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OS PRIMEIROS DADOS SOBRE AS CONCENTRAÇÕES DE METANO NOS GRIFOS DEGASADORES DO LAGO BASKUNCHAK.

THE FIRST DATA ON METHANE CONCENTRATIONS IN DEGASSING GRIFFINS OF LAKE BASKUNCHAK

LOS PRIMEROS DATOS SOBRE LAS CONCENTRACIONES DE METANO EN LOS GRIFOS DE DESGASIFICACIÓN DEL LAGO BASKUNCHAK.

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Resumo: Pela primeira vez, foi analisada a distribuição de metano na salmoura e nos sedimentos do fundo do riacho Ulan-Blag (afluente do Lago Baskunchak), alimentado por nascentes de degaseificação subterrâneas, bem como diretamente no Lago Baskunchak a uma distância das fontes subterrâneas. A composição dos principais íons na salmoura, as condições ácido-base e redox nos sedimentos do fundo foram estabelecidas. A mineralização da salmoura no Lago Baskunchak é de 312 g/dm3, o que é 2,1 vezes maior do que a mineralização do riacho Ulan-Blag. A composição química da salmoura de ambas as estações é classificada como tipo cloreto, com composição catiônica de sódio. A concentração de metano na salmoura das fontes subterrâneas de degaseificação estudadas no riacho Ulan-Blag atinge valores elevados (até 215 µl/dm3), excedendo em 1 a 2 ordens de magnitude sua concentração na salmoura do Lago Baskunchak. As baixas concentrações de metano na salmoura do lago provavelmente são devido ao seu fluxo insignificante dos sedimentos do fundo para a água devido à presença de uma crosta de sal que impede a emissão de gás, bem como devido às suas pequenas concentrações nas camadas superiores de sedimentos.

Revista Verde
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Palavras-chave: salmoura;sedimentos; degaseificação; mineralização.

Abstract: For the first time, the distribution of methane in the brine and bottom sediments of the Ulan-Blag stream (tributary of Lake Baskunchak), fed by underground degassing springs, as well as directly in Baskunchak Lake at a distance from underground sources. The composition of the main ions in brine, acid-base and redox conditions in bottom sediments have been established. The brine mineralization in Baskunchak Lake is 312 g/dm3, which is 2.1 times higher than the mineralization of the Ulan-Blag stream. The chemical composition of the brine of both stations is classified as chloride type, sodium cationic composition. The concentration of methane in the brine of the studied underground degassing sources in the ravine stream of the Ulan-Blag reaches high values (up to 215 µl/dm3), exceeding by 1–2 orders of magnitude its concentration in the brine of Lake Baskunchak. The low concentrations of methane in the brine of the lake are probably due to its insignificant flow from the bottom sediments into the water due to the presence of a salt crust that prevents gas emission, as well as due to its small concentrations in the upper layers of sediments.

Keywords: brine; sediments; degasification; mineralization.

Resumen: Por primera vez, se haestudiadoladistribución de metano en el agua salobre y sedimentos delfondodelarroyo Ulan-Blag (afluente del Lago Baskunchak), alimentado por manantialessubterráneos de desgasificación, así como directamenteenel Lago Baskunchak a distancia de fuentessubterráneas. Se haestablecidolacomposición de losprincipales iones enel agua salobre, las condiciones ácido-base y redox enlos sedimentos delfondo. La mineralizacióndelagua salobre enel Lago Baskunchak es de 312 g/dm3, lo que es 2,1 vecesmayor que lamineralizacióndelarroyo Ulan-Blag. La composición química delagua salobre de ambas estaciones se clasifica como tipo cloruro, con una composicióncatiónica de sodio. La concentración de metano en el agua salobre de losmanantialessubterráneos de desgasificaciónestudiadosenelarroyo Ulan-Blagalcanza valores altos (hasta 215 µl/dm3), superando en 1-2 órdenes de magnitudsuconcentraciónenel agua salobre del Lago Baskunchak. Las bajas concentraciones de metano enelagua salobre del lago probablemente se deben a suescasoflujo desde los sedimentos delfondohaciael agua debido a la presencia de

una costra de sal que impidelaemisión de gas, así como a sus bajas concentracionesenlas capas superiores de sedimentos.

Palabras Clave: Agua salobre; sedimentos; desgasificación; mineralización..

Introduction

Baskunchak Lake is a drainless, self–draining salt lake located within the Botkul-Baskunchak depression, part of the Caspian Lowland, about 270 km north of the Caspian Sea. Near the lake are the villages of Upper Baskunchak, Middle Baskunchak and Lower Baskunchak. Administratively, the lake belongs to the Akhtubinsky district of the Astrakhan region.

Lake Baskunchak is one of the largest of all known salt lakes in the world. Its area is about 96 km2, the length of the coastline is 42 km. The lake stretches from northwest to southeast for 16.5 km, the maximum width is up to 9 km. The water edge (brine) in the lake is 21 m below sea level. During the wet periods of the year (spring and autumn) oz. Baskunchak is a "brine" lake with a maximum level of brine up to 1 meter.

The salinity of the lake. Baskunchak averages about 300 g/l, which is due both to the entry of highly mineralized waters of watercourses into the lake and to the hot summer climate, which causes high water evaporation (Litovsky, 2018). Many authors who have studied oz. Baskunchak, allocated a different number of sources of water supply to the lake (see (Zelenkovsky and Kurylenko, 2013)). According to the results of monitoring works in 2004–2007, organized by the Faculty ofGeology of St. Petersburg State University together with the Institute of Galurgy(Zelenkovsky and Kurylenko, 2013), 22 watercourses and dry channels were identified. Especially large streams are formed on the northwestern and northern shores of the lake (Ulan-Blagov and Severny streams), as well as on the eastern shore of the lake in the Gorky Erik ravine (Gorky River). Streams are formed due to powerful ascending springs associated with heavily carded gypsum of the Kungursky tier (the lower part of the Permian System).

Revista Verde
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These sources come out in the form of powerful degassing griffins, as well as concentrated jets of various capacities both from fractured gypsum and at the bottom of small karst craters, as well as in silted bottoms of ravine valleys (Zelenkovsky and Kurylenko, 2013). The springs are located at the base of the slopes of the lake, as well as directly in the mouth parts of the gullies, and at some distance from them (500-800 m above the mouths) (Zelenkovsky and Kurylenko, 2013). These underground springs, as a rule, carry highly mineralized, bitter-salty waters (sodium chloride brines). Their mineralization varies somewhat from year to year, while there is no connection between the general decrease in the flow rates of sources in recent years and changes in mineralization (Zelenkovsky and Kurylenko, 2013). The high salinity of the waters of underground sources is due to the fact that, passing through salt lenses located under a layer of sedimentary rocks, the groundwater dissolves them, is saturated with salt and comes to the surface salty.

The variability of mineralization, cation-anion composition and flow rate of the waters of the largest ascending underground sources has been considered in a number of works (for example, (Zelenkovsky and Kurylenko, 2013;Golovachev and Ermolina, 2018)]). In many of these underground sources, along with the discharge of water, there is gas release in the form of jets of gases of varying intensity. However, there are no works in the scientific literature devoted to studying the levels of concentrations and fluxes of methane in the underground sources of Lake Baskunchak, which does not allow us to establish their potential for methane emission into the atmosphere.

This paper analyzes the results of expedition studies conducted in the spring period and aimed at studying the distribution of methane concentrations in the water (brine) and bottom sediments of one of the largest tributaries of Lake Baskunchak – the ravine stream Ulan-Blag. Baskunchak Lake was also explored, beyond the influence of ascending underground sources.

Materials and Methods

The expedition studies were carried out in the north-western (station 1) and western (station 2) coastal zones of the lake. Baskunchak (Fig. 1). During the observation period (May 21- 22), the air temperature varied from +12 °C (at night) to +29 ° C (during the day). During the daytime, as a rule, the weather was clear, clouds appeared in the late afternoon (cloud

Revista Verde
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cover up to 50%). There was no precipitation at least seven days before the start of the expedition, as well as during its conduct. The dirt roads providing access to the lake were dry and quite easily passable.

Station 1 is located on the northwestern shore of the lake, in the lower reaches of the ravine stream Ulan-Blag, where at least three underground sources are deciphered from satellite images. In the course of route observations, the authors examined ascending underground springs No. 1 and 2 (points 1-2 and 1-3), most closely located to the coastal zone of the lake – 140 and 360 meters, respectively (Fig. 2). The water of these springs during the observations had a temperature of 18 ° C and a salty taste.

The surveyed underground spring No. 2 (point 1-3), represented by a karst well with a diameter of up to 6 m and a depth of more than 5 meters (Fig. 3), has a high flow rate of clear water. In this source, during the observation period, several large water jets rose from the depth, with which gas bubbles of various sizes were periodically ejected to the surface. The sides of this source are composed of black, oily, fine-grained silts with a strong smellof hydrogen sulfide. Here (point 1-3) brine samples were taken over one of the ascending water-gas jets to determine methane concentrations.

Fig. 1. Schematic map of the location of sampling points in Lake Baskunchak.

Revista Verde
Green Journal
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Fig. 2. Satellite image (Google Earth) of the lower course of the ravine stream Ulan-Blag.

Below this source, closer to the coastal zone of the lake, a shallow sinkhole with a diameter of 6–8 meters with 15–20 separate fontanels of various flow rates was revealed (Fig. 4). In this debit field (underground source No. 1, point 1-2), most of the springs have a very low flow rate and 3 springs have a high flow rate. The latter form cone–shaped griffins with a diameter of 0.5–1 m; and fontanelles with a small flow rate are griffins with a diameter of 0.1–0.3 meters. From griffins, in addition to water, gas bubbles were released to the surface, when a burning match was brought to which ignition did not occur. In small griffins, constant discharge of bubbles was noted, in large griffins – periodic discharge with a frequency of 2-3 minutes to 5-6 minutes. The sides of the griffins are composed of black, oily, fine-grained silts with a pungent smell of hydrogen sulfide. In the debit field (point 1- 2) above one of the small griffins, brine samples were taken to determine methane concentrations.

Revista Verde
Green Journal
ISSN: 2764-9024 DOI: 10.5281/zenodo.10843534

Fig. 3. Underground spring No. 2 (point 1-3) in the lower reaches of the ravine stream Ulan-

Blag, represented by a karst well.

Fig. 4. Underground spring No. 1 (point 1-2) at the mouth of the ravine stream Ulan-Blag, represented by a debit field of degassing griffins.

Revista Verde
Green Journal
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Due to the dam erected at the mouth of the Ulan-Blag stream with a culvert that does not provide an unhindered discharge of its waters into the Lake Baskunchak(Pozdnyakov et. al. 2020), an extensive reservoir with clear water and a weak current was formed on the outside of the lake due to the overflowing waters of the stream (point 1-1). The depth of this reservoir does not exceed 15 cm. The lower horizons of bottom sediments in this reservoir are represented by brown, brown-brown refractory, saline clays, for which the parent rock is loam exposed at the base of the coastal slopes of the lake. Along the sharp border, black, soft-plastic, oily, saline fine-grained silts with a strong smell of hydrogen sulfide and inclusions of salt crystals of sandy and gravel dimensions lie above the clays. Brine samples were taken in the estuary of the ravine stream Ulan-Blag (point 1-1) to determine the concentrations of methane and major ions (HCO −, Cl−, SO 2−, Ca2+, Mg2+, Na+, K+), pH values and temperature. In addition, samples were taken from various horizons of bottom sediments (up to a depth of 35 cm), in which, in addition to methane concentrations, Eh and pH values, humidity and density were determined.

Station 2 is located on the western shore of Lake Baskunchak, 1.2–1.5 km south of the village of Nizhny Baskunchak, in the area of the destroyed ancient salt mining (Fig. 5). At a distance of 0.25–0.3 km from the shoreline of the lake (point 2-1), samples of transparent brine with a temperature of 11°C were taken to determine the concentrations of methane and major ions (HCO −, Cl−, SO 2−, Ca2+, Mg2+, Na+, K+), dry residue, pH and temperature values. The capacity of the rapa brine at the sampling point does not exceed 15 cm. The bottom is covered with a 1–2 cm crust of solid coarse-grained halite from pure white to light gray. Under the salt crust, underlain by a 0.1 cm layer of brown silt, lies a black, moist, fine-grained silt without the smell of hydrogen sulfide, in the surface horizon (0–2 cm) of which a sample was taken to determine the concentrations of methane. In addition, the determination of methane concentrations was carried out in the brine lake Baskunchak on the site of ancient salt production (point 2-2) and the water of a small brackish reservoir formed by the Dynamitka stream flowing into the lake (point 2-3).

Fig. 5. The western shore of Lake Baskunchak (point 2-1).

Bottom sediments were collected using a special plastic tube 500 mm long and 45 mm in diameter with sharply sharpened edges and a fluoroplastic piston for core extrusion. Sampling, transportation, storage of samples and subsequent determination of methane in water and sediment samples was carried out on a Chromatek-Crystal 5000 gaschromatograph.2" with an equilibrium vapor dispenser on a flame ionization detector according to certified methods (Hydrochemical Institute, 2012; Hydrochemical Institute, 2013). Methane was determined in bottom sediments at their natural humidity and expressed in µg/g of wet sediment. Simultaneously with sampling, a sample of bottom sediments was taken into pre-weighted and numbered buckets to determine humidity and density. The pH, Eh and temperature values were measured using the electrodes of the portable pH meter ionomer – "Ecotest 2000" immediately after sampling. The concentrations of the main ions in brine were determined according to standard methods generally accepted in the Roshydromet system (NOK, 2009).

Results

Brine mineralization at the mouth of the ravine stream Ulan-Blag (point 1-1) according to the data of the conducted expeditionary studies is 149.9 g/dm3. The chemical composition of

Revista Verde
Green Journal
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the brine at this point, represented below by the Kurlov formula, is classified as a chloride type, sodium cationic composition.

$$M_{149,86} \frac{(Cl)_{47,60}(SO_4)_{2,34}(HCO_3)_{0,06}}{(Na)_{47,47}(Ca)_{1,98}(Mg)_{0,45}(K)_{0,10}} pH7,1 \quad (1)$$

When naming waters, only the ions present in the water in an amount greater than 12.5% eq. are indicated (based on 50% of the amounts of anions and cations separately). In this case, the ions are listed according to their content from greater to lesser; first, the anionic composition is indicated, then the cationic one.

The data obtained in the course of these studies on the mineralization and the ratio of basic ions in groundwater discharged in the Ulan-Blag beam are consistent with previously published information (for example, (Myazina, 2006)).

The main physico-chemical parameters of the studied 35 cm layer of bottom sediments at the mouth of the ravine stream Ulan-Blag (point 1-1) are as follows: humidity – 15.3– 26.6%, density – 1.90–2.47 g/cm3; pH – 6.16–6.93 (slightly acidic medium), Eh -51.3 ...-

250.0 mV (reducing medium).

The brine mineralization in Baskunchak Lake (point 2-1) is 312.3 g/dm3, which is 2.1 times higher than the mineralization of the stream Ulan-Blag beam (point 1-1). The higher mineralization of the brine of the lake is probably due to the intense evaporation during the hot period. The chemical composition of the brine of Lake Baskunchak, as well as the stream of the beam Ulan-Blag, is classified as a chloride type, sodium cationic composition. At the same time, in the brine of the lake, in comparison with the stream Ulan-Blag, there is a noticeable increase in the proportion of magnesium ions.

$$M_{312,3} = \frac{(Cl)_{49,99}(SO_4)_{0,01}}{(Na)_{36,23}(Mg)_{10,68}(Ca)_{2,84}(K)_{0,25}} pH6,8 \quad (2)$$

The concentration of methane in the brine of ascending underground sources in the Ulan-Blag beam varies in the range of 46.9–215.0 µl/dm3 (on average 146.7 µl/dm3) with maximum values in degassing underground source No. 2 (207–215 µl/dm3), almost 2 times higher than its concentration in degassing underground source No.1.

The methane concentration in the brine of the mouth of the ravine stream Ulan-Blag (point 1-1), which is fed by ascending underground sources, decreases to 47.1–84.3 µl/dm3 (on average 65.7 µl/dm3). The decrease in concentration is probably due to the predominance in the balance of methane in the brine of the mouth of the stream of the processes of its oxidation and emission into the atmosphere over the intake from bottom sediments characterized by relatively low concentrations of the studied gas. Thus, themethane concentration in the bottom sediments of the mouth of the Ulan-Blag brine varies within 0.04–0.32 µg/g of wet sediment (on average 0.17 µg/g), with maximum values in the lower horizons (20–35 cm) and minimum values in the surface 0–2 cm layer, which correlates with the distribution of Eh ($r = -0.42$; $P < 0.05$). Low concentrations and the nature of the vertical distribution of gas in the bottom sediments of the mouth of the Ulan- Blag brine, despite the reducing environment and the flow of gas in the groundwater, may indicate intensive oxidation of methane by a consortium of anaerobic methane-oxidizing archaea and sulfate-reducing bacteria (Knittel, 2018).

The concentration of methane in brine collected directly in the lake. Baskunchak (points 2-1 and 2-2) at a considerable distance from the ravine stream Ulan-Blag and other groundwater sources, as well as in the salt reservoir formed by the Dynamitka stream (point 2-3), varies within 0.47–2.85 µl/dm3, averaging 1.53 µl/dm3. These concentrations are 1–2 orders of magnitude lower than in the brine of the studied degassing underground sources discharged in the lower reaches of the ravine stream Ulan-Blag. Methane concentration in the upper 0–2 cm layer of black clay silts sampled in the lake. Baskunchak (point 2-1) under a 1 cm crust of solid coarse-grained halite, was also low and was at the level of the detection limit – 0.01 µg/g of wet sediment.

Comparison with various fresh and mineralized lakes of Russia (Ivanovand Rusanov, 2001; Fedorovet. al., 2014; Garkusha et. al., 2023) shows that methane concentrations in the water of Lake Baskunchak are characterized by one of the lowest values. This is probably due to the insignificant flow of methane from the bottom sediments into the water due to the presence of a salt crust that prevents methane emission, as well as due to low concentrations of the studied gas in the upper horizons of the lake sediments. The latter is due to the fact that in highly mineralized lakes, such as Lake Baskunchak, due to the thermodynamic advantage of sulfate reducers over methanogens (Schönheit et. al., 1982), the capacity of the zone of sulfate-dependent anaerobic oxidation of methane increases in bottom sediments (Garkusha et. al., 2022), in which methanogenesis is usually suppressed (Knittel, 2018).

Conclusion

The concentration of methane in the brine of the two studied underground degassing sources in the ravine stream Ulan-Blag reaches high values (46.9–215.0 µl/dm3), exceeding by 1–2 orders of magnitude its concentration in the brine of the Lake Baskunchak (0.47–2.85 µl/dm3) in areas remote from groundwater sources. At the same time, there are noticeable differences between the concentrations of methane in the brine of the studied underground sources (on average by 2 times). Despite the recovery conditions, the bottom sediments of the stream Ulan-Blag are characterized by relatively low concentrations of methane. The latter may be related to the suppression of methane formation in the bottom sediments by the process of sulfate reduction and indicate the secondary role of modern sediments in the formation of high concentrations of methane in the brine of the studied degassing underground sources.

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