

# Comparison of experimental and calculated data on ion composition of precipitation in the south of Eastern Siberia

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The influence of the chemical composition of atmospheric air and condensation nuclei on the composition of atmospheric precipitation (AP) is analyzed using the mathematical modeling. Aerosols are represented in the form of solid salts of metals. Relationships between the chemical composition of precipitation and air mass traveling trajectories are analyzed based on 1999 data. To assess unambiguously the effect of the considered factors on the AP composition, it is necessary to carry out a similar analysis based on data for several years.

Continuous observations of the chemical composition of atmospheric precipitation (AP) conducted by the Limnological Institute SB RAS at monitoring stations in Southeastern Siberia (Irkutsk, Listvyanka, Mondy) allows one to reveal some peculiarities and, to some degree, estimate the anthropogenic effect on the AP chemical and ion composition. Unfortunately, it is difficult, based only on observations, to separate the contributions of natural and anthropogenic aerosol sources to concentration of some or other ions in droplets. Besides, formation of fogs and precipitation involves absorption of gaseous constituents from air.<sup>1</sup> This factor is especially important when assessing the effect of anomalous meteorological conditions on the level of urban pollution.<sup>2</sup>

In this paper we compare the experimental data with the results of numerical thermodynamic simulation of the equilibrium composition of precipitation in the clear and polluted atmosphere, as well as perform the trajectory analysis of the observed AP chemical composition in the south of Eastern Siberia.

We use thermodynamic models to describe complex atmospheric processes, including phase transitions and chemical interactions. The model of extreme intermediate states (MEIS) considered in Ref. 3 allows one to describe not only the state of final equilibrium of a reacting system, but also a series of intermediate (incomplete) equilibria, whose appearance is possible in the process of system relaxation to the final equilibrium state.

Different MEIS versions providing a detailed description of heterophase atmospheric processes are now under development in the Institute of Power Systems SB RAS. The first simplest model is a traditional final equilibrium unit of the model of extreme intermediate states:

$$\min \left[ G = \sum_{j \in J_g} \left( G_j^0 + RT \ln \frac{x_j}{\sigma} \right) x_j + \sum_{j \in J_c} G_j^0 x_j \right] \quad (1)$$

under the conditions

$$\mathbf{Ax} = \mathbf{b}, \quad (2)$$

$$x_j \geq 0, \quad (3)$$

where  $G$  and  $G_j^0$  are the Gibbs energy of the system and standard Gibbs energy of a mole of the  $j$ th component, respectively;  $J_g$  and  $J_c$  are the sets of the components of the gas and condensed phases;  $T$  is the temperature;  $R$  is the universal gas constant;  $\mathbf{x}$  is the  $n$ -dimension vector of the amounts of components in the reacting mixture;  $\sigma$  is the total amount of substances in the gas phase;  $\mathbf{A}$  [ $m \times n$ ] is the matrix of content of chemical elements in the system components;  $m$  is the number of balances,  $\mathbf{b}$  is the vector of the amounts of elements.

As is well-known, water droplets in the atmosphere do not consist of a pure substance, because watering of solid particles (condensation nuclei) requires lower energy, than formation of pure water nuclei. Therefore, the next modification of the model takes into account the possible presence of diluted solution of electrolytes in the system. The realized MEIS version describes diluted solutions of strong electrolytes based on the Debye–Huckel statistical theory.<sup>4</sup> For further improvement of the model, it is proposed to take into account Gibbs energy components determined by surface tension and electric charge of droplets.

Using the methods of mathematical modeling, we have analyzed the effect of the chemical composition of atmospheric air and condensation nuclei on the AP composition in the south of Eastern Siberia. Aerosols in

the system were represented as solid salts of metals (Table 1).

**Table 1. Example of calculation of atmospheric precipitation composition at  $T = 298$  K and  $P = 1$  atm.**

Substance	Gibbs energy $G^0$ , J/mol	Concentration, mol/kg	
		initial	equilibrium
<i>Gas phase</i>			
N <sub>2</sub>	-57072	26.7	26.7
O <sub>2</sub>	-61110	7.15	7.15
CO <sub>2</sub>	-457182	$1.19 \cdot 10^{-2}$	$1.19 \cdot 10^{-2}$
H <sub>2</sub> O	-298051	1.22	1.06
O <sub>3</sub>	70614	$1.42 \cdot 10^{-6}$	0.0
NO <sub>2</sub>	-37345	$4.26 \cdot 10^{-7}$	$3.40 \cdot 10^{-11}$
NO	28487	$6.04 \cdot 10^{-12}$	0.0
HNO <sub>3</sub>	-213410	$5.09 \cdot 10^{-8}$	$1.81 \cdot 10^{-11}$
CH <sub>3</sub> Cl	-151824	$3.50 \cdot 10^{-7}$	0.0
SO <sub>2</sub>	-370743	$3.49 \cdot 10^{-7}$	$2.48 \cdot 10^{-11}$
<i>Solid phase</i>			
C: CaSO <sub>4</sub>	-1466387	$3.49 \cdot 10^{-7}$	0
C: Na <sub>2</sub> CO <sub>3</sub>	-1169418	$3.49 \cdot 10^{-7}$	0
<i>Liquid phase</i>			
H <sub>2</sub> O	-306714	$3.49 \cdot 10^{-4}$	0.165
H <sup>+</sup> · NO <sub>3</sub> <sup>-</sup>	-243873	0	$1.96 \cdot 10^{-7}$
Ca <sup>2+</sup> · 2NO <sub>3</sub> <sup>-</sup>	-1027536	0	$6.35 \cdot 10^{-8}$
Na <sup>+</sup> · NO <sub>3</sub> <sup>-</sup>	-508125	0	$1.54 \cdot 10^{-7}$
CO <sub>2</sub>	-713359	0	$8.47 \cdot 10^{-7}$
Ca <sup>2+</sup> · 2HCO <sub>3</sub> <sup>-</sup>	-1966506	0	$8.94 \cdot 10^{-9}$
Na <sup>+</sup> · HCO <sub>3</sub> <sup>-</sup>	-977610	0	$3.53 \cdot 10^{-8}$
2H <sup>+</sup> · SO <sub>4</sub> <sup>2-</sup>	-900192	0	$2.68 \cdot 10^{-7}$
Ca <sup>2+</sup> · SO <sub>4</sub> <sup>2-</sup>	-1439981	0	$2.33 \cdot 10^{-7}$
2Na <sup>+</sup> · SO <sub>4</sub> <sup>2-</sup>	-1428694	0	$1.96 \cdot 10^{-7}$
H <sup>+</sup> · Cl <sup>-</sup>	-177537	0	$1.46 \cdot 10^{-7}$
Ca <sup>2+</sup> · 2Cl <sup>-</sup>	-894863	0	$4.32 \cdot 10^{-8}$
Na <sup>+</sup> · Cl <sup>-</sup>	-441788	0	$1.16 \cdot 10^{-7}$
System mass, kg		0.0286	0.0286
G, J		-68335.8	-68336.6

We considered a heterogeneous, but spatially homogeneous system – the sizes of aerosol particles and droplets were ignored. The process of watering of a solid nucleus accompanied by its solution and absorption of gaseous pollutants was imitated. It was an example of the polluted atmosphere, since the content of sulfur oxide in it exceeded 0.6 MPC (maximum permissible concentration), and the aerosol concentration was almost 2 MPC for inorganic dust (in Irkutsk the mean concentration of inorganic dust is 1.3 MPC, and the maximal one is 3 MPC; the mean concentration of sulfur oxide is 0.3, and the maximal one is 1 MPC).<sup>5,6</sup>

Table 2 compares the results calculated for the polluted atmosphere (see Table 1) with measurements in the region under study.

It should be noted that the anion ratio in the model example corresponds to that observed in atmospheric precipitation at St. Irkutsk in winter period. The calculated equilibrium solution concentration (sum of dissolved ions) proves to be five times higher than the

mean and two times higher than the maximal one measured at St. Irkutsk. When analyzing the results, the following circumstances should be taken into account:

– the concentrations of main pollutants in the initial data of the model example were set by us much higher than the mean values observed in Irkutsk;

– the chemical composition of the solid phase (aerosol) was taken conditionally, and we ignored the fact that actual particles contain insoluble compounds of silicon, aluminum, iron, and others as well.

Thus, at this stage the agreement between the measured and calculated concentrations of main pollutants in precipitation can be thought rather satisfactory.

**Table 2. Mean anion composition of atmospheric precipitation as calculated and measured experimentally, %**

Station, season	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>
Mondy, summer	12.75	33.14	18.90	35.50
Mondy, winter	35.97	24.11	14.39	25.52
Irkutsk, summer	26.72	46.79	13.24	13.25
Irkutsk, winter	24.70	47.40	12.40	15.50
Calculation	24.63	47.28	15.49	12.59

In calculation for the pure atmosphere (amount of the solid phase corresponds to the natural aerosol concentration), the equilibrium concentration of salt in precipitation decreases by the order of magnitude as compared with the polluted atmosphere and corresponds to precipitation mineralization at St. Mondy accurate to the order of magnitude.

The experimental data presented in Table 2 were obtained from primary statistical processing of the results of chemical analysis. We considered only the data for 1999 (three sites: Irkutsk, Mondy, and Listvyanka). It is obvious that the amount of sulfate ion in precipitation in Irkutsk increases sharply as compared with background regions of the south of Eastern Siberia (for example, St. Mondy).<sup>7</sup>

Figure 1 depicts the average annual observations (AP chemical composition) and mean many-year characteristics averaged over natural zones.<sup>8</sup> It can be seen from Fig. 1 that in the region under study the concentration of sodium ions is lower and that of calcium and ammonium ions is higher as compared with the mean zonal values. As to anions, the similar analysis has shown that the amount of SO<sub>4</sub><sup>2-</sup> increases at Sts. Irkutsk and Listvyanka. This marked increase, especially in winter period, is related to worse conditions for spread of anthropogenic pollutants.

An indicator of the anthropogenic effect is the winter increase in the concentration of hydrocarbonate, calcium, and other ions, which are present in emissions of heat and power plants, in precipitation at St. Irkutsk. At St. Mondy the sum of basic ions significantly increases in winter, but on the average it is five times lower than at St. Irkutsk. Important factors here are possibly small amounts of snow (20–25 mm), as well as wind speed and soil aerosol transport that intensify in winter.

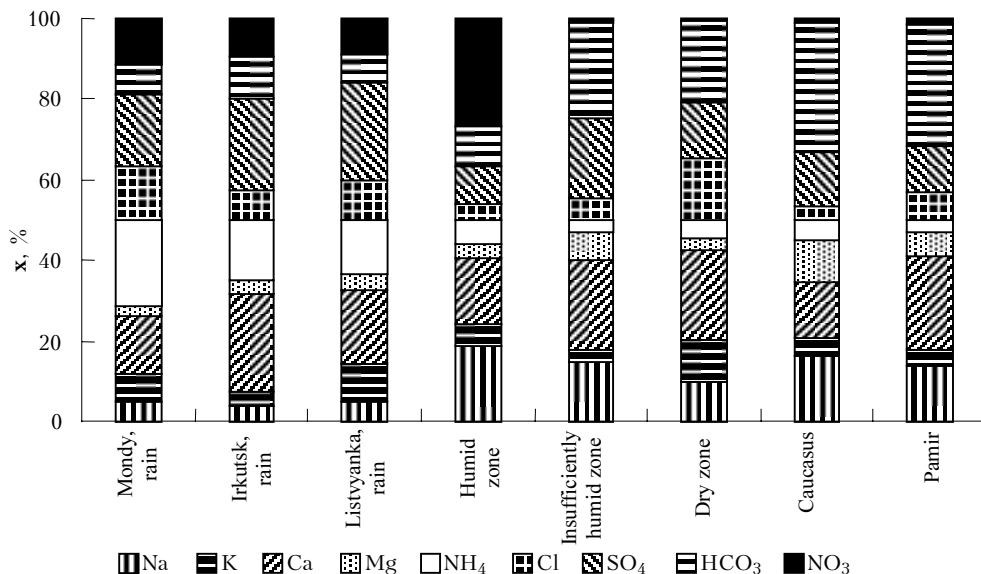


Fig. 1. Chemical composition of atmospheric precipitation.

It is obvious that the chemical composition and concentration of ions in AP depend on the composition of the atmosphere both at the site of their fall and along the path of air masses (AM). For precipitation days in 1999, we have analyzed backward trajectories using the trajectory model and the information available in the Internet (<http://www.arl.noaa.gov>). We have distinguished seven different types of trajectories for air masses at the height of 3000 and 5000 m. The pattern shown in Fig. 2 is a rather typical result of averaging.

At St. Irkutsk the maximal concentration of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$  ions was observed for northwestern trajectories, that is, when precipitation was formed above industrial areas of the Irkutsk and Krasnoyarsk Regions. When precipitation came from south and southwest, the content of ions in them was minimal. At St. Mondy the highest content of basic ions was observed in AP coming from southwest – from Mongolia and Kazakhstan. From Ref. 9 it is known that dust content in air masses and natural mineralization of precipitation increase from the north to the south.

In conclusion it should be noted that the comparison of experimental data with the results of numerical thermodynamic simulation, as well as the trajectory analysis of the observed chemical composition of atmospheric precipitation in the southeast of Siberia has shown that

- data obtained from thermodynamic simulation agree well with the measurements from the viewpoint of percentage of basic cations and anions;
- precipitation at St. Irkutsk is most polluted at the northwestern transport, and the ion content in atmospheric precipitations is minimal when they come from the south and southwest;
- at St. Mondy the highest content of basic ions is observed in precipitation transported from the southwest;

– at the sites subject to anthropogenic effect (Irkutsk, Listvyanka), the sum of the basic ions increases as compared with the background data (St. Mondy), that is, the part of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$  ions increases.

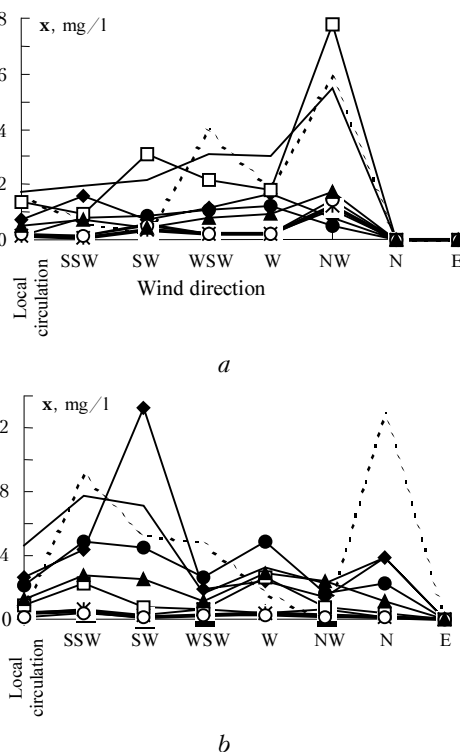


Fig. 2. Dependence of the chemical composition of atmospheric precipitation on air mass transport: St. Mondy (a) and St. Irkutsk (b);  $\text{HCO}_3^-$  (.....),  $\text{SO}_4^{2-}$  (—),  $\text{NO}_3^-$  (—◆—),  $\text{Cl}^-$  (—●—),  $\text{Na}^+$  (—■—),  $\text{K}^+$  (—\*—),  $\text{Ca}^{2+}$  (—△—),  $\text{Mg}^{2+}$  (—○—), and  $\text{NH}_4^+$  (—□—).

Thus, with a rather long observation series, thermodynamic simulation allows us to evaluate the role of anthropogenic and natural mechanisms of precipitation mineralization. Further development of thermodynamic models will likely open the possibility for studying the phenomena on the surface of liquid and solid aerosols, as well as for more accurate description of the properties of actual solutions.

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