Chemical composition and acidity of atmospheric precipitation in Baikal region

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Received February 29, 2000

The chemical composition of atmospheric precipitation was studied at three monitoring stations in the Baikal region in 1998–1999. Some atmospheric depositions were studied for the first time at Irkutsk and Mondy stations. It is shown that chemical composition of precipitation varies widely because of different geographic location of monitoring stations, meteorological conditions, and the degree of anthropogenic impact on the territory under study. Acidic rains were observed under some synoptic conditions in the studied region.

Introduction

Investigation of the chemical composition of precipitation is an important part of atmospheric observations. Precipitation removes pollutants from the atmosphere and thus takes part in air clearing.

In the 1980's, acid rains[1–5] became a key problem of environment in Western Europe, USA, and Canada. A transborder and macroscale transport of pollutants from Western Europe, as well as the effect of Russian large industrial centers on the environment has led to acidifying of precipitation in the western part of the European territory of the former USSR.[1]

In recent years, the problem of acid deposition arose also in some countries of South-East Asia[6] due to fast growing industry.

Vast expanses, point sources of pollution, and alkaline reaction of atmospheric deposition near industrial centers point to the absence of the problem of acidifying in Eastern Siberia in the 80's.[7] However, in Ref. 8 it was noted that precipitations with pH = 4.8–5.2 were observed in some Baikal areas, mostly in background northern regions.

It is commonly supposed that pH = 5.0 is the lower boundary of the natural acidity of precipitation.[1] The elevated acidity of precipitation in these regions most likely corresponds to the natural background. Such precipitation is most sensitive to acidifying due to low mineralization and low buffer capacity.[8] Some Baikal areas, especially, the south-west shore, are characterized by the great amount of precipitation in winter.[8,9] The increase of acid loading can lead to negative consequences for the whole unique ecosystem of Lake Baikal.

The purpose of our investigations was to study the peculiarities of formation of the chemical composition of atmospheric precipitation in Baikal areas with different anthropogenic load, to reveal seasonal differences of precipitation, and to determine the factors affecting possible acidifying of precipitation in the region.

1. Material and methods of investigation

Atmospheric precipitations were collected at three monitoring stations of the Baikal region (the city of Irkutsk, village Listvyanka, and station Mondy).

Irkutsk is a big industrial center with population of more than 700 thousand. The principal sources of air pollution in the city are emissions of industrial objects and exhausts of motor cars.

Listvyanka is a small village (population of about 3 thousand) situated on shore of the south edge of Lake Baikal 70 km far from Irkutsk. It has point sources of atmospheric pollution such as small boiler-houses and stove heating. Additional pollution comes with air masses from industrial plants of the Baikal region at the northwesterly wind.[10]

Station Mondy is an astronomic observatory of the Institute of Solar-Terrestrial Physics. It is situated on one of the plane tops of the Khamar-Daban ridge 2005 m above the sea level. The station uses power from an industrial supply line, so it has no its own sources of atmospheric pollution. The nearest populated areas are several tens kilometers far away. The station is more than 200 km far from large industrial centers (Irkutsk, Baikalsk) and is closed by the Khamar-Daban and East Sayan ridges.[11]

A total of about 150 samples of different precipitations were collected and analyzed since September 1998 until October 1999. Rainwater was sampled into automated precipitation samplers, and snow samples were collected in specialized vessels 35 cm in diameter. The pH value, electric conductivity, and ionic composition of the samples were determined. The samples were analyzed by the methods of ion chromatography,[12] atomic absorption, and spectrophotometry. The results were checked by

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calculating the error of the ion balance and the error of the calculated and measured electric conductivity.[6]

2. Discussion

Irkutsk. The mean ion sums of precipitations sampled at the monitoring stations are shown in Fig. 1. As is seen in the figure, atmospheric precipitations in Irkutsk in both winter and summer are more mineralized than those sampled at other stations (25.5 and 11.4 mg/l, respectively). The maximum ion sum in the sample of snow water at this station achieved 188 mg/l, and the minimum one was 2.5 mg/l. High concentrations of the determined components in snow water are explained by additional air pollution in the cold season by dust and gaseous emissions of heat and power enterprises, as well as by meteorological conditions preventing spread of industrial emissions.[13,14] The prevalent ions in precipitation of this period were Ca^{2+} and SO_4^{2-}, whose mean concentrations were 4.7 and 8.1 mg/l, respectively.

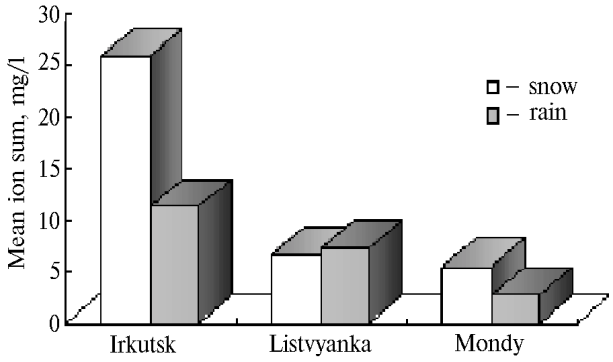

Fig. 1. Mean ion sums of atmospheric precipitation at monitoring stations of Baikal region (1998–1999).

The portion of NH_4^+ ions increased in summer and fall. These ions originate mostly from natural sources and agriculture.[2] The ion sum in rainwater varied from 1.8 to 54.0 mg/l.

The annual behavior of the pH value in precipitation at the stations under study is shown in Fig. 2. At the station Irkutsk, the pH value of snow water varied from 4.8 to 7.6 with the mean of 6.3, and pH of rainwater varied from 4.2 to 7.2 (the mean value was 5.6). The decrease of acidity was observed at this station in winter. The value of pH was maximum at the end of winter. Possibly, this is related to the fact that precipitation was minimum in February and March, and the atmosphere was less intensely cleaned of alkaline components. The maximum precipitation was observed in the warm season, especially, in June and July. Twenty four samples of rainwater were collected, and in 11 of them the pH value was lower than 5.0. The prevalent ions in some precipitations were H^+ and SO_4^{2-}. The increase of rainwater pH in September and October is also explained by the small amount of precipitation in this fall season. A great amount of suspended particles was accumulated in the atmosphere, thus increasing mineralization of precipitation.

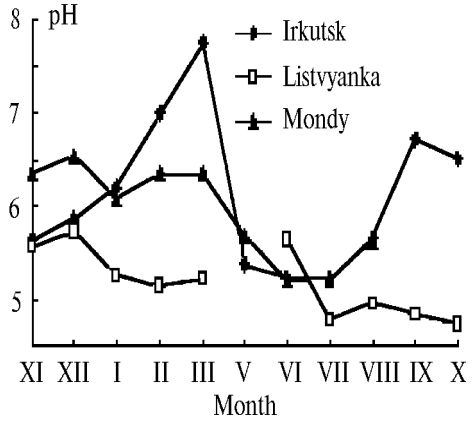

Fig. 2. Seasonal variations of pH at monitoring stations of Baikal region (1998–1999).

The analysis of meteorological conditions has shown that acid rains in Irkutsk are related to, as a rule, feebly marked local pressure formations causing slow motions of air masses in the region. These processes increase the contribution of regional anthropogenic sources to formation of the chemical composition of precipitation at weak generation of soil dust. In the periods when air masses came from the valley of the river Selenga and from the south of Lake Baikal, the SO_4^{2-} ion was prevalent in acid precipitation. Prevalence of the Cl^- ions was observed, as polluted air masses were transported from sources situated to the west of Irkutsk, from Sayansk and Usol'ye-Sibirskoe.

The gradual decrease of mineralization of precipitation with the simultaneous increase of their acidity occurs in the period of long snowfalls and long rains. In Ref. 14 it was also noted that most pollutants are washed out of the atmosphere by first portions of rain.

Listvyanka. The annually mean ion sum in precipitation sampled at the station Listvyanka was 7.0 mg/l. No marked difference was noticed between mineralization of winter (6.7 mg/l) and summer (7.2 mg/l) depositions. The prevalent anion in precipitation throughout the year was SO_4^{2-}. Its mean value in snow water is greater than in rainwater (3.0 and 2.2 mg/l, respectively). Such seasonal variations are also characteristic of NO_3^- ion. The winter increase of the concentrations of the SO_4^{2-} and NO_3^- ions in atmospheric precipitation in Listvyanka is related to the elevated winter content of sulfur and nitrogen compounds formed at fuel burning.[2]

The distribution of principal cations in precipitation in Listvyanka is also characterized by seasonal differences. The cations NH_4^+ and, to a lesser

degree, Ca^{2+} are prevalent in snow water. Their mean concentrations are 0.78 and 0.6 mg/l, respectively. Ammonium sulfate is the principal water-soluble component of the continental aerosol in the regions situated far from pollution sources.[2] The prevalence of this compound in snow water in Listvyanka indicates that the chemical composition of precipitation is affected by not only local sources of pollution, but also remote transport of pollutants along the valley of the river Angara.[10,13]

The portion of Ca^{2+} ions in rainwater in Listvyanka in summer was somewhat greater than that of NH_4^+ ions (mean values of 0.7 and 0.46 mg/l, respectively). The Cl^-, SO_4^{2-}, and NO_3^- ions with concentrations of 2.5, 4.5, and 2.2 mg/l, respectively, were observed in the rain sample collected in Listvyanka on August 15, 1999. In this case pH decreased down to 3.9. Thus, H^+ and SO_4^{2-} became prevalent ions. Precipitation with such acidity and ion ratio can be considered as "acid," and it was first observed in some rainwater samples in the Baikal region.

The mean value of pH in Listvyanka was 5.5 with variations from 4.9 to 5.9 in snow water and 5.2 with variations from 3.9 to 6.3 in rainwater. As at the station Irkutsk, the decrease of pH was observed here in summer. This decrease is related to the increasing amount of precipitation and, hence, more intense washing of the atmosphere (see Fig. 2). A half of rainwater samples collected since June until August had pH less than 5.0.

Mondy. The mean ion sum in snow water at the station Mondy was 5.5 mg/l, i.e., five times less than the analogous value for precipitation at the station Irkutsk. The mean pH value was 6.3 with variations from 5.8 to 6.6. The prevalent ions in precipitation of this period were HCO_3^- and Ca^{2+}. Such prevalence of ions and decrease of acidity in the background region in winter are related to the composition of surface rocks (limestone, dolomite, marble) and soils (turf-carbonate) of this region.[15,16,17] Winter at the station Mondy is usually characterized by small amount of precipitation (20–25 mm since October till March).[16] So erosion of ridges and soils not covered with snow significantly affects formation of the chemical composition of precipitation in this region.

The maximum amount of precipitation was observed at the station Mondy in June and July 1999. This led to the decrease of the ion sums in rainwater down to 2.8 mg/l, on the average, and pH down to 5.3. NH_4^+, Cl^-, and SO_4^{2-} became principal ions in rainwater. H^+, Cl^-, and SO_4^{2-} were prevalent in some precipitations at the station Mondy at pH from 4.7 to 5.1. The ion sum varied from 0.4 to 1.5 mg/l. Consideration of synoptic maps has shown that acid rains at the station Mondy are related to small-scale cyclones and anticyclones against the background of a low-gradient pressure field over Siberia. Under these conditions and at weak influence of natural factors, slow motions of air masses over the region favor penetration of regional anthropogenic pollutants into background regions (Fig. 3).

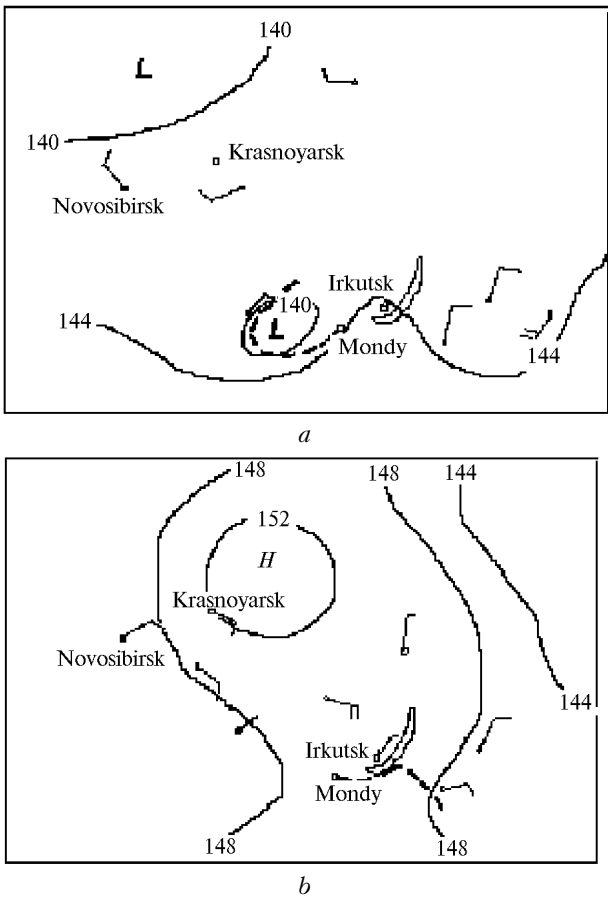

Fig. 3. Synoptic situation in the region for the period of atmospheric precipitation with low pH at the station Mondy: rain on July 20, 1999, pH = 4.70 (*a*) and rain on July 7, 1999, pH = 4.73 (*b*).

Conclusion

Thus, monitoring of atmospheric precipitation in the Baikal region has shown that the chemical composition of precipitation depends on the geographic location of monitoring stations and varies under the effect of climatic, meteorological, and anthropogenic factors.

Among the considered monitoring stations, Irkutsk is most strongly affected by emissions of pollutants and has the highest concentration of ions in atmospheric precipitation (18.5 mg/l). Listvyanka is less subjected to anthropogenic factors. The ion sum of atmospheric precipitation at this station is 7 mg/l. Precipitation at the station Mondy characterizes the background continental region. The ion sum is equal to 4.2 mg/l.

Acid precipitations at the monitoring stations are observed mostly in summer, resulting from passage of local cyclones and frequent long rains.

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