

## Geochemical features of Kulunda plain lakes (Altay region, Russia)

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**Abstract.** Geochemical specifics of lake water of the Kulunda Steppe territory (Altay region, Russia) are studied. The results show that in the territory mainly chloride and less soda lakes with sodium compound are developed. It is presented that calcite and soda saturation indexes (SI) of lake water increase with growth of pH, but decrease in such minerals as gypsum and barite. The opposite situation is typical for SI depending on the salinity. It is revealed that evaporation, secondary mineral formation and various biological processes have the greatest impact on accumulation of elements in solution.

### 1. Introduction

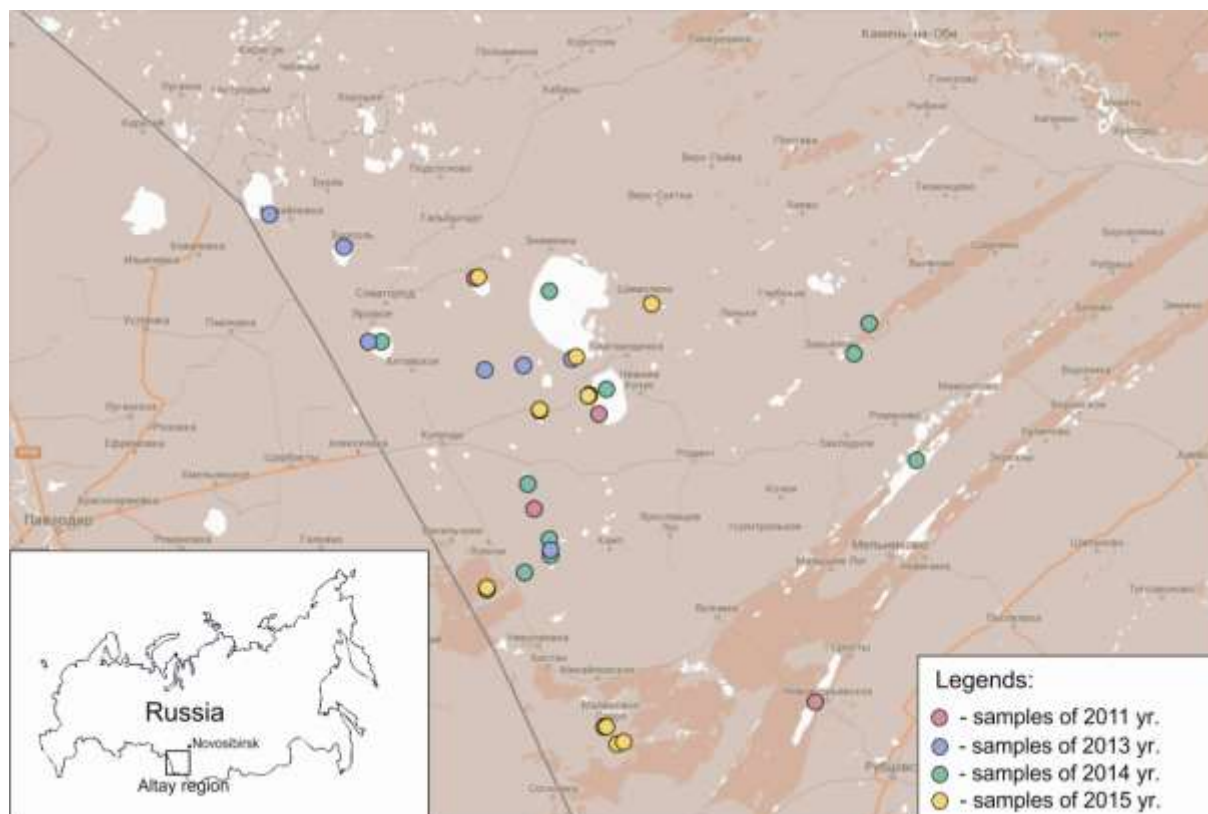
The studying of regularities of chemical elements distribution in natural water, features of their migration, and identification of possible sources of these elements is one of the fundamental problems of modern hydrogeochemistry. The research presented in this paper were carried out at the territory of Kulunda Steppe (Altay region, Russia) where more than 5000 saline lakes with total area about 4000 km<sup>2</sup> are located. In 1931 – 1933 the first extensive work of Kulunda expedition was held there under the leadership of N.S. Kurnakov (Academy of Sciences of the USSR) in order to study the main issues of formation of saline lake composition. In subsequent years, there were studies in calculation of reserves and conditions of a bedding of solid salts, also various methods of their operation were considered [1, 3]. The irreplaceable contribution to establishment of chemical types of lakes water on this territory was made by Yu.P. Nikol'skaya [9]. The research of saline lakes in the steppe area of Altai proceeds at present: the main directions of hydrological and morphological features [3, 8], flora and microbiological structure [7, 8], bottom sediments [10], etc. are being studied. For monitoring the current state of saline lakes we studied geochemical features of about 30 saline lakes and natural water which are in the territory of their reservoir within interdisciplinary expeditions of 2011-2015.



## 2. Materials and Methods

### 2.1. Study area

The studied lakes are located in forest-steppe and steppe landscapes and widespread in the southwest of Altay region, Russia (Figure 1). The lakes vary in sizes, chemical element sources, hydrogeological conditions, etc. For the territory of Kulunda steppe, which is characterized by salt accumulation and droughty climate, soil is one of the main sources of salts in lakes, their TDS can reach 0,15 % [7]. Interaction of internal and external factors [11] leads to a dynamic development of saline lake systems which can be easily affected by change of the environment conditions. Therefore, it is necessary to carry out regular comprehensive studies of water composition in such systems.



**Figure 1.** The location of Altay region and sampling points.

In most cases, the saline lakes of Kulunda steppe are shallow reservoirs with average depth less than 2,5m, the maximum depth of lake B. Yarovoe is 7.5m. Kuchukskoye and Kulundinskoye lakes are the largest system of connected lakes in this territory, the total area of their catchment area is about 24000 km<sup>2</sup>. Water level in lakes fluctuates within 0.4-1m; in droughty years the area of lakes is sharply reduced [4].

### 2.2. Water sampling

The collected samples of water were filtered and loaded into plastic bottles (0.5 L) for analysis of major components. Before sampling all bottles were prepared to prevent pollution. Lake waters were analyzed in the field conditions (pH, Eh, electric conductivity, temperature), as well as in the Fundamental Research Laboratory of Hydrogeochemistry of Education and Research Centre “Water” (Tomsk Polytechnic University, Russia).

## 3. Results and Discussion

Parameters of considered lakes vary in chemical composition and the degree of their salinity. The data obtained during fieldworks (Table 1) indicate the existence of two chemical types of lakes in the

territory of research (according to Kurnakov-Valyashko's classification): chloride and carbonate (soda).

The carbonate (soda) type of lakes differs in the wide range of TDS values which vary from the brackish to strong brines: TDS reaches 107 g/L, thus its average value is only 29 g/l. The share of carbonates ( $\text{CO}_3^{2-} + \text{HCO}_3^-$ ) in lakes seldom reaches 50%, the average value is 25%. The cationic component of the lakes water is always predominant by  $\text{Na}^+$  (average – 85%) against very low concentration of calcium and magnesium (2 and 11%, respectively). pH of water changes from 8,9 to 9,9 that defines reference of these waters to carbonate (soda) type.

The chloride lake type in comparison with soda type is characterized by higher salinity (20 – 590, average is 247 g/L, tab. 1), but considerably smaller values of pH (7.2 – 9.0, average – 7.75). Sodium prevails among cations (average – 74%), the content of magnesium is slightly higher than in soda lakes and can reach 26%.

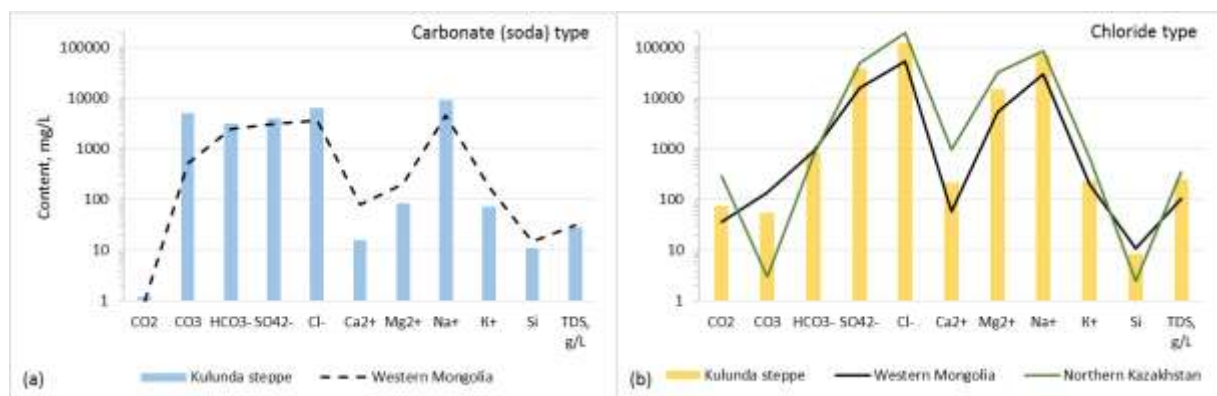
For lakes of both types the content of sulfate ions is the same and changes from 2 to 28%, average is 11-13%. The lack of accumulation of calcium and carbonate complexes in lakes is explained by formation of calcite at the early stages of chemical evolution of water [11]. The disproportional growth of sulfate relative to chloride [5] is associated with the formation of gypsum and microbiological processes in lakes [6].

**Table 1.** Minimum, maximum, and average values of chemical composition of Kulunda lakes, mg/L.

Chemical element	Carbonate (soda) type (number of objects – 10)			Chloride type (12)		
	Min.	Max.	Average	Min.	Max.	Average
pH	8.9	9.89	9,49	7.20	8.95	7.75
$\text{CO}_2$	n/d	4	1.2	n/d	255	75
$\text{CO}_3^{2-}$	24	25800	5044	n/d	396	54
$\text{HCO}_3^-$	415	8845	3156	46	1610	828
$\text{SO}_4^{2-}$	88	18840	4011	4865	97224	37359
$\text{Cl}^-$	188	26306	6451	6200	190400	120025
$\text{Ca}^{2+}$	5	32	16	0	993	218
$\text{Mg}^{2+}$	7	228	85	970	81630	14936
$\text{Na}^+$	250	35615	9216	5580	130000	70571
$\text{K}^+$	11	294	72	20	700	230
$\text{Si}^{4+}$	0.2	42	11	0.1	42	8
Total Dissolved Solids, g/L	1.0	107	29	20	591	247
Total Organic Carbon *	25	477	124	34	599	225
Fulvic Acid**	15.7	25.7	21.7	3.9	19.7	10.7
Humic Acid**	1.1	3.0	2.1	<0.5	0.8	0.6

n/d – not detected, \* - 2014 and 2015, \*\* - 2015 yr.

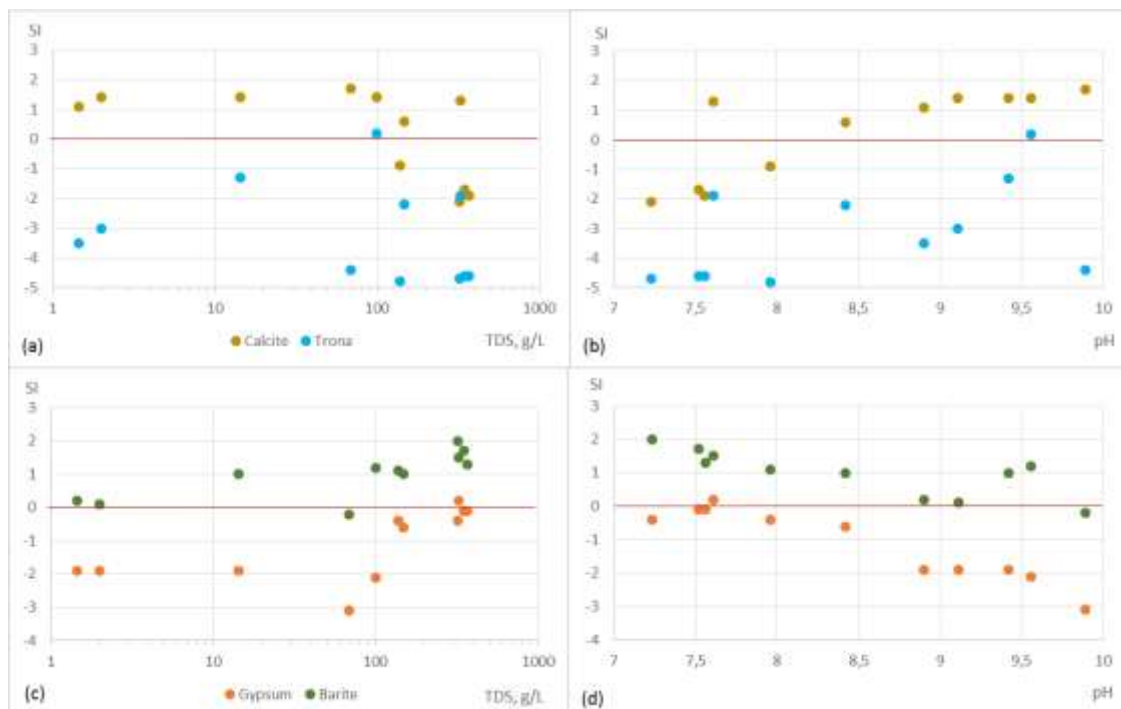
It should be noted that main anion composition of lakes in Kulunda Steppe is very similar to that of chloride lakes located in the nearby Ishimsk steppe territory (Northern Kazakhstan) but have higher values in comparison with lakes of chloride type in Western Mongolia [12]. As shown in Figure 2, the composition of considered lakes differs in smaller values of calcium (1 to 24 mg/L) in comparison with lakes of Northern Kazakhstan where  $\text{Ca}^{2+}$  content in lakes of this type reaches 3 g/L. At the same time, there are smaller concentration of Mg and  $\text{SO}_4$  in Kulunda steppe which is probably connected with the lack of additional sources of these elements.



**Figure 2.** Comparative characteristics of the composition of the lake water of carbonate (soda) and chloride types in the territories of the Kulunda steppe (Altai Territory), the Ishim steppe (Northern Kazakhstan) and the Great Lakes basin (Western Mongolia).

The important factor of the lakes geochemistry formation is the equilibrium-nonequilibrium state of water-rock interaction which results in secondary mineral formation connected with saturation of water by mineral phases. According to the thermodynamic calculations, the carbonate type of sedimentation is characteristic for the majority of lakes, the gypsum stage of the mineral formation is not typical for the studied lakes, which is mainly caused by calcium mobilization by carbonate minerals (Figure 3a). In some cases (pH>9.5 and TDS>100 g/L), lakes reach equilibrium with respect to soda (Figure 3 a, b).

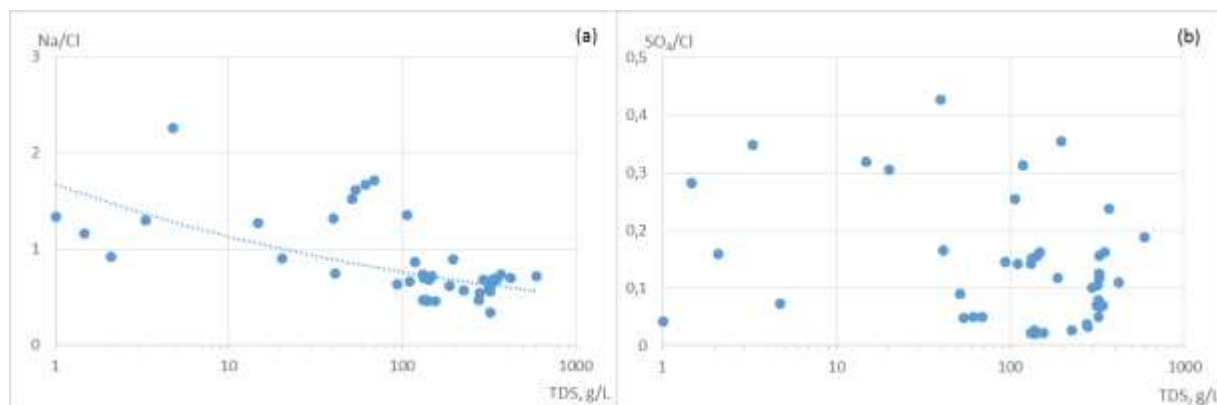
The sulphate content of saline lakes with pH values below 9.0 (chloride type) is sufficient for the formation of gypsum and barite (Figure 3c, d). It is obvious that the content of sulfates in the water can be limited only by the establishment of the equilibrium state of water with gypsum. Therefore, after this stage (gypsum precipitation) of the chemical composition transformation, the equilibrium of water with mirabilite does not reach.



**Figure 3.** Saturation index of lakes water with calcite and sodium carbonate (a, b), gypsum and barite (c, d) as a function of pH and the salinity of lakes.

Our studies [6] show that the accumulation of sulfate ions in the equivalent amounts with chloride does not occur due to, firstly, their bacterial reduction into  $H_2S$  and, secondly, their removing from the solution predominantly in the hydrotroilite form. Although there is an evidence that a portion of the hydrogen sulfide is oxidized, but in this case there is a possible loss in the form of elemental sulfur and iron polysulfide [6]. Nevertheless, the precipitation of gypsum and, rarely, other sulfate minerals is the main geochemical barrier of sulfate accumulation in chloride type of lakes (Figure 3). The study in the behavior of saturation index (SI) of gypsum with increasing of TDS (Figure 3c) and pH (Figure 3d) of lake water shows an inverse dependence. Thus, the saturation of water by gypsum and barite can reach faster in high saline lakes than in brackish lakes and, vice versa, the saturation by these minerals reduces by the increasing of pH.

It is known that the evaporative concentration is the major factor of both sodium and chlorine accumulation in solution [2]. However, in fig. 4a it is visible that the growth of these ions with the increasing of salinity is not uniform and sodium concentration becomes much smaller than the content of chloride ions in highly mineralized waters. It is explained by binding of sodium ions in clay minerals. At this stage of the "lake water - rock" system development, chloride ion does not form its own minerals and continues to accumulate in the solution up to the point of saturation with respect to halite or sylvite.



**Figure 4.** The relationships between the salinity of Kulunda steppe lakes and Na/Cl (a) and  $SO_4/Cl$  (b).

#### 4. Conclusion

Thus, in the territory of Kulunda Steppe mainly chloride and soda lakes with sodium cationic composition are developed. Lakes of sulfate type in the considered territory are not revealed. The TDS of lakes (in some years) reach 590 g/L, pH – 9.9. The growth of salinity of lakes water is followed by the increasing in the content of chemical components, however, their accumulation in lakes are uneven since the formation of a chemical composition of water affect the degree of evaporation, as well as geochemical and biological processes. The lack of sulfate ion accumulation in lakes (fig. 4b) is connected with sulfate reduction and precipitation of secondary minerals, in particular, gypsum.

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