

## Elemental composition of aerosol accumulated in snow cover of Altai Krai

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Based on experimental data, we revealed persisting (from year to year) pattern of quantitative distribution of concentrations of 12 chemical elements in samples of insoluble residuals in snow cover of Altai Krai on an area of 550×400 km. We present a summary of the data on geometrically mean concentrations of elements and variances of their logarithms. The obtained distribution is found to substantially differ from the standard distribution of elements for lithosphere. The approximate information on mean concentrations of minor elements supports a conclusion on the mesoscale distribution stability of elements in aerosols accumulated in snow cover.

The snow cover is known to be a good accumulator of atmospheric aerosol throughout the winter period.<sup>1,2</sup> Under winter conditions the main mechanisms of emission of continental natural particles to the atmosphere, namely, wind erosion of soils, blow-off of water bubbles by wind from the surface of water basins, and dispersion of pollen by plants, are absent; therefore, there are grounds to believe that in populated regions like the Altai, the aerosol accumulated in snow during winter is predominately of the anthropogenic origin. The aerosol admixture content in entire snow depth is usually large; therefore the analysis of its components can be made with a reasonable accuracy.

Based on the aforesaid, snow sampling expedition works were carried out in late February – early March 2002–2004 aimed at studying pollution of floodplains of Altai rivers by winter aerosol. The sampling points, remaining the same from year to year, were widely dispersed over the region and located both near industrial centers (cities of Barnaul, Biisk, Rubtsovsk, etc.) and rather far from them, i.e., under near-background conditions. A total of 161 samples have been collected for three years.

Snow cores of 20×20 cm area were collected by the method of “envelop” throughout the snow depth. The lowest 1.5–2-cm layer of the sample adjacent to the soil, was cut off. The sample weight and the snow depth were measured. Under laboratory conditions, the samples were placed on the *F* filter in Buchner funnels.

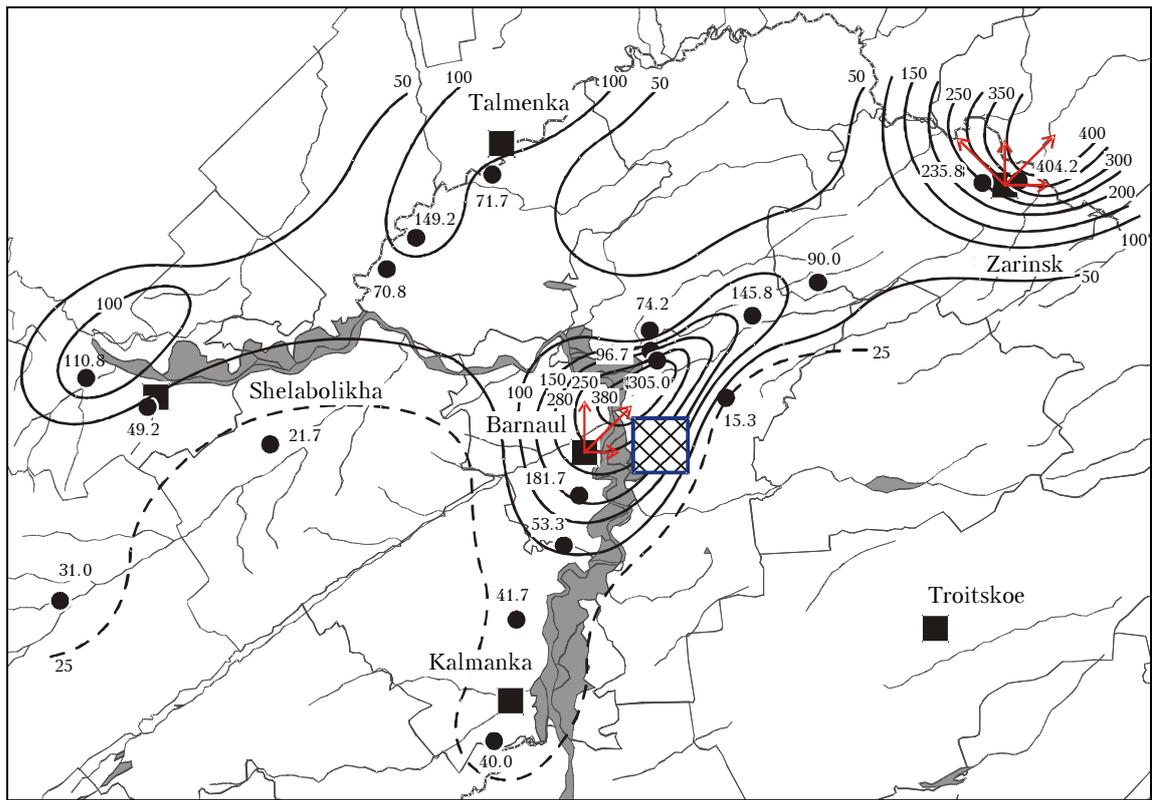
The processes of snow melting and filtering the resulting water proceeded almost simultaneously, which substantially reduced the losses of elements in aerosols in the process of their solution. Such losses are especially noticeable providing aerosol particles reside in acidified water for a long time.<sup>3</sup> After drying, the insoluble residuals (no less than 85% of the dried sample mass) were placed into glass weighing cups. By weighing the samples, we determined the total admixture concentrations in snow per liter of snow melt *C* (μg/l). Special tablets were pressed from the powder,

which then were analyzed for the presence of Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Br, Sr, Pb, Ni, W, Co, As, Zr, Mo, Se, Y, Hg, Nb, Rb, Bi, Ga, Ge, Th, and U by the roentgen-fluorescent method using synchrotron radiation at the Institute of Nuclear Physics SB RAS. The same method was also used to analyze the elemental composition of the matter remained on the filters. The results were summarized in tables of total concentration of elements in samples, calculated per liter of the snow melt *C* (μg/l) and per kilogram of the dry substance *C\** (μg/kg). They mainly characterize the coarse fraction of insoluble particles accumulated in snow cover during each winter.

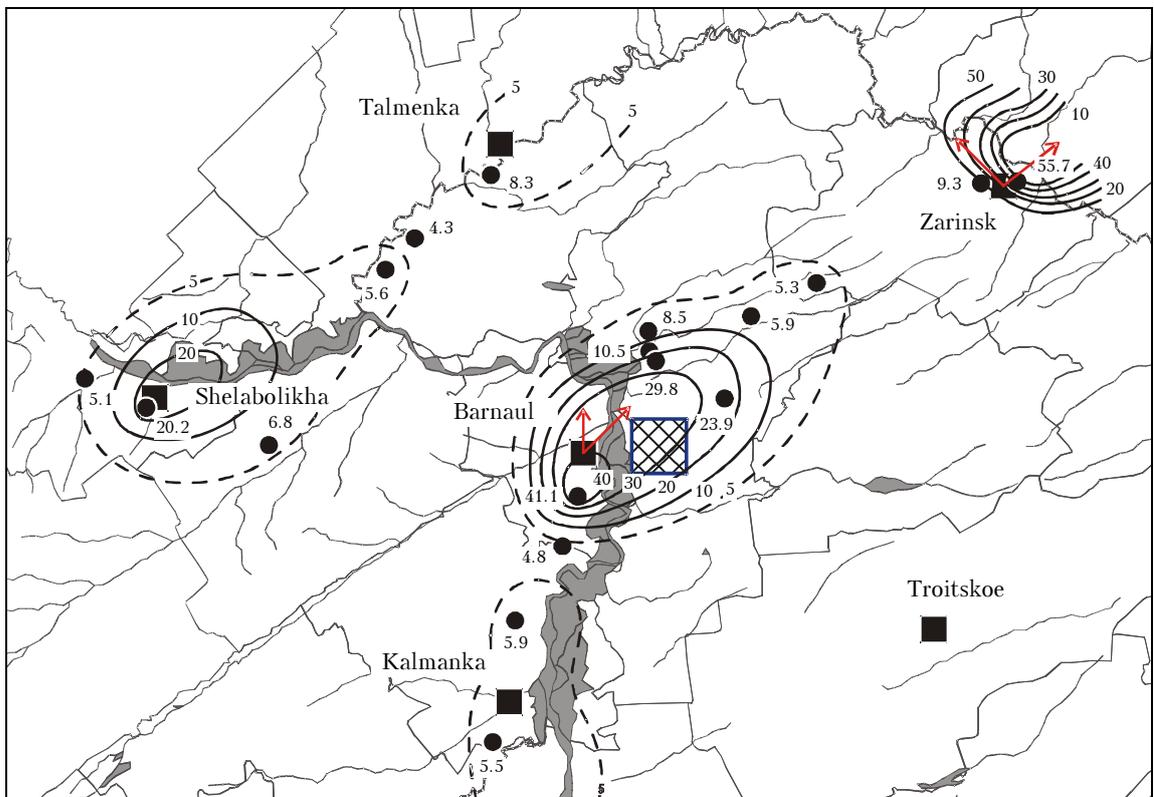
The obtained results can be treated using two approaches. The first widespread approach is in contouring the territories with approximately the same admixture content and, that is especially important, in identifying regions with an elevated toxicant abundance. As a rule, strongly polluted territories adjoin the cities and industrial centers. Examples of processing of winter “traces” of summarized aerosol admixtures in snow in the Altai region are presented in Fig. 1.

The contour lines of species concentrations deposited in snow were plotted taking into account the direction and speed of dominating winds in each winter. During winter 2003, the atmospheric processes favored accumulation of aerosol particles in snow; while in winter 2002, conversely, aerosols were actively dispersed and transported out of the studied region. It is seen that, at an elevated pollution of snow cover, the contour lines around individual sources close up and enclose vast territories.

Via such a mapping of spatial distributions of admixture concentrations, it is possible to determine their magnitudes on vast areas. For instance, within hatched squares of 100 km<sup>2</sup> area (Fig. 1), the total amount of the insoluble substance accumulated in snow was found to be  $1.6 \cdot 10^7$  (Fig. 1a) and  $3.2 \cdot 10^6$  kg (Fig. 1b), respectively. In the nearest future we plan



*a*

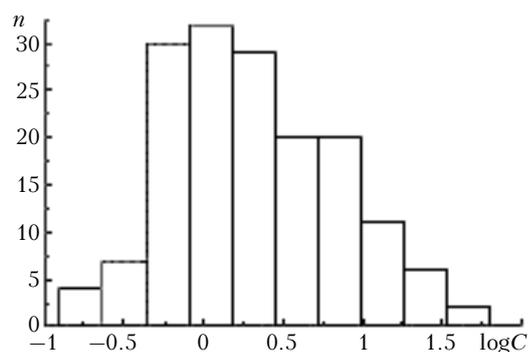


*b*

**Fig. 1.** Integrated pollution ( $\text{g}/\text{m}^2$ ) of snow cover on eastern territories of Altai Krai in 2003 (*a*) and 2002 (*b*).

to carry out the careful work on studying the total integrated aerosol content in snow cover and distribution of concentrations of separate elements over different regions. The primary purpose of this work was to find such general characteristics of winter aerosol, which describe it as an integral object over the vast Altai region (550×400 km).

Similar investigations dealing with distribution of concentrations of certain chemical elements in suspended substances of ocean and river waters had already been conducted before.<sup>4–9</sup> Assume that both summarized pollutant concentrations and concentrations of individual elements in snow samples are random quantities. Figure 2 presents the distribution of the number of samples over logarithms of concentrations of total admixtures for three winters throughout the region under study. A similar nearly logarithmically normal pattern of distribution functions is characteristic for individual elements as well. Therefore, in the resulting information on abundance of chemical elements in snow samples it is reasonable to use the geometrically means of concentrations and variances of their logarithms.



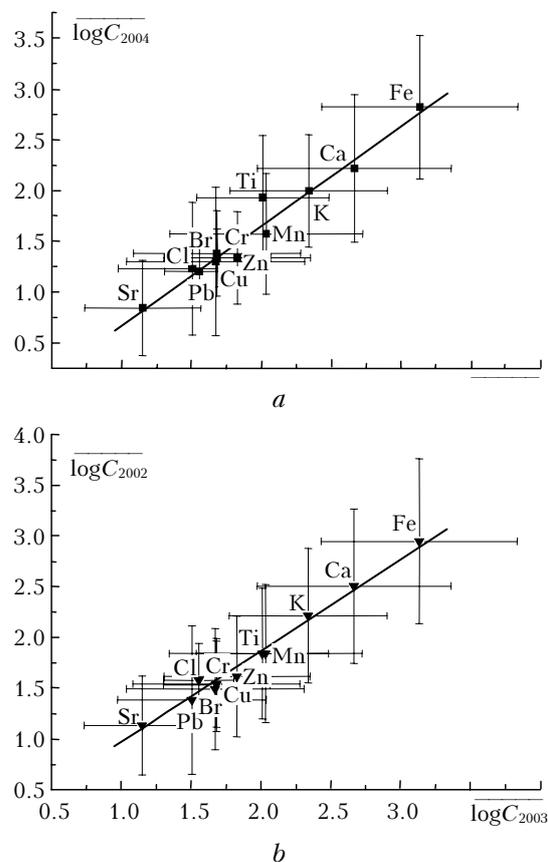
**Fig. 2.** Distribution of the number of samples over logarithms of concentrations ( $\mu\text{g}/\text{l}$ ) for total set of pollutants.

The necessity of using the geometrically means in statistical processing of experimental data imposes serious limitations on the number of analyzed chemical elements. We have to exclude from consideration the elements whose content cannot be determined with reasonable accuracy by the used method. Analysts usually assign zero values to these concentrations:  $C_i = 0$ .

Alternatively, it is possible to use in the calculations a larger number of elements excluding from the considered array the samples (and, hence, sampling sites) with “zero” concentrations. In this case, the generality of conclusions can be lost because of somewhat fewer sites under study.

In our case, if the number of sites is maintained at a level of 90%, we have to consider only 12 elements: Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Br, Sr, and Rb among the 28 ones, above enumerated. Calculate the average logarithms of concentrations of these elements  $\overline{\log C}$  successively for each winter and compare them. These results and the corresponding standard deviations

$\overline{\Delta \log C}$  are presented in Fig. 3. In the calculations, we used the data on content of the elements given in mass per liter of the snow melt, i.e., in  $\mu\text{g}/\text{l}$ .



**Fig. 3.** Comparison of logarithms of element concentrations in the snow cover for 2003–2004 (a) and 2002–2003 (b).

A good agreement between mean elemental compositions of aerosol in winters of 2002/03 and 2003/04 is clearly seen: the correlation coefficient  $r$  for logarithms of concentrations is  $0.98 \pm 0.01$ . The slope tangents are, respectively,  $0.93 \pm 0.06$  and  $0.99 \pm 0.05$ , i.e., close to unity. This indicates that not only the logarithms but the geometrically mean concentrations themselves are practically linearly related to each other within the standard error. The

large values of standard deviations  $\overline{\Delta \log C}$  are caused by strong variations of element concentrations from one sampling site to another. Actually, the weight content of insoluble deposit in samples varies in wide limits: between 26 and 5500  $\mu\text{g}/\text{l}$ . A similar result is obtained from comparison of the average logarithms of element concentrations in snow, calculated per unit mass of dry substance  $C^*$  ( $\mu\text{g}/\text{kg}$ ). The correlation coefficient  $r$ , as in the above case, is 0.98; however, the rms deviations  $\overline{\Delta \log C^*}$  are approximately a factor of 2 less than the deviations  $\overline{\Delta \log C}$  presented in Fig. 3.

The correlation coefficients for mean logarithms of concentrations are high only when analyzing

experimental data for the Altai territory as a whole (the number of samples is 51). When comparing the element concentrations in individual samples (in  $\mu\text{g}/\text{l}$ ), taken simultaneously at sites separated even by a few kilometers,  $r$  varies from 0.5 to 0.9, averaging about 0.7. Also, less than 0.98 values are obtained when comparing logarithms of the element concentrations in samples collected at the same site in different winters: the mean  $r$  is 0.86.

Of particular special interest may be the results of comparison of element concentrations in samples for cases of high and low aerosol content in the snow cover. We act as follows. Using the distribution function of the number of samples over logarithms of a substance mass concentrations (see Fig. 2), we divide the entire dataset into two groups, left and right relative to maximum. We calculate the mean logarithms of concentrations of chemical elements for three winters individually in each group, and compare them. The obtained results for 13 elements are presented in Fig. 4.

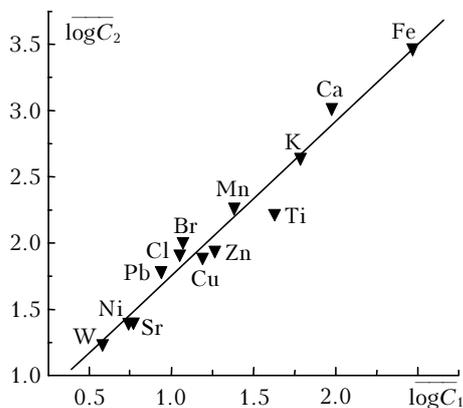


Fig. 4. Comparison of the average logarithms of small- ( $C_1$ ) and large-valued ( $C_2$ ) concentrations of elements ( $\mu\text{m}/\text{l}$ ) in snow samples, based on three-year measurements.

A similarity of the mean elemental composition of weakly and strongly polluted snow samples is clearly seen: the correlation coefficient is  $0.97 \pm 0.01$ . This again confirms the above conclusion that, even at large distances from cities and industrial centers, the role of anthropogenic factor in accumulation of aerosol admixtures in snow cover of Altai Krai is very important.

Table presents geometrically mean concentrations  $C$  and  $C^*$  of elements, average logarithms of concentrations  $\overline{\log C}$  and  $\overline{\log C^*}$ , as well as rms deviations  $\Delta \log C$  and  $\Delta \log C^*$  calculated for three winters. For comparison, the last column of the table presents mean concentrations of the studied elements in lithosphere, the so-called clarkes.<sup>10</sup> Comparing them with our experimental data, i.e., column 4 versus column 7, we can conclude the following. Average elemental composition of the insoluble substances in the Altai, persisting from one winter to another, differs substantially from total abundance of elements in lithosphere (correlation coefficient is no larger

than 0.7). A divergence for some elements exceeds an order of magnitude.

**Space and time average geochemical characteristics of snow pollutants in the Altai**

Element	$C, \mu\text{g}/\text{l}$			$C^*, \mu\text{g}/\text{kg}$			Clarke
	$C$	$\overline{\log C}$	$\Delta \log C$	$C^*$	$\overline{\log C^*}$	$\Delta \log C^*$	
	1	2	3	4	5	6	
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

Thus, for a series of 12 elements, it is possible to determine their stable concentration distribution in insoluble residual of particles deposited in snow cover of the Altai region.

The distribution of trace elements in the samples can be approximately judged from comparing the logarithms of arithmetically means, calculated for total data array in each winter. In this case, zero  $C_i$  values can also be included in the calculations. Figure 5 presents, in logarithmic coordinates, the results of the calculations based on data for 2003 and 2004 with the corresponding rms deviations. The correlation coefficient is  $0.98 \pm 0.01$ .

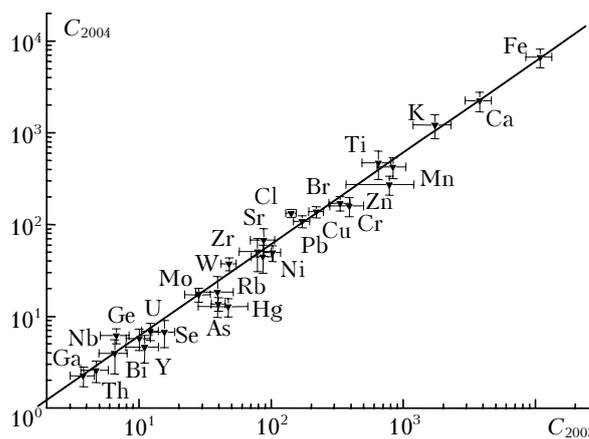


Fig. 5. Comparison of the mean concentrations of elements ( $\mu\text{g}/\text{l}$ ) in snow samples, collected in 2003 and 2004.

The regression equation has the following form:  $\log C_{2004} = A \log C_{2003} + B$ , where  $A = 1.00 \pm 0.03$  and  $B = -0.21 \pm 0.05$ . It is seen that the main conclusion about a good agreement between elemental compositions of snow samples in different winters holds also for arithmetically mean concentrations, including the cases with trace elements as well. In

other words, the distribution of elements in aerosol samples, accumulated in snow cover has a stable mesoscale character.

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