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Trend of atmospheric deposition of acidifying compounds at Čertovo Lake, southwestern Czech Republic (1992–1999)

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Abstract
Throughfall depositions at 2 plots (L and H) and one bulk precipitation have been investigated in the catchment of Čertovo Lake since May 1991. Throughfall deposition of sulfur was highest in 1992, being 40 and 52 kg/ha/y at the plot L (1045 m a.s.l) and H (1330 m a.s.l.), respectively, and lowest in 1999, when it reached only 9.1 and 12.5 kg/ha/y, respectively. Bulk deposition of sulfur was 12 kg/ha/y in 1992 and 6.3 in 1999. The large difference between throughfall and bulk precipitation fluxes documented the importance of dry and occult depositions in this high-elevated forested area. Similarly to sulfur deposition, the throughfall flux of inorganic nitrogen (IN = NO_3-N + NH_4-N) was highest in 1992. Bulk deposition of IN was 24 kg/ha/y in 1992. Since 1993, bulk deposition of IN has been roughly stable (8–14 kg/ha/y). Throughfall flux of IN was 27 and 35 kg/ha/y at the plot L and H, respectively, in 1992 and fluctuated there within 10–13 and 12–19 kg/ha/y, respectively, in the 1993–1999 period. Annual average pH of precipitation was 3.62 at both throughfall plots in 1992, then, it increased to 4.2–4.3 in 1995 and to 4.5–4.6 in 1999. Bulk precipitation pH increased from 4.5 in 1992 to 4.74 in 1999.

Key words: atmospheric deposition, anthropogenic acidification, throughfall, sulfur, nitrogen.

Introduction

Scientific investigations of glacier lakes in the Bohemian Forest (especially Černé Lake and Čertovo Lake) has a long history and tradition, namely in hydrobiology and botany. During the last two decades, the scientific effort has been focused on problems associated with atmospheric acidification of lake water like reduction in biodiversity (Fott & Pražáková 1994), changes in water chemistry (Veselý & al. 1998a,b), paleolimnology (Veselý & al. 1993, Hruška & al. 1999a), pollen analyses (Břízová, unpublished data), and nutrition status of water and sediments (Kopáček & al. 2000). The review of research history and the list of relevant publications has been published by Veselý (1994) and Vrba (2000), respectively (almost 400 records).

Despite the fact that atmospheric deposition of acidifying compounds was the major driving phenomena for environmental changes studied in the lakes, there are only sparse information in the literature on this aspect. Unfortunately, no data exist on the deposition of acidifying compounds in the region of Čertovo and Černé Lakes from the 1980's; the period

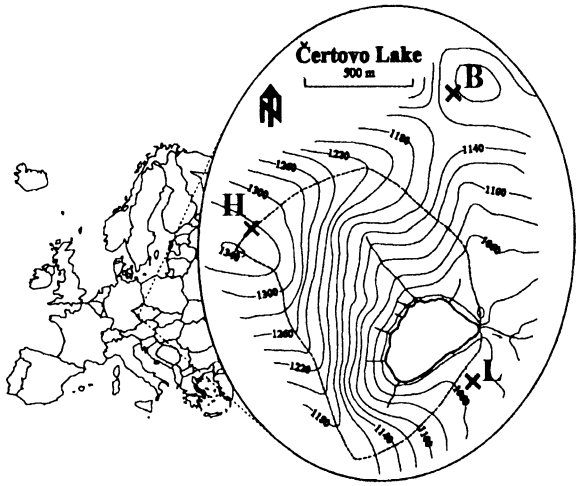

Fig. 1. – Location of precipitation plots within the Čertovo Lake catchment.

of the highest European emission rates of SO_2 and NO_x. The first estimation of atmospheric deposition of S and N compounds into the Čertovo and Černé lake catchments came from 1990 (Veselý & Majer 1992).

The aim of this study is to present the first consistent trend of atmospheric deposition of pollutants in the catchment of Čertovo lake, measured in the 1992–1999 period.

Site description

Čertovo lake is located on the northwestern part of the Bohemian Forest (49°10´ N, 13°12´ E). Lower throughfall plot (L) was located near the lake shore (altitude 1045 m a.s.l.) within ~100-year old Norway spruce (*Picea abies*) forest. Higher throughfall plot (H) was located near by Jezerní hora (the highest point of the catchment area, 1343 m a.s.l.) at 1330 m a.s.l. within >150-year old spruce forest. Bulk precipitation (B) was located at 1200 m a.s.l. in the open area (a small clear-cut; Hlavatý 1992). For a more detailed location of the plots in the catchment see Fig. 1.

Methods

Sampling

Between 1991 and 1994, each throughfall plot was equipped with 7 polyethylene rain collectors (area of one sampler was 115 cm^2) located in the middle of distance between trunk and canopy edge. Rain samples were taken biweekly. Snow was sampled using one large collector for the whole winter period. The collector was a large polyethylene barrel (50 l) with adjusted sampling area of 1200 cm^2 (Hlavatý 1992).

Since 1995, the network of throughfall collectors has consisted of 9 funnels randomly distributed with respect to trees in the square of 3x3 funnels. Samples were taken twice per month during the vegetation season (May-September) and monthly during winter (Novem-

ber-April). Winter samplers were larger (area of 167 cm^2) and deeper (50 cm) than the summer collectors and were made from thicker black polyethylene.

Bulk precipitation was sampled using two collectors. The identical sampling technique as for throughfall after 1995 has been used for bulk sampled since 1992.

Chemical analyses

Chemical analyses between 1991–1997 were done in the Czech Geological Survey, Prague, using following techniques: Concentrations of the inorganic anions Cl, SO_4, and NO_3 were determined by high-performance liquid chromatography (HPLC). Concentrations of Ca, Mg, Na, K, Sr, Zn, Mn, Al, SiO_2 and Fe were determined by atomic absorption spectroscopy. Solution pH was determined using a glass electrode and NH_4^+ with the indophenol blue colorimetry. Trace elements (As, Cd, Cu, Pb) were determined using graphite furnace atomic absorption spectroscopy.

Additionally, pH (glass electrode) and NH_4 (Nessler colorimetry) were measured as soon as possible after sampling in the laboratory of the hygiene station (OHES) in Klatovy and they were used for the period 1992–1995.

Since 1998, chemical analyses have been performed in Hydrobiological Institute AV CR. Glass electrode (Radiometer, GK 2321C) was used for pH determinations. Samples for ion determination (Ca, Mg, Na, K, NH_4, NO_3, SO_4, and Cl) were frozen immediately after sampling at -20 °C and analyzed by ion chromatography (Thermo Separation Products) within a month.

Concentrations of atmospheric SO_2 and NO_x at the German station Brotjacklriegel, located ~30 km southwest of Čertovo Lake at 1016 m a.s.l., were obtained from Umweltbundesamt, Berlin (Anonymus 1999).

Resultes and discussion

Precipitation amount

The average annual precipitation amount for the 1992–1999 period was 1158, 1490, and 1276 mm at the L, H, and B plot, respectively. The highest annual precipitation amount (2136 mm) was observed at plot H in 1995 and the lowest one (676 mm) at plot B in 1994. Generally, amount of precipitation was higher in throughfall plots compare to bulk precipitation (Figs. 3 and 4). This phenomenon was sometimes observed also for high altitude (>1000 m a.s.l.) Modrý potok spruce forested catchment in Krkonoše Mts., northeastern Czech Republic (Fottová 1999). Intensive water removal via spruce canopy from clouds and fog was probably responsible for the observed water enrichment.

Airborne SO_2 and NO_x concentrations

Concentrations of atmospheric SO_2 and NO_2 at Brotjacklriegel station are given in Fig. 2. The annual mean concentrations of SO_2 decreased after its peak (9–13 $\mu g/m^3$) in the late 1970's to the relatively stable level of 5 $\mu g/m^3$ in the 1985–1988 period. Then, SO_2 concentration declined steadily and its 1994–1998 level was 1–2 $\mu g/m^3$. Hence, the annual mean concentration of atmospheric SO_2 decreased by ~90% within last two decades and by ~60% during our study (1992–1998).

Compare to the steep decline of SO_2, atmospheric concentrations of NO_2 did not show any significant trend at Brotjacklriegel station between 1969 and 1998. NO_2 increased slightly from 5–6 $\mu g/m^3$ measured in the 1970s to ~6 $\mu g/m^3$ in the 1990s (Fig. 2). In contrast, atmospheric deposition of both NO_3^- and NH_4^+ declined sharply in the Czech Republic from the

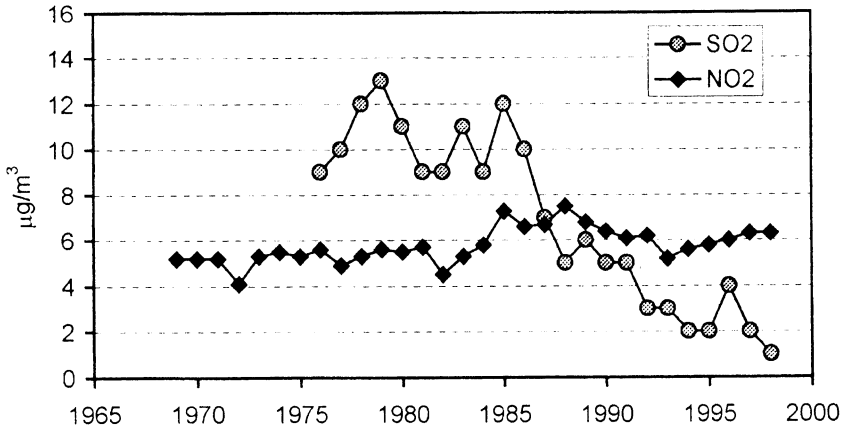

Fig. 2. – Time series of atmospheric concentrations of SO_2 and NO_2 measured at the German station Brotjacklrieger between 1968–1998 (NO_2) and 1976–1998 (SO_2). Data were derived from ANNONYMUS (1999).

relatively stable levels in the 1980's during the first half of the 1990's (KOPÁČEK & al. 1998). The above opposite trends are explained by relatively stable emission rates of nitrogen in Bavaria within the last 2 decades and the sharp decrease in NO_x emissions from stable sources and NH_3 emissions from agricultural sources after the political and economical changes in East European countries in 1989.

Concentrations and fluxes of SO_4

Sulfate concentrations in bulk precipitation decreased considerably from 2.73 mg/l in 1992 to ~1.5 mg/l in the 1998–1999 period (Fig. 3, Table 1). Even more pronounced change was observed in the composition of throughfall. Concentrations of SO_4 were ~11 mg/l in both L and H throughfall in 1992, i.e., ~4 times higher than in bulk precipitation. Then, high SO_4 concentrations in throughfall declined sharply (by ~70% between 1992 and 1995) and were stable until 1998. The lowest concentrations of SO_4 (2.29 and 2.60 mg/l at L and H plot, respectively) were observed in 1999.

Fluxes of sulfur (Fig. 5, Table 2) showed similar trend. Throughfall deposition of S was 39.8 and 52.1 kg/ha/y at L and H plot, respectively, in 1992, while bulk deposition of S was 4–5 times lower (11.9 kg/ha/y). Bulk deposition of S declined by 50% to 6.3 kg/ha/y in 1999. Throughfall fluxes declined predominantly between 1992 and 1995 (to ~20 kg/ha/y). Then, throughfall deposition of S was stable (9–10 kg/ha/y) at L plot in the 1997–1999 period, but continued to decline from 16.1 kg/ha/y in 1997 to 12.5 kg/ha/y in 1999 at H plot. Throughfall flux of S was only 1.5–2 times higher than the bulk flux in 1999, suggesting the decreasing importance of dry deposition of S into the Čertovo lake catchment in the late 1990's.

Dry and occult deposition of S comprised to very high throughfall fluxes of S reflecting the high loading of atmospheric S to the region. In areas of high S deposition the „net throughfall" of S (throughfall flux minus bulk precipitation flux) approximately equals the dry deposition of S to the forest ecosystem (LINDBERG & GARTEN 1988). This phenomenon was typical for spruce forested areas in the Central Europe (HRUŠKA & al. 1996, KRÁM & al. 1997, FOTTOVÁ 1999). However, 80% reduction in SO_2 emission in the Czech Republic within the last decade (HRUŠKA & al. 1999b) significantly contributed to the decrease in atmospheric concentrations of SO_2 and, consequently, to lower dry and occult deposition of S. The

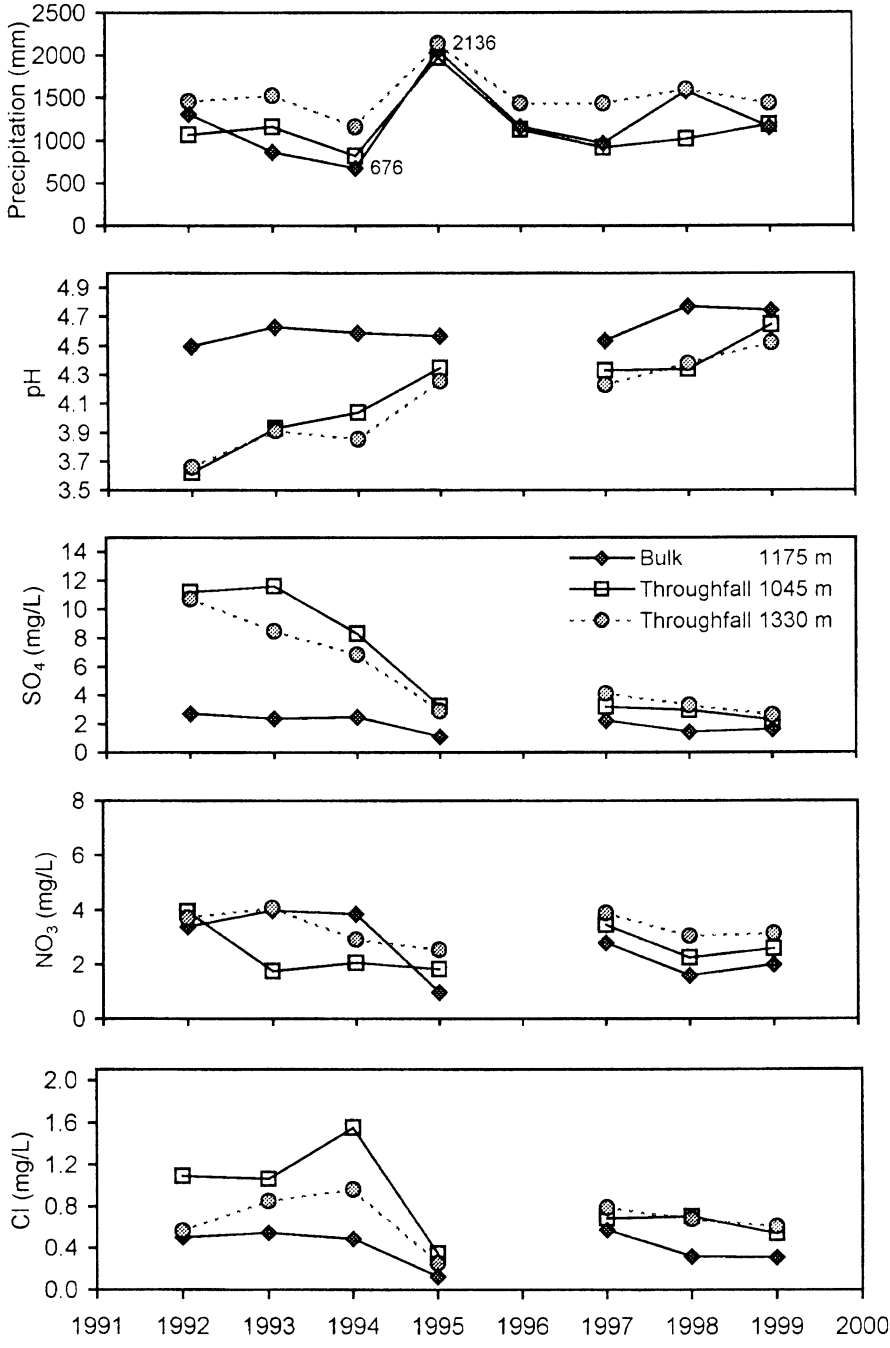

Fig. 3. – Time series of amount of precipitation and major anions measured within the Čertovo Lake catchment between 1992–1999.

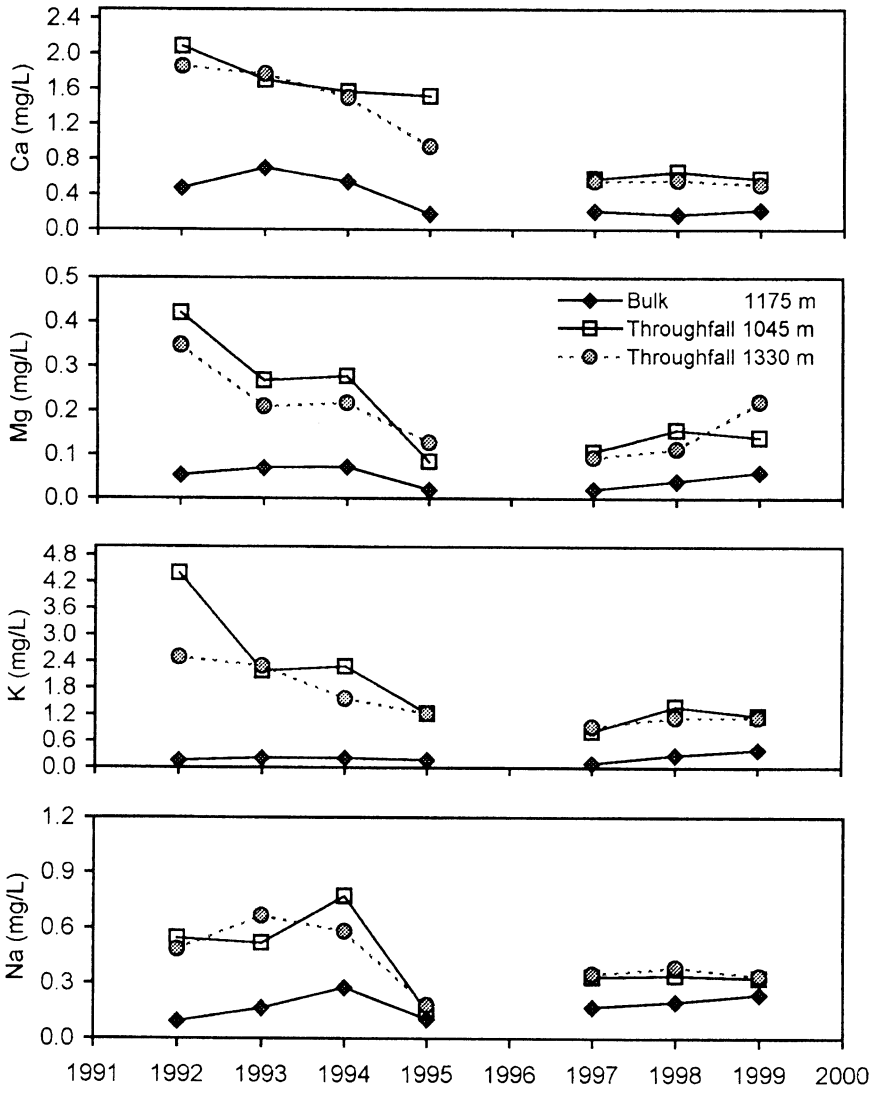

Fig. 4. – Time series of base cation concentrations measured within the Čertovo Lake catchment between 1992–1999.

observed ~70% decline in the throughfall deposition of S in the Čertovo Lake catchment between 1992–1999 corresponded with the decline in concentrations of atmospheric SO_2 (60–70%) during the same period (Fig. 2).

An extrapolation of the relationship between the throughfall deposition of S and atmospheric concentrations of SO_2 can be used to estimate an approximate level of S deposition to the Čertovo Lake catchment before 1992. The calculated levels of throughfall deposition of S varied between 90 and 100 kg/ha/year for the period of the maximum Central European emissions of SO_2, i.e. between the middle 1970's and the middle 1980's.

Table 1. – Volume weighted annual mean concentrations of solutes in bulk precipitation and throughfall within Čertovo lake catchment.

	pH	Cl	NO_3	SO_4	NH_4	Na	K	Mg	Ca	Mn	Zn	Fe	Al	SiO_2	Sr	As	Be	Cd	Pb	Cu
		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	µg/l	µg/l	mg/l	mg/l	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
Bulk (B)																				
1175 m																				
1992	4.50	0.50	3.38	2.73	1.38	0.10	0.16	0.05	0.47	4.2	32.4	0.04	0.05	0.13	2.5	0.38	<0.02	0.09	3.2	2.4
1993	4.63	0.55	3.98	2.37	0.64	0.17	0.22	0.07	0.70	4.7	52.7	0.05	0.15	0.21	2.6	0.45	<0.02	0.08	3.4	3.7
1994	4.59	0.49	3.84	2.48	0.76	0.28	0.22	0.07	0.55	7.4	51.2	0.09	0.14	0.24	3.5	0.42	<0.02	0.06	2.6	2.4
1995	4.57	0.12	0.97	1.13	0.26	0.10	0.18	0.02	0.18	5.9	33.2	0.03	0.03	0.08	0.5	0.11	<0.02	0.03	1.0	0.7
1996																				
1997	4.54	0.58	2.79	2.23	0.78	0.17	0.10	0.02	0.21											
1998	4.77	0.32	1.59	1.46	0.42	0.20	0.29	0.04	0.17											
1999	4.74	0.31	2.00	1.63	0.69	0.24	0.41	0.06	0.22											
Throughfall																				
1330 m (H)																				
1992	3.66	0.57	3.71	10.73	2.02	0.48	2.49	0.35	1.85	109.1	44.2	0.09	0.09	0.42	4.0	1.23	0.02	0.21	7.4	4.6
1993	3.91	0.85	4.06	8.47	0.47	0.67	2.29	0.21	1.77	135.9	67.7	0.11	0.13	0.37	2.9	0.74	0.02	0.16	4.8	5.0
1994	3.85	0.96	2.91	6.86	0.49	0.58	1.56	0.22	1.50	95.7	87.0	0.05	0.07	0.31	3.6	0.56	0.02	0.21	3.2	2.8
1995	4.26	0.25	2.53	2.88	0.26	0.18	1.23	0.13	0.94	31.6	88.3	0.03	0.04	0.19	2.2	0.12	<0.02	0.08	1.8	1.4
1996																				
1997	4.23	0.79	3.89	4.11	0.80	0.35	0.93	0.09	0.55											
1998	4.38	0.68	3.05	3.29	0.58	0.39	1.14	0.11	0.56											
1999	4.52	0.61	3.15	2.60	0.78	0.34	1.14	0.22	0.51											
Throughfall																				
1045 m (L)																				
1992	3.62	1.09	3.93	11.19	2.15	0.55	4.39	0.42	2.08	107.7	58.6	0.09	0.09	0.52	4.1	1.08	0.02	0.13	9.0	5.1
1993	3.93	1.06	1.74	11.62	0.61	0.52	2.19	0.27	1.70	146.3	142.0	0.11	0.08	0.33	3.1	0.51	<0.02	0.10	3.5	4.2
1994	4.04	1.55	2.05	8.30	0.97	0.77	2.28	0.28	1.57	58.0	98.7	0.12	0.20	0.40	3.1	0.38	0.02	0.09	2.6	3.9
1995	4.35	0.35	1.82	3.21	0.19	0.15	1.23	0.08	1.52	23.3	44.0	0.13	0.02	0.11	1.8	0.12	<0.02	0.03	1.4	1.0
1996																				
1997	4.33	0.69	3.45	3.20	0.82	0.33	0.83	0.11	0.58											
1998	4.34	0.71	2.25	2.96	0.69	0.34	1.38	0.16	0.66											

Table 2. – Annual fluxes of solutes in bulk precipitation and throughfall within Čertovo Lake catchment.

	Precip.	H	Cl	NO_3	SO_4	NH_4	Na	K	Mg	Ca	Mn	Zn	Fe	Al	SiO_2	Sr	As	Be	Cd	Pb	Cu	N tot	S tot
	mm	kg/ha	kg/ha	kg/ha	kg/ha	kg/ha	kg/ha	kg/ha	kg/ha	kg/ha	kg/ha	kg/ha	kg/ha	kg/ha	kg/ha	g/ha	g/ha	g/ha	g/ha	g/ha	g/ha	kg/ha	kg/ha
Bulk (B)																							
1175 m																							
1992	1306	0.42	6.5	44.1	35.7	18.0	1.2	2.1	0.7	6.2	0.05	0.42	0.59	0.64	1.7	32	4.6		1.0	39	28	23.9	11.9
1993	868	0.20	4.8	34.6	20.6	5.6	1.4	1.9	0.6	6.1	0.04	0.46	0.45	1.26	1.9	22	3.9		0.7	30	32	12.1	6.9
1994	676	0.18	3.3	26.0	16.8	5.2	1.9	1.5	0.5	3.7	0.05	0.35	0.61	0.97	1.6	24	2.8		0.4	18	17	9.9	5.6
1995	2061	0.56	2.6	20.0	23.4	5.3	2.2	3.7	0.4	3.6	0.12	0.68	0.52	0.59	1.6	11	2.2		0.7	20	15	8.6	7.8
1996	1162																						
1997	967	0.28	5.6	27.0	21.6	7.5	1.7	1.0	0.2	2.1												11.9	7.2
1998	1580	0.27	5.1	25.1	23.1	8.6	3.1	4.5	0.6	2.7												12.3	7.7
1999	1159	0.21	3.6	23.2	18.9	8.0	2.8	4.8	0.7	2.6												11.5	6.3
Throughfall																							
1330 m (H)																							
1992	1454	3.20	8.3	53.9	156.0	29.4	7.0	36.3	5.1	26.9	1.59	0.64	1.30	1.26	6.2	59	17.9	0.33	3.0	108	66	35.0	52.1
1993	1526	1.86	13.0	62.0	129.3	7.2	10.2	35.0	3.2	27.0	2.07	1.03	1.67	1.91	5.7	44	11.3	0.25	2.4	73	76	19.6	43.1
1994	1157	1.62	11.2	33.7	79.3	5.6	6.7	18.1	2.5	17.3	1.11	1.01	0.56	0.78	3.6	42	6.5	0.20	2.4	37	32	12.0	26.5
1995	2136	1.18	5.4	54.0	61.6	5.5	3.9	26.3	2.7	20.2	0.67	1.89	0.72	0.85	4.0	47	2.7		1.8	39	30	11.7	20.6
1996	1435																						
1997	1171	0.69	9.2	45.5	48.1	9.4	4.1	10.9	1.1	6.5												17.5	16.1
1998	1599	0.67	10.8	48.7	52.6	9.2	6.2	18.3	1.8	9.0												18.1	17.6
1999	1440	0.43	8.8	45.4	37.4	11.3	4.9	16.4	3.2	7.3												19.0	12.5
Throughfall																							
1045 m (L)																							
1992	1066	2.54	11.6	41.9	119.3	23.0	5.8	46.8	4.5	22.2	1.15	0.62	0.98	0.95	5.6	43	11.5	0.21	1.4	96	54	27.3	39.8
1993	1156	1.37	12.3	20.1	134.4	7.1	6.0	25.3	3.1	19.7	1.69	1.64	1.32	0.94	3.8	36	5.9		1.2	41	49	10.0	44.8
1994	820	0.75	12.7	16.8	68.1	7.9	6.3	18.7	2.3	12.8	0.48	0.81	1.02	1.64	3.2	25	3.2	0.16	0.7	21	32	10.0	22.7
1995	1973	0.88	6.9	36.0	63.3	3.7	2.9	24.3	1.7	29.9	0.46	0.87	2.55	0.47	2.1	36	2.3		0.5	28	20	10.9	21.1
1996	1128																						
1997	915	0.43	6.3	31.6	29.3	7.5	3.1	7.6	1.0	5.3												13.0	9.8
1998	1020	0.47	7.2	22.9	30.2	7.0	3.5	14.1	1.6	6.7												10.6	10.1
1999	1189	0.27	6.4	30.7	27.2	8.1	3.9	14.0	1.7	6.9												13.2	9.1

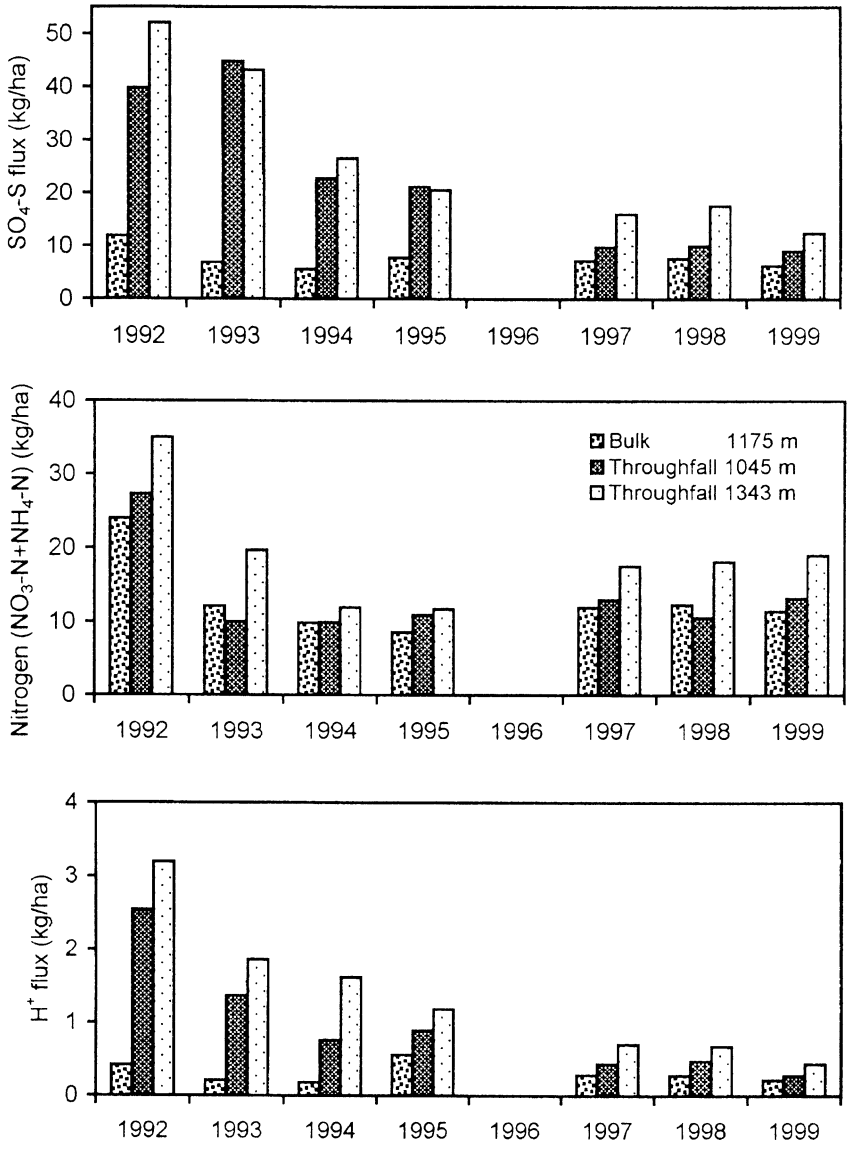

Fig. 5. – Annual fluxes of SO_4-S, inorganic N and H^+ measured in the Čertovo Lake catchment between 1992 and 1999.

Inorganic nitrogen

Annual volume weighted mean concentrations of NO_3 in bulk precipitation decreased from 3.4–4.0 mg/l in 1992–1993 to 2.0 mg/l in 1999. However, annual volume weighted mean concentrations of NO_3 in throughfall did not showed any significant decline during the study period, being ~3 mg/l at H plot and ~2.5 mg/l at L plot (Fig. 3, Table 1).

The contrast between the continuously decreasing trend in S deposition and relatively sta-

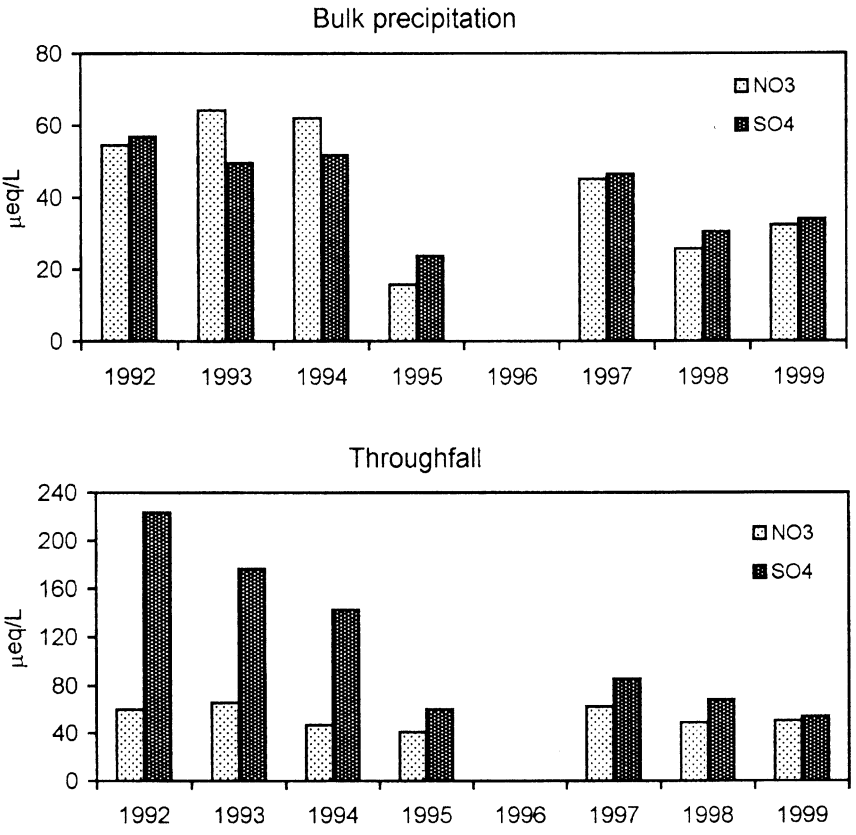

Fig. 6. – Comparison between SO_4^{2-} and NO_3^- concentrations in bulk precipitation and throughfall in the 1992–1999 period.

ble levels of N deposition can be explained by the differences in emission trends of S and N compounds (BERGE 1997). The major decline in the Central European emissions of NO_x and NH_3 occurred between 1989 and 1994, i.e. mostly before our study. Since 1994, it has been substantially less pronounced. In contrast, the decline in SO_2 emissions has continued throughout the whole 1990's.

The present Central European emission of inorganic N is ~35% lower than its maximum in the late 1980's. Thus, the maximum atmospheric deposition of inorganic N into the Čertovo Lake catchment can be roughly estimated using the present level of N deposition and the emission trend. The resulting values of atmospheric deposition of inorganic N in the 1980's are as follows: 16, 16, and 24 kg/ha/y at the plot B, L, and H, respectively. These results are very close to the deposition rate reported for the same area in 1990 by VESELÝ & MAJER (1992).

Relative importance of NO_3 and SO_4 (two major sources of atmospheric acidity) is shown in Fig. 6. NO_3 and SO_4 concentrations were comparable in bulk precipitation during the whole 1992–1999 period. In contrast, SO_4 was the dominant anion in throughfall in 1992 while comparable to NO_3 in 1999. Different patterns in sulfate to nitrate ratios in bulk precipitation and throughfall suggest important decline in dry deposition of S into the Čertovo Lake catchment between 1992 and 1999.

Concentrations of NH_4 varied within 0.26-0.78, 0.19-0.97, and 0.26-0.8 mg/l at the plot B, L, and H, respectively, between 1993 and 1999 (Table 1). Substantially higher concentrations were observed in 1992 (1.38 mg/l at B plot, 2.02 mg/l H plot, and 2.15 at L plot). These high values were responsible for higher fluxes of inorganic nitrogen in 1992 (Fig. 5, Table 2). Since 1993, fluxes of inorganic N has been roughly stable ranging between 8.6–12.3 kg/ha (B plot), 10.0–13.2 kg/ha (L plot), and 11.7–19.6 kg/ha (H plot).

The average equivalent ratio of NH_4 to NO_3 was 1.2 (B plot), 1.0 (L plot), and 0.8 (H plot) for the 1993–1999 period. In 1992 it was 1.5 (B plot), 2.1 (H plot) and 2.0 (L plot).

pH and proton fluxes

Bulk precipitation pH increased slightly during observed period (Fig. 2, Table 1). Lowest pH was measured in 1992 (pH = 4.50) and highest in 1998 (pH = 4.77). Significant changes of acidity has been observed in throughfall. In 1992, annual volume weighted pH was 3.62 at L plot and 3.66 at H plot. Until 1995, throughfall pH increased steadily to 4.35 (L plot) and 4.26 (H plot). Between 1995 and 1998, pH was relatively stable (Fig 3, Table 1) but increased again to 4.64 (L plot) and 4.52 (H plot) in 1999.

Proton fluxes are given in Fig. 5 and Tab. 2. Throughfall and bulk flux of H^+ decreased by 80–90% and ~50%, respectively, between 1992 and 1999. In 1992, throughfall flux of H^+ was ~8 times higher compare to the bulk flux (2.54–3.2 kg/ha/y compare to 0.42 kg/ha/y). The differences between the fluxes decreased steadily during the 1990s and in 1999, H^+ flux at L plot was only 25% higher than the bulk flux.

Observed patterns for throughfall fluxes of H^+ followed the changes in S fluxes with statistically significant correlation ($p<0.001$ at H plot and $p<0.02$ at L plot) (Fig. 7). This pattern suggests that S deposition was the most important source of atmospheric acidity for the Čertovo Lake catchment in the 1990's. Statistically significant correlation was not found for bulk precipitation fluxes.

Calcium, magnesium and sodium

Calcium concentrations were significantly higher between 1992 and 1995 than in the 1997–1999 period (Fig. 4, Table 1). Compare to bulk precipitation, throughfall concentrations and fluxes of Ca were ~5 times higher within 1992–1995 and ~3 times higher within 1997–1999 (Fig. 6., Table 2).

HLAVATÝ (1992) has estimated occult and dry deposition of Ca and Mg using the data mea-

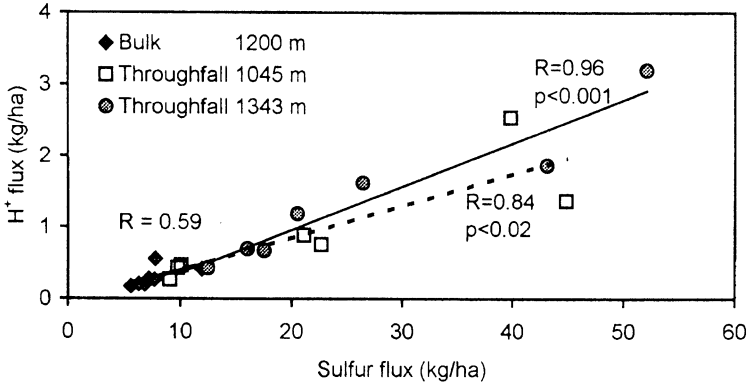

Fig. 7. – Relationship between the annual sulfur and H^+ throughfall fluxes for the catchment of Čertovo Lake.

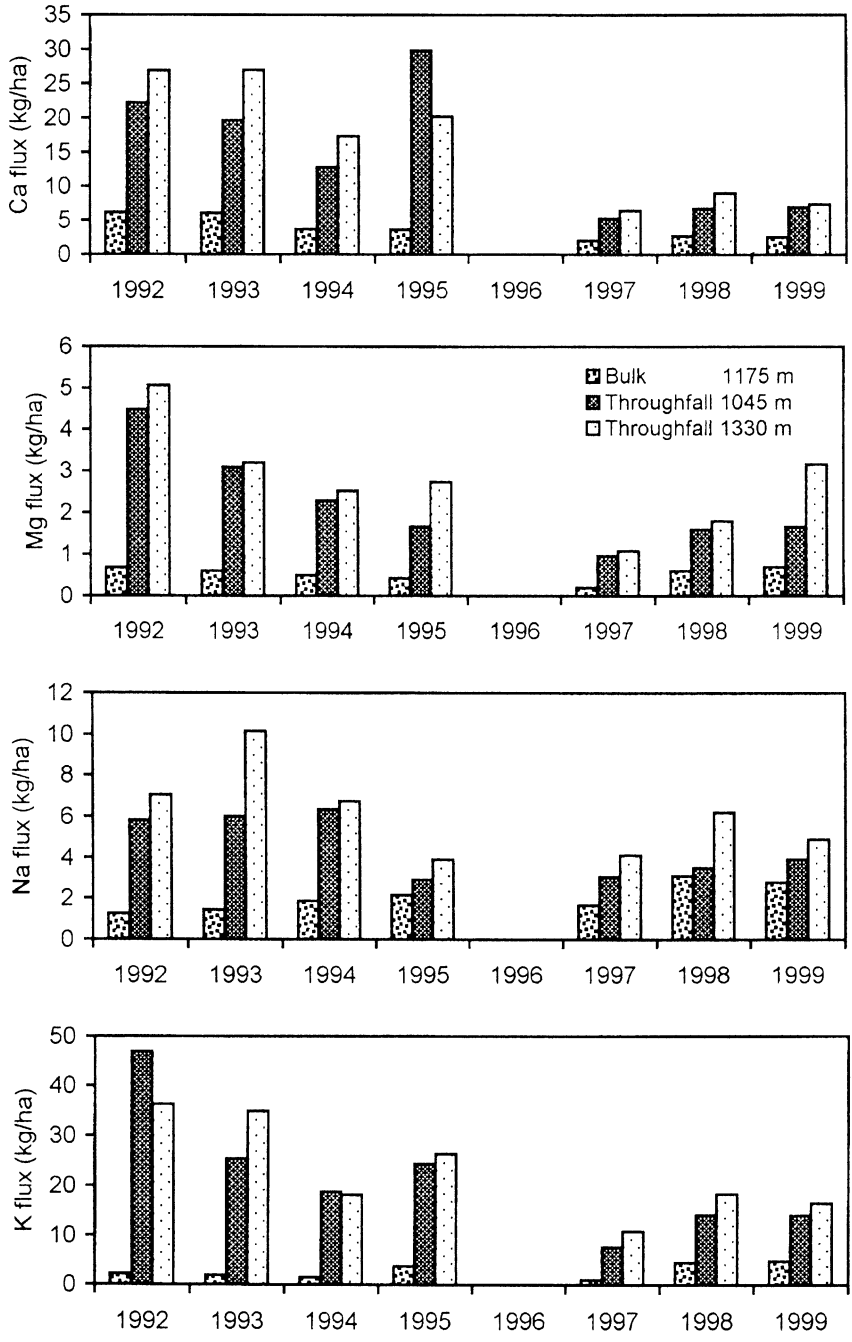

Fig. 8 – Annual fluxes of base cations measured in the Čertovo Lake catchment between 1992 and 1999.

sured between August 1991-March 1992. He used method by BREDEMEIER (1988), which is based on the assumption of biologically conservative behavior of sodium, i.e. canopy leaching of Na is negligible and throughfall flux of Na represents its total deposition. Ratio between the total and bulk fluxes calculated for Na is used for elements with a significant canopy leaching (Ca, Mg, K, Mn) to estimate their occult and dry deposition. The contribution of occult and dry deposition of Ca and Mg to their throughfall fluxes was 20–30% (HLAVATÝ 1992).

When we applied this method for the data from the 1992–1995 period, occult and dry deposition of Ca and Mg was equal or higher than their throughfall fluxes. However, we obtained more reasonable results (15–40% contribution of dry and occult deposition to the throughfall flux) for the 1997–1999 period. The unrealistic results for 1992–1995 resulted from very high Na fluxes in throughfall compare to bulk precipitation (3–4 times higher, Fig. 8). This high enrichment ratio of Na (the ratio of throughfall flux to bulk flux) was very different from data measured e.g. at the Lysina catchment (KRÁM & al. 1997), where the throughfall fluxes of Na were only ~50% higher than the bulk fluxes in the 1993–1994 period. It is questionable if the applied method is reasonable for high mountain's conditions, or if assumption about conservative Na behavior is valid. The mean enrichment ratio of Na for numerous forest areas throughout the word is approximately 2.4 (PARKER 1990). On the other hand MATZNER & MEIWEIS (1994) have observed that ~70% of Ca in throughfall (in Norway spruce forest, Solling, Germany) originated from the external sources.

Potassium

Compared to Ca and Mg, potassium concentrations were much higher in throughfall than in bulk precipitation. Throughfall concentrations of K were ~4.5 mg/l in 1992, then, they decreased to ~1.2 mg/l in 1999. Concentrations of K in bulk precipitation did not change significantly, and varied around 0.2 mg/l throughout the study period. Consequently, the enrichment ratio of K decreased from ~20 in 1992 to ~3 in 1999 (Fig. 8., Table 2). The published mean enrichment ratio for K is ~13 (PARKER 1990). Statistically significant relationship between the decline in K enrichment ratio and acidity load to the forest ecosystem of the Čertovo Lake catchment (Fig. 9) suggests a link between nutrient status of the forest (nutrient losses by canopy exchange) and the acidification level.

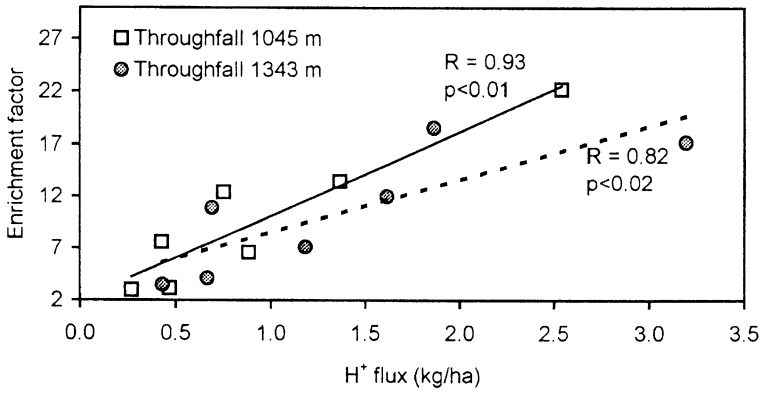

Fig. 9. – Relationship between the enrichment factors for potassium and annual throughfall fluxes of H^+ in the catchment Čertovo Lake.

HLAVATÝ (1992) has estimated 95% contribution of canopy exchange to the throughfall flux of K in 1991–1992. However this process contributed only 50% to the throughfall flux of K in 1999 due to the change in the K enrichment factor during the last decade.

Silica

Concentrations of Si in bulk precipitation and throughfall were measured between 1992 and 1995 only (Table 1, 2). Bulk precipitation concentrations and fluxes of Si did not change significantly during this period, while throughfall fluxes decreased by ~50%, suggesting decline of dust particles in the atmosphere.

Trace elements

All of the measured trace elements had higher concentrations in throughfall than in bulk precipitation (Table 1 and 2). The most pronounced enrichment factor (Fig. 10) was observed for Mn (22±14 in the 1992–1995 period). Similarly to potassium, the high enrichment factors of Mn were probably associated with the elevated acidity loads (Table 2) and higher leaching from foliage. External sources probably played minor role in the Mn throughfall flux.

Other trace elements (Cd, Fe, Zn, Sr, As, Pb, Cu, Al) showed different patterns. Their enrichment factors were ~2 with low standard deviation, suggesting predominantly external sources of examined elements.

Comparison with other areas

Deposition of S was used to compare acid load into the different mountain regions of the Czech Republic. At all the plots displayed in Fig. 11, the same method of throughfall sampling has been used as for the Čertovo Lake catchment. The region with the highest European deposition of S (border area between Czech Republic, Poland and Germany, so called „Black Triangle") was represented by Jezeří catchment in the Krušné hory (Erzgebirge), nearby town of Chomutov. Norway spruce throughfall was sampled there at 802 m a.s.l. Between 1991–1995, S deposition varied between 52–68 kg/ha/y and peaked in 1996 (88 kg/ha/y) (HAVEL & al. 1996, FOTTOVÁ 1999). Since 1997 it decreased sharply to 28 kg/ha/y in 1999.

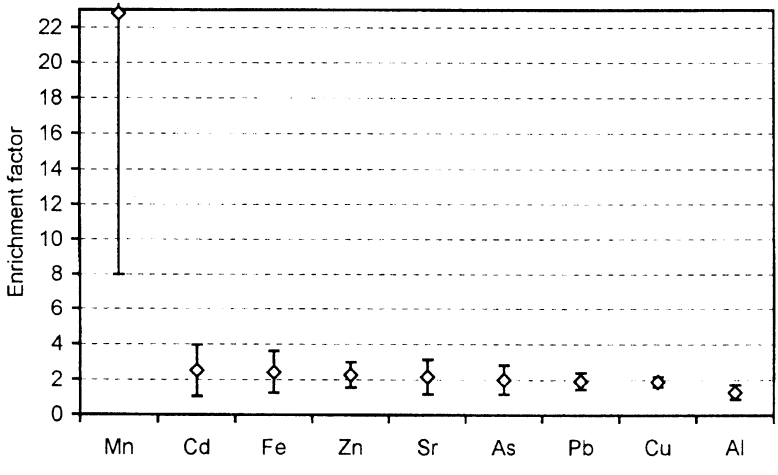

Fig. 10. – Average enrichment factors (± standard deviation) calculated for trace elements.

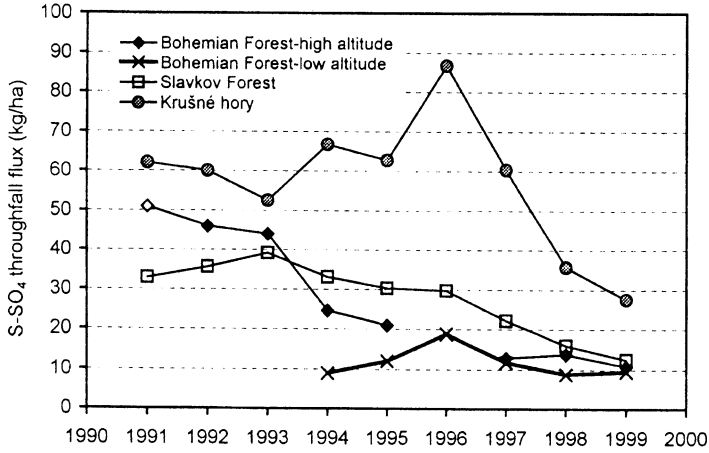

Fig. 11. – Comparison between sulfur depositions measured at different sites in the Czech Republic (1991–1999).

S deposition in the Čertovo Lake catchment in 1991–1993 (expressed as Bohemian Forest–high altitude in Fig. 8) was only 8–10 kg/ha/y lower than in the Jezeří catchment.

Similar trend as for the Čertovo Lake catchment was observed at the Lysina catchment in the Slavkov Forest, western part of the Czech Republic (HRUŠKA & KRÁM, unpublished data). Norway spruce throughfall of S was sampled there at 850 m a. s. l. S deposition was slightly lower there compared to the Čertovo Lake catchment between 1991 and 1993, then, it was higher in the 1994–1997 period and nearly identical in 1998 and 1999.

Finally, catchment Na Lizu, located at low altitude (deposition measured at 820 m a.s.l.) in the Bohemian Forest, was used for the comparison. At this catchment, very low throughfall deposition of S (9–18 kg/ha/y) without any trend was measured during the 1994–1999 period (FOTTOVÁ 1999). Except for the Jezeří catchment, all the other plots showed very similar S deposition in 1999 (between 10–11 kg/ha/y).

Conclusions

1) Atmospheric deposition of acidifying compounds in the Čertovo Lake catchment declined significantly during the period 1992–1999.
2) The most pronounced effect was observed for deposition of sulfur, which declined from 40–52 kg/ha/y in 1992 to 9–13 kg/ha/y in 1999. Similarly, proton input declined from 2.5–3.2 kg/ha/y to 0.3-0.4 kg/ha/y during this period.
3) No significant changes were observed for inorganic nitrogen deposition between 1993 and 1999 and varied between 11.5 and –19.0 kg/ha/y.
4) Compare to other areas in the Czech Republic, deposition of major acidifying compounds (SO_4-S, inorganic N, H^+) was relatively high at the beginning of the 1990's.
5) The maximum throughfall deposition rates of SO_4-S and inorganic N (sum of NO_3-N and NH_4-N) in the Čertovo Lake catchment occurred probably in the 1980's and were estimated to 90–100 and 16–24 kg/ha/y, respectively.

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