

Chemistry of tributaries to Plešné and Čertovo lakes during 1998–2012

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Abstract

Ionic and nutrient compositions of tributaries to Plešné Lake (PL, 4 inlets, granite bedrock) and Čertovo Lake (CT, 7 inlets, mica schist and quartzite bedrock) were analyzed in 3-week intervals from October 1997 to November 2012. Norway spruce stands, dominating both catchments, were damaged during this study: 93% of the PL mature trees died due to bark beetle infestation between 2004–2011; 14% of the CT forest was seriously damaged by windthrows and bark beetle in 2007–2011. Almost all dead biomass remained in the catchments. Prior to the forest damage, water chemistry of tributaries exhibited trends typical for areas recovering from strong atmospheric acidification, such as decreasing concentrations of strong acid anions, base cations, ionic aluminium (Al_i), and protons (increasing pH). Chemistry of tributaries draining the affected sub-catchments rapidly changed after the forest damage. Concentrations of nitrate immediately increased, reaching the maximum values (up to $350 \mu\text{mol.l}^{-1}$) within 3–6 years after the forest dieback, then started to decline. Nitrate became the dominant anion and its leaching was accompanied by similar trends in Al_i and potassium (K^+) concentrations, and decreasing pH. Increases in magnesium (Mg^{2+}) and calcium (Ca^{2+}) leaching were less steep than those of Al_i and K^+ , but continued at elevated rates until the end of the study. The elevated leaching of phosphorus (P) and dissolved organic carbon (DOC) and nitrogen (DON) occurred immediately after forest dieback. The DON concentrations increased more steeply than DOC, resulting in decreasing DOC:DON ratios. Because almost no biomass was removed from the damaged forest, leaching of K^+ , Mg^{2+} , Ca^{2+} , and P will probably last longer than after a clear-cut. The continuous liberation of base cations from dead biomass will have a positive effect on increasing base saturation of soils and on the surface water composition, mitigating its pH decline.

Key words: recovery from acidification, bark beetle, forest dieback, ions, nutrients, water chemistry

INTRODUCTION

Plešné (PL) and Čertovo (CT) lakes in the Bohemian Forest (Czech Republic) have been recovering from strong atmospheric acidification since the late 1980s, similarly to all lakes in this region (KOPÁČEK et al. 1998, VESELÝ et al. 1998). This continuous process has been delayed in the lakes due to chemical changes resulting from forest damages in their catchments (VESELÝ et al. 1998, KOPÁČEK et al. 2009a, VRBA et al. 2014). In general, forest disturbances such as windthrow, insect infestation, clear-cut or other harvesting methods result in abrupt increases not only in the amount of bioavailable fresh organic matter (litter, dead roots and aboveground tree parts) in soils, but also in the elevated soil temperature and moisture due to reduced shading effect of canopies and lower transpiration. These changes promote mineralization and nitrification in soils, and alter the natural cycles of elements.

The most important changes include an elevated availability of inorganic N in soils, manifested by increased NH_4^+ concentrations in soil solutions, and increased NO_3^- leaching (HUBER et al. 2004a,b, TAHOVSKÁ et al. 2010). The elevated concentrations of NO_3^- in soil solutions mobilize H^+ , base cations (especially K^+ , Mg^{2+} , and Ca^{2+} liberated from decaying tissue), and ionic aluminium (Al_i) (LIKENS & BORMANN 1995, BERDÉN et al. 1997, SWANK et al. 2001, FINÉR et al. 2003, HOULTON et al. 2003, HUBER 2005, BURNS & MURDOCH 2005, MCHALE et al. 2007).

Forest dieback in lake catchments thus usually significantly alters surface water composition. In the Bohemian Forest, these changes have been delaying lake water recovery from atmospheric acidification that has occurred since the late 1980s. While the adverse effects of forest damage on water chemistry already subsided in some lakes (e.g., RACHELSEE, VRBA et al. 2014), they have been affecting other lakes, including PL and CT, so far (OULEHLE et al. 2013a). Chemical responses of lake water to changes in the catchments are, however, mitigated by internal alkalinity production, resulting from nitrate assimilation, denitrification, sulphate reduction in sediments and photochemical degradation of DOC, and are also influenced by other in-lake processes like liberation and hydrolysis of organically bound metals (e.g., KOPÁČEK et al. 2004, 2009a, PORCAL et al. 2010). In contrast, chemical changes in lake tributaries (usually springs or short forest streams) more directly reflect influences of vegetation and soils on water composition, and are thus valuable straightforward indicators of the whole ecosystem status.

A regular monitoring of all known PL and CT tributaries has started in 1997 as a part of mass budget studies on element cycling within their catchments (KOPÁČEK et al. 2001a,b). Water composition of these tributaries has been so far evaluated with respect to (i) effects of bedrock composition and terrestrial characteristics of the individual sub-catchments (KOPÁČEK & HEJZLAR 1998) and (ii) seasonal patterns in concentrations of major ions and nutrients (KOPÁČEK et al. 2000a). The aim of this study is to evaluate 15-year trends in chemistry of the PL and CT tributaries with respect to (i) a chemical recovery of the PL and CT catchments from acidification and (ii) forest disturbances caused by bark beetle outbreak in the PL catchment and windthrows in the CT catchment.

MATERIALS AND METHODS

Site description

Plešné and Čertovo lakes are of glacial origin (>14,000 yr old; PRAŽÁKOVÁ et al. 2006), with areas of 7.6 and 10.7 ha, respectively (JANSKÝ et al. 2005). Plešné Lake has two surface tributaries (PL-I and PL-II) and two known subsurface inlets (PL-III and PL-IV; Fig. 1A). 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. Since then, the PL-III inlet forms a short surface stream. Čertovo Lake has seven surface tributaries (CT-I to CT-VII; Fig. 1B), of which CT-II is the major tributary, representing on average ~60% of the total water input by all tributaries (KOPÁČEK et al. 2001a). The lakes were atmospherically acidified already in the 1950s (pH <5.0) (PROCHÁZKOVÁ & BLAŽKA 1999, MAJER et al. 2003) and acidification progressed until the middle 1980s, when pH was ~4.6 in Plešné Lake and ranged between 4.1 and 4.4 in Čertovo Lake (VESELÝ et al. 1993, 1998). Since the early 1990s, chemistry of lakes and their tributaries has been recovering from acidification due to reduced sulphur and nitrogen emissions into the atmosphere in central Europe and the consequent decline in acidic deposition in the Bohemian Forest (MAJER et al. 2003, KOPÁČEK & HRUŠKA 2010). Both lakes are fishless and zooplankton species are present in low densities (VRBA et al. 2003).

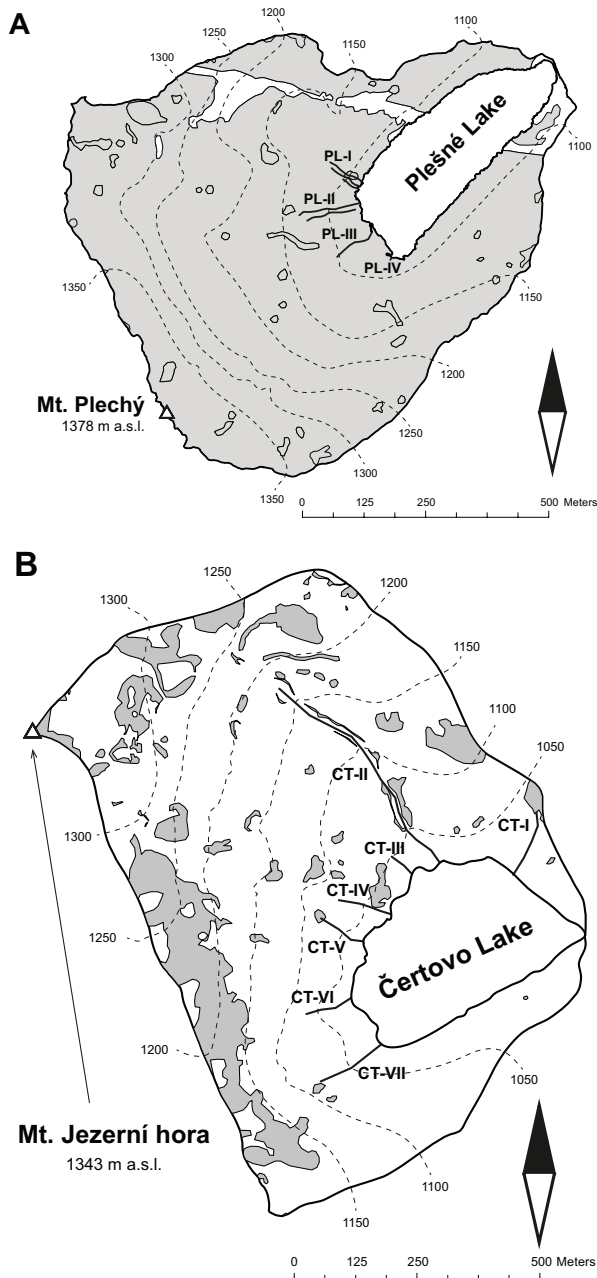


Fig. 1. Maps of the Plešné and Čertovo catchments with locations of lake tributaries (PL-I to PL-IV and CT-I to CT-VII). Gray colour denotes catchment parts with significant dieback of the original forest stands between 2000 and 2011: (A) areas with >80% reduction of living trees by bark beetle infestation in the Plešné catchment and (B) areas with >50% reduction of living trees by windthrows in 2007 and 2008 and the following bark beetle infestation in the Čertovo catchment.

The PL and CT catchments are 67 and 89 ha in size (including lakes) and steep, with maximum local reliefs of 288 and 315 m, respectively. The catchments differ in bedrock composition, soil pools and chemistry, with larger soil pools but more acidic soils in the CT catchment. The PL bedrock is formed by granite, while the CT bedrock is made up of micaschist (muscovitic gneiss), quartzite, and small amounts of pegmatite (VESELÝ 1994).

The PL catchment is covered with ~0.2 m deep leptosol (38%) and ~0.45 m deep podsol (29%) or spodo-dystric cambisol (27%); the rest is bare rocks (5%) and wetlands (~1%). Fine soil (< 2 mm, dry weight soil fraction) is rich in sand (~75%) and low in clay (~2%), and its catchment-weighted-mean pool is 92 kg.m⁻². Soil pH (CaCl₂ extractable; pH_{CaCl₂}) is 2.5–3.1 in A-horizons and reaches maximum values of 3.2–4.4 in the deepest mineral horizons. The mean effective cation exchange capacity of the soils is 129 meq.kg⁻¹ (NH₄Cl and KCl extractable; one equivalent is mole of charge), of which 15% is base saturation and the remaining is dominated by exchangeable Al³⁺ (57%) and protons (28%, KOPÁČEK et al. 2002a). The PL forest soils are important sources of P and organic C for the surface inlets and the lake (KOPÁČEK et al. 2004, KAŇA & KOPÁČEK 2006).

The CT catchment is covered with ~0.5 m deep spodo-dystric cambisol (58%), podsol (21%), and shallow (~0.2 m) leptosol (17%); wetlands and bare rocks represent ~3% and 1%, respectively. Fine soil is sandy (48–81%) with a low (1–4%) content of clay and a catchment-weighted-mean pool of 225 kg.m⁻². Soil pH_{CaCl₂} is 2.5–3.3 in A-horizons and 3.6–4.5 in mineral horizons. The mean effective cation exchange capacity of the CT soils is 104 meq.kg⁻¹, with 9, 62, and 29% proportions of base saturation, exchangeable Al³⁺, and H⁺, respectively (KOPÁČEK et al. 2002b).

The catchments weighted means of above-ground biomass of the understory vegetation (mostly *Vaccinium myrtillus* and *Calamagrostis villosa*) were 723 and 288 g.m⁻² in the PL and CT catchments, respectively, in 2004 (SVOBODA et al. 2006). At the same time, mature spruce forest (*Picea abies*) covered ~90% of the PL catchment (the rest was formed by steep slopes covered with grass and fern) and almost all area of the CT catchment.

Changes in the areal densities of healthy and dead (bark beetle attacked or broken) trees in the catchments during the study were calculated using colour aerial photographs (scales of 1 : 5000–7000), prepared by Argus Geo System Ltd. (Hradec Králové), Geodis Ltd. (Brno), and Georeal Ltd. (Plzeň) in 2000 and 2011. In 2000, dead forest occupied <3% of the PL catchment in small patches distributed over the whole catchment. The PL forest has been damaged by a bark beetle (*Ips typographus*) outbreak since the summer of 2004 (northwest part with the PL-I and PL-II sub-catchments) and 2006 (the rest of the catchment), and most of trees died within 2–3 years of the plot infestation. The trees lost most needles during first several months after the outbreak. Then, they have been continuously losing twigs, bark, and branches until the end of this study. Dead trees were continuously broken by winds, and >35% of the original trees was already broken in 2011. In the same year, 93% of the PL forest lost >80% of its original healthy trees (Fig. 1A). All dead biomass was left in the PL catchment.

The CT forest was almost intact in 2000 and was affected by windthrows in 2007 and 2008, which broke most of the trees along the south-western ridge of the catchment, i.e., in the upper parts of CT-IV to CT-VII sub-catchments (Fig. 1B). The only forest management practice used to deal with the damaged stands was bark removing from dead trees, and the most of dead biomass remained in the catchment. Other relatively small patches with broken trees and the following bark beetle outbreak occurred in the northern part and throughout the whole CT catchment in 2007–2011. Altogether, the total area of damaged forest (with >50% dead trees) in the CT catchment increased from ~4% to 18% during 2000–2011.

Sampling and analyses

Tributaries were sampled in usually three-week intervals (more frequently during snow-melt period) from November 1998 to October 2012. Samples were taken near the inlets to the lakes, except for subsurface tributaries that were sampled in a shallow artificial well (PL-IV, since autumn 1999) and in a small natural cave (P-III during 1998–2001). The water discharge of surface tributaries was estimated by means of a stop-watch and bucket method. In sub-catchments containing several tributaries in close proximity (PL-I, PL-II, CT-IV, and CT-VII), an integrated sample was taken with sample volumes proportional to the discharge of the individual streams. Samples were immediately filtered through a 40- μm polyamide sieve to remove coarse particles re-suspended from the streambed during sampling.

In the laboratory, samples were filtered with either membrane filters (pore size of 0.45 μm) for the determination of ions and dissolved reactive silica, or with glass-fiber filters (pore size of 0.4 μm) for other analyses, except for samples for pH, acid neutralizing capacity (ANC, determined by Gran titration), and total concentrations of aluminium (Al_T), phosphorus (TP), carbon, and nitrogen, which were not filtered beyond the field pre-filter. DOC was analyzed with a TOC 5000A analyzer (Shimadzu). Concentration of particulate organic C (POC) was calculated as the difference between concentrations of total organic C (TOC) and DOC, analyzed with a TOC/TN analyzers (Table 1) for the non-filtered samples and filtrate, respectively. Dissolved reactive P (DRP) was determined by the molybdate method (MURPHY & RILEY 1962). When the DRP concentration was below the detection limit of 0.05 $\mu\text{mol.l}^{-1}$, a half of this value was used in subsequent data evaluation. TP and dissolved P (DP) were determined by perchloric acid digestion and the molybdate method according to KOPÁČEK & HEJZLAR (1993), but samples were fourfold concentrated by evaporation (with perchloric acid at $\sim 100^\circ\text{C}$ prior digestion) to obtain a detection limit of 0.015 $\mu\text{mol.l}^{-1}$. Since 2001, DP and DRP were not determined in the CT inlets (except for CT-II and CT-VII) due to low TP concentrations. Dissolved reactive silica (Si) was determined by the molybdate method by GOLTERMAN & CLYMO (1969). Total and dissolved organic N (TON and DON; the difference between the respective Kjeldahl N and $\text{NH}_4\text{-N}$) were determined by Kjeldahl digestion according to PROCHÁZKOVÁ (1960), with 75 ml of samples previously evaporated to obtain a detection limit of $\sim 2 \mu\text{mol.l}^{-1}$. This method was used for PL-I, PL-IV, CT-II, and CT-VII throughout the study and for other tributaries during 1997–2001. In 2003–2012, TON concentrations were calculated as the difference between total N (TN, determined by the TOC/TN analyzers) and inorganic N. In this calculation, inorganic N was the sum of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$, whereas $\text{NO}_2\text{-N}$ (typically $< 1\%$ of $\text{NO}_3\text{-N}$) was neglected. Concentrations of NH_4^+ , NO_3^- and other ions (Cl^- , SO_4^{2-} , F^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+) were determined by ion chromatography (Table 1).

Fractionation of aluminium according to DRISCOLL (1984), i.e. Al_T , dissolved Al, and non-labile Al, were analyzed in non-filtered samples, filtered samples, and cation exchange treated samples after their filtration, respectively, using the method by DOUGAN & WILSON (1974). We assumed that concentrations of organically bound Al (Al_o) was equal to non-labile Al. Concentration of ionic positively charged Al species (Al_i) was the difference between dissolved Al and Al_o concentrations. The respective Fe fractions (Fe_T , Fe_i , and Fe_o) were obtained analogously to Al, and their concentrations were determined by the thiocyanate colorimetric method after sample evaporation and digestion with perchloric acid (KOPÁČEK et al. 2001c). Equivalent concentrations of Al_i and Fe_i (Al_i^{n+} and Fe_i^{m+} , $\mu\text{eq.l}^{-1}$) were obtained from their molar concentrations and the average charges of Al hydroxocomplexes (n) and Fe hydroxocomplexes (m), respectively. The n and m values were estimated from the theoretical distribution of ionization fractions of aqueous Al and Fe hydroxocomplexes, respectively, at

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

Abbreviation	Explanation	Assessment
ANC	Acid neutralizing capacity	Gran titration (Tacussel in 1997–2011, Radiometer in 2012).
H ⁺ (pH)	Proton concentration	pH electrode (combined, Radiometer)
NH ₄ ⁺ , Ca ²⁺ , Mg ²⁺ , Na ⁺ , K ⁺	Major cations	Ion chromatography (Thermo Separation Products in 1997–2000, Dionex IC25 in 2001–2011, Dionex ICF-3000 in 2012).
NO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻ , F ⁻	Major anions	Ion chromatography (Thermo Separation Products in 1997–2000, Dionex IC25 in 2001–2011, Dionex ICF-3000 in 2012).
Si	Dissolved silica	Molybdate method (GOLTERMAN & CLYMO 1969).
Al _p , Al _i , Al _o	Total, ionic, and organically bound Al	Fractionation according to DRISCOLL (1984), colorimetry (DOUGAN & WILSON 1974) throughout 1997–2012. Al _i = dissolved Al – Al _o .
Fe _p , Fe _i , Fe _o	Total, ionic, and organically bound Fe	Fractionation according to DRISCOLL (1984), colorimetry (KOPÁČEK et al. 2001c) throughout 1997–2012. Fe _i = dissolved Fe – Fe _o .
DOC	Dissolved organic C	Analyzer TOC 5000A (Shimadzu).
POC	Particulate organic C	Difference between total and dissolved C, analyzed with a TOC/TN analyzer (Formacs in 2002–2009 and Elementar in 2010–2012).
TON	Total organic N	Kjeldahl digestion (PROCHÁZKOVÁ 1960) for PL-I, PL-IV, CT-II and CT-VII in 1997–2012, for other tributaries in 1997–2002, then TOC/TN analyzer. ¹⁾
DON	Dissolved organic N	
PON	Particulate N	PON = TON – DON.
TP	Total P	Sample pre-concentration by evaporation, HClO ₄ digestion, molybdate method (KOPÁČEK & HEJZLAR 1993).
DP	Dissolved P	
PP	Particulate P	PP = TP – DP.
DRP	Dissolved reactive P	Molybdate method (MURPHY & RILEY 1962).

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

the sample pH (STUMM & MORGAN 1981), neglecting F⁻ and SO₄²⁻ complexes (KOPÁČEK et al. 2000b). Concentrations of organic acid anions (A⁻, µeq.l⁻¹) were obtained independently of ionic composition, from concentrations of DOC, Al_o, Fe_o, and pH (KOPÁČEK et al. 2000b).

The reliability of the analytical results was controlled by means of an ionic balance approach, a comparison between measured and calculated conductivities (KOPÁČEK et al. 2000b), and a standard sample (a frozen subsample of water annually taken from CT-II), which was melted and assayed with each series of samples. The differences between the sum of cations (including Al_i^{nt} and Fe_i^{mt}) and the sum of anions (including A⁻) was <±4% of the total ionic concentration in the individual samples. At higher differences, samples were re-analyzed.

Annual average compositions of surface tributaries were calculated for individual hydrological years (from November 1 to October 31) as discharge and period-weighted mean concentrations (*c*):

$$c = \frac{\sum c_i \cdot Q_i \cdot t_i}{\sum Q_i \cdot t_i} \quad (1)$$

where Q_i is water discharge, c_i is concentration of a water component during the sampling i (the average annual number of samplings is 17), and t_i is time period given as the sum of halves of intervals between the sampling and the previous one and between the sampling and the next one. In this calculation, we assumed that the actual discharge and component concentrations were representative for the whole period. For subsurface tributaries, with no data on discharge, annual average concentrations were calculated as period-weighted means. Linear regression analysis was used to estimate significances of temporal trends in annual average concentrations of water constituents.

Data on trends in chemical composition of bulk precipitation and throughfall in the PL and CT catchments (Appendix 1) were derived from KOPÁČEK et al. (2013). Throughfall deposition was calculated as average for low and high elevation plots in the CT and PL catchments. For original data, location of individual plots, sampling frequency and other details see KOPÁČEK et al. (2013).

RESULTS

Only four tributaries (PL-VI, CT-II, CT-VI, and CT-VII) were permanent in the PL and CT catchments, while all other tributaries were dry at least once during the study. Perennial tributaries (usually dry several times per year) were PL-II, CT-I, and CT-III. Stream water discharge varied within 0–80 l.s⁻¹, with highest values in CT-II, usually occurring during snowmelt. Average discharge of surface tributaries varied from 0.7 l.s⁻¹ in CT-I to 11.6 l.s⁻¹ in CT-II (Table 2). All samples of stream water had a depleted carbonate buffering system and were strongly acidic. Their pH varied between 3.9 and 4.9 for individual samples, with the lowest averages of 4.11 for tributaries CT-III and IV and the highest average value of 4.73 for PL-IV (Table 2). Annual average concentrations of water constituents are for all tributaries summarized in Appendix 2. Major ions and nutrients exhibited the following trends:

Annual average concentrations of SO₄²⁻ were 40–70 μmol.l⁻¹ during 1998–2000 and sulphate was the major anion in all tributaries (Fig. 2), contributing 35–66% to the total sum of anions on an equivalent basis, including organic acid anions. Concentrations of SO₄²⁻ exhibited monotonously decreasing trends in all tributaries throughout the study (Fig. 2C, D), with slopes varying between –1.6 and –3.0 μmol.l⁻¹.yr⁻¹ (Table 3).

Annual average concentrations of nitrate varied within 18–87 μmol.l⁻¹ prior to 2004 and contributed 8–38% to the total pools of anions on an equivalent basis. Nitrate was the dominant anion (42–48%) in all tributaries (except for CT-I) in 2004, due to its elevated leaching from soils, following exceptionally dry and hot summer 2003 (KOPÁČEK et al. 2009a). Since then, NO₃⁻ has become the most important anion in all PL tributaries, with annual average concentrations varying between 90 and 234 μmol.l⁻¹ (Fig. 2D) that exceeded the sum of NH₄⁺ and NO₃⁻ concentrations in throughfall deposition (Appendix 1). In the CT tributaries, NO₃⁻ concentrations decreased back to values typical for the 1998–2003 period during 2005–2007, and have increased again in most tributaries since 2008 (Fig. 2C).

Concentrations of base cations and their trends differed between catchments and individual tributaries (Fig. 3). The most pronounced increase was observed for K⁺ concentrations in the PL tributaries (especially PL-I and II), while concentrations of this cation remained stable in the CT tributaries (Fig. 3A,B), except for a significant increase in CT-V (Table 3). A similar pattern was observed for Mg²⁺ (Fig. 3C,D), but the steepest increase occurred in PL-IV among all PL tributaries (Table 3). The Mg²⁺ concentrations increased also in CT-V and CT-VI (Table 3). Concentrations of Ca²⁺ decreased in most of the CT tributaries similarly to throughfall (Appendix 1), while increased in the PL catchment (Fig. 3E,F), with the steepest trend in PL-IV (Table 3). Concentrations of Na⁺ generally decreased in both

Table 2. Average composition (arithmetical average of annual average discharge and period-weighted mean concentrations) of tributaries to Plešné (PL) and Čertovo (CT) lakes prior to (1998–2004) and after (2005–2012) bark beetle infestation in the PL catchment. Units are in $\mu\text{mol}\cdot\text{l}^{-1}$, except for discharge (Q , $\text{l}\cdot\text{s}^{-1}$) and pH [$\text{pH} = -\log(\text{mean } \text{H}^+ \text{ concentration})$]; ND = not determined.

Inlet	PL-I		PL-II		PL-III		PL-III		PL-IV		PL-IV		CT-I		CT-II		CT-III		CT-IV		CT-V		CT-VI		CT-VII	
	1998–2004	2005–2012	1998–2004	2005–2012	1998–2004	2005–2012	1998–2004	2005–2012	1998–2004	2005–2012	1998–2004	2005–2012	1998–2004	2005–2012	1998–2004	2005–2012	1998–2004	2005–2012	1998–2004	2005–2012	1998–2004	2005–2012	1998–2004	2005–2012	1998–2004	2005–2012
Q	2.0	2.1	1.4	1.4	3.5	4.4	ND	ND	ND	ND	ND	ND	0.7	11.6	1.6	2.3	0.8	1.9	2.2							
pH	4.23	4.13	4.32	4.19	4.58	4.42	4.73	4.72	4.73	4.72	4.72	4.72	4.31	4.26	4.11	4.11	4.15	4.49	4.51							
H ⁺	60	75	48	65	27	38	17	19	17	19	19	19	49	55	78	78	71	33	31							
Ca ²⁺	15	23	17	25	28	28	37	44	37	44	37	44	9	11	9	10	10	16	14							
Mg ²⁺	6	9	6	9	9	11	13	16	13	16	13	16	12	14	13	13	15	21	16							
Na ⁺	47	39	46	42	48	41	52	53	52	53	53	53	34	31	29	28	30	40	39							
K ⁺	9	32	8	28	10	18	12	16	12	16	16	16	8	8	7	8	9	10	11							
NH ₄ ⁺	1.6	1.0	1.4	0.6	1.1	0.7	1.2	0.5	1.2	0.5	1.2	0.5	1.0	0.7	0.6	0.8	0.8	0.8	0.7							
NO ₃ ⁻	56	143	59	155	77	140	99	171	99	171	171	171	32	70	67	78	79	76	63							
SO ₄ ²⁻	41	25	40	27	50	29	56	40	56	40	40	40	41	38	44	42	45	45	37							
Cl ⁻	15	14	13	14	13	14	13	15	13	15	15	15	16	16	15	16	17	18	18							
F ⁻	3	4	4	3	5	4	7	7	7	7	7	7	2	2	2	2	2	2	2							
DOC	969	1101	726	793	309	455	139	148	139	148	148	148	474	508	718	662	524	199	248							
POC	10	19	18	25	10	25	18	28	18	28	28	28	7	11	8	17	17	16	13							
TON	27	44	21	34	16	24	11	10	11	10	10	10	14	21	21	20	21	15	14							
DON	26	42	20	32	15	23	10	9	10	9	9	9	12	19	20	19	20	14	13							
TP	0.89	1.53	0.88	1.23	0.45	0.68	0.19	0.18	0.19	0.18	0.18	0.18	0.14	0.13	0.15	0.14	0.09	0.07	0.10							
DP	0.86	1.44	0.85	1.19	0.41	0.62	0.14	0.14	0.14	0.14	0.14	0.14	ND	0.09	ND	ND	ND	ND	0.07							
DRP	0.68	1.25	0.73	1.04	0.34	0.56	0.09	0.10	0.09	0.10	0.10	0.10	ND	0.02	ND	ND	ND	ND	0.02							
Si	140	127	134	124	142	117	143	135	143	135	135	135	76	71	72	67	67	85	91							
Al _T	31	33	29	33	27	32	27	34	27	34	34	34	11	20	22	24	24	18	15							
Al _I	17	20	17	23	22	25	23	31	23	31	31	31	6	15	15	16	17	15	11							
Al _O	14.5	12.1	11.4	9.6	5.4	6.4	2.6	2.0	2.6	2.0	2.0	4.8	3.7	3.0	3.6	3.2	2.3	2.6	3.4							
Fe _T	2.2	2.4	1.7	1.7	0.7	1.0	0.3	0.3	0.3	0.3	0.3	3.7	3.0	3.0	3.6	3.2	2.3	0.5	1.0							
Fe _I	0.6	0.7	0.5	0.6	0.2	0.3	<0.05	<0.05	<0.05	<0.05	<0.05	1.1	1.0	1.0	1.2	1.2	0.8	0.2	0.4							
Fe _O	1.6	1.6	1.2	1.1	0.5	0.6	0.2	0.2	0.2	0.2	0.2	2.6	1.8	2.4	2.0	2.0	1.4	0.3	0.6							

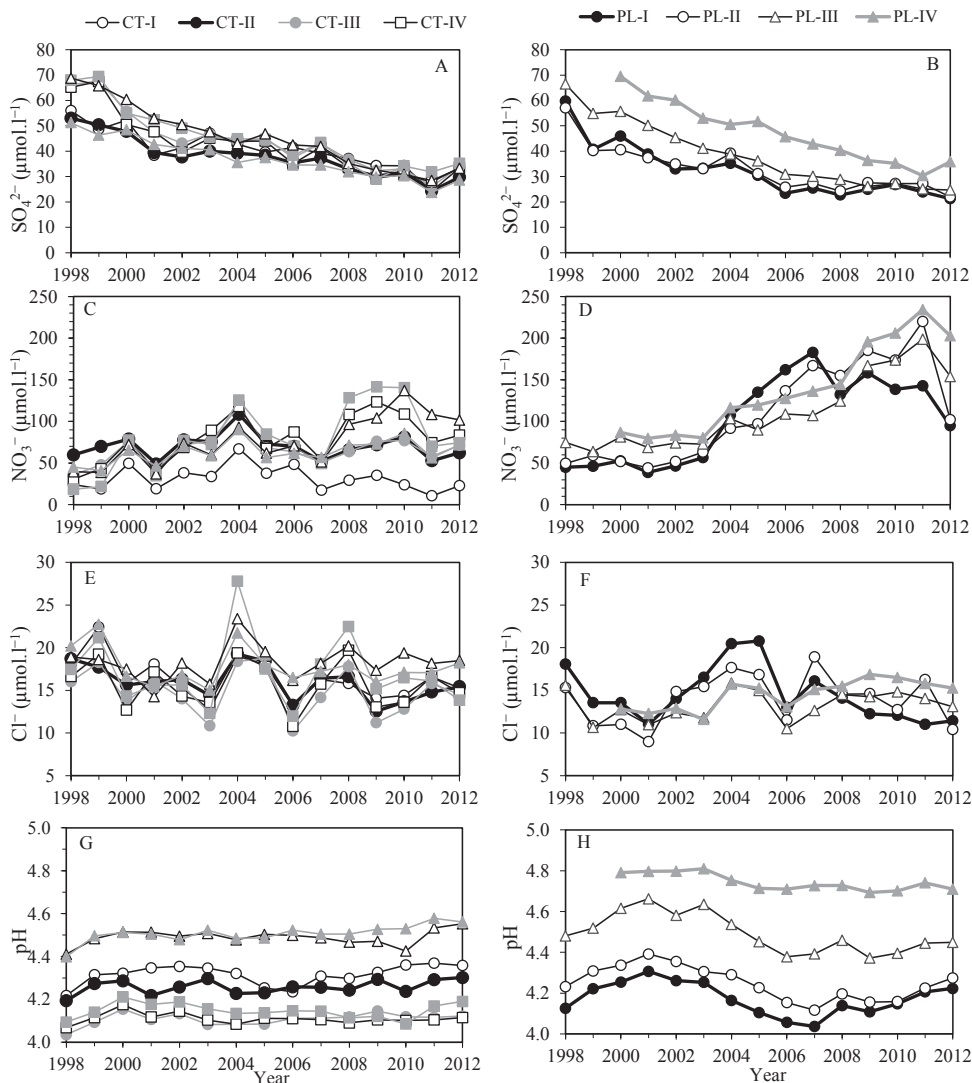


Fig. 2. Time series of annual average SO_4^{2-} , NO_3^- , and Cl^- concentrations, and pH values in tributaries to Čertovo (left: CT-I–VII) and Plešné (right: PL-I–IV) lakes. For location of tributaries see Fig. 1.

catchments during the study, but with significant trends only in five of eleven tributaries (Table 3, Appendix 2). In contrast to the differing trends in base cations in lake tributaries, their concentrations consistently decreased in throughfall throughout the study (Appendix 1; KOPÁČEK et al. 2013).

Concentrations of Al_1 consistently decreased in all CT tributaries, but increased in the PL tributaries (Fig. 3G,H), even though these changes exhibited significant trend only in three of them (Table 3). In contrast to Al_1 , concentrations of Al_0 decreased in all CT and PL tributaries, despite stable Fe_0 values and increasing DOC concentrations (Table 3). These changes resulted in significantly decreasing molar ratios of the sum of organically bound Al and Fe

Table 3. Slopes of linear regression between time (1998–2012) and annual average concentrations of water constituents in tributaries to Plešné (PL) and Čertovo (CT) lakes. Units are in $\mu\text{mol.l}^{-1}\cdot\text{yr}^{-1}$ for water constituents and yr^{-1} for their molar ratios. Asterisks denote significant trends: *, $p<0.05$; **, $p<0.01$, and ***, $p<0.001$).

	PL-I	PL-II	PL-III	PL-IV	CT-I	CT-II	CT-III	CT-IV	CT-V	CT-VI	CT-VII
NO_3^-	8.6**	11.0***	8.7***	13.1***	-0.7	-0.4	1.1	3.8*	5.3*	5.3***	1.6*
SO_4^{2-}	-2.1***	-1.7***	-2.8***	-3.0***	-1.6***	-1.6***	-2.4***	-2.4***	-2.5***	-2.7***	-1.7***
Cl^-	-0.3	0.1	0.1	0.3**	-0.3	-0.2*	-0.1	-0.1	-0.1	0.1	-0.1
H^+	0.9	1.4**	1.0**	0.3***	-0.4	-0.4	-0.5	0.2	0.1	-0.2	-0.5**
Ca^{2+}	0.8***	1.0***	0.2	1.3***	-0.4*	-0.4***	-0.2**	-0.1	0.1	0.0	-0.1
Mg^{2+}	0.4***	0.4***	0.3**	0.6***	-0.3*	-0.2	-0.1	0.1	0.3	0.3*	0.0
Na^+	-0.9*	-0.4	-0.7**	0.0	-0.4*	-0.4*	-0.3	-0.3	-0.2	-0.2	-0.5*
K^+	2.6***	2.4***	1.2***	0.9***	-0.1	-0.1	0.0	0.2	0.5**	0.1	0.1
Al_1	0.3	0.6	0.5	1.4***	-0.3**	-0.6***	-0.5**	-0.2	-0.2	-0.3	-0.3
Al_0	-0.31***	-0.29***	0.00	-0.11*	-0.10	-0.14	-0.23*	-0.23**	-0.19**	-0.10**	-0.14**
Fe_0	0.004	-0.012	0.008	-0.006	-0.011	0.022	0.019	0.025	0.011	-0.004	0.001
Si	-0.9	-0.2	-2.4**	-1.1*	-0.4	-0.3	-0.6	-0.6	-0.5	-0.2	-0.5
DOC	15.4	5.8	13.6**	1.6	10.1	6.8	8.0	7.1	4.3	-0.3	1.5
A^-	1.5*	0.8	0.9**	0.4***	1.0	0.7	1.0	0.8	0.6	0.2	0.4
DON	1.8***	1.3**	1.1*	0.0	0.2	0.5*	0.4	0.8	1.1*	0.8*	0.4*
TP	0.072***	0.034**	0.022***	0.001	0.003	<0.001	0.007	0.007	0.006	<0.001	<0.001
DOC:DON	-1.2**	-1.1*	-0.2	0.3	1.0	0.0	0.6	-0.1	-0.7	-0.6*	-0.2
$(\text{Al}_0 + \text{Fe}_0):\text{DOC}$	-0.0005*	-0.0005**	-0.0005*	-0.0010**	-0.0005*	-0.0004*	-0.0004*	-0.0004*	-0.0004*	-0.0005*	-0.0006**
DOC:DP ¹⁾	-4.1***	-2.0**	-4	3	5	59	-98	-68	-175*	-20	28

¹⁾DOC:DP for the PL tributaries and DOC:TP for the CT tributaries

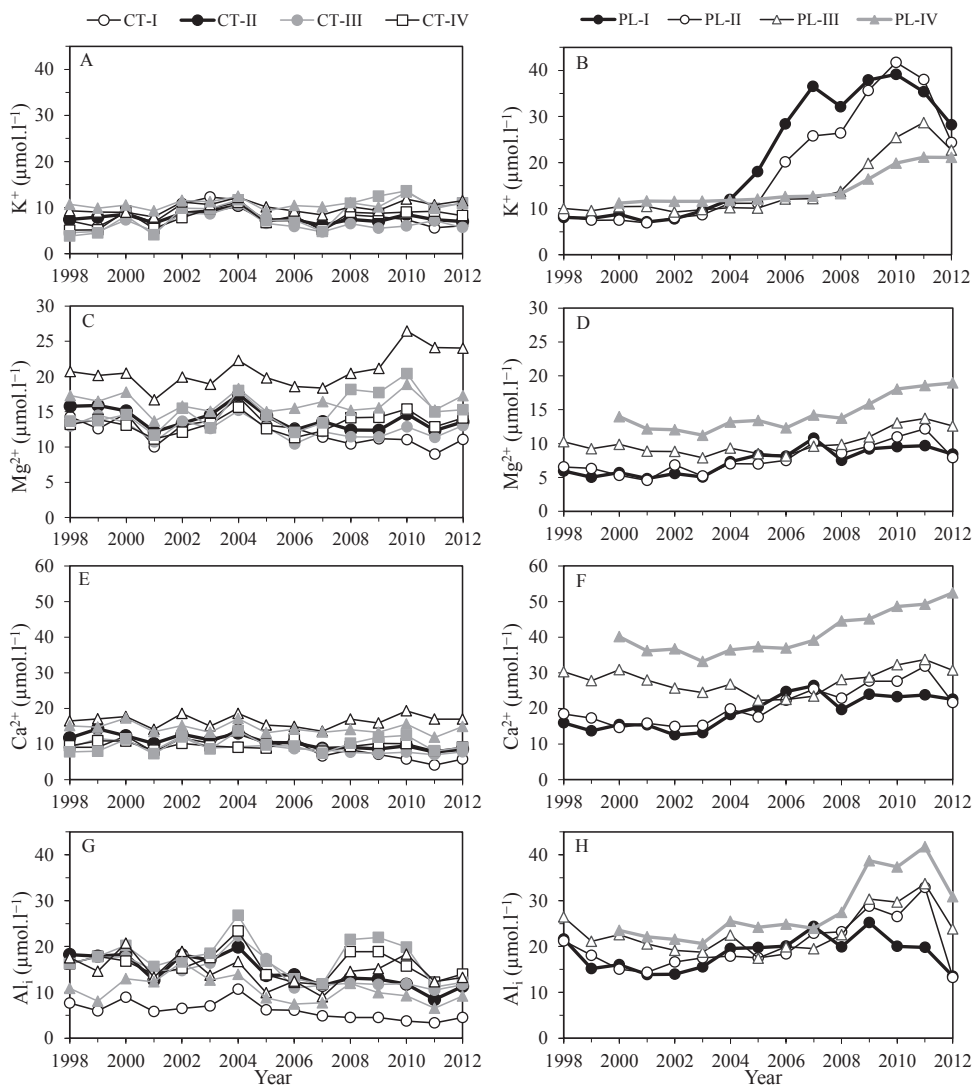


Fig. 3. Time series of annual average concentrations of K^+ , Ca^{2+} , Mg^{2+} and ionic aluminium (Al_I) in tributaries to Čertovo (left: CT-I–VII) and Plešné (right: PL-I–IV) lakes. For location of tributaries see Fig. 1.

to DOC concentrations [$(Al_I + Fe_o) : DOC$; Table 3] from 0.013–0.019 during 1998–2001 to 0.006–0.013 during 2009–2012.

Contrary to increasing Si concentrations in the Bohemian Forest lakes reported by VESELÝ et al. (2005), we observed stable or decreasing (PL-III and IV) concentrations of dissolved Si in all PL and CT tributaries throughout 1998–2012 (Table 3, Appendix 2).

Phosphorus and organic C and N were dominated by dissolved forms, with annual average concentrations of DP, DON and DOC representing 66–98%, 89–97%, and 88–99% of TP, TON, and TOC, respectively (Table 2). Concentrations of DRP were mostly below detection limit in the CT tributaries, while dominated (66–90%) the DP pool in the PL tributaries. The

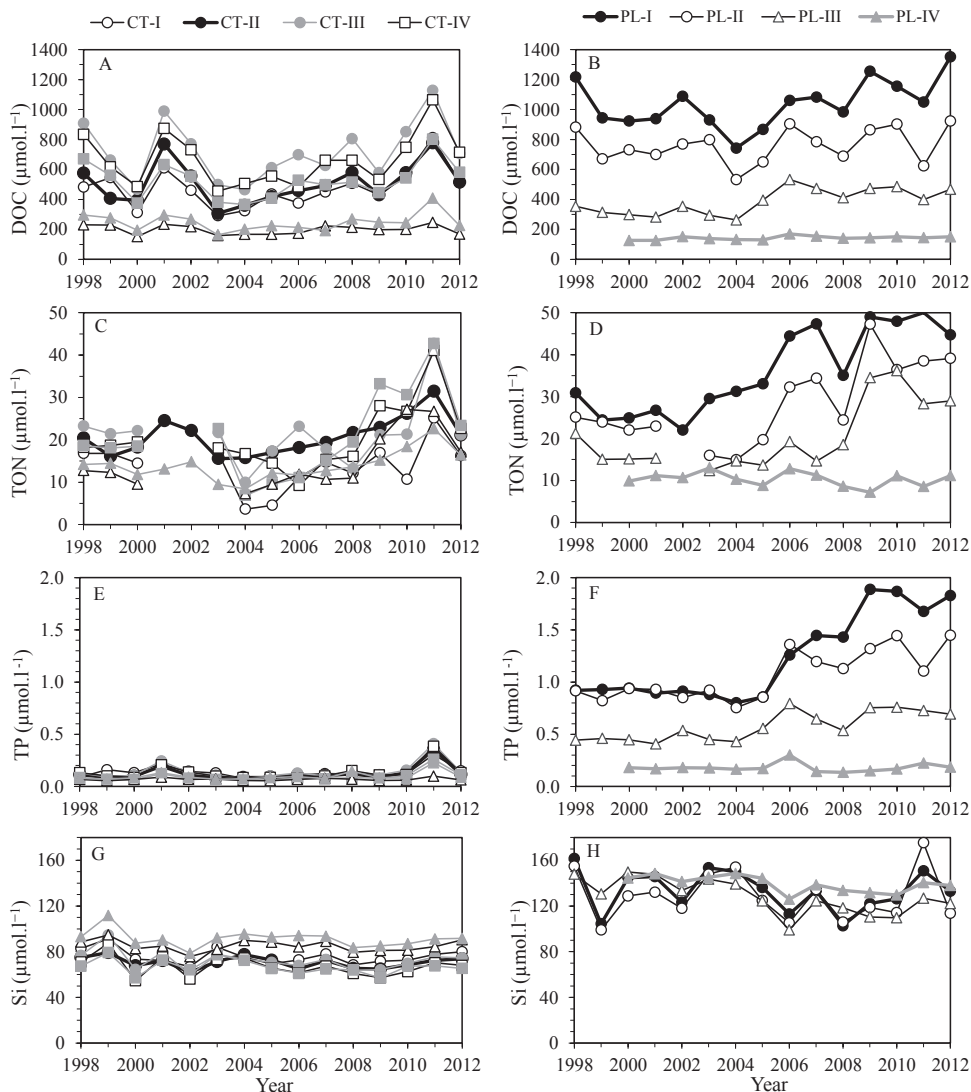


Fig. 4. Time series of annual average concentrations of dissolved organic carbon (DOC), total organic nitrogen (TON), total phosphorus (TP), and dissolved silica (Si) in tributaries to Čertovo (left: CT-I–VII) and Plešné (right: PL-I–IV) lakes. For location of tributaries see Fig. 1.

highest DOC and TON concentrations were in PL-I and II and the lowest values in PL-IV, CT-VI, and CT-VII. PL-I and PL-II also had the highest TP concentrations, with annual averages ranging from 0.75 to 1.89 $\mu\text{mol.l}^{-1}$ (Appendix 2). Trends in DOC, TON and TP concentrations differed between both catchments and individual tributaries (Fig. 4). Even though the DOC concentrations have been increasing in most tributaries (except for PL-IV, CT-VI, and CT-VII) since 2003–2004 (Fig. 4A, B), these trends were not significant over the whole 1998–2012 period (Table 3). In contrast, TON and DON concentrations significantly increased in most tributaries except for PL-IV (Fig. 4C, D). The greatest spatial difference

in the trends of nutrient leaching occurred for phosphorus. Concentrations of all P forms increased in most PL tributaries (PL-I, II, and III) while remained stable in the CT tributaries (Appendix 2).

DISCUSSION

Chemical composition of lake tributaries and long-term trends in concentrations of their major ions and nutrients reflected three major variables: (1) differences in bedrock and soil composition and morphological characteristics of individual sub-catchments, (2) recovery from acidification due to reduced acidic deposition, and (3) effect of forest dieback on element cycling in soils.

Effect of catchment characteristics

Similarly to previous studies (KOPÁČEK & HEJZLAR 1998, KOPÁČEK et al. 2000a, KAŇA & KOPÁČEK 2006) our result showed that the PL tributaries had higher concentrations of Ca^{2+} , Na^+ , TP, and DRP, while lower Mg^{2+} than the CT tributaries (Table 2) due to their different bedrock. Granite in the PL catchment has higher content of P, Ca, and Na, while lower content of Mg than mica-schist in the CT catchment (KOPÁČEK et al. 2002a,b). Phosphate is more easily liberated from granite than from mica-schist at ambient soil pH, causing higher phosphate concentrations in the PL soil waters. Moreover, phosphate is less intensively retained in the PL than CT soils, which have higher content of Fe oxyhydroxides. The higher phosphate production by weathering and its lower retention on the soil adsorption phase thus result in higher DRP leaching from the PL than CT soils (KAŇA & KOPÁČEK 2006).

Morphological characteristics of individual sub-catchments affected predominately NO_3^- and DOC concentrations and Al speciation. Concentrations of NO_3^- and DOC exhibited an inverse spatial relationship. The tributaries draining sub-catchments with more wetter and organic rich soils (PL-I and II, CT-I) had lower NO_3^- and higher DOC concentrations than tributaries draining steep slopes and receiving high proportion of subsurface water (PL-III and IV, and CT-VI and VII). The streams with higher concentrations of strong acid anions (predominantly SO_4^{2-} and NO_3^-) had higher concentrations of Al_1 , while DOC rich waters had higher concentrations of Al_0 . The sum of SO_4^{2-} and NO_3^- concentrations explained 82% of the observed spatial variability in the average Al_1 concentrations in the PL and CT tributaries (Fig. 5A). DOC concentrations explained 90% of the average Al_0 concentrations in tributaries, with the average molar Al_0 :DOC ratio of 0.013 (Fig. 5B). This ratio was within a range typical for surface waters with pH between 4 and 5 (DRISCOLL & POSTEK 1995).

Effect of reduced acidic deposition on stream water chemistry

Emissions of SO_2 , NO_x , NH_3 have declined by approximately 90, 64, and 50% in the Czech Republic and by 86, 51 and 34% in central Europe, respectively, causing significant declines in atmospheric deposition of SO_4^{2-} , NO_3^- , and NH_4^+ in the Bohemian Forest (85, 60, and 28%, respectively) since the 1980s (KOPÁČEK & HRUŠKA 2010, KOPÁČEK et al. 2011, 2013). In the same period, HCl emission originating from coal combustion (EVANS et al. 2011) and industrial sources declined by ~50% and atmospheric deposition of Cl^- decreased in the Czech Republic (VESELÝ et al. 2002). Trends in chemical composition of precipitation and throughfall in the PL and CT catchments (Appendix 1) were not as steep during 1998–2012 as the longer trends since the early 1990s (KOPÁČEK & HRUŠKA 2010, KOPÁČEK et al. 2011), but still showed significant declines in deposition of SO_4^{2-} , Cl^- , NO_3^- , H^+ , and base cations (KOPÁČEK et al. 2013). The reduced atmospheric pollution resulted in a rapid decline in concentrations of strong acid anions (SO_4^{2-} , NO_3^- , and Cl^-) in all Bohemian Forest lakes, with the

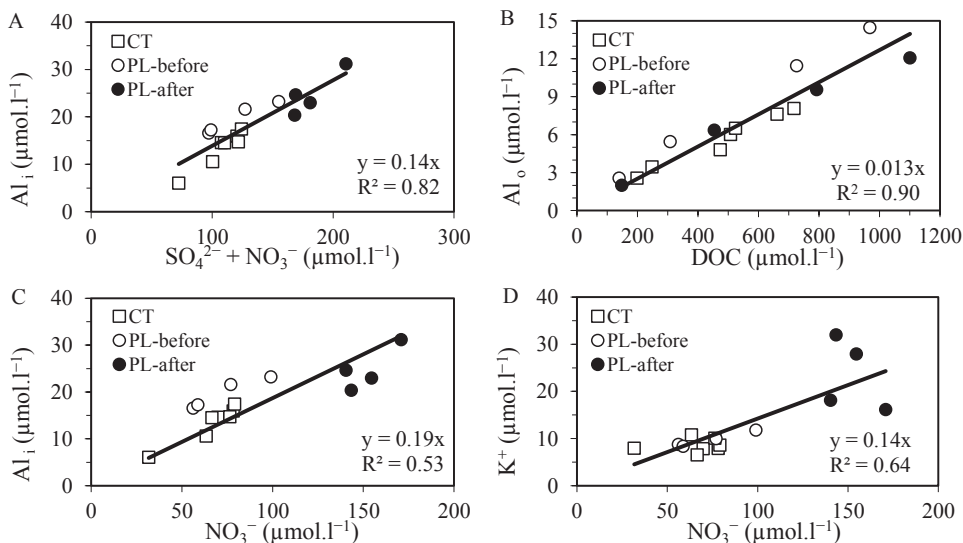


Fig. 5. Relationships between average concentrations of (A) Al_1 vs. $SO_4^{2-} + NO_3^-$, (B) Al_0 vs. DOC, (C) Al_1 vs. NO_3^- , and (D) K^+ vs. NO_3^- in 7 tributaries to the Čertovo (CT, the 1997–2012 averages) and 4 tributaries to the Plešné (PL) lakes before (PL-before, 1998–2004) and after (PL-after, 2005–2012) forest dieback by bark beetle infestation. Solid lines are the linear regression lines calculated for all data; $p < 0.001$ for all relationships except for Al_1 vs. NO_3^- ($p < 0.01$).

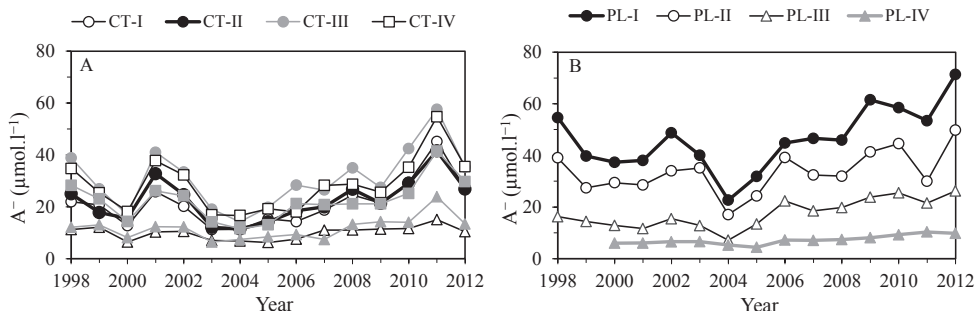


Fig. 6. Time series of annual average concentrations of organic acid anions (A^-) in tributaries to Čertovo (A: CT-I–VII) and Plešné (B: PL-I–IV) lakes. For location of tributaries see Fig. 1.

steepest trends in the 1990s (VESELÝ et al. 1998, MAJER et al. 2003). The decline in concentrations of strong acid anions in surface waters was compensated for by decreases in concentrations of Al_1 , Ca^{2+} , Mg^{2+} and H^+ and increasing concentrations of organic acid anions (e.g., KOPÁČEK et al. 1998, OULEHLE et al. 2013a). The increase in concentrations of organic acid anions may result from elevated leaching of DOC, accompanying reduction in SO_4^{2-} deposition (MONTEITH et al. 2007), as well as from higher dissociation of weak organic acids due to increasing pH of soil and surface waters (e.g., EVANS et al. 2012, OULEHLE et al. 2013b). Concentrations of A^- have increased especially since 2004 (Fig. 6A, B) in the PL and CT catchments, similarly to the DOC concentrations (Fig. 4A, B). Consequently, we assume that the DOC leaching rather than pH change was the principal factor responsible for trends in A^- concentrations in the lake inlets during the study.

Tributaries to Plešné and Čertovo lakes have exhibited clear signs of chemical recovery from atmospheric acidification, manifested predominantly by significantly decreasing concentrations of SO_4^{2-} (Table 3). The major reduction in SO_2 emissions and SO_4^{2-} deposition occurred in the 1990s (KOPÁČEK & HRUŠKA 2010), and SO_4^{2-} leaching has exceeded the atmospheric SO_4^{2-} inputs in the Bohemian Forest catchments since that time (KOPÁČEK et al. 2009a). Sulphate desorption from Al and Fe oxyhydroxides (KAŇA & KOPÁČEK 2005) and its formation by microbial oxidation of reduced S forms have currently become the dominant SO_4^{2-} sources in the Bohemian Forest soils. High pools of reduced S (organically bound S and sulphides) accumulated in central European forest soils during the 20th century due to microbial reduction of atmospherically deposited SO_4^{2-} (NOVÁK et al. 2000, 2005). Results of dynamic modelling suggest that this accumulated S will be responsible for the elevated SO_4^{2-} leaching until about the middle of the 21st century (MAJER et al. 2003). The continuous steep decline in SO_4^{2-} concentrations in the Bohemian Forest tributaries during 1998–2012 (Fig. 2A,B) thus reflected both the continuous decline in atmospheric SO_4^{2-} deposition (KOPÁČEK et al. 2013) and depletion of soil S pools.

Other typical signs of chemical recovery from atmospheric acidification, such as decreasing concentrations of Cl^- , H^+ (increasing pH), Al_i , and base cations occurred in most tributaries at the beginning of this study and then persisted only in sub-catchments not affected by forest damage and dieback (Figs. 2, 3).

Effect of forest damage on stream water chemistry

Forest dieback due to bark beetle infestation in the PL catchment and damaged stands by windthrows in the CT-IV–VII sub-catchments (Fig. 1) interrupted or even reversed the ongoing trends in fresh water recovery from atmospheric acidification. The change was manifested by elevated NO_3^- leaching (Fig. 2C, D), accompanied by almost the same trends in Al_i concentrations (Fig. 3G, H) in both catchments, and by pH decline (Fig. 2H) and increased terrestrial losses of K^+ , Mg^{2+} and Ca^{2+} (Fig. 3 B, D, F) in the PL catchment.

Increases in NO_3^- concentrations in seepage and surface waters after forest damage are often described in the literature (e.g., DAHLGREN & DRISCOLL 1994, LIKENS & BORMANN 1995, HUBER 2004a,b). An extent of these changes, however, varies between sites due to the type of forest damage, status of N saturation or limitation of forest ecosystems, and their productivity. Nitrate concentrations are lower in the receiving surface waters (streams and lakes) than in seepage water, and in N-limited than in N-saturated sites. For example, PIIRAINEN et al. (2002) observed NO_3^- concentrations $<20 \mu\text{mol.l}^{-1}$ in N-limited Finish sites after their clear-cutting. In contrast, very high NO_3^- concentrations (with average concentrations up to $2750 \mu\text{mol.l}^{-1}$) occurred in soil water after clear-cutting in N-saturated Norway spruce stands at Höglwald in southern Bavaria (HUBER et al. 2004b). BERDÉN et al. (1997) observed that NO_3^- losses from Norway spruce stands in Sweden increased with amount of artificially added N in fertilizers prior to their clear-cut. In the PL catchment, annual average concentrations of NO_3^- did not exceed $240 \mu\text{mol.l}^{-1}$ (Fig. 2D), and the observed maximum concentrations were $<350 \mu\text{mol.l}^{-1}$ in individual samples of the PL tributaries. Even though the PL catchment belongs among N-saturated sites, these concentrations were lower than NO_3^- concentrations ($<500 \mu\text{mol.l}^{-1}$) reported in the stream water after clear-cutting Hubbard Brook Experimental Forest (DAHLGREN & DRISCOLL 1994). Similar differences in the intensity of ecosystem responses to natural forest dieback by bark beetle infestation versus clear-cut occurred also elsewhere (HUBER 2004a,b). Major reasons for these differences include more biomass remains on the site after the natural dieback, its longer-lasting input to soils from continuously decaying trees, and the shading effect of standing dead trees, which mitigates changes in air and soil temperature (HAIS & KUČERA 2008). These factors spread minerali-

zation and nitrification over a longer time. Consequently, the amplitude of NO_3^- losses from soils is lower but has longer duration (7–8 years) after natural forest diebacks than after clear-cuts, when higher NO_3^- losses usually occur for a shorter period (3–5 years) (CUMMINS & FARRELL 2003, HUBER 2004a,b, McHALE et al. 2007).

Chloride concentrations have significantly decreased by 31–55 % in the Bohemian Forest lakes since 1984 (OULEHLE et al. 2013a). In contrast, no significant trend in Cl^- was observed in our study due to a high year-to-year variability in the data. Elevated Cl^- concentrations occurred in 2004 in all tributaries, then in 2005 in the PL tributaries and in 2008 in the CT-V–VII tributaries (Fig. 2 E,F). KAUFFMAN et al. (2003) have shown that a large amount of mineralizable chlorine is stored in the soil organic matter and may be rapidly leached as Cl^- from the decaying litter and roots, and liberated from decomposing soil organic matter after forest damage. The elevated mineralization in dry and hot year 2003 thus could be responsible for the 2004 peak in Cl^- concentrations (similarly to NO_3^- , Fig. 2C, D), then for the 2005 peak, following bark beetle attack in the PL catchment, and the 2008 peak after wind-throw in the CT catchment. These data suggest that Cl^- may exhibit an important short-term biochemical cycle, even though it is assumed to behave conservatively over a longer term.

NODVIN et al. (1988) observed decreased SO_4^{2-} leaching from soils at Hubbard Brook after forest damage. This change was explained by increased SO_4^{2-} adsorption in soils acidified by elevated NO_3^- fluxes. KAŇA et al. (2013), however, observed increasing soil pH in the PL catchment associated with elevated input of base cations to soils from litter after the forest damage by bark beetle infestation. Moreover, the decline in SO_4^{2-} concentrations was similar for the PL and CT tributaries (Table 3), suggesting that the effect of NO_3^- on SO_4^{2-} leaching was probably lower in the PL catchment than at Hubbard Brook (NODVIN et al. 1988), and that was probably mostly related to the ecosystem recovery from acidification.

The elevated leaching of NO_3^- after the forest damage and continuously decreasing SO_4^{2-} concentrations due to the ecosystem recovery from acidification caused the increasing nitrate contribution to the sum of strong acid anions in the PL and CT tributaries. Consequently, leaching of the most available and mobile cations in soil solutions (Al_i and K^+) exhibited trends similar to NO_3^- . Nitrate concentrations explained 53% and 64% of the observed spatial variability in the average Al_i and K^+ concentrations, respectively, during the study (Fig. 5 C,D). Increases in Mg^{2+} and Ca^{2+} concentrations were less steep than those of Al_i and K^+ , but still NO_3^- concentrations explained 30% and 55%, respectively, of their observed spatial variability. Similarly, NO_3^- concentrations explained most of temporal variation in cations in the PL tributaries: 56–88% for Al_i , 79–91% for K^+ , 73–88% for Mg^{2+} , and 29–93% for Ca^{2+} .

Differences in an extent of leaching of individual base cations from damaged forests result from differences in their liberation from decomposing plant material (PUHE & ULRICH 2001, PALVIAINEN et al. 2004, BERG & McCLAUGHERTY 2008). In general, potassium is highly soluble and is rapidly released from plant material at early stages of decay. Additionally, the decrease in nutrient uptake due to forest dieback enhances K^+ concentrations in soil water and increases the risk of its losses from soils to surface waters (HUBER et al. 2004b). Concentrations of magnesium decrease slowly in the litter without the fast leaching typical for K^+ . The Ca^{2+} leaching is usually slow during the early phase of litter decomposition, but rapidly increases later when lignin degradation begins (BERG & McCLAUGHERTY 2008). Actually, the present trends in leaching of base cations from the PL and CT catchments suggest that the elevated Mg^{2+} and Ca^{2+} leaching may persist longer than the already decreasing Al_i and K^+ concentrations (Fig. 3).

Similar responses of terrestrial export of base cations and Al_i to the NO_3^- leaching following forest damages have been reported by numerous studies, e.g., in the clear-cut Hub-

bard Brook Experimental Forest (DAHLGREN & DRISCOLL 1994) and in the bark beetle attacked stands in the Bavarian Forest National Park (HUBER et al. 2004a). The most probable reason for the elevated Al_i leaching is its exchange for other cations on the soil sorption complex. Decomposition of fresh litter is accompanied by a rapid and high production of NH_4^+ and K^+ during the first few years after the forest damage (HUBER et al. 2004a, KAŇA et al. 2013). These ions probably replace Al^{3+} on the soil sorption complex in the early stages of litter decay, while Mg^{2+} and Ca^{2+} contribute to this process in following years (KAŇA et al. 2013). Another source of Al_i in soil water is dissolution of solid Al phases such as gibbsite and imogolite due to pH decline (MCHALE et al. 2007), which results from H^+ production during nitrification of liberated NH_4^+ . The pH decline, however, lasted only 3–4 years, and then pH started to increase again (Fig. 2H) due to effective neutralization of soil water acidity by base cations liberated from decaying plant tissue.

The leaching of DOC, DON, and TP increased immediately after forest dieback in all surface tributaries in the PL catchment (Fig. 4), and probably originated from the decomposing fresh litter on the forest floor and in the uppermost soil organic horizons as observed elsewhere (e.g., ADAMSON & HORNUNG 1990, AHTIAINEN & HUTTUNEN 1999, PIIRAINEN et al. 2002, 2004). A part of the DOC (and DON) increase was probably associated with catchment recovery from acidification, because similar trend occurred also in most of the CT tributaries, including those with negligible changes in forest damage (Fig. 4A,C). In the sub-catchments, with damaged forests, however, the DON concentrations increased more steeply than DOC, resulting in decreasing DOC:DON ratios (Table 3).

Depending on litter type and environmental conditions, concentrations of P may either consistently decrease or (similarly to N) increase in the decomposing plant material (PALVIAINEN et al. 2004, BERG & MCCLAUGHERTY 2008). Net element losses from litter compared to the living tree tissue in the Bohemian Forest suggested rapid P release (similar to that of K^+ and Mg^{2+}) during a relatively short period (in an order of months) after the litter was shed (KOPÁČEK et al. 2009b). Phosphorus liberated from plant residues is mostly in inorganic forms and is partially adsorbed on Fe and Al oxyhydroxides in soils (PIIRAINEN et al. 2004, KAŇA & KOPÁČEK 2006). The increased stream water concentrations of P, following forest damage, thus probably occur when water table rises and runoff originates from the organic soil horizons, enabling export of P associated with DOC, as well as phosphate liberated from Fe oxyhydroxides due to their dissolution during periodic anaerobic conditions. This mechanism could explain higher TP, DP, and DRP concentrations in the surface PL tributaries (PL-I and II) than in PL-III and IV, with higher proportion of subsurface waters. The PL-I and PL-II sub-catchments are covered with shallow organic soils developed on big boulders, with almost absent mineral horizons (KOPÁČEK et al. 2002a). Water draining these soils is thus organic and phosphorus rich (Table 2), because neither DOC nor phosphate are adsorbed in mineral soil horizons. In contrast, tributaries PL-III and IV drain higher proportion of deeper water that passes through mineral soil horizons, which can reduce the DOC and phosphate fluxes from the upper organic soils. Forest streams with shallow catchment soils and aquifers are thus (similarly to seepage water) sensitive indicators of soil chemical changes in damaged forest ecosystems.

Unexpected results

The decreasing Al_o concentrations and (Al_o+Fe_o) :DOC ratios in all tributaries (Table 3) remain unexplained. They have been decreasing in both catchments, regardless of different trends in stream water pH (general decrease in the PL and increase in the CT catchments, Fig. 2G, H). This result was surprising because no significant change in Al_o concentrations occurred during forest disturbance and recovery in the Catskill Mountains, USA (MCHALE

et al. 2007) even though other chemical changes in surface waters were similar to our study. There may be at least two possible explanations to this pattern: (i) A decreasing ability of DOC to bind Al to metal organic complexes due to gradual changes in DOC composition, and (ii) decreasing concentration of $\text{Al}(\text{SO}_4)_2^-$ complexes in water due to decreasing SO_4^{2-} concentrations. The $\text{Al}(\text{SO}_4)_2^-$ complexes form in water at high $\text{SO}_4^{2-}:\text{Al}_i$ ratios (DRISCOLL & POSTEK 1995). These complexes are not retained in the cation exchange resin during determination of non-labile Al due to their negative charge and would overestimate Al_o concentrations in this study.

Increasing DOC concentrations in most tributaries since 2003–2004 (Fig. 4A,B) have probably resulted from two major processes: (i) the continuing ecosystem recovery from acidification (MONTEITH et al. 2007), and (ii) from litter decomposition after the forest damage (HUBER et al. 2004a). We speculate that both processes may result in production and leaching of DOC with higher proportion of organic C with lower ability to complex Al than the original DOC at the beginning of this study. The changing quality of DOC is also suggested by decreasing DOC:DON ratios, especially in tributaries most affected by forest damage (Table 3).

VESELÝ et al. (2005) observed a significant (36–51%) increase in Si concentrations in the Bohemian Forest lakes during 1986–2004, which was explained by elevated Si release from their catchments due to decreasing acidic deposition and related changes in Al speciation and mobility in soils. Possible mechanisms combining both Al and Si cycles and potentially explaining increasing Si at decreasing Al concentrations in soil solutions include (i) higher solubility of aluminosilicates, (ii) faster dissolution of biogenic opal (phytoliths), and (iii) lower Si precipitation as secondary aluminosilicates (VESELÝ et al. 2005). During our study, Al_i concentrations decreased in the CT tributaries and increased in the PL tributaries (Fig. 3G, H). In concordance with the mechanism proposed by VESELÝ et al. (2005), the highest decrease in Si concentrations occurred in PL-III and IV (Table 3, Fig. 4H), i.e., in tributaries with the steepest Al_i increase. Concentrations of Si, however, also decreased in all CT tributaries (Table 3, Fig. 4G), despite the continuing decrease in Al_i concentrations. This disproportion suggests that besides the Al cycling some other mechanisms could be responsible for mobilization and terrestrial export of dissolved Si.

CONCLUSIONS

Forest damage by bark beetle infestation and windthrows delayed and in some indicators (NO_3^- , pH, Al_i) even temporarily reversed chemical recovery of the Bohemian Forest streams from atmospheric acidification. Other studies from this and similar regions (e.g., HUBER et al. 2004a,b, McHALE et al. 2007, VRBA et al. 2014), however, showed that the effect of forest disturbances had only temporal (3–8 years) effects, and the affected ecosystem rapidly returned to the trajectories of pre-disturbance chemical trends. Similarly, our results suggest that water chemistry has begun to recover in 2012, after the reaching maximum concentrations of NO_3^- (Fig. 2D), K^+ (Fig. 3B), and Al_i (Fig. 3H) in the PL tributaries in 2009–2011. In contrast, terrestrial losses of nutrients such as Mg^{2+} , Ca^{2+} and P, which are slowly liberated from decaying plant tissue (BERG & McCLAUGHERTY 2008) and effectively retained in soils after their liberation (KAŇA et al. 2013) still continue at high rates (Figs. 3D,F and 4F). The future trends in the leaching of these nutrients are thus difficult to predict on the basis of our present data. Because no biomass was removed from the damaged forest, leaching of these nutrients will probably last longer than in clear-cut areas but should cease within the next few years as in the Bavarian Forest National Park (HUBER et al. 2004a). In any case, a continuous liberation of base cations from dead biomass has a positive effect on increasing base

saturation of soils (KAŇA et al. 2013) and water composition, mitigating and rapidly reversing pH decline that occurred immediately after the forest dieback (Fig. 2H). Our preliminary results thus confirm most of the results and experience gained from bark beetle disturbance in the Bavarian Forest National Park (HUBER et al. 2004a).

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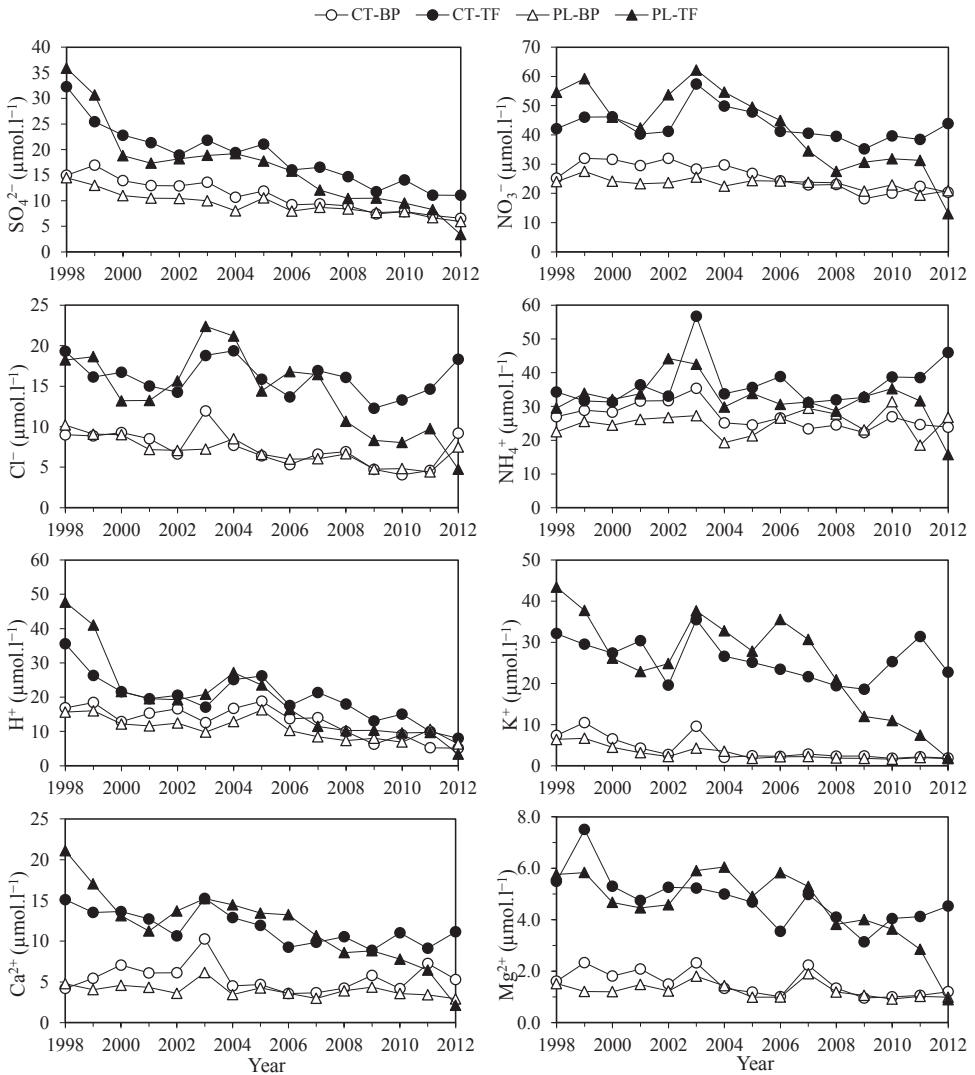
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Appendix 1. Chemical composition of bulk precipitation (BP) and throughfall (TF) in catchments of Plešné (PL) and Čertovo (CT) lakes. CT-TF and PL-TF data represent averages for low and high elevation plots in the CT and PL catchments, respectively. For original data and location of individual plots see KOPÁČEK et al. (2013).



Appendix 2. Annual average composition of inlets to Plešné (PL-I to PL-IV) and Čertovo (CT-I to CT-VII) lakes in the 1998–2012 hydrological years (November through October); pH = $-\log(\text{mean } \text{H}^+ \text{ concentration})$; ND = not determined.

Part	I/II	PL-I														
		1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Q	l.s ⁻¹	3.15	2.58	1.42	1.08	2.36	0.92	2.24	1.81	3.34	4.29	1.37	1.95	1.53	0.94	1.68
pH		4.13	4.22	4.25	4.31	4.26	4.25	4.16	4.10	4.06	4.04	4.14	4.11	4.15	4.21	4.22
H ⁺	μmol.l ⁻¹	74.9	60.1	55.8	49.4	54.8	55.9	68.6	78.7	87.8	92.0	72.7	78.0	71.1	62.2	59.8
Ca ²⁺	μmol.l ⁻¹	16.0	13.7	15.4	15.3	12.6	13.1	18.2	20.3	24.7	26.4	19.6	23.9	23.2	23.8	22.5
Mg ²⁺	μmol.l ⁻¹	5.9	5.0	5.7	4.8	5.6	5.1	7.3	8.3	8.2	10.8	7.5	9.2	9.5	9.7	8.4
Na ⁺	μmol.l ⁻¹	52.9	38.9	51.9	47.0	41.4	47.6	51.6	48.0	35.1	41.2	33.0	38.6	38.3	40.3	38.8
K ⁺	μmol.l ⁻¹	8.1	7.9	8.8	7.1	7.8	9.5	12.0	18.0	28.4	36.5	32.1	37.9	39.1	35.4	28.2
NH ₄ ⁺	μmol.l ⁻¹	0.55	1.28	2.75	0.62	2.73	1.92	1.60	0.62	2.06	1.87	0.66	1.39	0.65	0.18	0.79
NO ₃ ⁻	μmol.l ⁻¹	45	46	53	39	47	57	108	135	162	183	132	158	139	143	95
SO ₄ ²⁻	μmol.l ⁻¹	60	41	46	39	33	33	35	30	23	25	23	25	27	24	21
Cl ⁻	μmol.l ⁻¹	18	14	14	11	14	17	20	21	13	16	14	12	12	11	11
F ⁻	μmol.l ⁻¹	4.6	2.3	1.6	3.9	3.6	3.3	4.8	5.0	4.5	5.1	3.6	2.1	2.1	3.9	2.6
DOC	μmol.l ⁻¹	1217	945	924	938	1088	930	742	868	1061	1083	984	1255	1155	1050	1352
POC	μmol.l ⁻¹	ND	ND	ND	ND	ND	8	11	1	1	85	24	34	3	3	0
TON	μmol.l ⁻¹	31	24	25	27	22	29	31	33	44	47	35	49	48	50	45
DON	μmol.l ⁻¹	31	24	23	26	22	27	30	33	43	46	30	46	44	48	44
TP	μmol.l ⁻¹	ND	ND	0.94	0.89	0.91	0.88	0.80	0.86	1.26	1.45	1.43	1.89	1.87	1.68	1.83
DP	μmol.l ⁻¹	0.92	0.93	0.92	0.87	0.86	0.84	0.71	0.83	1.19	1.32	1.40	1.80	1.72	1.57	1.70
DRP	μmol.l ⁻¹	0.73	0.76	0.73	0.71	0.66	0.64	0.56	0.69	0.93	1.10	1.15	1.58	1.58	1.46	1.50
Si	μmol.l ⁻¹	162	104	145	146	123	154	150	136	113	133	103	122	126	151	133
Al _T	μmol.l ⁻¹	ND	ND	30	29	29	30	35	34	34	38	31	38	32	32	26
Al _I	μmol.l ⁻¹	22	15	16	14	14	16	20	20	20	24	20	25	20	20	14
Al ₀	μmol.l ⁻¹	15.2	13.6	14.5	14.8	14.7	13.7	14.9	14.1	13.5	13.1	11.0	12.4	10.7	10.1	11.6
Fe _T	μmol.l ⁻¹	ND	ND	2.5	2.6	2.4	1.7	2.1	2.2	2.0	2.4	2.3	2.5	2.5	2.5	3.1
Fe _I	μmol.l ⁻¹	0.6	0.6	0.8	0.6	0.6	0.3	0.4	0.4	0.2	0.7	0.6	1.1	0.9	0.8	0.8
Fe ₀	μmol.l ⁻¹	1.3	1.7	1.6	1.9	1.7	1.1	1.7	1.7	1.8	1.7	1.5	1.3	1.4	1.5	2.1

Appendix 2. Continued.

Part	2/11	PL-II														
		1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Q	l.s ⁻¹	1.53	1.71	0.79	1.10	2.75	0.54	1.62	0.93	2.90	2.05	1.34	1.43	0.92	0.27	1.13
pH		4.23	4.31	4.34	4.39	4.36	4.31	4.29	4.23	4.15	4.12	4.20	4.16	4.16	4.22	4.27
H ⁺	µmol.l ⁻¹	58.6	49.1	46.1	40.6	44.1	49.5	51.2	59.4	70.2	76.5	63.6	69.9	69.4	59.6	53.2
Ca ²⁺	µmol.l ⁻¹	18.4	17.3	14.6	15.8	14.9	15.2	19.8	17.5	22.3	25.4	22.9	27.6	27.6	31.8	21.6
Mg ²⁺	µmol.l ⁻¹	6.6	6.3	5.3	4.6	6.8	5.2	7.0	7.0	7.0	10.2	8.6	9.6	11.0	12.2	7.9
Na ⁺	µmol.l ⁻¹	53.4	39.1	46.0	44.9	42.7	46.7	52.1	46.2	34.9	44.6	38.3	41.0	38.1	54.7	37.6
K ⁺	µmol.l ⁻¹	8.5	7.5	7.5	6.9	8.1	8.7	11.1	11.2	20.1	25.8	26.4	35.6	41.7	38.0	24.4
NH ₄ ⁺	µmol.l ⁻¹	0.12	0.36	2.89	3.12	0.82	1.36	0.90	0.59	0.54	0.59	0.46	1.34	0.58	0.36	0.56
NO ₃ ⁻	µmol.l ⁻¹	50	59	52	44	52	63	92	97	137	167	155	185	174	220	102
SO ₄ ²⁻	µmol.l ⁻¹	57	40	41	37	35	33	39	31	26	27	24	28	27	27	22
Cl ⁻	µmol.l ⁻¹	15	11	11	9	15	15	18	17	12	19	15	15	13	16	10
F ⁻	µmol.l ⁻¹	4.4	2.9	2.2	3.4	5.0	3.0	4.2	4.0	3.2	3.7	4.4	2.5	2.1	4.2	2.8
DOC	µmol.l ⁻¹	882	670	732	700	770	798	533	650	904	784	689	864	902	624	923
POC	µmol.l ⁻¹	ND	ND	ND	ND	ND	28	7	0	9	42	42	10	17	22	56
TON	µmol.l ⁻¹	25	24	22	23	ND	16	15	20	32	34	24	47	36	38	39
DON	µmol.l ⁻¹	25	24	20	23	ND	15	14	20	31	29	21	41	37	34	39
TP	µmol.l ⁻¹	ND	ND	0.94	0.93	0.85	0.92	0.75	0.85	1.36	1.19	1.13	1.32	1.44	1.11	1.45
DP	µmol.l ⁻¹	0.92	0.82	0.91	0.89	0.81	0.90	0.71	1.16	1.29	1.10	1.04	1.22	1.34	1.06	1.33
DRP	µmol.l ⁻¹	0.79	0.73	0.76	0.80	0.70	0.73	0.60	0.71	1.05	0.99	0.88	1.13	1.26	1.03	1.26
Si	µmol.l ⁻¹	155	99	129	132	118	148	154	125	105	134	106	119	114	176	114
Al _T	µmol.l ⁻¹	ND	ND	27	27	29	30	30	29	31	34	33	39	36	41	22
Al _I	µmol.l ⁻¹	21	18	15	14	17	18	18	18	18	23	23	29	27	33	13
Al ₀	µmol.l ⁻¹	12.3	10.8	12.3	11.6	11.1	11.1	10.9	10.9	12.0	11.0	8.3	9.7	9.3	7.2	8.1
Fe _T	µmol.l ⁻¹	ND	ND	1.8	1.8	1.8	2.0	1.4	1.6	1.8	1.7	1.6	1.7	2.1	1.3	2.0
Fe _I	µmol.l ⁻¹	0.5	0.5	0.8	0.6	0.4	0.3	0.3	0.1	0.5	0.5	0.6	0.8	1.1	0.5	0.5
Fe ₀	µmol.l ⁻¹	0.9	1.0	1.0	1.3	1.4	1.6	1.0	1.4	1.3	1.2	1.0	0.8	0.9	0.8	1.3

Appendix 2. Continued.

Part	3/11	PL-III														
		1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Q	l.s ⁻¹	ND	ND	ND	ND	4.87	1.69	4.00	3.25	4.44	7.06	3.89	7.46	3.58	2.09	3.02
pH		4.48	4.52	4.62	4.66	4.58	4.63	4.54	4.45	4.38	4.39	4.46	4.37	4.40	4.44	4.45
H ⁺	µmol.l ⁻¹	33.1	30.3	24.2	21.8	26.2	23.2	29.0	35.3	41.9	40.5	34.7	42.5	40.2	35.9	35.6
Ca ²⁺	µmol.l ⁻¹	30.3	27.8	30.8	27.9	25.7	24.5	26.7	22.3	22.5	23.4	28.1	28.8	32.2	33.7	30.7
Mg ²⁺	µmol.l ⁻¹	10.3	9.2	9.9	8.9	8.8	7.9	9.3	8.5	8.2	9.6	9.9	11.0	13.0	13.7	12.6
Na ⁺	µmol.l ⁻¹	51.7	44.4	54.6	48.5	44.0	43.6	47.5	44.5	36.0	41.1	41.8	40.4	41.9	43.7	42.0
K ⁺	µmol.l ⁻¹	10.0	9.6	10.4	10.5	9.3	9.8	10.2	10.1	12.1	12.1	13.7	19.8	25.4	28.7	22.7
NH ₄ ⁺	µmol.l ⁻¹	0.17	0.75	2.46	0.99	0.70	1.60	1.02	0.47	0.41	0.39	0.54	1.48	1.11	0.19	0.86
NO ₃ ⁻	µmol.l ⁻¹	75	64	81	69	74	73	103	90	109	107	124	167	174	199	154
SO ₄ ²⁻	µmol.l ⁻¹	66	55	56	50	45	41	39	36	31	30	29	26	27	25	25
Cl ⁻	µmol.l ⁻¹	16	11	13	11	12	12	16	15	10	13	15	14	15	14	13
F ⁻	µmol.l ⁻¹	6.4	4.2	3.7	6.9	4.8	5.7	6.2	5.1	3.8	4.7	5.6	3.0	3.2	6.1	4.2
DOC	µmol.l ⁻¹	354	314	298	282	354	294	263	395	532	474	411	473	485	400	467
POC	µmol.l ⁻¹	ND	ND	ND	ND	ND	10	10	7	20	99	0	24	10	28	14
TON	µmol.l ⁻¹	21	15	15	15	ND	12	15	14	19	15	18	34	36	28	29
DON	µmol.l ⁻¹	21	15	12	15	ND	12	14	14	19	12	17	35	34	26	28
TP	µmol.l ⁻¹	ND	ND	0.45	0.41	0.54	0.45	0.43	0.56	0.79	0.64	0.53	0.75	0.76	0.73	0.69
DP	µmol.l ⁻¹	0.44	0.46	0.41	0.35	0.43	0.40	0.38	0.54	0.66	0.61	0.51	0.63	0.71	0.62	0.67
DRP	µmol.l ⁻¹	0.38	0.40	0.35	0.31	0.32	0.30	0.31	0.49	0.55	0.54	0.40	0.60	0.63	0.61	0.62
Si	µmol.l ⁻¹	148	131	150	148	134	144	139	125	99	124	118	110	110	127	122
Al _T	µmol.l ⁻¹	ND	ND	29	27	27	25	30	26	29	28	29	36	36	39	29
Al _I	µmol.l ⁻¹	26	21	23	21	19	19	23	17	20	20	23	30	30	34	24
Al ₀	µmol.l ⁻¹	5.5	4.8	5.2	5.2	6.0	5.0	6.4	8.1	8.6	8.3	5.7	5.8	5.5	4.4	4.6
Fe _T	µmol.l ⁻¹	ND	ND	0.8	0.9	0.8	0.7	0.6	0.9	1.3	1.0	1.0	0.9	1.0	0.8	0.9
Fe _I	µmol.l ⁻¹	0.1	0.2	0.4	0.3	0.2	0.1	0.1	0.1	0.3	0.2	0.4	0.4	0.5	0.2	0.3
Fe ₀	µmol.l ⁻¹	0.4	0.5	0.4	0.5	0.5	0.5	0.5	0.7	0.8	0.8	0.6	0.4	0.5	0.4	0.5

Appendix 2. Continued.

Part	4/11	PL-IV												
		2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Q		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
pH		4.79	4.80	4.80	4.81	4.75	4.71	4.71	4.73	4.73	4.69	4.70	4.74	4.71
H ⁺	μmol/l ⁻¹	16.2	16.0	15.9	15.5	17.6	19.3	19.5	18.7	18.7	20.2	19.9	18.2	19.5
Ca ²⁺	μmol/l ⁻¹	40.1	36.2	36.7	33.1	36.4	37.3	36.9	39.1	44.5	45.1	48.6	49.2	52.4
Mg ²⁺	μmol/l ⁻¹	14.0	12.2	12.0	11.2	13.2	13.4	12.3	14.2	13.7	15.8	18.1	18.6	19.0
Na ⁺	μmol/l ⁻¹	54.8	54.2	52.5	49.9	54.4	53.4	47.5	53.8	50.2	52.4	53.7	54.7	55.1
K ⁺	μmol/l ⁻¹	11.2	11.7	11.6	11.6	11.8	12.1	12.6	12.7	13.2	16.4	19.8	21.2	21.1
NH ₄ ⁺	μmol/l ⁻¹	2.30	1.61	1.34	1.56	0.84	0.45	0.28	0.48	0.35	0.54	0.51	0.25	0.74
NO ₃ ⁻	μmol/l ⁻¹	87	80	84	80	116	120	128	136	145	196	206	234	203
SO ₄ ²⁻	μmol/l ⁻¹	70	62	60	53	51	52	46	43	40	36	35	30	36
Cl ⁻	μmol/l ⁻¹	13	12	13	12	16	15	13	15	15	17	17	16	15
F ⁻	μmol/l ⁻¹	6.0	7.6	6.1	5.8	7.4	7.4	6.8	7.5	7.7	5.3	5.0	8.5	7.2
DOC	μmol/l ⁻¹	126	126	152	139	132	131	169	154	141	144	151	145	151
POC	μmol/l ⁻¹	ND	ND	ND	42	13	3	14	41	14	17	23	89	20
TON	μmol/l ⁻¹	10	11	11	13	10	9	13	11	9	7	11	9	11
DON	μmol/l ⁻¹	8	8	11	10	10	9	13	10	8	6	10	8	10
TP	μmol/l ⁻¹	0.18	0.17	0.18	0.18	0.16	0.17	0.30	0.14	0.13	0.15	0.17	0.22	0.18
DP	μmol/l ⁻¹	0.14	0.13	0.13	0.15	0.12	0.14	0.14	0.12	0.11	0.19	0.14	0.15	0.15
DRP	μmol/l ⁻¹	0.10	0.10	0.08	0.08	0.09	0.06	0.12	0.10	0.09	0.12	0.11	0.14	0.10
Si	μmol/l ⁻¹	145	148	141	145	148	144	126	139	134	132	130	140	138
Al _T	μmol/l ⁻¹	27	26	25	24	28	27	28	27	30	41	41	44	34
Al _I	μmol/l ⁻¹	23	22	22	21	25	24	25	24	27	39	37	42	31
Al ₀	μmol/l ⁻¹	2.1	2.0	2.8	2.3	2.6	3.0	3.0	2.6	1.9	1.8	1.5	0.8	1.2
Fe _T	μmol/l ⁻¹	0.2	0.2	0.2	0.2	0.2	0.3	0.5	0.2	0.4	0.2	0.2	0.2	0.2
Fe _I	μmol/l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Fe ₀	μmol/l ⁻¹	0.2	0.2	0.2	0.2	0.2	0.1	0.3	0.2	0.2	0.1	0.2	0.1	0.2

Part	5/11	CT-1														
		1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Q	l.s ⁻¹	0.45	0.57	0.81	0.79	1.01	0.30	1.18	1.33	0.89	0.48	0.95	0.53	0.43	0.40	0.33
pH		4.22	4.32	4.32	4.35	4.35	4.35	4.32	4.25	4.24	4.31	4.30	4.33	4.36	4.37	4.36
H ⁺	μmol.l ⁻¹	60.6	48.4	47.6	45.0	44.3	45.1	47.8	55.8	58.2	49.2	50.4	47.3	43.6	42.7	43.8
Ca ²⁺	μmol.l ⁻¹	9.1	9.1	12.3	7.7	11.7	10.2	14.1	9.6	11.0	6.6	8.4	7.1	5.7	4.1	5.7
Mg ²⁺	μmol.l ⁻¹	14.3	12.6	14.8	10.0	13.1	13.7	17.1	13.1	12.7	11.4	10.4	11.2	11.1	9.0	11.1
Na ⁺	μmol.l ⁻¹	38.7	41.9	36.3	35.1	34.1	32.9	33.2	32.7	30.5	35.6	31.3	32.3	32.8	32.6	34.7
K ⁺	μmol.l ⁻¹	7.1	5.9	8.9	6.8	10.8	12.3	11.7	6.9	8.2	5.0	8.4	8.0	7.4	5.6	6.1
NH ₄ ⁺	μmol.l ⁻¹	0.51	1.30	2.33	1.41	0.64	2.76	1.08	0.22	1.10	0.62	0.44	1.14	1.01	0.18	0.71
NO ₃ ⁻	μmol.l ⁻¹	24	19	50	19	38	34	67	38	48	17	29	35	24	11	23
SO ₄ ²⁻	μmol.l ⁻¹	56	49	52	38	41	47	43	40	41	39	37	34	34	24	33
Cl ⁻	μmol.l ⁻¹	18	22	16	18	15	13	19	18	13	16	16	14	14	17	15
F ⁻	μmol.l ⁻¹	2.8	1.7	2.1	2.5	3.3	2.7	3.5	3.1	1.9	2.4	2.4	1.4	1.3	1.8	1.7
DOC	μmol.l ⁻¹	482	545	313	610	461	291	325	436	376	449	508	430	558	812	512
POC	μmol.l ⁻¹	ND	ND	ND	ND	ND	11	1	17	4	5	23	11	0	0	0
TON	μmol.l ⁻¹	17	17	14	ND	ND	17	4	5	11	15	12	17	11	25	16
DON	μmol.l ⁻¹	17	17	13	ND	ND	15	3	4	11	14	10	16	8	19	14
TP	μmol.l ⁻¹	ND	ND	0.13	0.21	0.14	0.13	0.08	0.10	0.11	0.12	0.12	0.11	0.12	0.31	0.15
DP	μmol.l ⁻¹	0.09	0.16	0.05	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DRP	μmol.l ⁻¹	<0.05	<0.05	<0.05	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Si	μmol.l ⁻¹	83	91	73	72	67	84	75	69	73	78	68	72	73	78	80
Al _T	μmol.l ⁻¹	ND	ND	13	13	11	11	17	14	11	10	9	8	9	9	8
Al _i	μmol.l ⁻¹	8	6	9	6	7	7	11	6	6	5	5	5	4	3	5
Al _o	μmol.l ⁻¹	4.9	6.2	4.1	6.3	4.5	3.5	5.4	6.7	5.2	4.9	4.6	3.4	4.2	4.7	3.3
Fe _T	μmol.l ⁻¹	ND	ND	2.7	5.9	4.0	3.2	1.9	4.3	2.4	3.6	3.1	3.4	3.6	5.4	4.1
Fe _i	μmol.l ⁻¹	0.7	1.5	1.2	0.9	0.8	1.1	0.5	2.2	0.6	0.8	0.9	1.2	1.2	1.8	1.4
Fe _o	μmol.l ⁻¹	1.9	4.3	1.5	4.2	3.2	2.1	1.4	2.1	1.9	2.8	2.2	2.2	2.4	3.7	2.7

Appendix 2. Continued.

Part	6/11	CT-II														
		1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Q	ls ⁻¹	9.64	11.50	13.95	18.55	21.40	6.90	10.35	9.20	10.13	10.57	14.15	9.01	12.62	10.92	4.99
pH		4.19	4.27	4.29	4.22	4.26	4.30	4.23	4.23	4.26	4.26	4.24	4.29	4.24	4.29	4.30
H ⁺	μmol.l ⁻¹	64.0	53.2	51.7	60.5	55.2	50.5	59.2	58.8	55.1	55.4	57.1	50.9	57.9	51.0	49.9
Ca ²⁺	μmol.l ⁻¹	11.7	14.3	12.3	10.1	12.7	11.2	13.0	10.4	10.4	8.8	9.0	8.6	9.5	7.7	8.6
Mg ²⁺	μmol.l ⁻¹	15.8	15.9	15.1	12.2	13.4	14.6	17.4	14.4	12.4	13.6	12.4	12.4	14.7	12.3	13.6
Na ⁺	μmol.l ⁻¹	34.3	36.4	33.9	30.6	28.3	32.0	33.4	31.0	27.3	32.6	28.9	27.6	28.4	28.9	31.3
K ⁺	μmol.l ⁻¹	7.4	7.9	8.6	6.6	8.8	9.3	10.5	7.3	7.4	6.2	7.4	7.0	8.5	7.4	7.0
NH ₄ ⁺	μmol.l ⁻¹	0.13	0.36	2.43	0.32	0.58	0.81	0.68	0.44	0.77	0.71	0.44	0.53	0.72	0.33	0.94
NO ₃ ⁻	μmol.l ⁻¹	60	70	79	49	78	76	109	73	70	52	66	72	81	53	62
SO ₄ ²⁻	μmol.l ⁻¹	53	50	48	39	38	40	39	38	35	37	33	30	32	24	30
Cl ⁻	μmol.l ⁻¹	19	18	16	16	16	14	19	18	13	16	17	13	14	15	15
F ⁻	μmol.l ⁻¹	2.4	1.5	1.2	2.2	3.3	1.8	2.6	2.5	2.2	2.0	2.2	1.0	1.1	1.8	1.6
DOC	μmol.l ⁻¹	576	407	395	769	556	307	361	418	459	493	580	430	579	778	516
POC	μmol.l ⁻¹	ND	ND	ND	ND	ND	3	0	15	19	0	17	28	5	17	9
TON	μmol.l ⁻¹	20	16	18	25	22	16	16	17	18	19	22	23	26	31	21
DON	μmol.l ⁻¹	20	16	17	ND	ND	16	16	17	18	19	21	21	23	28	21
TP	μmol.l ⁻¹	ND	ND	0.10	0.19	0.11	0.08	0.09	0.09	0.11	0.10	0.12	0.09	0.13	0.35	0.12
DP	μmol.l ⁻¹	0.11	0.08	0.07	0.15	0.08	0.07	0.06	0.07	0.07	0.09	0.09	0.06	0.09	0.15	0.10
DRP	μmol.l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Si	μmol.l ⁻¹	75	79	68	72	62	71	77	73	65	72	65	65	69	72	74
Al _T	μmol.l ⁻¹	ND	ND	24	22	25	22	27	21	20	18	20	18	17	15	16
Al _I	μmol.l ⁻¹	18	18	18	13	18	17	20	14	14	11	13	13	12	8	11
Al _O	μmol.l ⁻¹	6.9	5.2	6.1	9.0	6.6	4.3	6.7	6.9	6.5	6.6	6.5	4.3	5.2	5.2	4.2
Fe _T	μmol.l ⁻¹	ND	2.4	2.4	4.6	2.8	2.1	2.0	2.6	2.4	3.1	3.0	2.6	3.2	5.4	3.3
Fe _I	μmol.l ⁻¹	0.8	1.2	0.5	1.3	0.9	0.8	0.8	0.7	0.6	0.9	1.1	1.2	1.4	1.3	1.2
Fe _O	μmol.l ⁻¹	1.8	1.3	1.1	3.2	1.9	1.3	1.2	1.9	1.6	2.0	1.7	1.2	1.6	3.1	1.7

Appendix 2. Continued.

Part	7/11	C1-H11														
		1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Q	ls ⁻¹	1.24	1.55	1.72	2.86	3.02	0.79	1.57	1.12	1.14	1.31	1.91	1.12	1.48	1.73	0.78
pH		4.04	4.09	4.15	4.11	4.13	4.08	4.08	4.08	4.11	4.11	4.12	4.15	4.12	4.12	4.12
H ⁺	μmol.l ⁻¹	92.2	80.7	70.0	78.2	73.6	82.6	82.4	82.3	77.4	77.2	76.2	71.5	76.1	76.5	75.5
Ca ²⁺	μmol.l ⁻¹	8.9	11.5	10.7	8.1	12.2	8.9	9.2	9.6	8.6	8.4	7.6	7.3	7.7	7.0	7.8
Mg ²⁺	μmol.l ⁻¹	13.0	14.5	13.5	10.7	13.7	12.6	15.2	12.8	10.4	12.2	11.5	11.4	12.9	11.4	13.0
Na ⁺	μmol.l ⁻¹	30.7	36.0	29.5	28.2	30.3	26.7	29.6	28.5	23.8	30.3	28.4	25.9	26.7	27.7	30.0
K ⁺	μmol.l ⁻¹	4.5	4.8	7.3	4.8	8.8	8.6	10.6	6.6	5.9	4.7	6.5	5.5	6.0	7.2	5.7
NH ₄ ⁺	μmol.l ⁻¹	0.06	0.36	1.35	0.99	0.62	1.15	1.25	0.39	0.44	0.36	0.37	0.52	0.67	0.31	0.85
NO ₃ ⁻	μmol.l ⁻¹	36	48	76	42	72	77	119	68	63	51	64	76	77	58	71
SO ₄ ²⁻	μmol.l ⁻¹	66	68	56	47	43	47	43	45	37	43	37	32	33	26	34
Cl ⁻	μmol.l ⁻¹	16	18	14	16	14	11	18	19	10	14	18	11	13	16	15
F ⁻	μmol.l ⁻¹	2.8	1.2	1.0	2.5	3.0	1.9	2.6	2.6	2.0	2.1	1.9	1.2	1.2	2.1	1.8
DOC	μmol.l ⁻¹	908	663	467	989	771	499	465	612	698	627	805	578	852	1128	707
POC	μmol.l ⁻¹	ND	ND	ND	ND	ND	17	0	27	14	0	8	12	0	1	4
TON	μmol.l ⁻¹	23	21	22	ND	ND	22	10	17	23	18	13	21	21	43	21
DON	μmol.l ⁻¹	23	21	22	ND	ND	21	10	17	20	18	13	20	16	43	21
TP	μmol.l ⁻¹			0.11	0.24	0.13	0.11	0.07	0.10	0.13	0.10	0.14	0.11	0.15	0.41	0.14
DP	μmol.l ⁻¹	0.13	0.09	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DRP	μmol.l ⁻¹	<0.05	<0.05	<0.05	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Si	μmol.l ⁻¹	77	95	65	80	60	78	73	71	68	73	64	64	70	75	75
Al _r	μmol.l ⁻¹	ND	ND	26	27	24	23	31	28	20	19	21	17	19	18	17
Al _i	μmol.l ⁻¹	16	18	18	15	15	16	22	17	11	12	12	12	12	10	12
Al _o	μmol.l ⁻¹	10.3	8.3	7.6	11.5	8.4	6.5	8.4	9.9	8.6	7.3	9.1	5.6	6.7	7.5	5.2
Fe _r	μmol.l ⁻¹	ND	ND	2.3	4.8	4.1	3.1	2.6	3.4	3.1	3.2	3.7	3.1	4.1	5.7	3.8
Fe _i	μmol.l ⁻¹	1.0	1.4	1.0	0.4	1.2	1.0	0.9	0.6	0.6	1.1	1.3	1.6	1.8	2.0	1.5
Fe _o	μmol.l ⁻¹	2.3	2.1	1.3	3.7	2.8	2.1	1.6	2.8	2.5	2.1	2.4	1.5	2.3	3.7	2.3

Appendix 2. Continued.

Part	8/11	CT-IV														
		1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Q	l.s ⁻¹	1.74	2.20	3.77	4.19	4.13	1.09	1.94	1.36	2.40	1.20	2.97	1.40	1.80	2.74	0.95
pH		4.07	4.12	4.18	4.12	4.15	4.10	4.08	4.11	4.11	4.11	4.09	4.10	4.10	4.10	4.12
H ⁺	μmol.l ⁻¹	85.6	76.7	66.7	76.2	71.6	78.8	82.4	77.3	77.6	78.4	81.2	78.6	79.2	78.6	76.7
Ca ²⁺	μmol.l ⁻¹	9.5	10.9	10.8	8.2	10.1	9.4	9.1	8.8	11.3	8.0	9.3	10.2	10.1	8.0	9.1
Mg ²⁺	μmol.l ⁻¹	13.2	13.9	13.1	11.1	12.1	13.3	15.6	12.6	11.3	12.3	14.2	14.2	15.4	12.9	14.1
Na ⁺	μmol.l ⁻¹	29.8	34.1	28.0	28.8	24.7	27.0	30.4	27.3	20.6	29.8	28.3	25.4	25.8	26.4	28.5
K ⁺	μmol.l ⁻¹	5.1	5.2	9.3	5.4	7.8	9.8	11.2	6.8	8.1	5.2	9.0	8.7	9.0	9.2	8.3
NH ₄ ⁺	μmol.l ⁻¹	0.11	0.91	2.36	1.87	0.77	1.78	0.85	0.51	0.77	0.56	0.34	0.42	0.58	0.35	0.50
NO ₃ ⁻	μmol.l ⁻¹	30	43	77	41	69	89	118	67	87	54	108	123	109	74	84
SO ₄ ²⁻	μmol.l ⁻¹	65	67	50	48	40	45	44	44	35	42	34	29	31	28	34
Cl ⁻	μmol.l ⁻¹	17	19	13	17	14	14	19	18	11	16	20	13	14	17	15
F ⁻	μmol.l ⁻¹	2.3	1.0	0.8	2.2	3.4	2.0	2.7	2.5	1.9	2.1	2.2	1.3	1.2	1.0	1.6
DOC	μmol.l ⁻¹	834	617	486	874	732	455	506	555	484	662	662	534	748	1065	715
POC	μmol.l ⁻¹	ND	ND	ND	ND	ND	11	4	68	10	20	11	9	11	15	12
TON	μmol.l ⁻¹	18	19	19	ND	ND	18	17	14	9	15	16	28	27	41	23
DON	μmol.l ⁻¹	18	19	18	ND	ND	17	16	14	6	15	15	26	18	41	23
TP	μmol.l ⁻¹	ND	ND	0.08	0.21	0.14	0.10	0.08	0.09	0.08	0.10	0.15	0.11	0.11	0.38	0.13
DP	μmol.l ⁻¹	0.13	0.10	0.03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DRP	μmol.l ⁻¹	<0.05	<0.05	<0.05	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Si	μmol.l ⁻¹	71	88	55	75	56	73	74	66	61	67	61	57	63	70	68
Al _r	μmol.l ⁻¹	ND	ND	24	25	24	24	33	22	20	19	27	24	23	20	20
Al _i	μmol.l ⁻¹	16	18	17	14	15	18	23	14	12	12	19	19	16	12	14
Al _o	μmol.l ⁻¹	9.8	7.7	7.6	10.8	8.0	6.5	8.8	8.7	7.3	7.4	7.6	5.0	6.5	6.7	5.6
Fe _r	μmol.l ⁻¹	ND	ND	2.6	4.6	3.5	2.6	2.5	2.9	2.2	3.5	2.9	2.5	3.5	4.9	3.3
Fe _i	μmol.l ⁻¹	1.0	1.3	1.3	1.9	1.0	0.9	1.0	0.8	0.9	1.2	1.2	1.3	1.0	1.5	1.3
Fe _o	μmol.l ⁻¹	2.6	1.9	1.3	1.9	2.5	1.7	1.5	2.1	1.4	2.3	1.7	1.1	2.5	3.4	2.1

Appendix 2. Continued.

Part	9/11	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Q		0.41	0.83	0.85	1.08	1.11	0.34	1.16	0.74	1.15	0.42	1.05	0.49	0.97	0.88	0.47
pH		4.09	4.14	4.21	4.18	4.19	4.16	4.13	4.14	4.15	4.15	4.11	4.12	4.09	4.17	4.19
H ⁺	μmol.l ⁻¹	80.5	72.4	61.5	66.6	64.8	69.9	73.3	72.8	71.3	71.6	76.9	75.8	82.1	67.8	64.5
Ca ²⁺	μmol.l ⁻¹	7.8	8.0	11.4	7.2	11.9	8.6	13.6	9.7	9.4	7.4	10.2	11.9	12.4	8.0	9.1
Mg ²⁺	μmol.l ⁻¹	13.7	13.7	14.6	11.7	15.5	12.7	18.0	14.5	12.1	13.4	18.2	17.7	20.4	15.0	15.3
Na ⁺	μmol.l ⁻¹	30.4	34.1	29.8	30.0	30.3	25.5	31.8	28.2	24.3	32.4	31.8	27.3	29.1	29.8	28.1
K ⁺	μmol.l ⁻¹	3.8	4.5	8.2	4.1	9.9	9.7	11.7	7.1	7.4	4.8	11.0	12.5	13.6	9.8	11.0
NH ₄ ⁺	μmol.l ⁻¹	0.06	0.59	2.24	1.37	0.79	2.23	0.87	0.20	0.80	0.48	0.47	0.60	1.29	0.16	0.59
NO ₃ ⁻	μmol.l ⁻¹	18	22	78	35	77	72	126	85	70	49	128	141	140	70	75
SO ₄ ²⁻	μmol.l ⁻¹	68	69	55	52	49	46	45	45	38	43	35	29	34	32	35
Cl ⁻	μmol.l ⁻¹	17	21	14	16	16	12	28	17	12	18	22	15	16	16	14
F ⁻	μmol.l ⁻¹	2.4	1.1	0.8	2.4	3.2	2.0	2.7	2.7	1.9	1.9	2.8	1.5	1.4	1.2	1.4
DOC	μmol.l ⁻¹	671	560	376	633	555	381	366	409	528	498	515	446	543	803	581
POC	μmol.l ⁻¹	ND	ND	ND	ND	ND	11	1	0	2	38	17	18	18	51	17
TON	μmol.l ⁻¹	19	18	18	17	ND	23	7	10	11	15	19	33	31	43	23
DON	μmol.l ⁻¹	19	18	17	ND	ND	22	7	10	11	14	18	31	28	39	21
TP	μmol.l ⁻¹	ND	ND	0.07	0.12	0.08	0.07	0.06	0.06	0.08	0.07	0.08	0.08	0.10	0.26	0.11
DP	μmol.l ⁻¹	0.08	0.07	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DRP	μmol.l ⁻¹	<0.05	<0.05	<0.05	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Si	μmol.l ⁻¹	67	79	57	73	64	77	72	65	61	65	64	57	67	68	65
Al _r	μmol.l ⁻¹	ND	ND	26	25	24	24	34	24	20	18	29	27	26	18	17
Al _i	μmol.l ⁻¹	16	18	20	16	17	19	27	17	13	12	22	22	20	11	12
Al _o	μmol.l ⁻¹	8.4	7.5	6.1	8.4	6.7	5.7	6.9	7.1	7.0	6.3	7.0	4.5	5.4	5.8	4.6
Fe _r	μmol.l ⁻¹	ND	ND	1.8	2.5	2.1	1.9	1.7	2.2	2.1	2.2	2.0	2.1	2.4	3.6	2.8
Fe _i	μmol.l ⁻¹	0.8	1.0	1.0	0.1	0.5	0.5	0.7	0.6	0.4	0.8	0.9	1.2	1.2	1.3	1.2
Fe _o	μmol.l ⁻¹	1.6	1.4	0.8	1.8	1.6	1.3	1.0	1.6	1.7	1.4	1.1	0.9	1.2	2.3	1.6

Appendix 2. Continued.

Part	10/11	CT-VI														
		1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Q	ls ⁻¹	2.21	3.26	2.71	2.89	3.37	1.36	2.37	1.78	1.01	1.31	1.80	1.12	1.41	1.12	0.79
pH		4.41	4.48	4.51	4.51	4.49	4.51	4.48	4.50	4.50	4.49	4.47	4.47	4.43	4.53	4.55
H ⁺	µmol.l ⁻¹	38.9	32.9	30.6	30.7	32.0	31.1	33.3	31.4	31.7	32.6	34.2	33.8	37.5	29.3	28.0
Ca ²⁺	µmol.l ⁻¹	16.5	17.0	17.7	14.1	18.6	15.0	18.5	15.3	14.9	13.6	17.0	15.9	19.3	17.0	17.0
Mg ²⁺	µmol.l ⁻¹	20.7	20.1	20.5	16.7	19.9	18.9	22.3	19.8	18.6	18.4	20.4	21.2	26.5	24.1	24.0
Na ⁺	µmol.l ⁻¹	41.0	45.3	45.2	36.9	36.2	37.9	41.2	40.6	37.1	40.4	37.7	38.2	38.7	39.7	41.8
K ⁺	µmol.l ⁻¹	9.3	9.0	9.0	7.9	11.2	10.6	12.2	10.2	9.2	8.4	10.2	9.4	11.8	10.6	11.5
NH ₄ ⁺	µmol.l ⁻¹	0.07	0.59	1.78	1.09	1.29	1.69	0.67	0.51	0.64	0.60	0.42	0.72	0.70	0.12	0.89
NO ₃ ⁻	µmol.l ⁻¹	40	39	72	37	74	60	93	62	71	51	96	104	137	108	102
SO ₄ ²⁻	µmol.l ⁻¹	69	66	60	53	51	48	43	47	42	42	35	33	31	28	33
Cl ⁻	µmol.l ⁻¹	19	19	17	14	18	16	23	20	16	18	20	17	19	18	18
F ⁻	µmol.l ⁻¹	2.7	1.6	1.4	2.2	4.6	1.6	2.3	2.3	1.8	1.8	2.5	1.4	1.5	2.1	1.7
DOC	µmol.l ⁻¹	230	229	152	234	218	159	167	167	174	223	214	199	201	247	169
POC	µmol.l ⁻¹	ND	ND	ND	ND	ND	ND	0	6	18	18	27	20	17	18	18
TON	µmol.l ⁻¹	13	12	9	ND	ND	ND	7	9	12	11	11	20	27	27	17
DON	µmol.l ⁻¹	13	12	8	ND	ND	ND	8	9	12	10	10	19	25	26	17
TP	µmol.l ⁻¹	ND	ND	0.07	0.09	0.07	0.07	0.06	0.05	0.07	0.08	0.07	0.06	0.06	0.10	0.06
DP	µmol.l ⁻¹	0.07	0.05	0.04	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DRP	µmol.l ⁻¹	<0.05	<0.05	<0.05	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Si	µmol.l ⁻¹	88	95	83	85	76	82	90	88	84	89	79	81	81	84	90
Al _T	µmol.l ⁻¹	ND	ND	24	18	22	17	20	14	17	12	18	18	21	15	15
Al _I	µmol.l ⁻¹	18	15	21	13	19	14	17	10	12	9	15	15	18	12	13
Al _o	µmol.l ⁻¹	3.0	2.6	2.6	3.7	3.0	2.5	2.8	3.1	2.8	2.9	2.6	1.8	1.7	1.9	1.3
Fe _T	µmol.l ⁻¹	ND	ND	0.6	0.9	0.4	0.6	0.4	0.5	0.5	0.5	0.6	0.5	0.4	0.7	0.4
Fe _I	µmol.l ⁻¹	0.3	0.2	0.4	0.1	0.1	0.3	0.0	0.1	0.1	0.1	0.3	0.2	0.2	0.3	0.1
Fe _o	µmol.l ⁻¹	0.3	0.4	0.2	0.5	0.3	0.3	0.3	0.4	0.4	0.4	0.3	0.3	0.2	0.4	0.2

Appendix 2. Continued.

Part	11/11	CT-VII														
		1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Q	l.s ⁻¹	1.70	1.63	3.22	3.63	4.89	1.73	2.53	1.64	1.78	1.69	2.16	1.39	1.91	1.54	1.25
pH		4.40	4.50	4.51	4.50	4.48	4.52	4.49	4.49	4.52	4.50	4.50	4.53	4.53	4.58	4.56
H ⁺	μmol.l ⁻¹	39.9	31.9	30.7	31.3	33.2	30.0	32.7	32.6	30.0	31.3	31.3	29.7	29.6	26.4	27.5
Ca ²⁺	μmol.l ⁻¹	15.1	14.7	17.3	13.5	15.1	13.3	17.1	13.2	14.1	13.3	14.0	13.3	15.6	11.9	14.9
Mg ²⁺	μmol.l ⁻¹	17.3	16.5	17.8	13.7	15.8	15.1	18.3	15.0	15.5	16.4	15.2	15.6	18.9	15.2	17.3
Na ⁺	μmol.l ⁻¹	41.1	48.7	43.9	37.8	34.6	37.5	40.5	38.1	38.3	38.6	34.7	36.4	37.2	35.8	38.5
K ⁺	μmol.l ⁻¹	10.7	9.9	10.5	9.3	11.6	11.3	12.5	9.3	10.4	10.2	11.1	10.1	13.4	10.2	10.9
NH ₄ ⁺	μmol.l ⁻¹	0.05	0.63	2.04	0.57	0.87	0.86	0.95	0.42	0.58	0.56	0.23	0.36	1.01	0.22	0.51
NO ₃ ⁻	μmol.l ⁻¹	45	41	66	46	70	59	90	57	62	57	72	73	86	56	72
SO ₄ ²⁻	μmol.l ⁻¹	51	46	48	43	41	41	36	37	35	35	32	30	30	24	29
Cl ⁻	μmol.l ⁻¹	20	23	17	15	17	15	22	18	16	17	18	16	17	17	18
F ⁻	μmol.l ⁻¹	2.1	1.2	1.3	1.8	2.5	1.3	1.9	1.8	1.6	1.5	1.6	1.0	1.1	1.6	1.3
DOC	μmol.l ⁻¹	297	277	195	297	268	165	202	224	214	192	269	247	244	408	226
POC	μmol.l ⁻¹	ND	ND	ND	ND	ND	75	2	8	5	0	21	15	0	0	0
TON	μmol.l ⁻¹	14	14	12	13	15	9	8	12	12	13	14	15	18	23	16
DON	μmol.l ⁻¹	14	14	10	ND	ND	8	8	12	11	11	13	14	15	20	14
TP	μmol.l ⁻¹	ND	ND	0.08	0.13	0.09	0.07	0.07	0.08	0.09	0.07	0.14	0.08	0.08	0.23	0.09
DP	μmol.l ⁻¹	0.08	0.07	0.05	0.10	0.06	0.05	0.05	0.07	0.06	0.05	0.06	0.05	0.05	0.12	0.07
DRP	μmol.l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Si	μmol.l ⁻¹	93	112	87	90	79	92	96	93	94	94	84	85	87	91	92
Al _r	μmol.l ⁻¹	ND	ND	16	18	21	16	18	13	11	11	17	12	12	11	12
Al _i	μmol.l ⁻¹	11	8	13	12	17	13	14	9	7	8	12	10	9	7	9
Al _o	μmol.l ⁻¹	4.9	3.7	3.3	4.9	3.9	2.9	3.9	4.0	3.3	3.4	3.6	2.3	2.4	3.5	1.9
Fe _r	μmol.l ⁻¹	ND	ND	0.8	1.3	0.9	0.9	0.8	1.2	1.0	0.9	1.1	0.9	0.9	1.8	0.9
Fe _i	μmol.l ⁻¹	0.4	0.5	0.4	0.4	0.4	0.4	0.4	0.5	0.4	0.4	0.6	0.4	0.5	0.8	0.4
Fe _o	μmol.l ⁻¹	0.6	0.7	0.4	0.7	0.5	0.5	0.4	0.7	0.6	0.6	0.5	0.5	0.4	1.0	0.5

Notes