Effect of atmospheric precipitation on the chemical composition of river waters in the South Baikal

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We discuss some results of investigations into the chemical composition of snow cover and river waters in the South Baikal region. It has been determined that acidity of anions of strong acids is not fully neutralized in snow waters of basins of some rivers. In a many-year aspect, pH of snow waters is gradually lowering, being a real threat of acidification of surface waters. It is shown that natural balance of ions in river waters is disturbed, the concentration of sulfates in them increases, while the concentration of hydrocarbonates and calcium decreases.

Introduction

Recent investigations[1,2] have shown the increasing role of anthropogenic factors in the formation of chemical composition of rivers in the South Baikal region. The sources of pollution in this region are the Trans-Siberian railway and the highway along the lake shore, as well as towns and villages situated in the lower part of valleys of the rivers, the largest of which is Baikalsk (on River Solzan), where the Baikalsk Pulp-and-Paper Mill (BPPM) is located.

We consider here some features of the chemical composition of snow cover in river valleys situated northwest side of the Khamar-Daban Ridge and the effect of atmospheric precipitations on the composition of river waters.

The mountain frame of the South Baikal hollow, the inversion stratification of the atmosphere, and the character of local circulation prevent the exchange between the air mass over the lake and these over its neighborhood. As a result, anthropogenic emissions disperse along the lakeshore, accumulate in foothills, and ascend the river valleys. River valleys most often become places of localization of anthropogenic emissions and accumulation of pollutants in various media, in particular, in the atmospheric precipitation. In addition, the northwestern side of the Khamar-Daban Ridge is on the way of airflows, which penetrate there across the Primorskii Ridge along the River Angara valley.[3,4]

Atmospheric precipitation is the main source of water for rivers of South Baikal region. The region of the Khamar-Daban Ridge is characterized by the largest amount of precipitations: up to 1060–1720 mm. The height of the show cover can achieve 2 m. Podzolic and brown forest soils are developed under dark coniferous forest on unstratified rock, while forest sod and meadow soils are formed along the river valleys and flood-lands under conditions of high moisture and low frost penetration. Uplands are characterized by stony placers and breakstone well-washed soils. Most soils show the acid reaction.[5]

Materials and methods

The paper analyzes the chemical composition of the rivers flown from the northwestern side of the Khamar-Daban Ridge (1996–2002) and the snow cover in the basins of these rivers (1997, 1999, 2001–2002). Water was sampled in river undercurrents (Fig. 1) in the main hydrological phases: winter low-water period, spring flood, summer low-water period, freshets, fall low-water period. Snow samples were collected in the river valleys in late February–early March over the entire height of the snow cover.

Fig. 1. Sampling map.

Chemical analyses were carried out by the methods commonly accepted in hydrochemistry of fresh water and atmospheric precipitations[6] and by the methods developed in the Limnological Institute.[7] Cations were detected by the atomic absorption method with the relative error of 2–3%; anions were determined by the HPLC method with the relative error of 5–10%. Ammonia nitrogen was determined by the colorimetric method with the relative error of 4–5%. The reliability of the obtained results was checked by calculating the anion and cation balance. In the river water the error of determination was within 3%, while in the snow water it did not exceed 8%.

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Results and discussion

Chemical composition of snow waters

The peculiarities of air mass circulation in the Southern Hollow of Lake Baikal govern the dispersion of atmospheric industrial emissions over the territory, their localization and accumulation in the river valleys and, consequently, affect the formation of the chemical composition of atmospheric precipitations. In the valleys of the rivers studied, the snow waters (SW) differ in the concentration of ions, their relative composition, and acidity. The maximum values of the sum of main ions are determined in SW of the River Solzan valley in the immediate vicinity of the main pollution sources: BPPM and Baikalsk (Fig. 2). However, now they are much lower than mineralization (150–170 mg/l) noticed in this region in 1979–1980.[8]

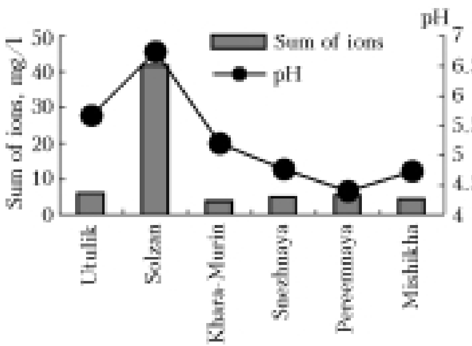

Fig. 2. Variation of ion sum and pH in snow water of the basins of the rivers in South Baikal region.

The contribution of hydrocarbonates to the ion composition of SW is quite significant (their concentration varies from 1.5 to 10.9 mg/l (10–20%-equ.)), and the contributions of sulfates and calcium are high too (Fig. 3). In the cation composition, as in the 1980s, the fraction of sodium ions – tracers of BPPM emissions – is rather high (Table 1).[9] The relative content of sodium in SW in River Solzan basin can achieve 19.4–23.2%-equ., sometimes exceeding the fraction of calcium. The effect of BPPM emissions on the SW ion composition and concentration is also observed in the valley of River Utulik, as is evidenced by the presence of hydrocarbonates in SW (up to 7%-equ.) in some periods. In the basins of other rivers, SW contains no hydrocarbonates, the sodium content varies within the background values, and the dominant cation is calcium (see Figs. 2 and 3). The content of chloride ions varies from analytical zero to 0.5 mg/l (River Solzan). The concentrations of ammonia nitrogen in SW are low and close in all the valleys studied (see Fig. 3). It is likely governed by the natural conditions of the region under study.

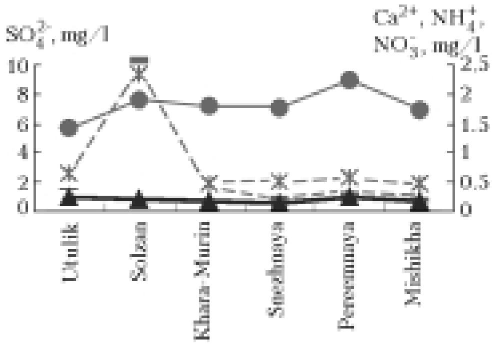

Fig. 3. Content of ions in snow water in basins of rivers of South Baikal: –■– SO_4, –✱– Ca, –▲– NH_4, –●– NO_3.

Consider the dynamics of the concentrations of main acid-forming components: sulfates and nitrates. As can be seen from Fig. 3, to the east and west of Solzan river, the concentrations of SO_4^{2-} ions in SW decrease with the increasing distance from the BPPM, while the concentrations of NO_3^- ions vary insignificantly, and only in the basin of the Pereemnaya river they slightly increase. The relative content of sulfates, nitrates, and hydrogen ions varies in a similar way (Table 1).

In SW of the Solzan river valley, the fraction of sulfates makes up, on the average, 30%-equ., while the fraction of nitrates is about 6%-equ. In the basin of Snezhnaya river, their values are already close, on the average, 22 and 24%-equ., respectively.

Farther to the east in the basins of the Pereemnaya and Mishikha rivers, the fraction of nitrate nitrogen increases up to 26–28%-equ., that is, the dominant ion here is nitrate (Table 1). The calculation of the ratios of equivalent concentrations SO_4^{2-}/NO_3^- also confirmed the significance of the nitrate contribution to SW acidity in the Khara-Murin–Mishikha region. This is evidenced by a gradual decrease of this ratio with the distance from the source of sulfate pollution: from 6.9 near the Solzan river to 0.8 near the Pereemnaya river (see Table 1).

Table 1. Variation of relative SW composition in the basin of South Baikal tributaries

Year	Sampling site	SO_4^{2-} %-equ.	NO_3^- %-equ.	Na^+ %-equ.	Ca^{2+} %-equ.	Mg^{2+} %-equ.	H^+ %-equ.	SO_4^{2-}/NO_3^-	C/A
1997	Solzan	37.4	5.7	21.2	19.4	2	0.1	6.5	1.0
1999	»	20.6	11.2	8.5	22.4	8	0.5	1.8	1.5
2001	»	25.3	5.0	23.6	20.2	1.8	0	5.2	1.5
2002	»	38.8	1.9	29.1	12.8	1	0	20.6	1.1
1997	Pereemnaya	20.2	22.6	5.3	21.3	6.0	14.0	0.9	0.9
1999	»	20.1	26.7	5.8	23.2	5.0	5.3	0.8	0.8
2001	»	25.5	28.0	2.8	24.2	4.8	5.8	0.8	0.7
2002	»	25.5	28.0	6.8	19.1	3.6	10.4	0.9	0.7

The decrease of the ratio SO_4^{2-}/NO_3^- is also observed in some countries of the East Asia due to the growing rate of NO_x emission and the increase of the nitrate concentration in precipitations.[10] The current level of the nitrate concentrations in the region studied, in particular, in the SW of the Pereemnaya river valley is rather high (2.23 mg/l) and approaches that in Irkutsk in 1999–2002 (2.29 mg/l).

Interannual variations of the ion sum and the concentrations of some SW components are most pronounced in the Solzan river (7.9–55.9 mg/l) and river Utulik (4.4–7.3 mg/l) valleys, which is most likely connected with the variations of the pollutant emissions by the BPPM and Baikalsk heat power plant and by the features of meteorological conditions of every particular year. The ion sums in SW in the basins of other rivers are low (see Fig. 2), and their variations in different years do not exceed 1–1.5 mg/l.

The values of accumulation of acidifying components in snow cover in the river basins also depend on the location with respect to Baikalsk. The highest sulfate accumulation was observed in the valley of Solzan river (Table 2), but the acid load was insignificant there, because accumulation of neutralizing cations of calcium (0.29 t/km^2) and sodium (0.43 t/km^2) is also high. With the increasing distance from Baikalsk, the accumulation of sulfates in snow decreases 4.5–8 times. The accumulation of nitrate nitrogen and hydrogen ions increases simultaneously (Table 2).

Table 2. Atmospheric income of sulfate sulfur, nitrate nitrogen, and hydrogen ions, t/km^2

Station	SO_4^{2-}(S)		NO_3^- (N)		H^+
	Winter	Year	Winter	Year	Winter
Baikalsk*[12]	1.24	3.86	0.07	0.32	0.00003
Khamar-Daban*[12,4]	0.39	1.2	0.04	0.18	0.003
Utulik	0.07	0.23	0.04	0.17	0.00053
Solzan	0.40	1.23	0.06	0.26	0.00007
Khara-Murin	0.09	0.28	0.07	0.32	0.0018
Snezhnaya	0.06	0.18	0.06	0.26	0.0015
Pereemnaya	0.07	0.21	0.07	0.34	0.0013
Mishikha	0.05	0.16	0.05	0.25	0.0015

* 1980–1986.

Analysis of many-year data has shown that the maximum income of sulfate sulfur and nitrate nitrogen in the region of Baikalsk and Khamar-Daban was observed in the 1980s.[11,12] In the recent year the ecological situation has improved in connection with nature-protection measures undertaken at the BPPM and Baikalsk heat power plant, in particular, the sulfur inflow from the atmosphere in the region of the Solzan river has decreased by 3 times, and the nitrogen inflow has decreased by 1.2 times (see Table 2). In the valleys of other rivers, the situation is somewhat different: the sulfur inflows from the atmosphere have decreased by 4 to 8 times, while the inflow of nitrogen has increased. The highest increase (by 1.9 times) of the nitrogen inflow is observed in the region of the Pereemnaya river, whose basin lies on the path of the main air mass transport along the valley of Angara river. Obviously, the increase of nitrate deposition is caused by the increase in the content of nitrogen oxides in the atmosphere. This is likely caused by their transport from industrial enterprises of the Angara region or by exhausts from traffic at the neighboring highway. It is quite possible that in the region under study the content of nitrogen oxides grows against the global level in the atmosphere due to large amount of precipitation. Thus, the global emission of NO into the atmosphere increased since 1975 to 2000 by 50%, while that of SO_2 increased only by 25% (Ref. 13). The increase of the nitrate deposition with precipitations was also observed in the European part of Russia.[14] The maximum accumulation of H^+ ions was noticed in the snow cover of the Khara-Murin river valley (see Table 2).

Based on the results obtained we have considered the possibility of SW acidification in the valleys of the rivers of the southeast shore of Lake Baikal. For this purpose, we have calculated the ratios of the equivalent concentrations of cations ($C = (Ca^{2+} + Mg^{2+} + NH_4^+ + Na^+)$) and anions ($A = (SO_4^{2-} + NO_3^-)$). The chlorine ions and potassium ions were neglected because of their low content. At the C/A ratios equal to or higher than unity, the acidity of anions of strong acids is fully neutralized in SW, and, consequently, there is no threat of acidification of the surface water and soil upon interaction with snowmelt water.

The calculations have shown that the situation is most favorable, in this respect, in the basins of Solzan and Utulik rivers; the C/A ratio is, on the average, higher than 1 there, and pH varies from 5.3 to 7.4. In the basins of other rivers, pH of precipitations varies from 4.6 to 5.5, and the ion ratios vary from 0.6 to 0.9 (see Table 1), that is, the acidity of anions is not fully neutralized in SW. It has been established that SW with low mineralization is subject to acidification.

Analysis of the interannual dynamics of the equivalent ion ratios has shown that since 1997 to 2002 the average C/A ratio in the region of the Khara-Murin and Mishikha rivers decreased, that is, the excess acidity remains increasingly not fully neutralized. In the basin of the Pereemnaya river the C/A ratio decreased from 0.9 to 0.7 (see Table 1), that is, in this region the risk of acidification of the surface water gradually increases.

Chemical composition of river water

The rivers flowing from the northwestern slope of Khamar-Daban are characterized by close natural conditions of the formation (mountain landscapes, washing water conditions, high moistening), but differ in the composition of the underlying rock in their catchment basin and in the chemical composition of incoming atmospheric precipitations. The tributaries of South Baikal have low water mineralization, varying from 14 to 110 mg/l depending on the river runoff. The annual variations of the concentration of some ions and their total content in the river water are similar, being governed by the dynamics of the water content.[2]

The highest mineralization of water is observed in the Utulik river (Fig. 4), which is connected with the carbonate strata situated within the basin of this river.[5] The lowest mineralization is characteristic of the Pereemnaya river, whose basin consists of acid silicate rock and has the abnormally high water content.[15,16]

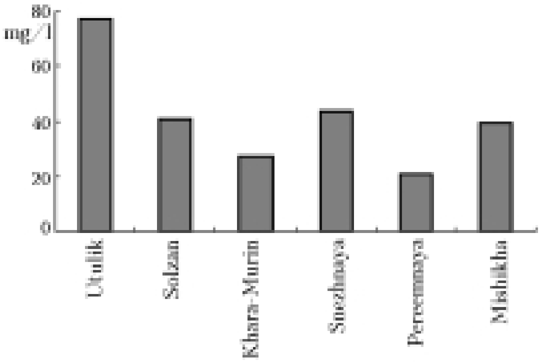

Fig. 4. Average annual ion sum in water of South Baikal, 2002.

In the composition of main ions, the waters of the studied rivers fall in the hydrocarbonate class of the calcium group, and only the water of the Pereemnaya river can alternate the hydrocarbonate class to the sulfate one. The unstable character of the water composition in this river is caused by the extremely low mineralization (14–28 mg/l). This results in that even an insignificant change in the content of some ions causes alternation of the water class.[1,16]

Analysis of the results of many-year investigations into the chemical composition of waters of the tributaries in the current period and the comparison made with the data of the 1950s[16] have shown that the relative ion composition in the river waters has changed: the sulfate content has increased, while the content of hydrocarbonates and calcium has decreased (Fig. 5).

Similar distortions of the chemical composition of the surface waters due to high inflow of the acidifying agents to the surface with precipitations are also observed in other regions of Russia and the world.[17–19] As was noted above, the SW in the Solzan river basin shows the basic reaction, and its income to the river does not cause the acidification of the river water. However, the increased income of sulfates into the river basin results in their accumulation in soil,[20] and, as a consequence, in the increase of their runoff and the concentration in the River Solzan water (Fig. 5).

The increase of the sulfate concentration and the variation of the relative ion composition in the water of Utulik river can be explained by the income of SO_4^{2-} from the basin. The river water is not acidified, because the carbonate rock forming the river basin provides for the efficient neutralization of the acid SW components in the runoff formation.

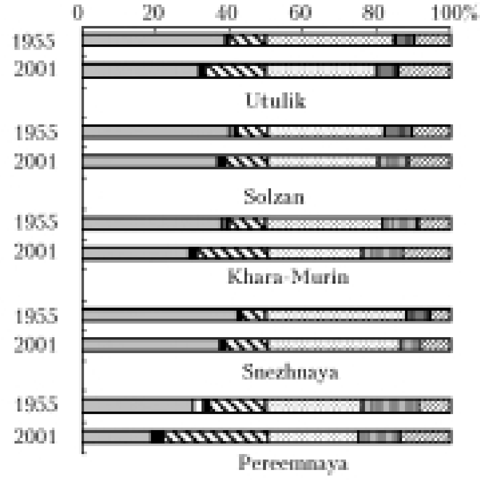

Fig. 5. Relative ion composition of river waters in Southern Baikal: HCO_3^-, Cl, NO_3^-, SO_4^{2-}, Ca^{2+}, Na^+K^+, Mg^{2+}.

The conditions of the runoff formation are quite different for the Khara-Murin, Snezhnaya, Pereemnaya, and Mishikha rivers, which are fed by precipitations with lower mineralization and increased acidity as compared with those in the Solzan and Utulik rivers. In addition, the acid rock in their basins does not provide for SW neutralization. As a result, in the snow-melting period, pH of the river waters decreases markedly. The lowest pH was observed in the Khara-Murin river (5.7), where the earlier pH did not drop lower than 6.0 (Ref. 15). When acid SW is mixed with low-mineralized river water, the established ion balance in these rivers is disturbed (see Fig. 5).

Conclusions

The investigations we have carried out revealed that the chemical composition of the surface waters in the region of the northwest slope of the Khamar-Daban ridge is largely determined by the composition of atmospheric precipitations. In the basins of the Solzan and Utulik rivers, the acid components coming into the basin are fully neutralized and, as a consequence, there is no threat of acidification of the surface waters.

Farther to the east, in the region between the Khara-Murin and Mishikha rivers, the influence of industrial emissions decreases. The SW mineralization and pH become lower. The continuous deficit of cations is observed in the SW composition, which causes incomplete neutralization of the total acidity of sulfates and nitrates. There is a real threat of acidification of the surface waters during snow melting, as is indicated by the shift of the balance of the basic ions in the river waters toward the increase of the sulfate fraction and the decrease of the fraction of hydrocarbonates and calcium. It has been established that the low-mineralized snowmelt and surface waters with low buffer capacity are most subject to acidification.

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