

# The Formation of the Chemical Composition of Karymsky R. Water As Affected by Hydrothermal and Volcanic Activity in Kamchatka

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**Abstract**—This paper examines the Karymsky Volcanic Center to estimate how much volcanic and hydrothermal activity affects the chemical composition of river water. We evaluate the volumes of major and trace elements coming to the Pacific Ocean via the Karymsky River. We assess the quality of river water in compliance with the regulations for potable water, water used for household work, and in fisheries. It is shown that the formation of ion load of the river water mostly occurs by inflow of thermal waters, as well as due to water-soluble complexes of ashes discharged by Karymsky Volcano and coming to the catchment area of the river. The annual volume of dissolved material transported by the river to the Kronotsky Bay of the Pacific Ocean amounts to more than 90 kilotons.

**Keywords:** Kamchatka, river, quantitative estimate, trace elements, chemical composition, caldera

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## INTRODUCTION

Volcanic areas play the key role in regulating the geochemical cycles of various important chemical elements that take part in climate change, as well as in changes affecting the Earth's atmosphere and biosphere. Eruptions discharge enormous masses of material onto the ground surface in the form of pyroclastics and lava flows. Arriving into the atmosphere, volcanic ash is transported by air currents over great distances, affecting the environment of man and the natural ecosystems. Along with pyroclastic material, eruptions also eject magmatic volatiles (CO<sub>2</sub>, SO<sub>2</sub>, HCl, HF, among others) that separate from magma by degassing. One of the most widely abundant and dangerous volcanic gases is sulfur dioxide. The arrival of SO<sub>2</sub> into the atmosphere occurs both during eruptions and during periods of passive volcanic degassing. When sulfur dioxide comes into the atmosphere, it interacts with water vapors, producing hydrogen sulfate, and this directly affects the ecosystems. Falling on the ground surface as acid rain, hydrogen sulfate removes nutrients from the soil that are necessary for vegetation, affects pH and the chemical composition of surface and ground waters.

There are other natural agents that affect onshore and offshore ecosystems; these are thermal waters having various physical and chemical properties, and which are also discharged in volcanic calderas. The chemical composition of waters in draining streams, after forming creeks with thermal runoff can change

radically, converting the water into a stream that is unsuitable for drinking and household activities.

The Karymsky Volcanic Center (KVC), which is situated in the central part of Kamchatka eastern coast on the shore of the Kronotsky Bay (Fig. 1a) is one of the more spectacular examples where one can fully evaluate the consequences of the influence exerted by both volcanic and hydrothermal activity on river drainage.

The center contains two active volcanoes, Karymsky and Malyy Semyachik, and discharges of thermal waters of varying volumes and chemical composition. A unique natural phenomenon occurred there in January 1996 that affected all ecosystems. A powerful, but short-lived, underwater eruption occurred in the Akademii Nauk caldera simultaneously with the beginning of an eruption cycle at Karymsky (Fedotov, 1997; Muraviev et al., 1997). The event gave rise to the appearance of a new peninsula (Novogodny) in the northern part of Lake Karymsky, causing a cardinal change in its geochemical and biotic regime, and producing new thermal springs both on shore and under water (Ushakov and Fazlullin, 1997; Vergasova et al., 1998; Vakin and Pilipenko, 1998, 2001; Karpov and Dvigalo, 2009). The recovery of the lake hydrochemical regime and microbiota were considered in detail in (Karpov et al., 2008; Taran et al., 2013; Nikolaeva et al., 2018).

Karymsky Volcano, which stands in the eponymous caldera, is one of the most active volcanoes in

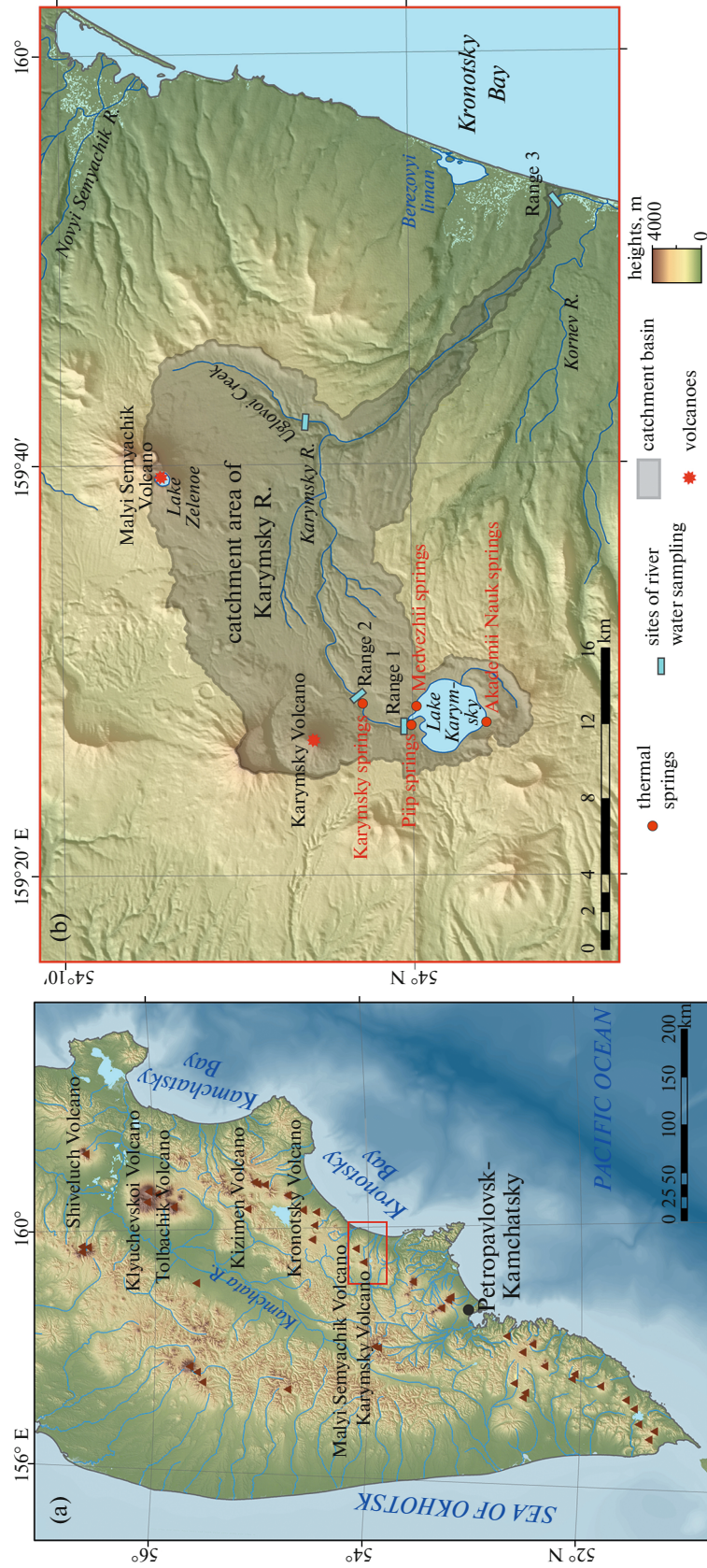


Fig. 1. The location of the Karymsky Volcanic Center (a) and sites where thermal and river water was sampled (b).



**Fig. 2.** The Karymsky River at different locations from the source to the mouth. (a) Lake Karymsky, which is the source of the eponymous river; (b) “Thermal Subsidence” in the Karymsky caldera; (c) Karymsky Volcano during the active phase; (d) confluence of Karymsky R. and Uglovoi Creek; (e) lower reaches of Karymsky R.

Kamchatka. It is a typical central-type stratovolcano about 1500 m high, and is composed of lava flows with interbeds of pyroclastic material. Its eruptions are typically explosive and explosive–effusive ones. Over 20 eruptions have occurred since 1771 (when the first historical evidence became available) (Ivanov et al., 1991). The last period of activity which began in January 1996 has continued until now with some interruptions. Small lava flows were discharged onto the volcano’s slopes until 2004. The most recent lava features (in the form of a lava dome in the crater) were noted in December 2005. After this the eruption became explo-

sive. Between 2005 and 2022 inclusive the volcano’s activity was medium in degree. The most frequent occurrences consisted in short-lived ejections of ash up to 3 km height above sea level, occasionally reaching 5–6 km above sea level, or even 10 km above sea level in some exceptional cases (Fig. 2c).

The Karymsky River is the only drainage element in the KVC. It maintains a practically constant level and volume of water in the eponymous lake in the Akademii Nauk caldera, and traverses the Karymsky caldera depression collecting all ground and thermal

runoff as it goes. In its middle reaches the river receives the waters of Uglovoi Creek which drains the slope of Malyi Semyachik Volcano, and empties into the Kronotsky Bay of the Pacific Ocean (see Fig. 1b). The river is 45 km long, its catchment area (together with that of Lake Karymsky) is 248 km<sup>2</sup>.

In spite of the enormous amount of work to study the impact of the 1996 underwater phreato-magmatic eruption on the environment (Fedotov et al., 1998; Andreev et al., 2003; Karpov et al., 2007; Dirksen and Dirksen, 2007; Andreev and Nikolaeva, 2012), river drainage has been little studied. There are no published data on the composition of the Karymsky River at the mouth, no quantitative or qualitative estimates have been made to assess the output of material (both dissolved and suspended) transported by the river waters of the Karymsky Volcanic Center into the Pacific Ocean both before and after the 1996 eruption. The dynamics of the river chemical composition along the riverbed and over time has been investigated.

In connection with the above, the goal of the present study is to make a general estimate of the impact of volcanic and hydrothermal activity on the chemical composition of the Karymsky River, including changes in water composition based on sampling over the years, quantitative and qualitative estimates for the output of volatile and rock-forming components into the Kronotsky Bay of the Pacific Ocean from the Karymsky Volcanic Center.

#### THE DRAINAGE AREA OF THE KARYMSKY RIVER

According to (*Vulkanicheskii...*, 1980), the Karymsky Volcanic Center is a powerful 3D system that has been draining the Earth's interior during the last 2 million years, with the total output of silicate material transported onto the ground surface being 1700 km<sup>3</sup>. As to structure, the Center is a tectonic dome complicated with caldera depressions and volcanic edifices in the axial part. The mutual locations of calderas and volcanoes suggest identifying the following three main sectors: Akademichesky, Karymsky, and Semyachinsky. There is a graben in the axial part of the structure, which can best be followed in the area where the calderas of Odnoboky, Akademii Nauk, and Karymsky volcanoes are adjacent to each other.

The Karymsky River has its source in the Akademichesky sector of the KVC (see Figs. 1, 2) as an outlet from Lake Karymsky. The lake has an area of ~12 km<sup>2</sup> and is ~4 km in diameter; it occupies the bulk of the bottom in the Akademii Nauk caldera. The lake receives the waters of about 30 constant and temporary streams, discharges of thermal water occur both onshore and offshore. The bulk of the hydrothermal discharge consists of boiling alkaline waters, including those functioning as geysers, of the Akademii Nauk springs situated on the southern shore. There are two

other groups of springs situated in the north part of the caldera near the source of the Karymsky River (Piipovskie and Medvezhii) which were formed after the 1996 underwater eruption (Muraviev et al., 1997; Vakin and Pilipenko, 1998; Vergasova et al., 1998). One consequence from the impact of the volcanic event was a burst in hydrothermal activity in the area. Several groups of springs have come into being with varying temperatures and chemical compositions. Some large discharges were situated directly in the bed of the Karymsky River near the source (Vakin and Pilipenko, 1998; Karpov et al., 2008). The number of these thermal occurrences and the intensity of hot water discharge were gradually diminishing (Taran et al., 2017; Nikolaeva et al., 2018). By the summer of 2018 only two small groups of hot (with temperatures reaching 60°C) springs were observed. One of the groups (the Medvezhii springs) discharges into the lake with a total output of ~1 L/s, while the other group (the Piipovskie springs) is drained by the Karymsky River.

The Karymsky River flows from the Akademii Nauk caldera into an adjacent caldera along a narrow ravine of tectonic origin as a violent stream with rapids and a small (below 3 m height) waterfall. The river traverses the Karymsky caldera in its southeastern part, which is the lowest and free of lava flows; the part is called "Thermal Subsidence" (Vakin and Pilipenko, 2001) (see Fig. 2b). The subsidence receives ground runoff of cold waters from an area of more than 40 km<sup>2</sup>, making the area a swamp. Acidulous thermal water is discharged at the center of the subsidence with a total output of ~700 L/s (Pilipenko, 1989). There are springs of two types: ascending springs that are surcharged with gas and have temperatures reaching 42°C with low discharge rates (below 1 L/s) and descending vigorous water streams charged with carbon dioxide and whose discharge rates can reach 100 L/s. The springs of the former type are situated directly in the swamped area, while those of the latter type are discharged from below lava flows along the northern rim of the subsidence.

The 1996 underwater eruption in the Akademii Nauk caldera has had an effect on the Karymsky caldera as well. Waves of a powerful flood have passed along the Karymsky River as far as the mouth twice, at once after the eruption, owing to a rapid melting of ice on the lake, as also in May 1996 after the dam formed by eruption ejecta was broken at the river source. An enormous volume of pyroclastic material was transported into the "Thermal Subsidence", with the river changing its bed at the inlet into the caldera (Vakin and Pilipenko, 2001). The new bed has persisted until now. The total volume of thermal discharge did not change after the eruption (Vakin and Pilipenko, 1998; Taran et al., 2017). The entire thermal and cold surface runoff in the subsidence is received by the Karymsky River.

Past the “Thermal Subsidence”, the Karymsky River flows again along a narrow box-shaped valley making numerous rapids and waterfalls. The river receives the waters of a few small creeks that flow down Karymsky Volcano and from the caldera sides. It receives the waters of a single large tributary ( $Q = 1.5 \text{ m}^3/\text{s}$ ) at a height of 343 m; this is Uglovoi Creek which drains the slopes of Malyi Semyachik Volcano (see Figs. 1, 2d). Malyi Semyachik stands in the north-eastern KVC; it is a massif  $\sim 3 \text{ km}$  in extent consisting of three coalesced edifices of different ages. Kraino-Semyachik is the only active cone crowned with a deep crater whose bottom is occupied by Lake Zelenoe, an ultra-acid ( $\text{pH} < 1$ ) mineralized water body. The lake was formed after the 1945–1946 eruption (Kalacheva et al., 2022 and the references therein).

As one moves toward the Kronotsky Bay, the Karymsky River changes its flow. As an example, in the lower reaches the riverbed becomes less sinuous, and the flow is gradually decelerated (see Fig. 2e). There are no significant tributaries. The total volume of water coming into the Kronotsky Bay (based on measurements at the mouth made in September 2021) is  $9 \text{ m}^3/\text{s}$  (at Range 3) (see Fig. 1b).

## METHODS OF STUDY

We studied the hydrothermal and volcanic contributions into the composition of the Karymsky R. water, as well as evaluated the output of dissolved components, by conducting hydrologic and hydrochemical surveys at three hydrologic gauging stations: at the source, below the Karymsky springs, and at the river mouth. We also sampled all groups of thermal waters that are discharged within the calderas, and the largest tributary (Uglovoi Creek). The field surveys were carried out in the summers and falls of 2018, 2019, 2021, and 2022.

At the sampling sites we measured pH, temperature, and electrical conductance (mineral content). Water samples for trace element analysis were collected in 0.5L bottles, with trace elements being determined from filtered samples put in test tubes of 50 mL each.

We determined water discharge in the Karymsky River at different cross-sections and in other streams by measuring current velocity along the river profile, measuring depths at a step of 1–2 m, and measuring river width. Current velocity was measured using an ISP-1M current meter.

Trace elements in water samples were determined at the Analytical Center IVS FEB RAS using standard methods. Trace elements were determined by the ICP-MS method (Agilent 7500 CE) at the Primorie Center for Local Elemental and Isotope Analysis (Far East Geological Institute FEB RAS, Vladivostok).

The OriginPro 2021 program package was used to display geochemical data and for interpretation of results.

The source of the digital relief model (see Figs. 1, 2) was Shuttle Radar Topography Mission (SRTM), images with resolution 1 s (30 m) SRTM 1 Arc-Second Global (DOI: /10.5066/F7PR7TFT). The bathymetric base map for offshore areas was the digital model of ocean bottom topography developed for the project GEBCO (The General Bathymetric Chart of the Oceans), version as of June 2022 GEBCO Compilation Group (2022) GEBCO 2022 Grid (DOI: 10.5285/e0f0bb80-ab44-2739-e053-6c86abc0289c).

Remote measurements of sulfur dioxide emission at Karymsky Volcano were made in 2011 using a scanning system based on differential optical absorption spectrometry (DOAS). In technical terms the scanner is consistent with the equipment developed for the project Network for Observation of Volcanic and Atmospheric Change (NOVAC) (Galle et al., 2010). Land measurements were made from the Karymsky caldera, with two temporary stations being installed within line of sight for volcanic plumes at distances of 3–3.5 km from the volcano’s summit (Fig. 3).

The satellite data we used were taken from the global catalog of large sources of  $\text{SO}_2$  emission based on measurements obtained with the spectrometers Ozone Monitoring Instrument (OMI), Ozone Mapping and Profiler Suite (OMPS), and TROPOspheric Monitoring Instrument (TROPOMI) (Fioletov et al., 2023). The catalog contains data from 2005 to 2021 inclusive.

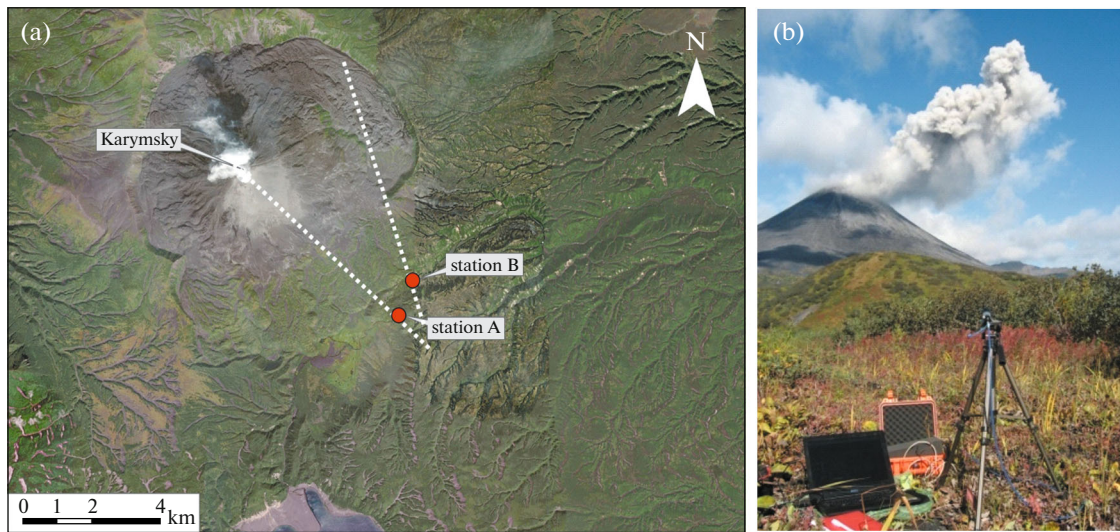
We determined the mass and area of volcanogenic  $\text{SO}_2$  contained in air using data obtained via an AIRS spectrometer (Atmospheric Infrared Sounder) installed at an AQUA satellite. AIRS is operated in the infrared range, unlike the OMI, OMPS, and TROPOMI instruments; in this range molecules of sulfur dioxide are intensively absorbed in a spectral window approximately equal to  $7.34 \mu\text{m}$ .

## RESULTS AND DISCUSSION

### *The Emission of $\text{SO}_2$ and Ash Plumes Discharged by Karymsky Volcano*

We studied the emission of sulfur dioxide discharged by Karymsky Volcano based on multiyear satellite-based and land-based observations. It was found from land-based observations by differential optical absorption spectrometry that there is a distinct pattern in the distribution of gas concentrations as a function of explosion intensity at the volcano (Table 1). The mean amounts of  $\text{SO}_2$  during ash emission reaching heights of 1.5–3 km above the volcano crater were 300–480 tons per day.

Continuous satellite-based observations of the volcano’s activity have been conducted for more than 15 years at the Institute of Volcanology and Seismol-



**Fig. 3.** Measuring concentrations of sulfur dioxide with a portable DOAS spectrometer. (a) temporary stations (dashed line represents the scanning axis), (b) a view of station A.

ogy FEB RAS. The main goals of this monitoring include the detection of ash plumes and clouds, the determination of their parameters (length, area, and azimuth of movement), and determining the concentration of sulfur dioxide both during passive degassing and during the active phase of an eruption (Girina et al., 2018). Satellite-based monitoring enables continuous observations to be made of all active volcanoes in Kamchatka and on the Kuril Islands. The result is to have multiyear data (Fioletov et al., 2023) that can be used to assess the total emission of sulfur dioxide for any active volcano. It has been found from these data that the mean annual emission of sulfur dioxide is 220–250 kilotons per annum for the period from 2005 to 2021 inclusive (Fig. 4), which is comparable with the data derived from land-based observations.

The dominant directions of travel for gas and ash plumes are east and southeast of the volcano (see Figs. 4b–4d), i.e., toward the Kronotsky Bay. Satellite images clearly show zones covered by ash deposits (see Fig. 4d). An example of spatial propagation of ash and gas plumes is furnished by the eruption of November 3, 2021 (see Fig. 4c). The plume was recorded on MODIS satellite images. The height of the ash ejection was 6–8 km above sea level ([\[net.ru/ivs/kvert/van/?n=2021-135\]\(http://www.ksc-net.ru/ivs/kvert/van/?n=2021-135\)\). The ash plume extended east–southeast of the volcano. Satellite images clearly show a differentiation between the ash plume and the gas plume. The gas plume \( \$\text{SO}\_2\$ \) was higher \(9 km above sea level\) compared with the ash plume \(6–7 km above sea level\).](http://www.ksc-</a></p>
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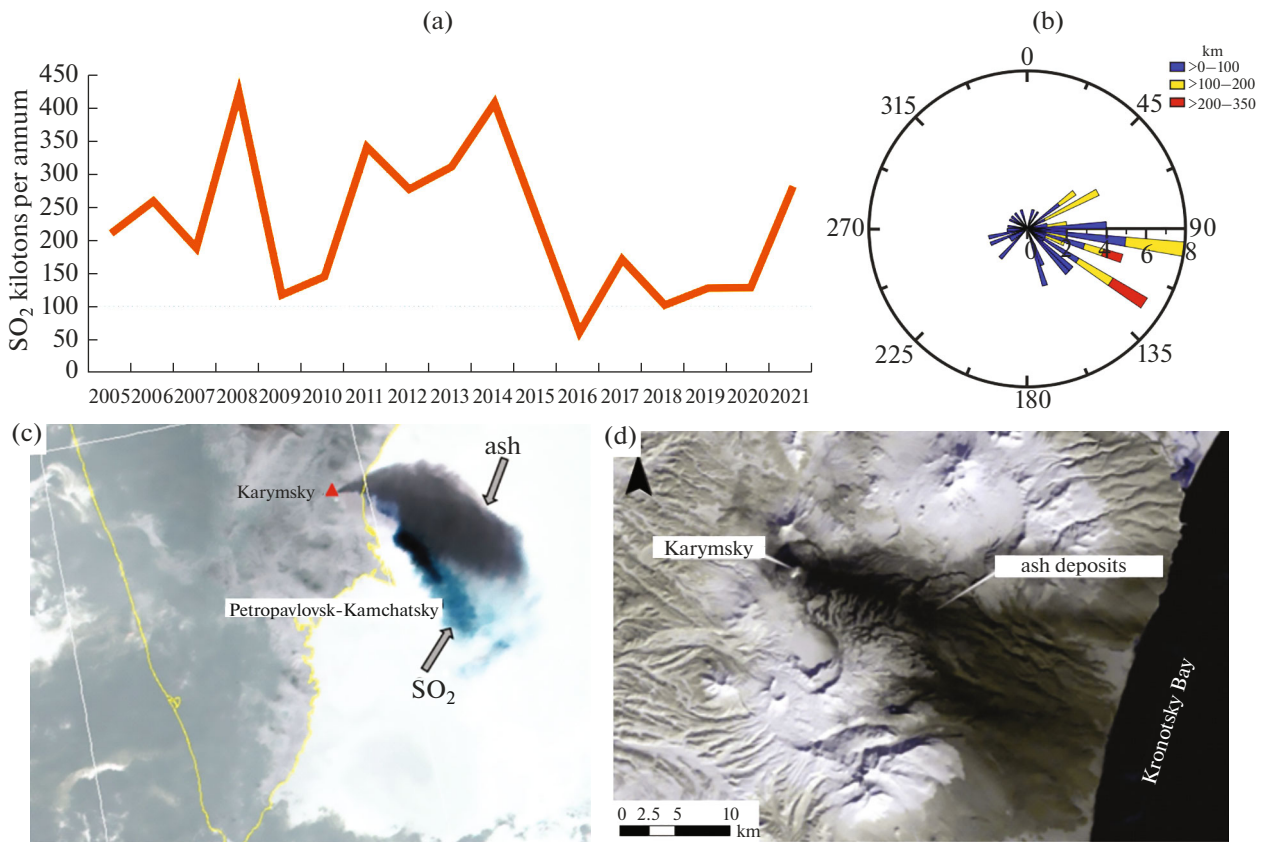
The issue of determining the mass of the volcanic ash ejected during an eruption is not simple. The existing methods of satellite analysis allow determining the ash mass only based on the upper limit of the ash cloud. However, a land-based infrared survey of the ash cloud yielded the lowest mass of the ejected ash during a sufficiently small eruption up to a height of 1.5 km above the crater of the volcano. This lowest value was 69 tons of ash (Lopez et al., 2013).

#### *The Chemical Composition of the Karymsky R. Water*

The major-element composition and its evolution over time. The Karymsky River is noted for high variability in the chemical composition of its water, both along the stream and over time (Table 2). Because the water composition at the source is consistent with the integrated composition of the eponymous lake, all

**Table 1.** The distribution of sulfur dioxide concentrations in relation to the activity of Karymsky Volcano (September 10–14, 2011) (Arellano et al., 2012)

	Number of measurements	Plume direction of travel	Speed of plume, m/s	Plume height, m	Flux of $\text{SO}_2$ , t/day		
					Range of values	mean	Rms deviation
Station A	189	$328 \pm 35$	6	$1375 \pm 340$	28–3145	<b>480</b>	429
Station B	243	$333 \pm 21$	6	$1375 \pm 340$	72–1159	<b>295</b>	202
A + B	432	$331 \pm 28$	6	$1375 \pm 340$	28–3145	<b>376</b>	334



**Fig. 4.** The emission of sulfur dioxide by Karymsky Volcano during the period 2005–2021 based on satellite data (a); a diagram of propagation (frequency of occurrence for directions of propagation in relation to the cardinal points and distance (in kilometers) for gas and ash plumes emitted by Karymsky Volcano (b); propagation of ash (dark) and gas (blue) plumes erupted by Karymsky. The total plume area is 24620 m<sup>2</sup>. A MODIS Terra image taken at 11:37 UTC, November 3, 2021 (c); a typical area of ash deposits for eruptions of Karymsky Volcano. A Landsat-8 image taken on March 2, 2019 (d).

changes occurring in the lake hydrochemistry affect the quantitative and qualitative parameters of the river ion drainage at the river section of interest. The chemical composition of Lake Karymsky water is controlled by the composition of atmospheric precipitation, as well as by that of surface and underground waters that go into the water body. The water at the source was of the hydrocarbonate–sodium hydrochemical type (Fig. 5) with mineral content <100 mg/L and pH ~ 7 before the 1996 event as derived from earlier observations carried out in 1984. The chemical analyses of water sampled in 1987 and in 1993 showed some changes in the relationships among major elements. The anion composition involved a trend toward increasing chlorine ions and decreasing hydrocarbonate ions, while the cation composition reveals a displacement toward increasing concentrations of Ca<sup>2+</sup> (from 1.2 to 6 mg/L). The limited amount of data does not enable us to draw more definite inferences; it is however quite possible that the eruption in question was preceded by degassing that contributed volatiles (S and Cl) into lake water.

The underwater eruption of 1996 started a geochemical evolution in Lake Karymsky due to fumarolic, postmagmatic, and hydrothermal activity (Nikolaeva et al., 2018). It was shown in this reference that sulfur, calcium, and magnesium came into the water along with erupted material, while increased hydrothermal activity enriched the solution in sodium, potassium, and chlorine. The result was to have a sharp change in the hydrochemical type of water. The water at the river source was classified as belonging to the sulfate–sodium hydrochemical type, pH decreased down to 3.2, while the mineral content increased to reach 0.7 g/L. As time went on, the role of the volcanic component in the formation of chemical composition for the water (which was brought into the lake once only) started to gradually decrease, while the hydrothermal contribution has remained at a constant level until the present time. Newly formed and constant patches where thermal chloride–sodium waters are discharged (both surface and underwaters waters) are the main agents to bring Na, K, and Cl into the lake until now. The main group of hot and boiling springs, including those operating in the geyser mode,

**Table 2.** The chemical composition of the Karymsky River during the period from 1984 to 2022 inclusive, mg/L

Date	T	pH	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>	SiO <sub>2</sub>	S <sup>1</sup>	PS <sup>2</sup>
River source (range 1)													
July 1984	1.0	7.05	10.4	1.6	1.6	0.5	8.5	3.8	35.1	0.10	30.0	92	a
April 1989	1.5	6.70	13.0	1.2	2.8	0.2	11.0	6.2	19.0	n.d.	33.1	87	b
August 1993	7.5	7.45	14.0	0.9	6.0	0.6	21.3	4.8	22.0	n.d.	45.0	115	h
July 1996	16.0	3.30	57.0	5.8	66.0	10.0	38.0	331.0	0.0	1.50	119.4	629	b
July 1997	17.0	3.76	49.5	4.1	38.5	9.7	36.2	211.3	0.0	0.80	89.4	439	c
August 1998	14.0	3.83	51.4	7.6	41.3	10.5	42.8	149.8	0.0	1.00	97.9	402	d
September 1999	16.0	4.00	62.0	8.4	40.0	11.7	45.0	221.0	0.6	0.80	100.6	490	b
August 2000	17.0	4.70	69.0	6.7	34.0	8.5	43.0	206.0	6.1	0.80	125.0	499	b
July 2001	16.0	4.86	44.0	n.d.	23.3	7.8	31.9	134.5	0.6	0.60	91.7	334	d
July 2002	15.0	4.87	51.0	7.5	29.7	8.3	43.3	172.9	1.2	n.d.	60.6	375	h
August 2003	14.8	5.29	51.5	6.0	26.5	7.8	36.9	148.9	1.2	0.70	91.9	371	e
August 2005	16.5	5.98	43.0	4.7	22.0	4.9	35.5	111.4	2.4	0.40	91.6	316	e
July 2006	17.1	6.35	47.0	4.5	22.4	8.3	41.2	127.7	9.8	n.d.	73.3	334	e
August 2007	14.5	6.80	46.9	3.9	16.8	6.1	42.6	105.6	7.3	n.d.	58.2	287	e
August 2009	16.0	6.48	35.8	3.8	32.9	4.4	32.6	76.8	12.2	0.40	50.0	249	e
September 2012	15.5	7.68	38.2	3.7	12.6	3.1	31.2	83.0	18.0	0.45	50.0	240	f
August 2013	14.0	7.20	32.3	3.3	11.2	2.4	31.2	56.0	14.0	n.d.	42.4	193	e
July 2015	17.4	7.25	30.0	3.4	10.0	1.7	31.2	48.0	13.4	n.d.	65.0	203	f
July 2018	10.1	6.90	31.7	2.8	7.6	1.7	30.2	32.4	27.0	0.24	63.3	197	h
August 2022	n.d.	7.37	30.2	2.7	6.8	1.7	26.3	23.2	37.0	0.25	59.4	187	h
At the outlet from Karymsky caldera (range 2)													
July 1984	8.5	7.80	35.0	5.2	16.0	20.0	30.0	66.0	137.0	0.10	43.1	352	a
August 1993	14.0	6.12	34.0	2.3	20.0	18.2	31.9	81.6	107.0	n.d.	48.6	343	h
May 1996	n.d.	3.25	57.4	6.6	66.0	15.1	38.3	374.0	0.0	0.13	119.4	677	g
July 1996	16.0	6.40	299.0	26.0	50.0	33.0	50.0	691.0	181.0	0.80	77.5	1408	b
August 1997	19.0	6.20	71.0	9.7	38.0	43.0	95.0	192.0	200.0	0.50	74.4	724	b
September 1999	17.0	6.90	102.0	10.0	40.0	52.0	91.0	221.0	223.0	0.60	92.5	832	b
August 2000	20.0	6.40	101.0	8.7	39.0	40.0	86.0	230.0	207.0	0.50	115.0	827	b
July 2015	19.5	6.40	62.0	6.8	22.0	29.0	51.0	134.0	132.0	0.45	59.0	496	h
July 2018	11.7	6.90	56.0	4.6	20.1	33.6	52.0	111.1	139.0	0.22	56.6	473	h
September 2019	14.7	6.21	57.5	4.8	21.2	35.4	54.1	111.6	143.0	0.31	57.1	485	h
River mouth (range 3)													
September 2021	10.0	7.22	33.0	3.6	19.0	15.3	28.4	84.5	107.0	0.40	74.4	366	h

<sup>1</sup> salinity; <sup>2</sup> published source: (a) (Pilipenko, 1989), (b) (Vakin and Pilipenko, 2001), (c) (Karpov, 2004), (d) (Andreev and Nikolaeva, 2012), (e) (Nikolaeva et al., 2018), (f) (Taran et al., 2017), (g) (Fazlullin et al., 2000), (h) the present paper.; n.d. means no data.

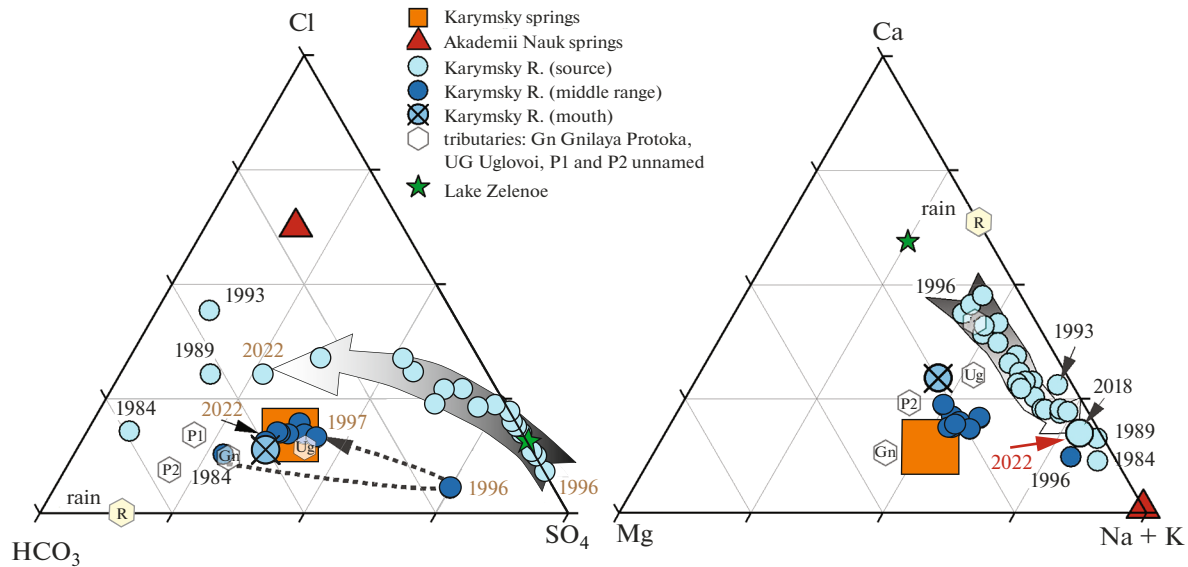


Fig. 5. Anion (a) and cation (b) compositions (mg/L) of river and thermal waters in the Karymsky Volcanic Center.

is situated on the south shore of the lake (the Akademii Nauk springs) (see Fig. 1b). They discharge chloride sodium water with the maximum concentration Cl  $\sim$  400 mg/L, while the concentration of sulfate ions and hydrocarbonate ions is slightly above 100 mg/L. The level of Na<sup>+</sup> is 300 mg/L, magnesium is absent from the cation composition, while sodium is at the level of a few units (see Table 2).

The long-continued hydrochemical evolution of the lake leads to continued transformation of the hydrochemical type of water at the source of the Karymsky River (see Fig. 5). During the entire period of observation the transformation was proceeding from the Na–HCO<sub>3</sub> type through Ca–SO<sub>4</sub> toward Na–HCO<sub>3</sub>–Cl. As of 2022, the water composition was similar to the 1989 data, judging by the cation relationship, while the anion composition has not yet reached the original relationships, although the tendency is to move in this direction, in spite of the appearance of a new underwater thermal discharge with a high concentration of Cl<sup>–</sup> after the 1996 eruption.

The relationship between cations and anions has remained constant at the outlet from the “Thermal Subsidence” (range 2) during the entire period of observation, except for 1996, when there was a sharp change in hydrochemical type (toward Na–SO<sub>4</sub>). This was caused by the arrival of a considerable volume of Na and SO<sub>4</sub> into the water owing to washout of products of ion exchange reactions from the fine-grained dispersed deposits of the mud flows that went along the Karymsky valley in the spring of 1996 (Vakin and Pilipenko, 2001).

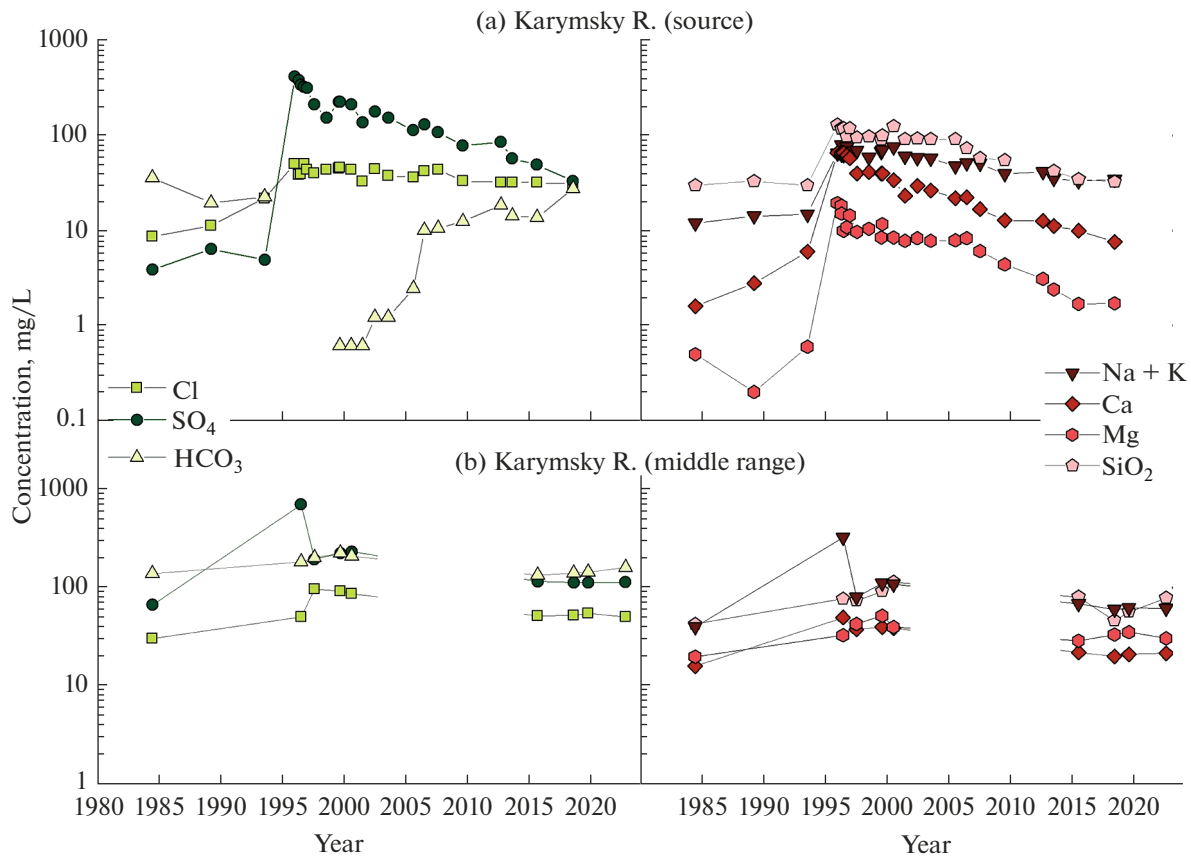
Figure 6 shows the variation in the chemical composition of river water over time based on measure-

ments made at two gauging stations (the source and outlet from the Karymsky caldera). The plots are based on our data and on all published results of chemical analyses of river water (Pilipenko, 1989; Vakin and Pilipenko, 2001; Fazlullin et al., 2000; Karpov, 2004; Karpov et al., 2008; Andreev and Nikolaeva, 2012; Nikolaeva et al., 2018).

One can see a sharp rise in the concentrations of all components in 1996 which was due to a sharp change in the chemical composition of lake water, both at the source and at the second gauging station.

Compared with 1993, the concentration of sulfate ions at the river source increased by a factor of 80 to reach 374 mg/L in 1996, and that of Cl reached 38 mg/L (the increase was by a factor of 2.5). Thanks to a considerable drop in pH (from 6.7 to 3.2), the concentration of HCO<sub>3</sub><sup>–</sup> decreased to reach zero. The water was found to contain one of the main elements accompanying volcanic exhalations, namely, fluorine (1.7 mg/L). The amount of major cations also increased considerably (see Table 2): Na<sup>+</sup> by a factor of 4, Ca and Mg by a factor of 10, and SiO<sub>2</sub> by a factor of 2.5. The total mineral content increased by a factor of 6 (reaching 0.6 g/L).

Subsequently, constant water exchange began to act toward a recovery of the lake hydrochemical regime, which was also recorded at the Karymsky R. source. As can be seen from the plot (see Fig. 6a), the anion composition showed a gradual decrease in the concentration of sulfate ions of SO<sub>4</sub> and an increase in HCO<sub>3</sub>, with this going on nearly 30 years since the 1996 events. A sharp increase in hydrocarbonate ions occurred, when pH increased to reach 6 (2005–2006). Nevertheless, the concentration of chlorine ions long (until 2007) persisted at the level that was observed



**Fig. 6.** The variation in the concentrations of major components in the water of the Karymsky River at the source (a) and at the outlet from Karymsky caldera (b).

since 1996 (~40 mg/L) and afterwards decreased down to 30–32 mg/L (2009–2018), which was due to a constant additional hydrothermal contribution into the lake water. The decreasing tendency was also recorded in 2022.

After the sharp spike in 1996, the cation composition shows (see Fig. 6a) decreasing concentrations of all components occurring at different rates. The slowest rate is for the concentration of Na<sup>+</sup>, as also for Cl<sup>-</sup>. The amounts of calcium and magnesium have been decreasing much faster than that of sodium, because these components were absent from the underwater discharges of hydrothermal fluids, but those amounts have not yet reached the pre-eruption levels. The mineral content in the water at the river source had decreased down to 157 mg/L by 2018, which exceeds the 1993 value by a factor of no more than 1.5.

The published data on the chemical composition of the river outside the Akademii Nauk caldera are not very numerous. Sampling at the outlet from the “Thermal Subsidence” was restricted to two time intervals: 1984–2000 (Pilipenko, 1989; Vakin and Pilipenko, 2001) and our measurements that started in 2015 and continue until now. Both of these time intervals cover the period before and after the 1996 erup-

tion, hence are sufficient to estimate the present state of the river for the river segment under discussion.

Figure 6b shows the evolution of the chemical composition for the river water at the eastern boundary of the Karymsky caldera (Range 2). It should be noted that the water chemical composition was different, even before the 1996 events, from the respective figures for the river source due to the arrival of large amounts of cold and thermal waters (whose total volume was ~4 m<sup>3</sup>/s) that are being discharged in the river valley in the southern part of the caldera. The Karymsky thermal springs typically exhibit high concentrations of sulfate ions and hydrocarbonate ions. The amounts of SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> at the hottest vents are approximately the same, being 600–700 mg/L (Table 3). The concentration of chlorine ions does not exceed 200–250 mg/L. The springs have an uncommon cation composition, which is dominated by Na<sup>+</sup> (304 mg/L), while the concentration of Mg<sup>2+</sup> is above that of Ca<sup>2+</sup>. The hydrothermal contribution is reflected in the composition of the river waters, with the latter becoming similar to the Karymsky springs as to the relationships among major components (see Fig. 5), but the mineral content is lower due to impoverishment by cold surface water and groundwater.

The plot in Fig. 6b clearly shows a spike in the concentration of  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  in the water of the Karymsky River at the outlet from the “Thermal Subsidence”. This was due to the impact of the 1996 eruption, resulting in a short-lived change for the relationships among major components (see Fig. 5) in the river water. However, the concentrations of these elements dropped rapidly as early as in 1997. The decreasing tendency has persisted until now, but the relationships among major components in this river segment are still different from the pre-eruption figures, now that more than 25 years have elapsed (in 2022).

We have not succeeded in discovering any published data of the hydrochemistry of the Karymsky River in its lower reaches, so it does not seem possible to trace the variation in the water composition in the lower reaches of the river. Our measurements were made in September 2021. The water at the river mouth is of the  $\text{Na-Ca-HCO}_3\text{-SO}_4$  type with a mineral content of 330 mg/L and  $\text{pH} = 6.8$ . The relationship between anions and cations is in agreement with the values obtained at the outlet from the Karymsky caldera (see Fig. 5). It follows that there are no additional springs that could have significantly altered the chemical composition of the Karymsky River in its lower reaches. The largest tributary (Uglovoi Creek) is also of the hydrocarbonate–sodium type of water. The water is fresh, near-neutral, with a mineral content of 100 mg/L. Uglovoi Creek is the only stream to drain the slopes of Malyi Semyachik Volcano inside the KVS. Its chemical composition is another confirmation of the fact that there is no hidden outlet from the lake that fills the crater of an active volcano. The chemical composition of Lake Zelenoe is cardinally different from that of the thermal springs in the Karymsky and Akademii Nauk calderas (see Fig. 5). The mineral content and temperature of the water varies depending on the state of the volcano, while invariably remaining ultra acid ( $\text{pH} < 1$ ). As of September 2021, the water was cold, mineralized (22 g/L), and a sulfate chloride one. The cation composition is dominated by aluminum and iron (Kalacheva et al., 2022 and references therein).

**The trace element composition.** In contrast to the major component composition, the study of trace elements in the Karymsky R. water for different segments of it has been practically neglected. The necessary data to reflect the period before the underwater eruption of 1996 are missing. It is therefore has not been possible to determine the degree of influence exerted by this volcanic event on the trace element composition of the river water. As shown by an analysis of the chemical composition of the water for a long period since 2015, the river is in a sufficiently stable condition for all components. We used data of hydrochemical sampling in 2018 and 2021 (Table 4) to estimate the present level of trace element loading at three key points along the river (at the source, at the outlet from the Karymsky caldera, and at the mouth). To make a comparative analysis possible, we also show data on the trace ele-

ment composition for the Karymsky springs and Uglovoi Creek. The total amount of trace elements at the source is 0.92 mg/L. The highest values are for boron (0.47 mg/L), iron (0.18 mg/L), zinc (0.063 mg/L), arsenic (0.047 mg/L), lithium (0.034 mg/L), aluminum (0.026 mg/L), strontium (0.022 mg/L), and barium (0.016 mg/L). The concentrations of Pb, Cs, Rb, Sb, Ge, Ni, Mn, Zr, Ti, and Sc (see Table 4) do not exceed 0.01 mg/L, while the remaining elements, including the total amount of rare earth elements, is 1 mg/L. At the other points (with the river discharge increasing) the concentration of trace elements in water shows a decreasing pattern. As an example, the total concentration of trace elements at the outlet from the Karymsky caldera is 0.73 mg/L. We observe an appreciable increase in the concentration of strontium (0.051 mg/L), barium (0.019 mg/L), and lithium (0.046 mg/L), while those of iron and boron remain at the level observed at the source. The total amount of trace elements at the mouth remains sufficiently high, 0.435 mg/L. For purposes of comparison we note that the total concentration of rare elements in the tributary of the river (Uglovoi Creek) is 0.154 mg/L. The concentrations of most elements including boron, iron, lithium, and copper, are lower by a few times. As well, we observed an increase of over 2 times (compared with the 1st and 2nd segments) in the concentration of vanadium (7.4 mg/L), while the amount of strontium and lead is at the level recorded at Range 2, and that of aluminum at the level of the source.

**The quality of the Karymsky R. water.** Water quality of the Karymsky River after the eruption (during 2002) is briefly considered in (Karpov et al., 2007). These authors pointed out that during that period there were considerable exceedances over maximum permissible concentrations (MPC) for household uses and drinking for magnesium, boron, lithium, and cadmium (by more than 7–10 times).

An analysis of our data on the present state of the Karymsky River gave the following results. Considered in relation to trace element composition and physico-chemical parameters ( $\text{pH}$ , temperature, and mineral content), the water at the source is within the current MPC regulations for household uses and drinking,<sup>1</sup> as well as for fisheries.<sup>2</sup> At the outlet from the Karymsky caldera (Range 2) there is a slight exceedance for sulfate ion (1.1 MPC). For several elements the MPC values for potable water and for fish farming water differ considerably (see Table 4), which prevents us from getting an unambiguous pattern in

<sup>1</sup> On the approval of sanitary regulations and norms SanPiN 1.2.3685-21 “Health-related normative standards and requirements on safety and/or harmlessness of environmental factors for man”: The Order of the Chief State Sanitary Inspector of the Russian Federation as of January 28, 2021.

<sup>2</sup> On the approval of water quality standards for water bodies for fish farming, including the regulations of maximum permissible concentrations of harmful substances in the waters used for fish farming and fisheries: The Order no. 552 of the Ministry of Agriculture of the Russian Federation as of December 13, 2016 (as amended October 12, 2018 and March 10, 2020).

the determination of water quality. The water at the source is unsuitable for fish farming because of contamination with compounds of copper (17 MPC), zinc (6 MPC), arsenic (4.7 MPC), molybdenum (2.9 MPC), vanadium (2.7 MPC), iron (1.8 MPC), and lead (1.2 MPC). As to the water for drinking and household needs, there is exceedances only in the concentrations of arsenic (4.7 MPC) and lithium (1.1 MPC). Observations at the second range of the Karymsky River tell us about lower concentrations of nearly all trace elements (caused by inflow of cold fresh waters and possible settling of mineral compounds), except alkaline and alkali-earth elements (strontium, rubidium, lithium, and barium) coming with thermal waters. The only exceedance above the standards prescribed to ensure safety for man exists for lithium (1.5 MPC). As to fish farming activities, the water persists in being unsuitable, similarly to the situation at the source, with regard to contamination with several elements (V, Fe, Cu, Mo). It should be noted that vanadium and lead contaminated the water of Uglovoi Creek (8 and 1.1 MPC, respectively). As the net result, the water at the source of the Karymsky River persists in exceeding the maximum permissible concentrations for these contaminating elements. Nevertheless, the water at the source is completely suitable for drinking and household needs with regard to the concentrations of trace elements.

*The Output of Major and Trace Elements  
by the Karymsky River into the Kronotsky Bay  
of the Pacific Ocean*

The variation in ion drainage (1st and 2nd segments of the river) over time. The first quantitative estimates of chemical drainage (major components) from the lake as transported by the Karymsky River with account being taken of the contribution of thermal springs before and after the 1996 eruption were made by Vakin and Pilipenko (1998, 2001).

We have not succeeded in finding published measurements of the river discharge made simultaneously with hydrochemical sampling for the period 2000 to 2015 inclusive. However, multiyear observations showed (Andreev and Nikolaeva, 2012) that the mean discharge at the source (Range 1, see Fig. 1b) is  $\sim 2 \text{ m}^3/\text{s}$ , and that at the outlet from the Karymsky caldera (Range 2, see Fig. 1b) is  $\sim 4.5\text{--}5 \text{ m}^3/\text{s}$ . Our measurements made in 2015 and 2018, both at the first and second ranges, gave similar results with due account of the measurement uncertainty ( $\sim 20\%$ ). Consequently, we can make use of chemical analyses and the mean statistical discharge in order to derive an approximate estimate for the ion drainage at two key segments of the river for different years, tracing the variation in the volume of transported material outside of both calderas for the entire period of observation. Figure 7 shows the variation in ion drainage at the river source (Range 1)

and at the outlet from the Karymsky caldera (Range 2) for the period 1984 to 2022 inclusive.

It is clearly seen that the pre-1996 behavior involved the minimum drainage of major elements at the source, this being equal to  $\sim 10 \text{ t/day}$ . The increase at the second segment (in the “Thermal Subsidence”) was  $\sim 110 \text{ t/day}$  for the period, primarily due to the inflow of thermal waters, resulting in the outward transport of  $\sim 120$  tons of dissolvable material beyond the two adjacent calderas, with practically half of the ion drainage consisting of hydrocarbonate (56 tons). The 1996 eruption caused a sharp increase in the amount of dissolved elements transported by the Karymsky River from Lake Karymsky, with volcanic sulfur being the most abundant element. With the total ion drainage being  $\sim 90 \text{ t/day}$ , the amount for sulfate ion is  $\sim 57 \text{ t/day}$ . At the second segment, the daily increment was  $\sim 450$  tons more during that anomalous year, with half of that figure being for  $\text{SO}_4^{2-}$ . Recalling that the volume of thermal water discharged in the Karymsky caldera did not change, as shown by Vakin and Pilipenko (2001), we find that the bulk of ion load (340 t/day) was due to leaching of the ejecta of the underwater eruption that were transported by a lahar into the “Thermal Subsidence” in May 1996. Just one year after the eruption, the summer of 1997 saw a sharp drop in the volumes of dissolved material transported from the lake, and the daily ion drainage at the first segment has been 22–25 tons ever since 2015, which is twice the amount recorded before 1996. The increment at the second segment was also considerably lower, being 150 t/day as given by the 2015–2019 measurements. Subtracting 110 tons of dissolved material coming in thermal water from the total amount, we find a surplus value on the order of 40 t/day. The amount of extracted carbon (in the form  $\text{HCO}_3$ ) is at the level observed before the 1996 eruption (50–55 t/day), while the amount of sulfur (as  $\text{SO}_4$ ), as well as of chlorine, magnesium, and sodium, have considerably increased. The surplus is most probably due to washing-out of water-soluble minerals from the Karymsky ashes which have been continually accumulated in the caldera since 1996.

The total output of major and trace elements into the Kronotsky Bay (the mouth of the Karymsky River). We used the 2018 measurements (Range 1 and Range 2 along the Karymsky River), as well as the measurements made in 2021 (the mouth of the Karymsky River and Uglovoi Creek), including hydrochemical sampling (see Tables 2, 3) and hydro-metric operations, to derive the annual drainage of dissolved material from the catchment area of the Karymsky River. The annual input of dissolved material into the river from Lake Karymsky is 11 kilotons, while the output into the Kronotsky Bay is  $\sim 93$  kilotons. More than a half of all elements ( $\sim 54$  kilotons) comes into the water stream in thermal waters in the Karymsky caldera. The distributions over individual

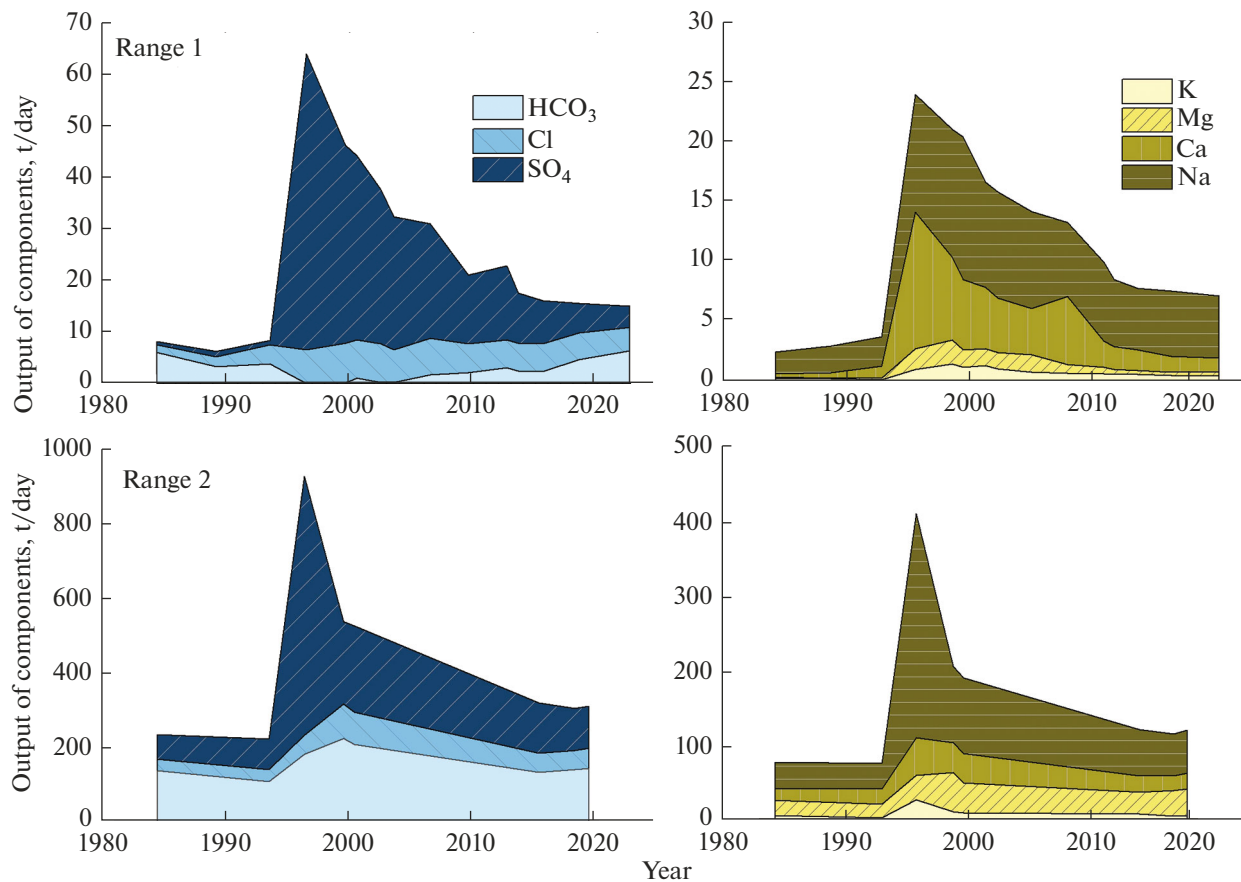


Fig. 7. The variation in the amount of ion drainage in the Karymsky River at the source (Range 1) and at the outlet from the Karymsky caldera (Range 2).

elements are not identical. Part of the ion drainage is formed in the “hydrothermal segment”, and remains at the same level as far as the mouth, while the other part is acquired from additional sources in the middle and lower reaches. Figure 8 shows the distribution of elements in groups (volatiles, rock-forming and trace elements) at different segments of the river. Also shown are the drainage values for the Karymsky springs and Uglovoi Creek.

The annual amount of major anion-generating elements (Cl, S, and C) that arrive via the Karymsky River into the Pacific Ocean is 8.3, 7.2, and 6.0 kilotons, respectively. The amounts for fluorine and boron are two orders of magnitude lower (65 and 72 t/yr, respectively). The quantity of chlorine output is on the whole in complete agreement with the values obtained for the “hydrothermal segment” as sampled at the outlet from the Karymsky caldera, and is similar to the values calculated for the springs situated in the “Thermal Subsidence”. From this it follows that there are no additional sources for this element in the middle and lower reaches of the river, and its main supply into the river network is due to the thermal waters that are discharged in the Karymsky caldera. The amounts of sul-

fur and carbon at the mouth are higher than those at the second range, which implies an additional source that supplies them to the river.

The individual fluxes of the main rock-forming elements (Fe, Al, Na, Mg, Ca, K, Si) are in the range between 1 kt/yr (K) and 7 kt/yr (Na). Comparison with data at the middle range and with the transport by the Karymsky springs shows well-expressed growth in calcium, silicon, and aluminum. The only large tributary of the river (Uglovoi Creek) has the lowest mineral load, and adds a small volume of dissolved elements into the main stream, while having a sufficiently high discharge (1.5 m<sup>3</sup>/s). In the case of iron we observe lower transported amounts from the source to the mouth. This is primarily due to the settling of iron hydroxides along the riverbed over a long segment.

The annual transport from Lake Karymsky to the river source is ~60 tons of trace elements; of this amount, about ~80 tons is acquired in the “Thermal Subsidence”. The total amount transported beyond the Karymsky caldera is thus ~140 tons. The calculated transport into the Kronotsky Bay is 123 tons based on sampling at the mouth, which is below the level determined at the second range. However, con-

**Table 3.** The chemical composition of surface streams and thermal springs in the Karymsky R. valley, mg/L

Sampling site	Date of sampling	$T, ^\circ\text{C}$	$\text{pH}_{\text{lab}}$	$\text{F}^-$	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\text{Na}^+$	$\text{K}^+$	$\text{Ca}_2^+$	$\text{Mg}_2^+$	$\text{HCO}_3^-$	$\text{SiO}_2$	M
Karymsky springs	September 2019	39.9	5.93	0.24	292	663	340	31.0	105	234	751	127	2543
Uglovoi Creek (mouth)	September 2021	5.9	7.01	0.11	5.7	17.1	11.6	1.4	7.5	4.4	17.1	27.6	92.5
Rain	July 2018	n.d.	5.18	n.d.	n.d.	1.5	0.3	n.d.	0.5	n.d.	8.0	<1.07	10.2
Gnilaya Protoka Creek (mouth)	July 2018	13.4	6.81	0.18	66.3	162	75.7	5.1	24.2	78.8	318	31.5	762
Creek near a permanent base	July 2018	0.8	6.8	0.08	4.4	5.3	2.8	1.6	3.9	1.1	16.0	<1.07	35.1

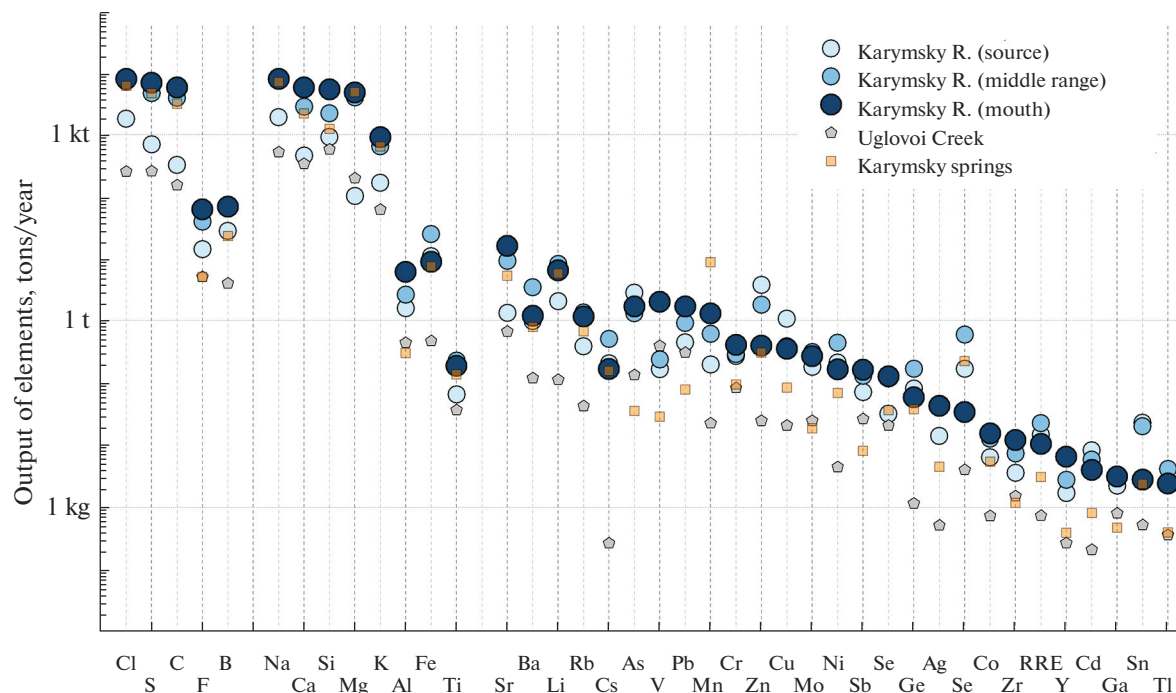
n.d. means *not detected*.

sideration of individual element transport values reveals significant supplies of material over the middle reaches of the river. This can best be seen for the concentration of strontium at Range 2 and at the mouth (10 t/yr and 16 t/yr, respectively), with the respective figures being 250 kg/yr and 2 t/yr for vanadium and 645 kg/yr and 1.4 t/yr for manganese.

One of the possible sources for additional supply of both major and trace elements may be surface/underground waters that come to the river in the middle reaches. Even some rough calculations of the hydrologic balance show an increment in the water stream amounting to  $\sim 2.5\text{--}3\text{ m}^3/\text{s}$  in the middle reaches. The chemical composition of the tributaries is unknown for this segment of the river. In addition, the drainage due to a group of thermal springs (Nizhnie Narzany

after Pilipenko, 1989) into the main water stream occurs beyond the “Thermal Subsidence” downstream of the waterfall series, and is not taken into account for measurements made at Range 2. It is possible that there are more discharges of thermal water downstream.

Another source of supply for elements, primarily sulfur and calcium, may be ashes, which are saturated with sulfur dioxide and other volcanic gases. These come directly, as well as are washed down into the narrow valley by rains and temporary streams due to snow melting. As was shown above (Section 3.1), the principal direction of ash and gas plumes discharged by Karymsky Volcano is eastward, including the area of the Karymsky R. valley. The mineral content in extracts from the ashes may reach 400 mg/L, with

**Fig. 8.** The annual drainage of elements along the bed of the Karymsky River at various segments.

**Table 4.** The trace element composition of thermal and river waters in the Karymsky R. valley, µg/L

Element	MPC, HD/FF	Karymsky River			Karymsky springs	Uglovoi Creek
		Range 1	Range 2	Range 3		
		July 2018		September 2021	July 2018	September 2021
Li	30/80	<b>34.140</b>	<b>45.840</b>	23.810	<b>277.680</b>	2.460
Be	0.2/0.3	0.006	0.003	0.001	0.005	0.001
<b>B</b>	500/500	467.390	405.830	254.85	<b>1096.560</b>	88.680
Al	20/40	26.440	14.570	22.56	14.410	9.800
Sc	–	2.793	3.289	0.124	10.567	0.087
Ti	100/60	1.071	1.260	0.686	6.495	0.798
<b>V</b>	<b>100/1</b>	<b>2.749</b>	<b>1.313</b>	<b>7.389</b>	<b>1.351</b>	<b>8.679</b>
Cr	50/20	4.470	1.601	1.503	4.471	1.823
<b>Mn</b>	100/10	3.262	3.409	4.808	<b>417.767</b>	0.488
<b>Fe</b>	<b>300/100</b>	<b>182.880</b>	<b>138.830</b>	32.860	<b>357.800</b>	10.430
Co	100/10	0.104	0.069	0.056	0.254	0.016
Ni	20/10	3.504	2.441	0.607	3.254	0.097
<b>Cu</b>	<b>100/1</b>	<b>17.782</b>	<b>2.142</b>	<b>1.303</b>	<b>3.966</b>	0.453
<b>Zn</b>	5000/10	<b>62.706</b>	10.040	1.460	<b>14.502</b>	0.539
Ga	–	0.036	0.018	0.011	0.022	0.017
Ge	–	1.334	0.931	0.214	1.772	0.025
<b>As</b>	<b>10/10</b>	<b>47.280</b>	7.320	6.248	1.680	2.952
Se	10/2	0.521	0.649	0.464	1.709	0.451
Rb	100/100	6.452	7.514	4.302	31.973	0.929
Sr	7000/400	22.320	50.928	59.005	253.156	14.877
Y	–	0.027	0.015	0.024	0.018	0.006
Zr	/70	0.058	0.040	0.044	0.055	0.033
Nb	10/	0.002	0.002	0.001	0.003	0.000
<b>Mo</b>	<b>70/1</b>	<b>2.971</b>	<b>1.723</b>	0.983	0.870	0.538
Ag	50/	0.230	0.219	0.157	0.209	0.011
Cd	1/1	0.133	0.032	0.014	0.038	0.004
Sn	–	0.373	0.109	0.010	0.111	0.011
Sb	5/112	1.169	0.709	0.598	0.378	0.574
Cs	1000	3.376	2.824	0.610	7.360	0.006
Ba	700/740	16.289	19.167	4.450	37.727	2.622
Σ REE	–	0.240	0.123	0.038	0.144	0.016
Hf	–	0.003	0.001	0.001	0.002	0.001
Tl	0.1/	0.038	0.022	0.009	0.018	0.008
<b>Pb</b>	<b>10/6</b>	<b>7.396</b>	5.103	<b>6.290</b>	3.696	<b>6.750</b>
Th	–	0.004	0.003	0.001	0.005	0.000

MPC (maximum permissible concentrations of harmful substances in water); HD stands for Household and Drinking needs (SanPiN 1.2.3685-21); FF stands for Fish Farming needs<sup>3</sup>; REE stands for rare-earth elements. **Bold face** highlights values above MPC.

<sup>3</sup> Order no. 552 as of December 13, 2016, Ministry of Agriculture of Russian Federation (version of October 12, 2018 and March 10, 2020) on Approval of Water Quality in Water Bodies of Fishing Importance, including Maximum Permissible Concentrations of Harmful Substances in the Waters of Water Bodies of Fishing Importance.

anions being dominated by sulfate ion and the cations by  $\text{Ca}^{2+}$  and  $\text{Na}^+$  (Manevich et al., 2012).

## CONCLUSIONS

The Karymsky Volcanic Center is a unique natural object where one can study both volcanic and hydrothermal activity as affecting the environment, including surface and underground waters.

The underwater eruption of January 2, 1996 has exerted considerable influence on the hydrochemistry of Lake Karymsky and its output, which was reflected in increased concentrations of all major components and in lowering of pH. Since 2015 we observe a stabilization in the chemical composition of the river at the mouth, but the concentrations of anions and cations remain higher than those observed before the increase in volcanic activity.

The river acquires the bulk of its mineral load in the Karymsky caldera which hosts a powerful discharge of thermal water, resulting in the fact that the mineral content of the river is sufficiently high for surface waters, even at the mouth (333 mg/L).

The upper reaches of the river (the source and the area of the Karymsky caldera) show considerable exceedances of maximum permissible concentrations of harmful substances as regulated for waters important for fish farming in relation to several trace elements (Cu (17 MPC), Zn (6 MPC), As (4.7 MPC), Mo (2.9 MPC), V (2.7 MPC), Fe (1.8 MPC), and Pb (1.2 MPC)). The contamination with V, Cu, and Pb remains as far downstream as the mouth. Considered with regard to uses of river water for drinking and household needs, there are only exceedances in arsenic (4.7 MPC) and lithium (1.1 MPC) at the river source.

The annual amounts of main anion-generating elements (Cl, S, and C) coming with the Karymsky River into the Kronotsky Bay of the Pacific Ocean is 8.3, 7.2, and 6.0 kilotons per annum, respectively. The amounts of fluorine and boron are two orders of magnitude lower (65 and 72 t/yr, respectively). The individual fluxes of major rock-forming elements (Fe, Al, Na, Mg, Ca, K, and Si) are in the range between 1 kt/yr (K) and 7 kt/yr (Na). The total amount of trace elements transported into the bay is over 120 t/yr. The maximum flux values were observed for Sr (16 t/yr), Li (6.8 t/yr), Ba (1.3 t/yr), Rb (1.2 t/yr), V (2.1 t/yr), As (1.8 t/yr), Pb (1.8 t/yr), and Mn (1.4 t/yr).

The amount of transported chlorine is in overall agreement with the values obtained for the “hydrothermal” segment, thus indicating an absence of any additional supply of that element in the middle and lower reaches of the river, while there must be additional sources for sulfur, carbon, calcium, silicon, aluminum, strontium, lead, vanadium, manganese, and copper.

Another possible source for additional supply of both major and trace elements may be surface/underground waters, including the thermal waters that come to the river in its middle reaches. The increment of the water stream in its middle reaches is  $\sim 2.5\text{--}3\text{ m}^3/\text{s}$ .

Still another source of elements, primarily sulfur and calcium, may be ashes saturated with sulfur dioxide and other volcanic gases. These directly arrive in the narrow river valley or else are washed down by rains and temporary water streams due to snow melting. The dominant direction of travel for the ash and gas plumes discharged by Karymsky Volcano is eastward, so as to completely cover the catchment area of the river in the middle and lower reaches.

## ABBREVIATIONS AND NOTATION

FEB RAS Far Eastern Branch Russian Academy of Sciences

IVS Institute of Volcanology and Seismology

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## CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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