Hydrochemistry of Low-temperature Thermal Water of Primorye Region (Russia) and Environmental Implications

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***Abstract*-The low-temperature thermal water in the Primorye Region of the Far East of Russia is traditionally important for medical purposes. A hydrogeochemical study based on 30 samples, including thermal springs, streams and well water has been carried out in the Goriachii geothermal area. The initial year-round survey on the condition of the spring water and the environment has shown that the thermal water demonstrates slight seasonal variation in chemical composition, but no significant seasonal variation in temperature and discharge. The geochemical testing of the surface stream indicated the influence of the thermal area on the surface water, which is exhibited in the hidden discharge. The testing of the head and mouth of the Teplii spring has shown that the increase in the water temperature has reached 2.5 °C for every 700 m distance. Simultaneous, the alkalinity and the mineralization increase by a magnitude of up to 1.5. The concentrations of sulphates and sodium likewise increase, while the concentrations of calcium and magnesium decrease.**

Keywords- Thermal Water; Primorye; Hydrogeochemistry; Goriachii Kliuch, Environmental Implications

I. INTRODUCTION

The study area is located in the Southern Primorye (the Far East of Russia) as displayed in Fig. 1, and represents four main groups of springs: Chistovodnoe, Sinegorsky, Goriachii, and Sukhoi Kliuch. The geology of south Primorye is dominated by the Sikhote-Alin Ridge and has been previously studied by Khanchuk (1995) [4]. According to the tectonic scheme, the geothermal area is located within the bounds of the Samarka terrain (Bazhanov & Oleinik, 1986) [1] within the Central Sikhote-Alin fault, the largest tectonic dislocation in Primorye.

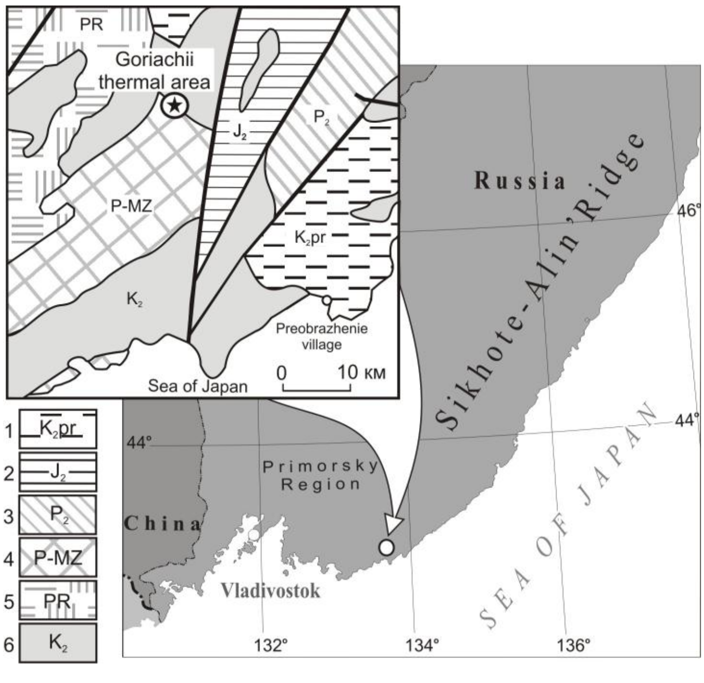

Fig. 1 General geological map of the area of the Goryachii spring [1]. (1) Cretaceous effusive rock (Primorye series): tuffs and rhyolite ignimbrite; (2) Jurassic sedimentary rock: sandstone, siltstone, and siliceous rock; (3) Upper-Permian rock: siltstone, sandstone, and siliceous rock; (4) Upper Permian–Mesozoic rock: clay slate, sandstone, siliceous rock, and limestone; (5) undissected Proterozoic formations: biotite and amphibole shale, marble (Sergeevka massif); (6) Late-Cretaceous granite

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The study of hydrogeochemistry of geothermal areas is important for understanding the processes of their genesis, rational use and environmental assessment. The temperatures and depths of the water formation of the Goriachii Kliuch thermal water, and the residence time were determined by previous work (Chelnokov et al., 2014) [2]. The annual variations in the geochemical components of the thermal and surrounding fresh water in the thermal springs of the Primorsky Region were obtained by this study for the first time. The influence of atmospheric precipitation on the temperature, composition, and discharge of the thermal spring was determined, allowing dynamic analysis of the processes affecting chemical composition of the thermal water. The results demonstrate the chemical impact of the thermal water of Goriachii spring on the surface water of the Teplii spring, expressed in the increased concentrations of Li, Fe, F, As, and Mo.

II. METHODOLOGY

Hydrogeochemical and hydrological monitoring studies were carried out in 2012–2013 on the Goriachii geothermal area to assess the conditions of the thermal water and define its environmental impact. The seasonal sampling was conducted, and ten water samples were analyzed completely (including microelements) along with five gas samples and five samples of isotope composition. Water samples were collected from Goriachii and Teplii springs. Groundwater samples were collected in acid-washed, high-density polyethylene sample bottles. Before sampling, all water samples were filtered through 0.45 μm cellulose filters. Water for cation analysis was acidified to pH < 2 with ultra-pure HNO_3. Water temperature, conductivity and pH were measured directly in the field. Major cations and anions were analyzed by ion chromatography. Carbonate species were titrated in the field with 0.1N HCl. Trace element and REE concentrations in groundwater were determined by ICP-MS (Agilent 4500). Analytical precision for the REEs, with the exception of Ce and Pr, was higher than 5% vs. relative standard deviation RSD; for Ce and Pr, precision was 6% and 9% vs. RSD, respectively. All analyses were made at the Analytical Centre of Far East Geological Institute (Vladivostok, Russia). The year-around variations in water temperature of the Goriachii thermal spring were first obtained using temperature data loggers (Solinst, Canada) and a flow-meter. Changes in water temperature and pressure (air and water) were registered at 1 hour intervals by the Solinst data loggers (LT F30/M10).

III. RESULTS AND DISCUSSION

A. *Hydrogeochemical Study*

Water samples were being collected during a two-year period (2012–2013) from the thermal well (Goriachii spring) and the Teplii spring (cold water). Additionally, hydrogeological and geophysical data for the period since 1962 to 2007 have been taken into consideration. Representative analyses are shown in Table 1.

TABLE 1 REPRESENTATIVE DATA OF THE STUDIED THERMAL AND COLD WATER

Source		Goryachii spring	Teplii spring	
			(springhead)	(mouth)
Type		thermal	cold	cold
Distance	m	0	1	700
Temp.	^{0}C	26	9.2	10.9
pH		9.1	7.1	7.5
TDS		128	36.6	50
TOC	mg/L	0.04	0.3	1.3
Na		32.1	2.9	8.2
Ca		3.37	4.9	4.6
Mg		0.13	0.7	0.6
K		0.7	0.8	0.8
NH_4		0.08	0.2	0.2
Cl		4.9	1.6	2.2
SO_4		10.6	3.8	5.2
HCO_3		68.8	18.1	28.7
SiO_2		41.2	3.7	8.2
Li		0.06	0.01	0.05
Fe		0.7	0.2	0.8
Al		0.009	0.002	0.03
F		6.1	0.07	1.12
As		0.01	0.003	0.008
Mo		0.02	0.0007	0.01

The thermal groundwater of the Goriachii is typically a sodium bicarbonate water with HCO_3 > Ca+Mg and Na > Cl+SO_4. It has low mineralization (< 170 mg/l) with increased concentrations of Si and F. Among the microelements, arsenic and molybdenum are characterized with high concentrations of 11.6 μg/L and 21.5 μg/L, respectively. The spring discharge is 0.83

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L/s. The water shows alkaline reaction, and the temperature falls within 26.9 – 30.1 °C. A major component of its bubbling gases is nitrogen (up to 72.2–97.2%). The total α-activity in the water amounts to 0.1–0.2 Bq/L; the total β-activity is 0.47 Bq/L or lower. The amount of organic carbon is less than 0.4 mg/L and is typical for fresh groundwater.

The thermal water is of atmospheric genesis. With soluble rocks and the absence of aggressive accessory gases (fluxes of deep-laid CO_2, H_2S, Cl, etc.), even under increased temperature, the process of element transition into solution remain slow, resulting in low mineralization (Chelnokov et al., 2014) [2]; thus, the water is undersaturated to most of the minerals of the water-bearing rocks. The temperature of the deep-seated reservoir, estimated geothermometers, is below 100 ° C, demonstrating the depth of penetration of the atmospheric waters as1-2 km (Kharitonova et al., 2012) [5]. The presence of helium and methane, as well as the absence of gases which are specific to volcanic and geothermal areas, testifies to the Central Sikhote-Alin fault relation. The data obtained is in accordance with the preceding data produced by Kiriukhin (1963) and Chudaev (2003) [3], who concluded that "the warming of the groundwater takes place under the circulation within a rock massif at depths over 1 km in the zone of quite recent tectonic shifts and igneous chambers." The springhead cold water of Teplii spring is characterized by Ca-Na-HCO_3 with low TDS values (36-80 mg/L). The spring discharge is 0.85 L/s. The water temperature is within 8.1-9.0 °C.

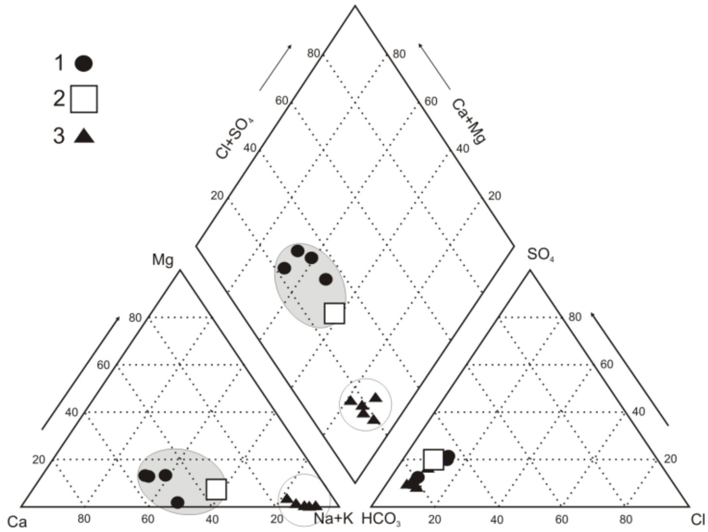

Fig. 2 Classification diagram of the examined waters. (1) Teplii spring (springhead); (2) Teplii spring (mouth); (3) thermal water the Goriachii spring

It is demonstrated in the below triangular diagram (Fig. 2) that despite the proximity of thermal and cold sources, their chemical composition and temperature varied over the testing time. However, the maximum values of the mineralization and the concentrations of the HCO_3 and Na are registered in the summer–autumn period.

B. Hydrological Observations

The cold water at the headlands of the Teplii spring and the thermal water of the Goriachii spring are close in proximity, at a distance of 1 m. The springhead of the thermal water of the Goriachii spring is located concrete well with a pipe. During the monitoring period, the spring discharge varied from 0.77 to 0.86 L/s, and the water temperature varied from 27.1 to 31.8 °C (the absolute minimum and maximum, respectively) with the maximum value registered once in January. The average daily temperature was not lower than 27.7 °C. The average monthly temperature of the water changed from 30.8 to 31.4 °C. The average annual water temperature reached 31.2 °C. The absolute minimum of the water temperature in the well was registered twice. The first decrease in temperature from 31.0 to 27.1 °C was registered on the May 26, 2013 during a rain storm in which the temperature decreased by 4 °C over two hours. The temperature increased during the following days and became as high as 31.1 °C by the June 1 (i.e., a little higher than the initial temperature before the decrease). The temperature decreased a second time from 31.3 to 29.4 °C on August 9, and returned to the initial temperature of 31 °C by August 15. The short-term decreases in water temperature in the well mentioned above are caused by intense cold rains of 8–10 °C in the spring, which result in the cooling of the rock masses, intense feeding of the surrounding cold water, and a decrease in water temperature in the spring. During the winter, small daily variations in water temperature were registered in the well; thus, the hourly average values of the temperature in February showed an amplitude of 0.6 ° C. In the summer, this amplitude amounted to 0.3 ° C (i.e. was comparable to the registration accuracy). Anomalies in the thermal field of the ground were found in the upper valley of the stream and associated with fracturing zones. The anomaly closest to the spring was 2.0 × 2.0 m in dimension, and

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demonstrated a temperature of 28.5 °C.

C. Environmental Implications

The objective of this section is to assess the environmental impacts of the thermal water on the nearby rivers in the Goriachii field. The determined amounts of organic carbon signify different sources and volumes of the supply of organic matter to the thermal water and to the cold groundwater of the Teplii spring.

The testing of the Teplii spring at its head and the mouth area has shown that the increase in water temperature amounted to 2.5 °C over a distance of 700 m (Table 1); this is a significant value for the stream discharge rate of 85 L/s. With the increase in water temperature, the alkalinity increases, the mineralization varies by an approximate magnitude of 1.5, the concentrations of sulphates and sodium increase, and concentrations of calcium and magnesium decrease. The influence of the thermal water on the chemical composition of the surface water is expressed by increased concentrations of Li, Fe, F, As, and Mo. The obtained results demonstrate the influence of the thermal water on the surface water of the Teplii spring, further exhibited in the latent discharge.

IV. CONCLUSIONS

Seasonal and annual monitoring of the hydrodynamic and hydrochemical parameters was performed for the thermal water of the Goriachii spring. This monitoring provided data on the genesis of the thermal water to evaluate the temperatures and depths of its formation, and to determine the time of the water circulation. It was determined that the thermal water had no significant seasonal variations in temperature over the year. The chemical composition of HCO_3-Na water and associated gases reflects geochemical processes that occur over time at this territory.

The geochemical testing of the Teplii spring at its springhead and mouth was undertaken to evaluate the dimensions of the thermal field and to characterize the environmental impact of the thermal water on the surface water. The environmental impact of the thermal contamination resulted in increased alkalinity and mineralization; increased concentrations of SO_4, Na, Li, Fe, F, As, and Mo; and decreased concentrations of Ca and Mg.

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