Estimation of some characteristics of sulfate formation and precipitation in the cities of Baikal region

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The development of power production system requires evaluation of primary SO_2 emissions converting into secondary aerosol (sulfates) within the considered area (a local zone). As a first approximation, the tentative estimations of conversion and precipitation of sulfur-bearing compounds can be obtained using data of chemical analysis of snow cover samples collected late in winter. The technique was developed using the data of detailed snow sampling on the territory of Irkutsk for four years (2000–2003) and in Slyudyanka and its outskirts for two years (2002–2003). The integral rates of precipitation of the sulfur-bearing compounds were determined; the values obtained for Baikal region in winter proved to be essentially different from those in Europe. The data on the background pollution of precipitation is shown to be useful for determination of the contribution of long-range transport to sulfate precipitation on the urban territory.

Introduction

It is an established fact that submicron aerosols of anthropogenic origin produce the most strong negative effect on the human health, because just this fraction is capable of penetrating deep into the human respiratory tract.[1] The sources of submicron aerosol in the atmosphere are, first, the industry, especially, power production industry emitting solid particles (primary aerosols) and, second, the processes of transformation of acid-forming gases (SO_2, NO_x, CO) into particles (secondary aerosols, which are characterized by the developed surface and high adsorptivity). It should be stressed that in solving some of the applied problems, for example, in developing ecological limits one should take into account the amount of secondary aerosols formed in a local zone through transformation of acid-forming gases. Thus, the aerosol concentration created by the jth industrial object at the point u is determined as

$$c'_{uj} = \left(\sum_{m \in L} c_{ujm} + \sum_{p \in P_{ag}} \beta c_{uj} \right), \qquad (1)$$

where L is the set of aerosol fractions; β is the coefficient of SO_2 transformation into the secondary aerosol; the first sum is the concentration of the primary aerosol, and the second sum is that of the secondary aerosol formed as a result of the transformation of gases emitted from the same object.

Our study was aimed, in particular, at the development of methods of estimating the fraction of SO_2 transformed into the sulfate aerosol in a local zone (urban area). The selection of the sulfur-bearing compounds as an object for our study is caused by the following reasons. First, in many towns of the region under study, in particular, in Irkutsk and Slyudyanka considered below, the main source of sulfur oxides in the atmosphere are the processes of organic fuel burning; second, chemical analyses aimed at the determination of the concentration of SO_4^{2-} ions in snow samples is cost effective.

Materials and objects of the study

To study the processes of anthropogenic income and transformation of sulfur-bearing compounds, we considered the towns of Baikal region: the city of Irkutsk as an industrial center characteristic of Eastern Siberia and Slyudyanka – orographically isolated town having several industrial enterprises and a network of small heat producing installations.

Some explanations should be given here. Irkutsk is an administrative center of the Irkutsk Region with the population of 600 000. The fraction of power production industry makes up to 86% of the total emission and 99% of sulfur oxide emission.[2] In Irkutsk there are 196 industrial and domestic boiling houses and one large heating plant. In some districts stove heating is still used. The total number of domestic stoves in Irkutsk is more than 30 000.

The town of Slyudyanka is situated on the shore of Lake Baikal in its southwestern part in the valley of the rivers Slyudyanka and Pokhabikha between spurs of the Khamar-Daban mountain ridge. The population of Slyudyanka is 21 100. There are 21 boiling houses in Slyudyanka, but the most part of people live in houses with stove heating (about 2200 houses).

To estimate the precipitation of SO_4^{2-} ions on the considered territory, we used the results of chemical

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analysis of snow cover samples that have been collected regularly in late winter in 2000–2003.[3] The amount of sulfates transported to the urban area from outside was approximately estimated based on the data on chemical composition of the atmospheric precipitation in Irkutsk, Mondy village, and Listvyanka village.

Besides, we took into account the data on the chemical composition of snow samples collected in the same years along the Irkutsk–Listvyanka and Irkutsk–Slyudyanka highways. For a comparison of the concentrations of the primary and secondary aerosols, we used the calculated characteristics obtained using the ISCST3 model a Gaussian plume dispersal.[4]

Calculation of emissions from stationary sources

The preset capacities, the installed heat loads, technical characteristics of the considered heat sources, and the types of the fuel burned were estimated using the results of power surveys carried out in 1995–2003 by specialists from MIPS SB RAS, as well as by analyzing the materials obtained within some international projects.[5,6] Instantaneous (g/s) emissions of SO_2 by boiling houses and domestic stoves were determined by the methods from Ref. 7 for the real loads of the heat stations and boiling houses. In the calculations, we used the specific emissions of SO_2 (kg/GJ) obtained from the results of burning West-Siberian coals of different kinds by different groups of boiling houses and domestic stoves.[8]

ISCST3 Gaussian model

To obtain the calculated characteristics of the concentration fields in Irkutsk and Slyudyanka, we used the standard ISCST3 dispersal model developed by U.S. Environmental Protection Agency.[4]

It should be noted that it is a local stationary model, which is now used most widely in the environmental protection organizations both in Europe and the USA. The version of the ISCST3 model used in this work provides the fields of dispersal from many sources. The surface concentrations for every source are calculated based on the solution of the Gaussian equation for the straight quasistationary emission plume.

In addition to the described features of the model, it should be noted that this version involves a unit accounting for the effect of terrain on the pollutant concentration. In the calculations, we used real meteorological information. The concentration field was calculated with the step of 1 km. For Irkutsk the considered territory was 16×22 km, and for Slyudyanka it was 10×14 km.

Technique for estimating the fraction of SO_2 transformation in a local zone

At the current stage of investigation of the processes of pollutant dispersion and transformation, it is quite difficult to estimate real fraction of the primary emission of SO_2 transformed into the secondary aerosol (sulfates) within the territory (local zone) considered.

In the course of the study, it was found that the model calculations show a wide spread in the parameter β. According to the observations of the chemical composition of the snow cover, the mean precipitations of sulfur-bearing compounds were estimated for the period of the stable snow cover ($P_{SO_4^{2-}}$, mg/(m^2 · h)). For the same period, the ISCST3 model has been used to calculate the mean surface sulfate concentrations ($c_{SO_4^{2-}}$, mg/m^3) (see Fig. 1).

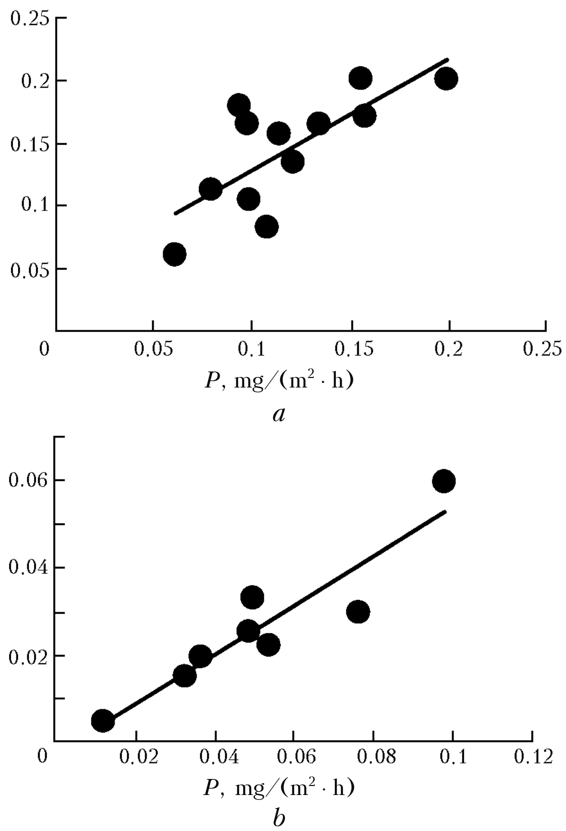

Fig. 1. Comparison of the observed sulfate precipitations, *P*, and the calculated surface concentrations, *c*, at the sampling points: Irkutsk (*a*) and Slyudyanka (*b*).

In simulating the processes of atmospheric pollution, it is commonly believed[9] that the pollutant precipitation is proportional to the surface concentration:

$$V_d = P_{SO_4^{2-}} / c_{SO_4^{2-}}, \quad (2)$$

where V_d, in m/h, is the rate of dry sedimentation. The experimental data available do not allow one to make separation of the processes of dry and wet sedimentation. In the first approximation, using Eq. (2), we can estimate some integral rate of precipitation of sulfur-bearing compounds. The average, over all sampling points, value of V is 0.024 cm/s for Irkutsk and 0.059 cm/s for Slyudyanka screened by Khamar-Daban spurs, while the rate of only dry precipitation of SO_2, according to the literature data,[9] is from 0.07 to 3–5 cm/s.

The obtained estimate of the precipitation rate is, certainly, quite rough and can include modeling errors, random errors, etc., but it should be noted, in the first turn, that the obtained value is much lower than the literature data. It is obvious that in the presence of snow cover under conditions of frequent occurrence of temperature inversions and weakening of turbulent exchange the rate of dry sedimentation decreases and, possibly, prove to be much lower than the earlier known values, because of the climate conditions in Eastern Siberia in winter (weak winds, powerful temperature inversions) have almost no analogs.

The difference between the values obtained for Irkutsk and Slyudyanka is, in principle, not so large and, probably, it is caused by the features of local circulation, which has a mountain-valley and breeze character in Slyudyanka, while in Irkutsk the urban circulation, namely, flows between the center and suburbs sometimes takes place. The ISCST3 model used for the calculations ignores local circulations, which arise at weak velocities of the principal flow.

For power problems, it is proposed to determine β from the results of snow sampling:

$$\beta = \frac{M_{SO_2}\left(P_{SO_4^{2-}} - P^{lt}_{SO_4^{2-}}\right)}{M_{SO_4^{2-}}\, G_{SO_2}}, \qquad (3)$$

where M is the molecular weight; $P_{SO_4^{2-}}$ is precipitation of SO_4^{2-} ions within the considered territory; $P^{lt}_{SO_4^{2-}}$ is the income of SO_4^{2-} ions to the considered territory due to the long-range transport of air masses; G_{SO_2} are emissions of SO_2 within the considered territory, in mg/h. When determining β, precipitations and emissions are estimated for the period rather than for 1h.

In this case, the precipitation of SO_4^{2-} ions within the considered territory is calculated by the equation

$$p_{SO_4^{2-}} = \sum_{n=1}^{N}\left(p_{SO_4^{2-}}\right)_n \Delta F_n, \qquad (4)$$

where $p_{SO_4^{2-}}$ is the specific precipitation of SO_4^{2-} ions in the nth zone of the industrial center (t/km^2 for the considered period); ΔF_n is the area of the nth zone of the considered territory, km^2.

Technique of $P^{lt}_{SO_4^{2-}}$ estimation

It is proposed to determine the income of SO_4^{2-} ions to the city territory from outside for the power problems, as well as for other problems of industrial ecology, by using the observed indices of their content in precipitations sampled at non-industrial sites of the region.

We have carried out specialized investigations, including:

(a) analysis of mineralization (ion composition) of atmospheric precipitations in the southern part of Irkutsk Region and in Buryatiya (from 51°N to 54°N, from 100°E to 105°E) beyond cities and industrial centers;

(b) analysis of the regions of precipitation formation using the HYSPLIT model of long-range transport.[10]

To justify the correctness of this technique, we have carried out detailed analysis of the factors affecting the composition of precipitations: seasonal, circulation, and local. Using the archived weather data, we have drawn the backward trajectories of air masses (AM) for different seasons of a year. Twelve most abundant types of AM trajectories at the height of 1500 and 3000 m were separated. The statistical analysis of the data on chemical composition of atmospheric precipitations suggests the following:

– in towns and cities of Baikal region, the precipitation of sulfates in winter is mostly determined by local anthropogenic sources of emissions, most of which are heating installations. In the first turn, this applies to old cities constructed before the end of the 20th century, heat supply in which is based on the large number of small heating installations;

– AM trajectories for Irkutsk, village Listvyanka, and village Mondy coincide in 90% cases;

– the seasonal behavior of the concentration of SO_4^{2-} ions in atmospheric precipitations has much similar features at different sites of the considered region.

Thus, on the one hand, the natural factors forming the chemical composition of precipitations at different sites of the studied region are quite close. On the other hand, in winter the dominant income of sulfates in cities is of local origin, that is, the income due to long-range transport is much lower.

Consequently, as an approximate estimate of the precipitation of sulfates formed due to the natural factors and long-range transport, we can take the value of sulfate income with precipitations in nonindustrial sites of the region (t/km^2), which is determined by the equation

$$P^{lt}_{SO_4^{2-}} = \sum_{\tau=1}^{\Phi}\left(c_{SO_4^{2-}}\right)_\tau V_\tau, \qquad (5)$$

where $c_{SO_4^{2-}}$ is the concentration of SO_4^{2-} ions in the studied sample, g/l; V_τ is the amount of precipitation per month τ, liter/m^2; Φ is the number of months in the considered period.

Results and discussion

The generalized estimates of wet precipitation of SO_4^{2-} (according to the observations) for the industrial (Irkutsk), remote or rural (Listvyanka), and background (Mondy) regions are summarized in Table 1.

Table 1. Estimated wet precipitation of SO_4^{2-}

Site. Season	SO_4^{2-}, t/km^2
Irkutsk	
Warm period	0.845
Cold period	0.685
Year	1.530
Listvyanka	
Warm period	0.456
Cold period	0.218
Year	0.674
Mondy	
Warm period	0.220
Cold period	0.036
Year	0.256

According to data on the wet precipitation with the allowance made for the results of chemical analysis of snow cover samples collected along highways, the specific precipitation of SO_4^{2-} ions in the nonindustrial zone of Baikal region for the cold period can be taken equal to 0.036 t/km^2. It should be emphasized that it is quite a rough estimate of the regionally mean precipitation and can be used only when studying pollution of cities, where the local income significantly exceeds that due to the long-range transport. The data on precipitations obtained based on the results of analysis of the chemical composition of snow samples are tabulated below.

Table 2. Estimated fraction of SO_2 transformation into sulfates at the territory of Irkutsk and Slyudyanka

Characteristics of sulfate formation and precipitation	Irkutsk	Slyudyanka
Emissions of SO_2 for the period of stable snow cover (G_{SO_2}), t	10650	195
Mean density of SO_2 emissions, t/km^2	30.3	1.4
Precipitation of sulfate ions at the city territory (as converted to SO_2) ($P_{SO_4^{2-}}$), t	186.6	10.5
Fraction of SO_2 transformed into sulfates, % of emission (β)	1.8	5.4
Contribution of long-range transport, % of precipitation	4.5	30.0
Fraction of SO_2 transformed into sulfates with allowance for $P^{lt}_{SO_4^{2-}}$	1.7	4.0

The percentage of sulfates coming from outside with respect to the total precipitation (P') is 4.5% for Irkutsk and 30% for Slyudyanka. It should be noted that the calculations of P' with the use of the dispersal models for Irkutsk give the scatter of ± 10–15% [Refs. 5 and 11].

The difference in the estimates of the parameter β is caused by the following main factors: the density and the mean height of SO_2 emissions in Irkutsk is much higher, and therefore the smaller territory of dispersal is taken into account; in Slyudyanka the mountain terrain and the local circulations arising as a result of the Lake Baikal effect prevent the pollutant removal from the local zone.

According to the data of snow sampling, the flow of secondary aerosol (sulfates) to the surface is 6–8% from the calculated precipitation of the primary aerosol (volatile soot).

Thus, the specialized snow sampling and the analysis of its results with Irkutsk and Slyudyanka taken as examples allow approximate determination of the fraction of primary emissions of SO_2 (β) transformed into the secondary aerosol within the considered territory. For rough estimation of the contribution of long-range transport to pollution of cities, it is recommended to use the averaged values of sulfate precipitations at some nonindustrial points of the region under study.

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