Chemistry for Sustainable Development **10** (2002) 497–521

Problem of Acid Deposition in West Siberia

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(Received March 25, 2002)

Abstract

The problem of acid deposition in West Siberia is discussed on the basis of the data on the ion composition of atmospheric aerosol, precipitation and surface waters, obtained for different natural climatic zones (from the tundra in the north to the steppe in the south) in 1996–2001. Regional features of the formation of aerosol and precipitation in the northern regions, conditioned by the insufficient efficiency of the terrigenous sources of neutralizing cations, lead to acidification, in spite of the small concentration of acid-forming anions. The extent of surface water acidification depends on the intensity of the interaction between snow-melted water with the ground. Some lakes of the tundra are acidified (pH 5–5.5) at low salt content of water not only in spring but all the year round. The concentration of the most toxic forms of metals in these lakes exceeds the level of safety for the plankton organisms. The conditions for the formation of aerosol, precipitation and surface water in the southern regions of West Siberia do not produce acidification.

INTRODUCTION

The problem of acid deposition is among global ecological problems caused by the distortions of the chemical composition of atmospheric components. Because of this, special attention of the complex integration project “Aerosol of Siberia” was paid to how the generation, transformation, transport and sink of atmospheric aerosol (AA) over West Siberia could affect the acidity of atmospheric precipitation (AP). However, investigation of the factors of the formation of AP acidity is only a part of the whole set of investigations, because negative consequences of acid precipitation for the functioning of land and water ecosystems are to a substantial extent determined by their properties. Because of this, it was necessary to investigate the chemical composition of surface water (SW) in different natural climatic regions of West Siberia in connection with the composition of AP. In addition, it was important to estimate the state of dissolved metals in local water reservoirs with different acidities, because the phenomenon of the secondary contamination of acidified SW with metals is known.

The necessity of the multi-aspect approach to the problem of acid deposition became evident in course of studying the situation in those regions where its negative consequences have already manifested themselves. The death of forests, loss of soil fertility and of fish resources in fresh-water reservoirs have involved vast territories of North America and Europe; these negative phenomena were accompanied by the formation of smog, which had a direct impact on human health. Acid rains are believed to accelerate the erosion and corrosion of industrial materials, buildings, and cultural heritage. By present, a series of monographs generalizing the results of many works in this area have been published [1–5].

In Russia, there are also regions with increased acidity of atmospheric precipitation; however, complex investigation into this problem is insufficiently developed yet. The region studied in most details is the region of the Kol’sky Peninsula. For example, in 1995, at the total amount of hazardous substances emitted into the atmosphere by automobiles and stationary sources being 660 thousand tons, the amount of SO_2 and nitrogen oxides was 450 and 25 thousand tons, respectively; 80 % of the total amount of emitted gases were produced by two plants, Severonikel and Pechenganikel [6]. The authors of [6] stress that the amount of SO_2 emitted by these plants increased after passing to the raw material with increased sulphur content obtained from the Noril'sk Mining Plant. The average pH of atmospheric precipitation on the Kolsky Peninsula was 4.4 to 4.7, while near industrial centres it was 3.4 and lower [7]. Among five hundred small lakes examined in the Kol'sky north, more than 10 % turned out to be in critical state; some lakes were strongly acidified having pH 4.2–4.5 [8]. For the Kolsky north, it is characteristic that the acidity of water in lakes, and especially in brooks increases for a short period of time during spring flood, which is connected with the enormous amount of snow-melted water.

Since a substantial amount of metals (58 thousand tons in 1995 [6]) is emitted into the atmosphere along with acid-forming gases, the routes of their admission into water reservoirs have been investigated in detail, along with the forms in which they are present in water and in bottom sediments, depending on the acidification of snow-melted, river, and lake waters [9, 10]. So, complex investigations of the problem of acid deposition in the Kol'sky Peninsula demonstrate that specific natural climatic conditions of northern regions enhance the negative consequences of man-made contamination of the atmosphere with metals and acid-forming compounds.

Unfortunately, no investigations of this sort have ever been performed over the vast territory of West Siberia. At the same time, it is known that this region also has large man-made sources of atmospheric pollution. For example, the emission of SO_2 in Noril'sk is estimated to be about 2 million tons per year; powerful man-made sources of SO_2 and nitrogen oxides are present in the industrial regions in the south of West Siberia and in the Urals. One ought to make a more detailed estimation of the stability of land and water ecosystems to acidifying, the possibility of secondary contamination of water with metals. It is also important to take into account the variety of natural climatic zones (from the tundra in the north to the steppe in the south), as well as non-uniformity of placing industrial urban zones in West Siberia.

It is clear that it is impossible to provide a detailed investigation of all the aspects of the problem of acid deposition in the absence of a developed monitoring system for AA, AP and SW in this region. At the first stage, the solution of this problem should consist in collecting the information on the action of factors potentially capable of provoking the problem of acid deposition for different natural climatic zones in the region. The fact that investigations of this problem within the project "Aerosol of Siberia" are closely conjugated with other sections has promoted the solution of this problem. This allows one to connect the aspects related to chemical transformations in the atmosphere and in surface waters with the aspects related to the identification of the sources of acidic and neutralizing substances, as well as their spatial and temporal dynamics.

In the present communication, the main factors are considered that determine the acidity of atmospheric precipitation and surface water, the state of metals in fresh water reservoirs, and the results obtained in 1996–2001 are presented.

CHEMICAL ASPECTS OF THE FORMATION OF THE ACIDITY OF ATMOSPHERIC COMPONENTS

The acidity of aqueous solutions is determined by the concentration (activity) of H^+ ions, which are the main constituent of ion balance between the cations and anions of all the dissolved salts. Using the concentrations of ion equivalents, this statement can be written down as follows:

$$\begin{aligned}[H^+] = \Sigma\,\mathrm{An} - \Sigma\,\mathrm{Cat} = \{&[HCO_3^-] + [SO_4^{2-}] \\ &+ [Cl^-] + [NO_3^-] + [F^-] + [CHOO^-] + \ldots\} \\ &- \{[NH_4^+] + [Ca^{2+}] + [Mg^{2+}] + [Na^+] \\ &+ [K^+] + \ldots\} \end{aligned} \qquad (1)$$

The major cations and anions included in the AP and water-soluble fraction of AA are represented in the eq. (1). This equation shows that an increase of $[H^+]$ is a consequence of the excess of anion equivalents with respect to the sum of cation equivalents. Hence, in the general case, the reasons of increased acidity of AA and AP can be either additional emission of the substances of acidic character into the atmosphere, or the lack of cations neutralizing those substances.

Along with salts brought from the land or water (oceanic) surface, the precursors of all the anions in the ion composition of AA and AP can be volatile substances, while among the cations represented in eq. (1) only ammonium has a volatile precursor (ammonia). In the absence of such substances, at the condensation of water vapour in atmospheric air containing the background concentrations of CO_2, SO_2 and NH_3, the calculated $[H^+]$ in water is about 1.6 10^{-6} g-ion/l (pH ~ 5.8) [5]. This pH value should be considered as a normal one for atmospheric precipitation in the background regions. In the regions with acid deposition, annual average pH of precipitation reach 4.1–4.3, being 2.1 in some rains [2]; a record for low pH in fog drops is 1.68 [4].

It should be noted that the decreased pH of rain (4.5 and below) is observed also in the background regions located far from both man-made and natural (volcanoes) sources of gas emission. Calculations show that this level of acidity can be achieved in the case when ammonia and calcium carbonate (product of the erosion of rocks and soils) are absent from the pure atmosphere over oceans [11].

Among cations, only ammonium has a gas-phase precursor; all the other cations do not have volatile forms and can enter AP and AA only with solid particles carried from the land or water surface. It follows from this consideration that the normal pH of precipitation can be a result of the neutralization of increased concentration of acid-generating anions (of gas-phase origin) by the cations of lithophile elements. Hence, in order to study the factors determining the acidity of AP, it is necessary to have the data on the ion composition of not only precipitation itself but also of aerosol, which is the precursor of cations in the AP.

An interconnection between the ion composition of AA and AP has a complicated character and is determined both by the composition of AA and by the in-cloud or under-cloud processes forming the AP composition. According to [1], the major ions in small aerosol particles (0.1–1 μm) are represented by SO_4^{2-}, NH_4^+, K^+, $RCOO^-$ while in larger particles (>1 μm) by Ca^{2+}, Mg^{2+}, Na^+, Cl^-, and NO_3^-. Hence, ion composition of precipitation varies depending on the size distribution of aerosol particles acting as the condensation nuclei for raindrops or captured by the drops while falling down. Ion concentration in raindrops can vary as a result of evaporation on the way from a cloud to the land surface. The processes of under-cloud washing out can affect the composition of raindrops also due to the absorption of gases. In addition, the composition of snow cover can vary with time due to dry deposition processes. Thus, the ion composition of AA and AP sampled in the same place at the same time moment is not identical to each other.

The dynamic character of atmospheric processes determines inconstancy of the composition of both AA and AP not only at the regional level but also at the local level. The joint investigation of the spatial and temporal dynamics of the ion composition of AA and AP within the acid deposition problem can turn to be more informative than the analysis of only atmospheric precipitation. It is convenient to use not absolute concentrations of ions for such a comparison but the fraction distribution of their equivalents in the sum of cations or anions. The reason is that the concentration of ions in precipitation is measured per 1 l of solution, while the concentration of ions in water-soluble AA fraction is related to the aerosol particle content of 1 m^3 of the air. The fraction of each ion in Σ Cat or Σ An is a dimensionless value, which allows one to compare AP and AA. It should be noted that in order to do this, one ought to know the complete ion composition of precipitation and aerosol but not only the content of some ions.

The self-descriptiveness of the combined investigation of the ion composition of AP and AA is defined by one more circumstance. Irregularity of precipitation, variability of its volume, duration, the size of raindrops or snowflakes bring additional complications into the identification of the sources of gaseous, terrigenous and sea precursors of their composition. The surface aerosol can be sampled periodically independent of weather. This provides prerequisites for a more detailed characterisation of the action of different sources and processes forming the components of the atmosphere taking into account the directions of air mass transfer.

Taking the above considerations into account, complex investigation of the ion composition of AP and AA was organized within the Project "Aerosol of Siberia" in several sites of West Siberia. It should be noted that such an approach has been very rarely applied by other investigators; the data obtained in the present study is of the general importance for the understanding of the factors that form acid deposition.

CHEMICAL ASPECTS OF THE ACIDIFICATION OF SURFACE WATER

The effects of acidification of soil and surface water in regions with increased acidity of atmospheric precipitation depend not only on the arrival of H^+ ions per unit surface but also on the buffer capacity. The latter is determined by total alkalinity Alk_{tot}, which is the sum of anion of weak acids included in SW. For the major part of SW, the most substantial contribution into Alk_{tot} is made by the carbonate alkalinity Alk_{carb} resulting from the weathering of carbonate rocks. In some situations, a substantial contribution into the sum of anion equivalents can be made by the organic substances of humus nature, designated in the integral form as Alk_{hum}. These substances enter water reservoirs from the drainage territory or are formed in water reservoirs during the decomposition of the dead organic matter; they can play an important role not only in the balance of cations and anions but also as complexing agents for dissolved metals. In these situations, Alk_{hum} should be taken into account in eq. (1) for the balance of cation and anion equivalents in SW; the Alk_{carb} value is incorporated into $[HCO_3^-]$.

Considering the acidification of SW as a result of large-scale natural titration of HCO_3^- in a water reservoir by the acids of atmospheric precipitation, the author of [12] generalized the data on pH and chemical composition of the water of 719 lakes of south Norway, and pH of precipitation; he represented these data in the coordinates: cation concentration (Ca^{2+} + Mg^{2+}) in the water of water reservoir *versus* pH (correlating with the concentration of SO_4^{2-}) of rainwater (Fig. 1). He revealed three groups of lakes: bicarbonate (pH > 5.3), transitional (4.7 < pH < 5.3), and strongly acidified (pH < 4.7). Each of these groups corresponded to a definite region of the nomogram depicting the pH of precipitation and the concentration of [Ca + Mg] in lake water (see Fig. 1). It turned out that the population of fish decreased sharply in the transitional lakes; in about 80 % of strongly acidified ones, it dropped down almost to zero (this means that there had been no fish species at all in those lakes).

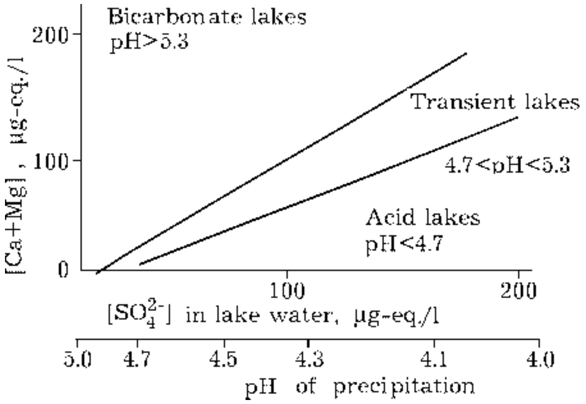

Fig. 1. Nomogram [12] to estimate the effects of lake water acidification in Norway, depending on water hardness and pH of atmospheric precipitation.

The lower boundary in Fig. 1 separating the transitional lakes from acidic ones corresponds to almost complete exhaustion of the buffer capacity of the carbonate system in water: at pH 4.7, the fraction of unbound HCO_3^- anions accounts for only 2 % of the sum of all the forms of the carbonate system. Transitional lakes are at the edge of exhaustion of the buffer capacity. At pH 5.3, the fraction of HCO_3^- is about 10 %, while at pH 6.3 it is about 50 %, which determines an increase in the stability of bicarbonate lakes to acidification.

The absolute concentration of the HCO_3^- ions affects the buffer capacity of lake water, too. Provided that HCO_3^- dominates in the ion composition of water, it is directly connected with the total salt content *W*. Hence, water reservoirs with low salt content and lowered pH of water are most prone to acidification.

For many SW in the region of extra moistening, including the lakes of Norway, a direct interconnection between the concentrations of HCO_3^- and basic cations Ca^{2+} and Mg^{2+} is characteristic. It is this condition that was used in [12] to build up a nomogram (see Fig. 1).

It is evident that this nomogram depicts a set of parameters for a common water reservoir of southern Norway. These parameters include annual amount of precipitation, their fraction in water balance of a water reservoir, the composition of soil and rocks at the drainage territory, hydrocarbonate-calcium type of surface water. One may expect deviations from the above-mentioned dependence in case if any parameters are changed. For example, for a deep lake with low fraction of annual refill by AP, acidification effects will be less significant. On the contrary, for shallow water reservoirs in regions with humid climate the situation will be more dangerous. Deviations from this dependence can be observed also in the case of the substantial contribution of other components into total alkalinity (*e. g.* not carbonate but humus alkalinity), or contribution from other cations (for example, sodium) into the sum of neutralizing cations. Because of this, it is reasonable to use the total alkalinity of water Alk_{tot}, which is equal to the sum of concentrations of the equivalents of all the anions able to bound H^+ ions, as a parameter that provides better characterization of the properties of a water reservoir.

It should be noted that seasonal variability of hydrological factors can lead to the situation of episodic acidification of water, which was called the acid shock. In the north, large amount of snow is accumulated during winter; its melting in spring is accompanied by intensive admission of snow-melted water into rivers and lakes. For shallow lakes with small drainage, the acid shock can be more lengthy than for flowing water; the ability to overcome it depends on the intensity of processes in the water reservoir, *i. e.* leaching of underlying rocks, and the biotic processes.

In the regions with low buffer capacity of SW, acid precipitation can lead to profound distortions of the functioning of not only separate fragments but also the entire water ecosystem. Natural biogeochemical cycles of a series of elements become distorted. In particular, immobilization of some metals (Me) present in the mineral components of soil, bottom sediments and underlying rocks occurs. Secondary contamination of water with soluble forms of Al, Fe, Cd, Cu and some other Me, which are toxic for hydrobionts, is a supplement to the negative consequences of the decrease of pH of water.

When estimating the toxicity of Me for water organisms, not only their total content is important but also the forms in which they are present in water. Low-toxic forms are those like MeL, bound with the dissolved organic matters (DOM), and strong complexes with inorganic ligands; the most toxic forms are free aqua ions Me^{z+} [13, 14]. Since the fractional distribution of different species of metals changes with changing pH, water acidification can affect migration, biological availability, and toxicity of metals that were initially present in the intact ecosystem.

Thus, the problem of acid precipitation is a complex one, including the characterization of sources and processes involved in the formation of the ion composition of AP, AA and SW, total content and state of Me in water reservoirs.

METHODS FOR THE DETERMINATION OF ION COMPOSITION OF ATMOSPHERIC PRECIPITATION, AEROSOL AND SURFACE WATER

When choosing the methods for the analysis of ion composition of atmospheric precipitation, water extracts of aerosol, and surface water, it is necessary to take into account the set and the concentration of ions to be determined, as well as sample volume. As a rule, the concentration of ions to be determined in these samples is not more than $1\ 10^{-4}$ M. In addition to the main cations and anions represented in eq. (1), other ions may also be present in natural samples. A test for the significance of their fraction is the balance between the sum of concentrations of the equivalents of the detected cations and anions, as well as the comparison between the calculated and measured specific electric conductance of the sample. These approaches are of special importance for the analysis of the aqueous extracts of aerosol, since their small volume (usually 10 ml) limits the possibilities of their repeated analysis.

The procedure for the determination of the ion composition of AP, AA and SW, used in the work on the Project "Aerosol of Siberia" [15], involved the following operations. A sample to be analyzed was divided into two parts. In one of them, the cations [NH_4^+], [Na^+], and [K^+] were determined by means of high-performance liquid chromatography (Katieks sorbent, HNO_3 as elutriator); so were the anions [F^- + $HCOO^-$], [Cl^-], [NO_3^-], [SO_4^{2-}] (KhIKS sorbent, carbonate-bicarbonate elutriator) with KhPI-01 chromatograph (conductometric detector). The sensitivity of determination was about 2 10^{-6} M. In this regime, the fluoride and formiate cannot be separated from each other having a similar peak height; that is why their sum was determined. This remark applies mainly to the samples of AP and AA, in which photochemical reactions in the atmosphere can be sources of formiate.

In the second part of a sample, specific electric conductance χ was measured, which is an integral parameter of the sum of all the ions in solution. It is reasonable to make this measurement at first, because the value of χ serves as a guiding line to estimate the necessity of diluting the sample for further analysis. After this, pH was measured in this aliquot; then it was divided into two parts. Alkali was added to one of them till pH 9, followed by titration with EDTA solution with the conductometric determination of the equivalence point of complexonometric titration of Ca^{2+} + Mg^{2+}. It is especially convenient to use conductometric titration when analyzing small concentrations, when the change of colour of the coloured indicators (which is usually applied version of the determination of these ions) can hardly be distinguished. Another part of the aliquot was titrated with HCl till pH 4.5 in order to determine total alkalinity (when analyzing AP and AA, this parameter coincides with the concentration of HCO_3^-). When analyzing SW, H_2CO_3 was removed from the resulting solution; reverse titration with the addition of NaOH was performed till the initial pH, in order to determine Alk_{hum} [16]. In this case, Alk_{carb} was determined as the difference between Alk_{tot} and Alk_{hum}.

After all the determinations were completed, specific electric conductance was calculated and compared with the experimental value. As a rule, the deviation did not exceed 10–15 %. The ΣAn and ΣCat values coincided within the same error. This agreement should be considered as satisfactory, taking into account low concentration of ions to be determined, as well as the absence of buffer in the AP and AA samples.

ION COMPOSITION OF ATMOSPHERIC AEROSOL

As it was mentioned above, the most informative aspect to investigate factors determining the formation of the acidity of atmospheric components is the examination of the ion composition of atmospheric aerosol. In the Project "Aerosol of Siberia", regular sampling of AA was performed in 1996–2001 in the observation sites listed below:

site 1: near Samburg settlement, to the north from the Polar Circle, 67 degrees of north latitude, 78 degrees of east longitude, the tundra zone;

site 2: near Tarko-Sale settlement, 65 degrees of north latitude, 78 degrees of east longitude, about 250 km to the south from site 1, forest-tundra zone;

site 3: Krasnosel'kup settlement, 66 degrees of north latitude, 83 degrees of east longitude, to the west from sites 1 and 2, forest-tundra zone;

site 4: Klyuchi settlement, Novosibirsk Region, 55 degrees of north latitude, 78 degrees of east longitude, forest-steppe zone;

site 5: near Karasuk settlement, Novosibirsk Region, 54 degrees of north latitude, 78 degrees of east longitude, about 500 km to the south-west from site 4, steppe zone.

In these sites, AA was sampled every day in the series of observations lasting for 30 days each, during different seasons of the year. High dynamics of the conditions of the formation of aerosol particles is illustrated by the data on variations of pH and specific electrical conductance of the aqueous extracts of AA, shown in Fig. 2 for two sites, Samburg and Karasuk, within the same period (January 10 to February 9, 2001). The range of pH variation during this period in the northern observation site

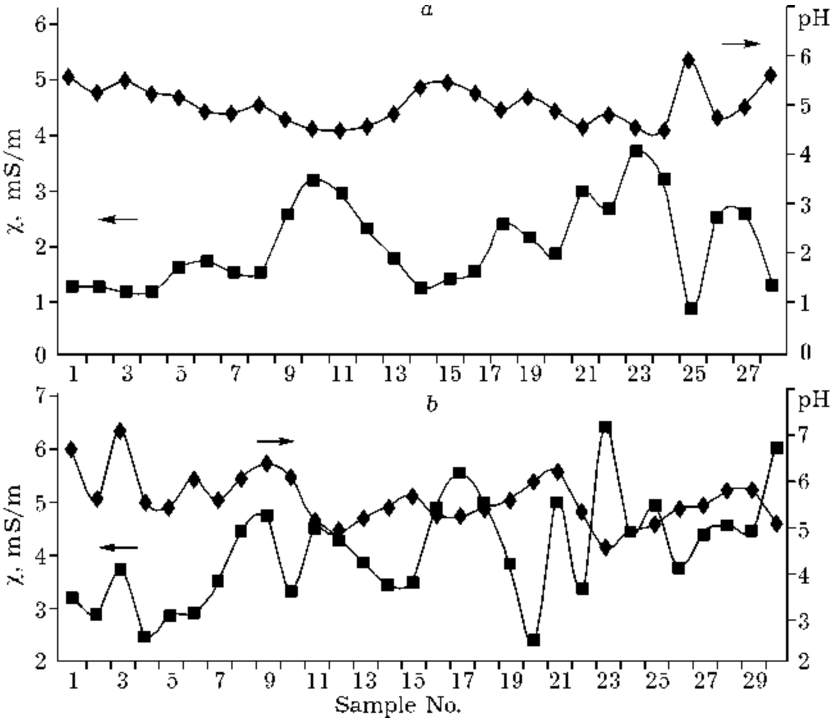

Fig. 2. Dynamics of specific electric conductance and pH of water extracts of discrete aerosol samples collected synchronously in Samburg (*a*) (site 1) and in Karasuk (*b*) (site 5) during the period from January 10 till February 9, 2001.

(Samburg) was 4.52 to 5.92, while in the southern site (Karasuk) it was 4.63 to 7.24. Total content of soluble salts in AA, for which χ value is the evidence, was lower in Samburg, where this parameter varied within the range 0.77–3.6 mS/m, while in Karasuk it was 2.31 – 6.29 mS/m. It is noteworthy that in Samburg the decrease of pH generally correlated with the increase of the concentration of dissolved salts, while in Karasuk the interconnection between the acidity and salt content of aqueous extracts of AA was of more complicated character.

For other periods and observation sites, the parameters of ion composition of the discrete AA samples were also highly variable. This undoubtedly reflects the dynamics of formation processes and sources of aerosol particles. It is reasonable to assume that the action of one or another source manifests itself as mutual correlation of the ions characteristic of it (for marine source, these are Na^+ and Cl^-; for erosion source, Ca^{2+} and HCO_3^-). The joint variability of NH_4^+, SO_4^{2-} and H^+ is the evidence of gas-phase processes of the formation of acid-containing aerosol; the absence of H^+ in this combination corresponds to the formation of the components of a “well-aged” aerosol from the gas phase [17]. Different sources of the AA can be identified by means of the statistical (factor) analysis of the ion composition of discrete samples in rather long series of observations.

The results of such an analysis and averaged data on the ion composition for separate observation series in sites 1, 2, 4, and 5, performed in 1997–2000, were published in [18]. In all the observation sites, the most frequently manifested fact is the effect of gaseous precursors of ion incorporated in AA. For example, the joint dynamics of NH_4^+ and SO_4^{2-} concentrations was exhibited in 10 of 11 series in the site 2, in all the 5 series obtained in site 3, in 12 of 16 series in site 4. In site 1, the conditions for the manifestation of an acid source were realized in 7 of 11 observation series, while in site 4 such a situation was observed only in 2 of 16 series. The action of the marine source of the formation of AA is most frequently exhibited in sites 1 and 2 (in 7 of 11 series), and more rarely in sites 4 and 5 (in 4 of 16, and 3 of 13 series, respectively). *Vice versa*, the action of the erosion source is more vividly expressed in sites 4 and 5, situated in the agricultural region in the south of West Siberia.

TABLE 1

Stoichiometric composition of AA averaged over many years

Site	M, μg/m^3	W, μg/m^3	Mean concentration of ions, ng-eq./m^3									
			NH_4^+	Ca^{2+}+ Mg^{2+}	Na^+	K^+	H^+	HCO_3^-	F^- + $HCOO^-$	Cl^-	NO_3^-	SO_4^{2-}
1	29.1	2.5	11.0	8.4	10.3	2.1	5.3	4.4	2.3	3.1	1.3	27.8
2	34.6	3.8	18.6	15.9	11.0	3.2	1.9	10.9	2.1	2.9	2.7	38.1
3	41.9	4.2	30.2	13.0	8.3	2.6	5.8	8.1	2.3	2.0	1.0	51.2
4	41.8	4.7	18.5	31.3	6.7	4.4	2.3	12.8	2.2	1.8	7.6	40.9
5	39.1	5.3	30.5	25.4	8.0	6.1	2.3	7.1	2.0	1.8	10.0	56.3

In order to estimate the contribution of each source of AA formation in different natural climatic zones of West Siberia, let us turn to the data on the concentrations of different ions. Arithmetic mean concentrations of the ions to be analyzed for all the observation series in sites 1–5 during 1997–2001 are shown in Table 1, along with mass concentrations (M) and the concentrations of water-soluble salts (W) in AA. Minimal M and W are observed in the northern observation site 1, which is in the tundra zone near the Arctic coast. Higher concentration of aerosol particles themselves and water-soluble salts in them is characteristic of site 3, which is situated in the north of West Siberia, too, and in sites 4 and 5 in the agricultural zone in the south of West Siberia. Among the cations of water-soluble salts in AA, when passing from north to south the concentrations of the products of erosion processes, *i. e.* potassium, calcium and magnesium, increase, while sodium concentration decreases, which depicts the weakening of the action of marine source of AA formation. This is confirmed also by the decrease of chloride concentration among anions. The concentration of nitrate increases substantially, while the concentration of F^- + $HCOO^-$ remains almost the same. No distinct regularities were observed in the spatial dynamics of the concentrations of ammonium, sulphate and hydrocarbonate.

For a more detailed analysis of the action of different sources of AA formation, it is useful to compare not the absolute concentrations but the distribution of ions from different sources in the water-soluble fraction of AA. These data, represented as the fraction of the equivalent of each ion in the sum of equivalents of cations or anions, are listed in Table 2. Attention should be paid to the prevailing role of sulphates among the anions, independently of the observation site. The fraction of hydrocarbonate occupied the second position among anions in sites 1–4; in site 5, the second position is occupied by nitrate. In general, no anion can compete with the sulphate. Hence, it is the sulphate that determines the possibility of the excess acidity of aerosol particles in all the natural climatic zones of West Siberia.

Only a half of sulphate in the water-soluble AA fraction can be neutralized by ammonium, the only cation having a gas-phase precursor. Another half must be compensated by non-volatile substances from erosion or marine sourc-

TABLE 2

Fractional distribution of cations and anions in AA in different observation sites, % of the sum of molar concentrations of equivalents

Site	NH_4^+	Ca^{2+}+ Mg^{2+}	Na^+	K^+	H^+	HCO_3^-	F^- + $HCOO^-$	Cl^-	NO_3^-	SO_4^{2-}
1	29.6	22.6	27.8	5.7	14.3	11.3	5.9	8.0	3.3	71.5
2	36.8	31.4	21.7	6.3	3.8	19.2	3.7	5.1	4.8	67.2
3	51.1	21.7	12.0	4.2	11.0	11.2	3.8	3.0	1.7	80.3
4	29.3	49.5	10.6	7.0	3.6	19.6	3.4	2.8	11.6	62.6
5	42.2	35.1	11.1	8.4	3.2	9.2	2.6	2.3	13.0	72.9

es. The necessary prerequisites are present, since, as one can see in Table 2, the AA contains sodium in excess with respect to chloride, and $Ca^{2+} + Mg^{2+}$ in excess with respect to HCO_3^-. Assuming as a first approximation that these pairs of ions characterize the action of the marine and erosion sources of AA, one may estimate the contribution from these sources into the neutralization of the excess of $SO_4^{2-} - NH_4^+$. The results of such an estimation are shown in Table 3. They demonstrate that the role of the products of erosion origin increases from the north to the south, while the contribution of the salts from the marine source decreases, though in the last site 5 it becomes higher than in site 4. The sum of contributions from both sources remains smaller than that required for the complete neutralization of the excess of sulphates in sites 1 and 3. As a result, the increased acidity of AA is observed in these sites, which is confirmed by the data on H^+ concentration (see Table 2).

It would be interesting to reveal the reasons of the different concentrations of sulphates in AA, the difference between sites 1 and 3 being 2-fold. Since the total concentrations of the cations of calcium, magnesium, sodium and potassium differ only insignificantly in these sites (20.8 and 23.9 ng-eq./m^3, respectively) nearly two-fold increase of the sulphate concentration in site 3 cannot be consequence of an additional income from land or sea sources. Hence, it may be believed that the action of a gas-phase source of volatile sulphur compounds in Krasnosel'kup is increased in comparison with Samburg. A source of this kind can be the Noril'sk industrial region, in which the emission of sulphur oxide into the atmosphere reaches 2 mln t per year. Really, it was demonstrated in series of simultaneous observations in sites 1–3 that at a definite direction of air mass transfer, a man-made source (Noril'sk) can be the additional source of sulphate; the extent of its influence is different for these sites [19]. The same authors established a correlation between the concentrations of SO_4^{2-} and a series of metals in aerosol and estimated the amount of their emission into the atmosphere by the Noril'sk industrial region. On the basis of these data, one can assume that the action of such a man-made source on the territory of the Krasnosel'kup and Purovsk regions of the Yamal Nenets Autonomous Okrug is exhibited both in the change of the acidity of atmospheric components and in the airborne income of metals.

TABLE 3

Contribution from different sources into neutralization of the excess sulphates in aerosol, %

Site	Marine	Erosion
1	47.3	27.0
2	54.6	40.1
3	30.8	36.0
4	18.0	69.1
5	28.7	84.4

Thus, the analysis of annual mean data on the ion composition of AA in 1997–2001 leads us to the conclusion that the prerequisite for the increased acidity of atmospheric components over West Siberia is the excess of the major anion with respect to the only cation among the products of the formation of aerosol particles from the gas phase. Neutralization of the excess sulphate can be provided by the products coming from erosion and marine sources in case if they are not deficient. The latter condition is fulfilled to a different extent in different natural climatic zones, judging from the data reflecting the annual mean composition of AA.

A specific feature of the climatic conditions of Siberia is long winter with the isolation of the land by the constant snow cover. This leads to seasonal non-uniformity of the action of local erosion sources of AA formation. The importance of seasonal factors for the ion composition of AA in different sites of West Siberia can be observed using the data related to winter and summer of the year 2000 (Table 4).

First of all, it should be noted that at the increase of AA mass concentration in summer, the concentration of water-soluble salts decreases in all the sites except site 3. So, the fraction of *W* in total *M* is substantially decreased. For example, in site 1, it is 34 % in winter decreasing to only 5.9 in summer. Hence, the increase of the mass of aerosol particles in summer is determined by the increase of the

TABLE 4

Ion composition of atmospheric aerosol in winter and in summer 2000

Site	M, µg/m^3	W, µg/m^3	Mean concentration of ions, ng-eq./m^3									
			NH_4^+	$Ca^{2+}+Mg^{2+}$	Na^+	K^+	H^+	HCO_3^-	F^-+HCOO^-	Cl^-	NO_3^-	SO_4^{2-}
						January–February						
1	10.0	3.40	20.0	9.2	9.7	4.2	4.5	1.6	2.5	2.2	1.0	46.1
2	24.0	5.67	42.0	12.5	10.9	7.1	1.2	4.0	3.6	3.5	3.3	73.5
3	42.9	5.12	37.7	18.9	7.1	3.5	2.3	3.5	2.5	1.7	1.8	70.5
4	15.0	4.87	31.8	21.9	8.0	8.4	0.1	4.2	1.6	1.9	5.0	57.2
5	26.4	4.68	38.3	16.4	8.6	4.7	0.6	1.8	0.6	0.7	3.1	62.6
						June–July						
1	22.0	1.18	4.3	2.0	5.7	1.1	7.1	2.0	1.0	1.9	0.5	13.7
2	24.7	2.61	8.5	14.2	9.0	1.5	1.3	13.7	1.9	2.1	1.2	19.3
3	20.4	5.06	40.9	11.6	10.0	3.8	7.0	6.5	1.7	2.1	0.7	64.0
4	51.0	3.08	7.6	26.8	5.0	2.4	0.3	17.4	2.1	1.7	2.6	19.8
5	66.0	3.37	11.7	24.0	7.3	3.0	0.2	14.6	1.2	2.0	3.3	26.8

fraction of water-insoluble substances, probably of erosion origin.

One can easily notice that the major contribution into the increase of W in winter is made by the ions of gas-phase origin: sulphate and ammonium. A confirmation of this fact is the data on the dynamics of the concentrations of sulphate, ammonium, sodium and $Ca^{2+} + Mg^{2+}$ during the whole observation period in sites 1, 2, 4, and 5 (Fig. 3). Cymbate changes of the sulphate and ammonium concentrations have the largest amplitude and do not coincide with the dynamics of the concentration of cations of erosion or marine origin. According to the data presented in Table 4, one can estimate seasonal variations of the contribution from the latter into the excess of sulphates over ammonium, as it has been done above.

Results of such an estimate are listed in Table 5. In the north of West Siberia (sites 1–3), in summer the role of the marine source increases sharply, while the contribution from the erosion source diminishes sharply. The former phenomenon is likely to be connected with the liberation of Arctic seas from ice, while the second one is due to the decrease of excess amount of $Ca^{2+} + Mg^{2+}$ with respect to HCO_3^-. For the sites 1 and 3, the total action of both sources turned out to be insufficient for the efficient neutralization of the excess of sulphates, which caused an increased concentration of H^+ in AA (see Table 4). Less dramatic situation was observed in January and February: in spite of the weakening of the contribution from the cations of marine source, the positive balance in the difference between the equivalents $[(Ca^{2+} + Mg^{2+}) - HCO_3^-]$ helped more efficient neutralization of the excess of sulphate. Nevertheless, an increased acidity of AA was observed in site 1 in winter. In the south of West Siberia, in sites 4 and 5, at the noticeable and almost constant contribution from the marine source, the major contribution into the neutralization of the excess of sulphates is made by the erosion source both in summer and in winter. As a results, no conditions for the formation of acidified AA are manifested.

The above estimations of the contribution from gas-phase, erosion, and marine sources into the acidity of the water-soluble fraction of aerosol are based on the actual data on the balance of cations and anions characteristic of these sources. Different explanations of the steady excess of sodium over chloride in AA are possible. One of them is based on the fact that only a part (from 1/3 to 1/5) of Na^+ originates from sea, while the major part of it originates from land, for example in the form of tenardite Na_2SO_4 (as it was mentioned above, sulphate prevails among anions) or in the

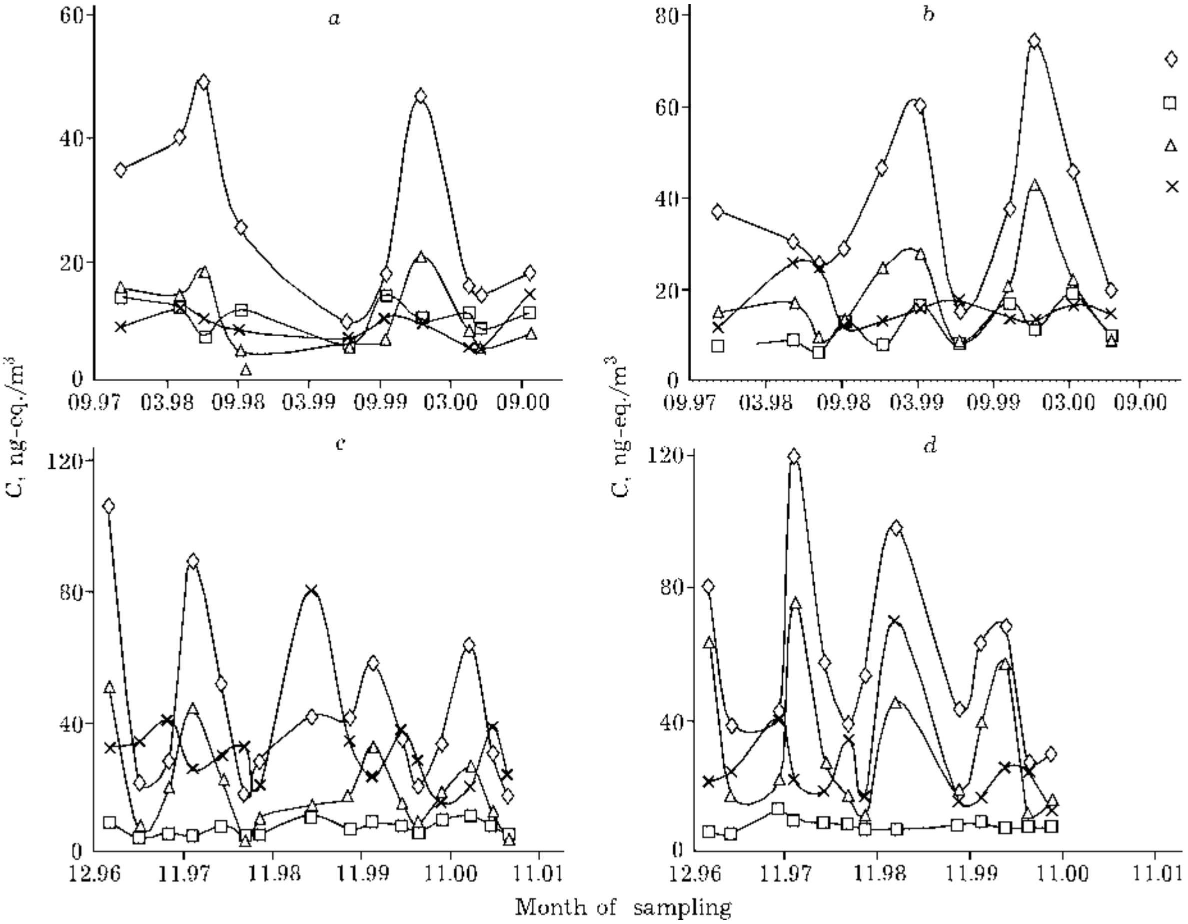

Fig. 3. Seasonal dynamics of the concentrations of major ions in the aerosol sampled at different observation sites from 1996 to 2001: *a* – Samburg, *b* – Tarko-Sale, *c* – Kluychi, *d* – Karasuk; *1* – SO_4^{2-}, *2* – Na^+, *3* – NH_4^+, *4* – $Ca^{2+} + Mg^{2+}$.

form of $NaHCO_3$. However, according to the data shown in Tables 1 and 4, no correlation is observed in the changes of sodium and sulphate or hydrocarbonate over seasons or observation sites. Because of this, without rejecting the possibility for a definite part of sodium to enter AA with the salts of land origin, one should recognize that these sources cannot provide the major part of sodium concentration. The HCO_3^- ions in AA are also deficient with respect to the sum $Ca^{2+} + Mg^{2+}$; only in summertime and in some observation sites, their concentration could provide the admission of the major part of sodium. At the same time, a definite correlation between $[Na^+]$ and $[Cl^-]$ is the evidence that the major part of sodium comes from the marine source. A substantial excess of sodium in AA can be the result of

TABLE 5

Seasonal variations of the contributions from the main sources into the neutralization of excess sulphates in AA, %

Site	Winter		Summer	
	Marine	Erosion	Marine	Erosion
1	28.7	29.1	40.4	0
2	23.5	27.0	63.9	4.6
3	16.5	47.0	34.2	3.5
4	24.0	69.7	27.0	77.0
5	32.5	60.1	35.1	62.2

displacement of chloride in the form of volatile HCl formed during the interaction of sulphuric acid, present in excess, with NaCl:

$$2NaCl + H_2SO_4 \rightarrow 2HCl + Na_2SO_4 \qquad (2)$$

The reaction (2) may occur in water film on the surface of aerosol particles because of the differences in the volatility of sulphur and hydrochloric acids; the result of this process is impoverishment of AA in chlorides and enrichment with sodium.

The situation with the excess of calcium and magnesium cations with respect to HCO_3^- ions, able to neutralize a part of acid-generating sulphates, is somewhat different. According to the data shown in Table 4, in winter $[Ca^{2+} + Mg^{2+}]/[HCO_3^-]$ ratio is equal to 3–5 in water-soluble fraction of AA in sites 1 and 2, while it reaches 9 in the southern site 5; in summer it is close to 1 both in the north and in the south. The major reason of these variations is higher variability of $[HCO_3^-]$ concentration, since the sum $[Ca^{2+} + Mg^{2+}]$ is more stable both over seasons and over observation sites. It should be noted that, independently of the origin, $[HCO_3^-]$ in the aqueous phase of aerosol is governed by the equilibrium of the dissociation of carbonic acid

$$H_2CO_3 \leftrightharpoons HCO_3^- + H^+ \qquad (3)$$

and gas exchange of this phase with the atmospheric CO_2. Under these conditions, the equilibrium concentration of HCO_3^- is a linear function of pH. However, this simple dependence is not fulfilled for the data shown in Table 4, because of different content of aerosol particles in 1 m^3 of the air. At the same time, the dependence is rather well fulfilled if one considers the fractional distribution of ions in the AA. For example, the decrease of the fraction of HCO_3^- from 36 to 10.5 % in the sum of anions of the water-soluble AA fraction in Samburg (site 1) with respect to another northern point (Tarko Sale, site 2) in June–July, 2000 is clearly correlated with the increase of the fraction of H^+ from 3.8 to 35 % among cations, *i. e.* is explained by the excess acidity of aerosol particles in site 1.

Another reason of the decrease in HCO_3^- concentration among the anions of AA is valid in the southern observation site (site 5), since no acidification of AA occurs in this point. According to the data shown in Table 2, in comparison with another point in the south of West Siberia (site 4), HCO_3^- fraction decreases from 19.6 to 9.2 %, or by 10.4 %, which is explained by the increase of the fraction of SO_4^{2-} by 10.3 %, which means the action of additional sources of sulphates. These can hardly be man-made sources because there are no powerful plants of power engineering and metallurgy near Karasuk. As we have noted earlier [20], this is most likely the action of natural sources of sulphates in AA, namely, aeolian carrying-out of salts into the atmosphere (including tenardite Na_2SO_4 from saline lands of the Kulunda and Caspian region, the annual flux being estimated to be 4–7 thousand t/(km^2 year) [21]).

Thus, results of the observation of ion composition of AA over West Siberia allow one to reveal some regional features important from the viewpoint of the formation of acid deposition. Total concentration of aerosol particles and the fraction of water-soluble fraction of AA in the atmosphere of northern regions, in the tundra and forest-tundra, is much lower than that observed in the steppe and forest-steppe of the southern regions. Over the whole territory, the major acid-forming anion is sulphate; its neutralization is only by half provided by ammonium, the sole cation in AA having a gas-phase precursor. Concentration of these ions increases in winter and decreases in summer in all the natural climatic zones of West Siberia. Neutralization of the excess of sulphate in water-soluble AA fraction can be provided by the cations of sodium, calcium and magnesium, having marine and erosion sources. The major contribution into the neutralization of the excess sulphate in the south of West Siberia is made by erosion sources both in summer and in winter. The efficiency of both sources is sufficient for almost complete neutralization of the excess sulphate; no acidification of AA is observed. In the north of West Siberia, the contribution from erosion sources is smaller (especially in summer); this is not compensated by an increase of the role of marine sources of aerosol. As a result, the conditions providing increased acidity of AA exist in the northern observation site near the Arctic coast, where the concentration of aerosol particles is minimal. The danger of aerosol acidification is somewhat lower in other observation sites in the north of West Siberia; however, it is much more clearly expressed than in the southern regions.

ION COMPOSITION OF ATMOSPHERIC PRECIPITATION

Regular observations of the ion composition of freshly precipitated snow and rain water were performed only in the vicinity of site 4: in winter near Akademgorodok (its southern border), and in summer at the bank of the Ob' Sea, 90 km to the south-west from Novosibirsk. Depending on the frequency of precipitation in 1996–2001, 20 to 40 samples per season were collected in these sites. A snow survey resulting in 30 samples of snow was performed in the north of West Siberia in Purovsk and Krasosel'kup regions of Yamal Nenets A. Okr. by the end of winter 1998–1999; a year before, 15 samples were taken only in Purovsk region. Because of this, information on the seasonal dynamics of the ion composition of atmospheric precipitation is scarcer than the data on aerosol. In addition, it should be taken into account that the data obtained by the analysis of the whole volume of snow accumulated during winter characterize a sum of dry and wet precipitation, while fresh samples relate only to wet precipitation.

The distribution of the frequency of discrete precipitation events with different pH in the vicinity of site 4 in 1996–2001 is shown in Fig. 4. During the winter 1996–1997, the largest number of samples had pH 5.5 to 6, corresponding to the normal acidity. However, the fraction of snow precipitations with lower pH exceeded the fraction of precipitations with higher pH; three samples had pH 4 to 4.5, and three samples had pH 4.5 to 5. In general, the distribution of discrete snow samples during that winter was shifted towards lower pH than the normal value for atmospheric precipitation (5.8). Snow precipitation samples during the winter 1997–1998 were even more acidic. In 1998–1999 and 2000–2001, the distribution of the frequency of precipitations with different pH was symmetrical with respect to the normal value, while in winter of 1999–2000 it was shifted to higher pH. For discrete rain samples, the variability from one year to another is also characteristic: increased acidity was observed in the summer of the year 1996, decreased acidity was observed in 1999; the range of acidity variation was broad in the summer of 1997, while in 2000 it was narrow. This suggests that the action of different factors forming the ion composition of atmospheric precipitation is subjected to variations from one year to another. It is essential that at the maintenance of the normal mean acidity over the whole season, separate precipitation events can be characterized by increased acidity (to pH 4.18). As a rule, an increase of acidity in the discrete samples of precipitation is not connected with the increase of the total salt concentration (for instance, the correlation coefficient between pH and electric conductivity χ in the series of snow precipitations of 1996–1997 is 0.136). This means that the reason of acidification of precipitation is not contamination by a man-made source. Hence, in the south of West Siberia, short-term conditions of natural character can occur for acid precipitation.

The data on seasonal mean concentrations of separate ions, pH, and total salt content (W) of snow and rain precipitations near site 4 in the Novosibirsk Region are shown in Table 6. Parameters for each type of precipitation, averaged over many years, are also shown there. If we compare these values to each other, we can observe a clear difference between the snow and rain precipitations seen in some parameters of the ion composition, at the constancy of others. Averaged over many years, the pH values for winter and summer precipitation (5.69 and 5.74) are close to each other and correspond to the normal level of acidity. The total salt content values averaged over many years are also close to each other (11.0 and 10.1 mg/l). The differences between snow and rain in the fractional distribution of the equivalents of calcium and magnesium, potassium, H^+ ions, nitrate, and sulphate are

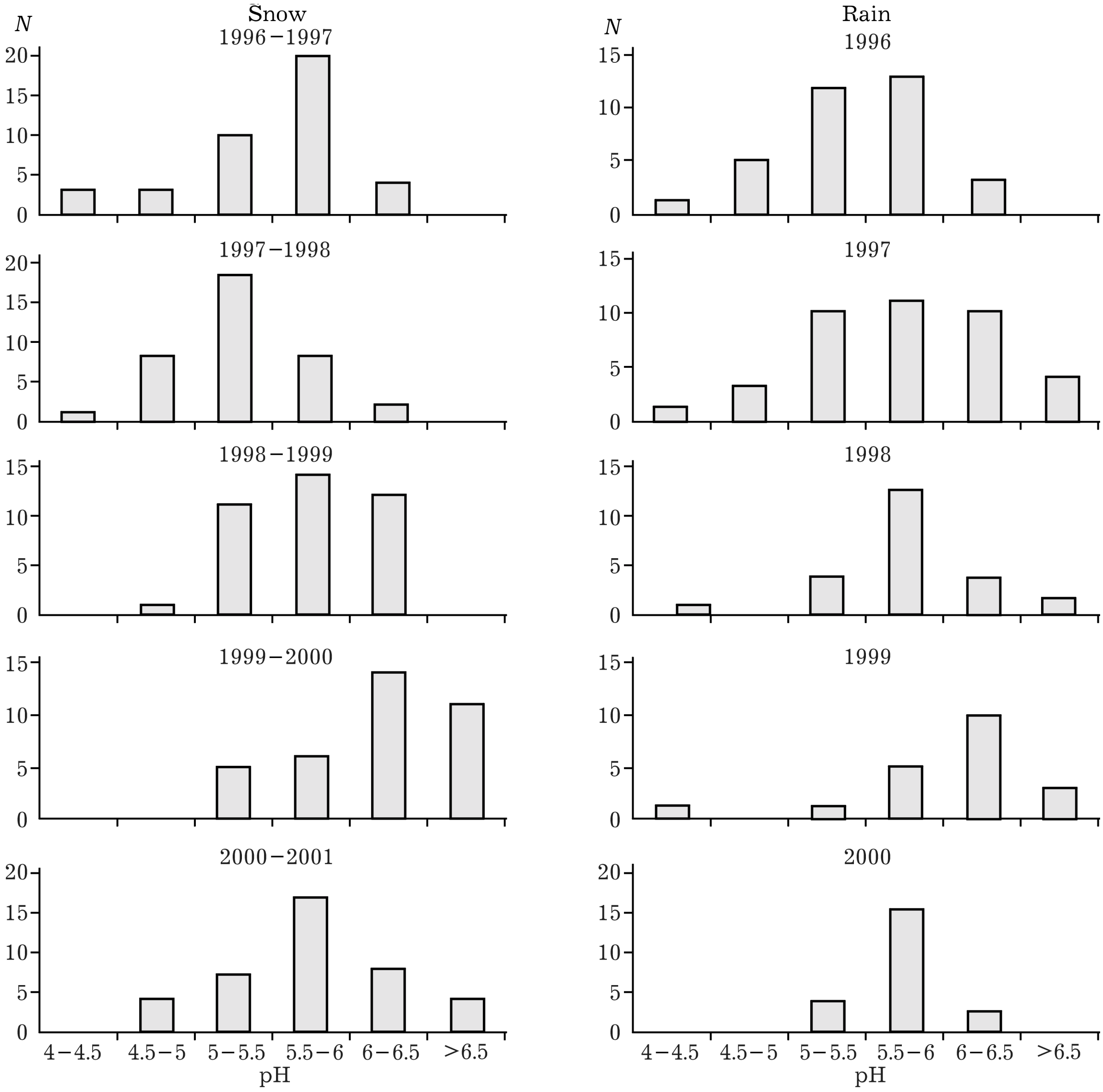

Fig. 4. Distribution of the number of discrete samples of snow and rain precipitations over pH.

not large. However, the fractions of ammonium and hydrocarbonate in the snow are 2–3 times lower, while those of sodium, chloride, and fluoride are 2–3 times higher than in rain. A decrease in the fraction of ammonium and HCO_3^- in winter can be explained by the decrease in the emission of ammonium and products of soil erosion, *i. e.* by the seasonal variations of the action of local factors. An increase in the fraction of sodium and chloride in precipitation in winter is likely to be due to another reason, namely, long-range atmospheric transport of salts from the regions of Kulunda and Caspian Sea.

When comparing the data on the fractional distribution of cations and anions in aerosol, rain and snow precipitation, presented for site 4 in Tables 2 and 6, one can see that the fraction of sulphates stops being prevailing in precipitation; it accounts for 25–27 % of the sum of the equivalents of anions (73 % in AA), while, quite contrary, the fraction of chlorides increases sharply (from 2.8 in AA to 15 % in rain, and up to 28 in snow). In our opinion, this is explained by the reaction (2), leading to enrichment of AA with sulphates and their impoverishment with chlorides. A similar reason, namely, evaporation of a part of nitrates in the form of HNO_3 from AA and their absorption by precipitations is likely to lead to the increase of the fraction of NO_3^- in precipitation, with respect to aerosol particles. We

TABLE 6

Ion composition of snow and rain precipitation in site 4 during 1996–2001

Year	Number of samples	W, mg/l	pH	NH_4^+	Ca^{2+}+ Mg^{2+}	Na^+	K^+	H^+	HCO_3^-	F^-	Cl^-	NO_3^-	SO_4^{2-}
						Snow precipitation							
1996–1997	40	10.9	5.50	29/16.9	106/61.6	21.5/12.5	9.1/5.3	6.1/3.6	24/15.4	14/8.8	29/18.2	39/24.4	53/33.1
1997–1998	37	9.0	5.26	17/12.8	50/37.3	43/31.9	17/12.6	7.2/5.3	19/14.2	11/8.5	40/30.6	27/20.4	34.5/26.2
1998–1999	39	10.7	5.73	14/6.9	84/44.8	69/36.3	20/10.3	3.1/1.6	29/15	17/8.7	61/31.1	38/19.3	51/26.2
1999–2000	36	14.2	6.19	26/13.1	100/49.8	53/26.6	21/10.3	1.0/0.5	64/30.4	28/13.3	50/23.5	31/14.9	38/17.8
2000–2001	40	10.4	5.77	8.4/4.9	63/40.7	65/41.3	17/11.1	3.1/2.0	28/17.9	11/7.1	57/37.0	27/17.2	32/20.9
Average	38	11.0	5.69	19.0/10.9	80.6/46.8	50/29.7	17/9.9	4.7/2.6	33/18.6	14/9.3	47/28.1	32/19.2	42/24.8
						Rain precipitation							
1996	34	7.8	5.44	42/35.7	46/39.1	16/13.6	11/9.4	3.6/3.1	32/28.3	4.0/3.5	16/14.2	18/15.9	43/38.1
1997	39	16.8	5.79	83/37.6	80/36.3	34/15.4	22/10	1.6/0.7	88/40.2	6.8/3.1	27/12.3	36/16.5	61/27.9
1998	23	12.3	5.83	38/24.7	87/56.5	18/11.7	9.6/6.2	1.4/0.9	72/51.3	0.7/0.5	12.6/9.0	24/17.1	31/22.1
1999	20	11.9	6.04	47/30.3	72/46.5	23/14.8	12/7.7	0.9/0.6	58/35.8	6.2/3.8	22/13.6	31/19.1	45/27.7
2000	23	5.1	5.74	19/27.1	34/48.6	10/14.3	5.2/7.4	1.8/2.6	29/39.7	3.1/4.2	18/24.7	10.5/14.4	12.4/17.0
2001	36	6.5	5.59	37/40.5	29/31.7	12/12.9	9.6/10.6	3.8/4.3	26/29.2	1.5/1.7	12/13.8	24/27.8	24/27.5
Average	29	10.1	5.74	44/32.7	58/43.1	19/13.8	12/8.6	2.2/2.0	51/37.4	3.7/2.8	18/14.6	24/18.5	36/26.7

Note. Numerator: concentration, mg-eq./l; denominator: fraction of equivalent, % of the sum of ion equivalents.

will see below that such a situation is also characteristic of the north of West Siberia: the fraction of sulphate in snow sampled at sites 1 and 2 decreases sharply in comparison with aerosol, while the concentration of chloride and nitrate increases. So, this difference in the ion composition of AA and precipitation is of general character and is not a local specific phenomenon.

Statistical (factor) analysis of the variability of the concentrations of separate ions in snow and rain precipitations shows that the acidic factor is not exhibited at any season. The total dynamics of Na^+ and Cl^- characterizes the action of marine source in all the seasons. In summer, its effect is not so obvious (can be distinguished in 3 of 6 seasons); the action of erosion factor can be noticed more frequently (the joint dynamics of Ca^{2+} and Mg^{2+}, HCO_3^-). Attention should be paid to the fact that many series (especially winter ones) demonstrate the mutual correlation of the concentrations of calcium, magnesium, and sulphate. This agrees with the above assumption that a part of sulphate in the aerosol of the south of West Siberia has not gas-phase but aeolian origin.

Similarities and differences in the ion composition of aerosol and wet precipitations are exhibited not only in the data averaged over rather long observation periods at a definite site, but also in comparing the results of the analysis of discrete samples. The fractional distribution of equivalents of the cations and anions in diurnal samples of AA and snow taken simultaneously in January–February, 2001, in site 4 is shown in Fig. 5. The fraction of ammonium in the cations of aerosol is somewhat higher and that of the sum of calcium and magnesium is lower than in snow precipitations. More substantial changes can be seen in the composition of anions. At the same state of atmosphere, the fraction of sulphates sharply decreases in the falling snow; because of this, the fraction of the anions of volatile acids (carbonic, hydrofluoric, hydrochloric and nitric) increases. This is the evidence that the wet precipitation only partially inherit the composition of AA during the in-cloud and under-cloud washing: cations to a major extent, while anions to a less extent. However, in order to understand the reasons that cause acidification of precipitation, the investigation of factors forming the ion composition and acidity of AA gives a good basis since it is not connected with limitations in the periodicity of precipitation.

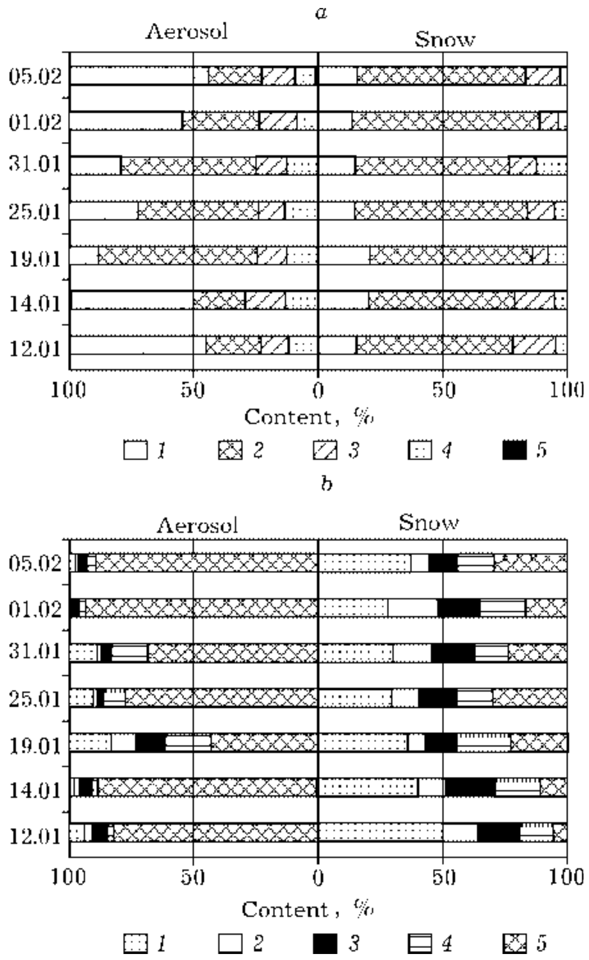

Fig. 5. Fractional distribution of the equivalents of some cations (*a*) and anions (*b*) in aerosol and snow samples collected synchronously in site 4 in January—February, 2001: *a* – NH_4^+ (*1*), Ca^{2+} + Mg^{2+} (*2*), Na^+ (*3*), K^+ (*4*), H^+ (*5*); *b* – HCO_3^- (*1*), F^- + $HCOO^-$ (*2*), Cl^- (*3*), NO_3^- (*4*), SO_4^{2-} (*5*).

As it was stressed above, systematic sampling of fresh atmospheric precipitation could not be organized in other sites of West Siberia. The data on the ion composition of the whole snow accumulated during winter, as obtained in the snow survey in Purovsk region (sites 1, 2) and Krasnosel'kup region (site 3) of Yamal Nenets A. Okr. (YaNAO) are shown in Table 7. Comparing the data for different regions one can note the elevated acidity of snow precipitation in the winter of 1997–1998, at the lower (about 2-fold) total salt content than that of

TABLE 7

Ion composition of snow precipitation in Purovsk and Krasnosel'kup regions*

Site	Year	Number of samples	W, mg/l	pH	NH_4^+	$Ca^{2+} + Mg^{2+}$	Na^+	K^+	H^+	HCO_3^-	$F^- + HCOO^-$	Cl^-	NO_3^-	SO_4^{2-}
1–2	1997–1998	32	4.6	4.89	8.3/11.3	25/34.1	19/25.9	8/10.9	13/17.7	8/33.3	13/10.6	15/17.3	14/20.0	25/18.7
	1998–1999	17	9.3	5.67	6.6/4.2	44/27.9	79/50.4	24/15.3	3.8/2.4	20/14.9	25/18.6	48/35.1	17/12.5	26/18.8
	1999–2000	5	8.7	5.16	23/21.4	34/31.6	26/24.2	17/15.8	7.5/7.0	26/23.9	13/11.9	25/22.9	23/21.1	22/20.2
3	1998–1999	16	8.1	5.66	15.4/12.3	37/29.5	50/40.3	20/15.8	3.4/2.7	22/17.4	28/22.4	37/29.8	17/13.2	21/16.8

*See Note to Table 6.

the winter of 1998–1999. The reason is the decrease of the concentrations of calcium, magnesium, and especially sodium, at the close concentrations of the major acid-forming anions sulphate and nitrate. The overall effect of the decrease in the concentrations of the mentioned cations (79 μg-eq./l) is not compensated by the decrease of the concentrations of anions (chloride, fluoride, and possibly formiate) by 56 μg-eq./l. As a consequence, the maintenance of balance between the equivalents of anions and cations requires the increase of the concentration of H^+ ions, which causes elevated acidity of snow. It is principally important that this occurs at the decrease of general salt content and not due to additional amount of acid-forming substances.

When comparing the data for the two neighboring regions (Purovsk and Krasosel'kup), obtained within one observation season, one can see the similarity of the ion composition of snow precipitation. Comparing ion composition of the snow over this territory (see Table 7) with the corresponding data for the south of West Siberia (see Table 6), one can conclude that the concentration of sulphates, nitrates and chlorides in the north of West Siberia is lower. However, this conclusion is erroneous, because the snow precipitations in the north contain substantially lower concentration and relative fraction of calcium and magnesium, *i. e.* cations that neutralize the anions of these strong acids. Because of this, a "purer" atmosphere in the north of West Siberia is by no means a sign of the decrease of the danger of acid rain. A fragile balance between the equivalents of cations and anions in this region can be easily distorted, as this happened in 1997–1998; the result will be elevated acidity of a huge amount of snow accumulated during long winter period.

In the ion composition of snow precipitation in sites 1–3 in the north of West Siberia, in comparison with AA, we observe the same differences as those characteristic of site 4 in the south. Comparing the data of Tables 2 and 7 on the fractional distribution of the equivalents of separate ions in AA and in snow, one can see that the fraction of the anions of volatile acids (HCl, HNO_3, HF) in snow has increased, due to a sharp decrease of the fraction of sulphates. Among cations, the fraction of Na^+ and K^+ increases due to the decrease of the contribution from ammonium, while the fraction of $Ca^{2+} + Mg^{2+}$ remains approximately at the same level. These differences are likely to reflect general regularities of the formation of AA and wet precipitation in West Siberia.

A substantial difference in the reasons of the elevation of AP acidity in West Siberia from those of some regions in the world, in which the problem of acid precipitation appears, should be noted. The author of [22] discovered that the concentrations of H^+ and SO_4^{2-} in precipitation over the territory of the USA and Canada are connected by a linear dependence

$$[H^+] = A + B\,[SO_4^{2-}] \qquad (4)$$

in which B decreases from 2 to 1 while the distance from industrially developed regions of the north-east of the USA becomes larger. According to the data of [2], the dependence (4) is also fulfilled for the territories of Norway and the European part of Russia. An increase of the acidity of precipitation in these regions is connected with the increase of the emission of sulphur dioxide and, as a consequence, with the increase of sulphate concentration in AP. However, according to our data shown in Table 6 (observations in site 4, averaged over many years), no correlation exists between $[H^+]$ and $[SO_4^{2-}]$; no correlation is exhibited also in each series of discrete samples of snow or rain. The dependence (4) is not obeyed, as suggested by the comparison of the same parameters in snow precipitation sampled in sites 1–3 (see Table 7). In addition, sulphate is not a prevailing anion in atmospheric precipitation in West Siberia.

The reason why the eq. (4) is not fulfilled is as follows: the distortion of the balance between acid-forming anions and neutralizing cations in AP over the vast territory of West Siberia is determined by the lack of cations from natural sources (gas-phase, terrigenous, marine), while in industrially developed regions acidification of AP is a result of increased emission of acid-forming gases from man-made sources. Under these conditions, the effect of man-made sources is exhibited even in the case of their relatively small capacity. In particular, near the oil-accompanying gas flare, an increased content of sulphates and nitrates was discovered [23], which can lead to an increased acidity of accumulated snow. The zone of such an influence turned out to be not large (about 1 km along the prevailing wind direction).

Thus, the analysis of the data on ion composition of atmospheric precipitation in West Siberia confirms some regional features that are also characteristic of aerosol. An increased danger of acidification of precipitation originates from the lack of cations in their composition due to overall decrease of the concentration of dissolved salts because of their insufficient income from terrigenous and marine sources. These conditions are most frequent in northern regions while in the south of West Siberia they are only occasional.

ION COMPOSITION AND ACIDITY OF SURFACE WATER

Atmospheric precipitation is an initial source of the formation of river and lake water. However, chemical composition of surface water is to a substantial extent determined by the interaction of precipitation with soils and rocks over the drainage territory, as well as by processes inside a water reservoir, including biotic ones. Drainage regime of rivers and lakes plays a substantial role, too. In a region with excess wetting, soil and rocks are well washed with precipitation; under the conditions of good drainage, they change the composition of atmospheric precipitation only slightly. Leaching processes in mountain rivers flowing from glacier foots are also exhibited only slightly. The situation is quite different in arid regions in which the connection between the composition of surface water and atmospheric precipitation is minimal, while the role of leaching processes is supplemented by the effects of evaporative concentrating, which often causes pickling.

Variety of natural climatic conditions in West Siberia leads to substantial differences in chemical composition of river and lake waters. Within the aspect of acid precipitation, we must be interested first in water with low salt content and relatively small buffer capacity; the formation of water of this type is to a major extent connected with their feeding by atmospheric precipitation rather than by subsoil or underground water. The water reservoirs of this type are those situated in the tundra and forest-tundra regions in the north of West Siberia, which are formed mainly by snow melting during spring high water. In the plains of the south of West Siberia, the major part of water reservoirs has low salt content only at the peak of spring high water, while the rest time those waters are characterized by high salt content; sodium carbonate pickling occurs over substantial territory (Baraba and Kulunda plains). This points to a substantial role of the interaction of atmospheric precipitation with soil and ground in forming surface water.

The accumulation of salts in soils and surface waters in the plains of the south of West Siberia was the subject of numerous investigations; recently, these investigations have been generalized and developed in [24]; in particular, it is demonstrated that one of the factors of the accumulation of salts in this region is their long-range transport with wind from south-west. Geographical and climatic factors promote not only salt accumulation but also their transformation with the formation of sodium bicarbonate lakes. It is typical that even in river systems the lowest pH during spring high water was never below 7 while during the rest part of the year pH was 8–8.5. It is natural that the problem of acid precipitation does not exist for such water reservoirs.

In sub-mountain and mountainous regions in the south of West Siberia, in particular in the Altay foothills, the formation of chemical composition of surface water is to a larger extent connected with direct feeding with atmospheric precipitation. In upper Ob' river, after the first flood, caused by snow melting in plains, a more powerful second flood comes, when the glaciers in the Altay Mts. start to melt. Thus, the period of washing river-beds with melted water becomes longer. These features of feeding water reservoirs and forming chemical composition of water help acidification effects to a more substantial extent than those of the steppe plain regions of the south of West Siberia. Because of this, in order to compare the effect of atmospheric precipitation on the acidity of surface water in different regions of West Siberia, we chose the Ob' Sea, situated in the upper Ob' river, for which the data of regular observations of chemical composition are available [25, 26].

In the north of West Siberia, only a few observations of the chemical composition of surface water are available; this forced us to perform special studies. Within the present project, in 1998–2001, we collected 33 samples of river and lake waters in the Purovsk and Krasnosel'kup regions of the YaNAO. Samples were collected at the end of winter snow accumulation period (April–May) and in summer (August). The data on the ion composition of these samples are shown in Table 8. Water samples from water bodies in Purovsk region were collected in the end of winter season of 1997–1998 and in the summer of 1998 in the sites: 1P – a lake 5 km to the south-east from Tarko-Sale settlement; 2P – a lake near the same settlement (summer cottages); 3P – lake Okunevoye; 4P – the Avaseida-Pur river; 5P – a lake 9 km to the south from Samburg; 6P – the Pur river, Samburg; 7P – lake Lebedinoye, Kharampur settlement; 8P – a lake 15 km to the east from Khanymey settlement; 9P, 10P – lakes around Samburg; 11P – lake Syrkovoye, Tarko-Sale settlement; 12P – a lake 15 km from Purne station; 13P, 14P – lakes 100 km from Purne station. The samples in sites 3P and 6P were successfully taken both in winter and in summer, while in other sites the samples were taken only once. In the end of winter 1999–2000, samples were collected in sites 9P, 15P – the river Pur near Tarko-Sale settlement, 16P – the Tretya river; in summer 2000 (August), samples were taken at sites 8P (this sample is designated as 8P-2, since a sample was taken at this site also in summer 1998), 17P – a lake 100 km to the north from site 8P.

In Krasnosel'kup region, sampling sites were as follows: 1K – a lake 6 km to the north from Krasnosel'kup; 2K – a closed canal near the right bank of the river Taz 3 km to south-east of Krasnosel'kup; 3K – the mouth of the Khudosey river; 4K – the mouth of the Karsavinskaya river; 5K – a lake ("warm") near site 4K; 6K – a lake 5 km to the north from Krasnosel'kup; 7K – the river Taz near

TABLE 8

Ion composition of surface water in the north of West Siberia, mg-eq./l

Sample	pH	*W*, mg/l	NH_4^+	Ca^{2+}+ Mg^{2+}	Na^+	K^+	Alk_{hum}	HCO_3^-	F^-	Cl^-	NO_3^-	SO_4^{2-}
						Summer						
3P	5.95	23	n/d	0.09	0.03	0.008	0.08	0.027	0.02	0.008	n/d	0.015
6P	7.08	18	n/d	0.23	0.12	0.013	0.26	0.14	n/d	0.03	0.01	0.017
8P	5.60	2.5	n/d	0.04	0.02	0.008	0.06	0.005	0.02	0.008	n/d	n/d
9P	6.29	28	n/d	0.35	0.08	0.02	0.08	0.24	n/d	0.02	0.05	0.03
10P	6.45	17	n/d	0.23	0.05	0.01	0.12	0.18	n/d	0.014	n/d	n/d
11P	5.70	28	n/d	0.09	0.03	0.009	0.07	0.042	n/d	0.006	0.002	n/d
12P	4.80	2	n/d	0.03	0.02	n/d	n/d	n/d	n/d	0.008	n/d	0.006
13P	4.50	3.5	n/d	0.02	0.05	0.003	n/d	n/d	n/d	0.042	n/d	0.008
14P	4.70	4.1	n/d	0.04	0.07	n/d	n/d	n/d	n/d	0.03	n/d	0.015
8P-2	5.72	7.7	0.03	0.05	0.04	0.011	0.11	0.06	n/d	0.096	n/d	0.017
17P	5.00	2.0	n/d.	0.014	0.005	0.015	0.025	n/d.	0.006	0.004	0.004	0.011
Mean	5.62	12.3	0	0.11	0.05	0.009	0.07	0.06	0.004	0.024	0.006	0.011
						Winter						
1P	6.00	21	n/d	0.28	0.10	0.03	0.17	0.20	n/d	n/d	n/d	n/d
2P	6.02	44	0.14	0.54	0.12	0.05	0.16	0.40	0.005	0.025	n/d	0.037
3P	6.60	58	n/d	0.78	0.16	0.03	0.23	0.64	n/d	0.01	n/d	n/d
4P	6.40	77	0.16	1.05	0.20	0.08	0.37	0.79	0.001	0.01	n/d	n/d
5P	5.76	13	n/d	0.13	0.07	0.014	n/d	0.10	n/d	0.03	0.01	0.02
6P	6.62	49	n/d	0.75	0.02	0.04	0.27	0.52	0.002	0.05	n/d	0.02
7P	6.31	50	0.26	0.75	0.12	0.07	0.62	0.41	0.01	0.027	n/d	0.02
9P	5.59	11	0.04	0.12	0.04	0.01	0.12	0.06	n/d	0.028	0.02	0.026
15P	5.98	53	n/d	0.52	0.19	0.05	0.20	0.56	0.004	0.08	n/d	n/d
16P	5.78	23	n/d	0.31	0.08	0.03	0.24	0.21	0.011	0.015	0.007	0.017
Mean	6.11	40	0.06	0.52	0.11	0.04	0.24	0.39	0.002	0.028	0.004	0.014
						Summer						
1K	6.53	37	n/d	1.12	0.20	n/d	1.28	0.16	0.020	0.019	0.014	0.009
2K	6.54	26	n/d	0.71	0.10	0.03	0.63	0.16	0.028	0.017	n/d	0.006
Mean	6.54	32	0	0.92	0.15	0.02	0.96	0.16	0.024	0.018	0.007	0.008
						Winter						
3K	6.99	266	n/d	2.95	0.80	0.06	0.28	3.14	0.009	0.009	0.023	0.045
4K	7.00	215	n/d	2.65	0.39	0.02	0.40	2.60	0.011	0.013	n/d	0.023
5K	6.30	127	0.077	1.75	0.11	0.16	0.46	1.50	n/d	0.009	n/d	0.011
6K	7.15	508	0.066	6.50	1.26	0.11	0.70	6.40	0.025	0.037	n/d	n/d
7K	7.21	183	0.167	2.35	0.20	0.04	0.34	2.08	0.006	0.16	n/d	0.045
8K	7.50	163	0.165	2.10	0.20	0.06	0.30	1.92	0.009	0.009	n/d	n/d
Mean	7.03	244	0.079	3.05	0.49	0.08	0.41	2.94	0.010	0.040	0.004	0.021

Note. P − Purovsk region, K − Krasnosel'kup region; n/d − ion content is below detection limit.

Krasnosel'kup; 8K – artesian well, Krasnosel'kup. Averaged data for different water bodies in summer and in winter represent the ion composition of a «mean» water body.

In summer, total salt content and pH of river and lake waters are much lower than those in the end of winter. This depicts the enhancement of the role of processes going in a water body, that involve leaching of the bed rocks after the freezing-over period, in comparison with the open-water period, when a more important role is played by the surface drainage of atmospheric precipitation. If we compare ion composition of snow-melted water (see Table 7) with that of surface water (see Table 8) in summer, we can conclude that the SW of Purovsk region only slightly differ from snow in total salt content. This means that the interaction of snow-melted water with the land surface has only a slight effect on the composition of river and lake waters. These processes play a more important role in water bodies of Krasnosel'kup region, where total salt content of SW is substantially higher than the total salt content of snow. This is likely to be due to landscape geochemical differences of the territories of these region; the contrast of these differences for the territory between the Pur and the Taz was stressed in [27]. Permafrost is characteristic of the territory of Purovsk region, while in the valley of the Taz (Krasnosel'kup region) «warm» lakes occur; they are rarely covered with ice in winter. Under these conditions, the contribution from sub-soil and underground water increases substantially, which is exhibited in an increase of the salt content of SW and a fundamental rearrangement of their chemical composition with respect to snow precipitation.

The fractional distributions of the ions in SW and AP are substantially different from each other. Among the cations of SW, the prevailing role is played by calcium and magnesium; among anions, carbonate and humus alkalinity is predominant. The concentrations of these components of ion composition of SW are much higher in winter than in summer. In river and lake water, concentrations of sulphates, nitrates and chlorides are lower than in snow-melted water. It is important to note that a substantial part of the cations of SW is bound with $\mathrm{Alk_{hum}}$, which is due to the decomposition of organic substances, *i. e.* due to the biotic factors of the formation of river and lake waters. In the case of their lower efficiency, concentrations of cations and total salt content, though low in summer, would be even lower. In addition, $\mathrm{Alk_{hum}}$ makes a contribution into total buffer capacity of SW.

In general, low efficiency of the interaction of snow-melted water with soil and bed rocks in Purovsk region is the reason why mean acidity of river and lake water in summer is close to the acidity of atmospheric precipitation. A nomogram of interconnection between the parameters of ion composition of lake water and pH of atmospheric precipitation, shown in Fig. 1, depicts a generalized form of the direct effect of sulphate concentration on the extent of the acidification of both SW and AP in Norway. In the north of West Siberia, there is no correlation between pH and sulphate concentration in lake water (see Table 8), similarly to snow precipitation (see Table 7). This fact allows us to conclude that the reason of acidification of water bodies in Purovsk region is not an increased emission of acid-forming gases into atmosphere but insufficient efficiency of soil and rock leaching by snow-melted water. This leads to decreased buffer capacity of river and lake water both in summer and in winter.

From the same point of view, the situation in Krasnosel'kup region is more favourable, which is promoted by higher efficiency of the interaction of atmospheric precipitation with soils and ground. Really, mean pH of lake water is more than that in water bodies of Purovsk region by about a unity; it approaches the optimal level 6.8–8.5 [28]. It is believed that at the decrease of pH below this level, features characteristic of ecological and metabolic regress develop in water ecosystem, while at pH < 6.0 the species diversity decreases, and nutrition sequence is distorted [29]. In addition to these negative ecological consequences, acidification of surface water affects water migration and toxicity of the species of some metals; their state in water bodies of West Siberia will be considered in the next section.

CONTENT AND SPECIES OF METALS IN WATER BODIES

The analytical data on the overall content (the sum of dissolved and suspended forms) of some metals for a series of the examined water reservoirs in the north of West Siberia are shown in Table 9. For comparison, the data of [30] for the water of the Ob' (middle part) are shown in the same Table. Comparison shows that metal concentration in the examined water bodies, devoid of intensive anthropogenic load, is higher than in the water of the Ob', accepting the contaminated waste waters from industrial centres. This is the evidence of the increased water migration of metals in SW in the north of West Siberia, insufficient efficiency of their deposition in bottom sediments. As it was stressed above, an additional source of metals in local water bodies can be atmospheric precipitation due to long-range atmospheric transport of AA, in particular from the Noril'sk region.

Regardless of the source of Me entering river and lake systems, the level of metal content in water depends on the transformation of metal speciation under specific physicochemical conditions in water bodies. For example, it is demonstrated in [9] that an occasional increase in the overall Me concentration in water bodies of the Kol'sky Peninsula occurs during spring high water periods at the temporary decrease in pH of water due to the admission of snow-melted water. This is accompanied by the increase in the fractions of the most toxic species of metals, *i. e.* aqua ions Me^{2+}, which the authors believe to be caused not only by acidification but also with low content of the dissolved organic substances.

For water reservoirs investigated in the present work, lowered pH and increased DOM content (indirectly exhibited through Alk_{hum}) are characteristic not only during the spring flood but also in winter and summer samples (see Table 8). Water bodies of Purovsk region of the YaNAO are especially unfavourable in this respect.

We performed chemical and thermodynamic modeling of the state of a series of toxic metals in solution in the investigated water bodies of the north of West Siberia and in the Ob' Sea using the WATEQ-4f software [31]. To take into account the formation of complexes with inorganic ligands, we used the data on the ion composition of water of a specific water body. Metal binding with DOM into MeL forms was taken into account in the integral form, by experimentally determining the binding parameters (a conventional constant K_{MeL}

TABLE 9

Total content of toxic metals in water bodies of Purovsk and Krasnosel'kup regions, μg/l

Sample, time	Hg	Cd	Cu	Pb
1P, winter	0.58	0.18	10.6	3.9
2P, winter	0.35	0.57	23.8	5.4
3P, winter	0.45	0.15	8.0	2.4
3P, summer	0.35	0.03	3.5	3.2
5P, winter	0.47	0.08	3.8	2.1
6P, winter	1.56	0.10	9.2	2.1
6P, summer	0.16	0.04	3.7	2.8
8P, summer	0.10	0.73	1.8	13.3
9P, summer	0.24	0.07	5.0	5.6
12P, summer	0.12	0.06	3.7	2.8
3K, winter	0.42	0.18	6.0	3.0
4K, winter	0.32	0.10	3.1	2.7
5K, winter	0.21	< 0.10	3.8	2.7
6K, winter	0.29	0.10	4.0	15.3
7K, winter	0.20	< 0.10	1.9	2.1
8K, winter	0.092	1.7	4.2	3.8
Middle Ob' [30]	0.02	0.24	2.3	0.8

TABLE 10

Content of the main forms of copper, lead, and cadmium in water of water bodies A, B, and C, %

Form	Copper			Lead			Cadmium		
	A	B	C	A	B	C	A	B	C
Me^{2+}	72.3	1.2	0.9	61.7	8.4	1.4	83.4	15.4	52.3
$MeOH^+$	<0.01	<0.01	1.3	<0.01	<0.01	1.5	<0.01	<0.01	4.8
$Me(OH)_2^0$	<0.01	0.25	26.0	<0.01	<0.01	0.7	<0.01	<0.01	0.01
$MeCO_3^0$	0.03	0.14	29.0	0.01	3.0	79.8	<0.01	0.08	7.0
MeL	26.5	98.2	42.8	36.8	87.2	16.5	16.1	84.3	36.0

and concentration of binding centres L) using the procedure described in [32]. The results of modeling show that in water reservoirs with low salt content in the north of West Siberia, the distribution of species of such metals as copper, lead, cadmium, in solution is quite different from that in the typical fresh-water reservoirs in the south of West Siberia [33]. As an illustration, Table 10 compares the results of the calculation of fractional distribution of the main forms of these metals in water reservoirs A and B of Purovsk and Krasnosel'kup regions of the YaNAO (for which the data on ion composition and metal content are shown in Tables 8 and 9, samples 12P and 1K, respectively), with the data obtained by calculations for the water of the Ob' Sea (water reservoir C).

One can see that the fraction of the most ecologically dangerous metal species (aqua ions Me^{2+}) is high in A reservoir. This fact deserves rapt attention, since the existing MPC standards (both for drinking water and for fishery water reservoirs) do not take into account the distribution of chemical forms of metals under natural conditions. For instance, total concentration of copper in reservoirs A, B and C (3.7, 1.3, and 2.3 μg/l) exceeds the MPC (1 μg/l for fishery water reservoirs) only slightly. However, at the Cu^{2+} fraction being 72.3, 1.2 and 0.9 % (see Table 10), the concentrations of this form are $4\ 10^{-8}$, $2\ 10^{-10}$ and $3\ 10^{-10}$ g-ion/l, respectively. The first value is two orders as much as the Cu^{2+} level causing oppression of plankton organisms (10^{-10}–10^{-12} g-ion/l [34]), while the situation in water reservoirs B and C is not so dramatic.

Depending on pH, salt content and DOM concentration, the distribution of metal forms is individual for each water reservoir. However, for the major part of the investigated water reservoirs of the Purovsk region, high fraction of aqua ions of metals is characteristic both in summer and in winter, because of low pH and *W*. Taking into account the fact that the overall concentration of a metal in water exceeds that in the sample 12P, one can see that the extent of ecological trouble is even higher in such water bodies. In water reservoirs of Krasnosel'kup region, as a rule, pH and *W* are much higher, which determines more favourable situation with the effects of their secondary contamination with metals.

CONCLUSIONS

A complex investigation of the ion composition of AA, AP and SW, performed within the integrative project "Aerosol of Siberia" for the vast territory of West Siberia, is the evidence of the regional features of their formation, in comparison with the regions of North America, Scandinavia, northern part of the European Russia, where the acid precipitation occurs causing negative consequences, in particular for water reservoirs.

Natural factors promoting this phenomenon include long winter with the snow isolation of land sources of the formation of atmospheric components, snow regime of feeding local water bodies, insignificant role of the interaction of snow-melted water with rocks at the drainage territories and in water bodies themselves. The most unfavourable situation is observed in Purovsk region of the YaNAO, where pH of water in some lakes reaches 5 or even lower during the whole year. Negative effect of water acidification itself is supplemented by the effects of secondary contamination with metals, because of the increase of the fraction of most mobile and toxic species of metals in solution (aqua ions). Better developed processes of the interaction of snow-melting water with ground and soil in the neighboring Krasnosel'kup region decrease the level of acidification, as well as the fraction of toxic metal species. In the south of West Siberia, natural climatic conditions help insignificant acidification of atmospheric precipitation and larger buffer capacity of water reservoirs, which diminishes the danger of the acid rain problem.

The major result of the present work, limited in periods and sites of natural observations, is the statement of the fact of acid deposition and its reason in the north of West Siberia. Some specific features of the manifestation of this problem in comparison with other regions must be mentioned. First, an increased acidity of atmospheric components is observed in sites where total concentration of aerosol particles and water-soluble salts in them is minimal. The interconnection between pH of atmospheric precipitation and sulphate content in them, observed in other regions, is not observed in the north of West Siberia.

A complex character of the problem of acid deposition requires a more detailed investigation. In particular, it is necessary to perform a retrospective analysis of metal content of bottom sediments, and populations of water organisms, in order to estimate the dynamics of the changes of pH of surface water. It is likely that the necessity exists to organize a natural ground to monitor the state of environment in this region. At the same time, it is necessary to investigate the efficiency of operations and technologies of lake water alkalization that are used in some countries to eliminate negative consequences of acid deposition.

Acknowledgements

The investigation has been supported by the Presidium of SB RAS (Integration Projects No. 64–00, 69–00), and the RFBR (Grant 01–05–64761).

REFERENCES

1 C. J. Brandt (Ed.), Acidic Precipitations, Formation and Impact on Terrestrial Ecosystems, VDI-Kommission, Düsseldorf, 1987.

2 Yu. A. Israel, N. M. Nazarov, A. Ya. Pressman *et al.*, Kislotnye dozhdi, Gidrometeoizdat, Leningrad, 1989.

3 Acid Deposition. Long-Term Trends, Washington, 1986.

4 G. E. Zaykov, S. A. Maslov, V. L. Rubaylo, Kislotnye dozhdi i okruzhayushchaya sreda, Khimiya, Moscow, 1991.

5 P. Brimblecomber, Air/ Composition & Chemistry, Cambrige University Press, 1986, 1986, 352 p.

6 T. I. Moiseenko, L. P. Kudryavsteva, S. S. Sandimirov, *Vodnye resursy*, 27 (2000) 91.

7 T. I. Moiseenko, L. P. Kudryavtseva, I. V. Rodushkin *et al.*, *Sci. Total Environ.*, 160/161 (1995) 715.

8 T. I. Moiseenko, A. N. Sharov, O. I. Vandysh *et al.*, *Vodnye resursy*, 26 (1999) 492.

9 T. I. Moiseenko, *Ibid.*, 25 (1998) 16.

10 T. I. Moiseenko, V. A. Dauvalter, N. V. Rodyushkin, *Ibid.*, 25 (1998) 231.

11 R. J. Charlson, H. Rodhe, *Nature,* 295, 5851 (1982) 683.

12 A. Henricsen, Proc. Intern. Conf. Impact Acid Precip. SNSF Project, Norway, 1980, pp. 68–74.

13 J. W. Moore, S. Ramamoorthy, Heavi Metals in Natural Waters, Applied Monitoring and Impact Assessment, New York, 1984.

14 F. M. M. Morel, Principles of Aquatic Chemistry, Wiley Intersci., New York, 1983.

15 B. S. Smolyakov, L. A. Pavlyuk, K. P. Koutsenogii *et al.*, *Chemistry for Sustainable Development*, 5 (1997) 193.

16 O. A. Alekin, A. D. Semenov, B. A. Skopintsev, Rukovodstvo po khimicheskomu analizu vod sushi, Gidrometeoizdat, Leningrad, 1973.

17 H. Sievering, *Atmos. Environ.,* 21, 12 (1987) 2525.

18 B. S. Smolyakov, K. P. Koutsenogii, L. A. Pavlyuk *et al., Optika atmosfery i okeana*, 14 (2001) 572.

19 K. P. Koutsenogii, A. I. Smirnova, B. S. Smolyakov, T. V. Churkina, Tez. dokl. konf. "Nauchnye aspekty ekologicheskikh problem Rossii", Moscow, 2000.

20 B. S. Smolyakov, L. A. Pavlyuk, A. M. Nemirovsky *et al.*, *Optika atmosfery i okeana*, 9 (1996)773.

21 M. A. Glazovskaya, Geokhimiya prirodnykh landshaftov SSSR, Vysshaya shkola, Moscow, 1988.

22 L. A. Barrie, *Atmos. Environ.,* 15 (1981).

23 V. F. Raputa, B. S. Smolyakov, K. P. Koutsenogii, *Sib. ekol. zhurn.*, 7 (2000) 103.

24 V. A. Kazantsev, Problemy pedogalogeneza, Nauka, Novosibirsk, 1998.

25 M. V. Chaikina, Gidrokgimicheskiy rezhim Novosibirskogo vodokhranilishcha, Nauka, Novosibirsk, 1975.

26 B. S. Smolyakov, L. A. Pavlyuk, A. M. Nemirovsky, *Chemistry for Sustainable Development*, 2 (1994) 493.

27 L. K. Karpov, E. P. Sorokina, N. K. Dmitrieva, N. L. Karpova, in: Geokhimiya biosfery, Tr. 2 Mezhdunar. soveshch., Novorossiysk, 1999, pp. 71–73.

28 E. D. Igolkina, in: Problemy ekologicheskogo monitiringa i modelirovaniya ekosistem, vol. XV, Gidrometeoizdat, St. Petersburg, 1993, pp. 108–121.

29 M. S. Galina, *Ibid.*, pp. 88–95.

30 S. S. Shvartsev, O. G. Savichev, *Vodnye resursy*, 24 (1997) 762.

31 J. W. Ball and D. K. Nordstrom, User's Manual for WATEQ4F, U. S. Geological Survey, Menlo Park, California, 1992.

32 L. Ruzic, *Anal. Chem. Acta,* 140 (1982) 99.

33 B. S. Smolyakov, V. I. Belevantsev, A. P. Ryzhikh *et al.*, *Khimiya v interesakh ustoychivogo razvitiya*, 7 (1999) 575.

34 L. Sigg, A. Kuhn, H. Xue *et al.*, in Ch. P. Huang, Ch. R. O'Melia, J. J. Morgan (Eds.), Aquatic Chemistry, Amer. Chem. Soc., Washington, DC, 1995, pp. 177–194.