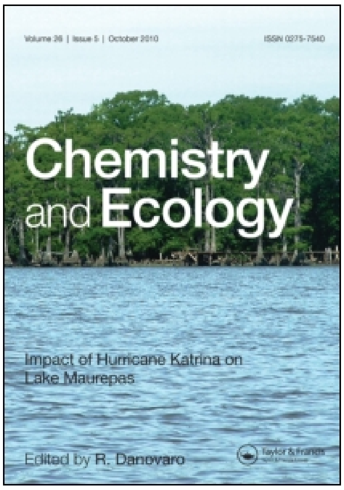

Chemistry and Ecology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

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To cite this Article Semenov, M. Yu. , Khodzher, T. V. , Obolkin, V. A. , Domysheva, V. M. , Golobokova, L. P. , Kobeleva, N. A. , Netsvetaeva, O. G. , Potemkin, V. L. , Van Grieken, R. and Fukuzaki, N.(2006) 'Assessing the acidification risk in the Lake Baikal region', Chemistry and Ecology, 22: 1, 1 — 11

To link to this Article: DOI: 10.1080/02757540500456955

URL: http://dx.doi.org/10.1080/02757540500456955

Chemistry and Ecology
Vol. 22, No. 1, February 2006, 1–11

Assessing the acidification risk in the Lake Baikal region

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(Received 11 July 2005; in final form 26 October 2005)

Data from 3-year-long observations on the chemical composition of precipitation, atmospheric gases, aerosols, soils, and surface waters at three monitoring stations in the Baikal region are presented. The stability of terrestrial ecosystems and surface waters to acidification has been estimated quantitatively. It has been shown that, unlike soils, surface waters of the Baikal watershed are more sensitive to acid deposition. The permissible acidity load for soils and surface waters of the territory varied from 0.30 to 20.00 keq ha^{-1} yr^{-1}, whereas the maximal contemporary acidity load attains 0.50 keq ha^{-1} yr^{-1}.

Keywords: Baikal watershed; Acid deposition; Monitoring; Critical load

1. Introduction

The problem of acid deposition is well known as a global ecological problem. Classical examples include forest decline in Europe [1] and degradation of small lakes in North America [2]. For the time being, intense economic development of Southeast Asian countries is taking place [3]. In this connection, governments and social organizations of the region are concerned about the expected increase in transfer of acidifying pollutants across state borders and appeal to international organizations dealing with environmental monitoring to timely detect possible negative tendencies in the environment. In 1999–2000, the Limnological Institute of the Siberian Branch of the Russian Academy of Sciences started its acid deposition monitoring program as a National Focal Center (NFC) of Acid Deposition Monitoring Network in East Asia (EANET). Besides the Russian Federation, 11 countries participate in the EANET monitoring activities: China, Japan, Mongolia, Republic of Korea, Cambodia, Indonesia, Malaysia, Lao PDR, Philippines, Thailand, and Vietnam. Most of the EANET monitoring stations are

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Chemistry and Ecology
ISSN 0275-7540 print/ISSN 1029-0370 online © 2006 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02757540500456955

shown in figure 1. The EANET acid-deposition monitoring program covers four environmental items – wet deposition, dry deposition, soil and vegetation, and inland aquatic environment. The available poor data on acid deposition and ecosystem tolerance to acidification in the Asian part of Russia [4–7], particularly the south of East Siberia, suggest that the risk of acidification in some especially sensitive ecosystems does exist, although the situation as a whole is still not critical. The data obtained during the monitoring activity under the aegis of EANET are aimed at extending our knowledge on the acidification problem in the region and used in the present study to evaluate the contemporary level of acidity deposition and critical loads.

2. Materials and methods

2.1 *Site selection and monitoring parameters*

During the preparatory phase, the main task was to choose several permanent monitoring stations characterized by different pollution levels: remote, rural, and urban. In accordance with the problem, three basic monitoring stations were established (see figure 1):

(1) Mondy station (51.6° N, 101.0° E). This station is located on the flat top (absolute height about 2000 m) of the eastern ridge of East Sayan mountains between the upper flow of the Irkut River and Lake Khubsugul. The nearest large industrial centres (cities of Irkutsk and Baikalsk) are located 200 km off Mondy; therefore, this station may be considered as remote.
(2) Listvyanka station (51.9° N, 104.7° E). This rural station is located on the flat top of the mountain (absolute height about 700 m) on the southern coast of Lake Baikal near the small settlement Listvyanka, 70 km from Irkutsk. The station is supplied with industrial electricity, and it produces hardly any pollution.
(3) Irkutsk station (52.3° N, 104.4° E). This station is situated in Irkutsk city on the west bank of the Angara River, 100 km upstream from the large industrial complexes in the Angara valley.

Every station has a set of monitoring objects for observation of atmospheric deposition, surface waters, and soil. All the monitoring parameters are listed in table 1.

For soil monitoring, two sites with different sensitivities to acid deposition (sensitive and control sites) were chosen within a radius of 50 km from each deposition sampling point. At each site, at least one sampling plot with the prevailing soil type for this area was established. During the process of preliminary survey, at Mondy station the sites were distinguished according to bedrock classes – acidic (granitoids) and basic (limestones). At Listvyanka station, a sensitive site was established at the Pereyomnaya River catchment of the Khamar-Daban Ridge, located on the southeastern shore of Lake Baikal, 40 km from Listvyanka. This territory is characterized by high amounts of precipitation – up to 2000 mm yr^{-1}, most of which (85–90% of the annual amount) falls from May to September, referred to hereafter as ‘summer’ (as opposed to ‘winter’, from October to April). High amounts of precipitation are caused by spatial orientation of the ridge, the northern slope of which faces the predominant north-west air current coming along the Angara River valley and being saturated with water over the Lake Baikal surface. In such a place, acidification is most probable. The soil cover at the Irkutsk station is to a considerable degree disturbed as a result of human activities, so the site has been selected empirically: on the base of soil analyses from different locations.

As regards acidification, the main criteria for choosing an object for surface-water monitoring are as follows: low alkalinity (up to 0.05 meq l^{-1}), electric conductivity, as well as several hydrological characteristics such as mean depth (up to 10 m), surface area (more than

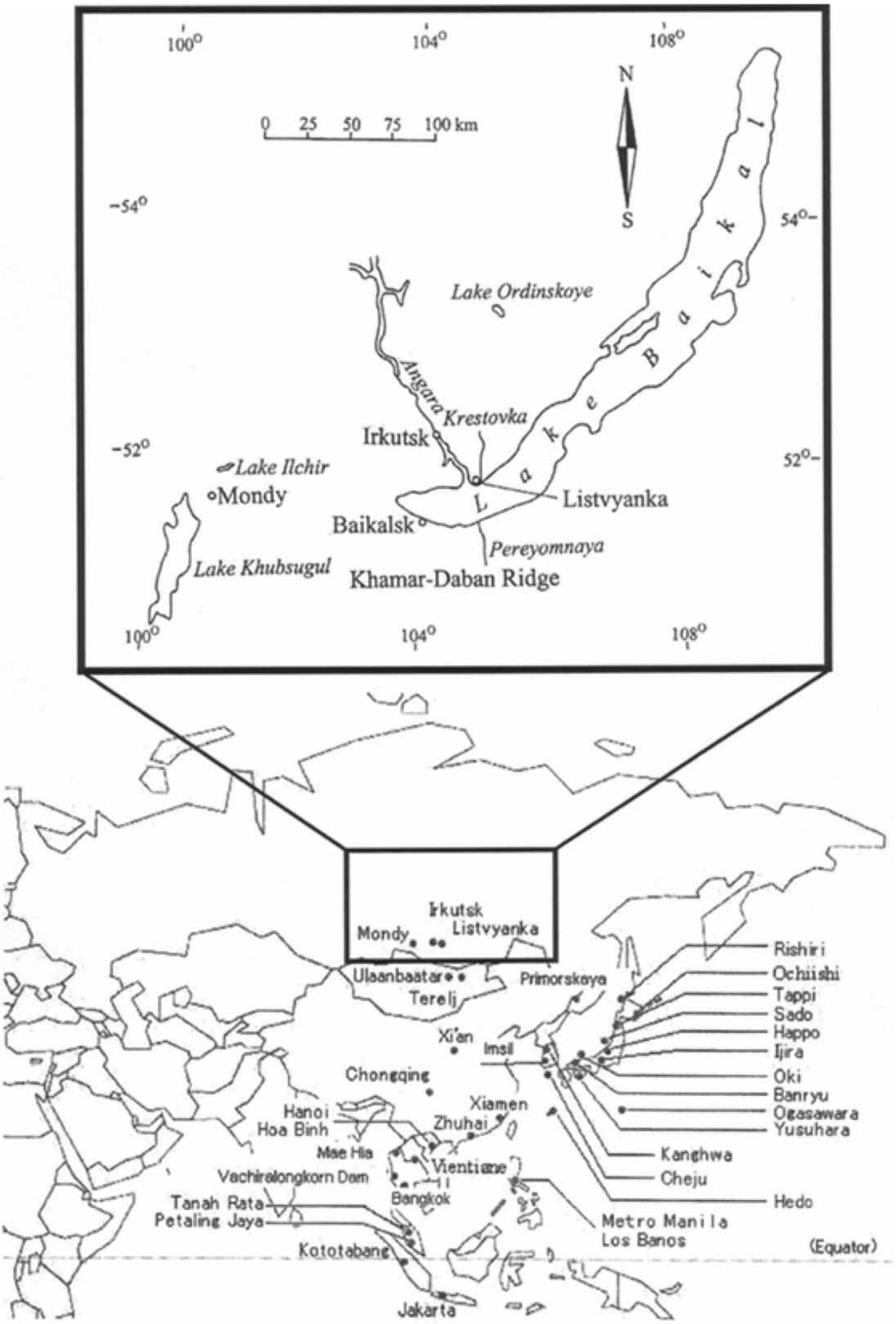

Figure 1. EANET monitoring stations.

Table 1. Monitoring parameters and analysis frequency.

Monitoring object	Monitoring parameters	Analysis frequency
Wet deposition	pH, EC, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-, Cl^-, HCO_3^- , NO_2^-, mg l^{-1}	Every time when deposition occurs
Dry deposition	SO_2, HNO_3, HCl, NH_3, mg m^{-3}, ionic composition of aerosols, μg m^{-3}	Weekly (week average)
Soil	pH_{H2O}, pH_{KCl}, exchangeable Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, H^+, meq kg^{-1}, carbonates, %, $C_{org.}$, %, $N_{org.}$, %	Once in 3–5 yr
Surface waters	Water temperature, pH, EC, $NH_4{}^+$, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-, Cl^-, HCO_3^-, mg l^{-1}	Monthly

1 ha), water residence time (less than 1 yr), and accessibility [8]. The objects chosen are Lake Ilchir, which is 40 km to the north from Mondy, Lake Ordynskoye located 80 km to the north from Irkutsk, and the Krestovka River located not far from the deposition sampling point in Listvyanka.

2.2 *Analytical procedures*

Samples of surface waters were collected in polyethylene vessels. Sampling of wet deposition was carried out with an automatic sampler for wet deposition (the vessel cap opens when rain starts, thus closing the electric circuit in the sampler, and it closes when rain stops, and the sensor is dry again).

The total C in soil was determined by wet oxidation using 9 M H_2SO_4 solution containing 0.4 N $K_2Cr_2O_7$ (Tyurin method), and total N was also determined by wet oxidation but with concentrated H_2SO_4 (Kjeldahl method) [9, 10]. Exchangeable cations were extracted from air-dried soil with 1 M ammonium acetate solution [9, 11]. For element-composition analysis, soil (after removing non-decomposed plant residues) was smelted with $KNaCO_3$ (47.5% Na_2CO_2 and 52.5% K_2CO_3) and then dissolved with HCl [9]. Calcium and magnesium ion concentrations in water and soil extracts were measured by flame atomic absorption spectrometry, and sodium and potassium ions by flame atomic emission spectrometry [9, 12]. Sulphate, chloride, nitrate, and bicarbonate concentrations were measured by high-performance liquid chromatography [13]. Ammonium concentration was estimated colorimetrically with Nessler reagent (without distillation). The pH was measured potentiometrically, and the electric conductivity (EC) electrochemically. EC was measured in the laboratory at 25° C using a water bath. $^{87}Sr/^{86}Sr$ ratios were measured by termal ionization mass spectrometry using a Finnigan MAT 262 apparatus [14].

Atmospheric particles and gases were sampled with a four-step impactor (Filter Pack method) using a pump with a flow rate of 1 l min^{-1}. In samples collected on the first polytetrafluoroethylene (PTFE) filter, the ion composition of the water-soluble aerosol fraction was analysed. Gas-originated anions (Cl^-, SO_4^{2-},NO_3^-) were measured on the second filter with subsequent expression in terms of gaseous SO_2, HNO_3, and HCl. The third and fourth filters (filter paper) were subjected to a special treatment. The third filter was soaked with a mixture of 6% K_2CO_3 solution and 2% glycerol solution for sorption of sulphur dioxide passing through the second filter. After extracting the filter with 0.3% hydrogen peroxide solution, the concentration of the formed SO_4^{2-} ions was measured. Further on, the sulphate content was expressed in terms of 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 NH_4^+ content of the extract was evaluated and expressed in terms of NH_3.

2.3 *Critical loads calculation*

Within the framework of this research, the integral ecosystem stability to acidification was evaluated. The critical load of acidity (CL(Ac)) was chosen as the measure of stability. According to the definition elaborated at an UN ECE expert workshop in Skokloster, Sweden in 1988, critical load is the deposition of acidifying compounds that will not cause chemical changes leading to long-term harmful effects on the ecosystem structure and function. Critical loads of acidity were calculated for both terrestrial and aquatic ecosystems. For terrestrial ecosystems, calculations were made using the Steady State Mass Balance (SSMB) [15]:

$$\mathrm{CL(Ac)} = \mathrm{BC_w} - \mathrm{ANC_{le(crit)}},$$

where CL(Ac) is the critical load of acidity (keq $\mathrm{ha^{-1}\ yr^{-1}}$), $\mathrm{BC_w}$ is the Ca, Mg, and K (base cations) release due to weathering (keq $\mathrm{ha^{-1}\ yr^{-1}}$), $\mathrm{ANC_{le(crit)}}$ is the critical value of acid neutralizing capacity (keq $\mathrm{ha^{-1}\ yr^{-1}}$), $\mathrm{ANC_{le(crit)}} = -Q \cdot ([\mathrm{Al^{n+}}]_{\mathrm{crit}} + [\mathrm{H^+}]_{\mathrm{crit}})$, Q is the runoff, *i.e.*water leaving the root zone ($\mathrm{m^3\ ha^{-1}\ yr^{-1}}$), and $[\mathrm{Al^{n+}}]_{\mathrm{crit}}$ and $[\mathrm{H^+}]_{\mathrm{crit}}$ are the critical concentrations of positively charged aluminium ions ($\mathrm{Al^{3+}}$, $\mathrm{AlOH^{2+}}$, $\mathrm{Al(OH)_2^+}$), with hydrogen set to 0.2 eq $\mathrm{m^{-3}}$ and 0.1 eq $\mathrm{m^{-3}}$, respectively. In the case of terrestrial ecosystems, CL(Ac) was calculated for the root-inhabited layer.

For aquatic ecosystems, the Steady State Water Chemistry (SSWC) method was applied [15]:

$$\mathrm{CL(Ac)} = ([\mathrm{BC}]_0 - [\mathrm{ANC}]_{\mathrm{limit}}) \cdot Q - \mathrm{BC_{dep.}} + \mathrm{BC_u},$$

where CL(Ac) is the critical load of acidity (keq $\mathrm{ha^{-1}\ yr^{-1}}$), $[\mathrm{BC}]_0$ is the base cation concentration in water (eq $\mathrm{m^{-3}}$), $[\mathrm{ANC}]_{\mathrm{limit}}$ is the desired ANC threshold (set to 0.02 eq $\mathrm{m^{-3}}$),

$$[\mathrm{ANC}]_{\mathrm{limit}} = [\mathrm{HCO_3^-}] + [\mathrm{A^-}] - [\mathrm{H^+}] - [\mathrm{Al^{n+}}],$$

where $[\mathrm{A^-}]$ and $[\mathrm{Al^{n+}}]$ are the concentrations of organic anions and positively charged aluminium respectively (eq $\mathrm{m^{-3}}$). Q is the runoff ($\mathrm{m^3\ ha^{-1}\ yr^{-1}}$), $\mathrm{BC_{dep.}}$ is the atmospheric deposition of base cations (keq $\mathrm{ha^{-1}\ yr^{-1}}$), and $\mathrm{BC_u}$ is the net long-term uptake in biomass (keq $\mathrm{ha^{-1}\ yr^{-1}}$). $\mathrm{BC_u}$ should be set to zero if there is no management.

The most important characteristic for assessment of terrestrial ecosystem susceptibility to acidification using SSMB is the soil-weathering rate. This was calculated from the comparison of $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios in soils, precipitation, and surface waters as described by [16–18], etc. The calculations were as follows:

$$\begin{aligned}\mathrm{Weathering} = \mathrm{BC/Ca} \cdot \mathrm{Ca_{dep.}} \cdot [((^{87}\mathrm{Sr}/^{86}\mathrm{Sr_R} - {}^{87}\mathrm{Sr}/^{86}\mathrm{Sr_D})/(^{87}\mathrm{Sr}/^{86}\mathrm{Sr_S}\\ - {}^{87}\mathrm{Sr}/^{86}\mathrm{Sr_D}))/((^{87}\mathrm{Sr}/^{86}\mathrm{Sr_R} - {}^{87}\mathrm{Sr}/^{86}\mathrm{Sr_S})/(^{87}\mathrm{Sr}/^{86}\mathrm{Sr_D} - {}^{87}\mathrm{Sr}/^{86}\mathrm{Sr_S}))],\end{aligned}$$

where BC/Ca is the $([\mathrm{Ca^{2+}}] + [\mathrm{Mg^{2+}}] + [\mathrm{K^+}] + [\mathrm{Na^+}])/[\mathrm{Ca^{2+}}]$ ratio in runoff, $\mathrm{Ca_{dep}}$ is the atmospheric deposition of calcium, keq $\mathrm{ha^{-1}\ yr^{-1}}$, $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ is the strontium isotope ratio in: $_\mathrm{R}$ denotes runoff, $_\mathrm{D}$ denotes deposition, $_\mathrm{S}$ denotes soils $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr_R} - {}^{87}\mathrm{Sr}/^{86}\mathrm{Sr_D})/(^{87}\mathrm{Sr}/^{86}\mathrm{Sr_S} - {}^{87}\mathrm{Sr}/^{86}\mathrm{Sr_D})$ is the soil contribution to runoff, and $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr_R} - {}^{87}\mathrm{Sr}/^{86}\mathrm{Sr_S})/(^{87}\mathrm{Sr}/^{86}\mathrm{Sr_D} - {}^{87}\mathrm{Sr}/^{86}\mathrm{Sr_S})$ is the contribution of atmospheric deposition to runoff.

The weathering rates obtained were extrapolated to nearby areas on the base of Arrhenius' equation [19]:

$$\mathrm{BC_{we}}(T) = \mathrm{BC_{we}}(T_0)\mathrm{e}^{(A/T_0 - A/T)},$$

where $\mathrm{BC_{we}}(T)$ is the weathering rate for the required location at local temperature T (K), $\mathrm{BC_{we}}(T_0)$ is the weathering rate measured for a certain monitoring plot at reference temperature T_0 (K), e is the base of the natural logarithm, and A is the pre-exponential factor (set to 3600 K).

3. Results and discussion

3.1 *Atmospheric deposition*

Wet deposition includes rain and fresh snow. The data given in this paper represent a 3-yr observation period. As expected, the sum of ions in atmospheric precipitation was the highest at Irkutsk station, and the lowest in Mondy. Average deposition rates are shown in table 2. The bulk of wet deposition falls in summer due to the annual distribution of precipitation. The distribution of low acidity values is unequal at the stations. The frequency of acid rains is the highest at rural station Listvyanka. Apparently, this is due to the predominant northwest wind bringing air pollutants from the industrial zone located in the upper stream of the Angara River. Acidity loads onto the north-western slope of the Khamar-Daban Ridge (on the opposite shore of Baikal) facing Listvyanka are also high.

Dry deposition observations include measurements of gases and aerosol composition. Data obtained from three stations are presented in table 3. For the Listvyanka station, dry deposition was calculated from literature data on deposition rates [20]. The seasonal distribution of wet and dry deposition of acidifying compounds at Listvyanka station is presented in figure 2. As it is clear from the figure, both wet and dry deposition rates are similar to each other during the summer. However, dry deposition is about twice as high as the wet deposition in the total annual flux due to its higher contribution in winter.

The total deposition of acidity (Ac(pot)) was calculated from wet deposition data using the formula [15, 21]:

$$\begin{aligned}\mathrm{Ac(pot)} = {} & \mathrm{SO_4^{2-}}_{\mathrm{dep.}} + \mathrm{NO}_x^{y-}{}_{\mathrm{dep.}} + \mathrm{Cl^-}_{\mathrm{dep.}} + \mathrm{NH_4^+}_{\mathrm{dep.}} \\ & - \mathrm{Ca^{2+}}_{\mathrm{dep.}} - \mathrm{Mg^{2+}}_{\mathrm{dep.}} - \mathrm{K^+}_{\mathrm{dep.}} - \mathrm{Na^+}_{\mathrm{dep.}},\end{aligned}$$

where $\mathrm{SO_4^{2-}}_{\mathrm{dep.}}$, $\mathrm{NO}_x^{y-}{}_{\mathrm{dep.}}$, $\mathrm{Cl^-}_{\mathrm{dep.}}$, $\mathrm{NH_4^+}_{\mathrm{dep.}}$, $\mathrm{Ca^{2+}}_{\mathrm{dep.}}$, $\mathrm{Mg^{2+}}_{\mathrm{dep.}}$, $\mathrm{K^+}_{\mathrm{dep.}}$, and $\mathrm{Na^+}_{\mathrm{dep.}}$ denote the deposition of the corresponding compounds. Ammonium was referred to acidifying substances because of soil nitrification producing two protons for every ammonium ion. The values

Table 2. Wet deposition of main ions.

		meq $\mathrm{m^{-2}\ yr^{-1}}$										Ac(pot) keq $\mathrm{ha^{-1}\ yr^{-1}}$
Station	Period	$\mathrm{HCO_3^-}$	$\mathrm{SO_4^{2-}}$	$\mathrm{NO_3^-}$	$\mathrm{Cl^-}$	$\mathrm{Na^+}$	$\mathrm{K^+}$	$\mathrm{Ca^{2+}}$	$\mathrm{Mg^{2+}}$	$\mathrm{NH_4^+}$	$\mathrm{H^+}$	
Irkutsk	Summer	4.79	22.03	7.69	3.36	2.44	1.69	30.11	3.29	0.05	0.29	
	Annual	10.64	31.67	10.90	6.32	3.91	2.35	47.50	5.26	0.11	0.39	−0.10
Listvyanka	Summer	3.47	11.47	4.66	2.03	1.39	1.46	7.25	1.49	6.54	3.51	
	Annual	4.08	15.47	7.32	2.48	2.00	2.28	10.09	2.96	7.92	4.10	0.16
Mondy	Summer	0.31	3.23	1.55	0.68	0.43	0.26	2.02	0.58	2.16	0.32	
	Annual	1.97	4.98	2.11	1.04	0.65	0.43	2.51	0.99	3.55	1.97	0.07

Table 3. Average concentrations of some aerosol compounds and gas admixtures in the atmosphere (μg m^{-3}).

	Irkutsk		Listvyanka		Mondy	
Substance	Winter	Summer	Winter	Summer	Winter	Summer
Aerosol						
HCO_3^-	1.4	3.6	1.0	4.1	0.2	0.5
SO_4^{2-}	4.6	0.8	3.1	0.8	0.6	0.4
NO_3^-	1.4	0.5	0.4	0.5	0.03	0.06
Cl^-	0.3	0.1	0.2	0.4	0.02	0.08
Na^+	0.2	0.2	0.1	0.01	0.02	0.07
K^+	0.1	0.8	0.04	0.4	0.05	0.18
Ca^{2+}	1.0	0.7	0.6	0.4	0.13	0.11
Mg^{2+}	0.1	0.1	0.1	0.1	0.02	0.02
NH_4^+	1.6	0.5	0.7	0.9	0.21	0.15
Gases						
SO_2	25.5	0.9	4.3	2.6	0.16	0.3
NH_3	0.5	3.1	0.5	1.2	0.22	0.9

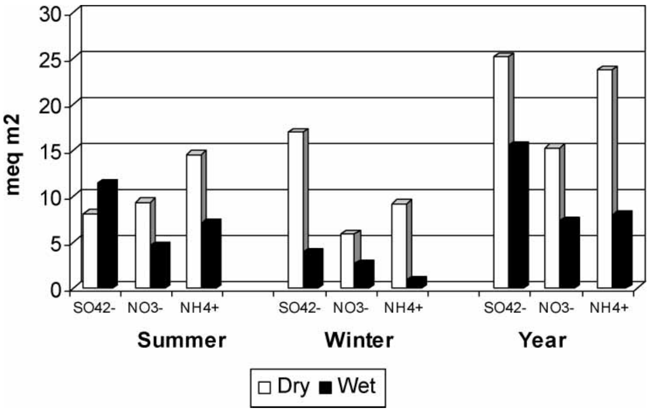

Figure 2. Comparison between the wet and dry deposition of acidifying ions at the Listvyanka station.

calculated are in the range of −0.10 to 0.16 keq ha^{-1} yr^{-1}. Negative values (predominance of base compounds) are typical of the inhabited localities (Irkutsk station), and positive values are common for remote and highland locations (Mondy and Listvyanka stations). Taking into account the twofold rate of dry deposition, the values of Ac(pot) obtained should be three times higher. Thus, the maximum value should reach 0.50 keq ha^{-1} yr^{-1}.

3.2 *Soil*

As mentioned above, two types of sites – sensitive and control – were chosen within a radius of 50 km from each deposition sampling point (see table 4). The profile distribution of exchangeable base cations is of an accumulative character (see table 5) in all the soils investigated except the soil of the 6th plot (the data on plots 3 and 5 are missing in the tables, since they are very close to data on plots 4 and 1 correspondingly but have less developed profiles). For all the horizons, the total amounts of base cations decrease in the row: $Ca^{2+} > Mg^{2+} > K^+ \geq Na^+$; calcium accounts for 40–95% of the total amount.

Table 4. Objects for soil monitoring.

	Sensitive		Control	
Station	Plot no.	Soil	Plot no.	Soil
Mondy	1	Gelic podzol	2	Calcic gleysol
	4	Gelic gleysol		
Listvyanka	7	Dystric leptosols*	6	Mollic leptosol
Irkutsk	8	Eutric regosol	9	Calcaric luvisol

*The seventh plot was established on the opposite Lake Baikal shore in the Pereemnaya River basin.

As expected, the highest amounts of base cations, as well as the highest pH values, were observed in control soils. The largest amounts of exchangeable acidity are coupled with the lowest pH_{KCl} values. The only exception is plot 7 established on the opposite Lake Baikal shore in the Pereyomnaya River basin. In this soil, both the content of exchangeable bases and the acidity content are quite low because of the absence of clay minerals, which was proved by X-ray diffraction analysis of the <1 μm fraction. Apart from the dynamic parameters, we also measured the total element composition of soil. In this connection, it is noteworthy that the soil of plot 2 was characterized by a considerable CaO content in A horizons – 10.84% (Ca measured in filtrate after SiO_2 precipitation), which amounted to 19.35% of $CaCO_3$ per total soil, or 34.54% of $CaCO_3$ per mineral substance. This was also confirmed by the results of acidimetric measurements of carbonates.

Table 5. Chemical properties of the soils investigated.

Plot no.	Layer	Depth (cm)	pH		Exchangeable cations (meq kg^{-1})					Total C(%)	Total N(%)
			H_2O	KCL	Ca^{2+}	Mg^{2+}	K^+	Na^+	$Al^{3+} + H^+$		
1	AO	3–6	5.05	3.80	152.61	40.91	9.54	0.91	17.42	13.81	3.12
	AB	6–9	5.05	3.50	46.43	8.92	1.73	0.94	87.44	3.63	0.71
	B	9–25	4.92	3.96	10.84	4.43	2.64	1.12	62.13	3.22	0.83
	BC	>25	5.66	4.00	31.91	11.92	1.02	0.92	12.55	1.22	0.52
2	Ok	0–2	7.62	–*	898.82	84.24	45.91	–	–	22.85	3.04
	Ak	2–20	7.84	–	1398.43	188.61	0.01	–	–	15.93	3.15
	Bkg	20–45	7.34	–	350.23	35.82	4.62	–	–	2.44	0.21
4	AO	8–18	4.90	3.95	135.23	48.51	5.32	0.72	20.81	7.42	1.22
	B	18–25	6.42	5.07	93.71	18.73	1.83	0.41	<d.l.**	0.83	0.61
	BCg	25–45	6.92	5.91	127.62	15.92	2.01	0.52	<d.l.	1.41	0.63
6	A	0–18	6.76	5.85	196.94	31.01	2.54	0.83	0.91	3.16	0.68
	B1	18–28	6.90	5.59	167.63	34.53	2.33	0.84	0.43	1.02	0.36
	B2	28–60	7.03	5.41	186.54	46.03	1.72	0.92	0.54	0.45	0.29
	BC	>60	6.90	5.43	168.91	46.72	1.21	0.73	0.42	0.31	0.20
7	AB	0–5	4.21	3.83	8.35	6.12	4.31	1.82	<d.l.	11.52	–
	BC	5–10	4.12	4.02	2.12	1.74	1.32	1.33	<d.l.	0.56	–
8	A	1–3	7.00	6.06	228.81	41.71	4.94	2.34	1.01	6.72	–
	B	3–15	6.56	4.47	113.32	23.03	2.12	1.25	1.92	1.32	–
	BC	15–60	6.18	4.00	115.44	23.02	1.31	1.44	3.81	0.95	–
9	A	0–6	6.65	5.79	266.23	64.22	2.33	1.84	–	9.12	0.50
	B	6–16	6.89	5.72	218.85	54.22	2.24	1.95	–	2.53	0.27
	BC	16–35	7.94	6.16	170.44	44.41	1.91	1.52	–	0.32	0.60
	Ck	35–55	7.99	6.66	237.01	44.15	2.12	1.63	–	0.26	0.04

*This parameter was not measured.

**<d.l.: value below the detection limit (<0.10 meq kg^{-1}).

3.3 *Surface waters*

In this study, several local freshwater water bodies were studied: Lake Ilchir (Mondy), Lake Ordynskoye (Irkutsk), and the Krestovka River (Listvyanka) (see table 6). Due to both low concentrations of ions in atmospheric precipitation and weathering rate, the water of Ilchir Lake is characterized by a low sum of ions during the ice-free season. Under the ice cover when the groundwater is the only supply, the sum of ions increases twofold. Within a year, the sum of ions is in the range of 3.8–6.9 meq l^{-1}, and the values of electric conductivity and alkalinity are in the range of 163–350 mS m^{-1} and 1.5–2.6 meq l^{-1}, respectively. pH values vary from 7.7 to 8.2. On the basis of chemical composition, the water of Ilchir Lake can be attributed to a calcium group of hydrocarbonate class (predominant ions are $\mathrm{HCO_3^-}$ and $\mathrm{Ca^{2+}}$). The sum of ions in Ordynskoye Lake water corresponds to the middle level: the annual average sum of ions is between 26.3 and 28.5 meq l^{-1}. For this lake, the highest alkalinity (5.3–6.2 meq l^{-1}) and the highest pH value (8.7) were registered. Ilchir Lake is also characterized by high pH values, but unlike Ordynskoye Lake, its alkalinity stock is much lower. Both the lowest alkalinity (0.5 meq l^{-1} on an average) and lowest pH (6.9) were observed in the Krestovka River. The concentration of alkalinity in Krestovka is close to the critical level.

3.4 *Critical loads and exceedances*

The weathering rates obtained vary within the range of 0.3–6.8 keq $\mathrm{ha^{-1}\ yr^{-1}}$ (see table 7). These values were extrapolated to nearby areas on the base of Arrhenius' equation [19]. The critical load values obtained on the base of weathering rates vary in the range of 0.4–20.0 keq $\mathrm{ha^{-1}\ yr^{-1}}$. Minimum values (0.3–1.3 keq $\mathrm{ha^{-1}\ yr^{-1}}$) were observed for highland ecosystems (mountain tundra and mountain forest-tundra) and maximum values (7.5–20.0 keq $\mathrm{ha^{-1}\ yr^{-1}}$) for the coniferous forests on various soils, especially on carbonate-rich soils. In general, surface waters of the Baikal watershed are more sensitive than soils to acid deposition (see tables 6 and 7). Comparing the triply enlarged (to obtain the total – wet plus dry deposition) values of present acidity load calculated on the base of wet deposition data (see table 2) and critical loads (see tables 6 and 7), exceedance is not observed for all the monitoring sites. However, in

Table 6. Chemical composition of surface waters.

	meq l^{-1}											
	$\mathrm{HCO_3^-}$	$\mathrm{SO_4^{2-}}$	$\mathrm{NO_3^-}$	$\mathrm{Cl^-}$	$\mathrm{Na^+}$	$\mathrm{K^+}$	$\mathrm{Ca^{2+}}$	$\mathrm{Mg^{2+}}$	$\mathrm{NH_4^+}$	pH	Q $\mathrm{m^3\ ha^{-1}\ yr^{-1}}$	CL(Ac) keq $\mathrm{ha^{-1}\ yr^{-1}}$
Baikal												
Year	1.09	0.11	0.00	0.02	0.17	0.05	0.75	0.26	0.00	7.75	1100	1.03
Ilchir												
Winter	2.56	0.85	0.00	0.02	0.05	0.02	2.25	1.11	0.01	7.86		
Summer	1.46	0.42	0.00	0.02	0.03	0.01	1.24	0.63	0.00	7.90	250	0.32*
Ordinskoye												
Winter	6.16	7.53	0.02	0.56	2.84	0.40	3.71	7.31	0.01	8.07		
Summer	5.28	7.29	0.00	0.56	2.98	0.36	3.39	6.38	0.01	8.74	300	1.03*
Krestovka												
Winter	0.54	0.20	0.01	0.01	0.14	0.01	0.33	0.22	0.01	6.86		
Summer	0.28	0.20	0.00	0.01	0.10	0.02	0.19	0.18	0.01	7.00	5000	–
Pereyomnaya												
Winter	0.14	0.21	0.02	0.00	0.06	0.02	0.19	0.08	0.00	6.49	13000	–
Summer	0.08	0.06	0.01	0.01	0.02	0.01	0.09	0.04	0.01	6.90		

*For CL calculations, summer $\mathrm{HCO_3^-}$ concentrations were used; the ion concentrations in Baikal water are the same all over the year.

Table 7. Critical loads for soils and parameters used for calculation.

Site	^{87}Sr/^{86}Sr			BC/Ca	Q m^3 ha^{-1} yr^{-1}	$Ca_{\text{dep.}}$	Weathering	CL(Ac)
	Soil	Surface water	Deposition			keq ha^{-1} yr^{-1}		
Pereyomnaya 1700 m a.s.l.*	0.716737 ± 12	0.713582 ± 10	0.70998 ± 11	1.46	3×10^3	0.16	0.27	1.17
Pereemnaya 600 m a.s.l.	0.715114 ± 15	0.713922 ± 20	0.710009 ± 10	1.59	8×10^3	0.98	5.12	7.52
Mondy 2000 m a.s.l.	0.70813 ± 11	0.70822 ± 10	0.70989 ± 12	1.57	1.5×10^3	0.03	0.87	1.32
Mondy 650 m a.s.l.	0.70813 ± 11	0.70822 ± 10	0.70989 ± 12	1.74	5×10^3	0.21	6.78	11.51
Irkutsk	0.712233 ± 15	0.711660 ± 12	0.710010 ± 11	1.16	2×10^3	0.48	1.60	2.20

*a.s.l.: above sea level.

mountain tundra and mountain forest-tundra zones, especially under excessive precipitation, the modelled CL and Ac(pot) values are close to each other.

4. Conclusion

This study has proved both the representativeness of monitoring stations with respect to land-use and pollution level, and the representativeness of monitoring objects with respect to sensitivity to acidification. That allows us to extrapolate the obtained data to the whole region. The most unfavourable area in the Baikal region is the northwestern slope of the Khamar-Daban Ridge facing Listvyanka where soil susceptibility to acidification and the amount of precipitation are very high. Surface waters of the Baikal watershed are more sensitive than soils to acid deposition. For the time being, the acidity deposition does not exceed critical loads of acidity for all the territory investigated; however, up in the mountains, these values are very close to each other.

Acknowledgements

This study was supported by Acid Deposition and Oxidant Research Centre (Niigata, Japan). The work of M. Semenov was also supported by a grant from the Belgian Office for Scientific, Technical, and Cultural Affairs, and a grant from the Russian Science Support Foundation.

References

[1] M. Hauhs, R.F. Wright. Regional pattern of acid depositiom and forest decline along a cross section through Europe. *Wat. Air Soil Pollut.*, **49**, 463 (1986).

[2] J.P. Baker, W.J. Warren-Hicks, J. Gallagher. Fish population losses from Adirondack lakes: the role of surhace water acidity and acidification. *Water Resour. Res.*, **29**, 861 (1993).

[3] V.N. Bashkin, S.-U. Park (Eds). *Acid Deposition and Ecosystem Sensitivity in East Asia*, p. 427, Nova Science, New York (1998).

[4] V.A. Obolkin, T.V. Khodzher, Yu.A. Anokhin, T.A. Prohorova. Kislotnost atmosfernih vipadenii v regione Baikala. *Meteorol. Gidrol.*, **1**, 55 (1991) (in Russian)

[5] A.O. Kokorin, S.V. Politov. Postupleniye zagryaznyayushchih veshchestv iz atmosferi s osadkami v yujnom Baikale. *Meteorol. Gidrol.*, **1**, 48 (1991) (in Russian)

[6] M.Y. Semenov, V.N. Bashkin, H. Sverdrup. Application of biogeochemical model 'PROFILE' for assessment of North Asian ecosystem sensitivity to acid deposition. *Asian J. Energy Environ.*, **2**, 143 (2000).

[7] M. Semenov, V. Bashkin, H. Sverdrup. Critical loads of acidity for forest ecosystems of North Asia. *Wat. Air Soil Pollut.*, **130**, 1193 (2001).

[8] Technical documents for monitoring on inland aquatic environment in East Asia, p. 46, Acid Deposition and Oxidant Research Center, Niigata, Japan (2000).

[9] E.V. Arinushkina. *Rukovodstvo po Khimicheskomu Analizu Pochv*, Moscow State University Press, Moscow (1970) (in Russian).

[10] J.M. Bremner. Nitrogen – total. In *Methods of Soil Analysis: Part 3 Chemical Methods*, J.M. Bartels (Ed.), pp. 1085–1121, ASA, SSSA Book Series No. 5, Madison, WI (1996).

[11] M.E. Sumner, W.P. Miller. Cation exchange capacity and exchange coefficients. In *Methods of Soil Analysis: Part 3 Chemical Methods*, J.M. Bartels (Ed.), pp. 1201–1229, ASA, SSSA Book Series No. 5, Madison, WI (1996).

[12] A.E. Greenberg, L.S. Clesceri, A.D. Eaton (Eds). *Standard Methods for the Examination of Water and Wastewater*, p. 297, American Public Health Association, Washington, DC (1992).

[13] G.I. Baram, A.L. Vereshchagin, L.P. Golobokova. Mikrokolonochnaya visokoeffiktivnaya gidkostnaya chromatographiya c UV-detectirovaniem dlya opredeleniya anionov v ob'ektah okrugayushchei sredi. *J. Anal. Himii*, **9**, 962 (1999) (in Russian).

[14] V.D. Pampura, G.P. Sandimirova. *Geohimiya i Izotopnii Sostav Strontsiya v Gidrotermalnih Sistemah*, Nauka, Novosibirsk (1991) (in Russian).

[15] H.-D. Gregor, B. Werner, T. Spranger (Eds). *Manual on Methodologies and Criteria for Mapping Critical Levels/Loads and Geographical Areas Where They are Exceeded*, p. 142, UN ECE Convention on Long-range Transboundary Air Pollution, Federal Environmental Agency, Berlin (1996).

[16] E. Miller, J. Blum, A. Friedland. Determination of soil exchangeable cation loss and weathering rates using Sr isotopes. *Nature*, **362**, 438 (1993).

[17] B.W. Stewart, R.C. Capo, O.A. Chadwick. Quantitative strontium isotope models for weathering, pedogenesis and biogeochemical cycling. *Geoderma*, **82**, 173 (1998).

[18] H. Sverdrup, P. Warfvinge, T. Wickman. Estimating the weathering rate at Gardsjon using different methods. In *Experimental Reversal of Acid Rain Effects; The Gardsjon Roof Project*, H. Hultberg, R. Skeffington (Eds), pp. 232–249, Wiley, Chichester, UK (1998).

[19] H. Sverdrup, W. De Vries, A. Henriksen. Mapping critical loads: a guidance to the criteria, calculations, data collection and mapping of critical loads. Miljorapport (environmental report), 14, Nordic Council of Ministers, Copenhagen (1990).

[20] R.G. Derwent, O. Hov, W. Asman, J.A. Van Jaarsveld, F. Deleeuw. An intercomparison of long-term atmospheric transport models – the budgets of acidifying species for the Netherlands. *Atmos. Environ.* **9**, 1893 (1989).

[21] P. Warfvinge, H. Sverdrup. Critical loads of acidity to Swedish forest soils. Methods, data and results. Reports in ecology and environmental engineering, 5, Lund University, Lund, Sweden (1995).