Features of the microelement composition of the liquid phase in snow cover from the towns of Usolye-Sibirskoe and Svirsk

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Abstract. We analyze the chemical composition of the liquid phase in the snow cover from industrial and residential zones, as well as the background region, the water area of Lake Baikal, to assess the atmospheric pollution of the towns of Usolye-Sibirskoe and Svirsk. We have determined the concentrations of trace elements (Fe, Co, Mn, V, Ni, Cu, Zn, As, Cd, Pb, Th, U, and Hg), and most of which have a high toxicity degree. The study has resulted in the identification of priority elements that pollute the atmosphere of the two cities, which differ significantly in the specifics of core enterprises. For the town of Usolye-Sibirskoe, such toxic elements in the liquid phase of snow are Hg, Zn and Pb; for the town of Svirsk – As and V. According to the dispersal halos of pollutants, we determined that their highest concentrations are in the industrial zones of the towns. At the same time, these elements have increased concentrations in the snow meltwater of residential areas of cities as well as in the water area of the Angara River, which is significant as the main source of drinking water supply to the region and fishery facilities. The revealed high concentrations of trace elements in the liquid phase of the snow cover show that a significant part of the pollutants is in the most dangerous dissolved mobile forms. Even in the period of a sharp decrease in the technogenic emission of potentially toxic elements, industrial sites of the investigated cities remain the main sources of air pollution.

1. Introduction

The property of atmospheric precipitation to accumulate a variety of substances characterizes it as one of the main objects of environmental monitoring in the study of environmental pollution in the area of industrial agglomerations [1]. The relevance of observations of changes in the chemical parameters of snowmelt in the Baikal region is associated with the period of stable snow cover, which is 180-200 days [2]. In terms of practical implementation, the data, indicating a deterioration of the ecological situation in the region, predetermined the need to study the chemical composition of the snow cover of cities in Eastern Siberia [3]. During 2012-2017, the Irkutsk Region ranked third in gas and dust emissions. The six most polluted cities revealed were Bratsk, Zima, Cheremkhovo, Usolye-Sibirskoe, Shelekhov, and Svirsk, in which, despite the currently used modern treatment facilities, pollution indicators increased compared to the previous period.

Environmental problems of the cities of Usolye-Sibirskoe and Svirsk located on the bank of the Angara River are mainly associated with their large-scale technogenic pollution from the core enterprises that have ceased operation. The main pollutant in the town of Usolye-Sibirskoe is mercury, which was released into the environment in large volumes for several decades (1972-1998) during the
2. Materials and methods

Snow samples in the towns of Usolye-Sibirskoe and Svirsk were collected at the end of the stable snow cover season before thawing (the last decade of February 2018-2019), taking into account the wind rose as well as the location of the main pollution sources and residential areas. A denser spaced sampling corresponded to areas close to technogenic sources. In total, 55 samples were taken.

The water area of Southern Baikal remote from the local influence of large industrial enterprises was chosen as the background region. Twelve snow cover samples were taken from the ice of Lake Baikal to calculate conditionally background concentrations. Furthermore, the median values for each of the studied trace elements were determined. The sampling stations were confined to two transverse sections from the western to the eastern shore of the lake: Listvyanka settlement - Tankhoi settlement; Maritui settlement – Murino settlement.

The elemental composition of snow meltwater was determined at the authorized Center for Collective Use "Isotope-Geochemical Research" SB RAS (Irkutsk). The water samples were analyzed for the content of trace elements (V, Mn, Fe, Co, Ni, As, Pb, Cd, Zn, Cu, Th, and U) using high-precision mass spectrometers with inductively coupled plasma (ICP MS FinniganElement2). Mercury was evaluated by atomic absorption on an "RA-915+" spectrometer.

The concentration coefficient (CC), showing the level of anomalous content of the elements, was calculated by the formula (1) [13] as the ratio of the element concentration in the selected samples (C) to its background concentration (Cф):

$$CC = \frac{C}{C_\phi}$$

(1)

The total pollution index ($Z_c$) was calculated by the formula (2) [13]:

$$Z_c = \sum K_c - (n - 1)$$

(2)

where $K_c$ is the concentration coefficient of the chemical element on the background level; $n$ is the number of elements taken into account with $K_c > 1$.

We processed all analytical data using the application programs Statistica” and Microsoft Excel as well as geoinformation systems to examine the available data on their spatial relationships and conduct an integrated assessment of the situation. This resulted in constructing maps of the distribution of chemical elements in the program Surfer 8 using the Kriging method, which is usually used when the analyzed data is distributed unevenly and have a low density of control points.

3. Results and discussion

Table 1 presents the concentrations of trace elements in the liquid phase of the snow cover from the conditional background region (Lake Baikal), Usolye-Sibirskoe and Svirsk. Based on average
concentrations of trace elements in the snow meltwater of Lake Baikal area, the following row was constructed:

Zn>Mn>Fe>Cu>Ni>V>As>Pb>Co>Cd>U>Th>Hg;

Usolye-Sibirskoe:
Mn>Zn>Fe>Cu>V>Ni>As>Co>Pb>U>Hg>Cd>Th;
Svirsk:
Mn>Fe>Zn>As>V>Cu>Ni>Pb>Co>U>Cd>Th>Hg

Table 1. The content of trace elements in snow meltwater from Usolye-Sibirskoe, Svirsk and Southern Baikal (µg/l).

| Element | Usolye-Sibirskoe | Svirsk | Southern Baikal |
|---------|------------------|--------|----------------|
|         | Industrial zone  | Residential areas | Industrial zone | Residential areas |               |
| V       | 0.6-10.6         | 0.4-4.2 | 2.3-13.8       | 1.3-2.4          | 0.8            |
| Mn      | 8.1-71.0         | 8.1-31.9| 7.5-97.8       | 17.3-49.8        | 8.8            |
| Fe      | 4.6-100.8        | 4.6-25.6| 6.93-46.7      | 4.0-16.2         | 5.4            |
| Co      | 0.1-1.7          | 0.1-1.4 | 0.09-1.1       | 0.3-0.4          | 0.10           |
| Ni      | 0.3-2.4          | 0.2-1.4 | 0.3-2.3        | 0.69-1.1         | 1              |
| Cu      | 0.9-30.1         | 0.9-9.8 | 1.17-5.4       | 1.23-2.2         | 2.01           |
| Zn      | 6.5-59.0         | 6.5-32.2| 1.69-27        | 7.4-13.7         | 29.6           |
| As      | 0.04-8.9         | 0.04-2.2| 0.98-27.4      | 0.2-1.5          | 0.5            |
| Cd      | 0.01-0.2         | 0.01-0.2| 0.05-0.1       | 0.03-0.07        | 0.03           |
| Pb      | 0.06-3.1         | 0.06-0.9| 0.16-1.0       | 0.06-2.01        | 0.12           |
| Th      | 0.001-0.09       | 0.001-0.09| 0.004-0.04   | 0.004-0.02       | 0.005          |
| U       | 0.01-0.45        | 0.01-1.3 | 0.02-0.7      | 0.01-0.06        | 0.02           |
| Hg      | 0.002-0.55       | 0.001-0.1| 0.002-0.02   | 0.002-0.01       | 0.001          |

The chemical composition of the soluble part of the snow cover depends substantially on natural and anthropogenic sources [14, 15]. The similarity of physical and geographical conditions supposes that the main factor, affecting the concentration of trace elements in snow meltwater in the study territories, is anthropogenic. In general, the concentrations of Mn, Fe and Zn are significantly higher than of other studied elements. The fluxes of Mn and Fe are mostly of natural origin since they relate to the basic elements of the earth's crust. An increase in the concentrations of Mn and Fe in the snow meltwater of towns (table 1) is due to the significant effect of urbanized territories. Noteworthy are the maximum concentrations of Zn in the region of Lake Baikal. A gradual reduction in its concentrations...
in snow meltwater, as it moves away from the lake, suggests that the zinc accumulation in snow meltwater in the water area is probably associated with the geochemical specificity of rocks and soils on the western shore of Lake Baikal, which is enriched with this element [16]. During aeolian transport from coastal territories, having a small amount of snow, a significant proportion of suspensions and aerosols accumulates on the lake, creating increased concentrations of Zn in the snow cover. At the same time, it is impossible to exclude the anthropogenic factor in the formation of Zn concentration in the snowy meltwater of Lake Baikal since Zn is one of the main elements of technogenic origin. One of the factors, affecting the concentration of impurities in the atmosphere on the territory of Southern Baikal, can be the industrial emissions from Irkutsk with prevailing northwest winds. The accumulation of zinc in the snow cover from the city is due to emissions into the atmosphere from the enterprises of the Irkutsk Aviation Plant, brick factory and steam power plant [17].

Snow meltwater from most stations of Usolye-Sibirskoe and Svirsk are significantly enriched with trace elements relative to background values. The high values of the microelement of the CC reflect the impact of technogenic factors on the ecological and geochemical situation of the urbanized territories (table 2). The bulk of the elements has the highest concentrations in the snow cover within the industrial zones of settlements and the lower concentrations within the residential areas. The exceptions are Mn and Pb (Svirsk) and U (Usolye-Sibirskoe), which accumulation in snow meltwater from the residential area is higher than in the industrial zone. Comparison of average concentrations of trace elements in snow meltwater from industrial zones shows specific components, which enter the atmosphere with dust and gas emissions located in the territories of enterprises. In Svirsk, such elements include As and V; in Usolye-Sibirskoe – Hg, Zn and Pb. Technogenic contribution to the accumulation of Mn, Fe, Co, Ni, Cd, Cu, Th, and U in snow cover from Usolye-Sibirskoe and Svirsk are comparable.

| Study area                        | CC                  |
|----------------------------------|---------------------|
| Usolye-Sibirskoe                 | Hg (90) – Co, Pb, U (5) – Fe (4) – Mn, V (3) – As, Cu, Cd, Th (2) – Ni (1) Zn (0.8) |
| (industrial zone)                |                     |
| Usolye-Sibirskoe                 | Hg (20) – U (5) – Co (4) – Pb (3) – Fe, Mn, V, Cd, Th (2) – Cu (1) As (1) Ni (0.9) Zn (0.5) |
| (residential areas)              |                     |
| Svirsk                           | As (13) – U (12) – Hg (10) – V (8) – Pb, Co, Fe (4) – Cd, Mn, Th (2) – Cu, Ni (1) – (1) – Zn (0.5) |
| (industrial zone)                |                     |
| Svirsk                           | Pb (6) – Hg (5) – Mn (4) – Co (3) – V, Th, U, As (2) – Fe, Cd, Ni (1) – Cu (0.8) – Zn (0.3) |
| (residential areas)              |                     |

Both in industrial and residential areas, concentrations of elements in snow meltwater are several times higher than background values. The values of CC in industrial and residential areas of towns differ. In the residential area of Svirsk, snow meltwater is more saturated with Pb, Hg, Mn, and Co, whereas in Usolye-Sibirskoe – with Hg and U. Enhanced concentrations of U and Th in the snow cover of the towns, where enterprises do not use these elements in production cycles, is probably related to the air transport from neighboring territories, in particular, with the influence of emissions from the Angarsk Electrolysis Chemical Plant, which enriches uranium.

Within the industrial zone of Usolye-Sibirskoe, the value of the total pollution index (Zc) vary from 29.3 (low pollution) to 604.5 (very high pollution), within the residential zone – from 0.47 (low pollution) to 133.9 (high pollution). On the territory of the industrial zone of Svirsk, the value (Zc) ranges from 11.8 (low pollution) to 97.4 (medium pollution), within the residential zone – from 3.51
(low pollution) to 31.4 (low pollution). The results indicate the local distribution of technogenic pollutants.

Despite significant closure of the UsolyeKhimProm enterprise in Usolye-Sibirskoe and elimination of the arsenic dumps of the Angarsk Metallurgical Plant in Svirsk, the main pollutants of these cities are still mercury and arsenic, respectively (table 2). Comparative analysis of As concentrations in samples from the towns of the Baikal region has shown that Svirsk has the highest concentrations of this trace element than other industrial centers, significantly exceeding the indices. According to our data, the maximum arsenic content in meltwater from Irkutsk was 1.87 μg/l, in Shelekhov – 1.14 μg/l, in Angarsk – 1.08 μg/l, and in Listvyanka – 0.97 μg/L, which 2-3.5 times exceeds background values. Within the industrial zone of Svirsk, arsenic concentrations in meltwater are 55 times higher than background values (table 1).

The dispersion halos of As show the local distribution of its high concentrations in meltwater. Moreover, it is predominantly limited to the industrial zone of operating enterprises (TPP and Battery Plant) and the territory where dumps of the Angarsk Metallurgical Plant were previously located. The maximum concentrations of As, Pb, Zn, Cd, and Fe in meltwater for the industrial zone of Svirsk were recorded on the reclaimed territory of the former Angarsk Metallurgical Plant. The high concentrations of these elements are due to the composition of arsenic production wastes. The cinders consisted of sulphide ore calcinates mainly represented by iron oxides and hydroxides (60-65%) and aluminosilicates (19-20%), and its arsenic content reached 14.2%, lead content – 1.4%, zinc – 0.23%, and cadmium – 7.6 mg/kg [11]. There is a fanning plume of arsenic in the water area of the Angara River as well as towards the northern part of Svirsk, which corresponds to the prevailing northwest wind direction in this area (figure 1).

![Figure 1. Distribution of arsenic in the liquid phase of the snow cover from Svirsk.](image-url)
Hg concentrations in the meltwater from the industrial zone in Usolye-Sibirskoe tens and hundreds of times exceed background values, which is associated with technogenic geochemical anomalies in the operation of the UsolyeKhimProm enterprise. The main suppliers of mercury to the environment are the mercury electrolysis workshop, under which approximately 345 t of Hg is concentrated in loose deposits, as well as sludge depository of the enterprise with approximately 620 t of Hg [4]. The technogenic load decreases markedly at a distance from the industrial site. At the same time, mercury concentrations at most stations in the residential zone of the Usolye-Sibirskoe field are ten times higher than the background value.

4. Conclusion
Long-term technogenic emission from pollutants has led to significant pollution of industrial sites of enterprises and adjacent territories, which affects the chemical composition of the liquid phase in the snow cover. The calculated CC of trace elements in the liquid phase of the snow cover indicates that the atmosphere of the towns is polluted by gases and water-soluble aerosols, which may be present in the form of various compounds, including toxic ones. The research findings of the chemical composition of the liquid phase in the snow cover enable to determine, with a sufficiently high degree of confidence, the sources of emission into the atmosphere of some potentially toxic elements specific to different types of industries even after a considerable time after the cessation of their operation. Thus, despite the closure of the UsolyeKhimProm in Usolye-Sibirskoe and the elimination of arsenic dumps in Svirsk, the main pollutants of these towns are still mercury and arsenic, respectively. Now, the main sources of these elements in the environment are large volumes of accumulated industrial waste, highly contaminated industrial sites and building structures of previously operating core enterprises. The dispersion halos of increased concentrations of priority pollutants in meltwater (Hg and As) from the industrial sites of the towns extend both to the residential areas and the water area of the Angara River, which is significant as a water body for drinking and fishery purposes. It should be also noted that the industrial sites of the towns of Usolye-Sibirskoe and Svirsk are located on elevated terrain in proximity to the Angara River, and in spring, untreated snow meltwater enters the river ecosystem with surface runoff, creating an additional source of pollution along with air transport as well as discharges of domestic and industrial wastewater.

The restoration of contaminated soils as well as the disposal of workshops, which are not operating now, and other technical facilities is required to minimize the continued flow of hazardous pollutants to urban areas and the Angara River. The obtained results of this study will expand the understanding of the migration paths of chemical elements and can clarify the balance of the biosphere circulation of substances in the Baikal region.

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