Actual and permissible acidity levels on the Asian part of Russia

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The actual and permissible acidity levels on the territory of the Asian part of Russia are evaluated. The critical acidity load was chosen as a measure of stability. To show the actual amounts of precipitation affecting the acidity balance in soil, sea-salt correction was applied. Such main calculated characteristics as precipitation of acid and base compounds, total acidity load, and critical acidity loads are mapped. It is shown that the critical acidity loads on the territory of the Asian part of Russia vary from 0 to 7 kEq·ha $^{-1}$ ·yr $^{-1}$.

Problem of acid precipitation and concept of the critical loads

The problem of acid rains is one of the most important in the contemporary Earth's science, since, in spite of the measures taken to decrease the atmospheric emissions of acidic pollutants, the scales of atmospheric acidification are still being enhanced.

It is well known that acidification cannot be evaluated only from the content of hydrogen ions. At the same time, simply the increase of the proton load on the system, as a whole, or the increase of the hydrogen ion concentration in that or other its component does not cause manifestation of adverse effects associated with the acidification. When dealing with complex natural objects capable of actively resisting changes in the environment, one should use quantitative characteristics of "capability to neutralize" expressed in the units of the amount of a substance to the time of action. As a quantitative measure of stability of ecosystems to acidification, we use here the critical acidity load, i.e., the maximum amount of acid precipitation not causing, for a long time, chemical changes accompanying by adverse effect on the ecosystem.1

Materials and methods Critical loads

As applied to our case, the critical acidity load CL(Ac) means the amount of acid (acid precipitation), which should be added to the system for the ratio of the summed concentration of physiologically active cations $(Ca^{2+} + Mg^{2+} + K^+)$ to the concentration of aluminum not bound by organic acids $(Al^{3+}, AlOH^{2+}, Al(OH)_2^+)$ in the soil solution to be equal to unity. At lower values, as was evidenced for many times, the absorption of the main elements of mineral nutrition by plants decreases and, correspondingly, the environmental

resistance of plants is affected.² The values of the critical loads were computed using the PROFILE biogeochemical model.³ As the input data, we used the parameters of biological circulation, as well as the parameters of physical and chemical state of soils and the atmosphere.

Atmospheric precipitation

The majority of qualitative and quantitative data on the composition of atmospheric precipitation have been borrowed from Refs. 4–9. The data on the Baikal Region have been obtained by scientists from the Laboratory of Hydrochemistry and Atmospheric Chemistry at the Limnological Institute, SB RAS.

It is well-known that snow is the most informative accumulator of substances coming into the ecosystem from the atmosphere. In contrast to liquid precipitation, snow not only removes solid pollutants from the atmosphere more efficiently, but also accumulates large amounts of dust due to gravitational sedimentation. About 5–20% of dust accumulated in snow is dissolved at snow thawing 10 and enriches snow water with alkaline and alkaline-earth elements. The chemical composition of snow also reflects partially the interaction between precipitation (snow) and crowns of trees. Taking into account the above-said, we calculated the arrival of substances from the atmosphere at the ecosystem from the data on the chemical composition of snow water and some climatic data.

It is also well-known that the World Ocean generally affects the chemical composition of atmospheric precipitation. Analyses of the chemical composition of precipitation in nival zones, on Antarctic glaciers, near the top of the troposphere, i.e., at places that are far from the water surface, gave similar results. The composition is mostly chlorine-sodium-magnesium, close to the composition of seawater. Salts of marine origin, the so-called cyclic salts, are neutral, i.e., cations of alkaline and alkaline-earth metals in them are

compensated for by anions of strong acids, and the acidity associated with them equals zero. 11 To exclude sea salts from the acidity balance, it is accepted that all sodium of atmospheric precipitation is of marine origin. According to this, an attempt was undertaken to subtract the "marine" fraction from the deposition of every element. The marine fraction was calculated from the ratio of the corresponding element to sodium in seawater by the following equation:

$$X_{\text{dep}}^* = X_{\text{dep}} - Na_{\text{dep}} (X_{\text{sw}}/Na_{\text{sw}}), \tag{1}$$

where X is S, Cl, Ca, Mg, and K; X_{dep} , Na_{dep} are depositions of the corresponding elements (components); $X_{\rm dep}^*$ are depositions of the elements after sea-salt correction; $X_{\rm sw}/{\rm Na_{\rm sw}}$ is the content ratio of the corresponding element to sodium in seawater (eq./eq.): S = 0.12, Ca = 0.044, Mg = 0.227, K = 0.021, and Cl = 1.164.

Ammonium and nitrates have no marine origin and therefore they are not subjected to correction. The sea-salt correction of depositions makes sense only in the regions, where the sole source of sodium in the atmosphere is the World Ocean. In the regions, where sources of anthropogenic or continental sodium (salt lakes, salt marches, etc.) are present instead of the oceanic source, sea-salt correction leads to underestimation of the inflow of all (expect for nitrogen) components of the atmospheric deposition 11 and distorts the pattern of the actual acid neutralizing capacity (ANC).

The Table presents the comparative data on the relation between the acid and base components of atmospheric deposition with the allowance made for their actual and corrected values: BC are the base components of the atmospheric deposition (Ca^{2+} + $+ Mg^{2+} + K^{+} + Na^{+}$); Bc are the physiologically active cations ($Ca^{2+} + Mg^{2+} + K^+$); Ac are the acid components except for nitrates; <u>ANC</u> is the acid neutralizing capacity of deposition = Bc - Ac neglecting ammonium and nitrates; ANC is the total value of the acid neutralizing capacity.

In the regions, where sodium is of marine origin only, the values of the acid neutralizing capacity remain unchanged. In addition to estimation of depositions actually influencing the acid-base balance in the land

ecosystems, this procedure allows identification of the regions with land (natural and anthropogenic) sources of sodium.

When calculating the acid depositions, we took into account ammonium along with the traditional acidifying sulfates, chlorides, and nitrates.

Although the ammonium ion is cation and in the acidity balance of deposition it is considered as a base, in this paper ammonium is considered as a potential source of acidity, since, falling in soil, it is completely nitrified, producing one hydrogen proton to every ion. Thus, the value of the current acidity load can be written in the form

$$Ac(pot)_{dep} = SO_{x dep}^* + NO_{y dep} + NH_{4 dep} - BC_{dep}^* + Cl_{dep}^*$$
, (2)

where $\text{Ac(pot)}_{\text{dep}}$ is the current acidity load, and the asterisk denotes the corrected values.

Spatial distribution of the components of atmospheric deposition

To estimate the current acidity load, we have mapped the main parameters used for its calculation: base and acid components of atmospheric depositions.

Base components

The obtained pattern of the spatial distribution of atmospheric depositions of physiologically active cations (Fig. 1) suggests that there exists atmospheric transport of aeolian particles from the regions subject to wind erosion: farmlands of the European territory, steppe and forest-steppe zones of the European and Asian territories, deserts and semi-deserts of Central Asia. The total influx of physiologically active cations varies from 0.05 to $1.30 \text{ kEq}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$. The maximum depositions were observed within the southern taiga and forest-steppe zones of the Western Siberia, whereas the minimal depositions were typical all over the tundra zone, except for the territory near the Northern Ural. At the territory to the east from the Central Siberian Plateau, the low values of depositions of physiologically active cations "go down" to the southern taiga zone.

Table. Comparison of actual and sea-salt corrected values of the acid-base balance of atmospheric deposition, in kEq·ha⁻¹·yr⁻¹

Region	Actual values				Corrected values			
	BC-Na	Ac	ANC	ANC	Вс	Ac	<u>ANC</u>	ANC
Without distortions								
Yakutsk	0.14-0.03	0.09	0.05	0.04	0.10	0.05	0.05	0.04
Mondy	0.24 - 0.02	0.78	-0.54	-0.56	0.21	0.75	-0.54	-0.56
Il'chir	0.50 - 0.02	0.20	0.30	0.24	0.47	0.17	0.30	0.24
Baikal Region	0.47 - 0.03	0.24	0.23	0.15	0.43	0.20	0.23	0.15
Golovnaya	1.08-0.09	0.62	0.56	0.28	0.92	0.36	0.56	0.28
With distortions								
Mirnyi	0.36-0.31	0.30	0.06	-0.03	0.017	0.15	-0.13	-0.22
Neryungri	0.49 - 0.26	0.10	0.39	0.35	0.16	0.00	0.16	0.12
Yamal	0.98 - 0.84	0.73	0.25	0.21	0.03	0.00	0.03	-0.01
Far East	1.31-0.55	0.49	0.82	0.62	0.60	0.25	0.35	0.15

Fig. 1. Atmospheric depositions of the base components (BC) at the territory of the Asian part of Russia, in kEq·ha⁻¹·yr⁻¹.

It is worth noting that the deposition isoline goes along the line of the Trans-Siberian Railway. In our opinion, this fact is connected not only with the so-called "western transport," but also with the human activity, which is most intense along the Trans-Siberian Railway. Thus, local transport on this territory may play a significant role (besides the tropospheric one).

Acid components

The spatial regularities in the distribution of deposition of acid components of atmospheric precipitation are close to those of the physiologically active cations (Fig. 2).

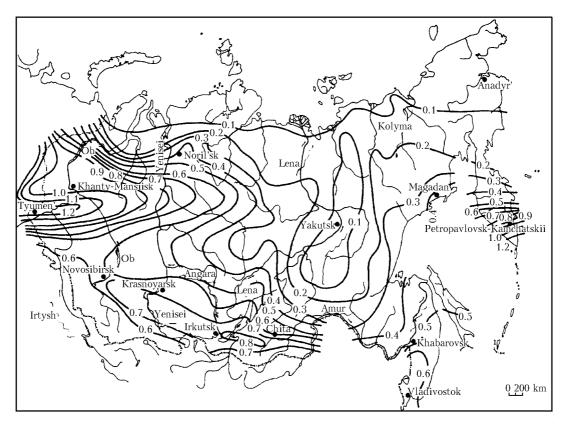
The main differences are localization of the high-concentration depositions and the gradient of the spatial distribution of the depositions. The clear localization of cations and the small spread area make an evidence of the aeolian origin of cation depositions. The spatial distribution of acid components has no clear reference to certain geographic objects, contours of the zones of high-concentration depositions are blurred, and the zones are far extended in both the latitudinal and meridional directions. As in the case with the physiologically active cations, we associate these peculiarities with the character of the aggregate state (gaseous, in this case) of compounds.

The largest meridional and latitudinal gradients of the spatial distribution of depositions are characteristic of Ural, Western Siberia, and Far East. The highest concentrations of depositions (up to 1.30 kEq·ha⁻¹·yr⁻¹) of acid components are also observed at the territories of Southern and Central Ural, the southern taiga zone of the Western Siberia, and Far East. As in the case with physiologically active cations, the lowest-concentration depositions were noticed in the tundra zone, subzones of northern, and central taiga within Yakutiya, Magadan Region, and Chukotka. These territories are also characterized by the lowest mean gradients of the spatial distribution of depositions.

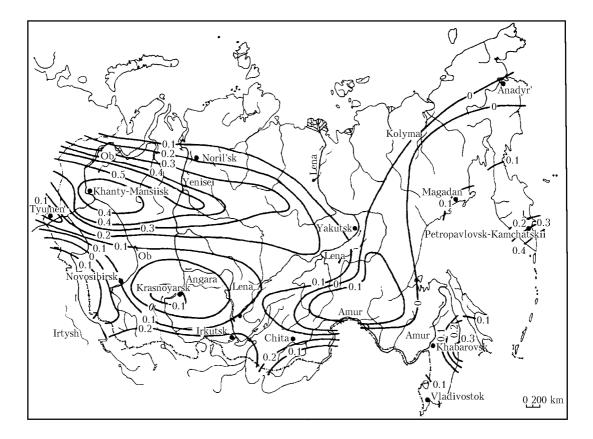
It is worth noting the tendency to lowering of acidifying depositions at the territories of large mountain systems, such as Altai, Western and Eastern Sayan, etc., observed in the direction of transport from periphery to the center. This is likely caused by the following circumstance: airflows carrying the acidifying compounds in the dissolved or gaseous form mostly flow around massifs, and in the flow-around zones the intensity of sedimentation of gaseous components and precipitation of dissolved ones can increase. ¹²

Current acidity load

As was mentioned above, we have made an attempt to exclude sea salts from the acidity balance according to the international sea-salt correction technique. The purpose was to demonstrate the actual amount of substances both acidifying and opposing to the detrimental effects of acidification.



 $\textbf{Fig. 2.} \ \, \textbf{Atmospheric depositions of the acid components (Ac) at the territory of the Asian part of Russia, in $k \text{Eq} \cdot ha^{-1} \cdot yr^{-1}$.}$



 $\textbf{Fig. 3.} \ \, \textbf{Current acidity of atmospheric depositions Ac(pot) at the territory of the Asian part of Russia, in kEq·ha^{-1}\cdot yr^{-1}.$

Fig. 4. Critical acidity loads CL(Ac) on ecosystems of the Asian part of Russia, in kEq·ha⁻¹·yr⁻¹: 0-1 (t), 1-2 (2), 2-3 (3), 3-4 (4), 4-5 (5), 5-6 (6), > 6 (7).

Mapping of the calculated results on the sum atmospheric depositions has shown (Fig. 3) the prevalence of the depositions of strong acid anions and ammonium over physiologically active cations ($Ca^{2+} + Mg^{2+} + K^+$) over vast expanses.

Within the tundra and taiga zones, the current acidity load Ac(pot)_{dep} equals 0.1–0.5 kEq·ha⁻¹·yr⁻¹ and decreases from south to north and from west to east. The largest values of the excess of acid components over the base ones $(0.5 \text{ kEq} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1})$ are observed in the south of the Western Siberia. Then, further to the north toward the polar circle and to the east toward Yakutiya the acidity load decreases down to 0.1 kEq·ha⁻¹·yr⁻¹. This phenomenon can be explained by the higher density of industrial enterprises in the south of the Asian part of Russia. Besides, some acidifying substances (sulfur and nitrogen oxides) are transported from the European part of Russia. A different situation occurs in the foreststeppe zone and the zone of deciduous forests, where the reverse pattern is observed: the base components of atmospheric depositions prevail over the acid ones. The current acidity load Ac(pot)_{dep} takes here negative values down to $-0.5 \text{ kEq} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$.

Spatial distribution of critical loads

Thanks to the wide variety of ecological conditions of Siberia and Far East, the critical acidity load over the territory under study varies from 0 to $7~\rm kEq\cdot ha^{-1}\cdot yr^{-1}$ (Fig. 4).

In general, the critical load increases in the direction from north to south and from east to west, that is, the spatial distribution of critical loads follows, in general, the zonal and facial distribution of soils and vegetation. The excess over critical loads was roughly estimated by the equation

$$Ex = Ac(pot)^* - CL(Ac).$$
 (3)

0 200 km

For the absolute majority of ecosystems occupying more than 90% of the area of tundra and taiga zones in Siberia the excess was negative. This points to the fact that no possibility exists of acidifying, and the accompanying harmful effects on the environment, at the current level of atmospheric depositions. In other words, the permissible "quote" of acid depositions ranges from 0 to 7 kEq·ha $^{-1}$ ·yr $^{-1}$. The values of Ac(pot)* and CL(Ac) are closest to each other in the belts of high and central taiga of the Eastern Sayan and in the Baikal Region.

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