

# Bulk deposition and throughfall fluxes of elements in the Bohemian Forest (central Europe) from 1998 to 2009

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We measured element concentrations and fluxes in bulk precipitation (at two sites) and throughfall (at four sites) in Norway spruce mountain stands in the Bohemian Forest (Czech Republic) from 1998–2009, with the aim to evaluate net atmospheric inputs of nutrients to the area, and (together with previous data from 1991–1997) long-term trends in acidic deposition. The average net atmospheric inputs of nutrients were 11, 4, 9, 62, 62, 45, 26, and 0.7–1.3 mmol m<sup>-2</sup> yr<sup>-1</sup> for Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, total organic N, S, and total P (TP), respectively. The TP deposition was affected by a notable contribution from local dust and pollen sources. Throughfall pH increased from 3.6–3.7 in 1991–1994 to 4.7–5.0 in 2006–2009, due to average declines in the SO<sub>4</sub><sup>2-</sup> plus NO<sub>3</sub><sup>-</sup> concentrations by 202 μeq l<sup>-1</sup> and the H<sup>+</sup> concentration by 147 μeq l<sup>-1</sup>. The decline in throughfall concentrations of SO<sub>4</sub><sup>2-</sup> (by 184 μeq l<sup>-1</sup>) was the dominant driving force for the pH increase.

## Introduction

Atmospheric deposition of pollutants and nutrients are usually important factors in environmental monitoring, enabling mass-budget studies, evaluations of element cycling within terrestrial and aquatic ecosystems, and reconstruction and prognoses of environmental biogeochemical trends (e.g., Likens *et al.* 1977). This paper presents the data from a twelve-year study of bulk and throughfall depositions in two mountain forest areas (the catchments of Plešné and Čertovo lakes), located in the Bohemian Forest about 150–200 km south of the most highly industrialised central European region, the so-called “Black Triangle” at the German–Polish–Czech borders (Fig. 1). In the past, this region was characterised by numerous electric power

plants burning S-rich lignite, which resulted in the highest European levels of SO<sub>2</sub> emissions into the atmosphere (a maximum of ~800 mmol m<sup>-2</sup> yr<sup>-1</sup> in the late 1980s; Berge 1997) and very high acidic deposition in the surrounding mountain regions (e.g., Moldan 1991, Alewell *et al.* 2000, Zimmermann *et al.* 2003). Political and economical changes in post-communist countries after 1989 (declines in energy and cattle production and the application of synthetic N-fertilizers) and emission controls of S and N oxides throughout Europe caused a rapid decline in central European emissions of SO<sub>2</sub>, NO<sub>x</sub>, and NH<sub>3</sub> (Kopáček and Veselý 2005). These reductions in emission rates resulted in a significant decline in acidic deposition in the region (e.g., Kopáček *et al.* 1997, Zimmermann *et al.* 2003, Oulehle *et al.* 2006).



**Fig. 1.** Locations of the deposition sites (catchments of Čertovo [CT] and Plešné [PL] lakes) and the Churáňov meteorological station in the Bohemian Forest (Czech Republic).

Hruška *et al.* (2000) evaluated chemical changes in the composition of precipitation and throughfall in the Bohemian Forest following the steepest decline in S and N emissions in the early 1990s. This research mostly focussed on acidifying pollutants [sulphate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), chloride ( $\text{Cl}^-$ ) and ammonia ( $\text{NH}_4^+$ )], base cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ), and heavy metals. In addition to data from previous acidic deposition monitoring, our current study includes phosphorus (P) forms, organic nitrogen, and organic carbon. The objectives were to use precipitation and throughfall chemistry data from the 1997–2009 period to (1) quantify the effect of altitude on atmospheric inputs of water and elements to the catchments and their seasonal patterns, (2) estimate the net atmospheric input of nutrients to the mountain forest, and (3) evaluate, together with previously published data (Veselý and Majer 1992, Hruška *et al.* 2000), long-term trends in acidic deposition in the Bohemian Forest.

## Material and methods

### Study sites

Atmospheric deposition was sampled at two throughfall plots and one open-area plot in both the Plešné Lake (PL) and Čertovo Lake (CT) catchments, situated on the north-eastern slope of the mountain ridge of the Bohemian Forest, along the border between the Czech Republic, Germany, and Austria (Fig. 1). Throughfall plots

were at low (L; < 1122 m; PL-L and CT-L) and high (H; ~1330 m; PL-H and CT-H) altitudes (Table 1), with annual average air temperatures of 5.5 and 3.9 °C, respectively, during the study period. 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 windstorm (broken branches, a high amount of twigs in litter fall) at the beginning of 2005. The plots PL-H and PL-L have been affected by a bark beetle (*Ips typographus*) outbreaks since the summers of 2004 and 2007, respectively, and all trees above the collectors died within two-three years of infestation. Even though they lost needles and some twigs and branches, which reduced the surface areas of their canopies, most of dead trees were still standing at both PL-L and PL-H plots at the end of this study, and chemical composition of throughfall at the PL plots remained similar to throughfall at the unaffected CT plots (*see below*).

Bulk precipitation (BP) was sampled in open areas without trees at the altitudes 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.

### Sampling and analyses

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 cm<sup>2</sup>) 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 cm<sup>2</sup>) 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 2009 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 were pre-filtered through a 200- $\mu$ m polyethylene sieve to remove coarse particles, either during collecting (rain collectors were equipped with a sieve) or immediately after melting the snow from the winter collectors. Then, samples were stored in the dark at 4 °C and subsamples for N and P analyses were frozen at –20 °C. Samples were analyzed within < 2 weeks after sampling.

Prior to analyses, samples were filtered through either membrane filters (pore size of 0.45  $\mu$ m) for the determination of ions, or through glass-fiber filters (pore size of 0.4  $\mu$ m) for other analyses, except samples for pH, alkalinity (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). Dissolved reactive P (DRP) was determined by the molybdate method (Murphy and Riley 1962). Total P (TP) was determined by perchloric acid digestion and the molybdate method; if necessary, samples were concentrated by evaporation (with perchloric acid at ~100 °C prior to digestion) to obtain a detection limit of ~0.02  $\mu$ mol l<sup>-1</sup> P (Kopáček and Hejzlar 1993). From 1998 to 2002, total organic N (TON; the difference between Kjeldahl N and NH<sub>4</sub>-N) was determined by Kjeldahl digestion according to Procházková (1960), with 25–75 ml of samples previously evaporated to obtain a detection limit of ~2  $\mu$ mol l<sup>-1</sup> N. From 2003 to 2009, concentrations of TON were calculated as the differences between concentrations of total N (TN, determined by the TOC/TN analyzer, Formacs) and inorganic N. In this calculation, inorganic N was the sum of NO<sub>3</sub>-N and NH<sub>4</sub>-N, whereas NO<sub>2</sub>-N (typically < 1% of NO<sub>3</sub>-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 ( $\pm$  SD) for the Kjeldahl digestion and TOC/TN analyzer of 21  $\pm$  18 and 21  $\pm$  19  $\mu$ mol l<sup>-1</sup>. Concentrations of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and other ions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>,

**Table 1.** Locations of bulk precipitation (BP) and throughfall study plots in the Bohemian Forest. Abbreviations: L = low altitude, H = high altitude.

	Plešné (PL) catchment			Čertovo (CT) catchment		
	PL-BP	Throughfall		CT-BP	Throughfall	
		PL-L	PL-H		CT-L	CT-H
Lat. °N (WGS-84)	48.7760	48.7752	48.7767	49.1754	49.1627	49.1696
Long. °E (WGS-84)	13.8708	13.8680	13.8547	13.1990	13.1993	13.1858
Elevation (m a.s.l.)	1087	1122	1334	1180	1057	1330

K<sup>+</sup>) were determined by ion chromatography (Dionex IC25, USA). Concentrations of HCO<sub>3</sub><sup>-</sup> were assumed to be equal to positive alkalinity values, while HCO<sub>3</sub><sup>-</sup> = 0 was used for all alkalinity values ≤ 0 μmol l<sup>-1</sup>.

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.* 2000), and a standard sample (a frozen subsample of water, with similar composition as throughfall), which was melted and assayed with each series of samples. Concentrations of organic acid anions (A<sup>-</sup>) for this control were estimated from DOC concentrations, using an empirical relationship of A<sup>-</sup> (μeq l<sup>-1</sup>) = 4 × DOC (mg l<sup>-1</sup>), 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<sup>-</sup>) were < ±10% of the total ionic content in individual precipitation and throughfall samples (at higher differences, samples were re-analyzed), and < ±4% for the annual volume weighted mean concentrations. Coefficients of variation for mean concentrations of the standard sample were 1%–5% for all ions (except for F<sup>-</sup>), DOC, TP, and pH; < 10% for TON and DRP; and < 20% for F<sup>-</sup> (e.g., 55 ± 2, 36 ± 3, 1.12 ± 0.06, 0.84 ± 0.08, and 1.1 ± 0.2 μeq l<sup>-1</sup> for NO<sub>3</sub><sup>-</sup>, TON, TP, DRP, and F<sup>-</sup>, respectively, in 2009, *n* = 36).

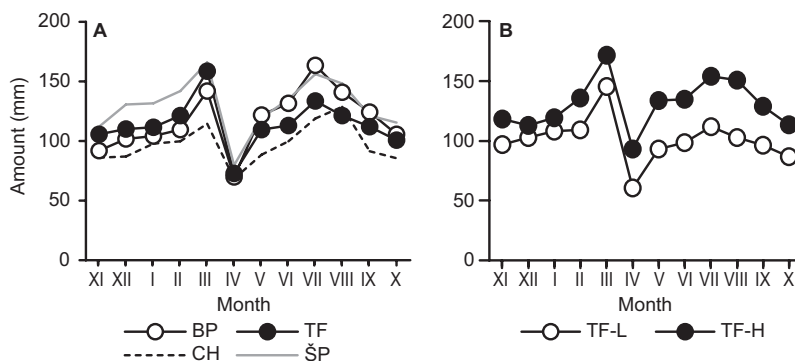
## Data evaluation

Annual average compositions of precipitation and throughfall were calculated as volume weighted mean concentrations. When the DRP and F<sup>-</sup> concentrations were below their detection limits of 0.05 and 0.1 μmol l<sup>-1</sup> (~2% and ~25% of all samples), respectively, a half of these values were used in subsequent data evaluation. Concentrations of other constituents were always above their detection limits. Averages (± SD) of element concentrations and fluxes during the whole study period were calculated for each plot from annual volume weighted mean concentrations and fluxes, respectively. To

compensate for differences between the individual plots caused by their altitudes and geographical positions, we calculated the average throughfall and precipitation fluxes (TF and PF) in the Bohemian Forest as arithmetical averages for all four throughfall plots and both bulk precipitation plots, respectively. Data on bulk precipitation and throughfall composition (annual volume weighted mean concentrations) and fluxes in the CT catchment prior to 1998 were from Veselý and Majer (1992), and Hruška *et al.* (2000).

Characteristic curves of average monthly element fluxes and concentrations were obtained as arithmetical means for the respective monthly data over the study period. The monthly data were recalculated from the original 2–4 week intervals using (i) the distribution of daily precipitation amounts measured at the Špičák meteorological station, situated ~2 km east of the CT catchment at the altitude of 950 m, and the Churáňov station, situated in the central part of the Bohemian Forest (Fig. 1; 49.067°N, 13.617°E, altitude 1118 m; data from the Czech Hydrometeorological Institute), and (ii) continuous summer (May to November) measurements of precipitation with automatic weather stations situated at the outlets from the PL and CT catchments. For this calculation, the element flux was attributed to individual days proportionally to the daily precipitation amount, assuming constant element concentrations throughout the sampling interval. The average seasonal cycles of element fluxes in the Bohemian Forest were then calculated as arithmetical averages of the respective monthly data for PL-BP and CT-BP (bulk precipitation at open area plots; BP), PL-L and CT-L (throughfall at low-altitude plots; TF-L), and PL-H and CT-H (throughfall at high-altitude plots, TF-H).

We used the Wilcoxon matched pairs test (STATISTICA, StatSoft ver. 9.1, www.statsoft.com) with the significance level of 0.05 to test for differences in (1) element concentrations and fluxes between the high- and low-altitude plots in both catchments: PL-H vs. PL-L (*n* = 107, monthly data from 2001–2009) and CT-H vs. CT-L (*n* = 144, monthly data from 1998–2009) and (2) TP and K<sup>+</sup> fluxes and precipitation amounts between the PL-BP and CT-BP plots (*n* = 143, monthly data from 1998–2009). The



**Fig. 2.** Average seasonal patterns of bulk precipitation (BP) and throughfall (TF) in the Bohemian Forest from 1998 to 2009: **(A)** comparison of precipitation (average for PL-BP and CT-BP) and throughfall (average for PL-L, PL-H, CT-L, and CT-H) amounts at the study plots with precipitation at the Churáňov (CH) and Špičák (ŠP) meteorological stations; **(B)** comparison of throughfall amounts at low altitude (TF-L, average for PL-L and CT-L, < 1122 m) and high altitude (TF-H, average for PL-H and CT-H, ~1330 m).

null hypothesis was that the sample means were equal. A non-parametric procedure was selected because of inhomogeneous variances.

Evaluation of the relative importance of local sources and long-range transport at the PL-BP and CT-BP plots followed Kopáček *et al.* (1997). We compared the particular slopes and significances of linear regressions between annual precipitation amounts and volume-weighted mean concentrations and/or annual fluxes of elements assuming that: (i) if dry deposition dominated the total deposition of an element then a negative correlation should exist between its concentration and precipitation amount, while its flux should be independent of precipitation amount; and (ii) if long-range transport (and wet deposition) was prominent then the concentration of an element would be independent of precipitation amount, while there should be a positive correlation between the element flux and precipitation amount. This evaluation is based on the fact that dry deposition is the dominant pathway in areas that are close to sources of pollutant emissions, while the importance of wet deposition increases with the distance from pollutant sources (e.g., Moldan 1991, Erisman *et al.* 1997, Asman 1998).

Average rates of change in precipitation and throughfall fluxes of elements were based on a regression of their annual fluxes against time over the study period. The PL-H plot was excluded from this trend analysis due to the shorter records than those for other plots, and the

long duration of forest dieback in this part of the PL catchment.

## Results and discussion

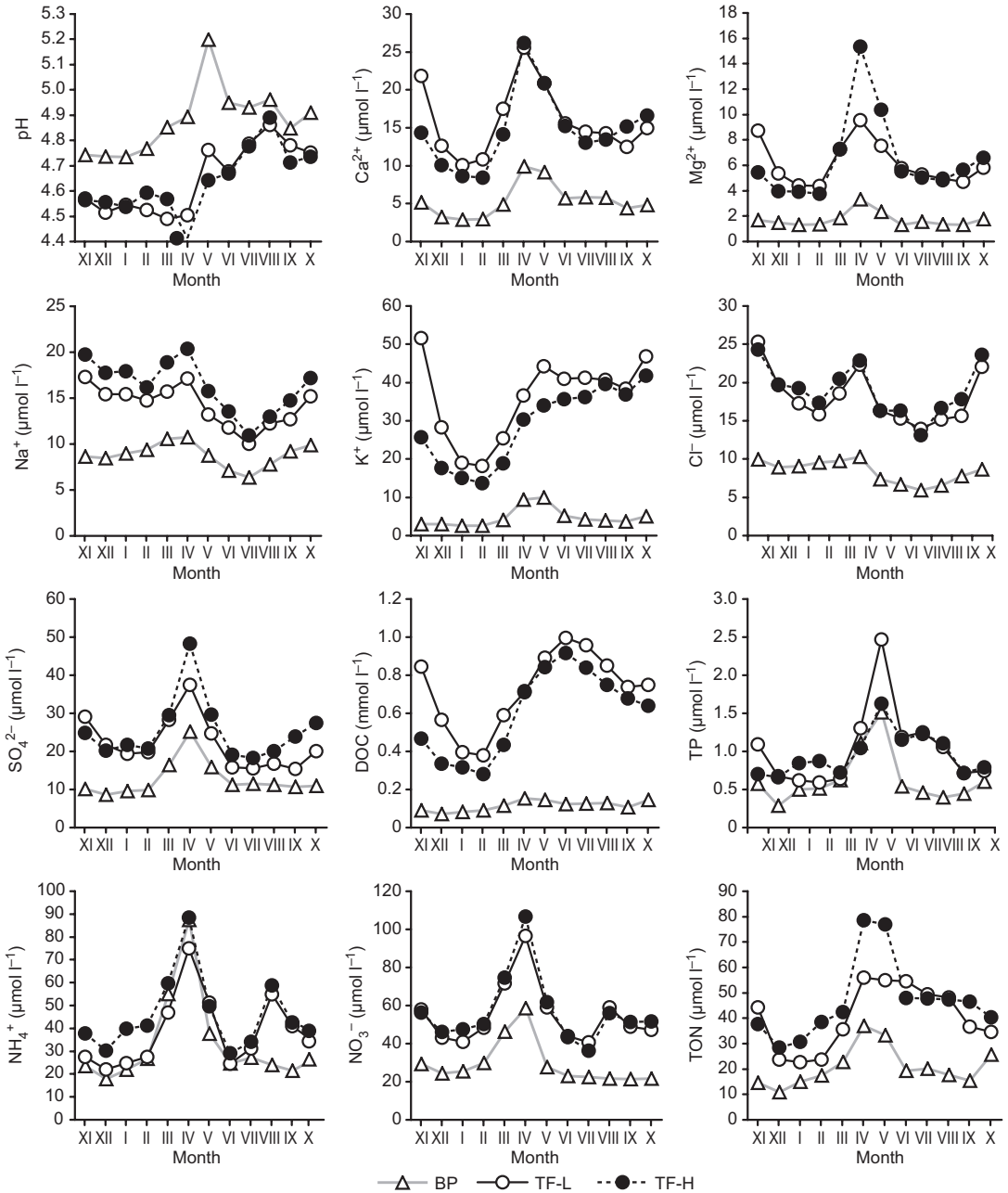
### Precipitation and throughfall fluxes

The annual average precipitation and throughfall amounts (mostly rain from May–October and snow from November–April) varied within 1057–1981 and 838–2053 mm, respectively, in both study catchments from 1998 to 2009. These precipitation amounts were in accordance with the long-term (1961–2009) range of 866–2211 mm at the Churáňov and Špičák stations. Throughfall amounts were significantly higher ( $p < 0.001$ ) at the high- versus low-altitude plots in both catchments (Table 2 and Fig. 2B), with altitude gradients of 1.9 vs. 1.2 mm m<sup>-1</sup> in the PL and CT catchment, respectively. No statistical difference ( $p > 0.05$ ) was observed between annual precipitation amounts at the PL-BP and CT-BP plots. On a seasonal basis, throughfall amount was the highest in March (while maximum precipitation was in July–August), and minima occurred in October–November and, especially, in April. Similar precipitation minima occurred also at the open area Churáňov and Špičák stations in the 1998–2009 period (Fig. 2A), indicating that the observed pattern was characteristic for the whole Bohe-

**Table 2.** Average ( $\pm$  SD) annual concentrations and fluxes of bulk precipitation (PL-BP, CT-BP) and throughfall (PL-L, PL-H, CT-L, CT-H) in the Bohemian Forest from 1998–2009. Abbreviations: PL, Plešné catchment; CT, Čertovo catchment; BP, bulk precipitation; L, low altitude; H, high altitude. Asterisks denote significant differences (Wilcoxon matched pairs test; \*  $p < 0.05$ , \*\*  $p < 0.01$ , and \*\*\*  $p < 0.001$ ) in element concentrations and fluxes between the low and high altitude throughfall plots (PL-L vs. PL-H,  $n = 107$ ; CT-L vs. CT-H,  $n = 144$ ) calculated for monthly data.

	Average concentrations ( $\mu\text{mol l}^{-1}$ )						Average fluxes ( $\text{mmol m}^{-2}\text{yr}^{-1}$ )					
	PL-BP	PL-L	PL-H	CT-BP	CT-L	CT-H	PL-BP	PL-L	PL-H	CT-BP	CT-L	CT-H
Amount <sup>1)</sup>	1413 $\pm$ 215	1170 $\pm$ 218***	1550 $\pm$ 230	1419 $\pm$ 258	1256 $\pm$ 188***	1601 $\pm$ 262						
pH <sup>2)</sup>	4.95 $\pm$ 0.12	4.64 $\pm$ 0.21***	4.84 $\pm$ 0.15	4.86 $\pm$ 0.13	4.71 $\pm$ 0.10***	4.65 $\pm$ 0.13						
H <sup>+</sup>	12 $\pm$ 3	25 $\pm$ 11***	15 $\pm$ 5	14 $\pm$ 4	20 $\pm$ 5***	23 $\pm$ 7	16 $\pm$ 4	28 $\pm$ 11	24 $\pm$ 9	20 $\pm$ 7	25 $\pm$ 5***	37 $\pm$ 13
Ca <sup>2+</sup>	4.2 $\pm$ 0.8	14 $\pm$ 4***	11 $\pm$ 2	5.5 $\pm$ 1.9	11 $\pm$ 3**	13 $\pm$ 2	5.8 $\pm$ 1.0	16 $\pm$ 4**	17 $\pm$ 3	7.7 $\pm$ 2.6	14 $\pm$ 3***	20 $\pm$ 3
Mg <sup>2+</sup>	1.3 $\pm$ 0.3	5.3 $\pm$ 1.1*	4.8 $\pm$ 0.8	1.6 $\pm$ 0.5	4.6 $\pm$ 0.9	5.2 $\pm$ 1.5	1.9 $\pm$ 0.4	6.0 $\pm$ 1.1**	7.4 $\pm$ 1.6	2.3 $\pm$ 0.7	5.8 $\pm$ 1.3***	8.3 $\pm$ 2.4
Na <sup>+</sup>	7.9 $\pm$ 1.8	13 $\pm$ 4*	14 $\pm$ 3	8.1 $\pm$ 2.2	12 $\pm$ 2***	15 $\pm$ 3	11 $\pm$ 2	15 $\pm$ 4***	21 $\pm$ 4	11 $\pm$ 3	15 $\pm$ 3***	24 $\pm$ 6
K <sup>+</sup>	3.4 $\pm$ 1.7	33 $\pm$ 10***	23 $\pm$ 6	4.6 $\pm$ 3.1	25 $\pm$ 6	26 $\pm$ 5	4.5 $\pm$ 1.9	38 $\pm$ 9	36 $\pm$ 8	6.3 $\pm$ 3.8	31 $\pm$ 7***	41 $\pm$ 7
NH <sub>4</sub> <sup>+</sup>	25 $\pm$ 3	32 $\pm$ 9**	36 $\pm$ 8	27 $\pm$ 4	30 $\pm$ 7***	41 $\pm$ 9	35 $\pm$ 8	37 $\pm$ 11***	55 $\pm$ 13	39 $\pm$ 10	37 $\pm$ 8***	65 $\pm$ 12
NO <sub>3</sub> <sup>-</sup>	24 $\pm$ 2	49 $\pm$ 16**	42 $\pm$ 8	27 $\pm$ 4	38 $\pm$ 5***	50 $\pm$ 8	34 $\pm$ 5	56 $\pm$ 16***	65 $\pm$ 14	39 $\pm$ 11	47 $\pm$ 7***	78 $\pm$ 10
SO <sub>4</sub> <sup>2-</sup>	10 $\pm$ 2	19 $\pm$ 8	16 $\pm$ 3	12 $\pm$ 3	18 $\pm$ 6***	23 $\pm$ 5	14 $\pm$ 3	21 $\pm$ 7***	25 $\pm$ 6	17 $\pm$ 5	22 $\pm$ 6***	36 $\pm$ 9
Cl <sup>-</sup>	7.4 $\pm$ 1.6	16 $\pm$ 5	15 $\pm$ 4	7.7 $\pm$ 2.0	15 $\pm$ 2***	18 $\pm$ 3	10 $\pm$ 2	18 $\pm$ 4***	24 $\pm$ 6	11 $\pm$ 3	18 $\pm$ 2***	28 $\pm$ 5
F <sup>-</sup>	0.3 $\pm$ 0.2	1.0 $\pm$ 0.7	0.7 $\pm$ 0.3	0.5 $\pm$ 0.4	0.9 $\pm$ 0.5	0.9 $\pm$ 0.4	0.5 $\pm$ 0.3	1.2 $\pm$ 0.9	1.1 $\pm$ 0.6	0.8 $\pm$ 1.0	1.1 $\pm$ 0.8	1.5 $\pm$ 0.9
HCO <sub>3</sub> <sup>-</sup>	1.9 $\pm$ 1.6	2.1 $\pm$ 2.3	2.9 $\pm$ 3.2	3.1 $\pm$ 4.8	2.7 $\pm$ 5.4	1.3 $\pm$ 1.9	2.7 $\pm$ 2.0	2.4 $\pm$ 2.6	4.1 $\pm$ 4.5	3.9 $\pm$ 5.0	3.3 $\pm$ 6.2	1.8 $\pm$ 2.3
DOC	96 $\pm$ 22	743 $\pm$ 121***	548 $\pm$ 95	104 $\pm$ 16	569 $\pm$ 122	554 $\pm$ 59	134 $\pm$ 29	859 $\pm$ 167	838 $\pm$ 124	146 $\pm$ 31	702 $\pm$ 110***	883 $\pm$ 154
TON	18 $\pm$ 6	43 $\pm$ 11	41 $\pm$ 13	18 $\pm$ 5	39 $\pm$ 7***	52 $\pm$ 15	24 $\pm$ 9	48 $\pm$ 10***	60 $\pm$ 16	26 $\pm$ 7	46 $\pm$ 10***	80 $\pm$ 23
TP	0.48 $\pm$ 0.2	0.93 $\pm$ 0.24	0.90 $\pm$ 0.19	0.65 $\pm$ 0.26	0.90 $\pm$ 0.28	0.92 $\pm$ 0.27	0.65 $\pm$ 0.22	1.1 $\pm$ 0.3***	1.4 $\pm$ 0.2	0.90 $\pm$ 0.32	1.1 $\pm$ 0.3***	1.5 $\pm$ 0.4
DRP	0.18 $\pm$ 0.16	0.10 $\pm$ 0.08	0.11 $\pm$ 0.06	0.26 $\pm$ 0.16	0.19 $\pm$ 0.14	0.20 $\pm$ 0.16	0.24 $\pm$ 0.20	0.12 $\pm$ 0.12***	0.16 $\pm$ 0.09	0.35 $\pm$ 0.20	0.23 $\pm$ 0.16***	0.31 $\pm$ 0.25

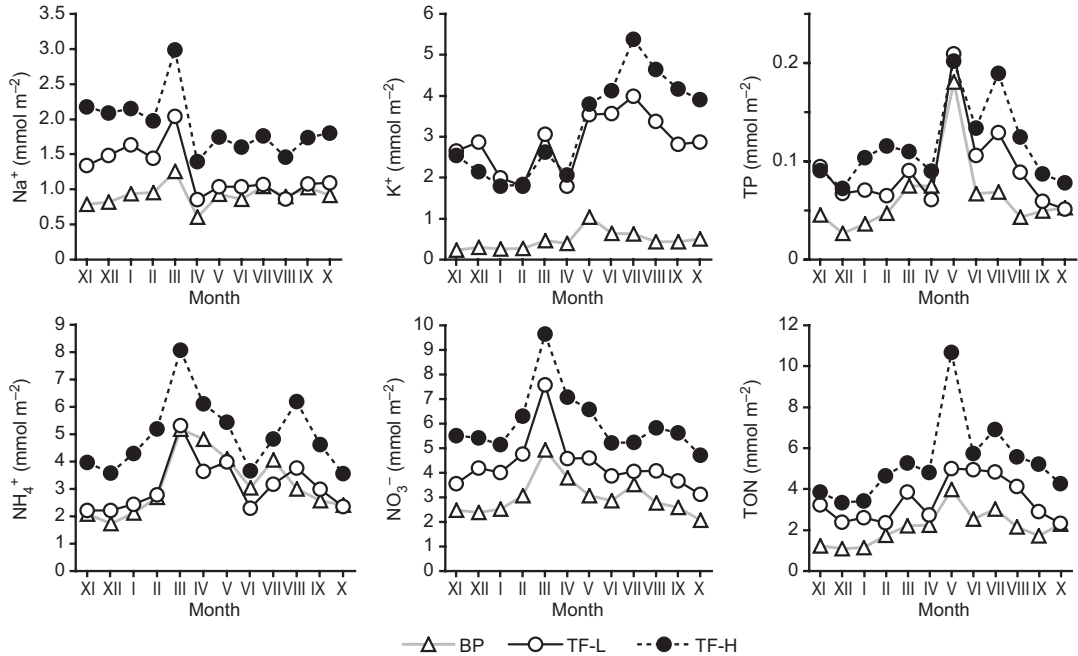
<sup>1)</sup> Precipitation amount is given in mm. <sup>2)</sup> pH =  $-\log(\text{average H}^+ \text{ concentration})$ .



**Fig. 3.** Average seasonal patterns of element concentrations in bulk precipitation (BP, average for PL-BP and CT-BP) and throughfall at low (TF-L, average for PL-L and CT-L) and high (TF-H, average for PL-H and CT-H) altitudes in the Bohemian Forest from 1998–2009. For site abbreviations see Table 1.

mian Forest during the study period. The differences between throughfall amounts at the high- and low-altitude plots were greater in summer than in winter (Fig. 2B). The plot altitude thus affected both the annual throughfall amount and its seasonal pattern.

Concentrations and fluxes of most elements exhibited pronounced seasonal cycles both in precipitation and throughfall (Figs. 3 and 4). While the seasonal cycles of element concentrations were similar at both altitudes (Fig. 3), higher throughfall fluxes occurred for



**Fig. 4.** Average seasonal patterns of element fluxes by bulk precipitation (BP, average for PL-BP and CT-BP) and throughfall at low (TF-L, average for PL-L and CT-L) and high (TF-H, average for PL-H and CT-H) altitudes in the Bohemian Forest from 1998–2009. For site abbreviations see Table 1.

all elements at the high- than low-altitude plots throughout the year, and especially in summer (Fig. 4), due to higher throughfall amounts at the higher altitude (Fig. 2B). Seasonal cycles of individual elements differed due to their different sources and transformations and/or enrichment in the canopies. Throughfall fluxes of  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , and DOC were more enriched relative to precipitation (especially in summer) than the conservative  $Na^+$ ,  $Cl^-$ , and  $SO_4^{2-}$  ions (Fig. 4 shows  $K^+$  and  $Na^+$  as examples).

The seasonal throughfall cycles of  $K^+$  were almost identical to those of DOC (Fig. 3), and both constituents had similar enrichment, with stable  $K^+$  to DOC ratios throughout the year. The leaching of  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  associated with DOC export from tissue and exchange for  $H^+$  was the most likely reason for their increased concentrations in canopy, as also observed elsewhere (e.g., Johnson and Lindberg 1992, Balistrini and Tagliaferri 2001), and were discussed in detail by Kopáček *et al.* (2009). Throughfall and precipitation fluxes of  $NH_4^+$  and  $NO_3^-$  had their maxima in March (Fig. 4) due to their high concentrations in spring (March–May; Fig. 3)

and the maximum precipitation amount in March (Fig. 2A). The highest fluxes of TP and TON occurred in spring (Fig. 4) due to high concentrations of TP and TON in both precipitation and throughfall (Fig. 3), usually associated with the presence of pollen in the samples. Throughfall fluxes of TON were elevated relative to their precipitation values especially in summer, due to the microbial transformation of  $NH_4^+$  to organic N forms in canopies (Kopáček *et al.* 2009). Thus, the ratio between throughfall and precipitation fluxes (TF:PF) for  $NH_4^+$  decreased and that of TON increased when precipitation passed through the canopies. This process is especially pronounced in wetter forests favouring green algae, lichen, and other epiphytic microflora (Ferm and Hultberg 1999), and consequently, very important in the Bohemian Forest stands, lowering the  $NH_4^+$  throughfall flux by ~22% on average in these canopies (Kopáček *et al.* 2009). The reduction of  $NH_4^+$  fluxes was more pronounced at the low-altitude plots (with milder climate), where the throughfall  $NH_4^+$  flux was similar to its precipitation flux, or even lower in summer (Fig. 4). In contrast, the  $NO_3^-$  through-



fall fluxes were higher than the precipitation flux at both altitudes throughout the year.

The annual average throughfall fluxes of almost all elements were significantly higher at the high- versus low-altitude plots in both catchments (Table 2). The primary reason for these higher fluxes were ~30% higher throughfall amounts at the high-altitude plots, while differences in the element concentrations contributed to the higher throughfall fluxes only in the CT catchment (Table 2). The increasing throughfall fluxes with altitude were ecologically important especially for acidic deposition (S and N compounds), with their averages being 1.2–1.8 times higher at the high-altitude plots. This pattern was probably the reason for differences in the litter fall composition along the altitude gradient in the Bohemian Forest, with significantly higher N concentrations and N:Mg ratios at the high- than low-altitude plots (Kopáček *et al.* 2010).

Surprisingly, throughfall composition at the defoliated PL-H plot remained more similar to that at the unaffected CT-H plot than to bulk precipitation even five years after the bark beetle attack (*see* average concentrations and their variability in Table 2). For example, the average ( $\pm$  SD) concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Ca}^{2+}$ , and  $\text{K}^+$  prior to (2000–2004) versus after (2005–2009) the bark beetle attack of the PL-H plot were  $17 \pm 1$  vs.  $15 \pm 4$ ,  $46 \pm 10$  vs.  $39 \pm 6$ ,  $12 \pm 2$  vs.  $11 \pm 1$ , and  $24 \pm 6$  vs.  $23 \pm 7 \mu\text{mol l}^{-1}$ , respectively. At the end of this study, the remaining twigs and branches covered with lichens in the damaged canopies probably still effectively enriched throughfall as compared with bulk precipitation.

### Net atmospheric input of elements to the Bohemian Forest

Slopes and significances of the relationships between annual precipitation amounts and volume-weighted mean concentrations and/or annual fluxes of elements (Table 3) suggested three main deposition pathways for the Bohemian Forest sites: (1) Concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  were not dependent on precipitation amount while their fluxes significantly increased with precipitation amount (Table 3),

indicating that these components originated from long-range transport. Even though a large fraction of emitted  $\text{NH}_3$  is deposited near the sources due to the relatively short residence time in air (hours to days), some of this N may be deposited as  $\text{NH}_4^+$  in remote locations hundreds of kilometers away (Asman *et al.* 1998). Sulphur and N oxides have longer lifetimes than  $\text{NH}_3$  in the atmosphere (on the order of days) and can be transported far away from their sources (Seinfeld and Pandis 1998). The fact that the throughfall fluxes of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  were also related to throughfall amounts and their TF:PF ratios were between 1.3 and 1.7 suggests that wet deposition was the major source of these constituents for the study plots in 1998–2009. (2) Concentrations of  $\text{K}^+$  and TP significantly decreased while their fluxes were roughly constant with increasing precipitation amounts, indicating that these components originated predominantly from local sources and were deposited primarily via dry deposition. (3) Concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$  (i.e., components mostly associated with terrestrial dust, e.g., Ulrich 1983) exhibited negative relationships with precipitation amount (like components from local sources), while their fluxes increased with precipitation amount (like components from distant sources). Neither of these relationships was significant (most likely

**Table 3.** Correlation coefficients of linear regressions between annual precipitation amount (mm) and volume-weighted mean concentration and/or annual flux, calculated for bulk precipitation in the Plešné (PL-BP) and Čertovo (CT-BP) catchments from 1998–2009. Number signs indicate either positive (+) or negative (–) regression line slopes. Asterisks denote significant relationships (\*  $p < 0.05$ , \*\*  $p < 0.01$ , and \*\*\*  $p < 0.001$ ;  $n = 12$ ).

	Concentration		Flux	
	PL-BP	CT-BP	PL-BP	CT-BP
$\text{Ca}^{2+}$	–0.45	–0.17	+0.39	+0.48
$\text{Mg}^{2+}$	–0.25	–0.13	+0.42	+0.48
$\text{Na}^+$	–0.50	–0.12	+0.28	+0.54
$\text{K}^+$	–0.60*	–0.26	–0.32	+0.05
TP	–0.68*	–0.58*	–0.35	+0.06
$\text{NH}_4^+$	+0.24	+0.16	+0.86***	+0.87***
$\text{NO}_3^-$	–0.41	+0.24	+0.92***	+0.85***
$\text{SO}_4^{2-}$	–0.32	+0.13	+0.67*	+0.73**

due to the low number of observations), but the patterns were consistent for both catchments and all elements (Table 3). This suggests that both dry fallout of dust particles from local sources and long-range transport contributed significantly to the base cation fluxes at the study sites.

For conservative constituents ( $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ ), the enrichment of throughfall as compared with bulk precipitation can be mostly attributed to dry and horizontal deposition, and their net fluxes to the forested areas are approximately equal to throughfall fluxes (Ulrich 1983, Erisman *et al.* 1997, Balestrini *et al.* 2007). Consequently, the current averages of net  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  fluxes equal 19, 22, and 26  $\text{mmol m}^{-2} \text{yr}^{-1}$  (i.e., 4.3, 7.8, and 25  $\text{kg ha}^{-1} \text{yr}^{-1}$ ), respectively, in the Bohemian Forest. The net atmospheric input of base cations to the study catchments can be estimated as their precipitation flux (Table 2) multiplied by a factor of 1.7 (the TF:PF ratio for  $\text{Na}^+$ ), because dry and horizontal depositions of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$  are assumed to be similar to that of  $\text{Na}^+$ , due to the same physical size and aerodynamic properties of base cation-containing aerosols (Ulrich 1983, Draaijers and Erisman 1995). From 1998 to 2009, the average calculated net atmospheric inputs of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$  to the Bohemian Forest catchments were 11, 4, and 9  $\text{mmol m}^{-2} \text{yr}^{-1}$  (or 4.5, 0.9, and 3.6  $\text{kg ha}^{-1} \text{yr}^{-1}$ ), respectively. The net  $\text{K}^+$  flux should be, however, considered as its maximum estimate, due to the significant contribution of local  $\text{K}^+$  sources to its flux (Table 3), similarly as in the case of TP (*see* below).

The net flux of TN can be assumed to be similar to the throughfall flux (i.e., 169  $\text{mmol m}^{-2} \text{yr}^{-1}$  or 24  $\text{kg ha}^{-1} \text{yr}^{-1}$ ), because the contribution of fragmented litter to the throughfall TN flux is negligible (~10% of the throughfall flux of particulate N, Kopáček *et al.* 2009) and the  $\text{NH}_4^+$  lost in canopies is transformed into TON. In the throughfall TN flux, on average 37%, 29%, and 34% was  $\text{NO}_3\text{-N}$ ,  $\text{NH}_4\text{-N}$ , and TON, respectively. However, after correction for  $\text{NH}_4^+$  transformation (22% of its flux) to TON in the canopies (Kopáček *et al.* 2009), the net TN atmospheric input was composed on average of 37%  $\text{NO}_3\text{-N}$ , 37%  $\text{NH}_4\text{-N}$ , and 26% TON, and their average fluxes were 62, 62, and 45  $\text{mmol m}^{-2} \text{yr}^{-1}$  (or 9,

9, and 6  $\text{kg ha}^{-1} \text{yr}^{-1}$ ), respectively. Similarly to Mustajärvi *et al.* (2008), our results show that a relatively high proportion of N passes through the Norway spruce canopies in organic forms. No correction was applied for  $\text{NO}_3^-$ , because its net flux can be considered equal to its throughfall flux in European mountain forested areas (e.g., Zimmermann *et al.* 2006, Balestrini *et al.* 2007). Moreover, the seasonal  $\text{NO}_3^-$  cycle showed a negligible effect of canopy interactions on its throughfall flux in the Bohemian Forest (Fig. 4).

Caution is necessary when evaluating net P fluxes. The dry contribution of P to its total deposition is probably not the same as that for Na, because aerosols containing Na and P differ in sizes and surface properties (Newman 1995). Because the contribution of litter fragmentation to throughfall flux of TP was negligible, similarly to that of TN, and most of the loss of DRP after passing through canopies occurred as organic P in throughfall (Kopáček *et al.* 2009), we can roughly estimate that the maximum total flux of TP to the Bohemian Forest was roughly equal to its throughfall flux, i.e., 1.3  $\text{mmol m}^{-2} \text{yr}^{-1}$ . This value, however, was affected by a high contribution of pollen and dust, which probably originated mostly from local sources and apparently caused an overestimation of net long-range P transport to the study sites. The contribution of local dust to TP (as well as  $\text{K}^+$ ) deposition was suggested by the significantly ( $p < 0.05$ ) higher TP ( $\text{K}^+$ ) fluxes at the CT-BP than PL-BP plot, differing in the nature of their terrain, while precipitation amounts were similar at both plots (Table 2). The grassy terrain of the CT-BP plot could be a more significant source of local dust than the stony ground of the PL-BP plot, due to the recycling of local organic and inorganic dust taken up from the grass by wind and settling within short distances (Kopáček *et al.* 1998). Thus, the CT-BP collectors probably accumulated more dust of local origin than those at PL-BP, and overestimated the actual long-range dust transport to the CT catchment. Nevertheless, the average precipitation fluxes of TP in the Bohemian Forest were similar to those measured elsewhere in the Czech Republic (0.65 and 0.90  $\text{mmol m}^{-2} \text{yr}^{-1}$  at PL-BP and CT-BP, respectively, *versus* 0.5–0.8  $\text{mmol m}^{-2} \text{yr}^{-1}$  at the Slapy and Římov reservoirs; Kopáček *et al.* 1997).

Consequently, we can assume that the actual net atmospheric input of TP to the Bohemian Forest was probably a value between its precipitation flux (partly elevated by dust and pollen from local sources, but not including dry deposition from long-distance sources) and throughfall fluxes (including both the dry deposition and local TP sources), i.e., within 0.7–1.3 mmol m<sup>-2</sup> yr<sup>-1</sup> (or 0.2–0.4 kg ha<sup>-1</sup> yr<sup>-1</sup>). The importance of local sources in the TP flux (Table 3) suggests that the net long-range TP transport to the Bohemian Forest is probably at the lower part of this range. About ~39% of this TP flux was in the form of DRP (Table 2). Similar results have often been reported from other non-agricultural sites (e.g., ~44% in northern Italy, Mosello and Tartari 1984; 40% in south-western Sweden, Persson and Broberg 1985; 32% at Lake Victoria, Tamatamah *et al.* 2005) and for mineral aerosols and other atmospheric TP sources (~10%–50%, Mahowald *et al.* 2008), suggesting that net TP deposition is a significant source of bio-available P for terrestrial and aquatic mountain ecosystems. For example, the average DRP deposition on the surface of the Bohemian Forest lakes (0.24–0.35 mmol m<sup>-2</sup> yr<sup>-1</sup>, Table 2) has been a significant source of bio-available P. The direct atmospheric input of DRP to the CT lake surface comprised 7%–33% of the annual TP loadings (and the dominant DRP flux) from both terrestrial and

atmospheric sources from 1998 to 2009, because of the low terrestrial TP (and negligible DRP) export from its catchment (Kopáček *et al.* 2006, J. Kopáček unpubl. data).

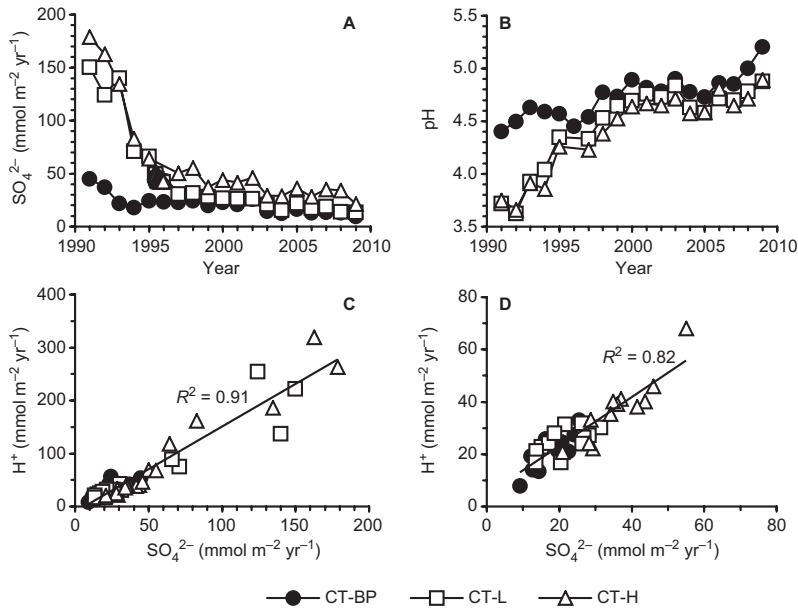
### Long-term trends in acidic deposition in the Bohemian Forest

Sulphate and H<sup>+</sup> were the only pollutants exhibiting significant declines throughout both the 1991–2009 and 1998–2009 periods at the open area and throughfall plots (Table 4). In contrast, fluxes of NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and divalent base cations (Ca<sup>2+</sup> + Mg<sup>2+</sup>) declined significantly between 1991 and 2009, but were almost stable (exhibiting only few significant trends) during the 1998–2009 period (Table 4). The average concentrations of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> in the Bohemian Forest throughfall decreased by 184 and 18 µeq l<sup>-1</sup>, respectively, between the 1991–1994 and 2006–2009 periods, while H<sup>+</sup> concentrations declined by “only” 147 µeq l<sup>-1</sup>. The difference between declines in concentrations of strong acid anions and protons was due to parallel declines in concentrations of NH<sub>4</sub><sup>+</sup> and base cations (Hruška *et al.* 2000).

The long-term deposition trends closely reflected the respective trends in emission rates of S and N compounds and particulates in the Czech Republic and central Europe (Kopáček

**Table 4.** Trend analysis for annual fluxes of H<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and sum of Ca<sup>2+</sup> + Mg<sup>2+</sup> in the Bohemian Forest from 1991–2009 (*n* = 19) and 1998–2009 (*n* = 12). Plot abbreviations: PL-BP and CT-BP, bulk precipitation in the Plešné (PL) and Čertovo (CT) catchments; PL-L, CT-L, and CT-H, throughfall at the low (L) and high (H) altitude plots. Numbers are average rates of deposition change (Δ, mmol m<sup>-2</sup> yr<sup>-1</sup>) during the study period and asterisks denote significant declines (\* *p* < 0.05, \*\* *p* < 0.01, and \*\*\* *p* < 0.001).

Pollutant	Period	Plot				
		PL-BP	PL-L	CT-BP	CT-L	CT-H
ΔH <sup>+</sup>	1991–2009			-1.6***	-9.6***	-12.8***
	1998–2009	-0.7*	-2.2**	-1.2*	-0.6	-2.3*
ΔSO <sub>4</sub> <sup>2-</sup>	1991–2009			-1.2***	-6.7***	-6.9***
	1998–2009	-0.5*	-1.7***	-1.3***	-1.6***	-2.0**
ΔNO <sub>3</sub> <sup>-</sup>	1991–2009			-1.3**	-1.6***	-1.0*
	1998–2009	0	-2.0	-1.8*	-0.6	-0.4
ΔNH <sub>4</sub> <sup>+</sup>	1991–2009			-1.4*	-2.8**	-1.5
	1998–2009	0.6	-0.4	-1.5*	-0.7	1.2
Δ(Ca <sup>2+</sup> + Mg <sup>2+</sup> )	1991–2009			-0.4*	-2.9***	-2.9***
	1998–2009	0	-0.7	-0.4	-1.0***	-0.8



**Fig. 5.** Trends in concentrations of (A)  $\text{SO}_4^{2-}$  and (B) pH in bulk precipitation (CT-BP) and throughfall (CT-L, CT-H) in the Čertovo catchment (Bohemian Forest), and relationships between  $\text{SO}_4^{2-}$  and  $\text{H}^+$  concentrations during the (C) 1991–2009 and (D) 1998–2009 periods. For site abbreviations see Table 1.

and Veselý 2005), because the majority of their deposition in the Czech Republic originated from central European emission sources (Berge 1997). Sulphur and nitrogen emissions in the region including Austria, Czech Republic, Germany, Poland, and Slovakia declined by 86% for  $\text{SO}_2$ , 53% for  $\text{NO}_x$ , and 35% for  $\text{NH}_3$  between the 1980s and the 2005–2007 period (EMEP; <http://www.ceip.at/emission-data-webdab/>). Emission control of particulates from stationary sources occurred almost simultaneously to (in some countries prior to) S emission control, which significantly reduced dust emissions to the atmosphere (e.g., by 94% in the Czech Republic in 2005–2007 as compared with their 1980–1985 levels). The largest reduction in pollutant emissions occurred in the early 1990s. Consequently, the most rapid declines in acidic deposition and base cation fluxes occurred in the Bohemian Forest in the early 1990s (Hruška *et al.* 2000), and then their trends levelled off (or moderated,  $\text{SO}_4^{2-}$  and  $\text{H}^+$ ) during the 2000s. One probable reason for the slower chemical recovery of acidic deposition than we might have expected from the large reductions in  $\text{SO}_2$  and  $\text{NO}_x$  emissions in central Europe was the decline in long-range transport of particulates, as observed elsewhere (e.g., Hedin *et al.* 1994, Moldan *et al.* 2001). In addition, the reduction in element fluxes associ-

ated with dust to forested areas caused changes in tree nutrient usage and resulted in decreasing Ca and Mg concentrations in the foliage of central European forest sites over the last two decades (e.g., Alewell *et al.* 2000, Oulehle *et al.* 2006).

The decline in concentrations of the major anion  $\text{SO}_4^{2-}$  was the dominant driving force for the reduction in acidic deposition (Fig. 5) and for the increase in throughfall pH from 3.6–3.7 in the early 1990s to current values between 4.7 and 5.0 (Fig. 5B). The throughfall fluxes of  $\text{SO}_4^{2-}$  exhibited steeper declines than bulk precipitation fluxes (Fig. 5A), indicating that the change in acidic deposition resulted primarily from the decline in dry S deposition. For example, the dry S deposition dominated (77% on average) its throughfall fluxes in the Bohemian Forest in the 1991–1994 period, and the TF:PF ratio for  $\text{SO}_4^{2-}$  (4.6) was 2–3 times higher than current values. The long-term changes in the chemistry of atmospheric deposition in the Bohemian Forest are well in line with those reported for different European regions (e.g., Evans *et al.* 2001, Moldan *et al.* 2001, Rogora *et al.* 2006), showing the dominant role of S emission controls on acidic deposition during the last three decades. However, despite the large reduction in S emissions, sulphate has remained the major factor, explaining on average 82% of the variability in

H<sup>+</sup> concentrations observed in the Bohemian Forest during the last decade (Fig. 5D). Even though the changes in absolute values of SO<sub>4</sub><sup>2-</sup> fluxes were relatively small in 1998–2009 (Fig. 5A), they caused a significant decrease in H<sup>+</sup> concentrations, because fluxes of base cations remained stable during this period (Fig. 5B and Table 4). However, this additional decline in H<sup>+</sup> concentrations was minor and the Bohemian Forest precipitation remained acidic during the last decade, with still negligible HCO<sub>3</sub><sup>-</sup> concentrations (Table 2).

## Conclusions

Atmospheric deposition of ecologically important elements was measured at one open area and two throughfall plots located in Norway spruce stands at different altitudes in both the PL and CT catchments in the Bohemian Forest from 1998 to 2009.

The net atmospheric inputs of nutrients to the Bohemian Forest by long-range transport were estimated at 11, 4, 9, 169, 26, and 0.7–1.3 mmol m<sup>-2</sup> yr<sup>-1</sup> for Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, TN, S, and TP, respectively, and DRP contributed on average 39% to TP.

We observed that element deposition was higher at higher altitudes, due predominately to higher throughfall amounts, while differences in the concentrations of individual elements between the high- and low-altitude plots were less marked. The highest concentrations and fluxes of major acidifying pollutants (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>) occurred in April and March, respectively, and their dry deposition significantly (~40%) contributed to the total acidic deposition in 1998–2009. Despite the respective 86% and 53% reductions in central European SO<sub>2</sub> and NO<sub>x</sub> emissions since the middle 1980s, the current level of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> deposition remains a strong acidifying potential for forest ecosystems in the Bohemian Forest, especially at high-altitude plots and in spring.

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