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Nano- and Microparticles of Metals in Urban Atmosphere (by the Example of the Vladivostok and Ussuriysk Cities)

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Abstract

Atmospheric aerosols inherent in two areas of the Far East cities such as the Vladivostok and Ussuriysk were studied. Three of the 21 pairs of the samples of fresh snow and dry air suspensions taken in different parts of these cities exhibited the presence of iron, chromium, lead and zinc nano- and microparticles. Therewith, the nanoparticles were registered for the samples taken near the electroplating production enterprises, whereas the microparticles were observed near the roads with an intense traffic.

Key words: nanoparticles, microparticles, atmospheric aerosol, metals

INTRODUCTION

Life on Earth evolved in the presence of mineral nanoparticles in the atmosphere, which was caused by volcanic eruptions as well as by wind carrying the soil, rocks and sea salt particles. As the technocratic civilization developed, artificial nanoparticle sources appeared. The origin thereof is connected with engine exhausts, industrial fumes, and all the sorts of explosive processes [1–4]. The authors of [5] consider that about a half of artificial nanoparticles in urban atmosphere represent organic compounds the remaining ones being presented by metal oxides, elemental carbon, sulphates, nitrates, chlorides, and ammonium. The effect of this new environmental factor exerted on the biota is only under beginning the investigation [4], however, the fact is already established [3, 6, 7] that micro- and nanosized particle fractions of metals and metal oxides are the most toxic with respect to human beings.

Earlier [8] we revealed the presence of nano- and microparticles in the atmospheric air of the Vladivostok. In this paper, we have made an attempt to reveal and identify nano- and microparticles of metals in atmospheric aerosols within a number of the areas of the two Far East cities such as the Vladivostok and the Ussuriysk.

MATERIALS AND METHODS

In order to study the composition of atmospheric aerosols we used two types of samples and two technologies for sampling, respectively. We took fresh snow with further studying the aerosol particles immediately in the liquid and after drying. The samples of atmospheric air were taken in a week after snowfall; using a special sampling apparatus, we took the dry suspension by means of pumping air through membrane filters to further investigate the dry dust on the filters. At the Vladivostok we took 12, whereas at the Ussuriysk we took 10 pairs of samples. All the samples were collected in the winter of 2011–2012 within different urban areas immediately in the course of snowfall. The snow samples were taken from the top layer of fresh snow to collect in 1 L containers.

After thawing the snow in the containers, the resulting liquid was agitated, and then we took a 40 mL aliquot from each sample into a cuvette to analyze with the help of an Analysette 22 NanoTech laser particle analyzer (Fritsch, Germany). This method allowed us to determine the shape of the particles under investigation and to reveal the size distribution thereof.

For further studying the particles in the liquid samples, water was evaporated. The resulting dry residue was investigated with the use of an electron microscope, a part of the residue after dissolving thereof in an acid was analyzed by means of a Shimadzu 6800 atomic absorption spectrometer (Japan) in the Laboratory of Applied Ecology and Toxicology, at the FSUE "TINRO-centre". The analyses were also performed using an Element XR mass spectrometer with inductively coupled plasma (Thermo, USA) in the Laboratory of X-ray investigation methods at FEGI of the FEB RAS.

In order to obtain dry samples immediately from atmospheric air we used a LSV 3.1 sampler used (Derenda, Germany) with a MGG filter (glass microfiber paper) with a diameter of 47 mm (Munktell, Germany) employing a PM_{10} end cap, as well as a PU-3E/12 sampler with AFA type filters (perchlorovinyl). The further type of sampler was used in the Vladivostok, the latter type was used in the Ussuriysk.

Electron micrographic imaging and identification of the material composition of individual particles was performed using scanning electron microscopes such as Zeiss EVO 40XVP with an INCA Energy energy dispersion attachment and Hitachi S3400 with a Thermo Scientific energy dispersion attachment. The quantitative calculations of the composition of microparticles were normalized (total amounts were reduced to 100 %).

RESULTS AND DISCUSSION

Metal nanoparticles

Metal nanoparticles were found in snow samples taken from the western (industrial) part of the Ussuriysk, where there are the Ussuriysk railway station with the federal highway located in the immediate vicinity (cargo

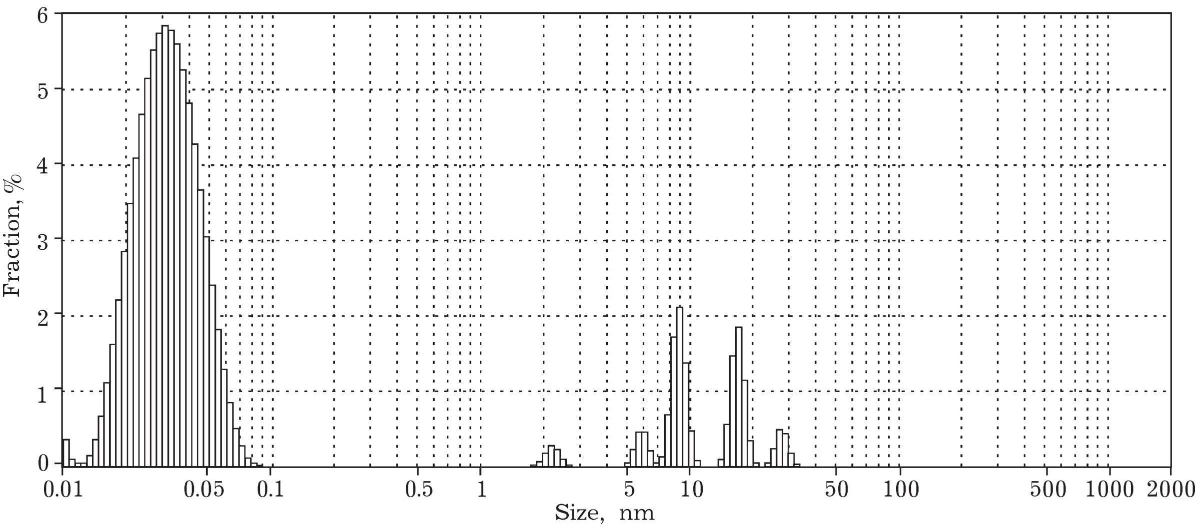

Fig. 1. Particle size distribution and the fraction thereof in the suspension (snow samples selected in the western part of the Ussuriysk).

TABLE 1

Morphometric parameters of metal particles revealed in snow samples taken at the western part of the Ussuriysk

Parameters	Value
Arithmetic mean diameter, μm	2.06
Mode, μm	0.031
Median, μm	0.034
Deviation, μm^2	29.05
Standard deviation, μm	5.39
Deviation ratio, %	260.96
Specific surface, cm^2/cm^3	1 711 471.75

traffic 1200 cars/h), the Ussuriysk Locomotive Repair Plant (ULRP) and refrigerator railcar depot. Snow samples were taken in front of an apartment house at the Blucher Ave., 38, at a distance of 5 m from the road. Sampling the snow was performed when the weather was windless. The distribution pattern of the particles suspended in a liquid sample is demonstrated in Fig. 1. The content of the particles with a diameter of 0.01–0.07 μm was equal to 84 %, 2–3 μm – 1 %, 5–7 μm – 3 %, 7–12 μm – 5 %, 20–30 μm – 5 %, and 30–40 μm – 2 %. Table 1 demonstrates the morphometric parameters of metal particles in the suspension of snow samples taken at the western part of the Ussuriysk.

Judging by a high concentration level of nanoparticles in the suspension (see Fig. 1), the mentioned particles could be, to all appearance, presented by metals or oxides thereof being the products of the "dusting" from a galvanizing-bath plant. The validity of this hypothesis is indicated by the fact that the official website of the ULRP advertises the service of recovering the component parts by chromium plating, steel plating, tin plating, zinc plating, nickel plating, *etc*. (URL: http://www.ulrz.ru).

In order to verify this assumption a part of the snow sample as transformed into an acidic solution to be analyzed by means of atomic absorption spectrophotometry (AAS), as well as by means of mass spectrometry with inductively coupled plasma (ICP-MS). In both cases, we revealed the presence of chromium, in the sample, whereby the AAS method exhibited the content thereof equal to 0.001 μg/mL, whereas the ICP-MS exhibited the content amounting to 0.3 μg/mL. Alongside with chromium, the ICP-MS method also revealed the presence of iron in the sample (10–12 μg/L).

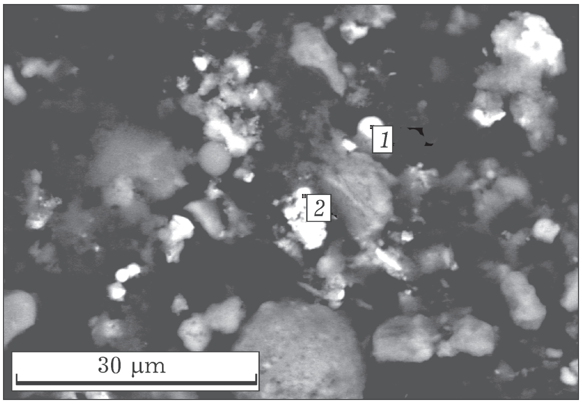

Fig. 2. Overview micrograph of particles inherent in snow samples taken at the western part of the Ussuriysk obtained in a mode of reflected electrons: *1*, *2* – the spectra of iron microparticles with different morphology.

TABLE 2

Composition of iron microparticles with different morphology according to EDS analysis

Elements	Spectrum *1*		Spectrum *2*	
	mass %	at. %	mass %	at. %
O	7.11	20.52	24.20	50.44
Al	abs.	abs.	2.93	3.62
Si	3.18	5.24	4.12	4.89
Fe	89.71	74.24	68.75	41.05
Total	100.00	100.00	100.00	100.00

Note. Here and in the Tables 3–7: abs. – absent.

In order to confirm the working hypothesis that these particles represent the nanoparticles of metals we investigated a dry suspension obtained from the collected snow using an electron microscope. Figure 2 demonstrates an overview micrograph, whereas Table 2 presents the results of X-ray energy dispersion spectroscopy (EDS) analysis of the two particles among the heaviest ones. The size of the particles under investigation is less than or comparable with the diameter of the microprobe electron beam, so in the course of the EDS analysis, the signals from aluminum silicate adjacent particles contribute in the signal registered, which is confirmed by revealing the signal from Si and Al impurities. It can be seen that the iron microparticles are oxidized. Thereby, shapeless (xenomorphic) particles are oxi-

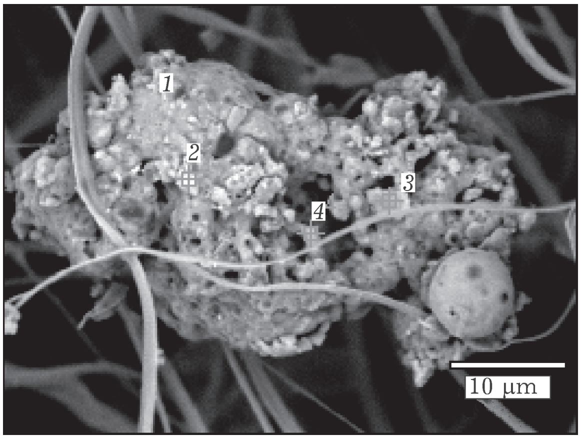

Fig. 3. Overview micrograph of the particles collected on the filter of the sampler from the western part of the Ussuriysk, obtained in a mode of reflected electrons. Spectra of particles: *1* – aluminosilicate; *2* – iron oxide; *3*, *4* – titaniferous minerals; light-coloured filaments represent filter fibres.

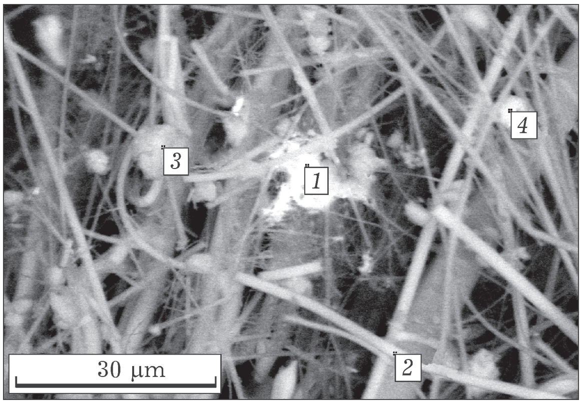

Fig. 4. Overview micrograph of aerosol particles collected on the filter of the air sampler from the region of Zarya (the Vladivostok), obtained in a mode of reflected electrons. Spectra of particles: *1* – barium-containing mineral (to all appearance, barite); *2* and *3* – filter material; *4* – iron; light-coloured filaments represent filter fibres.

TABLE 3

Composition of the microparticles of aluminosilicate, iron and titanium-containing minerals according to EDS analysis

Elements	Spectrum *1*		Spectrum *2*		Spectrum *3*		Spectrum *4*	
	mass %	at. %	mass %	at. %	mass %	at. %	mass %	at. %
C	2.54	4.65	1.82	4.28	2.55	4.94	1.71	3.18
O	37.86	52.05	29.26	51.68	32.41	47.25	44.02	61.66
Na	0.58	0.55	abs.	abs.	abs.	abs.	abs.	abs.
Mg	1.47	1.33	5.26	6.11	0.84	0.80	abs.	abs.
Al	16.55	13.50	3.36	3.52	14.51	12.54	11.93	9.91
Si	25.59	20.04	4.87	4.90	28.24	23.45	15.56	12.42
Cl	2.08	1.29	2.71	2.16	2.94	1.94	1.76	1.11
K	abs.	abs.	abs.	abs.	1.43	0.85	abs.	abs.
Ca	8.63	4.74	3.29	2.32	2.65	1.54	abs.	abs.
Fe	4.69	1.85	49.43	25.02	4.99	2.08	abs.	abs.
Ti	abs.	abs.	abs.	abs.	9.44	4.59	25.03	11.71

TABLE 4

Composition of the microparticles of iron (to all appearance, chromium-containing steel), barium-containing minerals and aluminosilicates according EDS analysis

Elements	Spectrum *1*		Spectrum *2*		Spectrum *3*		Spectrum *4*	
	mass %	at. %	mass %	at. %	mass %	at. %	mass %	at. %
O	33.22	53.49	48.06	61.37	49.32	62.52	34.73	53.51
Na	10.62	11.90	11.27	10.02	8.36	7.37	7.15	7.67
Mg	abs.	abs.	abs.	abs.	2.88	2.41	abs.	abs.
Al	2.54	2.43	4.37	3.31	6.84	5.15	7.09	6.47
Si	20.34	18.65	31.26	22.74	27.86	20.12	22.53	19.77
S	7.03	5.65	abs.	abs.	abs.	abs.	abs.	abs.
K	1.59	1.05	abs.	abs.	2.58	1.34	abs.	abs.
Ca	4.85	3.11	5.03	2.57	2.15	1.09	abs.	abs.
Fe	abs.	abs.	abs.	abs.	abs.	abs.	28.51	12.58
Ba	19.81	3.72	abs.	abs.	abs.	abs.	abs.	abs.

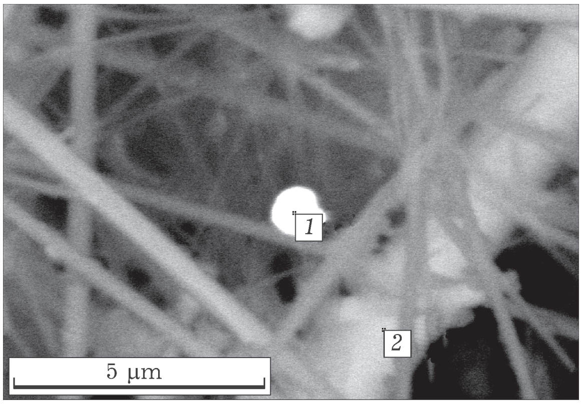

Fig. 5. Micrograph of a lead particle (*1*) on the filter of the air sampler from the region of Zarya factory (Vladivostok) and of filter fibres (*2*), obtained in a mode of reflected electrons.

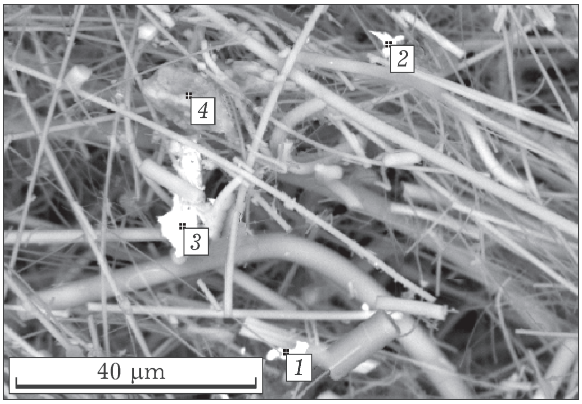

Fig. 6. Overview micrograph of particles on the filter of the air sampler from the region of the Pushkinkaya Street (Vladivostok), obtained in a mode of reflected electrons: *1–3* – oxides of chromium-containing steel; *4* – zinc and barium containing minerals. Grey-coloured filaments represent filter fibres.

TABLE 5

Composition of lead microparticles according to EDS analysis

Elements	Spectrum *1*		Spectrum *2*	
	mass %	at. %	mass %	at. %
O	38.37	66.61	42.87	56.43
Na	7.55	9.12	11.45	10.49
Mg	abs.	abs.	1.63	1.41
Al	2.61	2.68	2.89	2.26
Si	17.17	16.98	34.59	25.94
K	abs.	abs.	2.13	1.15
Ca	abs.	abs.	4.44	2.33
Pb	34.29	4.60	abs.	abs.

dized to a much greater extent (spectrum *2*), rather than spheroidal ones (spectrum *1*).

In the course of studying the microparticles on the filter of the air sampler those ere taken from the western part of the Ussuriysk it was found that, as far as metals are concerned, there are only iron (probably oxides), aluminosilicates and titaniferous minerals (probably ilmenite or rutile) present therein.

The complex of investigations performed (Fig. 3 and Table 3) indicates with a high reliability level that the nanoparticles we found in the fresh snow at the western part of the Ussuriysk are presented by iron and chromium (or their oxides).

The microparticles of metals have also been found in several samples of snow and air tak-

TABLE 6

Composition of different microparticles according to EDS analysis

Elements	Spectrum *1*		Spectrum *2*		Spectrum *3*		Spectrum *4*	
	mass %	at. %	mass %	at. %	mass %	at. %	mass %	at. %
O	13.31	29.64	16.97	34.40	abs.	abs.	44.60	60.82
Na	7.30	11.31	7.99	11.27	abs.	abs.	8.47	8.04
Mg	abs.	abs.	abs.	abs.	abs.	abs.	0.79	0.71
Al	abs.	abs.	1.70	2.05	abs.	abs.	2.96	2.39
Si	12.42	15.75	15.50	17.90	1.54	2.99	30.00	23.31
K	abs.	abs.	abs.	abs.	abs.	abs.	1.74	0.97
Ca	1.04	0.92	2.34	1.89	abs.	abs.	3.57	1.95
Cr	6.96	4.77	6.39	3.98	15.8	16.58	abs.	abs.
Fe	58.98	37.62	49.11	28.52	82.60	80.43	abs.	abs.
Zn	abs.	abs.	abs.	abs.	abs.	abs.	3.24	1.08
Ba	abs.	abs.	abs.	abs.	abs.	abs.	4.62	0.73

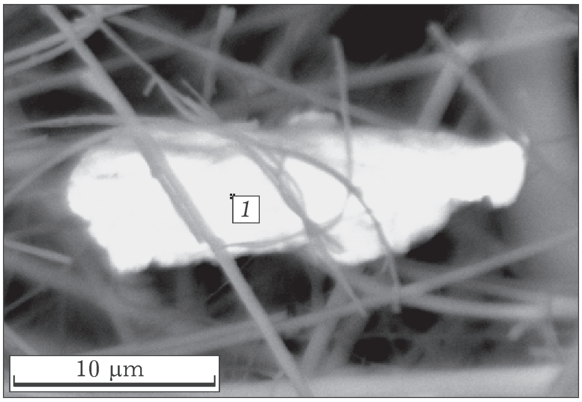

Fig. 7. Micrograph of a zinc particle (*1*) on the filter of the air sampler from the region of the Pushkinskaya Street (Vladivostok) obtained in a mode of reflected electrons. Grey-coloured filaments represent filter fibres.

TABLE 7

Composition of zinc microparticles according to EDS analysis

Elements	Spectrum	
	mass %	at. %
C	23.22	53.25
O	8.21	14.14
Al	3.04	3.10
Si	3.38	3.32
Cu	0.90	0.39
Zn	61.24	25.80

en in the Vladivostok. So, the samples taken within the area of the Zarya factory contain metal microparticles of iron, lead, barium and minerals (Figs. 4, 5 and Tables 4 and 5).

The microparticles of metals have also been found in snow samples taken at the Pushkinskaya Str.; they are predominantly presented by chromium particles (to all appearance chromium-containing-steel), zinc, and aluminosilicates (see Figs. 6, 7 and Tables 6, 7).

CONCLUSION

Nano- and microparticles of many metals and their oxides, including Cr, Pb, Fe, Ti, Zn, according with the concepts developed in the field of classical toxicology and nanotoxicology [2] exhibit pronounced toxic properties. Therewith, the nanoparticles have the highest reactivity among other size groups (micro-, meso-, and macrogroups). The presence of metal nano- and microparticles already in the first dozen of atmospheric air samples determines the urgency studying the mentioned ecological and hygienic factor at a detailed level. Special attention in the course of studying this issue should be given to the places, where technologically obsolete chemical and electroplating production facilities are located.

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