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Complex research of water and bottom sediments of the Tmaka river in Tver city

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As a result of comprehensive research of water and bottom sediments of the Tmaka River the estimation of the water quality in terms of SCWPI (specific combinatorial water pollution index) and the criteria of toxicity for aquatic organisms are given. Pollutants priority for the Tmaka River (Ba, Cd, Cr, Cu, Mn, P, Pb, Sr, Zn, Hg, as well as oil products), are identified. Special attention in the monitoring of river and wastewater of the city should be given to the elements mentioned.

Key words: ecology, pollution of water and bottom sediments, biogenic matter, organic matter, anthropogenic pollution

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The complex investigation on the assessment of water quality and the identification of the most polluted sites of the Tmaka River has been conducted. Recommendations have been given on the development of the system of ecological monitoring of the river.

The Tmaka is the right tributary of the Volga. The length of the Tmaka is 73 km, the catchment area is 582 km^2. The main source of water feeding of the river is snow (more than 50 % of annual volume). Rain waters give 15–20 % and ground waters give 30–35 % of annual volume.

Throughout all its length the river suffers the anthropogenous influence. In the upper and medium stream the river accepts the runoff from drying peatlands and agricultural grounds. In the lower stream (including Tver) the river is used for recreation and as the receiver of household, storm water and production sewage. The last 11 km of the lower stream of the river within the city have been studied in this work.

Four water sampling points on the river were chosen which characterize the different level of anthropogenous pressing: No.1–11 km upstream the mouth of the river (background point), No.2–7 km upstream the mouth (residential area), No.3–4 km upstream the mouth (industrial area), No.4–0.3 km upstream the mouth (before the flowing into the Volga).

The samples of water were taken during the main hydrological phases in the period from May 2010 till June 2011. The following indices were determined in water:

1) Hydrolodical (water level);
2) Physical (water temperature, conductivity, color, turbidity, smell);
3) Dissolved oxygen;
4) pH and Eh;
5) The main ions (HCO_3^-, SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+);
6) Biogenic components (NH_4^{2+}, NO_2^-, NO_3^-, Phosphates, Total iron, Si);
7) Permanganate oxidizability (PO);
8) Oil products (OP) and heavy metals (Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}).

Temperature, pH, Eh, dissolved oxygen and conductivity were measured *in situ*. Zinc, cadmium, lead and copper were measured with a method of inversion voltammetry on a mercury film electrode [*ФР.1.31.2004.00987 (2009)*].

Statistical parameters (maximal, minimal and medium concentrations, standard deviation) of the examined indices are given in table 1. Complex assessment of water quality with using of combinatory indices of pollution [*РД 52.24.643-2002 (2002)*] are shown in table 2.

During low water on March 23, 2011 the samples of water and bottom sediments were taken for the detailed microelement analysis. The maximum concentrations of all the tested elements were found in the mouth of the Tmaka (table 3).

Besides the chemical studies the biological testing was carried out of the samples of water and water extracts of bottom sediments using *Daphnia magna Straus* and *Chlorella Vulgaris Beijera* [*ФР.1.39.2007.03222 (2007), ПНДФ Т 14.1:2:3:4.10-04*]. In all the samples the intensive development of alga was observed. There is a correlation between toxic frequency rate of diluting of water and concentration of ammonium in water. In the bottom sediments' extracts the increasing of toxicity was recorded downstream the river from "slightly toxic" to the "hyper toxic".

By the results of biotesting with using *Daphnia* no toxic influence was revealed in spite of the high content of many pollutants, in particular, metals: iron, manganese, molybdenum and mercury. The results allow assuming that the complex formation occurs of these metals with some natural ligands and, as a result, their toxicity is decreasing [*Edigarova I.A. (1989)*].

It was shown that most serious impacts on the river Tmaka within the city of Tver are the following:

1. Communal waste water discharge in Nikolsky settlement causes pollution of the river by biogenic elements, detergents and pathogenic microorganisms;
2. Disposal of oil reservoirs near Nikolsky within water protection zone of the river creates the risk of pollution of ground waters and storm drain by oil products;
3. Disposal of ash residues from the heating station on the right bank of the river can be the source of polluting substances going to the river with ground waters;
4. Private housing estate on the right bank can be the source of sewage from the houses and grounds.
5. Sand extraction near Stroiteley St. causes the destruction of the right bank and dumping of the wastes.
6. Industrial waters going from the heating station, the Proletarka factory, the worsted plant and the Rozhdestvenskaya textile mill lead the increasing of water temperature in Tmaka;
7. Automobile bridges crossing the river can be the source of oil and salt pollution;
8. There are many damps and fallen trees on banks and bed of the river.

The water pollution, the declining of self-cleaning processes, the soiling of riverbed and the eutrophication of the river are the results of intensive anthropogenous impact on the Tmaka.

In the lower course of the river the accumulation of Ba, Cd, Cr, Cu, Mn, P, Pb, Sr, Zn, Hg and oil products is under way. These substances should be entered in the list of specific substances for the ecological monitoring of the Tmaka and the monitoring of the industrial sewages.

Table 1. Values of hydrochemical indices in water samples of the river Tmaka

Sample point No	Index	Color	pH	h	NH_4^{2+}	NO_2^-	NO_3^-	PO_4^{2-}	Fe^{3+}	Si	PO*	HCO_3^-	Ca^{2+}	Mg^{2+}	Na^+	SO_4^{2-}	Mn^{2+}	Cl^-	K^+	O_2	OP**	Zn^{2+}	Cd^{2+}	Pb^{2+}	Cu^{2+}
1	Max C	166	8.2	600	**1.84**	**0.090**	13.1	**0.27**	**1.97**	6.04	48	319	85	21	9.6	98	0.90	31	2.0	14	0.032	0.0006	0.0036	0.0055	<0.0006
	Min C	40	6.9	199	**0.58**	0.001	0.65	<0.01	0.18	0.94	1.6	94	36	0	3.1	0	<0.01	3.4	0.7	2.8	0.007	<0.0005	<0.0002	<0.0002	<0.0006
	$\overline{C}$	92	7.5	312	**0.98**	0.034	3.29	0.07	**0.75**	3.16	22	219	63	11	5.1	25	**0.25**	12	1.4	8.1	0.018	0.0002	0.0010	0.0014	<0.0006
	σ	42	0.4	138	0.40	0.030	3.65	0.11	0.64	2.10	14	82	18	6.1	2.4	29	0.39	8.6	0.6	3.0	0.009	0.0002	0.0011	0.0017	0
2	Max C	165	7.9	476	**1.84**	**0.097**	12.3	**0.29**	**1.69**	5.92	45	299	81	21	8.9	96	**0.87**	25	2.2	10	0.023	0.0014	0.0031	0.0052	<0.0006
	Min C	41	6.8	208	0.44	0.000	1.30	<0.01	0.12	0.86	3.2	97	38	0	3.1	0	<0.01	3.4	0.7	2.2	0.006	<0.0005	<0.0002	<0.0002	<0.0006
	$\overline{C}$	91	7.4	273	**0.91**	0.041	3.65	0.08	**0.64**	2.96	20	220	62	12	6.1	31	**0.25**	13	1.4	7.3	0.015	0.0005	0.0008	0.0019	<0.0006
	σ	42	0.4	72	0.44	0.037	3.25	0.12	0.54	2.05	13	79	17	8.0	2.6	34	0.40	7.0	0.6	2.5	0.007	0.0004	0.0009	0.0020	0
3	Max C	157	7.9	650	**1.88**	**0.115**	12.3	**0.27**	**1.73**	5.80	35	265	75	17	9.6	78	**0.44**	22	2.7	10	0.021	0.0009	0.0020	**0.0064**	0.0006
	Min C	39	6.5	200	0.44	0.000	1.01	0.00	0.10	0.86	3.2	97	40	0	2.6	0	0.02	3.8	0.7	5.1	0.013	<0.0005	0.0002	0.0007	<0.0006
	$\overline{C}$	86	7.4	373	**1.01**	0.045	3.50	0.07	**0.64**	2.86	16	201	56	9.8	5.8	25	**0.15**	12	1.4	8.1	0.017	0.0005	0.0008	0.0031	<0.0006
	σ	41	0.4	171	0.43	0.043	3.38	0.11	0.63	1.85	13	62	11	5.8	2.7	24	0.20	5.9	0.6	1.9	0.003	0.0004	0.0005	0.0020	0.0002
4	Max C	154	8.3	600	**1.90**	**0.132**	12.3	**0.41**	**1.25**	5.88	42	274	74	16	23	84	**0.65**	26	6.3	10	**0.075**	0.0009	0.0030	**0.0065**	**0.0017**
	Min C	31	6.9	195	0.36	0.003	0.50	0.00	0.06	0.28	4.8	97	36	0	2.4	0	<0.01	4.4	0.7	6.8	0.005	<0.0005	0.0005	0.0033	<0.0006
	$\overline{C}$	79	7.5	340	**0.94**	0.051	3.80	0.08	**0.53**	2.95	17	204	56	9.5	8.4	21	**0.17**	14	2.2	8.4	0.031	0.0006	0.0018	0.0047	<0.0006
	σ	40	0.4	144	0.51	0.047	3.40	0.15	0.44	2.13	11	63	13	5.4	7.1	26	0.26	7.5	1.8	1.0	0.022	0.0002	0.0010	0.0012	0.0007

PO* - Permanganate oxidizability, OP** - Oil products

Concentrations which exceed the admissible concentration limit are allocated with a bold print

Table 2. Combinatory indices of pollution of water in four points of the River Tmaka in Tver

Point No.	CWPI*	SCWPI**	Quality class	Priority pollutants (in descending order)
	37.46	2.34	Polluted (3 a)	Mn, Fe,NH_4^+, PO_4^{3-}, deficiency in O_2
	39.02	2.44	Very polluted (3 b)	Mn, Fe, NH_4^+, PO_4^{3-}, deficiency in O_2, NO_2^-
	40.69	2.54	Very polluted (3 b)	Mn, Fe, NH_4^+, NO_2^-, deficiency in O_2, PO_4^{3-}, Pb
	47.21	2.95	Very polluted (3 b)	Mn, Fe, NH_4^+, PO_4^{3-}, NO_2^-, Cu, Pb

* Combinatory water pollution index

** Specific water pollution index [*РД 52.24.643-2002 (2002)*].

Table 3. Concentrations of microelements in samples of water and bottom sediments of the Tmaka

Bottom Sediments	**As**	**Ba**	**Be**	**Cd**	**Co**	**Cr**	**Cu**	**Li**	**Mn**	**Mo**	**Ni**	**P**	**Pb**	**S**	**Sr**	**Ti**	**V**	**Zn**	**Hg**
Sample point No 1	0.40	43.9	0.17	22	1.8	3.67	6.01	4.4	198	0.3	4.5	542	0.9	2299	8.4	209	7.06	9.05	<20
Sample point No 2	0.30	39.6	0.13	22	1.5	2.93	6.76	3.5	152	0.4	3.8	401	1.0	2279	10.7	168	5.52	9.68	<20
Sample point No 4	0.75	99.9	0.25	90	3.04	12.1	54.2	7.19	483	0.29	7.9	1500	9.09	4009	24.2	258	10.1	46.4	80,5
Water	**Al**	**As**	**Ba**	**Ca**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Li**	**Mg**	**Mn**	**Mo**	**Na**	**Ni**	**Si**	**Sr**	**Zn**	**Hg**
Sample point No 1	0.016	<0.0001	0.049	52.9	<0.00001	<0.002	<0.002	<0.001	**1.95**	0.003	14.4	**0.81**	**0.009**	6.81	<0.002	5.04	0.14	0.006	<10
Sample point No 2	0.011	<0.0001	0.046	53.9	<0.00001	<0.002	<0.002	<0.001	**1.01**	0.003	14.9	**0.81**	**0.007**	8.27	<0.002	5.10	0.15	0.006	<10
Sample point No 4	0.018	<0.0001	0.044	53.8	<0.00001	<0.002	<0.002	<0.001	**1.77**	0.003	14.4	**0.71**	**0.008**	9.05	<0.002	4.90	0.18	0.003	**11**

Concentrations which exceed the admissible concentration limit are allocated with a bold print

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