

# *Fluorides in Surface and Underground Waters of Southeastern Coast and in Parts of Navigable Channels of Azov Sea*

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**Abstract**—The concentration of fluorides in the surface and underground waters of the studied areas of the Azov sea does not exceed the maximum permissible concentrations. In the direction of the Eastern region of the Taganrog Bay → Central area → West Bay area → East Azov Sea, the concentration of fluorides in the water of the coastal zone increases. In the same direction, their concentration in underground aquifers increases. It is shown that the tributaries may be one of the main sources of fluoride inflow into the coastal zone of the sea, while the role of groundwater is secondary. In the areas of dredging and dumping soil, a slight excess of fluoride concentrations was revealed, compared with their concentrations in the water of the background sites, which may indicate the local influence of the functioning of navigable channels on the formation of the concentration of fluorides in the sea water.

**Keywords**—fluorides; concentrations; surface and underground waters; navigable channels

## I. INTRODUCTION

The tendency of an increase in the background fluoride content in combination with their high chemical and biological activity and the ambiguity of the resulting effects [1, 7, 12-14, etc.] necessitate a comprehensive consideration of the sources and distribution of fluoride in environmental objects.

The maximum permissible concentration (MPC) of fluoride in drinking water is 1.2 mg / dm<sup>3</sup> with a toxicity-limiting hazard indicator. Exceeding MPC for fluorine in drinking water causes bone disease - fluorosis [2, 6, 12, 13]. The main sources of pollution of surface and groundwater with fluorides are enterprises for the production of steel, aluminum, thermal power plants, cryolite and glass factories [3, 8, 9].

Fluorine belongs to those elements whose lack is also dangerous. So, in areas where the content of fluoride in drinking water is low (less than 0.1 mg / dm<sup>3</sup>), people develop dental caries more often [2, 4, 6, 13].

The purpose of this work is to study the distribution of fluorides in surface and underground waters of the southeastern coast of the Azov Sea, as well as the influence of the functioning of navigable canals on their contents.

## II. MATERIALS AND METHODS OF THE RESEARCH

This study is based on materials obtained by the authors during the two ground expeditions to the southeastern coast of the Azov Sea, and five water expeditions in the areas of navigable canals, and dumping of soils in the Taganrog Bay.

From 10 to 13 August 2016 and from 29 to 31 August 2017, ground-based expeditionary studies of the coastal zone of the Russian part of the Sea of Azov were conducted, including its bays (Taganrog, Yeisk and Yasensky), as well as the Kagalnik, Eya, Sukhaya and Mokraya Chuburka rivers flowing into it. Furthermore, it included water sampling to determine fluoride concentration, ion composition and salinity, pH values, and temperatures in order to study patterns of the distribution of fluoride concentrations in the coastal zone of the sea (Fig. 1).

Five expeditions were conducted in the areas of navigable canals and dumping of soils, as well as at a distance from them in the Taganrog Bay from April to June 2017. In addition, establishing fluoride levels far from the coast were considered. The expeditions aimed to study the impact on their distribution of works on dredging shipping channels and soil dumping (Fig. 2). At the same time, 4 surveys were carried out at stations located in the waters of the Taganrog seaport, the

Taganrog approach channel, and underwater dump No. 956 seized during port construction and dredging. Moreover, one survey was made at the stations located in the Azov-Don Sea Canal (ADMK), underwater dump soil number 970, and "background" areas. During expeditions in the areas of navigable canals and soil dumping, water was sampled from the vessels of the FSUE "Rosmorport" Azov Basin Branch at local environmental monitoring stations [5]. At all stations, water was taken from the surface layer.

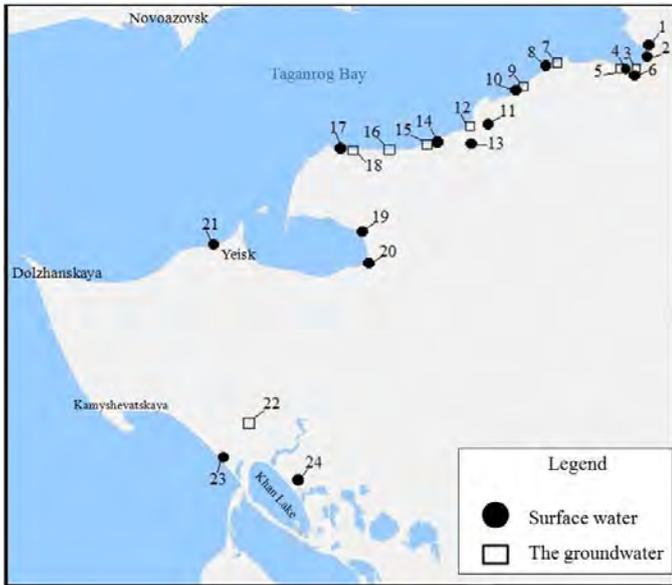


Fig. 1. Map of sampling stations on the southeast coast of the Azov Sea

The sampling, transportation, storage of samples, the subsequent determination of the content of fluorides and other ingredients, as well as indicators in them were carried out according to standard methods accepted in the Roshydromet system [10, 11].

### III. RESULTS AND ITS DISCUSSION

The fluoride concentration in the investigated waters of the southern coastal areas of the Taganrog Bay varies between 0.342-0.516 mg / l (average content is 0.402 mg / l) (Table 1). In groundwater, their content is, as a rule, somewhat lower and varies in the range of 0.112-1.022 mg / l (on average, 0.309 mg / l), except for a single sample with a maximum concentration of fluoride (1.022 mg / l) close to the MPC taken in the public well of Port Caton village (Primorskaya street). Based on the establishment of lower fluoride concentrations in groundwater waters (first aquifer from the surface) discharging into the coastal areas of the southeastern coast of the Sea of Azov, it can be concluded that groundwaters play a secondary role in the formation of fluoride concentrations in the water of the coastal zone of the sea.

There is a tendency of increased fluoride concentration with increasing depth, on which the groundwater is located. Thus, in groundwater collected in public wells up to 10 m in depth, the fluoride concentration averages 0.202 mg / l. Whereas in water collected in the inter-layer aquifer from a

depth of 10-12 meters, the average amount was found to be 0.242 mg / l (station 18), and from a depth of 20 meters, it showed an average of 0.445 mg / l (station 22). Probably, this is due to the duration of interaction of groundwater with host rocks: the deeper the groundwater level, the older it is and the more fluoride is leached from the rocks. There is a clear trend of increasing fluoride concentrations in the coastal zone water in the following direction: the eastern region of the Taganrog Bay (average of 0.352 mg / l) → central bay area (average of 0.425 mg / l) → western region of the Taganrog Bay (0.514 mg / l) → eastern region - Sea of Azov (0,650 mg / l). In the same direction, an increase in their concentrations was also recorded in underground aquifers: the eastern region of the Taganrog Bay (average 0.202 mg / l) → the central bay area (average 0.374 mg / l) → the eastern ariar of the Sea of Azov (0.445 mg / l).

In the studied rivers, fluoride concentrations vary from 0.325 to 0.606 mg / l (average 0.446 mg / l) with their maximum concentrations (0.408-0.606 mg / l) found in the small tributaries Mokraya and Sukhaya Chuburka, flowing into the southern coast of the central region of Taganrog Bay, and a minimum (0.325-0.348 mg / l) found in the water of the more abundant rivers Don and Kagalnik, flowing into the eastern region of the Taganrog Bay. Thus, the concentrations of fluorides in the waters of the studied tributaries are similar in value to their concentrations in the waters of the coastal areas of the Taganrog Bay, which may indicate that the tributaries are one of the main sources of fluoride in the Taganrog Bay. Besides, an increase in fluoride concentrations in surface and underground waters of the investigated coastal zone of the Azov Sea, and in the waters of tributaries can be noted in the subsequent direction: tributaries of the eastern region of the Taganrog Bay (average of 0.337 mg / l) → tributaries of the southern coast of the central region of the bay (average of 0.507 mg / l).

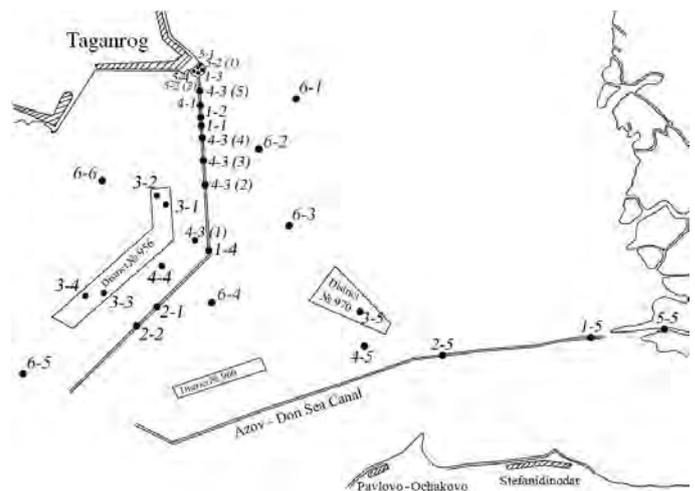


Fig. 2. Location of observation stations in the water area of the Taganrog Bay at the Taganrog seaport, Taganrog approach channel, the sea part of the Azov-Don channel, underwater landfill sites No. 956 and 970, and background areas.

In the Taganrog Bay, there is a positive correlation between the concentration of fluoride and the total content of

basic ions in water, which causes the above trend of increasing concentrations of fluoride in the water of the coastal zone in the direction of the eastern area of the Taganrog Bay → central area of the bay → the western area of the Taganrog Bay → eastern Azov area seas. The correlation of the concentration of fluoride with the temperature of the water is weak.

TABLE I. FLUORIDE CONCENTRATION IN SURFACE AND UNDERGROUND WATERS OF THE COASTAL ZONE OF THE SOUTHEASTERN COAST OF THE AZOV SEA, AS WELL AS IN THE WATER OF ITS TRIBUTARIES

Sea of Azov areas	Fluoride content, mg / l
<b>East district of Taganrog Bay (stations 1 - 8)</b>	
Surface waters of the coastal zone of the eastern region of Taganrog Bay	<u>0,342-0,359</u> * 0,352 (4)
Groundwaters of the coast of the eastern region of the Taganrog Bay	<u>0,186-0,211</u> 0,202 (3)
R. Kagalnik, estuary, 1 km from the confluence of the Taganrog Gulf	0,325 (1)
R. Don estuary, 1 km from the confluence of the Taganrog Gulf	0,348 (1)
<b>Central District (stations 9-20)</b>	
Surface waters of the coastal zone of the central region of Taganrog Bay	<u>0,371-0,516</u> 0,425 (4)
Groundwaters of the coast of the central region of Taganrog Bay	<u>0,112- 1,022</u> 0,374 (5)
R. Wet Chuburka, estuary, 1 km from the confluence of the bay	0,408 (1)
R. Dry Chuburka, estuary, 1 km from the confluence of the bay	0,606 (1)
Surface waters of the coastal zone of the western region of Taganrog Bay (station 21))	0,514 (1)
Total for surface waters of coastal areas of the entire southern coast of the Taganrog Bay	<u>0,342-0,516</u> 0,402 (12)
Total for groundwater of the entire southern coast of the Taganrog Bay	<u>0,112 - 1,022</u> 0,309 (8)
Total for the waters of the rivers of the south coast of the Taganrog Bay	<u>0,325-0,606</u> 0,446 (3)
<b>East region of the Azov Sea (stations 22, 23)</b>	
Surface waters of the coastal zone of the eastern region of the Azov Sea	0,650
Groundwater coast of the eastern region of the Azov Sea	0,445
* Here and below in table 2 the numerator shows the limits of change, in the denominator - the average values, in brackets - the number of measurements.	

In the water of the studied area of the Sea of Azov, direct proportional dependencies were established between the concentration of fluorides and the concentrations of sulphate ions ( $r = 0.80$ ;  $P < 0.01$ ), magnesium ions ( $r = 0.54$ ;  $P < 0.01$ ), sodium ( $r = 0.47$ ;  $P < 0.01$ ), chloride ions ( $r = 0.31$ ), pH values, as well as inverse proportional relationships between the concentration of fluorides, and the concentrations of calcium ions ( $r = -0.53$ ;  $P < 0.01$ ) and bicarbonate ions ( $r = -0.54$ ;  $P < 0.01$ ), which are intracontinental in origin ( $\text{Ca}^{2+}$  ions and  $\text{HCO}_3^-$  come mainly as part of surface runoff - river runoff and precipitation).

The authors also analyzed the materials of expeditionary research aimed at studying the influence of navigable canals and storage areas of soil formed during the clearing of canals, on the distribution of fluoride concentrations in the Taganrog Bay (Table 2). In the Taganrog Bay, two shipping canals were investigated: The Taganrog approach channel (TPK, 19 km

long, 80 m wide, 5.0–5.5 m deep), crossing the Taganrog coast and providing sea approaches to the Taganrog port complex, and the Azov-Don sea canal (ADMK, length 26 km, width 80 m, depth 4–5 m), laid parallel to the center line of the Taganrog Bay.

TABLE II. FLUORIDE CONCENTRATION AT THE TAGANROG SEAPORT IN THE WATER AREA OF THE TAGANROG BAY, TAGANROG APPROACH CHANNEL, THE SEA PART OF THE AZOV-DON CHANNEL, UNDERWATER DUMPS OF SOIL NO. 956 AND 970 AND BACKGROUND STATIONS

Azov Sea areas	Fluoride content, mg / l
Seaport of Taganrog, including: away from the dredger	<u>0,334-0,438</u> 0,386 (4) <u>0,334-0,403</u> 0,369 (3)
near the dredger	0,438 (1)
Taganrog approach channel (TPK), including: away from the dredger	<u>0,304-0,481</u> 0,421 (8) <u>0,455-0,481</u> 0,469 (3)
near the dredger	<u>0,304-0,450</u> 0,391 (5)
Azov-Don Sea Canal (ADMK)	<u>0,332-0,354</u> 0,343 (2)
Landfills including: landfill No. 956 landfill No. 970	<u>0,330-0,473</u> 0,407 (4) <u>0,370-0,473</u> 0,432 (3) 0,330 (1)
Background, Taganrog Bay, 10 km from 0 km at a distance from ADMK	0,355 (1)

Fluoride concentrations in the navigable canals varied within 0.304-0.481 mg / l (average of 0.405 mg / l) with slightly higher concentrations in the water of the Taganrog approach channel (0.304-0.481 mg / l, average of 0.421 mg / l) compared with the Azov-Don Sea Canal (0.332-0.354 mg / l, an average of 0.343 mg / l). At the same time, in the water of samples taken near working dredgers, fluoride concentrations, as a rule, were slightly lower (on average 1.2 times) than at a distance from working dredgers, which may indicate that the bottom developed in shipping canals are a significant source of fluoride in the water of the Taganrog Bay.

The concentrations of fluoride in ADMK water are close to its concentrations in the water of the Don River (0.348 mg / l), as well as in the water of the background area remote from ADMK (0.355 mg / l). This is probably due to the fact that the waters of the ADMK and in general, in the eastern region of the Taganrog Bay, are in fact low-transformed waters of the Don river.

In areas of bottom dumping, fluoride concentrations are close to or slightly higher than their content in the waters of the background section and the Don River, and vary between 0.330-0.473 mg / l (mean of 0.407 mg / l) with lower values in the landfill No. 970, on which the grounds of ADMK are stored.

#### IV. CONCLUSION

The concentration of fluoride in all samples taken in the water of the southeastern coastal zone of the Sea of Azov, in tributaries flowing into it (the Don, Kagalnik, Yeya, Sukhaya

and Mokraya Chuburka rivers), in the water area of the Taganrog seaport, Taganrog approach canal I, Azov-Don - the sea canal, underwater dumps of the soil, as well as in the ground and interstratal horizons of groundwater, does not exceed the maximum permissible levels (MAC - 1.2 mg / l).

The fluoride concentration in the investigated waters of the coastal areas of the southern coast of the Taganrog Bay varies between 0.342-0.516 mg / l (average content is 0.402 mg / l). There is a distinct trend of increasing fluoride concentrations in the water of the coastal zone in the direction of the Taganrog Bay → central area of the Bay → the western area of the Taganrog Bay → eastern Azov area seas. In the same direction, an increase in their concentrations was recorded in the aquifers.

In groundwater, the fluoride content is, as a rule, somewhat lower than in the waters of the investigated coast of the Azov Sea and varies in the range of 0.112-1.022 mg / l (on average, 0.309 mg / l). It is concluded that groundwater plays a secondary role in the formation of fluoride concentrations in the water of the coastal zone of the sea. There was a tendency to increase the concentration of fluoride with increasing depth, on which the groundwater horizon is located, which is probably due to the interaction of groundwater with host rocks: the deeper the groundwater, the older it is and the more fluoride is leached from the rocks.

In the studied rivers, fluoride concentrations vary from 0.325 to 0.606 mg / l (average 0.446 mg / l) with their maximum concentrations in the small tributaries of the Mokraya and Sukhaya Chuburka, flowing into the southern coast of the central area of the Taganrog Bay, and their minimal amount found in the waters of more saturated rivers. Don and Kagalnik flow into the eastern area of the bay. Thus, the concentrations of fluorides in the waters of the studied tributaries are similar in values to their concentrations in the waters of the coastal areas of the bay, which may indicate tributaries water as one of the main sources of fluoride in the Taganrog Bay. Concerning the surface and underground waters, and to the waters of the tributaries, one can note an increase in fluoride concentrations in the following direction: tributaries of the eastern region of the Taganrog Bay → tributaries of the southern coast of the central region of the bay.

Finally, in areas of dredging and underwater storage of soils, a slight excess of fluoride concentrations was detected in general compared to their concentrations in background water and the coastal zone of the eastern region of Taganrog Bay. This may indicate a slight effect of navigation canals on the concentration of fluoride in the Taganrog Gulf.

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