HEAVY-METAL MICROPARTICLES AS ATMOSPHERIC POLLUTANTS. ELECTRON-MICROSCOPE DATA ANALYSIS

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Abstract: *This study is focused on metal contamination in atmosphere and presents analysis of results related to elemental composition, size distribution and morphology of fine dust particles with size below 10* μm *(PM10). Samples from Bulgaria and Czech Republic, collected from air, fog and rime, were studied by using of electron microscopy methods (SEM and EDX). A special attention was paid to the identification of micro- and nano-size particles enriched by heavy metals. It was established that some heavy metals are concentrated predominantly in single-particles, often smaller than 0,5-2* μm. *Such enriched of heavy metals PM10 are more dangerous for human health. Besides they could serve also as tracers for specific emission sources.*

СЪДЪРЖАЩИ ТЕЖКИ МЕТАЛИ МИКРОЧАСТИЦИ КАТО АТМОСФЕРНИ ЗАМЪРСИТЕЛИ. АНАЛИЗ НА ЕЛЕКТРОННО-МИКРОСКОПСКИ ДАННИ

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Ключови думи: *Атмосферни замърсители, прахови частици, тежки метали, СЕМ-ЕДХ анализ*

Резюме: *Това изследване е фокусирано върху замърсяването на атмосферата с метални частици и представя анализ на резултати, свързани с елементния състав, разпределението по размери и морфологията на фини прахови частици с размер под 10* μm *(ФПЧ10). Образци от България и Чешката република, събрани от въздух, мъгла и скреж, бяха изследвани с електронно-микроскопски методи (SEM и EDX). Специално внимание се отделя на идентификацията на микро- и нано-размерни частици, обогатени на тежки метали. Беше установено е, че някои тежки метали са концентрирани предимно в отделни частици, често по-малки от 0,5-2* μm. *Такива ФПЧ10, обогатени на тежки метали, са по-опасни за човешкото здраве. Освен това те биха могли да служат и като маркери за източниците на специфични емисии.*

Introduction

Solid aerosol particles in the air are involved in all natural circulation processes and in almost every air pollution problem. As the heavy metal pollution has a harmful effect on life; in recent years much such environmental problems. According to Bulgarian standards for air quality [1], which is synchronized to European legislation on protection of atmospheric air, the atmospheric particles have to be monitored periodically and much attention has to be paid to presence of heavy metals like Pb.

The contribution of dust particles to atmospheric pollution and human health is of great importance [2-4], especially concerning particles smaller than 10 µm, so called particulate matter (PM10).

Heavy metal (HM) enriched particles are important trace constituents of the ambient particles [4]. Main anthropogenic emissions of HM are result of a traffic intensification and rapid urbanization and industrialization world-wide last century. As all other air born PM10, they go through long distance transfer before to fall down the land or water surfaces by dry or wet deposition. All this makes important our interest for the origin, composition and morphology of such individual particles together with integral analysis of the collected dust material. Having such information for some non-typical metal-rich particles, we could use them as tracers for specific emission sources [12].

A great number of particles from Bulgarian and Czech sources have been analyzed by us last years, and some of the obtained results have been already published [5-11]. This paper aims not so much to discuss them as to demonstrate the possibilities of electron microscope techniques for identification of HM particles and to present some newly analyzed unpublished data.

Sampling and methods

A dozen sampling points (close or remote from industrial regions) were carefully selected in Bulgaria and Czech Republic and different sampling techniques were applied to gather typical solid atmospheric particles, see Fig. 1.

Dust particles from the low atmosphere of Bulgarian sites were collected by free sedimentation on smooth carbon surfaces (protected against rainfall) from several Sofia districts (urban samples) and from some green villages (rural sites) [5,6]. Additionally, fine ash particles were taken directly from electro-filters of some of the biggest Bulgarian Thermo-Power-Plants (TPP). Details are given in [7,8]. Both dust and ash sampling sites are indicated in Fig. 1a.

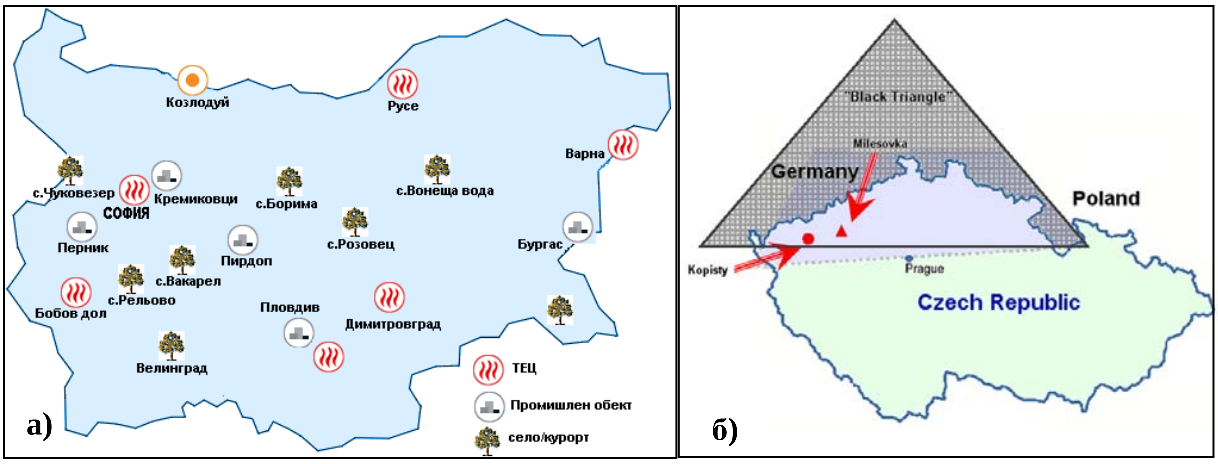

Fig. 1. Schematic illustration of the sampling sites in Bulgaria (a) and Czech Republic (b)

Meteorological stations of Mt. Milesovka, 837 m a.s.l., and the industrial town Kopisty, 240 m a.s.l., 20 km distance from each other, are located in the north Bohemian brown coalfield - one of the most polluted areas in the Czech Republic (Fig. 1b.).

Particles from fog (FP) and rime (RP) water were caught by wet-filter technique during fog or rime events at Milesovka. Particles from ambient air (AP) of Kopisty and Milesovka were collected by dry filter technique. Details of the sampling procedure and preparation of filters before the analysis of water-insoluble particles are given in [9-11].

All microscopic investigations in this study were performed by using of electron microscopes JSM-6390 (equipped with EDX of Oxford Instruments) and JSM-5300, JEOL. Their main regimes of operation are illustrated in Fig. 2. EDX-ray analysis determines the chemical contents of individual or group of particles.

The electron-microscope image formed by secondary electrons (SEI mode) reveals various morphological characteristics, like shape, faceting, surface structure, elongation, agglomeration, etc. They are shown in Fig. 3.

The image formed by back-scattered electrons (BEI mode) is influenced by the contrast with respect to the atomic number of the chemical elements, so that the HM particles could be seen as white spots on dark field, see Fig. 4.

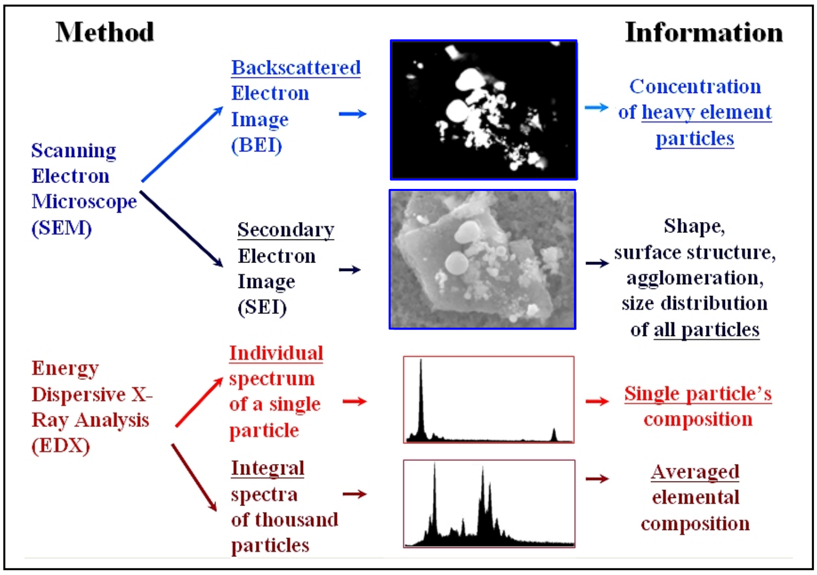

Fig. 2. Schematic relation of the used electron-microscope methods and the expected information

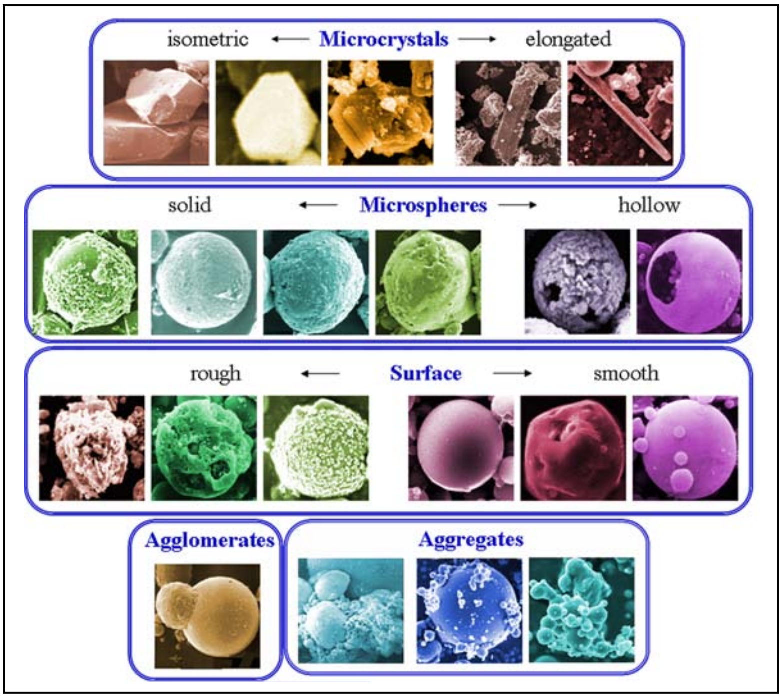

Fig. 3. Morphological characteristics of micro- and nano-size particles

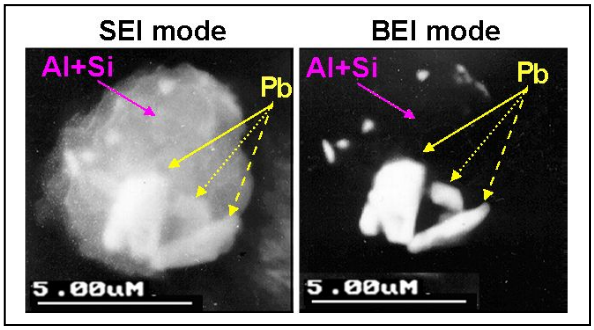

Fig. 4. SEI and BEI images of Al-Si-particle (size ~5 μm) with incorporated Pb pieces, collected from Sofia

Results and discussion

About 3000 particles from Bulgarian and Czech sources, collected by different sampling techniques, have been analyzed electron microscopically.

Integral spectra of their elemental contents reflect mostly the influence of the background soil-mineral particles from each sampling region. Elements like Al, Si, K, Ca, Fe, Ti are usually estimated as habitual ones for most of the typical continental atmospheric dusts. Mineral particles are generally identified by the peaks of presence of: Si for quartz; Mg and Ca for dolomite; S and Ca for gypsum, etc. Most often they have easily distinctive irregular shape, sometimes faceted. Clay particles are complex mixtures of alkaline earth silicates (Na, Mg, Al, Si, K, Ca, Ti, Fe).

Various heavy metals (like Mn, Cu, Zn, Co, Ni, Cr, Pb, etc.) are usually associated with big plants and power stations, traffic, etc. They are known as characteristic elements for technogenic pollution of a given region.

The integral spectra analysis is express one, but it can distinguish only to some extent the air quality of urban and rural sites.

Although the manual processing of samples is slower, it allows one to see specific characteristics of the particles and some mutual relations between morphology and elemental composition, i.e. all those obvious and hidden parameters by which particles are identified in different categories. After manual (or automatic) determination of the size and specific features (shape, morphology, surface structure, etc.) of selected particles, observed in SEI mode, followed by their recognition in BEI mode, and final EDX analysis, they were attributed to a particular category.

A. Bulgarian dust samples from near-ground urban and rural atmosphere

Firstly, a series of integral spectra were taken (at spectrum accumulation 300s) from each one sample. The obtained information is demonstrated on an example of two dust aerosols from Sofia districts (Fig. 5a), and by comparison of typical rural (Fig. 6a) and urban (Fig. 6b) sites in Bulgaria.

Characteristic presentation of size distribution of individual dust particles is shown in Fig. 5b with a maximum of the number of particles with sizes below 2 micrometers.

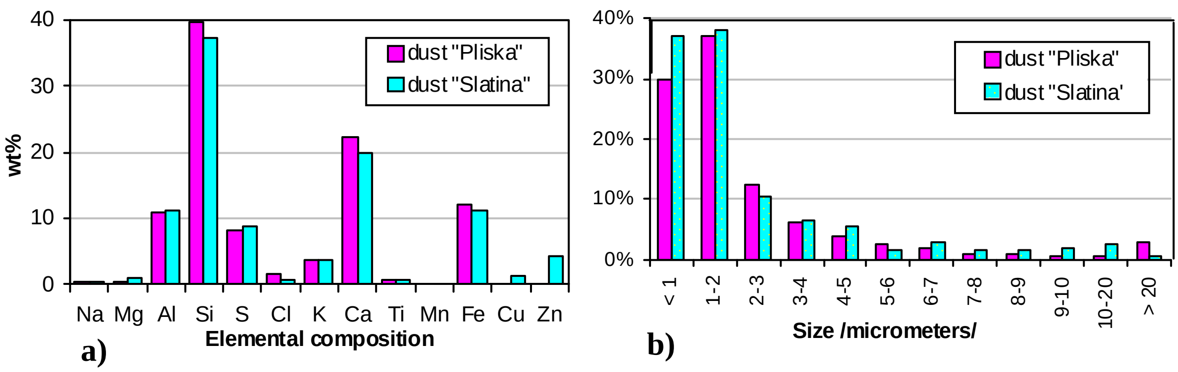

Fig. 5. Typical chemical composition in wt% (a) and size distribution in % (b) of dust-particles from background atmosphere of two Sofia-East districts, collected near two busy crossings

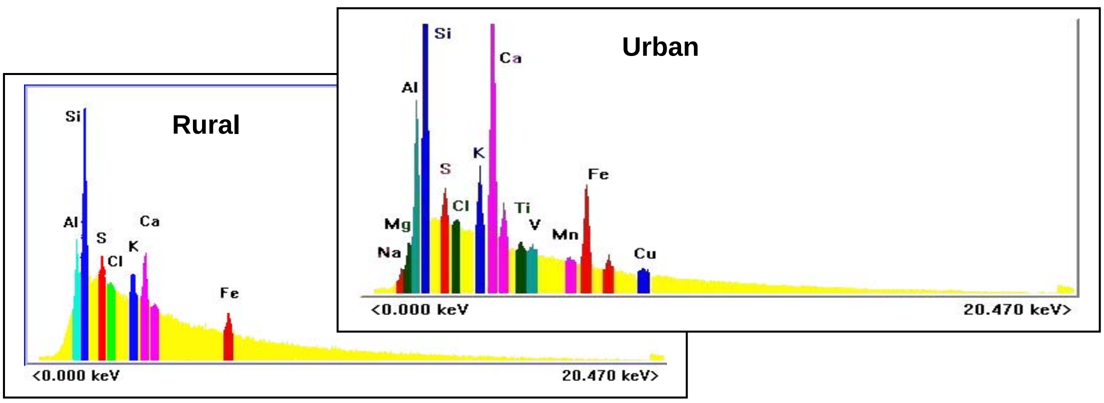

Fig. 6. Integral spectra illustrating qualitatively typical chemical compositions from rural and urban sites

Microphotos of some of inhaled noxious PM10 are seen in Fig. 7. Majority of them are almost always directly related to human activity. For example, the iron-rich particles (Fe more than 70wt%) come from metropolitan areas, where their number is two to four times more than in rural ones. Elemental spectrum of pure iron-rich PM10 with spherical form is seen in Fig. 7a. The spherical shape of micro- and nano- particles usually is a result from high-temperature processes, and therefore could be almost directly correlated to an anthropogenic origin. Impressing is the great variety of HM elements in particles from urban atmosphere, while for comparison, the rural atmosphere is extremely pure of them. Among the potentially most dangerous to human health are the inhalatory size particles rich of Pb and Cd (Fig. 7b,d). Particles of coal burned ashes found in air are easily identified by their porous spherical shape and the presence of the characteristic V and S (Fig. 7e).

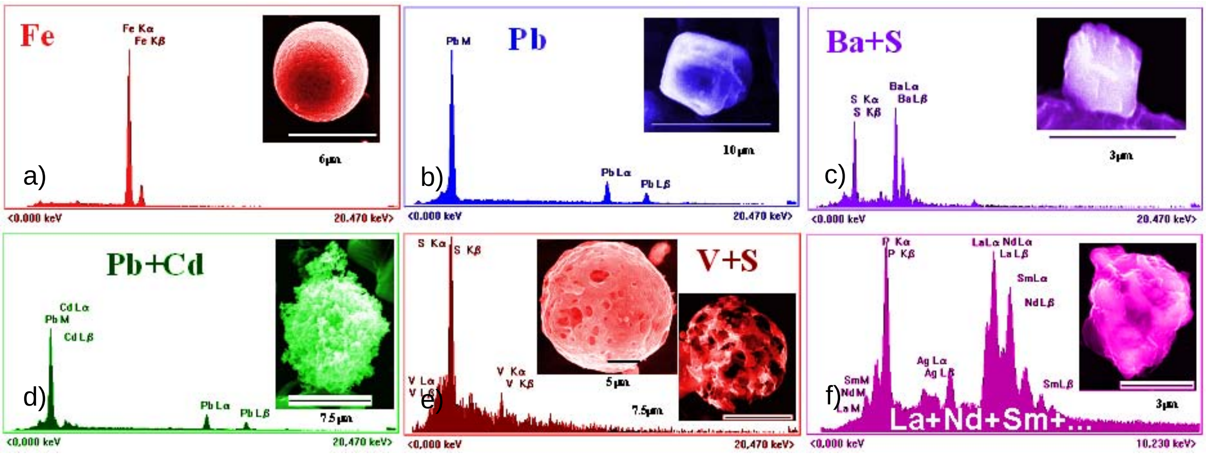

Fig. 7. Elemental spectra and images of individual dust particles, collected from Bulgaria

B. Bulgarian fly ashes samples from TPP

Although fly ashes generated from different power plants have to a certain extent similar composition, their chemical and physical properties vary widely, because strongly depend on the type of coal fired, on burning regime, etc. Both the qualitative and quantitative analyses confirmed that the initial fly ashes, collected from three Bulgarian power plants ("Varna", "Bobovdol" and "Maritza-Iztok I"), are rather inhomogeneous materials as particles' size and shape, surface structure and chemical composition. As seen in Table 1, more than half of the studied ash particles from several TPP were submicron in size and most of them, enriched of heavy elements, were of respiratory size (<10µm).

Table 1. The number of sorted by size HM-rich fly ash particles, collected from three different TPP in Bulgaria

Heavy metal particles	**Varna**			**Bobovdol**			**Maritza-Iztok I**	
	<1µm	**1÷10µm**	**>10µm**	**<1µm**	**1÷10µm**	**>10µm**	**1÷10µm**	**>10µm**
Fe>65wt%	2	62	2	5	28	19	32	58
Pb>55wt%	1	2		8	21	4		
Ba>20wt%; (Ba+Tl+Cu),(Ba+Sr),Sr>30wt%; (Ba+Cu)>60wt%;(Ba+Tl)>80wt%	1	14			1		1	1
Cu>60wt%;(Cu+Zn)>90wt%		2		1	3			1
Ti>55wt%; (Ti+V)>80wt%		2			1			
Cd>60wt%; Ag,Hg >70wt%; Sn,Co,Pt,W >80wt%		4			10			
Y,(Y+Zr),(Y+Lantanides)>50wt%	1	5			2			
Mn~0.5÷7wt%; Cr ~1wt%; As ~1÷8wt%; Zn~1wt%	2xCr,Mn	51xCr,Mn	2xCr,Mn	2xZn,Mn 1xAs	12xZn,Mn 2xAs	13xMn,Zn		8xMn
Number of studied ash particles	11	178	13	17	152	74	50	78
Number of all heavy metal particles	54%	77%	38%	82%	53%	31%	76%	83%

A brief qualitative comparison points at ash “Bobovdol” as the most abundant of heavy metal and trace elements, followed by “Varna”, and in the end - the fly ash “Maritza-Iztok I”. The obtained results demonstrate that many of the heavy metals are concentrated in discrete particles and are not homogeniously distributed in the ash volume.

Fig. 8 reveals some typical interconnections established on the base of elemental composition study of hundred fly ash particles enriched of HM, originating from a lignite coal burning in TPP “Varna”. Such interconnections are different and specific for each one fly ash sample.

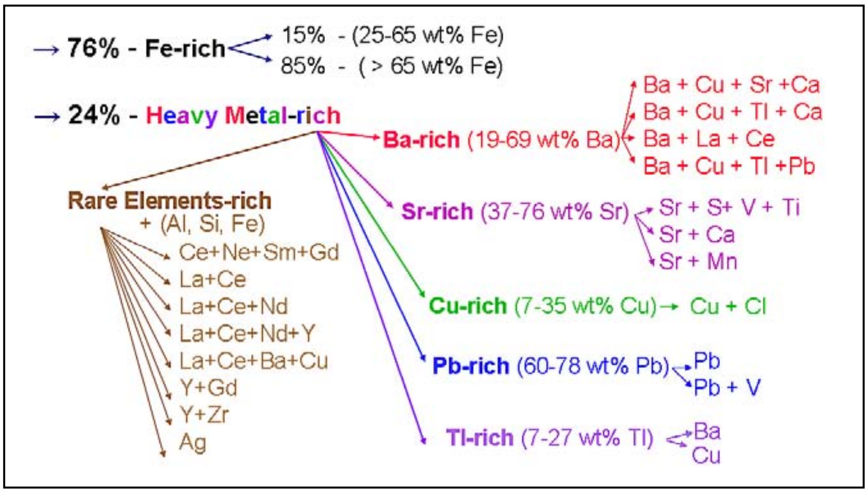

Fig. 8. Interconnections between HM-compositions of fly ash particles from TPP Varna

C. Czech dust samples from air, fog and rime in an industrial region

Hundreds particles were analysed, collected by using of an impactor directly from ambient air (AP) of Milešovka and Kopisty, and water-insoluble particles (FP and RP), obtained after filtering of fog and rime water in the vicinity of Milešovka, respectively. Many of the results were obtained in the frame of AS CR and BAS collaboration. Elemental composition of insoluble components identified in fog/rime water and of air-born dust particles reflect the presence of elements included in phonolite composition of the region. The morphology of FP and RP are similar to that of AP, as seen from their electron-microscope images, shown in Fig. 9. The marker line below each photograph is 1 μm.

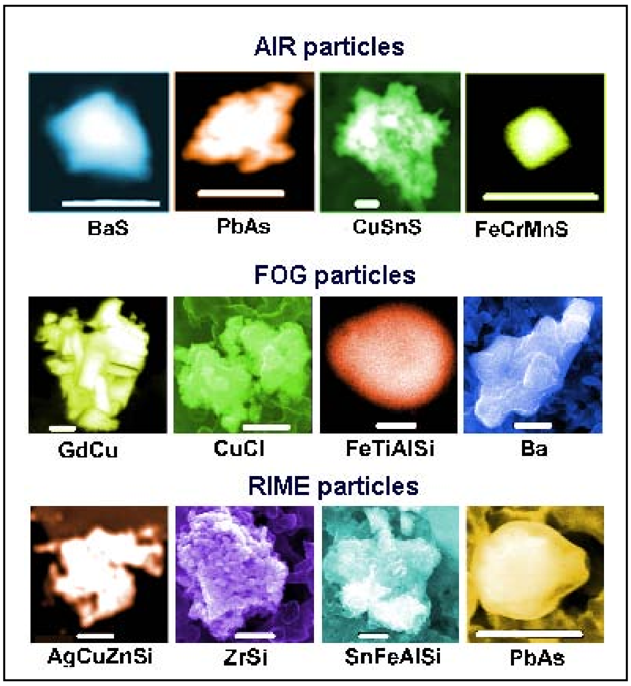

Fig. 9. Particles collected from Air, Fog and Rime samples of Czech Republic. The marker line is 1 μm

The distribution of HM among the particles of given sample is listed in Table 2 through the number of enriched AP, RP and FP. Most often HM were found in the air of industrial zone Kopisty - 54% of all studied air-collected particles (compared to 34% in Milesovka). In addition, the Fe-rich particles (Fe>60wt%) prevail in "K" (48%) also. They reflect the industrial and urban influence in near vicinity of Kopisty.

Table 2. Number of HM-rich AP, RP and FP, obtained from different experimental sets, sampling ways and sites, and classified in groups according to their elemental composition

Sampling	AIR										RIME						FOG				
Site	Kopisty					Milesovka					Milesovka						Milesovka				
Elements / Number	K1	K2	K3	K4	K5	M6	M7	M8	M9	M10	R1	R2	R3	R4	R5	R6	F1	F2	F3	F4	F5
Pb(+As,Cr)		2		2		5	1	1	1	1						1					
Ba(+Cu)	1	2	1			2															
Cu(+Zn,Ni)			1	3				1	1		1			1			1			1	
Au,Ag,W,Tl,Gd,Ta			1					1				1					2	1			
Zr,Ti,Al	2	1		2	2	1		4	1	1	4	6	2	3	3	3	4		5	6	5
Cr,Sn					1	1						3									
Fe(+Cr,Mn,Zn,Ni,Cr,Mo)	10			3		4					1	10	2	3	9	5	3		2	2	
Fe	37	41	45	58	26	33	7	21	12	6	6	11	8	5	19	13	2				2
Wind direction	W	W	W	W	SE	W	W	W	S	W	N	S	N	W	N	E	S	W	N	W	N
PM10-analysed	66	83	101	103	90	78	74	72	64	60	111	83	120	77	115	85	59	50	66	59	63
HM-rich analysed	50	46	48	68	29	46	8	28	15	8	12	32	12	12	31	22	12	1	7	9	7
PM10 total	443					348					591						293				
PM10 average size, µm	3,0±2,4					2,8±2,2					2,7±2,2						4,0±2,3				
HM/PM10, %	54%					30%					20%						12%				
HM average size, µm	2,5±1,9					2,2±1,6					1,4±1,26						2,5±1,9				

Independent of the way of collection, Fe-rich particles are most abundant with respect to other HM particles everywhere (Air, Fog, Rime). Their industrial origin is evident from their composition often including typical technogenic elements as Cr,Mn,Zn,Ni,Mo.

Particles rich of Pb, Au, Zr, Al, Ti, and Pb+Ba, Pb+Ba+Cr, Cu+Zn, Cu+Zn+Ni were detected in M, and similar - in K (W, Zr, Mn, Ba, Cu+Zn, Cu+Sn, Zn+Zr).

The concentration of As registered in AP from Kopisy is three times higher than in Milešovka. Additionally, the (Pb+As) enriched RP from Milešovka were observed at wind direction from Kopisty. That is why the presence of As could serve as a tracer for pollution distribution in the studied region, as proposed by other authors [12].

Some elements (Cu, Ag, Ca, Cl,) were present largely in fog and others (Fe, Al, Si, Ti) prevailed in rime samples. Particles containing Cu were found in bigger quantity in fog than in rime. Rime water contained Fe, Mg, and Ti.

The highest heavy metal concentrations were recorded at the air transfer from south direction and lower pollutant concentration from north direction. It is valid for both fog and rime events. Apparently, the majority of trace elements found in fog were transported to Milesovka from the industrial region (Kopisty and the other towns in south direction).

Conclusion

Thousands particles have been analyzed by using of electron microscope SEM and EDX analysis. A special attention was paid to the identification of micro- and nano-size particles enriched by HM. Such particles were included in almost every air pollution sample, but most often were found in ashes originating from coal combustion, near traffic jam crossings or in the vicinity of factories and industrial zones. The results of the carried out analysis of air born particles and solid particles caught by water during fog or rime events confirm this statement. The inhallatory HM particles (with technogenic origin) are met in the urban regions of Sofia three to four times more frequently in comparison with green rural regions. Almost the same is situation with HM transported to Milesovka from the region of Kopisty and the other industrial towns in its vicinity. A natural expectation is confirmed, that the environmental pollution is strongly influenced by the concentration of people, industry and motor vehicles in the large cities.

The obtained data were classified in several principal groups and compared. It was established that many HM are present predominantly in single-particles. Most often their size is smaller than 0,5-2 µm. The results of many other authors lead to the same observation, namely that in the finest fraction of atmospheric aerosols (below 2,5 μm) the concentration of crustal elements is very low while many anthropogenic elements (such as S, Pb and heavy metals) with a strong environmental impact have higher concentrations (see for example [13]). Also the anthropogenic inputs for Pb, Cr, Zn and Cu have been confirmed by other authors [14,15].

Due to the increased solubility and enhanced reactivity, these particles pose additional health risks.

The HM-enriched particles from air, fog or rime also could serve as tracers for specific emission sources [12].

In conclusion we state that electron microscope analysis proposes unique possibilities to investigate simultaneously the size distribution, morphology and elemental composition of individual dust particles, giving in the same time (through the integral spectra) information for dust material as a whole. The applied here method allows demarcation of HM from phonolite soil-mineral particles present in the near-ground atmospheric layer. So, studies of morphology and element composition of particles shed light about the technogenic or natural origin of the particles and help one to clarify their transport and transformation, as well as to identify some technogenic source emissions.

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