Hydrochemical Research and Geochemical Classification of Salt Lakes in the Pavlodar Region

A Ubaskin[1], A Kassanova[1,2], A Lunkov[1], K Ahmetov[1], K Almagambetova[1], N Erzhanov[1] and T Abylkhassanov[1]

[1]S. Toraighyrov Pavlodar State University, 64 Lomov Street, Pavlodar, 140000, Kazakhstan
[2]National Research Tomsk Polytechnic University, 30 Lenin Avenue, Tomsk, 634050, Russia

E-mail: asiyakass@mail.ru

Abstract. This paper presents the results of a study of the macrocomponent composition of 15 salt lakes of the Pavlodar region. For the first time, based on the data of the chemical composition and pH of the waters, the geochemical classification of the lakes of this region has been proposed. The study shows that the majority of the analyzed objects are lakes of chloride type with sodium cationic composition.

1. Introduction

Salt lakes are important sources of mineral salts - mirabilite, halite, soda, gypsum and others [1-3], in addition, recreational use of the territory of salt lakes is highly popular [4, 5]. Salt lakes that are unique in their physicochemical properties are rarely lifeless, their biota is represented by specific halophilic forms, in particular, to the crustacean Artemia Leach, 1819 [6-8]. Artemia is widely used as a starter feed for growing fish, crustaceans, farm birds [9, 10] in industrial conditions, for obtaining valuable medicinal and cosmetic products [11].

In the hydrochemical study of natural waters, an important issue is their classification. According to the Kurnakovo-Valyashko classification, salt lakes are usually divided into carbonate, sulfate and chloride chemical types. Sometimes they are also distinguished by their acidic and basic types, sodium and magnesium subtypes. Lakes with a pH of more than 9.0 are usually classified as basic types, lakes with a pH less than 9.0 and the predominant Cl^- anion are typical of chloride types; lakes with a pH less than 9.0 and the predominant SO_4^{2-} anion are typical of sulfate types [12, 13]. Hydrochemical characteristics of salt lakes are subject to significant chronological changes. The reason for the change in hydrochemical characteristics is cyclic fluctuations of climatic conditions, leading to periodic filling and drying of lakes [14,15].

Numerous brackish and salty lakes are widespread in the Pavlodar region. The ecosystems of these reservoirs located in the Irtysh plain and the Kazakh Uplands function in transgressive-regressive cycles [16]. Significant climate and water regime variability over years and seasons causes instability, both of individual components of aquatic ecosystems, and of all of them in total. Therefore, it is very important to study their geochemical typing, both from a scientific point of view, and for the development of recommendations for the protection and rational use of lake minerals and valuable hydrobionts.

Thus, the purpose of this study is to explore the chemical composition of salt lakes in the Pavlodar region, to establish the type of lakes and the seasonal change in the type of lakes over the period spring-autumn 2018.

It is known that the spatial arrangement of lakes of different salinity and chemical types does not have a definite pattern. Lakes with different water composition and salinity can often be located at a small distance from each other. In this regard, when choosing the lakes for hydrochemical analysis, we were guided, firstly, by the value of the lake for the commercial use of brine shrimp resources, and secondly, by lakes, with abiotic factors limiting the existence of brine shrimp populations, and thirdly, by geographical location (to cover most of the district centers) (table 1).

Table 1. The name and location of the investigated salt lakes

Name of the lake	Geographical coordinates	S, km^2	Water Regime	Ice Regime
Bastuz	52°39′ N, 75°01′ E	7.7	Dries out periodically	Does not freeze
Tuz	50º34′ N, 75°13′ E	7.1	Does not dry out	Gets frozen
Big Kosor	51°18′ N, 78°15′ E	2.9	Dries out periodically	Gets frozen
Muzdykol	53°43′ N, 76°02′ E	1.7	Dries out periodically	Does not freeze
Bayanbay	53°00′ N, 74°37′ E	2.8	Does not dry out	Gets frozen
Kalatuz	51º53′ N, 77º30′ E	8.5	Does not dry out	Does not freeze
Borly	51°49′ N, 77°58′ E	16.0	Does not dry out	Does not freeze
Aydarsha	51º45′ N, 78º48′ E	2.8	Does not dry out	Gets frozen
Seiten	51º55′ N, 78°07′ E	15.5	Does not dry out	Does not freeze
Zhamantuz	51°33′ N, 77°44′ E	2.1	Dries out periodically	Does not freeze
Uyaly	51°18′ N, 78°15′ E	3.8	Does not dry out	Gets frozen
Sharbakty	51°23′ N, 78°15′E	6.8	Does not dry out	Does not freeze
Balkazy	53°10′ N, 77°03′ E	4.8	Dries out periodically	Does not freeze
Kyzyltuz	51°52′ N, 75°58′ E	10.7	Does not dry out	Does not freeze
Kudaikul	51º39′ N, 78º11′ E	6.2	Does not dry out	Does not freeze

2. Results and discussions

Sampling and preservation of water was carried out according to the standard technique [17]. The total chemical composition of the water was determined in an accredited laboratory of the Kazakhstan Project-Research Institute "Kazakhstan Project" LLP. The total mineralization index was determined by the gravimetric method [17]. A potentiometric method was used to determine the pH of the samples. The content of Cl^-, NO_3^-, NO_2^-, PO_4^{3-} and SO_4^{2-} ions was determined by capillary electrophoresis [19], the content of Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+ cations by capillary electrophoresis according to [20]. The permanganate oxidizability, the total content of CO_3^{2-} and HCO_3^- ions were performed by titrimetric methods of analysis [18]. Determination of total iron content was performed by photocolorimetric method using sulfosalicylic acid [18]. For the analysis were used reagents brand "pure for analysis".

The results of the chemical analysis of the composition of water samples of salt lakes of Pavlodar region in the spring-autumn 2018 period are presented in table 2.

Table 2. The results of the chemical analysis of the composition of water samples of salt lakes

Name of the lake	Season	pH	Total minera-lisation	Fe	PO	Cl$^-$	SO$_4^{2-}$	HCO$_3^-$	CO$_3^{2-}$	PO$_4^{3-}$	Na$^+$	Ca^{2+}	Mg^{2+}	K$^+$
			g/l	mg/l		g/l				mg/l	g/l			mg/l
Bastuz	spring	7.70	190.5	0.06	29.7	104.3	19.10	0.37	<0.008	<0.25	59.59	0.670	6.39	<0.5
	autumn	7.61	275.8	0.11	25.5	142.1	26.53	0.50	<0.008	<0.25	96.53	0.0004	10.14	<0.5
Tuz	spring	8.21	39.1	0.07	19.7	22.0	4.54	0.36	0.096	<0.25	10.42	0.083	1.32	<0.5
	autumn	8.60	110.5	0.07	28.2	12.0	3.24	0.34	0.072	<0.25	93.40	0.190	1.15	46.2
Big Kosor	spring	7.72	73.3	0.09	23.8	40.6	4.51	0.23	<0.008	<0.25	19.41	1.800	5.96	<0.5
	autumn	7.50	199.8	0.12	28.2	122.6	8.42	0.38	<0.008	<0.25	51.62	0.770	15.98	<0.5
Muzdykol	spring	7.72	200.1	0.10	31.6	104.5	19.10	0.39	<0.008	<0.25	61.54	0.730	13.18	<0.5
	autumn	7.32	319.2	0.10	32.6	188.1	29.44	0.51	<0.008	<0.25	84.28	0.0004	16.81	<0.5

Bayanbay	spring	7.47	292.2	0.12	23.0	14.3	4.32	0.35	<0.008	<0.25	8.65	0.260	1.05	28.5
	autumn	7.30	356.7	0.10	30.3	176.5	53.06	1.15	<0.008	<0.25	105.50	0.0004	20.49	<0.5
Kalatuz	spring	7.92	167.4	0.19	28.3	90.1	7.98	0.49	0.1350	<0.25	55.24	0.410	11.99	<0.5
	autumn	7.40	192.1	0.09	31.0	104.4	11.35	0.61	<0.008	<0.25	62.80	0.300	12.67	<0.5
Borly	spring	9.16	57.2	0.08	24.8	26.7	5.49	2.32	1.380	<0.25	21.19	0.009	0.17	<0.5
	autumn	8.89	62.6	0.06	26.7	26.0	6.22	2.81	1.200	<0.25	26.17	0.012	0.20	<0.5
Aydarsha	spring	8.50	68.9	0.05	6.1	22.9	5.88	0.66	<0.008	<0.25	70.71	0.084	0.98	494
	autumn	8.70	74.4	0.04	6.4	36.9	7.81	1.01	<0.008	<0.25	64.11	0.057	0.92	442
Seiten	spring	7.80	115.9	0.05	3.7	49.4	6.47	1.04	<0.008	<0.25	99.73	0.045	0.13	365
	autumn	8.00	124.8	0.04	5.4	59.5	11.40	1.22	<0.008	<0.25	100.30	0.019	0.35	422
Zhamantuz	spring	9.00	157.4	0.05	4.6	67.8	17.11	0.22	<0.008	<0.25	101.40	0.430	2.07	479
	autumn	9.10	215.6	0.04	5.7	101.6	22.70	0.36	<0.008	<0.25	132.90	0.570	2.01	1012
Uyaly	spring	9.50	23.4	0.09	24.9	2.7	3.06	3.59	0.910	<0.25	11.99	0.015	0.08	17
	autumn	9.47	27.3	0.07	23.8	4.8	6.49	2.75	1.500	<0.25	11.62	0.0056	0.09	48
Sharbakty	spring	8.95	57.4	0.10	28.2	12.9	0.82	1.49	0.420	<0.25	40.56	0.020	0.43	11
	autumn	8.77	119.0	0.06	28.0	67.1	5.92	1.39	0.750	<0.25	43.47	0.004	0.54	<0.5
Balkazy	spring	8.40	131.1	0.10	25.0	32.1	51.28	0.51	0.096	<0.25	42.03	0.470	3.76	<0.5
	autumn	8.35	145.5	0.06	29.2	48.0	41.76	0.74	0.048	<0.25	47.77	0.296	6.92	<0.5
Kudaikul	spring	7.39	246.2	0.13	27.3	141.4	20.27	0.31	<0.008	<0.25	73.73	0.600	9.84	<0.5
	autumn	7.12	368.1	0.12	31.2	204.1	57.77	0.29	<0.008	<0.25	122.20	0.0004	15.49	<0.5
Kyzyltuz	spring	7.50	239.9	0.90	6.6	119.7	17.16	0.20	0.120	0.12	145.90	0.258	2.29	652
	autumn	9.00	282.6	0.04	5.7	252.7	22.39	0.42	<0.008	0.14	150.00	0.211	2.00	848

The content of total iron in the analyzed objects varies from 0.04 to 0.19 mg/l and varies slightly from spring to autumn and meets the standards for the maximum permissible concentration for water of reservoirs of the 1-2 categories (maximum permissible concentration of maximum 0.3 mg/l). In most water bodies, the content of nitrate and nitrite ions does not exceed 0.2 mg/l and does not change within six months, with the exception of the lakes Aydarsha and Zhamantuz, in which by the autumn the content of nitrate ions increases 13 and 57 times respectively, while according to the standards for water of water bodies of categories 1 and 2, their content does not exceed the norm (MPC_{NO2} not more than 3.3 mg/l, MPC_{NO3} not more than 45.0 mg/l). The content of phosphate ions in all salt lakes is less than 0.25 mg/l and does not vary during the spring and autumn periods.

Indicator content of organic substances is permanganate oxidation (PO). The minimum value of PO is observed for Lake Seiten and is 3.7 mg/l (spring), the maximum value is 32.6 mg/l and is typical for Lake Muzdykol (autumn). As a rule, the permanganate oxidation slightly rises from spring to autumn and is directly dependent on the total salinity. For lakes with high total mineralization, PO has the greatest value, lakes with lower mineralization have lower PO.

For further geochemical classification of salt lakes in the Pavlodar region, an important role is played by such indicators as pH, total mineralization, the content of anions Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-; Na^+, Ca^{2+}, Mg^{2+} cations. It is these cations and anions that are the basis of the macro-component analysis of lakes.

The total mineralization of water in lakes varies from 23 to 268 g/l in the spring, and significantly increases in the autumn from 27 to 367 g/l (figure 1).

According to the degree of mineralization, the lakes are divided as follows:
- slightly salted (Lake Uyala (spring, autumn), Lake Bayanbai (spring));
- highly salty (Lake Tuz (spring));
- slightly concentrated brines (Big Kosor (spring), Borley, Aydarsha, Sharbakty (spring));
- strong brines (Kalatuz, Seyten, Zhamantuz, Balkazy, Kyzyltuz);
- very strong brines (Bastuz and Muzdykol during the autumn period);
- super strong brines (Kudaykul and Bayanbay in autumn).

The findings show that the optimal levels of mineralization for the growth of the crustacean population are in the range from 34 to 299 g/l, in rare cases 320 g/l [20].

The pH value in the spring period ranges from 7.39–9.5. During the autumn period in most of the analyzed objects, the pH level rises or decreases slightly (figure 2).

The highest pH values are characteristic for lakes with lower mineralization, for example, the pH of Borly and Uyaly lakes are more than 9, and the total salinity is less than 60 g/l. The minimum pH values (7.12-7.3) are fixed in brine-type lakes. In all the lakes studied, this trend continues, with the exception to this rule being Lake Zhamantuz, which has a pH of more than 9 with a high level of salinity (more than 250 g/l).

It is known that the indicator of mineralization of natural waters is directly dependent on the content of such anions as Cl^-, SO_4^{2-}, CO_3^{2-} and HCO_3^-, and the pH of natural waters depends on the concentration of carbonate and bicarbonate ions [21].
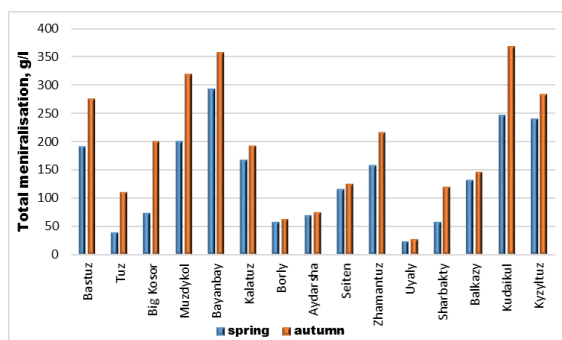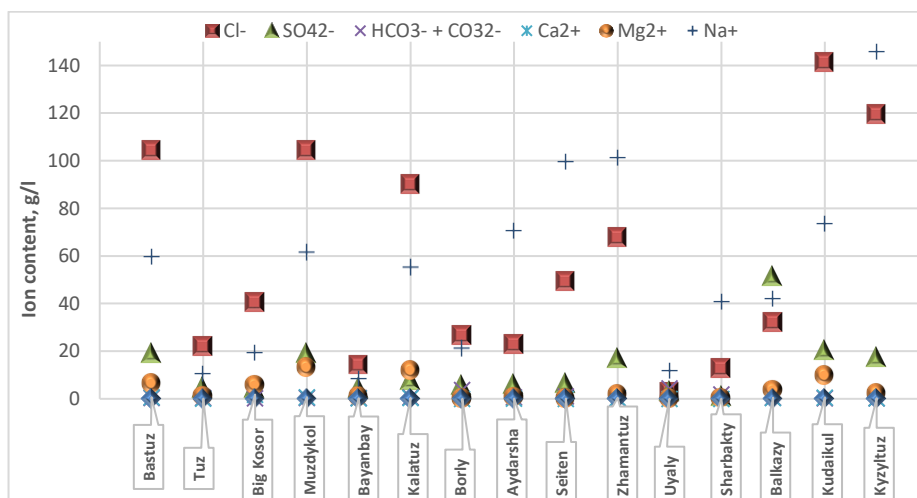

Figure 1. Graph of changes in the total mineralization of lakes in the period spring - autumn 2018.
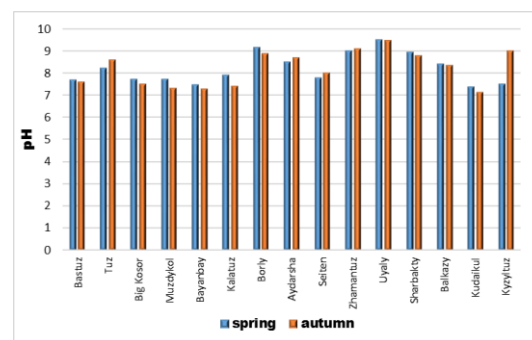
Figure 2. Graph of changes in the pH of the analyzed objects for the period spring-autumn 2018.

Figure 3 shows a graph of the dependence of the total salinity of lake waters on the content of the above-mentioned ions in the spring.

Figure 3. Graph of the content dependence of basic ions on the level of total mineralization in the spring period

As can be seen from the graphs presented, the predominant anion in salt lakes in the Pavlodar region in the spring is Cl^-, so most lakes can be attributed to chloride-type lakes. In spring, two lakes can be distinguished, where the dominant anion is not Cl^-. This is Lake Uyaly, where carbonate and bicarbonate ions are the predominant anion, and Lake Balcas, where the main anion is SO_4^{2-}. At the same time, taking into account the classification proposed in [13], lakes with pH> 9 can be attributed to basic or carbonate lakes. These are the lakes Uyaly and Borley.

To determine the cation composition of the analyzed objects, the dependence of the total mineralization index on the concentration of the main cations: Na^+, Ca^{2+}, Mg^{2+} was built.

According to the classification of lake types, all the studied lakes during the spring period can be divided into the following: carbonate or soda type (with a pH greater than 9) of the sodium subtype - 2 lakes (13% of the total); sulfate type of sodium subtype - 1 lake (7%); chloride type of sodium subtype - 12 lakes (80%).

The directional transformation of the chemical composition of lake waters is due to the concentration in the summer and autumn periods, changes in the chemical composition leads to a change in the types

of lakes: from carbonate to sulfate and then to chloride [22]. This sequence of change of the chemical type of lakes is explained by the different solubility and, accordingly, precipitability of salts. First of all, the least soluble calcium and magnesium carbonates precipitate, then calcium, magnesium, sodium sulfates, and finally of all precipitate chlorides from the supersaturated brine.

Given that the Pavlodar region is located in a sharply continental climate zone, we should expect a change in the type of lakes from carbonate to sulfate, from sulfate to chloride. To confirm these hypotheses, a graph was constructed of the dependence of the content of basic ions on the level of total mineralization in the autumn period (Figure 4).
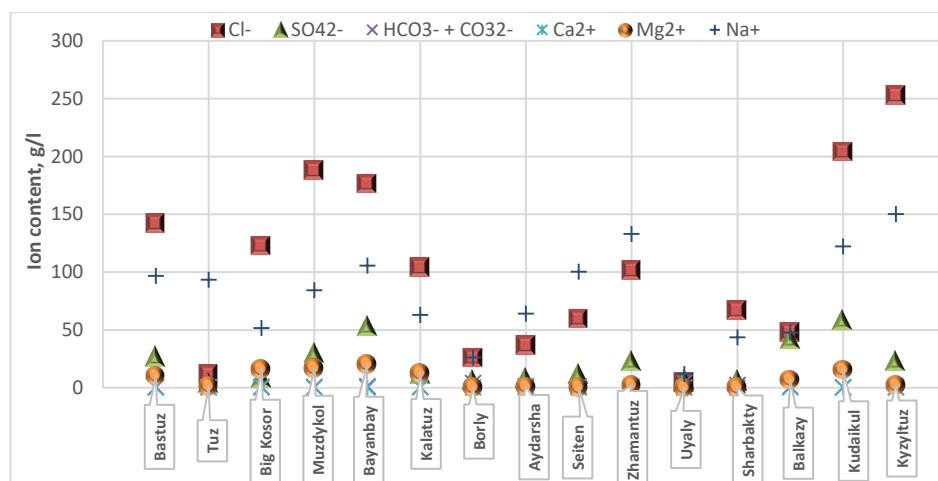
Figure 4. Graph of the content dependence of basic ions on the level of total mineralization in the autumn period

As can be seen from the presented graph, in 14 of 15 analyzed lakes the main anion is the Cl^- ion, one lake (Lake Uyala) has almost the same content of anions, the main anion is SO_4^{2-}, but the pH of the lake is more than 9 and by classification [14] it is carbonate.

The predominant cation, as in the spring, is the sodium cation.

During the autumn period, the following types of lakes can be distinguished: carbonate type of sodium subtype - 1 lake (7% of the total); - sodium chloride-type subtype - 14 lakes (93%).

The results of the geochemical classification of the analyzed salt lakes of the Pavlodar region for the purpose of clarity were summarized in Table 3.

Table 3. Geochemical types of salt lakes of Pavlodar region in the period spring-autumn 2018

Name of the lake	Geo-chemical type	
	Spring	Autumn
Bastuz	Chloride-sodium Cl-Na-II	Chloride-sodium Cl-Na-II
Tuz	Chloride-sodium Cl-Na-II	Chloride-sodium Cl-Na-II
Big Kosor	Chloride-sodium Cl-Na-III	Chloride-sodium Cl-Na-III
Muzdykol	Chloride-sodium Cl-Na-II	Chloride-sodium Cl-Na-II
Bayanbay	Chloride-sodium Cl-Na-II	Chloride-sodium Cl-Na-II
Kalatuz	Chloride-sodium Cl-Na-I	Chloride-sodium Cl-Na-II
Borly	Carbonate-sodium C-Na-I	Chloride-sodium Cl-Na-I
Aydarsha	Chloride-sodium Cl-Na-II	Chloride-sodium Cl-Na-I
Seiten	Chloride-sodium Cl-Na-I	Chloride-sodium Cl-Na-I
Zhamantuz	Chloride-sodium Cl-Na-II	Chloride-sodium Cl-Na-II
Uyaly	Carbonate-sodium C-Na-I	Carbonate-sodium C-Na-I
Sharbakty	Chloride-sodium Cl-Na-I	Chloride-sodium Cl-Na-I
Balkazy	Sulfate-sodium S-Na-II	Chloride-sodium Cl-Na-II
Kudaikul	Chloride-sodium Cl-Na-II	Chloride-sodium Cl-Na-II
Kyzyltuz	Chloride-sodium Cl-Na-I	Chloride-sodium Cl-Na-I

Thus, the study of the hydrochemical composition and geochemical classification of salt lakes in the Pavlodar region was conducted for the first time. Most of the objects analyzed belong to the lakes of the sodium-type sodium subtype. On the territory of the region there are several carbonate and sulphate type lakes, characterized by a gradual transition to chloride type lakes.

The results of the research will make it possible to use these lakes extensively both for the extraction of sodium mineral salts and for the development of Artemia crustaceans. In addition, data on the geochemical classification of saline lakes will allow to predict the nature of groundwater feeding the lakes; their geology, formation and other worth-exploring issues.

References

[1] Sklyarov E V, Sklyarova O A, Men'shagin Yu V and Danilova M A 2005 *Geography and Natural Resources* **32** 323–332

[2] Sovolov V P Bodies of Altai Territory: Biological Productivity and Prospects for Use 1999 *Novosibirsk Nauka* 285

[3] Novoselova S I and Novoselov V A 2000 *Sib. Ecolog. J.* **3** 80–85

[4] Pasynkov A A, Sockova L M and Chaban V I 2014 *Scientific notes of the Tauric National University named after V I Vernadsky Geography* **27** 97–117

[5] Vasil`ev O F, Kazancev V A, Popov P A and Kirillov V V 2005 *Sib. Ecolog. J.* **2** 167–173

[6] Ivanova V I 2012 *X International Scientific and Practical Conference, ICSN "Science and Education* 38–40

[7] Volf L A 2011 Ecological features of the gill-footed crustacean (Artemia parthenogenetica Varigozzi, 1974) in the salt reservoirs of Northern Kazakhstan (Republic of Kazakhstan) *Omsk* 17

[8] Ubaskin A V 2005 Ecological and biological features of the crustacean Artemia (Crustacea, Anostraca) of salt lakes in Pavlodar region (Republic of Kazakhstan *Omsk* 21

[9] Litvinenko L I, Kozlov A V, Matveeva E P and Guzhenko M V 2006 *Bulletin of KSU Natural Sciences* **4** 49– 51

[10] Studenikina T L 1984 Biological resources of inland waters of Siberia and the Far East *Moscow Nauka* 117–124.

[11] Litvinenko L I 2009 Gill-footed crustaceans of the genus Artemia Leach, 1819 in the hyperhaline reservoirs of Western Siberia (geography, biodiversity, ecology, biology, and practical use) *Perm`* 46

[12] Shirokova V A 2013 *Bulletin of TSU* **18** 1023–27

[13] Kolpakova M N 2014 Geochemistry of salt lakes in Western Siberia *Tomsk* 21

[14] Shwarcev S l, Kolpakova M N, Isupov V P, Vladimirov A G and Ariunbileg S 2014 *Geochemistry* **3** 1-18

[15] Kolpakova M N, Borzenko S V and Isupov V P 2015 *Water: chemistry and ecology* **1** 18–23

[16] Ubaskib A V and Ubaskina N V 2002 *History, nature, economics. Mater. Int. scientific-practical conf.(Omsk)* 188–191

[17] Leonova G A, Bobrov V A, Bogush A A, Bychinsky V A and Anoshin G N 2007 *Geochemistry* **10** 1114–28

[18] GOST 31861-2012. Water. General sampling requirements

[19] GOST 26449.1-85. Stationary distillation desalination plants. Methods of chemical analysis of salt water

[20] KZ.07.00.01998-2014. MVI of the mass concentration of chloride ions, nitrite ions, sulfate ions, nitrate ions, fluoride ions and phosphate ions in samples of natural, drinking and treatment waste water using the capillary electrophoresis system Kapel

[21] KZ.07.00.01529-2017. MVI of the mass concentration of cations of ammonium, potassium, sodium, lithium, magnesium, strontium, barium, calcium in samples of drinking, natural (including mineral) and wastewater using the capillary electrophoresis system Kapel

[22] Litvinenko L I and Guzhenko M V 2007 *Siberian Bulletin of Agricultural Science* **2** 81–85