Element composition of the insoluble fraction of winter atmospheric precipitation in some of the Southern Baikal regions

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Received February 16, 2004

We present some results of the investigation of the element composition of insoluble particles in the snow cover at some urban and rural sites of the southern part of Irkutsk Region, as well as at the background Mondy station. The deposition values of 21 chemical elements accumulated in the snow cover are estimated. It is shown that insoluble particles in snow water are less enriched with heavy metals than those in the atmospheric aerosol. This means that a significant part of anthropogenic admixtures being deposited in snow is transferred into the solution during the snow melting. Some elements were identified as possible tracers of the atmospheric emissions from large cities in the region under study.

The snow cover is a convenient natural plate for sampling the total (dry and wet) atmospheric depositions for several winter months. Samples of the snow column are used for a long time to study chemical composition, amount, and spatial distribution of atmospheric depositions of different chemical substances. However, by now, in the most of cases analysis was restricted to only determination of the chemical composition of snow water (that is, the composition of the soluble fraction). At the same time, only minor attention was paid to analysis of the composition of the insoluble and hardly soluble fractions of the atmospheric depositions. However, these data are important for in-depth understanding of the migration of some chemical elements, for example heavy metals, in different natural media.

In this paper, we present some results of the investigation of the element composition of solid insoluble suspensions sampled from the snow cover at different sites of the southern Irkutsk Region characterized by different degrees of the anthropogenic impact. The particular attention was paid to the southern part of Lake Baikal.

Material and methods of analysis

Snow was sampled in February–March of 2001 and 2002. Overall of 500 samples have been collected and analyzed at the sites with different degrees of the anthropogenic impact (Fig. 1). The cleanest background conditions are observed at the Mondy station, while the industrial regions are represented by snow samples from Irkutsk, Baikalsk, and Slyudyanka. The Listvyanka village and the valleys of the Pereemnaya, Snezhnaya, Khara-Murin, and Utulik rivers can be classified as rural sites.

The samples of the snow water were filtered through standard (47 mm) membrane filters with the pore diameter of 0.45 μm. The suspended matter collected on the filters was analyzed for the element composition by the method of X-ray fluorescence using the synchrotron radiation (XFA-SR) on the setup of the Institute of Nuclear Physics SB RAS (Novosibirsk, Russia). The detailed description of this method can be found in Ref. 1.

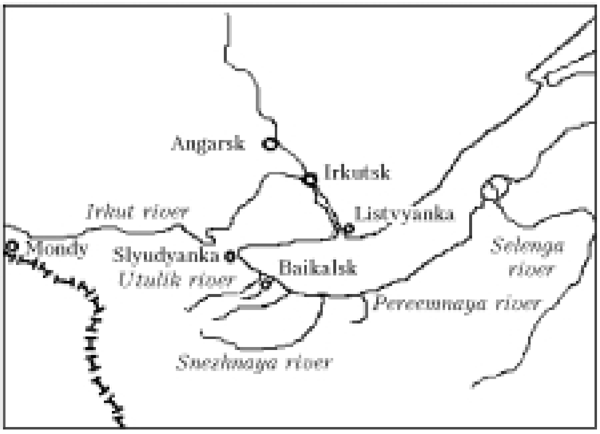

Fig. 1. Region under study.

Discussion

Figure 2 shows the concentrations of 21 chemical elements present in the solid particles suspended in the snow water (from here on, for simplicity, they will be referred to as suspension). It can be seen from Fig. 2 that, though the element composition of the suspensions from different sites is generally similar, the concentrations of the elements differ widely, in particular, almost tenfold between the urban (Irkutsk) and background (Mondy) conditions. In the rural areas (Listvyanka) and small towns (Slyudyanka), the concentrations of the elements have intermediate values. The significant increase of the calcium concentration in Slyudyanka as compared to that in Irkutsk is, obviously, connected with the many-year opencast mining of marble in this area.

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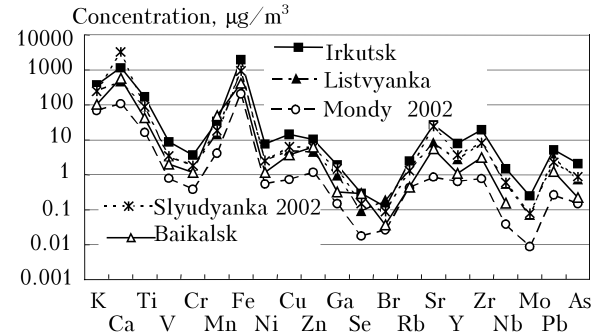

Fig. 2. Average element composition of the solid snow suspension at some sites of Southeastern Siberia.

However, those large differences in the element concentrations in the snow suspensions cannot be fully explained by the anthropogenic impact. In particular, the extremely low element concentrations in the suspensions from Mondy station can be connected, in the first place, with the high-altitude location of the station. It should also be kept in mind that the element concentrations in this case are relative parameters that depend not only on the air pollution, but also on the amount of snow. Therefore, for a comparison of sites differing for precipitation, the amount of the element accumulated per unit area is usually used. This characteristic is determined as a product of the element concentration to the moisture stored in the snow cover. Such estimates for some sites of the Southern Baikal region are summarized in Table 1.

The Baikalsk site is distinguished by high amounts of all elements accumulated in the snow cover. In the other places of the southern Baikal shore, the accumulated amounts of the elements are close to data obtained earlier[2] for the Khamar-Daban mountain ridge adjacent to Lake Baikal. The amount of the elements accumulated in the solid snow suspensions sampled from the mountain area turned out to be 10–50% lower than those on the shore. The maximum differences are observed for typically anthropogenic elements As, Sr, and Mn.

The main sources of the atmospheric continental aerosol are the soil and the earth's crust, so the relative content of the elements in the atmospheric aerosols from different continents is very close and corresponds to that of the earth's crust.[3–5] In this connection, it is often difficult to estimate the contribution of the anthropogenic component against the background of the absolute concentrations of elements. Therefore, this analysis is performed with the use of the so-called enrichment factor for elements in the atmosphere with respect to the earth's crust or soil.

The idea of using the enrichment factor consists in the following: the element ratio in the atmospheric admixtures of soil origin should correspond to that in the soil or the earth's crust. The enrichment factor Φ_{en} is calculated with respect to the element most abundant in the soil or the earth's crust; usually, it is Si, Al, Fe, or Sc. In this paper, the enrichment factor was calculated with respect to Fe:

$$\Phi_{en} = (X/Fe)_{susp}/(X/Fe)_{crust},$$

where X is the element, for which Φ_{en} is being calculated.

According to this equation, the enrichment factor of an atmospheric admixture of the soil origin should be close to unity. Actually, when transported from the soil to the atmosphere, some elements are enriched to one or another degree due to natural processes and chemical properties of the compounds (fractionating, volatility). In spite of this, useful properties of the enrichment factors are their higher constancy and higher sensitivity to the effect of other (non-soil), e.g., anthropogenic sources as compared to mere concentrations.

Table 1. Accumulation of elements in solid snow suspensions in winter of 2001/02, mg/m²

Elements	Baikalsk	Valleys of the rivers				Khamar-Daban mountain ridge (Ref. 2*)
		Utulik	Khara-Murin	Snezhnaya	Pereemnaya	
K	7.3	3.4	2.2	2.8	1.1	–
Ca	40.1	5.7	3.5	4.5	3.2	–
Ti	3.0	0.9	1.0	1.1	0.6	1.0
V	0.14	0.05	0.05	0.08	0.04	–
Cr	0.08	0.025	0.037	0.039	0.037	–
Mn	3.4	0.19	0.17	0.28	0.12	0.09
Fe	29.1	8.7	10.2	20.6	8.1	9.0
Ni	0.083	0.027	0.032	0.043	0.031	–
Cu	0.26	0.07	0.07	0.09	0.07	0.05
Zn	0.44	0.08	0.07	0.07	0.05	0.04
Ga	0.023	0.001	–	0.024	0.023	–
As	0.015	–	–	0.005	–	0.008
Se	0.0206	0.0024	0.0004	–	–	–
Br	0.0026	0.0024	0.002	0.0016	0.001	–
Rb	0.03	0.02		0.02	–	–
Sr	0.39	0.07	0.06	0.18	0.04	0.03
Y	0.078	0.012	0.018	0.019	0.011	
Zr	0.22	0.05	0.06	0.07	0.05	0.03
Nb	0.011	0.003	0.002	0.004	0.004	–
Mo	–	0.001	–	0.002	–	0.01
Pb	0.09	0.02	0.04	0.04	0.02	0.03

* The data presented in Ref. 2 in g/km² are converted into mg/m².

Figure 3 shows the enrichment factors of the elements in the suspensions at three sites and, for a comparison, in winter aerosols. The data for the aerosols were obtained in 1995/96 by the XFA-SR method.[6]

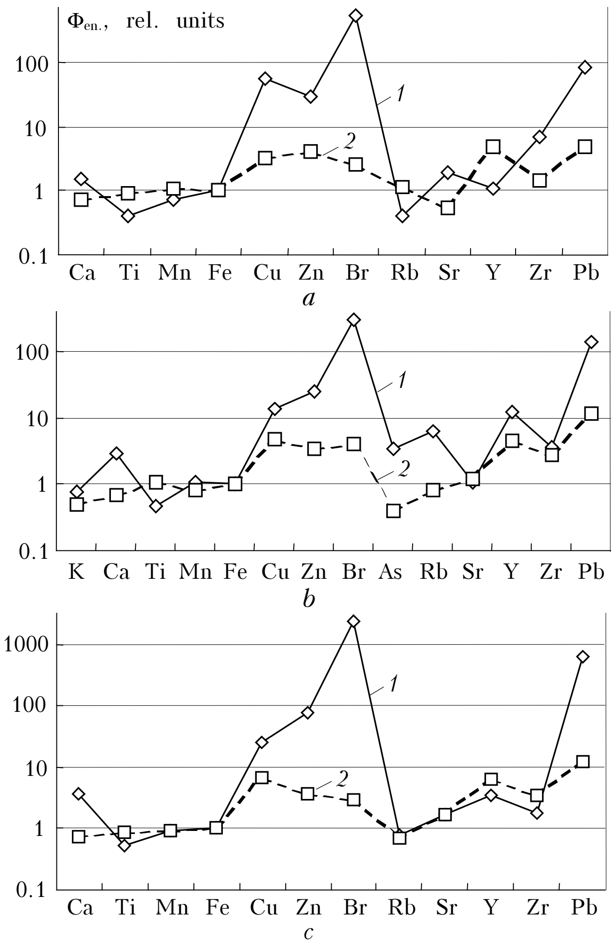

Fig. 3. Enrichment factors of elements in aerosol and solid snow suspension at the sites: (*a*) Mondy, (*b*) Listvyanka, (*c*) Irkutsk; aerosol (curve *1*), suspension (*2*).

The first to be noticed in Fig. 3 is the much higher enrichment of the atmospheric aerosol, as compared with that of the suspension, with such elements as Ca, Cu, Zn, As, Br, and Pb. This means, first, that the atmospheric aerosol is much more polluted by the contaminants of the anthropogenic origin than the solid insoluble particles of the snow cover and, second, that the major part of the atmospheric depositions accumulated in the snow cover transforms into the dissolved state upon snow thawing.

From analysis of Fig. 3, it follows that the amount of some elements (Br, Pb) in Irkutsk is higher (as compared with the background sites) in both aerosols and suspensions, which suggests that they are partly emitted from the local anthropogenic sources. Usually, Br and Pb are associated with the automobile exhausts. The contribution of local anthropogenic sources to accumulation of chemical elements in snow suspensions can be estimated by comparing the enrichment factors of elements in Irkutsk to those in Mondy (Mondy is considered as a background site, whose atmosphere is characterized by the prevailing global background of soil and anthropogenic admixtures). This comparison is shown in Table 2. It can be seen that, in the suspensions from Irkutsk and Listvyanka, the elements Cu, Br, Sr, Zr, and Pb are enriched much higher (1.5 to 3 times) as compared to the suspensions from the background site, and this excess can be attributed to the contribution of anthropogenic sources of Irkutsk and Listvyanka. For aerosols, these ratios likely are many times higher.

Table 2. Ratios of the enrichment factors of some elements in solid snow suspensions from Irkutsk and Listvyanka to those from Mondy

Site	Ca	Ti	Mn	Cu	Zn	Br	Sr	Y	Zr	Pb
Irkutsk/ Mondy	1.0	1.0	0.8	2.1	0.9	1.1	3.1	1.4	2.4	2.5
Listvyanka/ Mondy	1.0	1.2	0.8	1.5	0.85	1.6	2.2	0.9	1.9	2.3

The element ratio in aerosol admixtures over industrial centers is often used as a tracer of long-range transport of atmospheric emissions.[3–5] In this connection, it is interesting to consider the possibility of using the element ratio in solid snow suspensions for this purpose. To do this, we should first find the elements specific for the considered urban sites (Irkutsk, Baikalsk, Slyudyanka) and then follow their presence in solid snow suspensions from the neighboring rural and background areas. Since the element ratio is very similar for all the sites (see Fig. 2), while the concentrations are strongly different, the concentrations at every site were normalized to Fe to facilitate revealing of the specific elements and then to the element concentrations at the unpolluted site – Mondy. Thus obtained ratios should be close to unity for the elements having only some common regional sources and much higher than unity if the effect of a local source is present. These estimates are summarized in Table 3 (only the elements most significantly deviating from unity are presented). According to the results obtained, Se, Mn, Sr, Ca, Zn, Cu are more specific for Baikalsk, Nb, Mo, Sr, Zr, As are specific for Irkutsk, and Ca and Sr are specific for Slyudyanka.

The correlation analysis carried out between the source and receptor sites shows that the effect of Baikalsk, as judged from the solid insoluble snow suspensions, is seen only in the area of the Utulik River (correlation $R = 0.5$). This can mean that specific insoluble admixtures in the atmosphere over Baikalsk are mostly contained in large particles and not transported far from the source. The effect of Irkutsk, to the contrary, is seen on an extended territory: $R = 0.84$ in Listvyanka, and $R = 0.72$ and $R = 0.55$ in the areas of the Pereemnaya and Snezhnaya Rivers situated opposite to the Angara River valley, along which the emissions of the Irkutsk–Angarsk industrial center can be transported

Table 3. Relative excess of the content of chemical elements in solid snow suspensions at some Baikal sites over the background values

Sites, rivers	Ca	Mn	Cu	Zn	As	Se	Sr	Zr	Nb	Mo	Pb
Baikalsk	2.63	5.84	2.52	2.62	0.75	8.16	3.26	1.99	1.99	–	2.34
Khara-Murin	0.66	0.83	2.02	1.16	–	0.44	1.51	1.57	1.27	–	3.32
Snezhnaya	0.42	0.68	1.28	0.61	0.32	–	2.17	0.86	0.97	2.39	1.68
Pereemnaya	0.49	0.76	2.37	1.02	–	–	1.34	1.51	2.41	–	2.33
Irkutsk	1.01	0.81	2.06	0.91	2.09	2.46	3.02	2.96	4.55	3.64	2.53
Listvyanka	0.94	0.77	1.49	0.84	1.09	1.15	2.14	2.36	3.11	1.75	2.66
Slyudyanka	6.69	0.98	1.91	1.75	1.33	1.87	6.27	2.33	3.5	1.99	1.91
Utulik	1.24	1.08	2.3	1.57	–	3.19	1.83	1.63	1.66	1.26	1.92

to this area. However, the depositions are most likely determined by some mixed regional background of atmospheric admixtures including the emissions from numerous natural and anthropogenic sources located upstream Angara River valley, rather than only by the emissions from Irkutsk. The emissions from Slyudyanka are observed in no one of the sites studied, that is, they are deposited just near the town.

The increased content of strontium in the solid snow suspensions from Slyudyanka (two to three times higher than at other sites) is mostly connected with marble mined near this town.

Conclusions

1. Most of the chemical elements accumulated in the snow cover are dissolved upon snow thawing. This is especially true for some metals, whose presence in the atmosphere is most often associated with anthropogenic emissions (As, Zn, Cu, Br, Pb, and others). The typically soil elements mostly remain in the solid state (Ti, Mn, Fe, and some rare-earth elements).

2. The soluble fraction of the atmospheric aerosol and atmospheric depositions is much higher polluted with anthropogenic pollutants than the insoluble fraction remaining after snow thawing.

3. The area of pollutant spread from Irkutsk covers an extended territory along the Angara River valley. The effect of Baikalsk and Slyudyanka, because of the orographic isolation of these sites, was revealed at a local territory.

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