

# Ion composition and acidity of atmospheric precipitation in Novosibirsk Region during the period from 2000 until 2005

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We present some results on the ion composition and acidity of rain and snow precipitation in Novosibirsk Region (south of the Western Siberia) obtained during the period from 2000 until 2005. Seasonal variations in mineralization, acidity, concentration, and a fraction of some ions in precipitation were considerable. We can conclude that the main sources of ions in precipitation are the continental aerosol particles, and an additional source of  $\text{NH}_4^+$  is the gaseous  $\text{NH}_3$ . Activity of the first one is enhanced in winter whereas that of the second in summer. Precipitation acidity increases when its mineralization reduces. Rainfalls acidity (mean value of pH equal 5.55) is somewhat higher than that of snowfalls (pH equal 5.87), but overall it remains close to the standard level (pH equal 5.8). The results are compared with similar data obtained at the same observation sites during the period from 1996 until 2001 as well as with the data for other regions in Russia and in the World.

## Introduction

Atmospheric precipitation (AP) are of great value not only for climate, landscape formation, ecosystem functioning, but also for a material exchange in the atmosphere–surface system, providing the return of substances removed into the atmosphere due to various processes back to the earth's surface. The chemical composition of AP is determined by the nonvolatile and volatile components.<sup>1–4</sup> Atmospheric aerosols (AA) serving the centers of vapor condensation or entrapped by the drops generated in the processes of inside- and undercloud washout are the sources of nonvolatile components. The volatile components are formed due to the absorption of atmospheric gases. Variety of formation conditions of snow and rain precipitation leads to a considerable difference in their chemical composition in time and space. Apart from the natural factors, human activity increasingly influences the AP composition. The results of human activity are observed not only in places of the concentrated population, industry, transport, farm-production, but also in distant territories. All this has favored, during the past decades, the researches into the AP chemistry at a regional level.

A considerable place in these researches is given to studying the AP ion composition. To a certain degree, it is connected with the known problem of acid precipitation since the cationic and anionic balance of water-soluble salts determines the AP acidity. Data on the AP ion composition are informative for estimation of the flux of macronutrient elements coming to the earth's surface with precipitation, their transfer from distant sources, and for other practical and theoretical

aspects of the atmospheric chemistry. In some regions of the world, on-line monitoring of the AP ion composition has been arranged that allows one to reveal long-term trends of its variation caused by the changes in the level of atmospheric pollution. In particular, we can mark a tendency toward the decrease of sulfate, nitrate (to a lower degree), and the basic cations in precipitation on the territory of Finland and Germany from the middle of 1980s that could be connected with realization of measures on the restriction of technogenic effluents of their precursors in Europe.<sup>5,6</sup> Trends in the ion composition of AP on the territory of Japan during the period from 1987 until 1997 differed in a more sharp increase of the concentration of nitrates and ammonium, as we assume, due to their transfer from other regions.<sup>7,8</sup> In Russia, the total concentration of salts in AP has increased since 1958 until 1990 and the concentration of basic cations has increased in a greater extent, than the concentration of sulfates. Therefore, the precipitation acidity has a little bit decreased.<sup>9</sup>

The numerous researches have been carried out recently in different regions of the world on a shorter time scale. In particular, the ion composition of snow precipitation in distant territories has been investigated in Alaska<sup>10</sup> and in the high-mountainous regions (near Everest) (see Ref. 11), and the ion composition of rains has been investigated in India<sup>12</sup> Turkey,<sup>13</sup> and in the tropical zone of Brazil.<sup>14</sup> It should be noted that combination of composition monitoring of the AP and AA discrete samples (fresh precipitated) with the data on trajectories of the air mass transport allows one to estimate the contribution of the local and distant sources of ions in precipitation collected at the observation point.

Monitoring of the AP and AA ion composition on the territory of the Western Siberia is being carried out within the framework of the interdisciplinary project "Siberian Aerosols." The results of observations carried out since 1996 until 2001, can be found in Ref. 15. In this paper, we present some results obtained on snow (SP) and rain (RP) precipitation in Novosibirsk Region during the period from 2000 until 2005. Thus, we have an opportunity to isolate trends in the AP ion composition in this region for the 10-year period and compare them with similar data acquired in other regions of the world.

## Technique

Discrete samples of SP (since November until May) were taken at the site located 30 km to the southwest from Novosibirsk (in the environs of Akademgorodok) in a sparse mixed forest. A polyethylene film was spread on the snow surface. Right after the precipitation ceased, the snow sample was taken in a clean polyethylene sack. We delivered the sample to the laboratory, weighed, melted by means of the infrared lamp and filtered. Before the analysis (as a rule, no more than two days), the filtrate was stored at a temperature of 2–4°C in a refrigerator. Analysis was carried out by means of the ion chromatography method with conductometric detection ( $F^- + HCOO^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$  – with the carbonate eluent,  $NH_4^+$ ,  $Na^+$ ,  $K^+$  – with the eluent of  $HNO_3$ ) and by the method of conductometric titration ( $HCO_3^-$ ,  $Ca^{2+} + Mg^{2+}$ ). The measurements of pH and electric conductivity (EC) were carried out with an ANION-210 ionometer and an ELWFO 5711 apparatus measuring conductivity. The errors of AP analysis were estimated by the interlaboratory intercalibration; for pH it made 0.01–0.02 units of pH, for EC –  $0.01 \text{ mCm} \cdot \text{m}^{-1}$ , for the concentration of individual ions 5–15%. (see Ref. 16). Additional monitoring of completeness and correctness of the ion composition of each sample was carried out by means of the equivalent balance comparison of the cationic and anionic sum and by means of the measured and calculated values of EC. As a rule, discrepancies between these values did not exceed 10–15% that corresponds to the criteria accepted in practice of similar researches.

Discrete RP samples were taken since June until October at the site located 90 km to the southwest from Novosibirsk, in a forest zone on the coast of Novosibirsk reservoir. We weighed the fresh rain samples and stored them at a temperature of 2–4°C in a refrigerator. As a rule, during 7 to 10 days, the samples were delivered to the laboratory, where they were analyzed by means of the methods, mentioned above. The results of analysis of the SP and RP samples were expressed in  $\text{eq} \cdot \text{l}^{-1}$  and in  $\text{mg} \cdot \text{l}^{-1}$ , that allowed us to estimate the ion balance, by calculating the value of EC, a fraction of each ion in the sum of cationic Cat and anionic An equivalents, and the total mineralization  $W$ .

## Results and discussion

### Ion composition of snow and rain precipitation

For each season, in the observation periods, we have taken from 21 up to 43 samples of SP and RP. Minimum, maximum, and arithmetic mean values of pH,  $W$ , ion concentration for the whole observation periods are presented in Table 1.

**Table 1. Minimum, maximum, and arithmetic mean values of mineralization  $W$ ,  $\text{mg} \cdot \text{l}^{-1}$ , pH, and ion concentration,  $\text{meqv} \cdot \text{l}^{-1}$ , for samples of fresh rain and snow precipitation during the period from 2000 until 2005**

Parameter	Min	Max	Mean	Min	Max	Mean
	Rain precipitation			Snow precipitation		
$W$	1.37	26.0	6.2	4.38	55.	11.3
pH	4.57	6.68	5.55	4.28	6.92	5.87
$NH_4^+$	3.9	194	36.6	4.5	93.0	16.5
$Ca^{2+} + Mg^{2+}$	2.1	144	24.1	14.6	397	81.9
$Na^+$	1.3	72.6	13.0	4.0	327	48.4
$K^+$	1.4	52.6	9.5	2.2	97.1	16.3
$HCO_3^-$	5.0	110	25.1	1.0	160	35.9
$F^- + HCOO^-$	1.4	24.2	4.4	0.9	65.1	12.0
$Cl^-$	1.0	45.3	13.3	7.2	292	43.8
$NO_3^-$	1.0	53.1	17.4	2.5	164	31.9
$SO_4^{2-}$	1.7	178	28.5	2.2	248	41.2

The most considerable concentration variations (by 100 times and more) were shown for  $SO_4^{2-}$  and  $HCO_3^-$ , but for other ions, the maximum and minimum values also differ by tens times. Such a variability of the ion concentration in discrete precipitation samples points to the high dynamics of the processes of their composition formation. A certain role play such strongly variable factors of meteorological environment as amount, periodicity, and duration of precipitation, direction of air mass transport that has been shown earlier for the same observation sites.<sup>17</sup> Besides, variability of the total mineralization and concentration of different ions in precipitation is connected with nonuniform activity of their volatile and nonvolatile precursors emitted from local and distant sources.

Information on contribution of various sources to formation of the AP composition can be obtained in analyzing a fraction of individual ions in the sum of their equivalents. Table 2 presents the data for each observation season on the number of samples  $N$ , mean values of total mineralization  $W$ , pH, and concentration of each ion (numerator) and its fraction (denominator) in the sum of Cat and An, respectively.

The many-year mean values of these parameters for the whole observation period since 2000 until 2005 and similar data for the period from 1996 until 2001 are printed in bold type. The interannual variability of  $N$  and  $W$  of snow precipitation during the period from 2000 until 2005 was small. However, for the SP, a tendency to the growth of  $SO_4^{2-}$  and  $NO_3^-$  concentrations, and even to a greater extent of the cations ( $Ca^{2+} + Mg^{2+}$ ) has manifested itself that

resulted in a tendency of pH values to grow. A fraction of these cations makes ½ of the equivalent sum of all cations. In different seasons, Na<sup>+</sup> competes with these cations, on the average, for 5 years, its fraction appeared to be noticeably lower. The contribution of K<sup>+</sup> is even lower and its concentration varied in SP a little, both in some years and for the whole ten-year period. The only sources of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> ions in the AP are the aerosols, overall they made almost 90% of all cations in snow precipitation, whereas a fraction of NH<sub>4</sub><sup>+</sup>, which can have NH<sub>3</sub> as an additional source from the free air, makes only 10%.

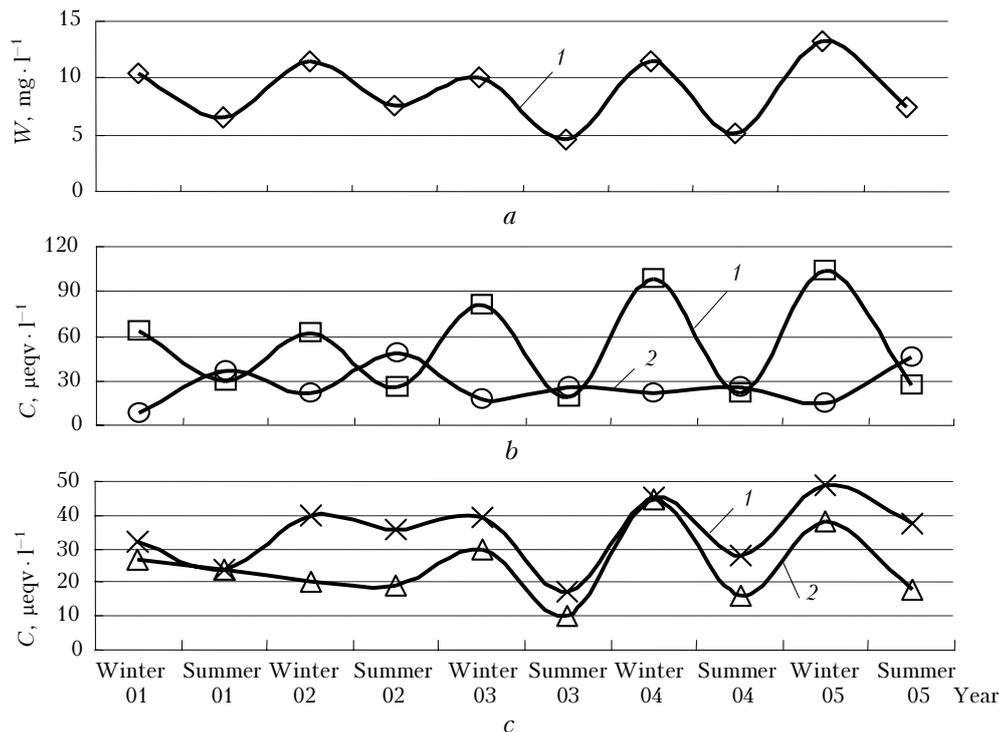
In rains, the concentration and fraction of NH<sub>4</sub><sup>+</sup> appeared to be considerably higher, and this obviously points to the higher contribution of the additional absorption of NH<sub>3</sub> by raindrops in summer. The natural source of NH<sub>3</sub> in the free air is the decomposition processes of organics on the earth's surface. Since in Siberia, in winter, they are considerably decelerated due to the low temperature and isolation of the earth's surface by snow, the concentration of NH<sub>3</sub> in the atmosphere is lower than in summer. The concentration of NH<sub>4</sub><sup>+</sup> in AA is lower in summer than in winter (see Ref. 18); this fact

favors the assumption of that ammonium absorption by raindrops from the air in summer increases thus increasing the influx of NH<sub>4</sub><sup>+</sup> from the aerosol particles. The interannual variability of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> concentration in rains during the period from 2001 until 2005 had no expressed tendency. However, in comparison with the period from 1996 until 2001, they appeared to be lower, especially for Ca<sup>2+</sup> + Mg<sup>2+</sup> that also manifested itself in a decrease of the RP total mineralization.

If in the AP cation composition it is possible to distinguish an ion cluster, the source of which can be only aerosols (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>), the sources of all anions can be both aerosols and atmospheric gases. As follows from the data presented in Table 2, the concentration of all anions in SP is higher than in RP, but the relative fraction of HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> is lower, that of Cl<sup>-</sup> and (F<sup>-</sup> + HCOO<sup>-</sup>) is higher, but the fraction of NO<sub>3</sub><sup>-</sup> is the same both in SP and RP. There is no obvious tendency in the interannual variability of anionic concentration in the AP composition. The annual mean values for the period from 2001 until 2005 for SP appeared to be practically the same during the period from 1996 until 2001, but they have decreased for RP.

**Table 2. Ion composition of snow and rain precipitation during the period of 2001–2005**

Year	N	W	pH	NH <sub>4</sub> <sup>+</sup>	Ca <sup>2+</sup> + Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	H <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup> + HCOO <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
<i>Snow precipitation</i>													
2000–2001	40	10.4	5.77	<u>8.4</u> 4.9	<u>63</u> 40.7	<u>65</u> 41.3	<u>17</u> 11.1	<u>3.1</u> 2.0	<u>28</u> 17.9	<u>10.9</u> 7.1	<u>57</u> 37.0	<u>27</u> 17.2	<u>32</u> 20.9
2001–2002	32	11.4	5.1	<u>21</u> 11.8	<u>62</u> 34.9	<u>67</u> 37.8	<u>22</u> 12.4	<u>5.4</u> 3.0	<u>33</u> 19.3	<u>8.0</u> 4.7	<u>62</u> 36.3	<u>27</u> 15.8	<u>41</u> 24.0
2002–2003	46	10.1	5.69	<u>18</u> 12.4	<u>81</u> 56.2	<u>29</u> 20.2	<u>12</u> 8.4	<u>4.1</u> 2.8	<u>35</u> 23.7	<u>14.6</u> 9.8	<u>31</u> 20.6	<u>30</u> 20.2	<u>39</u> 25.7
2003–2004	43	11.5	6.08	<u>21</u> 13.2	<u>99</u> 61.5	<u>25</u> 15.7	<u>14</u> 8.9	<u>1.1</u> 0.7	<u>37</u> 21.7	<u>11.1</u> 6.7	<u>29</u> 17.3	<u>45</u> 26.9	<u>45</u> 27.4
2004–2005	39	13.3	6.08	<u>15</u> 7.6	<u>104</u> 54.0	<u>57</u> 29.3	<u>16</u> 8.4	<u>1.3</u> 0.7	<u>48</u> 25.0	<u>15</u> 8.1	<u>40</u> 21.1	<u>38</u> 20.1	<u>49</u> 25.7
2000–2005	<b>40</b>	<b>11.3</b>	<b>5.87</b>	<u>16.7</u> <b>10.0</b>	<u>82</u> <b>49.5</b>	<u>49</u> <b>28.9</b>	<u>16.2</u> <b>9.8</b>	<u>3.0</u> <b>1.8</b>	<u>36</u> <b>21.5</b>	<u>11.9</u> <b>7.3</b>	<u>44</u> <b>26.5</b>	<u>33</u> <b>20.0</b>	<u>41</u> <b>24.7</b>
1996–2001 (Ref. 15)	<b>38</b>	<b>11.0</b>	<b>5.69</b>	<u>19.0</u> <b>10.9</b>	<u>80.6</u> <b>46.8</b>	<u>50</u> <b>29.7</b>	<u>17</u> <b>9.9</b>	<u>4.7</u> <b>2.6</b>	<u>33</u> <b>18.6</b>	<u>14</u> <b>9.3</b>	<u>47</u> <b>28.1</b>	<u>32</u> <b>19.2</b>	<u>42</u> <b>24.8</b>
<i>Rain precipitation</i>													
2001	36	6.5	5.59	<u>37</u> 40.5	<u>29</u> 31.7	<u>12</u> 12.9	<u>9.6</u> 10.6	<u>3.8</u> 4.3	<u>26</u> 29.2	<u>1.5</u> 1.7	<u>12</u> 13.8	<u>24</u> 27.8	<u>24</u> 27.5
2002	31	7.6	5.49	<u>48</u> 45.9	<u>25</u> 23.8	<u>13</u> 12.5	<u>14</u> 13.4	<u>4.7</u> 4.4	<u>34</u> 32.0	<u>4.0</u> 3.7	<u>13</u> 12.3	<u>19</u> 18.2	<u>36</u> 33.8
2003	21	4.6	5.49	<u>26</u> 37.8	<u>19</u> 26.9	<u>15</u> 21.7	<u>4.8</u> 8.9	<u>4.7</u> 6.7	<u>22</u> 33.0	<u>3.4</u> 5.1	<u>14</u> 20.6	<u>10</u> 15.3	<u>17</u> 26.0
2004	30	5.2	5.46	<u>26</u> 37.4	<u>21</u> 30.4	<u>9.5</u> 13.6	<u>7.9</u> 11.3	<u>5.1</u> 7.3	<u>16</u> 21.0	<u>5.0</u> 6.5	<u>13</u> 16.7	<u>16</u> 20.3	<u>28</u> 35.5
2005	22	7.3	5.71	<u>46</u> 44.7	<u>27</u> 26.5	<u>16</u> 15.4	<u>11</u> 11.0	<u>2.4</u> 2.4	<u>28</u> 26.1	<u>7.9</u> 7.5	<u>15</u> 14.0	<u>18</u> 16.8	<u>38</u> 35.6
2001–2005	<b>28</b>	<b>6.2</b>	<b>5.55</b>	<u>37</u> <b>41.3</b>	<u>24</u> <b>27.9</b>	<u>13</u> <b>15.2</b>	<u>9.5</u> <b>11.0</b>	<u>4.1</u> <b>4.1</b>	<u>25</u> <b>28.3</b>	<u>4.4</u> <b>4.9</b>	<u>13</u> <b>15.5</b>	<u>17</u> <b>19.7</b>	<u>29</u> <b>31.7</b>
1996–2000 (Ref. 15)	<b>30</b>	<b>10.1</b>	<b>5.74</b>	<u>45</u> <b>32.7</b>	<u>58</u> <b>43.1</b>	<u>19</u> <b>13.8</b>	<u>11.6</u> <b>8.5</b>	<u>2.2</u> <b>2.1</b>	<u>38</u> <b>31.7</b>	<u>3.8</u> <b>3.2</b>	<u>18</u> <b>15.0</b>	<u>24</u> <b>20.0</b>	<u>36</u> <b>30.1</b>



**Fig. 1.** Variability of the ion composition parameters of atmospheric precipitation in Novosibirsk Region in summer and winter seasons during the period from 2000 until 2005: (a) the total mineralization  $W$  (1); (b) the concentration of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  (1) and  $\text{NH}_4^+$  cations (2); (c) the concentration of  $\text{SO}_4^{2-}$  (1) and  $\text{NO}_3^-$  anions (2).

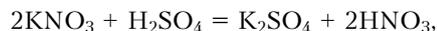
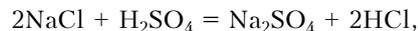
Dynamics of mineralization  $W$  and concentration of some ions in AP for the entire period of observations is shown in Fig. 1.

For variability of  $W$  (Fig. 1a) and ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ) (Fig. 1b), the same seasonal cyclicality is typical at high cross correlation ( $r^2$  equals 0.927), whereas dynamics of the  $\text{NH}_4^+$  concentration was completely different ( $r^2$  equals  $-0.567$ ). Cyclic variations (with its maximum in winter) of the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration as well as of other cations ( $\text{Na}^+$  and  $\text{K}^+$ ) have the AA as the only source. It is possible to relate the cyclic variations with the higher ability of snowflakes to entrain aerosol particles, compared with raindrops, in the processes of intra- and under-cloud washout. Action of the second formation factor of the cation composition, the absorption of gaseous  $\text{NH}_3$  from air, is shown to be considerable only in summer and it manifests itself only weakly in the value of  $W$ .

Seasonal dynamics of the anion concentration in the AP composition is shown in Fig. 1c for  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . The high value of correlation coefficient between the variations of  $W$  and  $\text{SO}_4^{2-}$  ( $r^2$  equal 0.874),  $W$  and  $\text{NO}_3^-$  (0.802) appeared to be typical also for other anions: 0.866 for  $\text{HCO}_3^-$ , 0.831 for ( $\text{F}^- + \text{HCO}_3^-$ ). Similar result we have mentioned above for the dynamics of cation concentration  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ , having no volatile precursors, but not for  $\text{NH}_4^+$ , an additional source of which in AP can be the absorption of  $\text{NH}_3$ .

These facts allow one to conclude that the main sources of anions in AP are the AA particles, and not

free atmospheric gases. However, earlier we have established the essential difference between the contents of anions in the AA and AP in Novosibirsk Region. The sulfates, a fraction of which exceeds 60% of the sum of all anions dominate in AA, whereas it is sharply reduced in AP due to the increase in a fraction of  $\text{Cl}^-$  and  $\text{NO}_3^-$  (from 2.6 up to 15% and from 12.2 up to 20%, respectively) (see Ref. 15). One would think that this fact points to different sources of anions in AA and AP. In particular, a high fraction of  $\text{Cl}^-$  in AP could be connected with the action of marine source, and a fraction of  $\text{NO}_3^-$  with the action of technogenic source. In discussing this assumption, possible reactions, like



in the AA particles should be taken into account. Their volatile products ( $\text{HCl}$ ,  $\text{HNO}_3$ , etc.) pass from the aerosol surface into the atmosphere and then can be absorbed by precipitation. As a result, aerosols are "depleted," and precipitation are "enriched" with the anions of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , whereas  $\text{SO}_4^{2-}$  is stored in aerosols. On this basis, it is possible to assume that difference in the anion composition of AA and AP in Western Siberia is conditioned by the AA transformation with the emission of volatile products and their absorption by precipitation. Thus, we consider the particles of a continental aerosol as the basic source of both anions and cations (except for  $\text{NH}_4^+$ ) in the AP composition at insignificant contribution of aerosols of marine origin. An

additional source of  $\text{NH}_4^+$  in AP, especially in summer, is the gaseous  $\text{NH}_3$ .

### Acidity of rain and snow precipitation

Dynamics of the ion composition of SP and RP is reflected in their acidity. Calculated pH value of condensed water vapor, in the atmosphere at a background content of  $\text{CO}_2$ ,  $\text{SO}_2$ , and  $\text{NH}_3$  in it, makes 5.8 (see Ref. 3). This value is accepted as “standard” for atmospheric precipitation. The lower values of pH point to the existence of other acid, while the higher ones to alkaline components in AP. In such situations, the balance between the sum of anions An and cations Cat (ignoring  $\text{H}^+$ ) is disturbed, in the first case – in favor of An, in the second case

– for Cat. Owing to this, the data on the distribution of  $N$ , the number of the AP samples, over pH values taken with a 0.5 units increment, shown in Fig. 2, demonstrate variability of the factors, determining the balance between An and Cat. The maximum variations of these factors occurred during the period from 2000 to 2003, especially in winter, their action was more stable over a period of two next years. The shift attracts attention in the number of the SP samples with the values of  $\text{pH} > 5.8$  in winter of 2003/04 and 2004/05. In contrast to SP, the distribution of the RP samples is constantly shifted to the values of  $\text{pH} < 5.8$ . These effects also manifested themselves in the mean values of pH for several seasons and for the entire period of observations (see Table 2).

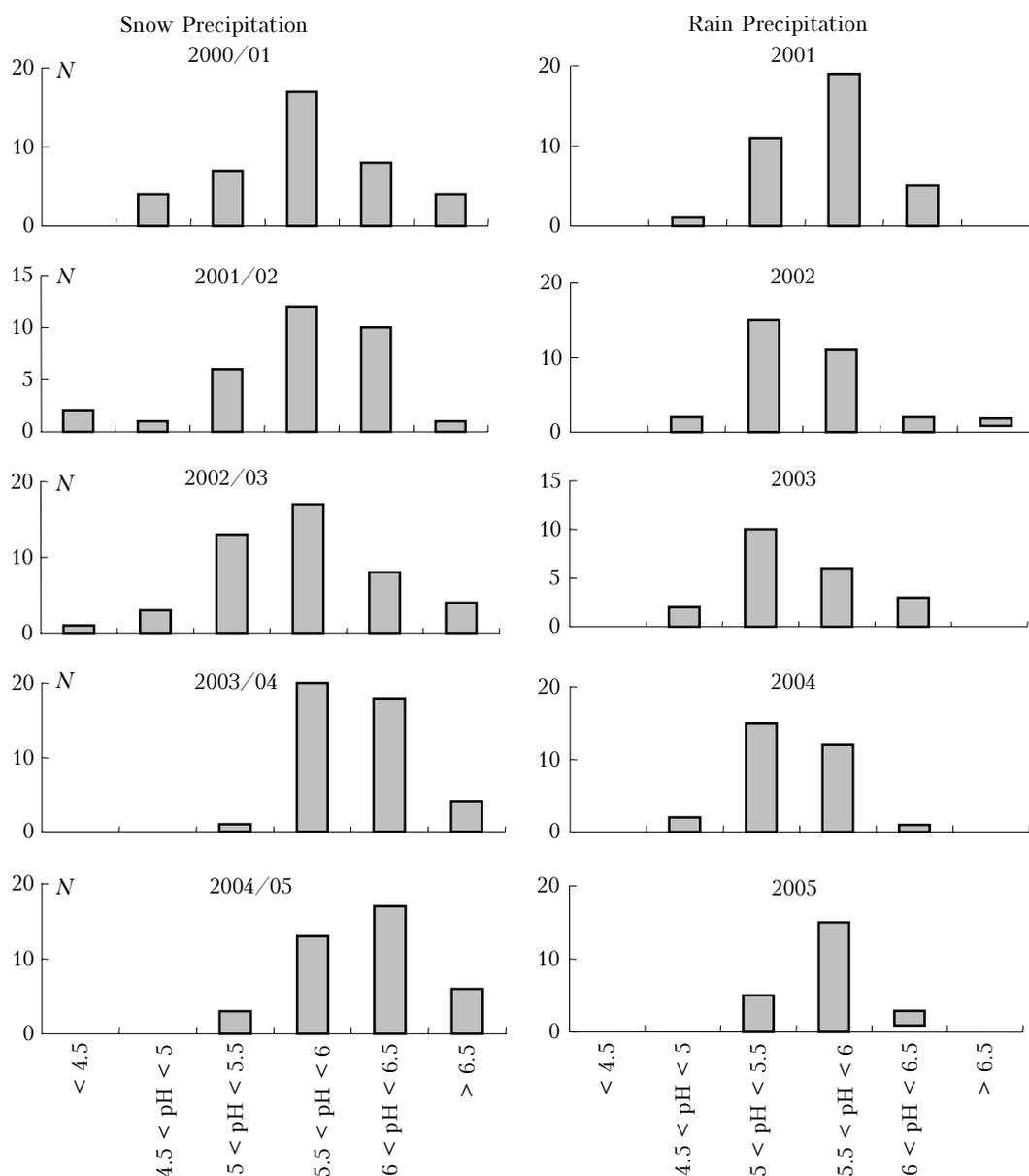


Fig. 2. Number distribution of discrete samples of snow and rain precipitation in the pH values.

As follows from the data in Table 2, the many-year mean pH values of rain precipitation were lower, than of snow precipitation, with the concentration of a series of ions and total mineralization  $W$  being of the same proportion. This is also confirmed by the high values of correlation coefficients of the pH precipitation variability for the period from 2001 until 2005 with the variability of  $W$  ( $r^2$  equal 0.868),  $(Ca^{2+} + Mg^{2+})$  (0.905),  $SO_4^{2-}$  (0.791),  $HCO_3^-$  (0.780).

It has been found that interrelations between pH and  $W$ , pH and cationic concentration  $(Ca^{2+} + Mg^{2+})$  can be presented by the following equations:

$$pH_{cal} = 5.13 + 0.065W, \quad (1)$$

$$pH_{cal} = 5.38 + 0.006(Ca^{2+} + Mg^{2+}). \quad (2)$$

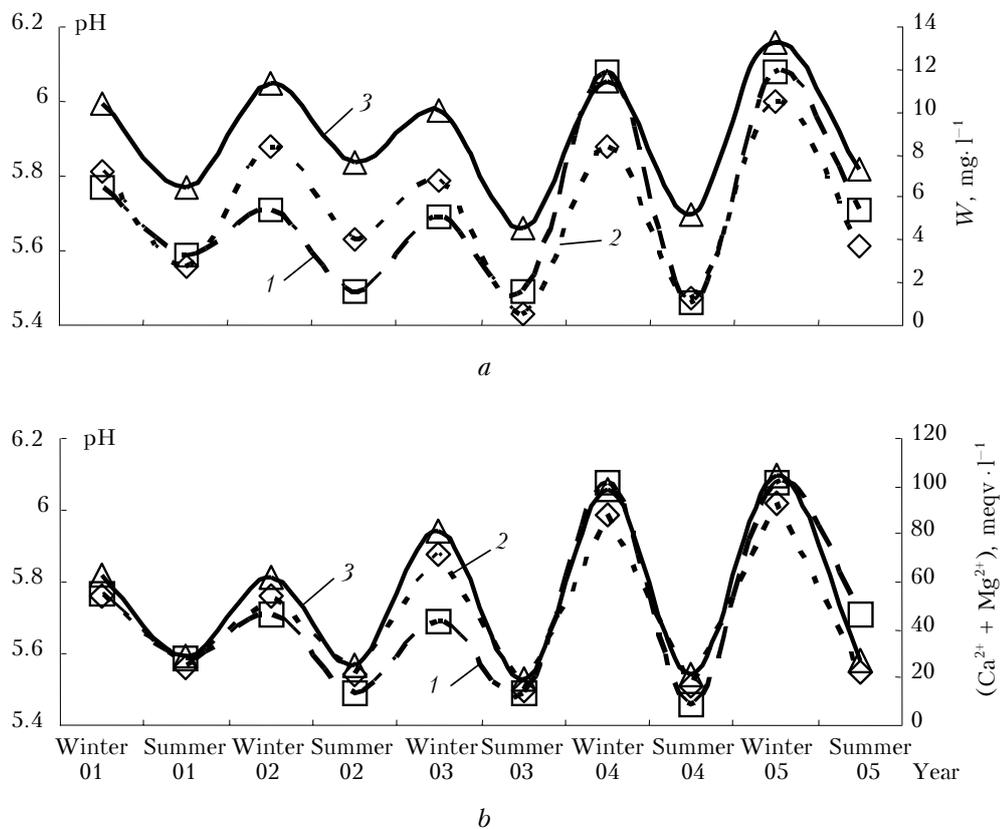
Comparison of the pH values (mean for each season) observable and calculated by the Eqs. (1) and (2) with the data on  $W$  and  $(Ca^{2+} + Mg^{2+})$  is shown in Fig. 3. The higher precipitation mineralization and content of  $(Ca^{2+} + Mg^{2+})$  in them is, the lower their acidity level (the higher pH values) and it is common both for RP and SP.

The correlation being high for pH values with the concentration of a series of ions (the sources of these ions in AP are the AA particles), it was absent

between pH and the  $NH_4^+$  concentration ( $r^2$  equal  $-0.497$ ). Based on this fact, we can ascertain that AA particles play smaller role in the formation of the precipitation composition, at a higher acidity of the precipitations in the observation region. The AP acidity increase in Novosibirsk Region takes place not due to the increase in content of soluble salts in it, but, on the contrary, due to reduction of  $W$ , this fact points to the main role of natural, but not technogenic factors. Thus, the higher aerosol contribution to the AP ion composition, the lower their acidity hazard.

### Comparison of the AP ion composition in Novosibirsk Region and other regions

It is interesting to compare the obtained data on the ion composition of SP and RP in Novosibirsk Region to similar data for other regions. In order to reveal the contribution of different sources to the AP formation, it is convenient to use a fraction of ions in the sum of equivalents Cat and An instead of the absolute ion concentrations which considerably differ in various observation sites. Since the ion concentrations in precipitation in different works are presented in various units (fractions of equivalents,  $mg \cdot l^{-1}$ ,  $eqv \cdot l^{-1}$ ,  $eqv \cdot m^2 \cdot year^{-1}$ ), we have recalculated and presented them in Table 3.



**Fig. 3.** Dynamics of the observable  $pH_{obs}$  (curve 1) and calculated values of  $pH_{calc}$  (curve 2) for atmospheric precipitation during the period from 2000 until 2005 as compared with the data for  $W$  (a) and  $(Ca^{2+} + Mg^{2+})$  (b) (curve 3).

**Table 3. Comparison of the ion composition of atmospheric precipitation in different areas of the world**

Place and period of observations	W	pH	NH <sub>4</sub> <sup>+</sup>	Ca <sup>2+</sup> + Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	H <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup> + HCOO <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
<i>Snow precipitation</i>												
Western Siberia, our data	11.3	5.87	10.0	49.5	28.9	9.8	1.8	21.5	7.3	26.5	20.0	24.7
Eastern Siberia, Mondy, 1998–2002 (Ref. 19)	–	6.27	16.4	71.8	7.2	3.8	1.8	40.6	–	11.4	13.0	33.6
Alaska, Alert, 1990–1994 (Ref. 10)	1.89*	5.28*	5.2	56.1	21.7	1.4	15.7	–	3.3**	39.1	13.8	43.8
<i>Rain precipitation</i>												
Western Siberia, our data	6.2	5.55	41.3	27.9	15.2	11.0	4.1	28.3	4.9	15.5	19.7	31.7
Eastern Siberia, Mondy, 1998–2002 (Ref. 19)	–	5.45	42.0	31.8	5.4	2.8	20.8	8.8	–	11.8	30.0	44.2
India, Hyderabad, 2000 (Ref. 12)	9.7	6.4	20.4	56.2	16.2	6.7	0.5	17.4	–	52.1	19.2	11.3
Brazil, Campinas (Ref. 14)	2.9	4.5	27.5	8.9	4.8	6.1	52.9	0.5	5.6	12.9	38.6	42.3
<i>Mid-annual data for observation sites in Finland (1) and Russia (2–5)</i>												
1. Central part, 1991–2000 (Ref. 8)	–	4.90	34.9	20.1	14.9	7.5	22.3	–	–	15.4	31.6	53.0
2. Voeikovo, 1990 (Ref. 9)	12.0	5.3	39.6	34.5	15.9	7.7	3.0	9.2	–	14.4	17.8	58.6
3. Barabinsk, 1990 (Ref. 9)	34.9	6.7	15.7	52.8	23.8	7.8	0.04	41.9	–	20.3	6.8	31.0
4. Ayan, 1990 (Ref. 9)	130.4	6.6	2.0	31.1	63.9	2.8	0.01	4.6	–	84.2	0.3	10.8
5. Norilsk, 1990 (Ref. 9)	242.6	6.8	2.7	92.2	3.1	2.0	0	6.1	–	4.8	0.5	88.6

Note. Empty boxes mean the absence of data; \* shows the values calculated from the data on the ion concentration; \*\* denote the authors' data for the sum of impurity anions, including the anions of organic acids.

The data on concentration of some ions in AP are presented in Ref. 8, with the contribution of the marine source subtracted. We have recalculated their actual concentrations using the technique explained by the authors. At minimum content of salts in SP in distant points of Alaska (1.89 mg · l<sup>-1</sup>), their acidity appeared to be increased (pH = 5.28) as compared with SP in the south of the Western and Eastern Siberia (5.87 and 6.27, respectively). For all observation sites, a fraction of NH<sub>4</sub><sup>+</sup> is small and the main role (determinant in the high-mountainous point of Mondy in the Eastern Siberia) in the neutralization of SP anions belongs to by cations Ca<sup>2+</sup> and Mg<sup>2+</sup>. Their deficiency in snows of Alaska also leads to the precipitation acidity, in spite of their general mineralization and, respectively, content of the acid-forming anions in this distant area appeared to be the lowest.

Rain precipitation in Brazil appeared even more acid (pH = 4.5), also being characterized by low mineralization (2.9 mg · l<sup>-1</sup>). As in the other regions, a fraction of NH<sub>4</sub><sup>+</sup> in rains and its role in neutralization of anions are higher than in SP, but its content appears to be insufficient that leads to the RP acidity in Brazil in combination with low contribution of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup>.

We have a different situation in India, where at higher contribution of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup>, the level of precipitation acidity is below the "standard" (pH = 6.4). Thus, in India a fraction of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> in RP was considerably less than in Brazil. On the territory of the south of the Western and Eastern Siberia, a fraction of these anions in rains is less than in Brazil, but is higher, than in India, and a fraction of NH<sub>4</sub><sup>+</sup> appeared to be considerably higher, than in those regions. Probably, it reflects the higher efficiency of the NH<sub>3</sub> absorption by the rainfalls in Siberia. However, it is not enough for a full neutralization of the acid-forming anions as well as higher than in Brazil fraction of other neutralizing

cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup>) and the pH values of Siberian rains appeared to be lower than in rains on the territory of India.

Thus, distinctions in contribution of the nonvolatile and volatile precursors to the SP and RP ion composition, conditioned by distinctions in their formation conditions in different regions, is also reflected in variations of precipitation acidity. Action of these factors is well seen for the annual mean data on precipitation as a whole, presented in Table 3 for five observation sites: 1 – in the Central part of Finland, 2–5 in Russia (2 is the overmoistened zone, 3 is the insufficiently moistened zone, 4 is the seaside zone, 5 is the industrial zone with an intense atmospheric pollution). The annual mean value of precipitation mineralization in these observation sites varied from 12 up to 242.6 mg · l<sup>-1</sup>. Concentration of single ions varied in a wide range as well as their fractional contribution to the AP ion composition. In spite of the low precipitation mineralization and high fraction of NH<sub>4</sub><sup>+</sup>, the highest acidity, conditioned mainly by sulfates, was recorded in overmoistened zones (sites 1–2). The lowered AP acidity was observed at sites 3–5, but the reasons for low acidity in each of them were different. Growth of the cationic contribution (Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup>) is general for these sites, the source of these cations in AP are the aerosols of natural origin (erosive origin for the site 3 and marine origin for the site 4) or technogenic origin (for the site 5).

Role of the composition of technogenic effluents in the AP acidity is clearly shown in comparing the data on the SP in Alaska and on the AP at the site 5 (Norilsk), located in the zones similar by natural-climatic conditions. Snow mineralization, content and fraction of the basic acid-forming anion, sulfate, in snows of Alaska is much lower, than in the AP of Norilsk, but in the first of these sites, acidity was observed, while in the second one the precipitation alkalization was detected. The cause of this effect is

in high content of the neutralizing cations  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in precipitation on the territory of Norilsk, anomalously high fraction of this precipitation, obviously, points to their technogenic source.

## Conclusion

Ion composition of atmospheric precipitation in Novosibirsk Region is subjected to considerable variations for short time intervals and this is confirmed by the data for fresh precipitation samples. Such variations are determined by the dynamics of meteorological conditions (amount and periodicity of the precipitation, change of direction of the air mass transfer). Total content of salts, concentration of individual ions, and precipitation acidity in summer and in winter appreciably differ. One can see the tendency to growth of the  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations and, even to a greater extent, of the cations ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ), which is observed for the SP and not in the RP during the period from 2000 until 2005. At the same time, the many-year mean values of parameters of the SP ion composition for this period appeared similar to the data for the period from 1996 until 2001. On the contrary, the total mineralization, concentration of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  and especially of the cations ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ) appeared lower for RP but the precipitation acidity was higher. Thus, the trends of the SP and RP ion composition in Novosibirsk Region during the period from 1996 until 2005 did not coincide. They differed from the growth tendencies of  $W$ ,  $\text{SO}_4^{2-}$ , basic cations and decrease in the AP acidity on the territory of Russia during the period from 1958 until 1990 (see Ref. 9).

When considering the ion contributions, with the volatile and nonvolatile atmospheric components as the precursors in the RP and SP composition, and comparing to similar data for other regions of the world, it is possible to reveal the regional features in action of these factors in the south of the Western Siberia. The determining role in formation of the ion composition of atmospheric precipitation in this region belongs to natural factors. The basic sources of water-soluble salts in the AP composition are the aerosol particles of a continental origin. In summer, contribution of this source is reduced due to the smaller efficiency of the AA entrainment by raindrops, compared to that by snowflakes. This leads to the balance disturbance between the acid-forming anions and the cations neutralizing them owing to the AP acidity. The smaller concentration of salts, the greater the balance disturbance. The contribution of other source, gaseous  $\text{NH}_3$ , on the contrary, increases in summer due to the higher emission from the ground

surface. As a result, a fraction of  $\text{NH}_4^+$  in rains in the south of the Western Siberia reaches 40% of the equivalents of all cations, capable of neutralizing the acid-forming anions. However, reduction of the AA contribution to formation of the RP appears to be more considerable, and deficiency of the total sum of cations leads to the greater precipitation acidity in summer as compared with snowfalls in winter.

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