

Fluxes of ecologically important solutes in the Čertovo catchment–lake system from 1998–2017

Jiří Kopáček*, Josef Hejzlar, Jiří Kaňa, Petr Porcal & Jan Turek

Biology Centre CAS, Institute of Hydrobiology, Na Sádkách 7, 37005 České Budějovice, Czech Republic
*jkopacek@hbu.cas.cz

Abstract

Fluxes of major ions and nutrients were measured in the catchment–lake system of atmospherically acidified Čertovo Lake between 1998 and 2017 hydrological years. Water balance was calculated from precipitation and throughfall amounts, and measured outflow from the lake. The average water outflow from the system was $1216 \pm 247 \text{ mm} \cdot \text{yr}^{-1}$ (i.e., $39 \pm 8 \text{ l} \cdot \text{km}^{-2} \cdot \text{s}^{-1}$), and the water residence time in the lake averaged 649 ± 139 days. The Čertovo catchment remained an average net source of H^+ ($44 \pm 13 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$) despite significant reductions in sulphur and nitrogen deposition since the late 1980s. Nitrogen saturation of the catchment soils caused low retention of the deposited inorganic N (23% on average) and the terrestrial NH_4^+ removal and NO_3^- production via nitrification (50 and $25 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$, respectively) were the major terrestrial H^+ sources. Net terrestrial SO_4^{2-} production (the second most important H^+ source) decreased from ~ 49 to $\sim 31 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ between 1998–2002 and 2013–2017, and this decrease was accompanied by decreasing production of ionic Al (Al_i) forms from ~ 47 to $26 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$. The increasing terrestrial production of organic acid anions (A^-) compensated for the decreasing SO_4^{2-} leaching and maintained (and stabilized) low pH (4.1–4.5) in lake tributaries during the study period. Compared to precipitation, the catchment was a net source of all ions and nutrients (except for NH_4^+). The in-lake biogeochemical processes reduced the incoming H^+ by $\sim 40\%$ (i.e., neutralized on average $223 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1} \text{ H}^+$, on a lake-area basis). The NO_3^- and SO_4^{2-} reductions and photochemical and microbial oxidation of A^- were the most important H^+ neutralizing processes (184 , 38 , and $140 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$, respectively), while hydrolysis of Al_i was the dominant H^+ generating process ($79 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$). The lake was a net sink for all nutrients, removing on average 13–38% of total (terrestrial and atmospheric) inputs of dissolved organic carbon, phosphorus, nitrogen, and silicon.

Key words: recovery from acidification, nitrogen, sulphur, organic carbon, aluminium, base cations, phosphorus, pH.

INTRODUCTION

Čertovo Lake has been the most atmospherically acidified among all eight natural lakes situated in the mountain area of the Bohemian (and Bavarian) Forest along the Czech-German border (VESELÝ et al. 1998, VRBA et al., 2003). The lake was acidified (pH < 5.0 and with the depleted carbonate buffering system) already in the 1950s (PROCHÁZKOVÁ & BLAŽKA 1999, OULEHLE et al. 2012) and its acidification further progressed until the middle 1980s, when pH ranged between 4.1 and 4.4 (VESELÝ et al. 1993, 1998). The lake water chemistry has been recovering from acidification since the late 1980s (OULEHLE et al. 2012), exhibiting steadily decreasing concentrations of SO_4^{2-} , Cl^- and base cations ($\text{BCs} = \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$), and increasing pH (KOPÁČEK et al. 2016). The chemical recovery of Čertovo Lake is, however, slow and significantly delayed after the rapid decreases in emissions of S and N compounds into the atmosphere and acidic deposition in the Bohemian Forest (KOPÁČEK & HRUŠKA 2010). Our previous investigations of major fluxes and transformations of ions and

nutrients in the Čertovo catchment–lake system showed that its terrestrial part was a significant source of acidity (due to net terrestrial production of SO_4^{2-} , NO_3^- , and H^+ in soils), while the in-lake processes (SO_4^{2-} and NO_3^- reduction and oxidation of organic acid anions) only neutralized a small part of this additional H^+ produced in the catchment (KOPÁČEK et al. 2000a, 2001a, 2006). This terrestrial source of acidity is a legacy of long-term atmospheric acidification and N-saturation of the Čertovo catchment and was predicted to persist for decades considering the anticipated trends in atmospheric pollution (MAJER et al. 2003, OUL-
EHLE et al. 2012).

The aim of this study is to evaluate how terrestrial sources of acidity and its in-lake neutralization have progressed in the Čertovo catchment–lake system during the last two decades. Relying on measured annual fluxes of major elements in precipitation, throughfall, tributaries, and output from the lake, we calculate mass balances for major ions and nutrients, quantify their sinks and sources within the catchment and the lake, and evaluate their changes during the whole 1998–2017 period. For this purpose, we review and synthesize already published studies on element fluxes in the Čertovo catchment–lake system, recalculate previous mass balances of elements (KOPÁČEK et al. 2000a, 2001a, 2006) using new data on lake and catchment characteristics (KOPÁČEK et al. 2016, ŠOBR & JANSKÝ 2016), and supplement them with unpublished data from 2006–2017.

MATERIALS AND METHODS

Site description

Čertovo Lake is situated near the Czech-German border at 13°12' E, 49°10' N, and an elevation of 1027 m a.s.l. It is a dimictic, oligotrophic lake of glacial origin, with surface area of 10.7 ha and maximum depth of 35 m. The lake volume is $1.86 \times 10^6 \text{ m}^3$, of which 26%, 41%, 31%, and 2% are in the 0–5 m, 5–15 m, 15–30 m, and deeper than 30 m layers, respectively (ŠOBR & JANSKÝ 2016). Čertovo Lake is fishless, most crustacean zooplankton are extinct, the phytoplankton is dominated by dinoflagellates and Chrysophyceae, and filamentous microorganisms dominate the bacterioplankton (VRBA et al. 2003, 2016). Submersed littoral macrophytes are absent. The lake has seven surface tributaries (CT-I to CT-VII, Fig. 1), of which CT-II is the major tributary.

The Čertovo catchment (89 ha including the lake) is steep, with a maximum elevation gradient of 315 m. The bedrock consists of mica-schist (muscovitic gneiss), quartzite, and small amounts of pegmatite (VESELÝ 1994). The catchment soils are comprised of ~0.5 m deep dystric cambisol (58%), podsol (21%), and shallow (~0.2 m) leptosol (17%); wetlands and bare rocks represent ~3% and 1%, respectively. Fine soil is sandy (48–81%) with a low (1–4%) content of clay and a catchment weighted mean pool of $225 \text{ kg} \cdot \text{m}^{-2}$ (<2 mm, dry weight soil fraction). Soil pH (CaCl₂ extractable) is low, with minimum values of 2.5–3.3 in A-horizons and maximum values of 3.6–4.5 in deeper mineral horizons. The mean effective cation exchange capacity of the soils is $104 \text{ meq} \cdot \text{kg}^{-1}$ (NH_4Cl extractable Ca^{2+} , Mg^{2+} , Na^+ and K^+ , and KCl extractable Al^{3+} and H^+), of which 9% is base saturation and 62% and 29% is exchangeable Al^{3+} and H^+ , respectively (KOPÁČEK et al. 2002). The Čertovo catchment has been N-saturated (resulting in elevated in-lake NO_3^- concentrations) since the ~1960s (PROCHÁZKOVÁ & BLÁŽKA, 1999, MAJER et al. 2003).

The catchment is forested with mature Norway spruce (*Picea abies*), with a minor admixture of European beech (*Fagus sylvatica*). The current forest was established after a severe disturbance that occurred between 1860 and 1870, and there had not been any important disturbances until windthrows in the winters of 2007 and 2008, which broke most of the trees along the south-western ridge of the catchment, mostly in the upper parts of the CT-IV

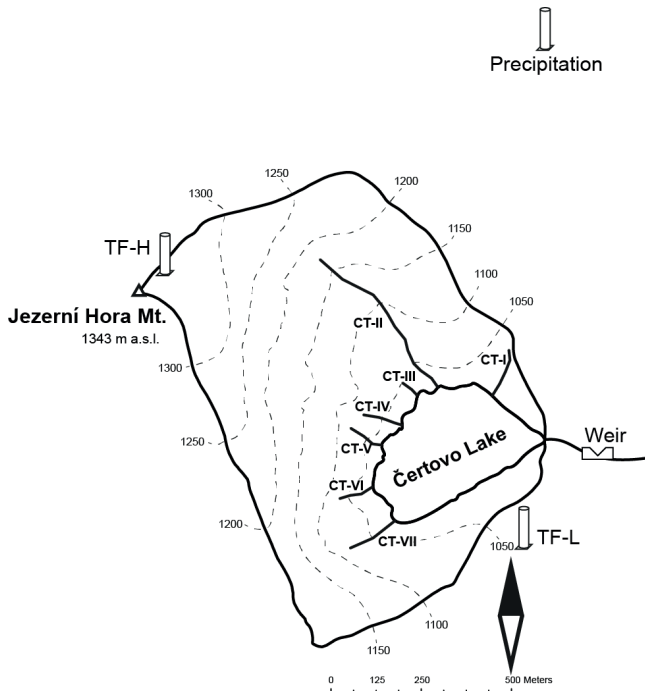


Fig. 1. Map of the Čertovo Lake catchment with the locations of sampling and measuring sites (tributaries, CT-I to CT-VII; outlet equipped with weir; precipitation in treeless area; and throughfall at low and high elevation plots, TF-L and TF-H, respectively).

to CT-VII sub-catchments (KOPÁČEK et al. 2013b, 2016). Other relatively small patches with broken trees and a subsequent bark beetle outbreak occurred and spread throughout the whole Čertovo catchment from 2007–2011. Altogether, the total area of damaged forest (with >50% dead trees) increased from ~4 to 18% between 2000 and 2011 (KOPÁČEK et al. 2016). Another windthrow occurred in October 2017, damaged forest close to the ridge of the catchment, but did not affect results of this study. For details on history of land use and forest composition in the Čertovo catchment see VESELÝ et al. (1993) and VESELÝ (1994). Details on the dominant understory vegetation are given by SVOBODA et al. (2006).

Water sampling

Water and elements fluxes have been determined since November 1997. Atmospheric deposition was collected at three sites (Fig. 1). Precipitation was sampled in an open area without trees (2 samplers) at an elevation of 1175 m, <1 km north of the lake catchment. Throughfall was sampled at two forest plots (9 samplers at each plot) at elevations of 1045 m (TF-L) and 1330 m (TF-H). For details on the sampling plots see KOPÁČEK et al. (2013c). At each plot, water volume was measured in each sampler, but for chemical analyses they were combined in an integrated sample. Rain was sampled in two-week intervals, and snow in four-week intervals. Samples from all seven tributaries and the outlet were taken in three-week intervals and biweekly (weekly during snowmelt period), respectively. Discharges of tributaries were estimated using a stop-watch and bucket method. These discharge values were used for calculation of volume-weighted mean composition of terrestrial export (see later). Samples were immediately filtered through a 40- μ m polyamide sieve to remove coarse particles re-

suspended from the streambed during sampling. The discharge from the lake was continuously monitored using a gauge-recorder (part of an MS16 automatic weather station; J. Fiedler, České Budějovice; readings in 15-minute intervals) at a weir, situated ~150 m downstream of the lake. A water column profile (5–6 depths equally distributed between the surface and bottom) was sampled at the deepest part of the lake. Data from each October were used in mass budget studies (see below).

Water chemistry analysis

Samples of precipitation, throughfall, and stream and lake water were analysed using identical methods. Samples were filtered with either membrane filters (pore size of 0.45 μm) for the determination of ions and dissolved reactive silicon, or with glass-fiber filters (pore size of 0.4 μm) for other analyses, except for samples for pH, acid neutralizing capacity (ANC, determined by Gran titration), and total concentrations of aluminium (Al_T), phosphorus (TP), organic carbon (TOC), and nitrogen (TN), which were not filtered beyond the field pre-filtration. Dissolved organic carbon (DOC) was analysed as CO_2 with several TOC analysers (Table 1), all with a detection limit of $<4.0 \mu\text{mol.l}^{-1}$. Particulate organic C (POC) in

Table 1. Methods used for the determination of individual elements and nutrient forms and their abbreviations.

Abbreviation	Explanation	Assessment
ANC	Acid neutralizing capacity	Gran titration (Tacussel in 1997–2011, then Radiometer).
H^+ (pH)	Proton concentration	pH electrode (combined, Radiometer)
NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NO_3^- , Cl^- , SO_4^{2-} , F^-	Major cations and anions	Ion chromatography (Thermo Separation Products in 1997–2000, Dionex IC25 in 2001–2011, then Dionex ICF-3000).
Si	Dissolved reactive silicon	Molybdate method (GOLTERMAN & CLYMO 1969).
Al_T , Al_i , Al_o , Al_p	Total, ionic, organically bound, and particulate Al	Fractionation according to DRISCOLL (1984), colorimetry (DOUGAN & WILSON 1974) throughout 1997–2017. Al_i = dissolved Al – Al_o . Al_p = Al_T – dissolved Al.
Fe_T , Fe_p , Fe_o , Fe_d	Total, ionic, organically bound, and particulate Fe	Fractionation according to DRISCOLL (1984), colorimetry (KOPÁČEK et al. 2001b) throughout 1997–2017. Fe_i = dissolved Fe – Fe_o . Fe_p = Fe_T – dissolved Fe.
DOC	Dissolved organic C	LiquiTOC analyser (Foss-Heraeus, Germany) in 1997–1999 and Shimadzu analysers TOC 5000A in 2000–2015 and then TOC-L.
POC	Particulate organic C	Analysed on glass-fiber filters (pore size of 0.4 μm) in TOC analysers (Foss-Heraeus LiquiTOC, Shimadzu TOC 5000A/SSM, and Elementar vario Micro cube in 1997–1999, 2000–2015, and 2016–2017, respectively).
TON, DON, PON	Total organic N, dissolved organic N, particulate organic N.	Kjeldahl digestion (PROCHÁZKOVÁ 1960) for precipitation, CT-II and CT-VII, for throughfall in 1997–2001, otherwise TOC/TN analyzer. ¹⁾ PON = TON – DON.
TP, DP, PP	Total P, dissolved P and particulate P.	Sample pre-concentration, HClO_4 digestion, molybdate method (KOPÁČEK & HEJZLAR 1993). PP = TP – DP.
SRP	Soluble reactive P	Molybdate method (MURPHY & RILEY 1962).

¹⁾ Concentrations of TON and DON were calculated as the differences between concentrations of total and dissolved N, respectively (determined by TOC/TN analysers Formacs (Skalar, the Netherlands) in 2002–2009 and vario TOC cube (Elementar, Germany) in 2010–2012) and inorganic N.

the lake outlet was determined on glass-fibre filters using several TOC analysers (Table 1). POC in the other samples was calculated as $POC = TOC - DOC$. Soluble reactive P (SRP) was determined by the molybdate method (MURPHY & RILEY, 1962), with the detection limit of $0.05 \mu\text{mol.l}^{-1}$. TP and dissolved P (DP) were determined by perchloric acid digestion and the molybdate method (KOPÁČEK & HEJZLAR 1993), but samples were 3- to 4-fold concentrated by evaporation (with perchloric acid at $\sim 100^\circ\text{C}$ prior digestion) to obtain a detection limit of $0.015 \mu\text{mol.l}^{-1}$. Particulate P (PP) was calculated as $PP = TP - DP$. Dissolved reactive silicon (Si) was determined by the molybdate method (GOLTERMAN & CLYMO 1969). Total and dissolved organic N (TON and DON; the difference between the respective Kjeldahl N and $\text{NH}_4\text{-N}$) were determined by Kjeldahl digestion according to PROCHÁZKOVÁ (1960), with 75 ml of samples previously evaporated to obtain a detection limit of $\sim 2 \mu\text{mol.l}^{-1}$. This method was used for CT-II, CT-VII, outlet and precipitation throughout the study and for throughfall from 1997–2001, otherwise concentrations of TON (DON) were the difference between total (dissolved) N, determined by the TOC/TN analysers, and inorganic N (Table 1). In this calculation, inorganic N was the sum of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$, whereas $\text{NO}_2\text{-N}$ (typically $<1\%$ of $\text{NO}_3\text{-N}$) was neglected. Particulate organic N (PON) was calculated as $PON = TON - DON$. Concentrations of NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NO_3^- , Cl^- , SO_4^{2-} , and F^- were determined by ion chromatography (Table 1). Detection limits for F^- and NH_4^+ were 0.1 and $0.4 \mu\text{mol.l}^{-1}$, respectively. Concentrations of other ions were always higher than detection limits of the respective methods.

Fractionation of aluminium according to DRISCOLL (1984), i.e. Al_T , dissolved Al, and non-labile Al, were analysed in non-filtered samples, filtered samples, and cation-exchange-treated samples after their filtration, respectively, using the method by DOUGAN & WILSON (1974). We assumed that concentration of organically bound Al (Al_o) was equal to non-labile Al. Concentration of ionic positively charged Al species (Al_i) was the difference between dissolved Al and Al_o concentrations. Concentration of particulate Al species (Al_p) was the difference between Al_T and dissolved Al concentrations. The respective Fe fractions (Fe_T , Fe_i , Fe_o , and Fe_p) were obtained analogously to Al, and their concentrations were determined by the thiocyanate colorimetric method after sample evaporation and digestion with perchloric acid (KOPÁČEK et al. 2001b). Equivalent concentrations (one equivalent is one mole of charge) of Al_i and Fe_i (Al_i^{m+} and Fe_i^{m+} , $\mu\text{eq.l}^{-1}$) were obtained from their molar concentrations and the average charges of Al hydroxocomplexes (n) and Fe hydroxocomplexes (m), respectively. The n and m values were estimated from the theoretical distribution of ionization fractions of aqueous Al and Fe hydroxocomplexes, respectively, at the sample pH (STUMM & MORGAN 1981), neglecting F^- and SO_4^{2-} complexes (KOPÁČEK et al. 2000b). Concentrations of organic acid anions (A^- , $\mu\text{eq.l}^{-1}$) in stream and lake water were calculated from pH and concentrations of DOC, Al_o , and Fe_o according to KOPÁČEK et al. (2000b). Concentrations of A^- in precipitation and throughfall were calculated from the empirical relationship of A^- ($\mu\text{eq.l}^{-1}$) = $4 \times \text{DOC}$ (mg.l^{-1}) according to MOSELLO et al. (2008) and KOPÁČEK et al. (2009).

The reliability of the analytical results was controlled by means of an ionic balance approach, a comparison between measured and calculated conductivities (KOPÁČEK et al., 2000b), and a standard sample (a frozen subsample of water annually taken from CT-II tributary), which was melted and assayed with each series of samples. For example in 2009, coefficients of variation for mean concentrations of the standard sample were 1–5% for all ions (except for F^-), DOC, TP, and pH; $<10\%$ for TON and SRP; and $<20\%$ for F^- (e.g., 55 ± 2 , 36 ± 3 , 1.12 ± 0.06 , 0.84 ± 0.08 , and $1.1 \pm 0.2 \mu\text{mol.l}^{-1}$ for NO_3^- , TON, TP, SRP, and F^- , respectively, $n = 36$) (KOPÁČEK et al. 2011). The differences between the sum of cations and the sum of all anions (including A^-) were $< \pm 10\%$ of the total ionic content in individual precipitation and throughfall samples, and $< \pm 4\%$ for the annual volume weighted mean concentrations.

Similarly, the differences between the sums of cations and anions (including Al_i^{n+} , Fe_i^{m+} and A^-) were $<\pm 5\%$ of the total ionic concentration in the individual samples of stream and lake water. At higher differences, samples were re-analysed. For these ion balance controls, a half of detection limit was used when measured concentrations were lower than this limit. Positive ANC values were assumed to represent HCO_3^- concentrations and $HCO_3^- = 0$ was used for all ANC values $\leq 0 \mu\text{mol.l}^{-1}$.

Average rates of change in chemical composition of element fluxes were based on a regression of their annual fluxes against time over the study period.

Mass balance and net terrestrial and aquatic production of water constituents

Mass balance of chemical constituents in the catchment soils and lake was calculated for individual hydrological years according to equations (1) and (2), respectively (KOPÁČEK et al. 2016):

$$Q_{DEP} C_{DEP} + \pi_C = Q_{TE} C_{TE} + \Delta M_C \quad (1)$$

$$Q_{TE} C_{TE} + Q_{PR} C_{PR} + \pi_L = Q_{OUT} C_{OUT} + \Delta M_L \quad (2)$$

where π_C and π_L (both in mol.yr^{-1}) are the net mass production (when positive) or retention (when negative) of a constituent in the catchment and lake, respectively. Q_{DEP} , Q_{TE} , Q_{PR} , and Q_{OUT} (all in $\text{m}^3.\text{yr}^{-1}$) are water fluxes of atmospheric deposition (DEP) to the catchment soils (i.e., bulk deposition in the open area and throughfall deposition in forests), terrestrial export (TE) to the lake from the catchment (tributaries), direct atmospheric deposition to the lake surface (precipitation, PR), and total (measured) water output (OUT) from the lake, respectively. C_{DEP} , C_{TE} , C_{PR} , and C_{OUT} (all in mol.m^{-3}) are annual mean concentrations of water constituents in the atmospheric deposition to the catchment soils, in terrestrial export via tributaries, in direct atmospheric deposition to the lake surface (precipitation), and in the lake output, respectively. The concentrations were calculated as annual volume weighted means (VWM) for C_{DEP} and C_{PR} and discharge and period weighted means (DPWM) for C_{TE} and C_{OUT} . The annual DPWM value of C_{TE} was calculated using the compositions and discharges of all seven tributaries throughout the hydrological year (LIKENS & BORMANN 1995):

$$C_{TE} = \frac{\sum C_{y,i} Q_{y,i} \tau_i}{\sum Q_{y,i} \tau_i} \quad (3)$$

where y and i denote lake tributaries (CT-I to CT-VII, Fig. 1) and sampling period, respectively, $C_{y,i}$ is concentration of a water constituent and $Q_{y,i}$ water discharge in a tributary y during sampling i , and τ_i (days) is length of sampling period i . In this calculation, each flux was assumed to represent the whole period i given as the sum of halves of intervals between the sampling and the previous one and between the sampling and the next one. The annual DPWM value of water output from the lake (C_{OUT}) was calculated similarly by linking continuously monitored discharge data of the outlet with the corresponding weekly to biweekly concentration data.

ΔM_L (mol.yr^{-1}) in equation (2) is the change in storage of a constituent in the lake and was calculated from equation (4):

$$\Delta M_L = V (C_2 - C_1) \quad (4)$$

where V (m^3) is lake volume and C_1 and C_2 (both in kg.m^{-3}) are volume weighted mean concentrations of water constituents. The C_1 and C_2 values were obtained from data on all sampled depths (usually five) between the surface and bottom at the beginning and the end of

each hydrological year, respectively, by linking the volumes of sampled water layers with the corresponding concentrations. We usually used data from October sampling for this purpose. An analogous change in storage of a constituent in the catchment (ΔM_C ; mol.yr⁻¹) was not measured, but was assumed to be negligible in a one-year balance compared to the total element pools in the catchment. The equation (1) was thus rearranged to

$$\pi_C^* = Q_{TE} C_{TE} - Q_{DEP} C_{DEP} = \pi_C - \Delta M_C,$$

where π_C^* includes both the net mass production and change in storage of a constituent in the catchment.

The water balance was determined from the annual amounts (m.y⁻¹) of precipitation in the open area (H_{PR}) and throughfall (TF) at the low (L) and high (H) elevation plots (H_{TF-L} and H_{TF-H} , respectively), Q_{OUT} , and the budget for Cl⁻. The Q_{OUT} was continuously monitored using a gauge-recorder at a weir (Fig. 1). Because the total catchment area above the weir was 2.3% higher than the Čertovo catchment, the measured Q_{OUT} values were corrected accordingly to obtain water discharge from Čertovo Lake. Previously published data on element mass balances in the Čertovo catchment–lake system (KOPÁČEK et al. 2000a, 2001a, 2006) were accordingly corrected in this study. Q_{DEP} was calculated, assuming that 10% and 90% of the catchment area (estimates based on aerial photographs) received atmospheric deposition in the form of precipitation and throughfall, respectively, and that each of sites TF-L and TF-H represented 50% of the total throughfall deposition in the study catchment:

$$Q_{DEP} = (A_C - A_L) (0.1H_{PR} + 0.9(0.5H_{TF-L} + 0.5H_{TF-H})) \quad (5)$$

where A_C and A_L (m²) is area of the catchment (including lake) and lake, respectively, and coefficients 0.1 and 0.9 represent portions of the catchment, receiving atmospheric deposition in the form of precipitation and throughfall, respectively.

The total water input into the lake (Q_{IN}) was the sum of Q_{TE} and Q_{PR} . $Q_{PR} = H_{PR}A_L$ and Q_{TE} was calculated from equation (2), using the measured Q_{OUT} and Q_{PR} fluxes and annual VWM concentrations of Cl⁻ in precipitation (Cl_{PR}), annual DPWM concentrations of Cl⁻ in lake tributaries (Cl_{TE}) and outlet (Cl_{OUT}), and change in storage of Cl⁻ in the lake (ΔCl_L , calculated from equation 4). The net removal or production of Cl⁻ in the lake was assumed to be negligible (e.g., VAN DER PERK 2006) and thus π_L of Cl⁻ was set to zero:

$$Q_{TE} = \frac{Q_{OUT} Cl_{OUT} - Q_{PR} Cl_{PR} + \Delta Cl_L}{Cl_{TE}} \quad (6)$$

Annual VWM concentrations of elements deposited to the catchment soils via atmospheric deposition and canopy leaching were calculated from the amounts and VWM compositions of precipitation (C_{PR}) and throughfall at the low (C_{TF-L}) and high (C_{TF-H}) elevation plots:

$$C_{DEP} = \frac{0.1 C_{PR} H_{PR} + 0.9 (0.5 C_{TF-L} H_{TF-L} + 0.5 C_{TF-H} H_{TF-H})}{0.1 H_{PR} + 0.9 (0.5 H_{TF-L} + 0.5 H_{TF-H})} \quad (7)$$

where coefficients 0.1, 0.9, 0.5 are the same as in equation (5).

Mass balance of protons in terrestrial and aquatic ecosystems

Net terrestrial and aquatic production (or consumption) of protons and the contributions of individual constituents to these processes were calculated from budgets for ions, using the equation of electroneutrality:

$$[H^+] = [SO_4^{2-}] + [NO_3^-] + [Cl^-] + [F^-] + [A^-] + [HCO_3^-] - [NH_4^+] - [Na^+] - [K^+] - [Ca^{2+}] - [Mg^{2+}] - [Al_i^{n+}] - [Fe_i^{m+}] \quad (8)$$

where brackets represent equivalent concentrations of components. According to this approach, any increase in concentration of cations and decrease in concentration of anions are H^+ consuming processes. In contrast, any decrease in concentration of cations and increase in concentration of anions are H^+ producing reactions. Changes in concentrations of ionic P and Si forms were neglected.

RESULTS

Concentrations

All tributaries were more acidic than precipitation (pH of 4.1–4.5 vs. 5.0) and atmospheric deposition to the catchment soils (pH of 4.8), and had higher concentrations of SO_4^{2-} , NO_3^- , H^+ , and Al forms (Table 2). In contrast, deposited NH_4^+ was almost completely retained in soils and its concentration in tributaries was permanently low ($<1 \mu\text{mol.l}^{-1}$). All tributaries had lower concentrations of DOC, TP, and TON than deposition to the catchment soils, and stream water SRP was always below the detection limit of $0.05 \mu\text{mol.l}^{-1}$. Tributaries CT-I to CT-V represented $\sim 80\%$ of the total terrestrial input to the lake and their chemistry was similar to that in the major tributary CT-II (Table 2), except for lower NO_3^- concentrations in CT-I, due to a small wetland in its sub-catchment. The chemistry of tributaries CT-VI and CT-VII differed from the other tributaries, being significantly less acidic (pH of 4.5 vs. 4.1–4.3) and having higher concentrations of BCs and Si, and lower DOC concentrations (Table 2). Such a different composition implies a higher proportion of groundwater (base flow) in these tributaries than in other sub-catchments.

The lake output had lower concentrations of H^+ , NO_3^- , DOC, SO_4^{2-} , Al_i , Al_o , Fe_o , and Si, but higher concentrations of particulate forms of all nutrients (POC, PON, PP) compared to tributaries and precipitation (Table 2). Concentrations of NH_4^+ behaved differently to other ions, being higher in the lake output than in tributaries.

Details on annual average chemical composition of major fluxes in the Čertovo catchment–lake system are for individual hydrological years summarized in Appendixes 2 to 6.

Secchi disc transparency varied between 2–6 m during the study. The thermal stratification of Čertovo Lake developed characteristically for a dimictic temperate lake. The ice cover usually lasted from December to April, with the minimum, maximum, and average ice-on period of 92, 160, and 130 days, respectively, during 1998–2017. The autumn and spring overturns usually occurred in December and April, respectively, but were not always complete and bottom layers below ~ 25 m were not mixed in some years (e.g. in 2000; KOPÁČEK et al. 2001a). Anoxia only occurred in a thin (~ 1 – 3 m) layer above the bottom in the deepest part of the lake during the late stages of winter and summer thermal stratification (Fig. 2). At low redox potentials above the lake bottom, dissimilatory reduction processes occurred, decreasing NO_3^- and SO_4^{2-} concentrations and increasing concentrations of NH_4^+ and Fe forms, while concentrations of conservative Cl^- remained stable along the whole water column (Fig. 2). The changes in ionic composition increased the hypolimnetic pH (to ~ 6 from ~ 4.5 in the epilimnion; Fig. 2C), as well as ANC concentrations that reached positive values (the carbonate buffering system was re-established above the bottom; Fig. 2D). With the pH increase towards neutrality, ionic Al species hydrolyzed and formed Al_p (colloidal hydroxides). Concentrations of Al_i were thus lower in the anoxic zone than in the rest of water column profile, while Al_p concentrations sharply increased above the bottom (Fig. 2I,J). These high Al_p concentrations were accompanied with elevated TP concentrations

Table 2. Average (\pm standard deviation) values of discharge (Q), for annual data see Appendix 1) and mean composition of precipitation (C_{PR} for annual data see Appendix 2), atmospheric deposition to the catchment soils (C_{DEP} precipitation in treeless area and throughfall in forest, for annual data see Appendix 3), tributaries (CT-I to CT-VII), terrestrial export via tributaries (C_{TE} for annual data see Appendix 4), total input to Certovo Lake (C_{IN} , terrestrial export and precipitation to the lake surface, for annual data see Appendix 5), and output from the lake (C_{OUT} for annual data see Appendix 6) during the period between November 1997 to October 2017. Units: $\mu\text{mol}\cdot\text{l}^{-1}$, except for discharge (Q , $\text{l}\cdot\text{s}^{-1}$) and pH. For location of tributaries see Fig. 1.

	C_{PR}	C_{DEP}	CT-I	CT-II	CT-III	CT-IV	CT-V	CT-VI	CT-VII	C_{TE}	C_{IN}	C_{OUT}
Q	*4.5 \pm 0.9	**36 \pm 5	0.7 \pm 0.3	11.2 \pm 3.8	1.6 \pm 0.6	2.1 \pm 1.0	0.8 \pm 0.3	1.7 \pm 0.8	2.0 \pm 0.9	31 \pm 6	36 \pm 7	35 \pm 7
pH	4.96 \pm 0.18	4.79 \pm 0.17	4.32 \pm 0.04	4.26 \pm 0.03	4.11 \pm 0.03	4.11 \pm 0.03	4.16 \pm 0.04	4.51 \pm 0.06	4.53 \pm 0.06	4.26 \pm 0.03	4.30 \pm 0.03	4.52 \pm 0.08
H ⁺	12 \pm 4	17 \pm 7	48 \pm 5	56 \pm 4	78 \pm 6	78 \pm 4	70 \pm 6	31 \pm 4	30 \pm 4	56 \pm 4	50 \pm 4	31 \pm 6
Ca ²⁺	5 \pm 2	10 \pm 2	8 \pm 3	10 \pm 2	8 \pm 2	9 \pm 1	9 \pm 2	16 \pm 2	14 \pm 1	11 \pm 2	10 \pm 2	10 \pm 2
Mg ²⁺	1.5 \pm 0.5	4.4 \pm 0.7	12 \pm 2	14 \pm 2	12 \pm 1	13 \pm 1	15 \pm 2	21 \pm 2	16 \pm 1	14 \pm 2	13 \pm 1	12 \pm 1
Na ⁺	7 \pm 2	12 \pm 2	34 \pm 3	31 \pm 3	29 \pm 3	28 \pm 3	30 \pm 3	40 \pm 4	39 \pm 4	32 \pm 3	29 \pm 3	27 \pm 2
K ⁺	3 \pm 3	24 \pm 5	8 \pm 2	8 \pm 1	6 \pm 2	8 \pm 2	9 \pm 3	10 \pm 1	11 \pm 1	8 \pm 1	8 \pm 1	8 \pm 1
NH ₄ ⁺	27 \pm 4	36 \pm 7	0.9 \pm 0.7	0.6 \pm 0.5	0.6 \pm 0.4	0.8 \pm 0.6	1.2 \pm 2.1	0.7 \pm 0.5	0.6 \pm 0.4	0.6 \pm 0.4	4 \pm 1	5 \pm 1
NO ₃ ⁻	25 \pm 4	41 \pm 6	28 \pm 15	66 \pm 16	65 \pm 18	75 \pm 27	72 \pm 37	77 \pm 26	62 \pm 13	67 \pm 16	62 \pm 14	46 \pm 7
SO ₄ ²⁻	10 \pm 3	16 \pm 6	40 \pm 8	35 \pm 8	41 \pm 12	40 \pm 11	43 \pm 11	43 \pm 12	35 \pm 8	37 \pm 9	34 \pm 8	36 \pm 9
Cl ⁻	7 \pm 2	15 \pm 2	16 \pm 2	16 \pm 2	15 \pm 3	16 \pm 3	17 \pm 5	18 \pm 2	18 \pm 2	16 \pm 2	14 \pm 2	15 \pm 1
F ⁻	0.5 \pm 0.5	0.9 \pm 0.5	2.4 \pm 0.6	1.9 \pm 0.6	2.0 \pm 0.6	1.9 \pm 0.7	2.0 \pm 0.7	2.1 \pm 0.7	1.6 \pm 0.4	1.9 \pm 0.5	1.7 \pm 0.5	1.8 \pm 0.5
DOC	96 \pm 17	514 \pm 66	513 \pm 159	555 \pm 171	768 \pm 208	717 \pm 204	561 \pm 135	202 \pm 42	266 \pm 67	519 \pm 158	467 \pm 139	282 \pm 35
POC	32 \pm 17	84 \pm 52	8 \pm 9	11 \pm 8	12 \pm 13	15 \pm 16	15 \pm 14	15 \pm 7	11 \pm 19	12 \pm 6	15 \pm 7	46 \pm 16
DON	11 \pm 3	25 \pm 9	13 \pm 5	20 \pm 4	20 \pm 7	19 \pm 7	19 \pm 8	13 \pm 6	14 \pm 4	19 \pm 4	18 \pm 4	15 \pm 2
PON	7 \pm 4	10 \pm 6	2.6 \pm 3.1	0.9 \pm 1.0	1.2 \pm 1.8	1.2 \pm 2.1	1.8 \pm 1.7	1.1 \pm 1.2	1.3 \pm 1.2	1.4 \pm 1.1	2 \pm 1	5 \pm 1
TP	0.54 \pm 0.26	0.87 \pm 0.21	0.14 \pm 0.04	0.13 \pm 0.05	0.15 \pm 0.07	0.14 \pm 0.06	0.10 \pm 0.03	0.07 \pm 0.02	0.10 \pm 0.04	0.12 \pm 0.05	0.17 \pm 0.05	0.14 \pm 0.02
PP	0.26 \pm 0.11	0.53 \pm 0.13	ND	0.09 \pm 0.03	ND	ND	ND	ND	0.07 \pm 0.2	0.03 \pm 0.02	ND	0.09 \pm 0.02
SRP	0.20 \pm 0.15	0.18 \pm 0.11	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.03 \pm 0.01	0.05 \pm 0.02	<0.05
Si	0.3 \pm 0.1	ND	78 \pm 9	71 \pm 7	73 \pm 9	68 \pm 9	68 \pm 8	88 \pm 8	92 \pm 9	74 \pm 7	65 \pm 6	57 \pm 4
Al _T	0.4 \pm 0.4	ND	11 \pm 2	20 \pm 3	21 \pm 4	23 \pm 4	22 \pm 6	16 \pm 4	14 \pm 3	20 \pm 3	18 \pm 3	16 \pm 3
Al _I	ND	ND	6 \pm 2	13 \pm 4	14 \pm 3	15 \pm 3	15 \pm 5	13 \pm 4	10 \pm 3	14 \pm 3	12 \pm 3	12 \pm 3
Al _o	ND	ND	5 \pm 1	6 \pm 1	8 \pm 2	8 \pm 1	7 \pm 1	3 \pm 1	4 \pm 1	6 \pm 1	5 \pm 1	3 \pm 1
Fe _T	ND	ND	3.6 \pm 1.1	3.2 \pm 0.9	3.8 \pm 0.9	3.4 \pm 0.8	2.4 \pm 0.5	0.5 \pm 0.1	1.1 \pm 0.3	2.8 \pm 0.8	2.5 \pm 0.7	2.8 \pm 0.6
Fe _I	ND	ND	1.1 \pm 0.4	1.0 \pm 0.3	1.2 \pm 0.4	1.3 \pm 0.4	0.9 \pm 0.4	0.2 \pm 0.1	0.5 \pm 0.2	0.9 \pm 0.2	0.8 \pm 0.2	1.0 \pm 0.4
Fe _o	ND	ND	2.5 \pm 0.9	1.9 \pm 0.7	2.6 \pm 0.8	2.1 \pm 0.6	1.5 \pm 0.4	0.3 \pm 0.1	0.6 \pm 0.2	1.7 \pm 0.6	1.5 \pm 0.5	0.8 \pm 0.2

Explanations: * Precipitation amount deposited to the lake surface, ** water amount deposited to the lake catchment with precipitation and throughfall. ND – not determined.

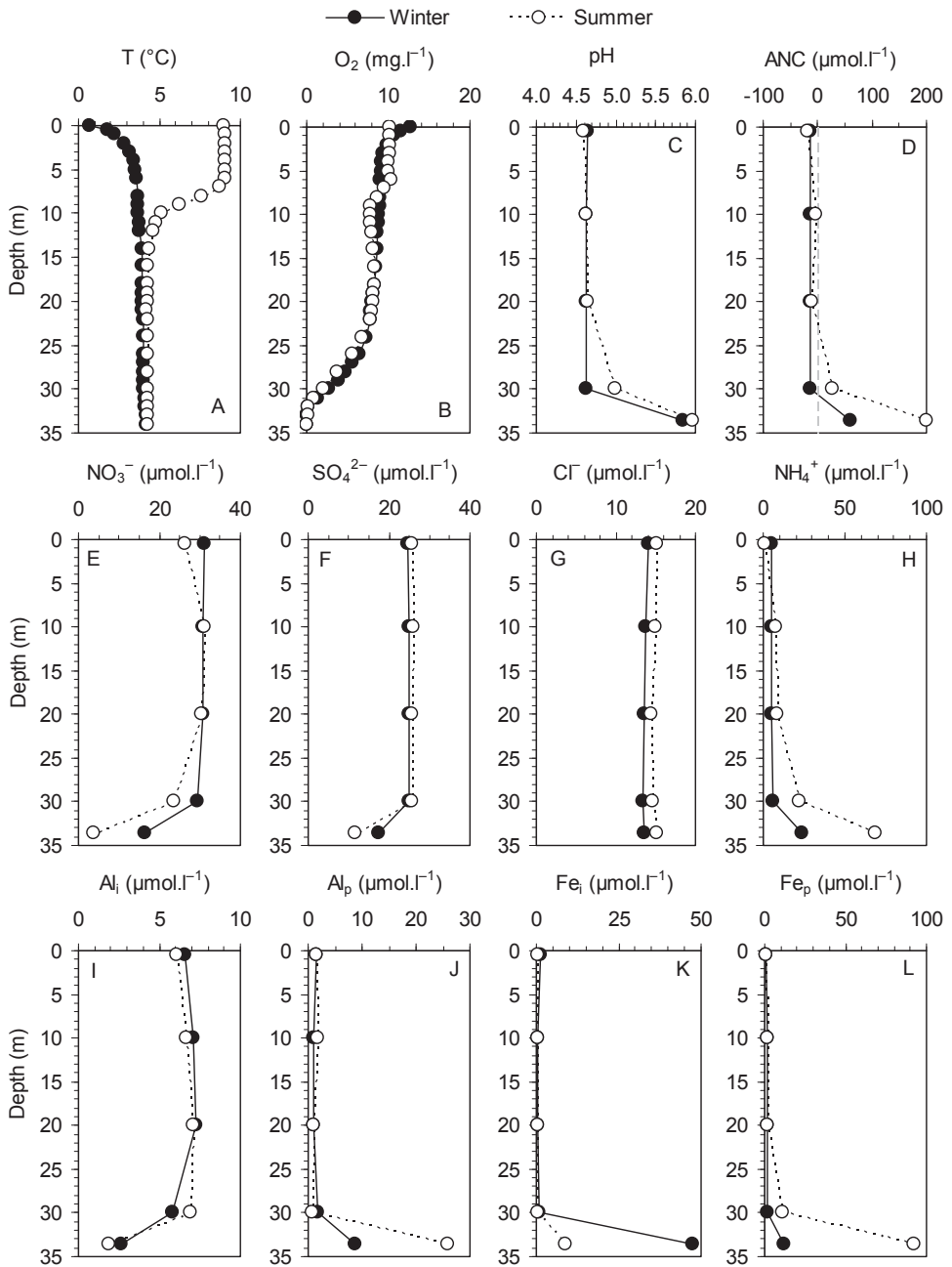


Fig. 2. Depth diagrams of temperature (T), dissolved oxygen (O_2), pH, acid neutralizing capacity (ANC), NO_3^- , SO_4^{2-} , Cl^- , NH_4^+ , ionic and particulate aluminium (Al_i , Al_p) and iron (Fe_i , Fe_p) during winter (22 March 2017) and summer (23 October 2017) thermal stratification of Čertovo Lake.

Table 3. Mean (\pm standard deviation) element fluxes in precipitation (*PR*), deposition to the catchment soils (*DEP*), terrestrial export (*TE*), net production of water constituents in the catchment ($\pi_c^* = \pi_c - \Delta M_c$, calculated from equation 1), and the associated H^+ production/removal in soils of the Čertovo catchment in the 1998–2017 hydrological years.

	<i>PR</i>	<i>DEP</i>	<i>TE</i>	π_c^*	H^+ source [†]
	mmol.m ⁻² .yr ⁻¹				meq.m ⁻² .yr ⁻¹
H ⁺	16±8	25±10	69±14	44±13	
Ca ²⁺	6.6±2.6	15±3	13±4	-1±3	3±5
Mg ²⁺	1.9±0.8	6±1	18±3	12±3	-23±7
Na ⁺	9.4±3.9	18±3	39±7	22±6	-22±6
K ⁺	4.7±3.8	33±5	10±2	-23±6	23±6
NH ₄ ⁺	35±10	51±8	0.8±0.5	-50±8	50±8
NO ₃ ⁻	33±11	59±7	84±25	25±24	25±24
SO ₄ ²⁻	14±6	23±9	46±15	24±9	47±18
Cl ⁻	9±4	21±3	19±4	-2±3	-2±3
F ⁻	1±1	1±1	2±1	1±1	1±1
DOC (A ⁻)	126±36	727±94	648±209	-79±170	(-6±10)
HCO ₃ ⁻	4±4	5±6	0±0	-5±4	-5±4
TON	23±8	47±20	25±8	-21±18	
TP	0.7±0.3	1.2±0.3	0.15±0.06	-1.1±0.3	
Si	0.4±0.1	ND	92±15	91±15	
Al _T	0.5±0.4	ND	26±7	25±7	
Al _i (Al _i ^{net})	ND	ND	17±5	17±5	(-45±14)
Fe _T	ND	ND	3.5±1.1	3.4±1.1	
Fe _i (Fe _i ^{net})	ND	ND	1.1±0.3	1.1±0.3	(-1±0.4)

Explanations: Values are given on a catchment-area basis; ND – not determined. When deposition of an element on the catchment soils was not determined, its net production was set equal to its terrestrial export. Positive π_c^* values indicate net production, while negative values indicate net removal; for their annual values see Appendix 7. [†] Release of cations and removal of anions are proton-consuming processes, while removal of cations and release of anions are proton-producing reactions. One meq = mmol of charge. Sum of H^+ sources and sinks gives a net production of 45 mmol.m⁻².yr⁻¹.

(maximum of $\sim 1 \mu\text{mol.l}^{-1}$) above the bottom, while its concentrations were one order of magnitude lower in the rest of water column (not shown), similarly to the lake outlet (Table 2). Despite these elevated TP concentrations, DP remained low above the lake bottom, with SRP values close to or below the detection limit.

Water fluxes

The average (\pm standard deviation) precipitation was $1309 \pm 273 \text{ mm.yr}^{-1}$, with minimum and maximum values of 780 and 2080 mm.yr⁻¹ (in 2015 and 2002), respectively. The deposition to the catchment (precipitation in treeless areas plus throughfall in forest) was $1429 \pm 206 \text{ mm.yr}^{-1}$ and ranged from 1045 to 2018 mm.yr⁻¹ (Appendix 1). The average water outflow from the lake was $1216 \pm 247 \text{ mm.yr}^{-1}$ (i.e., specific outflow of $39 \pm 8 \text{ l.km}^{-2}.\text{s}^{-1}$). The resulting average evapotranspiration from the catchment–lake system, based on precipitation and

throughfall amounts, was 15%. This value was, however, lowered by interception. Consequently, the actual total evapotranspiration from the catchment–lake system was >15% due to the direct water evaporation from canopies. Water residence time in the lake varied between 395 and 1005 days, with an average of 649 ± 139 days over the study period.

Element fluxes in catchment

Terrestrial part of the Čertovo catchment was a net sink for atmospherically deposited NH_4^+ , but a net source of most water solutes, with exception for Cl^- (Table 3). The average fluxes of Cl^- deposition and leaching were almost equal on a long-term (Table 3), but varied in some

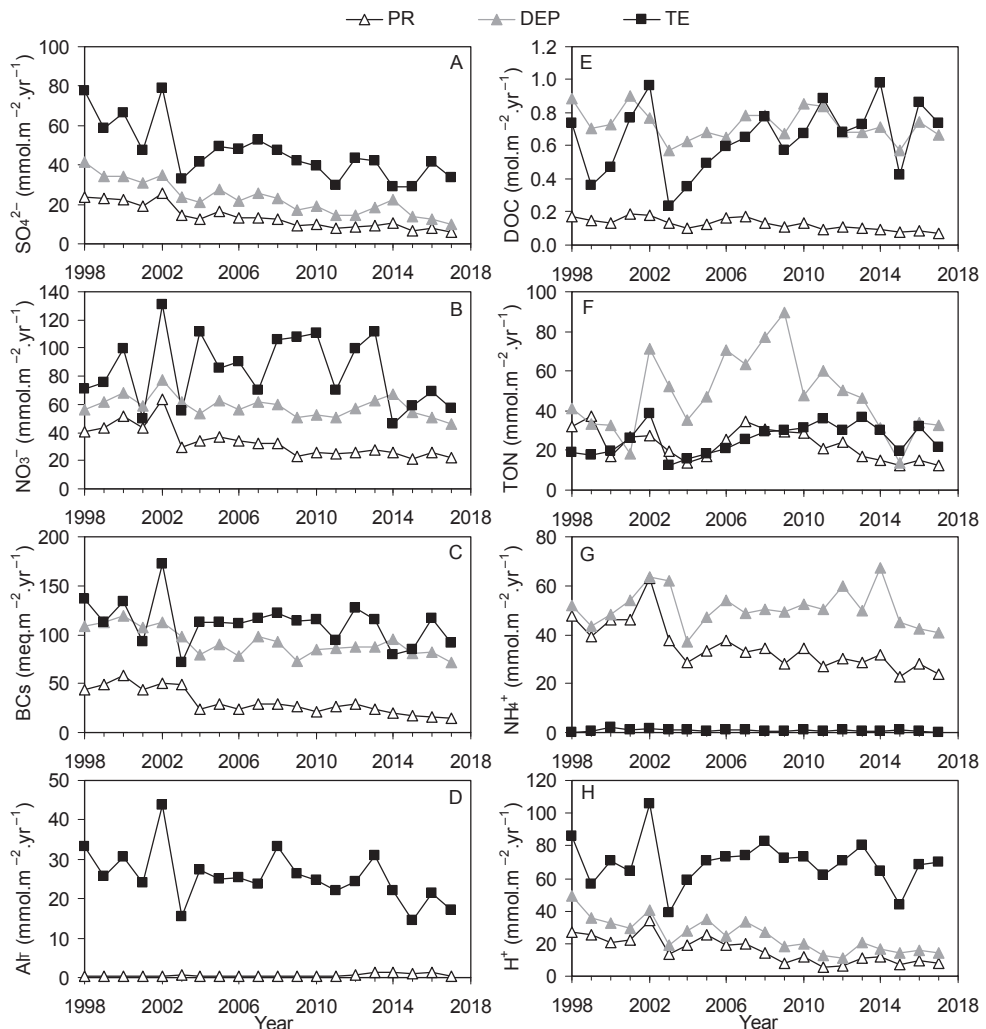


Fig. 3. Time series of annual fluxes (based on a catchment area basis) of SO_4^{2-} , NO_3^- , base cations (BCs = sum of Ca^{2+} , Mg^{2+} , Na^+ and K^+), total aluminium (Al_t), dissolved organic carbon (DOC), total organic nitrogen (TON), NH_4^+ , and H^+ in precipitation (PR), deposition to the catchment soils (DEP), and terrestrial export via tributaries (TE) in the Čertovo catchment in the 1998–2017 hydrological years.

years. Terrestrial exports of NO_3^- , SO_4^{2-} , and Al_i were higher than inputs to the catchment soils by precipitation and throughfall deposition throughout the study period (Fig. 3). This change in ionic composition resulted in a significant terrestrial H^+ production of $44 \pm 13 \text{ meq. m}^{-2} \cdot \text{yr}^{-1}$ on a catchment-area basis, and in permanently higher terrestrial exports than was the atmospheric H^+ input (Fig. 4H). This H^+ production, resulting from the H^+ mass balance (based on pH measurements) in precipitation, throughfall and tributaries, was in good concordance with H^+ production calculated from equation (8) as the sum of individual H^+ sources (terrestrial production of anions and removal of cations) and sinks (terrestrial production of cations) that averaged $45 \text{ meq. m}^{-2} \cdot \text{yr}^{-1}$ from 1998–2017. Both estimates thus differed by

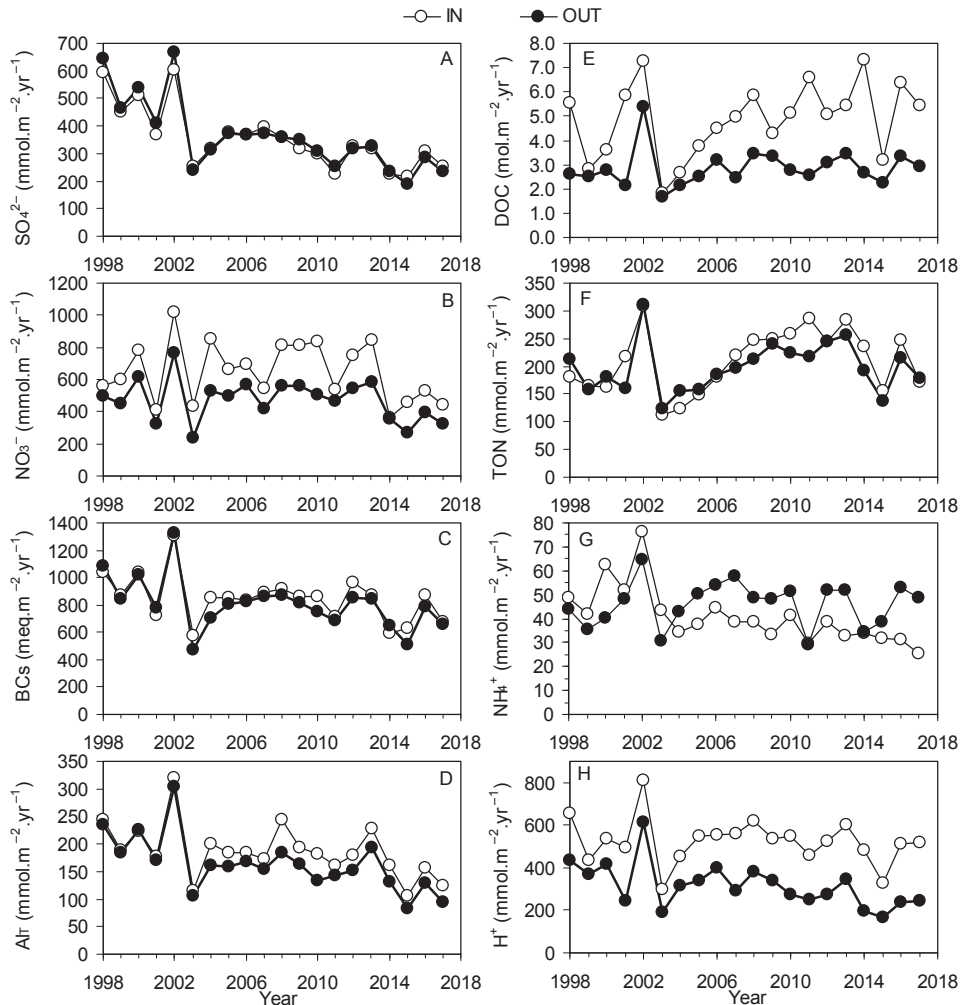


Fig. 4. Time series of annual fluxes (based on a lake area basis) of SO_4^{2-} , NO_3^- , base cations (BCs = sum of Ca^{2+} , Mg^{2+} , Na^+ and K^+), total aluminium (Al_i), dissolved organic carbon (DOC), total organic nitrogen (TON), NH_4^+ , and H^+ in total input (IN, tributaries and precipitation) to and outlet (OUT) from Čertovo Lake in the 1998–2017 hydrological years.

<2% on average. The most important H^+ sources were net retention and nitrification of NH_4^+ (50 and 25 $meq.m^{-2}.yr^{-1}$, respectively), SO_4^{2-} production (leaching of 47 $meq.m^{-2}.yr^{-1}$), while terrestrial production of Al_1 , Mg^{2+} , and Na^+ ions represented the most important H^+ sinks (45, 23, and 22 $meq.m^{-2}.yr^{-1}$, respectively).

Terrestrial exports of DOC and TON were lower than their deposition to the catchment soils (amended by contribution of canopy leaching to throughfall deposition), but were higher than their inputs via precipitation (Fig. 3). However, sources of DOC and TON in precipitation and throughfall are fundamentally different from their stream water sources. In contrast to DOC, terrestrial export of TP was even lower than its flux in precipitation, and Čertovo catchment was a net sink of deposited P, averaging 1.1 $mmol.m^{-2}.yr^{-1}$ during this study (Table 3).

Element fluxes in lake

The in-lake processes caused reductions in NO_3^- , A^- , SO_4^{2-} , and Al_1 fluxes (Table 4, Fig. 4) and a pH increase in the lake outlet compared to their inputs by tributaries and precipitation (4.5 vs. 4.3 on average; Table 2); i.e., the input H^+ flux decreased by ~40% from 524 to 316 $meq.m^{-2}.yr^{-1}$ on a lake area basis (Table 4). The net in-lake H^+ removal (calculated on the basis of pH values in precipitation, tributaries and lake outlet) averaged 223 $meq.m^{-2}.yr^{-1}$. This value is not a simple difference between the input and output fluxes because it also includes a net change in H^+ storage in the lake (equation 2) that decreased by 15 $meq.m^{-2}.yr^{-1}$ during the study. The pH-based estimate was similar to the H^+ removal calculated from equation (8) that averaged 234 $meq.m^{-2}.yr^{-1}$. Both estimates thus differed by <5% on average. The most important internal H^+ sinks were NO_3^- , A^- and SO_4^{2-} removals (184, 140, and 38 $meq.m^{-2}.yr^{-1}$, respectively), while Al_1 transformations were the most important in-lake H^+ sources of 79 $meq.m^{-2}.yr^{-1}$ on average (Table 4). In contrast to H^+ , the lake was negligible sink for BCs (Fig. 4C), and was a net source of NH_4^+ in most years (Fig. 4G), with the long-term average production of 4 $mmol.m^{-2}.yr^{-1}$.

The lake was a net sink for all nutrients, removing on average 22% of TP, 36% of total N, 38% of DOC, and 13% of Si inputs (Table 4). Precipitation to the lake surface was the major SRP source, while its concentrations were <0.05 $\mu mol.l^{-1}$ in tributaries (Table 2).

DISCUSSION

Major processes affecting mass budget of protons in Čertovo catchment

Terrestrial transformations of inorganic N were the most important H^+ producing process in the Čertovo catchment (Table 3). This H^+ production due to N transformations was almost twofold higher than the maximum observed at 17 European forest sites (-5 to 46 $meq.m^{-2}.yr^{-1}$) by FORSIUS et al. (2005). The progressed stage of N-saturation of the Čertovo catchment and its low ability to retain the deposited inorganic N (on average only 23%) even after significantly reduced N deposition compared to the 1980s (KOPÁČEK & HRUŠKA 2010) thus contribute to the high proportion of NO_3^- in the total terrestrial export of strong acid anions (= $SO_4^{2-} + NO_3^- + Cl^-$) (Appendix 4), as also observed in other N-saturated areas (ROGORA 2007). The terrestrial NO_3^- export usually increases after vegetation disturbances in catchments (HOULTON et al. 2003, HUBER et al. 2004, HUBER 2005, MCHALE et al. 2007). The elevated NO_3^- leaching also occurred in Čertovo sub-catchments CT-IV to CT-VI that were affected by windthrows in 2007–2008 (KOPÁČEK et al. 2016), and resulted in elevated terrestrial export of NO_3^- during 2008–2013 (Fig. 3B). This excess NO_3^- likely resulted from the mineralization of fresh dead biomass (litter and fine roots) and ceased N uptake by dead trees (KAŇA et al. 2015). Similar (and even more pronounced) ecosystem response to forest

Table 4. Mean (\pm standard deviation) element fluxes in total input to lake [IN , sum of atmospheric deposition on the lake surface (see precipitation in Table 3) and terrestrial export], output from lake (OUT), net in-lake production of water constituents (π_L), and the associated H^+ production/removal in Čertovo Lake in the 1998–2017 hydrological years.

	IN	OUT	π_L	H^+ source [†]
	mmol.m ⁻² .yr ⁻¹			meq.m ⁻² .yr ⁻¹
H ⁺	524±109	316±104	-223±58	
Ca ²⁺	103±28	101±31	-7±11	14±22
Mg ²⁺	133±26	126±27	-9±11	18±23
Na ⁺	298±55	275±58	-24±26	24±26
K ⁺	79±18	78±17	-1±6	1±6
NH ₄ ⁺	41±12	46±9	4±22	-4±22
NO ₃ ⁻	647±184	473±130	-184±57	-184±57
SO ₄ ²⁻	354±112	363±130	-19±26	-38±52
Cl ⁻	150±30	152±37	ND	
F ⁻	18±8	19±8	0±8	-0.8±10
HCO ₃ ⁻	3±14	0±0	-3±14	-3±14
DOC (A ⁻)	4875±1530	2861±766	-1875±1132	(-140±71)
TON	210±56	198±45	-140±71	
TP	1.8±0.5	1.4±0.3	-0.4±0.4	
Si	671±111	576±108	-91±67	
Al _T	187±49	164±50	-33±26	
Al _i (Al _i ^{nt+})	126±40	126±44	-14±23	(79±41)
Al _o	57±16	26±9	-30±14	
Al _p	4±2	12±3	11±13	
Fe _T	26±8	28±11	4±17	
Fe _i (Fe _i ^{mt+})	8±2	11±7	1±11	(-0.2±10)
Fe _o	16±6	8±3	-7±7	
Fe _p	2±2	9±4	10±15	

Explanations: Values are given on a lake-area basis; ND – not determined. Values of π_L were calculated from equation (2), data on the average annual change in storage of elements in the lake are not given. Positive values indicate net production, while negative values indicate net removal; for their annual values see Appendix 8. † Release of cations and removal of anions are proton-consuming processes, while removal of cations and release of anions are proton-producing reactions. One meq = mmol of charge. Sum of H^+ sources and sinks gives a net retention of 234 mmol.m⁻².yr⁻¹.

damage, manifested by elevated terrestrial NO₃⁻ exports, have occurred across the Bohemian Forest (OULEHLE et al. 2013), especially in the catchment of Plešné Lake (KOPÁČEK et al. 2017) and Rachelsee (VRBA et al. 2014), where the majority of mature Norway spruce stands were killed by bark beetle.

The release of SO₄²⁻ was two times higher than deposition to the catchment soils (46 vs. 23 mmol.m⁻².yr⁻¹ on average) during the study (Table 3). The source of this extra SO₄²⁻ originated from S accumulated in soils during high atmospheric deposition in the 2nd half of the

20th century. The deposited SO_4^{2-} is retained in soils (i) partly by adsorption on Al and Fe hydroxides, especially as soils acidify and the positive charge of these hydroxides increases (e.g., COSBY et al. 1986, KAŇA & KOPÁČEK 2005), and (ii) predominantly due to organic cycling of deposited SO_4^{2-} that is microbially reduced to S^0 or S^{-II} compounds and stored in soils (e.g., NOVÁK et al. 2000, 2005). The reduced S is further used by S-oxidizing bacteria (and oxidized back to SO_4^{2-}) as an electron donor after aeration of the originally anoxic micro-sites (CLARK et al. 2006). Despite the net annual terrestrial export of SO_4^{2-} decreased from ~ 49 to ~ 31 $\text{meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ during the study period ($p < 0.001$), i.e., close to the prediction by MAGIC model (MAJER et al. 2003, OULEHLE et al. 2012), the H^+ fluxes remained almost stable (Fig. 3H). This disproportion resulted from the temporarily elevated NO_3^- leaching from 2008–2013 (Fig. 3B), and importantly from the significantly ($p < 0.001$) increasing terrestrial DOC (and also A^-) export after 2003 (Fig. 3E). The decrease in terrestrial SO_4^{2-} production was mostly compensated for by significantly ($p < 0.001$) decreasing net terrestrial production of Al_i (from 47 to 26 $\text{meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ between 1998–2002 and 2013–2017), manifested by the decreasing Al_i leaching (Fig. 3D). The water in lake tributaries thus remained strongly acidic, with pH ranging from 4.2–4.3 throughout this study (Appendix 4), despite decreasing leaching of SO_4^{2-} and Al_i (Fig. 3A,D).

The Cl^- behaved conservatively in the Čertovo catchment indicating balanced conditions in Cl^- retention and release in a long-term perspective (Tables 2 and 3). However, annual Cl^- fluxes in deposition (Appendix 3) and terrestrial export (Appendix 4) differed $>10\%$ during dry years (e.g., in 2003 and 2015), when Cl^- input exceeded its export. In contrast, higher Cl^- exports than inputs occurred in wet years. Chloride has been considered a conservative ion, with negligible retention in ecosystems, because annual Cl^- leaching from undisturbed catchments is usually similar to the total annual Cl^- input from atmospheric deposition (e.g., PECK & HURLE 1973), especially at sites where atmospheric Cl^- inputs exceed 17 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ (SVENSSON et al. 2012). The average Cl^- deposition to the Čertovo soils of 15 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ was close to this threshold (Appendix 3). On average 11% higher terrestrial export of Cl^- than its deposition also occurred from 2008–2011, i.e., in years following the partial damage of Čertovo forest in 2007 and 2008. This response was in concordance with other studies. For example, KAUFFMAN et al. (2003) and HUBER et al. (2004) have shown that a large amount of mineralisable chlorine is stored in the soil organic matter and may be leached as Cl^- from decaying litter and roots, and liberated from decomposing soil organic matter after forest damage.

Terrestrial export of Al_i decreased from ~ 30 to ~ 20 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ during the study period (Fig. 3D) and was mostly associated with decreasing leaching of Al_i and its concentrations in tributaries (from 17–19 to 9 $\mu\text{mol}\cdot\text{l}^{-1}$; Appendix 4). The decreased Al_i leaching (despite stable stream water pH; Fig. 3H) occurred due to decreasing leaching of SO_4^{2-} and represents the most important change in water recovery from acidification (VRBA et al. 2006). The Al_i leaching was the major terrestrial factor mitigating the net terrestrial H^+ production (Table 3).

Net terrestrial sources of base cations and organic acid anions

The interpretation of π_C^* values for BCs (Table 3) is not very straightforward except for conservative Na^+ . These values are related to BC deposition to the catchment soils that also includes canopy leaching (elements released during precipitation passing through the canopies), i.e., a part of their internal cycling between soils and vegetation. Thus calculated π_C^* values suggest net Ca^{2+} and K^+ retention in soils and underestimate terrestrial Mg^{2+} production. The actual net terrestrial production of Ca^{2+} , Mg^{2+} , and K^+ (without the soil-vegetation exchange) can be estimated as the difference between their terrestrial exports and net atmos-

pheric inputs to the catchment. Total deposition of conservative ion Na^+ was on average 1.87 fold higher than that of precipitation. The Na^+ exchange was negligible in Norway spruce canopies in the study catchment (KOPÁČEK et al. 2009), hence, we can assume that its total (wet, dry, and horizontal) atmospheric input into the catchment was equal to the deposition to the catchment soils. Moreover, dry depositions of Ca^{2+} , Mg^{2+} , and K^+ are assumed to be similar to that of Na^+ , due to the same physical size and aerodynamic properties of base cation-containing aerosols (DRAAIJERS & ERISMAN 1995). Total atmospheric input of the rest of BCs can thus be roughly estimated from their precipitation fluxes, multiplied by a factor of 1.87. This provides net (without contribution of canopy exchange) atmospheric inputs of Ca^{2+} , Mg^{2+} and K^+ to the catchment of 11.2, 4.2, and 1.5 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ and their 1998–2017 average terrestrial production of 0.8, 14.2, and 1.3 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively. The catchment was thus higher source of Mg^{2+} than Ca^{2+} , which is consistent with its almost one order of magnitude higher concentration in the Čertovo bedrock (KOPÁČEK et al. 2002).

Similarly corrected for canopy leaching as BCs, the catchment was a net source of 18 ± 13 $\text{meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ A^- .

Net phosphorus retention in catchment soils

The Čertovo soils were a net sink for atmospherically deposited P. The TP fluxes averaged 0.7 and 1.2 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ in precipitation and deposition to the catchment soils, respectively, while its average terrestrial export was 0.15 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ (Table 3). The P pool in Čertovo soils has probably increased since their development (throughout Holocene), and the present average P concentration (catchment weighted mean for all soil horizons and soil types) is almost two fold higher than in the dominant (mica-schist) bedrock (24 vs. 13 $\text{mmol}\cdot\text{kg}^{-1}$; KOPÁČEK et al. 2002). The retained P is probably adsorbed on soil Al and Fe hydroxides that are responsible for high phosphate adsorption capacity of the Čertovo soils (11.9 $\text{mol}\cdot\text{m}^{-2}$; KAŇA & KOPÁČEK 2006). The present average P pool is about a half (~ 5.4 $\text{mol}\cdot\text{m}^{-2}$) of the total phosphate adsorption capacity of the Čertovo soils (KOPÁČEK et al. 2002), which suggests that soils may remain a net P sink for a long time even in future.

Major processes affecting element fluxes in Čertovo Lake

The in-lake H^+ neutralization was dominated by denitrification that reduced the input flux of NO_3^- by 28% on average (Table 4). Similar high importance of NO_3^- reduction on internal H^+ cycle was also observed in other acidified lakes with elevated NO_3^- inputs (SCHINDLER 1986, KELLY et al. 1987). The settling (removal) velocity of NO_3^- calculated according to KELLY et al. (1987) averaged 4.4 ± 1.7 $\text{m}\cdot\text{yr}^{-1}$ in Čertovo Lake, and was within the range of similar data (2.8–12.7 $\text{m}\cdot\text{yr}^{-1}$) reported for 20 European and North American lakes (KELLY et al. 1987, KASTE & DILLON 2003). The annual SO_4^{2-} retention in Čertovo Lake (5% on average) was within the range of data reported for lakes with water residence times <4 years (5–19%; KELLY et al. 1987, THIES 1997) and its mass transfer coefficient (also called “settling velocity”) averaged 0.6 ± 0.8 $\text{m}\cdot\text{yr}^{-1}$. The SO_4^{2-} role in the internal H^+ neutralization was thus small during the study and will probably further decrease together with the decreasing in-lake SO_4^{2-} concentrations, anticipated by modelling (MAJER et al. 2003, OULEHLE et al. 2012). Most of the NO_3^- and SO_4^{2-} removal probably occurred in sediments, even though denitrification also could occur in the anoxic hypolimnion. The zone with depleted O_2 (<1 $\text{mg}\cdot\text{l}^{-1}$) was, however, relatively thin in Čertovo Lake and only occurred in the deepest parts of the lake during winter and summer temperature stratification (Fig. 2; KOPÁČEK et al. 2000a, 2001a).

The removal of A^- , the second most important in-lake H^+ neutralizing process after NO_3^- reduction (Table 4), mostly occurs in the epilimnion. This H^+ neutralizing process is associ-

ated with the partial photochemical degradation of allochthonous DOC (KOPÁČEK et al. 2003, PORCAL et al. 2010) that oxidizes DOC and produces biologically available small molecular weight compounds for bacterial growth (e.g., WETZEL et al. 1995). The DOC (and A⁻) is thus photochemically and/or microbially oxidized to CO₂ and H₂O, removing one mole of H⁺ per each equivalent of the oxidized A⁻; e.g., for formic acid:



The role of A⁻ oxidation on in-lake H⁺ neutralization will probably further increase due to almost generally increasing DOC leaching from European catchments recovering from atmospheric acidification (MONTEITH et al. 2007, EVANS et al. 2012), which also occurs in the Bohemian and Bavarian Forest surface waters (KOPÁČEK et al. 2013a, BEUDERT & GIETL 2015).

Photochemical degradation of allochthonous DOC and its increased availability for bacteria can explain the high proportion of bacteria in the total plankton biomass observed in Čertovo Lake (VRBA et al. 2003). Having a possibility to utilize the transformed allochthonous DOC, bacterial grow is not limited by availability of organic exudates from primary (algal) production, which is small in this oligotrophic lake due to low P inputs. The lower in-lake production of algal exudates than the photochemical and microbial degradation of DOC resulted in net DOC removal in Čertovo Lake (Fig. 4E). Photochemical cleaving of allochthonous organic N to NH₄⁺ and NO₃⁻ (PORCAL et al. 2014) was probably the major reason for net TON retention in the lake (Fig. 4F, Table 4).

Photochemical cleaving of DOC also significantly affects in-lake metal chemistry (KOPÁČEK et al. 2003, PORCAL et al. 2010) and was responsible for liberating ~50% of Al_o and Fe_o from their organic complexes as Al_i and Fe_i (Table 4). The Al_o and Fe_o concentrations were thus lower in the outlet than in the lake tributaries (Table 2) and the liberated metals contributed to their ionic forms, supplied by tributaries, in modifying in-lake H⁺ budgets.

The higher output fluxes of NH₄⁺ from Čertovo Lake than its input by tributaries and atmospheric deposition to the lake surface (Fig. 4G) resulted from internal NH₄⁺ generation by dissimilatory processes in the hypolimnion (Fig. 2H). The major source of NH₄⁺ for primary producers in the epilimnion is atmospheric deposition (Table 2). After its depletion, algae can utilize NO₃⁻ as an alternative source of reactive N (PROCHÁZKOVÁ et al. 1970). The produced biomass settles and the organic matter is continuously microbially decomposed. The liberated NH₄⁺ accumulates in the anoxic zone, but is usually rapidly nitrified in the oxic parts of water column in circum neutral lakes (WETZEL 2001). However, nitrification was likely suppressed in Čertovo Lake due to its strong acidification as described for North American lakes by RUDD & al. (1988). Consequently, the liberated NH₄⁺ was not nitrified in Čertovo Lake, and entered its outlet after mixing to the whole water profile during spring and autumn overturns. The lake thus became the net NH₄⁺ source in years when its dissimilative production in the hypolimnion exceeded its assimilation in the epilimnion and the water column was completely mixed.

Hydrolysis of Al_i (equation 10) was the most important in-lake acidity source, producing on average 79±41 meq.m⁻².yr⁻¹ of H⁺ (Table 4):



The hydrolysis occurs along pH gradients between the input and output water (Table 2), and between the lake surface and bottom (Fig. 2C), resulting in a decreasing positive charge of hydroxyl-Al complexes, and a net in-lake production of Al_p (mostly colloidal Al(OH)₃) (KOPÁČEK et al. 2008). A part of this Al_p left the lake via outflow (11 mmol.m⁻².yr⁻¹), the rest (33 mmol.m⁻².yr⁻¹) was deposited in sediments (Table 4). A similar effect of Fe_i on the in-

lake H^+ budget was negligible, due to its lower concentrations.

The formed colloidal Al hydroxides have large specific surfaces and a strong ability to bind orthophosphate from the liquid phase. Thus, orthophosphate liberated from the sedimenting organic matter by dissimilatory processes was removed from the liquid phase by adsorption on (or co-precipitation with) Al_p and transformed to PP (KOPÁČEK et al. 2000c). This process explains low DP and SRP concentrations above the lake bottom despite elevated TP, but also HN_4^+ concentrations (Fig. 2H) from microbial decomposition of settling seston.

The annual removal of Si in Čertovo Lake averaged $91 \pm 67 \text{ mmol.m}^{-2}.\text{yr}^{-1}$. The reduction of dissolved Si in lakes is commonly associated with diatom production (WETZEL 2001). Pelagic diatoms are, however, absent in Čertovo Lake, but Chrysophyceae form an important portion of the phytoplankton biomass (VRBA et al. 2003, NEDBALOVÁ et al. 2006). The sedimentation of chrysophycean cysts and scales seems to be the most likely biological mechanism contributing to the Si depletion in the lake.

CONCLUSIONS

Despite substantial reduction of central European anthropogenic emission and the consequent deposition of S and N compounds since the late 1980s (KOPÁČEK & HRUŠKA, 2010), Čertovo Lake remains strongly acidic and its chemical and biological recovery from acidification is slow (VRBA et al. 2006, 2016). The H^+ production associated with N cycle (NH_4^+ assimilation and nitrification) and the excess SO_4^{2-} leaching (desorption and microbial oxidation of reduced S forms) play the most important role among the water acidifying processes in the lake catchment. The terrestrial export of SO_4^{2-} decreased by 50% during the last two decades, but this source of terrestrial acidity was partly replaced by (i) temporally elevated NO_3^- leaching from sub-catchments affected by windthrows in 2007 and 2008, (ii) continuously increasing leaching of organic acid anions as a response to decreasing SO_4^{2-} and NO_3^- deposition (KOPÁČEK et al. 2013a), and (iii) decreased leaching of Al_i from soils. Lake tributaries are thus strongly acidic, with pH between 4.1 and 4.5 (Table 2) and the depleted carbonate buffering system. The most important change in stream water recovery from acidification is decreasing Al_i concentration in the lake tributaries (Appendix 4) and output (Appendix 6).

The in-lake H^+ removal processes neutralize ~40% of the total (terrestrial and atmospheric) H^+ input into the lake. This internal acidity removal, however, increases lake water pH only slightly, from 4.3 to 4.5. Water leaving the whole Čertovo catchment–lake system thus remains significantly more acidic than precipitation (pH of ~5.0; Table 2). The most important in-lake neutralizing processes are NO_3^- reduction and A^- oxidation, while Al_i hydrolysis most importantly mitigates the H^+ decrease associated with the former processes. Changes in in-lake concentrations of SO_4^{2-} , BCs, and NH_4^+ only play minor roles in the internal H^+ balance (Table 4).

Results of this study suggest that chemical (and most probably also biological) recovery of Čertovo Lake will remain slow and may be even temporally reversed in future due to forest damages. The reason for such a high sensitivity of Čertovo catchment to acidification is low base saturation of soils that probably resulted from historical forest harvesting for wood, charcoal, and potash (VESELÝ 1994). The negative effect of acid rain thus could be strengthened by previous anthropogenic activities, highlighting the importance of cumulative stresses on ecosystems even in seemingly remote and protected areas.

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Appendix 1. Water balance in Čertovo Lake and its catchment in hydrological years (from November 1997 to October 2017). Precipitation amount (H_{PR} mm.yr⁻¹), deposition to the catchment soils (Q_{DEP} mm.yr⁻¹; precipitation in the open area and throughfall in the forest), terrestrial export from catchment via all lake tributaries (Q_{TE} mm.yr⁻¹), water output from lake (Q_{OUT} mm.yr⁻¹), specific runoff from catchment-lake system (SR , l.km⁻².s⁻¹), and water residence time in lake (WRT , day).

	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
H_{PR}	1580	1359	1625	1464	2080	1057	1167	1368	1413	1401	1410	1253	1289	1108	1268	1220	1085	780	1298	962
Q_{DEP}	1418	1406	1564	1527	2018	1156	1150	1375	1424	1599	1564	1481	1362	1350	1447	1505	1335	1045	1594	1257
Q_{TE}	1347	1050	1321	1108	1926	763	1057	1238	1334	1358	1422	1374	1236	1150	1401	1446	1051	909	1329	1144
Q_{OUT}	1364	1071	1319	1100	1920	755	1078	1217	1301	1334	1376	1329	1200	1094	1351	1386	1024	802	1262	1085
SR	43.2	34.0	41.8	34.9	60.9	24.0	34.2	38.6	41.3	42.3	43.6	42.1	38.0	34.7	42.8	43.9	32.5	25.4	40.0	34.4
WRT	557	708	575	690	395	1005	704	623	583	569	552	571	633	694	562	548	741	946	601	699

Appendix 2. Precipitation amount (H_{pr}) and volume weighted mean composition of precipitation (C_{pr}) in the catchment of Čertovo Lake in hydrological years between November 1997 and October 2017. Units: $\mu\text{mol.l}^{-1}$, except for H_{pr} ($\text{m}^3 \cdot \text{yr}^{-1}$) and pH. ND – not determined.

	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
H_{pr}	1.58	1.36	1.63	1.46	2.08	1.06	1.14	1.37	1.41	1.40	1.41	1.25	1.29	1.11	1.27	1.22	1.09	0.78	1.30	0.96
pH	4.77	4.74	4.89	4.82	4.78	4.90	4.78	4.73	4.86	4.85	5.00	5.21	5.05	5.28	5.29	5.04	4.97	5.06	5.11	5.08
H ⁺	17.1	18.4	12.9	15.3	16.6	12.6	16.7	18.8	13.7	14.0	9.9	6.2	9.0	5.2	5.1	9.2	10.8	8.8	7.7	8.3
Ca ²⁺	4.2	5.4	7.1	6.1	5.8	10.3	4.5	4.7	3.6	3.7	4.2	5.8	4.2	7.3	5.3	4.6	3.7	4.6	2.9	3.2
Mg ²⁺	1.6	2.3	1.8	2.1	1.4	2.3	1.3	1.2	1.0	2.2	1.3	1.0	1.0	1.1	1.2	1.5	1.4	1.7	0.8	1.0
Na ⁺	8.6	10.5	11.4	8.9	6.9	11.7	7.6	6.9	5.4	6.3	7.4	5.2	4.5	4.9	8.3	5.4	5.9	7.1	3.4	4.7
K ⁺	7.4	10.5	6.5	4.3	2.6	9.6	2.0	2.4	2.3	2.8	2.3	2.4	1.8	2.2	1.8	2.0	2.1	2.4	1.1	1.3
NH ₄ ⁺	30.2	28.8	28.3	31.6	30.2	35.3	25.1	24.5	26.6	23.4	24.5	22.3	26.9	24.6	23.8	23.5	29.1	29.5	21.6	25.0
NO ₃ ⁻	25.5	32.0	31.6	29.5	30.5	28.3	29.7	26.9	24.3	22.9	23.1	18.2	20.1	22.4	20.4	22.8	24.1	26.6	19.5	22.8
SO ₄ ²⁻	15.2	17.0	13.9	13.0	12.3	13.6	10.7	11.9	9.2	9.4	9.0	7.4	7.9	7.1	6.6	7.6	9.9	8.1	5.9	6.2
Cl ⁻	9.1	8.9	9.3	8.5	6.3	11.9	7.7	6.4	5.3	6.6	6.9	4.7	4.1	4.6	9.2	5.5	5.9	6.7	3.5	4.0
F ⁻	ND	ND	0.2	0.2	1.8	0.6	0.3	1.0	0.5	0.2	0.3	0.3	0.2	0.2	0.3	1.5	0.5	0.6	0.2	0.4
HCO ₃ ⁻	0.0	0.0	1.2	1.7	1.0	17.0	0.1	1.7	2.1	4.1	2.1	6.8	6.8	7.6	4.5	2.7	3.1	5.0	2.8	3.4
DOC	108	108	80	126	87	124	90	90	115	124	97	90	106	82	84	82	83	99	65	75
POC	ND	ND	ND	ND	ND	81.5	22.4	25.9	38.0	29.7	56.5	40.9	20.7	32.3	20.5	24.4	24.5	17.7	20.5	17.0
DON	14.2	8.6	7.3	12.7	8.4	7.2	7.4	10.1	12.6	14.5	14.4	16.8	14.7	8.8	13.4	8.1	7.3	9.6	7.5	8.0
PON	6.3	19.0	3.2	5.6	4.8	11.1	4.9	2.5	5.4	10.1	7.5	6.6	7.5	10.0	5.5	5.9	6.3	6.5	4.0	4.7
TP	0.43	0.53	0.48	0.90	0.39	1.18	0.34	0.49	0.94	0.56	0.65	0.87	0.58	0.47	0.27	0.34	0.27	0.75	0.23	0.23
PP	0.27	0.39	0.26	0.33	0.23	0.56	0.20	0.19	0.44	0.27	0.18	0.36	0.23	0.34	0.14	0.17	0.21	0.22	0.14	0.16
SRP	0.08	0.11	0.20	0.43	0.07	0.56	0.08	0.24	0.32	0.23	0.35	0.39	0.07	0.09	0.09	0.13	0.03	0.34	0.06	0.04
Si	ND	ND	0.36	0.49	0.27	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29
Al _r	0.2	0.3	0.3	0.2	0.1	0.5	0.3	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.6	1.1	1.3	1.1	1.0	0.2

Appendix 3. Deposition amount (Q_{DEP}) and volume weighted mean composition of atmospheric deposition to the catchment soils (C_{DEP} ; precipitation in the open area and throughfall in the forest; calculated from equation 7) in the catchment of Certovo Lake in hydrological years between November 1997 and October 2017. Units: $\mu\text{mol}\cdot\text{l}^{-1}$, except for Q_{DEP} ($\text{m}^3\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) and pH. ND – not determined.

	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
Q_{DEP}	1.42	1.41	1.56	1.53	2.02	1.16	1.13	1.38	1.42	1.60	1.56	1.48	1.36	1.35	1.45	1.51	1.34	1.045	1.594	1.257
pH	4.46	4.59	4.68	4.72	4.69	4.78	4.61	4.60	4.77	4.68	4.76	4.91	4.84	5.02	5.12	4.87	4.91	4.87	5.00	4.93
H^+	34.9	25.7	20.8	19.2	20.2	16.6	24.4	25.4	17.0	20.8	17.4	12.4	14.5	9.6	7.6	13.5	12.3	13.5	9.9	11.7
Ca^{2+}	12.9	12.4	12.7	10.8	9.6	14.4	11.9	11.0	8.5	9.3	10.1	8.6	10.4	8.8	10.1	10.0	9.5	10.8	6.9	7.7
Mg^{2+}	4.6	7.0	4.8	4.4	4.6	4.8	4.6	4.3	3.2	4.7	3.9	2.9	3.8	3.8	4.0	4.2	5.0	5.3	3.2	3.9
Na^+	14.1	13.9	16.7	12.5	10.6	13.5	13.3	12.3	11.0	13.8	13.5	9.6	10.5	10.6	11.8	9.6	13.7	15.4	9.1	11.6
K^+	27.1	27.0	24.6	27.2	16.7	32.3	23.8	22.7	20.8	19.7	18.1	16.3	23.2	28.0	20.1	20.2	28.9	29.4	22.3	21.8
NH_4^+	36.5	30.8	30.7	35.3	31.4	53.5	32.8	34.3	37.9	30.5	32.2	33.1	38.4	37.2	41.3	33.1	50.4	43.1	26.6	32.2
NO_3^-	39.4	44.1	43.8	38.7	38.2	53.4	47.4	45.2	39.4	38.8	38.5	34.3	38.6	37.4	39.2	41.7	50.2	52.0	32.0	36.7
SO_4^{2-}	29.1	24.2	21.7	20.3	17.4	20.6	18.5	20.0	15.2	15.9	14.5	11.6	13.9	10.7	10.0	12.3	17.0	13.2	7.8	7.7
Cl^-	17.1	15.2	15.8	13.3	12.7	17.7	18.0	14.8	12.6	15.9	15.6	11.8	12.8	13.6	16.6	11.7	16.6	19.5	11.5	14.5
F^-	ND	ND	0.5	0.5	1.9	0.7	0.8	0.9	1.0	1.0	0.7	0.5	0.3	0.4	1.3	1.8	1.2	1.5	0.7	1.2
HCO_3^-	0.0	0.0	0.8	1.2	1.4	2.0	0.4	0.3	3.3	0.7	1.0	2.9	4.2	9.5	7.8	1.5	5.8	6.8	5.7	4.5
DOC	62.4	503	467	590	379	498	557	494	459	491	503	456	627	623	474	453	534	550	469	533
POC	ND	ND	ND	ND	ND	169	110	103	108	186	97	108	75	61	11	23	21	25	75	92
DON	29.0	23.6	20.8	12.2	23.2	21.4	19.8	24.7	28.8	27.2	39.1	49.0	26.6	35.9	27.6	27.2	21.5	10.5	15.1	19.1
PON	ND	ND	ND	ND	11.9	23.8	11.4	9.6	20.7	12.4	10.1	11.5	8.4	8.5	7.4	3.5	2.2	2.5	6.0	6.9
TP	0.63	0.85	0.91	0.85	0.51	1.38	0.71	0.63	1.06	0.86	0.99	1.05	0.77	1.22	0.70	0.61	0.83	0.87	0.95	0.92
PP	0.31	0.52	0.54	0.60	0.38	0.45	0.50	0.43	0.62	0.60	0.48	0.60	0.50	0.94	0.42	0.39	0.62	0.61	0.60	0.51
SRP	0.19	0.12	0.23	0.10	0.03	0.47	0.09	0.09	0.32	0.12	0.30	0.30	0.10	0.12	0.15	0.10	0.07	0.14	0.22	0.30

Appendix 4. Mean annual discharge (Q_{TE}) and discharge and period weighted mean concentrations of water constituents (C_{TE}) of terrestrial export via all tributaries to Čertovo Lake (calculated from equation 3) in hydrological years between November 1997 and October 2017. Units: $\mu\text{mol}\cdot\text{l}^{-1}$, except for Q_{TE} ($\text{m}^3\cdot\text{yr}^{-1}$), given on a catchment-area basis) and pH. ND – not determined.

	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
Q_{TE}	1.35	1.05	1.32	1.11	1.93	0.76	1.04	1.24	1.33	1.36	1.42	1.37	1.24	1.15	1.40	1.45	1.05	0.91	1.33	1.14
pH	4.20	4.27	4.27	4.24	4.26	4.29	4.24	4.24	4.26	4.26	4.24	4.28	4.23	4.27	4.29	4.25	4.21	4.32	4.29	4.22
H^+	63.6	53.7	53.5	58.1	55.0	51.0	56.9	57.3	54.6	54.6	58.2	52.4	59.1	53.9	50.7	55.6	61.3	48.4	51.5	60.9
Ca^{2+}	12.3	15.2	13.2	10.3	12.3	11.4	13.5	10.9	10.8	9.2	10.0	9.7	10.7	8.7	10.2	9.0	8.0	9.8	8.6	7.9
Mg^{2+}	16.4	15.3	15.6	12.4	13.4	14.8	17.9	14.7	12.8	14.0	13.5	13.6	16.1	13.5	15.1	13.3	12.2	15.5	14.2	13.1
Na^+	35.9	36.9	35.2	31.6	29.4	32.3	34.6	32.1	28.4	33.3	30.1	29.0	29.8	29.7	32.6	26.1	28.9	34.6	34.8	30.7
K^+	7.8	9.6	8.9	6.6	8.5	9.8	11.1	7.7	7.7	6.4	8.2	7.7	9.3	8.1	8.1	9.0	5.9	7.4	7.6	6.9
NH_4^+	0.1	0.3	1.7	0.7	0.9	1.1	0.8	0.4	0.7	0.6	0.4	0.5	0.8	0.3	0.8	0.4	0.3	1.3	0.3	0.1
NO_3^-	52.5	71.9	75.2	44.8	67.7	72.2	107	69.3	67.9	51.3	74.8	78.3	89.7	61.0	71.0	77.1	44.2	65.3	51.9	50.1
SO_4^{2-}	57.8	55.6	50.4	43.0	41.0	42.9	40.0	40.1	36.2	38.5	33.1	30.5	31.8	25.6	30.9	29.3	27.7	31.8	31.0	29.3
Cl^-	18.4	16.0	16.1	15.9	13.3	15.0	20.3	16.8	13.3	16.9	17.6	13.0	14.5	15.4	16.1	14.0	14.6	14.0	15.0	14.8
F^-	2.4	1.6	1.2	2.2	3.1	1.8	2.5	2.5	2.1	1.9	2.2	1.1	1.2	1.7	1.6	2.6	1.6	2.0	1.7	1.6
DOC	545	347	358	697	502	304	338	402	445	481	548	417	548	772	486	506	937	465	647	641
POC	ND	ND	ND	ND	ND	17	1.7	19	6	3	17	23	8	16	10	8	20	14	13	11
DON	13.9	16.6	14.9	23.6	17.4	16.4	15.0	13.0	15.2	17.5	19.9	20.3	24.4	29.5	20.5	22.4	24.0	21.1	22.6	17.8
PON	ND	ND	ND	ND	2.48	0.31	0.00	1.60	0.58	1.09	0.95	1.62	1.06	1.96	0.91	2.73	4.65	0.31	1.29	1.22
TP	0.16	0.08	0.09	0.18	0.11	0.08	0.08	0.08	0.10	0.10	0.12	0.09	0.12	0.22	0.11	0.13	0.27	0.08	0.13	0.10
PP	0.05	0.00	0.04	0.04	0.03	0.00	0.02	0.02	0.04	0.02	0.03	0.03	0.04	0.06	0.01	0.02	0.09	0.00	0.02	0.01
SRP	0.02	0.02	0.02	0.03	0.01	0.01	0.03	0.02	0.03	0.03	0.03	0.02	0.03	0.04	0.03	0.03	0.04	0.02	0.04	0.04
Si	79.5	74.5	69.7	76.3	66.1	77.7	80.3	75.0	69.3	75.6	67.3	67.2	70.7	74.5	76.6	62.0	65.6	87.3	82.9	84.2
Al_r	24.6	24.5	23.1	21.7	22.6	20.4	26.3	20.2	18.9	17.4	23.4	19.2	20.0	19.2	17.5	21.4	20.8	15.9	16.0	14.8
Al_l	17.6	19.5	17.5	12.9	16.2	15.8	19.7	13.1	12.4	10.9	15.7	14.3	13.8	11.6	12.6	13.8	10.5	9.9	9.1	9.0
Al_o	6.5	4.5	5.6	8.5	6.1	4.3	6.2	6.6	6.1	6.2	7.1	4.4	5.6	6.4	4.2	7.7	9.6	5.7	6.7	5.5
Fe_r	2.9	2.0	2.0	3.9	2.6	1.9	1.8	2.7	2.2	2.8	2.7	2.3	2.8	4.7	2.8	2.6	4.5	2.5	3.5	3.3
Fe_l	0.8	0.8	1.0	1.2	0.6	0.7	0.6	0.5	0.5	0.9	0.9	1.1	1.2	1.2	1.0	0.9	0.9	0.9	1.0	0.9
Fe_o	1.8	0.9	1.0	2.5	1.7	1.2	1.1	1.7	1.6	1.8	1.6	1.1	1.5	2.8	1.5	1.6	3.1	1.4	2.3	2.1

Appendix 5. Total water input (Q_{IN}) and mean annual composition of water input (terrestrial export and precipitation to the lake surface) to Čertovo Lake in hydrological years between November 1997 and October 2017. Units: $\mu\text{mol}\cdot\text{l}^{-1}$, except for Q_{IN} ($\text{m}^3\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, given on a lake-area basis) and pH. ND – not determined.

	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
Q_{IN}	11.4	9.0	11.3	9.6	16.2	6.6	8.7	10.4	11.2	11.3	11.8	11.3	10.3	9.5	11.5	11.8	8.8	7.4	11.0	9.3
pH	4.24	4.32	4.32	4.29	4.30	4.35	4.29	4.28	4.31	4.31	4.28	4.33	4.28	4.32	4.34	4.29	4.26	4.35	4.33	4.26
H ⁺	57.2	48.4	47.7	51.6	50.0	44.8	51.7	52.3	49.4	49.5	52.4	47.3	52.9	48.2	45.7	50.8	55.0	44.2	46.4	55.5
Ca ²⁺	11.2	13.7	12.3	9.6	11.5	11.2	12.4	10.1	9.9	8.6	9.3	9.3	9.9	8.5	9.6	8.6	7.4	9.2	7.9	7.4
Mg ²⁺	14.4	13.3	13.6	10.8	11.9	12.8	15.7	12.9	11.3	12.5	12.1	12.2	14.2	12.0	13.6	12.1	10.9	14.1	12.6	11.9
Na ⁺	32.1	32.9	31.8	28.1	26.5	29.1	31.0	28.8	25.5	30.0	27.4	26.4	26.6	26.8	29.9	23.9	26.0	31.7	31.1	28.0
K ⁺	7.7	9.8	8.5	6.3	7.8	9.7	9.9	7.0	7.0	6.0	7.5	7.1	8.4	7.5	7.5	8.3	5.4	6.9	6.8	6.3
NH ₄ ⁺	4.2	4.6	5.5	5.4	4.7	6.6	4.0	3.6	4.0	3.4	3.3	2.9	4.0	3.1	3.3	2.8	3.9	4.3	2.8	2.7
NO ₃ ⁻	48.8	65.9	68.9	42.5	62.9	65.2	97.1	63.8	62.4	47.8	68.6	71.6	81.0	56.5	65.4	71.5	41.7	61.3	48.1	47.3
SO ₄ ²⁻	51.9	49.8	45.1	38.4	37.3	38.2	36.1	36.4	32.8	34.9	30.2	27.9	28.8	23.5	28.2	27.1	25.5	29.3	28.1	26.9
Cl ⁻	17.1	14.9	15.1	14.8	12.4	14.5	18.7	15.4	12.3	15.6	16.4	12.1	13.2	14.1	15.4	13.1	13.5	13.3	13.7	13.7
F ⁻	2.1	1.4	1.0	1.8	2.9	1.6	2.2	2.3	1.9	1.7	2.0	1.0	1.1	1.6	1.4	2.5	1.4	1.8	1.5	1.4
DOC	484	311	318	610	449	275	306	361	404	437	494	381	493	692	442	462	831	427	579	583
POC	ND	ND	ND	ND	ND	27	4	20	10	6	22	25	10	17	11	10	21	14	14	12
DON	14.0	15.4	13.8	21.9	16.3	14.9	14.0	12.6	14.9	17.1	19.2	19.9	23.2	27.1	19.7	20.9	21.9	19.9	20.8	16.8
PON	1.90	6.91	0.46	0.86	2.78	2.03	0.21	1.72	1.20	2.20	1.74	2.17	1.87	2.89	1.42	3.06	4.86	0.96	1.60	1.57
TP	0.15	0.15	0.15	0.29	0.14	0.26	0.11	0.14	0.21	0.16	0.18	0.18	0.18	0.25	0.13	0.15	0.27	0.15	0.14	0.11
PP	0.04	0.06	0.07	0.09	0.05	0.09	0.05	0.04	0.09	0.05	0.05	0.06	0.06	0.09	0.02	0.04	0.11	0.02	0.04	0.03
SRP	0.03	0.03	0.04	0.09	0.02	0.10	0.03	0.05	0.07	0.06	0.07	0.06	0.04	0.05	0.04	0.04	0.04	0.06	0.05	0.04
Si	68.5	63.3	59.7	64.7	57.6	65.4	69.8	65.2	60.6	66.3	59.4	59.8	61.9	65.8	68.2	55.6	57.5	78.1	73.2	75.6
Al _T	21.3	20.9	19.8	18.4	19.8	17.3	22.9	17.6	16.5	15.3	20.6	17.1	17.5	17.0	15.6	19.3	18.4	14.3	14.3	13.3
Al _I	15.2	16.6	15.0	11.0	14.2	13.3	17.1	11.4	10.8	9.6	13.8	12.7	12.1	10.3	11.2	12.4	9.2	8.9	8.0	8.0
Al ₀	5.6	3.8	4.8	7.2	5.3	3.6	5.4	5.8	5.4	5.4	6.3	3.9	4.9	5.6	3.8	6.9	8.4	5.1	5.9	5.0
Fe _T	2.6	1.7	1.7	3.3	2.2	1.6	1.5	2.3	1.9	2.4	2.4	2.0	2.5	4.1	2.5	2.3	4.0	2.2	3.1	2.9
Fe _I	0.7	0.7	0.8	1.0	0.6	0.6	0.6	0.4	0.4	0.8	0.8	1.0	1.0	1.1	0.9	0.8	0.8	0.8	0.9	0.8
Fe ₀	1.5	0.7	0.8	2.2	1.5	1.0	0.9	1.5	1.4	1.6	1.4	1.0	1.3	2.4	1.3	1.4	2.8	1.3	2.0	1.9

Appendix 6. Water output (Q_{OUT}) and mean annual composition of water output from Cértovo Lake (C_{OUT}) in hydrological years between November 1997 and October 2017 Units: $\mu\text{mol.l}^{-1}$, except for Q_{OUT} ($\text{m}^3 \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$, given on a lake-area basis) and pH. ND – not determined.

	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
Q_{OUT}	11.4	8.9	11.0	9.2	16.0	6.3	8.6	10.1	10.8	11.1	11.5	11.1	10.0	9.1	11.2	11.5	8.5	6.7	10.5	9.0
pH	4.42	4.39	4.42	4.58	4.41	4.51	4.44	4.47	4.43	4.58	4.47	4.52	4.56	4.57	4.61	4.53	4.64	4.60	4.65	4.56
H^+	38.2	41.1	38.1	26.5	38.5	30.7	36.3	33.7	37.0	26.4	33.5	30.5	27.5	27.2	24.4	29.8	23.1	25.2	22.6	27.3
Ca^{2+}	12.6	12.9	12.2	11.5	12.0	10.1	10.4	10.2	10.9	9.7	9.8	8.7	8.8	8.7	8.6	8.3	8.6	7.4	8.3	7.6
Mg^{2+}	14.8	14.5	13.5	12.5	12.6	11.3	13.1	12.3	11.2	12.2	11.5	11.5	12.4	12.4	12.5	12.2	12.4	13.0	12.1	11.8
Na^+	30.9	30.4	32.7	29.7	26.4	25.2	26.5	26.7	24.5	26.4	26.0	25.9	25.6	26.1	26.5	25.2	27.1	27.9	27.0	27.1
K^+	9.5	9.1	9.2	7.2	7.6	7.9	8.7	7.7	7.8	7.0	7.3	7.4	7.4	7.6	7.4	7.3	7.4	7.5	7.3	6.9
NH_4^+	3.9	4.0	3.7	5.3	4.1	4.9	5.0	5.0	5.0	5.2	4.3	4.4	5.2	3.2	4.6	4.5	4.0	5.8	5.0	5.4
NO_3^-	43.7	50.2	55.9	35.0	48.1	38.2	61.0	49.2	52.8	37.4	48.9	50.7	51.0	51.4	48.2	50.7	41.6	39.8	37.3	35.7
SO_4^{2-}	56.9	52.0	49.2	45.0	41.6	38.3	36.4	36.8	34.0	33.7	31.6	31.5	31.1	27.6	28.2	28.3	27.6	28.1	27.0	26.2
Cl^-	18.3	16.1	16.3	15.4	15.8	13.4	17.5	16.3	13.7	15.2	15.4	13.9	13.7	13.8	14.8	13.2	14.4	14.4	14.3	14.1
F^-	2.4	1.9	1.3	2.1	2.7	1.3	2.0	2.3	1.8	1.9	1.9	1.1	1.1	1.4	1.1	2.2	1.9	2.7	1.7	1.6
DOC	232	280	254	231	337	268	246	250	296	223	301	302	275	282	272	299	311	335	317	324
POC	ND	ND	ND	ND	ND	64	48	48	50	48	54	79	49	37	22	20	18	53	52	46
DON	14.2	12.7	12.9	13.3	12.7	12.9	13.2	11.3	12.7	13.1	13.1	17.0	18.3	19.6	17.4	17.3	16.0	16.8	16.1	15.9
PON	4.5	4.9	3.6	4.1	6.9	6.7	4.8	4.2	4.4	4.7	5.4	4.8	4.0	4.3	4.3	4.9	6.5	3.8	4.5	3.8
TP	0.14	0.15	0.11	0.16	0.16	0.20	0.13	0.14	0.14	0.13	0.15	0.16	0.13	0.15	0.12	0.13	0.16	0.15	0.13	0.12
PP	0.08	0.08	0.06	0.12	0.10	0.14	0.09	0.09	0.09	0.09	0.09	0.12	0.07	0.09	0.08	0.09	0.11	0.10	0.09	0.09
SRP	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.04	0.03	0.03	0.03	0.02	0.03	0.04	0.03	0.03	0.03	0.03	0.02	0.01
Si	59.2	58.2	56.7	58.2	55.1	53.8	56.6	55.5	50.3	56.3	54.6	53.0	55.7	59.7	57.2	53.7	57.3	63.4	61.1	65.9
Al_T	20.7	20.6	20.5	18.5	19.0	16.9	18.6	15.8	15.5	13.8	16.1	14.9	13.5	15.6	13.6	16.8	15.5	12.4	12.4	10.4
Al_D	17.4	17.7	17.0	14.7	14.6	12.5	14.1	11.9	11.0	10.7	12.4	11.6	10.6	12.2	11.0	12.3	11.1	8.0	7.6	7.0
Al_o	2.6	2.4	2.7	2.3	3.4	2.7	3.3	2.6	3.2	2.1	2.5	2.2	1.6	1.7	1.3	2.9	3.0	3.2	2.9	2.0
Fe_T	3.2	2.6	2.2	3.3	4.5	3.4	2.9	2.5	2.0	2.7	2.6	2.8	2.5	2.5	2.7	2.2	2.2	3.1	2.7	2.4
Fe_D	1.6	0.8	0.9	1.7	2.1	0.4	1.4	1.0	1.0	1.2	1.0	1.0	1.0	0.9	0.9	0.5	0.7	0.8	0.6	0.5
Fe_o	0.6	0.9	0.8	0.7	1.3	0.4	0.8	0.9	0.8	0.7	1.0	1.0	0.8	0.8	0.8	0.8	0.5	1.1	0.8	0.8

Appendix 7. Net production of water constituents in the catchment of Čertovo Lake (π_{C}^* calculated from equation 1) in hydrological years between November 1997 and October 2017. Units: $\mu\text{mol}\cdot\text{L}^{-1}$. Positive values indicate net production, while negative values indicate net removal. ND – not determined.

	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
H ⁺	27	19	29	32	34	26	30	29	36	30	39	39	43	43	43	42	46	33	40	48
Ca ²⁺	-1.3	-1.4	-1.8	-4.6	2.3	-11	0.6	-1.3	1.7	-1.7	-1.1	0.4	-0.7	-1.7	-0.3	-1.4	-4.2	-2.7	0.3	-0.6
Mg ²⁺	12	6	10	6	9	7	13	10	9	8	9	10	12	9	11	9	6	9	10	9
Na ⁺	21	18	15	14	18	12	20	18	17	17	15	19	18	17	20	16	11	17	24	18
K ⁺	-21	-27	-20	-31	-9	-39	-15	-17	-15	-17	-12	-10	-16	-25	-13	-12	-31	-26	-19	-17
NH ₄ ⁺	-38	-41	-35	-48	-32	-80	-35	-38	-40	-35	-35	-35	-42	-43	-42	-34	-64	-48	-32	-35
NO ₃ ⁻	11	13	23	-8	28	-9	56	19	26	6	32	41	47	17	31	34	-20	6	13	10
SO ₄ ²⁻	27	23	25	15	23	12	20	18	20	20	17	18	16	13	21	17	6	17	22	21
Cl ⁻	0.5	-4.3	-2.7	-2.4	0.0	-12	0.7	0.4	-0.2	-1.8	0.5	0.3	0.4	-0.5	-1.0	1.8	-6.5	-8.4	1.2	-1.1
F ⁻	1.5	1.6	0.6	2.2	1.1	0.7	1.7	1.4	1.0	0.8	1.4	0.6	0.8	1.3	0.2	0.7	0.0	0.3	0.8	0.2
DOC	-113	-326	-195	-116	104	-451	-268	-146	-44	-97	-5	-75	-143	40	-4	34	258	-167	85	56
POC	ND	ND	ND	ND	-1	-239	-118	-95	-110	-217	-89	-94	-75	-55	-1	-16	-7	-16	-77	-90
DON	-17	-15	-10	-1	-7	-16	-7	-14	-16	-15	-23	-33	-5	-13	-8	-6	-3	9	5	-3
PON	ND	ND	ND	ND	-10	-36	-13	-9	-22	-13	-10	-11	-8	-8	-7	-1	2	-3	-6	-6
TP	-0.5	-1.1	-1.0	-1.0	-0.4	-2.0	-0.7	-0.6	-1.0	-0.9	-1.0	-1.0	-0.7	-1.2	-0.6	-0.5	-0.8	-0.9	-1.0	-0.9
PP	-0.3	-0.7	-0.6	-0.8	-0.4	-0.7	-0.5	-0.5	-0.6	-0.7	-0.5	-0.6	-0.5	-1.0	-0.4	-0.4	-0.7	-0.7	-0.7	-0.6
Si	79	75	68	76	66	78	80	75	69	76	67	67	71	74	76	62	66	87	83	84
Al _T	24	24	23	22	23	20	26	20	19	17	23	19	20	19	17	21	21	16	16	15
Al _i	18	20	17	13	16	16	20	13	12	11	16	14	14	12	13	14	10	10	9	9
Al _o	6.5	4.5	5.6	8.5	6.1	4.3	6.2	6.6	6.1	6.2	7.1	4.4	5.6	6.4	4.2	7.7	9.6	5.7	6.7	5.5
Fe _T	2.0	2.0	2.0	3.9	2.6	1.9	1.8	2.7	2.2	2.8	2.7	2.3	2.8	4.7	2.8	2.6	4.5	2.5	3.5	3.3
Fe _i	0.8	0.8	1.0	1.2	0.6	0.7	0.6	0.5	0.5	0.9	0.9	1.1	1.2	1.2	1.0	0.9	0.9	0.9	1.0	0.9
Fe _o	1.2	0.9	1.0	2.5	1.7	1.2	1.1	1.7	1.6	1.8	1.6	1.1	1.5	2.8	1.5	1.6	3.1	1.4	2.3	2.1

Appendix 8. Net production of water constituents in Čertovo Lake (π_p , calculated from equation 2) in hydrological years between November 1997 and October 2017. Units: $\mu\text{mol.l}^{-1}$. Positive values indicate net production, while negative values indicate net removal. ND – not determined.

	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
H ⁺	-22	-20	-17	-35	-9	-34	-13	-17	-19	-25	-18	-20	-22	-34	-19	-23	-39	-24	-22	-27
Ca ²⁺	-0.4	-0.8	1.0	-0.4	-2.2	-0.4	-1.5	-1.3	0.7	-0.2	-0.6	0.6	-2.3	-0.7	-0.3	-0.3	0.8	-2.8	-0.4	-2.2
Mg ²⁺	0.1	0.0	-1.0	0.1	-2.0	-0.7	0.1	-1.9	-0.9	0.0	-2.6	-0.6	-1.4	-0.6	-0.6	-0.6	1.3	-4.0	-1.6	-0.4
Na ⁺	0.2	-3.7	0.3	0.3	-4.1	-3.8	-3.3	-3.3	-2.2	-3.6	-2.8	-5.0	0.3	-2.4	-2.6	-0.7	2.5	-5.9	-8.0	0.9
K ⁺	3.3	-5.0	4.4	-1.6	-0.6	-1.2	-0.4	-0.9	0.9	0.0	-0.1	-0.7	-0.8	-0.1	-0.2	0.0	0.9	-0.3	-0.8	-0.3
NH ₄ ⁺	1.1	-1.7	-1.2	0.0	-3.4	2.0	-0.3	1.3	0.4	2.8	0.9	-0.3	1.1	-3.3	3.7	0.0	3.6	-0.5	1.8	1.6
NO ₃ ⁻	-10	-20	-17	-13	-16	-28	-27	-17	-18	-11	-21	-23	-21	-12	-13	-24	-9	-38	-18	-20
SO ₄ ²⁻	-0.6	-2.2	1.7	-6.3	-6.3	-2.9	0.0	-3.6	-1.5	-2.4	-2.3	0.1	0.4	-2.9	0.1	-0.6	0.4	-3.5	-3.2	-1.3
Cl ⁻	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
F ⁻	0.3	0.5	0.3	0.2	-1.1	1.7	0.5	0.1	-1.1	0.8	-0.4	-1.4	0.0	1.2	0.1	0.1	-0.2	0.2	-0.6	0.6
DOC	-103	-187	-82	-333	-54	-107	-154	-83	-76	-229	-231	-41	-297	-420	-148	-97	-537	-305	-246	-198
POC	ND	ND	ND	ND	ND	88	39.7	-25	80	54	109	-15	-63	41	17	-17	32	23	89	57
DON	5.7	-3.1	-2.2	-6.2	-4.9	-11	-5.1	5.5	-6.5	-5.0	-2.8	1.1	-3.2	-10	7.4	-17	-9.0	2.9	-11.1	8.2
PON	4.0	-3.6	3.6	0.5	0.4	11	1.7	-1.2	9.6	3.0	-2.2	6.3	0.9	3.5	-2.6	7.4	4.7	-4.0	3.0	1.4
TP	-0.04	-0.12	-0.04	-0.07	-0.03	-0.09	0.02	-0.05	0.01	-0.06	-0.05	0.01	-0.11	-0.11	0.01	-0.03	-0.08	-0.06	-0.01	0.01
PP	0.02	-0.03	0.00	0.04	0.04	0.05	0.00	0.04	0.08	-0.02	-0.01	0.07	0.00	0.05	0.05	-0.01	0.10	0.03	0.06	0.07
SRP	-0.07	-0.02	0.00	-0.06	-0.03	-0.09	0.03	-0.03	-0.03	-0.05	-0.05	-0.02	0.00	-0.03	-0.02	0.00	-0.03	-0.05	-0.04	-0.05
Si	-9.9	-6.1	-6.1	-11	-4.8	-11	-14	-13	-15	-11	-5.4	-18	6.9	-11	-17	-1.4	1.5	-25.2	-5.4	-9.4
Al _r	-1.2	-2.4	-1.6	-3.3	-2.8	-1.3	-6.7	-2.8	-3.8	0.0	-9.2	-4.4	-3.8	0.6	-0.1	-4.4	-4.7	-7.8	-2.2	-5.8
Al _l	-1.3	0.3	0.7	-3.0	-1.4	-2.0	-7.1	0.3	-1.9	2.3	-5.1	-2.8	0.0	3.6	-2.1	-1.4	-0.5	-2.0	-2.3	-2.4
Al _o	-0.5	-2.9	-2.2	-4.2	-1.8	-2.1	-2.0	-3.2	-3.2	-2.7	-4.8	-2.4	-3.9	-5.5	-0.2	-3.1	-6.0	-2.3	-2.7	-4.2
Fe _r	1.7	-1.4	3.0	0.5	1.3	5.6	-1.3	0.3	1.6	-1.9	0.8	0.8	-2.1	0.1	-1.0	2.0	-2.3	-1.5	0.7	0.5
Fe _l	-0.3	-0.5	2.4	-1.9	1.5	0.5	-0.1	0.1	1.5	0.2	-0.6	0.7	-0.4	0.5	-0.9	-0.2	0.5	-1.6	0.5	-1.2
Fe _o	-0.3	-0.4	0.0	-1.2	0.1	-0.2	-0.9	-0.5	0.0	-1.1	-0.4	-0.6	-0.5	-1.8	-0.6	-0.6	-2.9	0.9	-1.1	-1.8