Contaminants bound to solid part of falling precipitation and throughfall at the Milešovka observatory

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Abstract Content of selected elements bound to solid part of falling precipitation (open place, beech- and spruce throughfall) has been monitored at the Milešovka Observatory. This part of pollutants bound to solid matter will be further named as insoluble. Data of Al, Fe, Na, K, Ca, Mg, Mn, P, Ba, Cd, Co, Li, Sr, Ti, Zn are available. The impact of the above–ground forest vegetation on the entrapment of solid aerosol is clearly detectable in the throughfall samples. The correlation analysis of the individual deposited elements divided them into three main groups according to their origin. Elements Al, Ba, Fe, Ti (Li) come mainly from the terrigenous dust; Ca, K, Mg, Mn and P are of predominantly organogenic origin, and Cd, Co, Mg, Sr and Zn indicate the anthropogenic sources. The seasonal distribution of the elements in the monitored deposition fluxes also confirms their distribution into the three main groups. The results of backward trajectories of precipitation events generally show decrease of the amount of insoluble pollutants during the prevailing western and northwestern flow with more pronounced daily precipitation amounts. Low total concentrations were also recorded in case of eastern or southeastern transport with very low or nil precipitation. Recent environmental hazards of the sampling locality connected with the deposition of inorganic pollutants bound to solid matter are assessed.

Key words: insoluble pollutants, throughfall, bulk precipitation, wet deposition, sources, backward trajectories

Sampling and methods

Long term monitoring of major ions and trace metals in bulk atmospheric deposition and throughfall was started in June 2004 at the Milešovka Mt., located in the industrial area of north-western Bohemia. The monitoring is a part of broader study oriented on physical and chemical processes taking place in the forest ecosystems (Fišák et al. 2006, Tesař et al. 2006, Buchtele et al., 2006, Skřivan et al. 2000, Navrátil et al. 2002). In the period of May 2005 to June 2006 the monitoring was supplemented by the analysis of insoluble precipitation components captured during the sample filtration.

Precipitation sampling and the laboratory treatment

Bulk deposition was sampled into 4 collectors. The first 2 collectors were used to collect bulk precipitation samples determined for the study of major cations and anions and the other 2 collectors were used for samples determined for the study of the trace element concentrations. The throughfall sampling site was equipped by 4 collectors used for sampling of spruce throughfall and 5 collectors used for sampling the beech throughfall. All throughfall collectors were used for collecting of samples determined for both analyses of major ions and trace elements (see also Fisak et al., 2006).

The collectors determined for the study of major cations and anions consisted of a 1L collecting polyethylene bottle and a polyethylene funnel with a nylon sieve placed in the neck of the funnel to prevent sampling of debris. The collector of samples determined for the study of the trace element concentrations was almost the same, but furthermore it was equipped with a glass funnel inserted into the polyethylene funnel. The mouth of the glass funnel was protected from falling organic debris and insects by a small glass bubble. The throughfall collector was additionally equipped with a glass conical bulb placed onto the funnel so that the throughfall flowed down into the collecting bottle without additional contamination by needles or other organic debris.

The samples were filtered in the laboratory using the 0.45 μ m nitrocellulose membrane filter. The insoluble solid components of precipitation captured during the filtration were then subjected to further study. The filters with solid particles were dried to constant weight and digested in the mixture of 4 ml HF and 10 ml HNO₃ (both Suprapur, Merck) using the microwave digestion unit (Milestone, MLS 1200 mega). After the digestion the acid solution was heated to 150 °C to evaporate the HF and then filled up to 50 ml by 1% HNO₃ (Merck, Suprapur). All employed laboratory vessels were leached in HNO₃ (1:3) for at least 24 hours and then rinsed with deionized water (Elga, >18 MΩ.cm).

Analytical methods

The concentration of studied elements was determined with IRIS Intrepid II XPS spectrometer (ICP-EOS) using axial plasma view and cyclone type nebulizer. The standard operational conditions were used (plasma power 1150 W, nebulizer pressure 25.0 psi, auxiliary gas flux 1.0 ml/min, sample uptake 2.40 ml/min). The calibration curves were constructed using four points (blank and multi-element standards in 1% ultrapure nitric acid) covering full range of the concentrations measured. The detection limits were following (wavelength/nm; detection limit/ μ g.L⁻¹): Al (328.1; 0.4); Ca (393.4; 0.05); Fe (259.9; 0.6); K (766.5; 10.0); Mg (280.3; 0.1); Mn (259.3; 0.6); Na (589.0; 1.0); P (213.6; 10.0); Ba (455.4; 0.5), Cd (214.4; 0.2), Co (228.6; 0.6), Li (670.7; 0.8), Sr (407.7; 0.05), Ti (334.9; 0.5), Zn (206.2; 0,3). Each sample was analysed twice. Quality control was ensured through inserting QC sample into the analytical run after each ten unknown samples.

Data treatment

The values are expressed as concentrations of studied elements/ions in the solid phase related to the unit volume of filtered solution.

To eliminate differences in the total amount of insoluble precipitation components collected in the individual samples, the determined value of analytical concentration of each individual element was divided by the sum of concentrations of all studied elements. Through this operation we obtained values of the *relative abundance of individual elements* in the solid portion for all bulk and throughfall samples.

The mutual correlation of values of the relative abundance of studied elements was computed using Spearman correlation coefficient.

Backward trajectories

The backward trajectories were employed for the evaluation of dependence between the concentration of insoluble components and the direction of their transport. The trajectories were computed using the HYSPLIT model (Draxler & Rolph, 2003; Rolph, 2003).

Results and discussion

Correlations of the elements in solid matter

The distinct determination of sources of elements in solid part of the deposition solely from the correlation analysis is not possible, in particular with respect to their varied and diverse potential sources. The correlation nevertheless enables to estimate several groups of elements with common access to the atmosphere.

Values of correlation coefficients (R), together with the significance levels (α) and number of correlated values (n) of relative abundance of individual elements in the solid portion of bulk and throughfall samples are presented in the Tables 1, 2, and 3. Our correlated elements can be dissected into three main groups, according to their origin:

• The predominantly terrigenous elements, originating from the soil minerals and the bedrock: Al, Ba, Ca, Fe, Li, Na, P, Sr, and Ti.

Table 1: Correlation matrix of the relative abundances of elements in bulk precipitation. (R- correlation coefficient, α- significance level, n- number of correlated pairs.)

	(I	R- correla			t, α- sigi	nificanc	e level,	n- num			d pairs.)					
elem		٨I	Ch	Fe	Ľ.	Цş	1-fu	\mathbf{p}_{1}	Р	Bh	Co	Lı	йr	Τı	20	C J
	R.	1	-0 +11	0 210	-0 212	-01'4	-0 490	0.241	-0100	0.196	-0 10"	-0.009	0 100	0.308	001+	3000-
٦	C	0	0108	0 10	0 001	0.600	0106	0 4 4 3	0.071	0 742	0.744	0.087	0.421	0 0001	0.966	0 0 0 0 1
	ш	12	12	12	12	12	12	12	12	12	12	10	12	12	12	12
	E.	-0 + 11	1	0 070	0 140	0.317	0.04.2	-0.049	-0.10°	0 100	0 091	0.047	0.182	0.077	0.028	0.028
Ch	C1	0138	0	0.829	0.667	0.211	0.897	0.830	0.744	0.421	0.779	0.811	0 172	0 21 2	0.901	0.901
	1	12	12	12	12	12	12	12	12	12	12	10	12	12	12	12
	E.	0 210	0.070	1	-0 301	-0.344	-0182	0.042	-0.617	0 ##1	-0 203	0.172	-0.119	0.62.9	-0 640	-0 687
Fe	C	0 * 10	0.829	0	0.042	0.247	0 172	0.897	0.000	0.172	0 527	0.676	0 713	0.028	0.024	0014
	ъ	12	12	12	12	12	12	12	12	12	12	10	12	12	12	12
	R.	-0 515	0140	-0 301	1	0.200	0427	-0 4 34	0 ± 62	-0.381	0 322	0.018	0.182	-0420	0.007	0 101
F.	C	0 0 0 1	0.667	0.342	0	0.127	0147	0119	0131	0/217	300 0	0.940	0 172	0.175	0.900	0.075
	1ı	12	12	12	12	12	12	12	12	12	12	10	12	12	12	12
	R.	-0 1'4	0.317	-0 364	0/203	1	-0.24 1	-0 608	390.0	-0.266	0.092	-0.4729	0.273	-0.692	0101	0483
M_{f}	(1)	0 400	0.2 **	0.247	0.127	0	0440	0.034	0.742	0 +0+	0 208	0.142	0.091	0 01 3	0.74.4	0112
	ъ	12	12	12	12	12	12	12	12	12	12	10	12	12	12	12
	E.	-0 490	0.042	-0.122	0.427	-0.247	1	0.0 %	0.329	-0.028	0.028	0.234	-0.272	-0.016	-0.11.2	0 3 0 1
1-fn	C	0106	0.897	0 172	0.147	0.443	0	0.843	0.297	0.991	0.991	0 '11	0.400	0.863	0.72.9	0.342
	1	12	12	12	12	12	12	12	12	12	12	10	12	12	12	12
	R.	0.247	-0.049	0.042	-0 +3+	-0.408	0016	1	-0.2.24	04""	-0 490	0 11 '	-0.119	0.434	0.091	-0.270
17_{2}	C	0443	0830	0 897	0.119	0.00%	0.060	0	0 1 84	0 138	0 104	0.7'1	0.713	0.02%	0 779	0091
	ъ	12	12	12	12	12	12	12	12	12	12	10	12	12	12	12
_	R.	-0 708	-0 10'	-0 617	0 462	390.0	0.32.9	-0.2.24	1	-0.266	-0 224	0.094	-0.381	-0 10	0.280	0174
Р	C.	0071	0.746	0 000	0.131	0.762	0.297	0 1 81	0	0 +0+	0 +8+	0.260	0.217	0.050	0.379	0.600
	ъ	12	12	12	12	12	12	12	12	12	12	10	12	12	12	12
	E.	0196	0100	0 ##1	-0.381	-0.266	-0.028	0477	-0.2.66	1	-0 308	0.1∞	0.049	0.762	-0.21.0	-0 102
Bh	C	0 742	0.631	0.172	0.217	0 +0+	0.991	0100	0 + 0 +	0	0 001	0 600	0 330	0 00 +	0 10	0071
	ъ	12	12	12	12	12	12	12	12	12	12	10	12	12	12	12
	E.	-0 10'	0.091	-0 200	0.322	0.092	0.028	-0 4 90	-0.2.24	-0 308	1	-0 648	0.119	-0.310	0.399	0187
Co	C	0.744	0.779	0.527	300 0	0.208	0.991	0104	0 4 84	0 001	0	0.043	0.019	0.241	0 199	0.04"
	ъ	12	12	12	12	12	12	12	12	12	12	10	12	12	12	12
	R.	-0 009	0.047	0 172	0 018	-0.479	0.20%	0117	0.3.94	0.1∞	-0 648	1	-0.479	0 000	-0.318	-0 4 11
Ŀт	<1 C	000	0.811	0.676	0.940	0142	0 '11	0 7 1	0.2.40	0 400	0 043	0	0 1 42	0.047	0 310	0187
	1	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	P.	0133	0182	-0 119	0 182	0.273	-0.212	-0.119	-0.381	0.049	0,119	40,479	1	390.0	0 11 2	0476
Сr.	C	0 6 81	0 172	0 713	0 172	0.091	0430	0 713	0.217	0 330	0.019	0.142	0	0.762	0.72.9	0118
	14	12	12	12	12	12	12	12	12	12	12	10	12	12	12	12
_	E.	0000	0.077	0.629	-0 420	-0.692	-0.014	0.636	-0 10	0.742	-0.310	0 000	320.0	1	-0.219	-0 611
Τı	C.	0 3 3 1	0 812	0.028	0.17'	0 013	0.060	0.026	0.0.90	0 00+	0.245	0.047	0.742	.0	0417	0000
	1	12	12	12	12	12	12	12	12	12	12	10	12	12	12	12
_	P.	0014	0.028	-0 640	0 007	0 10 7	-0 11 2	0091	0.2.50	-0 210	0.000	-0 3°C	0 112	-0.219	1	0.210
20	C1	0.946	0.901	0.024	0.900	0.744	0.72.9	0.779	0.379	0 10	0 199	0 310	0.729	0 +1 7	0	0 * 10
	1	12	12	12	12	12	12	12	12	12	12	10	12	12	12	12
	R.	-0 308	0.028	-0 601	0 101	0483	0 301	-0.273	017+	-0 100	0 187	-0 + 11	0 474	-0 41 1	0.210	1
Ca	C.	0 3 31	0.901	0 014	0.075	0 112	0.342	0091	0 600	0 071	0.04"	0 187	0118	0.000	0 13	0
	<u> </u>	12	12	12	12	12	12	12	12	12	12	10	12	12	12	12

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	1	(R-come			ι, α - ε				iber of ()				
elenen		ăl –	Ch		Ľ.	Мg	1-fu	\mathbf{D}_{2}	Ρ	Ba	Co	Lı	йr	Τı	20	CJ
	R.	1	-0 + + 6	0 132	-0 310	-0.607	-0.492	0 0 1 1	-0.727	0 702	-0 +'1	0 23 7	-0191	0.040	-0.709	-0 750
٦L	C.	0	0110	0 500	0.231	0 01 "	0 00 6	0.970	0.0 "+	0 000	0 122	0 00 0	0 13	0 0 0 0	0.007	0 001
	14	1+	1+	1+	1+	1+	1+	1+	1+	1+	10	1+	1+	1+	13	1+
	E.	-0 ++ 6	1	0 108	0 103	0 "40	0 187	-0 4 64	-0.172	-0.007	0.416	-0411	0.200	-0.081	0 330	0 41'
Ch	C	0110	0	0 714	0.721	0.04.	0.027	0.0.9"	0.607	0.329	0.117	0102	0490	0.17°	0.271	0 140
	ъ	1+	1+	1+	1+	14	1+	1+	1+	1+	10	1+	1+	1+	13	1+
_	R.	0182	0108	1	-0 41°	-0.020	-0.270	-0.271	0172	0.191	-0 110	0.275	-0 0 20	0.0.90	-0.209	-0.389
Fe	С.	0 "33	0.714	Û	0 140	0.94%	03*0	0.342	0 60"	0 "13	0.721	0.34.2	0.2.40	0.719	0 494	0.149
	ъ	1+	1+	1+	14	1+	1+	1+	14	1+	10	1+	1+	1+	10	1+
	R.	-0.310	0103	-0 +1"	1	0.319	0419	0 712	-0.116	-0 024	0.264	-0.314	361.0	-0 341	0 149	0 429
Ľ.	C.	0.281	0.721	0 140	0	0.247	0.098	0.041	0194	0.991	43C 0	0.21 °	0.047	0.200	0.012	0 126
	ш	1+	1+	1+	1+	1+	1+	1+	1+	1+	13	1+	1+	1+	13	1+
	E.	-0.601	0 140	-0 020	0.019	1	0.747	-0.336	0.2.62	-0 +81	0 421	-0 ## S	0 4 24	-0.763	0 49C	0.704
M_{f}	C.	0 01 '	0.04,	0.944	0.247	0	0 00 1	0.240	0.344	0.031	0.024	0 01 2	0131	0 0 0 2	0 000	0 000
	ъ	1+	1+	1+	14	14	1+	1+	1+	1+	10	1+	1+	14	13	1+
	R.	-0.692	0 1 87	-0.270	0.419	0.747	1	3400	0.0.64	-0.074	0 434	-0 604	0.279	-0_741	0	0 741
1-10	C.	0 00 6	0.027	0.370	320.0	0 001	0	0.817	0.829	0 21 7	0 138	0.02.2	00004	0 0 0 2	0.049	0.002
	ц	1+	1+	14	14	14	1+	1+	14	14	13	14	1+	14	13	14
	P.	0 011	-0 4 64	-0.27"	0 '12	-0.336	0.048	1	-0.218	0.132	-0-297	0143	0112	-0 000	-0.090	-0.14°
17γ	C.	0.970	0.0.91	0 042	0.041	0.240	0 31 7	0	0+11	0.607	0.321	0.62.6	0 700	0.911	0.762	0 170
	14	1+	1+	1+	14	14	1+	14	14	1+	13	14	14	14	13	1+
	E.	-0 12 1	-0112	0 172	-0.1%	0.242	0.064	-0.218	1	-0.633	-0.016	-0 090	-0.275	-0 4 ***	0.227	9,000
Р	С	0.014	0.40*	0 40"	0 '94	0.366	0829	0 + 11	0	0 007	0.917	0144	0.342	0102	0.419	0 1 49
	μ.	1+	1+	14	14	14	1+	1+	14	14	13	1+	14	14	13	14
-	R.	0 702	-0.007	0 191	-0.024	-0 481	-0.374	0138	-0 633	1	-0.100	0 763	-0149	0 714	-0 738	-0 613
Bh	C.	0 00 3	0.000	0 13	0.951	0.051	0.21 *	0 637	0 0 0 7	0	0.03*	0 00 2	016	0 0 04	0.012	0 020
	1	1+	1+	14	14	14	1+	1+	14	1+ -0 'SS	13	1+	1+	14	13	14
<i>a</i> .	P.	-041	04%	-0 110	0.244	0 421	0434	-0.2.97	-0 014		1	-0 777	0.713	-0 423	0.447	0 '9)
Co	C.	0122	0117	0 721	430.0	0.024	0138	0.325	0.917	0.03"	0	9 (0 0	0 0 0 0	0170	0 108	0 033
	ц В	1) 0827	1) -0 + ""	13 0-275	1) -0 374	1) -0 648	1) -0:04	1)	1) -0 090	10 0 740	10 -0 177	1)	1)	1) 0 8 44	1) -0 736	1) -0 311
т.		0.000	-0+	0 22 0 342	-05+	-0 640	-0 60+	0143 0626	-0.595	0.002	0.039	1	-0.248 0.392	0.000	-0 .5% 0 004	-0 311 0 000
Ъı	с h	1+	1+	14	14	14	1+	1+	14	14	13	14	14	14	1)	14
	Ē	-0 191	0 2 0 0	-0 323	0 100	0 424	0.279	0112	-0.271	-0169	0 773	-0.248	1	-0 213	0.475	0 323
й г		0 13	0490	0 240	0.047	0131	0.334	0 703	0.342	0.16	0 000	0 392	0	0 4 64	0 103	0 260
н F	С h	1+	0 + 20	0 260	14	14	1+	0 /05	14	14	13	0.5%2	1+	14	13	14
	Ē	0.040	-0381	0.050	-0 341	-0.763	-0.741	-0.033	-0 + 17	0.714	-0 +23	0.064	-0.213	1	-0 604	-0 710
Τı	С.	0 000	0171	0.719	0 200	0 002	0.002	0.911	0102	0 004	010	0 000	0 + 6+	0	0.029	0 004
- 1	11	1+	1+	14	14	1+	14	14	14	14	Î)	1+	1+	1¥	13	14
	E	-0.70.9	0.00	-0 209	0 749	71 394 0	0	-0.093	0.227	-11 -0 "38	0.447	-0 73 6	0 4 70	-0 i0i	10	0.749
2.0	L. C.	-0.7057	0.550	0 194	0.012	0.000	0.010	0.742	0110	-0 JC 0 0'S	0 102	0.004	0103	-0 104	1	0.002
611	с 1	1)	13	13	13	13	13	10	13	13	13	1)	13	13	Ď	13
	Ē	-0.750	0+11	-0.329	0 429	0.736	0.741	-016	0.20	-0 (1)	0 10	-0 311	0 3 2 3	-0 710	0.769	15
сa	- C	0.001	0140	0169	0 126	0.003	0 00 2	0170	0149	0 020	0.000	0 000	0240	0 0 0 4	0.002	0
C a		1+	14	14	1+	14	1+	14	14	1+	13	1+	1+	14	1)	1)
	ц	11	1+	1†	11	14	1†	1†	11	14	10	1+	1†	11	15	15

Table 2: Correlation matrix of the relative abundances of elements in spruce throughfal	1.
(R- correlation coefficient, α- significance level, n- number of correlated pairs	0

Table 3: Correlation matrix of the relative abundances of elements in beech throughfall.

elein		ăl –	Ch	Fe	Ľ.	gnifica 119	1-fn	I^{1}	Р	Bh	Cō	Lı	й г	Τı	20	Cd
	R.	1	-0.749	0.200	-0.019	-0.270	-0 191	-0 341	-0.44.2	0.77%	-0.270	0401	-0.749	0.370	-0 410	-0.17.
āl –	C	0	0.002	0 0 0 0	0 0 0 0	0.370	0.026	0 200	0114	0.001	0.091	0.1.74	0 002	0 000	0.019	0.003
	14	10	1+	1+	1+	1+	1+	1+	1+	1+	12	10	1+	10	1+	1.
	E .	-0.74.9	1	-0.410	0486	0.701	0.798	0.007	0.244	-0481	0.636	-0/200	0 720	-0.742	0 771	0.62
Ch	C	0.002	0	0011	0.070	0.00'	0 001	0.322	0401	0 0 0 1	0.024	0.01	0 000	0 004	0 001	0.01
	ъ	1+	10	1+	1+	1+	1+	1+	1+	1+	12	13	1+	10	1+	1.
	R.	0.908	-0.610	1	-0.921	-0.147	-0 °C+	-0-297	-0481	0.448	-0.201	0 4 42	-0 666	0.32°	-0.417	-0.12
Fe 👘	C	0 00 0	0011	0	0 0 0 0	0 170	0.049	0 000	0.021	0.012	$0 \neq 71$	0112	0.009	0 000	0 011	0.04
	ъ	1+	1+	10	1+	1+	1+	1+	1+	1+	12	13	1+	13	1+	1
	R	-0.519	0486	-0.921	1	-0.029	0.374	0.374	0 + 9 -	-0.734	0139	-0 ++*	0 772	-0 754	0.730	0.31
Ľ.	C	0 00 0	0.078	0 0 0 0	0	0.920	0 217	0 217	0.072	0 00 3	0117	0128	0 0+1	0 001	0.01	0.25
	ц	1+	1+	1+	13	1+	1+	1+	1+	1+	12	1)	1+	1)	1+	1
	E	-0.270	0.701	-0.145	-0.029	ī	0 🖾	-0.772	0178	-0.011	0 4 42	-0.044	0.279	-0 ++0	0.442	0.63
Líg	C.	0.310	0.00	0 775	0.925	ō	0.007	0 0+1	0 4 3	0.244	0101	0.501	0.004	0 100	0 11+	0 01
uş.	11	1+	1+	14	14	Ď	1+	14	14	14	12	13	1+	13	1+	1
	Ē	-0 791	0 798	-0 104	034	0 🖾	1	-0 0+6	0 244	-0.213	0 3 2 2	-0 203	0 444	-0 (1)	0 601	0.74
t-fo	ā.	0.026	0 0 0 1	0.049	0.217	0.007	Ô	0.874	0 4 01	0 + 6 +	0.505	0.01	0 013	0.021	0 016	0 00
	ц	1+	14	14	1+	14	Ď	1+	14	14	12	Ď	14	1)	1+	1
	Ē	-0 341	0.007	-0 297	0.014	-0 112	-0 046	1	-0.288	-0 + 7 7	-00Sł	0014	0 4 68	-0 121	-0 102	-017
ITa			0.0007	0.000		0 0+1			0.000	0102	0.795				-0105	-01
τų	C.	0 200			0.21°		0.876	0				0.917	0 091	0 694		
	14	1+	1+	14	14 0495	14	14	13	1+	14	12	13	1+	13 -0 166	14	1
-	E.	-0 44 2	0.244	-0 481 0 0 62		0.178	0 244	-0.283 0.220	1	-0.244	-0.2.19	-0.242	-0.020		0 424	013
Р	C.	0114	0 + 01	0031	0.072	0 743	0 +01	0 318	0	0401	0 + 17	0426	0.946	0 044	0 101	0.66
	ъ	1+	1+	1+	14	1+	1+	1+	10	1+	12	13	1+	13	1+	1
_	E.	0.776	-0 + 31	0.648	-0.734	-0.01	-0.213	-0 411	-0.244	1	-0.196	011	-0.147	0 199	-0.217	-0.25
Bh	С.	0 001	0031	0.012	0 0 0 3	0 864	0 + 6+	0 102	0401	0	0 142	0.1.0	0.040	0 031	0.375	0.07
	ъ	1+	1+	1+	1+	1+	1+	1+	1+	10	12	13	1+	13	1+	1
	P .	-0.270	0.636	-0/201	0.139	0.442	0 322	430 OF	-0.219	-0.10	1	0.208	0 772	-0.022	0 '00	042
Co	C	0 091	0.026	0 + 71	0117	0 101	300 0	0.791	0417	0.742	0	0 # 17	0.040	0.311	0.097	017
	ш	12	12	12	12	12	12	12	12	12	12	12	12	11	12	1
	R.	0401	-0.200	0 4 62	-0 447	-0.066	-0 203	0 014	-0.24.2	0181	0.208	1	0.049	0 741	-0 011	-0.20
Lт	C	0.174	0 0 0 0 0	0112	0128	$0 \ \odot 1$	0 00	0.917	0.42.6	0 ** 3	0417	0	0 870	0.00%	0.972	0.47
	ъ	10	10	10	13	13	13	13	10	10	12	12	13	12	13	1
	R.	-0.74.9	0 720	-0 ééé	0 1 12	0.279	0 644	344 O	-0.020	-0.147	0 1 12	0.049	1	-0 127	0.409	0.64
Сr	C	0.002	0.000	0.009	00+1	0 33 1	0 013	0.091	0.94.6	0.040	0.040	0.873	0	0.044	0.021	0 01
	ъ	1+	1+	1+	1+	1+	1+	1+	1+	1+	12	13	13	13	1+	1
	Ē.	0.000	-0.742	0.85	-0.784	-0 ++0	-0 41	-0 121	-0 166	0 599	-0.032	0741	-0 127	1	-0 421	-0.5
Τı	C	0 00 0	0 0 0 4	0 0 0 0	0 0 0 1	0 100	0.027	0.694	0.044	0 0001	0 811	0.00%	0.044	0	0.024	0.01
	ц	10	10	10	13	13	13	13	10	10	11	12	10	12	13]
	Ē	-0 418	0771	-0 677	0,50	0 442	0 601	-0 10E	0 +2 +	-0.217	0'03	-0 011	0 609	-0 421	1	0.6
2.0	- C	0.019	0 0 0 1	0011	001	0 114	0 014	0 714	0 13 1	0.375	0.095	0.972	0 021	0 024	0	0.02
	L L	1+	1+	14	14	14	14	14	1+	1+	12	13	14	13	13	1
	Ē	-0 177	0631	-0 127	0 3 1 3	0.487	0.747	-01'4	0 13 2	-0.280	0 4 20	-0 201	0 440	-0 166	0.41	
CJ .		-0 //		-0 22	0.297	0 010	0.003	-01+ 0416	0155	-01200 -01210	017	-0 251 0 4 71	0 018	0.011	0.027	
C d	C.															
	1L	10	10	13	13	13	10	10	10	10	12	12	13	12	13	1

• The predominantly organogenic elements, commonly present in the vegetation tissues: Ca, K, Mg, Mn, P, (Sr).

• The predominantly technogenous elements originating in emissions from the electricity supply- and other kinds of industry: Ca, Cd, Sr, Zn (Co, Fe, Mg) and probably others.

The evaluation of strong and fair correlations between the elements found in Tables 1, 2 and 3, focused on the estimate of their primary sources, is complicated by the fact that several elements are common to more than a single above mentioned group. Nevertheless, repeating strong or fair correlation between several distinct pairs of elements in the solid portion of bulk precipitation and both kinds of throughfall indicates their predominant source.

Correlations between Al-Ba, Al-Ti, Ba-Fe, Fe-Ti, and Li-Ti indicate that the elements Al, Ba, Fe, Li and Ti really originate mainly in the terrigenous dust. On the other hand, strong or fair correlations between Ca-K, Ca-Mg, Ca-Mn, K-P, Mg-Mn (and Sr-K) certify the predominantly organogenic origin of these elements in the solid portion of the deposition.

Repeating fair correlations of Cd-Mg, Cd-Sr, Cd-Zn, Co-Mg, Co-Sr, Co-Zn, Mg-Zn, and Sr-Zn indicate that at least the elements Cd, Co, Mg, Sr and Zn have common, and probably anthropogenic sources.

The comparison of the number of valid correlations in bulk precipitation and both types of throughfall indicates the somewhat diverse composition of solids present in these deposition fluxes. The number of valid correlations is the highest in beech throughfall, which is, according to expectations, especially obvious in the correlations of organogenic elements.

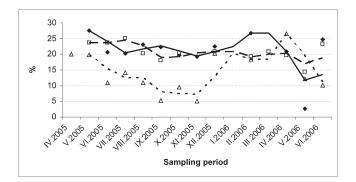


Fig. 1 Temporal course of Fe in bulk and both types of throughfall. (Legend is in Fig. 4.)

The common origin of selected elements is also documented by the similarities of the temporal patterns of their normalized concentrations, especially in beech throughfall. The similarity of the courses of terrigenous elements is evident in the diagrams depicting Al, Fe, Ba and Ti. The typical pattern of this group of elements is shown in Fig. 1 displaying Fe The common peaks of Ca, Mg, Sr, Zn, Cd (and K?) throughout the cold months of the year indicate their origin in the combustion processes (see Fig. 2 depicting the patterns of Zn), while the peaks of Ca, Mg, and Mn in spring months should suggest their common organogenic origin. Typical pattern exhibits the temporal course of Ca (Fig. 3), especially for the beech throughfall. The temporal course of other elements (Na, Co, P) is ambiguous either due to their diverse emission sources, or to the insufficient accuracy of applied analytical methods. The moving average of each two successive sampling periods was employed for the expression of temporal pattern of the normalized concentrations.

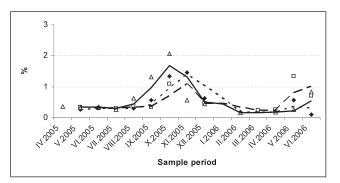


Fig. 2 Temporal course of Zn in bulk and both types of throughfall. (Legend is in Fig. 4.)

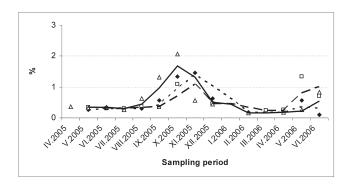


Fig. 3 Temporal course of Ca in bulk and both types of throughfall. (Legend is in Fig. 4.)

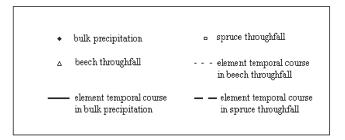


Fig. 4 Legend to Figures 1 -3.

Concentrations of pollutants bound to solid atmospheric aerosol and directions of its transport

Our further interest was oriented on the question whether there exists any dependence between the concentration of insoluble components and the direction of their transport. The backward trajectories were employed for this purpose. The trajectories were computed for the time span of 24 hours. Time 06 UTC was selected as a ending time. To this ending time is, according to the climatologic rules, (Fisak, 1994) assigned the daily precipitation amount (from 06 hrs. yesterday to today's 06 hrs.). We shall presume that the atmospheric particles will move along the same trajectory. The trajectory then describes through what way flow the atmospheric particles that form the daily precipitation amount.

As the time span of the sample collecting varies, the individual samples are assigned to that month, in which their maximum sampling time occurred. The individual pictures displaying the 24 hr. backward trajectories then contain various numbers of trajectories in dependence on the time span of sample collection.

The whole concentration of pollutants, calculated for each type of precipitation samples (bulk, beech- and spruce throughfall) as a sum of concentrations of individual components, was then employed for the evaluation of the effect of pollutant transport.

It was evaluated 12 sampling periods between May 2005 and June 2006. Each of the periods lasted approx. 1 calendar month. Two periods were removed from the elaboration – 1.2006, when we were unable to collect analyzable precipitation sample, and 3.2006, when the collectors were destroyed by gale. The review of elaborated sampling periods, together with whole concentrations of pollutants in samples of individual kinds of precipitation, is presented in the Table 4.

Table 4 Whole pollutant concentration in precipitation samples $[mg.L^{-1}]$.

Sample	Bulk	Throughfall						
period	precipitation	spruce	beech					
V.2005	0.239	0.354	0.165					
VI.2005	0.296	0.344	0.098					
VII.2005	0.253	1.860	0.295					
VIII.2005	0.083	0.210	0.043					
IX.2005	0.358	0.546	0.111					
X.2005	0.128	0.549	0.062					
XI.2005	0.182	1.658	0.094					
XII.2005	2.903	0.172	1.499					
II.2006	0.381	3.614	1.529					
IV.2006	0.323	3.522	0.968					
V.2006	0.066	0.181	2.934					
VI.2006	1.162	0.288	0.255					

The Table evidently reveals that the maximum whole concentrations did not occur in the individual kinds of precipitation simultaneously (bulk – XII.2005, Fig. 5; spruce throughfall – II.2006, Fig. 6; beech throughfall – V.2006, Fig. 7). The same holds for the minimum concentrations (bulk – V.2005, Fig. 8; spruce throughfall – XII.2005, Fig. 5; beech throughfall – VIII.2005, Fig. 9).

The view of trajectories of atmospheric particles throughout periods with maximum concentrations of "insoluble" pollutants in the collected samples evidently shows that the western and northwestern transport with not too high precipitation amounts prevails for bulk precipitation and spruce throughfall (Figs. 5 and 6). Typically for the bulk precipitation, number of days without any precipitation (or with non-measurable precipitation) prevails over the number of days with precipitation events.

Maximal concentrations of "insoluble" pollutants in beech throughfall were indicated in the sampling period 5/2006, when precipitation events, including those with considerable daily amounts, came from the west and simultaneously there existed sufficiently long period with eastern transport, prevailingly without any precipitation (Fig. 7.). It can be concluded that low concentrations of "insoluble" pollutants are indicated during the western or northwestern flow with pronounced daily precipitation amounts. It is possible to expect lower occurrence of trace elements of terrestrial origin that – owing to wet earth surface – less easily enter the atmosphere.

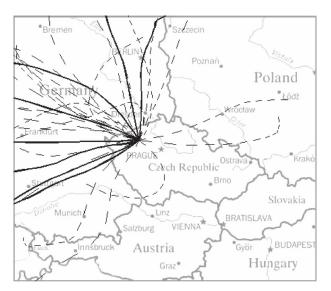


Fig. 5 Backward trajectories in sampling period XII.2005 (legend is in Fig. 10)

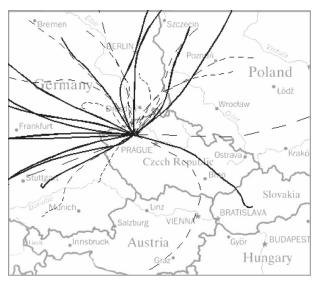


Fig. 6 Backward trajectories in sampleing period II.2006 (legend is in Fig. 10)

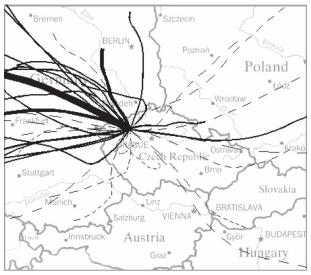


Fig. 7 Backward trajectories in sampling period V.2006 (legend is in Fig. 10)

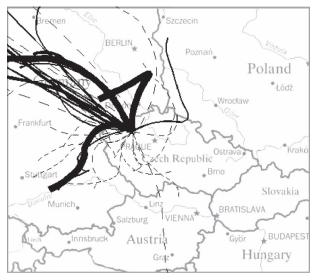


Fig. 8 Backward trajectories in sampling period V.2005 (legend is in Fig. 10)



Fig. 9 Backward trajectories in sampling period VIII.2005 (legend is in Fig. 10)

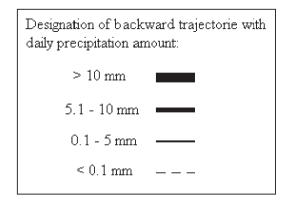


Fig. 10 Legend to Figures 5 - 9

Conclusions

The correlation analysis allowed us to divide the studied elements into three main groups according to their origin in insoluble part of precipitation. Elements Al, Ba, Fe, Ti (Li) come mainly from the terrigenous dust; Ca, K, Mg, Mn and P certify their predominantly organogenic origin, and at least Cd, Co, Mg, Sr and Zn probably come from the anthropogenic sources. The throughfall samples generally contain higher amount of organogenic elements than the bulk precipitation. The seasonal distribution of concentrations of the elements in studied deposition fluxes confirms their distribution into the three main groups mentioned above.

The presented results of study of the backward trajectories are affected through seasonal character of occurrence of some of the discussed pollutants. A distinct effect has also the relatively short evaluated time period, and in beech throughfall it also affects the changing level of foliage. Nevertheless, it can be generally concluded the decrease of the amount of "insoluble" pollutants during the prevailing western and northwestern flow with more pronounced daily precipitation amounts. Low total concentrations are also recorded in case of the occurrence of eastern or southeastern transport without precipitation or with not measurable precipitation amount. In this case it is possible, especially in throughfall precipitation, to consider low amount of pollutants washed off from the above – ground surface of the growth.

Acknowledgment

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References

[1] Buchtele, J., Buchtelová, M. & Tesař, M., 2006: Role of vegetation in variability of water regimes in Sumava Mts. Forests. Biologia, 61, Suppl. 19, S246-S250.

[2] Draxler, R.R. & Rolph, G.D., 2003. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website http://www.arl. noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD.

[3] Fišák, J., 1994: Manual for observers at the meteorological stations. Metodological guide of CHMI No. 11. CHMI, Prague. ISBN 80-85813-12-2

[4] Fišák J., Skřivan P., Tesař M., Fottová D., Dobešová I. & Navrátil T., 2006: Forest vegetation affecting the deposition of atmospheric elements to soil. Biologia, 61, Suppl. 19, S255-S260.

[5] Navrátil, T., Skřivan, P., Minařík, L. & Žigová, A., 2002: Beryllium geochemistry in the Lesni Potok Catchment (Czech Republic), 7 years of systematic study. Aquatic Geochemistry, 8 (2), 121-134.

[6] Rolph, G.D., 2003. Real-time Environmental Applications and Display System (READY) NOAA Air Resources Laboratory, Silver Spring, MD. Website (http://www.arl.noaa.gov/ready/hysplit4.html).

[7] Skřivan, P., Navrátil, T., & Burian, M., 2000: Ten years of monitoring the atmospheric inputs at the Černokostelecko region, Central Bohemia. Scientia Agriculturae Bohemica 31, (2) : 139-154.

[8] Tesař, M., Sír, M., Lichner, L. & Zelenková, E., 2006: Influence of vegetation cover on thermal regime of mountainous catchments. Biologia, 61, Suppl. 19, S311-S314.