

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

J. FIŠÁK ⁽¹⁾, J. ŠPIČKOVÁ ⁽²⁾, J. ROHOVEC ⁽²⁾, P. SKŘIVAN ⁽²⁾ and M. VACH ⁽²⁾

⁽¹⁾ Institute of Atmospheric Physics ASCR, v.v.i., Prague 4, Czech Republic (e-mail: fisak@ufa.cas.cz)

⁽²⁾ Institute of Geology ASCR, v.v.i., Prague 6, Czech Republic (e-mail: skrivan@gli.cas.cz)

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 µm 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/ $\mu\text{g.L}^{-1}$): 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.)

element	Al	Ca	Fe	K	Mg	Mn	Na	P	Ba	Co	Li	Sr	Ti	Zn	Cd
Al	R: 1 n: 12	R: -0.477 n: 12	R: 0.210 n: 12	R: -0.338 n: 12	R: -0.174 n: 12	R: -0.490 n: 12	R: 0.247 n: 12	R: -0.138 n: 12	R: 0.194 n: 12	R: -0.107 n: 12	R: -0.309 n: 10	R: 0.133 n: 12	R: 0.308 n: 12	R: 0.014 n: 12	R: -0.308 n: 12
Ca	R: 0.138 n: 12	R: 1 n: 12	R: 0.070 n: 12	R: 0.140 n: 12	R: 0.377 n: 12	R: 0.042 n: 12	R: -0.049 n: 12	R: -0.107 n: 12	R: 0.133 n: 12	R: 0.091 n: 12	R: 0.047 n: 10	R: 0.182 n: 12	R: 0.077 n: 12	R: 0.028 n: 12	R: 0.028 n: 12
Fe	R: 0.210 n: 12	R: 0.070 n: 12	R: 1 n: 12	R: -0.301 n: 12	R: -0.344 n: 12	R: -0.182 n: 12	R: 0.042 n: 12	R: -0.417 n: 12	R: 0.441 n: 12	R: -0.203 n: 12	R: 0.172 n: 10	R: -0.119 n: 12	R: 0.429 n: 12	R: -0.443 n: 12	R: -0.487 n: 12
K	R: 0.138 n: 12	R: 0.070 n: 12	R: -0.301 n: 12	R: 1 n: 12	R: 0.203 n: 12	R: 0.427 n: 12	R: -0.434 n: 12	R: 0.442 n: 12	R: -0.387 n: 12	R: 0.322 n: 10	R: 0.018 n: 12	R: 0.182 n: 12	R: -0.420 n: 12	R: 0.007 n: 12	R: 0.731 n: 12
Mg	R: 0.377 n: 12	R: 0.377 n: 12	R: 0.344 n: 12	R: 0.203 n: 12	R: 1 n: 12	R: -0.247 n: 12	R: -0.408 n: 12	R: 0.098 n: 12	R: -0.244 n: 12	R: 0.392 n: 10	R: -0.479 n: 12	R: 0.273 n: 12	R: -0.492 n: 12	R: 0.107 n: 12	R: 0.483 n: 12
Mn	R: 0.042 n: 12	R: 0.042 n: 12	R: -0.182 n: 12	R: 0.427 n: 12	R: -0.247 n: 12	R: 1 n: 12	R: 0.074 n: 12	R: 0.329 n: 12	R: -0.028 n: 12	R: 0.028 n: 10	R: 0.234 n: 12	R: -0.272 n: 12	R: -0.074 n: 12	R: -0.112 n: 12	R: 0.301 n: 12
Na	R: -0.107 n: 12	R: -0.107 n: 12	R: -0.417 n: 12	R: -0.434 n: 12	R: -0.408 n: 12	R: 0.074 n: 12	R: 1 n: 12	R: 0.484 n: 12	R: 0.477 n: 12	R: -0.490 n: 12	R: 0.117 n: 10	R: -0.119 n: 12	R: 0.434 n: 12	R: 0.091 n: 12	R: -0.379 n: 12
P	R: 0.133 n: 12	R: 0.091 n: 12	R: 0.047 n: 12	R: 0.322 n: 12	R: 0.442 n: 12	R: -0.387 n: 12	R: 0.442 n: 12	R: 1 n: 12	R: 0.138 n: 12	R: 0.404 n: 10	R: -0.308 n: 12	R: 0.049 n: 12	R: 0.742 n: 12	R: -0.210 n: 12	R: -0.388 n: 12
Ba	R: -0.107 n: 12	R: -0.107 n: 12	R: -0.417 n: 12	R: -0.434 n: 12	R: -0.408 n: 12	R: 0.074 n: 12	R: 0.329 n: 12	R: -0.028 n: 12	R: 0.477 n: 12	R: -0.490 n: 12	R: 0.117 n: 10	R: -0.119 n: 12	R: 0.434 n: 12	R: 0.091 n: 12	R: -0.379 n: 12
Co	R: 0.047 n: 12	R: 0.047 n: 12	R: 0.028 n: 12	R: 0.018 n: 12	R: 0.392 n: 12	R: 0.234 n: 12	R: -0.272 n: 12	R: 0.028 n: 12	R: -0.244 n: 12	R: 0.392 n: 10	R: -0.479 n: 12	R: 0.273 n: 12	R: -0.492 n: 12	R: 0.107 n: 12	R: 0.483 n: 12
Li	R: -0.309 n: 10	R: 0.387 n: 10	R: 0.474 n: 10	R: 0.940 n: 10	R: 0.142 n: 10	R: 0.711 n: 10	R: 0.771 n: 10	R: 0.240 n: 10	R: 0.403 n: 10	R: 0.403 n: 10	R: 0.043 n: 10	R: 0.142 n: 10	R: 0.347 n: 10	R: 0.310 n: 10	R: 0.187 n: 10
Sr	R: 0.133 n: 12	R: 0.182 n: 12	R: -0.119 n: 12	R: 0.182 n: 12	R: 0.273 n: 12	R: -0.272 n: 12	R: -0.119 n: 12	R: -0.388 n: 12	R: 0.049 n: 12	R: 0.779 n: 10	R: -0.479 n: 12	R: 1 n: 12	R: 0.098 n: 12	R: 0.112 n: 12	R: 0.474 n: 12
Ti	R: 0.308 n: 12	R: 0.077 n: 12	R: 0.429 n: 12	R: -0.420 n: 12	R: -0.492 n: 12	R: -0.074 n: 12	R: 0.434 n: 12	R: -0.710 n: 12	R: 0.742 n: 12	R: -0.379 n: 10	R: 0.333 n: 12	R: 0.098 n: 12	R: 1 n: 12	R: -0.279 n: 12	R: -0.417 n: 12
Zn	R: 0.014 n: 12	R: 0.028 n: 12	R: -0.443 n: 12	R: 0.007 n: 12	R: 0.107 n: 12	R: -0.112 n: 12	R: 0.091 n: 12	R: 0.280 n: 12	R: -0.210 n: 12	R: 0.399 n: 10	R: -0.378 n: 12	R: 0.112 n: 12	R: -0.279 n: 12	R: 1 n: 12	R: 0.210 n: 12
Cd	R: -0.308 n: 12	R: 0.028 n: 12	R: -0.487 n: 12	R: 0.731 n: 12	R: 0.483 n: 12	R: 0.301 n: 12	R: -0.379 n: 12	R: 0.174 n: 12	R: -0.388 n: 12	R: 0.787 n: 10	R: -0.477 n: 12	R: 0.474 n: 12	R: -0.417 n: 12	R: 0.210 n: 12	R: 1 n: 12

- 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.

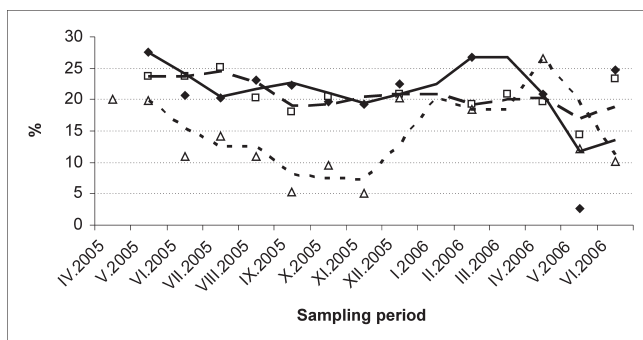


Fig. 1 Temporal course of Fe in bulk and both types of throughfall. (Legend is in Fig. 4.)

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.

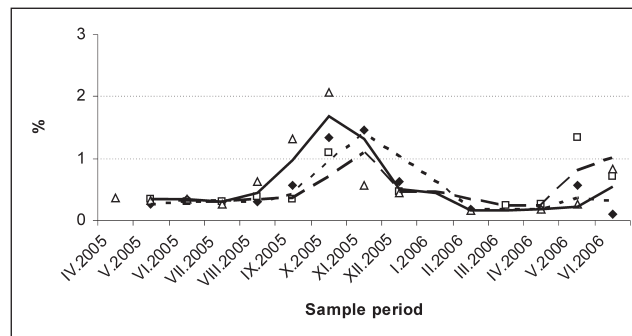


Fig. 2 Temporal course of Zn in bulk and both types of throughfall. (Legend is in Fig. 4.)

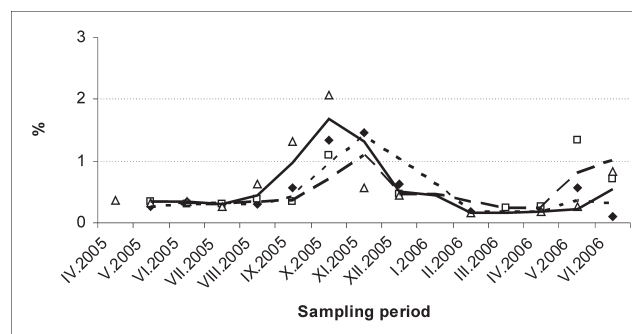


Fig. 3 Temporal course of Ca in bulk and both types of throughfall. (Legend is in Fig. 4.)

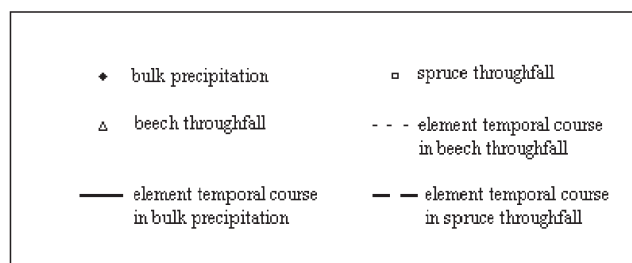


Fig. 4 Legend to Figures 1 -3.

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 period	Bulk precipitation	Throughfall	
		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, prevailing 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 sampling period II.2006 (legend is in Fig. 10)



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



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

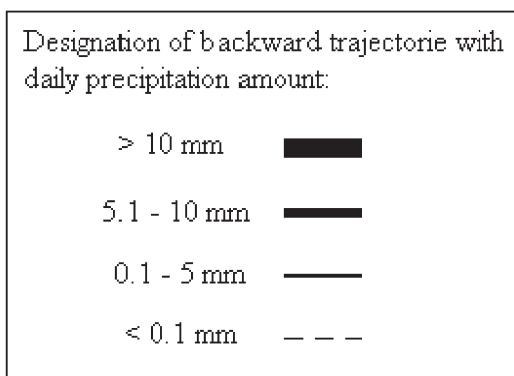


Fig. 10 Legend to Figures 5 - 9



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

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.

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