

## Fluxes of ecologically important solutes in the Plešné catchment–lake system from 2000–2017

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 Plešné Lake between 2000 and 2017 hydrological years. The system has been recovering from acidification since the late 1980s. Bark beetle killed ~90% of mature Norway spruce trees in the catchment from 2004–2008 and all dead biomass was left in the catchment. The average water outflow from the system was  $1087 \pm 232 \text{ mm.yr}^{-1}$  (i.e.,  $34 \pm 7 \text{ l.km}^{-2}.\text{s}^{-1}$ ) and the water residence time in the lake averaged  $338 \pm 70$  days during 2000–2017. The Plešné catchment was an average net source of  $\text{H}^+$  ( $35 \pm 18 \text{ meq.m}^{-2}.\text{yr}^{-1}$ ) throughout the study. The most important  $\text{H}^+$  sources were net release of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  (76 and  $37 \text{ meq.m}^{-2}.\text{yr}^{-1}$ , respectively) and retention of  $\text{NH}_4^+$  in soils ( $41 \text{ meq.m}^{-2}.\text{yr}^{-1}$ ), while terrestrial production of  $\text{Al}_1$  and base cations represented the most important  $\text{H}^+$  sinks ( $53$  and  $78 \text{ meq.m}^{-2}.\text{yr}^{-1}$ , respectively). The maximum terrestrial  $\text{H}^+$  production of  $58 \text{ meq.m}^{-2}.\text{yr}^{-1}$  occurred after the tree dieback (an average for 2006–2010). The in-lake biogeochemical processes reduced the incoming  $\text{H}^+$  by ~65% (i.e., neutralized on average  $267 \text{ meq.m}^{-2}.\text{yr}^{-1}$   $\text{H}^+$  on a lake-area basis), and reached maximum values of  $359 \text{ meq.m}^{-2}.\text{yr}^{-1}$  on average from 2006–2010. The  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  reductions and photochemical and microbial oxidation of organic acid anions ( $\text{A}^-$ ) were the most important  $\text{H}^+$  neutralizing processes ( $395$ ,  $25$ , and  $151 \text{ meq.m}^{-2}.\text{yr}^{-1}$ , respectively), while hydrolysis of  $\text{Al}_1$  was the dominant  $\text{H}^+$  generating process ( $243 \text{ meq.m}^{-2}.\text{yr}^{-1}$ ). The  $\text{H}^+$  concentrations in the lake have started to decrease since 2009, because inputs of  $\text{NO}_3^-$  and  $\text{A}^-$  have remained high enough to neutralize  $\text{H}^+$  by  $\text{NO}_3^-$  reduction and  $\text{A}^-$  oxidation, while  $\text{H}^+$  production by  $\text{Al}_1$  hydrolysis has decreased due to decreasing terrestrial  $\text{Al}_1$  export. The changes in composition of tributaries after the tree dieback thus caused rapid pH increase to  $>5$  and a reestablishment of the carbonate buffering system in Plešné Lake.

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

### INTRODUCTION

Plešné Lake is the most productive among the glacial lakes in the Bohemian Forest (VRBA et al., 2003, 2016). After sparse historical studies from the end of the 19<sup>th</sup> century (FRÍČ 1874) and the early 1960s (PROCHÁZKOVÁ & BLAŽKA 1999), the limnology of Plešné Lake has become the subject of regular monitoring since 1984 (VESELÝ et al. 1998a, b). The historical data on chemical and biological research of Plešné Lake were summarized by VESELÝ (1994) and HEJZLAR et al. (1998). The lake was atmospherically acidified already in the early 1960s (pH < 5.4) and acidification progressed until the middle 1980s, when pH ranged between 4.4 and 4.7 (VESELÝ et al. 1998a). The lake has been recovering from acidification since the late 1980s (MAJER et al. 2003). HEJZLAR et al. (1998) performed the first complex limnological study of Plešné Lake including water and sediment chemistry and biota. Since 2000, regular research on the lake has been further intensified, focusing on fluxes of major ions within the whole catchment–lake system, including water–sediment and soil–water interactions, and in-lake nutrients cycles (e.g., KOPÁČEK et al. 2001a, 2004, 2006, KAŇA et al. 2013, 2015).

Scientific interest in Plešné Lake further increased in the middle 2000s, when bark beetle killed most of mature spruce trees in its catchment. Since the tree dieback, element leaching from soils and lake water chemistry have started to change (OULEHLE et al. 2012, KOPÁČEK et al. 2017). The aim of this paper is to (i) evaluate major sources and sinks of acidity in the terrestrial and aquatic parts of the Plešné catchment–lake system in the 2000–2017 period using mass budget study on major ions and nutrients, (ii) evaluate their changes after the onset of tree dieback in 2004, and (iii) compare how major fluxes of elements differ from those in Čertovo catchment–lake system (KOPÁČEK et al. 2018b), a similar acidified ecosystem in the same mountain area, but with predominately healthy forest and lower terrestrial phosphorus export. For this purpose, we review and synthesize already published studies on element fluxes in the Plešné catchment–lake system, recalculate previous mass balances of elements (KOPÁČEK et al. 2001a, 2006) using new data on lake and catchment characteristics (ŠOBR & JANSKÝ 2016, KOPÁČEK et al. 2017), and supplement them with unpublished data.

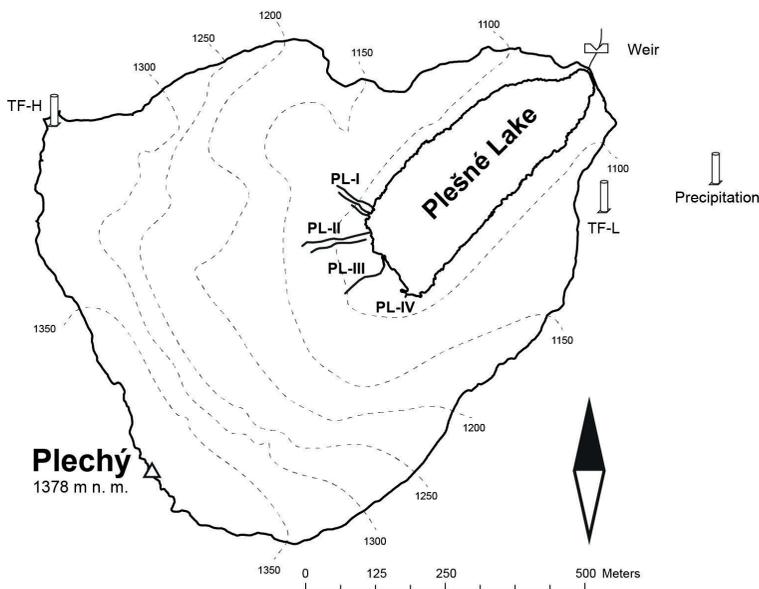
## MATERIALS AND METHODS

### Site description

Plešné Lake is situated near the Czech-Austrian border at 13°52' E, 48°47' N, and an elevation of 1087 m a.s.l. It is a dimictic, oligotrophic lake of glacial origin, with surface area of 7.2 ha and maximum depth of 17.7 m. The lake volume is  $553 \times 10^3 \text{ m}^3$ , of which 48%, 33%, 18%, and 1% are in the 0–5 m, 5–10 m, 10–15 m, and deeper than 15 m layers, respectively (ŠOBR & JANSKÝ 2016). Plešné Lake is fishless at present, with recovering plankton and littoral communities. Acid-tolerant species of green algae, dinoflagellates, and filamentous cyanobacteria dominate in phytoplankton biomass, while two abundant copepods and scarce pelagic rotifers form the current zooplankton (VRBA et al. 2003, 2016). Littoral and submerged macrophytes (*Carex rostrata*, *Isoëtes echinospora*) were sparse 1–2 decades ago, but their area rapidly increased during the last decade and reached ~0.28 ha in 2016 (ČTVRTLÍKOVÁ et al. 2016). Anoxia occurs regularly in the PL hypolimnion during both winter and summer stratification periods (KOPÁČEK et al. 2004). Plešné Lake has two surface tributaries (PL-I and PL-II) and one known subsurface inlet (PL-IV) (Fig. 1). The PL-III tributary was subsurface until 2001, when the PL water level was decreased by ~0.5 m after a reconstruction of its outlet and a short inlet into the lake has appeared.

The Plešné catchment (67 ha including the lake) is steep, with a maximum elevation gradient of 288 m. The bedrock consists of granite (VESELÝ, 1994). The catchment is covered with ~0.2 m deep leptosol (38%), and ~0.45 m deep podsol (29%) or dystric cambisol (27%); the rest is bare rocks (5%) and wetlands (~1%). Fine soil is rich in sand (~75%) and low in clay (~2%), and its catchment-weighted-mean pool is  $92 \text{ kg} \cdot \text{m}^{-2}$  (<2 mm, dry weight soil fraction). Soil pH (CaCl<sub>2</sub> extractable) is low, with minimum values of 2.5–3.1 in A-horizons and maximum (3.2–4.4) in the deepest mineral horizons. The mean effective cation exchange capacity of the soils was  $129 \text{ meq} \cdot \text{kg}^{-1}$  (NH<sub>4</sub>Cl and KCl extractable) in 2000, of which 15% was base saturated and the remaining was dominated by exchangeable Al<sup>3+</sup> (57%) and protons (28%) (KOPÁČEK et al. 2002).

In 2000, mature Norway spruce forest (*Picea abies*) covered ~90% of the Plešné catchment, was dominated by healthy trees, and dead trees (~7% of all adult trees) occupied <3% of the forest area in small patches distributed over the whole catchment (KOPÁČEK et al. 2013a, 2017). The rest of vegetation cover (in steep slopes) was dominated by grass (*Calamagrostis villosa*) and fern (*Athyrium distentifolium*). Blueberry (*Vaccinium myrtillus*) and fern formed the dominant understory vegetation in forest in 2004 (SVOBODA et al. 2006). Forest in Plešné catchment has been damaged by a bark beetle (*Ips typographus*) outbreak since the



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

summer of 2004 (northwest part with the PL-I and PL-II sub-catchments; Fig. 1) and around 2006 (the rest of the catchment). Most of trees died within 2–3 years after the onset of infestation in the individual catchment parts. The trees lost most needles during first several months after the infestation. Then, they have been continuously losing twigs, bark, and branches until the end of this study, and were continuously broken (but not uprooted) by winds. Most of the trees died by 2009. In 2013, 88% of the original ~17,700 adult spruce trees in the PL catchment were dead, 66% were broken, and 93% of the Plešné forest area lost more than 80% of its original healthy trees. All dead biomass was left in the catchment (KOPÁČEK et al. 2013a, 2017).

### Water sampling and analyses

Precipitation was sampled in a treeless area (2 samplers; 13.871 E, 48.776 N) at an elevation of 1087 m, close to the lake catchment (Fig. 1). Throughfall was sampled at two forest plots (9 samplers each) at low elevation of 1122 m (TF-L; 13.868 E, 48.775 N; situated close to the lake) and high elevation of 1334 m (TF-H; 13.855 E, 48.777 N; situated close to the summit). Both throughfall plots were located in flat areas in mature Norway spruce forests (>150 years old). The TF-H and TF-L plots have been affected by a bark beetle outbreak since the summers of 2004 and 2006, respectively, and all trees above the collectors died within 2–3 years of infestation. By 2015, all the original adult trees were already broken by winds at both plots. Rain was regularly sampled in two-week intervals (May to October). Snow was sampled in two to four-week intervals (November to April). Samples were pre-filtered through a 200  $\mu\text{m}$  polyethylene sieve to remove coarse particles, either during collecting (rain collectors were equipped with a sieve) or immediately after melting the snow from the winter collectors. Then, samples were stored in the dark at 4°C and subsamples for analysis

of nitrogen and phosphorus forms were frozen ( $-20^{\circ}\text{C}$ ). Samples were analysed within  $<3$  weeks after sampling. For more details see KOPÁČEK et al. (2013b).

Samples from lake tributaries were taken in approximately three-week intervals (more frequently during the snowmelt period) from November 1999 to October 2017, except for the PL-IV tributary that was sampled from January 2000. Samples were taken near the inlets to the lakes, except for subsurface tributaries that were sampled in a shallow artificial well (PL-IV) and in a small natural cave (PL-III during 1998–2001). The water discharge of surface tributaries was estimated by means of a stop-watch and calibrated bucket at small natural waterfalls or rapids. In sub-catchments containing several tributaries in close proximity (PL-I and PL-II), an integrated sample was taken with sample volumes proportional to the discharge of the individual streams. Samples were immediately filtered through a  $40\text{-}\mu\text{m}$  polyamide sieve to remove coarse particles re-suspended from the streambed during sampling. For more details see KOPÁČEK et al. (2013a).

Samples from lake outlet were taken biweekly (weekly during the snowmelt period) and immediately filtered through a  $200\text{-}\mu\text{m}$  polyamide sieve to remove zooplankton and coarse particles. 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  $\sim 20$  m downstream of the lake (Fig. 1). A water column profile (5 depths equally distributed between the surface and bottom) was sampled at the deepest part of the lake each October.

Methods for water analyses were identical to those used for water samples in the Čertovo catchment–lake system (KOPÁČEK et al. 2018b). For abbreviations of individual water constituents and other methodological details see Table 1. Equivalent concentrations (one equivalent is one mole of charge) of ionic Al ( $\text{Al}_i$ ) and Fe ( $\text{Fe}_i$ ), i.e.  $\text{Al}_i^{n+}$  and  $\text{Fe}_i^{m+}$  ( $\mu\text{eq.l}^{-1}$ ) 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  $\text{F}^-$  and  $\text{SO}_4^{2-}$  complexes (KOPÁČEK et al. 2000a). Concentrations of organic acid anions ( $\text{A}^-$ ,  $\mu\text{eq.l}^{-1}$ ) in stream and lake water were calculated from pH and concentrations of DOC and organic Al and Fe forms ( $\text{Al}_o$  and  $\text{Fe}_o$ ) according to KOPÁČEK et al. (2000a). Concentrations of  $\text{A}^-$  in precipitation and throughfall were calculated from the empirical relationship of  $\text{A}^-$  ( $\mu\text{eq.l}^{-1}$ ) =  $4 \times \text{DOC}$  ( $\text{mg.l}^{-1}$ ) 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., 2000a), and a standard sample, which was melted and assayed with each series of samples. The differences between the sum of cations and the sum of all anions (including  $\text{A}^-$ ) were  $\leq \pm 10\%$  of the total ionic content in individual precipitation and throughfall samples, and  $\leq \pm 4\%$  for the annual volume weighted mean concentrations. Similarly, the differences between the sums of cations and anions (including  $\text{Al}_i^{n+}$ ,  $\text{Fe}_i^{m+}$  and  $\text{A}^-$ ) were  $\leq \pm 5\%$  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 (Table 1).

### Mass balance and net terrestrial and aquatic production of water constituents

Mass balance of chemical constituents in the Plešné catchment and lake was based on previous studies (KOPÁČEK et al. 2001a, 2004, 2006) and was calculated for individual hydrological years from November 1 to October 31 according to equations (1) and (2), respectively:

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

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

Abbreviation	Explanation	Assessment
ANC, $\text{HCO}_3^-$	Acid neutralizing capacity, bicarbonate	Gran titration (Tacussel in 1997–2011, then Radiometer). ANC = $\text{HCO}_3^-$ for ANC >0 $\mu\text{mol.l}^{-1}$ ; $\text{HCO}_3^- = 0$ for ANC $\leq 0$ $\mu\text{mol.l}^{-1}$ .
$\text{H}^+$ (pH)	Proton concentration	pH electrode (combined, Radiometer)
$\text{NH}_4^+$ , $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{NO}_3^-$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{F}^-$	Major cations and anions	Ion chromatography (Thermo Separation Products in 1997–2000, Dionex IC25 in 2001–2011, then Dionex ICF-3000). Detection limits for ions were 0.1–0.4 $\mu\text{mol.l}^{-1}$ .
Si	Dissolved reactive silicon	Molybdate method (GOLTERMAN & CLYMO 1969).
$\text{Al}_T$ , $\text{Al}_D$ , $\text{Al}_O$ , $\text{Al}_P$	Total, ionic, organically bound, and particulate Al	Fractionation according to DRISCOLL (1984), colorimetry (DOUGAN & WILSON 1974) throughout 1997–2017; detection limit of 0.1 $\mu\text{mol.l}^{-1}$ . $\text{Al}_T$ = dissolved Al – $\text{Al}_O$ . $\text{Al}_D$ = $\text{Al}_T$ – dissolved Al. Dissolved Al = $\text{Al}_D$ + $\text{Al}_O$ .
$\text{Fe}_T$ , $\text{Fe}_D$ , $\text{Fe}_O$ , $\text{Fe}_P$	Total, ionic, organically bound, and particulate Fe	Fractionation according to DRISCOLL (1984), colorimetry (KOPÁČEK et al. 2001b) throughout 1997–2017; detection limit of 0.3 $\mu\text{mol.l}^{-1}$ . $\text{Fe}_D$ = dissolved Fe – $\text{Fe}_O$ . $\text{Fe}_P$ = $\text{Fe}_T$ – dissolved Fe. Dissolved Fe = $\text{Fe}_D$ + $\text{Fe}_O$ .
DOC	Dissolved organic C	LiquiTOC analyser (Foss-Heraeus, Germany) in 1997–1999 and Shimadzu analysers TOC 5000A in 2000–2015 and then TOC-L; detection limit of <4.0 $\mu\text{mol.l}^{-1}$ .
POC	Particulate organic C	Analysed on glass-fiber filters (pore size of 0.4 $\mu\text{m}$ ) 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 <sup>1)</sup> ; detection limit of ~2 $\mu\text{mol.l}^{-1}$ . PON = TON – DON.
TP, DP, PP	Total P, dissolved P and particulate P.	Sample pre-concentration, $\text{HClO}_4$ digestion, molybdate method (KOPÁČEK & HEJZLAR 1993); detection limit of 0.015 $\mu\text{mol.l}^{-1}$ . PP = TP – DP.
SRP	Soluble reactive P	Molybdate method (MURPHY & RILEY 1962), detection limit of 0.05 $\mu\text{mol.l}^{-1}$ .

<sup>1)</sup> 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.

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

In these equations,  $\pi_C$  and  $\pi_L$  (both in  $\text{mol.yr}^{-1}$ ) are the net mass production (when positive) or removal (when negative) of a constituent in the catchment and lake, respectively.  $\Delta M_C$  and  $\Delta M_L$  (both in  $\text{mol.yr}^{-1}$ ) are annual changes in storage 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., precipitation in the treeless area and through-

fall 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<sup>-3</sup>) are annual mean concentrations of water constituents in the atmospheric deposition to the catchment soils, in tributaries, in direct atmospheric deposition to the lake surface (precipitation), and in the lake output, respectively.

The water balance was determined from the annual amounts ( $H$ , m.y<sup>-1</sup>) of precipitation in the treeless area ( $H_{PR}$ ) and throughfall at plots  $H_{TF-L}$  and  $H_{TF-H}$ , continuously monitored  $Q_{OUT}$  and the budget for Cl<sup>-</sup>.  $Q_{DEP}$  was calculated from equation (3):

$$Q_{DEP} = (A_C - A_L) (0.2H_{PR} + 0.8(0.5H_{TF-L} + 0.5H_{TF-H})) \quad (3)$$

where  $A_C$  and  $A_L$  is area of the catchment (including lake) and lake, respectively, and coefficients 0.2 and 0.8 represent portions of the catchment, receiving atmospheric deposition in the form of precipitation (treeless area and thin forest) and throughfall (dense forest), respectively. These estimates were based on aerial photographs. In this calculation we assumed that each of plots TF-L and TF-H represented 50% of the total throughfall deposition in the study catchment (coefficients of 0.5).

The total water input into the lake ( $Q_{IN}$ , m<sup>3</sup>.yr<sup>-1</sup>) was the sum of  $Q_{TE}$  and  $Q_{PR}$ .  $Q_{PR} = H_{PR} \cdot A_L$  and  $Q_{TE}$  was calculated from equation (2), using the measured  $Q_{OUT}$  and  $Q_{PR}$  fluxes and annual volume weighted mean concentrations of Cl<sup>-</sup> in precipitation ( $Cl_{PR}$ ), annual average concentrations of Cl<sup>-</sup> in lake tributaries ( $Cl_{TE}^*$ ) and outlet ( $Cl_{OUT}$ ), and change in storage of Cl<sup>-</sup> in the lake ( $\Delta Cl_L$ ). The  $Cl_{TE}^*$  values were calculated as arithmetical mean for all tributaries, because Cl<sup>-</sup> concentrations in tributaries were similar. The net removal or production of Cl<sup>-</sup> in the lake was assumed to be negligible (e.g., VAN DER PERK 2006) and thus  $\pi_L$  of Cl<sup>-</sup> was set to zero in equation (2) that was rearranged to:

$$Q_{TE} = \frac{Q_{OUT} Cl_{OUT} - Q_{PR} Cl_{PR} + \Delta Cl_L}{Cl_{TE}^*} \quad (4)$$

The  $\Delta M_L$  (mol.yr<sup>-1</sup>) in equation (2), as well as  $\Delta Cl_L$  in equation (4), is the change in storage of a constituent in the lake and was calculated from equation (5):

$$\Delta M_L = V(C_2 - C_1) \quad (5)$$

where  $V$  (m<sup>3</sup>) is lake volume and  $C_1$  and  $C_2$  (both in mol.m<sup>-3</sup>) are volume weighted mean concentrations of water constituents. The  $C_1$  and  $C_2$  values were obtained from data on samples taken from five depths between the surface and bottom in the deepest part of the lake at the beginning and the end of each hydrological year, respectively, by linking volumes of the 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 ( $\Delta M_C$ ; mol.yr<sup>-1</sup>) was not regularly measured. The equation (1) was thus rearranged to:

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

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

The annual average compositions of precipitation and throughfall were calculated as volume weighted means (VWM) for  $C_{PR}$  and throughfall at the low ( $C_{TF-L}$ ) and high ( $C_{TF-H}$ ) elevation plots. When the SRP and F<sup>-</sup> concentrations were below their detection limits of 0.05 and 0.1  $\mu\text{mol.l}^{-1}$  (~2% and ~25% of all samples; KOPÁČEK et al. 2011), respectively, a half of these values were used in subsequent data evaluation.

Annual average composition of deposition to catchment soils ( $C_{DEP}$ ) by both precipitation and throughfall (i.e., via atmospheric deposition and canopy leaching) were calculated from the respective precipitation and throughfall amounts and VWM compositions:

$$C_{DEP} = \frac{0.2 C_{PR} H_{PR} + 0.8 (0.5 C_{TF-L} H_{TF-L} + 0.5 C_{TF-H} H_{TF-H})}{0.2 H_{PR} + 0.8 (0.5 H_{TF-L} + 0.5 H_{TF-H})} \quad (6)$$

where coefficients 0.2, 0.8, and 0.5 are the same as in equation (3).

Annual average compositions of surface tributaries (PL-I and PL-II during the whole study and PL-III from 2002) were calculated for individual hydrological years as discharge and period-weighted mean (DPWM) concentrations (LIKENS & BORMANN 1995):

$$C = \frac{\sum C_i Q_i \tau_i}{\sum Q_i \tau_i} \quad (7)$$

where  $Q_i$  is water discharge and  $C_i$  is concentration of a water constituent during the sampling  $i$  (the annual number of samplings was 17–19), and  $\tau_i$  (days) is the 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.

For subsurface tributaries, with no data on discharge (PL-IV during the whole study and PL-III prior to 2002), annual average concentrations were calculated as period-weighted means.

Annual average compositions of terrestrial export to the lake from the catchment via tributaries ( $C_{TE}$ ) was calculated as follows: Because discharge of subsurface tributaries was unknown, annual average values of  $C_{TE}$  (representing a mixture of surface and subsurface tributaries) were calculated from annual average composition of subsurface ( $C_{SUBSUR}$ ) and surface ( $C_{SUR}$ ) tributaries and their relative proportions ( $r$  and  $1 - r$ , respectively) to the total terrestrial water export. The  $r$  value was estimated from the balance for  $Ca^{2+}$  ions, because  $Ca^{2+}$  concentrations were about twofold higher in subsurface than in surface PL tributaries and could be used as a tracer (KOPÁČEK et al. 2001a, 2017):

$$r Q_{TE} C_{SUBSUR} + (1 - r) Q_{TE} C_{SUR} + Q_{PR} C_{PR} + \pi_L = Q_{OUT} C_{OUT} + \Delta M_L \quad (8)$$

The  $\pi_L$  value ( $-503 \text{ mol.yr}^{-1}$ ) was estimated from a net Ca accumulation in the lake sediments. This value was based on the average mass accumulation rate in the Plešné sediments ( $85 \text{ g.m}^{-2}.\text{yr}^{-1}$ ), the average concentration of Ca in the uppermost sediment layer ( $78 \text{ } \mu\text{mol.g}^{-1}$  dry weight), and lake area. The average mass accumulation rate was calculated from the average accumulation rate of sediment ( $5.3 \text{ mm.yr}^{-1}$ ) and the water content of the uppermost sediment layer (98.4%) in the Plešné sediments (SCHMIDT et al. 1993). For more details see (KOPÁČEK et al. 2001a). The  $\Delta M_L$  values were calculated from equation (5). The computed  $r$  values were 0.3–0.4 during the study, suggesting that ~30–40% of the  $Q_{TE}$  entered the lake via the subsurface tributaries. Then, the  $C_{TE}$  values of all water constituents (except for Cl<sup>-</sup>) were computed as:

$$C_{TE} = \frac{r Q_{TE} C_{SUBSUR} + (1 - r) Q_{TE} C_{SUR}}{Q_{TE}} \quad (9)$$

The annual average  $C_{SUBSUR}$  values were arithmetical means of annual concentrations of water constituents in the PL-III and PL-IV tributaries. The annual average  $C_{SUR}$  values were calculated using compositions and discharges of PL-I and PL-II as:

$$C_{SUR} = \frac{\sum C_{y,i} Q_{y,i} \tau_i}{\sum Q_{y,i} \tau_i} \quad (10)$$

where  $y$  and  $i$  denote lake tributary and sampling period, respectively,  $C_{y,i}$  is concentration of a water constituent, and  $Q_{y,i}$  is water discharge in a tributary  $y$  during sampling  $i$ .

Annual average compositions of the total water input into the lake ( $C_{IN}$ ) was calculated from the total input of water constituents into the lake, i.e. the sum of their fluxes by tributaries ( $Q_{TE}C_{TE}$ ) and atmospheric deposition ( $Q_{PR}C_{PR}$ ) according to equation (11):

$$C_{IN} = \frac{Q_{TE}C_{TE} + Q_{PR}C_{PR}}{Q_{TE} + Q_{PR}} \quad (11)$$

Annual average composition of lake output ( $C_{OUT}$ ) was calculated from equation (7) by linking continuously monitored discharge data of the outlet (average discharges for  $\tau_i$  periods) with the corresponding weekly to biweekly concentration data.

### 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 estimated from budgets for ions, using the equation of electroneutrality:

$$[H^+] = [SO_4^{2-}] + [NO_3^-] + [Cl^-] + [F^-] + [A^-] + [HCO_3^-] - [NH_4^+] - [Na^+] - [K^+] - [Ca^{2+}] - [Mg^{2+}] - [Al_i^{n+}] - [Fe_i^{m+}] \quad (12)$$

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.

### In-lake nitrate and sulphate removal

The lake ability to remove  $NO_3^-$  and  $SO_4^{2-}$  was assessed using the following two coefficients (e.g. for  $NO_3^-$ ): (i)  $R_{NO_3}$  is the  $NO_3^-$ -removal coefficient (the ratio of net in-lake  $NO_3^-$  removal to the total  $NO_3^-$  input, and (ii)  $S_{NO_3}$  is the mass transfer coefficient for  $NO_3^-$  (also called “settling velocity”,  $m.yr^{-1}$ ). The relationship between  $S_{NO_3}$  and  $R_{NO_3}$  values is given by equation (13) (KELLY et al. 1987):

$$S_{NO_3} = R_{NO_3} \frac{q_s}{1 - R_{NO_3}} \quad (13)$$

where  $q_s$  ( $m.yr^{-1}$ ) is the areal water load per unit area of the lake. The  $q_s$  value was calculated as  $q_s = Q_{TE}/A_L$  (KASTE & DILLON 2003).

## RESULTS

### Concentrations

The average chemical composition of Plešné tributaries differed from atmospheric deposition to the catchment soils in higher concentrations of  $H^+$ ,  $SO_4^{2-}$ ,  $NO_3^-$ , metals, DOC, TON, TP and Si, and in one order-of-magnitude lower  $NH_4^+$  concentrations (Table 2). The compo-

sition of surface inlets differed from the subsurface inlets predominantly in lower concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , and higher concentrations of TP, SRP, DOC, DON,  $\text{Al}_o$  and  $\text{Fe}_o$  (Table 2). The TP pool was dominated by SRP (on average ~80%).

Annual average chemical composition of tributaries exhibited pronounced changes during the study period (Appendix 4). Concentrations of  $\text{NO}_3^-$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{H}^+$ , and  $\text{Al}_i$  started to increase immediately after the tree dieback (after 2004), reached their maxima in 2009–2011, and then decreased almost to their pre-disturbance levels by 2017. In contrast, concentrations of DOC and P forms started to increase more slowly, and their increase continued until the end of this study (Appendix 4). Concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ , and Si were not affected by the tree dieback.

Compared to the chemistry of surface and subsurface tributaries and total water input to the lake (including precipitation), composition of the lake output had lower concentrations of  $\text{H}^+$ ,  $\text{NO}_3^-$ , Al forms, DOC, DON, TP, SRP and Si, but higher concentrations of  $\text{NH}_4^+$ ,  $\text{HCO}_3^-$ , POC, PON and PP (Table 2). Changes in in-lake concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ , base cations ( $\text{BCs} = \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$ ), and Fe forms were almost negligible.

The thermal stratification of Plešné 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 100, 170, and 135 days, respectively, during 2000–2017. Secchi disc transparency varied between 0.8–1.5 m during the study and the thermocline depth between 3–5 m. The autumn and spring overturns usually occurred in December and April, respectively. Dissolved  $\text{O}_2$  was depleted above the lake bottom within a month after the development of thermal stratification and the anoxic layer increased up to 12 m depth before the overturns (Fig. 2B). At low redox potentials above the lake bottom, dissimilatory reduction processes occurred, decreasing  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations and increasing concentrations of  $\text{NH}_4^+$  and Fe forms, while concentrations of conservative  $\text{Cl}^-$  remained stable along the whole water column (Fig. 2). Concentrations of  $\text{NO}_3^-$  also rapidly decreased in the epilimnion due to assimilation by algae, and the  $\text{NO}_3^-$  maxima (persisting from spring overturn) usually were in the middle of the water column during its summer thermal stratification (Fig. 2E).

The changes in ionic composition were accompanied by changes in water ANC and pH. The carbonate buffering system was depleted in the most of water column after spring overturns until 2013, then it has re-established and ANC concentrations have become positive throughout the year, with elevated values in the hypolimnion (Fig. 2D). The hypolimnetic pH increased toward ~6 during both winter and summer stratification (Fig. 2C). During winter stratification, the lowest pH values were below the ice, because water from surface tributaries (with temperature close to freezing point) had lower density than the rest of water column and flew through the surface layer. During summer stratification, water from tributaries was colder and denser than that in the epilimnion and mixed with the deeper water layers. In addition, pH increased in the epilimnion due to assimilative processes ( $\text{NO}_3^-$  removal, see later) in summer. Consequently, the lowest pH values were in the middle of the water column in summer (Fig. 2C). With the pH increase towards neutrality, ionic Al species hydrolyzed and formed  $\text{Al}_p$  (colloidal hydroxides). Hence,  $\text{Al}_p$  concentrations were higher in summer than in winter and in the hypolimnion than in the epilimnion (Fig. 2J). In contrast, concentrations of  $\text{Al}_i$  were higher in winter than in summer (Fig. 2I). The high  $\text{Al}_p$  concentrations were accompanied with elevated TP concentrations (maximum of ~3.3  $\mu\text{mol.l}^{-1}$ ), while concentrations of dissolved P forms (DP and SRP) were an order of magnitude lower above the bottom (not shown).

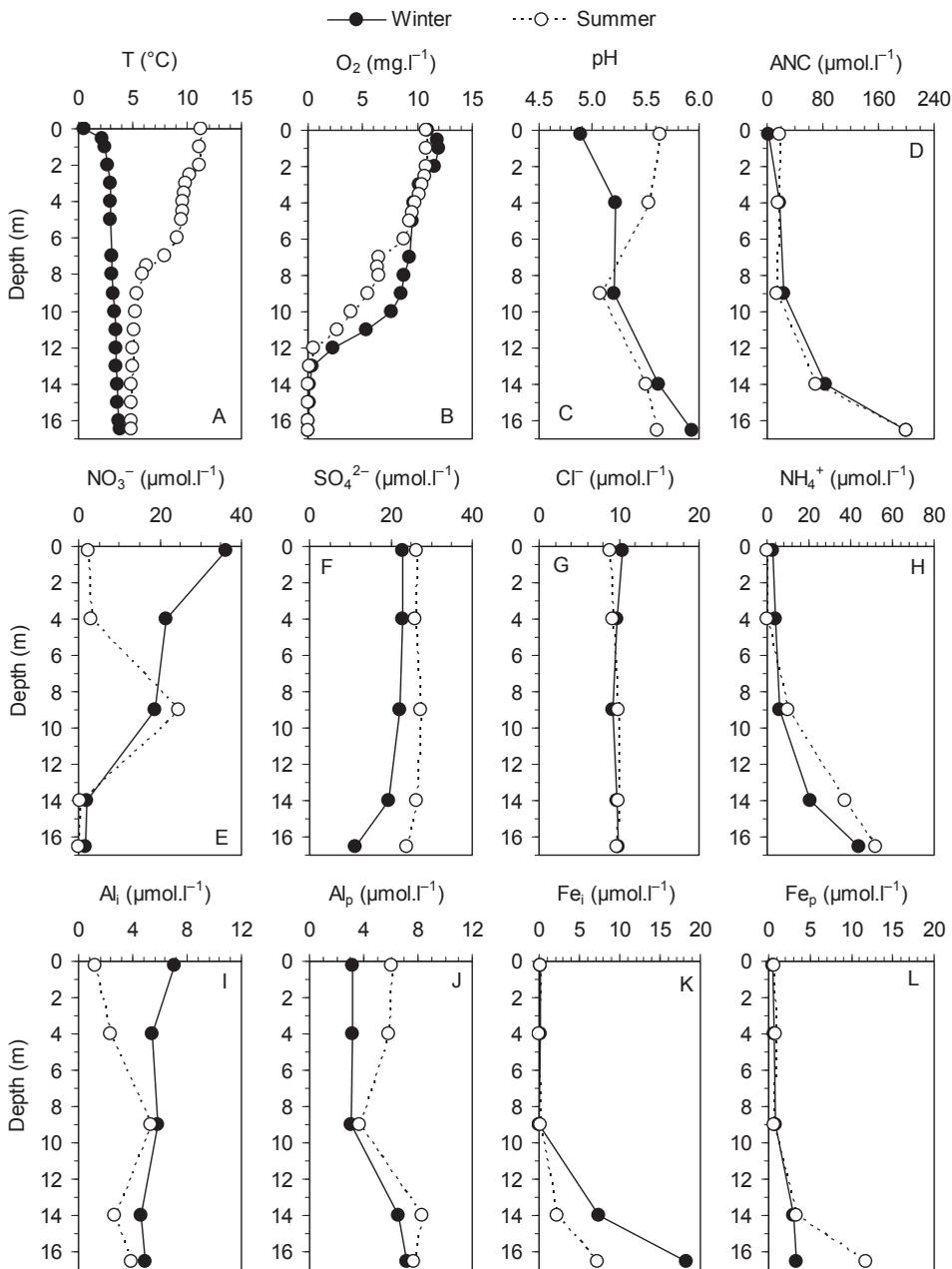
**Table 2.** Average ( $\pm$  standard deviation) values of discharge ( $Q$ , for annual data see Appendix 1) and mean composition of precipitation ( $C_{PR}$ , for annual data see Appendix 2), atmospheric deposition to the catchment soils ( $C_{DEP}$ , precipitation in treeless area and throughfall in forest, for annual data see Appendix 3), tributaries (PL-I to PL-IV), terrestrial export via tributaries ( $C_{TE}$ , for annual data see Appendix 4), total input to Plešné 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 1999 to October 2017. Units:  $\mu\text{mol.l}^{-1}$ , except for discharge ( $Q$ ;  $\text{l.s}^{-1}$ ) and pH. For location of tributaries see Fig. 1.

	$C_{PR}$	$C_{DEP}$	PL-I	PL-II	PL-III	PL-IV	$C_{TE}$	$C_{IN}$	$C_{OUT}$
$Q$	* $3.3\pm 0.6$	** $27\pm 5$	$1.7\pm 0.9$	$1.3\pm 0.7$	$3.4\pm 1.8$	ND	$19.4\pm 4$	$22.6\pm 5$	$21.9\pm 5$
pH	$5.07\pm 0.17$	$4.95\pm 0.23$	$4.21\pm 0.09$	$4.27\pm 0.09$	$4.49\pm 0.09$	$4.74\pm 0.04$	$4.33\pm 0.08$	$4.38\pm 0.08$	$4.88\pm 0.21$
$\text{H}^+$	$9\pm 3$	$13\pm 7$	$63\pm 14$	$55\pm 11$	$33\pm 6$	$18\pm 2$	$48\pm 9$	$42\pm 8$	$15\pm 6$
$\text{Ca}^{2+}$	$4.0\pm 0.8$	$8.2\pm 3.3$	$20\pm 4$	$21\pm 5$	$27\pm 4$	$41\pm 6$	$25\pm 4$	$22\pm 4$	$22\pm 4$
$\text{Mg}^{2+}$	$1.2\pm 0.3$	$3.2\pm 1.3$	$7.4\pm 1.8$	$7.6\pm 2.1$	$10\pm 2$	$15\pm 3$	$9\pm 2$	$8\pm 2$	$9\pm 2$
$\text{Na}^+$	$6.7\pm 1.3$	$10\pm 3$	$42\pm 6$	$43\pm 7$	$43\pm 5$	$52\pm 3$	$45\pm 5$	$39\pm 4$	$38\pm 2$
$\text{K}^+$	$2.3\pm 0.9$	$14\pm 10$	$22\pm 11$	$20\pm 11$	$16\pm 6$	$16\pm 4$	$19\pm 8$	$17\pm 7$	$16\pm 7$
$\text{NH}_4^+$	$27\pm 5$	$31\pm 6$	$0.8\pm 0.6$	$0.9\pm 0.8$	$0.8\pm 0.6$	$0.6\pm 0.6$	$0.6\pm 0.6$	$4\pm 1$	$5\pm 1$
$\text{NO}_3^-$	$23\pm 2$	$34\pm 10$	$95\pm 51$	$106\pm 54$	$117\pm 40$	$143\pm 51$	$110\pm 43$	$98\pm 38$	$58\pm 31$
$\text{SO}_4^{2-}$	$8.1\pm 1.8$	$12\pm 5$	$28\pm 7$	$28\pm 6$	$33\pm 9$	$44\pm 11$	$32\pm 7$	$28\pm 6$	$29\pm 7$
$\text{Cl}^-$	$6.3\pm 1.3$	$11\pm 4$	$13\pm 3$	$13\pm 3$	$13\pm 2$	$14\pm 2$	$13\pm 3$	$12\pm 2$	$13\pm 2$
$\text{F}^-$	$0.6\pm 0.5$	$0.8\pm 0.4$	$3.5\pm 1.0$	$3.4\pm 0.9$	$5.0\pm 1.3$	$7.0\pm 1.3$	$4.4\pm 1.0$	$3.8\pm 0.9$	$4.1\pm 0.8$
$\text{HCO}_3^-$	$4.5\pm 4.0$	$5.3\pm 4.3$	0	0	0	0	0	$0.6\pm 0.6$	$3.3\pm 5.2$
DOC	$93\pm 18$	$367\pm 190$	$1165\pm 280$	$841\pm 177$	$432\pm 102$	$153\pm 22$	$766\pm 159$	$669\pm 142$	$408\pm 104$
POC	$33\pm 30$	$109\pm 211$	$11\pm 23$	$24\pm 20$	$20\pm 25$	$24\pm 23$	$21\pm 16$	$21\pm 16$	$197\pm 73$
DON	$12\pm 4$	$18\pm 6$	$35\pm 8$	$28\pm 8$	$20\pm 7$	$10\pm 2$	$27\pm 6$	$25\pm 68$	$20\pm 5$
PON	$6\pm 2$	$8\pm 6$	$2\pm 2$	$2\pm 2$	$1\pm 2$	$1\pm 1$	$1\pm 1$	$2\pm 1$	$18\pm 6$
TP	$0.44\pm 0.16$	$0.66\pm 0.22$	$1.39\pm 0.42$	$1.18\pm 0.26$	$0.63\pm 0.15$	$0.18\pm 0.04$	$0.98\pm 0.23$	$0.91\pm 0.20$	$0.46\pm 0.10$
PP	$0.24\pm 0.09$	$0.42\pm 0.18$	$0.07\pm 0.05$	$0.04\pm 0.03$	$0.05\pm 0.06$	$0.03\pm 0.04$	$0.06\pm 0.02$	$0.09\pm 0.02$	$0.37\pm 0.09$
SRP	$0.15\pm 0.11$	$0.13\pm 0.07$	$1.10\pm 0.37$	$0.99\pm 0.23$	$0.51\pm 0.14$	$0.11\pm 0.02$	$0.78\pm 0.21$	$0.70\pm 0.18$	$0.04\pm 0.02$
Si	$0.5\pm 0.3$	ND	$138\pm 24$	$131\pm 25$	$129\pm 17$	$142\pm 9$	$134\pm 18$	$115\pm 15$	$101\pm 9$
$\text{Al}_T$	$0.4\pm 0.3$	ND	$31\pm 4$	$30\pm 5$	$29\pm 5$	$30\pm 7$	$31\pm 4$	$26\pm 4$	$20\pm 3$
$\text{Al}_I$	ND	ND	$17\pm 5$	$18\pm 6$	$22\pm 6$	$26\pm 7$	$20\pm 5$	$17\pm 5$	$10\pm 3$
$\text{Al}_O$	ND	ND	$14\pm 3$	$11\pm 2$	$6\pm 1$	$2\pm 1$	$10\pm 1$	$8\pm 1$	$5\pm 2$
$\text{Fe}_T$	ND	ND	$2.7\pm 0.6$	$1.9\pm 0.3$	$0.9\pm 0.1$	$0.2\pm 0.1$	$1.7\pm 0.3$	$1.5\pm 0.2$	$1.6\pm 0.3$
$\text{Fe}_I$	ND	ND	$0.6\pm 0.2$	$0.5\pm 0.2$	$0.3\pm 0.1$	$0.0\pm 0.0$	$0.4\pm 0.2$	$0.4\pm 0.1$	$0.3\pm 0.1$
$\text{Fe}_O$	ND	ND	$1.9\pm 0.6$	$1.3\pm 0.3$	$0.6\pm 0.1$	$0.2\pm 0.1$	$1.2\pm 0.3$	$1.0\pm 0.2$	$0.7\pm 0.2$

Explanations: \* Precipitation amount deposited to the lake surface, \*\* water amount deposited to the lake catchment with precipitation and throughfall.

## Water fluxes

The average ( $\pm$  standard deviation) precipitation was  $1346\pm 241$   $\text{mm.yr}^{-1}$  and varied between 1020 and 1953  $\text{mm.yr}^{-1}$  in 2015 and 2002, respectively. The deposition to the catchment soils (precipitation in treeless areas plus throughfall in forest) was  $1338\pm 223$   $\text{mm.yr}^{-1}$  and ranged



**Fig. 2.** Depth diagrams of temperature (T), dissolved oxygen (O<sub>2</sub>), pH, acid neutralizing capacity (ANC), NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, ionic and particulate aluminium (Al<sub>I</sub>, Al<sub>P</sub>) and iron (Fe<sub>I</sub>, Fe<sub>P</sub>) during winter (17 March 2017) and summer (2 October 2017) thermal stratification of Plesné Lake.

between 1019 and 1969 mm.yr<sup>-1</sup> (Appendix 1). The average water outflow from the lake was 1087±232 mm.yr<sup>-1</sup> (i.e., specific outflow of 34±7 l.km<sup>-2</sup>.s<sup>-1</sup>). The resulting average evapotranspiration from the catchment–lake system, based on precipitation and throughfall amounts, was 19±8 % during 2000–2017. This value was, however, lowered by interception in the period of healthy forest. Consequently, the actual average evapotranspiration from the Plešné catchment–lake system was >19% due to the direct water evaporation from canopies during the study period.

The tree dieback only had small effect (increase) on water outflow from Plešné catchment–lake system relatively to the atmospheric water input. The ratio between water outflow and water input to the catchment soils increased from 0.72 to 0.84 (averages for 2000–2004 and 2005–2017 periods, respectively, Appendix 1). In contrast, evapotranspiration from the catchment decreased due to ceased transpiration of dead trees, while soil wetness increased (for more details see KOPÁČEK et al. 2017). The increased runoff was similar to other catchments in the Bohemian and Bavarian Forest where disturbance exceeded 30% of forest areas (BEUDERT et al. 2018).

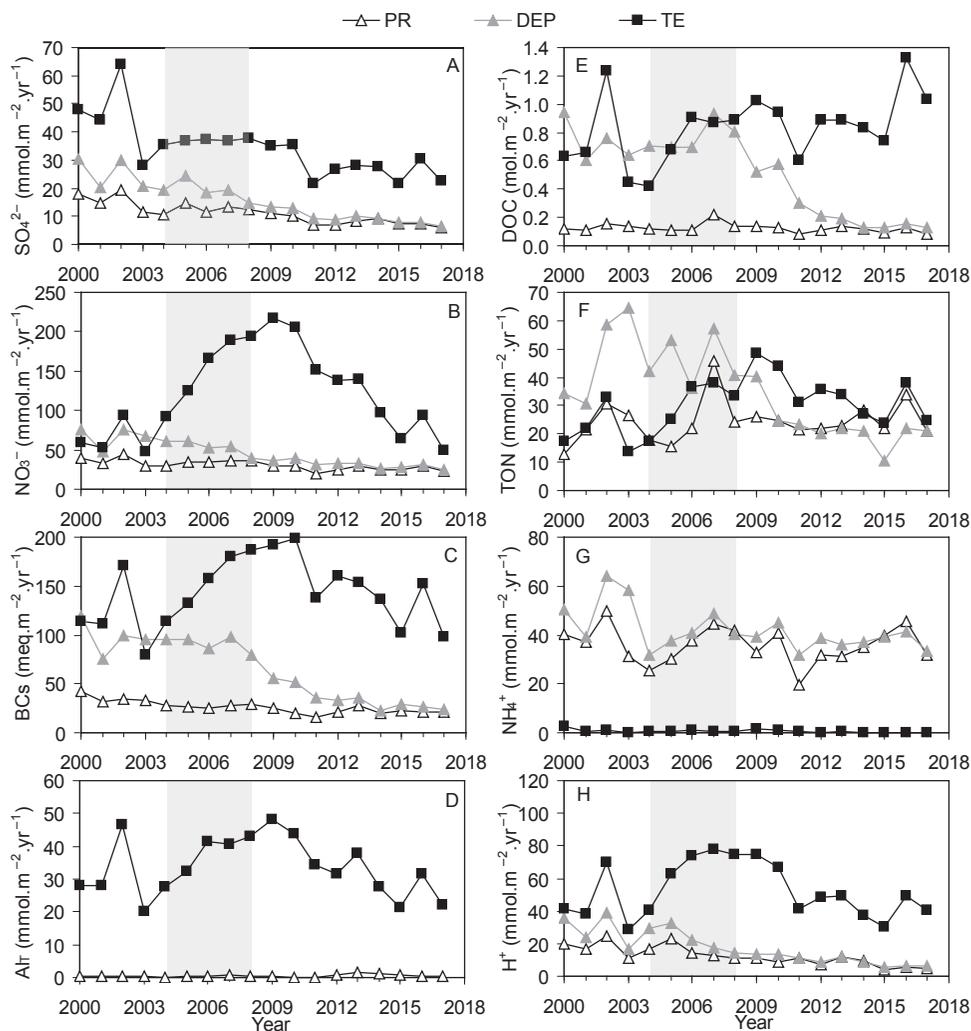
Water residence time in Plešné Lake varied between 211 and 481 days, and averaged 338±70 days during the study period.

### Element fluxes in catchment

Terrestrial exports of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, BCs (except for Na<sup>+</sup>), and Al<sub>T</sub> were higher than their inputs to the catchment by precipitation and throughfall throughout the study period, and further increased after the tree dieback (Fig. 3). Terrestrial exports of DOC and TON were lower than their deposition to the catchment soils prior to 2009, but then higher (Fig. 3E,F). Terrestrial exports of TP and SRP (not shown) behaved similarly to DOC and increased until the end of this study. The Plešné catchment was a net P source, averaging 0.19±0.51 mmol.m<sup>-2</sup>.yr<sup>-1</sup> during this study (Table 3).

On a long-term basis, the Plešné catchment was a net sink for atmospherically deposited NH<sub>4</sub><sup>+</sup> (Table 3) both prior to and after tree dieback (Fig. 3). The average Cl<sup>-</sup> deposition and leaching were almost equal on a long-term (Table 3), but differed on the annual basis. The Plešné catchment usually accumulated Cl<sup>-</sup> prior to the tree dieback, but became a net Cl<sup>-</sup> source from 2008 to 2017, when both fluxes equalled (Fig. 4A). Terrestrial export of Na<sup>+</sup> was stable (except for elevated flux in 2002), permanently higher than its atmospheric input, and was not affected by the tree dieback (Fig. 4B). The elevated Na<sup>+</sup> export in 2002 resulted (as in the case of other water constituents; Figs. 3 and 4B) from extremely high discharge (Appendix 1), associated with a summer heavy rain event. Patterns in terrestrial export of Si were similar to Na<sup>+</sup> and their concentrations in tributaries were closely correlated (KOPÁČEK et al. 2017).

Terrestrial transformations of ionic fluxes resulted in a net terrestrial H<sup>+</sup> production of 35±18 meq.m<sup>-2</sup>.yr<sup>-1</sup> on a catchment-area basis during 2000–2017 (Table 3), with maximum production of 58 meq.m<sup>-2</sup>.yr<sup>-1</sup> from 2006–2010. The average pH of tributaries was thus permanently lower than pH of precipitation and deposition to the catchment soils (Table 2). The average H<sup>+</sup> production, based on pH values in precipitation, throughfall and tributaries, was in good concordance with H<sup>+</sup> production calculated from equation (12) as the sum of individual H<sup>+</sup> sources (terrestrial production of anions and removal of cations) and sinks (terrestrial production of cations) that averaged 36.5 meq.m<sup>-2</sup>.yr<sup>-1</sup> during 2000–2017. Both estimates thus differed by <4% on average. The net terrestrial H<sup>+</sup> production (the difference between annual terrestrial export and deposition to the catchment soils; see Fig. 3H) was highest after the tree dieback (56 meq.m<sup>-2</sup>.yr<sup>-1</sup> on average during 2006–2010). The most important H<sup>+</sup> sources were net release of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and A<sup>-</sup> (76, 37, and 15 meq.m<sup>-2</sup>.yr<sup>-1</sup>,



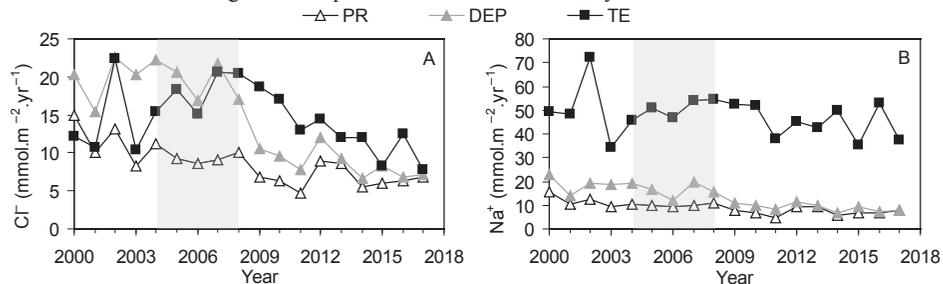
**Fig. 3.** Time series of annual fluxes (based on a catchment area basis) of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , base cations (BCs = sum of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ), total aluminium ( $\text{Al}_p$ ), dissolved organic carbon (DOC), total organic nitrogen (TON),  $\text{NH}_4^+$  and  $\text{H}^+$  in precipitation (PR), deposition to the catchment soils (DEP), and terrestrial export via tributaries (TE) in the Plešné catchment in the 2000–2017 hydrological years. Grey area indicates the period of bark beetle outbreak in the Plešné catchment.

respectively) and retention of  $\text{NH}_4^+$  in soils (41 meq.m<sup>-2</sup>.yr<sup>-1</sup>), while terrestrial production of  $\text{Al}_i$  and BCs represented the most important  $\text{H}^+$  sinks (53 and 78 meq.m<sup>-2</sup>.yr<sup>-1</sup>, respectively). The contribution of  $\text{NO}_3^-$ , BCs, and  $\text{Al}$  to modifying terrestrial  $\text{H}^+$  export reached maximum values during 2005–2011 (Fig. 3), while that of  $\text{A}^-$  in 2016–2017 (see high terrestrial export of DOC in Appendix 4).

**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 Plešné catchment in the 2000–2017 hydrological years.

	<i>PR</i>	<i>DEP</i>	<i>TE</i>	$\pi_c^*$	$H^+$ source <sup>†</sup>
	mmol.m <sup>-2</sup> .yr <sup>-1</sup>				meq.m <sup>-2</sup> .yr <sup>-1</sup>
H <sup>+</sup>	12±6	18±11	53±17	35±18	
Ca <sup>2+</sup>	5.4±1.2	11±5	27±7	16±9	-32±19
Mg <sup>2+</sup>	1.6±0.5	4.4±2.0	10.1±3	5.7±3.4	-11±7
Na <sup>+</sup>	9.0±2.6	13±5	48±9	34±9	-34±9
K <sup>+</sup>	3.2±1.4	20±14	21±10	1.1±20	-1±20
NH <sub>4</sub> <sup>+</sup>	36±8	42±9	0.7±0.6	-41±9	41±9
NO <sub>3</sub> <sup>-</sup>	31±6	45±17	121±57	76±63	76±63
SO <sub>4</sub> <sup>2-</sup>	11±4	16±8	34±11	19±6	37±12
Cl <sup>-</sup>	9±3	14±6	15±4	0.3±5.3	0±5
F <sup>-</sup>	0.8±0.6	1.0±0.6	5±2	5±1	5±1
DOC (A <sup>-</sup> )	124±30	507±291	834±241	326±426	(15±24)
HCO <sub>3</sub> <sup>-</sup>	6±4	6±4	0±0	-6±4	-6±4
TON	24±7	35±16	30±9	-3±20	
TP	0.6±0.2	0.9±0.4	1.1±0.3	0.19±0.51	
Si	0.7±0.3	ND	144±23	143±24	
Al <sub>T</sub>	0.5±0.4	ND	34±9	33±9	
Al <sub>i</sub> (Al <sub>i</sub> <sup>n+</sup> )	ND	ND	22±8	22±8	(-53±20)
Fe <sub>T</sub>	ND	ND	1.8±0.5	1.4±0.5	
Fe <sub>i</sub> (Fe <sub>i</sub> <sup>m+</sup> )	ND	ND	0.5±0.2	0.5±0.2	(-0.5±0.2)

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  $\pi_c^*$  values indicate net production, while negative values indicate net removal; for their annual values see Appendix 7. <sup>†</sup> 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 36.5 mmol.m<sup>-2</sup>.yr<sup>-1</sup>.



**Fig. 4.** Time series of annual fluxes (based on a catchment area basis) of Cl<sup>-</sup> and Na<sup>+</sup> in precipitation (*PR*), deposition to the catchment soils (*DEP*), and terrestrial export via tributaries (*TE*) in the Plešné catchment in the 2000–2017 hydrological years. Grey area indicates the period of bark beetle outbreak in the Plešné catchment.

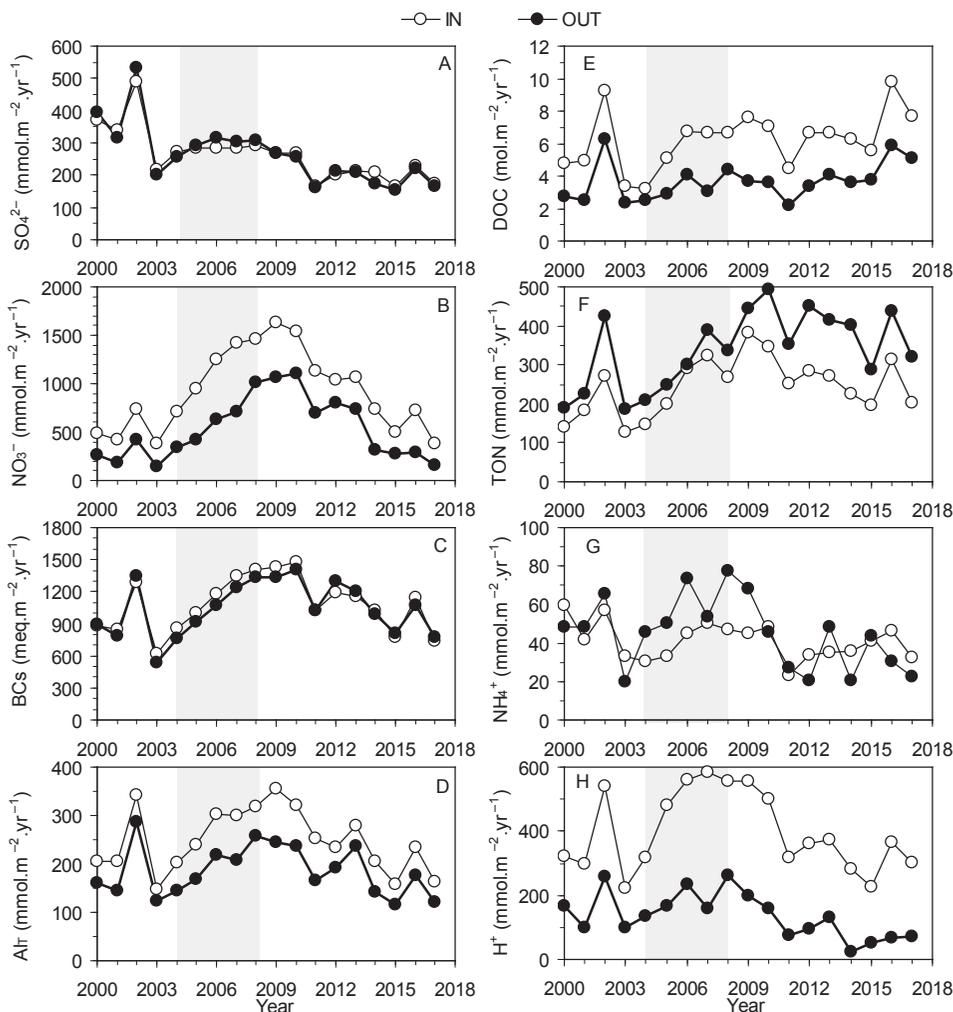
## Element fluxes in lake

The internal processes caused reductions in  $\text{NO}_3^-$ ,  $\text{A}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Al}_i$  fluxes (Table 4, Fig. 5) and increased pH in the lake outlet compared to their values in the lake input by tributaries and precipitation. The average input flux of  $\text{H}^+$  decreased by ~65% from 403 to 136  $\text{meq.m}^{-2}.\text{yr}^{-1}$  on a lake area basis (Table 4). The net in-lake  $\text{H}^+$  removal (calculated on the basis of pH values in precipitation, tributaries and lake outlet) averaged 267  $\text{meq.m}^{-2}.\text{yr}^{-1}$  during the

**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 2, and terrestrial export), output from lake (*OUT*), net in-lake production of water constituents ( $\pi_L$ ), and the associated  $\text{H}^+$  production/removal in Plešné Lake in the 2000–2017 hydrological years.

	<i>IN</i>	<i>OUT</i>	$\pi_L$	$\text{H}^+$ source <sup>†</sup>
	$\text{mmol.m}^{-2}.\text{yr}^{-1}$			$\text{meq.m}^{-2}.\text{yr}^{-1}$
$\text{H}^+$	398±125	136±70	-266±71	
$\text{Ca}^{2+}$	205±53	201±51	-6±21	13±41
$\text{Mg}^{2+}$	76±22	78±21	3±10	-6±20
$\text{Na}^+$	361±66	343±73	-21±36	21±35
$\text{K}^+$	157±75	145±64	-10±19	10±19
$\text{NH}_4^+$	41±10	45±19	3±32	-3±32
$\text{NO}_3^-$	920±419	531±320	-395±129	-395±123
$\text{SO}_4^{2-}$	263±81	364±94	-12±17	-25±34
$\text{Cl}^-$	115±33	117±36	ND	
$\text{F}^-$	36±11	37±12	1±10	1±9
$\text{HCO}_3^-$	5±4	27±42	33±52	33±52
DOC (A <sup>-</sup> )	6251±1778	3673±1170	-2400±673	(-151±65)
TON	246±73	339±98	93±70	
TP	8.5±2.4	4.1±1.2	-4.3±1.3	
Si	1056±172	907±171	-136±85	
$\text{Al}_T$	248±65	186±52	-62±33	
$\text{Al}_i$ ( $\text{Al}_i^{\text{net}}$ )	163±57	91±43	-74±33	(243±81)
$\text{Al}_o$	78±19	47±19	-29±14	
$\text{Al}_p$	7±3	48±16	41±22	
$\text{Fe}_T$	14±4	14±4	1±4	
$\text{Fe}_i$ ( $\text{Fe}_i^{\text{net}}$ )	3±2	3±1	-1±2	(1±2)
$\text{Fe}_o$	10±3	6±2	-3±2	
$\text{Fe}_p$	1±0.4	5±2	5±3	

Explanations: Values are given on a lake-area basis; ND – not determined. Values of  $\pi_L$  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. <sup>†</sup> Release of cations and removal of anions are proton-consuming processes, while removal of cations and release of anions are proton-producing reactions. One  $\text{meq}$  =  $\text{mmol}$  of charge. Sum of  $\text{H}^+$  sources and sinks gives a net retention of 258  $\text{mmol.m}^{-2}.\text{yr}^{-1}$ .



**Fig. 5.** Time series of annual fluxes (based on a lake area basis) of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , base cations (BCs = sum of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ), total aluminium ( $\text{Al}_r$ ), dissolved organic carbon (DOC), total organic nitrogen (TON),  $\text{NH}_4^+$ , and  $\text{H}^+$  in total input (IN, tributaries and precipitation) to and outlet (OUT) from Plešné Lake in the 2000–2017 hydrological years. Grey area indicates the period of bark beetle outbreak in the Plešné catchment.

whole study, and reached maximum values of  $359 \text{ meq.m}^{-2}.\text{yr}^{-1}$  on average during 2006–2010. This value is not a simple difference between the input and output fluxes because it also includes a net change in  $\text{H}^+$  storage in the lake (equation 2) that decreased by  $4 \text{ meq.m}^{-2}.\text{yr}^{-1}$  during the study (lake water pH during autumn overturns increased from 5.0 in 1999 to 5.4 in 2017). The pH-based estimate was similar to the  $\text{H}^+$  removal calculated from equation (12) that averaged  $257 \text{ meq.m}^{-2}.\text{yr}^{-1}$ . Thus, both estimates differed by  $\sim 4\%$  on average.

The most important internal  $\text{H}^+$  sinks were  $\text{NO}_3^-$ ,  $\text{A}^-$  and  $\text{SO}_4^{2-}$  removals (395, 151, and 25

meq.m<sup>-2</sup>.yr<sup>-1</sup>, respectively), while Al<sub>i</sub> transformations were the most important in-lake H<sup>+</sup> sources of 243 meq.m<sup>-2</sup>.yr<sup>-1</sup> on average (Table 4). In contrast to H<sup>+</sup>, the lake was negligible sink for BCs (Fig. 5C) and was a net source of NH<sub>4</sub><sup>+</sup> in most years (especially in 2004–2009; Fig. 5G), with the long-term average production of 3 mmol.m<sup>-2</sup>.yr<sup>-1</sup>.

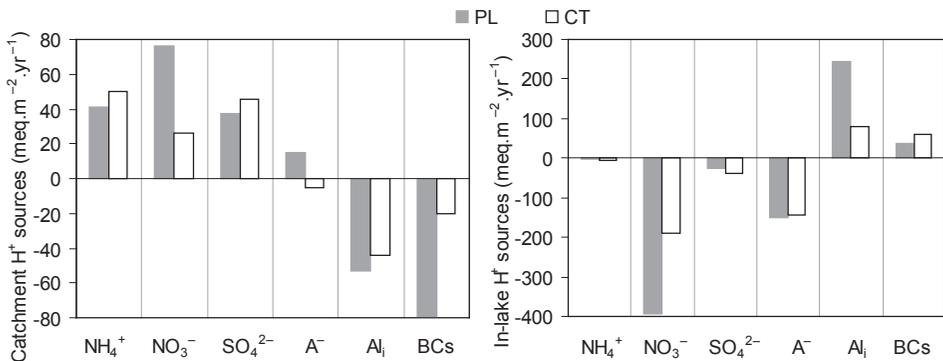
The lake was a net sink for all nutrients, removing on average 51% of TP, 25% of total N, 38% of DOC, and 13% of Si inputs (Table 4). Terrestrial export via tributaries was the major SRP source for the lake (6.3 meq.m<sup>-2</sup>.yr<sup>-1</sup>) and represented ~74% of TP input to the lake. Organic dissolved P and PP from soils formed together 20% of the TP input, while atmospheric inputs of all P forms only represented 6% of the total TP input to Plešné Lake during the study.

## DISCUSSION

### Major processes affecting mass budget of protons in Plešné catchment

Terrestrial transformations of inorganic N (IN = NO<sub>3</sub>-N + NH<sub>4</sub>-N) were the most important H<sup>+</sup> producing process in the Plešné catchment, with the 2000–2017 average of 117 meq.m<sup>-2</sup>.yr<sup>-1</sup> (Table 3). This value was 2.5 times higher than the maximum observed at 17 European forest sites (–5 to 46 meq.m<sup>-2</sup>.yr<sup>-1</sup>) by FORSIUS et al. (2005), and even higher than in strongly N-saturated Čertovo catchment in the same mountain area (Fig. 6). The IN-related production of H<sup>+</sup> in the Plešné catchment was significantly affected by tree dieback, with averages of 51 and 142 meq.m<sup>-2</sup>.yr<sup>-1</sup> in 2000–2004 and 2005–2017, respectively, and the maximum of 219 meq.m<sup>-2</sup>.yr<sup>-1</sup> in 2009. The ability of the N-saturated Plešné catchment to retain the deposited IN was thus low already prior to the tree dieback, averaging 38% during 2000–2004. After the tree dieback, however, the catchment became a significant net source of NO<sub>3</sub><sup>-</sup> and its terrestrial export exceeded IN deposition to the catchment soils by 85% on average during 2005–2017, with the maximum of 189% in 2009 (Fig. 3B). Similar steep increase in NO<sub>3</sub><sup>-</sup> leaching after vegetation disturbances in catchments usually results from the mineralization of abundant dead biomass (litter and fine roots) and diminished N uptake by dead trees (HOULTON et al. 2003, HUBER 2005, McHALE et al. 2007, KAŇA et al. 2015).

The release of SO<sub>4</sub><sup>2-</sup> was more than twice higher as deposition to the catchment soils (34



**Fig. 6.** Comparison of mean sources (when positive) and removal (when negative) of H<sup>+</sup> in Plešné (PL) and Čertovo (CT) lakes and their catchments, associated with fluxes of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, organic acid anions (A<sup>-</sup>), ionic Al forms (Al<sub>i</sub>) and base cations (BCs) in the 2000–2017 hydrological years. Data for CT were derived from database given by KOPÁČEK et al. (2018b).

vs. 16 mmol.m<sup>-2</sup>.yr<sup>-1</sup> on average) during the study (Table 3). The most likely source of this extra SO<sub>4</sub><sup>2-</sup> was S accumulated in soils from high atmospheric deposition during the preceding decades as in the case of Čertovo Lake (Fig. 6). The net annual terrestrial exports of SO<sub>4</sub><sup>2-</sup> decreased by ~50% during the study (as predicted by MAGIC modelling on the basis of development of its atmospheric deposition and S retention in soils; MAJER et al. 2003, OULEHLE et al. 2018) and were not affected by the tree dieback (Fig. 3A).

On a long-term, the Cl<sup>-</sup> behaved conservatively in the Plešné catchment, only with negligible average production during 2000–2017 (Table 3). However, the terrestrial Cl<sup>-</sup> export exceeded its atmospheric input after the tree dieback (Fig. 4A), similarly as observed in other disturbed forests (e.g., KAUFFMAN et al. 2003, HUBER et al. 2004). This elevated Cl<sup>-</sup> leaching originates from mineralization of organically bound chlorine, stored in the soil organic matter (LOVETT et al. 2005, BASTVIKEN et al. 2007, ÖBERG & BASTVIKEN 2012).

Leaching of A<sup>-</sup> started to contribute to the terrestrial H<sup>+</sup> production with ~5 year delay after the tree dieback, when leaching of DOC increased (Fig. 3). The increase in DOC occurred as concentrations of NO<sub>3</sub><sup>-</sup>, H<sup>+</sup>, and polyvalent cations started to decrease in soil water, suggesting that disturbance-induced changes in N cycling strongly influenced DOC leaching via both chemical and biological mechanisms (KOPÁČEK et al. 2018a). Elevated DOC leaching after tree dieback was also observed elsewhere and was mostly attributed to increasing soil wetness due to disrupted or diminished transpiration by dead trees (e.g., NIEMINEN 2004, MIKKELSON et al. 2013, BEARUP et al. 2014).

The leaching of BCs and Al<sub>i</sub> peaked in 2009–2010, and then started to decrease to their pre-disturbance levels (Fig. 3). Their fluxes were affected by the tree dieback similarly to NO<sub>3</sub><sup>-</sup> (Fig. 3) that became the dominant strong acid anion in water, and cations accompanied predominantly its leaching as counter-ions. Consequently, the decreasing terrestrial export of SO<sub>4</sub><sup>2-</sup> from the Plešné catchment was not accompanied by decreasing Al<sub>i</sub>, as observed in the Čertovo catchment during the same period (KOPÁČEK et al. 2018b).

### Net terrestrial sources of base cations

The interpretation of  $\pi_C^*$  values for BCs (Table 3) is not very straightforward because they were related to deposition of BCs to the catchment soils that also included canopy leaching (elements released during precipitation passing through the canopies) prior to the tree dieback. Later, BCs were also released from decaying dead biomass. The calculated  $\pi_C^*$  values thus underestimated net terrestrial production of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup> in soils until 2004 and then overestimated this production for all BCs after the tree dieback. The actual net terrestrial production of BCs can be roughly estimated as the difference between their terrestrial exports and net atmospheric inputs to the catchment during 2000–2004, when the net accumulation of BCs in mature trees was low. This period also preceded effects of tree dieback on throughfall composition and terrestrial export of BCs (Fig. 3C). Deposition of Na<sup>+</sup> to the catchment soils was on average 1.6 fold higher than that of precipitation during 2000–2004. Because the Na<sup>+</sup> exchange is negligible in Norway spruce canopies in the study catchment (KOPÁČEK et al. 2009), we can assume that its total (wet, dry, and horizontal) atmospheric input into the catchment was equal to its deposition to the catchment soils. Moreover, dry depositions of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup> are assumed to be similar to that of Na<sup>+</sup>, due to the same physical size and aerodynamic properties of base cation-containing aerosols (DRAAIJERS & ERISMAN 1995). Total atmospheric inputs of BCs to the Plešné catchment can thus be roughly estimated from their precipitation fluxes, multiplied by a factor of 1.6. This provides net atmospheric inputs of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> to the catchment of 10.2, 3.3, 18.8, and 8.2 mmol.m<sup>-2</sup>.yr<sup>-1</sup>, and their 2000–2004 average terrestrial production of 11.2, 4.4, 31.2, and 1.5 mmol.m<sup>-2</sup>.yr<sup>-1</sup>, respectively. The higher net terrestrial source of Ca<sup>2+</sup> than Mg<sup>2+</sup> is consistent

with its almost twofold higher concentration in the Plešné granitic bedrock (KOPÁČEK et al. 2002). Thus estimated net terrestrial production of BCs is similar to their weathering rate assessed by modelling (64 vs. 75 meq.m<sup>-2</sup>.yr<sup>-1</sup>; OULEHLE et al. 2018).

After the tree dieback, terrestrial export of BCs increased, while their atmospheric deposition to the catchment soils continually decreased (Fig. 3C) due to thinning of dead canopies, and consequently, decreasing horizontal deposition and ceasing their canopy exchange (KOPÁČEK et al. 2013b, 2017). The average ratio of Na<sup>+</sup> fluxes in total deposition vs. precipitation decreased to 1.4 on average for the 2005–2017 period. The net terrestrial productions of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> during 2005–2017 (corrected using the Na-related factor of 1.4) were respectively 22.4, 8.9, 35.9, and 21.8 mmol.m<sup>-2</sup>.yr<sup>-1</sup>, and were thus higher by 11.2, 4.5, 4.7 and 20.3 mmol.m<sup>-2</sup>.yr<sup>-1</sup> than prior to the tree dieback. This excess leaching of BCs can be considered as their average annual loss from the decaying dead biomass to receiving waters during the last 13 years. The tree dieback and release from dead biomass are important sources of BCs for soil solutions (e.g., BERG & McCLAUGHERTY 2008, PALVIAINEN et al. 2004). The increased availability of BCs in the Plešné soils caused their rapid recovery from acidification. The released BCs replaced a part of H<sup>+</sup> and Al<sub>i</sub> from the soil sorption complex and significantly increased soil base saturation in the upper soils (from 39–65% and from 21–38% in the O and A horizons, respectively) between 2000 and 2015 (KAŇA et al. 2013, unpublished data).

### Net phosphorus release from catchment soils

The forest soils of the Plešné catchment are an important source of P for the lake (Table 3), and the terrestrial P export closely correlates with DOC leaching (KOPÁČEK et al. 2017). This terrestrial P flux, dominated by SRP, is ~5-times higher than that to the Čertovo Lake (KOPÁČEK et al. 2018b), and is the major reason for Plešné Lake having the highest productivity of the Bohemian Forest lakes (VRBA et al. 2003, 2016). The most probable reasons for the high terrestrial P export from the Plešné catchment are (i) higher P release from the granitic bedrock (while mica schist dominates in the rest of the Bohemian Forest lake district), (ii) a lower overall phosphate sorption capacity of the Plešné soils (due to the lower concentrations of Fe hydroxides and lower pools of podsol and dystric cambisol, and a higher proportion of less-adsorbing leptosol), and (iii) high microbial P transformations and enzymatic P hydrolysis (ŠANTRŮČKOVÁ et al. 2004, KAŇA & KOPÁČEK 2006, TAHOVSKÁ et al. 2018).

### Major processes affecting element fluxes in Plešné Lake

The in-lake H<sup>+</sup> neutralization was dominated by NO<sub>3</sub><sup>-</sup> removal (Table 4, Fig. 6). The process removed on average 395±132 meq.m<sup>-2</sup>.yr<sup>-1</sup> NO<sub>3</sub><sup>-</sup> (and H<sup>+</sup>), i.e., 43% of the total NO<sub>3</sub><sup>-</sup> input to the lake by inlets and atmospheric deposition. This internal acid neutralizing process is typical for acidified lakes with elevated NO<sub>3</sub><sup>-</sup> inputs (KELLY et al. 1987, SCHINDLER 1986). Contribution of denitrification and assimilation in the total NO<sub>3</sub><sup>-</sup> removal was approximately 1/3 and 2/3, respectively, in Plešné Lake (KOPÁČEK et al. 2006). Acidified lakes with elevated NO<sub>3</sub><sup>-</sup> inputs usually receive low P inputs, their primary production is P-limited, the algal uptake of N is low, and their NO<sub>3</sub><sup>-</sup> removal is dominated by denitrification in the sediments (SCHINDLER 1986, MOLOT & DILLON 1993, KASTE & DILLON, 2003). While Čertovo Lake (KOPÁČEK et al. 2018b) represents such a typical acidified oligotrophic lake, Plešné Lake receives both high NO<sub>3</sub><sup>-</sup> and P inputs (Table 2). Due to high primary production in Plešné Lake (KOPÁČEK et al. 2004), N assimilation was higher than the NH<sub>4</sub><sup>+</sup> input (the primary N source for freshwater phytoplankton) and NO<sub>3</sub><sup>-</sup> assimilation became an alternative N source for the plankton. Consequently, NO<sub>3</sub><sup>-</sup> assimilation prevailed in the NO<sub>3</sub><sup>-</sup> removal in Plešné Lake, while denitrification was the major NO<sub>3</sub><sup>-</sup> sink in Čertovo Lake (KOPÁČEK et al. 2018b). The

average  $S_{NO_3}$  values were two-fold higher in Plešné than in Čertovo Lake (9.4 vs. 4.4  $\text{m}\cdot\text{yr}^{-1}$ ), but both values were within the range of similar data (2.8–12.7; on average 6.4  $\text{m}\cdot\text{yr}^{-1}$ ) reported for 20 European and North American lakes by KELLY et al. (1987) and KASTE & DILLON (2003).

The annual  $\text{SO}_4^{2-}$  retention in Plešné Lake (5% on average, the mass transfer coefficient of  $0.5\pm 0.7 \text{ m}\cdot\text{yr}^{-1}$ ) was similar to Čertovo Lake, as well as lakes with short (<4 years) water residence times (KELLY et al. 1987). The  $\text{SO}_4^{2-}$  role in the internal  $\text{H}^+$  neutralization was thus small during the study (Fig. 6) and will further decrease together with the decreasing in-lake  $\text{SO}_4^{2-}$  concentrations, anticipated by modelling (MAJER et al. 2003, OULEHLE et al. 2018).

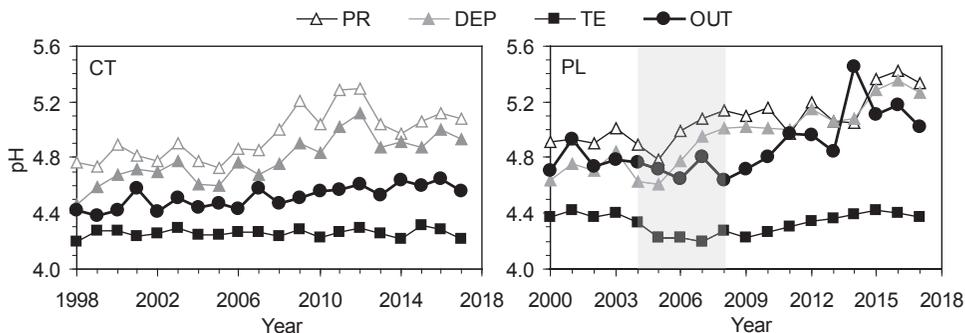
The in-lake removal of  $\text{A}^-$  ( $151 \text{ meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ ) was the second most effective  $\text{H}^+$  neutralizing process. This  $\text{H}^+$  neutralizing process is associated with the partial photochemical degradation of allochthonous DOC (KOPÁČEK et al. 2003, PORCAL et al. 2004, 2010) that oxidizes DOC and produces biologically available small molecular weight compounds for bacterial growth (e.g., WETZEL et al. 1995). The DOC (and  $\text{A}^-$ ) is thus photochemically and/or microbially oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , removing one mole of  $\text{H}^+$  per each equivalent of the oxidized  $\text{A}^-$ ; e.g. for formic acid:



The photochemical and microbial decomposition removed 38% of DOC supplied by surface inlets and decreased DOC concentrations in the outlet (Fig. 5E). This acid neutralizing process will likely remain important in all the Bohemian and Bavarian Forest lakes due to the continuing increase in DOC leaching to surface waters in this area (BEUDERT & GIETL 2015, KOPÁČEK et al. 2018a).

The photochemical cleaving of DOC liberated 30–40% of  $\text{Al}_0$  and  $\text{Fe}_0$  from their organic complexes as  $\text{Al}_i$  and  $\text{Fe}_i$  (Table 4) and thus the  $\text{Al}_0$  and  $\text{Fe}_0$  concentrations were lower in the outlet than in the lake tributaries (Table 2). This proportion of liberated metals was lower than in Čertovo Lake (~50%; KOPÁČEK et al. 2018b) due probably to the lower water transparency, higher pH, and shorter water residence time. The liberated metals contributed to their ionic forms, supplied by tributaries, in modifying in-lake  $\text{H}^+$  budgets.

Hydrolysis of  $\text{Al}_i$  (equation 15) was the most important in-lake source of acidity, producing on average  $243\pm 81 \text{ meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  of  $\text{H}^+$  (Table 4, Fig. 6):



**Fig. 7.** Time series of annual average pH of precipitation (PR), deposition to the catchment soils (DEP), and terrestrial export via tributaries (TE), and output (OUT) from lake in the Čertovo (CT; data from KOPÁČEK et al. 2018b) and Plešné (PL) catchment–lake systems in the 1998–2017 hydrological years. Grey area indicates the period of bark beetle outbreak in the Plešné catchment.

The hydrolysis occurs along pH gradients between the input and output water (Table 2), and between the lake surface and bottom (Fig. 2C,J), 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 particulate Al left the lake via outflow ( $41 \text{ mmol.m}^{-2}.\text{yr}^{-1}$ ), the rest ( $62 \text{ mmol.m}^{-2}.\text{yr}^{-1}$ ) was deposited in the sediments (Table 4). The  $H^+$  production associated with the  $Al_i$  hydrolysis was three times higher in Plešné than in Čertovo Lake (KOPÁČEK et al. 2018b), due to higher terrestrial  $Al_i$  exports after the tree dieback and higher water pH, and consequently, higher proportion of  $Al_i$  transformed to  $Al_p$ .

Similarly to  $Al_i$ , the  $Fe_i$  partly hydrolyzed in the lake along pH gradients, but its effect on the in-lake  $H^+$  budget was negligible, due to lower concentrations. The lake was a small net source of  $Fe_T$  (Table 4), similarly to Čertovo Lake (KOPÁČEK et al. 2018b). This suggests that both lakes receive some unmeasured  $Fe_p$  source, e.g., deposition of needles from shoreline trees (PSENNER 1984) or overland flow.

The net internal  $H^+$  neutralization was more pronounced in Plešné than Čertovo Lake throughout the study period, and has further accelerated since 2009 (Fig. 7) together with decreasing leaching of  $Al_i$  (Fig. 3). The  $H^+$  concentrations in the lake have started to decrease since 2009 (Fig. 5H), because terrestrial exports of  $NO_3^-$ ,  $A^-$  (DOC), and TP have remained high enough to neutralize  $H^+$  by  $NO_3^-$  reduction and  $A^-$  oxidation, while  $H^+$  production by  $Al_i$  hydrolysis has decreased. The changes in composition of tributaries thus caused the rapid pH increase in Plešné Lake (while its values only slightly increased in Čertovo Lake; Fig. 7), and a reestablishment of the carbonate buffering system (see annual average  $HCO_3^-$  concentrations in the lake outlet; Appendix 6).

Plešné Lake was a net sink for all nutrients (Table 4, Fig. 5). The in-lake retention of total N ( $297 \pm 142 \text{ mmol.m}^{-2}.\text{yr}^{-1}$ ) was caused by high  $NO_3^-$  removal, while the lake was a net source of TON and also  $NH_4^+$  (as in Čertovo Lake; KOPÁČEK et al. 2018b). The net  $NH_4^+$  production shows that the internal  $NH_4^+$  source can exceed its sinks in acidified lakes, which have ceased nitrification (RUDD & al. 1988) and have significant assimilation of  $NO_3^-$ . This pattern was for Plešné Lake discussed in detail elsewhere (KOPÁČEK et al. 2004, 2006).

The lake was an average sink of  $4.3$  and  $6.2 \text{ mmol.m}^{-2}.\text{yr}^{-1}$  of TP and SRP, respectively, during the whole study. The percent retention of P was twice as high in Plešné as in Čertovo Lake (51% vs. 22%) despite a ~50% shorter water residence time. The disproportion could be partly caused by higher abiotic PP production in Plešné Lake. Dissolved P can be converted to PP by both biomass production and abiotic P immobilization by colloidal  $Al_p$  in acidified lakes with elevated Al inputs (KOPÁČEK et al. 2000a, 2004). The  $Al_p$  production was three times higher in Plešné than in Čertovo Lake.

The average Si removal of  $136 \pm 85 \text{ mmol.m}^{-2}.\text{yr}^{-1}$  was probably too high to be explained by sedimentation of diatoms, which are absent in the plankton of Plešné Lake (VRBA et al. 2003, NEDBALOVÁ et al. 2006, 2016). Similarly, as in Čertovo Lake (KOPÁČEK et al. 2018b), we assume that some abiotic processes could contribute to the internal Si sink in Plešné Lake, besides the sedimentation of biogenic Si.

## CONCLUSIONS

Recovery of Plešné Lake from atmospheric acidification was disrupted by bark beetle outbreak in its catchment that killed ~90% of mature Norway spruce trees during 2004–2008. All dead biomass was left in the catchment.  $NO_3^-$  became the dominant anion, with maximum concentrations within 5–7 years after the tree dieback, and then started to decrease. Terrestrial exports of  $Al_i$ ,  $K^+$ ,  $H^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$  accompanied  $NO_3^-$  leaching. Elevated losses of TP, SRP, and DOC continued until the end of the study. These changes affected  $H^+$

balance in both terrestrial and aquatic ecosystems.

The terrestrial  $H^+$  production was dominated by  $NH_4^+$  removal and the excess leaching of  $SO_4^{2-}$  from soils (desorption and microbial oxidation of reduced S forms) during 2000–2004, i.e., prior to the tree dieback. Then, net terrestrial  $NO_3^-$  production became the dominant  $H^+$  producing process for 10 following years (Fig. 3). Since 2008, the relative importance of  $A^-$  in the terrestrial  $H^+$  production has steadily increased, and has become the dominant process in 2017. The future trend in terrestrial  $H^+$  production will be probably governed by  $A^-$  leaching,  $NH_4^+$  retention, and also (despite its continuous decrease) by net  $SO_4^{2-}$  release, while the importance of  $NO_3^-$  will further decrease due to increasing N consumption by regenerating forest. The elevated  $A^-$  leaching will probably last until the decrease of elevated soil wetness back to their pre-disturbance levels (KOPÁČEK et al. 2018a) and termination of the enhanced production of DOC from dead biomass that can continue (albeit with decreasing intensity) for up to three decades after a mortality event, as observed elsewhere (HYVÖNEN et al. 2000, SHOROHVA & KAPITSA 2016).

In the lake, microbial processes significantly decreased concentrations of  $NO_3^-$ ,  $A^-$ ,  $H^+$ , and  $Al_1$ . Their net effect was ~65% reduction of the total (terrestrial and atmospheric)  $H^+$  input into the lake. The in-lake acidity removal neutralized almost all  $H^+$  production in the catchment, and consequently, the water leaving the whole Plešné catchment–lake system had pH similar to that in precipitation (Fig. 7). The most important in-lake neutralizing processes were  $NO_3^-$  reduction and  $A^-$  oxidation, while  $Al_1$  hydrolysis most importantly mitigated the  $H^+$  decrease associated with the former processes. Despite the decreasing  $NO_3^-$  leaching, its input to the lake remains higher than its present in-lake biological demand. The present terrestrial export of  $NO_3^-$  (together with TP) thus results in a still high  $H^+$  neutralization due to  $NO_3^-$  assimilation. Moreover,  $H^+$  neutralization by photochemical and microbial oxidation of  $A^-$  remains high due to still elevated leaching of DOC (Fig. 3E). In contrast,  $Al_1$  leaching and its in-lake hydrolysis decrease, resulting in lower  $H^+$  production. The net result of these processes is that lake water pH increases and the carbonate buffering system has established in the lake after more than a half of century (OULEHLE et al. 2018). These favourable conditions for biological recovery of Plešné Lake from acidification will probably persist until the terrestrial exports of  $NO_3^-$ , TP, and DOC will decrease back to their pre-disturbance levels.

Further research of Plešné Lake should include more detailed studies on the development of in-lake food web structure and sediment diagenesis. It is probable that (i) the role of sulphur controls on the fate of geochemical elements in the lake sediment will decrease with decreasing terrestrial export of  $SO_4^{2-}$  (COUTURE et al. 2016), and (ii) the settling particulate organic carbon will become more available for microbial decomposition due to decreasing load of Al and decreasing formation of organic-Al complexes that are substantially stabilized against microbial decay (MULDER et al. 2001, SCHEEL et al. 2007).

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**Appendix 1.** Water balance in Plešné Lake and its catchment in hydrological years (from November 1999 to October 2017). Precipitation amount ( $H_{PR}$  mm.yr<sup>-1</sup>), deposition to the catchment soils ( $Q_{DEP}$  mm.yr<sup>-1</sup>; precipitation in the open area and throughfall in the forest), terrestrial export from catchment via all lake tributaries ( $Q_{TE}$  mm.yr<sup>-1</sup>), water output from lake ( $Q_{OUT}$  mm.yr<sup>-1</sup>), specific runoff from catchment–lake system ( $SR$ , l.km<sup>-2</sup>.s<sup>-1</sup>), and water residence time in lake ( $WRT$ , day).

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
$H_{PR}$	1655	1408	1953	1146	1315	1406	1425	1516	1513	1418	1293	1050	1186	1351	1068	1020	1465	1041
$Q_{DEP}$	1549	1349	1969	1160	1265	1337	1356	1553	1453	1403	1366	1090	1209	1335	1093	1019	1459	1115
$Q_{TE}$	971	1017	1655	723	886	1060	1236	1218	1386	1252	1230	838	1069	1126	906	799	1248	947
$Q_{OUT}$	1011	1018	1667	730	921	1060	1229	1216	1371	1227	1196	835	1052	1113	860	803	1243	923
$SR$	32.0	32.3	52.9	23.2	29.2	33.6	39.0	38.6	43.5	38.9	37.9	26.5	33.4	35.3	27.3	25.5	39.4	29.3
$WRT$	348	345	211	481	382	332	286	289	256	286	294	421	334	316	409	438	283	381

**Appendix 2.** Precipitation amount ( $H_{pr}$ ) and volume weighted mean composition of precipitation ( $C_{pr}$ ) in the catchment of Plesné Lake in hydrological years between November 1999 and October 2017. Units:  $\mu\text{mol.l}^{-1}$ , except for  $H_{pr}$  ( $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ ) and pH. ND – not determined.

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
$H_{pr}$	1.66	1.41	1.95	1.15	1.32	1.41	1.43	1.52	1.51	1.42	1.29	1.05	1.19	1.35	1.07	1.02	1.47	1.04
pH	4.91	4.94	4.91	5.01	4.89	4.79	4.99	5.08	5.14	5.10	5.16	4.97	5.20	5.07	5.05	5.37	5.42	5.34
$\text{H}^+$	12.2	11.6	12.4	9.8	12.9	16.3	10.3	8.4	7.3	8.0	6.9	10.6	6.3	8.6	8.9	4.3	3.8	4.6
$\text{Ca}^{2+}$	4.6	4.3	3.4	6.2	3.4	4.3	3.6	3.0	3.9	4.4	3.6	3.4	2.9	4.7	4.3	5.1	3.4	4.2
$\text{Mg}^{2+}$	1.2	1.5	1.2	1.8	1.4	1.0	1.0	1.9	1.2	1.1	0.9	1.0	1.0	1.2	1.2	1.6	0.8	1.0
$\text{Na}^+$	9.6	7.4	6.4	8.2	7.9	6.9	6.5	6.5	7.2	5.5	5.0	4.3	7.8	6.8	5.4	6.7	4.7	7.4
$\text{K}^+$	4.5	3.1	2.1	4.3	3.5	1.8	2.2	2.2	1.8	1.8	1.6	2.0	1.7	2.0	2.1	2.3	1.3	1.9
$\text{NH}_4^+$	24.4	26.2	25.4	27.3	19.3	21.3	26.5	29.4	27.8	23.0	31.4	18.5	26.7	23.0	32.6	39.2	31.1	30.7
$\text{NO}_3^-$	24.2	23.3	22.5	25.6	22.5	24.4	24.2	23.8	23.6	20.8	22.9	19.4	20.9	21.4	23.8	24.6	20.3	22.9
$\text{SO}_4^{2-}$	11.0	10.5	9.9	10.0	8.0	10.5	8.0	8.7	8.4	7.7	7.9	6.7	5.9	6.2	8.6	7.3	5.1	5.6
$\text{Cl}^-$	9.0	7.2	6.7	7.2	8.5	6.6	6.0	6.0	6.6	4.8	4.8	4.4	7.5	6.4	5.2	5.9	4.4	6.6
$\text{F}^-$	0.2	0.2	0.6	0.3	0.4	0.4	0.5	0.4	0.4	0.2	0.0	0.4	1.4	2.0	1.3	0.7	0.5	0.7
$\text{HCO}_3^-$	0.7	2.1	0.9	4.9	1.1	0.3	3.9	1.6	3.1	3.6	5.2	2.0	3.8	5.9	7.0	15.5	9.9	9.6
DOC	70	77	79	123	94	81	78	142	89	94	97	78	92	104	111	92	85	80
POC	ND	ND	ND	109	15	40	31	82	45	52	7	10	6	24	15	4	24	39
DON	5.5	8.2	10.4	11.2	10.1	7.1	10.7	21.9	9.2	11.3	13.7	13.3	12.5	12.6	17.9	14.7	15.2	13.7
PON	2.3	6.9	5.4	12.1	3.6	4.0	4.7	8.2	6.7	7.1	5.6	7.2	6.2	4.3	8.8	7.0	7.7	6.5
TP	0.37	0.65	0.29	0.71	0.48	0.30	0.33	0.68	0.37	0.32	0.41	0.73	0.23	0.33	0.46	0.61	0.30	0.42
PP	0.23	0.21	0.15	0.44	0.25	0.24	0.22	0.27	0.22	0.19	0.21	0.45	0.14	0.16	0.23	0.24	0.13	0.28
SRP	0.10	0.40	0.10	0.15	0.23	0.04	0.05	0.42	0.10	0.07	0.07	0.20	0.05	0.13	0.16	0.19	0.14	0.10
Si	0.07	0.07	0.22	0.38	0.38	0.38	0.38	0.38	0.68	0.67	1.04	0.86	0.86	0.86	0.46	0.68	0.68	0.68
$\text{Al}_L$	0.2	0.2	0.2	0.3	0.1	0.2	0.2	0.4	0.2	0.4	0.1	0.1	0.6	1.1	1.2	0.8	0.3	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 6) in the catchment of Plešné Lake in hydrological years between November 1999 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.

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
$Q_{DEP}$	1.55	1.35	1.97	1.16	1.27	1.34	1.36	1.55	1.45	1.40	1.37	1.09	1.21	1.34	1.09	1.02	1.46	1.12
pH	4.64	4.76	4.71	4.85	4.63	4.61	4.78	4.95	5.01	5.02	5.02	5.00	5.15	5.06	5.08	5.29	5.35	5.26
H <sup>+</sup>	22.9	17.4	19.7	14.2	23.5	24.5	16.6	11.2	9.8	9.6	9.6	10.0	7.1	8.7	8.3	5.1	4.5	5.5
Ca <sup>2+</sup>	13.4	9.8	9.1	14.1	12.0	12.0	10.3	9.0	8.0	7.3	7.2	6.3	4.9	5.8	4.0	5.5	3.8	4.5
Mg <sup>2+</sup>	4.7	3.5	3.5	4.9	5.0	4.4	3.8	4.7	3.8	2.9	3.2	2.7	2.2	1.8	1.5	2.0	1.3	1.5
Na <sup>+</sup>	14.9	10.2	9.9	16.0	15.0	12.5	8.6	12.8	10.7	7.9	7.3	7.7	9.6	7.3	6.1	9.3	5.0	6.9
K <sup>+</sup>	26.3	19.2	15.1	28.6	26.2	25.5	26.1	22.8	20.5	11.0	9.2	7.2	3.7	3.8	3.2	3.7	2.8	2.9
NH <sub>4</sub> <sup>+</sup>	32.5	29.2	32.6	50.1	25.2	28.2	30.0	31.4	27.8	28.1	33.0	29.1	31.8	27.1	33.7	38.6	28.2	29.7
NO <sub>3</sub> <sup>-</sup>	49.3	35.6	38.7	58.1	47.6	44.9	38.3	35.1	27.3	26.1	28.7	28.8	27.1	24.7	24.8	26.8	20.9	22.3
SO <sub>4</sub> <sup>2-</sup>	19.5	15.2	15.2	17.9	15.2	18.1	13.6	12.3	10.0	9.4	9.5	8.4	7.2	7.6	8.6	7.7	5.3	5.9
Cl <sup>-</sup>	13.1	11.4	11.4	17.5	17.6	15.4	12.5	14.0	11.8	7.5	7.0	7.2	9.9	6.9	6.1	8.1	4.7	6.5
F <sup>-</sup>	0.5	0.6	1.0	0.6	0.4	0.8	1.5	0.9	0.6	0.4	0.0	0.6	0.8	1.7	0.9	1.2	0.5	0.8
HCO <sub>3</sub> <sup>-</sup>	1.1	1.0	0.3	7.5	1.1	0.4	4.5	1.4	5.8	5.8	4.0	4.8	4.8	6.4	8.2	16.7	9.8	10.8
DOC	607	451	386	553	558	518	512	603	555	371	419	276	173	146	117	130	109	117
POC	ND	ND	ND	158	136	914	147	154	166	119	56	9	7	11	8	18	22	32
DON	22.1	22.6	23.0	33.6	19.2	25.9	17.1	22.9	13.4	19.1	9.9	15.1	13.1	14.5	13.0	8.5	11.6	14.8
PON	0.0	0.0	6.8	22.0	14.0	13.6	9.6	13.8	14.7	9.6	8.1	6.5	3.6	2.1	6.1	1.8	3.3	4.2
TP	0.82	0.65	0.49	0.84	0.76	0.82	0.81	1.07	0.89	0.72	0.71	0.73	0.31	0.51	0.63	0.43	0.28	0.33
PP	0.61	0.41	0.36	0.63	0.56	0.59	0.55	0.67	0.61	0.48	0.44	0.48	0.18	0.23	0.25	0.23	0.13	0.23
SRP	0.12	0.14	0.05	0.08	0.10	0.13	0.10	0.26	0.11	0.10	0.08	0.15	0.06	0.21	0.30	0.11	0.11	0.05

**Appendix 4.** Mean annual discharge ( $Q_{TE}$ ) and period weighted mean concentrations of water constituents ( $C_{TE}$ ) of terrestrial export via all tributaries to Plešné Lake (calculated from equation 9) in hydrological years between November 1999 and October 2017. Units:  $\mu\text{mol}\cdot\text{l}^{-1}$ , except for  $Q_{TE}$  ( $\text{m}^3\cdot\text{m}^2\cdot\text{yr}^{-1}$ , given on a catchment-area basis) and  $\text{pH}$ . ND – not determined.

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
$Q_{TE}$	0.97	1.02	1.66	0.72	0.89	1.06	1.24	1.22	1.39	1.25	1.23	0.84	1.07	1.13	0.91	0.80	1.25	0.95
pH	4.37	4.43	4.37	4.40	4.34	4.23	4.22	4.19	4.27	4.23	4.27	4.31	4.34	4.36	4.39	4.42	4.41	4.37
H <sup>+</sup>	42.2	37.5	42.3	39.8	46.1	59.0	60.0	64.0	53.7	59.4	54.3	49.5	45.3	43.7	40.8	38.1	39.3	42.5
Ca <sup>2+</sup>	21	21	18	20	24	23	26	28	27	30	31	31	30	27	27	24	23	19
Mg <sup>2+</sup>	7.5	6.5	7.3	6.9	8.8	8.8	8.8	11.1	9.4	10.8	12.3	12.3	11.2	10.7	10.4	9.1	7.9	6.6
Na <sup>+</sup>	51	48	44	47	51	48	38	44	39	42	42	45	42	38	55	44	42	40
K <sup>+</sup>	9.0	8.2	8.6	9.8	11.4	14.4	19.6	24.8	23.8	30.4	33.1	32.1	24.7	22.8	20.0	18.3	17.9	13.2
NH <sub>4</sub> <sup>+</sup>	2.7	0.7	0.6	0.3	0.8	0.4	0.8	0.6	0.5	1.3	0.9	0.6	0.2	0.5	0.1	0.2	0.1	0.1
NO <sub>3</sub> <sup>-</sup>	62	51	57	66	105	118	134	155	140	174	167	180	130	125	107	81	76	52
SO <sub>4</sub> <sup>2-</sup>	49	44	39	39	40	35	30	30	27	28	29	26	25	25	30	27	24	24
Cl <sup>-</sup>	13	11	14	14	17	17	12	17	15	15	14	15	13	11	13	10	10	8
F <sup>-</sup>	2.7	4.8	4.6	4.2	5.4	5.2	4.4	5.2	4.9	2.9	2.9	5.1	3.9	6.4	4.9	4.0	3.8	3.3
DOC	653	644	748	615	472	638	732	717	641	816	764	716	832	790	923	929	1059	1094
POC	ND	26	ND	13	10	0.1	9	71	24	23	11	25	16	17	22	34	9	19
DON	18.1	20.7	19.9	18.4	18.8	23.5	29.1	30.4	22.2	37.3	33.8	36.1	33.0	30.1	28.8	27.3	29.1	25.7
PON	ND	0.82	ND	0.86	0.83	0.06	0.48	0.63	1.88	1.33	1.78	1.24	0.48	0.23	0.87	2.36	1.47	0.53
TP	0.75	0.72	0.75	0.66	0.59	0.71	1.00	0.98	0.95	1.23	1.21	1.17	1.18	1.33	1.09	1.18	1.17	1.00
PP	0.03	0.03	0.05	0.04	0.06	0.03	0.10	0.08	0.05	0.08	0.09	0.09	0.09	0.06	0.04	0.06	0.05	0.03
SRP	0.59	0.59	0.56	0.48	0.42	0.57	0.73	0.77	0.75	1.03	1.02	1.02	0.99	1.11	0.87	0.87	0.93	0.83
Si	141	142	125	149	149	133	111	133	112	121	121	148	127	106	183	138	135	148
Al <sub>T</sub>	28.7	27.4	28.2	27.7	31.2	30.7	33.4	33.4	31.2	38.4	35.5	41.1	29.7	33.6	30.5	26.6	25.4	23.5
Al <sub>I</sub>	17.8	16.3	16.7	17.6	20.7	19.5	22.1	23.0	22.7	29.5	26.9	31.6	20.5	22.4	18.2	13.7	13.7	11.7
Al <sub>0</sub>	10.6	10.5	10.6	9.1	9.7	10.8	10.7	9.7	7.6	8.6	7.5	8.0	7.9	10.1	11.3	12.3	11.3	11.3
Fe <sub>T</sub>	1.7	1.7	1.7	1.2	1.3	1.6	1.5	1.6	1.5	1.6	1.7	1.6	1.8	1.6	2.1	2.0	2.1	2.3
Fe <sub>I</sub>	0.6	0.5	0.4	0.2	0.2	0.2	0.3	0.4	0.5	0.7	0.7	0.5	0.5	0.3	0.4	0.3	0.3	0.5
Fe <sub>0</sub>	1.0	1.2	1.3	0.9	1.0	1.3	1.2	1.1	1.0	0.8	0.8	1.0	1.2	1.2	1.5	1.6	1.7	1.7

**Appendix 5.** Total water input ( $Q_{IN}$ ) and mean annual composition of water input (terrestrial export and precipitation to the lake surface) to Plešné Lake in hydrological years between November 1999 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.

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
$Q_{IN}$	8.79	8.88	14.1	6.46	7.83	9.19	10.5	10.5	11.7	10.6	10.3	7.21	9.04	9.62	7.73	6.89	10.6	8.00
pH	4.44	4.48	4.42	4.46	4.39	4.28	4.27	4.25	4.32	4.28	4.32	4.36	4.40	4.41	4.44	4.48	4.46	4.42
H <sup>+</sup>	36.6	33.4	38.2	34.5	40.5	52.4	53.2	56.0	47.7	52.6	48.4	43.9	40.2	38.8	36.4	33.1	34.4	37.6
Ca <sup>2+</sup>	18	18	16	17	21	20	23	24	24	26	28	27	26	24	24	21	20	17
Mg <sup>2+</sup>	6.3	5.7	6.5	6.0	7.6	7.6	7.8	9.8	8.3	9.5	10.8	10.7	9.9	9.3	9.1	7.9	6.9	5.9
Na <sup>+</sup>	43	41	38	40	44	42	34	39	35	37	37	39	38	34	48	39	37	35
K <sup>+</sup>	8.2	7.4	7.7	8.8	10.1	12.5	17.3	21.5	20.9	26.5	29.2	27.7	21.7	19.9	17.5	15.9	15.6	11.7
NH <sub>4</sub> <sup>+</sup>	6.8	4.7	4.0	5.1	3.9	3.6	4.3	4.8	4.0	4.2	4.7	3.2	3.7	3.6	4.6	6.0	4.3	4.1
NO <sub>3</sub> <sup>-</sup>	55	47	52	59	91	103	119	136	125	153	149	156	116	110	96	73	68	48
SO <sub>4</sub> <sup>2-</sup>	42	38	35	34	35	31	27	27	25	25	26	23	22	22	27	24	22	22
Cl <sup>-</sup>	12	10	13	13	16	16	11	15	14	14	13	14	13	10	12	10	9	8
F <sup>-</sup>	2.3	4.0	4.1	3.5	4.6	4.4	3.9	4.5	4.3	2.6	2.5	4.4	3.6	5.8	4.4	3.6	3.4	3.0
DOC	543	554	655	528	408	553	643	634	570	720	680	623	735	694	811	805	925	962
POC	ND	28	10	30	11	6	12	72	27	27	11	23	15	18	21	29	11	21
DON	15.7	18.7	18.6	17.1	17.3	21.0	26.6	29.2	20.5	33.8	31.3	32.8	30.3	27.7	27.3	25.4	27.2	24.2
PON	0.44	1.79	0.74	2.84	1.30	0.66	1.05	1.73	2.50	2.11	2.26	2.10	1.23	0.41	1.96	3.04	2.33	1.30
TP	0.68	0.71	0.68	0.67	0.57	0.65	0.91	0.93	0.87	1.11	1.11	1.11	1.06	1.19	1.01	1.10	1.05	0.92
PP	0.06	0.06	0.07	0.11	0.09	0.06	0.12	0.11	0.07	0.09	0.11	0.14	0.10	0.08	0.07	0.09	0.06	0.06
SRP	0.50	0.56	0.50	0.42	0.39	0.49	0.63	0.72	0.66	0.90	0.90	0.90	0.86	0.97	0.78	0.77	0.82	0.74
Si	114	120	107	122	124	113	96	114	98	105	106	127	110	91	158	117	117	128
Al <sub>T</sub>	23.4	23.0	24.3	22.9	26.0	26.0	28.9	28.6	27.2	33.3	31.1	35.1	25.8	29.1	26.5	22.8	22.0	20.5
Al <sub>I</sub>	14.5	13.7	14.4	14.5	17.2	16.5	19.1	19.7	19.8	25.5	23.5	27.0	17.8	19.2	15.6	11.6	11.8	10.2
Al <sub>O</sub>	8.6	8.8	9.2	7.5	8.1	9.2	9.2	8.3	6.6	7.5	6.6	6.8	6.8	8.7	9.7	10.4	9.7	9.8
Fe <sub>T</sub>	1.4	1.5	1.5	1.1	1.1	1.4	1.4	1.4	1.4	1.5	1.5	1.4	1.6	1.4	1.9	1.7	1.9	2.0
Fe <sub>I</sub>	0.5	0.4	0.3	0.2	0.2	0.2	0.2	0.3	0.4	0.6	0.6	0.4	0.4	0.3	0.4	0.2	0.3	0.5
Fe <sub>O</sub>	0.9	1.0	1.1	0.8	0.8	1.1	1.0	1.0	0.8	0.7	0.7	0.8	1.1	1.1	1.3	1.3	1.5	1.5

**Appendix 6.** Water output ( $Q_{OUT}$ ) and mean annual composition of water output from Plesné Lake ( $C_{OUT}$ ) in hydrological years between November 1999 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.

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
$Q_{OUT}$	8.44	8.50	13.9	6.10	7.69	8.85	10.3	10.2	11.4	10.2	9.99	6.97	8.79	9.29	7.18	6.70	10.4	7.70
pH	4.70	4.93	4.73	4.79	4.76	4.72	4.64	4.81	4.64	4.71	4.80	4.97	4.97	4.85	5.44	5.11	5.18	5.02
H <sup>+</sup>	19.9	11.7	18.6	16.3	17.3	19.1	22.7	15.5	22.8	19.3	15.8	10.8	10.8	14.2	3.6	7.8	6.6	9.5
Ca <sup>2+</sup>	21	18	18	17	19	20	21	24	22	25	28	29	29	25	27	22	19	17
Mg <sup>2+</sup>	7.4	6.1	7.2	6.0	7.4	7.5	7.2	9.6	8.6	9.8	10.8	11.6	11.7	10.0	10.6	8.8	7.6	7.2
Na <sup>+</sup>	41	37	38	34	38	39	36	40	37	38	37	40	41	35	41	39	35	36
K <sup>+</sup>	8.8	8.1	7.7	8.2	9.0	9.3	11.9	15.1	17.5	21.7	26.4	26.1	25.6	24.1	21.6	19.3	15.8	14.9
NH <sub>4</sub> <sup>+</sup>	5.7	5.7	4.7	3.3	5.9	5.7	7.2	5.3	6.8	6.7	4.6	3.9	2.3	5.2	2.8	6.5	2.9	2.9
NO <sub>3</sub> <sup>-</sup>	31	22	30	23	44	48	61	70	88	104	110	100	91	80	45	40	27	21
SO <sub>4</sub> <sup>2-</sup>	47	37	38	33	34	33	31	30	27	26	26	23	24	23	24	23	21	21
Cl <sup>-</sup>	13	10	14	11	15	15	13	15	15	14	14	14	14	12	12	11	11	9
F <sup>-</sup>	3.4	3.7	5.1	3.3	3.7	4.3	3.7	4.6	4.6	2.7	3.0	5.1	3.5	5.7	4.9	4.4	3.8	3.4
HCO <sub>3</sub> <sup>-</sup>	0.0	0.0	0.1	0.3	0.2	0.0	0.0	0.1	0.3	0.4	0.1	2.4	2.5	3.4	14.9	12.2	12.2	10.9
DOC	328	295	453	386	326	325	396	305	386	362	364	312	380	435	497	562	565	664
POC	0	223	264	165	158	152	157	202	158	252	213	260	156	151	350	207	235	249
DON	14.2	12.9	15.5	14.4	13.1	12.2	16.0	19.6	18.9	24.5	26.2	24.5	27.3	23.0	24.2	23.1	21.8	22.6
PON	8.3	13.8	15.0	15.9	13.9	16.0	13.4	18.6	10.6	19.0	23.3	25.9	24.0	21.5	31.6	19.7	20.2	19.1
TP	0.34	0.34	0.40	0.39	0.31	0.36	0.41	0.37	0.42	0.55	0.52	0.48	0.53	0.66	0.61	0.51	0.49	0.54
PP	0.27	0.26	0.29	0.30	0.24	0.30	0.30	0.30	0.33	0.39	0.46	0.39	0.45	0.54	0.53	0.42	0.41	0.43
SRP	0.01	0.03	0.03	0.02	0.03	0.04	0.06	0.04	0.04	0.04	0.07	0.03	0.05	0.06	0.03	0.03	0.04	0.05
Si	89	87	95	100	104	100	90	104	96	100	99	116	115	94	110	110	102	111
Al <sub>i</sub>	19.2	16.9	20.6	20.2	18.8	18.9	21.3	20.5	22.5	24.0	23.7	23.7	21.8	25.5	19.7	17.1	17.0	15.6
Al <sub>t</sub>	10.4	8.5	10.2	10.2	9.9	9.3	11.5	11.3	13.9	15.7	15.2	10.8	9.5	11.2	3.8	5.3	5.3	4.2
Al <sub>o</sub>	4.6	3.8	6.3	5.3	5.0	5.1	6.1	4.0	4.4	3.3	3.1	2.4	3.2	6.8	6.7	8.2	7.9	7.0
Fe <sub>i</sub>	1.5	1.5	1.9	2.0	1.8	1.5	1.5	1.2	1.4	1.4	1.4	1.2	1.3	1.5	1.8	1.8	1.9	2.0
Fe <sub>t</sub>	0.4	0.4	0.2	0.3	0.4	0.3	0.4	0.3	0.3	0.4	0.4	0.3	0.4	0.3	0.1	0.3	0.3	0.2
Fe <sub>o</sub>	0.6	0.5	0.9	1.0	0.7	0.7	0.7	0.6	0.7	0.4	0.4	0.3	0.4	0.5	0.6	0.9	0.9	1.0

**Appendix 7.** Net production of water constituents in the catchment of Plešné Lake ( $\pi_c^*$  calculated from equation 1) in hydrological years between November 1999 and October 2017. Units:  $\mu\text{mol.l}^{-1}$ . Positive values indicate net production, while negative values indicate net removal. ND – not determined.

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
H <sup>+</sup>	5.6	14.4	18.9	17.1	12.6	28.1	41.7	49.8	43.4	48.7	43.6	36.6	37.2	33.3	30.8	31.6	34.1	36.0
Ca <sup>2+</sup>	-0.2	7.5	7.3	-2.8	6.8	7.4	14.7	16.6	18.1	21.3	23.1	23.0	24.4	20.5	22.3	16.9	18.8	13.6
Mg <sup>2+</sup>	-0.1	1.8	3.2	-0.9	1.7	3.2	4.7	5.1	5.4	7.5	8.7	8.7	8.8	8.5	8.6	6.5	6.4	4.8
Na <sup>+</sup>	27.2	34.1	31.9	21.4	30.0	32.1	28.4	28.1	28.0	33.1	33.9	35.5	31.5	29.3	48.0	32.3	36.4	31.5
K <sup>+</sup>	-32.9	-17.2	-9.4	-36.1	-26.1	-17.8	-9.1	-4.3	2.3	18.0	22.8	22.7	20.6	18.3	16.2	13.5	14.6	9.8
NH <sub>4</sub> <sup>+</sup>	-49.2	-38.1	-38.1	-79.9	-35.2	-35.2	-32.1	-39.4	-28.6	-30.1	-35.7	-37.3	-35.7	-31.6	-40.5	-49.0	-32.9	-34.9
NO <sub>3</sub> <sup>-</sup>	-16.8	3.9	10.7	-27.1	36.5	60.8	92.2	110.6	111.8	144.6	135.0	142.3	99.2	95.3	77.5	47.1	51.1	25.9
SO <sub>4</sub> <sup>2-</sup>	18.2	23.4	20.7	10.1	18.3	11.8	15.4	14.5	16.9	17.3	18.1	14.9	16.8	15.9	20.0	17.3	18.0	17.0
Cl <sup>-</sup>	-8.3	-4.6	0.0	-13.7	-7.8	-2.1	-1.5	-0.9	2.4	6.5	6.1	6.1	2.2	2.4	5.8	0.1	4.6	0.6
F <sup>-</sup>	1.9	4.0	3.5	3.2	4.9	4.1	2.8	4.1	4.3	2.5	2.9	4.4	3.0	4.4	3.9	2.5	3.2	2.4
DOC	-315	46	288	-271	-326	-15	170	-51	60	400	298	357	636	617	782	763	932	957
POC	ND	ND	ND	-241	-184	ND	-152	-126	-150	-111	-51	13	7	4	12	10	-16	-19
DON	-17.2	-9.3	-7.5	-35.5	-8.7	-9.2	10.4	1.3	8.2	16.0	22.8	16.4	18.2	12.9	13.2	16.4	15.5	8.3
PON	ND	27	-8	-34	-19	-17	-10	-17	-14	-9	-7	-7	-4	-3	-7	0	-2	-4
TP	-0.56	-0.14	0.16	-0.68	-0.50	-0.33	0.10	-0.39	0.02	0.43	0.42	0.23	0.83	0.73	0.34	0.63	0.85	0.61
PP	-0.95	-0.50	-0.38	-0.97	-0.74	-0.71	-0.51	-0.78	-0.59	-0.47	-0.39	-0.53	-0.12	-0.21	-0.26	-0.23	-0.10	-0.24
SRP	0.40	0.41	0.50	0.36	0.28	0.41	0.62	0.44	0.63	0.92	0.93	0.82	0.91	0.86	0.51	0.74	0.80	0.77
Si	138	142	124	148	148	133	111	132	111	120	120	147	126	105	182	138	135	147
Al <sub>r</sub>	28.0	27.3	28.0	27.2	31.0	30.5	33.1	32.8	31.0	38.0	35.4	40.9	29.0	32.4	30.2	25.6	25.3	23.5
Al <sub>i</sub>	17.8	16.3	16.7	17.6	20.7	19.5	22.1	23.0	22.7	29.5	26.9	31.6	20.5	22.4	18.2	13.7	13.7	11.7
Al <sub>o</sub>	10.6	10.5	10.6	9.1	9.7	10.8	10.7	9.7	7.6	8.6	7.5	8.0	7.9	10.1	11.3	12.3	11.3	11.3
Fe <sub>r</sub>	1.7	1.3	1.2	0.6	0.7	1.1	1.1	1.0	0.9	0.9	1.2	1.3	1.6	1.4	1.4	1.8	2.0	2.2
Fe <sub>i</sub>	0.6	0.5	0.4	0.2	0.2	0.2	0.3	0.4	0.5	0.7	0.7	0.5	0.5	0.3	0.4	0.3	0.3	0.5
Fe <sub>o</sub>	1.0	1.2	1.3	0.9	1.0	1.3	1.2	1.1	1.0	0.8	0.8	1.0	1.2	1.2	1.5	1.6	1.7	1.7

**Appendix 8.** Net production of water constituents in Plesné Lake ( $\tau_T$ , calculated from equation 2) in hydrological years between November 1999 and October 2017. Units:  $\mu\text{mol.l}^{-1}$ . Positive values indicate net production, while negative values indicate net removal. ND – not determined.

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
H <sup>+</sup>	-22	-25	-18	-25	-22	-34	-34	-40	-27	-34	-36	-36	-33	-27	-35	-28	-27	-29
Ca <sup>2+</sup>	1.7	-0.7	-0.8	0.1	0.1	-1.4	-0.3	0.7	-0.9	0.3	0.5	-0.8	1.8	-1.9	-0.3	-1.5	-7.8	-0.1
Mg <sup>2+</sup>	1.1	0.9	-0.5	0.6	1.1	-0.8	-0.4	1.1	-0.4	1.5	0.2	0.2	1.7	-1.1	2.0	0.8	-2.0	2.1
Na <sup>+</sup>	-7.5	-10.3	-1.1	-2.0	-5.6	-3.9	-0.8	3.1	-0.9	1.6	-2.6	-1.6	6.1	-3.4	-4.8	-4.5	-6.9	2.7
K <sup>+</sup>	-0.1	0.1	-0.4	0.2	-1.2	-3.1	-3.5	-4.0	-2.3	-2.2	-0.3	-2.6	2.7	0.4	2.0	0.1	-3.2	1.5
NH <sub>4</sub> <sup>+</sup>	1.0	1.6	-1.5	1.5	0.3	3.9	4.0	-0.4	4.2	0.4	2.2	-9.4	4.4	2.1	-3.8	0.6	-3.3	-6.4
NO <sub>3</sub> <sup>-</sup>	-31	-28	-21	-31	-39	-58	-54	-51	-38	-33	-45	-82	-31	-54	-78	-49	-47	-33
SO <sub>4</sub> <sup>2-</sup>	-3.2	-4.2	-1.5	-2.6	-2.5	0.2	1.4	-0.9	0.5	0.6	-1.7	-5.0	2.7	-1.2	-3.3	-2.3	-3.0	-0.7
Cl <sup>-</sup>	ND																	
F <sup>-</sup>	1.0	-1.3	0.7	0.3	-0.9	0.5	-1.4	2.0	0.1	-1.5	0.4	1.8	0.3	-0.1	1.4	-1.1	-0.6	1.0
HCO <sub>3</sub> <sup>-</sup>	9.1	3.2	-4.9	3.3	-0.5	1.3	1.6	-0.7	1.6	-4.2	6.6	5.7	3.3	9.4	21.8	15.1	3.3	4.0
DOC	-209	-237	-139	-362	-168	-211	-276	-279	-232	-362	-336	-393	-348	-168	-267	-331	-309	-265
POC	ND	194	263	243	55	234	133	159	85	272	28	343	106	141	343	169	277	288
DON	-0.1	-5.2	-3.9	-6.5	-7.7	-9.5	-10.4	-13.6	1.1	-8.3	2.7	-14.0	-9.9	-8.3	1.8	-9.3	-7.4	-2.6
PON	5.9	12.5	16.3	16.5	8.0	21.0	3.2	21.1	2.9	23.1	16.8	31.4	25.2	17.6	26.1	13.9	19.7	19.9
TP	-0.29	-0.41	-0.26	-0.29	-0.38	-0.34	-0.45	-0.59	-0.55	-0.45	-0.51	-0.81	-0.48	-0.62	-0.46	-0.71	-0.54	-0.43
PP	0.25	0.18	0.27	0.20	0.08	0.20	0.21	0.19	0.14	0.47	0.49	0.09	0.42	0.39	0.50	0.24	0.38	0.37
SRP	-0.51	-0.57	-0.48	-0.42	-0.36	-0.47	-0.59	-0.71	-0.64	-0.85	-0.91	-0.86	-0.86	-0.92	-0.85	-0.74	-0.81	-0.72
Si	-22	-32	-14	-24	-21	-19	-15	-7	-6	-12	-2	2	-14	-4	-42	-35	-7	-17
Al <sub>T</sub>	-3.7	-6.6	-2.9	-5.6	-10.4	-6.2	-9.7	-5.2	-9.5	-6.5	-4.8	-20.8	-0.7	-5.2	-10.5	-11.2	-2.5	-8.1
Al <sub>I</sub>	-5.8	-4.1	-3.4	-11.3	-8.2	-7.0	-8.1	-7.8	-7.5	-6.9	-8.4	-26.9	-7.0	-8.2	-14.6	-8.5	-6.3	-6.3
Al <sub>0</sub>	-2.1	-4.2	-2.6	-4.1	-5.0	-3.1	-4.8	-3.2	-3.4	-4.9	-3.5	-6.3	-1.7	-0.5	-0.2	-4.2	-1.0	-4.7
Fe <sub>T</sub>	0.66	0.12	0.58	1.32	-0.25	-0.01	0.07	-0.44	0.12	-0.52	0.19	-0.72	0.00	0.43	-0.21	0.27	0.19	-0.38
Fe <sub>I</sub>	-0.02	-0.04	-0.05	-0.23	0.25	-0.13	0.27	-0.15	0.01	-0.10	-0.20	-0.49	0.05	0.06	-0.36	-0.24	0.06	-0.33
Fe <sub>0</sub>	-0.03	-0.27	-0.11	-0.03	-0.47	-0.27	-0.40	-0.43	-0.25	-0.58	-0.26	-0.74	-0.56	-0.53	-0.44	-0.32	-0.56	-0.64

