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OPTICS OF CLUSTERS, AEROSOLS, AND HYDROSOLES

Material and Elemental Composition of Surface Aerosols on the North-Western Coast of the Kandalaksha Bay of the White Sea

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Abstract—Continuous sampling of aerosols is carried out on the north-western (NW) coast of the Kandalaksha Bay of the White Sea. Aerosol matter from 30 filters collected in summer and autumn, 2013, and spring, 2014, was studied by scanning electron microscopy. The elemental composition of aerosol matter was determined by the inductively-coupled plasma mass-spectrometry (ICP-MS). The major portion of aerosol particles collected in summer is of biogenic origin. Heavy metal concentrations in aerosols are at the Arctic background level. The distribution of trace element concentrations is characterized by simultaneous peaks of different elements. The backward trajectory analysis shows an increase in Ni and Cu concentrations corresponding to the arrival of air masses from the western part of the Kola Peninsula. That suggests the influence of smelters.

Keywords: aerosols, heavy metals, copper, nickel, long-range atmospheric transport, backward trajectories
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INTRODUCTION

The atmospheric transfer of aerosol particles is the most rapid channel for the arrival of pollutants in remote regions [1–3]. This channel is of great importance for environmental conditions in the Arctic [4, 5]. Studies of the chemical composition of aerosols in the Russian Arctic were started in the mid-1980s at polar stations at Severnaya Zemlya and Wrangel Island [5, 6]. The results of later studies were generalized in [7]. Interest in the study of aerosols in Arctic and subarctic regions of Russia has grown in recent years [8–14]. In all the above-mentioned works, the chemical composition of aerosols was studied for a short period over the Arctic sea water areas during cruises of research vessels. This approach does not allow seasonal features of atmospheric transfer of heavy metals to be ascertained.

Continuous sampling of aerosols is carried out at the territory of the White Sea Biological Station of the Department of Biology of Moscow State University (WSBS MSU) (66°34′ N, 33°08′ E) to provide for long-term study of aerosols on the north-western coast of the Kandalaksha Bay of the White Sea [15]. The territory is distant from strong pollutant sources (75 km to the nearest town Kandalaksha). The Station is electrically heated; therefore, the site is considered background. The aerosol studies carried out at WSBS MSU include the study of organic and elemental carbon in aerosols [15] and their particle-size distribution [16]. To study insoluble winter aerosol particles, snow composition has been studied at the Station for several years [17], since snow is a natural accumulator of all aerosol precipitation for the period when the ground is snow-covered.

MATERIAL AND TECHNIQUES

The atmospheric aerosol sampling at WSBS MSU is carried out with a UAS-310 air sampler on filters 22.5 × 31 cm in size. Different filter types can be used, i.e., fiberglass, cellulose, and quartz fiber [18]. The air pumping rate is 270 L/min, the sampling time of an individual sample is about a week, and the air volume pumped for the sampling time is about 2500–3000 m^3. The device does not operate in winter due to the weather conditions.

In this work, we present the results of sampling on Whatman 41 cellulose filters, which trap particles smaller than 2.5 μm (PM2.5), in 2013 (in summer and autumn) and 2014 (spring), 10 filters for each season. To detect the aerosol material composition, pieces of filters 0.5 × 0.5 cm in size were studied by scanning electron microscopy (SEM) with a VEGA 3 SEM microscope (Tescan) with an INCA Energy microprobe (Oxford Instruments).

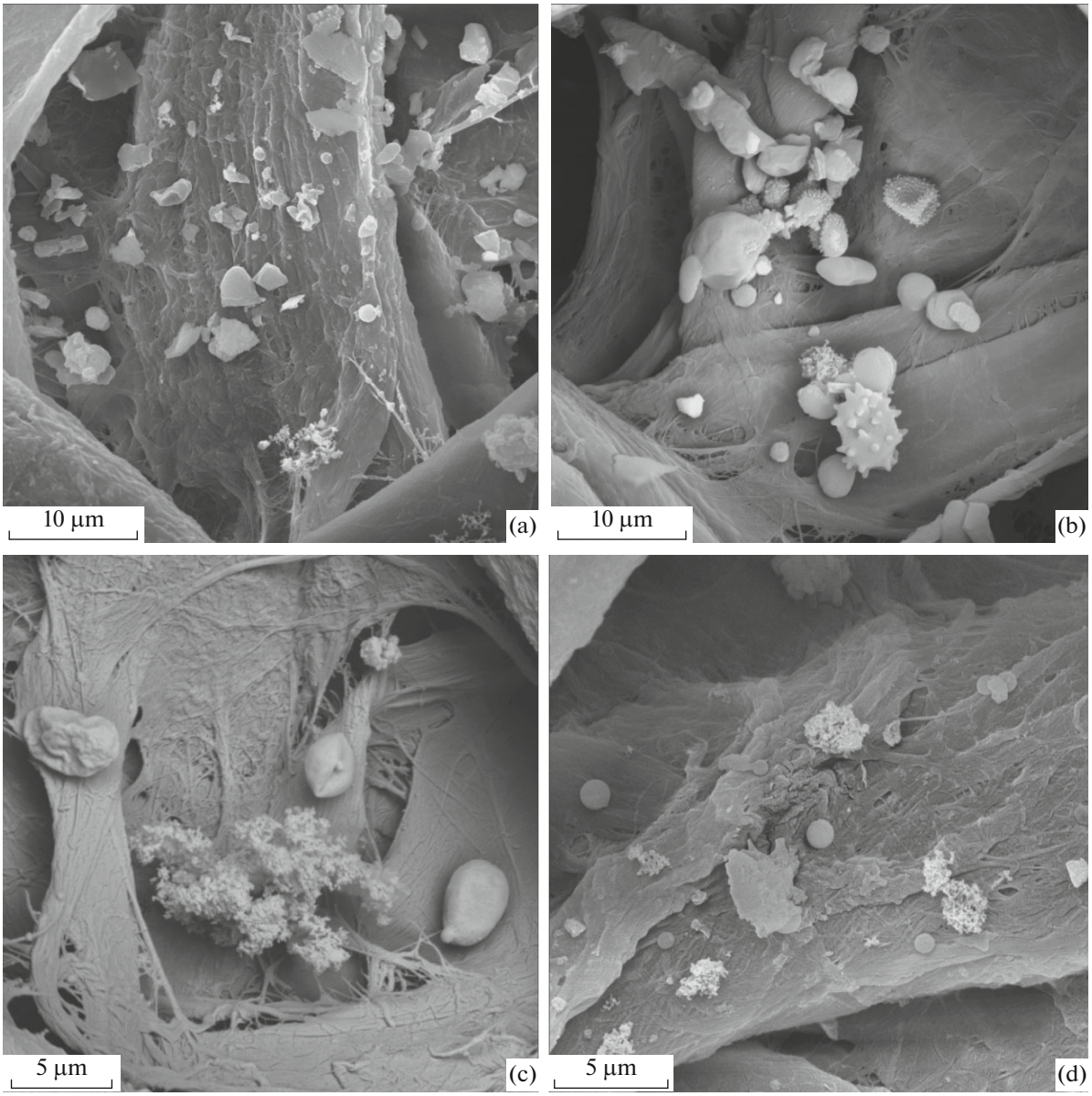

Fig. 1. TEM images of different aerosol particles: (a) mineral aluminosilicate particles; (b and c) biogenic particles (spores); (d) soot aggregates and combustion spheres.

Pieces of the same filters 4 × 8 cm in size were digested in a mixture of concentrated acids (nitric, hydrofluoric, and perchloric); then the resulting solution evaporated using an IR lamp and the solution deposit was brought to the required volume by a 3% nitric acid solution. The elemental composition of the aerosol filters digested was detected by inductively-coupled plasma mass-spectrometry (ICP-MS) using an Agilent 7500 device. The concentrations of the following metals were measured: V, Ni, Cu, Zn, Ga, Rb, Sr, Zr, Cd, Sb, Cs, Y, Ba, La, Pr, Nd, Pb, and Bi. The resulting concentrations in the solution were recalculated to the concentration in air.

RESULTS AND DISCUSSION

Aerosol Material Composition

SEM results allow division of aerosol particles into four genetic groups (Fig. 1): biogenic particles (spores, pollen, and plant fragments); lithogenic particles represented by debris; anthropogenic particles (combustion spheres and soot aggregates); and sea salt as an admixture that forms a haze on other particles, which is revealed during the microprobe analysis.

Analyzing the seasonal particle distribution, one may note that biogenic particles are the most frequent in summer samples and make up to 80–90% of the aerosol matter volume (according to visual estimates).

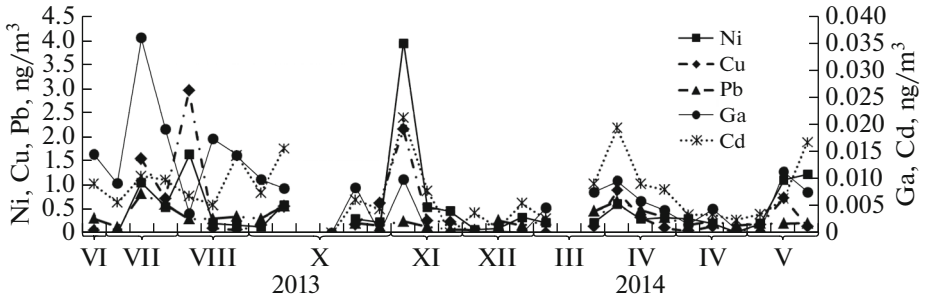

Fig. 2. Concentrations of microelements in aerosol particles.

The biogenic particle concentration in spring and autumn samples is much lower. Soot aggregates and combustion spheres are detected in aerosols during all the three observation seasons.

Aerosol Elemental Composition

Figure 2 shows concentrations of elements in aerosols. Peaks in the element concentrations can be both synchronous for a number of elements and specific for one or several elements. The comparison with literature data (table) shows that the mean microelement concentrations correspond to the Arctic background level [19, 20].

To reveal connections between elements, the Pearson correlation coefficients were calculated. The correlation coefficients for Cu and Ni are high (0.75), which is evidence of their common source. A cluster of lithogenic elements Ga, Rb, and Ba is also notable: the correlation coefficient between Ga and Rb is 0.78 and between Ga and Ba is 0.92. A significant correlation coefficient between Zn and Cd (0.59) is probably explained by their chemical affinity, but not by their common source. The correlation coefficients are significant for Pb and Zn (0.61) and Pb and Cd (0.53).

To identify the source of the material arriving, the enrichment factors (EF) with respect to the average Earth's crust composition were calculated by the equation

$$EF = (El./Ga)_{sample}/(El./Ga)_{E.c.},$$

where (El./Ga) is the ratio of the element concentration to the Ga concentration in a sample and in the Earth's crust (E.c.) [21], respectively. In this case, Ga was used as a lithogenic source indicator. If an aerosol matter source is close in composition to the average Earth's crust composition, then EF is close to unity. High (>10) EFs are characteristic for those elements that arrived from a source different in composition from the Earth's crust (marine, biogenic, and anthropogenic aerosols). EFs are close to unity for Rb, Sr, Cs, Ba, and rare earth elements. The highest EFs (> 10 in all samples) are characteristic for Zn (102), Cd (270), Sb (321), and Pb (62). The mean EFs for Ni and Cu are also higher than 10 and are 37 and 52, respectively; however, there are samples free of Cu and Pb. This witnesses that sources of Pb, Zn, Cd, and Sb continuously arrive at the observation site from different directions, while Cu and Ni sources are localized.

Three-D backward trajectories of air masses that arrive at a sampling point were calculated with the HYSPLIT software at a level of 20 m with a step of 12 h for the whole sampling period to reveal sources of the metals [22]. Three-day trajectories were calculated for summer, and five-day trajectories for other seasons. The analysis of the backward trajectories showed that low EFs for Cu and Ni are characteristic for samples collected in the periods where the air mass trajectories did not approach smelters on the Kola Peninsula. Those samples were also characterized by the absence of combustion spheres, according to SEM data.

Figure 3 shows a correlation between Ni and Pb concentrations in the samples. All samples in Fig. 3 are conventionally divided into three groups. A similar division of the samples into three groups is also typical for Cu. The first group is characterized by increased Ni and low Pb concentrations; EFs for Ni and Cu in this group are the highest (103 and 175, respectively) (*1*). In the second group, high Pb concentrations correspond to low Ni concentrations; EFs for Ni and Cu are below

Concentrations of microelements in different Arctic regions (ng/m^3)

Region	V	Ni	Cu	Sb	Pb	Cd
Finnish Arctic [19]	0.79	0.97	14.10	0.14	4.62	–
The White Sea [13]	–	0.40	7.60	–	0.12	0.02
Central Arctic, August–October 1991 [20]	–	0.18	0.16	0.019	0.20	–
WSBS MSU (the mean, this work)	0.21	0.57	0.53	0.079	0.30	0.01

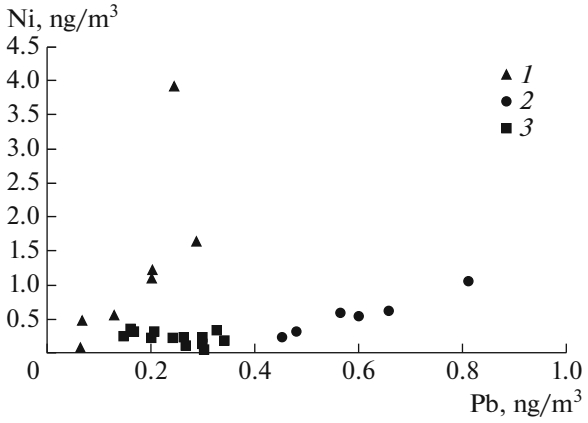

Fig. 3. Correlation between Ni and Pb concentrations in aerosols.

the means (16 and 32) (*2*). In the third group, both Pb and Ni concentrations are low; EFs for Ni and Cu are also below the means (22 and 10) (*3*). That is, Pb significantly enriches the samples with low element concentrations, which shows that it is washed out from the atmosphere less effectively than other elements.

The backward trajectory analysis has shown that each of these three groups is characterized by the proper back trajectory distribution. The characteristic backward trajectories of the first group pass through smelters on the Kola Peninsula; backward trajectories of the second group arrive from the south and west; and backward trajectories of the third group arrive from the polar regions.

CONCLUSIONS

Aerosols near WSBS MSU in summer are mainly composed of biogenic particles; the fraction of the mineral component increases in autumn and winter. Anthropogenic particles (soot aggregates and combustion spheres) are homogeneously distributed over seasons. The heavy metal concentrations in aerosols are at the Arctic background level. The correlation analysis allowed the following group of elements to be distinguished: (1) lithogenic (Ga, Rb, and Ba) and (2) anthropogenic, consisted of two subgroups, i.e., with far sources (Pb, Zn, and Cd) and close sources (Cu–Ni pair); EFs by such heavy metals as Pb, Zn, Sb, and Cd exceed 10 in all samples, which witnesses long-range atmospheric transfer and mixing of these metals. Cu and Ni sources are localized in the western part of the Kola Peninsula.

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