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## Assessment of Groundwater Impact on Water Quality in the Built-up Areas at the Lower Don

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**Abstract**—The impact is assessed that the groundwater flow from the built-up areas on the left bank of the Don River in the Rostov oblast produces on the chemical composition and quality of surface water in the lower river reaches. It is demonstrated that the total average annual groundwater flow from the built-up areas on the left river bank is very small and equals 0.002 km<sup>3</sup>/year on average or 0.01% of the average annual water flow in the estuarine outlet. Despite the rather high degree of contamination of groundwater and the high content of principal ions, this causes the insignificant impact of groundwater runoff on water quality in the Lower Don. The average total mass of substances that annually come from the left-bank urbanized areas in the groundwater flow is about 4.9 · 10<sup>3</sup> t or 0.04% of total mass of substances transported by the Don River to the Taganrog Bay.

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### INTRODUCTION

According to the existing classification, in the last quarter of the 20th century and at the beginning of the 21st century water of the Lower Don is considered as polluted from the Tsimlyansk hydroelectric power station dam to the river estuary and as very polluted and dirty between Rostov-on-Don and Azov cities [9]. The changes in water quality in the Don River are caused by the increase in the concentration of biogenic elements, oil products, heavy metals, and water mineralization [15]. The deterioration of surface water quality is mostly caused by the anthropogenic load. At the same time, the groundwater also acts as the source and transporter of surface water contamination. The surface water is basically associated with the groundwater of the first (from the surface) aquifer [11]. Due to the natural factors typical of the south of the Rostov oblast, it is largely vulnerable to the infiltration pollution and is classified as unprotected or poorly protected [2]. The groundwater contamination increases manifold under the influence of the processes of anthropogenic underflooding [5, 13] which are currently often observed both on agricultural lands and on the territory of settlements in the south of the Rostov oblast [1].

Unfortunately, such important aspect as the mass transport of pollutants with the groundwater flow is not taken into account, as a rule, for assessing and forecasting environmental conditions in surface water bodies and coastal areas. The impact of groundwater on water contamination in the Lower Don has not been studied so far despite the fact that the main components of water balance of the Lower Don taking into account the groundwater inflow to the stream channel was studied as early as in the 1960s–1980s [3, 10]. According to the data of these studies, the total volume of water coming as a groundwater inflow to the Lower Don channel is 0.14 km<sup>3</sup>/year.



The schematic map of the research area. (1) Water bodies; (2) key areas where groundwater surveys and routine observations were carried out; (3) settlements where routine observations were not carried out.

We aimed at estimating the groundwater flow from the built-up areas on the left bank of the Don River in the Rostov oblast and the groundwater impact on surface water contamination in the lower reaches of the river.

#### THE AREA AND METHODS OF RESEARCH

In 2008–2013 the authors carried out works including the hydrogeological survey (the scale is 1:50000), the drilling of wells for testing groundwater inflow and for the determination of physical and mechanical properties of soil as well as stationary routine observations of the level, composition, and contamination of groundwater in the built-up areas on the left bank of the Lower Don.

The length of the left-bank part of the Don River within the Rostov oblast is 319 km, and the catchment area is more than  $160 \cdot 10^3 \text{ km}^2$  [4] (17 and 38% of the total length and catchment area of the river, respectively). As to the terrain, the area of research is flat with small surface slopes mainly not exceeding 1–3 [6]. The most of the territory is weakly drained, hence, the volume of groundwater flowing towards natural and artificial discharge zones (rivers, streams, canals, etc.) is insignificant. The low ruggedness of the terrain defines the relatively small surface runoff of precipitation (hence, its high infiltration) and the small depth of groundwater (as a rule, not more than 10 m). The latter causes the significant role of underground evaporation in the discharge part of groundwater balance and the relatively high mineralization of groundwater [6].

At the initial stage the authors collected data from the archival datasets and published materials of Territorial Geological Databases, Institute of Urban Development, and other organizations in Rostov-on-Don and the Rostov oblast. All initial data for the territory under study taken from the borehole passports, observations diaries, sampling logbooks, etc., were analyzed and systematized.

To carry out the groundwater survey, the existence of wells, boreholes, and springs was revealed, the depth of the groundwater level was registered [1], and the sources of anthropogenic infiltration recharge and pollution of groundwater were identified.

The drilling of boreholes was carried out to create the stationary routine network, to sample soil in order to determine physical properties, and to carry out the testing of the groundwater inflow as a result of which the filtration coefficients and transmissibility of water-bearing rocks were determined using the data of cluster and single pumping tests. The total number of the drilled observation boreholes is 36.

Stationary routine observations of the level and chemical composition of groundwater were conducted from 2008 to 2013 on the territory of eight large settlements situated on the left bank of the Don River considered to be key areas (see the figure). As a rule, the observations were carried out every quarter at the points of the created routine network (boreholes and wells). Due to similar geomorphological and hydrogeological conditions, the data obtained by the authors in the key areas and archival data were used for the settlements on the left bank of the Don River which were not located in the zone under study.

The laboratory study of the chemical composition and degree of contamination of groundwater determined the concentration of iron, lead, copper, cadmium, zinc, calcium, magnesium, sodium, potassium, hy-

**Table 1.** Engineering-geological and hydrogeological parameters of soils and groundwater in the settlements in the south of the Rostov oblast

Settlement	Gradient of hypsometric groundwater table	Filtration flow width, m	Filtration coefficient, m/day		Effective porosity, m/day		Groundwater filtration rate, m/day	
			min	max	min	max	min	max
Semikarakorsk	0.00020	10350	0.10	3.0	0.50	0.90	0.00002	0.00060
Manychskaya	0.00170	3630	0.02	3.0	0.75	0.80	0.00003	0.00510
Bagaevsкая	0.00035	6190	0.41	3.0	0.50	1.00	0.00014	0.00105
Koisug	0.00100	7000	0.10	3.0	0.60	1.20	0.00010	0.00300
Bataisk	0.00090	7240	0.10	3.0	0.60	0.20	0.00009	0.00270
Romanovskaya	0.00208	4000	0.10	3.0	0.60	0.80	0.00021	0.00625
Kagal'nik	0.00667	4000	0.24	3.0	0.60	0.80	0.00160	0.02000
Azov	0.00638	5650	0.15	3.0	0.60	0.80	0.00096	0.01915
Shmat	0.00476	1900	0.15	3.0	0.60	0.80	0.00071	0.01429
Ust'-Koisug	0.00286	2800	0.15	3.0	0.60	0.80	0.00043	0.00857
Rostov-on-Don (left bank)	0.00300	19500	0.15	3.0	0.60	1.20	0.00045	0.00900
Makhin	0.00250	1100	0.15	3.0	0.60	1.20	0.00038	0.00750
Rybatskii	0.00125	2600	0.15	3.0	0.50	1.00	0.00019	0.00375
Alitub	0.00133	3600	0.15	3.0	0.50	1.00	0.00020	0.00400
Arpachin	0.00118	4300	0.15	3.0	0.50	1.00	0.00018	0.00353
Chebachiі	0.00188	4200	0.15	3.0	0.50	0.90	0.00028	0.00563
Novozolotovskaya	0.00077	6000	0.15	3.0	0.50	0.90	0.00012	0.00231
Kargal'skaya	0.00333	1100	0.15	3.0	0.50	0.90	0.00050	0.01000
Volgodonsk suburb	0.00208	15200	0.15	3.0	0.60	0.80	0.00031	0.00625

drocarbons, sulfates, chlorides, silicon, nitrogen compounds, phosphorus of phosphates, total content of oil components, total hardness, synthetic surfactants, methane, and pH. The total number of groundwater samples taken and analyzed in the key area of the left bank of the Don River over the period of observations is above 100. Before the water sampling the borehole was washed to clear water. The sampling of water and the preparation and determination of its chemical composition were carried out using the Roshydromet standard methods used in Hydrochemical Institute [14].

To study the processes of mass transport of dissolved migrants with the groundwater flow to the Don River, the scheme of convective transport was used as the base one. According to the data presented in [16], the main parameter of this scheme was the real filtration rate  $u_0$  related to the filtration rate by the relationships  $u_0 = \frac{Q}{n_0}$  for neutral migrants and  $u = \frac{Q}{n_e}$  for sorbed migrants, where  $n_0$  and  $n_e$  are active and effective rock porosities, respectively.

According to the data of [16], the velocity of the solute at the displacement front ( $u_d$ ) is equal to

$$u_d = \frac{Q}{(n_0 + k_d)} \cdot \frac{1}{n_{ef}} \quad (1)$$

where  $Q$  is the filtration flow discharge in the flow element with the area  $S$ ,  $m^3/day$ ;  $u_d$  is the filtration rate at the displacement front,  $m/day$ ;  $k_{distr}$  is the distribution coefficient being constant under these physical and chemical conditions:

$$k_{distr} = \frac{N - N_0}{c - c_0} \quad (2)$$

Here,  $N - N_0$  is the variation in sorptive capacity of rocks;  $c - c_0$  is the variation in migrant concentration in the separated flow element.

As follows from (1) that  $Q = n_e u_d$ , then  $Q = mB$  (where  $m$  is the flow thickness,  $m$ ;  $B$  is the flow width,  $m$ ) and  $u_d = kJ$  ( $k$  is the filtration coefficient of water-bearing rocks,  $m/day$ ;  $J$  is the gradient of hypsometric groundwater table); then, if  $B = 1$  m,

**Table 1.** (Contd.)

Real groundwater velocity, m/day		Specific discharge of the plane filtration flow with the width of 1 m		Discharge of the filtration flow from the settlement territory, m <sup>3</sup> /day		
min	max	min	max	min	max	mean
0.00004	0.00067	0.00030	0.00900	3.105	93.150	48.128
0.00005	0.00638	0.00051	0.07650	1.851	277.695	139.773
0.00029	0.00105	0.00215	0.01571	13.286	97.214	55.250
0.00017	0.00250	0.00150	0.04500	10.500	315.000	162.750
0.00015	0.00225	0.00135	0.04050	9.774	293.220	151.497
0.00035	0.00781	0.00312	0.09374	12.498	374.940	193.719
0.00267	0.02500	0.02400	0.30002	96.005	1200.060	648.032
0.00160	0.02394	0.01436	0.28723	81.144	1622.872	852.008
0.00119	0.01786	0.01071	0.21429	20.357	407.143	213.750
0.00071	0.01071	0.00643	0.12857	18.000	360.000	189.000
0.00075	0.00750	0.00675	0.13500	131.625	2632.500	1382.063
0.00063	0.00625	0.00563	0.11250	6.188	123.750	64.969
0.00038	0.00375	0.00281	0.05625	7.313	146.250	76.781
0.00040	0.00400	0.00300	0.06000	10.800	216.000	113.400
0.00035	0.00353	0.00265	0.05294	11.382	227.647	119.515
0.00056	0.00625	0.00422	0.08438	17.719	354.375	186.047
0.00023	0.00256	0.00173	0.03462	10.385	207.692	109.038
0.00100	0.01111	0.00750	0.15000	8.250	165.000	86.625
0.00052	0.00781	0.00469	0.09374	71.239	1424.772	748.005

$$q = kJm \quad (3)$$

where  $q$  is the specific discharge of the plane flow with the width of 1 m, m<sup>3</sup>/day.

Then the filtration flow discharge in the zone with the length  $l$  (m) is

$$Q = ql. \quad (4)$$

The estimation of  $q$  and  $Q$  was based on the determined filtration coefficients: both on the minimum and maximum ones (Table 1). The transport of chemical ingredients with the groundwater flow was computed using the values of their mean concentration in groundwater sampled in the settlements located on the left bank of the Don River close to the regional discharge area. For the settlements, where the observations of the chemical composition of groundwater were not conducted (Makhin, Rybatskii, Alitub, Arpachin, Chebachii, Novozolotovskaya, and Kargal'skaya), the transport was estimated using the mean concentration of chemical elements computed for the whole dataset obtained as a result of studying groundwater in the Don left-bank settlements.

The data was analyzed of in situ groundwater investigations in the south of the Rostov oblast which were carried out to determine the parameters of water-bearing rocks and specific features of hydrogeological conditions of groundwater. The analysis demonstrated that the geological structure of the area under study was basically defined by alluvial and diluvial deposits of the Quaternary age represented by sands, clays, and loams whose filtration coefficients vary from 0.02 to 3.0. The mean aquifer thickness revealed for the territory under consideration is 15 m [1]. The gradients of the hypsometric groundwater table  $J$  were computed using the schematic map of local runoff basins (is prepared for publication). For different settlements  $J = 0.0002\text{--}0.007$ . The width of filtration flows  $l$  for each settlement was determined using ARCGIS and Google Earth software. The total length of the left-bank line for all built-up areas is 100 km that makes up 16% of the total length of the Lower Don bank line (the right and left banks).

**Table 2.** Concentration of principal ions and methane in the groundwater of settlements located on the left bank of the Don River (summary for 2008–2013)

Settlement	N	Ionic composition (MPC), mg/dm <sup>3</sup>							CH <sub>4</sub> , l/l
		Ca <sup>2+</sup> (180)	Mg <sup>2+</sup> (50)	Na <sup>+</sup> (200)	K <sup>+</sup> (50)	HCO <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup> (500)	Cl <sup>-</sup> (350)	
Kagal'nik	3	<u>288–346</u> 326 (100)	<u>91–250</u> 146 (100)	<u>345–1656</u> 827 (100)	1	<u>466–636</u> 546	<u>1108–2110</u> 1560 (100)	<u>231–1134</u> 535 (33)	–
Koisug	3	<u>278–360</u> 314 (100)	<u>129–227</u> 167 (100)	<u>332–509</u> 421 (100)	<1–67 23 (33)	<u>376–609</u> 484	<u>997–1680</u> 1371 (100)	<u>175–297</u> 227	<0.1–11.6 3.9
Bataisk	23	<u>52–499</u> 202 (61)	<u>12–195</u> 86 (78)	<u>46–811</u> 262 (61)	<1–204 45 (48)	<u>164–1194</u> 464	<u>73–2090</u> 781 (74)	<u>36–566</u> 189 (9)	<0.1–32.2 3.1
Manychskaya	18	<u>29–563</u> 190 (39)	<u>25–383</u> 96 (44)	<u>147–1313</u> 371 (83)	<1–26 5	<u>244–944</u> 508	<u>245–2100</u> 678 (61)	<u>8–1505</u> 268 (33)	<0.1–20.6 2.0
Bagaevskaya	29	<u>70–806</u> 226 (69)	<u>43–250</u> 103 (93)	<u>64–532</u> 273 (79)	<1–53 9 (40)	<u>248–1026</u> 579	<u>160–1440</u> 626 (48)	<u>127–1134</u> 299 (21)	<0.1–18.6 1.5
Semikarakorsk	24	<u>32–432</u> 226 (70)	<u>46–325</u> 127 (96)	<u>108–613</u> 330 (88)	<1–32 4	<u>393–1793</u> 693	<u>213–1136</u> 647 (79)	<u>97–814</u> 277 (42)	<0.1–106.0 0.3
Romanovskaya	3	<u>189–201</u> 194 (100)	<u>29–30</u> 30	<u>66–91</u> 83	<3–3 3	<u>383–432</u> 403	<u>272–318</u> 289	<u>85–93</u> 90	–
Volgodonsk suburb	12	<u>219–507</u> 415 (100)	<u>77–381</u> 197 (100)	<u>202–1002</u> 829 (100)	1–8 2	<u>377–659</u> 563	<u>784–3720</u> 2460 (100)	<u>169–793</u> 427 (67)	–
Mean	115	<u>29–806</u> 249 (68)	<u>12–383</u> 109 (82)	<u>46–1665</u> 359 (79)	<1–204 12 (11)	<u>164–1793</u> 522	<u>73–3720</u> 990 (70)	<u>8–1505</u> 234 (29)	<0.1–106.0 2.2

Note: *N* is number of samples. For principal ions the values of MPC for the drinking water are given in brackets (for the ions of calcium and potassium and for ammonium nitrogen the values for the fishery water are presented); here and in the other tables, the variation range is given in the numerator, the mean concentration is given in the denominator, and the number of samples (%) where MPC was exceeded, is given in brackets; the dash means that the observations were not conducted.

## RESULTS AND DISCUSSION

The computations have demonstrated that the average total volume of groundwater coming from the built-up areas on the left bank of the Don River to water in the lower reaches is 5038 m<sup>3</sup>/day (0.002 km<sup>3</sup>/year) or 0.01% of average long-term water discharge in the estuarine outlet of the river (16.82 km<sup>3</sup>/year [7]) (Table 1). This value does not exceed 1.5% of the value of the total groundwater flow to the Lower Don channel computed before [3, 10]. The small runoff is probably caused by the fact that the length of the investigated left-bank line makes up only 16% of the total length of the bank line in the lower reaches of the river. Also, the basic part of the groundwater flow is assigned to the right bank characterized by much more significant surface slopes and drainage conditions.

As a whole, among all left-bank built-up areas, the maximum groundwater flow ( $Q = 1382$  m<sup>3</sup>/day) is typical of the industrial zone of Rostov-on-Don. The mean real velocity of groundwater  $u_0$  in the built-up areas towards the discharge area varies from 0.0004 to 0.0138 m/day, and the maximum real velocity is typical of the towns of Azov and Kagal'nik that are located hypsometrically relatively high.

The data on the chemical composition of groundwater in the built-up areas revealed [8] that MPC of sulfate ions, sodium ions, magnesium ions, nitrate nitrogen, chloride ions, and the total content of oil components for the sources of drinking water supply was exceeded in the majority of the samples taken (Tables 2 and 3). The periodic exceeding over MPC was registered for ammonium nitrogen, silicon, iron, potassium ions, and cadmium ions. The concentration of the ions of zinc, copper, synthetic surfactants, and phosphorus of phosphates was below MPC for the sources of drinking water supply. The high concentration of nitrate nitrogen, ammonium nitrogen, and other specific pollutants in the groundwater of settlements indicates the great influence of household and industrial wastes on the degree of contamination of poorly protected groundwater [8]. It was found [1] that the sewage system is absent and the hydraulic engineering systems are damaged or do not operate in the majority of settlements in the south of the Rostov oblast.

**Table 3.** Concentration of pollutants in the groundwater of settlements located on the left bank of the Don River (summary for 2008–2013)

Settlement	N	Pollutants (MPC)					
		Fe <sub>tot</sub> (0.3)	Oil products (0.1)	NO <sub>3</sub> (10)	NO <sub>2</sub> (1)	NH <sub>4</sub> (0.4)	PO <sub>4</sub> <sup>3-</sup> (3.5)
Kagal'nik	1	<0.2	0.1 (100)	299.1 (100)	0.01	0.03	0.04
Koisug	3	<0.02	<u>0.06–3.30</u> 0.82 (80)	<u>38.08–77.0</u> 53.1 (100)	<u>0.01–0.15</u> 0.07	<u>&lt;0.02–0.04</u> 0.03	<u>0.01–0.28</u> 0.11
Bataisk	23	<u>n/d–0.08</u> 0.03	<u>0.05–8.79</u> 0.51 (55)	<u>0.02–43.1</u> 9.9 (39)	<u>n/d–0.15</u> 0.02	<u>&lt;0.02–0.98</u> 0.10 (7)	<u>&lt;0.01–1.18</u> 0.15
Manychskaya	13	<u>&lt;0.02–0.08</u> 0.02	<u>0.02–1.10</u> 0.37 (82)	<u>0.10–171.0</u> 17.6 (18)	<u>n/d–0.28</u> 0.07	<u>0.01–0.27</u> 0.06	<u>0.02–0.68</u> 0.14
Bagaevskaya	25	<u>n/d–0.18</u> 0.03	<u>0.02–2.63</u> 0.39 (72)	<u>0.21–95.0</u> 24.7 (66)	<u>0–0.10</u> <0.02	<u>&lt;0.02–0.37</u> 0.04	<u>0.01–0.36</u> 0.09
Semikarakorsk	23	<u>n/d–6.38</u> 0.61 (17)	<u>n/d–26.5</u> 1.3 (70)	<u>0.01–141.0</u> 39.0 (70)	<u>n/d–0.6</u> 0.04	<u>0.01–1.34</u> 0.17 (10)	<u>0.05–0.85</u> 0.17
Romanovskaya	3	<u>n/d–0.02</u> 0.01	<u>&lt;0.02–0.25</u> 0.23 (67)	<u>4.04–5.95</u> 5.10	<u>n/d–0.01</u> 0.01	<u>&lt;0.02–0.03</u> 0.03	<u>0.12–0.16</u> 0.14
Volgodonsk suburb	9	<u>&lt;0.02–0.06</u> 0.03	<u>&lt;0.02–5.16</u> 1.49 (78)	<u>0.07–6.5</u> 1.38	<u>&lt;0.01–0.14</u> 0.04	<u>&lt;0.02–0.37</u> 0.07	<u>&lt;0.01–0.23</u> 0.05
Mean	100	<u>n/d–6.38</u> 0.08 (5)	<u>n/d–26.5</u> 0.50 (89)	<u>0.01–171.0</u> 65.90 (63)	<u>n/d–0.6</u> 0.04	<u>&lt;0.02–1.34</u> 0.07 (5)	<u>&lt;0.01–1.18</u> 0.09

**Table 3. (Contd.)**

Settlement	N	Pollutants (MPC)					
		Si (10)	Synthetic surfactants (0.1)	Pb <sup>2+</sup> (30)	Cd <sup>2+</sup> (1)	Cu <sup>2+</sup> (1000)	Zn <sup>2+</sup> (5000)
Kagal'nik	1	8.80	–	–	<0.10	1.2	69.7
Koisug	3	<u>6.5–8.8</u> 7.7	<u>&lt;0.01–0.02</u> 0.02	<u>0.75–7.8</u> 4.4	<u>0.3–0.3</u> 0.29	<u>5.0–11.2</u> 7.7	<u>39.0–90.0</u> 62.3
Bataisk	23	<u>0.7–15.0</u> 5.3 (6)	<u>0.01–0.03</u> 0.02	<u>n/d–11.6</u> 2.0	<u>n/d–0.5</u> 0.16	<u>n/d–30.0</u> 6.6	<u>n/d–123.0</u> 37.7
Manychskaya	13	<u>3.2–7.4</u> 5.4	<u>&lt;0.01–0.10</u> 0.03	<u>0.4–2.4</u> 0.8	<u>n/d–0.2</u> 0.11	<u>n/d–11.7</u> 4.9	<u>n/d–44.8</u> 20.5
Bagaevskaya	25	<u>3.9–13.4</u> 9.9 (66)	<u>&lt;0.01–0.01</u> 0.01	<u>n/d–4.6</u> 1.1	<u>n/d–1.6</u> 0.21 (3)	<u>n/d–18.0</u> 4.3	<u>n/d–104.0</u> 23.8
Semikarakorsk	23	<u>4.06–24.6</u> 9.96 (40)	<u>&lt;0.01–0.02</u> 0.01	<u>0.46–11.2</u> 3.0	<u>n/d–1.5</u> 0.30 (3)	<u>n/d–16.0</u> 6.0	<u>n/d–103.0</u> 33.5
Romanovskaya	3	<u>11.1–12.7</u> 12.0 (100)	–	n/d	0.1	<1.0	<u>n/d–19.7</u> 11.7
Volgodonsk suburb	9	<u>5.61–6.42</u> 5.92	–	<u>&lt;2.0–3.0</u> 2.5	<u>&lt;0.10–1.22</u> 0.30 (11)	<u>1.7–12.1</u> 4.7	<u>4.4–22.0</u> 14.1
Mean	100	<u>0.7–24.6</u> 8.43 (38)	<u>&lt;0.01–0.1</u> 0.05	<u>n/d–11.6</u> 2.20	<u>n/d–1.6</u> 0.15 (3)	<u>n/d–30.0</u> 4	<u>n/d–123.0</u> 29

Note: N is number of samples. For the pollutants the values of MPC for the drinking water are given in brackets; n/d is “not detected.” Units for Pb<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> are g/dm<sup>3</sup>, for the other elements, mg/dm<sup>3</sup>. The rest of explanations are the same as in Table 2.

**Table 4.** The average annual flow of chemical components in the Don River outlet and average annual flow of chemical components with the groundwater from the left-bank built-up areas of the Lower Don in 2008–2013

Component	Average annual flow of chemical components in the Don River outlet, t/year [9]	Average annual flow of chemical components with the groundwater of settlements to the Don River channel, t/year
Ca <sup>2+</sup>	1316165	<u>48.244–908073</u> 478.159 (0.04)
Mg <sup>2+</sup>	629909	<u>19.630–379.738</u> 199.648 (0.03)
Na <sup>+</sup>	–	<u>68.685–1306.038</u> 687.362
K <sup>+</sup>	–	<u>1.731–36.923</u> 19.327
HCO <sub>3</sub>	3641530	<u>93.320–1801046</u> 947.183 (0.03)
SO <sub>4</sub> <sup>2-</sup>	3957325	<u>196.111–3696.114</u> 1946.113 (0.05)
Cl <sup>-</sup>	2649150	<u>43.336–817.961</u> 430.648 (0.02)
NO <sub>3</sub>	11450	<u>17.773–280.593</u> 149.183 (1.30)
NH <sub>4</sub>	1082	<u>0.011–0.236</u> 0.124 (0.01)
NO <sub>2</sub>	291	<u>0.011–0.222</u> 0.116 (0.04)
Oil products	764	<u>0.098–2.020</u> 1.059 (0.14)
PO <sub>4</sub> <sup>3-</sup>	2020	<u>0.014–0.287</u> 0.150 (0.03)
Si	52275	<u>1.481–28.321</u> 14.901 (0.03)
Synthetic surfactants	–	<u>0.008–0.168</u> 0.088
Cd <sup>2+</sup>	–	<u>0.029–0.574</u> 0.302
Zn <sup>2+</sup>	93	<u>0.006–0.107</u> 0.057 (0.06)
Cu <sup>2+</sup>	24	<u>0.001–0.012</u> 0.006 (0.02)
Pb <sup>2+</sup>	–	<u>0.329–6.942</u> 3.635
Fe <sub>tot</sub>	–	<u>0.011–0.224</u> 0.117
CH <sub>4</sub>	–	<u>0.280–5.530</u> 2.900
Mean	12262080	4874.284 (0.04)

Note: The percentage of average annual flow of chemical components in the Don River outlet is given in brackets; the unit for Cd<sup>2+</sup>, Pb<sup>2+</sup>, and CH<sub>4</sub> is kg/year.

Proceeding from the mean concentration of chemical components and average annual discharge of groundwater flow, the concentration of substances transported with the groundwater of left-bank settlements to the Lower Don was determined. The computations have demonstrated that 4874 t/year (determined by the authors) of chemical components or 0.04% of their total average annual runoff in the closing outlet of the Don River come to the Don River with the groundwater from the left-bank built-up areas (Table 4). As clear from the computations, the transport of chemicals with the groundwater of left-bank settlements within the territory under study (from Volgodonsk to the Don estuary) makes up a small part of

the total river runoff of these components to the Taganrog Bay that is caused by the insignificant average annual groundwater flow from the areas under consideration.

The maximum contribution to the groundwater flow of chemical components from the territory of the Don River settlements is made by sulfate ions and hydrocarbon ions. This is related to the fact that the chemical composition of groundwater in the Don River basin is mainly formed of the water-soluble fraction of water-bearing sedimentary rocks the most part of which contain the significant amount of calcium carbonate, gypsum, and highly soluble salts (chlorides and sulfates) [12]. In terms of the degree of the impact on the total flow to the Lower Don, the principal ions are in the following order:  $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{Na}^+ > \text{Ca}^{2+} > \text{Cl}^- > \text{Mg}^{2+} > \text{K}^+$ .

The flow of the studied chemical components coming to the Don River with the groundwater runoff from the left-bank built-up areas is insignificant and, as a rule, makes up the hundredths of a percent of average annual flow of chemical components in the Don River outlet. The slightly greater contribution is typical of the groundwater flow of such anthropogenic pollutants as nitrate nitrogen (1.30% of its average annual flow in the outlet) and oil products (0.14%) that is caused by the impact of agricultural enterprises and oil storages (Semikarakorsk, Bataisk, and the industrial zone of Rostov-on-Don) located on the left bank of the Don River.

### CONCLUSIONS

The total average annual groundwater flow to the Lower Don is very small and equals 0.002 km<sup>3</sup>/year or 0.01% of average annual water discharge in the estuarine outlet. Despite the rather high degree of contamination of groundwater and the high content of principal ions in it, this causes the insignificant impact of groundwater runoff on the water quality in the lower reaches of the river. The total average mass of substances annually coming from the left-bank urbanized areas as a part of the groundwater flow is about  $4.9 \cdot 10^3$  t or 0.04% of total mass of substances transported by the Don River to the Taganrog Bay. As a rule, the groundwater flow of the investigated chemical components to the Don River makes up the hundredths of a percent of average annual flow of these chemicals in the Don River outlet except the groundwater flow of nitrate nitrogen whose contribution reaches 1.30%.

Thus, the groundwater flowing from the studied left-bank built-up areas in the limits of the Rostov oblast does not play a significant role in the formation of the chemical composition and quality of water in the lower reaches of the river.

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