

Chemical composition of atmospheric deposition in the catchments of Plešné and Čertovo lakes in 1998–2012

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Abstract

The 1998–2012 average composition of bulk precipitation was dominated by NH_4^+ ($25 \mu\text{mol.l}^{-1}$) among cations and NO_3^- ($21 \mu\text{mol.l}^{-1}$) among anions in catchments of Plešné (PL) and Čertovo (CT) lakes in the Bohemian Forest. Concentrations of other ions averaged between 0.8 and $8.3 \mu\text{mol.l}^{-1}$. The average precipitation amount was 1372 mm, bulk deposition fluxes of major nutrients were 5.0, 4.7, and $3.5 \text{ kg.ha.yr}^{-1}$ of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and TON, respectively, and 22, 4.5, 2.6, 1.9, 0.5, 0.23 kg.ha.yr^{-1} of TOC, $\text{SO}_4\text{-S}$, Ca^{2+} , K^+ , Mg^{2+} , and TP, respectively. Prior to bark beetle infestation in the PL catchment in 2004–2006, the average throughfall fluxes (TF) of Na^+ , H^+ , SO_4^{2-} , NO_3^- , Cl^- , and TP, were on average 1.5–2.1 fold higher than their precipitation fluxes (PF). Higher TF:PF ratios (2.1–9.8) were observed for Mn, K^+ , Mg^{2+} , Ca^{2+} , and organic C, N, and P forms, while lower ratios (0.6–1.3) occurred for dissolved reactive P and NH_4^+ . After the forest infestation, throughfall deposition of ions and nutrients started to decrease in the PL catchment compared to the CT catchment. The greatest and most rapid changes occurred for K^+ , DOC, Mg^{2+} , and Ca^{2+} . Their fluxes rapidly decreased to values similar to precipitation fluxes within 6–8 years after the infestations. Slower changes occurred in throughfall fluxes of SO_4^{2-} , NO_3^- , and Cl^- , and negligible changes so far occurred in the throughfall fluxes of NH_4^+ . The major reason for differing response of throughfall deposition of individual elements to forest dieback (and reduced surface area of canopies) was different contribution of canopy leaching (export from living and decaying canopy tissue) and microbial transformations to the elemental throughfall fluxes.

Key words: throughfall, precipitation, ions, nutrients

INTRODUCTION

Chemical composition of precipitation and throughfall has been measured in the uppermost Bohemian Forest range (catchment of Čertovo Lake) since 1991 (HLAVATÝ 1992, VESELÝ & MAJER 1992). The early studies evaluated changes in acidic deposition resulting from reductions in European emissions of sulphur (S) and nitrogen (N) compounds to the atmosphere during the 1990s. This research was mostly focused on fluxes of acidifying pollutants, like sulphate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), and ammonium (NH_4^+), as well as base cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+), which mitigated negative effects of acidic deposition (HRUŠKA et al. 2000). These studies have been extended to the catchment of Plešné Lake and also included fluxes of major forms of phosphorus (P), organic nitrogen, organic carbon (C), and sili-

ca (Si) since 1997. Data on atmospheric deposition of pollutants and nutrients in precipitation and throughfall have enabled us to (i) estimate net atmospheric inputs of elements to the mountain forest and their seasonal patterns (KOPÁČEK et al. 2011), (ii) quantify canopy leaching of elements and changes in their fluxes during passage through canopies (KOPÁČEK et al. 2009), (iii) calculate mass-budgets, evaluating element cycling within lakes and their catchments (KOPÁČEK et al. 2000a, 2001a,b), and (iv) reconstruct and predict environmental biogeochemical trends in element fluxes within terrestrial and aquatic ecosystems (MAJER et al. 2003, OULEHLE et al. 2012).

This study presents data from the fifteen-year research on composition of precipitation and throughfall in the catchments of Plešné and Čertovo lakes. Chemical composition of atmospheric deposition differed only negligibly between the catchments in the early 2000s (KOPÁČEK et al. 2009, 2011), with the exception for less acidic deposition in the Plešné catchment due to its geographical position further downwind of the major central European emission sources of S and N compounds (KOPÁČEK & HRUŠKA 2010). Forest in the Plešné catchment has been, however, seriously affected by a bark beetle outbreak since the middle 2000s (see below), resulting in a forest dieback, disintegration and decay of canopies, and a continuous change in throughfall composition, compared to unaffected throughfall plots in the Čertovo catchment. The objectives of our study are to evaluate data on precipitation and throughfall amounts and chemistry in both catchments to (i) quantify differences in composition of throughfall deposition caused by forest dieback and (ii) compare extents and rapidity of changes in throughfall fluxes of individual elements.

MATERIALS AND METHODS

Site description and sampling

Atmospheric deposition was sampled at two throughfall plots and one open area plot in catchments of both Plešné (PL) and Čertovo (CT) lakes, situated on the north-eastern slope of the mountain ridge of the Bohemian Forest. Throughfall plots were at low (L; <1122 m; PL-L and CT-L) and high (H; ~1330 m; PL-H and CT-H) elevations (Table 1). All throughfall plots were located in flat areas in mature Norway spruce forests (~150 years old), with a negligible proportion of beech at CT-L. Trees at all plots were partly damaged by a wind-storm (broken canopies, branches, and a high amount of twigs in litter fall) at the beginning of 2005 and in 2007 (KOPÁČEK et al. 2010). The plots PL-H and PL-L have been affected by a bark beetle (*Ips typographus*) outbreak since the summers of 2004 and 2006, respectively,

Table 1. Locations of bulk precipitation and throughfall study plots in the Bohemian Forest. Abbreviations: PL, Plešné Lake; CT, Čertovo Lake; BP, bulk precipitation; L, low elevation; H, high elevation; ND, not determined.

	PL catchment			CT catchment		
	BP	Throughfall		BP	Throughfall	
	PL-BP	PL-L	PL-H	CT-BP	CT-L	CT-H
Latitude (°N, WGS-84)	48.7760	48.7752	48.7767	49.1754	49.1627	49.1696
Longitude (°E, WGS-84)	13.8708	13.8680	13.8547	13.1990	13.1993	13.1858
Altitude (m)	1087	1122	1334	1180	1057	1330
Average air temperature^{*)} (°C)	5.7	5.4	3.9	ND	5.5	3.9

^{*)} Data on annual average air temperature are based on hourly records in 2003–2007 (KOPÁČEK et al. 2009).

and all trees above the collectors died within 2–3 years of infestation. The dead trees lost most needles within a year 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, in 2011, ~74% and 50% of the original trees (in 2000) were already broken at the PL-L and PL-H plots, respectively (Table 2). The CT-H and CT-L plots were less affected than the PL plots and only ~6% and 24% of the vigour trees was broken between 2000 and 2011 (Table 2). The areal densities of healthy, dead (bark beetle attacked), and broken trees were calculated at each plot (1 ha area with the centre in the middle of the plot) using colour aerial photographs (scales of 1 : 5000–7000), prepared by Argus Geo System Ltd. (Hradec Králové, Czech Republic) and Georeal (Plzeň, Czech Republic) in 2000, 2003, 2005, and 2007–2011.

Bulk precipitation (BP) was sampled in open areas without trees at elevations of 1087 (PL-BP) and 1180 m (CT-BP). The PL-BP plot was in a stony area (moraine) sparsely covered with small dwarf pine bushes, while the CT-BP plot was in a small mountain meadow. In spring 2007, the CT-BP samplers were shifted ~20 m from their original position due to new birch trees growing in their vicinity.

Each of the throughfall plots was equipped with nine bulk collectors that were situated in north-south and east-west oriented crosses, with the central collector placed randomly and the others placed at exactly 10-m distances. Each of the open-area plots was equipped with two collectors. Rain was regularly sampled in two-week intervals (May to October) using polyethylene collectors (the area of each sampler was 115 cm²) situated 1.5–2 m above the ground, and protected against light, bird perching, and sample evaporation (each sample was collected in a bottle connected to the collector funnel by a 1 mm diameter tube). Snow was sampled in two to four-week intervals (November to April) using high-density polyethylene cylinders (height of 1 m, area of 167 cm²) situated 2–2.5 m above the ground. After heavy snowfall or rain, the sampling interval was shortened to avoid loss of samples. The sampling lasted from November 1997 to October 2012 at all plots, except for the PL-H plot that was operated from November 2000. At each plot, precipitation amounts collected by individual samplers were measured individually, and then were combined into one integrated sample. Samplers were visually inspected for contamination, and samples containing animal droppings were not used. Snow from all collectors at each plot was combined in a polyethylene barrel, transported to the laboratory, melted, and water equivalent was measured. Samples

Table 2. Number of healthy (Heal.), dead (due to bark beetle attack) and broken (Brok.) trees of Norway spruce (ind.ha⁻¹) at the throughfall plots in the Bohemian Forest.

Year	PL-L			PL-H			CT-L			CT-H		
	Heal.	Dead	Brok.									
2000	591	36	0	662	47	1	355	10	1	347	27	0
2003	558	69	0	562	147	1						
2005	424	187	16	366	314	28	342	15	8	314	42	18
2007	95	447	85	95	493	130						
2008	11	490	126	89	466	163	335	19	12	295	22	57
2009	11	490	126	51	478	189						
2010	0	273	354	42	391	286						
2011	0	192	435	42	344	333	332	14	21	263	24	87

were pre-filtered through a 200- μm 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 N and P analysis were frozen at -20°C. Samples were analyzed within <2 weeks after sampling (KOPÁČEK et al. 2011).

Chemical analyses and data evaluation

Prior to analysis, samples were filtered with either membrane filters (pore size of 0.45 μm) for the determination of ions and Si, or with glass-fiber filters (pore size of 0.4 μm) for other analyses, except samples for pH, acid neutralizing capacity (ANC, determined by Gran titration), and total concentrations of P, C, and N, which were not filtered beyond the field pre-filtration. Dissolved organic C (DOC) was analyzed with a TOC 5000A analyzer (Shimadzu). Concentration of particulate C (PC) was calculated as the difference between concentrations of total organic C (TOC) and DOC, analyzed with a TOC/TN analyzers (Table 3) for the non-filtered samples and filtrate, respectively. Dissolved reactive P (DRP) was determined by the molybdate method (MURPHY & RILEY 1962). Total and dissolved P (TP and DP) were determined by perchloric acid digestion and the molybdate method according to KOPÁČEK & HEJZLAR (1993). If necessary, samples were concentrated by evaporation (with perchloric acid at ~100°C prior to digestion) to obtain a detection limit of ~0.02 $\mu\text{mol l}^{-1}$ P. Particulate P (PP) was the difference between TP and DP. In 1998 to 2002, 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 25–75 ml of samples previously evaporated to obtain a detection limit of ~2 $\mu\text{mol l}^{-1}$ N. From 2003 to 2012, concentration of TON was calculated as the difference between concentrations of 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 $\text{NO}_3\text{-N}$ in all types of samples) was neglected. For comparison, TON concentrations were determined by both methods for the precipitation samples from 2003–2009 ($n = 198$), with respective resulting averages (\pm standard deviation) for the Kjeldahl digestion and TOC/TN analyzer of 21 ± 18 and 21 ± 19 $\mu\text{mol l}^{-1}$; these differences were insignificant according to a paired t-test at a 95% significance level (KOPÁČEK et al. 2009, 2011). Particulate organic N (PON) was the difference between TON and DON. Methods used for the determination of C, P, and organic N forms and their abbreviations are summarized in Table 3.

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 3). Concentrations of HCO_3^- were assumed to be equal to positive ANC values, while $\text{HCO}_3^- = 0$ was used for all ANC values ≤ 0 $\mu\text{mol l}^{-1}$. Concentrations of Al, Fe, and Mn were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) and atomic absorption spectroscopy (AAS) in 1998–2000 and 2009–2012, respectively (Table 3). In 2001–2008, Al was determined in PL-BP and CT-BP according to DOUGAN & WILSON (1974), and Fe in the PL-BP samples according to KOPÁČEK et al. (2001c). Concentration of dissolved reactive Si was determined in bulk precipitation samples in 2000–2012, using a molybdate method by GOLTERMAN & CLYMO (1969).

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, with similar composition as throughfall), which was melted and assayed with each series of samples. Concentration of organic acid anions (A^-) for this control was estimated from DOC concentration, using an empirical relationship of A^- ($\mu\text{eq l}^{-1}$) = $0.048 \times \text{DOC}$ ($\mu\text{mol l}^{-1}$), where equivalent (eq) is one mole of charge; this relationship was obtained for precipitation and throughfall sampled at all study

plots from 1998–2007 (KOPÁČEK et al. 2009). The differences between the sum of cations and the sum of all anions (including A^-) were below $\pm 10\%$ of the total ionic content in individual precipitation and throughfall samples (at higher differences, samples were re-analyzed), and below $\pm 4\%$ for the annual volume weighted mean concentrations. Coefficients of variation for mean concentrations of the standard sample were 1–5% for ions (except for F^-), DOC, TP, DP, and pH; $< 10\%$ for TON, DON, DRP, Al, Fe, and Mn; and $< 20\%$ for F^- (for details see KOPÁČEK et al. 2011).

Annual average compositions of precipitation and throughfall were calculated for hydrological years (from November 1 to October 31) as volume weighted mean concentrations. When the DRP and F^- concentrations were below their detection limits of 0.05 and 0.1 $\mu\text{mol l}^{-1}$ ($\sim 2\%$ and $\sim 25\%$ of all samples; KOPÁČEK et al. 2011), respectively, a half of these values were used in subsequent data evaluation. Concentrations of other constituents were always above their detection limits. We used the Wilcoxon matched pairs test STATISTICA (Stat-

Table 3. 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).
HCO_3^-	bicarbonate	$HCO_3^- = ANC$ for all ANC values $> 0 \mu\text{mol l}^{-1}$.
Si	dissolved silica	Molybdate method (GOLTERMAN & CLYMO 1969).
Mn	total manganese	Flame AAS in 1997–2000 and cuvette AAS in 2009–2012 (Varian AA240Z).
Al	total aluminium	ICP-OES in 1997–2000, colorimetry (DOUGAN & WILSON 1974) in 2001–2008, and cuvette AAS (Varian AA240Z) in 2009–2012.
Fe	total iron	ICP-OES in 1997–2000, colorimetry (KOPÁČEK et al. 2001c) in 2001–2008, and cuvette AAS (Varian AA240Z) in 2009–2012.
DOC	dissolved organic C	Analyzer TOC 5000A (Shimadzu).
PC	particulate 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) in 1997–2002, then TOC/TN analyzer. ¹⁾
DON	dissolved organic N	
PON	particulate organic 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.

Soft, Inc., Electronic Statistics Textbook, version 9.1, www.statsoft.com) with a significance level of 0.05 to test for differences in precipitation amounts and element concentrations and fluxes between (1) the PL and CT catchments: PL-BP vs. CT-BP ($n = 15$, 1998–2012), PL-L vs. CT-L ($n = 10$, 1998–2007), and PL-H vs. CT-H ($n = 5$, 2001–2005); years with results affected by forest dieback in the PL catchment were excluded from this analysis; and (2) the high and low elevation plots in both catchments: PL-H vs. PL-L ($n = 12$, 2001–2012) and CT-H vs. CT-L ($n = 15$, 1998–2012). The null hypothesis was that the sample means were equal. A non-parametric procedure was selected because of inhomogeneous variances. Linear regression analysis was used to estimate significances of temporal trends in precipitation amounts and element concentrations and fluxes.

RESULTS AND DISCUSSION

Precipitation and throughfall amounts

The annual average precipitation and throughfall amounts (mostly rain from May to October and snow from November to April) varied within 1050–1981 and 838–2134 mm, respectively, in both study catchments from 1998 to 2012 (Fig. 1). Throughfall amounts were significantly higher ($p < 0.001$) at the high versus low elevation plots in both catchments, with steeper elevation gradient in the PL than CT catchment, with the averages of 1.5 vs. 1.3 $\text{mm}\cdot\text{m}^{-1}$, respectively, for the whole study. The CT gradient was similar to the average elevation-precipitation gradient in the Czech Republic (1.3 $\text{mm}\cdot\text{m}^{-1}$ in the elevation range of 900–1300 m, KOPÁČEK et al. 2012) and did not exhibit any significant trend ($p > 0.05$), because the ratio between throughfall amounts at CT-H and CT-L plots was stable during the study (Fig. 2A). In contrast, the ratio between throughfall amounts at PL-H and PL-L plots decreased significantly ($p < 0.001$) in time (Fig. 2B). The average PL gradient thus decreased from 2.0 to 0.8 $\text{mm}\cdot\text{m}^{-1}$ between the 2001–2005 and 2006–2012 periods. The higher PL than CT gradient prior to the bark beetle outbreak resulted from significantly lower (by 7% on average; $p < 0.05$) annual throughfall amounts at the PL-L than CT-L plot, despite being 85 m higher in elevation. The difference between the PL-L and CT-L plots was probably caused by their topography rather than geography because the high elevation plots (situated at similar elevations near the catchment summits) received similar ($p > 0.05$) water inputs prior to the bark beetle outbreak. No significant difference ($p > 0.05$) was observed between annual precipitation amounts at the PL-BP and CT-BP plots.

The plot elevation affected both the annual throughfall amount and its seasonal pattern, and differences between throughfall amounts at the high and low elevation plots were greater in summer than in winter (KOPÁČEK et al. 2011). These patterns are typical for mountain forest areas (TESAŘ et al. 2000) and result from (i) higher contributions from horizontal deposition (mostly fog and frost deposits in canopies) to the throughfall that occurs at high elevations and in winter (MOLDAN 1991), and (ii) higher evaporation from canopies (due to 1.6°C higher annual average air temperature, Table 1) that occurs at the low elevation plots and especially in summer. After the bark beetle outbreak, spruce rapidly lost needles (within a year) and fine twigs, which significantly reduced specific surface area of canopies. The effects of higher evaporation at PL-L in summer and higher horizontal deposition at PL-H in winter thus continuously decreased and throughfall amounts at both throughfall plots became similar to each other (Fig. 2B), as well as to precipitation amount in the open area (Fig. 1B). In contrast, no apparent change occurred in throughfall amounts in the CT catchment (Fig. 1A). Precipitation amount, however, decreased at the CT-BP relatively to the CT-H plot after the shift of samplers in 2007.

Concentrations and fluxes of elements unaffected by forest dieback

Element concentrations (Appendix 1) and fluxes (Fig. 3–5) were similar in the CT and PL bulk precipitation throughout the study. The 1998–2012 average composition of bulk precipitation in the Bohemian Forest (average for CT-BP and PL-BP) was dominated by NH_4^+ ($25 \mu\text{mol.l}^{-1}$) among cations and NO_3^- ($21 \mu\text{mol.l}^{-1}$) among anions (Appendix 1). Concentrations of other ions averaged 4.1, 1.1, 8.0, 1.8 and $5.7 \mu\text{mol.l}^{-1}$ for Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and H^+ , respectively, and 6.2, 8.3, 0.8, and $4.2 \mu\text{mol.l}^{-1}$ for SO_4^{2-} , Cl^- , F^- , and A^- , respectively. The respective concentrations of TOC, TON, TP, and Si averaged 136, 18, 0.54, and $0.48 \mu\text{mol.l}^{-1}$, and

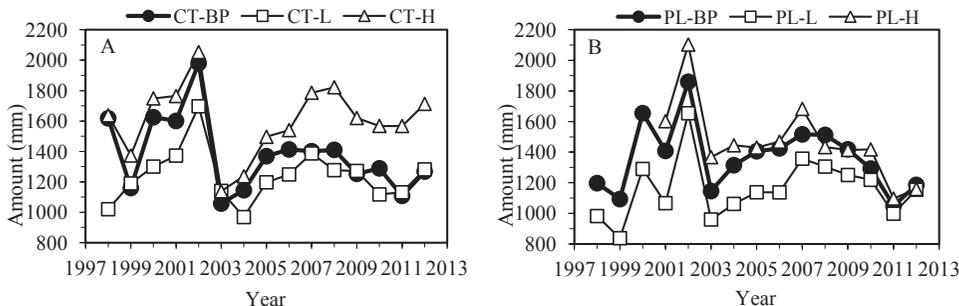


Fig. 1. Annual (November–October) amounts of bulk precipitation (BP) and throughfall at low (L) and high (H) elevations in (A) the Čertovo catchment (CT) and (B) the Plešné catchment (PL).

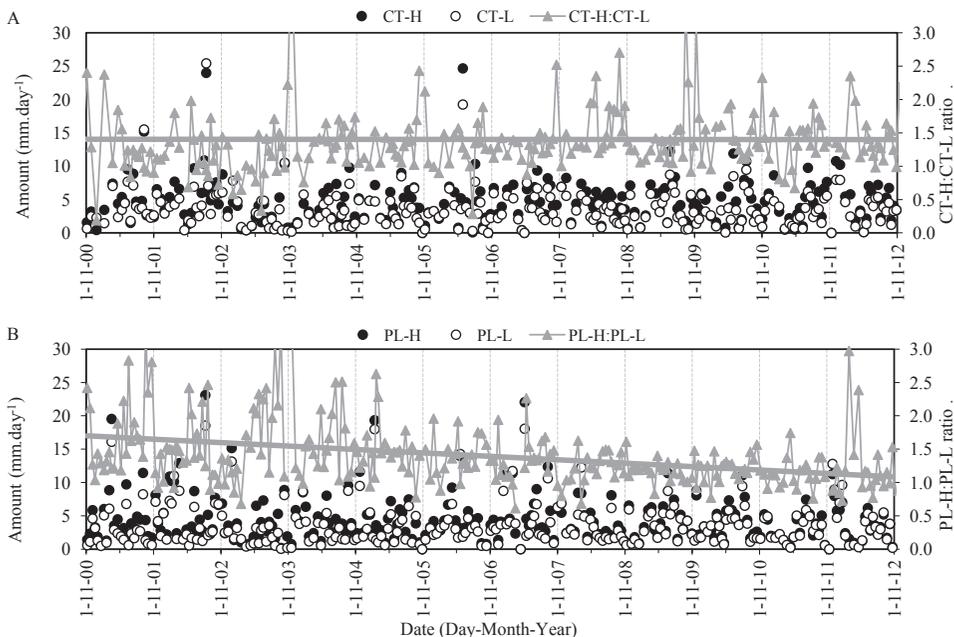


Fig. 2. Daily average amounts of throughfall at low (L) and high (H) elevations and their H:L ratio in (A) the Čertovo catchment (CT) and (B) the Plešné catchment (PL). Average values are calculated for individual sampling intervals (1–4 weeks). Solid gray lines are the linear regression lines between time and H:L ratios ($p > 0.05$ for CT and $p < 0.001$ for PL).

the average concentrations of Al, Fe, and Mg varied within 0.05–0.33 $\mu\text{mol}\cdot\text{l}^{-1}$. At the average precipitation amount of 1372 mm, bulk deposition represented the following fluxes of major nutrients to terrestrial and aquatic ecosystems: 5.0, 4.7, and 3.5 $\text{kg}\cdot\text{ha}\cdot\text{yr}^{-1}$ of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and TON, respectively, and 22, 4.5, 2.6, 1.9, 0.5, 0.23, and 0.18 $\text{kg}\cdot\text{ha}\cdot\text{yr}^{-1}$ of TOC, $\text{SO}_4\text{-S}$, Ca^{2+} , K^+ , Mg^{2+} , TP, and Si, respectively. Concentrations and fluxes of most ions (except for NH_4^+ , Ca^{2+} , F^- , and A^-) exhibited significant decreases (with $p < 0.001$ for SO_4^{2-} , Cl^- and NO_3^- , Fig. 3; and $p < 0.05$ for Mg^{2+} , Na^+ and K^+ , Figs. 4, 5) during the study period. Because the decrease in fluxes of strong acid anions was greater than that in base cations, the difference was compensated for by a decrease in H^+ fluxes ($p < 0.001$; Figs. 5C, D) and an increase in HCO_3^- fluxes ($p < 0.001$; for concentrations see Appendix 1). As a result, average precipitation pH increased from 4.8 to 5.2 and ANC of individual samples increased from predominantly negative to mostly positive values within the 1998–2012 period. Concentrations and fluxes of C and P forms and metals did not exhibit any significant trend ($p > 0.05$) during the study.

Differences between the CT and PL throughfall fluxes at similar elevations were small and statistically insignificant until the onset of bark beetle infestation in 2004 and 2006 at the PL-H and PL-L plots, respectively (Figs. 3–5). Deposition fluxes of elements were greater at higher elevations due to higher throughfall amounts (Fig. 1), because throughfall composition was similar at all the Bohemian Forest plots (Appendix 1). Prior to the bark beetle infestation, the average throughfall flux (TF, average for CT-L, CT-H, PL-L, and PL-H) of the conservative ion Na^+ was on average 1.67 fold higher than that of the bulk precipitation flux (PF, average for CT-BP and PL-BP) in the open areas. Similar average ratios of throughfall to precipitation fluxes (TF:PF) of 1.5–2.1 occurred for H^+ , SO_4^{2-} , NO_3^- , Cl^- , F^- , TP, TN, Al, and Fe, indicating relatively small changes in their fluxes during precipitation passing through canopies (KOPÁČEK et al. 2009). Throughfall fluxes of the other constituents were, however, substantially increased by canopy interactions, with TF:PF ratios of 9.8 for Mn, 6.5 for K^+ , 5.1 for TOC, 3.3 for Mg^{2+} , 2.6 for Ca^{2+} , and 2.1–2.4 for DON, PON, DOP, and PP. In contrast, TF:PF ratios were lower than those for conservative constituents for NH_4^+ (1.3) and DRP (0.6) fluxes, due mostly to their biological uptake and transformation to organic forms in the canopies (KOPÁČEK et al. 2009).

The effect of forest dieback on throughfall fluxes and concentrations of elements

While the differences between throughfall vs. bulk precipitation compositions and fluxes remained relatively stable in the CT catchment throughout the study, they have begun to change for most constituents in the PL catchment since the bark beetle attack. In general, only negligible changes (hardly distinguishable from year-on-year variability) occurred within 2–3 years from the infestation, then they rapidly accelerated with the progressing forest decline (Table 2), and presently the throughfall concentrations and fluxes of elements have been approaching composition typical for the open area. The rapidity and extend of these changes, however, differ for individual constituents (Fig. 3–5), depending on the tree effect on modifying precipitation chemistry as it passes through the canopy. We have observed the following patterns:

(1) The greatest changes in throughfall composition occurred in DOC and K^+ fluxes, which increased for a short (1–2 yr) period after the infestation (especially at the PL-L plot), and then rapidly decreased at both PL throughfall plots to levels similar to the bulk precipitation (Figs. 3B, 4H). Similar pattern is evident also for concentration ratios between throughfall composition at the PL and CT plots of corresponding elevations (i.e., PL-L:CT-L and PL-H:CT-H ratios; Fig. 6E, H). In contrast to relatively stable PL-BP:CT-BP ratios of K^+ and DOC concentrations in bulk deposition, they almost doubled at the infested PL throughfall plots

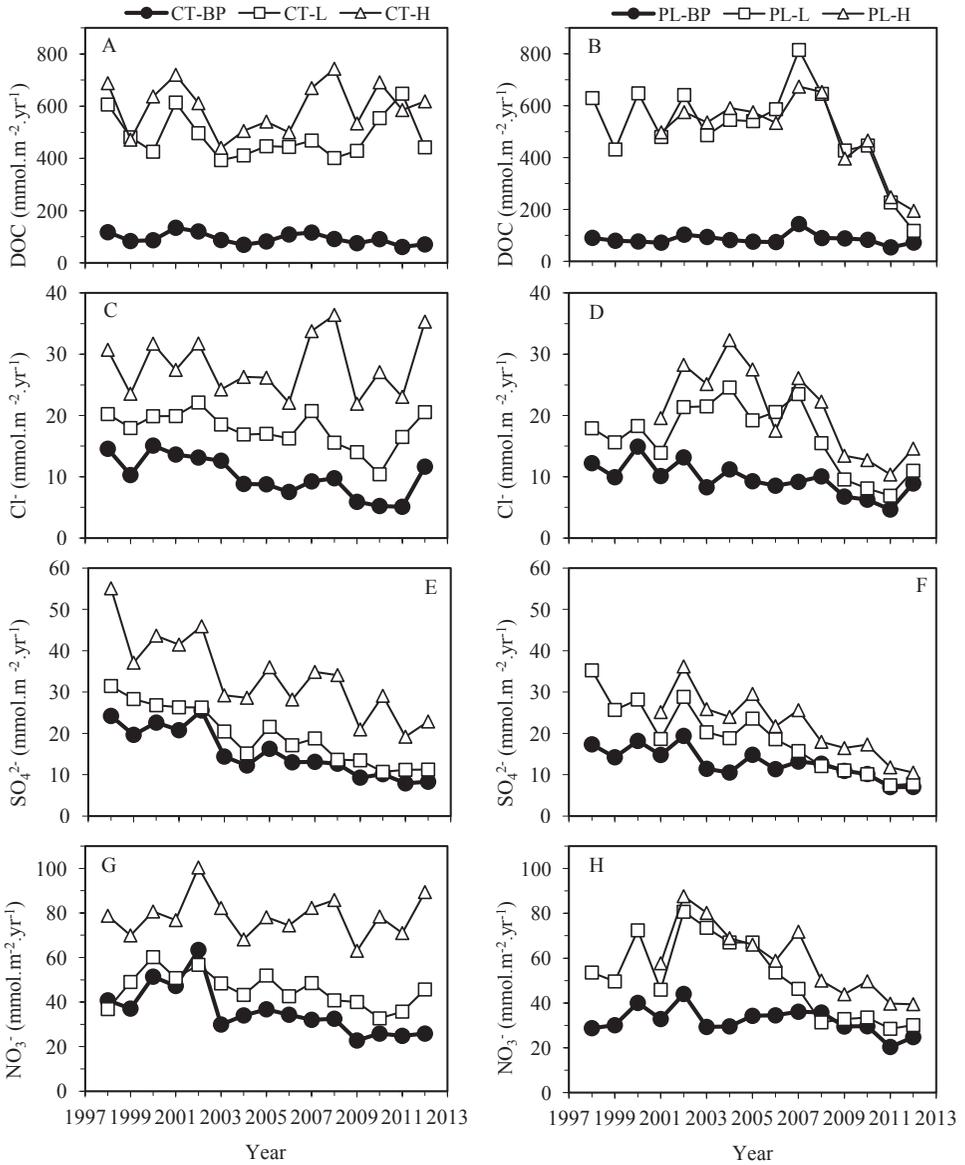


Fig. 3. Annual (November–October) average fluxes of dissolved organic carbon (DOC), Cl⁻, SO₄²⁻, and NO₃⁻ in bulk precipitation (BP) and throughfall at low (L) and high (H) elevations in the Čertovo (CT; left column) and Plešné (PL; right column) catchment.

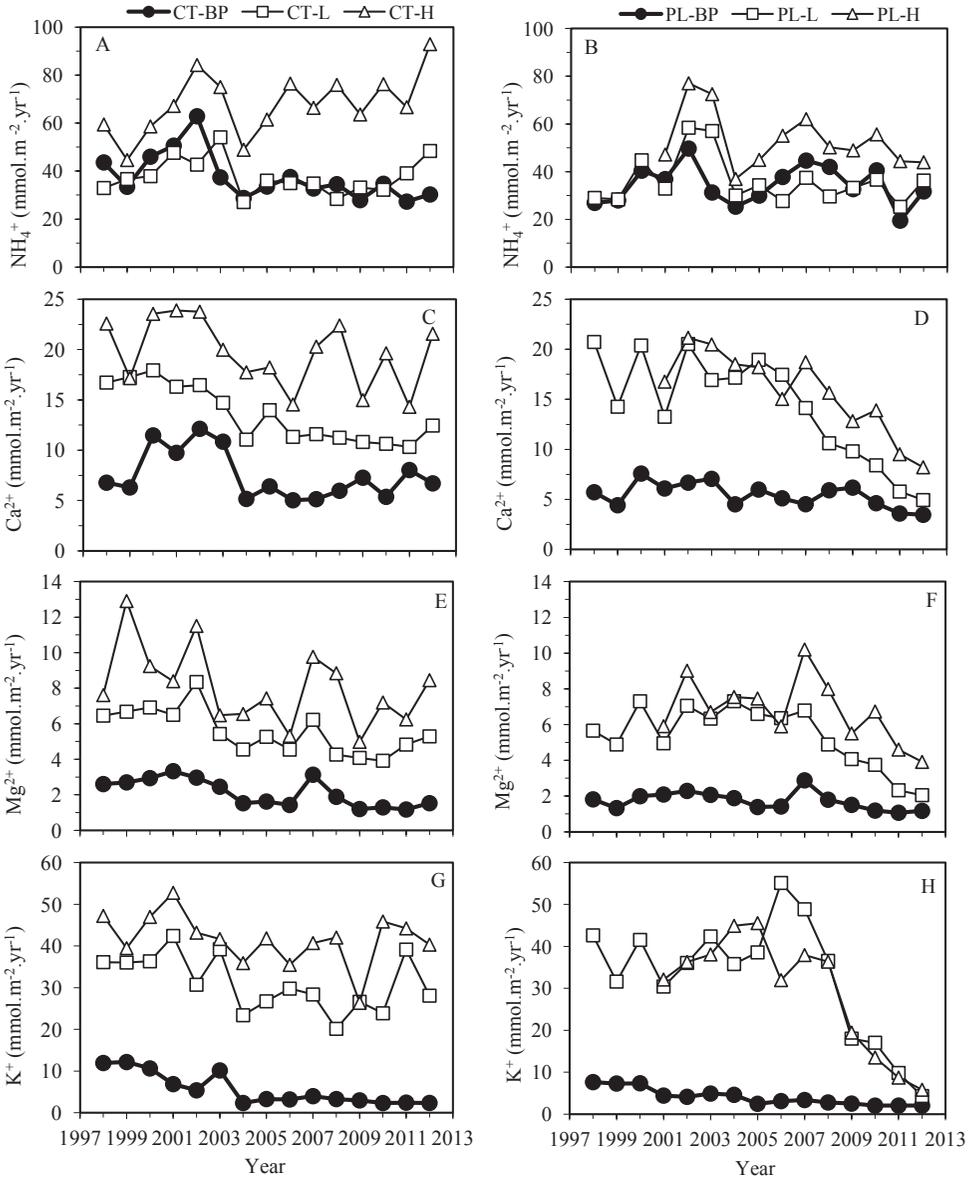


Fig. 4. Annual (November–October) average fluxes of NH_4^+ , Ca^{2+} , Mg^{2+} , and K^+ in bulk precipitation (BP) and throughfall at low (L) and high (H) elevations in the Čertovo (CT; left column) and Plešné (PL; right column) catchment.

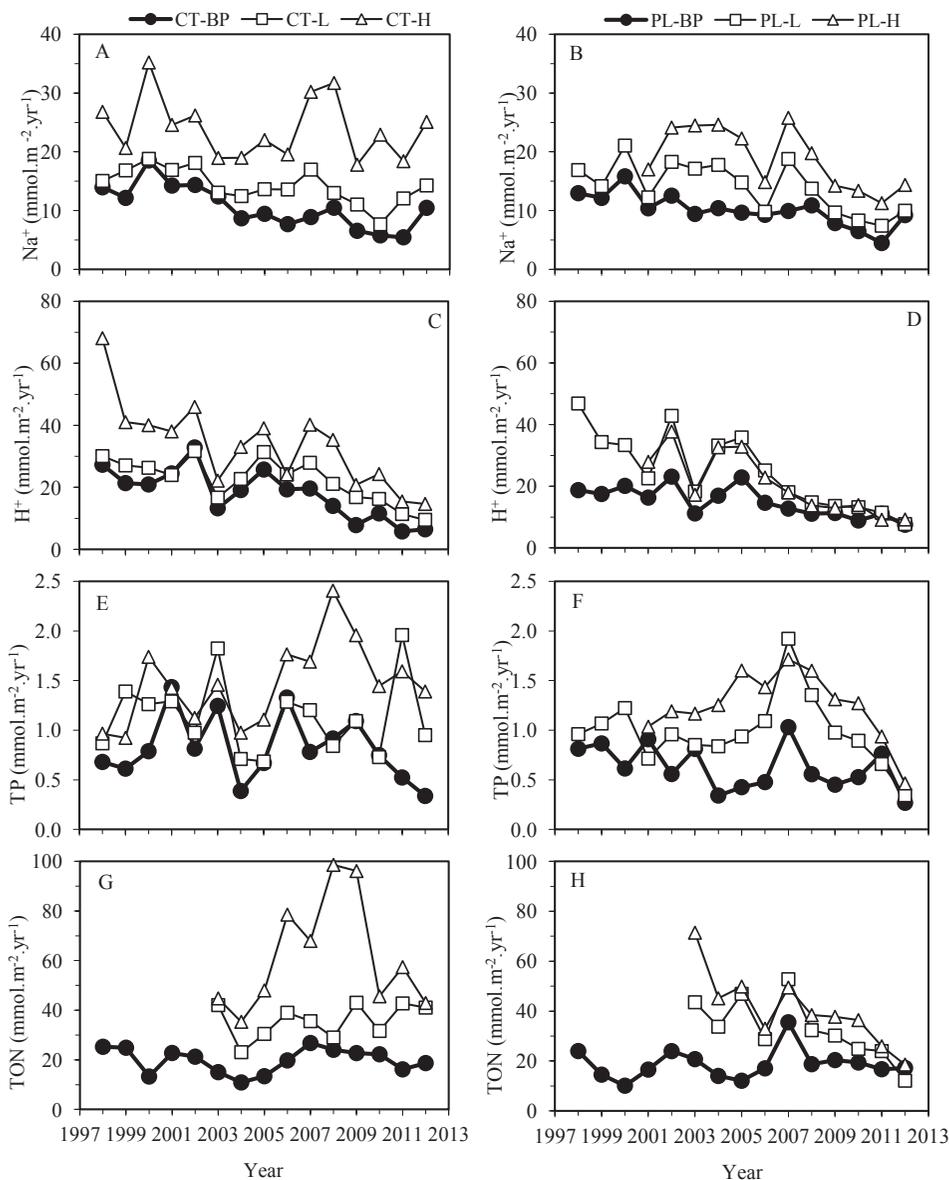


Fig. 5. Annual (November–October) average fluxes of Na⁺, H⁺, total phosphorus (TP) and total organic nitrogen (TON) in bulk precipitation (BP) and throughfall at low (L) and high (H) elevations in the Čertovo (CT; left column) and Plešné (PL; right column) catchment.

relatively to the unaffected CT plots in 2004–2008, and then, the ratios decreased to ~20% (K^+) and 30–50% (DOC) of the CT throughfall concentrations by 2012.

Canopy leaching of K^+ is usually greatest among base cations and originates from senescing tissue (BALESTRINI & TAGLIAFERRI 2001) and from decaying needles during the first decay stages (BERG & McCLAUGHERTY 2008), and was the most probable reason of the elevated K^+ throughfall fluxes immediately after the infestation (Fig. 4H). On an equivalent basis, the canopy leaching of K^+ was almost identical to that of A^- in the Bohemian Forest (KOPÁČEK et al. 2009), confirming the dominant role of K^+ as the cation compensating for leaching of organic acid anions from plant cells (BALESTRINI & TAGLIAFERRI 2001). With the continuing loss of the decaying needles and twigs from canopies in the years following infestation, leaching of K^+ and DOC ceased (Fig. 3B, 4H).

(2) The effect of bark beetle infestation on throughfall fluxes of Ca^{2+} and Mg^{2+} was less pronounced (Figs. 4D, F) than that on K^+ fluxes, and was negligible for Na^+ (Fig. 5B). The PL-L:CT-L and PL-H:CT-H concentration ratios for Mg^{2+} exhibited similar (even though not such a steep) trend as K^+ , with elevated canopy leaching immediately after the infestation, and then with continuously decreasing concentrations to ~50% of values measured at the unaffected CT throughfall plots in 2012 (Fig. 6F).

BERG & McCLAUGHERTY (2008) showed that Mg^{2+} release from decaying needles is much slower than that of K^+ , which is consistent with the observed differences between canopy contributions of these elements to throughfall fluxes. Proton exchange for Mg^{2+} in decaying tissue is the most probable processes explaining canopy leaching of this element in spruce stands (FRITSCHÉ 1992, JOHNSON & LINDBERG 1992). In contrast, H^+ exchange for Ca^{2+} in decaying biomass is usually small (JOHNSON & LINDBERG 1992) and canopy leaching of Ca^{2+} largely originates from the living tissue (KOPÁČEK et al. 2009). Plants can immobilize excess (and potentially toxic) Ca by the formation of poorly soluble Ca oxalate that accumulates in specialized cells. But Ca oxalate can also accumulate outside the mesophyll cell walls in Norway spruce needles (McLAUGHLIN & WIMMER 1999). A proportion of this Ca oxalate can be probably dissolved and exported from mechanically damaged (or insect attacked) needles, and the co-transport of Ca^{2+} and A^- can be an important factor contributing to Ca^{2+} canopy leaching. Oxalate was not determined in this study, but its peak has often occurred in chromatograms of anions from throughfall samples (KOPÁČEK et al. 2009). In contrast to Mg^{2+} and K^+ , the Ca^{2+} throughfall fluxes did not increase after the infestation, but they have been continuously decreasing (Fig. 4D), probably due to continuously reducing amount of living tissue in the canopies, as the infestation of trees in the study plots progressed.

(3) Throughfall fluxes of NH_4^+ changed only negligibly at the PL-L and PL-H plots after the infestation (Fig. 4B), as well as the PL-L:CT-L and PL-H:CT-H concentration ratios (Fig. 6D). The lack of changes was probably caused by two contrasting effects of defoliation on NH_4^+ fluxes. We assume that the lowered density and specific surface of the thinning canopies reduced dry and horizontal inputs of NH_4^+ to the canopies. In contrast, these changes reduced water residence time in the canopies and surface area where NH_4^+ uptake by microorganisms (living on needles and twigs) occurs, and, consequently, NH_4^+ transformation to organic nitrogen. This transformation plays an important role in reducing throughfall NH_4^+ fluxes (FERM 1993), especially in plots with higher wetness favouring green algae, lichens, and other epiphytic microflora (FERM & HULTBERG 1999), and was responsible for ~22% reduction of the NH_4^+ flux in the unaffected Bohemian Forest plots (KOPÁČEK et al. 2009). The reduced throughfall fluxes of TON at both PL plots after the infestation (Fig. 5H) suggest that the reduced NH_4^+ transformation probably roughly compensated for the decreasing NH_4^+ inputs and resulted in the relatively stable NH_4^+ throughfall fluxes despite the forest dieback.

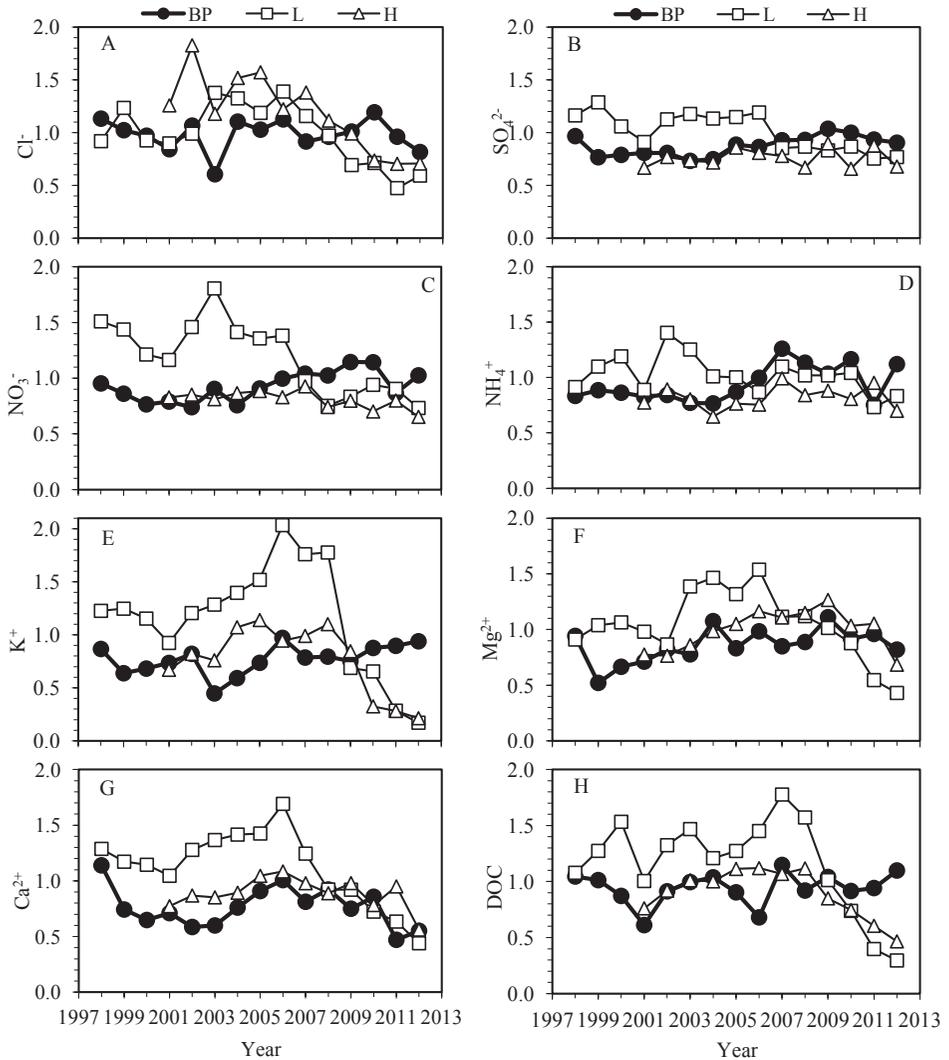


Fig. 6. Ratios of element concentrations measured in the Plešné (PL) vs. Čertovo (CT) catchment at the bulk precipitation (BP) and throughfall plots situated at low (L) and high (H) elevations. Abbreviations indicate the following ratios: BP, PL-BP:CT-BP; L, PL-L:CT-L; and H, PL-H:CT-H. For individual concentration data see Appendix 1.

(4) The SO_4^{2-} and NO_3^- concentrations significantly ($p < 0.05$) decreased at all the Bohemian Forest plots except for stable NO_3^- concentrations at the CT-H plot (Appendix 1). The steeper decline in SO_4^{2-} and NO_3^- concentrations expectedly occurred at the PL-L than CT-L plot, but the PL-H:CT-H concentration ratio remained stable (Fig. 6B, C), despite earlier infestation and more advanced canopy decay at the PL-H than PL-L plot (Table 2). The lack of difference between the PL-H and CT-H plots in their throughfall SO_4^{2-} and NO_3^- concentrations is surprising, especially because the PL-H:CT-H ratio for Cl^- concentrations significantly decreased (Fig. 6A).

Canopy leaching of SO_4^{2-} and NO_3^- is usually negligible in central European Norway spruce forests and their elevated TF:PF ratios result from dry and horizontal deposition of their compounds adsorbed on canopy surfaces (ULRICH 1983, ZIMMERMANN et al. 2006, BALESTRINI et al. 2007). The decreasing throughfall fluxes of SO_4^{2-} and NO_3^- at both PL plots after infestation (Figs. 3F, H) thus mostly resulted from their decreased adsorption onto the reduced canopy surface, rather than from changes in tissue vigour (as in the case of base cations). A part of this decrease was associated with continuing reduction in central European SO_2 and NO_x emissions to the atmosphere (KOPÁČEK & HRUŠKA 2010).

(5) Throughfall fluxes and concentrations of Cl^- continually decreased at both throughfall PL plots after their infestation (Fig. 3D, 6A). Similar decrease occurred also in the Na^+ throughfall fluxes at the PL plots (Fig. 5B), but was less steep than that of Cl^- . Consequently, the $\text{Na}^+:\text{Cl}^-$ ratios significantly increased in throughfall deposition at the PL-L ($p < 0.05$) and PL-H ($p < 0.001$) plots after their infestation (not shown). This disproportion between changes in the Na^+ and Cl^- fluxes suggests their partial origin from other sources besides marine aerosol. Even though the molar $\text{Na}^+:\text{Cl}^-$ ratio in the Bohemian Forest throughfall (0.85) was close to that in seawater (0.86) prior to infestation, this similarity was probably only accidental (KOPÁČEK et al. 2009). We assume that the average molar $\text{Na}^+:\text{Cl}^-$ ratio in the Bohemian Forest precipitation (1.05) was increased relative to the marine sources by Na^+ originating from terrestrial dust. Then, the throughfall $\text{Na}^+:\text{Cl}^-$ ratio was lowered in canopies by a relatively higher dry deposition of Cl^- than Na^+ . This additional Cl^- flux probably originated from HCl emissions from industrial sources and coal combustion. EVANS et al. (2011) have shown that the measures to reduce S emissions from coal combustion have led to a significant (95%) reduction also in HCl emissions in the United Kingdom. VESELY et al. (2002) have suggested that the industrial HCl emissions declined by ~50% in the Czech Republic during 1985–2000. The decreasing contribution of coal combustion to energy production in the Czech Republic thus probably caused decreasing HCl emissions, which resulted in significantly ($p < 0.01$) decreasing bulk precipitation fluxes of Cl^- during the study period (Figs. 3C, D). The disproportion between changes in Na^+ and Cl^- throughfall fluxes after the forest dieback thus may reflect different effects of decreasing canopy surface on adsorption of dust (source of Na^+) and HCl. An alternative explanation for this pattern is that Cl^- is not as conservative ion as we usually assume and is partly leached by canopy tissue. Foliar leaching of Cl^- has been observed elsewhere (e.g., DRAAIJERS & ERISMAN 1995, CORNU et al. 1998). The decreasing amount of canopy tissue after the infestation could thus partially contribute to lower canopy leaching and throughfall fluxes of Cl^- in the PL catchment.

(6) Throughfall fluxes of TP continuously decreased at the PL-L and PL-H plots after the infestation and reached values similar to bulk precipitation at the PL-BP plot in 2011–2012 (Fig. 5F), while remained higher at the unaffected CT throughfall plots (Fig. 5E). Canopy leaching of TP was small in the unaffected Bohemian Forest plots (KOPÁČEK et al. 2009). It is well known that P is not leached from decaying tissue as easily as other nutrients, being bound to complex organic matter during decomposition (BERG & McCLAUGHERTY 2008). The

reduced throughfall TP fluxes in the PL catchment thus probably resulted from lower horizontal input of dust particles, which could also explain decreasing throughfall fluxes of a conservative cation Na^+ (Fig. 5B).

CONCLUSIONS

Bark beetle infestation of Norway spruce stands in the catchment of Plešné Lake caused significant changes in proportion of vigour, dead, and broken trees at the study plots (Table 2) and, consequently, in throughfall deposition of most elements in this area compared to unaffected forests in the Čertovo Lake catchment. The changes, however, were not uniform for individual elements and reflected both their reduced input to the canopies by dry and horizontal deposition (due to reducing surface area of the infested canopies), as well as changes caused by element leaching from living and decaying canopy tissue. The greatest and most rapid changes occurred for K^+ , Mg^{2+} , and DOC (Fig. 4H, 4F, and 3B, respectively), i.e. elements whose throughfall fluxes were typically enriched by canopy leaching. Their fluxes increased immediately after the infestation and then rapidly decreased to values similar to bulk precipitation fluxes within the following 4–6 years. Similar trend occurred also for Ca^{2+} (Fig. 4D), but did not exhibit increasing flux after the infestation, and decreased more slowly than the K^+ and Mg^{2+} fluxes. Even slower changes occurred in throughfall fluxes of SO_4^{2-} , NO_3^- , and Cl^- (Fig. 3F, 3H, and 3D, respectively), which exhibit negligible or small (possibly Cl^-) canopy leaching. Negligible changes so far occurred in the throughfall fluxes of NH_4^+ (Fig. 6D), probably due to offsetting effects of its reduced input from dry and horizontal depositions and reduced microbial transformation in canopies, both caused by the reduced canopy surface.

By 2011, almost all trees were dead and ~75% and 50% of trees was broken and without canopies at the PL-L and PL-H plots (Table 2). The remaining trees are expected to fall within the following 2–5 years, depending on weather conditions and severity of storm events. The changes in throughfall chemistry and amounts thus will continue and slowly approach their values in the open areas for all constituents.

In contrast to forest clear-cut or wind-fall, when the throughfall deposition abruptly changes to bulk precipitation, the slow breakdown of forest after bark beetle attack represents longer (about one decade) and slower transition from throughfall to bulk precipitation character of atmospheric deposition.

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Appendix 1. Chemical composition of atmospheric deposition in the catchments of Čertovo and Plešné lakes in 1998–2012. Concentrations are volume weighted means ($\mu\text{mol.l}^{-1}$) for hydrological years (November–October). Height in mm; $\text{pH} = -\log(\text{VWM concentration of H}^+)$; ND, not determined.

Part 1/6		Čertovo Lake, bulk precipitation at elevation of 1180 m (CT-BP)														
		1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Height		1618	1159	1625	1600	1981	1057	1145	1368	1413	1401	1410	1253	1289	1108	1268
pH		4.77	4.73	4.89	4.82	4.78	4.90	4.78	4.73	4.86	4.85	5.00	5.20	5.05	5.28	5.29
H ⁺		16.9	18.4	12.9	15.3	16.6	12.6	16.7	18.8	13.7	14.0	9.9	6.2	9.0	5.2	5.1
Ca ²⁺		4.2	5.4	7.1	6.1	6.1	10.3	4.5	4.7	3.6	3.7	4.2	5.8	4.2	7.3	5.3
Mg ²⁺		1.6	2.3	1.8	2.1	1.5	2.3	1.3	1.2	1.0	2.2	1.3	1.0	1.0	1.1	1.2
Na ⁺		8.6	10.5	11.4	8.9	7.2	11.7	7.6	6.9	5.4	6.3	7.4	5.2	4.5	4.9	8.3
K ⁺		7.4	10.5	6.5	4.3	2.7	9.6	2.0	2.4	2.3	2.8	2.3	2.4	1.8	2.2	1.8
NH ₄ ⁺		26.9	28.8	28.3	31.6	31.7	35.3	25.1	24.5	26.6	23.4	24.5	22.3	26.9	24.6	23.8
NO ₃ ⁻		25.2	32.0	31.6	29.5	32.0	28.3	29.7	26.9	24.3	22.9	23.1	18.2	20.1	22.4	20.4
SO ₄ ²⁻		15.0	17.0	13.9	13.0	12.9	13.6	10.7	11.9	9.2	9.4	9.0	7.4	7.9	7.1	6.6
Cl ⁻		9.0	8.9	9.3	8.5	6.6	11.9	7.7	6.4	5.3	6.6	6.9	4.7	4.1	4.6	9.2
F ⁻		0.5	0.1	0.2	0.1	1.9	0.6	0.3	0.5	0.5	0.2	0.3	0.3	0.2	0.2	0.3
HCO ₃ ⁻		0.0	0.0	1.2	1.7	1.0	17.0	0.1	1.7	2.1	4.1	2.1	6.8	6.8	7.6	4.5
DOC		109	108	80	126	91	124	90	90	115	124	97	90	106	82	84
POC		ND	ND	ND	ND	ND	82	22	26	38	30	57	41	21	32	21
DON		13.9	8.6	7.3	12.7	8.8	7.2	7.4	10.1	12.6	14.5	14.4	16.8	14.7	8.8	13.4
PON		6.2	19.0	3.2	5.6	5.0	11.1	4.9	2.5	5.4	10.1	7.5	6.6	7.5	10.0	5.5
DP		0.15	0.14	0.23	0.56	0.17	0.62	0.14	0.30	0.50	0.29	0.47	0.51	0.35	0.13	0.13
PP		0.27	0.39	0.26	0.33	0.24	0.56	0.20	0.19	0.44	0.27	0.18	0.36	0.23	0.34	0.14
DRP		0.08	0.11	0.20	0.43	0.07	0.56	0.08	0.24	0.32	0.23	0.35	0.39	0.07	0.09	0.09
Al		0.10	0.13	0.12	0.07	0.07	0.24	0.14	0.09	0.08	0.11	0.11	0.18	0.12	0.20	0.14
Fe		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.26	0.12	0.22
Mn		0.07	0.07	ND	0.04	0.04	0.06	0.06								
Si		ND	ND	0.39	0.49	0.29	1.28	0.29	0.50	0.17	0.61	0.64	0.36	0.61	0.63	0.38

Appendix I. Continued.

Part 2/6	Čertovo Lake, throughfall deposition at elevation of 1057 m (CT-L)														
	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Year	1020	1189	1300	1372	1697	1140	968	1197	1249	1387	1277	1272	1117	1131	1282
Height	4.53	4.64	4.69	4.76	4.73	4.83	4.63	4.58	4.71	4.70	4.78	4.88	4.84	5.00	5.14
pH	29.5	22.8	20.2	17.5	18.7	14.6	23.4	26.2	19.4	20.1	16.5	13.3	14.6	10.1	7.3
H ⁺	16.4	14.5	13.8	11.9	9.7	12.9	11.4	11.7	9.1	8.4	8.8	8.5	9.5	9.1	9.9
Ca ²⁺	6.3	5.6	5.3	4.7	4.9	4.8	4.7	4.4	3.6	4.5	3.3	3.2	3.5	4.3	4.2
Mg ²⁺	14.7	14.2	14.5	12.3	10.7	11.4	12.9	11.4	10.9	12.2	10.2	8.7	6.9	10.7	10.8
Na ⁺	35.4	30.3	27.9	30.9	18.1	34.4	24.2	22.3	23.8	20.5	15.8	20.9	21.4	34.6	22.3
K ⁺	32.3	30.8	29.1	34.7	25.1	47.4	28.0	30.1	28.0	25.1	22.2	26.1	28.8	34.5	37.7
NH ₄ ⁺	36.1	41.2	46.3	37.0	33.4	42.4	44.6	43.4	34.1	35.0	31.9	31.5	29.3	31.6	36.6
NO ₃ ⁻	30.8	23.8	20.6	19.2	15.5	17.9	15.6	18.0	13.7	13.5	10.7	10.6	9.6	9.9	8.6
SO ₄ ²⁻	19.8	15.1	15.3	14.5	13.0	16.2	17.5	14.2	13.0	14.9	12.2	11.0	9.3	14.6	15.9
Cl ⁻	1.2	0.5	0.5	0.4	2.0	0.7	0.7	1.2	1.0	1.0	0.6	0.4	0.4	0.4	1.2
F ⁻	0.0	0.0	0.6	1.1	1.4	19.3	0.3	0.2	4.5	0.6	0.4	4.0	3.5	11.9	9.0
HCO ₃ ⁻	892	606	491	671	439	517	637	560	533	507	472	506	744	859	516
DOC	ND	ND	ND	ND	ND	157	97	113	85	187	75	124	60	117	124
POC	32	31	21	ND	ND	20	20	25	19	20	21	30	27	40	29
DON	ND	ND	ND	ND	ND	27	11	8	21	13	8	14	9	9	10
PON	0.45	0.58	0.39	0.25	0.16	0.73	0.23	0.18	0.33	0.29	0.29	0.25	0.23	0.41	0.32
DP	0.40	0.59	0.58	0.69	0.42	0.87	0.50	0.39	0.70	0.57	0.37	0.61	0.42	1.33	0.47
PP	0.29	0.23	0.23	0.08	0.05	0.58	0.11	0.07	0.23	0.14	0.14	0.11	0.03	0.15	0.17
DRP	0.19	0.19	0.14	ND	0.31	0.24	0.39	0.38							
Al	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.31	0.24	0.31
Fe	0.99	0.88	ND	0.38	0.52	0.39	0.32								
Mn															

Appendix I. Continued.

Part 3/6	Čertovo Lake, throughfall deposition at elevation of 1330 m (CT-H)														
	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Year	1637	1373	1749	1764	2053	1137	1237	1496	1540	1786	1822	1620	1567	1567	1713
Height	4.38	4.52	4.64	4.67	4.65	4.71	4.57	4.58	4.80	4.65	4.71	4.89	4.81	5.01	5.07
pH	41.6	29.9	22.9	21.6	22.4	19.5	26.7	26.1	15.7	22.5	19.4	12.8	15.5	9.9	8.6
H ⁺	13.8	12.5	13.5	13.5	11.6	17.6	14.3	12.2	9.4	11.4	12.3	9.2	12.5	9.1	12.6
Ca ²⁺	4.7	9.4	5.3	4.8	5.6	5.7	5.3	5.0	3.5	5.5	4.9	3.1	4.6	4.0	4.9
Mg ²⁺	16.4	15.0	20.1	13.9	12.7	16.7	15.4	14.7	12.7	16.9	17.4	11.0	14.6	11.7	14.6
Na ⁺	28.8	28.7	26.9	29.9	21.0	36.6	29.0	28.0	23.0	22.8	23.1	16.3	29.3	28.2	23.5
K ⁺	36.3	32.5	33.5	38.1	41.0	66.0	39.5	41.1	49.7	37.1	41.7	39.3	48.6	42.5	54.2
NH ₄ ⁺	48.1	50.9	46.1	43.5	48.9	72.3	55.1	52.2	48.3	46.1	47.1	38.9	50.0	45.3	52.2
NO ₃ ⁻	33.7	27.0	25.0	23.5	22.4	25.7	23.1	24.1	18.3	19.5	18.7	12.9	18.6	12.3	13.4
SO ₄ ²⁻	18.8	17.2	18.1	15.6	15.5	21.3	21.3	17.5	14.3	18.9	20.0	13.5	17.3	14.7	20.6
Cl ⁻	0.9	0.7	0.6	0.6	2.1	0.8	1.0	0.7	1.1	1.1	0.9	0.6	0.4	0.4	1.3
F ⁻	0.0	0.0	0.7	0.6	1.6	6.9	0.5	0.0	2.4	0.0	1.0	1.5	3.5	5.7	6.7
HCO ₃ ⁻	630	515	547	612	447	581	613	542	487	562	612	494	662	560	542
DOC	ND	ND	ND	ND	ND	207	142	114	146	219	122	112	99	26	119
POC	33	22	24	ND	ND	27	23	29	41	36	57	65	29	39	29
DON	ND	ND	ND	ND	ND	24	13	13	25	13	12	11	8	8	4
PON	0.30	0.17	0.41	0.21	0.10	0.61	0.22	0.22	0.53	0.23	0.70	0.57	0.30	0.23	0.30
DP	0.29	0.50	0.59	0.60	0.44	0.67	0.57	0.52	0.61	0.71	0.62	0.64	0.62	0.79	0.51
PP	0.17	0.04	0.24	0.06	0.02	0.38	0.09	0.08	0.40	0.10	0.42	0.38	0.16	0.11	0.17
DRP	0.21	0.15	0.20	ND	0.35	0.55	0.43								
Al	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.36	0.34
Fe	0.65	0.75	ND	0.49	0.66	0.44	0.38								
Mn															

Appendix 1. Continued.

Part 4/6	Plešné Lake, bulk precipitation at elevation of 1087 m (PL-BP)															
	Year	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Height	1197	1093	1655	1408	1860	1860	1146	1315	1406	1425	1516	1513	1418	1293	1050	1186
pH	4.81	4.80	4.91	4.94	4.91	5.01	5.01	4.89	4.79	4.99	5.08	5.13	5.10	5.16	4.98	5.20
H ⁺	15.7	16.0	12.2	11.6	12.4	9.8	9.8	12.9	16.3	10.3	8.4	7.3	8.0	6.9	10.6	6.3
Ca ²⁺	4.8	4.0	4.6	4.3	3.6	6.2	6.2	3.4	4.3	3.6	3.0	3.9	4.4	3.6	3.4	2.9
Mg ²⁺	1.5	1.2	1.2	1.5	1.2	1.8	1.8	1.4	1.0	1.0	1.9	1.2	1.1	0.9	1.0	1.0
Na ⁺	10.8	11.1	9.6	7.4	6.7	8.2	8.2	7.9	6.9	6.5	6.5	7.2	5.5	5.0	4.3	7.8
K ⁺	6.4	6.7	4.5	3.1	2.2	4.3	4.3	3.5	1.8	2.2	2.2	1.8	1.8	1.6	2.0	1.7
NH ₄ ⁺	22.5	25.5	24.4	26.2	26.7	27.3	27.3	19.3	21.3	26.5	29.4	27.8	23.0	31.4	18.5	26.7
NO ₃ ⁻	24.0	27.5	24.2	23.3	23.7	25.6	25.6	22.5	24.4	24.2	23.8	23.6	20.8	22.9	19.4	20.9
SO ₄ ²⁻	14.5	13.0	11.0	10.5	10.4	10.0	10.0	8.0	10.5	8.0	8.7	8.4	7.7	7.9	6.7	5.9
Cl ⁻	10.2	9.1	9.0	7.2	7.1	7.2	7.2	8.5	6.6	6.0	6.0	6.6	4.8	4.8	4.4	7.5
F ⁻	0.4	0.0	0.2	0.2	0.6	0.3	0.3	0.4	0.4	0.5	0.4	0.4	0.2	0.3	0.4	0.4
HCO ₃ ⁻	0.6	0.5	0.7	2.1	0.9	4.9	4.9	1.1	0.3	3.9	1.6	3.1	3.6	5.2	2.0	3.2
DOC	114	109	70	77	83	123	123	94	81	78	142	89	94	97	78	92
POC	ND	ND	ND	ND	ND	109	109	15	40	31	81	45	52	7	10	6
DON	16.2	7.9	5.5	8.2	10.9	11.2	10.1	10.1	7.1	10.7	21.9	9.2	11.3	13.7	13.3	12.5
PON	9.6	9.2	2.3	6.9	5.6	12.1	3.6	4.0	4.0	4.7	8.2	6.7	7.1	5.6	7.2	6.2
DP	0.25	0.56	0.14	0.43	0.14	0.26	0.12	0.12	0.06	0.11	0.41	0.15	0.13	0.20	0.27	0.08
PP	0.43	0.23	0.23	0.21	0.16	0.44	0.14	0.14	0.24	0.22	0.27	0.22	0.19	0.21	0.45	0.14
DRP	0.17	0.49	0.10	0.40	0.11	0.15	0.08	0.04	0.04	0.05	0.38	0.10	0.07	0.07	0.20	0.05
Al	0.10	0.19	0.11	0.07	0.08	0.17	0.07	0.07	0.09	0.11	0.21	0.08	0.26	0.20	0.19	0.18
Fe	ND	ND	ND	ND	ND	0.43	0.39	0.54	0.49	0.52	0.58	0.58	0.29	0.24	0.17	0.21
Mn	0.05	0.07	ND	0.05	0.04	0.04	0.03									
Si	ND	ND	0.08	0.16	0.23	0.38	0.14	0.22	0.48	0.47	0.66	0.67	1.04	0.87	0.87	0.42

Appendix I. Continued.

Part 5/6	Plešné Lake, throughfall deposition at elevation of 1122 m (PL-L)														
	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Height	982	838	1290	1067	1654	960	1062	1138	1137	1357	1306	1251	1219	998	1154
pH	4.32	4.39	4.59	4.67	4.59	4.72	4.50	4.50	4.66	4.88	4.95	4.96	4.97	4.94	5.17
H ⁺	47.7	41.0	25.9	21.2	25.9	19.1	31.3	31.5	22.1	13.3	11.3	10.9	10.8	11.5	6.7
Ca ²⁺	21.1	17.0	15.8	12.4	12.4	17.6	16.2	16.7	15.3	10.4	8.1	7.8	6.9	5.8	4.3
Mg ²⁺	5.8	5.8	5.7	4.6	4.3	6.6	6.9	5.8	5.6	5.0	3.7	3.3	3.1	2.3	1.8
Na ⁺	17.2	16.9	16.3	11.5	11.1	17.8	16.7	13.0	8.6	13.8	10.5	7.7	6.8	7.4	8.6
K ⁺	43.4	37.8	32.2	28.5	21.8	44.2	33.7	33.9	48.5	36.0	28.0	14.4	14.0	9.8	3.7
NH ₄ ⁺	29.5	33.9	34.7	30.8	35.3	59.4	28.3	30.2	24.3	27.6	22.7	26.6	30.0	25.3	31.4
NO ₃ ⁻	54.6	59.2	56.1	43.1	48.8	76.6	63.1	58.9	47.2	34.1	24.0	26.2	27.5	28.6	26.1
SO ₄ ²⁻	35.9	30.7	21.8	17.5	17.4	21.1	17.7	20.7	16.4	11.6	9.3	8.8	8.3	7.5	6.7
Cl ⁻	18.2	18.6	14.2	13.0	12.9	22.4	23.1	16.9	18.1	17.3	11.9	7.6	6.6	6.9	9.5
F ⁻	1.2	0.7	0.6	1.0	1.0	0.7	0.4	1.3	1.3	1.2	0.7	0.4	0.4	0.6	0.6
HCO ₃ ⁻	2.2	0.9	0.7	0.4	0.1	4.8	0.0	0.4	7.0	1.1	4.4	3.8	2.6	2.4	4.5
DOC	961	772	753	674	581	760	771	713	774	900	741	513	549	342	153
POC	ND	ND	ND	ND	ND	138	109	260	249	158	166	125	33	1	6
DON	35	28	27	ND	ND	36	24	32	20	32	17	20	18	24	10
PON	ND	ND	ND	ND	ND	22	17	21	12	18	15	11	8	7	3
DP	0.21	0.19	0.24	0.20	0.14	0.19	0.23	0.16	0.20	0.55	0.38	0.24	0.25	0.17	0.15
PP	0.77	1.08	0.71	0.47	0.44	0.70	0.56	0.67	0.76	0.87	0.66	0.54	0.48	0.49	0.15
DRP	0.05	0.07	0.12	0.07	0.02	0.05	0.09	0.05	0.08	0.34	0.16	0.07	0.09	0.06	0.07
Al	0.19	0.21	0.26	ND	0.44	0.45	0.35	0.24							
Fe	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.50	0.31	0.28	0.30
Mn	0.64	0.62	ND	0.26	0.24	0.14	0.10								

Appendix 1. Continued.

Part 6/6 Year	Plešné Lake, throughfall deposition at elevation of 1334 m (PL-H)											
	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Height	1602	2104	1367	1445	1430	1468	1683	1433	1415	1418	1097	1159
pH	4.76	4.75	4.90	4.65	4.64	4.81	4.97	5.02	5.04	5.01	5.08	5.10
H ⁺	17.4	17.9	12.6	22.6	23.0	15.6	10.7	9.6	9.2	9.8	8.3	8.0
Ca ²⁺	10.5	10.1	15.0	12.8	12.7	10.2	11.1	10.9	9.1	9.8	8.7	7.1
Mg ²⁺	3.7	4.3	4.9	5.2	5.2	4.0	6.1	5.6	3.9	4.7	4.2	3.4
Na ⁺	10.6	11.5	17.9	17.0	15.6	10.1	15.3	13.8	10.1	9.4	10.3	12.4
K ⁺	20.0	17.3	27.8	31.1	31.9	21.8	22.5	25.4	13.7	9.5	8.0	5.0
NH ₄ ⁺	29.5	36.6	53.0	25.6	31.4	37.5	36.9	35.0	34.6	39.2	40.5	37.9
NO ₃ ⁻	36.0	41.7	58.7	47.7	46.2	40.1	42.7	34.9	31.0	35.1	36.2	34.1
SO ₄ ²⁻	15.7	17.2	18.9	16.6	20.7	14.8	15.2	12.5	11.6	12.2	10.8	9.1
Cl ⁻	12.2	13.4	18.4	22.4	19.2	11.9	15.5	15.5	9.5	9.0	9.4	12.6
F ⁻	0.5	1.3	0.7	0.4	0.8	0.8	0.9	0.7	0.5	0.4	0.8	0.7
HCO ₃ ⁻	0.4	0.2	4.5	1.1	0.4	2.3	0.9	8.2	7.8	4.2	6.0	5.0
DOC	466	410	588	614	603	545	600	684	420	493	339	252
POC	ND	ND	ND	211	203	132	191	246	159	103	17	11
DON	25	ND	ND	24	32	19	23	15	24	23	25	17
PON	ND	ND	ND	16	13	9	14	20	11	10	6	3
DP	0.20	0.14	0.20	0.17	0.40	0.39	0.28	0.28	0.30	0.35	0.32	0.15
PP	0.45	0.43	0.66	0.70	0.72	0.58	0.73	0.83	0.62	0.55	0.53	0.25
DRP	0.06	0.05	0.06	0.05	0.23	0.15	0.13	0.08	0.14	0.10	0.23	0.07
Al	ND	ND	ND	ND	ND	ND	ND	ND	0.41	0.36	0.32	0.31
Fe	ND	ND	ND	ND	ND	ND	ND	ND	0.35	0.25	0.24	0.34
Mn	ND	ND	ND	ND	ND	ND	ND	ND	0.52	0.52	0.42	0.24

Notes