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## OPTICS OF CLUSTERS, AEROSOLS, AND HYDROSOLES

# Elemental Composition of Aerosols in the Near-Surface Air of Moscow: Seasonal Changes in 2019 and 2020

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**Abstract**—The seasonal changes in the elemental composition of surface aerosol in Moscow are considered in four data series: for summer and autumn 2019 and winter and spring 2020. The surface aerosol is significantly enriched with sulfur, heavy metals, and metalloids (Cu, Zn, Cd, Sb, Pb, Bi, etc.). The mass concentrations, mass percentages, and enrichment factors for different elements in aerosol particles are determined and compared for different seasons. The spatial distribution of elements in surface aerosol is not uniform through the city, which may be associated with the specificity of local sources, underlying surface, and wind regime in different regions of Moscow. The highest concentrations of a number of terrigenous and anthropogenic elements are revealed in the Central Administrative District of Moscow. The causes for seasonal variability in the elemental composition of surface aerosol in the Moscow megalopolis and possible sources of elements are discussed.

**Keywords:** atmosphere, aerosol, elemental composition, seasonal variability, mass concentration, percentage, enrichment factor, Moscow

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## INTRODUCTION

The elemental composition of aerosol particles is an important characteristic necessary for quantitative estimates of the aerosol role in the climate change and ecosystem state [1–3]. First, physicochemical and optical properties of atmospheric aerosols significantly depend on how chemical compounds are distributed in particles. Second, the elemental composition of aerosol serves as an indicator of different sources of atmospheric contamination, especially in large urban agglomerations. The soil and biomass burning are the main natural sources of primary urban aerosols; their principal anthropogenic sources are transport and industrial plants, including those of the fuel and energy complex. Secondary aerosols are formed as products of gas-phase and heterogeneous photochemical reactions in the atmosphere with the participation of water vapor, organic compounds, and different gaseous precursors ($NO_x$, $SO_x$ et al.) [1–3]. Therefore, in a large megalopolis, one can expect spatiotemporal variability of the elemental composition and particle size of the surface aerosol under the action of a combination of natural and man-induced factors.

At present, information on the elemental composition of surface aerosols in different regions of Russia is not systematized and episodic, which is due to the arduousness and expensiveness of analytical investigations of aerosol samples. One should mention a series of publications devoted to such investigations in the arid zones of Central Asia and the southern European part of Russia (EPR) [4–6], the Arctic [7], cities of Siberia [8–10], as well as in the Moscow region [11–16]. In addition, careful attention is paid to studying the elemental composition of solid particles of road dust in the Moscow megalopolis [17, 18].

This paper discusses new results of the study of spatiotemporal variability of the elemental composition of the aerosol in the surface layer of the atmosphere of the Moscow megalopolis. The results were obtained at the A.M. Obukhov Institute of Atmospheric Physics (IAP), Russian Academy of Sciences, within the intensive complex experiment on the study of the composition of the atmosphere in 2019–2020.

**Fig. 1.** Observation points in Moscow in 2019 and 2020.

## RESEARCH OBJECTS, METHODS, AND TOOLS

In this work, data obtained on the elemental composition of surface aerosol in Moscow within the intensive complex field investigations carried out in different seasons of 2019 and 2020 at IAP are considered. The observation periods lasted 5–7 weeks in every season: June 10–July 9, 2019; October 2–November 13, 2019; January 10–February 16, 2020; and March 25–May 4, 2020.

As the experimental points, megalopolis districts with different man-induced load were chosen (Fig. 1): point *1* was in the territory of IAP, in a densely built-up area in the administrative center of Moscow (Pyzhevskii per. 3); point *2* was in the living zone of a densely built-up area in the Central Administrative District of Moscow (Podsosenskii per. 18/5); points *3* (Moscow State University (MSU), zone 1M, Vorobyovy Gory) and *4* (ul. 26 Bakinskikh Komissarov 2, residential sector) were selected in the zone of moderately dense development and verdured landscapes in the Western Administrative District of Moscow.

In the course of the complex experiment, aerosol samples for the elemental and gravimetric analysis were collected on AFA analytical filters with the use of aspirating samplers. At point *1*, samples were taken for every 24 hours (from 09:00 to 09:00 of the next day); at points *2*–*4*, the sampling time was several days with allowance for the synoptic situation and meteorological conditions. The laboratory analysis of aerosol samples with the aim of determining the elemental composition was carried out using inductively coupled plasma mass spectrometry [19]. The elemental analysis of each sample was carried out without fractionation.

To estimate the selective accumulation of chemical elements in aerosol particles of the near-surface air layer in the Moscow megalopolis, as well as the sources of elements into aerosol, enrichment factors of elements relative to clarkes (mean content of elements in the Earth's crust) [7, 20, 21] were calculated:

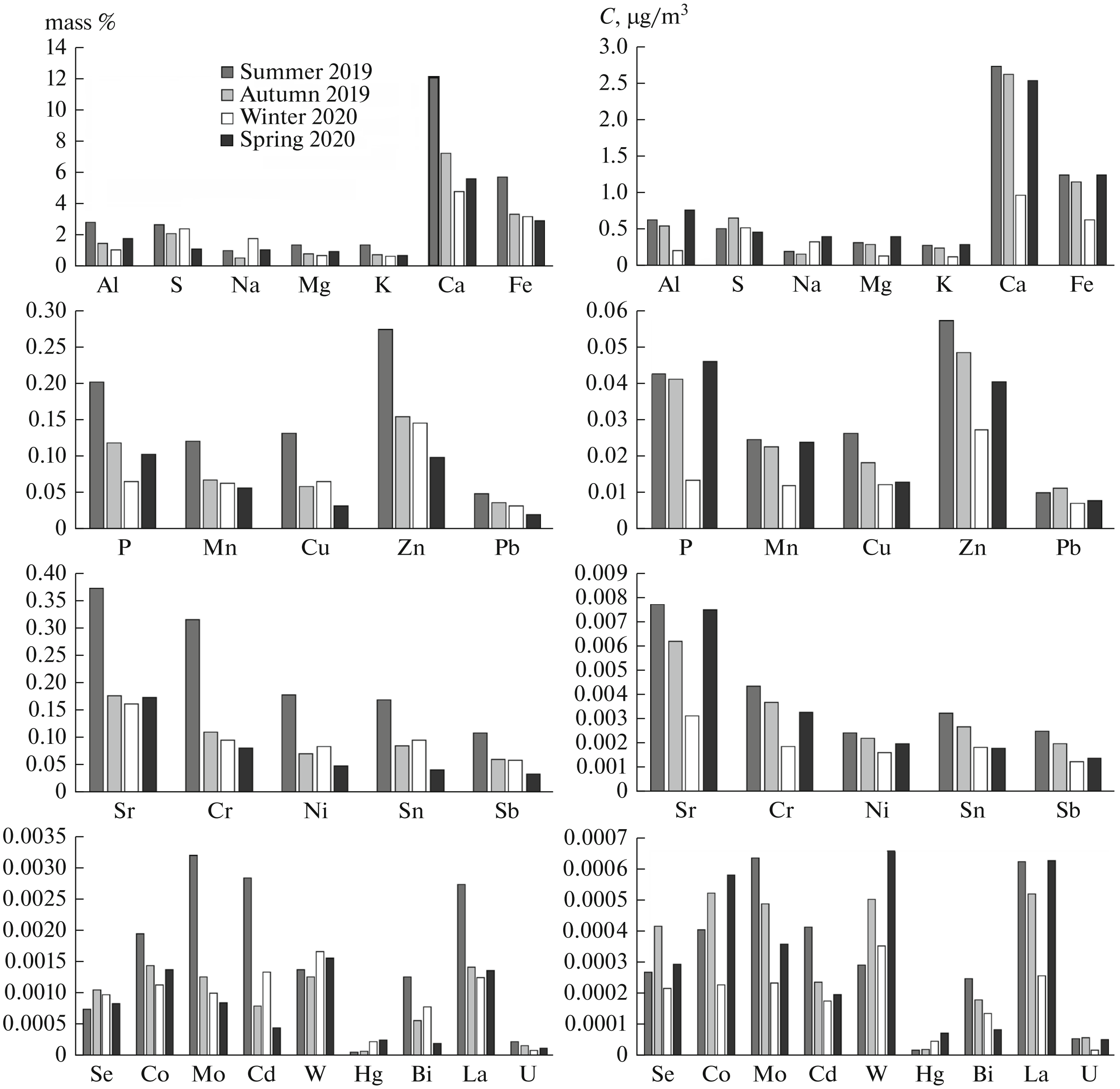

**Fig. 2.** Variations of the mass percentage composition and absolute values of mass concentration of chemical elements (arranged pairwise for similar elements) in surface aerosol.

$$\mathrm{EF} = \frac{(C_{\mathrm{e}}/C_{\mathrm{La}})_{\mathrm{sample}}}{(C_{\mathrm{e}}/C_{\mathrm{lan}})_{\mathrm{crust}}},$$

where $C_{\mathrm{e}}$ and $C_{\mathrm{La}}$ are the concentrations of the considered element and lanthanum (an element of terrigenous origin chosen as a reference element).

## RESULTS AND DISCUSSION

### *Elemental Composition: General Comments*

Based on results of the laboratory elemental analysis, 65 chemical elements (from Li to U) were determined in the composition of the aerosol samples. They all were classified in four groups depending on their origin and taking into account the enrichment factor [22]: globally distributed elements, heavy metals and metalloids of predominantly terrigenous or anthropogenic origin, and radioactive elements. For visual interpretation, 26 elements were selected from the abovementioned groups. They are characterized by most significant values of the mass concentration and enrichment factors and are tracers of urban aerosol sources.

Figure 2 presents diagrams of season average variations (mean values averaged over 35–40 aerosol samples) in the mass percentage composition of elements (mass %) (mass concentration of each element normalized to the total mass concentration of all elements identified in an aerosol sample) and absolute values of mass concentrations of elements accumulated in surface aerosol of Moscow. For convenience of representation, the elements are grouped depending on the order of magnitude of the mass concentration and mass percentage composition.

As seen from Fig. 2, values of mass concentration for globally distributed elements Al, S, Na, Mg, K, Ca, and Fe are highest in the absolute value; Al is mostly treated as of mineral origin; Na, Mg, K, and Ca, as of marine origin; Fe is classified as a heavy metal of terrigenous nature [1]; S stands apart in this series because it has many natural and man-induced sources and, as shown by investigations in different regions of the ETR, e.g., [5, 6, 14], is characterized almost everywhere by a higher content. The lowest values of mass concentration were revealed for a series of heavy metals (Cr, Co, Ni, Mo, Cd, W, Hg, and Pb), metalloids (Bi, Sb, and Sn), and radioactive elements. Minimal mass concentrations of almost all considered elements are observed in the winter period, which is related to a considerable extent to the decrease in the intensity of natural sources in cold months. Maximal mass concentrations of a series of globally distributed elements, some heavy metals, and metalloids were revealed in warm months (in spring and summer), which indirectly indicates the mixed nature of these elements and aggregate contribution of different technology-related and terrigenous sources to their emissions.

### *Enrichment Factors: On the Nature of Element Origin in Surface Aerosol of Moscow*

It is known [1, 7] that the origin of elements in the composition of surface aerosols, i.e., the degree of lithogenic/man-induced impact on the elemental composition of atmospheric aerosol in the near-surface layer, is determined by the enrichment factor EF. If $EF \leq 10$, the origin of element can be treated as predominantly natural. When $EF > 10$, the presence of elements in the atmosphere can be caused by several factors:

—significant value of other sources (of man-induced origin or the ocean) on concentrations of corresponding elements in atmospheric aerosol;

—secondary aerosol transformations of different kinds in the atmosphere;

—fractionation of aerosol particles along the path of air mass transport.

Figure 3 presents the enrichment factors of elements in the composition of surface aerosol in Moscow according to observations at IAP in different seasons of 2019–2020. The values of the enrichment factors are averaged over each season. All the elements are divided into two groups depending on the order of magnitude of the enrichment factor ($EF \leq 10$ and $EF > 10$), which makes it possible to estimate their origin: terrigenous or anthropogenic.

As seen from Fig. 3, elements of anthropogenic origin in the composition of surface aerosols of the Moscow megalopolis include heavy metals and metalloids (Cu, Zn, Mo, Cd, Sn, Sb, W, Hg, Pb, Bi), as well as sulfur. Sulfur is an indicator of sulfate aerosols forming in atmospheric oxidation processes. Sulfur-containing aerosols are as a rule nano- and submicron particles, long-lived and subjected to chemical transformation and long-range transport. Such particles are the most dangerous for human life and activities and take an active part in climate-forming processes [2, 3]. The higher concentration of sulfur in the atmosphere of the Moscow region is related, in particular, to such sources as vehicle exhaust gases and products of industrial fuel and natural gas combustion. First results of our study of the elemental composition in terms of fractions of aerosol particles [15] demonstrate that sulfur is mainly concentrated on small aerosol particles of the $PM_{2.5}$ fraction. As mentioned above, a higher content of sulfur is typical for surface aerosol of different ETR regions (both urbanized and background ones), which is caused by physicochemical properties of sulfur-containing aerosol particles and widespread occurrence of numerous sulfur sources.

The anthropogenic origin of the majority of heavy metals and metalloids in surface aerosol in Moscow is predominantly related to the main urban source—motor transport, as well as its maintenance and production. In particular, it is known [17, 18] that vehicle exhaust gases contain Cu and Pb and engine oil contains Mo, Zn, Cu, Pb, and Sb. Scuffing of tires serves a source of Cd, Zn, Pb, Cu, and Sb, and brake pad wear favors the Cu, Sb, Zn, and Pb emission. In addition, antifriction Sn- and Pb-based alloys are used in the production of bearings; their composition also includes Sb, Cu, and Cd.

It should be noted that first results of the comparative analysis of the elemental composition of surface aerosol and road dust in Moscow show a significant correlation between the heavy metals and metalloids considered above and reveal a larger degree of accumulation of these elements in surface aerosol as compared to road dust [15].

The majority of globally distributed elements (P, Al, Na, Mg, K, and Ca) gets into the near-surface layer of the Moscow atmosphere from natural sources of mineral and marine origin. Most often, these elements (with the exception of phosphorus) are concentrated in the coarse, micron fraction of particles [15].

The main contribution to enrichment of surface aerosol in Moscow with some heavy metals (Cr, Mn, Fe, Co, Ni) is also made by terrigenous sources. However, the origin of heavy metals in surface aerosol under conditions of the megalopolis is of mixed (natural-anthropogenic) character. The specific contribution of different highly intense local sources concentrated in the urban area is very hard to determine. However, one can indirectly determine the nature of

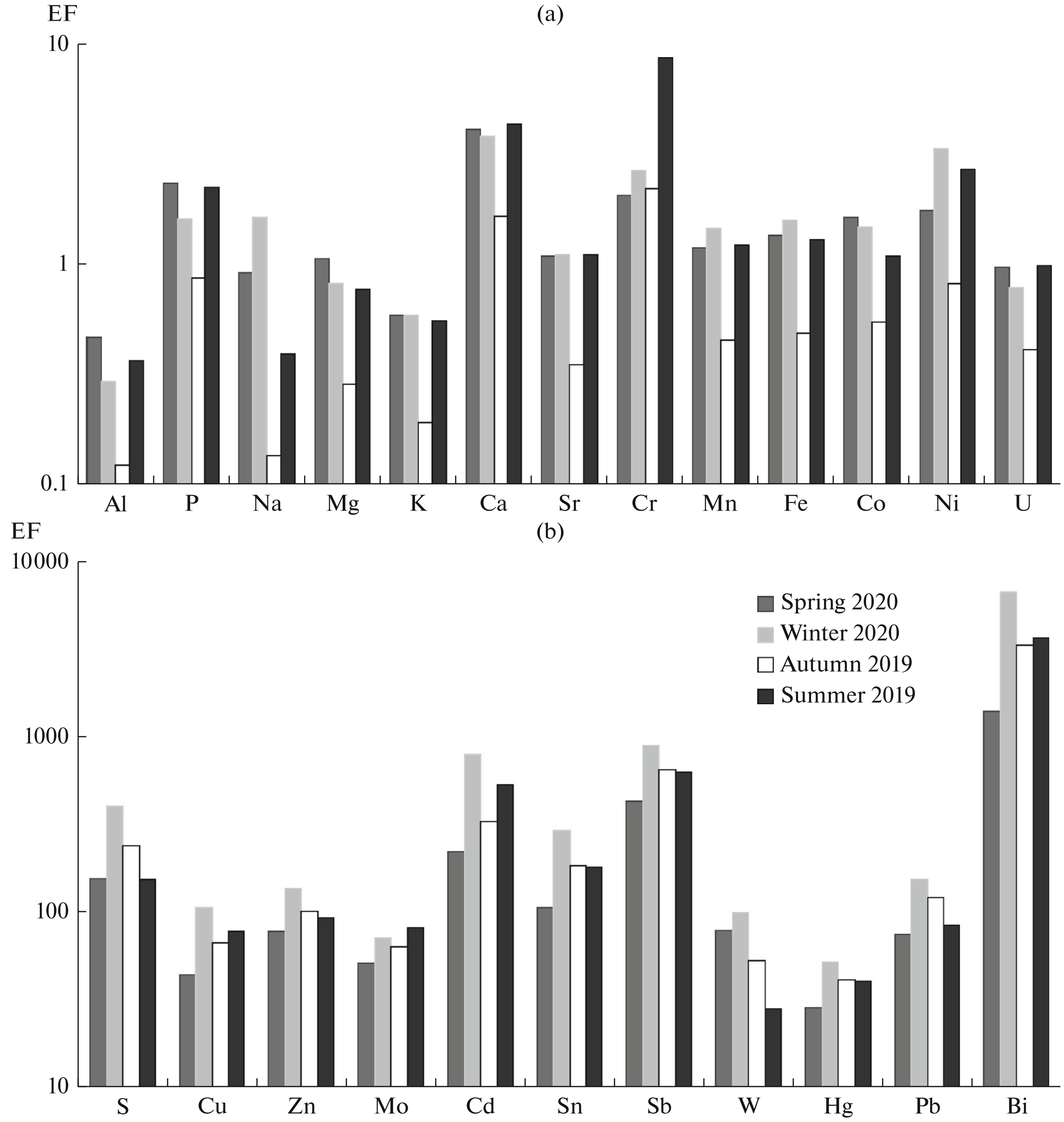

**Fig. 3.** Variations in the enrichment factor in surface aerosol for elements of (a) terrigenous and (b) anthropogenic origin.

elements in the surface aerosol composition in Moscow based on combined features of seasonal variability of such elemental composition characteristics as mass concentration, percentage, and enrichment factors of elements.

### *Features of Spatiotemporal Variability of the Elemental Composition*

Figure 4 shows diagrams of seasonal variability (in relative units) of elemental composition characteristics of surface aerosol in Moscow during the period of observations (from summer 2019 to spring 2020). Winter 2020, which was characterized by the least concentrations of almost all considered elements as compared to other seasons, was taken as the reference period. To interpret seasonal changes, the ratios $(n_i - n_{\text{winter}})/n_{\text{winter}}$ were calculated. Here, $i$ is spring, summer, or autumn, and $n$ is a characteristic (mass concentration, percentage, or enrichment factor).

As seen from the diagrams, the character of their seasonal variation is different. In particular, the relative content of most of the considered elements takes the highest values in summer 2019; in spring, the mass percentage composition of almost all heavy metals and

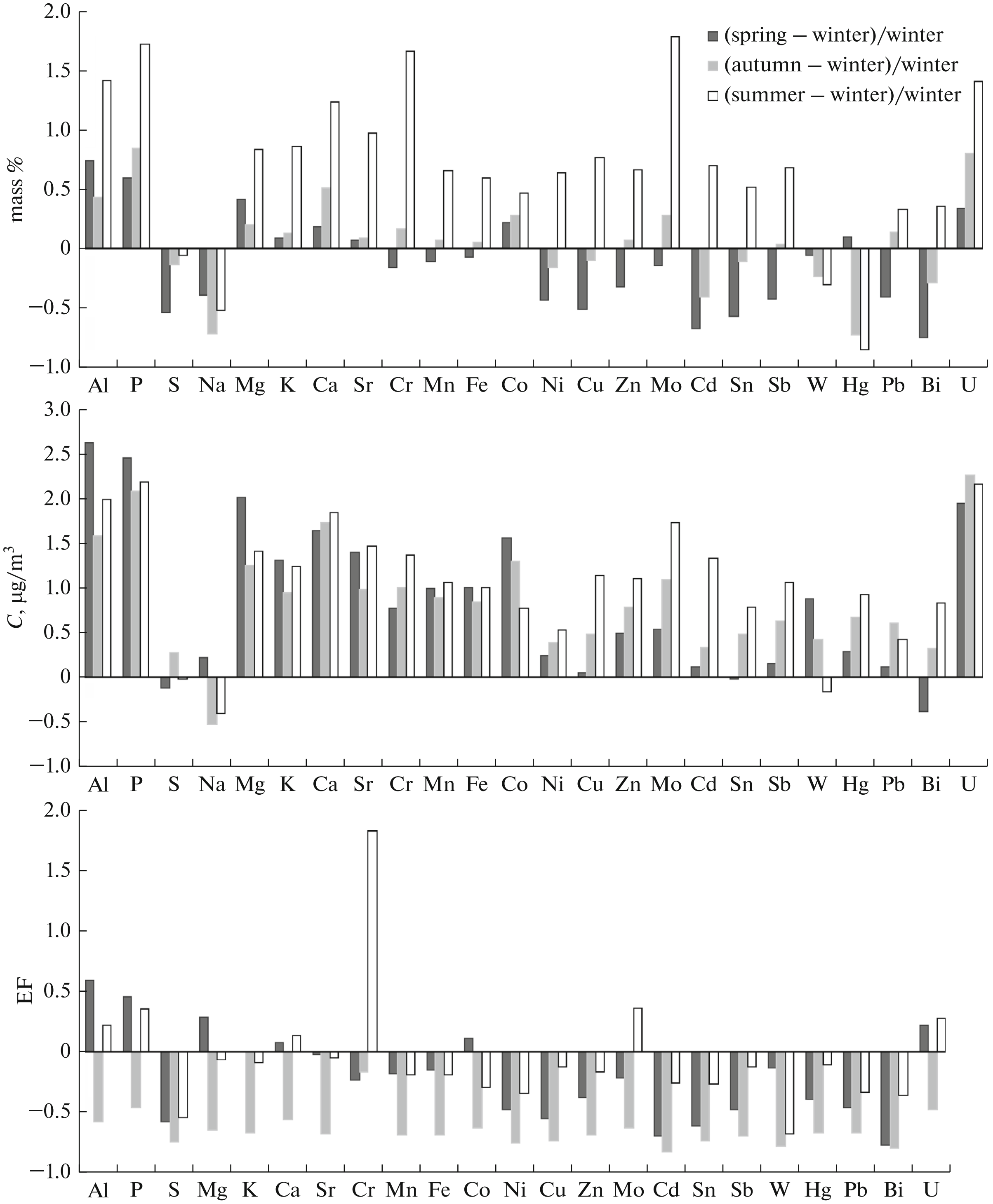

**Fig. 4.** Seasonal variability of some characteristics of the elemental composition of surface aerosol according to IAP observation data in 2019–2020.

sulfur is minimal. The mass concentrations of globally distributed elements (mainly of natural origin) were maximal in spring 2020; mass concentrations of almost all heavy metals, in summer 2019, which is apparently related to an increase in the contribution of natural sources. In winter 2020, enrichment factors of most elements of anthropogenic origin were maximal, which is explained by an increase in the intensity of some of the main local anthropogenic sources (enterprises of fuel and energy industry, community facilities, and exhausts of motor transport) in cold months. For terrigenous (globally distributed) ele-

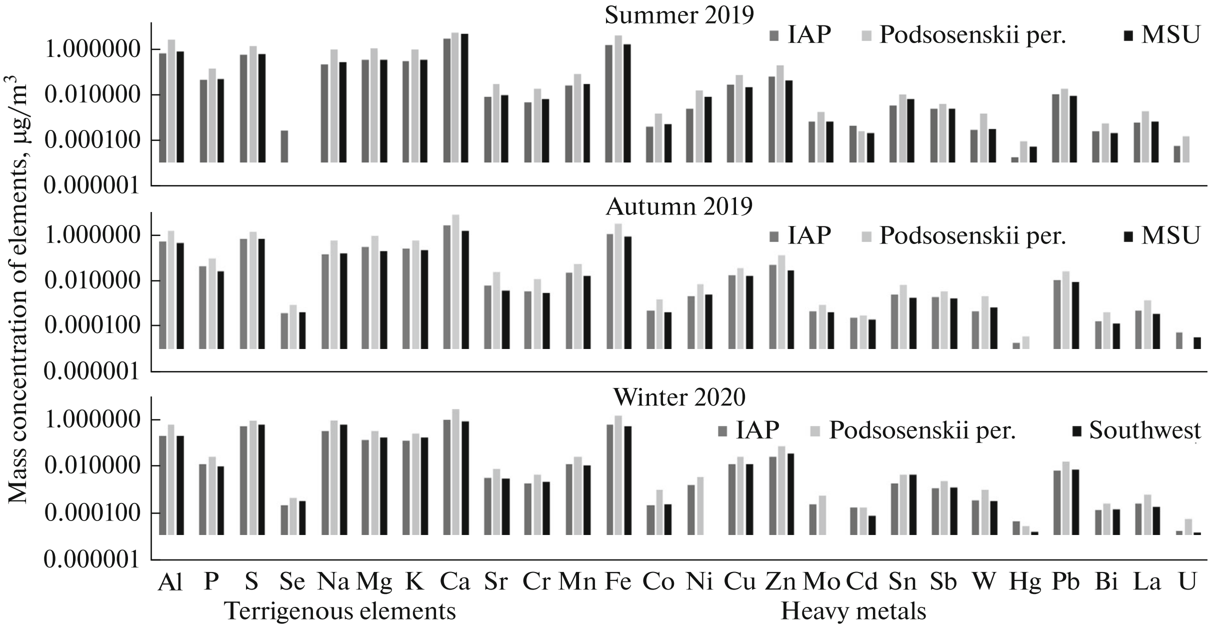

**Fig. 5.** Spatial variability of the mass concentration of elements in surface aerosol according to observation data at different points in Moscow in 2019–2020.

ments, the seasonal variations (with the exception of autumn) in the enrichment factors are weak.

The first results have been obtained on the spatial distribution of the elemental composition of surface aerosol in Moscow districts with different anthropogenic load and degree of greening. Figure 5 presents diagrams of spatial variability of the elemental composition of surface aerosol in Moscow depending on the season. It is seen that the distribution of elements in surface aerosol in different districts of Moscow is nonuniform, which is related to the specificity of local sources, particularities of the underlying surface, and wind regime in different districts. In our experiment, the highest values of mass concentration of both heavy metals and elements of terrigenous origin were revealed in the Central Administrative District (Podsosenskii per.), in the densely built-up area, and near highways with moderate and high transport loads, in cold and warm months.

Contrary to the expectations, concentration of some heavy metals in the area of moderate built-up and planted landscapes (Vorobyovy Gory, Moscow State University) turned out to be rather high (comparable with the administrative zone of dense development of the city center, IAP) and increased in winter.

In general, the spatiotemporal variability of different characteristics of the elemental composition is of complex ambiguous character and requires a more detailed and long-term study of the whole combination of factors having an effect on the composition of urban surface aerosol, including the allowance for meteorological and synoptic conditions.

## CONCLUSIONS

The first results of the study of spatiotemporal variations in elemental composition characteristics of surface aerosol in Moscow made it possible to reveal significant values of the mass concentration of some terrigenous elements, heavy metals, and sulfur. In winter, the lowest values of their concentration are found. However, the aerosol enrichment factors for such heavy metals and metalloids as Cu, Zn, Mo, Cd, Sn, Sb, W, Hg, Pb, and Bi, reach the highest values in winter, which indicates an increase in the contribution of anthropogenic sources (enterprises of fuel and energy industry and transport) to enrichment of surface aerosol in cold months. For terrigenous elements, the absolute values of enrichment factors and their seasonal variations are low.

The distribution of elements in surface aerosol in different regions of Moscow is not uniform, which is related to the specificity of local sources, features of the underlying surface, and wind regime in different districts of the megalopolis. In particular, the highest absolute values of concentrations of terrigenous and some anthropogenic elements are observed in summer, which indicates an increase in the total contribution of natural and anthropogenic sources to atmospheric contamination in warm months.

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## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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