ISSN 1068-3739, Russian Meteorology and Hydrology, 2022, Vol. 47, No. 3, pp. 232–240. Allerton Press, Inc., 2022.
Russian Text The Author(s), 2022, published in Meteorologiya i Gidrologiya, 2022, No. 3, pp. 106–117.

Spatiotemporal Dynamics of Copper and Zinc Concentrations in the Lower Don Water

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Received March 22, 2021
Revised July 29, 2021
Accepted September 23, 2021

Abstract—Spatiotemporal dynamics of concentrations of dissolved forms of copper and zinc in the water of the lower Don River was studied and compared with changes in mineralization, temperature, and concentrations of major ions, suspended matter, O_2, NO_2, NO_3, NH_4, PO_4^3, pH, BOD_5, and COD. For all periods, there is a steady excess of the maximum permissible concentration standards for dissolved copper, while the concentrations of zinc are mostly within the normal range. Maximum concentrations of copper and zinc are recorded on the river reach adjacent to the big industrial city of Rostov-on-Don. Minimum concentrations of copper and zinc are registered in the spring-summer period, maximum ones were recorded after the spring-summer and summer-autumn phytoplankton outbursts. The formation of the levels of both metals in the Don River water is significantly influenced by anthropogenic factors and processes, while the pattern of their intraannual dynamics is mainly due to natural factors.

DOI: 10.3103/S1068373922030098

Keywords: Copper, zinc, dissolved form, river water, intraannual dynamics

INTRODUCTION

The Don River is one of the largest rivers in the European part of Russia, which belongs (in terms of water regime) to the East European type with strongly pronounced spring floods, relatively stable winter and summer low water, and insignificant water level rise in autumn [18]. In addition to seasonal changes in water content, the water level regime in the lower Don River (Lower Don) is highly affected by wind-induced water level fluctuations and water releases from the Tsimlyansk Reservoir [3].

Priority pollutants in the Don River basin also include such heavy metals as copper (Cu) and zinc (Zn) [9, 11, 14, 15, 20, 25], whose effect on the vital activity of organisms, including humans, is ambiguous. On the one hand, they are needed for a normal course of physiological processes: copper is involved to the processes of photosynthesis, synthesis of proteins, fats, and vitamins, while zinc is associated with the activity of some ferments and hormones, with the synthesis of RNA and DNA ([9, 10, 23] etc.). On the other hand, in case of their high concentrations, they are toxic for most living organisms [7, 10] and are considered as the most dangerous polluting components of the aquatic environment, since they are almost not subjected to detoxication due to some physical and chemical properties [5].

Copper and zinc are transported to the Don River from both natural and industrial sources. The natural sources are the processes of chemical and microbiological leaching of minerals of rocks and soils composing the catchment surface, precipitation, as well as the deposition of dust and aerosol involved to the air transport from the atmosphere ([1, 10, 11] etc.). Anthropogenic pollution of the Lower Don water with copper and zinc is caused by the transport of their compounds with industrial, domestic, and municipal wastewater, diffuse washout of mineral fertilizers and chemical plant protection products from agricultural lands located in the catchments of the Don basin rivers [11].

Copper and zinc compounds may exist in the aquatic environment in three main forms: suspended, colloidal, and dissolved ones. The ratio between them is largely determined by the value of pH and by the

Fig. 1. The schematic map of observation station location in the Lower Don: (*1*) the Don River upstream of the Aksai stream confluence, the middle; (*2*) the Don River, water intake area of Rostov-on-Don, the middle; (*3*) the Don River, 0.5 km downstream of the Temernik River influx, the middle; (*4–6*) the Don River, 0.5 km downstream of the Vodokanal spillway area, (*4*) the middle, (*5*) left bank, and (*6*) right bank; (*7*) the Don River, 0.5 km downstream of Koluzaevo village, the middle; (*8)* the Bol'shaya Kalancha arm, Dugino settlement, the middle; (*9*) the Don River, upstream of the city of Azov, water intake area, the middle; (*10*) the Don River, downstream of Azov, spillway, the middle.

chemical composition of water (for example, [7, 10, 15]). The dissolved forms of copper and zinc are the most dangerous for aquatic organisms. They are most capable to penetrate through the cell membrane and to be accumulated in tissues and internal organs of living organisms, causing toxic effects [7, 23]. The maximum permissible concentration (MPC) of copper and zinc in fishery water bodies [13] is 1 and 10 μg/dm^3, respectively.

The studies of the spatiotemporal distribution of copper and zinc concentrations in the water of the Lower Don, which is of great economic importance for the largest Rostov-on-Don agglomeration in southern Russia, are of crucial importance. However, there are few papers dealing with this problem, and they are episodic, as a rule [6, 8, 9, 12, 14, 16, 20].

Originality and scientific novelty of the present study is that along with studying spatiotemporal dynamics of concentrations of dissolved copper and zinc in the Lower Don water, the temporally and spatially conjugated changes in mineralization, temperature, and concentrations of major ions, suspended matter, O_2, NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, pH, BOD_5, and COD are investigated for comparison.

DATA AND METHODS

Periodic observations (July, August, September, and October in 2002, May and July in 2003) of concentrations of copper and zinc dissolved in the surface water layer were carried out during six complex expeditions in the Lower Don at ten stations that are relatively evenly distributed along the longitudinal profile of the river on the "upstream of Aksai–downstream of Azov" reach (Fig. 1). Synchronously with copper and zinc concentrations in the water, the following were determined: temperature, mineralization, and concentrations of major ions (Ca^{2+}, Mg^{2+}, $Na^+ + K^+$, HCO_3^-, SO_4^{2-}, Cl^-), mineral compounds of nitrogen and phosphorus (NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}), oxygen, suspended matter, the values of pH, BOD_5, and COD. Thus, over the whole observation period, the concentrations of the analyzed heavy metals and other hydrochemical parameters were determined in 60 samples taken from the Lower Don surface water layer.

The water samples were taken with GR-18 Molchanov bathometer from a small vessel along the fairway (except for stations 5 and 6 located 0.5 km downstream of the Vodokanal spillway area (Rostov-on-Don), where the samples were taken near the left and right banks, respectively). The sampling, transportation, storage of samples, and subsequent determination of the listed parameters in them were carried out using standard methods generally accepted in the Roshydromet system [17, 19]. The values of pH were measured with Ekotest 2000 portable ionomer immediately after the samples had been lifted on board the vessel.

The filtering of water samples through preliminarily purified and weighted MFAS-VA Vladipor membrane filters with a pore size of 0.45 m was performed using a portable filtering unit immediately after the sampling. After that in accordance to the technique [17], filtrate was conserved by nitrogen acid to pH 2 to exclude the sorption of dissolved copper and zinc on the walls of containers in which the water sample is placed. The preparation of the samples for measurements and the quantitative determination of metals in them were carried out at Hydrochemical Institute (Roshydromet) by the atomic absorption analysis with a direct electrothermal atomization of the samples with a KVANT-Z.ETA instrument according to the technique [17]. The error in determining the concentration of metals in water samples does not exceed 10–15%.

RESULTS AND DISCUSSION

The summarization of the dataset that includes all six periods of field studies (from July 2002 to July 2003) shows that the Don River water temperature varied from 15.8–16.0 C in October 2002 to 24.3– 25.8 C in July 2002 and July 2003. During the other periods, temperature had intermediate values: 17.3– 23.5 C (Fig. 2a). No considerable changes were recorded in water temperature along the analyzed profile of the Don River.

The mineralization of the Don water varied within 622.8–987.0 mg/dm^3 (an average is 795.2 mg/dm^3). The highest values (825.6–987.0 mg/dm^3, an average is 920.4 mg/dm^3) were typical of October 2002, the lowest ones (622.8–670.3 mg/dm^3, an average is 650.7 mg/dm^3) were typical of May 2003. There was a certain increase in water mineralization toward the Don mouth (Fig. 2b). The modern class, type, and group of the Lower Don water can be described by the formula by O.A. Alekin $S_{II}^{Na, Ca}$ (sulfate class, type 2, sodium and calcium group).

The values of pH for the Don water varied in the weakly alkaline range of 7.9–8.6, an average was 8.2. The maximum pH (8.3–8.6) was observed in August 2002 during the intensive blooming of blue-green algae, the minima were recorded in July 2003 (7.9–8.3). During the other periods, pH did not go beyond 8.1–8.4. For all observation periods, there was an increasing trend in pH towards the Don delta (Fig. 2c).

The concentration of suspended matter in the Don water during the period of seasonal observations varied within 5.3–66.5 mg/dm^3 (an average is 27.5 mg/dm^3). The highest concentration of suspended matter (45.0–66.5 mg/dm^3, an average is 54.4 mg/dm^3) was registered at the beginning of September 2002, when the intense blooming of blue-green algae was visually observed. The minimum concentration (5.3–30 mg/dm^3, an average is 11.3 mg/dm^3) was recorded in October 2002, which is probably associated with a dramatic decrease in the vegetation activity of phytoplankton due to a temperature drop. For the other periods, the concentration of suspended substances on average ranged from 19.7 to 30.3 mg/dm^3. Most observation periods were characterized by an increase in the amount of suspended matter in the Don delta (Fig. 2e).

The concentration of dissolved oxygen in the water varied within 6.0–11.9 mg/dm^3 (an average is 8.61 mg/dm^3; Fig. 2g). In general, except for single samples, its concentration was not below 80–85% of saturation, which indicated a good aeration of the river water during the study periods.

The concentration of copper in the water of the analyzed reach varied within 1–14 mg/dm^3 (an average is 3.5 g/dm^3; Fig. 2d) and exceeded the MPC almost everywhere, which is consistent with papers [6, 8, 9, 12, 14, 20] and the opinion expressed in [12] about the chronic pollution of the Don River with this metal.

The concentration of zinc in the Don water ranged within 1–10 g/dm^3 (an average is 5.6 g/dm^3; Fig. 2f), which is below the MPC. In general, the revealed values correspond to the data on the concentration of dissolved zinc in the river water, which is available in scientific literature (for example, [6, 8, 9, 20]).

High concentrations of both copper (an average is 3.5–5.5 g/dm^3) and zinc (an average is 5.5–6.8 g/dm^3) in the Don River were registered within the reach adjacent to Rostov-on-Don (stations 3–6). One of the main sources of river water pollution in this reach in addition to industrial, domestic, and municipal wastewater of the Rostov-on-Don agglomeration is the small plain Temernik River. A half kilometer downstream of its influx (station 3), the highest concentrations of copper (up to 9–14 g/dm^3, an average is 5.5 g/dm^3) and zinc (up to 10 g/dm^3, an average is 6.8 g/dm^3) were found for the whole analyzed reach of the Don. Within the catchment area of the Temernik River flowing on the territory of Rostov-on-Don, about 600000 people live and more than 50 enterprises are located [2], including the largest zoo in southern Russia. Taking insufficiently treated and untreated wastewater from industrial enterprises and municipal sector, as well as pollutants together with storm runoff and washout from the catchment area, the Temernik River transports them to the Don River.

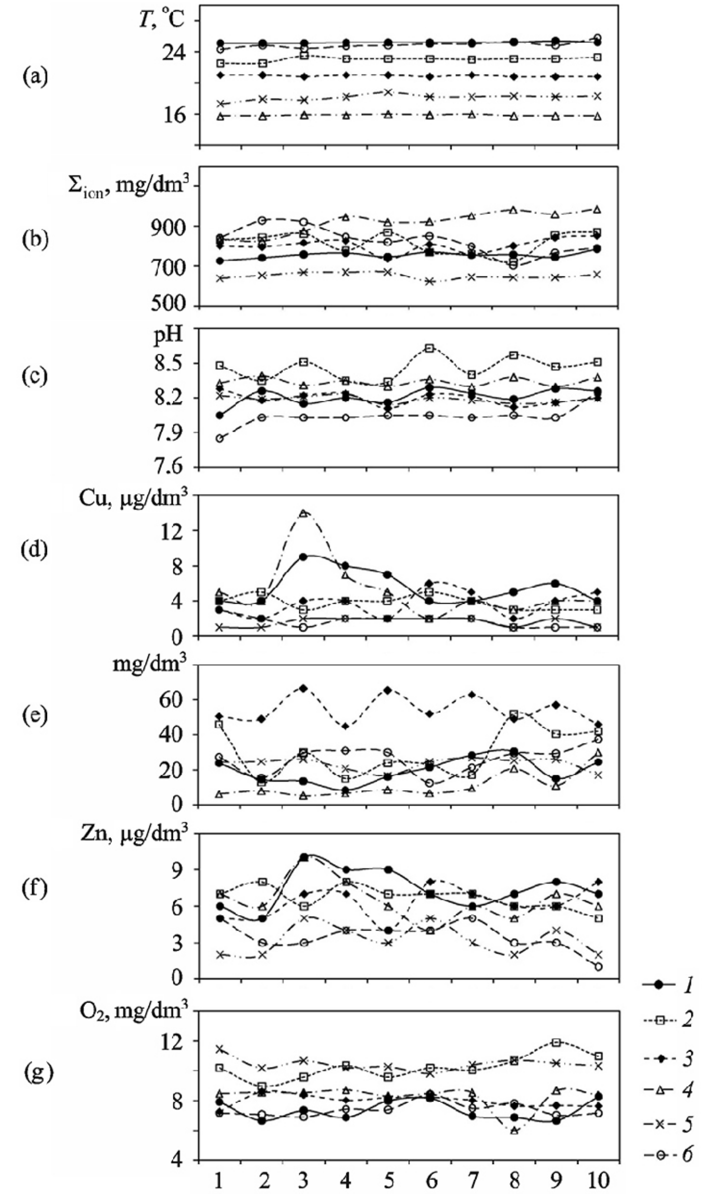

Fig. 2. The intraannual variations in (a) temperature, (b) mineralization, (c) pH, and concentrations of (d) dissolved Cu, (e) suspended matter, (f) dissolved form of Zn, and (g) O_2. The numbers of observations stations are given along the *x*-axis (the location of stations 1–10 here and in Fig. 4 corresponds to the one presented in Fig. 1). The sampling dates in 2002: (*1*) July 24; (*2*) August 20; (*3*) September 4; (*4*) October 8; in 2003: (*5*) May 20; (*6*) July 14.

A possible significant source of copper and zinc inflow to the river water is precipitation and atmospheric dust fallout. For example, according to the summarized data [16], concentrations of copper and zinc in solid fallouts over Rostov-on-Don exceeded those at background sites (Veshanskaya village) on average by 12.5 and 35.7 times.

At stations 7–10 located downstream of Rostov-on-Don, average concentrations of copper and zinc were 2.5–3.5 g/dm^3 and 4.8–5.7 g/dm^3, respectively. Minimum concentrations of both metals were observed in the Bol'shaya Kalancha arm in the Don delta (station 8). This arm is subjected to the smallest anthropogenic load from the municipal sector, agricultural landscapes, and navigation as compared to other observation stations.

It should be noted that for the reach situated upstream of the Aksai stream confluence (see Fig. 1, station 1), in particular, upstream of the Rostov-on-Don agglomeration, concentrations of copper in the Don

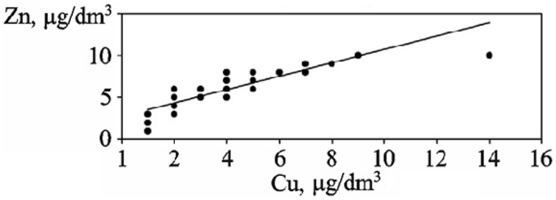

Fig. 3. The dependence between the concentrations of Cu and Zn in the Don River water along the "upstream of Aksai–downstream of Azov" longitudinal profile. The constraint equation: $y = 0.7965x + 2.746$, the coefficient of determination $R^2 = 0.7486$.

water during all observation periods, except for May 2003, has already exceeded the MPC for copper by 2–5 times (on average by 3.3 times). Possible significant sources of the Don water contamination with copper on the reach from the Tsimlyansk Reservoir to the Aksai stream confluence, in addition to municipal, domestic, and industrial wastewater from the settlements relatively uniformly distributed along the river (the largest ones are Bagaevskaya village, the cities of Semikarakorsk and Konstantinovsk with total population of ~70000), are the tributaries Severskii Donets River (water flow is ~6.31 km^3/year) subjected to high anthropogenic pollution and, to a lower extent, the Sal (~0.32 km^3/year) and Manych (~0.15 km^3/year) rivers, as well as the washout of mineral fertilizers and pesticides, which contain copper (for example, kuprosil, kuproksat, etc.) coming from agricultural lands [12].

Apparently, the steady increase in the concentration of dissolved copper and zinc in the water to the values close or above the MPC is associated not only with anthropogenic pollution but also with the increased transport of these elements due to the large-scale ploughing of soil in the Lower Don basin catchments in the second half of the 20th century. Currently, about 85% of the Lower Don territory is occupied by agricultural lands [1], and ~90% of the analyzed agrolandscapes are characterized by the concentrations of copper and zinc in the upper soil layer, which noticeably exceed the clarks of these elements in soil: by 4.5 and 1.6 times, respectively, an average is 89 mg/kg (or 1.6 MPC in soil) for copper and 80 mg/kg (0.8 MPC) for zinc. Concentrations of copper and zinc in soil of unplowed landscapes are slightly smaller than in agrolandscapes: 85 and 68 mg/kg, respectively, but are still higher than the clarks of these elements in soil [1]. It is noteworthy that dust storms typical of the Lower Don can essentially activate the inflow of metals to the river water. For example, during three days in September 2020, strong northeastern wind was observed in the Lower Don, which caused an intense dust storm and river water downsurge that exposed bottom sediments, on the surface of which, according to the authors' observations, up to 1.0–1.5 cm of siltstone-lutaceous soil dust fell.

Within the analyzed Don reach, there is a high significant correlation between the concentration of dissolved copper and zinc ($r = 0.87$, $P < 0.01$) (Fig. 3), the trend toward which was also observed in the Sea of Azov [9], where a rather high and significant positive correlation between these components was found ($r = 0.69$, $P < 0.01$). The presence of this correlation requires further investigation. It is possible that this is caused both by the unity of sources of the inflow of these heavy metals to water and by similar dynamics of their concentrations under conditions of intraannual changes in the hydrological, hydrobiological, and hydrochemical regimes of water bodies.

At most stations, the intraannual variations in concentrations of copper and zinc in the water are synchronous (Figs. 4a and 4b), which indicates the dominance of the impact of natural factors on their dynamics. The changes in the concentration of the metals in the water are less synchronous at station 6 located near the right bank of the river within the reach adjacent to Rostov-on-Don. This is probably associated with a certain difference in hydrological and hydrochemical conditions along the river cross-section.

In general, maximum concentrations of dissolved copper and zinc were typical of July and October in 2002, the minima were typical of May and July in 2003. As the temporal dynamics at the sampling stations for the analyzed hydrochemical parameters is almost identical, for greater clarity, the lines corresponding to the change in the values of the parameters at each station during different study periods were combined into one line averaging the values over all observation stations for each parameter (Figs. 4c, 4d, 4e, and 4f). For calculating average values, data for eight stations were considered, at which the samples were taken along the fairway. Thus, stations 5 and 6 were removed from the calculation: these are the left and right banks of the river, where the changes in the values of the analyzed parameters are characterized by the lowest synchrony as compared to the other eight stations.

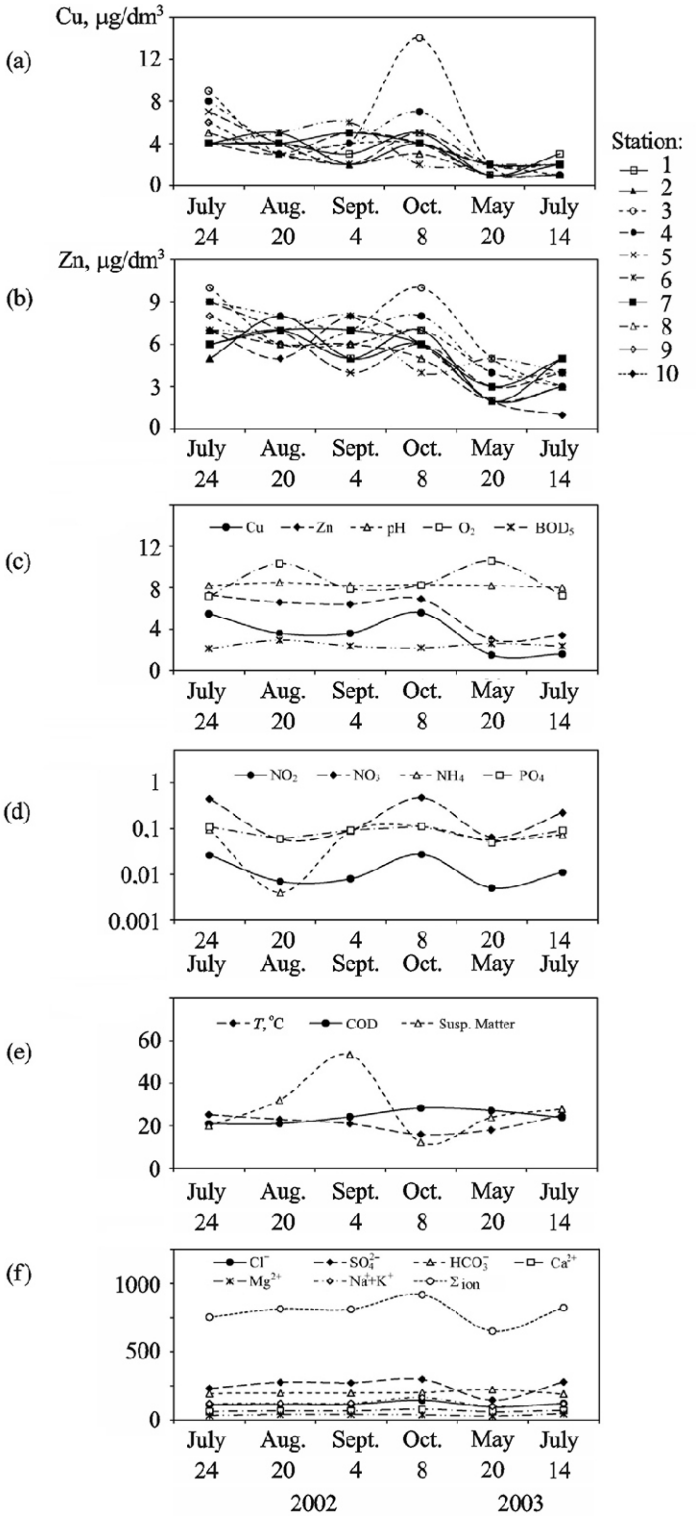

Fig. 4. The intraannual changes in the concentration of (a) copper and (b) zinc at observation stations 1–10 and (c–f) in the average values of the analyzed hydrochemical parameters in the Lower Don water.

The analysis of available data shows that maximum concentrations of copper and zinc in 2002 were caused by their inflow to the water resulting from the mineralization of organic matter after the spring-summer and summer-autumn phytoplankton outbursts, which were typical of the Sea of Azov basin as a whole [4]. This is confirmed by the synchronous dynamics of concentrations of the analyzed metals and mineral forms of nitrogen and phosphorus (NO_2, NO_3, NH_4, and PO_4^3), the main source of whose inflow to the river water, in addition to the surface flow from the catchment basin, is the decomposition of organic matter. The coefficients of correlation of Cu and Zn concentrations with NO_2, NO_3, NH_4, and PO_4^3 concentrations are 0.83 and 0.60, 0.74 and 0.47, 0.45 and 0.21, and 0.71 and 0.56, respectively ($P < 0.01$).

Due to the prewinter decrease in phytoplankton biomass, which is typical of the Don River [8], the consumption of the products of the autumn mineralization of organic substances that arrived to the water, in particular, of nitrogen and phosphorus, copper and zinc compounds actively accumulated by living matter is considerably reduced. This probably causes a synchronous growth of concentrations of dissolved heavy metals and biogenic components in the river water. A decrease in the number of particles suspended in the water which can adsorb soluble metal compounds, was observed during the periods of maximum copper and zinc concentrations. It does not favor the transition of copper and zinc from the solution to suspended matter and the decrease in their concentrations.

Minimum concentrations of dissolved copper and zinc in May 2003 are probably caused by the dilution with meltwater that came from the catchment surface, which is indicated by the significant decrease in the mineralization of river water (on average to 650.7 mg/dm^3). In addition, high (at the moment) oxygen concentrations in the water against a background of minimum concentrations of the analyzed metals may point out binding into suspended matter of copper and zinc dissolved in the water by oxides and hydroxides of iron, manganese [7], iron phosphates [21] and the subsequent sedimentation in the suspension into bottom sediments. In general, there is a rather low but significant correlation between the dissolved form of the analyzed metals and the oxygen concentration in the water (the coefficient of correlation between Cu and O_2 is –0.36, and the one between Zn and O_2 is –0.27; $P < 0.01$).

A possible important factor causing minimum concentrations of copper and zinc in May and July in 2003 is the spring-summer phytoplankton outburst associated with an increase in the river water temperature and the amount of biogenic substances that arrived with the meltwater. The increased phytoplankton population provides the transition of dissolved copper and zinc into living matter of the suspension and, hence, a decrease in their concentrations in water. The latter is also favored by the sorption of dissolved metals on the mineral and organic components of the suspension that came from the catchment surface with the meltwater and on the particles of autochthonous organic detritus.

In 2002, minimum concentrations of copper and zinc were recorded in August–early September. On the one hand, this may be associated with their assimilation by blue-green algae that actively vegetates during that period. On the other hand, the absorption of metals by living matter may be overlapped by the adsorption of dissolved cooper and zinc by iron and manganese hydroxides and organomineral suspension particles, which also causes the decrease in their concentrations.

The copper and zinc compounds accumulated by phytoplankton and macrophytes are retained in them during the whole growing season until their death and decay [22], from the beginning of which the metals accumulated by living matter begin to be released and pass into an aqueous solution. As shown above, this is observed for the analyzed Don reach at the end of the spring-summer and summer-autumn phytoplankton outbursts (at the end of July and at the beginning of October), when the synchronous growth of concentrations of nitrogen and phosphorus compounds and dissolved copper and zinc compounds is registered. Apparently, during the cold season, along with the transport of copper and zinc with the river flow to the Taganrog Bay, which is typical of all periods, some part of metals is sorbed on iron and manganese hydroxides and oxides, as well as on organomineral suspension particles and settles to the bottom. It is accumulated in the bottom sediments of the Lower Don, mainly on the reaches with relatively calm hydrodynamic conditions. If equilibrium conditions at the bottom sediments–water interface are disturbed and especially if there is a significant decrease in pH and a lack of dissolved oxygen, an increase in the migration mobility of metals and their transition to an aqueous environment are possible [7]. The migration of copper and zinc compounds from bottom sediments to the aqueous solution can also be intensified by stirring and the transition of silty particles of bottom sediments to a suspended state, which occurs at a significant increase in flow velocity, usually during high water, as well as in case of wind-induced mixing [24].

CONCLUSIONS

During all observation periods, the concentration of dissolved copper in the water of the analyzed reach of the Don River steadily exceeds the MPC, while the concentration of zinc, as a rule, does not exceed the MPC. At the same time, there is a high significant correlation between the concentrations of dissolved forms of these metals (which is evidently caused both by the single sources of their inflow to the river water) and by the similar dynamics of concentrations under conditions of intraannual changes in the hydrological, hydrobiological, and hydrochemical regimes of the river.

The highest concentrations of copper and zinc were recorded on the river reach adjoining Rostov-on-Don, rather high concentrations were registered in the Don delta in some periods. However, on the river reaches upstream of the Rostov agglomeration in all seasons, the copper concentration has already exceeded the MPC on average by 3.3 times. Apparently, the steady increase in the concentration of dissolved copper and zinc in the water up to the values that are close or exceed the MPC is associated not only with anthropogenic pollution but also with the intensified transport of these elements as a result of the large-scale ploughing of soil in the Lower Don river catchments in the second half of the 20st century.

The pattern of intraannual variability of dissolved forms of copper and zinc in the Lower Don is mainly determined by the natural (hydrological, hydrobiological, and hydrochemical) factors, which is indicated by the strongly pronounced synchrony in the intraannual variations in metal concentrations in the water at most observation stations. This synchrony highly correlates with changes in the concentration of other analyzed hydrochemical parameters (NO_2 , NO_3 , NH_4 , PO_4^3 , O_2, suspended matter).

Two maxima of the concentration of copper and zinc were registered, which were associated with their inflow to the water as a result of organic matter mineralization after the spring-summer and summer-autumn phytoplankton outbursts, respectively. Minimum concentrations of copper and zinc in the spring-summer period are caused, on the one hand, by the dilution with meltwater that came from the catchment surface. On the other hand, they are determined by the removal of dissolved metals from the water as a result of both the intensive assimilation by living matter during the spring-summer phytoplankton outburst and the binding into suspended matter by iron and manganese oxides and hydroxides under conditions of water saturation with oxygen (as well as the sorption of organomineral suspended substances that came from the catchment surface in the meltwater and their subsequent sedimentation into bottom sediments).

FUNDING

The research was supported by the Russian Foundation for Basic Research (grant 19-05-50097).

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