Analysis of mechanism of formation of ion composition of atmospheric precipitation in the south of Eastern Siberia

E.V. Molozhnikova, E.V. Kuchmenko,* O.G. Netsvetaeva, and N.A. Kobeleva

Limnological Institute, Siberian Branch of the Russian Academy of Sciences, Irkutsk
** Energy Systems Institute, Siberian Branch of the Russian Academy of Sciences, Irkutsk*

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The aim of this paper is to specify the mechanisms of anthropogenic impact on the composition of atmospheric aerosols and precipitation. In this study we made use of data obtained by snow sampling during 5 years in Irkutsk and in 2002 in Slyudyanka settlement. Attention was primarily paid to revealing the relationship between the ion composition of atmospheric precipitation and the operating characteristics of industrial emission sources. An attempt was made to balance sulfur-containing compounds in the atmosphere of various populated settlements (by using local and regional transport models). Estimation of the anthropogenic impact on the precipitation composition in the regions calls for the knowledge of natural mechanisms that form the background characteristics. If there is no anthropogenic impact, the composition of precipitation is determined, first of all, by the source and region of the condensation nuclei formation as well as by the atmospheric pollution on the way of air mass that carries precipitation. The trajectories of air masses, characterized by most mineralized atmospheric precipitation, were determined for the background and industrial areas in the near-Baikal region.

Chemical composition of atmospheric precipitation (AP) is determined by the source and the region of formation of condensation nuclei, as well as by the state of the atmosphere along the travel path of an air mass (AM) carrying precipitation to the region. The goal of this paper is to reveal the mechanisms of formation of chemical composition of AP depending on the direction of air mass motion (long-range transport) and the effect of local sources of anthropogenic pollution. The paper analyzes data on chemical composition of AP fallen in Irkutsk over a period from 1999 to 2002 and the snow cover sampled late in winter during 5 years (1998–2002) in Irkutsk and in 2000 – in Slyudyanka settlement.

To construct the air mass trajectory the model HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory Model) of the USA National Oceanic and Atmospheric Administration[1] was used. Using the archives of meteorological data the back trajectories were constructed for different seasons (no less than 30 days in every season). We have separated 12 most widely met types of trajectories for air masses at heights of 3000 m and 5000 m, including "local circulation" (LC) corresponding to low winds. As part of the investigations it was confirmed that in the south of Eastern Siberia the western, northwestern and southwestern transport of air masses prevailed; transport of air masses from the east is rare in occurrence (with the account of the southeastern and northeastern directions – from 3 to 10%) (Table 1).

At the western and northwestern trajectories of motion of air mass we can observe the increase of annual mean ion concentrations in the atmospheric precipitation (primarily sulfates). In this case this dependence can be clearly seen from the data collected in cold period (Fig. 1*a*) that, evidently, is connected with the effect of anthropogenic sources of aerosols located in Irkutsk–Cheremkhovo Fuel and Energy Plant as well as in the Krasnoyarsk Territory along the northwestern trajectory of the air mass motion. Similar analysis of annual mean data (for 1999) for Mondy Station makes it possible to argue that in the background regions the maximum content of basic ions is observed in the atmospheric precipitation transported from the southwest – from Mongolia and Kazakhstan.[2]

Table 1. Repetition of trajectories of different types, %

Direction	Annual mean			
	1999	2000	2001	2002
N	9.6	4.2	5.8	6.0
N-N-W	0.8	2.5	2.2	0.7
N-W	15.7	12.5	11.5	6.7
W-W-N	15.7	17.2	14.5	17.3
W	19.0	15.5	16.4	23.3
W-W-S	13.2	15.2	16.2	12.0
S-W	6.9	10.0	9.3	14.0
S-S-W	3.8	4.4	5.8	8.0
S	2.5	3.9	2.5	1.3
E	1.4	1.4	6.0	1.3
N-E	3.3	2.2	2.7	1.3
Local circulation	8.2	11.1	7.1	8.0

During warm period (May–October) the western transport of air masses also prevailed though the repetition of meridian types of circulation increased, during which the repetition of cases of the southwest circulation increased up to 30% and of the northwest circulation decreased to 15%. The occurrence of local circulations increased.

The most polluted precipitation came also from the west and northwest (Fig. 1*b*). The sum of ions in the atmospheric precipitation of Irkutsk in summer decreased, on the average, by a factor of two (the ion

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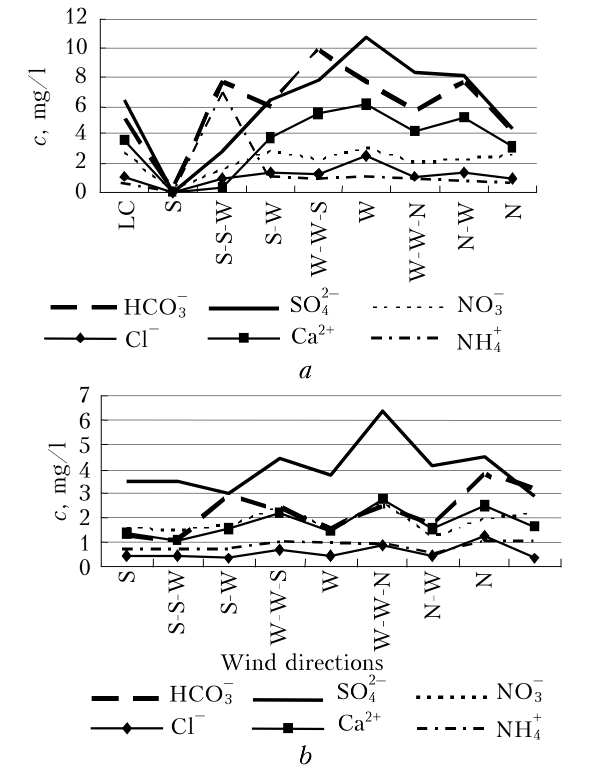

Fig. 1. Variation of chemical composition of atmospheric precipitation in Irkutsk depending on the trajectory of air masses: winter period (*a*); summer period (*b*).

concentration in the AP during winter period was 24 mg/l, and during summer period it was 11.6 mg/l). It is expected that this minimum is due to the following four reasons:

(1) the increase of total quantity of precipitation (by a factor of 2.7) and the number of days with precipitation that favors the acceleration of processes of atmospheric self-purification;

(2) variations in trajectories of motion of air masses, including the decrease of repetition of the northwestern trajectories;

(3) the decrease in the wind velocity as compared with spring months that results in the reduction of soil aerosol lifting.

(4) completion of heating season and, respectively, a sharp decrease of the amount of anthropogenic emissions owing to the heat-and-power engineering enterprises performance.

Having considered the monthly mean chemical composition of AP in Irkutsk (Fig. 2) it should be noted that the peaks of pollution could be observed during winter months (February) and spring months (April–May). It is evident that the main reason of the increase of AP mineralization in spring is the increase in wind speed resulting in the growth of soil aerosol concentrations in the atmosphere. Besides, this period is characterized by small amount of precipitation. Based on our data, from 2.1% (1999) to 12.6% (2001) of the annual amount of precipitation fell in the April and May period.

It may be supposed that the winter maximum depends on large volumes of industrial emissions, first from the heat and power production plants as well as by insignificant dispersal during this period. Figure 2 shows the annual secondary maximum of mineralization, mainly for October, and in 2001 – for November. The sharp increase of ion concentration during this period is connected with the decrease of number of cases and the amount of precipitation. Large intervals between those and the increase of repetition of trajectories of the northwestern type, carrying out more polluted air masses (Fig. 2) at increasing wind speed also favored the increase.

The subsequent drop in the mineralization of AP (to 9 mg/l), observed in different years in November or December, being connected with the formation of snow cover and, respectively, with the decrease of soil aerosol lifting, not only at an observation point but along the trajectory of air masses. The minimum of precipitation mineralization, occurred in December for some years, it can be attributed to a large amount of precipitation.

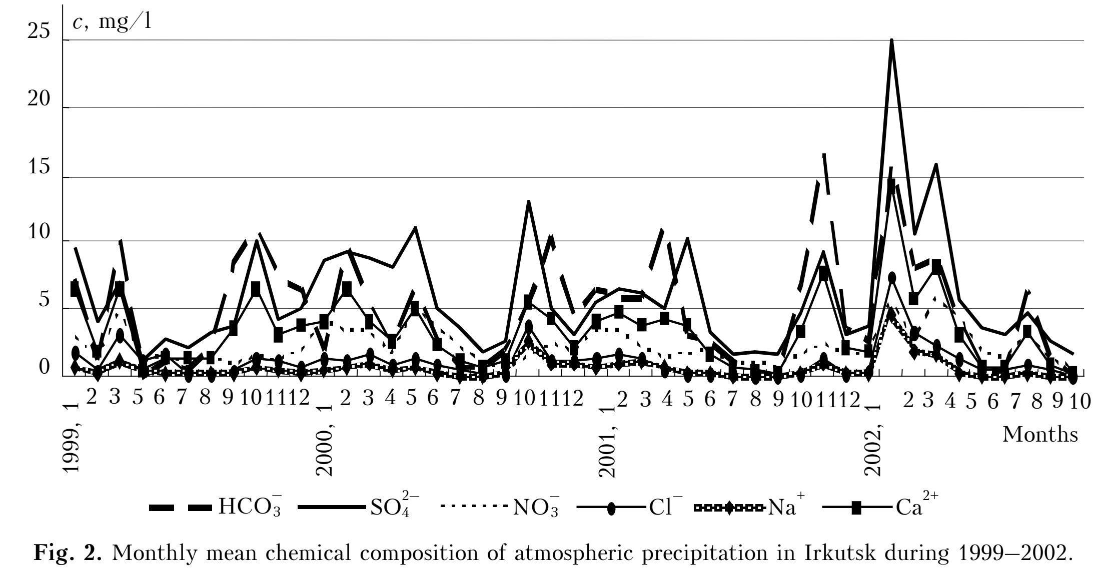

Fig. 2. Monthly mean chemical composition of atmospheric precipitation in Irkutsk during 1999–2002.

The results of snow survey also make it possible to draw some conclusions about the role of anthropogenic sources of emissions of different types in the processes of variation of AP composition.[3,4] In this case Irkutsk is considered as a typical for Eastern Siberian industrial center, and Slyudyanka – as an orographically isolated populated area with several industrial enterprises and a network of small thermal sources.

It should be explained that Irkutsk is an administrative center of Irkutsk Region with the population more than 600 thousand people. The contribution of industrial emissions of heat and power production plants is 86% of total emission and 99% of sulfur oxide emissions.[6] In the city there are 236 industrial and public boiler-houses operating in addition to one large heat and electric power plant. In some regions the stove heating still exists.

The town of Slyudyanka is situated on the bank of Lake Baikal in its southwestern end in the valleys of rivers Slyudyanka and Pokhabikha between the spurs of the Khamar-Daban ridge. The population of the town is 21.1 thousand people. The industrial enterprises of the city are: enterprises of industry of building materials, metal working industry and mining industry. In the town of Slyudyanka there is one of large carriage-passenger stations. In the town, a series of small boiler-houses is located, although in recent years the number of boiler-houses considerably decreased. The majority of population lives in private houses with stove heating.

Every year in the end of winter season in Irkutsk the snow survey is carried out and the ion analysis of sample composition is performed. The concentrations of anions SO_4^{2-}, NO_3^-, HCO_3^-, Cl^- and cations Ca^{2+}, Na^+, K^+, Mg^{2+}, NH_4^+ are determined. Traditionally, no more than 10 samples are selected on the city territory in different regions that enabled us to evaluate the pollution of precipitation in Irkutsk as compared with other places and background points. However, for a detailed study of the structure of city pollution and identification of emission sources in recent three years the number of sampling sites was increased. In March 2000 36 samples (19 points) were selected in Irkutsk and 3 samples in the near-by vicinity of the town, and in 2001 – 70 samples (38 points) were selected, in 2002 – 26 samples (13 points) were selected. Besides, in 2002 17 samples (10 points) were selected in Slyudyanka and its vicinity as well as 5 samples (5 points) along the route Irkutsk–Slyudyanka.

As a reference compound the sulfate-ion was considered, because the sulfur-containing compounds in Irkutsk and Slyudyanka are present only in the industrial emissions of thermal power plants. To compare the snow survey data with the data on emissions and estimation of the effect of different sources on the snow pollution the numerical models of emission scattering were used.[5] The major part of calculations was performed using a stationary local model based on the Gaussian plume, which at present is used widely in the environmental protection organizations of European Community, USA (version ISC3). A comparison of the configuration of experimental and calculated fields of pollution by sulfates allows one to argue for their satisfactory agreement.

To assess the impact of anthropogenic emissions on the atmospheric precipitation composition on the local and regional scales an attempt was made to prepare the balance of sulfur-containing compounds for Irkutsk and Slyudyanka (see Table 2).

Table 2. The balance of sulfur-containing compounds based on the snow-survey data in Irkutsk and Slyudyanka

Parameter	Irkutsk	Slyudyanka
Number of sampling points	13	8
Years of observation	2000–2002	2002
Number of boiler-houses	236	21
Emissions, t	27198.2	567.8
Fallout, t	191.5	10.45
Fallout (%) of emission	0.70	1.8
Correlation coefficient	0.7	0.93

For Slyudyanka the preparation of the balance appeared to be a simpler problem than for Irkutsk, in spite of such peculiarities as a complex terrain and inhomogeneity of the underlying surface, which complicated essentially the calculation of the pollution dispersal. The correlation coefficient between the calculated and measured characteristics of sulfate fallout for Slyudyanka reaches 0.93, while for Irkutsk the correlation coefficient is about 0.7. Theoretically falling out in a local area for boiler-houses should be from 5% to 10% of the emission.

The relation obtained (0.7–1.8%) between the emission and fallout is due to, first, overestimating of calculated emissions in Irkutsk, at least, twice, and, second, due to underestimating of the quantity of sulfur fallout when evaluating this quantity based on the results of snow sampling that is connected with the sulfate migration over a period of thaws (to 30% of losses).[6] Besides, the sulfur loss is due to the fact that the sulfur is determined in the filtered snow water. In this case, the sulfur, contained in an insoluble form, is deposited on the filter and is not considered in the total balance.

It should be noted that by the results of snow sampling the ion concentration of Ca^{2+} and HCO_3^- in Slyudyanka is higher than in Irkutsk, although the net emission of ash in Irkutsk is by several orders of magnitude greater (Table 3).

Table 3. Anion composition based on data of snow sampling (% equiv.)

Site	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-
Slyudyanka	**53.1**	35.4	0.5	11
Irkutsk	20.5	**55.1**	11.5	12.9

This phenomenon is due to a joint action of two factors:

• the impact of the marble open pit located several kilometers from the city on the spur of the ridge Khamar-Daban;

• the absence of cleaning structures and ineffective burning of coal in small boiler-houses of Slyudyanka as well as very low rates of emission dispersal in the atmosphere due to both a complex relief of the town and the presence of elevated temperature inversions formed during winter time under the action of Lake Baikal.

Separating the degree and the sphere of influence of these two factors calls for further investigations, however, the significance of the second factor gives proof to the following fact. Maximum concentrations of calcium as well as hydrocarbonates and sulfates are found directly in the region of application of boiler-houses.

The results of snow sampling enable us to argue that in low populated areas the snow cover pollution can be compared with such pollution in large industrial centers. Thus, on the average, for all the samples of snow cover, selected in Irkutsk late in winter 2001–2002, the amount of ions is 29.1 mg/l, and for the samples selected in Slyudyanka – 33.2 mg/l.

Such a high pollution level of snow cover in the towns depends upon functioning of a large number of small boiler-houses, their incompetent exploitation, the lack of systems of emission cleaning as well as ineffective burning of fuel. In this case the fraction of HCO_3^- ions in snow cover increases connected first with ash emissions, while in the large cities the fraction of sulfates is much higher formed at high-temperature burning of coals (Table 3).

Thus, statistical analysis of data on chemical composition of atmospheric precipitation in Irkutsk and Slyudyanka has made it possible to draw the following conclusions:

• the largest amounts of ions in atmospheric precipitation observed in Irkutsk occur at western transport of air masses;

• the concentration of ions in atmospheric precipitation during winter period is, on the average, twice as large as in summer period;

• the chemical composition of atmospheric precipitation in large and small towns of Baikal area in winter is mainly determined by local anthropogenic emission sources;

• in spring (April–May) and fall (September, October) months in the absence of snow cover and high winds the role of natural aerosols due to soil-erosion origin becomes greater that results in an increase of AP mineralization.

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References

1. R.R. Draxler and G.D. Hess, Meteorol. Magazine, No. 47, 295–308 (1998).
2. E.V. Molozhnikova, E.V. Kuchmenko, O.G. Netsvetaeva, N.A. Kobeleva, L.P. Golobokova, and T.V. Khodzher, Atmos. Oceanic Opt. **15**, No. 5–6, 401–404 (2002).
3. V.F. Raputa and V.V. Kokovkin, Khimiya v Interesakh Ustoichivogo Razvitiya **10**, No. 5, 669–682 (2002).
4. S.B. Smolyakov, Khimiya v Interesakh Ustoichivogo Razvitiya **10**, No. 5, 521–554 (2002).
5. E.V. Kuchmenko, E.V. Molozhnikova, and S.P. Filippov, Atmos. Oceanic Opt. **15**, No. 5–6, 490–493 (2002).
6. I.S. Lomonosov, in: *Geochemistry of Technogenic Processes* (Nauka, Moscow, 1990), pp. 26–60.