

Features of the Formation of Chemical Composition of Snow Drainage in the Closed Drainage of the Ob' – Irtysh Interfluve

SERGEY V. TEMEREV¹, VLADIMIR P. GALAKHOV², ALLA N. EYRIKH¹ and TATIANA G. SERYKH¹

¹*Institute for Water and Environmental Problems, Siberian Branch of the Russian Academy of Sciences, Ul. Papanintsev 105, Barnaul 656099 (Russia)*

E-mail: temerev@chemwood.dcn-asu

²*Altay State University, Pr. Lenina 61, Barnaul 656000 (Russia)*

(Received May 31, 2001; in revised form July 10, 2002)

Abstract

Results of field observations of the formation and distribution of the chemical sink of mineral substances and heavy metals in the closed drainage of the Ob' – Irtysh interfluve in 1995–1997 are presented. By means of snow-measuring monitoring, laboratory analysis of snow melt and lake water, solid snow particles, suspended matter and bottom sediments of the largest salt lakes: Kulundinskoye, Kuchukskoye and Bol'shoe Yarovoye, the quantitative estimations of the drainage and distribution of heavy metals are obtained. Physicochemical features of this distribution are discussed. With the help of the indication method of chemical analysis, we demonstrate the effect of point sources of chemical substances released by chemical plants, and diffuse sources from which chemical substances enter the closed drainage water ecosystems of the interfluve.

INTRODUCTION

Problems of sustainable development of Siberia are at present to a large extent determined by ecological problems, including the status of water ecosystems. The features of the formation of chemical snow drainage affect the quality of surface water [1] during spring high water when chemical substances accumulated during autumn and winter periods of snow accumulation enter water reservoirs and water flows with snow melt within a short time interval.

The goal of the present study is to estimate chemical composition of the snow drainage and the features of its formation under the influence of natural factors (blind drainage, increased mineralization of surface water, aeolian transport of mineral salts, high natural content of mineral forms of sulphur in the components of the environment, *etc.*), and point sources of anthropogenic load onto water ecosystems from chemical plants: Altaykhimprom

JSC (Yarovoye, Slavgorod district, Altay) and Kuchuksulfat JSC (Stepnoye Ozero settlement, Blagoveshchenka district, Altay Territory). Both plants are powerful manufacturers of chemical reagents and materials in Russia. The former manufactures mercury oxide, the raw material being metal mercury. Till 1994, Altaykhimprom JSC was importing 160–200 t of mercury annually. The second plant is a monopolist in Russia for the production of sodium sulphate from natural mirabilite. In addition, Kuchuksulfat JSC manufactures sodium sulphide by reducing the sulphate sulphur with carbon. According to the data of the regional ecological committee, such a technology leads to the release of hydrogen sulphide, 112.1 t/year, sulphur dioxide, 234.2 t/year, and sodium sulphate, 835.0 t/year. In the 70-ies of the previous century, the water area of the Kulundinskoye Lake had been intensively used as a proving ground for aviation bombing for the Warsaw treaty countries.

Long ago, the mentioned salt lakes had been used not only as the sources of mineral salts but also as recreation territory for mud cure. Because of this, the investigation of ecological status of water ecosystems and water-collecting basin of the blind drainage area is of scientific and practical interest. The features of the formation of snow drainage within the range of the influence of large chemical plants (point anthropogenic sources) and natural distributed sources of mineral salts, *i. e.* blind drainage lakes of the Kulunda depression, have not been investigated yet.

EXPERIMENTAL

A blind-drainage area between the Ob' and the Irtysh was selected as the subject of investigation [2]. In order to reveal the ecological status of the components of water ecosystems of this drainage-free region, complex monitoring hydrochemical investigations of the snow cover, surface water, bottom sediments and soil were performed in the basin of Bol'shoye Yarovoye lake in 1995; in 1997, complex monitoring hydrochemical investigation of the snow cover, surface water, and bottom sediments in the water bodies of Blagoveshchenskoye district of Altay was carried out; the largest among

these water bodies are Kulundinskoye and Kuchukskoye lakes.

The Kulundinskoye, Kuchukskoye, and Bol'shoye Yarovoye lakes are situated in the western part of the Kulunda depression (Fig. 1); these lakes are among the largest acrid lakes of the blind-drainage region between the Ob' and the Irtysh [2]. The Kulundinskoye lake has the area of water mirror 728 km², its drainage area is 24 100 km². The Kulunda river flows into it. The Kuchukskoye lake has moderate hydrological characteristics: 181 and 3240 km² [3]. The Kuchuk river flows into it. In the mouth, it has a regulated stream. The salt content of the water of Lake Kuchukskoye exceeds that of Lake Kulundinskoye by a factor of more than 5. Lake Kuchukskoye is situated in the central part of the Kulunda depression and is the most salty one in the blind drainage area. It is so salty that it does not become frozen during some winters. While going farther from the Kuchukskoye lake, total salt content of the lake water in the Kulunda depression decreases [4]. Total salt content of the water of Lake Bol'shoye Yarovoye is 170–250 g/l, which is less than that of Lake Kuchukskoye. Among the cascade of lakes of the blind drainage area of the Ob'-Irtysh basin, Lake Bol'shoye Yarovoye has a medium size. Its length is 11 km,

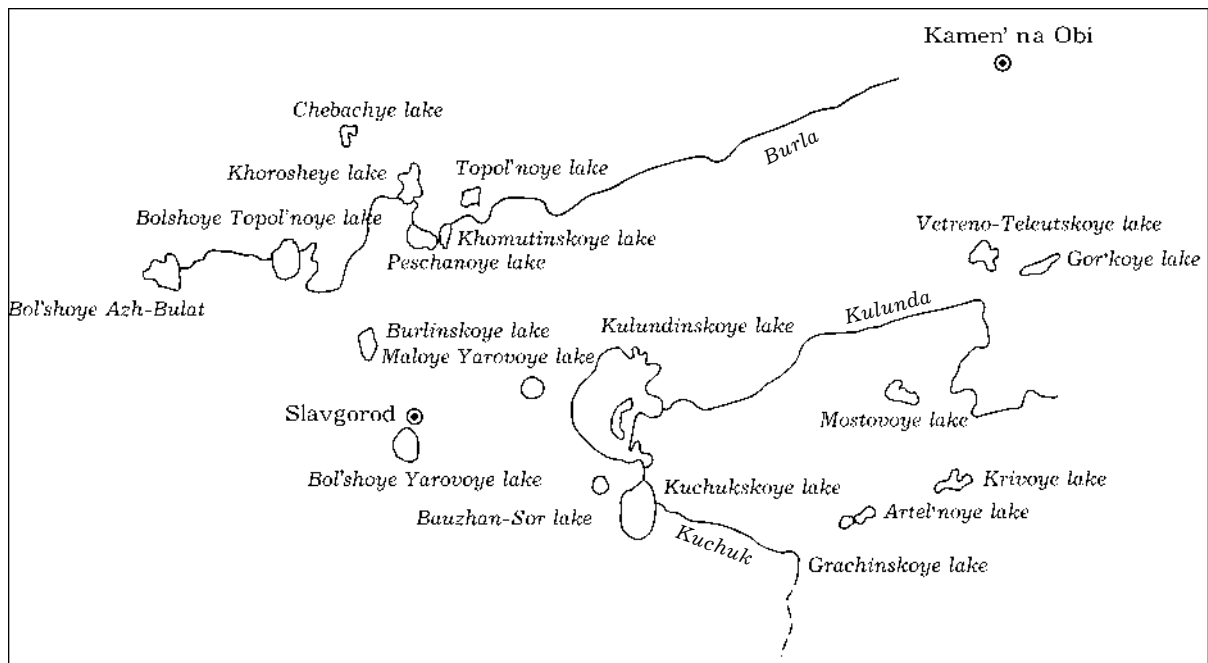


Fig. 1. Scheme of lakes at the northwest of the Altay Territory.

width 7.9 km, mean mirror area 66.7 km². Total drainage area, including the mirror, is 1210 km² [4]; among these, the blind-drainage area is 582 km². The lake hollow is up to 25 m deep. The lakesides are steep with the height variation 10–15 m; they are cut by deep ravines; the lakesides are composed of clay sand. In the region of shore line, there are shows of subterranean waters at the sides. Bottom sediments are composed of silt with mirabilite layers 0.6 to 1.5 m thick. In the natural climatic aspect, the drainage area is a dry soddy grassy steppe with small amount of atmospheric precipitation (250–300 mm per year) [5]. The soils are represented by chestnut soil with inclusions of saline lands [6].

In order to determine the sources from which chemical compounds come, and their spatial distribution, we used the indicative method of determining ion composition and heavy metals (HM) in the components of water ecosystems: in snow cover over the drainage area (schemes of sampling sites are shown in Figs. 2 and 3), suspended matter (SM) and bottom sediments (BS). For the integral estimation of the atmospheric emission of mercury from the Altaykhimprom plant on the surface of drainage area of Bol'shoje Yarovoye lake, we investigated the snow cover because the snowing period lasts for more than 5 months a year in this region. The territory at which samples were taken embraced 40 km²; it was chosen taking into account the wind rose, because the southern winds are prevailing during the snow accumulation period [5]. Atmospheric precipitation of the cold season usually account for about one third of the amount per the warm season [7].

The snow was sampled during the period of maximal snow accumulation (March 1–3, 1995; 17 samples; see Fig. 2) over the whole depth of snow layer. Snow sampling was also performed in the basins of Lakes Kulundinskoye and Kuchukskoye in March, 1997; 22 samples were collected at the territory with the total area of 1024 km² (see Fig. 3) during the maximal snow accumulation period (March 12–14, 1997) over the entire depth of snow layer with a special plastic sampler with the sampling area of 0.0314 m². In each sampling

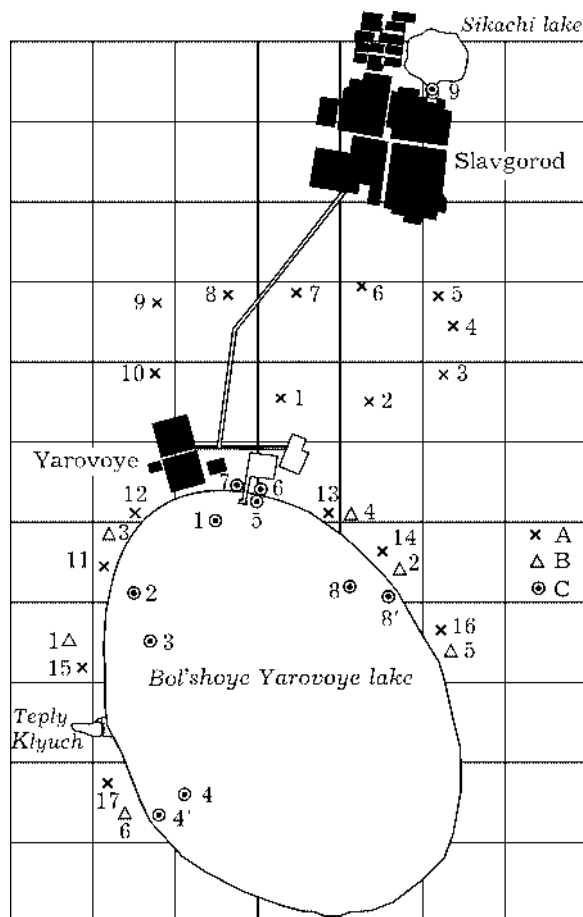


Fig. 2. Schematic map of sampling sites: A – snow samples, B – samples of soil from tailings, C – samples of water, suspended matter and bottom sediments.

site, 2 to 7 core samples were taken at a distance of 1–3 m from each other.

Thus sampled cores were placed in pure double polyethylene bags and delivered to the analytical laboratory in the frozen state. Under the laboratory conditions, the snow was thoroughly mixed in the packed state. Then, 3–4 portions of snow were taken from each bag; the portions were placed in separate 2 l flasks, closed with Petri dishes and kept at room temperature to obtain melted water. Then, 50 ml of water was poured off each flask in order to perform direct potentiometric measurements. The pH of melted water was determined with a glass electrode, E_h was measured by the wire Pt electrode at a temperature of 20 °C with respect to the reference silver chloride electrode and calculated for the hydrogen scale. Then the snow water was filtered under the argon pressure of 1–2 kg/m² in aliquots of 1 l through



Fig. 3. Schematic map of snow cover sampling sites in March, 1997.

the membrane nuclear filters with pore diameter of 0.45 μm . The filtrate was acidified with nitric acid (chemically pure reagent grade, State Standard GOST 4461-77) and analyzed, immediately after filtering, for heavy metal content by means of atomic spectrometry with different versions of atomization of liquid samples. Cadmium, copper, lead, and zinc were determined in a graphite cell (AAS 30 ETA), iron and manganese were atomized in flame (AAS 1N), arsenic and selenium were determined with the hydride method by reducing with sodium borohydride (AAS 30 HS), mercury was determined by means of the cold vapour (mercury analyzer Yulia 2) by reducing with the chloride of divalent tin in hydrochloric acid [8]. The major anions: chloride, sulphates and nitrates – were determined within 3 h after filtering in all the 22 samples of snow water.

Additionally, the hydrochemical analysis of the snow water was performed. All the hydrochemical characteristics were determined using the standard analysis procedures for surface waters [9–11]. Total mass of snow sampled in each site was measured preliminarily by weighing with technical balance. Specific chemical sinks were calculated. When calculating, we took into account the snow accumulation period of 150 days [7] and sink coefficients [12]. The filters with solid particles from the snow water were dried at room temperature and weighed with the analytical balance. The gravimetric data were used to estimate the solid snow sink. Solid particles were washed off the filters with nitric acid (1 M), then decomposed with a mixture of acids $\text{HNO}_3 : \text{H}_2\text{SO}_4 : \text{HCl} = 2 : 1 : 1$; in order to exclude the losses of mercury, the resulting solution was evaporated with the reflux con-

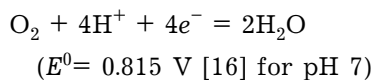
denser till humid salts, and diluted with bidistilled water to 30 ml.

RESULTS AND DISCUSSION

Snow cover as an indicator of chemical pollutants

The hydrochemical characteristics of the snow and lake water of the blind drainage part of the territory between the Ob' and the Irtysh are shown in Tables 1-4.

Comparing the obtained hydrochemical data one should note higher activity of snow water in comparison with the lake water of the same region (see Tables 1, 3). A more positive redox potential E_h characterizes its higher oxidizing ability, a 10 000 times lower salt content and pH lower by 2-3 units are the evidence of the dissolving ability. The major part in the formation of sink of chemical substances is played by the oxidation and dissolution processes, which go on more actively in the melted water for the case of snow sink; the processes that play the most important part in the physicochemical and spatial distribution are the reverse processes for reduction - sorption (accumulation) in the porous waters of BS with the participation of natural minerals, organic substances, biogenic elements, and reducing anaerobic bacteria [13, 14]. Snow water contains much higher amount of dissolved oxygen during melting (1.62-1.75 mmol/l) [10] (for comparison: 0.4-0.7 mmol/l for lake water). Oxygen dissolved in snow water determines more positive oxidative-reductive potential E_h [15] (see Tables 1, 3). The equilibrium potential of water under standard conditions is described by the following semi-reaction:



Oxygen serves as an oxidizer in snow water. Reducing agents are sulphite, sulphide ions, and elementary sulphur, which are formed during snow melting from sulphur dioxide and hydrogen sulphide present in atmospheric precipitation, especially in the vicinity of the chemical plant (sample No. 15, see Table 2). It

TABLE 1
Hydrochemical characteristics of the snow (water drainage area) and lake water of the Bol'shoye Yarovoye lake (numerator: scattering; denominator: mean)

Water (number of samples)	pH	E_h , mV	Mercury content		Turbidity, g/l	Mercury sink module per day, mg/km ²
			in filtrate, µg/l	in solid particles, µg/g		
Melted (10)	4.74-6.39	509-636	0.004-0.018	0.31-1.27	0.075-0.259	14 [18]
	5.73	567	0.006	0.57 ± 0.23	0.147	
Lake (12)	8.05-8.24	375-443	0.004-0.006	0.1-0.4	0.032-0.071	3.1*
	8.16	404	0.005	0.22 ± 0.21	0.042 ± 0.019	

*Taking into account the sink coefficient [12].

TABLE 2

Hydrochemical characteristics of the snow water of the basin of Kulundinskoye and Kuchukskoye lakes

Sample No.	Salt content, mg/l	Alkalinity, mmol/l	Hardness		Mg ²⁺ , mg/l	Cl ⁻ , mg/l	SO ₄ ²⁻ , mg/l	SO ₃ ²⁻ , mg/l	S ²⁻ , mg/l	NO ₃ ⁻ , mg N/l	NO ₂ ⁻ , mg N/l	NH ₄ ⁺ , mg N/l	PO ₄ ³⁻ , mg P/l	Si, mg/l	Oxidability by KMnO ₄ , mg O/l	COD, mg O/l
			mg CO ₃ ²⁻ /l	mg HCO ₃ ⁻ /l												
1	25.25	4.6	0.18	1.8	1.1	10.3	4.3	3.1	0.005	1.7	0.02	0.09	0.40	0.5	4.8	17.1
12	25.25	6.1	0.15	1.7	0.8	7.4	4.7	2.3	0.010	2.0	0.02	0.07	0.20	0.5	6.6	27.8
15	64.75	18.6	0.51	5.7	2.7	10.3	82.3	2.3	0.013	1.5	0.03	0.15	0.36	0.5	6.7	25.7
18	34.75	3.1	0.25	2.8	1.3	11.2	7.4	2.2	0.005	3.5	0.01	0.17	0.23	0.5	3.2	19.3
MPC [11]	-	-	-	-	20	100	250	-	-	45	3.3	2.0	0.05	-	<2.0	30
Weakly contaminated water [9]	-	-	-	-	250	500	-	-	45	3.3	2.0	0.10	-	8-10	30	

Note. Snow sampling was performed on the 12-14 March, 1997. Sample numbers see in Fig. 3.

TABLE 3

Hydrochemical characteristics of snow (from the drainage area) and lake water of the Kulundinskoye and Kuchukskoye lakes (numerator: scattering; denominator: mean)

Water (number of samples)	pH	E_h , mV	χ , $\mu\text{S}/\text{cm}$ (mS/cm)*	SO ₄ ²⁻ , g/m ² (g/l)*	Cl ⁻ , g/m ² (g/l)*	NO ₃ ⁻ , g N/m ²
Melted (22)	<u>5.29 -6.68</u> 6.18	<u>487-588</u> +575	<u>14.2-344</u> 45.4	<u>0.12-3.93</u> 0.51	<u>0.14-4.42</u> 0.95	<u>0.04-1.34</u> 0.12
Lake						
Kuchukskoye lake (18)	<u>8.11-8.31</u> 8.19	<u>374-475</u> +444	<u>182-200</u> 190	<u>42.1-61.4</u> 48.0	<u>190.9-221.1</u> 208.4	- -
Kulundinskoye lake (12)	<u>8.11-8.31</u> 8.19	<u>374-475</u> +444	<u>1.11-6.12</u> 3.1	<u>12.1-25.9</u> 14.8	<u>25.1-25.9</u> 28.6	- -

Note. Bidistilled water had the following characteristics: pH 5.86; E_h = +582 mV; χ = 3.15 $\mu\text{S}/\text{cm}$.

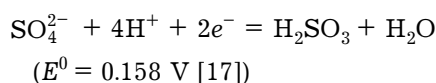
TABLE 4

Specific snow sink of HM bound with the solid particles of snow, and the dissolved anionic forms, corresponding to the maximal snow accumulation in 1997 at the area of 1024 km² of the Blagoveshchensky region

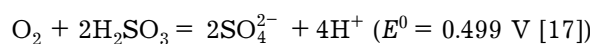
Characteristics	Fe	Cd	Mn	Cu	As	Hg	Pb	Se	Zn	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
Specific sink:												
scattering	17-416	0.1-29 (3-10 [23])	0.3-6.1	0.14-2.1	1-22	0.7-4.7	0.03-1.0	2-13	0.2-1.8	236-4423	119-3932	36-372
mean	81 (648)	6 (0.018)	1.3 (6.2)	0.6 (2.93)	5 (0.023)	2.1 (0.0054)	0.12 (0.213)	6 (0.031)	0.84 (4.44)	945	508	118
Total, t	82.9	0.006	1.33	0.614	0.005	0.002	0.123	0.006	0.86	902	468	184
Sink module per day, g/km ²	450	0.03	7.4	3.0	0.03	0.011	0.67	0.03	4.7	4890	2540	1000 (4650 [22])

Note. Units for Fe, Mn, Cu, Pb, Zn, Cl⁻, SO₄²⁻, NO₃⁻ - mg/m²; for Cd, As, Hg, Se - µg/m²; mean in parentheses: mmol/kg.

is evident that the equilibrium concentration of oxygen will be lower during snow melting due to the effect of reducing agents. The concentration of sulphite ions in snow water, determined by us (0.03-0.04 mmol/l), was likely to correspond to the equilibrium because the concentrations of sulphate and sulphite ions in the snow water are of the same order of magnitude. This equilibrium is described by the following semi-reaction:



Summing these two equations according to the rules [17], we obtain the overall equation for the electrode potential of platinum with respect to the hydrogen electrode under aerobic conditions:



Thus, during snow melting in the area affected by the atmospheric emission of the reduced sulphur species, sulphuric acid is formed, which renders additional dissolving activity to melted water. It is evident that the sulphide ions also participate in establishing the equilibrium potential but only to an insignificant extent. It should be noted that the above equations provide only schematic characterization of sulphur oxidation process in the case of its increased natural content in snow. Even the reference data on standard potentials [16, 17] differ substantially for different sulphur forms. The reduced ionic forms of sulphur (sulphite and sulphide ions) are hydrolyzed during snow melting, which is evident even from the increase of pH (see Table 3) in comparison with more acidic melted water from the drainage basin of Bol'shoye Yarovoye lake (see Table 1). This difference is due to the indirect influence of sulphide production at the Kuchuksulfat plant (Stepnoye Ozero settlement, see Fig. 3) because of atmospheric precipitation containing sulphur dioxide, hydrogen sulphide, and because of aeolian transport of sodium salts from the plant to the north-northeast (see Fig. 4 demonstrating the spatial distribution of the mineral composition of snow cover).

In the lake water, the concentrations of chloride and sulphate ions are thousand times

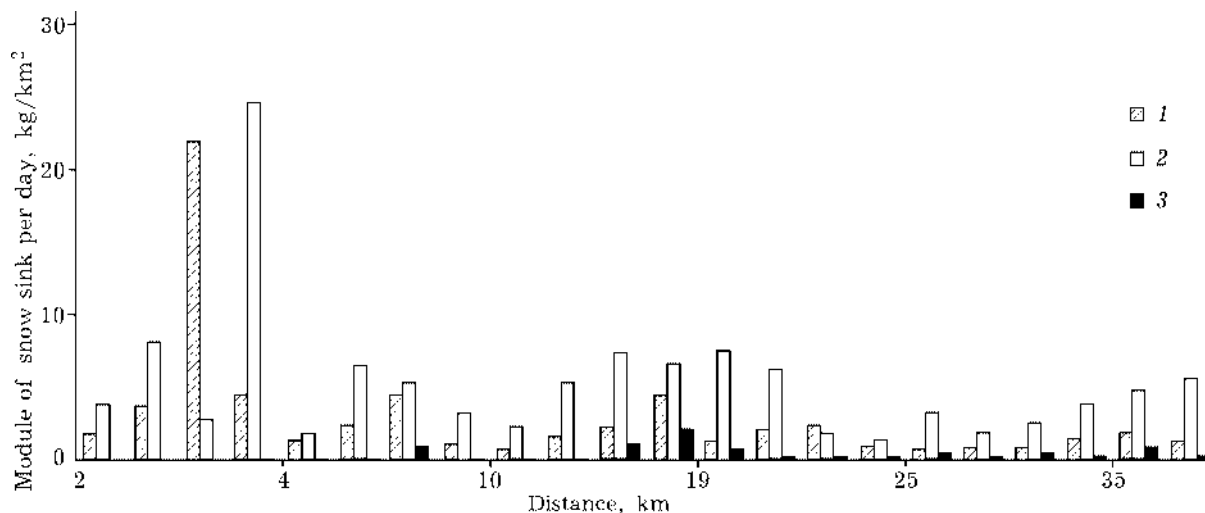
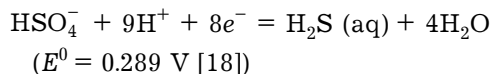


Fig. 4. Dependence of the module of snow sink for the main anionic forms on the distance between sampling sites and the Kuchuksulfat Plant (see Fig. 3): 1 - sulphates, 2 - chlorides, 3 - nitrates.

higher, pH is higher by 2–3 units at the increase of carbonate alkalinity [18, 19], the decrease of E_h by about 100 mV is observed. The brine of the investigated lakes is rather stable with respect to the mineral composition and does not exhibit any changes. However, some freshening of water is noticed, as compared with the 50-ies of the previous century [18], and seasonal variations of salt content not connected with chemical reasons.

Under anaerobic conditions, insignificant acidifying (by a pH unit) of the porous water of bottom sediments occurs along with very substantial decrease of the E_h potential (Table 5). The decrease of oxygen concentration is connected with the emission of hydrogen sulphide:



which is rather efficient reducing agent. No substantial acidifying of the bottom sediments is observed because of the hydrolysis of the reduced ionic forms of sulphur and insignificant solubility of hydrogen sulphide in water. The reductive processes in porous waters are multiple-factor ones; they depend on the organic substance, anaerobic sulphur bacteria and living organisms, *i. e.* the reduction of sulphate is most likely a biochemical process [14]: (SO_4^{2-} , sulphates) \leftarrow sulphur bacteria, SH groups of organisms \rightarrow (H_2S , sulphides).

The emission of hydrogen sulphide is most intensive in sites where fresh waters enter salty lakes, in the estuaries of the Kulunda and the Kuchuk rivers (the most negative E_h in Table 5). In these places, there are the developed bottom sediments with intensive smell of hydrogen sulphide. Thus, the oxidation reactions (reduction for the porous waters of BS) affect the formation of chemical composition and the surface waters of the investigated region [3, 4, 13]. More essential physicochemical processes that must be taken into account when estimating the sinks of mineral substances and HM from the drainage basin under the increased salt content of soil will be heterogeneous processes [1] (dissolution, sorption/desorption), and physical processes (sedimentation of SM in BS, denudation of soil, infiltration, evaporation, *etc.* [20]).

The closed drainage under investigation belongs to natural complexes with the increased natural content of sulphur forms (see Table 2). The dependence of the module of the snow sink of the main anions on the distance between the sampling sites and the plant is shown in Fig. 4. One can see that the effect of the plant is restricted to a 5 km region and is expressed as a substantial increase of the sink of sulphates, because the isolation of sodium sulphate from the brine of the Kuchukskoye Lake is performed by open-cut mining. However, with increasing distance from the plant, this influence is leveled by the strong aeolian trans-

TABLE 5
Ranges of the variations of chemical composition of BS

Water body	pH	E _h , mV	Se, µg/g	Cu, µg/g	Pb, µg/g	Cd, µg/g	Zn, µg/g	Co, µg/g	Fe, µg/g	Mn, µg/g	As, µg/g
Plotava lake (fresh water)	9.2	30	0.19 (2.4)	3.9 (61)	0.3 (1.4)	1.1 (9.8)	3.4 (512)	1.2-2.3 (30)	1.3-2.7 (35.8)*	31-93 (1.1)*	0.6-0.7 (8.7)
Kulundinskoye lake (n = 4)	7.32-9.08	-6...+204	0.10-0.56 (3.9)	3.6-7.8 (85)	0.27-0.92 (2.5)	0.16-0.76 (3.1)	2.1-19 (214)	1.3-4.1 (87)	1.2-8.8 (77.8)*	47-279 (2.2)*	1.4-5.3 (29)
Kuchuk lake (n = 6)	7.00-8.19	-21...+179	0.22-0.70 (3.6)	0.85-37 (190)	0.11-1.2 (1.8)	0.17-2.3 (6.1)	2.3-75 (320)	1.1-5.7 (45)	1.4-14.7 (91.8)*	43-354 (2.9)*	2.4-5.2 (52)
The Kuchuk river (n = 2)	7.52-7.80	-18...-20	0.28-0.31 (3.7)	4-35 (351)	1.9-2.8 (7.7)	0.49-0.57 (5.3)	62-73 (851)	1.7-4.2 (44)	2.7-20.1 (231)*	92-590 (7.5)*	3.3-6.1 (66)
The Kulunda river (n = 2)	7.89-8.14	-12...-154	0.10-0.48 (3.7)	8.3-21 (231)	0.85-2.4 (8.7)	0.18-0.26 (2.2)	24-41 (558)	4.2-5.2 (80)	8.3-9.4 (159)*	243-343 (5.3)	3.1-3.9 (47)
Molar ratio											
SP : BS (lakes)			8.9	16	48	3.4	9	-	5.4	1.6	0.6

Note. The contents of all the components are calculated for dry samples; in parentheses: micro(*milli)moles per kilogram.

port of sulphates from the surface of the Kuchukskoye Lake and, to a less extent, from the Kulundinskoye lake in the northeast direction. The occurrence of the aeolian transport is confirmed by the cymbate dependence of the sink module of chloride ions on the distance from the plant (which is situated on the northern shore of the Kuchukskoye lake). An increase of the sinking amount of nitrates at a distance of 15-20 km (see Fig. 4) is connected with the influence of the delta of the Kulunda river, which serves as a specific collector of agricultural sewage containing high concentrations of nitrates, organic substances [13] and cadmium, brought with mineral fertilizers on the surface of the drainage basin during the formation of snow cover.

According to the data averaged over many years [21], the duration of spring high water in the Kuchuk river is 20 to 70 days; during this time, 26 to 88 % of the total amount of annual water flow enters the water ecosystem of the Kuchukskoye lake. The major hydrochemical characteristics of the melted and lake water and the quantitative estimates of chemical sink of HM from the investigated part of the Kulunda depression are shown in Tables 1-4. HM are rather dangerous toxic agents; under the conditions of naturally increased salt content of water ecosystems of the closed drainage between the Ob' and the Irtysh, HM can affect the ecological state of the ecosystems, especially during intensive melting of snow.

The obtained hydrochemical data allowed us to estimate total sink of Hg into the Bol'shoje Yarovoye lake and into the Kuchuk-Kulunda set of lakes. In spite of the background values of sink module, according to the data shown in Tables 1 and 4, the module of snow sink in the Slavgorod region is somewhat higher than that in the Blagoveshchenka region, which can be an indirect confirmation of the effect of mercury emission from the Altaykhimprom Plant (Yarovoye). Using suspended forms of arsenic as a chemical indicator, we stated the effect of the chemical plant on the water ecosystem of the Bol'shoje Yarovoye lake, as a point source of arsenic. By analyzing the suspended forms of arsenic, we stated a negative gradient of its concentration in the suspended

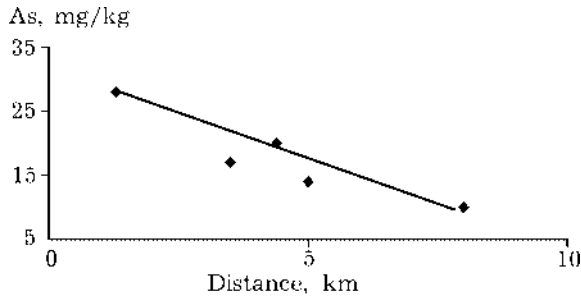


Fig. 5. Dependence of specific concentration of arsenic in the suspended matter on the distance from the Altaykhiprom Plant to the south.

matter while the distance from the point source (Altaykhiprom Chemical Plant) increases (Fig. 5).

The analysis of mercury content of the snow cover and soil (Table 6) allowed us to identify the main diffuse source of mercury in the water ecosystem of the lake; this source is the tailings of the chemical plant at the shore, especially during intensive snow melting. A quantitative estimation of the chemical snow sink of mercury has been performed with and without taking into account the secondary contamination with mercury [18, 19]. The generalized data on the sink of HM bound with the solid particles in the snow at the investigated territory of the Blagoveshchenka region are shown in Table 4 (see Fig. 3). The authors of [22] dealing with the influence of the Severonikel' metallurgical plant on the snow cover at the Kol'sky Peninsula report a hundred times larger sink module for copper, while the specific annual sink of sulphates is of the same order of magnitude (see Table 4). An estimation of the specific atmospheric precipitation of cadmium in the coastal region of the Japanese Sea, described in [23], was 3–10 $\mu\text{g}/\text{m}^2$.

TABLE 6

Meanmercury content of conservative components of the water ecosystem of Bol'shoye Yarovoye lake and heavy metals in biota, mg/kg

Hg					Pb	Cd	Cu	Ni	Zn	Fe	Mn	Hg	As
SP	SM	BS	PS										
0.57 ± 0.23	0.22 ± 0.21	0.16 ± 0.14	140 ± 103	< 2.5	0.3	2.2	3.5	24	388	306	0.39 ± 0.12	5.9 ± 1.4	
[19]													

Note. The SP : SM : BS : PS molar ratio is 2.8 : 1.1 : 0.8 : 700. Mercury Clarke for clays: 0.4 mg/kg (according to A. P. Vinogradov [20]).

Higher cadmium content of the snow cover of the Kulunda depression is connected with the intensive agricultural activities in the basic of the Kulunda river and the migration of metal into the delta followed by its transportation into the snow cover. This way of Cd emission is confirmed by the data of [13] stressing the increased Cd content of water in the Kulunda river and especially in the Kulundinskoye lake.

Thus, the effect of salt lakes in the blind drainage area of the territory between the Ob' and the Irtysh on the chemical snow sink has been demonstrated experimentally at the level of the effect of seas on their shores. A higher dissolving and oxidizing activity of the snow water with respect to the brine of salt lakes is stated; the amount of chemical sink follows the same regularity. By means of indication procedure, the spatial distribution of snow sink of the main anion has been obtained; the effect of the diffuse natural sources of mineral salts situated on the surface of salt lakes is confirmed. By means of chemical indication (arsenic, mercury), the point and diffuse sources of the anthropogenic emission of these toxic agents into the water ecosystem of the blind-drainage lake are identified.

Distribution of HM snow sink over the water reservoirs

In order to investigate the physicochemical distribution of the solid snow sink of HM over the components of water ecosystems, we used molar ratios in the row: snow particles (SP) : SM : BS. The comparison of natural data presented in Tables 3 and 4 shows that the mineral sink of chlorides, sulphates and nitrates

prevails over the sink of HM. The content of the sorbed forms of HM in snow exceeds that of their dissolved forms substantially: Hg – 4–10 times, Cd – 5–6 times, Pb – 2–3 times, As – 2–4 times, Fe – 35–40 times, Mn – 3–9 times. The determination of the concentration of HM in snow water is limited by the possibilities of the technique. For example, Cu content of the snow water was less than 1 µg/l, As less than 0.04, and Se less than 0.1 µg/l. Because of this, when calculating total amount of sink, the content of HM chemically bound with the solid particles of snow (0.03–0.05 g/l), flowing into the lakes in the form of suspended matter and entering bottom sediments, was calculated taking into account the concentration of solid particles in snow.

Comparative analysis of the specific content of mercury bound with the solid particles of snow and soil (PS) that enters the components of the water ecosystem of the Bol'shoye Yarovoye lake is shown in Table 6. Judging from molar ratios, its content diminishes in the following sequence: PS > SP > SM > BS. Thus, soil of the tailings of the chemical plant serves as a diffuse source of the contamination of the water area. The data presented in Table 6 are also confirmation of the absence of any noticeable bioaccumulation of mercury in the blind-drainage ecosystem of the Bol'shoye Yarovoye lake. According to the data shown in Table 5, the molar ratio SP/BS increases in the row: Cd < Zn < Cu < Pb. This is connected with the presence of smaller fractions in the snow bulk and with their subsequent distribution between soil, SM and BS. The SP/BS molar ratio for selenium is nearly an order of magnitude higher than that for arsenic. This fact can be explained by the general increase of the selenium background accompanying sulphur. On the other hand, this may be the influence of mercury binding selenium under anaerobic conditions (negative E_h , reducing hydrogen sulphide medium) to form mercury selenide [16]. This assumption is confirmed by the fact that no selenium was detected in the bottom sediments of the Bol'shoye Yarovoye lake [19], while there are diffuse sources of secondary contamination with mercury.

CONCLUSIONS

Thus, the molar ratio of the forms of HM sorbed by the solid particles of snow bulk and by bottom sediments is determined for the salt blind-drainage lakes. It is stated that this ratio depends both on the chemical nature of metal and on the physicochemical properties of the solid and liquid phases determining the distribution of the chemical snow sink.

Acknowledgements

The investigation has been supported by the Altay Committee for Natural Resources and the Administration of the Blagoveshchenka district.

The authors express their deep gratitude to the researchers from the Laboratory of Water Ecology M. I. Kaveshnikov and E. N. Krylova, as well as to Z. I. Novoselova for assistance in organizing and performing the field measurements.

REFERENCES

- 1 H. F. David, Béla G. Lipták, Groundwater and Surfacewater Pollution, CRC Press LLC, N. W. Corporate Blvd, Boca Raton, Florida.
- 2 V. M. Savkin, Ekologo-geograficheskiye izmeneniya v basseynakh rek Zapadnoy Sibiri, Nauka, Novosibirsk, 2000.
- 3 Resursy poverkhnostnykh vod Sibiri. Gidrogeologicheskaya izuchennost', vol. 15, Altay i Zapadnaya Sibir', issue 2, Srednyaya Ob', Gidrometeoizdat, Moscow, 1967.
- 4 Ravninnye rayony Altayskogo kraya i Yuzhnaya chast' Novosibirskoy oblasti, issue 6, Gidrometeoizdat, Leningrad, 1962.
- 5 Prirodnoye rayonirovaniye Altayskogo kraya, in A. N. Rozanov (Ed.), Izd-vo AN SSSR, Moscow, 1958.
- 6 Atlas Altayskogo kraya, Izd-vo MGU, Moscow, 1978.
- 7 Spravochnik po klimatu SSSR, issue 20, part 3, Gidrometeoizdat, Leningrad, 1969.
- 8 Yu. S. Zelyukova, Posledniye dostizheniya v oblasti atomno-absorbtsionnogo analiza, Nauka, Leningrad, 1976.
- 9 Rukovodstvo po khimicheskomu analizu poverkhnostnykh vod sushi, in A. D. Semenov (Ed.), Gidrometeoizdat, Leningrad, 1977.
- 10 O. A. Alekin, Osnovy gidrokhimii, Gidrometeoizdat, Leningrad, 1970.
- 11 Kontrol' khimicheskikh i biologicheskikh parametrov okruzhayushchey sredy, in L. K. Isaev (Ed.), Moscow etc., 1998.
- 12 I. V. Babkina, Mestny stok yuga sredney Sibiri, Ph. D. Thesis, Irkutsk, 1997.
- 13 E. I. Tretyakova, T. S. Papina, *Khimiya v interesakh ustoychivogo razvitiya*, 8 (2000) 429.

- 14 N. Grin, U. Staut. D. Teilor, *Biologiya*, vol. 1, in R. Soper (Ed.), Mir, Moscow, 1996, pp. 313–314.
- 15 P. N. Linnik, B. I. Nabivanets, *Formy migratsii metallov v presnykh poverkhnostnykh vodakh*, Gidrometeoizdat, Leningrad, 1986.
- 16 Yu. Yu. Lurie, *Spravochnik po analiticheskoy khimii*, Moscow, 1989.
- 17 Ya. I. Turyan, *Okislitel'no-vosstanovitel'nye reaktsii i potentsialy v analiticheskoy khimii*, Khimiya, Moscow, 1989.
- 18 S. V. Temerev, T. S. Papina, E. I. Tretyakova, V. N. Morozova, *Chem. Chinese Univ.*, 20 (1999) 538.
- 19 S. V. Temerev *et al.*, *Ekologicheskiy analiz regiona (teoriya, metody, praktika)*: Sb. nauch. trudov, Izdvo SO RAN, Novosibirsk, 2000, pp. 120–135.
- 20 A. I. Perelman, *Geokhimiya*, Vysshaya shkola, Moscow, 1989.
- 21 *Osnovnye gidrogeologicheskiye kharakteristiki*, Gidrometeoizdat, Leningrad, 1975, vol. 6, issue 1.
- 22 V. Barcan, A. Sylina, *Water, Air and Soil Pollution*, 89 (1996) 49.
- 23 A. P. Nedashkovskiy, *Tez. dokl. 6 konf. "Analitika Sibiri i Dal'nego Vostoka-2000"*, Novosibirsk, 2000.