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Analysis of Dust Particles in Snow Cover in the Surroundings of the City of Ostrava: Particle Size Distribution, Zeta Potential and Heavy Metal Content

Roman Marsalek

Abstract**—**In this paper, snow samples containing dust particles from several sampling points around the city of Ostrava were analyzed. The pH values of sampled snow were measured and solid particles analyzed. Particle size, zeta potential and content of selected heavy metals were determined in solid particles. The pH values of most samples lay in the slightly acid region. Mean values of particle size ranged from 290.5 to 620.5 nm. Zeta potential values varied between -5 and -26.5 mV. The following heavy metal concentration ranges were found: copper 0.08-0.75 mg/g, lead 0.05-0.9 mg/g, manganese 0.45-5.9 mg/g and iron 25.7-280.46 mg/g. The highest values of copper and lead were found in the vicinity of busy crossroads, and on the contrary, the highest levels of manganese and iron were detected close to a large steelworks. The proportion between pH values, zeta potentials, particle sizes and heavy metal contents was established. Zeta potential decreased with rising pH values and, simultaneously, heavy metal content in solid particles increased. At the same time, higher metal content corresponded to lower particle size.

Keywords**—**Dust, snow, zeta potential, particles size distribution, heavy metals.

I. Introduction

ONE of the most studied topics in industrially developed regions is the issue of solid emissions. Solid particles are released into the air from anthropogenic activities, in particular from burning of fossil fuels, automobile traffic, heavy industry etc. The diversity of sources also leads to very heterogeneous composition of these particles; they have varying sizes, different surface charges or specific surface areas. Ostrava is an industrial centre of Northern Moravia situated in the eastern part of the Czech Republic. In the surroundings of Ostrava, there are black coal mines, several large ironworks and steelworks and numerous other industrial plants. The city is characterized by a dense road network and its inhabitants also burn wood and coal in local furnaces during the winter months. All this, together with current meteorological conditions, contribute to the formation of smog. Smog situations occur especially during the winter months. These adverse conditions are reflected in the health of inhabitants, with increased occurrence of respiratory diseases and asthma, particularly in children.

Mobile monitoring devices measuring actual levels of nitrogen oxides, sulphur oxides, air dust concentrations etc. are deployed in the city. Emission particles are sampled and analyzed using defined procedures, i.e. at a certain height above the ground and with approved filters. One of the other ways to sample solid particles is to sample snow cover in the winter months and subsequently analyze solid particles contained in the snow. This procedure is also known from literature; solid particle size and heavy metal contents were analyzed in snow cover in the surroundings of Novi Sad in Serbia, as in [1].

Negative effects of solid emissions are often connected with the particle size itself. Very small particles penetrate through the respiratory tract down to the lungs and can cause many serious disorders. The surface charge of these particles, or their zeta potential, plays a very important part. The sign and level of zeta potential jointly decide about a range of physical and chemical processes on the particle surface, such as adsorption. Cations of heavy metals are quite easily adsorbed on negatively charged particles. Heavy metals are released into the environment primarily from anthropogenic activities. Here are at least some examples: major constituents of coal combustion processes are Al, Fe and Ca, as in [1]; products of oil combustion include Mn, Fe and Pb, as in [2]; Pb, Fe and Zn are products of vehicle exhausts, as in [3], [4]; Ca and Zn are often added to motor oil, as in [5]; wood burning processes result in generation of K, as in [6]; car brakes are one of the major sources of Cu release, as in [7].

Practically all the above processes also take place directly in the city of Ostrava or in its close vicinity. This paper was aimed at collecting upper layers of snow cover in various places in Ostrava. Collection points were located near busy crossroads, close to large industrial plants and one locality with relatively low air pollution was chosen as a reference point. Specifically, pH of melted snow, solid particle size distribution and their zeta potential were measured. Moreover, concentrations of selected heavy metals in these particles were determined.

II. Experimental

A. Sampling

In February 2013 snow layers from ten sampling points all over the city of Ostrava were collected. Ostrava is the third largest city in the Czech Republic with developed industry and

R. Marsalek is with the Faculty of Science, University of Ostrava, 30. Dubna 22, Ostrava, 701 03, Czech Republic (phone: 402-737-443663; e-mail: roman.marsalek@osu.cz).

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heavy automobile traffic. Ostrava covers an area of 214 km^2, and its population is approximately 320,000. Average annual temperature is 8.6°C. Samples were collected in February 2013; February is the second coldest month of the year with an average temperature of approximately 0°C. After three days of snowing, all snow samples were collected on 11th February in the afternoon hours. Air temperature was -2°C. Snow cover was around 15 cm thick. Collection points are shown on the map of Ostrava, Fig. 1. Places near large crossroads (1-4), places close to large industrial plants (5-9) and a reference point (10) were chosen.

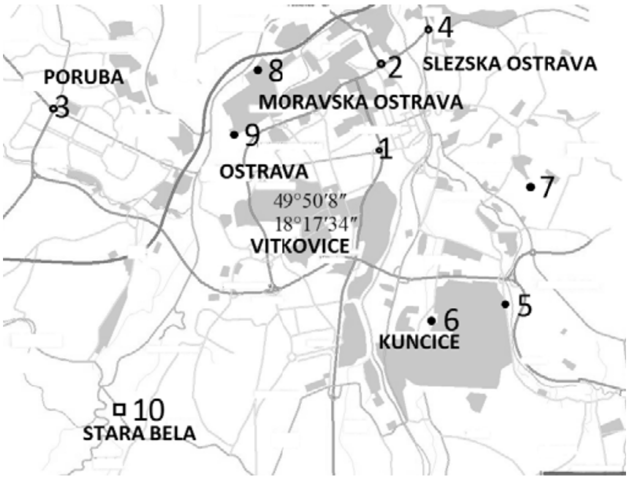

Fig. 1 Collection points: 1-4 heavy traffic crossroads, 5-9 large industrial plant premises (ArcelorMittal, BorsodChem), 10 reference point situated outside Ostrava

B. Instrumentation

Prior to decantation, pH of melted snow was measured. Measurement was performed using the inoLab pH meter 730 (Czech Republic). The pH value indicates acidity or alkalinity of the melted snow suspension with dust particles but it is also important information related to zeta potential.

1. Zeta Potential Measurements

The zeta potential was measured by analyzing suspensions of PM in melting snow using the Zetasizer Nano ZS (Malvern Instruments Ltd., GB). Before zeta potential measurements all samples were sonicated for 5 minutes. Zetasizer Nano ZS uses Laser Doppler Velocimetry to determine electrophoretic mobility. The zeta potential was obtained from the electrophoretic mobility by the Smoluchowski equation. Each sample was analyzed in three replicates.

2. Particle Size Distribution

For dynamic light scattering measurements 12 mm cell (DTS 0012) was used. Samples were sonicated for 5 minutes. Size distributions of the nanoparticles were determined with a Malvern Zetasizer Nano ZS (Malvern Instruments Ltd., GB) by the DLS technique. The suitable parameters (viscosity, absorption and refractive index) were chosen. Each sample was analyzed in twenty replicates.

3. Heavy Metals Determination

When pH, zeta potential and particle size measurements were completed, residual suspensions were filtered and dried out at laboratory temperature. Solid particles were weighed and then heavy metal content was related to 1 g of solid particles. Solid fractions were transferred into beakers and concentrated nitric acid added (2 ml). The mixture was poured into an autoclave and closed. The autoclave was heated in a drier for 4 hours at 130°C. The non-decomposed fraction (mainly silicates and carbon) was removed by filtration. The levels of copper, iron, manganese and lead in the filtrate were determined by atomic absorption spectroscopy using Varian AA 240 FS.

III. Results and Discussion

A. pH, Zeta Potential and Particles Size Distribution

Measured values of pH in suspensions, zeta potential values and particle sizes are summarized in Table I. Zeta potential values and mean particle sizes are reported as an average of all measurements. Zeta potential of each sample was measured in three replicates. Relative error of determination did not exceed 5%. Particle size for each sample was measured in twenty replicates. Samples were highly polydisperse and the average was determined using a statistical method: Horn's procedure. The used parameter is D (0.5), which means that 50% of particles are lower than or equal to the given size value.

TABLE I
THE VALUES OF PH, ZETA POTENTIAL AND PARTICLE SIZE MEAN VALUE

Sample	GPS	pH	Zeta potential (mV)	D (0.5) (nm)
1	49°49'45.131"S, 18°16'54.925"V	6	-9	580
2	49°50'20.822"S, 18°17'45.425"V	5.9	-8	561
3	49°50'5.258"S, 18°9'58.281"V	5.5	-7	620.5
4	49°51'35.842"S, 18°17'38.591"V	6.1	-10	509.5
5	49°47'54.295"S, 18°19'42.054"V	6.9	-15.03	446.5
6	49°47'41.538"S, 18°18'16.284"V	7.5	-21.4	420.5
7	49°49'27.334"S, 18°20'7.868"V	7.72	-25.6	290.5
8	49°50'33.660"S, 18°14'16.934"V	6.7	-14	495.5
9	49°50'2.034"S, 18°13'52.826"V	6.3	-12	517
10	49°46'7.575"S, 18°11'50.953"V	5.32	-5.05	609.5

The pH values of all samples lie in the acid region, except for samples 6 and 7. These two samples were taken near the large ArcelorMittal steelworks. The table also demonstrates a typical relation between pH value and zeta potential. All samples show negative zeta potential, while the lowest values were found in sample 7, namely -25.6 mV. This is the sample with the highest pH value. On the contrary, sample 10 shows zeta potential value of – 5.05 mV and it has the lowest pH value, too. This is the sample from the relatively least polluted area, away from busy crossroads and far from industrial plants. Moreover, it is a known fact that the zeta potential value indicates further possible interactions, such as heavy metal adsorption. In other words, heavy metal cations will more readily adsorb on samples with significantly negative potential. Heavy metal contents are shown in Table II.

B. Content of Heavy Metals

TABLE II
CONTENTS OF COPPER, LEAD, MANGANESE AND IRON AND TOTAL CONTENT OF THESE HEAVY METALS RELATED TO 1 G OF SOLID PARTICLES

Sample	Cu (mg/g)	Pb (mg/g)	Mn (mg/g)	Fe (mg/g)	Total (mg/g)
1	0.28	0.74	0.53	46.52	48.06
2	0.30	0.80	0.53	31.42	33.05
3	0.46	0.88	0.36	30.43	32.12
4	0.67	0.90	0.79	65.43	67.79
5	0.65	0.33	3.45	200.56	205.00
6	0.75	0.34	3.65	205.68	210.42
7	0.24	0.30	5.90	274.03	280.46
8	0.26	0.70	1.27	110.84	113.06
9	0.22	0.26	0.86	88.84	90.18
10	0.08	0.05	0.45	25.12	25.70

Several facts can be observed from the table. The lowest content of heavy metals was found in sample 10; it is the reference sample. On the contrary, definitely the highest concentrations (mainly of iron and manganese) were found in samples 6 and 7; they come from localities in the vicinity of the steelworks. A high content of these metals was also found in sample 5, taken from a locality near the steelworks in the direction of prevailing winds. This locality is considered to be the most affected by ArcelorMittal activities. Samples 1-4, were collected in the vicinity of large crossroads, show mainly high contents of lead and copper, which can be connected with heavy traffic. Particles of similar sizes and composition were also found in the paper by Greek authors, as in [8].

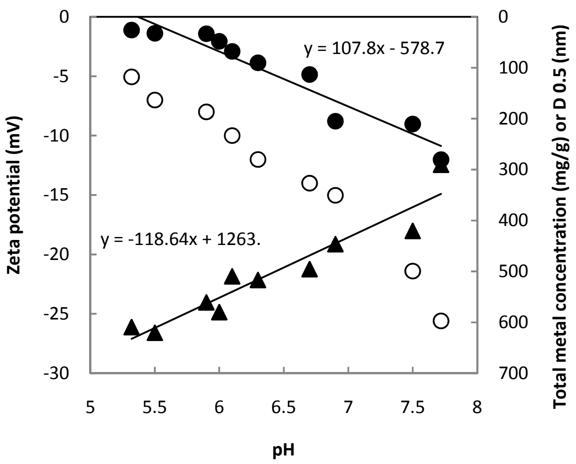

Fig. 2 Relations among pH, zeta potential, particle size and heavy metal concentrations. Empty circles represent zeta potential values, full circles total contents of monitored heavy metals and triangles particle sizes

All monitored quantities are plotted in a single graph. The x-axis shows pH and zeta potential values (empty circles) are plotted on the left (primary y-axis). The values of particle sizes and total heavy metal contents are of the same order of magnitude; they are expressed in hundreds of mg in case of heavy metal levels or hundreds of nanometres in case of particle sizes. Both quantities are plotted simultaneously on the secondary y-axis. Heavy metal contents are represented by full circles, particle sizes by triangles.

As mentioned above, zeta potential values decrease with increasing pH values; zeta potential assumes more negative values. At the same time, it was suggested that negatively charged particles have higher tendency to adsorb heavy metal cations. It has been confirmed in this case, as samples with the highest pH value and thus the lowest negative zeta potential value show the highest content of heavy metals. In other words, the decreasing trend of zeta potential is similar to the increase in heavy metal levels. The connection between zeta potential value and heavy metal adsorption is also known from other systems, such as adsorption on coal or clay minerals, as in [9].

It is also interesting that we can find certain dependence between heavy metal content and the size of particles where heavy metals were analyzed. The slope of heavy metal level increase and the slope of particle size decrease are practically identical. In other words, higher heavy metal concentrations were found in smaller particles. If the charge (weight) is identical, smaller size particles have a higher surface area. Specific surface size plays an important part in heavy metal adsorption. The heavy metal concentrations in analyzed particles may thus be related to the surface charge (zeta potential) of the particles, but also to their size or their specific surface value.

IV. CONCLUSIONS

Air quality in Ostrava is significantly affected by the industrial character of the region and heavy automobile traffic. High dust particle content has negative impacts predominantly in winter months. Snow analysis in selected localities demonstrated a high content of solid particles with wide particle size distribution, from units up to hundreds of nanometres. In addition to ash and carbon, particles contain a considerable proportion of heavy metals. The sources of these heavy metals include first of all metallurgical industry and automobile traffic. The total content of dust particles in the atmosphere decreases with the distance from pollution sources and, along with it, heavy metal content in these particles also decreases. In terms of chemistry, the composition of dust particles is also influenced by pH of the environment and the charge of dust particles, expressed as zeta potential in the liquid environment.

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