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Fluorine in the Surface Water of Bering Island

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Abstract—First data have been collected to characterize fluorine concentrations in the surface water of Bering Island (the Komandorskie Islands). The average fluorine concentration is 0.23 mg F/L with variations within the range of 0.08–0.42 mg F/L, which is ~2 times higher than the average fluorine concentration in world rivers (~0.1 mg F/L) but corresponds to its occurrence in rivers in the Russian Eastern Arctic and Kamchatka (0.15–0.21 mg F/L). The major fluorine sources have been shown to be weathering products and atmospheric precipitation.

Keywords: fluorine, surface water, background concentration, Bering Island

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INTRODUCTION

The analysis of regularities in water migration of fluorine—a physiologically active element, which shows pronounced toxic properties—is mostly hampered by problems with the identification of its genesis, primarily, the determination of its natural and anthropogenic sources. The global dispersion of anthropogenic fluorine undoubtedly has its effect on the quantitative characteristics of the environmental migration of this element [1]; however, the extent of these changes is difficult to assess because of the rapid decrease in the areas that have not been radically disturbed by human activity. Clearly, studying geochemical processes in slightly affected areas can provide useful data on the natural migration of chemical elements in general and fluorine, in particular. The objective of this study was to examine the distribution and genesis of fluorine in the surface water in Bering Island, subject to a minimal anthropogenic impact because of its geographic position.

OBJECT AND METHODS OF STUDIES

Bering Island is the largest (1667 km^2) in the group of the Komandorskie Islands, located in the western margin of the Aleutian arc. The natural and climatic characteristics [3, 5, 9, 13] are as follows.

The climate of the island is cold, wet oceanic with the annual precipitation of 470 mm. The maximal precipitation falls in October and November, and the minimum, from February to June. At high air moisture content, the precipitation rate is low—0.1–5 mm/day (drizzling rain). Snow cover lies from late November to middle May.

The northern part of the island has a smooth relief, while its middle and southern parts are represented by low mountains with strongly dissected relief. The river network is well developed. The lowland rivers in the northern part are commonly deeper and wider than those in the central and southern parts of the island, which often end with beach scarps and waterfalls 10 to 100–200 m in height. Few lowland rivers show the penetration of tidal impact up to 1 km upstream. Most rivers originate in the mountains and have snow or mixed nourishment. The island contains many lakes, the largest of which—Lake Sarannoe—has a water area of ~31 km^2 and lies in the northern part; it has a lagoon origin.

The lithogenic basement of drainage area is composed of volcanic and volcanogenic–sedimentary rocks of andesite–basalt composition, as well as sedimentary rocks that have formed due to the erosion and redeposition of lava and pyroclastic strata. The soils that have developed on these rocks contain large amounts of unstable minerals, which are due to the low rate of weathering within the soil. The island shows no modern volcanic activity.

In June–July 2006, I.R. Zaripov, a student of the Moscow State University, took 18 samples from water bodies in the island. The sampling sites are shown in Fig. 1. The concentration of dissolved fluorine was determined by potentiometric method with a fluorine ion-selective electrode with a membrane made of LaF_3 monocrystal according to the procedure described in [10]; the concentrations of the components of main salt composition were determined by standard analytical procedures recommended in [6]. The measurement error of the concentrations of fluo-

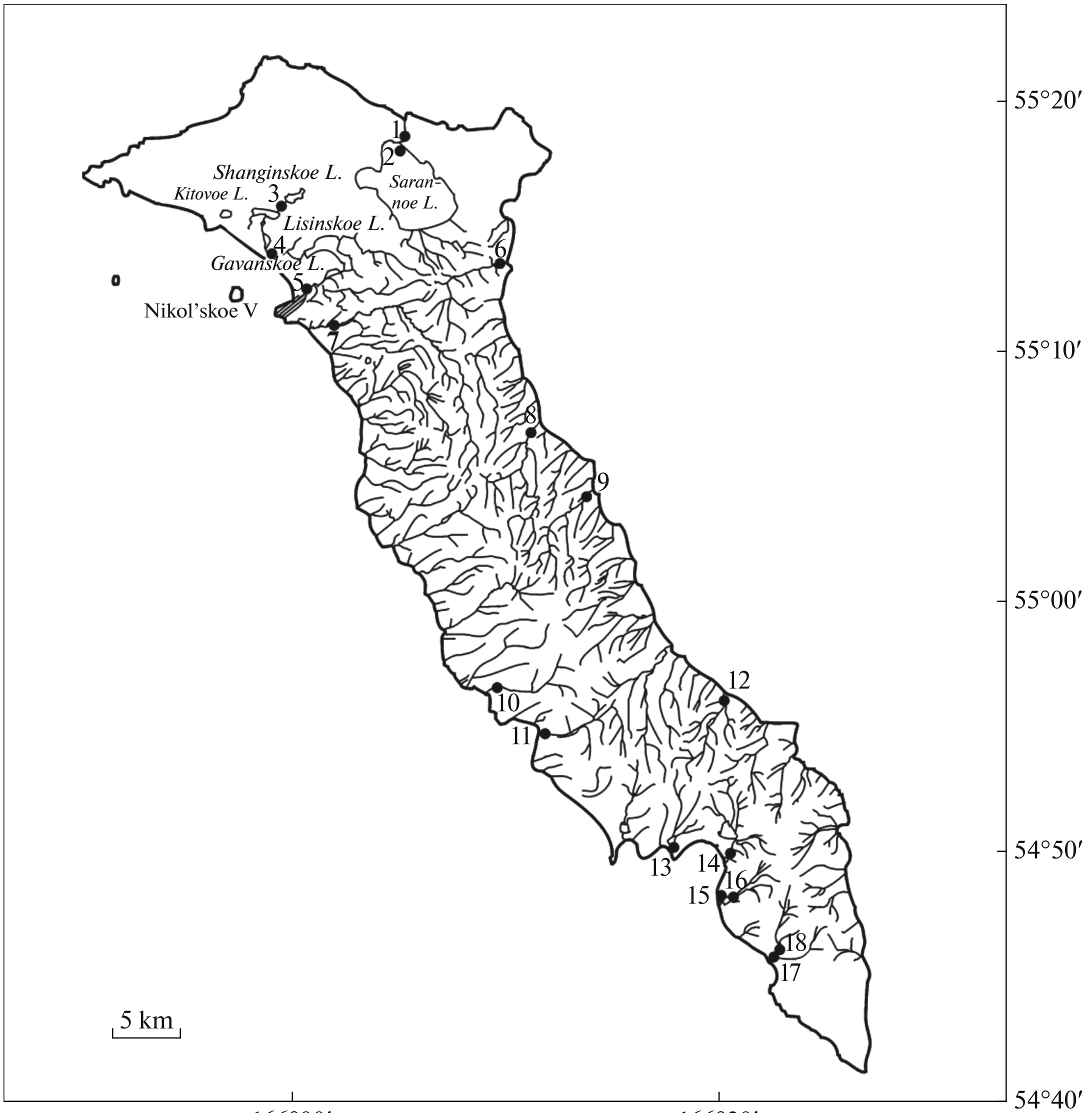

Fig. 1. Layout of (black circles) the sampling stations of surface water on Bering Isl.

rine and major ions was ±4%. Fluorine detection limit is solution was of the order of 10^{-6} M (0.02 mg/L).

RESULTS AND DISCUSSION

The results of fluorine analyses, along with total dissolved solids, the main salt composition of water from Bering Island, and its typification according to O.A. Alekin classification are given in Table 1. The variation range of fluorine concentrations in the samples is relatively narrow (0.08–0.42 mg F/L), and the average concentrations of fluorine in the northern, central, and southern parts of the island differ only slightly—0.24, 0.28, and 0.21 mg F/L, respectively. The overall average concentration of fluorine in the surface water in Bering Island is 0.23 ± 0.08 mg F/L. These values are in agreement with the long-term mean concentrations of fluorine in river water in the nearby areas: 0.21 for the Indigirka, 0.15 for the Kolyma, 0.19 for the Anadyr, and 0.18 mg F/L for the Kamchatka [4]. The average fluorine concentration in the world rivers is about half this value (0.1 mg F/L) [2].

Two water samples taken in the Golodnaya and Gavanskaya rivers in the zone of tidal impact showed anomalously high chloride concentrations of 569 and 301 mg/L. Clearly, this is due to seawater inflow during high tides, and a part of the fluorine is of the same origin. The amount of fluorine of tidal–marine origin can be evaluated using the available concentrations of fluorine and chlorine in seawater (1.3 and 19374 mg/L, respectively [8]) and assuming that the entire chlorine in these samples of river water is of tidal–marine origin. Under such assumption, the

Table 1. Total dissolved solids (M) and the concentrations of major ions in the surface water on Bering Island and their classification by chemistry

Station no.	Water body	M	F^-	Cl^-		SO_4^{2-}		HCO_3^-		Na^+		K^+		Mg^{2+}		Ca^{2+}		Water type
		mg/L	mg/L	mg/L	%-equiv.	mg/L	%- equiv.	mg/L	%- equiv.	mg/L	%- equiv.	mg/L	%- equiv.	mg/L	%- equiv.	mg/L	%- equiv.	
1	Sarannaya R.	66.0	0.08	11.0	16.6	8.17	9.1	26.8	23.5	8.60	20.0	0.60	0.8	0.72	3.2	10.1	26.9	C_{II}^{Ca}
2	Sarannoe Lake	102	0.22	34.4	30.5	12.0	7.9	23.2	12.0	19.4	26.5	2.00	1.6	4.10	10.6	6.92	10.9	Cl_{III}^{Na}
3	Shanginskaya R.	145	0.34	43.0	28.2	12.0	5.8	42.7	16.3	31.2	31.5	4.10	2.4	2.66	5.1	9.22	10.7	Cl_{I}^{Na}
4	Ladyginskaya R.	212	0.42	74.6	32.0	13.9	4.4	50.6	12.6	55.8	36.9	5.10	2.0	5.55	6.9	6.80	5.2	Cl_{I}^{Na}
5	Gavanskaya R.	586	0.18	301	42.4	27.9	2.9	31.1	2.5	187	40.6	9.70	1.2	17.3	7.1	12.6	3.1	Cl_{III}^{Na}
6	Starogavanskaya R.	97.3	0.22	19.8	19.0	13.2	9.3	34.8	19.4	12.5	18.5	1.20	1.0	5.55	15.5	10.2	17.3	C_{III}^{Na}
7	Kamenka R.	137	0.26	21.0	14.9	30.0	15.7	47.6	19.7	18.6	20.4	1.20	0.8	6.87	14.2	11.4	14.3	C_{II}^{Na}
8	Buyan R.	108	0.20	16.0	14.4	12.0	8.0	49.4	25.9	14.1	19.6	0.80	0.7	5.73	15.1	10.3	16.4	C_{II}^{Na}
9	Nikitinskaya R.	142	0.35	13.5	9.6	24.0	12.6	66.5	27.4	13.1	14.3	0.50	0.3	6.87	14.2	17.2	21.5	C_{II}^{Ca}
10	Vodopadnaya R.	102	0.29	14.9	14.4	12.0	8.5	45.8	25.6	13.3	19.8	0.60	0.5	3.74	10.5	12.1	20.7	C_{II}^{Ca}
11	Gladkovskii Cr.	69.4	0.19	9.94	14.4	8.17	8.8	32.3	27.3	6.40	14.3	0.50	0.7	2.05	8.7	10.1	25.9	C_{II}^{Ca}
12	Komandor R.	95.9	0.23	19.9	19.9	8.17	6.0	37.8	22.0	14.4	22.2	1.00	0.9	2.77	8.1	11.9	21.0	C_{II}^{Na}
13	Golodnaya R.	1050	0.26	569	44.8	47.4	2.8	60.4	2.8	293	35.5	13.3	0.9	44.0	10.1	22.8	3.2	Cl_{III}^{Na}
14	Lisinskaya R.	79.9	0.14	14.9	17.9	8.17	7.3	32.3	22.6	11.5	21.3	0.80	0.9	2.77	9.7	9.50	20.2	C_{II}^{Na}
15	Serebrennikova R.	114	0.18	33.4	27.7	8.17	5.0	37.8	18.2	20.2	25.8	2.20	1.7	4.10	9.9	8.00	11.7	Cl_{III}^{Na}
16	Serebrennikova L.	74.4	0.13	12.4	15.7	13.9	13.0	26.9	19.8	8.20	16.0	0.60	0.7	4.82	17.8	7.56	16.9	C_{III}^{Mg}
17	Bobrovaya R.	163	0.25	27.0	16.8	15.8	7.3	76.9	27.8	21.7	20.8	2.40	1.4	7.33	13.3	11.4	12.6	C_{I}^{Na}
18	The same	75.8	0.25	13.5	17.2	12.0	11.3	29.9	22.1	7.82	15.3	0.50	0.6	4.33	16.1	7.77	17.5	C_{III}^{Ca}

Table 2. Correlations between the concentrations of fluorine and major ions in the surface water on Bering Isl.

Component	M	Cl^-	SO_4^{2-}	HCO_3^-	Na^+	K^+	Mg^{2+}	Ca^{2+}
r	0.82	0.64	0.43	0.57	0.71	0.61	0.46	0.21

shares of the tidal seawater (α_{sw}, %) and tidal–marine fluorine ($\alpha_{sw\text{-}F}$, %) will be

$$\alpha_{sw} = 100\frac{[Cl^-]_{rw}}{[Cl^-]_{sw}}, \quad (1)$$

$$\alpha_{sw\text{-}F} = 100\alpha_{sw}\frac{[F^-]_{sw}}{[F^-]_{rw}}, \quad (2)$$

$[Cl^-]_{sw}$, $[F^-]_{sw}$, $[Cl^-]_{rw}$, and $[F^-]_{rw}$ are the concentrations (mg/L) of chlorine and fluorine in seawater and river water. The shares of seawater in the samples taken from the rivers of Golodnaya and Gavanskaya, evaluated by (1) and (2), were 2.9 and 1.6%, respectively, and the shares of fluorine of marine origin in them were 1.4 and 1.1%, respectively; this has practically no effect on the total fluorine content.

With the exclusion of the two rivers that were subject to the effect of tides during sampling (the Golodnaya and Gavanskaya), fluorine concentration and total dissolved solids (M), as well as the concentrations of major anions, sodium, potassium, and magnesium showed a positive correlation (Table 2).

Bering Island shows no modern volcanic activity nor any significant anthropogenic sources of fluorine, and the island is far from areas with intense economic activity. This allows us to assume that the surface water of the island receives soluble fluorine from two major sources. The first source is wet and dry atmospheric fallouts, represented mostly by cyclic marine salts; and the second source is the soluble weathering products from rocks in the drainage basin:

$$[F^-]_{rw} = x[F^-]_a + y[F^-]_w, \quad (3)$$

where x and y are the mass fractions of soluble substances in river water, associated with the input of cyclic marine salts from the atmosphere and soluble substances from rocks in the drainage basin because of their weathering; $[F^-]_{rw}$, $[F^-]_a$, and $[F^-]_w$ are the concentrations of soluble fluorine in river water, atmospheric fallout, and weathering products.

Chlorine is commonly used as an indicator to cyclic marine salts [7, 12]. Because of the small size of the island, the effect of marine aerosols should extend all over its area. The result is the high concentrations of chlorides in the precipitation over the island compared with the concentrations typical of the areas located several tens of kilometers from the coasts [7]. The soluble substances, including fluorides, in atmospheric fallouts over the ocean and small islands are almost completely represented by seawater salts, of which chlorides are the main component [11, 12]. Therefore, it can be assumed that the contribution of the atmospheric source of fluoride to its concentration in surface water on Bering Island (x) is proportional to the chloride concentrations observed there:

$$x[F^-]_a = k_1[Cl^-]_{rw}. \quad (4)$$

The best indicator of soluble weathering products seems to be the bicarbonate ions that form during silicate weathering from volcanogenic rocks, which constitute the lithogenic basis of Bering Island territory:

$$\begin{aligned} &2Na_{1-x}Ca_xAl_{1+x}Si_{3-x}O_8 \\ &+ 2(1+x)CO_2 + 3(1+x)H_2O \\ &= (1+x)Al_2Si_2O_5(OH)_4 + 2xCa^{2+} \\ &+ 2(1-x)Na^+ + 2(1+x)HCO_3^- + 4(1-x)SiO_2. \end{aligned}$$

In that case, the amount of fluorine mobilized from rocks in the process of weathering should be proportional to the concentration of dissolved bicarbonates:

$$y[F^-]_w = k_2[HCO_3^-]_{rw}. \quad (5)$$

Substituting (4) and (5) into (3), we obtain the linear dependence of the ratio F^-/Cl^- on HCO_3^-/Cl^-:

$$\frac{[F^-]_{rw}}{[Cl^-]_{rw}} = k_1 + k_2\frac{[HCO_3^-]_{rw}}{[Cl^-]_{rw}}. \quad (6)$$

The dependence of $[F^-]_{rw}/[Cl^-]_{rw}$ on $[HCO_3^-]_{rw}/[Cl^-]_{rw}$ shown in Fig. 2 corresponds to (6) with parameters k_1 and k_2, equal to 0.0013 and 0.0047, at a coefficient of correlation $r = 0.89$. This confirms the assumption regarding the dominating role of the two sources of fluorine in the surface water in Bering Island: weathering products and atmospheric fallouts.

CONCLUSIONS

The average concentration of fluorine in the surface water in Bering Island is 0.23 mg F/L at a range of concentrations of 0.08–0.42 mg F/L. This is somewhat higher than the average fluorine concentration in the world rivers (~0.1 mg F/L), but is similar to its occurrence in the rivers of the Russian Eastern Arctic and Kamchatka (0.15–0.21 mg F/L).

The major sources of fluorine in the surface water of the island are weathering products and cyclic sea salts arriving through the atmosphere.

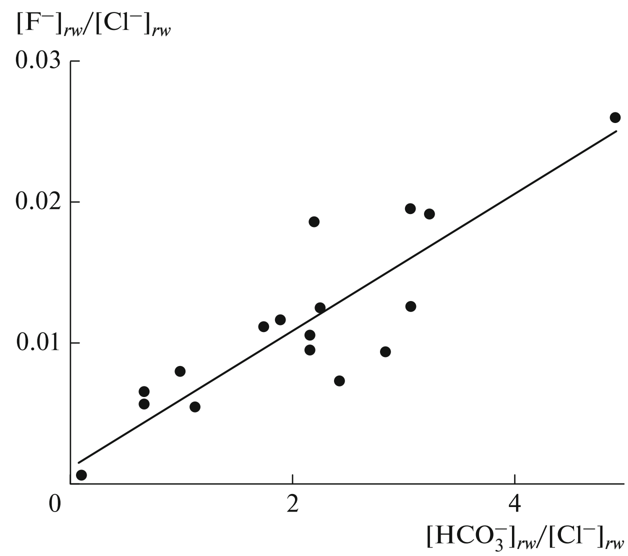

Fig. 2. Dependence between the ratios F/Cl and HCO_3/Cl in the surface water on Bering Isl.

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