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OPTICS OF CLUSTERS, AEROSOLS, AND HYDROSOLES

Elemental Composition of Near-Ground Aerosol Near the Northwestern Coast of Kandalaksha Bay of the White Sea

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Abstract—Aerosol samples $PM_{2.5}$ (44 filters), collected in 2013–2014 on the coast of the White Sea, were examined for the presence of trace elements. The entire sampling period was divided into conventional seasons: one snow-covered season, when the effect of terrigenous dust is minimal, and two snow-free seasons, when the effects of both anthropogenic and terrigenous sources are distinctly manifested. The snow-free seasons are characterized by the largest dispersion of elemental concentrations. The snow-covered season differs from snow-free seasons by the predominance of the western directions of air mass transport. Analysis of the directions of transport of air masses and aerosol admixtures to the observation site made it possible to identify a few groups of trace elements of natural (La, Nd, Sr, Ga) and predominantly anthropogenic origin (V, Ni, Cu and Pb, Bi, Cd).

Keywords: White Sea, aerosols, $PM_{2.5}$, heavy metals, atmospheric transport, background regions, backward trajectories

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INTRODUCTION

Study of the elemental composition of atmospheric aerosols in remote regions has given, for many years, valuable information on the possible origin of substances observed there. Transport in the atmosphere plays a major role in determining the aerosol composition. Sources of different trace elements may be located at large distances (as large as a few thousand kilometers) from observation sites [1, 2]. Atmospheric transport delivers pollutants most rapidly to environment. Information on the amount and composition of pollutants is required for further estimates of their distribution over food chains and their potential influence on different components of environment, flora and fauna of the region [3].

Atmospheric chemical composition can be studied both in the process of continuous observations at monitoring stations [4], and in short-term investigations during individual expeditions [5–7]. The information obtained in that manner is fragmentary and, as such, should be complemented by model estimates of dispersal of pollutants in the atmosphere [8].

The White Sea as a whole and the vicinity of N.A. Pertsov White Sea Biological Station of Moscow State University (WSBS MSU) are in the area impacted by the complexes of mining and metallurgic industries located on the Kola Peninsula (mainly near Nikel settlement and Monchegorsk) [9, 10]. In addition, the anthropogenic contribution to aerosols in the study region comes from the thermal power plants and industry of the Republic of Karelia, Murmansk and Arkhangelsk oblasts, as well as European industrial regions due to trans boundary atmospheric transport [11]. An important factor in determining the aerosol composition in the summer period is winnowing, blowing, and mixing (in air) of soil and dust particles from the snow-free land surface.

The presence of powerful anthropogenic sources on the Kola Peninsula, which emit to the atmosphere such metals as nickel, copper, and other chemical elements, has stimulated, for many years, the neighbor-

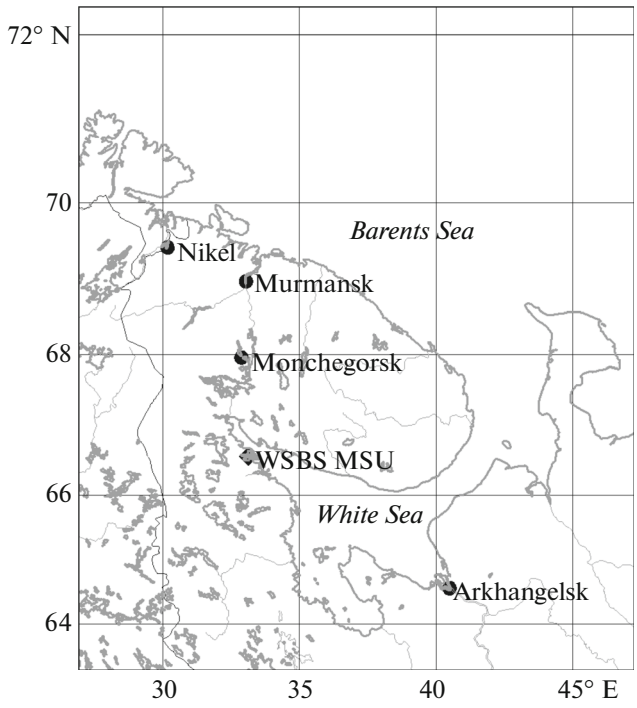

Fig. 1. Locations of aerosol sampling site.

ing European countries to monitor the composition of aerosol, atmospheric precipitation, and natural archives of aeolian matter, i.e., snow, moss, and other natural objects on the territories of these countries. Such studies were performed in Finland in regions near the border with Russia [12, 13]. The authors of work [14] analyzed the composition of precipitation and snow from data of the Murmansk and Arkhangelsk regional administrations of the Hydrometeorological service. Research into the composition of precipitation on the Kola Peninsula has been regularly performed by staff of the Kola Science Center, Russian Academy of Sciences, since the 1990s [15, 16]. Model estimates of the long-range transport of anthropogenic components from Russian sources to the territory of Karelia, the Kola Peninsula, and Arkhangelsk oblast were obtained in work [10].

In our work, we present the results of experimental measurements of concentrations of several chemical elements in aerosol in the vicinity of WSBS MSU, obtained during implementation of the White Sea System project (with academician A. P. Lisitsin as leader), and analysis of the origins of diverse components in different seasons.

MATERIALS AND METHODS

The study region was located near MSU WSBS (66°34′ N, 33°8′ E, Fig. 1), where aerosol samples have been collected since 2010 [17–20]. The territory of the stations adjoins the Kandalaksha nature reserve; the station is heated by electricity and, as such, can be thought to be unaffected by local pollution (the nearest mining and smelting complex, Severonikel, in Monchegorsk, is at a distance of about 150 km). Aerosol sampling is being performed at WSBS MSU year-round, interrupted only in the coldest winter months. In the present paper, we analyze aerosol particles less than 2.5 μm in size ($PM_{2.5}$), with one sample collected about once a week.

We analyzed 44 aerosol samples, collected on Whatman 41 filter paper in the following periods: June 18–August 24, 2013, September 26–December 2, 2013, and March 5–September 9, 2014. Aerosol filters were digested using a mixture of concentrated acids and examined for the concentrations of 15 elements by the method of inductively coupled plasma mass spectrometry (ICP-MS) using an Agilent 7500a instrument. Standard specimens of bottom sediments SDO-1 and SDO-2 were subject to the same procedures as aerosol specimens.

Data on aerosol chemical composition were complemented by the calculations of backward trajectories of air masses arriving to the sampling site [21] and by their statistical processing by the method described in [8].

RESULTS AND DISCUSSION

The entire aerosol sampling period was divided into specific conventional seasons (Table 1): one snow-covered (sn) period, when the effect of terrigenous sources (dust, soil) is minimal, and two snow-free (sf13 in 2013 and sf14 in 2014) periods, when the effects of both anthropogenic and terrigenous sources are distinctly manifested. The boundaries between snow-covered and snow-free periods were assumed to be average dates of the beginning and end of the climatic winter for the given terrain (mid-October and mid-April) [22].

We note that open-cast mines and rock debris at ore-mining locations are anthropogenic sources of terrigenous material, supplied by the sources year-round. Analysis of these sources and certain estimates of iron and aluminium amounts emitted from the Kostomuksha industrial complex were presented in work [10].

Trans-boundary atmospheric transport also brings aerosol to the observation site. This channel supplies anthropogenic and terrigenous aerosol which, in the study materials, can be extracted and estimated neither in total nor by parts. Lead and cadmium fluxes from anthropogenic and terrigenous sources for the study area were estimated crudely in work [23].

The concentrations of trace elements in WSBS MSU aerosols show strong time variations. We can identify episodes with a simultaneous increase or decrease in concentrations of almost all elements, interpretable as periods of strengthening or weakening of the dust load. Certain groups of elements (such as

Table 1. Average concentrations of trace elements in air (aerosol $PM_{2.5}$); standard deviations of concentrations for three identified conventional seasons are given in parentheses, ng/m^3

Period	V	Ni	Cu	Ga	Rb	Sr	Cd	La	Ce	Nd	Pb
sf13	0.13 (0.08)	0.78 (1.14)	0.86 (1.00)	0.014 (0.009)	0.043 (0.022)	0.16 (0.08)	0.010 (0.005)	0.012 (0.010)	0.027 (0.023)	0.009 (0.007)	0.35 (0.20)
sn	0.27 (0.13)	0.45 (0.17)	0.42 (0.26)	0.006 (0.003)	0.016 (0.011)	0.09 (0.06)	0.008 (0.005)	0.007 (0.004)	0.015 (0.006)	0.002 (0.002)	0.34 (0.18)
sf14	0.18 (0.10)	0.79 (0.77)	0.79 (0.92)	0.009 (0.010)	0.058 (0.094)	0.30 (0.48)	0.026 (0.046)	0.015 (0.017)	0.034 (0.032)	0.010 (0.010)	0.48 (0.21)

copper and nickel) are characterized by the presence of specific maxima.

For a further analysis, we selected 11 trace elements for which the most reliable and comprehensive (no less than 70% of samples) results were obtained (Fig. 2). Average concentrations of elements in air in different seasons and their standard deviations are presented in Table 1. The largest dispersion of the measured values from one sample to another (up to 100% and larger) is characteristic for snow-free seasons when dust component plays an important role in determining the aerosol composition. Authors of work [24], in which summertime aerosol $PM_{2.5}$ in the forested area of Finland was studied, estimated the content of terrigenous material in this fraction at 3%. However, this is an average value, and the dispersion of the content of terrigenous dust in fine fractions may be considerable.

Seasonal differences in the directions of air mass input to the study region are shown in Fig. 3. It can be clearly seen that the snow-covered period differs from both snow-free seasons by the predominance of air transport from western directions. The main difference in distributions between two snow-free seasons is a marked predominance of northern and northeastern directions, with the corresponding decrease in the frequency of transports from western rhumbs, in 2014 (as compared to 2013). Most rarely throughout the observation period, air was supplied from the southern direction to the observation site.

Figure 4 presents the average distributions of transport directions, characteristic for groups of elements either of different origins or coming from different sources (natural or anthropogenic). The calculations took into account weighted average concentrations of elements in accordance with air mass transport directions for each aerosol sample. As a result, we created five groups of trace elements, the atmospheric transport of which to WSBS MSU has specific features: V, Ni, and Cu arrive most often from north; two groups comprise elements predominately natural in origin, i.e., Nd, La, Ga (wide distribution, elongated in direction from southwest to northeast), and Rb and Sr (a smaller percentage from the northeastern direction of transport and a larger fraction from the western direction); and anthropogenic groups Pb–V–Bi and Cd, for which southwestern and western directions predominate, respectively.

These results indicate the reason for the possible in-phase variations in the concentrations of elements

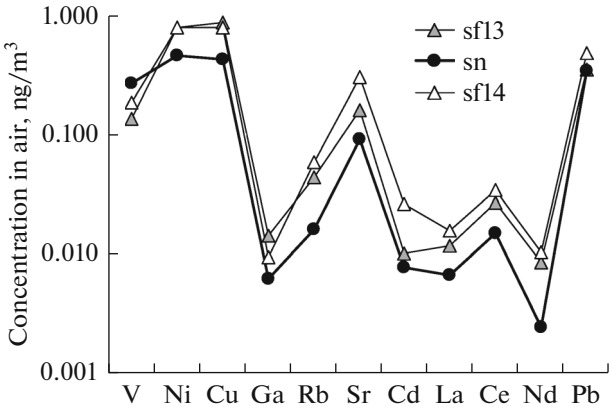

Fig. 2. Profiles of concentrations of trace elements for three conventional seasons.

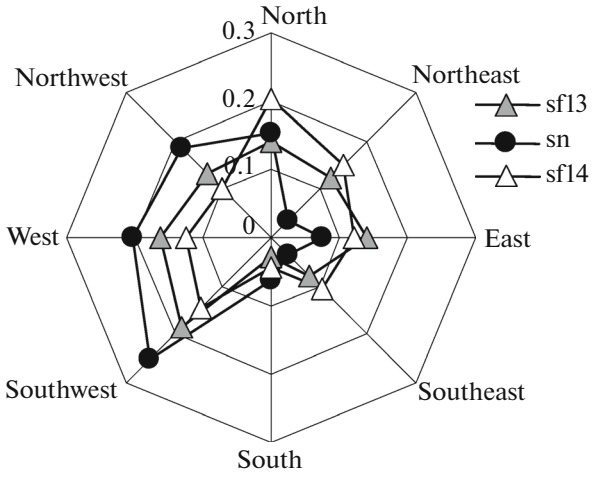

Fig. 3. Average distributions of the frequency of occurrence of air mass transport over the sides of horizon for the identified seasons. Figures indicate fractions of the total number.

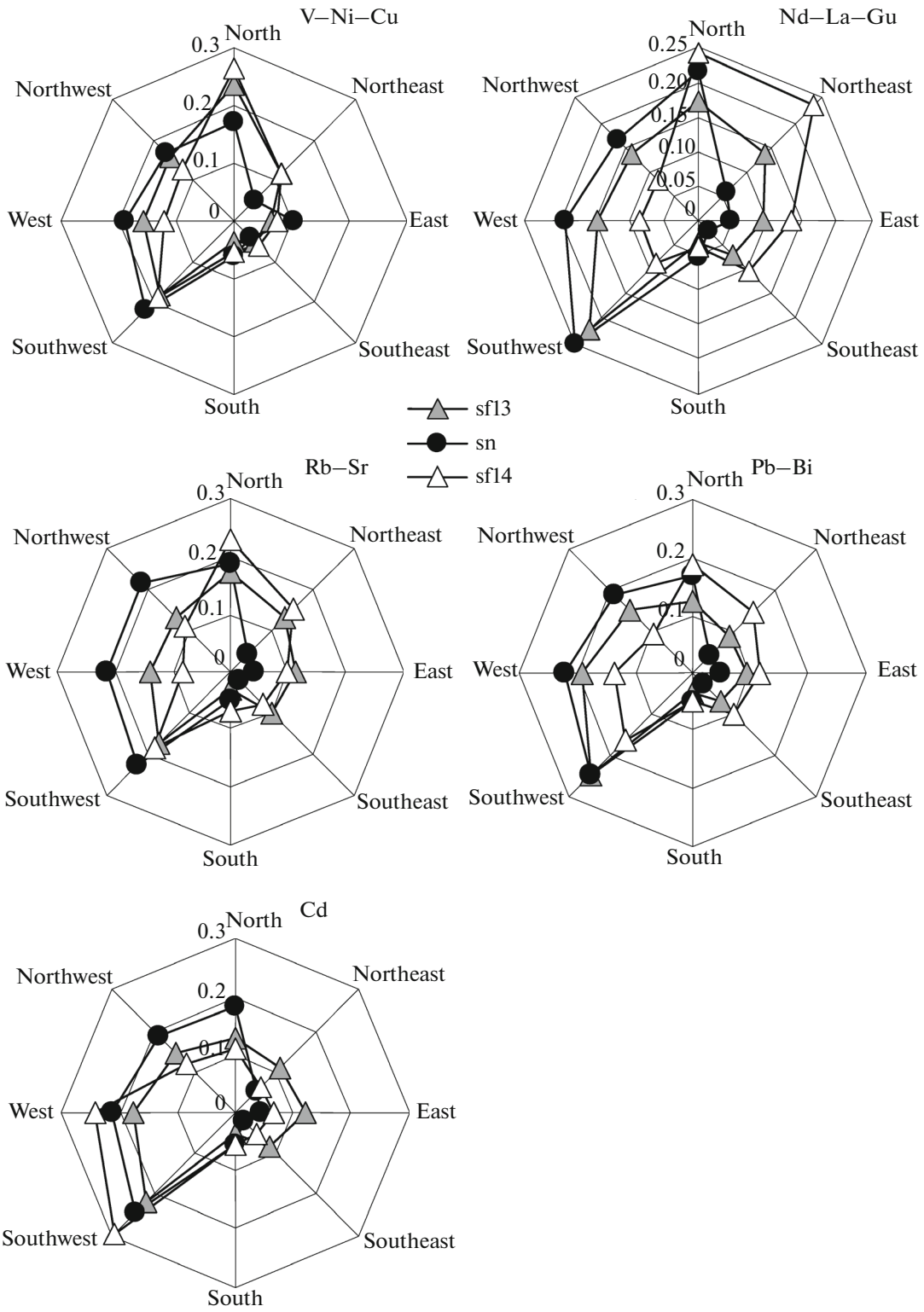

Fig. 4. Average distributions of transport directions of different trace elements.

in one group, associated with the spatially common character of atmospheric transport. However, based on these results, we cannot identify a common source of these elements, except for nickel and copper, powerful anthropogenic sources of which are located at a relatively short distance, i.e., on the Kola Peninsula, which determines the main directions of supply of these elements and their main source. However, for

Table 2. Average concentrations of trace elements in air, measured in polar and subpolar regions, ng/m^3

Sampling site	Period	V	Ni	Cu	Cd	Pb
Northern Finland (Sevettijärvi) [13]	Summer 1997		2	1.9		
Western Finland (Kalajoki) [12]	Summer 2007	0.74	0.54	0.52	0.048	1.58
Southern Finland (Ähtäri) [12]	2007	0.71	0.41	0.56	0.074	1.67
Barents Sea [6]	July 2001		0.3	3.8	0.023	0.13
White Sea [6]	July 2001		0.4	7.6	0.02	0.12

these elements we also know nothing about the fractions of material of terrigenous origin, both in snow-free seasons and in the snow-covered one.

Correlation analysis with clustering of variables makes it possible to identify three groups of elements, characterized by significant correlations inside groups, which can be interpreted as a geochemical affinity, common origin, or similar transport mechanisms. (1) Maximal correlations in the total sample or in individual seasons are characteristic for La and Nd, probably explained by their membership in the group of rare-earth elements (REEs). Sr adjoins the La–Nd group. We associated this group with terrigenous material, subject to the effect of local dust in many respects. (2) A high (0.72) correlation is also found between Ni and Cu, which are adjoined by V, having, though a lower, but significant correlation coefficient with the former. This group is associated with the activity of metallurgic plants in Murmansk oblast. (3) The Ga–Rb group is associated with long-range transport because these elements adhere to the pelitic fraction. The element Pb correlates significantly with this group. In turn, Cd has nearly the same correlation coefficients with groups (2) and (3). This tendency toward different groups corresponds well to the isolation of directional pattern of supply of this element (Fig. 4), having similar features to the arrival patterns of both Pb/Rb (with a prevailing southwesterly direction), and Ni/Cu (the northern direction is very important for Cd, but only in the snow-covered season).

The grouping of elements differs slightly among individual seasons. The Ni–Cu–V group is unchanged for all seasons. All the other elements join the second group in the snow-covered period. It is clear why the concentrations of predominantly terrigenous elements Ga, Rb, Sr, La, and Nd correlate. In snow-covered periods, the anthropogenic elements (Pb, Cd, Bi) join this group because all of them are associated with long-range transport or nearest mine openings and tailing dumps in this period. Division of elements into groups in snow-free periods, generally, corresponds well to the grouping carried out for the total sample.

We note that the total number of samples is small, and samples divided into seasons are even fewer; therefore, the conclusions about the origin of trace elements can be regarded just as preliminary, even though they do not contradict qualitatively the general understanding and publications of other authors. If these data are confirmed by further observations, conclusions can be drawn about the predominant transport of different trace elements to the WSBS MSU region under different synoptic conditions.

Table 2 presents the results of other works, in which the concentrations of the above-mentioned trace elements in air and snow were measured on territories nearest to Kandalaksha bay of the White Sea.

The maximal concentrations of nickel and copper in the WSBS MSU region throughout the observations as part of this research had been 4.0 and 3.4 ng/m^3 respectively. The concentrations of these elements, measured in northern Finland, reached 10 ng/m^3 when air masses were transported from the direction of Nikel settlement [13]. Thus, the results agree reasonably well, especially considering that only fine-mode aerosols $PM_{2.5}$ participate in our analysis and the period of collection of each sample far exceeds the time of existence of the same synoptic situation with any characteristic direction of air mass transport.

CONCLUSIONS

The main results of the work are as follows: (1) we measured concentrations of 11 trace elements in the atmospheric aerosol $PM_{2.5}$, (2) calculated their dispersion, and (3) determined time variations in snow-covered and snow-free seasons of the year. Higher concentrations of most elements in snow-free period of the year indicate an important effect of environmental pollution during dispersal of dust and soil particles. Study of these characteristics in the WSBS MSU region, considered as a background area, give an idea of the state of the environment in this region, which is important for the different activities of nature conservation organizations.

Analysis of directions of transport of air masses and aerosol admixtures to the observation site gives information on the specific features of atmospheric circulation and the relation of these processes to the level of anthropogenic pollution of the air and the ground. The conclusions about the origin of trace elements can be considered only preliminary; however, they do not contradict qualitatively the general understanding and data of other authors. If these results are confirmed by further observations, more justified conclusions can

be drawn about predominant mode of transport of different trace elements to the MSU WSBS region under different synoptic conditions.

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