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WATER QUALITY AND PROTECTION: ENVIRONMENTAL ASPECTS

Fluorine in Surface and Subsoil Waters in the Middle Klyaz'ma Basin

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Abstract—Data on fluorine concentration in water in the Middle Klyaz'ma Basin during summer low-water period have been obtained. Fluorine background concentration has been determined in streams (Klyaz'ma R., small rivers, and creeks), water bodies (drainage ditches, lakes), and subsoil waters. Anthropogenic fluorine hydrochemical anomalies have been determined and localized with respect to urbanized industrial areas. An assumption has been made and experimentally substantiated, according to which fluorine concentration in subsoil water is governed by the processes of its distribution between water and host rocks. It has been established that the interaction of soils with snowmelt water and alluvial deposits with river water in neutral and acid media is accompanied by fluorine removal from solution, while in a weakly alkaline medium, fluorine passes from solid phase into solution. The effect of dissolved organic matter on the process of fluorine leaching from rock minerals also depends, primarily, on the equilibrium pH value: in weakly alkaline media, the presence of organic acids contributes to fluorine mobilization, while in weakly acid media, it reduces mobilization rate.

Keywords: fluorine, surface waters, subsoil waters, background concentrations, anthropogenic hydrochemical anomalies, Klyaz'ma R.

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INTRODUCTION

Fluorine is a biologically active element with pronounced physiological functions. Its major amount (~70%) enters the human organism with drinking water, so a deficiency or excessive amount of fluorine causes the development of specific pathologies: its low fluorine concentration (<0.1–0.2 mg/L) causes dental caries, while its high concentration (>5 mg/L) causes dental and skeletal fluorosis [3, 4, 6]. Some signs indicate that fluorine affects the accumulation of metals in the bone tissue of animals [5, 9]. Moreover, it is supposed that large amounts of fluorine in the organism can cause oncological diseases [1, 13]. The optimal concentration of fluorine in drinking water is believed to be the range of 0.5–1.5 or 0.7–1.2 mg/L [1, 4].

Fluorine occurrence in natural waters, in particular, in Russian territory, was studied in many works. However, many regions have not been covered by detail studies. These include the middle Klyaz'ma basin, in which urban zone with centralized water supply neighbor with relatively sparsely populated areas, where local sources of water supply are in use. The objective of this work was to study fluorine distribution in different water bodies in the region, which serve as currently used or potential water supply sources. In addition to this task, the concentration of fluorine in surface waters in the "Elk Island" National Park.

OBJECTS AND METHODS OF STUDY

The study area covers the northeastern part of Smolensko–Moskovskaya Highlands (Yur'evskoe Opol'e), as well as the northern and central parts of Meshchera Lowland.

Yur'evskoe Opol'e is a hilly moraine plain, occupying elevated, dissected, and well drained areas with absolute elevations of 180–240 m. The part of the Yur'evskoe Opol'e that was studied is situated in the zone of forests and podzol soils. The most widespread are sod-podzol soils; peat-gley and silty-gley soils occur in relief depressions; grey forest soils occur in water divides.

Meshchera Lowland, of which the Klyaz'ma R. is the northern boundary, is mostly represented by very swampy areas, 50–60% of which are forests, which absolute elevations of 100–140 m, and overgrown lakes, branches, and oxbows. Almost 35% of the area of Meshchera Lowland is occupied by impassable or heavy-going swamps, which occur in relief depressions. The soils are acid: sod-podzol, podzol-gley, and podzol.

The Klyaz'ma is a typical river in East European Plain with mixed nutrition and high spring flood. In spring, the main source of its nutrition is snowmelt water; in summer and autumn, this is rain and subsoil water; and in winter, the nutrition is mostly due to subsoil water discharge. In the examined segment from Noginsk C. to Kosterevo Settl., river depth averages

1.5–2.5 m, increasing to 7 m in some reaches. Flow velocity varies within 0.3–0.7 m/s. Since 1937, river runoff is regulated by the Klyaz'ma Reservoir.

"Elk Island" National Park is situated near the contact of Meshchera Lowland and Klin–Dmitrov Ridge, which serves as a water divide between Moskva and Klyaz'ma basins. One-third of park area lies within the administrative boundaries of Moscow (Sokol'nicheskii, Babushkinskii, and Kuibyshevskii districts), while the rest belongs to the suburban zone (Balashikhinskii, Mytishchinskii, and Shchelkovskii districts of Moscow oblast). Forests, wetlands, and water bodies occupy 85, 5, and 1% of the area. The most widespread soils are sod-podzol (mostly loamy, rarer, clay sand, and sand).

Water samples from different water bodies were taken into clean plastic vessels during summer low-flow period. Several snow samples were taken in winter near Meshchera Educational–Scientific Station of Geological Faculty, Moscow State University. Fluorine concentration in the solution was determined with the use of fluorine ion-selective electrode by direct ionometry method, described in [11]. The repeatability of potentiometric measurements varied within ±1 mV, which corresponded to the measurement accuracy of fluorine concentration ±4%. The comparison of the results of fluorine determination by direct ionometry and by precision addition technique showed no systematic error and the agreement between the results within ±0.01 mg F/L (Table 1). The total of 200 water samples were analyzed for fluorine concentration. To reveal the possible correlation between the concentrations of fluorine and other dissolved components, 62 samples of different types of waters (snowmelt, river, lake, subsoil, and artesian groundwaters) were analyzed for the concentrations of components of main salt composition with the use of standard analytical techniques recommended in [8].

RESULTS AND DISCUSSION

Data on fluorine concentration in water bodies in the basins of the Middle Klyaz'ma Basin are given in Table 2. In areas remote from the sources of anthropogenic pollution, the mean concentration of fluorine in the Klyaz'ma R. and in 28 small rivers during summer dry period almost coincide (0.29 and 0.28 mg/L, respectively). The mean fluorine concentrations in waters of drainage ditches are also similar, though, in their absolute values, they are much lower compared with watercourses (0.19 and 0.18 mg/L). The occurrence frequency of concentrations in surface waters of background areas obeys the normal distribution law (Fig. 1a). No significant correlations were found to exist between the concentrations of fluorine and components of main salt composition (the correlation coefficients of fluorine and Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-,

Table 1. Comparison of results of fluorine determination in natural waters by direct ionometry and addition technique

Object	[F], mg/L		
	direct ionometry	addition technique	difference
Malaya Dubna R.	0.25	0.24	0.01
Verkhul'ka R.	0.35	0.36	–0.01
Sherna R.	0.32	0.32	0
Laska R.	0.34	0.33	0.01
Vokhonka R.	0.67	0.65	0.02
Well, Molodino V.	0.04	0.03	0.01
Well, Bogdarnya V.	0.25	0.27	–0.02
Snow, Meshchera Education–Scientific Station	0.08	0.09	–0.01

SO_4^{2-}, HCO_3^-, and mineralization are 0.13, 0.38, –0.05, 0.16, 0.17, 0.19, 0.02, and 0.13).

Fluorine concentration in surface water of the Middle Klyaz'ma Basin is somewhat higher its mean concentration in World rivers (0.1 mg/L [14]), but it corresponds to the range of earlier measurements in river waters of the Upper Volga (0.14–0.75 mg/L [7]). Fluorine concentration in subsoil water in the study area shows a little difference from the mean value for subsoil water in the zone of leaching of moderate climate (0.26 mg/L [12]).

Fluorine concentration near urban areas are higher: 0.42–0.84 mg/L with a mean value of 0.56 mg/L. Even higher concentrations were recorded in the settling ponds of the cities of Elektrostal' (0.71 mg/L) and Stavrovo (0.97–2.08 mg/L). Those data suggest that anthropogenic fluorine hydrochemical anomalies are confined to urbanized industrial areas, never extending far beyond their limits. The atmospheric transport of anthropogenic pollutants seems to have no significant effect on the fluorine concentration in surface water, as can be seen from its low concentrations (0.07–0.22 mg F/L) in different water bodies (small rivers, creeks, ponds, small bogs) in the "Elk Island" National Park, which lies in the zone of permanent presence of urban air masses.

A characteristic feature of the Middle Klyaz'ma Basin are low fluorine concentrations in subsoil water: 0.10 (0.02–0.26) mg/L, with minimal values typical of Meshchera Lowland, and higher values confined to the well-drained Yur'evskoe Opol'e. In accordance this, the occurrence frequency of fluorine concentration in subsoil water has two peaks 0.04 and 0.19 mg/L (Fig. 1b).

As noted in [2], lower fluorine concentrations are recorded in rivers flowing through very boggy and densely forested areas of modern within-platform depression, of which Meshchera Lowland is an exam-

Table 2. Fluorine concentrations in different water objects in the Middle Klyaz'ma Basin

Object	Number of samples	[F], mg/L	
		mean	range
Areas with relatively small anthropogenic load			
Snow, Meshchera Educational–Scientific Station	4	0.08	0.07–0.10
Rivers:			
Klyaz'ma	35	0.29	0.19–0.49
Bol'shaya Dubna	2	0.35	0.23–0.47
Bol'shaya Lipnya	2	0.30	0.22–0.38
Bol'shaya Ushma	1	0.25	–
Verkhul'ka	3	0.34	0.34–0.35
Vol'ga	4	0.32	0.22–0.39
Vorsha	2	0.29	0.25–0.32
Vorya	2	0.35	0.33–0.37
Vyrka	1	0.24	–
Drezna	1	0.25	–
Dubenka	1	0.25	–
Il'movka	1	0.28	–
Kirzhach	6	0.32	0.21–0.58
Koloksha	7	0.31	0.27–0.41
Laska	2	0.33	0.31–0.34
Malaya Dubna	2	0.28	0.25–0.30
Melezha	1	0.25	–
Molodyn'	1	0.24	–
Obod	1	0.17	–
Peksha	4	0.28	0.18–0.43
Plotnya	1	0.26	–
Polya	2	0.35	–
Sen'ga	5	0.28	0.21–0.35
Tanka	2	0.34	0.26–0.41
Chernaya	2	0.35	0.31–0.39
Shalovka	2	0.24	0.22–0.26
Sheredar'	1	0.32	–
Sherna	4	0.27	0.23–0.32
Shchitka	2	0.17	0.14–0.20
Ruch'i	7	0.32	0.20–0.37
Drainage ditches	6	0.19	0.06–0.28
Lakes:			
Bogdarnenskoe	1	0.17	–
Ershevik	1	0.08	–
Ignatovka	1	0.21	–
Chashcha	1	0.07	–
Voinovo	1	0.38	–
Subsoil waters (wells)	50	0.10	0.02–0.26
Artesian water, well in limestones of Myachkovskii aquifer	1	1.95	–
Areas subject to a strong anthropogenic impact			
Klyaz'ma R., Orekhovo-Zuevo C.	2	0.46	0.42–0.49
Berezka R., Petushki C.	4	0.57	0.43–0.84
Vokhonka R., Elektrostal' C.	1	0.67	–
Shchitka R., Pokrov C.	1	0.54	–
Silty plats of Klyaz'ma R.	4	0.88	0.54–1.20
Settling pond, Elektrostal' C.	1	0.71	–
Settling ponds, Stavrovo T. Motor-and-tractor plant	5	1.65	0.97–2.08

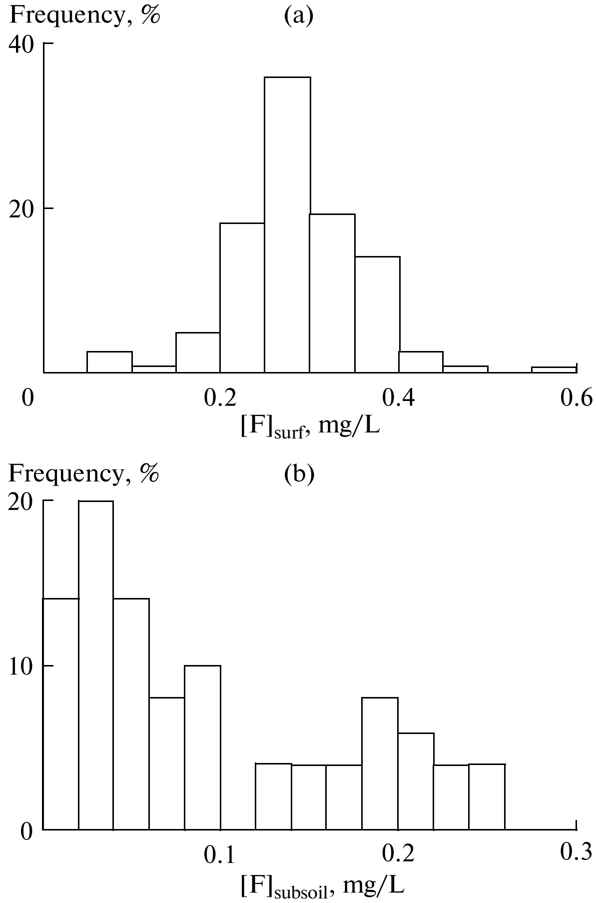

Fig. 1. Occurrence frequency of fluorine concentrations in (a) surface and (b) subsoil waters of background regions in the Middle Klyaz'ma Basin.

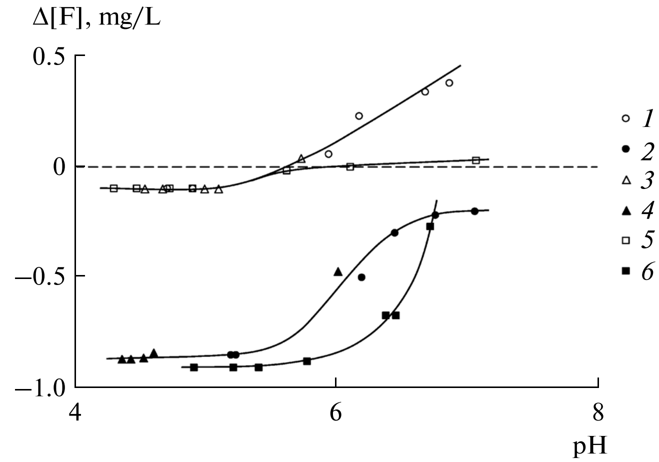

Fig. 2. The effect of the acidity of the medium on changes in fluorine concentration in snowmelt water at its interaction with soils. Floodplain sod soil, layered, in the initial solution [F]: (*1*) 0.10 mg/L, (*2*) 0.94 mg/L; sod-gley podzolized soil, in the initial solution [F]: (*3*) 0.10 mg/L, (*4*) 0.94 mg/L; sod forest unpodzolized soil, in the initial solution [F]: (*5*) 0.10 mg/L, (*6*) 0.94 mg/L.

ple. A correlation of low fluorine concentrations with a large amount of aquatic humus [12]; however, this regularity seems to be an artefact, since it is difficult to find a chemical process, leading to such effect. In addition to this, experiments for studying the interaction of fluorine-containing solutions with clay minerals [10] showed a considerable increase in fluorine sorption with increasing acidity of the medium. If the relationship between the fluorine sorption rate and pH has a universal character, the lower fluorine concentration in the subsoil water of Meshchera Lowland with the ubiquitous occurrence of acid soils and peat bogs receives a logical explanation.

To check the latter assumption, experiments were carried out for studying fluorine distribution between water and soil, as well as between water and bottom sediments in rivers.

The experiments used three types of soils divided into horizons (floodplain soddy laminated, soddy-gley slightly podzolic, and soddy forest podzol-free), and four types of river silts. All samples were taken in the study area. In the first series of experiments with soils, finely pulverized soil samples were mixed with filtered snowmelt water, containing 0.10 mg F/L; in the second series, it was mixed with the same water with fluorine concentration increased to 0.94 mg/L. Experiments with river sediments, pulverized to a fraction of <0.1 mm, consisted of four series with fluorine concentration successively increasing from 0.15 to 2.3 mg/L. In experiments with soils, the value of pH was artificially kept unchanged and established as a result of water interaction with soil samples from different horizons; in experiments with silts, the acidity of medium varied by adding small amounts of HCl or NaOH. The ratio of solid phase to solution in all experiments was constant and equal to 1 : 10, and the exposure time was 3 weeks with weekly mixing.

The results of experiments aimed to study fluorine distribution between water and soils (Table 3) showed that, in experiments with the initial concentration of 0.10 mg F/L, fluorine either left the water or entered it, depending on pH: at pH < 5.6, fluorine concentration in solution decreased, while at pH > 5.6, it increased (Fig. 2). In experiments with the initial concentration of 0.94 mg F/L, the removal of fluorine from solution was observed throughout the examined acidity range (pH 4.36–7.06) with its maximal immobilization at low pH. Experiments for studying fluorine distribution between water and river silts (Table 4) yielded the same regularities as those obtained for soils: an increase in acidity caused the removal of fluorine from solution or a decrease of its input from solid phase (Fig. 3).

The effect of dissolved organic matter on fluorine leaching from rock minerals also depends, primarily, on the equilibrium pH value. As follows from the experimental data given in Table 5, in the case of

Table 3. Changes in fluorine concentration in snowmelt water at its interaction with soils (the solid phase to solution mass ratio is 1 : 10)

Soil section		Equilibrium solution		
horizon	depth, cm	pH	[F], mg/L	Δ[F], mg/L
Floodplain sod soil, layered, in the initial solution [F] = 0.10 mg/L				
A	0–9	6.68	0.44	0.34
AB	9–25	6.86	0.48	0.38
B	25–40	6.17	0.33	0.23
Cg	40–120	5.94	0.16	0.06
[A]g	120–140	4.90	N.d.*	–0.10
CD	>140	4.71	The same	–0.10
The same in the initial solution [F] = 0.94 mg/L				
A	0–9	6.45	0.64	–0.30
AB	9–25	7.06	0.74	–0.20
B	25–40	6.76	0.72	–0.22
Cg	40–120	6.19	0.44	–0.50
[A]g	120–140	5.23	0.09	–0.85
CD	>140	5.19	0.09	–0.85
Sod-gley podzolized soil, in the initial solution [F] = 0.10 mg/L				
A	0–7	4.99	N.d.	–0.10
AEg	7–16	5.10	The same	–0.10
Eg	16–24	4.67	"	–0.10
Bf, h, (g)	24–38	4.53	"	–0.10
Cg	>38	5.73	0.14	0.04
The same in the initial solution [F] = 0.94 mg/L				
A	0–7	4.52	0.08	–0.86
Aeg	7–16	4.60	0.10	–0.84
Eg	16–24	4.43	0.07	–0.87
Bf, h, (g)	24–38	4.36	0.07	–0.87
Cg	>38	6.01	0.41	–0.47
Sod forest unpodzolized soil, in the initial solution [F] = 0.10 mg/L				
A	0–17	4.73	N.d.	–0.10
Bf	17–44, top	4.48	The same	–0.10
The same	The same, bottom	4.30	"	–0.10
Bf, i	44–68	4.90	"	–0.10
The same	68–103	5.62	0.08	–0.02
BC	103–176, top	6.11	0.10	0
Cp, s	>176	7.07	0.13	0.03
The same in the initial solution [F] = 0.94 mg/L				
A	0–17	4.91	0.03	–0.91
Bf	17–44, top	5.21	0.03	–0.91
The same	The same, bottom	5.41	0.03	–0.91
Bf, i	44–68	5.78	0.06	–0.88
The same	68–103	6.38	0.27	–0.67
BC	103–176, top	6.46	0.27	–0.67
Cp, s	>176	6.72	0.67	–0.27

* Below detection limit.

Table 4. Variations in fluorine concentration in water of the Klyaz'ma R. at the interaction with river silts (the solid phase to solution ration is 1 : 10)

Equilibrium pH	[F], mg/L		
	original solution	equilibrium solution	Δ[F]
Black sandy silt			
6.92	0.15	0.19	0.04
8.09	"	0.18	0.03
8.90	"	0.24	0.09
7.13	1.17	1.11	–0.06
8.05	"	1.14	–0.03
8.95	"	1.22	0.04
7.11	2.31	2.15	–0.16
8.04	"	2.21	–0.10
8.99	"	2.31	0.0
Sandy-clayey silt			
6.95	0.15	0.17	0.02
8.07	"	0.17	0.02
8.91	"	0.22	0.07
7.01	0.66	0.65	–0.01
8.06	"	0.66	0
8.90	"	0.72	0.06
7.07	1.17	1.13	–0.04
8.02	"	1.15	–0.02
8.90	"	1.18	0.01
Black sandy-clayey silt			
6.55	0.15	0.18	0.03
7.47	"	0.21	0.06
8.51	"	0.27	0.12
6.36	0.66	0.63	–0.03
7.43	"	0.63	–0.03
8.53	"	0.74	0.08
6.46	1.17	1.00	–0.17
7.47	"	1.04	–0.13
8.45	"	1.29	0.12
6.39	2.31	1.79	–0.52
7.45	"	1.98	–0.33
8.46	"	2.37	0.06
Blue–black clayey silt			
6.73	0.15	0.11	–0.04
7.70	"	0.10	–0.05
8.63	"	0.27	0.12
6.59	0.66	0.33	–0.33
7.20	"	0.37	–0.29
8.64	"	0.67	0.01
6.60	1.17	0.55	–0.62
7.53	"	0.64	–0.53
8.64	"	1.16	–0.01
6.48	2.31	0.99	–1.32
7.66	"	1.10	–1.21
8.38	"	2.04	–0.27

Table 5. Fluorine leaching from micas in the presence of dissolved organic matter (the solid phase to solution mass ratio is 1 : 100, exposure time is 3 weeks with weekly mixing)

Acid (0.01 M solution)	Equilibrium solution		
	pH	[F], mg/L	$[F]_{org} - [F]_{dist}$, mg/L
Muscovite			
H_2O	5.79	0.23	–
Sulfanilic	5.26	0.16	–0.07
Citric	6.51	0.13	–0.10
Amygdalic	6.93	0.19	–0.04
Salicylic	6.65	0.17	–0.06
Acetic	6.94	0.16	–0.07
Phthalic	5.13	0.17	–0.06
Ethane	6.79	0.10	–0.13
Amber	7.03	0.18	–0.05
Tartaric	6.15	0.08	–0.15
Ferryphlogopite			
H_2O	9.19	0.07	–
Sulfanilic	8.17	0.11	0.04
Citric	7.59	0.13	0.06
Amygdalic	8.24	0.10	0.03
Salicylic	7.91	0.09	0.02
Acetic	7.99	0.09	0.02
Phthalic	7.96	0.10	0.03
Ethane	8.19	0.14	0.07
Amber	8.07	0.09	0.02
Tartaric	7.79	0.10	0.03
Biotite			
H_2O	8.32	0.23	–
Sulfanilic	7.36	0.29	0.06
Citric	7.00	0.30	0.07
Amygdalic	7.60	0.31	0.08
Salicylic	7.31	0.26	0.03
Acetic	7.23	0.27	0.04
Phthalic	5.96	0.18	–0.05
Ethane	6.56	0.08	–0.15
Amber	7.53	0.29	0.06
Tartaric	6.69	0.19	–0.04

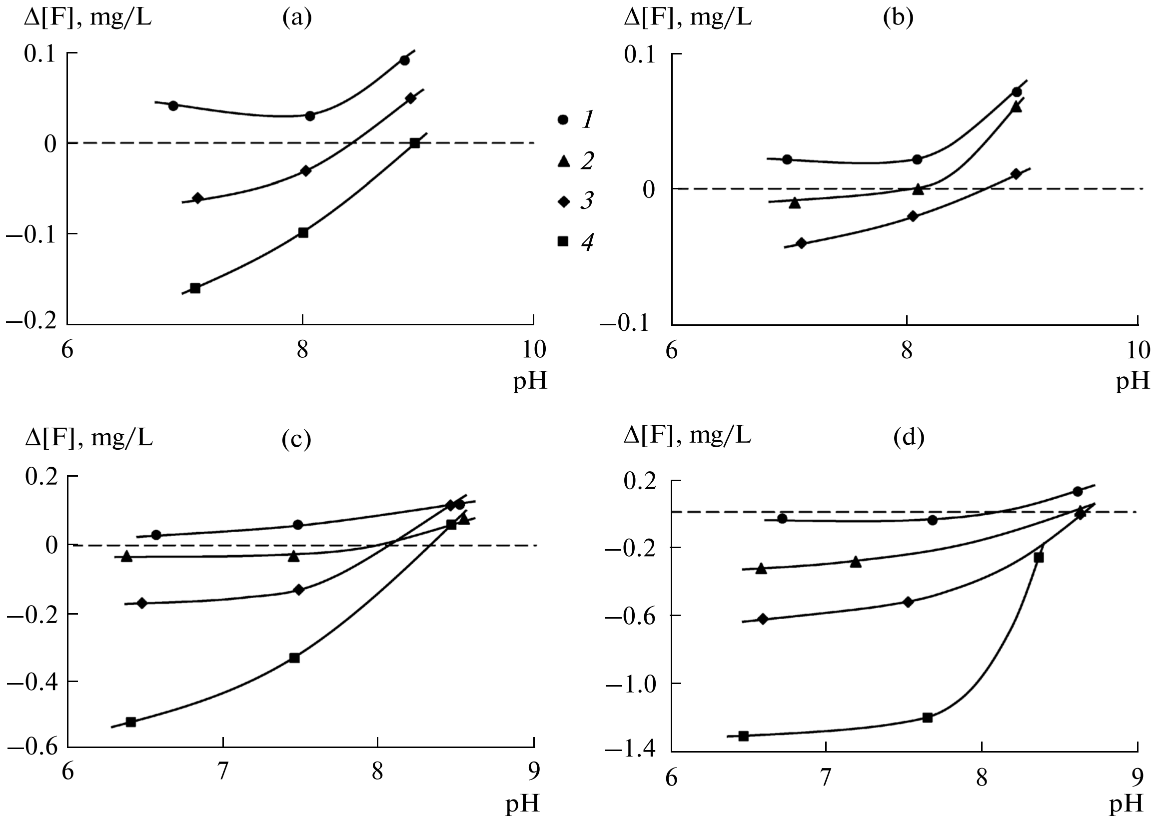

Fig. 3. The effect of the acidity of the medium on changes in fluorine concentration in Klyaz'ma R. water at its interaction with river silts: (a) black sandy, (b) sandy-clayey, (c) black sandy-clayey, (d) blue–black clayey; in the initial solution [F]: (*1*) 0.15, (*2*) 0.66, (*3*) 1.17, (*4*) 2.31 mg/L.

leaching of monomineral mica fractions with a size <0.1 mm (muscovite, ferryphlogopite, and biotite) the difference between the concentrations of the fluorine that has passed from the solid phase into 0.01 M solutions of organic acids ($[F]_{org}$, mg/L), and distilled water ($[F]_{dist}$, mg/L), decreases proportionally to the increase in the acidity of the medium in accordance with the relationship common for all samples:

$$[F]_{org} - [F]_{dist} = 0.058pH - 0.43, \quad r = 0.69.$$

In this case, in weakly alkaline media, the presence of organic acids facilitates fluorine mobilization, while in weakly acid media, it, conversely, decreases its intensity (Fig. 4).

Thus, the experiments confirm the previously established fact of an increase in the adsorption capacity of various mineral phases with respect to fluorine at a decrease in pH. This phenomenon seems to cause the lower fluorine content of subsoil water in the swampy areas of Meshchera Lowland.

CONCLUSIONS

The background fluorine concentration in watercourses in the Middle Klyaz'ma Basin is 0.29 mg/L (0.29 in the Klyaz'ma R., 0.28 in small rivers, and 0.32 mg/L in creeks); in the water bodies in the area (drainage ditches and lakes), it was 0.19 mg/L; and in subsoil waters of Yur'evskoe Opol'e and Meshchera Lowland, it was 0.19 and 0.04 mg/L, respectively.

Anthropogenic fluoride hydrochemical anomalies, exceeding the background concentrations by 2–9 times, are confined to urbanized industrial regions and not extend far beyond their limits. Maximal fluorine concentrations, reaching 1.20–2.08 mg/L, were recorded in silty sewage intake basins at the Klyaz'ma R. and in settling ponds of industrial plants. The effect of atmospheric transport of anthropogenic pollutants on fluorine content of surface waters is insignificant.

Fluorine concentration in subsoil water is controlled by its distribution between water and host rocks, and the rate of the corresponding process depends on pH: in acid media, the immobilization of dissolved fluorine is maximal; the adsorption capacity of mineral phases decreases with increasing pH, and in neutral and weakly alkaline media, fluorine can enter the solution. The low fluorine concentrations in subsoil waters in Meshchera Lowland are due to its

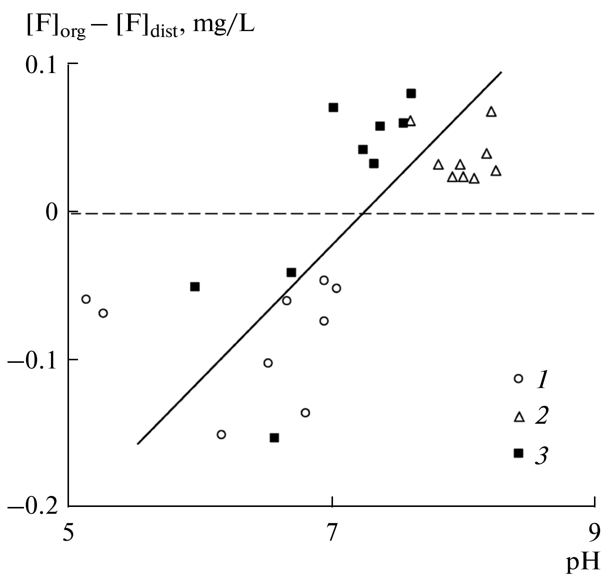

Fig. 4. The effect of dissolved organic matter on fluorine leaching from micas at different acidity of the medium. (*1*) Muscovite, (*2*) ferryphlogopite, (*3*) biotite.

adsorption by soils with higher acidity, which are widespread in the area.

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