ACIDITY AND ION COMPOSITION OF ATMOSPHERIC PRECIPITATION AND AEROSOL IN NOVOSIBIRSK REGION

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Experimental data on the ion composition of 97 samples of rain and snow and 73 aerosol samples for two sites in Novosibirsk region in 1994−1995 are presented. The mean pH *value of wet precipitation proved to be close to the calculated one* (5.6) *for the equilibrium of distilled water with the atmospheric* CO_2. *The fractions of different ions in aerosol and wet precipitation are discussed. It was proposed that the atmospheric transport of mineral salts from other regions plays an appreciable role for the region under study.*

INTRODUCTION

Monitoring of the ion composition of atmospheric precipitation and aerosols is now being widely developed in a number of regions all over the world in connection with the problem of acid rains. Generalization of the data of routine observations at the network of stations, located in the background rural and industrial urban zones, has revealed a number of regularities in the spatial and temporal dynamics of the concentration of separate ions, whose proportion regulates the acidity of atmospheric precipitation.[1−3] In particular, the role of natural and technogenic sources of solid and gaseous substances in the atmosphere was revealed, as well as the characteristics of main processes of their transformation and washing out with precipitation. On this basis, the models of the matter exchange in the atmosphere−surface system are being developed taking into account factors of global, regional, and local scales.

Thus, the rain acidity closely relates to a wide circle of problems on formation, transformation, and transport of atmospheric constituents and their effect upon the state of terrestrial and water ecosystems.

The organization of a network to monitor the atmospheric composition throughout the vast territory of Siberia playing an important role in the global processes cannot be put into being in the near future. At the same time, the peculiar features of the region (geographic and climatic ones, local displacement of industrial urban zones) distinguish it from the regions for which large bulk of sufficiently detailed information is accumulated about the dynamics of atmospheric constituents.

The Program of the Complex Project "Siberian Aerosols,"[4] aimed at a comprehensive study of the regularities in the process of formation, transport, and action of atmospheric constituents in Siberian region at global, regional, and local levels, includes the organization of monitoring of the ion composition at different sites: background and situated near industrial centers. Earlier we have investigated the ion composition of aerosols at different sites of Novosibirsk region.[5] This paper presents the results of simultaneous observations of the composition of aerosols and precipitation that have been made in summer and winter periods of 1994−1995.

TECHNIQUE OF OBSERVATIONS

As a background site (No. 1), we have chosen the forested area ashore the Novosibirskoe reservoir 80 km to south-south-west from Novosibirsk. Point No. 2 was situated near Akademgorodok 30 km to south-south-east from Novosibirsk (approximately 54°N and 84°E). Fresh precipitation was sampled into polyethylene ware and analyzed for ions of ammonium, sodium, potassium, calcium, magnesium, fluoride, chloride, nitrate, and sulfate using the methods of ionometry (NH_4^+, Na^+, K^+, F^-, and NO_3^-), ionic chromatography (F^-, Cl^-, NO_3^-, and SO_4^{2-}), and conductimetric titration ($Ca^{2+} + Mg^{2+}$). In addition, these samples were analyzed for pH factor and electric conductivity $\varkappa$. Rain water was analyzed at the observation point as soon as it was sampled, snow was analyzed in the stationary laboratory once the sample was melted. For this purpose an "Anion-210B portable ionometer−conductometer a KhPI portable ionic chromatograph and an ELWFO conductometer 5711 were used.

From the data on pH the equilibrium concentration of H^+ and HCO_3^- ions was calculated; for the samples with pH > 5 the HCO_3 concentration was determined experimentally using the technique from Ref. 6. The calculational data on [HCO_3^-] coincides well (accurate to

10−20% depending on pH) with the experimental ones. So, the conclusion can be drawn that main source of carbonates in precipitation is the atmospheric CO_2 rather that their washing out from solid particles of terrestrial origin.

From the results of the analysis, the difference between the sums of equivalents of anions ΣAn, and cations, ΣCat, was within 15%, while that between measured and calculated values of electric conductivity was 20%. This confirms not only good accuracy of the analysis of ion composition, but also the fact that the fraction of other ions in precipitation is insignificant.

Aerosol was sampled every day onto AFA−KhA filters at the volume rate of air pumping through of 6−13 m^3/h during 10−15 days in every cycle of observations. Filters were weighed before and after the exposition. After exposition a part of the filter was cut out and placed into a container with 5−10 ml of deionized water for a day to obtain the aqueous extract. Anion content in the aqueous extract obtained was determined by the method of ion chromatography, whereas for cations (with previous one-fifth dilution) the methods of ionometry and conductimetric titration were used, similarly to the analysis of atmospheric precipitation. The results of the analysis were then reduced to the aerosol particle content in 1 m^3 of air.

RESULTS AND THEIR DISCUSSION

The dynamics of pH and electric conductivity $\varkappa$, characterizing the total ion content, in the discrete samples of atmospheric precipitation is shown in Fig. 1 (June−September 1994, point No. 1 (a), December 1994−February 1995, point No. 2 (b), June−September 1995, point No. 1 (c)). Horizontal lines are for the mean values for the given period. With pH varying in some samples from 4.5 to 7.4, the mean values for rain (5.53 (a) and 5.25 (c)) and snow (5.76 (b)) precipitation proved to be close to the value (5.6) calculated for the equilibrium of distilled water with the atmospheric CO_2. This allows us to conclude that at the observational sites there are no constant factors (natural and technogenic) causing acidation or alkalization of precipitation in both summer and winter periods.

The mean values of $\varkappa$ (1.78 (a), 3.12 (b), and 1.53 mS·m^{-1} (c)) are much less than those observed for regions with marked manifestation of acid rains (thus, from the data of Ref. 7, in 1994 the average annual $\varkappa$ was 5.26 mS·m^{-1} with pH = 4.22 for the Uhlirska Catchment observation site in the Central Europe), although they are much higher than that for Antarctic snow ($\varkappa$ = 0.15 mS·m^{-1} (Ref. 8)). It is interesting to note that for the Antarctic region the clear relation was revealed between pH and $\varkappa$, which is not evident in Novosibirsk region as follows from the data of 97 samples shown in Fig. 1 No correlation between pH and sulfate and nitrate concentrations that control the acidity of precipitation on the vast areas of the northern hemisphere[1] was found too. One can assume that the excess or deficiency of free H^+ ions (relative to the calculated concentration for the equilibrium between the distilled water and CO_2 in the atmosphere) in our case is due to small disturbance of the balance between ΣAn and ΣCat (without H^+), that is not related to the evident pollution of atmosphere with S and N oxides.

This is confirmed by the comparison of our data on fractions of ion equivalents in precipitation, averaged over month periods of observations with the values we recalculate from the data[7] for average annual ion concentrations (mg/l) for the region with acid rains (Fig. 2). In our observations, the fraction of chlorides every time proved to be higher than in this region, sometimes reaching and even exceeding the total contribution from sulfates and nitrates. And the sodium fraction in the composition of cations is markedly higher (especially for winter period, when the fraction of ammonium, calcium, and magnesium becomes lower). The fraction of free H^+ ions, compensating the difference between ΣAn and ΣCat in our observations cannot be directly associated with the excess of sulfate as is clearly seen for the data of Ref. 7, or some other anion.

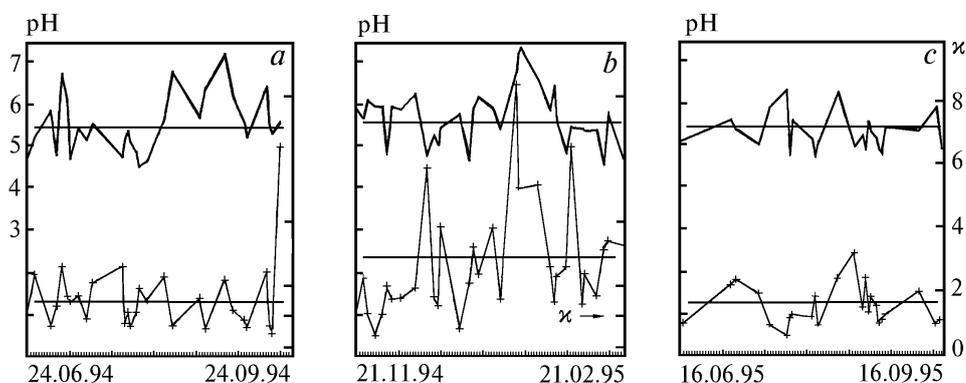FIG. 1. Dynamics of pH and electric conductivity $\varkappa$ (ms/m) in samples of rain (a, c, point No. 1) and snow (b, point No. 2) precipitation in 1994−1995.
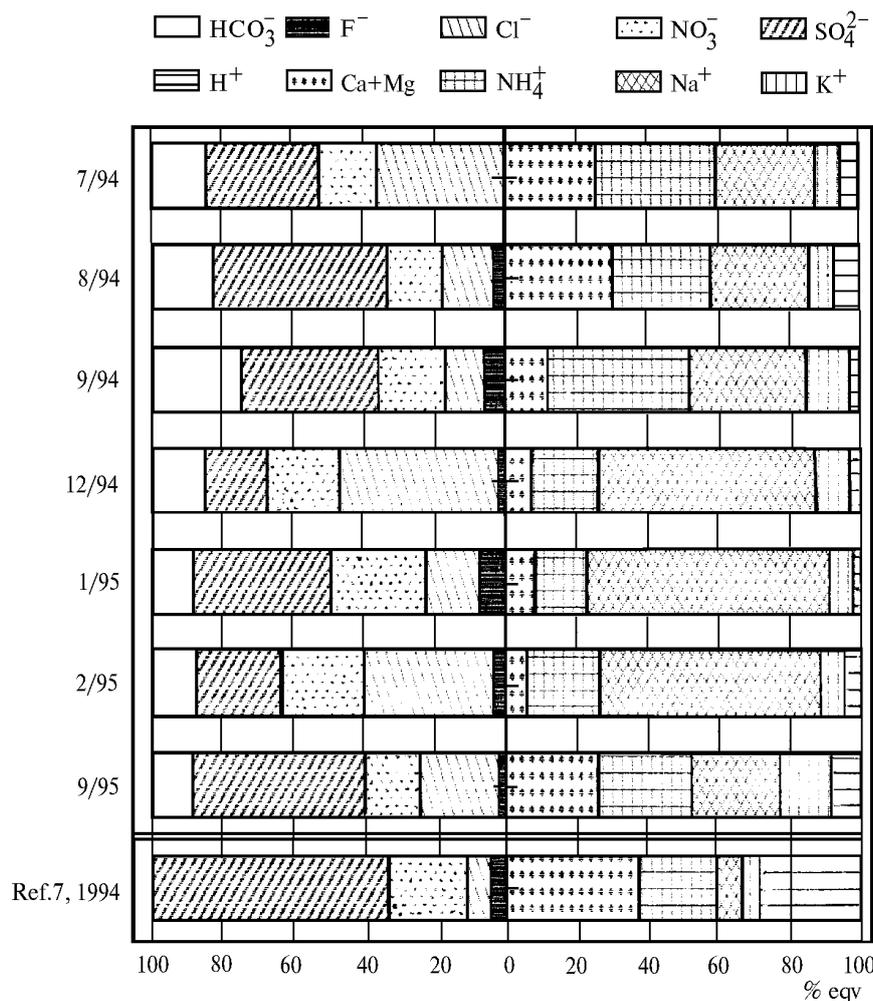
FIG. 2. *Fractional distribution of ion equivalents in wet precipitation in Novosibirsk region (our data) in comparison with the data[7] for the Central Europe region.*

TABLE I. *Ion composition of the aqueous extraction of aerosols sampled at point No. 1 (numerator in $\mu g/m^3$, denominator in per cent of equivalents).*

Period	F^-	Cl^-	NO_3^-	SO_4^{2-}	ΣAn	NH_4^+	$Ca^{2+}+Mg^{2+}$	Na^+	K^+	ΣCat	Σ_{total}	% of aerosol mass
24.06–13.07.95	$\dfrac{0.029}{2.4}$	$\dfrac{0.19}{7.6}$	$\dfrac{1.08}{16.8}$	$\dfrac{3.07}{73.1}$	$\dfrac{4.37}{100}$	$\dfrac{0.049}{1.9}$	$\dfrac{1.06}{44.4}$	$\dfrac{1.43}{45.4}$	$\dfrac{0.45}{8.4}$	$\dfrac{2.99}{100}$	$\dfrac{7.36}{-}$	14.2
21.08–07.09.95	$\dfrac{0.017}{3.0}$	$\dfrac{0.06}{4.7}$	$\dfrac{0.44}{16.2}$	$\dfrac{1.51}{76.2}$	$\dfrac{2.03}{100}$	$\dfrac{0.15}{12.0}$	$\dfrac{0.44}{35.7}$	$\dfrac{0.80}{48.9}$	$\dfrac{0.09}{3.3}$	$\dfrac{1.48}{100}$	$\dfrac{3.51}{-}$	9.1

Quite different situation is typical for the fractions of anions in aerosol particles. As is seen from the data shown in Fig. 3, regardless of season, sulfate dominates in the aerosol composition, even for the period of observations, when its fraction in wet precipitation was lower than the contribution given by chlorides or nitrates. In Ref. 5 we have shown that significant part of sulfates is in particles less that 3 μm in size, whereas the main part of nitrates, chlorides, and fluorides is in larger particles. This distribution of ions in aerosol was

also noticed in Ref. 1. Since different-size particles have different lifetime, different-scale atmospheric processes, for example, distant transport, have different effect upon the formation of ion composition of aerosols.

The table presents data on ion composition of aerosols at point No. 1 at the beginning and the end of the summer season of 1995 along with the fraction of water-soluble salts in the net aerosol mass on a filter. The lower aerosol content in air by the end of summer

period is apparently due to the washing out effect of rains, in this case the fraction of water-soluble part in the total mass of aerosol particles is also somewhat lower.
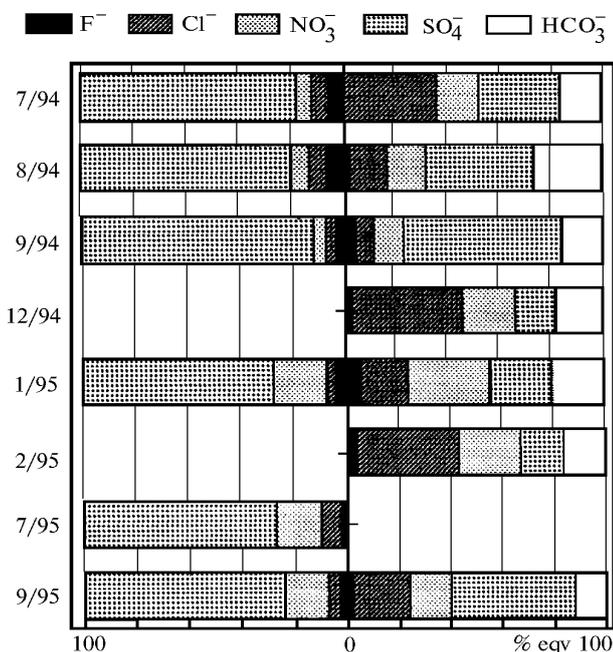

FIG. 3. Fractional distribution of anions in aerosols (to the left) and wet precipitation (to the right) for different periods of observations.

Low fraction of ammonium in the composition of cations, among which the main contribution comes from sodium, calcium, and magnesium, with the dominating contribution from sulfates into the composition of anions engages our attention. It is not characteristic of continental aerosols, the main mass of whose water-soluble part is given by the ammonium sulfate as well as for oceanic aerosols with the high content of sodium chloride.[8] Obviously, the fact that in our observations the water-soluble part mainly contains sodium, calcium, and magnesium sulfates is indicative of the presence of a specific source from which these salts come into the atmosphere. It should be noted that in the composition of cations the contribution of sodium, calcium, and magnesium is also high, and in winter the dominating contribution comes from sodium (Fig. 2).

Probably these regularities can be connected with the effect of a great amount of salts coming into the atmosphere from the solonchak zones of Kulunda and Prikaspii, including the intense dispersal of Na_2SO_4 thenardite, whose flow is estimated as 4–7 thousand ton/(km^2 year) (Ref. 9). When the earth's surface is isolated by snow cover at the points of our observations (December–March), the local inflow of lithophile elements (sodium, calcium, magnesium, potassium) due to erosion processes drops sharply that must result in a decrease of their content in aerosols and precipitation. The observed increase of general mineralization and, especially, sodium concentration in snow, as well as its

high fraction in summer aerosols, is indicative, in our opinion, of a significant role of mineral salts transport with atmospheric flows from regions to south–west from the sites of observations in Novosibirsk region.

CONCLUSION

Analysis of the ion composition of aerosols, rain and snow precipitation for two observation points in Novosibirsk region in 1994–1995 allows us to conclude that in this region the conditions still exist that do not result in the enhanced atmospheric pollution. The mean acidity of precipitation is close to the background one, and their total mineralization is significantly lower than in regions with clear manifestation of acid rains. From the ion fraction composition the conclusion can be drawn about a marked contribution of the processes of natural rather than technogenic origin, and the atmospheric transport of mineral salts from other regions probably plays an appreciable role. Certainly, these conclusions do not apply to the local effects from industrial urban zones, whose influence could be estimated in the future with regard to the data we obtained for relatively clear sites of Novosibirsk region.

ACKNOWLEDGMENT

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