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WATER AND ALLUVIUM OF A SMALL RIVER WITHIN THE URBAN TERRITORY: CHEMICAL POLLUTION

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ABSTRACT

The article contains the results of the assessment of chemical pollution in water and bottom sediments of the Tvertsa River across Tver city 2.5-5 km from its influx into the Volga River. The Tvertsa has domestic, drinking, recreational and fishery importance; receives some amount of municipal sewage. Sanitary hygienic standards in water were exceeded slightly: up to 1.5 times in some places by the indicators of biological (BOD_5) and chemical (COD) oxygen consumption because of the oxidation of organic substances and 2.7-5 times all over the places by Fe content (from 0.42-0.95 mg / l in the river to 1.53 mg / l in the runoff). Fishery standards are exceeded 1.2-15 times: Fe, Mn, Cu, Co, Ni, petroleum products (PP), suspended substances (S.s), COD and BOD_5. The instability in chemical concentrations is largely due to seasonal fluctuations of the water content, including the effects of steady rains. The state of bottom sediments in this section of the river was recorded for the first time. The level of total accumulation (Zc) of metals (Fe, Co, Cu, Ni, Zn, Cd, Mn) and PP was in the "low" category (Zc = 0.8-6.5). The water of the Tvertsa will not have a negative impact on the ecological and sanitary hygienic state of the Volga River. In fisheries the situation may be get worse by the introduction of toxic metals Cu, Co, Ni into the receiving watercourse.

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INTRODUCTION

The relevance of assessments of chemical pollution in the water bodies increases in relation to small rivers, which drain urban lands and feed large waterways. Such rivers can increase the level of chemical pollution in the receiving watercourses. The condition of bottom sediments depositing pollutants is derived from the manmade load as well as the quality of water (Bogdanov N.A. *et al*, 2011; Sinitsyna O.O. *et al*, 2017). As an example the Tvertsa may be considered as drinking, recreational, fisheries and domestic water consumption river of great significance. Before join the river Volga it crosses Tver city and is affected by municipal runoff (domestic, industrial, storm, etc.). Seasonal control over the runoffs and river water is carried out by local environmentalists. Data on the accumulation of pollutants in the alluvium is missing. *The goal* is to assess the state of the river Tvertsa across Tver city by the content of chemicals in water and sediments before its influx into the river Volga.

OBJECT AND METHODS

The Tvertsa (188 km long) is a left tributary of the Volga. A hydraulic backwater is made 9 km to the confluence. On the territory of the city, the water of the river is used for domestic and technological needs of the municipal CHPP-3 (it produces electrical and heat energy; the main type of fuel is natural gas; water is taken from the river, 5 km from the mouth). 3.5 km from the mouth sewage is discharged into the river through the metal pipe of the underground collector (periodic discharge of the volley is practiced) and into the river siphon from the by-channel (BC) of the open type, Figure. The main feed for the river is the melting snow and groundwater (up to 85% of the annual flow). Soils of exceed acidity (sod-marsh-podzolic, etc) and those containing mobile forms of Fe, Al, Mn (Soil ..., 1991) are widespread in the catchment area. Under the conditions of the washing regime, metals are transferred outside the soil profile and fall into watercourses. There were examined the river Tvertsa between river stations, located 5 and 0.6 km from its mouth (samples (Sp.) 1-4, 7, 8, 11); process water of CHPP-3 (Sp. 5, 6, 9, 10), Figure. Water and sandy-silty-clayey alluvium samples were collected over the short time period in July between steady rains. Samples, immediately after their collecting, were passed to the chemical laboratory (it has a Certificate of Accreditation; it was determined> 20 ingredients in water and 7 in alluvium). The assessment of pollution was based on sanitary hygienic

(Maximum Permissible ..., GN 2.1.5.1315-03) and fishery (Water Quality .., 2017) standards (maximum permissible concentrations - MPC), as well as at the ratio of concentrations (Kc) of substances (Kc = Ci / Cb) resulting the sampling across surveying sites (Ci) and on the backgrounds (Cb). It was considered *global* (rivers of the world), *regional* (Western Siberia, Upper Volga) and *local background* (Sp. 4 is located at a distance from the influence of residential waste water and above the place of water discharge from CHPP-3 Figure). For a comprehensive assessment of water quality, we offered “General Water Pollution Index”- GWPI. The fixed complex of ingredients (n) consisted of substances exceeding MPC (n = 9). Pollution estimates were based on the principle of calculation and the gradation scale for a standard indicator “Water Pollution Index” (Yanin E.P, 2002; Hydrochemical Indicators ..., 2007). It was calculated the index of nitrification of ammonium nitrogen $K_{NH4} = NH_4^+ / NO_3^-$ (Krainov S.R., Shvets V.M., 1992; Bogdanov N.A. *et al*., 2004). The rise of its value indicates the proximity of the pollution source due to an increase in the intensity of a “new” supply of NH_4^+ ions (minor neutralization by oxidation and mineralization). The quality of alluvium was determined by the content of metals Fe, Co, Cu, Ni, Zn, Cd, Mn and petroleum products (PP) using the general pollution index Zc (Sayet Y.E, *et al*., 1990; Yanin E.P, 2002). The composition of substances was compared with their quantity on a *regional* and *local basis* (Aleksinskaya L.N., 1987; On the approval of a practical guide…, 2014).

RESULTS AND DISCUSSION

Water: The state of calcium-hydrocarbon poorly mineralized fresh river water was normal. The reaction pH = 7.9-8.1 from the “input” (Sp. 1) to the “output” from the survey site (Sp. 11) was shifted (within the framework of standard values) towards an alkaline medium (pH = 8-8.1 which is characteristic for industrial runoffs. The composition of most of 27 analyzed substances corresponded to (pH, O_2) or was lower than the MPC (dry residue — DR, anions, cations, phosphates, PP; metals, except for Fe).

Backgrounds: Regarding Fe, the situation is largely result from the natural factor. Fe content (0.42-1.53 mg / l) in the Tvertsa river slightly exceeded *global* (0.67 mg / l, average concentration in the hypergenesis zone — 0.5 mg / l) and *regional backgrounds* (the rivers of Western Siberia: 0.6-1.3 mg / l). However, the amount of Fe was significantly higher than in the rivers of the Upper Volga basin (Moskva, Vazuza, Volga, etc. - 0.20–0.32 mg / l) (A practical guide to the geochemical…, 1982; Aleksinskaya L.N, 1987; Saet Yu.E. et. al., 1990; Ivanov S.S, 1995; Yanin E.P, 2002; Hydrochemical indicators ..., 2007). Concentrations of a number of substances in relation to the local background increased significantly (> 8 times in the representative sites of the survey; the multiplicity in the values of Rc are shown in parentheses after the symbol of a substance):

“*Input*” (Sp. 1, residential sewage): S.s (2.3) Mn (1.9) COD (1.4) PP (1.3) Fe (1.2) and slightly - pH, BOD_5, NO_2, Ca, DR (1.1);

"*Backwater of CHPP-3 water intake*" (Sp. 2, accumulation of pollutants and natural phenol, dynamically stagnant conditions): Cu (8.2) Phenol (2.4) Co (2.1) S.s (1.9) PP (1.7) Mn, BOD_5, COD (1.5) and slightly - pH, NO_2, Ca, DR (1.1);

"*Discharge*" (Sp. 7, discharge of process water into the river): Cu (2.2) S.s (2.1) Fe (1.9) SO_4 (1.8) Mn (1.5) CoCl (1.3) COD (1.2) and slightly Ca, Mg, DR, NO_2 (1.1).

Sanitary hygienic MPCs are exceeded only for Fe (2.7-5 MPCs) as well as indicators of biological (BOD_5) and chemical (COD) O_2 consumption for the oxidation of organic natural and man-made substances that depress ecological situation (up to 1.5 MPCs). almost all of the water became unsuitable for irrigation through Fe content > 0.5 mg / l (0.5 mg / l - *FAO* standard: Food and Agriculture Organization of the United Nations). An increase in Fe concentrations up to 1.53 mg / l in the river is in agreement with anthropogenic factor (discharge point of CHPP-3, Sp. 7). The quality of the removing process water almost corresponded to that in the river (except for Ni - 1.2 MPCs, Sp. 5).

***Commercial Fishing Standards*:** 30% of the ingredients (9 of 27) did not correspond to *commercial fishing standards* (MPC_{fs}). When there was enough dissolved O_2 (7.5–8.1 mg / l), the maximum overshoot was as follows: MPC_{fc}: 15–10, mostly natural, except copper, (Fe, Mn, and Cu) and 3.1–2.3 toxic technogenic metals (Co, Ni); slightly suspensions and hydrocarbons 1.9-1.2 (BOD_5, S.s, COD and PP), Table 1. The K_{NH4} indicator everywhere exceeded the conventional norm (0.01), indicating an intense “*new*” intake of NH_4^+ ions from nearby sources of pollution (10-17 times in the river, 21-28 times in industrial storm runoff). The river water at the CHPP-3 water intake (Sp. 2) was of lower quality (GWPI = 2.9 “*polluted*” category; phenol — natural genesis) than in the storm intercepting receivers (GWPI underground tunnel wells = 2.1-2.8). By the quality it is comparable to that at the point of release into the river (GWPI = 3.1). In the backwater of the intake there was an accumulation of substances of household waste, from dirt roads and from the territories of the fruit and vegetable gardens located along upper course (GWPI = 2.5), Figure, Table 1. At the "*output*" (Sp. 11) river water is also of “*polluted*” quality (GWPI = 2.1). In general, on the estuary of the Tvertsa water pollution spectrum is formed by the cumulative impact of domestic and industrial effluents from the territory of Tver.

Process wastewater in comparison with the river “*alkaline background*” had high alkalinity (up to pH = 8.1), mineralization (up to 255 mg / l), as well as the enrichment with dissolved O_2, ions Cl^-, SO_4^{-2}, NO_2^-, Ca^{+2}, Mg^{+2}, NH_4^+, phosphates, metals (Cu and Ni). As the industrial storm runoff approaches the point of discharge into the river, they are somewhat cleared, but remain “*polluted*”. Wastewater differs in composition at each of the two outputs into the river, Table 1.

Upper output water is significantly saturated with metals, especially Cu (up to 10 MPC_{fs}. In the collector near the discharge into the river (Sp. 6) the amount of Fe, Mn, BOD_5 and DR increases. The phenomenon is related to periodic over drying, accumulation of metals and organic substances on the walls of the pipe which is half submerged into the river and washing out the rusty pipes of the collector way by the “*volley*” discharges. At the discharge point the “*moderately polluted*” river water becomes “*polluted*.” The amount of Fe in the river above the point of discharge (8 MPC_{fs}) is filled up with the substances from industrial-storm sewage (5.3 MPC_{fs} , Sp. 6) and becomes 15 MPC_{fs} in the river. Below the points of discharge, the concentrations of pollutants are reduced by dilution.

Table 1. Water quality in the Tvertsa river and industrial and storm runoffs from CHPP-3: ingredients of GWPI ranking by MPC_{fs} multiplicity

№ sample	GWPI	Series of ingredients*	Water quality**	Sample location
1	2.5	Fe(9.5) Mn(6.2) S.s(1.8) COD,BOD(1.2)		River "input"
2	2.9	Fe(8.2) Mn(4.8) Cu(4.1) Co(3.1) BOD(1.8) S.s(1.5) COD(1.4)	Polluted	River, intake chamber
3	3.2	Mn(12) Fe(8.2) BOD(1.9) Co(1.7) COD(1.4) PP(1.2)		River, below intake
4	1.9	Fe(8) Mn(3.3) Co(1.5) BOD(1.1)	Medium polluted	River, 150 m above a discharge point
5	2.8	Cu(10) Fe,Mn(4) Ni(2.3) S.s(1.3)		well, conducting underground collector
6	2.1	Fe(5.3) Mn(5) Ni,Cu(2) S.s(1.2) BOD(1.1)		Same as above, before discharge to the river
7	3.1	Fe(15) Mn(5) Co(2) S.s(1.6) BOD,Cu,COD(1.1)		River, sewage discharge
8	2.1	Fe(8) Mn(4) Co,S.s(1.5) BOD(1.2) COD(1.1)		River, 100 m above a discharge point
9	2.6	Fe(12) Mn(5) Co(1.6) COD,BOD,S.s(1.1)	Polluted	Discharge into a take-out channel
10	2.4	Fe(8) Mn(5) Co,Cu,COD(1.4) S.s(1.3) BOD(1.2)		Discharge from the channel into a river backwater
11	2.1	Fe(9) Mn(5) Co(1.4) BOD(1.2) COD(1.1)		River, "output" below backwater and 150 m above rail-and-road bridge

* the series contain a fixed amount (n = 9) of ingredients (S.s., BOD_5, COD, PP, Fe, Co, Cu, Ni, Mn). Substances with concentrations > MPC_{fs}, are given in the table, Figure;
** - according to (Hydrochemical indicators ..., 2007).

Table 2. Metals and petroleum products (PP): alluvium of the Tvertsa river and background concentrations, mg / kg

Matter	Tvertsa river, sample №							Backgrounds		
	1	2	3	4	7	8	11	*A*	*B*	*C*
Fe	8030	9205	8402	12813	16525	18685	6565	8216	-	-
Co	3.1	4.7	4.2	4.5	3.8	4.7	3.7	3.6	5	3
Cu	5.4	8.6	5.8	6.3	9.5	15.5	7.9	5.6	30	21
Ni	14	13	9.2	9.9	9.6	10	6.6	12	19	16
Zn	29	33	26	29	24	40	28	27	123	19
Cd	0.22	0.33	0.26	0.26	0.18	0.33	0.20	0.24	-	-
Mn	166	165	231	228	392	256	178	198	635	458
PP	23	32	22	23	44	47	96	22	-	-
Zc	0.8	1.9	1.2	2.1	4.1	6.5	3.9	1.0	-	-

A – up-to-day local background: the average content in samples No. 1 and 3 (the Tvertsa); B – waterways of the upper course of the river Volga, in the alluvium - 23000 mg / kg Fe; C – the Istra river (A practical guide..., 1982; Aleksinskaya L.N., 1987; Ivanov V.V., 1995). Dash - no data

Lower output (open take-out channel). At the headwater of the discharge into the canal the water is substantially enriched with Fe (12 MPC_{fs}) and Mn (5 MPC_{fs}) while concentrations of other substances are at the level of the MPC_{fs}. The open conditions in the canal and the pan sludge contribute to the accumulation of pollutants from municipal sewages (domestic and industrial). The spectrum of pollutants extends beyond the MPC_{fs}, Cu, PP, and S.s with organic matter (BOD_5 and COD). However, at the discharge point into the river backwater, the amount of Fe decreases to the concentration special for the river (8 MPC_{fs}).

Seasonal changes in the quality of natural waters are complicated by fluctuations in the river content. It was seen the dynamics of the concentrations of substances in the backwater at the intake during the summer periods: dry 2016 and rainy 2017. *The increase* in the amount of substances through washing off by precipitation from the shore and municipal sewage in the rainy season is marked "+" (concentration ratio: 07.2017 /08.2016). *The decrease* in their concentrations by diluting "─" (08.2016 / 07.2017 respectively). The trends in the development of a hydrochemical situation are expressed by ranked series of multiplicity for concentrations of substances (enclosed in parentheses after the ingredient symbol):

Increase: "+" NO_2(6) NO_3(3.5) BOD_5(2.7) COD(2.6) S.s(1.9)

PP(1.7) Fe(1.3) D.r.(1.2);

Reduction: "─" SO_4(5.3) C_{NH4}(3.6) Cl(1.8) P(1.5).

The variation of the concentration of ingredients in the effluent of process water is largely related to the quality of consumed river water. For the period 2014-2017 stable fluctuations in concentrations which exceed MPC_{fs} were seen in the *water of the Tvertsa River* - BOD_5, COD, S.s, SO_4, NO_3, K_{NH4} (they increase mostly in summer); *process waters* - BOD_5, S.s, SO_4, NO_3, K_{NH4}, PP (in spring and summer; they are determined by the river water quality). The technology of purification of industrial storm runoffs let reduce the concentration of PP, Fe, nitrogen compounds, simply oxidizable organic matter and pH to the quality of river water.

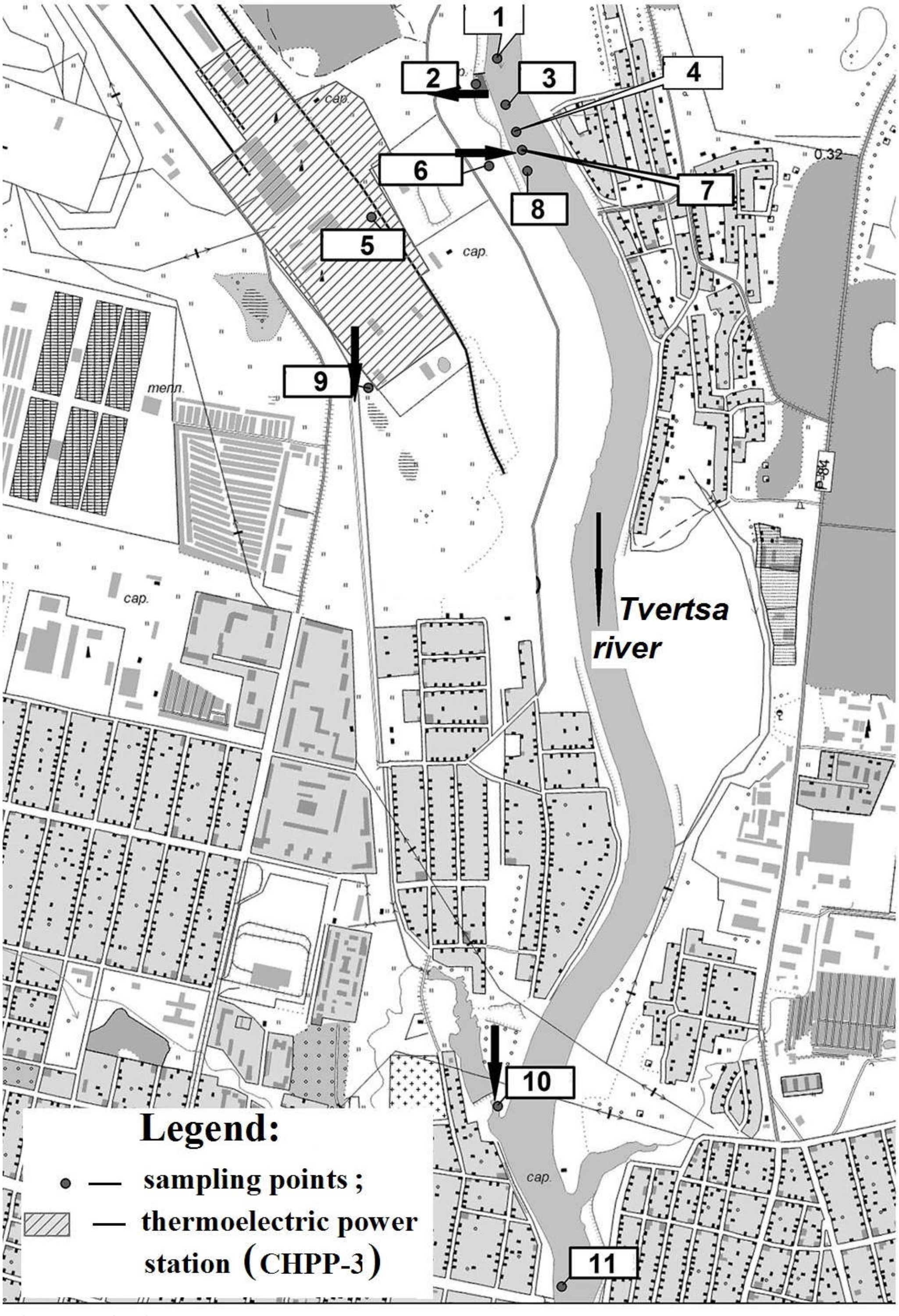
Bottom Sediments

The *present local background* of metals had lower values than the regional or was at the same level, Table 2. The level of the total pollution of alluvium with metals and petroleum products along the Tvertsa was "*low*", Table 3. In the series of maximum values of Kc there were the follow pollutants: PP(4.3) Cu(2.8) Fe(2.3) Mn(2) Zn(1.5) Cd,Co(1.4) Ni(1.2). The spectrum of substances expanded in the backwater of the intake (Sp. 2) and 100 m below the discharge point of wastewater from CHPP-3 (Sp. 8). The accumulation involved metals both of the asphaltene fraction of PP and those from washing out the underground collector pipes during volley discharge of water.

Table 3. Total accumulation of metals and petroleum products (PP) in the alluvium of the Tvertsa River: Zc (FeCoCuNiZnCdMnPP)

Sample №	*Zc*	Series of ingredients*	Pollution**
1	0.8	Ni(1.2)Zn(1.1)	≈ background
2	1.9	Cu(1.5)PP (1.4)Cd,Co(1.3)Zn,Ni(1.2)Fe(1.1)	low
3	1.2	Co,Mn(1.2)Cd(1.1)	≈ background
4	2.1	Fe(1.6)Co,Mn(1.2)Cu,Zn(1.1)	
7	4.1	Fe,Mn(2)PP (1.9)Cu(1.7)	low
8	6.5	Cu(2.8)Fe(2.3)PP(2)Zn(1.5)Cd(1.4)Co,Mn(1.3)	
11	3.9	PP(4.3)Cu(1.4)	

* the table displays substances with a concentration of Kc > 1 (in relation to the current local background, see A, Table 2); No. of samples - Figure;
** pollution level in Zc values: <10 low, 10-30 - medium, 30-100 - high,> 100 - very high (according to Saet Yu.E. *et al*., 1990; Yanin E.P., 2002).



Signature to the Figure:

Figure. Scheme of the sampling at the site, Tver city. Thick arrows - water intake from the river and discharge of process water from CHPP-3

Conclusion

Water and alluvium conditions along the area before the mouth of the river Tvertsa within Tver is quite normal. Hygienic standards in the water are slightly exceeded in BOD_5, COD and everywhere in iron 2.7-5 MPCs (mostly of natural genesis). The influence of all of the municipal runoffs is seen locally: at the discharge points and in the dynamically stagnant river basin backwaters. Bottom sediments conditions in terms of total accumulation of metals and PP was recorded for the first time. The pollution level is "*low*" (Zc = 0.8-6.5). Seasonal alterations in the quality of natural waters are complicated by fluctuations in the water content of the river and are contrasted in spring and summer. During rainy periods washouts and run-offs from urban villages increase the concentrations of NO_3 and NO_2 in the river, easily and hardly oxidizable organic matter (BOD_5 and COD), petroleum products and iron (mainly of natural genesis). They are reduced by diluting the amount of sulfates, chlorides and phosphates as well as "new" ammonium nitrogen. The variation in the quality of technological discharges is largely related to the quality of the consumed river water. Sewage treatment allows to bring their chemical characteristics to the quality of the river water. The Tvertsa water does not have a significant negative impact on the sanitary and hygienic quality of the river Volga, but in fisheries it can increase the content of toxic metals Cu, Co, Ni.

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