cl^- concentrations in the tributaries throughout the study (Fig. 2) also suggested non-steady state conditions in the Čertovo watershed. These non-steady state conditions probably led also to the ~5% difference in the estimated water balance compared to the measured lake outflow.

Conclusions

The total atmospheric inputs of H^+ onto the forest floor and the lake surface of the Čertovo watershed-lake ecosystem were 39 and 3 keq y^{-1}, respectively, in the 1998 hydrological year. H^+ output from the lake with the outflow was 46 keq y^{-1}. Thus, the watershed-lake ecosystem was a net annual source of ~4 keq H^+ y^{-1}.

The watershed was a net source of H^+ (0.36 keq ha^{-1} y^{-1}) with sulfate release from soils as the most pronounced terrestrial proton-generating process.

The lake was a net sink of H^+ (2.5 keq ha^{-1} y^{-1}) with photochemical and microbial decomposition of allochthonous organic matter and denitrification being the most important aquatic proton-consuming processes.

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