

## Monitoring of Acid Deposition in the Baikal Region

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### Abstract

Data of 3-year-long observations of the chemical composition of precipitation, aerosol, soils and surface waters at three monitoring stations in the Baikal region are presented. The choice of observation objects is substantiated. Problems of "natural objects" resistance to acidification are considered. The resistance of terrestrial ecosystems to acidification has been estimated quantitatively, and that of surface waters has been done so qualitatively. It has been demonstrated that symptoms of acidification are manifested most strongly in regions lee with respect to regional industrial centers at a distance of several tens and hundreds kilometers from them. The permissible acidity load for the soils of the territory under consideration varies from 1.25 to 1.4 keq / (ha yr), while the maximal modern acidity load attains only 0.4 keq / (ha yr).

### INTRODUCTION

The problem of acid deposition is well known as one of global ecological problems. Classical examples thereof are the degradation of small lake ecosystems and the weakening of forests in Scandinavia and Canada brought about by the transfer of anthropogenic sulphur and nitrogen oxides from the Central Europe and the USA, respectively.

Lately, an intense economical development of the South-East Asian countries is taking place, and in this regard the governments and social organizations of the region are justly concerned with the expected increase in transfer of acidifying compounds across state borders and call to organization of an international system of monitoring of acid deposition with the purpose of timely detection of possible negative tendencies in the environment.

The available scanty data [1–4] on the Asian part of Russia, and particularly the south of West Siberia, suggest that the risk of development of acidification process in some especially sensitive areas of ecosystems

does exist, although the situation as a whole is still not critical. In this regard, in 1999–2000 the Limnological Institute, SB RAS, started the studies of this problem within the framework of the international program of monitoring of acid precipitation in East Asia – EANET.

### EXPERIMENTAL

In 1998–1999, three stations were set up for all-year-round monitoring of acid deposition representing different levels of anthropogenic influence:

– the Irkutsk station (52.3° north latitude, 104.4° east longitude) characterizing the acidification processes under urbanized conditions where observations were carried out within the boundaries of the city, in its southern outskirts;

– the Listvyanka station (51.9° N.L., 104.7° E.L.) representing rural territories under the influence of regional pollution sources, situated at the distance of 70 km to the south-east of Irkutsk, *i. e.* leeward with respect to it;

TABLE 1

Parameters measured and observation frequency

Object	Parameters	Observation frequency
Wet deposition	pH, electric conductivity, concentration of $\text{NH}_4^+$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{SO}_4^{2-}$ , $\text{NO}_3^-$ , $\text{Cl}^-$ , $\text{HCO}_3^-$ , $\text{NO}_2^-$ , $\text{F}^-$ , $\text{Br}^-$ , mg/l	Each case of precipitation
Dry deposition	Concentration of $\text{SO}_2$ , $\text{HNO}_3$ , $\text{HCl}$ , $\text{NH}_3$ , mg/m <sup>3</sup> , ionic composition of aerosols, mg/m <sup>3</sup>	Every week (week average)
Soils	$\text{pH}_{\text{H}_2\text{O}}$ , $\text{pH}_{\text{KCl}}$ , content of exchange cations $\text{Na}^+$ , $\text{K}^+$ , $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Al}^{3+}$ , $\text{H}^+$ , cmol(+)/kg, carbonates, %, $\text{C}_{\text{org}}$ , %, $\text{N}_{\text{org}}$ , %	Once in 3 years
Vegetation	Ca, Mg, K, N in assimilation organs, %	Once in 3 years
Surface waters	$t$ , °C, pH, electric conductance, concentration of $\text{NH}_4^+$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{SO}_4^{2-}$ , $\text{NO}_3^-$ , $\text{Cl}^-$ , $\text{HCO}_3^-$ , mg/l	Monthly

– the Mondy station (51.6° N.L., 101.0° E.L.) located in one of the cleanest background regions of the Vostochny Sayan at the altitude of 2000 m above sea level (its distance from the nearest industrial centers and cities is about 200 km).

In the same localities, examination of soils and surface waters was carried out for the purpose of estimating their actual condition and potential sensitivity to acidification. The parameters studied and the frequency of their observation are presented in Table 1.

Samples of surface waters were taken into polyethylene vessels. Sampling of wet deposition was carried out employing an automatic sampler. Calcium and magnesium ions measurement was performed by means of flame atomic absorption spectrometry, that of sodium and potassium ions was made by means of flame emission spectrometry [5]. Sulphate, chloride, nitrate, bicarbonate, fluoride and bromide concentrations were determined by means of ion chromatography (HPLC) [6], ammonium concentration was estimated spectrophotometrically using Nessler reagent [7]. pH was determined potentiometrically, electric conductivity electrochemically.

Dry deposition was sampled employing a four-step impactor (Filter Pack method) using a pump with a pumping rate of 1 liter per minute. In the samples collected on the first filter (PTFE), the ion composition of the water-soluble aerosol fraction was analyzed. The

second filter was subjected to gas-originated anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  only) composition measurement, with subsequent expression in terms of gaseous  $\text{SO}_2$ ,  $\text{HNO}_3$ ,  $\text{HCl}$  [8]. The third and the fourth filters (Filter Paper), before air pumping, were subjected to a special treatment. The third filter was soaked with a mixture of 6 %  $\text{K}_2\text{CO}_3$  solution and 2 % glycerol solution for sorption of sulphur dioxide passed through the second filter. After extracting the filter with 0.3 % hydrogen peroxide solution, the concentration of the formed  $\text{SO}_4^{2-}$  ions was determined. Further on, the sulphate content was expressed in terms of  $\text{SO}_2$  and summarized with that of the second filter. The fourth filter was treated with a mixture of 5 % solution of phosphoric acid and 2 % glycerol solution for absorption of gaseous ammonia. After extracting the filter with twice distilled water, the  $\text{NH}_4^+$  content of the extract was estimated and expressed in terms of  $\text{NH}_3$ . The content of gases was calculated in terms of concentration of respective ions in the aqueous extract [8].

The chemical composition of soils was estimated according to conventional methods [9].

## RESULTS AND DISCUSSION

### Wet deposition

The highest mineralization of precipitation, as could be expected, was observed at the Irkutsk station, the lowest one at the

TABLE 2

Fluxes of wet deposition of main ions onto the underlying surface in 2000, mg/m<sup>2</sup>

Station	Period	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>
Irkutsk	Summer	292	1058	477	119	56	66	327	40	233
	Year	649	1521	676	224	113	92	596	64	301
Listvyanka	Summer	212	551	289	72	32	57	168	23	127
	Year	249	743	454	88	46	89	252	36	143
Mondy	Summer	19	169	96	24	10	10	42	7	39
	Year	120	239	131	37	15	17	80	12	64

background Mondy station. The amount of wet deposition onto the underlying surface corresponded to mineralization of the precipitation (Table 2).

As one can see in Table 2, the major part of the annual sum of wet deposition of ions falls on summer, that corresponds to the annual distribution of atmospheric precipitation in the region, 70 to 90 % of which fall out as rains during the warm period of the year.

The reiteration of low pH values of deposition at the three monitoring stations is not equal (Fig. 1). Most frequently, acidification of deposition occurs at the rural Listvyanka station which is situated at 70 km from Irkutsk in the direction of prevalence of north-western winds (*i. e.* leeward of the main anthropogenous sources of the region). This is consistent with some theoretical estimates [10] according to which the maximal transformation of SO<sub>2</sub> into H<sub>2</sub>SO<sub>4</sub> takes place at a distance of 100–600 km from the SO<sub>2</sub> source in the air transfer direction.

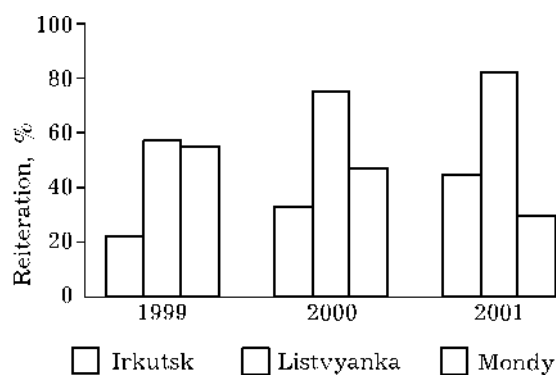


Fig. 1. Reiteration of deposition with pH < 5.6 at the three monitoring stations.

### Dry deposition

In Table 3, the mean concentration of the main ions of the soluble aerosol fraction and of the main acidifying gases in the air at the three monitoring station is presented.

For calculation of dry deposition of acidifying substances, it is necessary to know the rate of their precipitation. In the future, it is planned to carry out a special study of the rate of dry ion precipitation at each observation point, and for the time being, for preliminary estimation one may use the known mean precipitation rates which are often used, *e. g.*, in mathematical models [11]. These estimates are presented in Fig. 2 in comparison with wet deposition (see Table 2).

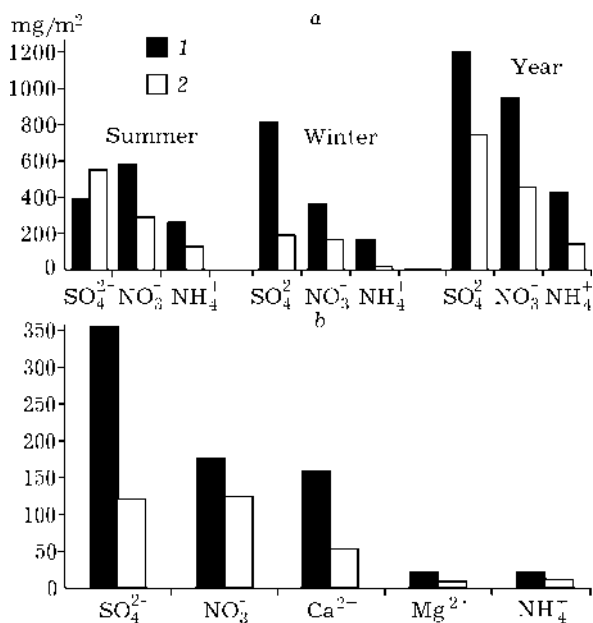


Fig. 2. Seasonal correlation acidifying (a) and annual correlation between prevalent (b) ions in dry (1) and wet (2) deposition at the Listvyanka station in 2000.

TABLE 3

Mean concentrations of the main ions in the aerosol and of some gaseous admixtures in the atmosphere at the three monitoring stations,  $\mu\text{g}/\text{m}^2$

Component	Irkutsk		Listvyanka		Mondy	
	Winter	Summer	Winter	Summer	Winter	Summer
<i>Aerosol</i>						
$\text{HCO}_3^-$	1.4	3.6	1.0	4.1	0.2	0.5
$\text{SO}_4^{2-}$	4.6	0.8	3.1	0.8	0.6	0.4
$\text{NO}_3^-$	1.4	0.5	0.4	0.5	0.03	0.06
$\text{Cl}^-$	0.3	0.1	0.2	0.4	0.02	0.08
$\text{Na}^+$	0.2	0.2	0.1	0.01	0.02	0.07
$\text{K}^+$	0.1	0.8	0.04	0.4	0.05	0.18
$\text{Ca}^{2+}$	1.0	0.7	0.6	0.4	0.13	0.11
$\text{Mg}^{2+}$	0.1	0.1	0.1	0.1	0.02	0.02
$\text{NH}_4^+$	1.6	0.5	0.7	0.9	0.21	0.15
<i>Gases</i>						
$\text{SO}_2$	25.5	0.9	4.3	2.6	0.16	0.3
$\text{NH}_3$	0.5	3.1	0.5	1.2	0.22	0.9

The amount of dry deposition was calculated as the product of concentrations of the components studied by the rate of their precipitation and by the period of time during which the precipitation was recorded. One can see that in summer dry and wet deposition in the region under consideration had values close to each other; however, in the annual flux of ions dry deposition considerably prevailed due to its large contribution during winter.

### Soils

For a long-term observation of chemical properties of soils in the territory controlled by each station (within the radius of 50 km from the deposition sampling point) it was necessary to choose in each territory two plots with soils differing in acidification sensitivity. For this purpose, at the preliminary stage, in the region of the Mondy station two large plots were chosen by the soil map using the data on the bedrocks. At the field stage, 4 plots were set up in a potentially sensitive site (No. 1, 3, 4 and 5) with soils of two types: No. 1 and 5 belonged to Gelic Podzol, No. 3 and 4 to Gelic Gleysol. In a non-

sensitive (control) site, a Galcic Gleysol was chosen (plot 2).

In the region of the Listvyanka station the situation with preliminary choice became difficult because of uniformity of the soil cover; for this reason, the most widespread relief elements were chosen – a hillside (plot No. 6, Mollic Leptosol) and a river valley (plot No. 7, Umbic Leptosol) which soils, having different origin, could presumably differ in acidification resistance. Further on, the plausibility of such a choice was confirmed by field and laboratory studies, wherein it was demonstrated that it was the soil of plot No. 6 that had to be considered as control.

The soil cover at the Irkutsk station is to a considerable degree disturbed as a result of human economic activities, and for this reason the choice was made empirically. As a result, two plots with Eutric Regosol and Calcaric Luvisol were chosen.

In all the soils analyzed, the distribution of exchangeable cations across the profile was of accumulative character (Table 4). For all the horizons, a decrease in exchangeable cations' concentration in the series  $\text{Ca} > \text{Mg} > \text{K} > \text{Na}$  was characteristic, wherein  $\text{Ca}^{2+}$  made up 40–95% of the sum of all cations. The sum of ex-

TABLE 4

Some chemical characteristics of soils

No. of the plot	Horizon	Depth, cm	pH		Exchangeable cations, cmol(+)/kg					C <sub>org</sub> , %	N, %
			H <sub>2</sub> O	KCl*	Ca	Mg	K	Na	Al + H		
1	Ad	3-6	5.05	3.80	15.26	4.09	0.95	0.09	1.74	13.81	3.12
	AB	6-9	5.05	3.50	4.64	0.89	0.17	0.09	8.74	3.63	0.71
	B	9-25	4.92	3.96	1.08	0.44	0.26	0.11	6.21	3.22	0.83
	BC	>25	5.66	4.00	3.19	1.19	0.10	0.09	1.25	1.22	0.52
2	Oca	0-2	7.62	-	89.88	8.42	4.59	-	-	22.85	3.04
	AdT2ca	2-20	7.84	-	139.84	18.86	0.00	-	-	15.93	3.15
	Bgca	20-45	7.34	-	35.02	3.58	0.46	-	-	2.44	0.21
4	Ad	8-18	4.90	3.95	13.52	4.85	0.53	0.07	2.08	7.42	1.22
	B	18-25	6.42	5.07	9.37	1.87	0.18	0.04	0.00	0.83	0.61
	BCg	25-45	6.92	5.91	12.76	1.59	0.20	0.05	0.00	1.41	0.63
5	OAd	1-3	4.42	3.63	12.46	3.23	1.97	0.76	1.58	25.61	2.33
	A	3-7	4.59	3.64	9.02	1.57	0.53	0.16	4.67	18.53	1.91
	B1	7-40	5.69	4.05	1.96	0.32	0.10	0.08	1.81	0.82	0.24
	B2	40-55	5.85	4.42	3.41	0.30	0.07	0.05	0.51	2.32	0.86
	BC	>55	6.06	4.40	2.37	0.16	0.07	0.07	0.45	0.74	0.23
6	AdA1	0-18	6.76	5.85	19.69	3.10	0.25	0.08	0.09	3.16	0.68
	B1	18-28	6.90	5.59	16.76	3.45	0.23	0.08	0.04	1.02	0.36
	B2	28-60	7.03	5.41	18.65	4.60	0.17	0.09	0.05	0.45	0.29
	BC	>60	6.90	5.43	16.89	4.67	0.12	0.07	0.04	0.31	0.20
7	Ad	0-10	4.95	4.03	14.53	4.16	0.72	0.07	0.89	11.52	3.22
	AE	10-14	4.78	3.71	10.09	2.44	0.28	0.06	1.27	8.12	1.15
	EB	14-19	4.71	3.61	3.12	0.97	0.11	0.07	3.83	3.65	0.47
	BC	>19	5.13	3.99	1.39	0.54	0.26	0.15	2.16	0.56	0.15

\*pH of salt suspension.

changeable bases in all the soils is well correlated with the organic carbon content. The largest amount of exchange bases, just as the highest pH value of aqueous suspension, were observed, as it was expected, in the soils of control plots, whereas the lowest one was found in presumably acidifiable ones. The highest exchange acidity was linked with the lowest salt suspension pH values.

Apart from the parameters reflecting the dynamics of soil properties, we estimated also the total element composition of soil. In this regard, it is noteworthy that the soil of profile 2 was characterized by a considerable CaO content (64.08 %), which, in terms of the mineral substance, amounted to 19.35 %, or 34.54 % CaCO<sub>3</sub>. This also confirms the results of acidimetric estimation of carbonates. In the section of plot No. 7, the molecular SiO<sub>2</sub>/R<sub>2</sub>O<sub>3</sub> ratio

becomes lower from horizon AE to horizon EB, which confirms the presence of podsolization process in this soil.

Studies with the help of the biogeochemical model PROFILE [12] have demonstrated that the permissible acidity load for the soils studied varies from 1 to 14 keq/(ha yr). At the same time, according to snow sampling data, the modern acidity load calculated by the formula  $H_{dep}^+ = SO_4^{2-} + NO_x^{y-} + Cl^- + NH_4^+ - Ca^{2+} - Mg^{2+} - K^+ - Na^+$  where deposition of respective components are indicated, is within the limits of -0.10 to 0.40 keq/(ha yr). This permits assuming that the permissible load is not exceeded. We ascribed the ammonium ion to acidic components of precipitation, because, when it gets into the soil, it is completely nitrified, producing one hydrogen proton per ion. The lowest H<sup>+</sup> deposition values were found at

the Irkutsk station, the maximal ones at the Listvyanka station.

### Surface waters

The basic criteria for the choice of water object for estimation of its potential sensitivity to acidification are low alkalinity (up to 0.05 meq/l), electric conductivity of its waters, and such hydrological characteristics as the mean depth (less than 10 m), water surface area (more than 1 ha), and the water residence time (below 1 year). We failed to find any water body having the required alkalinity and water electric conductivity in the region of acid deposition monitoring stations. Lakes which met the hydrological criteria were chosen as observation objects: Lake Il'chir – in the region of the Mondy station, and Lake Ordynskoye – 80 km to the north of Irkutsk. Because of the absence of small lakes near the Listvyanka station, observations were carried out on the Krestovka river, which is permitted by the EANET program.

The water of Lake Il'chir is low mineralized during the period of atmospheric feeding and moderately mineralized in winter when the main feeding source are ground waters. The sum of ions during the year changes from 107 to 260 mg/l, the electric conductivity from 163 to 350 mS/m, the carbonate alkalinity from 1.4 to 2.4 meq/l. By its chemical composition, the water of the lake belongs to hydrocarbonate class (calcium group). The pH value is within the limits of 7.7–8.2.

The water of Lake Ordynskoye is mineralized, the sum of main ions varies throughout the year from 915 to 1025 mg/l, electric conductance from 1328 to 1485 mS/m, carbonate alkalinity from 5.2 to 6.5 meq/l. The prevalent ions are sulphate and magnesium. The location of the lake in the forest-steppe zone and the small amount of precipitation in this region cause insignificant variations of the concentration of the main ions of salt composition throughout the year (5–10 % of the mean annual value). The pH varies from 7.6 to 8.5.

The water of the Krestovka river has a low mineralization and belongs by its chemical composition to hydrocarbonate class (cal-

cium group). The sum of the main ions during the year varies from 32 to 172 mg/l, electric conductance from 6 to 25 mS/m, carbonate alkalinity from 0.2 to 1.5 meq/l, pH from 6.5 to 7.2.

Lake Ordynskoye has the highest alkalinity and electric conductivity, and in Lake Il'chir their values are much lower. The largest supply of atmospheric precipitation to the water bodies occurs during the snow thawing. At this period the pH decreases slightly, its minimal values are recorded in winter when, due to oxidation of the organic substance and the absence of gas exchange with the atmosphere, accumulation of carbon dioxide in the water bodies takes place (Fig. 3)

The insignificant decrease in pH in the water of Lake Il'chir in July–August seems to be linked with the decrease in photosynthetic activity of algae.

The influence of atmospheric precipitation on some hydrochemical parameters is well noticeable on the example of the Krestovka river due to the low alkalinity and electric conductance of its water, as well as to the small volume of its drainage. Minimal pH values are observed not in winter, but at the snow thawing period and after long rains. In the same region, as it was shown above, the precipitation possesses the highest acidity. Nevertheless, the carbonate rocks and the well-drained soils with which the river waters have contact, as well as the subterranean waters which are a constant source of hydrocarbonates hinder the decrease in alkalinity to a critical level at which acidification of water bodies and water flows takes place.

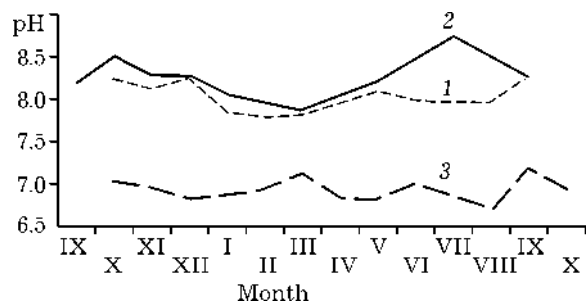


Fig. 3. Seasonal changes of pH value in Lakes Il'chir (1) (1998–1999), Ordynskoye (2) (1999–2000) and the Krestovka river (3) (2000–2001).

## CONCLUSIONS

Observations of the chemical composition of atmospheric precipitation and surface waters demonstrate that the acidification processes are most clearly manifested in regions leeward with respect to regional industrial centers and remote from them at tens or hundreds kilometers. In the region under consideration, such a territory is the southern part of the Lake Baikal hollow. Due to the large amount of atmospheric precipitation (up to 122 mm per year), the hazard of acidification processes is the greatest for the north-west macroslope of the Khamar-Daban ridge (120–140 km from Irkutsk). Even at low concentrations of acidifying components, the total amount of acids precipitated from the atmosphere may turn out to be critical. In the very industrial centers, the high flows of acidifying substances from the atmosphere are balanced by the high content of basic components of precipitation, and for this reason no acidity load is observed. The permissible acidity load for the soils of the territory under consideration varies from 1 to 14 keq/(ha ar), while the actual acidity load on the territory of the region is within the limits of  $-0.10$  to  $0.40$  keq/(ha yr). In this way, in the region under study there is yet no excess of actual acidity load over the permissible one.

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