
OPTICS OF CLUSTERS,
AEROSOLS, AND HYDROSOLES

Analysis of the Content of Chemical Elements in Aerosols Using Data from Passive Sampling at Fonovaya Observatory

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Abstract—Data from passive sampling are used to compare the chemical compositions of water- and acid-soluble forms of aerosols in background forested regions during autumn, winter, and spring periods. We calculated the coefficients of aerosol accumulation and absolute values of aerosol enrichment, and analyzed back trajectories. Seasonal changes in the chemical composition of aerosol fractions are shown, and the presence of elements indicating the activity of thermal power plants is noted.

Keywords: aerosol, dry depositions, passive sampling, back trajectories

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INTRODUCTION

The anthropogenic load on the environment is currently rapidly increasing and the scales of anthropogenic activity are becoming comparable to those of natural processes. This is accompanied by technogenic pollution of natural systems, with the most dangerous consequence being ever-growing atmospheric pollution. By virtue of this, studying the dynamics of regional changes in the chemical composition of aerosols in the near-surface atmosphere is one of the priority tasks. The control over the content of organic and inorganic substances in the near-surface air with the purpose of estimating the quality of environmental components (atmosphere, hydrosphere, soil, and biota) is a very important current problem. In this regard, there is a need for a qualitative assessment of the state of atmospheric air, including monitoring studies [1–3].

Much of the current effort is concentrated on the development of reliable and, at the same time, maximally simple and accessible methods for collecting and preparing aerosol samples. Active methods envisage collecting a great number of samples at a given location, which is expensive and time consuming.

A well-known active method of aerosol sampling incorporates deposition of dry aerosols on multilayer filters by pumping the airflow (via aspiration) through filters using special ventilation installations (aspirators) [4, 5]. A disadvantage of the aspiration method is that the data obtained show aerosol content in the pumped air volume, which characterizes air pollution from the hygienic rather than ecologic point of view.

Recently, scientists have shown increasing interest in the method of passive sampling, based on molecular diffusion of the pollutant from object analyzed to sorbent, which is a specially prepared substrate with a selective chemical reactant [6, 7]. However, as practical applications showed, in order to be used in ecological studies, a passive sampler should be preliminarily calibrated [8, 9], including laboratory and field tests. It is noteworthy that the exposure time is limited by the capacity of the chemical reactant.

The passive method of collecting dry aerosols with the use of chemically inert sorbents consists in separation of the deposition process of dry aerosol particles with extraction for a subsequent chemical analysis of those whose deposition is determined by turbulent diffusion (their sizes are 0.01–10.0 μm). The interaction between these particles in airflow and with the substrate surface of substrate are determined by the van der Waals forces; therefore, molded fine-fiber plates with a microporous structure and large-area active surface were used as a depositing substrate. The deposition process is also activated by design features of the sampler. For instance, due to the differences in the specific heats between materials of the depositing substrate and the device, exposure to solar radiation causes a temperature gradient in the inner volume of the device accompanied by the formation of convective and turbulent airflows over the substrate. Inside the device, this causes a high probability of diffuse and turbulent deposition of dry aerosols from the boundary layer onto the sorbent surface.

Table 1. Coefficients of aerosol accumulation of elements for water and acid extracts

Chemical element	Extract						Chemical element	Extract					
	water-soluble			acid-soluble				water-soluble			acid-soluble		
	Fall	Winter	Spring	Fall	Winter	Spring		Fall	Winter	Spring	Fall	Winter	Spring
Li	1.15	0.57	0.62	1.15	0.64	0.93	Ag	0.80	0.28	2.75	0.41	0.60	1.22
Be	1.00	1.00	1.25	1.00	1.00	1.03	Cd	2.30	12.35	15.91	2.70	11.32	21.13
Na	1.42	1.06	1.01	1.42	1.67	2.21	In	29.47	10.00	50.00	1.00	0.22	1.12
Mg	2.28	5.26	4.62	1.21	1.86	2.35	Sn	0.95	0.94	1.08	1.99	4.89	1.70
Al	3.58	65.24	39.28	1.74	8.07	8.02	Sb	1.28	2.95	3.82	1.87	20.76	9.32
Si	1.09	2.13	1.21	0.96	0.09	0.14	Cs	2.48	8.36	6.79	2.17	3.53	6.24
P	1.39	1.07	1.65	1.19	0.51	1.28	Ba	2.59	17.10	16.31	1.43	5.45	6.80
K	1.59	1.42	1.67	1.31	0.87	1.45	La	3.23	12.85	15.44	2.17	5.36	5.97
Ca	2.54	3.71	3.07	1.18	1.12	1.30	Ce	6.69	21.53	27.18	1.89	3.73	4.20
Sc	2.38	2.08	5.57	1.00	1.00	10.00	Pr	4.10	13.77	15.32	1.57	4.89	5.75
Ti	1.52	0.56	0.69	2.05	1.40	1.88	Nd	3.74	8.42	12.64	1.67	4.80	6.39
V	1.14	1.04	1.30	1.48	1.09	2.05	Sm	3.67	10.04	10.55	1.17	4.04	4.46
Cr	1.87	1.32	2.00	1.11	0.37	0.51	Eu	2.61	8.86	14.80	1.56	4.67	5.26
Mn	2.57	16.67	13.96	1.01	3.45	3.97	Gd	5.07	11.06	14.43	1.62	4.62	5.91
Fe	3.13	7.20	6.76	1.23	1.63	2.14	Tb	2.45	5.97	9.50	1.59	4.16	4.72
Co	4.04	2.94	3.97	1.63	1.34	2.32	Dy	4.65	10.51	13.79	1.47	2.95	4.07
Ni	2.19	1.28	2.38	6.47	5.62	3.33	Ho	3.44	5.14	8.62	1.44	2.41	3.27
Cu	3.47	1.61	1.83	1.55	0.55	0.75	Er	2.51	1.85	3.90	1.71	2.31	3.25
Zn	15.62	68.26	125.16	4.32	11.44	41.41	Tm	1.00	2.38	2.75	1.70	1.71	2.21
Ga	1.20	8.46	7.98	2.01	4.06	5.77	Yb	6.69	5.87	11.11	1.56	2.02	2.88
Ge	1.71	0.44	0.08	4.44	6.12	0.53	Lu	0.97	0.98	1.07	0.97	1.28	1.70
As	1.80	5.64	3.27	2.07	4.29	4.86	Hf	3.53	1.58	2.56	2.07	0.66	0.47
Se	10.48	187.12	24.93	6.55	22.39	5.44	Ta	1.09	0.65	2.28	1.14	0.20	0.40
Rb	1.51	1.34	1.96	1.35	1.14	2.21	W	0.52	0.03	0.18	3.53	0.62	0.42
Sr	2.38	1.54	1.55	1.12	0.52	0.70	Tl	2.69	9.98	8.28	2.08	7.54	7.97
Y	4.04	5.45	8.51	1.44	2.35	3.21	Pb	0.93	1.85	1.03	3.18	5.07	5.42
Zr	3.90	2.09	2.96	2.13	0.76	0.36	Bi	9.52	4.42	3.17	16.89	4.98	0.97
Nb	1.36	1.02	1.40	1.80	0.76	0.90	Th	3.27	6.84	8.47	2.73	3.24	1.91
Mo	1.11	0.14	0.65	1.12	0.45	1.90	U	2.89	3.64	4.85	1.37	1.62	2.00

This method of passive aerosol sampling makes it possible to organize in a new way the aerosol air pollution monitoring in remote and hard-to-reach regions. The device is simple in construction, cheap in fabrication, and, as such, makes it possible to organize simultaneous observations of the dynamics of variations in the geochemical background under different landscape conditions and over a large area, which, in contrast to existing methods, improves the quality of research into the atmospheric cycle of migration of chemical elements.

In this paper, we considered the observations of seasonal variations in the elemental composition of dry aerosol deposits that were collected by the method of passive sampling. This work is a continuation of earlier studies at the Fonovaya Observatory [10].

METHOD OF STUDY

In fall 2016, based at the Fonovaya Observatory, V.E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences (60 km west of Tomsk), a site was created for the passive collection of

aerosols using special devices, namely, impulverators [11]. The installation comprised 160 impulverators with a sorbent inside, i.e., four paper filters of the “white strip” type. The aerosol material was sampled during three seasons: fall (from September 6 to November 8, 2016), winter (from November 8, 2016 to March 4, 2017), and spring (from March 4 to June 1, 2017). After being demounted, the filters were used to prepare water and acid extracts. The chemical analysis was performed by the method of inductively coupled plasma mass spectroscopy at the Chemical-Analytical Center “Plasma” (Tomsk). In addition, extracts from unexposed filters were prepared to estimate the effect of the filters. Results of analyzing the composition of dry aerosol deposits for the fall period were considered in [10].

The contents of elements may differ by orders of magnitude; therefore, in accordance with [11, 12], we calculated the coefficients of aerosol accumulation and absolute values of aerosol enrichment for each extract type by the formula

$$A_{\text{sol}} = c_i/C_i, \quad (1)$$

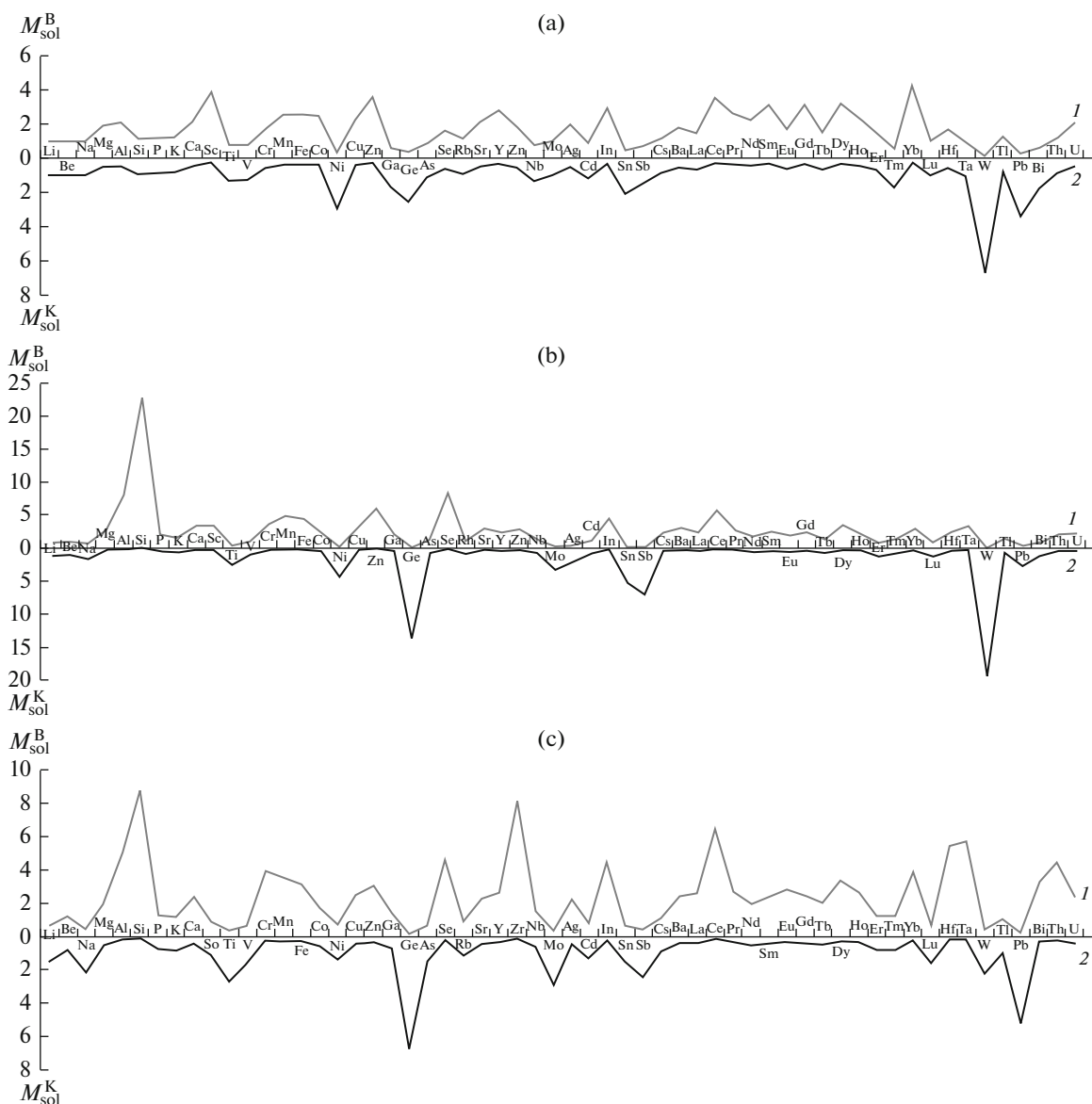


Fig. 1. Ratio of water- to acid-soluble fraction: (a) in fall; (b) in winter; and (c) in spring; water- (curve 1) and acid- (curve 2) soluble extracts.

where c_i is the content of the i th element in an exposed sample; C_i is the average content of this element in the standard (the chemical composition of clean filter is used as a standard).

The method of back trajectories was used to estimate the contribution of long-range transport to the total aerosol pollution of the territory [13]. The calculations were performed using the HYSPLIT model for the whole sampling period from September 6 to June 1 at altitudes of 500, 1000, and 1500 m for 72 h.

RESULTS

Coefficients of aerosol accumulation for elements in water and acid extracts (Table 1) showed that there are seasonal variations in the aerosol chemical compo-

sition in both extract types. It follows from Table 1 that certain chemical elements are equally actively accumulated in both acid- and water-soluble extracts; whereas differences in concentrations are more marked for other elements.

To compare seasonal accumulations of chemical elements in water and acid extracts [11] we calculated the modulus of aerosol accumulation, which allowed us to figure the quantitative measure of difference in metal accumulation between them (Fig. 1) on the basis of the equation:

$$\left(M_{\text{sol}}^{\text{B}} = \frac{A_{\text{sol}}^{\text{B}}}{A_{\text{sol}}^{\text{K}}} \right), \quad (1)$$

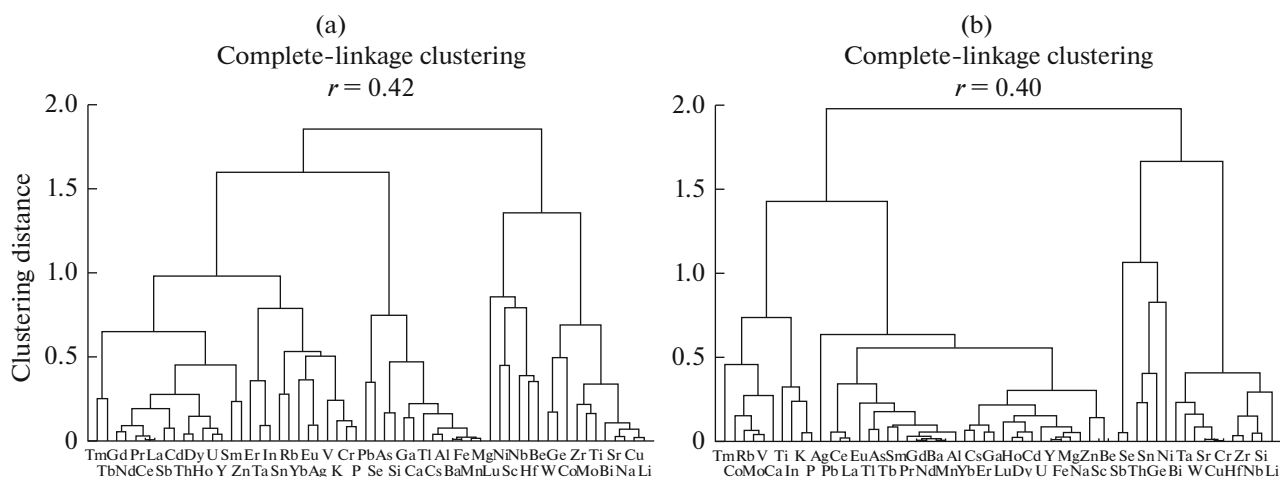


Fig. 2. Dendrogram of correlation matrices of geochemical spectra for 58 elements: (a) water- and (b) acid-soluble extracts.

where M is the modulus of aerosol enrichment of water/acid extracts; $A_{\text{sol}}^{\text{B}}$ is the coefficient of aerosol accumulation in the water extract; $A_{\text{sol}}^{\text{K}}$ is the coefficient of aerosol accumulation in the acid extract (in the figure, this parameter is plotted along the ordinate above the origin). If ratio (1) was smaller than unity, we used the reverse equation:

$$\left(M_{\text{sol}}^{\text{K}} = \frac{A_{\text{sol}}^{\text{K}}}{A_{\text{sol}}^{\text{B}}} \right), \quad (2)$$

(this parameter is plotted along the ordinate below the origin). This simplifies plotting and makes Fig. 1 clearer because parameters are always rendered to be larger than or equal to unity.

The analysis of Fig. 1 showed that enrichment in water extracts was maximal in absolute value for Ca, Sc, Mn, Fe, Co, Zn, Y, and In (a group of rare earth elements) in the fall; for Al, Si, Cu, Zn, In, and Ce in the winter; and for Al, Si, Ca, Cr, Mn, Fe, Co, Cu, Zn, Sr, Zr, In (a group of rare earth elements), Hf, and Ta in the spring.

The enrichment in acid extracts was maximal in absolute value for Ni, Ge, Sn, W, and Pb in the fall; for Ge, Sn, Sb, and W in the winter; and for Na, Ti, Ge, Mo, Sb, W, and Pb in the spring.

The presence of such elements as Rb, Cs, Sr, Ba, Tl, Y, Pr, Nd, Sm, Gd, Dy, Ho, Er, Yb, Ga, and Ge can be explained by activities of the coal-fueled thermal power plants in the Tomsk–Seversk industrial agglomeration.

From the comparison of water and acid extracts, it can be seen that the numerical values of the modulus of aerosol enrichment for most elements are larger in water extracts; they are maximal in acid extracts for such elements as Na, Li, Ni, Ge, and W. It should be noted that the content of chemical elements is larger in the water- than acid-soluble fraction for all seasons,

especially for spring (see Fig. 1). The causes for this are not quite clear and require an additional study.

For data processing in the STATISTICA software package, we grouped together samples of water and acid extracts over the entire sampling period (Fig. 2). The values of the Pearson's correlation coefficients (also called Pearson's r) had been 0.58 for water extracts and 0.6 for acid extracts.

The analysis of correlation dependences allowed us to single out three large clusters in the water extracts. The first cluster includes Gd, Nd, Pr, Ce, La, Sb, Cd, Th, Dy, Ho, U, and Y; the second cluster includes Ga, Ca, Tl, Cs, Al, Ba, Fe, and Mn; and the third cluster includes Zr, Mo, Ti, Bi, Sr, Na, Cu, and Li.

Estimation of interrelation between elements in the acid extracts revealed four clusters, with Co, Rb, Mo, V, and Ca in the first cluster; Pb, Ce, La, Eu, Tl, As, Tb, Sm, Pr, Gd, Nd, Ba, Mn, and Al in the second cluster; Yb, Cs, Er, Ga, Lu, Ho, Dy, Cd, U, Y, Fe, Mg, Na, Zn, Sc, and Be in the third cluster; and Bi, Ta, W, Sr, Cu, and Cr in the fourth cluster.

Earlier studies of snow cover at this background site revealed high contents of such elements as Cr, Sb, Hf, Cs, Rb, and Ta, as well as of rare earth and radioactive elements within the spectrum under study, attributable to effect of thermal power plants in Tomsk and Seversk and boilers located in nearby settlements [14]. In [15], it is suggested that Na, Sm, Yb, Ba, Sr, La, Ta, Th, and U are the elements indicating the activity of the complex of coal-fueled thermal power plants; while multiproduct industries are characterized by Mg, Na, Ca, Fe, Ba, and Pb.

There may also be a contribution to aerosol pollution from natural processes: erosion of coasts, dusting in fall and spring periods, as well as long-range transport. For instance, trajectory analysis carried out using HYSPLIT model showed that in the fall period, the air masses were predominantly transported from southern

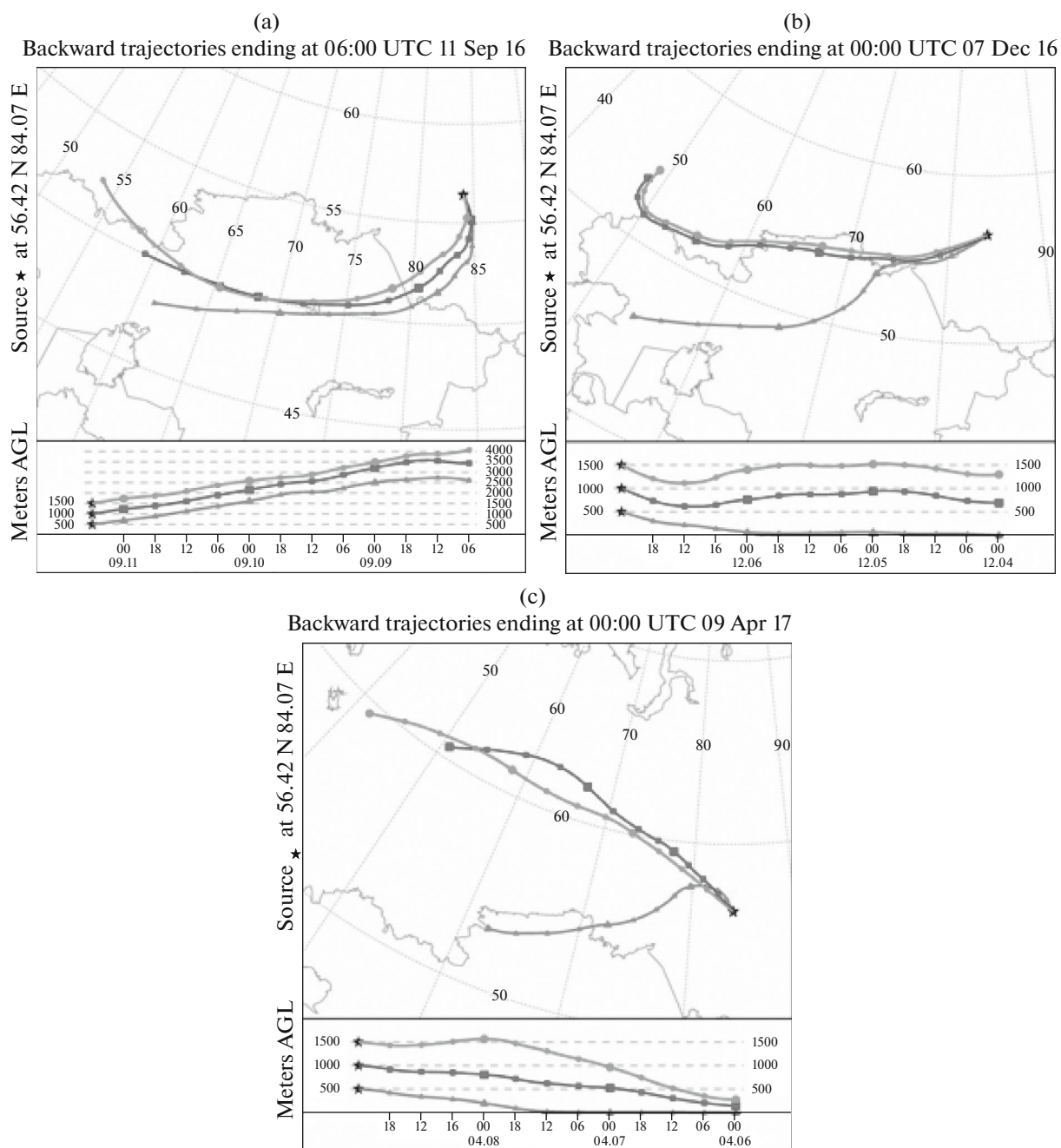


Fig. 3. Examples of back trajectories for (a) fall, (b) winter, and (c) spring.

directions (Fig. 3a), encompassing Novosibirsk oblast, Altai krai, and the north of Kazakhstan.

In the period from September 21 to October 6, the northern direction prevailed. The winter is characterized by air mass motion from the south-southwest (Fig. 3b). In the spring, the air masses moved predominantly from the west and northwest, encompassing a part of Western Siberia and the Urals (Fig. 3c).

It should be noted that in the first half of September, in early October, and in the second half of March,

air masses moved from the direction of Tomsk, which could contribute to introducing indicator elements.

CONCLUSIONS

We carried out observations of the dynamics of seasonal variations in the elemental composition of dry aerosol deposits collected by passive sampling. The calculations of the coefficients of aerosol accumulation and the subsequent comparison of the modules of aerosol enrichments in different seasons showed that

chemical elements were more abundant in water- than acid-soluble extracts. Therefore, most chemical elements, participating in seasonal migration, were in the most mobile, water-soluble form. This is more pronounced in spring than in fall and winter. The fact that Na, Sm, Yb, Sr, La, Ta, Th, and U showed anomalous increases in winter and fall, indicates that, in their migrations, both (acid- and water-soluble) forms were equally represented. These elements are indicators of emissions from thermal power plants, located south of the Fonovaya Observatory. Presumably, the seasonal variations in the contents of chemical elements in water- and acid-soluble fractions, contained in the samples of dry aerosol deposits, are mainly determined by the air mass motion. Southerly (western and northwestern) directions of air mass motion are predominant in fall and winter (spring).

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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