Time-Space Estimate of the Variation in a Level of Mercury Pollution of the Altai Atmosphere According to Layer-by-Layer Analysis of High Mountain Glacier Core of Belukha Mountain

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Abstract

Time-space estimate of a level of mercury pollution of Altai atmosphere has been performed according to layer-by-layer analysis of high mountain glacier core sample that was taken by joint Russian-Swiss expedition in 2001 in a saddle of Belukha Mountain of the Altai hills (Katun ridge, Altai). The results arrived at have demonstrated that mercury content of glacier layers that had been shaped during the industrial time varies within the limits of 0.2–6.3 ng/kg and it is comparable with mercury level of alternative high mountain glaciers of the Northern hemisphere. Data of the layer-by-layer analysis of glacier core sample for a period of 1940 to 2001 testify that Aktash Mercury Integrated Works, a large local source of mercury, exerts no significant effect on the pollution of the atmosphere of the Western Altai. A calculation technique has been suggested to quantitatively estimate the regional component of mercury pollution of a territory. It has been found that the contribution of the regional component almost 3.5 times exceeds the contribution of the global component to the total present-day level of the pollution by mercury of the atmosphere of the Altai (Central Asian) region. A conclusion has been made that Altai-Sayan mercury province and industrial metallurgical centres of East Kazakhstan may act as the main sources in terms of the regional level of mercury pollution of the atmosphere of northwest part of the Altai territory.

Keywords: high mountain glaciers, pollution of the atmosphere, mercury, layer-by-layer analysis, types of circulation, orographic barriers

INTRODUCTION

Carrying out direct monitoring observations [1–3] and theoretical calculations of the emissions of pollutants to the atmosphere [4, 5] fall into the basic methods to estimate the modern-day level of contamination of the atmosphere. Currently, to provide generalized information on the ecological state of the atmosphere both for a past epoch and for a present-day interval of time, the use is made of various stratified natural holding lagoons [6]. Among them, high mountain glaciers occupy a special place [7]. Heightened interest to these ground stratified holding lagoons is determined by their observed intensive degradation, which results in that their use as "paleoarchives" will be impossible any more in a short time [8, 9].

A methodology of the way to estimate a scale of atmospheric pollution using data of layer-by-layer chemical analysis of high mountain glacier cores has its origins in the following factors:
- Existence of correlation between atmosphere pollution and concentrations of pollutants in layers of ice core sample, these pollutants having been formed at that time;
- Comparison of data of chemical analysis of a core sample with information on the pollution sources, on meteorological and orographic conditions of the region.
High mountain glaciers represent much interest to make an estimate of a level of atmosphere pollution by substances with the capacity for transportation to significant distances. Mercury is a typical representative of such class of substances [3]. A potential for global spread of mercury is determined by the fact that it exists in free air for the most part (95–99%) in the form of elementary gaseous mercury, the life time of which in the atmosphere comprises approximately 1–2 years [10, 11]. Owing to the global spread of mercury, practically every emission source may have an influence on any remote region; therefore, its intercontinental transfer along with local and regional sources makes also a contribution to mercury pollution of the environment. For Altai (Fig. 1), this toxic metal is a priority contaminant, since large natural and anthropogenic sources of mercury emission exist in the territory of the region [12]. The purpose of this work is to determine modern-day and retrospective levels of mercury pollution of the atmosphere of Altai and to estimate the contribution of regional and global components to mercury pollution.

SUBJECT OF THE RESEARCH

High mountain glaciers of Tien Shan-Pamir and Altai hills can serve as few in number paleoarchive indicators of pollutants and aerosol particles entering the atmosphere of the Central Asian region [13]. To make an estimate of modern-day and retrospective level of atmosphere pollution of Altai, a joint Russian-Swiss expedition took an ice core from the depth of 140 m in a saddle of the Belukha Mountain (lat. 49°48' N, long. 86°34' E, height of 4062 m; Katun ridge, Altai) in July, 2001.

Freedom from mixing and thawing of the layers of a glacier during its formation is a necessary condition to use the ice core sample as a “paleoarchive”. Glaciological and glaciochemical studies of a glacier in a saddle of the Byelukha Mountain that have been performed jointly by Paul Scherrer Institute (Switzerland) and the Institute for Water and Environmental Problems, SB RAS (Barnaul, Russia) have shown the freedom from effects of melting and mixing of the ice layers, which bears witness to the suitability of this glacier for further paleoarchive studies [14, 15]. As a consequence of these works, snow accumulation of the given glacier has been also determined from the variation in the content of $^{18}\text{O}$ and $^{}\delta^D$ stable isotopes for an annual period, and dating of layers with the use of reference-point dates (1963 and 1945, in terms of a maximum concentration of tritium and plutonium, respectively) has been performed; activity of $^{210}\text{Pb}$ and seasonal changes in the concentration of $^{18}\text{O}$ and ions of ammonium [16, 17] has been measured. Thus far the most part of the selected glacier core of Belukha mountain has been dated and analysed for its layer-by-layer content of the main substances that are related to biogenic ($\text{NH}_4^+$, $\text{COOH}^-$), soil ($\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Cl}^-$, $\text{Na}^+$), and anthropogenic ($\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{NH}_4^+$) emission to the atmosphere [15–18].

METHODS OF THE RESEARCH

Method of atomic fluorescence spectroscopy (AFS) was applied to determine ultralow mercury concentrations in samples of ice and snow (at a level of nanograms per kilogram and less). When sampling and analysing the core sample, we performed all field and analytical works with the observance of technique of “ultrapure report” [19]. An ice core sample for the layer-by-layer analysis was cut in “a cold room” (with the resolution of 10–20 cm) and later after the appropriate decontamination procedure, the samples were prepared to conduct an assay for total and reactive mercury.
To determine reactive mercury, i.e., easily reduced forms, the samples were oxidized by 0.4% HCl solution according to recommendations of [20], and to determine total mercury, the sample was oxidized by BrCl by the US EPA Method 1631 [21].

The possibility to apply AFS method for mercury analysis in ice and snow samples were studied with the use of mercury analyser Mercur (Analytik Jena, Germany) that depends on combination of “cold steam” technique with atomic fluorescence detecting. Amalgamation regime makes it possible to enhance focusing of mercury peak approximately by 7–8 times as compared with a direct injecting of the sample. Further improvement of the sensitivity by way of concentrating the greater volume of the sample (3 mL) and by way of optimising the instrument parameters (the voltage of the photocell multiplier of 475 V, the reaction time of 18 s, time to anneal the sorbent of 20 s) in combination with an original procedure of sample preparation has allowed us to determine the presence of mercury in ice and snow samples with the detection limit of 0.025 ng/kg [22, 23]. To control the correctness of the given procedure certified reference standards ORMS-2 (river waters) that are manufactured by Natural Research Council Canada (NRCC) have been used. Data that have been obtained for three parallel determinations (30.1±0.45 ng/kg) are comparable with the certificated value (30.6±2.3 ng/kg). The relative standard deviation for samples and standards was as large as 1–6%.

Using the developed procedure, we analysed layers of a glacier core sample of Belukha Mountain that were dated 1925–2001.

RESULTS AND DISCUSSION

The results arrived at have demonstrated that mercury content of the glacier layers that have been shaped during industrial time varies over a wide range, from 0.2 to 6.3 ng/kg (Fig. 2).

To make an estimate of the pollution level and of the contribution of regional sources to the total balance of mercury entering the air basin of the Altai region, acquired data of chemical layer-by-layer analysis of ice core of a glacier of Belukha Mountain were compared to current reliable literary data on mercury content in layers of core samples of other glaciers and in superficial snow of the remote places of Northern hemisphere (Tables 1, 2). These data involve the results of investigations that

<table>
<thead>
<tr>
<th>Sampling place</th>
<th>Sample type</th>
<th>Years</th>
<th>Mercury content, ng/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>total</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>reactive</td>
</tr>
<tr>
<td>Altai, a glacier of Belukha Mountain (3895 m) [30]</td>
<td>Superficial snow</td>
<td>2000</td>
<td>0.8–1.4 (n = 29)</td>
</tr>
<tr>
<td></td>
<td>Upper firn layer</td>
<td>1998–2001</td>
<td>1.7–3.5 (n = 17)</td>
</tr>
<tr>
<td>Swiss Alps, Jungfraujoch (3450 m) [30]</td>
<td>Superficial snow</td>
<td>2002</td>
<td>1.5–2 (n = 13)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.6–1.4 (n = 26)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&lt;0.8 (n = 14)</td>
</tr>
<tr>
<td>Swalbard, Norway [32]</td>
<td>Seasonal snow</td>
<td>2003</td>
<td>1.2–32 (n = 28)</td>
</tr>
<tr>
<td>Kuujarapik, Canada [32]</td>
<td></td>
<td>2002</td>
<td>3.4–24.5 (n = 6)</td>
</tr>
<tr>
<td>Central Greenland, Summit, 3238 m [27]</td>
<td>Snow core</td>
<td>1949–1989</td>
<td>&lt;0.05–2.0 (n = 56)</td>
</tr>
</tbody>
</table>

Note. n is the number of averaged values.
TABLE 2
Comparison of data on the content of total mercury in ice core samples of various glaciers of the world during the industrial time

<table>
<thead>
<tr>
<th>Sampling place</th>
<th>Sample type</th>
<th>Year of the formation of the glacier layers</th>
<th>Content, ng/kg of the glacier layers</th>
<th>Average*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Altai, glacier of Belukha Mountain (4062 m)</td>
<td>Firn, ice</td>
<td>1941–2001</td>
<td>0.19–6.29</td>
<td>1.95 (n = 61)</td>
</tr>
<tr>
<td>Alps, Mont Blanc (4250 m) [33]</td>
<td>The same</td>
<td>1913–1990</td>
<td>0.86–5.76</td>
<td>2.20 (n = 9)</td>
</tr>
<tr>
<td>The USA, Upper Fremont glacier (4100 m) [34]</td>
<td>-</td>
<td>1900–1993</td>
<td>-</td>
<td>10.0 (n = 39)</td>
</tr>
<tr>
<td>Central Greenland, Summit, 3238 m [27]</td>
<td>Snow core</td>
<td>1949–1989</td>
<td>&lt;0.05–2.0</td>
<td>0.43 (n = 31)</td>
</tr>
</tbody>
</table>

*Average content of mercury was calculated from mid-annual values for the specified period; n is the number of averaged values.

were performed with the observance of expressly developed technique of «an ultrapure analysis” [24–26]. The technique has been applied and substantiated for the first time to explore a content of heavy metals in snow and ice cores from the polar regions [27, 28]. Meanwhile, the data that had been received before the middle 1980s were considered mostly bankrupt in the context of sample contamination problems at the stage of sampling and analysis [29].

Comparison of the results we obtained to literary data has demonstrated that mercury content of the top snow layer of a glacier core sample from Belukha Mountain that is representative of the modern levels of atmospheric pollution of the region under study (see Table 1) is at a low level and it is comparable with concentrations of mercury for other high mountain glaciers and remote regions of Northern hemisphere (Central Greenland). The content of both total and reactive mercury for the Swiss Alps and Altai is about identical. Meanwhile, the levels of content, and the ratio of total and reactive mercury for French and Swiss Alps are significantly different, which invites for further investigations.

In general, mercury content in the top snow layer of a glacier core sample of Belukha Mountain and in superficial snow are significantly less by comparison to other investigated places of the Northern hemisphere [31, 32]. This fact bears witness that total emission of mercury and its transportation to long distances presently define a level of the contamination of the environment of Altai and the Central Asian region as a whole.

From data of Table 2 it will be obvious that layers of the glacier of Belukha Mountain are characterized by the lowest mercury content among all considered high mountain glaciers, and most close values of mercury content have been determined in a glacier of Mont Blanc.

To make a quantitative estimate of the regional component of mercury pollution we suggested the following calculation technique. It is possible that mercury concentration in the atmosphere that is reflected in glaciers of Central Greenland, the area that locates at significant distance from industrial centres of our planet be accepted as the global background modern-day (industrial time) mercury level of the Northern hemisphere. By means of comparative analysis of mercury concentrations in layers of a glacier of Belukha Mountain that has shaped during industrial time, and in analogous layers of snow core taken in Greenland, it is possible to determine the contribution of regional and global components to mercury emission in the atmosphere of Altai (Central Asian) region. If the total contribution of mercury to the atmosphere of the region under study measures 1.95 ng/kg (the average content for the mentioned period), and the global component is 0.43 ng/kg, then the regional component that is determined as the difference of these two magnitudes, is equal to 1.52 ng/kg. Thus the contribution of the regional component almost 3.5 times exceeds the contribution of the global component to the total modern-day level of mercury pollution of the atmosphere of Altai (Central Asian) region. It was found in analogous way that the modern contribution of the regional component for the Central European region almost 4 times exceeds the contribution of the global component, and that for the USA exceeds almost 22 times.
To characterize a regional component of mercury emission to the atmosphere of Altai (Central Asian) region we shall consider the main local and regional sources, i.e., the main components of mercury emission in this region. Among local sources of mercury pollution, Aktash Mercury Integrated Works (AMIW) that is located in the immediate proximity (~80 km) of the place of core sampling (within the limits of 100-km zone, see Fig. 1) may have the maximum effect on the research area and, particularly, on the content of mercury in layers of a glacier core sample of Belukha Mountain. Altai-Sayan mercury province [35] and industrial metallurgical centres of East Kazakhstan and Southwest Siberia may act as significant regional sources of mercury in the given area.

In estimation of the modern-day level of the environment pollution of the Altai region, AMIW, in opinion of ecologists, serves the largest source of mercury pollution since this integrated works was one of the largest ones in terms of mercury production in the USSR up to the middle 1980s. The maximum peak in the rates of its production fell on 1970–1986. Aktash mine started its functioning since 1941 when the first experiments had been performed in metallurgical sublimation of mercury and production of metallic mercury of R-2 grade. The sublimation of mercury at the first stage of the mine functioning was conducted in primitive retort furnaces without industrial condenser recovery devices. The coefficient of mercury extraction comprised as little as 30–35 %. Repeated emissions of mercury to the atmosphere occurred because of imperfection of the technologies; cases of mercury poisoning of people were recorded [36].

An intensive increase in the rates of mercury output at the AMIW begins since the late 50s of the 20th century when more productive rotor plants are put into operation. At that time, the rates of production at the integrated works amount to as much as almost 80 t/year, and in 1970–1980, they were equal to 120–130 t/year [37–39]. Since the second half of 1980s, a sharp setback in its production is evidenced that leads to disintegration of Aktash mine group into separate manufacturers. In 1990, mining operations have been stopped, and later on, all developments of the ore mine have been closed, flooded, and destroyed. However in 1990–2000, the manufacturer processed 1300 t of mercury waste and produced 71.5 t of secondary mercury of R-1 and R-2 grade [40].

To determine the contribution of AMIW to atmospheric mercury pollution of the region under study, graphic comparison of mercury concentrations in the ice core sample of Belukha Mountain and the rates of mercury production at AMIW has been performed for a period of 1940–1991 (Fig. 3). It is evident that direct correlation dependence between the rate of production and the trend of the changing mercury concentration in the ice core is observed only at the initial stage of operation of the integrated works (till 1960s), when the imperfection of the production technology led to significant mercury emissions in the atmosphere. Starting with the 1960s, such correlation is no longer evidenced.

We will consider the principal causes that restrict the influence of AMIW on mercury pollution of the layers of the glacier core sample from Belukha Mountain.

To make pollutants from sources of their emission reach the glacier surface and be buried in it, a favourable action of several factors is necessary. They involve, particularly, the features of the source of entering (its capacity and geographical disposition with respect to the glacier) as well as meteorological and orographic conditions. Aktash mercury integrated works was the largest manufacturer of mercury in

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**Fig. 3.** Comparison of the rates of mercury production at Aktash Mercury Integrated Works and mercury content in glacier core of Belukha Mountain for a period of 1940–2001.
Fig. 4. Distribution of circulation types during year seasons in the territory of Central Asian region.

It is advisable that the influence of meteorological conditions for mountain territories be considered within the limits of regional scale, since the frameworks of local scale for mountain territories are limited by conditions of their mountain-valley circulation. In this relation, to make an estimate of the influence of meteorological conditions on a high mountain glacier, we cannot use data from meteorological stations that are nearest to the glacier, first of all, because of a difference in the position heights for the meteorological station and the glacier.

This factor taken into account, to estimate the influence of meteorological conditions on the glacier of Belukha Mountain we have systematized and calculated a percentage ratio of eight types of circulation during year seasons with the use of data on the types of atmospheric circulation and with dissected kinematic maps of the natural synoptic period for the region under study for a period of 1951–1990 (Fig. 4).

It is evident that western, southwest, and northwest anticyclonic types of circulation dominate in the region in winter and spring periods, however their proportion drops down in spring at the expense of an increase in a cyclonic component. Southwest and western cyclonic types of circulation dominate in summer and in autumn, the contribution of ultrapolar intrusions and stabilization of cyclones being additionally augmented in summer, and their proportion decreasing in autumn period. Thus, with preferential movement of air masses from the west, southwest, and northwest, the sources that are located to the west, to the northwest, and to the southwest of Belukha Mountain will make the maximum influence on the glacier. The influence of the sources that are located to the east of Belukha Mountain that involve AMIW will be limited.

Orographic conditions of the area under study are mainly represented by orographic barriers of the Great Altai (Fig. 5). Orographic barrier is diversified forms of the relief that form obstacles on the way of the movement of air currents in the general circulation of the atmosphere. All other conditions being equal, the more are the barriers; the more intensive is their action upon the movement of the air masses [41]. It has been apparent in Fig. 5 that the AMIW is blocked from Belukha Mountain by a massive orographic barrier (two ridges, >3500 m in height), which will hinder the direct spread of mercury from the integrated works to the glacier.

Thus the freedom from any significant influence of AMIW, the powerful local contami-
nant of air basin of the Altai region, on the layers of the core sample of the glacier of Belukha Mountain is determined first by unlikely transfer of air masses from the integrated works to the glacier, and second, by the presence of orographic barriers that block the glacier and all northwest territory of Altai with a double ring from the influence of AMIW. Consequently, the layer-by-layer analysis of the glacier core sample of Belukha Mountain allows us to determine regional mercury pollution of only northwest part of the territory of Altai. The freedom from orographic barriers and the preferential movement direction of air masses should be favourable to spread mercury pollution from AMIW to the areas located to the east and to the southeast of the integrated works. From this, it is inferred that a reliable estimate of scales of the modern-day and retrospective levels of mercury emission to the atmosphere the Central-Asian region.

To estimate the influence of meteorological conditions on a glacier of Belukha Mountain depending on the types of atmospheric circulation during year seasons with the use of dissected kinematic maps of the natural synoptic period.

A procedure of layer-by-layer atomic fluorescence determination of ultralow mercury contents in ice and snow samples has been developed (the detection limit of 0.025 ng/kg), by means of which the ice core sample of Belukha Mountain has been analysed. The results arrived at made it possible:

- To pioneer in estimating the variation in the level of mercury pollution of the atmosphere of the Central Asian region for the recent 75 years.
- To reveal the freedom from the direct influence of Aktash mercury integrated works on the atmosphere pollution of the Western Altai.
- To estimate for the first time the contribution of global and regional components of mercury emission to the atmosphere the Central-Asian region.
- To estimate the influence of meteorological conditions on a glacier of Belukha Mountain depending on the types of atmospheric circulation during year seasons with the use of dissected kinematic maps of the natural synoptic period.

REFERENCES

16. S. Oliver, Atmospheric and Climate History of the Past Two Centuries from Belukha Ice Core, Siberian Altai.


38 Gosudarstvenny arkhiv Altayskogo kraya: Podlinniki, delo 2075, delo 20. delo 4480, Barnaul.

