FACTORS AFFECTING THE CONTENT OF HEAVY METALS IN BULK ATMOSPHERIC PRECIPITATION, THROUGHFALL AND STEMFLOW IN CENTRAL BOHEMIA, CZECH REPUBLIC

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Abstract. Content of copper, manganese, lead, and zinc in samples of bulk precipitation, throughfall and stemflow has been studied in a forest area in central Bohemia. The sampling localities are situated on two types of bedrock, granite and cenomanian sandstones. The content in bulk precipitation reflects the impact of fossil fuel emission sources and the vehicular sources of lead. The deposition rate of elements in throughfall, in comparison with that of the deposition on an open land, exhibits increased values in essential microelements (in Mn approx. 45 times, Zn - 5 times, Cu and Cd - 2 times), with significant seasonal fluctuations. The value of the same ratio for ecotoxic lead is 0.23. The enhanced flux of elements in throughfall is ascribed mainly to the metabolic processes of the trees. Differences in the chemical composition of throughfall and stemflow collected on stands with different kind of bedrock are ascribed to various degree of accessibility of the micronutrients and various intensity of their vegetation uptake.

Key words: Heavy metals, precipitation, throughfall, stemflow, soil, metabolic activity, trees, uptake

1. Introduction

Heavy metal content in various types of atmospheric deposition reflects above all their emission sources, and their chemical properties. In case of the *bulk precipitation* sampled in central Bohemia, the content of heavy metals reflects the chemical composition of large air masses, affected by the anthropogenic emission sources. On the other hand, the chemistry of *throughfall* and *stemflow* reflects, besides the primary chemical composition of the bulk precipitation resulting from the wash-out effect of the rain- and snowfall, the intensified impact of the near-surface aërosol attached in the tree canopy, and in some elements the vegetation metabolic activity. High concentrations of K, Mg, and Ca in throughfall below various tree species were documented by a number of authors (Tukey, 1970, Norden, 1991, Potter, 1991, Novo *et al.* 1992, Arthur and Fahey, 1993). The ion exchange of the redundant ionic species excreted from the tree assimilation organs for the atmospheric protons is supposed to be the main mobilization mechanism of these elements (Hoffman *et al.* 1980, Adams and Hutchinson, 1984, Morrison *et al.* 1992, Capellato *et al.* 1993). Data concerning the content of heavy metals in throughfall are not so plentiful, and their interpretation is not unambiguous (Heinrichs and Mayer, 1980, Atteia and Dambrine, 1993). The chemistry of *stemflow* (Kazda and Glatzel, 1984) mirrors all the above mentioned factors, together with the tree bole leaching (Potter, 1992).

The aim of this work was to assess the major factors affecting the content of the studied microelements in the bulk precipitation, throughfall and stemflow of a forested area in central Bohemia with considerable load of atmospheric pollution, to compare the obtained results with the published data from other regions of Europe, and to discuss the impact of the atmospheric deposition chemistry on the position of the studied elements in soil.

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2. Materials and Methods

Sampling of the studied types of atmospheric deposition was caried out at the experimental station of the Faculty of Forestry, Czech Agricultural University (locality "Truba") and in the afforested Nature State Reserve "Voděradské bučiny" (locality "Lesní potok" catchment). The mutual distance of these two sampling sites is about 5 km and they are situated approx. 30 km SE from Prague. Both the localities have a background character, considering the Central European standards.

The bulk atmospheric precipitation was sampled on a forest clearing (loc. Truba), at least 50 m from the trees. Samples of the average throughfall were collected in an adjacent mixed forest site, into a set of nine sampling devices evenly distributed on a 20 m x 20 m square measuring plot. The species growing on the plot (beech, spruce, oak, pine, birch, larch) represent an average species composition of a forest surrounding the studied area. Sampling of beech throughfall and stemflow has been carrying out in both sampling areas (Truba and Lesní potok).

The procedures of bulk precipitation and throughfall sampling were in principle similar to those of Berg *et al.* (1994). Samples were collected in a polyethylene (PE) devices on a monthly basis. The collectors consist of a PE funnel (11.8 cm in diameter) equipped with a nylon sieve, screwed to 1 L PE bottle. The device for stemflow sampling is similar to those for bulk precipitation and throughfall, with PE stemflow collector adjustable to the tree trunk. Prior to their installation on a sampling site, the recycled sampling bottles were carefully washed (hot water, 0.5% HNO_3, distilled and bidistilled water), and in case of the bulk precipitation sampling, 5 ml of diluted (22% v/v) HNO_3 (Merck, Suprapur) were inserted into each sampling bottle.

At the end of each sampling period the bottles were replaced by new ones and were transported into the laboratory in sealed PE bags. The bottles were weighed to check up the volume of the liquid. The samples were filtered using a 0.45 μm membrane filters to remove minute solid particles which could negatively affect the final analytical procedure. The filtrate was stored at +4°C in a cooler until the analysis (graphite furnace- or flame AAS). In case of throughfall and stemflow, the samples were acidified in a laboratory (after the bulking of the average throughfall samples), and after 1 day they were filtered through the membrane filters. Samples determined for the laboratory pH measurements were sampled separately.

The soil samples were collected at the beech forest hillside in the catchment "Lesní potok", in selected distances from the tree trunk, up- and down the slope. In the laboratory they were dried at room temperature and sieved through a 1 mm nylon sieve. The <1 mm fraction was extracted for 24 hrs. with 0.1M HNO_3 (V/m=100) and filtered through the membrane filters.

3. Results and Discussion

3.1. BULK ATMOSPHERIC PRECIPITATION

statistical values of element concentrations and pH in samples collected since May 1989, together with their annual flux in 1994 (when most reliable data were available - Kotková *et al.*, in press), are presented in Table I. They are approx. 1.5 - 3 times higher in Cu, Zn, and Pb in comparison with the data of Berg *et al.* (1994) for the sampling site *Birkenes* (which shows the highest concentrations in most of the 27 studied elements among the six monitored rural and remote sites in Norway). The median value of Mn is

6.5 times higher than the corresponding values of the most polluted rural sites *Birkenes* and *Nordmoen* in Norway. Our 1994 elemental flux compared with the station *Birkenes* in 1990 is lower in all elements except for Mn, owing to the significantly higher annual precipitation (at *Birkenes* 1861 mm in 1990) than in central Bohemia (605 mm in 1994). The sequence of the enrichment factors (normalized to Fe) follows that of Berg *et al.* (1994). Zinc and lead are highly enriched (EF>100), Cu>Mn are moderately enriched.

TABLE I

Summary of the analytical data on the studied elements in ***bulk precipitation*** at the locality Truba since May 1989 till Feb. 1995, conc. in *ppb* ($ng.ml^{-1}$). Enrichment factor (EF) of the elements is normalized to Fe.

element	n	median	total range	lower and upper quart.	vol. wt. mean	1994 vol. wt. mean	flux 1994 (F_D, $\mu g.m^{-2}$)	EF
Mn	69	15	1.3-310	7.8-30	30	22	14000	12
Cu	69	2	<0.5-20	1-3	2.3	1.8	1100	34
Zn	68	30	<10-590	15.5-80	46	11	7200	290
Pb	70	5	0.5-15	3-6.7	5.3	4.6	2900	250
pH	12	4.15	3.42-4.42					

3.2. THROUGHFALL

Table II summarizes data on the content of studied elements in the average throughfall.

TABLE II

Summary of the analytical data on the studied elements in ***throughfall*** at the locality Truba since May 1993 till Jan. 1995, n=21, conc. in *ppb*.

element	median	total range	lower and upper quart.	1994 vol. wt. mean	flux 1994 (F_{TH}, $\mu g.m^{-2}$)	F_{TH}/F_D* 1994
Mn	1190	660-5990	870-2140	1200	470000	33
Cu	4.6	1.9-15.5	3.3-7.8	4.6	1700	1.7
Zn	43	20-870	40-68	46	17000	2.4
Pb	1.35	<0.5-5.9	1.1-2.9	2.0	690	0.24
pH	4.69	3.76-5.87				

* - ratio of the elemental fluxes in throughfall and in bulk precipitation

Comparison of the median and the volume weight mean concentration reveals enrichment in throughfall with the exception of Pb. The comparison of the elemental fluxes (F_{TH}/F_D), which reveal similar characteristics, is more exact showing considerable enrichment in Mn. High Mn concentrations in throughfall have been reported by a number of authors (Heinrichs and Mayer, 1980, Atteia and Dambrine, 1993) and they were confirmed through laboratory experiments (Fritsche, 1992). They are interpreted as a consequence of the Mn role in the carbohydrate metabolism and in the photolysis of water. Excess metabolic Mn cations are then secreted from the assimilation organs of the vegetation and leached through the ion-exchange mechanism. The course of the Mn deposition flux in the bulk precipitation and throughfall plotted vs. time is shown in Figure 1. The maximum values in deep autumn samples result from the metabolic role of Mn, when more intensified secretion of the excessive cations proceedsin the time period preceding the winter stagnation of the forest vegetation. The fact that the Mn curve

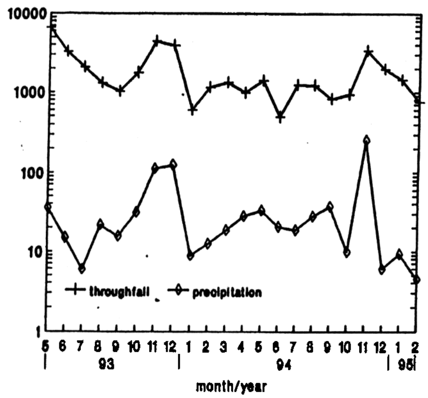

Fig. 1.Mn deposition flux (in $\mu gMn.m^{-2}.day^{-1}$) through the bulk precipitation and throughfall.

of bulk precipitation resembles that for Mn in throughfall can be explained by the possibility of the local reverse effect of the throughfall chemistry on that of the bulk precipitation. Rains occuring in windy periods may be contaminated by small droplets of water arising from the collision of the rain drops with the surface of the tree assimilation organs.

3.3. BEECH THROUGHFALL

Beech througfall has been sampled at two localities with different kind of bedrock, in order to find out any effect of the various degree of accessibility of the soil elements on the throughfall chemistry. Results are shown in the Table III. Values representing

TABLE III

Content of elements in *beech throughfall* collected on stands with different kind of bedrock. G - granite, S - sandstones, conc. in *ppb*.

element	bed-rock	median	total range	lower and upper quart.	F_{THB}* ($\mu g.m^{-2}$)	F_S/F_G+
Mn	G	230	29-1190	49-370	76000	7.54
	S	770	140-4370	330-1600	570000	
Cu	G	3.0	1.5-6.2	2.3-4.9	1300	1
	S	2.9	0.7-7.5	1.6-5.4	1300	
Zn	G	24	<10-42	22-36	8300	1.6
	S	32	<10-50	20-38	13000	
Pb	G	1.9	0.6-8.3	1.5-3.3	960	1.03
	S	1.6	<0.5-6.55	1.2-2.2	990	
pH	G	5.42				
		4.51				

* - flux in the beech troughfall since April 1994 till January 1995
+ - ratio of the fluxes on the sandstone/granite bedrock

the locality with granitic bedrock are lower in Zn and especially in Mn, which is clearly shown in the values of the ratio of elemental fluxes on both types of the bedrock (F_S/F_G). This finding could be explained by the lower accessibility, of Mn (and Zn) in the granitic bedrock. The appropriate data have not been available up to now, to confirm this idea.

3.4. BEECH STEMFLOW

The stemflow chemistry allows us to formulate an idea about the extent of the input of these elements into the soil and about their interactions with the soil components. Data for the beech stemflow, collected on both types of the bedrock (Table IV) resemble those for the beech throughfall (Table III) except for the pH values. Higher concentration of protons in the stemflow results from leaching of the excess atmospheric anions of strong acids (SO_4^{2-}, NO_3^-) deposited and adsorbed on the tree surface. The elevated metal and proton concentrations in the stemflow, together with the high amount of this deposition flux occuring in the close stem vicinity, should strongly affect the vertical and lateral distribution of heavy metals in the forest soil. To confirm this, samples of the topsoil were collected for the study of their content of leachable elements, together with the sampling of the undisturbed soil samples for the soil mesofauna study (Kopeszki, 1988, Kopeszki, 1992, Rusek, unpublished data). Table V shows the lateral changes in the element concentrations in dependence on the position of the individual sampling site with respect to the stemflow discharge.

TABLE IV

Content of elements in *beech stemflow* collected on stands with different kind of bedrock. G - granite, S - sandstones, conc. in *ppb*.

element	bedrock	median	total range	lower and upper quart.
Mn	G/S	480/770	330-1600/300-2530	360-730/560-980
Cu	G/S	4.4/2.4	2.2-12.1/0.6-16.1	3.9-5.1/1.8-9.1
Zn	G/S	17/30	<10-80/<10-120	16-30/10-51
Pb	G/S	2.3/1.7	0.8-3.5/0.5-4.3	1.1-2.9/1.0-2.1
pH	G/S	4.04/4.00	3.15-4.88/3.17-5.03	

Presented values reflect the chemical behaviour of elements in the soil environment, and the role of the stemflow pH value. Low Pb mobility and high Cu affinity to the soil organic matter results in the accumulation of these two elements close to the stem base (sampling locality +0.5 m). On the other hand, the soil of this locality exhibits the lowest concentrations of extractable forms of Zn and Mn, which are the elements easily mobilized in acidic conditions of the soil environment. Fixation of the mobilized metals in soil proceeds farther, where the acidic solution is partly neutralized by the mineral soil cations. Described mechanism could explain the elevated values of the extractable Zn and Mn found in samples far below the stemflow discharge (sampling localities +1.0 and +2.0 m).

TABLE V

Lateral changes in the content of soil leachable elements in dependence on the site of the stemflow discharge (content in *ppm* d.w.). Soil samples on the slope in *m* below (-) and above (+) the stem base.

element	distance from the stemflow discharge (*m*)					
	-4.0	-2.0	-1.0	+0.5	+1.0	+2.0
Mn	46.0	114.6	80.7	25.7	61.9	153.4
Cu	2.53	3.62	5.01	6.35	4.52	3.42
Zn	18.7	34.6	30.6	12.5	26.7	33.6
Pb	55.0	65.7	82.7	84.0	85.9	61.7

4. Conclusions

Comparison of the content of studied elements in bulk precipitation of central Bohemia with values of the rural and remote localities of Norway shows the considerably higher degree of contamination in all studied elements (Mn, Zn, Cu, Pb). Values of the enrichment factors of studied elements and their sequence correspond to the Norwegian sampling site *Birkenes*. Elemental fluxes in the average throughfall reveal the enrichment in all elements except for Pb, which is ascribed to the leaching of tree metabolites from their assimilation organs and to the ion exchange with the atmospheric protons. The effect of metabolites is particularly strong in Mn, where the flux intensity oscillations throughout the year are supposed to be connected with the role of Mn in the photosynthesis. The similarity of the annual course of Mn fluxes in throughfall and in bulk precipitation is explained by the reverse effect of the throughfall chemistry on that of precipitation collected on an open place. Varying Mn (and Zn) content in the beech throughfall collected at sites with different type of bedrock is ascribed to the various accessibility of these elements in the corresponding soil types. Fluctuations in the content of leachable microelements of the beech forest topsoil samples collected at various distance from the stemflow discharge are explained by the chemical composition and pH of this deposition flux, together with the chemical character of the studied elements.

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References

Adams, C.M. and Hutchinson, T.C.: 1984, *New Phytologist* **97**, 463-478.
Arthur, M.A. and Fahey, T.J. 1993, *Canad. J. Forest Res.* **23**, 738-742.
Atteia, O. Dambrine, É.: 1993, *Ann. Sci. For.* **50**, 445-459.
Berg, T., Royset, O. Steinnes, E.: 1994, *Atmosph. Environ.* **21**, 3519-3536.
Capellato, R., Peters, N.E. and Ragsdale, H.L.: 1993, *Canad. J. Forest Res.* **23**, (6), 1114-1124.
Fritsche , U.: 1992, *Environ. Pollut.* **75**, 251-257.
Heinrichs, H. and Mayer, R.: 1980, *J. Environ. Pollut.* **9**, 111-118.
Hoffman, W.A. Jr., Lindberg, S.E. and Turner, R.R.: 1980, *J. Environ. Qual.* **9**, 95-100.
Kazda, M. and Glatzel, G.: 1984, *Z. Pflanzenernaehr. Bodenk.* **147**, 743-752.
Kopeszki, H.: 1988, *Zool. Anz.* **221**, 368-378.
Kopeszki, H.: 1992, *Pedobiologia,* **36**, 295-305.
Kotková, P., Skřivan, P. and Burian, M.: *Ecol. Environ. Statistics* (in press).
Morrison, I.K., Foster, N.W. and Nicholson, J.A.: *Water, Air, and Soil Pollut.* **61**, 243-252.
Norden, U.: 1991, *Water, Air, and Soil Pollut.* **60**, 209-230.
Novo, A., Buffoni, A. and Tita, M.: 1992, *Environ. Pollut.* **75**, 199-208.
Potter, C.S.: 1991, *Canad. J. Forest Res.* **21**, 222-229.
Potter, C.S.: 1992, *Plant and Soil,* **140**, 249-254.
Rusek, J.: *Unpublished data.*
Tukey, H.B. Jr.: 1970, In:*Ecology of leaf surface micro-organisms,* (Ed. T.F. Preece, C.H. Dickinson), pp 68-80, Academic Press, New York.