

Nalychevo Hydrothermal System - A Unique Combination of Natural and Man-Caused Hydrothermal System

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ABSTRACT

Nalychevo National Park is host to a great number of hydrothermal fields, natural hot springs, travertine terraces and cold mineral water sources. The park, with a total area of about of 2,871 km², is located 25 km to the north of the Petropavlovsk-Kamchatsky city. Nalychevo is the largest hydrothermal system in the Nalychevo National Park. It contains over 1,000 thermal springs distinguished by scale, temperature, and water chemistry. The thermal waters are characterized by high concentration of boron, arsenic, iron, calcium, magnesium, sodium, potassium, rubidium, lithium, cesium, silicon, and bromine. The springs are classified as special balneological carbonaceous fresh-medium-mineralized, arsenic boric siliceous chlorine-sulfur-calcium-sodium thermal mineral waters group, which does not have any other analogues in the world and has a special name – Nalychevo balneological water type. Travertine, continuously deposited from the thermal waters, is characterized by high concentrations of arsenic, iron, calcium, magnesium, manganese, strontium, barium, and antimony.

1. INTRODUCTION

The Nalychevo National Park is host to a great number of the hydrothermal fields, natural hot springs, travertine terraces, and cold mineral water sources. The National Park, with a total area of about of 2,871 km², is located 25 km to the north of the Petropavlovsk-Kamchatsky city (Fig. 1a) in South Kamchatka, which belongs to the Eastern Kamchatka volcanic belt consisting of many active volcanoes. The Nalychevo National Park is enlisted as a UNESCO World-Wide Cultural and Nature Heritage since 1995.

The Nalychevo Park is surrounded by mountain ranges of ancient and active volcanoes. Among the active volcanoes, four are show present fumarolic activities. These are the Koryaksky and Avachinsky volcanoes in the south of the Nalychevo Park, whereas the Zhupanovsky and Dzen-dzur volcanoes are located in the north. The Pinachevsky and Ivulk mountain ranges enclose the National Park from the western side.

The Koryaksky Volcano is a large andesitic basalt volcano with an elevation of 3,456 m. It is located 22 km southeast of the Nalychevo Park. Seismic activities have arisen beneath the volcano in 2008–2009, resulting in week to moderate fumarolic streams.

The Avachinsky Volcano, with an elevation of 2,751 m, is a typical composite volcano with a crater shape of Somma-Vezuvi, located next to the Koryaksky Volcano. It is the most well-known and picturesque volcano in Kamchatka. Several streams of fumaroles are often seen on the top of the volcano. Craters are filled by lavas erupted in 1991.

The Zhupanovsky and Dzen-dzur volcanoes are located to the west of the Nalychevo Park. The Dzen-dzur volcano, with an elevation of 2,285 m, is almost destroyed. The Zhupanovsky volcano (2,985 m) is a complex volcano with four merging volcanic necks. Fumarolic streams were noted on the top of the Zhupanovsky Volcano in 2013.

These active volcanoes are probably providing the heat source feeding the thermal features of the Nalychevo Park.

The Nalychevo hydrothermal system is the largest identified in the National Park. It contains over 1,000 thermal springs distinguished by scale, temperature, and water chemistry. Most important and largest ones are the Nalychevskie, Zheltorechenskie, Talovskie, Kraevedcheskie, and Shaibny hot springs (Fig. 1b). The healing properties of these springs are known since a scientific trip of Karl von Ditmar in 1851–1855. The Nalychevo hydrothermal system is one of the most original hydrothermal systems, not only in South Kamchatka but probably also in the whole Pacific Fire Rim. There are no analogues of Nalychevo waters, so they got a special name – the Nalychevo balneological water type (Litvinov et al., 1999; Okrugin et al, 2009). Similar types of mineral waters are used for prophylaxis and treatment of cardiovascular, gastrointestinal, and nervous system diseases, and for curing people (e.g., astronauts, chemical industry workers, and sportsmen) by ionization and microwave radiation.

Ivanov's Gryphon of the Nalychevo hydrothermal system is a unique, world's only man-made thermal feature (Fig. 2, 3). Ivanov's Gryphon was formed as a result of collapsing of the exploration wells drilled in 1959–1960. A basin of high temperature thermal waters was developed at the location where the well was collapsed (Fig. 3). The term «gryphon» is used in the Russian geological literature to describe the crater formed as a result of the blow up of the deep-seated hydrothermal fluids to the surface with formation of a crater. The Nalychevo crater was named as the Ivanov's Gryphon after famous Russian hydrogeologist Ivanov, who visited the Nalychevo hydrothermal springs in 1951 (Firstov et al., 2011).

A hot, naturally-formed travertine terrace is located next to Ivanov's Gryphon (Fig. 2). This travertine terrace named as Kotyol.

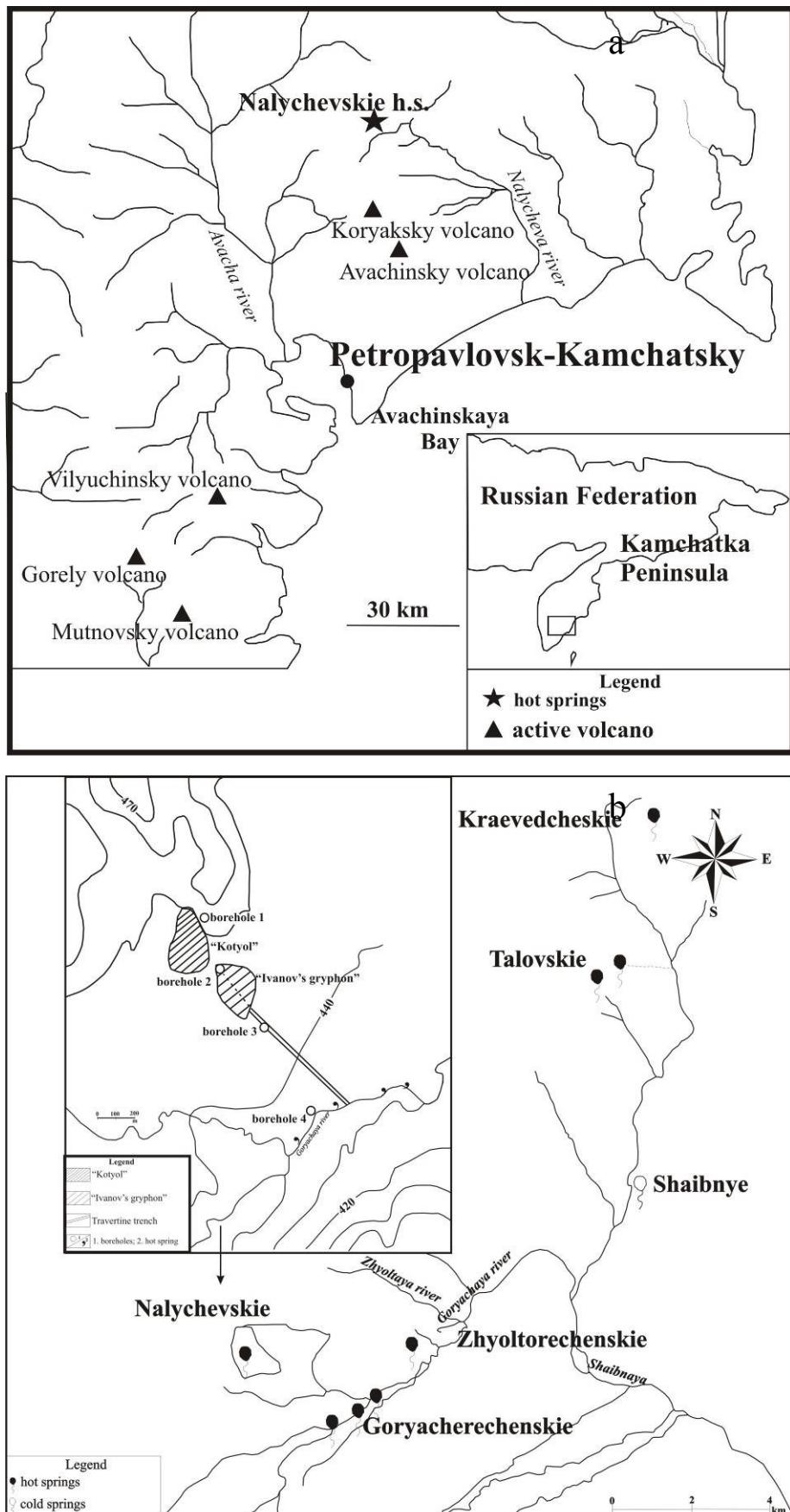


Figure 1. a: Map of South Kamchatka showing locations of the Nalychevskie springs, active volcanoes, and the Petropavlovsk-Kamchatsky city; b: Thermal springs of the Nalychevo hydrothermal system showing location of the Kotyol travertine terrace, exploration boreholes 1, 2, 3, 4, and Ivanov's Gryphon in the Nalychevo National Park.



Figure 2. View of the Kotyol travertine terrace and Ivanov's Gryphon.



Figure 3. General view of the Ivanov's Gryphon.

Some water analyses were reported by Piip (1937), Kovalev et al. (1969), and other researchers. Nishikawa and Okrugin with co-workers first identified the rare arsenic-bearing hydrous mineral yukonite in deposits of the Nalychevo springs. Yukonite from the Nalychevo springs contains high Si (up to 8.7 wt.%), Ca (up to 22.3 wt.%), and lower Fe and As. The latter is substituted by Si (Nishikawa et al., 2006).

Sheshkanova (2006) reported the variation of the chemical compositions of the travertine at the Ivanov's Gryphon.

Geophysical data of from this area was reported by Firstov et al. (2011) and Rashidov et al. (2013).

The Nalychevo hydrothermal waters are also favorable for different kinds of bacteria and plants, giving the springs a colorful appearance.

This study was completed with an aim to constrain the model of the modern precipitation mechanism of arsenic-enriched deposition from the thermal springs in South Kamchatka. Water-chemistry data from numerous sample sites along with mineral compositions of the deposits from the Nalychevo hydrothermal system are reported in this paper.

2. GEOLOGICAL BACKGROUND

The Nalychevo National Park is situated in the valley of the Nalycho River. There are several hydrothermal systems in this area but Nalychevo is the largest and most interesting. Human factor played a special role in formation of the Nalychevo hydrothermal system. This fact is raising a special interest to the Nalychevo springs. The travertine terrace and Ivanov's Gryphon are located in the central area of the Nalychevo Park in the valley of the Goryachaya River (Fig. 2). These two thermal features are the main springs of the Nalychevo hydrothermal system. They represent one naturally-formed thermal spring and a man-made one.

Vigorous volcanic eruptions took place during the late Pliocene and early Pleistocene in South Kamchatka. As a consequence, basaltic lava plateaus and shield volcanoes were formed (Saji et al., 2004). Active volcanoes of Koryaksky, Avachinsky, and Zhupanovsky, along which Nalychevo springs are distributed, were developed in the middle Pleistocene–Holocene interval (Fig. 4). The area hosting the Nalychevo hydrothermal system is composed of andesite, basaltic tuffs, and breccias interbedded with pyroxene lava flows (Fig. 4). The ages of tuffs and breccias are determined as Pliocene (Piip, 1937).

The travertine terrace is often called in the literature as the thermal spot "Kotyol" and a travertine dome. The terrace is oval in shape with an area of 180 m x 200 m and height of 5–7 m. It consists of travertine interlayered with layers of volcanic ash, belonging to eruptions of the Avachinsky Volcano (Piip, 1937). A bowl-shaped crater was observed on the eastern top of the travertine terrace. Until the middle of the 20th century the crater of the travertine dome was filled with thermal waters (Firstov et al., 2011; Rashidov and Firstov, 2012; Rashidov et al., 2013). This crater was named as Kyotel by hunters (Piip, 1937). Temperature of the thermal water is 72°C. Other thermal springs existed on the travertine terrace were smaller and flowed into a small creek running from the top of the terrace. The gentle slope of the western side of the terrace allows for self-discharge of thermal waters into the creek. The temperature of the creek has arisen due to the continuous inflow of thermal waters. The creek discharges into the Goryachaya River, which is located 100 m away from the travertine terrace (Piip, 1937).

The man-made Ivanov's Gryphon is a unique characteristic of the Nalychevo hydrothermal system and the entire Nalychevo National Park. Exploration work by drilling of four boreholes at the travertine terrace and surrounding area were done in 1959–1960 (Fig. 2b). The intensely flowing boreholes 1 and 2 discovered the hottest thermal waters. In consequence, borehole 2, the deepest hole (217 m), collapsed and a thermal water basin was formed with a size of 5 m x 6 m (Kovalev et al., 1969; Saji et al., 2004; Shishkanova, 2006; Firstov et al., 2011). Maximum depth of the basin is about 8 m (Firstov et al., 2011). This basin was named as Ivanov's Gryphon.

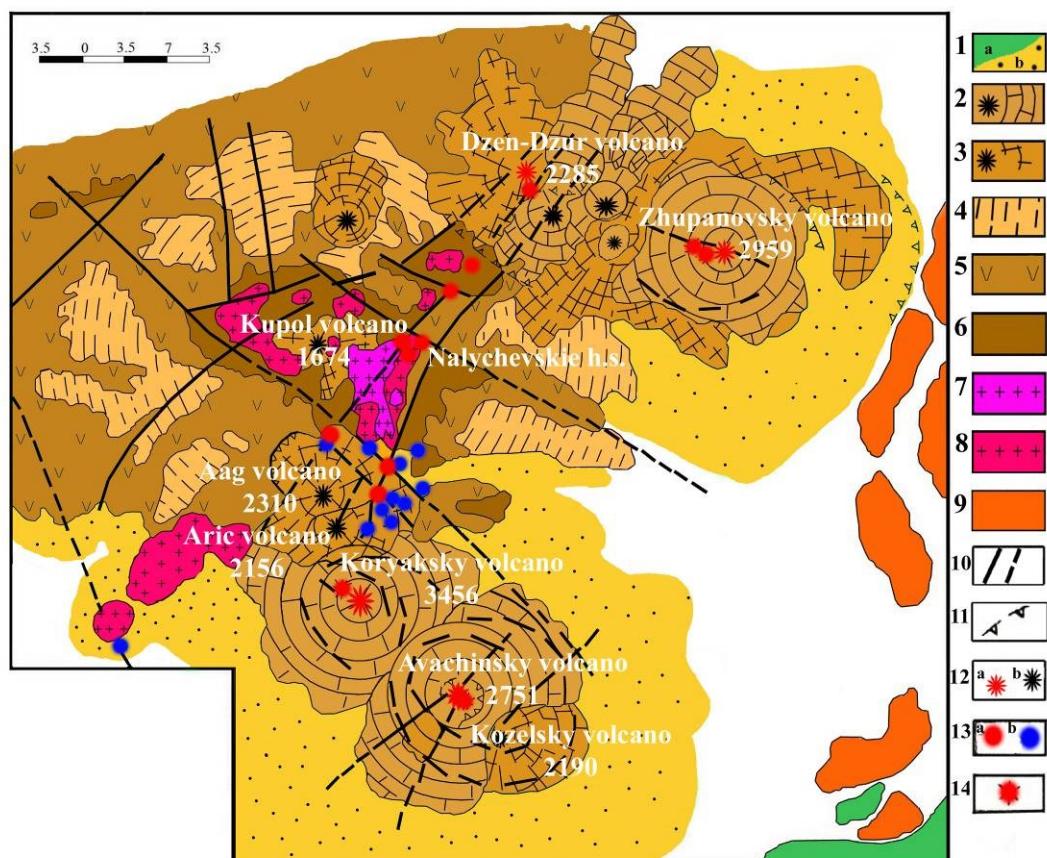
The Nalychevo hydrothermal system recently shows a combination of natural thermal features and man-made thermal springs. The bright contrast between the green line of the birch forest and destructive activities of the thermal waters can be clearly seen in Figures 2 and 3. Before the exploration was undertaken, the birch forest closely approached to the travertine terrace. Gashing of thermal waters from the crater by collapsing of the exploration borehole 2 led to spreading out of aggressive thermal solutions with temperatures of over 70°C and pH values of 6.3–7.1. The only way to cope with this catastrophic event and to protect the vegetation was to develop an artificial discharging system by a drainage channel connecting Ivanov's Gryphon with the Goryachaya River (Fig. 3). The birch forest (90 m x 100 m) died and forest rehabilitation was impossible near the Ivanov's Gryphon thermal spot (Fig. 5a). Thermal springs of the travertine terrace are steaming without the presence of water.

3. SAMPLES AND ANALYTICAL METHODS

Over 100 samples were collected from the thermal waters, travertines, and other precipitates of the Nalychevo hydrothermal system during field surveys of 2006 and 2009.

Water samples were taken from the basin of Ivanov's Gryphon as close to the center as possible, along the drainage channel, and the Goryachaya River. Water and precipitate samples were collected from Ivanov's Gryphon along the drainage channel towards the Goryachaya River at every 20 m until the sampling point of 200 m, after which the sampling interval was 100 m. Temperatures of waters were measured in the field using a mercury thermometer passing through an aluminum tube and pH measurements were done at the sampling point by a portable pH meter. Waters were collected in plastic bottles for chemical analysis.

Travertine and precipitate samples were collected simultaneously with water samples at the sampling points.



Legend

1. Glacial and fluvial deposits: a) river valley; b) volcanic deposits
2. Upper-Pleistocene volcanics
3. Middle-, Upper-Pleistocene volcanics
4. Volcanic uplands
5. Pliocene volcanics
6. Miocene volcanics
7. Quartz diorite (porphyry)
8. Andesite-dacite
9. Upper-cretaceous deposits
10. Faults
11. Caldera rim
12. a) Active volcano; b) Inactive volcano
13. a) Hot springs; b) cold springs
14. Fumarole field

Figure 4: Geological map of the Nalychevo hydrothermal system.



Figure 5: Outline of Ivanov's Gryphon, the drainage channel, travertine deposition, and samples: a - Ivanov's Gryphon basin with first 60 m of the drainage channel. The birch forest can be seen in the background; b - the drainage channel pathways with increasing travertine deposits: c - sampling point of the drainage channel of 350 m with maximum deposition of travertine in volume. Green colors indicate presence of microorganisms; d - amorphous precipitations at a sampling point 70 m from Ivanov's Gryphon; e - crystalline travertine at the sampling point of 200 m; f - travertine taken at the sampling point of 900 m.

Concentration of major cations and trace metals in the samples of the thermal waters, travertines, and precipitates were determined by inductively-coupled plasma mass spectroscopy (ICP-MS) at the Analytical Laboratory of the Institute of Problem Microelectronic Technology of Russian Academy of Science, Chernogolovka.

Travertine and precipitate samples were also examined with X-ray power diffraction analysis at the Moscow State University in Russia, and at the Hokkaido University in Sapporo, Japan.

Structures and chemical compositions of the travertines were determined by scanning electron microscope and electron micro probe analyses at IViS (Russian Academy of Science).

4. RESULTS

Drainage channel extending from the basin at the Ivanov's Gryphon down to the Goryachaya River has a total length of 970 m with different amounts of precipitation products. Ivanov's Gryphon was chosen as the sampling point 0, and the Goryachaya River as the sampling point of 970 m. At and within 200 m of Ivanov's Gryphon precipitations are small in amount (Fig. 5a). Large amounts of precipitation were recorded at a distance of 300 (Fig. 5d, c).

Water temperatures and pH values are plotted as a function of distance from the Ivanov's Gryphon basin (Figure 6a, b). Temperature is gradually decreasing from Ivanov's Gryphon along the drainage channel. Highest temperature is measured within 200 m of Ivanov's Gryphon. Temperatures of thermal waters are almost constant within 200 m with little variation (62–69°C; Fig. 6a). After sampling point of 300 m temperatures decrease rapidly. Intensive travertine precipitation was identified at sampling points between 300 and 400 m.

The pH values of waters vary from 6 to 8. Water are weakly acidic at the discharge source. As temperature drops, pH values shift to alkaline values (Fig. 6a, b).

The Nalychevo thermal waters are characterized by extremely high concentrations of boron, arsenic, iron, calcium, magnesium, sodium, potassium, rubidium, lithium, cesium, silicon, and bromine. Springs are distinguished by special balneological carbonaceous fresh-medium-mineralized, arsenic boric siliceous chlorine-sulfur-calcium-sodium thermal mineral water group.

Orkugin and Yablokova (2013) reported that sulfides precipitated from some of the hydrothermal systems in Central and South Kamchatka. At the Nalychevo springs, precipitation of sulfides or native metals was not observed. Precipitations are mostly amorphous. Some crystalline forms were identified at certain sampling points (Fig. 5e, f). Products of the thermal waters vary in color from reddish brown and dark red to pale brown, indicating high heavy element concentrations such as arsenic and iron (Fig. 5d-f).

Travertines precipitated at different distances from Ivanov's Gryphon due to cooling of thermal waters and breaching of various geochemical barriers. They are characterized by complex chemistries and mineralogies. Extremely high concentrations of toxic elements such as arsenic, iron, and boron were detected in Nalychevo travertines. The travertines also contain calcium, magnesium, manganese, strontium, barium, and antimony.

Approximately 1,000 kg of arsenic is being deposited annually at the Nalychevo hydrothermal system (Okrugin et al., 2009).

Arsenic concentrations exceed 5,000 mg/l in water and reach over 3,000 mg/g in most of the travertine samples. Waters are enriched in arsenic at and within 400–450 m of Ivanov's Gryphon (Fig. 6c). Arsenic is a typical element of the hydrothermal systems in Kamchatka (Marusenko and Komkova, 1978; Okrugin and Zelensky, 2004), but such anomalous concentrations were found only in waters of the Nalychevo springs.

Travertines are characterized by extremely high concentrations of arsenic, iron, and calcium. No difference was observed between travertines deposited at the discharge source and travertines located along the drainage channel.

The XRD data show that calcite is the most common mineral in the travertines, and is present at each sampling point. Samples collected at sampling points of 0, 250, 400, 500, 600, 700, 800, 900 and 970 m are almost completely made up of calcite with small amounts of aragonite, dolomite, and potassium feldspar. Calcite is present either as pure calcite or high magnesium calcite. The latter variety is a rare form of carbonate.

Aragonite is the second most common mineral deposited at the Nalychevo springs. Precipitates at sampling points of 100 and 200 m contain 50–86 % of aragonite.

Dolomite is a rare mineral, associated with calcite and potassium feldspar.

Small amounts of gypsum and smectite were identified at the sampling point of 60 m. Gypsum is associated with thenardite, tridymite, and jarosite.

Rare yukonite ($\text{Ca}_3\text{Fe}_7(\text{AsO}_4)_6(\text{OH}) \cdot 18\text{H}_2\text{O}$) was identified by Nishikawa et al. (2006) in precipitates from the Nalychevo hydrothermal system. This was the first discovery of yukonite in Russia and in the eastern part of Eurasia. Yukonite occurs as spherulitic aggregates of thin flakes close to the discharging source. Both amorphous and crystalline yukonite were found. Chemical composition of the Nalychevo yukonite shows variable contents of calcium, iron, arsenic, and siliceous.

Some additional minerals were previously reported from the travertines such as opal, rivermandite, limonite, zeolite, micas, and goethite (Vasilevskii et al., 1977a,b; Litvinov et al., 1999; Saji et al., 2004).

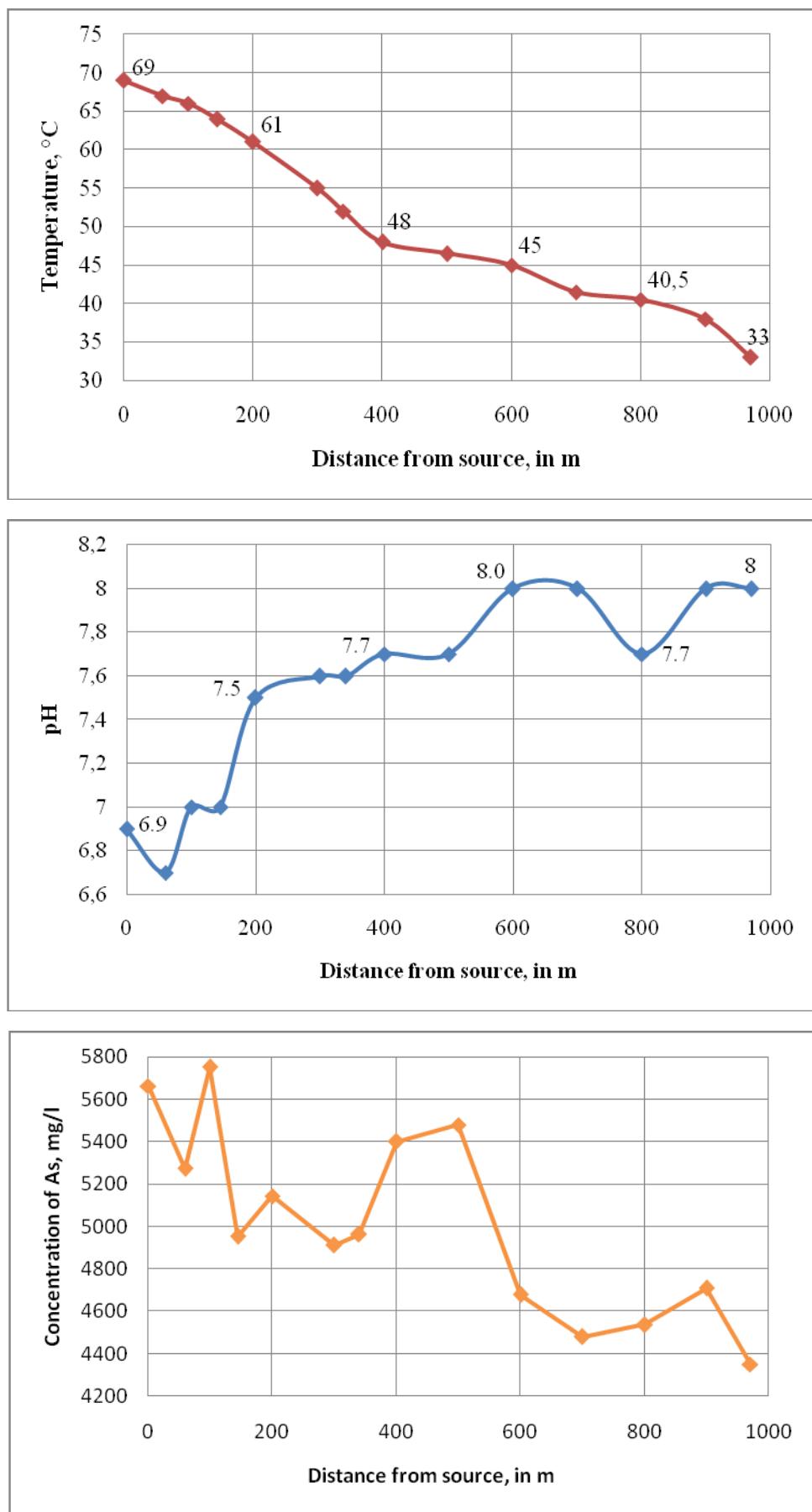


Figure 6: Plots showing: a - temperatures of thermal waters along the drainage channel; b - variations in water pH along the drainage channel; c – arsenic concentrations of Ivanov's Gryphon and the drainage channel.

Kamchatkan hydrothermal systems are also known as a favorable environment for different kinds of bacteria and plants (Okrugin et al., 2002; Okrugin and Zelensky, 2004; Nishikawa et al., 2006). The Nalychevo springs are enriched in toxic elements generating microorganism colonies.

5. CONCLUSIONS

The Nalychevo hydrothermal system is a unique occurrence formed by both humans and natural causes.

The thermal springs are of carbonaceous fresh-medium-mineralized, arsenic boron siliceous chlorine-sulfur-calcium-sodium thermal water group.

Thermal waters of the Nalychevo hydrothermal system are classified as a special Nalychevo balneological water type. Analogues of this water type have not yet been found.

Arsenic is a main element in the thermal waters and in the travertine.

Travertine deposits along the drainage channels develop in all seasons. They contain anomalous concentrations of iron, boron, and arsenic, some of the most toxic elements.

Approximately 1,000 kg of arsenic is being deposited each year along the drainage channel.

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REFERENCES

Firstov, P.P., Rashidov, V.A., Melnikova, A.V., Andreev, V.I., and Shulzhenkova, V.N.: Nuclear-geophysical investigation in Nalychevo National Park (Kamchta), *Vestnik Kraunc. Science of Earth*, **17**, (2011), 91-101.

Kovalev, G.N., Komkova L.A., Marusenko, Yu. P.: Connection of some physico-chemical parameters of Nalychevo hydrothermal system, *Bulletin of Volcanic Stations*, **45**, (1969), 39-46.

Litvinov, A., Patoka, M., Frolov, Yu., Kolyada, A., Pozdeev, A., and Pavlova, L.: Mineral map of Kamchatka region 1:500 000. Catalog of ore deposits, manifestation, point of mineralizations, *Geological survey of Kamchatka*. St. Petersburg VSEGEI Print, (1999).

Masurenko, Yu. P., and Komkova L.A.: Geodynamics and ore-forming processes in the Dome-ring structure of a volcanic belt, *Nauka Print*, Moscow, (1978). In Russian.

Nishikawa, O., Okrugin, V., Belkova, N., Saji, I., Shiraki, K., and Tazaki, K.: Crystal symmetry and chemical composition of yukonite: TEM study of specimens collected from Nalychevskie hot springs, Kamchatka, Russia and from Venus Mine, Yukon Territory, Canada, *Mineralogical Magazine*, **70**, (2006), 73-81.

Okrugin, V. M., Belkova, N.L., and Tazaki, K.: Biogenic formation in modern hydrothermal systems of Kamchatka Peninsula (Mutnovsko-Asachinsky volcanogenic centre), *Abstracts*, 1st International Symposium on Life and Rock, (2002).

Okrugin, V.M., and Zelensky, M.E.: Miocene-to-Quaternary centre of volcanic, hydrothermal, and ore-forming activity in Southern Kamchatka, *Metallogeny of the Pacific Northwest (Russian Far East): Tectonic, Magmatism, and Metallogeny of Active Continental Margins*, (2004), 147-176. In Russian.

Okrugin, V.M., Andreeva, E.D., Bukhanova, D.S., and Kulikov, V.V.: Medical-balneological importance of arsenic in the thermal waters of Nalychevo and Vilyuchinsky hydrothermal systems in South Kamchatka, *Proceedings*, Conference on Kamchatka is a health resort in North-Eastern regions of Russia. Petropavlovsk-Kamchatsky, (2009).

Okrugin, V. M., and Yablokova, D.A.: Comparative analysis of sulfide sferoloidov gold-bearing conglomerates of the Witwatersrand in South Africa and modern hydrothermal systems in Kamchatka, *Vestnik Kraunc. Earth Science*, **22**, (2013), 196-204.

Okrugin, V.M., Yablokova, D.A., Andreeva, E.D., Sheshkanova K.O., Chubarov, V.M., Philosophova, T.M., Moskaleva, S.V., and Chubarov, M.V.: New data on pyrite from modern and extinct hydrothermal systems in Kamchatka region, *Proceedings*, Conference on Volcanism and related processes. Institute of Volcanology and Seismology, Petropavlovsk-Kamchatsky, (2014). In Russian.

Piip, B. I.: Thermal springs of Kamchatka, *AN USSR*, (1937).

Rashidov, V.A., and Firstov, P.P.: Students' research camp "Geophysic-10" and "Geophysic-12" at the Nalychevo national Park (Kamchta), *Vestnik Kraunc. Earth Science*, **20**, (2012), 207-213. In Russian.

Rashidov, V.A., Fedorchenko, I.A., Dolemen, I.F., Dubrovskaya, I.A., Melnikova, A.V., and Andreev, V.I.: The study of the thermal spots at the Nalychevo hydrothermal system in the summer field of 2012, *Proceedings, Conference on Volcanism and related processes. Institute of Volcanology and Seismology, Petropavlovsk-Kamchatsky*, (2013). In Russian.

Saji, I., Nishikawa, O., Belkova, N., Okrugin, V., and Tazaki, K.: Chemical and microbiological investigations of hot spring deposits found at the hydrothermal systems of Kamchatka Peninsula, Russia, *Sci. Rep. of Kanazawa University*, **48**, (2004), 73-106.

Tazaki, K., Okrugin, V., Okuno, V., Belkova, N., Islam, A. R., Chaerin, S. K., Wakimoto, R., Sato, K., and Moriichi, Sh.: Heavy metallic concentration in microbial mats found at hydrothermal systems, Kamchatka, Russia, *Sci. Rep. of Kanazawa University*, **47**, (2003), 1-48.

Vasilevskii, M.M., Okrugin, V.M., and Stefanov, Yu. M.: Mineral fancies of deep ore-forming regions, *Bulleten vulkanstanstii*, **53**, (1977b), 111-114. In Russian.

Sheshkanova K.O.: New data on composition of precipitates from Grifon Ivanova Nalychevskaya hydrothermal system, East Kamchatka, *Vestnik Kraunc. Earth Science*, **8**, (2006), 201-205.