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GEOPHYSICS

Mesoscale Stability in the Distribution of Some Chemical Elements Based on Concentrations in Snow Cover of the Altai Territory

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Experimental data have established the preservation of mesoscale stability from year to year in the distribution of 12 chemical elements in samples of insoluble particles in the snow cover of the Altai Territory over an area of 550×400 km. Geometric means for the concentrations of elements and dispersion of their logarithms are presented. A substantial difference between the established distribution and the clarke values is pointed out.

Snow cover is a good indicator of aerosol pollution of the lower atmosphere. Due to the gravitational settling of particles and their washout by winter sediments, an appreciable amount of aerosol is accumulated in snow. This provides a high degree of reliability for the subsequent determination of its elemental composition.

In winter, the eolian erosion of soil is appreciably smoothed by the freezing of surface particles and the presence of a snow cover. Therefore, the material accumulating in snow on habitable territories similar in type to that of the Altai Territory will necessarily be mainly of human origin. Discharges of heating plants, industrial enterprises, and transport are the main sources of snow pollution.

To study snow cover pollution in drainage basins of large rivers on the Altai Territory, expeditions were undertaken in this region in February and March, 2002–2004. Samples were taken both near large settlements (Barnaul, Biisk, Rubtsovsk, and others) and in remote areas (Fig. 1). Snow cores, 20×20 cm in size, were taken according to the "envelope" technique [1]. The cores included the entire thickness of the snow cover, except the near-soil layer 1–1.5 cm thick. The sample weight and snow depth were measured. Geographical coordinates of the sampling site were determined in order to take samples at the same points in the future. Snow samples were melted in laboratories on "F" filters in Buchner funnels. The filters were dried and weighed. The insoluble residue was then collected in glass bottles. The residue accounted for not less than 85% of the filtered substance. The samples were then pressed and converted into tablets. The tablets were analyzed for 28 elements by the X-ray fluorescence method using synchrotron radiation at the Institute of Nuclear Physics, Siberian Division, Russian Academy of Sciences. The results obtained made it possible to compile tables of element concentrations in each sample calculated for 1 l of thaw water (C_i, μg/l) and 1 kg of dry substance (C_i^*, mg/kg). A total of 160 samples were analyzed.

The results obtained can be treated in two ways. The first approach, a common one, consists in contouring regions with nearly similar pollutant concentrations and revealing the areas with an elevated content of toxicants. Usually (and in our case as well) highly polluted territories share a border with cities and industrial centers. Another way of treating the results is to search for general properties of aerosol, which would characterize it as a single object in the study region. We previously solved a similar problem for suspended matter in water of the Ob River system [2–4]. The present work is an attempt to compile a mesoscale (~550×400 km) stable scheme of element distribution in winter aerosol accumulated in snow cover of the Altai Territory.

The analysis of experimental data convincingly showed that functions of distribution of both total aerosol concentrations and individual elements in samples were similar to normal logarithmic functions. Therefore, the subsequent analysis of the elemental composition is based on geometric mean values of concentrations C and corresponding logarithmic mean-square deviations $\overline{\Delta \log C}$.

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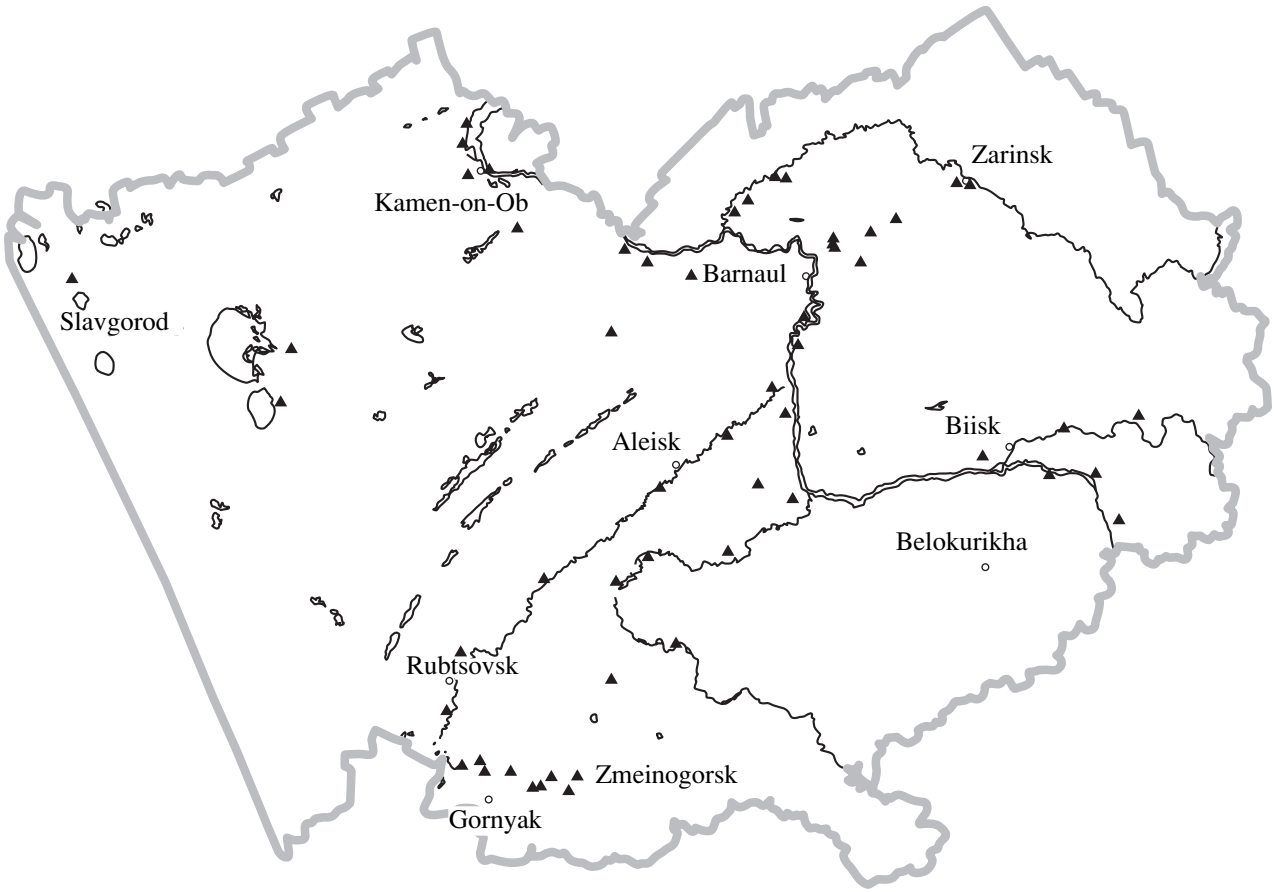

Fig. 1. Snow sampling sites in the Altai region.

The use of geometric means sets significant limits on the number of elements analyzed. We were forced to exclude minor elements, concentrations of which in some samples cannot be determined by the applied method with an adequate accuracy. Such elements are characterized by $C_i = 0$. Therefore, we could calculate C values for only 12 elements (Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Br, Sr, and Pb) out of the 28 that were ana-

Geochemical characteristics of snow pollutants in the Altai Territory averaged over time and space

Element	C, μg/l			C*, mg/kg			
	C	$\overline{\log C}$	$\overline{\Delta \log C}$	C*	$\overline{\log C}$ *	$\overline{\Delta \log C}$ *	Clarke value
Sr	11	1.04	0.47	42	1.63	0.30	230
Pb	24	1.37	0.62	86	1.94	0.31	16
Cl	28	1.45	0.32	107	2.03	0.09	170
Br	31	1.49	0.67	118	2.07	0.36	2.5
Cu	33	1.52	0.39	126	2.10	0.15	22
Cr	34	1.53	0.49	120	2.08	0.28	34
Zn	39	1.59	0.56	151	2.18	0.36	51
Mn	65	1.82	0.68	246	2.39	0.40	700
Ti	84	1.93	0.57	303	2.48	0.31	3300
K	153	2.18	0.61	585	2.77	0.28	27000
Ca	290	2.46	0.75	1114	3.05	0.34	25000
Fe	927	2.97	0.75	3556	3.55	0.40	36000

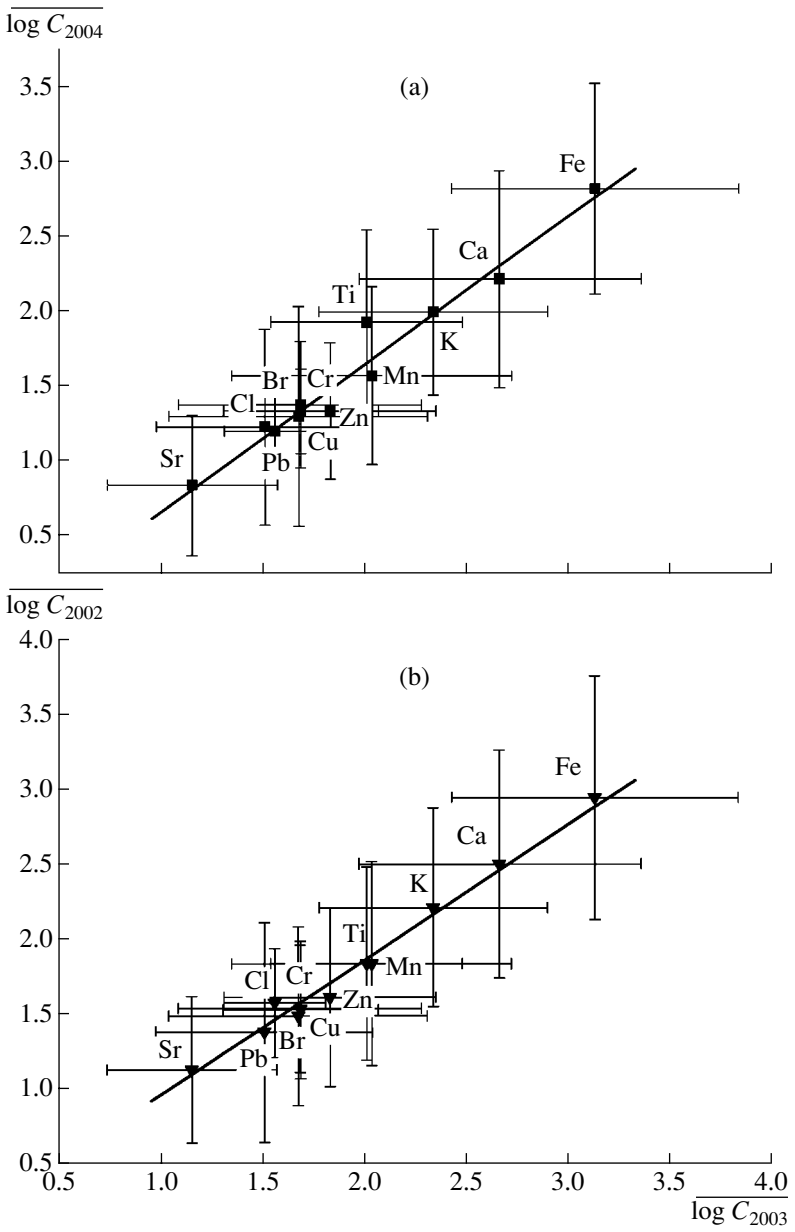

Fig. 2. Logarithmic concentrations of elements in snow in (a) 2003–2004 and (b) 2002–2003.

lyzed, and other elements, such as Ni, W, Co, As, Zr, Mo, Se, Y, Hg, Nb, Rb, Bi, Ga, Ge, Th, and U, were excluded from consideration.

Figure 2 presents the average logarithms of element concentrations (in μg/l) in the winters of 2002–2003 and 2003–2004 for all the samples with corresponding mean-square deviations. The correlation coefficient r is equal to 0.98, which is indicative of a great similarity of the average elemental composition of aerosol accumulated each winter in the snow cover of the entire Altai Territory. It should be pointed out that the weight content of the insoluble residue in thaw water samples varied from 26 to 5500 mg/l depending on the sampling site and different effects of the human factor. This was the main cause of high $\overline{\Delta \log C}$ values.

A similar result is obtained when comparing logarithms of element concentrations normalized to a unit of the dry matter mass C^* (in mg/kg). The correlation coefficient r in this case remains the same (~0.98), but mean-square deviations $\overline{\Delta \log C^*}$ are half as high as deviations $\overline{\Delta \log C}$.

Such significant values of correlation coefficients for the average logarithms of chemical element concentrations in aerosol in different winters appear only when we use the whole experimental data array related

to the entire study territory. When comparing element concentrations in individual samples (in μg/l) taken close to one another (at a distance of several kilometers) and practically at the same time, r_i values vary from 0.5 to 0.9 (average 0.7). Correlation coefficient values noticeably lower than 0.98 are also obtained when comparing logarithms of element concentrations in samples taken in one and the same site in different winters: the average r_k value equals 0.86.

Table demonstrates geometric means of element concentrations C and C^*, average logarithmic concentrations $\overline{\log C}$ and $\overline{\log C^*}$, and mean-square deviations $\overline{\Delta \log C}$ and $\overline{\Delta \log C^*}$ calculated for all three winters. The last column in the table presents clarke values of concentrations (mg/kg) of the studied elements in the lithosphere [5]. Comparing them with our experimental data (C^*), we can make the following inference. The average elemental composition of insoluble substances in the snow cover of the Altai region is stable from winter to winter, but it substantially differs from the general elemental composition in the lithosphere. The discrepancy is more than one order of magnitude for some elements.

Thus, it is possible to draw up a temporally stable scheme of the distribution of 12 elements in insoluble particles polluting the snow cover over an area of 550 × 400 km in the Altai Territory.

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