

## Posteruptive chemical evolution of a volcanic caldera lake: Karymsky Lake, Kamchatka

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[1] The 1996 short-lived subaqueous eruption at the Karymsky caldera lake suddenly changed the composition of the lake water. The lake, with a surface area of  $\sim 10 \text{ km}^2$  and a volume of  $\sim 0.5 \text{ km}^3$ , became acidic, increased its salinity to  $\sim 1000 \text{ mg/kg}$ , and became dominated by  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$ . Since the eruption, the lake chemistry has evolved in a predictable manner described by simple box model. As a result of dilution by incoming  $\text{SO}_4$ -Ca-Mg-poor water,  $\text{SO}_4$ , Ca, and Mg concentrations follow a simple exponential decrease with a characteristic time close to the residence time of the lake. Na, K, and Cl decrease relatively significantly slower, indicating a continuing input of these constituents into the lake that was initiated during the eruption. Thus, the dynamics of two groups of lake water solutes can be predicted by a simple box model for water and solute mass balance. **Citation:** Taran, Y., S. Inguaggiato, C. Cardellini, and G. Karpov (2013), Posteruptive chemical evolution of a volcanic caldera lake: Karymsky Lake, Kamchatka, *Geophys. Res. Lett.*, 40, 5142–5146, doi:10.1002/grl.50961.

### 1. Introduction

[2] Karymsky Lake is a caldera lake in southern Kamchatka (Figure 1). The caldera with an age of  $\sim 40 \text{ ka}$  is characterized by significant thermal activity hosting a boiling geothermal system (Akademii Nauk springs) and associated with the old Akademii Nauk volcano [e.g., Ivanov, 1974; Vakin and Pilipenko, 1998; Karpov et al., 2008]. The Akademii Nauk caldera merges to the north with the caldera of Karymsky volcano, which is the most active volcano in Kamchatka [Ivanov, 1996; Izbekov et al., 2004, and references therein]. An eruption from the Karymsky Lake floor occurred on 2 January 1996. It lasted several hours, erupted several tens of millions of cubic meters of juvenile and secondary pyroclastic material, extensively changed the morphology of both calderas, triggered the appearance of new thermal springs, and dramatically affected the chemical composition of the Karymsky Lake water [Leonov, 1997; Gordeev et al., 1998; Belousov and Belousova, 2001; Fazlullin et al., 2000; Izbekov et al., 2004 and references therein]. After a sudden change in the lake chemistry (more

than one order of magnitude in salinity and acidification from pH 7.5 to 3.2), the lake water composition started to gradually change back to its new steady state. Dynamics of this process is governed by the parameters of the Karymsky Lake-Karymsky River hydrologic system and by hydrothermal activity within the Akademii Nauk caldera. Vakin and Pilipenko [1998] and Fazlullin et al. [2000] reported the first data on changes in the lake chemistry and the surrounding hydrothermal activity immediately after the 1996 eruption. Karpov and Esikov [2005] and Karpov et al. [2008] conducted chemical and temperature monitoring of the lake during 1997–2006. We sampled the lake water in August 2012. In this paper, we use and analyze all data on the chemistry of the Karymsky Lake water from 1996 to 2012 to evaluate the chemical dynamics of the lake and the Akademii Nauk hydrothermal system.

[3] The approach used in this study is similar to those applied for other lake systems with outflow (and a constant volume,  $dV/dt = 0$ ) for evaluating the dynamics of anthropogenic and natural solutes [e.g., Varekamp, 1988, 2003, 2008] and is based on a simple dynamic box model for nonreactive species [Albarède, 1995].

### 2. Mass and Chemical Balance of a Well-Mixed Lake With Outflow and the One-Box Model for the Chemical (Contaminant) Dynamics

[4] A water balance of a lake is expressed as

$$Q_{\text{in}} + Q_{\text{th}} - Q_{\text{out}} - Q_{\text{ev}} = dV/dt = 0 \quad (1)$$

where  $Q_{\text{in}}$  is the rate of the input (rainfall on the lake surface + runoff from the catchment area);  $Q_{\text{th}}$  is the inflow rate of a permanent source of water not depending on precipitation, for example, thermal waters;  $Q_{\text{out}}$  is the outflow rate (of a stream or river + seepage through the lake floor); and  $Q_{\text{ev}}$  is the rate of evaporation.

[5] Let  $C$  be the concentration of a chemical component in the lake water (Cl,  $\text{SO}_4$ , Na, Ca, etc.). The total amount of this component in any moment of time  $t$  in the lake is  $C(t)V$ , where  $V$  is the volume of the lake. If  $V = \text{constant}$  (a lake with a draining river) and the lake water is ideally mixed,

$$dC/dt = (1/V)[C_{\text{th}}Q_{\text{th}} - C(t)Q_{\text{out}}] \quad (2)$$

where  $C_{\text{th}}$  is the concentration of the component in a permanent source (for example, Cl in thermal springs).

[6] Let  $C_{\text{th}}Q_{\text{th}}/Q_{\text{out}} = C_s$  (the thermal source has a constant discharge rate and concentrations of species) and  $V/Q_{\text{out}} = \tau$ . By definition,  $\tau$  is the residence time for the system [e.g., Albarède, 1995]. In this case,

$$dC/dt = C_s - \tau^{-1}C \quad (3)$$

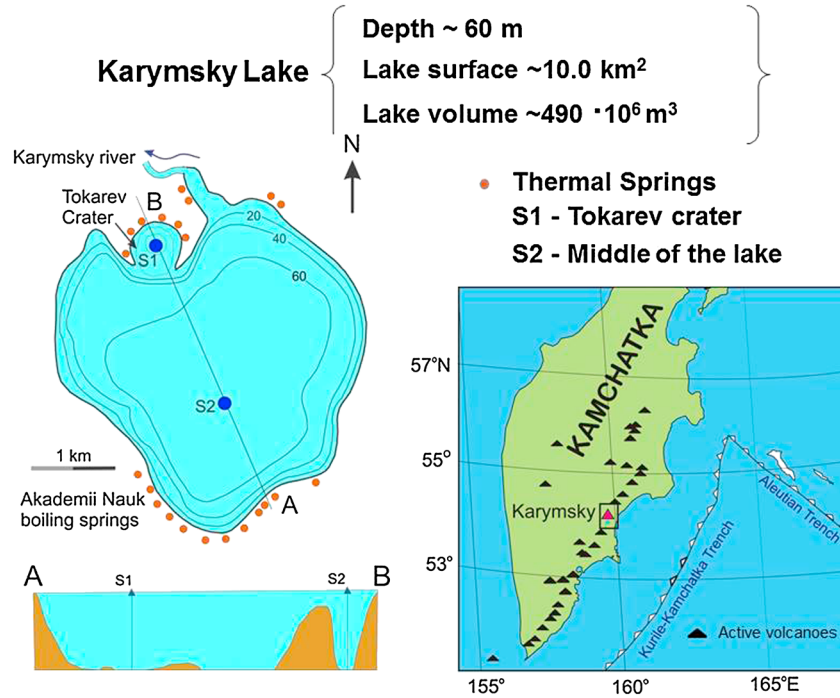
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**Figure 1.** A map of Karymsky Lake with the bathymetry from *Fazlullin et al.* [2000] and the depth profile along the cross section (a-b) from *Karpov et al.* [2008]. Hot springs areas and the sampling sites S1 (Tokarev crater) and S2 (middle of the lake) are also shown. The location of the Karymsky volcano and the Karymsky caldera lake are shown in the inserted Kamchatka map.

[7] The solution of this equation is expressed as follows:

$$C(t) = C_s + (C_o - C_s) e^{-t/\tau} \quad (4)$$

where  $C_o$  is the concentration of the component at  $t = 0$ .

[8] At  $t = \infty$ ,  $C(t) = C_s = C_{th}Q_{th}/Q_{out}$ , i.e., the stationary (steady state) concentration depends only on the properties (concentrations of species and flow rate) of the permanent source of chemicals and the ratio between the source input rate and the total outflow rate.

### 3. Application to the Karymsky Lake After the 1996 Eruption

#### 3.1. Chemistry of the Lake Before the Eruption and Water Balance Parameters

[9] Karymsky Lake has a surface area of about  $10 \text{ km}^2$  and a flat bottom at depth  $\sim 60 \text{ m}$  (Figure 1). The volume of the lake can be calculated from the bathymetry given by *Fazlullin et al.* [2000] as  $\sim 0.49 \text{ km}^3$ . The catchment area is about 1.5 times the lake surface area, and the lake volume is controlled by the outflow rate of the Karymsky River that comes out of the lake on the northern shore (Figure 1). For the input and output rates of the lake system, different authors give different values. *Vakin and Pilipenko* [1998] accepted the annual precipitation as  $\sim 2000 \text{ mm}$  and the total runoff of cold streams to the lake as  $\sim 1 \text{ m}^3 \text{ s}^{-1}$ . This gives for the  $Q_{in}$  term a value of  $\sim 1.6 \text{ m}^3 \text{ s}^{-1}$ . For the outflow rate of the Karymsky River during the summer time, same authors reported one result of the direct measurement to be  $2.04 \text{ m}^3 \text{ s}^{-1}$ . They also estimated the seepage rate to be lower than  $100 \text{ kg s}^{-1}$  for the whole lake. *Karpov and Esikov* [2005] suggested a value of  $1000 \text{ mm}$  for the average annual

precipitation based on the data of a meteorological station located within the Kamchatka River valley. For the outflow rate of the Karymsky River, they give values of  $1.4$  and  $1.7 \text{ m}^3 \text{ s}^{-1}$ , without mentioning the date of measurements. Taking the mean value for the river outflow rate of  $1.7 \text{ m}^3 \text{ s}^{-1}$  (with a corresponding uncertainty of  $\sim 30\%$ ), for the annual outflow rate, we have a value of  $5.35 \times 10^7 \text{ m}^3 \text{ yr}^{-1}$ . Thus, the residence time for the Karymsky Lake-Karymsky River system can be estimated as  $\tau = V_{lake}/Q_{out} = 49/5.35 \approx 9$  years. We assume here that the evaporation and seepage rates are small (within errors) compared to the river outflow. High evaporation rates should be compensated by a decrease in the drainage rate and thus result in an increase of the residence time.

[10] A thermal field of Akademii Nauk is located on the southern side, with numerous boiling springs and small geysers extending for about  $3 \text{ km}$  along the lake shore. Before the eruption, the inflow rate of these boiling springs was estimated between  $0.025$  and  $0.05 \text{ m}^3 \text{ s}^{-1}$  of hot water with  $\sim 350 \text{ mg/kg}$  of Na and  $\sim 420 \text{ mg/kg}$  of Cl [*Vakin and Pilipenko*, 1998]. Before the 1996 eruption, the lake had a salinity of  $\sim 100 \text{ mg/kg}$  (including  $\text{HCO}_3^-$  and  $\text{H}_4\text{SiO}_4$ ) with relatively high Na and Cl ( $\sim 12$  and  $\sim 11 \text{ mg/kg}$ , respectively) and low sulfate, K, Mg, and Ca ( $< 4 \text{ mg/kg}$  of each one; Table 1, first column). The Akademii Nauk springs could provide such amount of the dissolved Cl in the lake at the total discharge rate of  $0.04 \text{ m}^3 \text{ s}^{-1}$ . It follows from the definition of  $C_s$  term:  $C_s = C_{th}(Q_{th}/Q_{out})$ . For  $C_{th} = 420 \text{ mg/kg}$ ,  $Q_{out} = 1.7 \text{ m}^3 \text{ s}^{-1}$ ,  $Q_{th} = 0.04 \text{ m}^3 \text{ s}^{-1}$ ,  $C_s \approx 10 \text{ mg/kg}$ , which is close to the observed Cl concentrations ( $8.5\text{--}14 \text{ mg/kg}$ ) before the eruption. It is worth noting that Na, K, and Cl varied in concentration in the lake water before the eruption, (e.g.,  $7 \text{ ppm} < \text{Cl} < 14 \text{ ppm}$ ; *Fazlullin et al.*, 2000 and references therein) which can be caused by at least two reasons: variations

**Table 1.** Chemical Composition (mg/kg) of the Karymsky Lake Water Sampled at the Middle of the Lake<sup>a</sup>

Year of Sampling	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	pH
1984	10.4	1.6	1.6	0.5	8.5	3.8	7.0
1993	13	0.7	1.8	0.6	11.3	6.9	7.4
1996	76.8±5.1	17.4±2.0	65.3±0.5	15.5±0.5	46.5±4.8	394±58	3.2
2000	69.7±3.2	8.5±0.5	39.6±2.6	12.0±1.2	47.6±2.9	226±15	4.5
2001	57.5±5.7	7.2±0.7	35.3±4.3	10.0±3.6	44.3±4.5	189±32	4.63
2002	60.5±1.9	7.0±0.4	32.4±2.5	9.5±0.4	44.5±2.1	193±20	4.9
2003	55.6±4.2	6.9±0.4	31.2±2.1	8.2±0.5	44.7±2.8	169±15	4.9
2004	49.9±3.1	6.7±0.5	26.5±0.6	6.3±0.1	43.3±1.9	156±3.4	5.01
2005	50.9±3.8	6.0±0.5	24.5±1.4	7.1±1.5	40.1±3.2	152±13	5.9
2006	46.2±2.3	4.7±0.1	22.9±1.8	5.8±0.7	36.2±1.6	128±1.0	7.0
2012	38.2	3.7	12.4	3.1	36.9	70.9	7.54

<sup>a</sup>The data before the 1996 eruption are from *Karpov and Esikov* [2005]. The 1996–2006 data are from *Karpov et al.* [2008]. Data for 2012 are from this work. Uncertainties are standard deviations from the mean for six measurements of the water column (surface to –60 m). Temperature of samples varied from 10°C–12°C at the surface to 4°C near the bottom.

in the hydrothermal input rates and annual variations in the sea salt aerosol input from the ocean (20 km to east).

### 3.2. Chemical Consequences of the 1996 Eruption and Initial Conditions After the Chemical “Pulse”

[11] As the result of the eruption, which lasted several hours, a half kilometer wide, ~60 m deep crater was formed (the Tokarev crater), and a new peninsula with a “hot beach” on the northern coast of the lake appeared about 0.7 km from the Karymsky River outlet (Figure 1). New groups of hot and warm springs were formed along the northern shoreline, within the new peninsula and to the east of the Akademii Nauk field on the southern shore. Some of these new thermal manifestations could be controlled by the convection mechanism proposed by *Cardenas et al.* [2012] for the crater lake of Taal volcano, Philippines, with the increased heat flux due to fresh pyroclastic deposits of the 1996 eruption. *Vakin and Pilipenko* [1998] have mapped in detail all thermal fields as they appeared in 1996, half a year after the eruption. They also presented the measured flow rates of thermal waters from each of nine groups of thermal springs that represent the Karymsky geothermal system. *Karpov et al.* [2008] reported data on the chemical and temperature monitoring of the lake water column at two sites: the middle of the Tokarev crater and the middle of the lake (Figure 1). Table 1 shows the chemical data from *Karpov et al.* [2008] and our data obtained in August 2012 from the middle lake site.

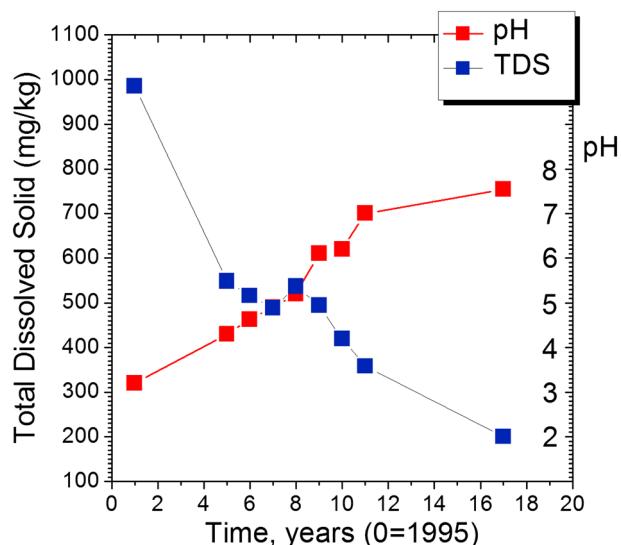
[12] The salinity of the lake as the result of the eruption increased more than an order of magnitude, from <100 to 1000 mg/kg [*Karpov et al.*, 2008]. The water became acidic and enriched with sulfate and Ca (Table 1), with a composition typical for diluted acidic SO<sub>4</sub>-Cl waters of volcano-hydrothermal systems [e.g., *Giggenbach*, 1997]. However, even with relatively high initial concentrations of Ca and SO<sub>4</sub> ions (about 65 and 400 mg/kg, respectively; Table 1), the lake water is far from the saturation with gypsum or anhydrite, and these ions cannot decrease their concentrations by mineral precipitation.

### 3.3. Time Evolution of the Chemistry of Karymsky Lake

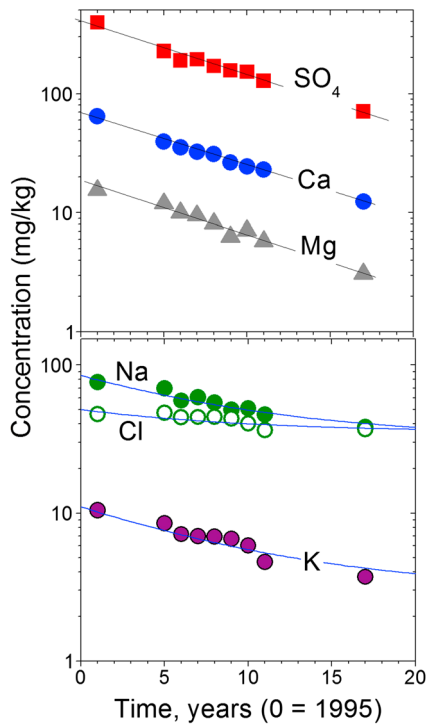
[13] Previous data and our study show that the lake is well mixed; the concentrations of the main species in the water column vary within less than 10% of their mean values (Table 1), although *Karpov et al.* [2008] noted that there is

a weak chemical stratification of the water column with respect to some of the components. The lake water, 16.5 years after the eruption became neutral, and the salinity (total dissolved solids, TDS) of the lake systematically decrease (Figure 2). Concentrations of the main ions in the Karymsky Lake water as a function of time since the 1996 eruption are shown in Figure 3. There are two distinct behaviors of the main components: (i) a simple exponential decrease for SO<sub>4</sub>, Ca, and Mg and (ii) a slower and more complicated decrease of Na, Cl, and K.

[14] The residence time for the Karymsky Lake-Karymsky River system is ~9 years (see above). The slopes on the semilog plot of Figure 2 for the time dependence of SO<sub>4</sub>, Ca, and Mg (corrected for natural logarithm) are between 0.11 and 0.12, or  $1/\tau=1/9=0.11$ . Therefore, it can be suggested that Ca, Mg, and sulfate in the Karymsky Lake water occurred there as the result of the 1996 eruption, which, after that time, had no additional sources and decreased through a simple dilution with Ca-Mg-SO<sub>4</sub>-free (or almost free) water in agreement with the main hydrological characteristics of the lake-river system. This is not the case for Na, K, and Cl, which decrease significantly slower than the other ions (Figure 3). The rate of decrease for Na

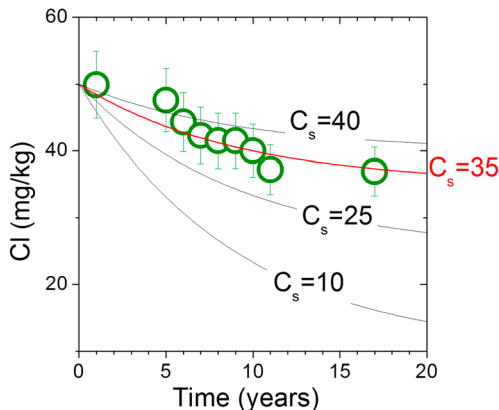


**Figure 2.** The time evolution of pH and total dissolved solids in water of Karymsky Lake since the 1996 eruption.

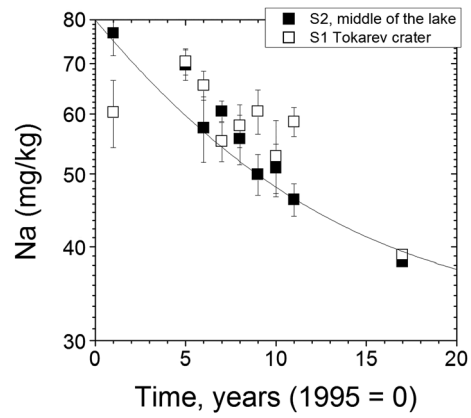


**Figure 3.** Time evolution of main chemical components in the Karymsky Lake water after the 1996 eruption. Components of the upper panel decrease with the same rate which is close to  $1/\tau$ , where  $\tau$  is the residence time for the Karymsky Lake-Karymsky River system. Components of the lower panel decrease significantly slower, indicating existence of an additional input of Na-Cl water into the lake. The fitting curves are computed at  $1/\tau=0.11$  and different  $C_s$  using equation (4) (see text for details).

and K is similar to each other, whereas Cl decreases still slower. The first group of components ( $\text{SO}_4$ , Ca, and Mg) is typical for the acid-sulfate-chloride volcanic waters; the second group is typical for Na-Cl thermal waters of water-dominated geothermal systems. With a Na/K weight ratio equal to  $\sim 10$  (like in the boiling springs of the Akademii Nauk field; *Vakin and Pilipenko* [1998]), the temperature of equilibrium for these waters can be estimated as  $\sim 230^\circ\text{C}$ . Therefore, the first group of components and a part of the



**Figure 4.** Fitting of the Cl evolution data with a curve:  $\text{Cl}(t) = C_s + (\text{Cl}_0 - C_s)e^{-0.11t}$ . The best fit is achieved at  $C_s = 35$ .



**Figure 5.** Comparison of time evolution for Na in the middle of the lake and in the middle of the Tokarev crater (data from *Karpov et al.*, 2008 and from this work). The fitting curve is as that in Figure 3. Errors bars are from Table 1.

second group that occurred in the lake water as the result of the underwater eruption from dissolved magmatic and hydrothermal gases and leaching of the erupted pyroclastics have no other sources and decrease their concentrations through a dilution that has a characteristic time close to the residence time for the lake. The second group, the “hydrothermal” group, obviously has an additional source that in a first approximation can be assumed as having a constant flow rate and concentrations of components similar to those of the Akademii Nauk waters. The appearance of this source can be a result of the local tectonic changes associated with the eruption [*Leonov*, 1997], such as a system of fractures which partially increased the permeability of the roof of the Akademii Nauk hydrothermal system.

### 3.4. Estimation of the Discharge Rate of the Permanent Source of Na-Cl Thermal Water

[15] The simplest box dynamic model for a lake-river system has a solution  $C(t) = C_s + (C_0 - C_s)e^{-t/\tau}$  (equation (4)) with only two parameters. The parameter  $C_s$  characterizes a permanent source of a component, and  $\tau$  is a ratio between the volume of the system and the outflow rate. For the Karymsky system, we estimated  $1/\tau \approx 0.11$ . The curves in Figure 3 fitting the data for Cl, Na, and K are computed using equation (4) with  $C_s(\text{Na}) = 32$ ,  $C_s(\text{Cl}) = 35$ , and  $C_s(\text{K}) = 3$ , at  $1/\tau = 0.11$ . Figure 4 demonstrates how different  $C_s$  values fit the data for chloride. Boiling water of the Akademii Nauk springs on average contains 420 mg/kg of chloride. With  $Q_{\text{out}} = 1.7 \text{ m}^3 \text{ s}^{-1}$ ,  $Q_{\text{th}}$  should be  $\sim 0.14 \text{ m}^3 \text{ s}^{-1}$  (of water with 420 mg/kg of chloride). All these estimations are valid if the lake is well (ideally) mixed. The time evolution of concentrations of Na in both the water column of the new explosive Tokarev crater and the water column in the middle of the lake [*Karpov et al.*, 2008] is shown in Figure 5. The Tokarev crater points are systematically higher than those at the lake center, but the difference is small and the behavior of both columns is very similar, indicating that the lake water is well mixed.

[16] *Vakin and Pilipenko* [1998] reported the outflow rates for all nine groups of thermal springs that represent the whole Karymsky geothermal system, including hot springs of the caldera of Karymsky volcano to the north. Six groups are located within the Akademii Nauk caldera and feed the lake. Five of them appeared after the eruption. For all six groups,

the total discharge of thermal water was measured by *Vakin and Pilipenko* [1998] as  $0.18 \pm 0.02 \text{ m}^3 \text{ s}^{-1}$ . More than a half of this flow was measured for the thermal input to the Tokarev crater. *Karpov and Esikov* [2005] presented field values of 0.175 and  $0.152 \text{ m}^3 \text{ s}^{-1}$  for the thermal input to the lake in 1997 and 1998, respectively. Taking into account that these field estimations include thermal waters from different groups with  $\text{Cl} \leq 420 \text{ mg/kg}$  and the assumption about the constant rate of the new hydrothermal input, the agreement with our calculated value ( $0.14 \text{ m}^3 \text{ s}^{-1}$ ) based on the box model is quite good. The total measured chloride output from Karymsky Lake by the Karymsky River in 2012 can be estimated as  $\sim 63 \text{ g s}^{-1}$  of Cl taking  $1.7 \text{ m}^3 \text{ s}^{-1}$  of the river outflow rate at the source and the analyzed 36.9 mg/kg of Cl in the lake water. The calculated input of chloride by thermal springs is  $59 \text{ g s}^{-1}$ . This should be the steady state output from the lake in three to four decades after the eruption. The calculated steady state Cl concentration in the lake water is 35 mg/kg, which is  $\sim 3.2$  times higher than the mean value before the 1996 eruption.

#### 4. Conclusions

[17] The chemical evolution of the Karymsky Lake water after the 1996 subaqueous volcanic eruption is captured by a box model that explains the different behaviors of two groups of solutes:  $\text{SO}_4$ , Ca, and Mg were suddenly introduced into the lake along with the erupted material, whereas most of the Na, K, and Cl were introduced into the lake by the increased hydrothermal activity which began immediately after the eruption and persists to this day. The old and new hydrothermal vents, Na-Cl in composition and poor in  $\text{SO}_4$ , Ca, and Mg, currently contribute about  $0.14 \text{ m}^3 \text{ s}^{-1}$  of hot Na-Cl water, which is 3–3.5 times higher than before the 1996 eruption.

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