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The typical insoluble particles in fog water at Milešovka Observatory (Czech Republic)

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Abstract:

The vicinity of Milesovka Mountain is one of the most polluted areas in the Czech Republic. In this study the input and possible sources of solid pollutants into the fog are studied. 25 sets of samples were collected in the period between August 2006 and July 2007 by different wind direction situations. Samples of fog water were filtered. Dried filters were examined by Scanning Electron Microscope. Number of particles is in the interval from 53 to 116 in every filter. Content of solid pollutants, especially elements like Al, Si, K, Fe or Ca, sizes and shapes of the particles were detected. In accordance to the content of observed elements these particles were divided into categories. After that particles in these groups were collated according to the meteorological conditions.

1. INTRODUCTION

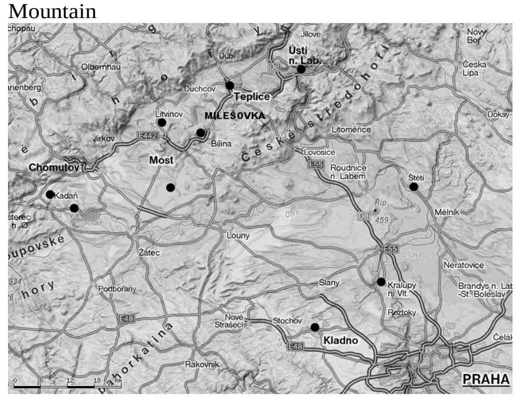
The pollution in the atmosphere markedly influences human health and ecosystems. Formation of fog and low clouds plays a significant role in washout processes in the atmosphere. Therefore fog chemistry investigations are very important. It must be noted that some pollution in fog and low clouds is natural and the presence of condensation nuclei projects the requirement for fog and cloud genesis. It is quite necessary to examine character of the material which occurs in fog water and after that to try to determine possible sources of this pollution. It is advisable to learn how to distinguish natural and anthropogenic sources discovered in the fog samples. Identification of such sources is very complicated task.

This study is considering with the analysis of 25 samples of fog water collected at the Milešovka Mountain (837 m a.s.l.), Czech Republic. The sampling proceeded in the years 2006 and 2007 by chosen fog episodes. After that, the samples were filtered and dried filters were analyzed in the laboratory of the IPC BAS (Institute of Physical Chemistry, Bulgaria). The aim of this analysis has been to determine the typical insoluble particles in collected samples. Consequently the samples were assigned to the wind directions noticed in the day of sampling to find possible sources of detected particles. Precipitation amounts measured 24 hours before every foggy period were compared for content of particles rich in particulate element.

2. SITE OF MESUREMENT AND METHODS

The observatory Milešovka of the IAP ASCR is located on the highest mountain of České středohoří Mountains in the Czech Republic. The vicinity of this area belongs to the most polluted areas in the Republic [1] (Picture 1).

Picture 1 – Map of the biggest pollution sources (black spots) in the surroundings of Milešovka Mountain



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25 fog samples were collected by the active fog water collector in the episode from August 2006 till July 2007. Nitrocellulose filters with pore sizes 0,45 μm were used to filter insoluble particles from water.

From each sample were recognized from 53 to 116 particles. Altogether that was more than 2000 particles. These filters were dried up and covered with very thin carbon coating. Each individual particle on filters was analyzed by mean of JEOL JSM 6390 scanning electron microscope. Scanning electron microscopy (SEM), coupled with Energy Dispersive X-ray Spectrometer (EDX) was used to detect parameters of the particles. In SEI mode particle's size and morphology were ascertained. BEI (backscattering) mode helped to recognize heavy metals-rich particles. EDX analysis was used to detect elemental composition of the particles [2]. Because of the necessity of covering the particles in filters by carbon layer carbon was excluded from the dataset as well as oxygen.

After getting data from analysis the statistics was made. Particles were divided into groups according to the most represented elements.

3. THE RESULTS AND DISCUSSION

3.1 Typical insoluble particles

Almost 100% of all particles in our dataset belong to PM10 (particles with size smaller than 10 μm). 62% belong to very small particles of category PM2,5 (2,5 μm diameter) (see Table 1). Approximately 23% of all particles have spherical shape. From among the spherical particles predominate those with size under 2,5 μm. Greatest shares of spherical-shaped particles have those rich in Zn (53%) and Mn (44%).
Most typical elements (Si, Al, Fe, K, Mg, Ca, P, S, Na, Ti, Mn, Zn and Cr) in fog particles were found. Representation of these elements in every fog episode is from 1,65 to 87,06 % of the whole dataset (see Table 2). The absolutely most abundant elements are Si, Al, Fe and K which are in almost 50 to 90 percent of all found particles.
Particles having more then 5% of given element were labeled as element-rich. The highest number (1752 - almost 90%) of particles includes more then 5 % of Silicium with 25% substitution of spherical particles. In between Al-rich particles there were found 26% of spherical shaped particles, in Fe-rich particles it was almost 30% and in K-rich particles it was almost 20% of particles.

There are also lots of Al-Si-rich particles, which mean particles containing 5 % and more of Al as well as Si. There are 65,47% of these particles in the dataset. In these particles quite a lot of Fe (up to 25%) and K (20%) was found. 42% of Al-Si rich particles have spherical shape.

Much less but still significantly represented are elements Ca, P, Mg, S, Na, and Ti. Each of them is represented by more then 10% in the data set.
Cl, Mn, Zn and Cr were found in more then 1% but less then 10% of all particles and were also denoted as considerable elements.

Table 1 – Sizes of particles in samples divided to 3 categories (PM2,5, PM10 and particles sizes bigger then 10 μm)

Filter	**PM 2.5 [%]**	**PM 10 [%]**	**> 10 μm [%]**
1	70.89	93.67	6.33
2	50.65	97.4	2.6
3	77.01	95.4	4.6
4	86.21	100	0
5	75.95	98.73	1.27
6	67.78	95.56	4.44
7	79.78	95.51	4.49
8	85.42	98.96	1.04
9	89.25	96.77	3.23
10	55.67	93.81	6.19
11	6.25	100	0
12	5.61	93.46	6.54
13	68.32	95.05	4.95
14	64.15	96.23	3.77
15	40.28	90.28	9.72
16	63.74	92.31	7.69
17	7.23	100	0
18	80.58	99.03	0.97
19	86.6	98.97	1.03
20	60	92.5	7.5
21	67.86	97.62	2.38
22	47.95	89.04	10.96
23	70.83	94.79	5.21
24	77.05	96.72	3.28
25	72.41	94.83	5.17

Table 2 – Particle quantity (PQ) and share of spherical particles (sph)

ELEMENT	PQ	PQ [%]	sph [%]
Particle total	2187	100	23.00
Si	1904	87.06	25.00
Al	1688	77.18	26.32
Fe	1321	60.4	29.72
K	1091	49.89	19.49
Mg	618	28.26	14.09
Ca	523	23.91	9.35
P	476	21.76	18.60
S	449	20.53	13.56
Na	279	12.76	10.26
Ti	265	12.12	32.77
Cl	127	5.81	7.46
Mn	56	2.56	44.44
Zn	55	2.51	52.83
Cr	36	1.65	27.27

3.2 Possible sources of fog pollution

Solid particles in the atmosphere are produced by both sources – natural and/or anthropogenic. Natural sources of air-borne dust are sea salt, terrestrial dust, volcanoes, forest fires and bioaerosol. These particles have usually size of approximately 10 µm. Anthropogenic sources are primarily combustion processes from vehicle traffic and power plant combustion, cement factories, lime-kilns, quarries and mining or particles from building sites or areas devoid of vegetation. These kinds of aerosol particles have usually smaller sizes. Another anthropogenic source of solid pollutants in atmosphere is agriculture. Solid aerosol can rise also secondarily directly in the atmosphere [3, 4].

To demark natural and anthropogenic sources of pollutants in atmosphere is very difficult. Most of elements found in our dataset are usual components of natural ambience. Also most of them can originate as products of anthropogenic activity.

The most represented elements in the dataset – Si, Al, Fe and K and also other detected particles like Ca, Na, and Mg belong to ones of the most represented elements in the crust of the earth. Silicium was found in about 90% of all particles and it is an element which is found in almost every igneous rock. Also it is second most represented particle in the earth crust. This means that significant content of these elements in fog water is natural and that most of particles with prevailing content of Si, Al, Fe, K, Ca, Na and Mg could originate from the earth. On the other hand these elements could possibly get into the fog water also from anthropogenic sources. Quite a big part of detected particles have a spherical shape. Majority of spherical particles are considered to be produced by burning processes at high temperatures (about 1200°C and more). The fact that there are lots of power plants, incineration plants and other industrial works in the surrounding of Milešovka Mountain turns out the probability of the presence of anthropogenic products in collected fog water.

Particles were divided into 3 sectors according to prevailing wind directions – NNW (north-north-west, 3 samples), WNW (west-north-west, 5 samples) and WSW (west-south-west, 5 samples). Some particles rich in particular element such as Al-rich, Si-rich or P-rich particles don't embody any significant pertinence to any sector. On the other hand certain particles show considerable dependence on wind direction. Among such particles belong primarily Cl (NNW), Cr (NNW) and Zn (WSW).

Precipitation amounts (PA) measured 24 hours before every foggy period were compared for content of particles rich in particulate element. Surprisingly there was not found significant decrease of total amount of particles in fog water. The decrease was found in Zn, Fe, Na, Cl-rich particles occurrence and on the contrary P, Ti, Mg, Si-rich particles occurrence increased by increasing PA. Investigations concerning dependence of insoluble pollutants in fog water on meteorological indicators are at the beginning and the research will continue.

5. ACNOWLAGEMENT

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