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Content of heavy metals in urban surface water bodies

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Today urban territories became the main habitat for people, but together with the rising level of economic and social advantages, they also have some ecological problems. And one of them is the pollution of urban water bodies with different toxicants, such as heavy metals. In this study, the analysis of surface water bodies carried out to containing of some heavy metals, such as: Pb, Fe, Mn, Sr, Zn, Cd and Cu, as well as comparison of obtained results with the results of previous research in 2006. During the research it was found that the main heavy metal contaminating town water bodies is cadmium (Cd), which average concentration is thirtyfold higher then allowed statutory level of contaminants for water bodies to amenity needs. Maximal concentration of Cd is 37 MPC_{an} (maximum permissible concentration in water bodies to amenity needs) was evidenced in the pond inside the industrial area. The other heavy metals found in water bodies and benthic sediments in concentrations 2-5 MPC_{an} were Pb, Fe and Mn. The results were compared with the previous research data in 2006, and it should be noticed, that during the eleven years concentrations of Pb and Mn lowered a bit, but they are still higher than MPC_{an}. At the same time, concentrations of Fe and Cd have slightly increased. In regards to heavy metals' concentrations in sediments, their dynamics changed a little. Basing to the obtained data, the specific combinatorial water pollution index (SCWPI) was calculated. This index characterizes water pollution rate, and for water bodies in Dzerzhinsky town SCWPI was 11 points, which indicates that surface waters in the town could be classified as "strongly polluted waters".

Keywords: surface water bodies, heavy metals, benthic sediments, specific combinatorial water pollution index, Dzerzhinsky town.

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Содержание тяжёлых металлов в городских водоёмах

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В данной работе был проведён анализ воды и донных отложений из поверхностных водоёмов г. Дзержинский Московской области на содержание ряда тяжёлых металлов (ТМ): Pb, Fe, Mn, Sr, Zn, Cd и Cu, а также сравнение полученных результатов с данными исследования, проводившегося в 2006 г. В результате исследования было установлено, что основным TM, оказывающим негативное влияние на городские водные объекты, является кадмий, средняя концентрация которого в воде находится на уровне 30 ПДКк-б (предельно допустимая концентрация для водоёмов культурно-бытового назначения), а максимальная – достигает 37 ПДКк-б для водоёма в промышленной зоне города. Другими TM, находящимися в воде и донных отложениях в концентрациях 2–5 ПДКк-б, являются свинец, железо и марганец. На основании полученных данных был рассчитан удельный комбинаторный индекс загрязнения воды (УКИЗВ), характеризующий степень загрязнённости поверхностных водных объектов в г. Дзержинский, составивший 11 баллов, из чего следует, что поверхностные воды города относятся к 4 классу, разряд «Г» – «очень грязные воды».

Ключевые слова: поверхностные водоёмы, тяжёлые металлы, донные отложения, удельный комбинаторный индекс загрязнения воды, г. Дзержинский.

Nowadays water pollution with heavy metals (HM) is one of the most serious problems for all urban territories. Heavy metals are highly toxic substances, which are able to accumulate in living organisms and transfer to food chain, influence negatively both on the environment and human health. World Health Organization (WHO) introduced standards of drinking water quality [1] including heavy metals content, which is similar to Russian maximum permissible concentration (MPC) standards.

Nevertheless, annual researches indicate the presence of heavy metals in water and ben-

36

thic sediments all over the world, but HM in dangerous concentrations mainly pointed in water bodies of the developing countries, like Vietnam [2], Bangladesh [3], Argentina [4] and also China [5–7]. In Europe strong concentrations of HM in sediments are pointed for countries of the East and Central Europe, for example, in Poland (the Upper Silesian region) [8], but also there are some works, dedicated HM water pollution in the West Europe, such as in Great Britain [9, 10].

In Russia, the problem of water bodies' pollution with heavy metals is also well-known for a long time, but, according to number of researches, it's still actual one. So, in annual report "Surface water quality in Russian Federation" with annexfor 2016 [11] there is pointed, that the highest pollution level of surface water bodies was for manganese, cuprum, iron, zinc, cadmium, and hexavalent chromium Cr (VI) compounds. Concentrations of these heavy metals exceedmaximum permissible concentration in water bodies to amenity needs $(\mathrm{MPC}_{\mathrm{an}})\,\mathrm{up}$ to $10{-}50$ times. Exceeding $\mathrm{MPC}_{\mathrm{an}}$ level for lead is average 10 times. Data from annual report is equal with results of the other independent researches of surface water bodies in Russia [12, 13].

For Moscow region as a high-urbanized territory, the estimation of the environmental conditions, including water bodies, is one of the high-priority task necessary for creating and maintaining safe and healthy environment. This is right to Dzerzhinsky town as well. Being a satellite town of Moscow city, Dzerzhinskyhas a serious anthropogenic pressure on landscapes and water bodies from Moscow industries, like Kurianovskyie wastewater treatment facilities or Moscow Refinery plant, and from its own industrial objects, like Central Heating and Power plant No. 22 (CHPP-22) and so on.

Besides that, another possible source of anthropogenic influence could be a farming company "NIVA" situated near CHPP-22, and its fertilizes, mainly phosphates, could pollute the river with heavy metals with flush water [15].

According to this, the actual task of this research is to analyze water and sediments to define their HM pollution level according to standard of MPC_{an} . And the research objective is to analyze HM concentrations in the water and sediments in 2017 and comparing them with the data of previous research in 2006. To achieve this the following tasksit was done:

- to collect samples of water and sediments and analyze them to heavy metals concentrations; - to compare the results with the data of previous research in 2006;

- to count the specific combinatorial water pollution index (SCWPI) of surface water bodies in Dzerzhinsky.

Subjects and methods of research

Water and sediments' samples were taken from all the town surface water bodies at the beginning of October 2017. There are nine points: the Moskva river (points T1 and T9); the pond in the territory of the Ugreshsky Monastery of St. Nicholas (the Monastery pond) – point T2; the Upper pond (point T3) in the Victory public garden; two depleted sand pits – the Little sand pit (points T4 and T5) and the Large sand pit (points T7 and T8), and one pond in the industrial area (point T6). All sampling points are shown at Figure 1.

All the samples were analyzes with atomic absorption spectrophotometer "Shimadzu AA-6200" to the next heavy metals: Zn,Sr, Cd, Cu, Pb, Fe and Mn. Water samples were prepared according to mass concentration of HM in water definition method. Accomplish this 100 ml of analyzed water was taken into the 250 ml beaker and acidified with concentrated nitric acid (HNO₃) to pH = 1-2. Then, 50 ml of prepared water sample was placed into 50 ml flask and analyzed to seven heavy metals with atomic absorption spectrophotometer (AAS).

Sediments' samples were prepared according to definition methods of total HM and mobile forms of HM in soils and dust. Accomplish this sediments' samples were placed to the 250 ml beaker and dried a few days at room temperature. Then, 1 g of sediments was triturated, weighted with the analytical balances, placed into 50 ml heat-resistantbeaker and acidified with 20 ml 1 n. HNO₃ for total HM and with 20 ml 0.1 n. HCl formobile forms of HM. After that sample was brought to boil on sand bath, then cooled down and infiltrated through ashless paper filter into 25 ml flask then made up to volume with distilled water. After that, prepared samples analyzed with atomic absorption spectrophotometer.

Then, according to HM data, SCWPI [16] was calculated for all urban surface water bodies. SCWPI is a relatival integrated index, which estimates a complex water pollution from different pollutants in different combination, and the contribution of each pollutant in the total water object pollution [17]. The specific combinatorial water pollution index was counted in Microsoft Excel for all seven HM, the total value for all pollut-

ХИМИЯ ПРИРОДНЫХ СРЕД И ОБЪЕКТОВ



Fig. 1. Points of water sampling from Dzerzhinsky surface water bodies

ants in the water body equals eleven (SCWPI = 11), which indicates that in accordance with "K" Annex of RD 52.24.643-2002 [17] surface waters in Dzerzhinsky town could be classified as "strongly polluted waters".

Results and discussion

The result of this research was, that all surface water bodies in Dzerzhinsky town were strongly polluted with cadmium (Cd_{max} = 37 MPC_{ap}) as well as Pb, Fe and Mn heavy metals

 $(2-5 MPC_{an})$. Obtained results were compared with the results of previous research in 2006 [14], as demonstrated at Figure 2 (see color insert). The results for all water bodies in mg/L and their MPC_{an} [18] are shown in Table 1.

It should be noticed, that cadmium pollution level has been increased for most water bodies in 2017 in comparison with 2006 (Fig. 2) Besides that, as it was told before, practically in all urban water bodies the HM concentrations are higher than MPC_{an} . It's 2–5 MPC_{an} for Pb, 2–3 MPC_{an} for Mn and nearly 2–2.5 MPC_{an} for Fe (Fig. 2).

Water body	HM in water samples in 2017 (mg/L)											
	Zn	Pb	Cu	\mathbf{Sr}	Fe	Mn	Cd					
Point T1	0.05	0.020	0.068	5.17	0.777	0.258	0.030					
Point T2	0.09	0.028	0.078	2.76	0.633	0.318	0.035					
Point T3	0.01	0.017	0.034	3.12	0.611	0.364	0.028					
Points T4–T5	0.12	0.031	0.049	5.95	0.259	0.068	0.028					
Point T6	1.00	0.049	0.058	4.61	0.683	0.122	0.037					
Points T7–T8	0.04	0.033	0.427	6.02	0.270	0.273	0.017					
Point T9	0.25	0.021	0.082	5.17	0.734	0.246	0.035					
MPC _{an} [18]	1	1 0.01 1 7		7	0.3	0.1	0.001					

 Table 1

 Concentrations of heavy metalsin surface water bodies in Dzerzhinsky town (mg/L) in 2017 year

Теоретическая и прикладная экология. 2019. № 1 / Theoretical and Applied Ecology. 2019. No. 1

E. G. RIABOVA CONTENT OF HEAVY METALS IN URBAN SURFACE WATER BODIES, P. 36



Fig. 2. HM content above MPC_{an} in urban water bodies in 2006 and 2017. Left to right: Pb, Fe, Mn, Cd. **MPC**_{an} **2006**/**2017**: $C_{Pb} = 1.2-14.2 \text{ MPC}_{an} / C_{Pb} = 1.6-4.8 \text{ MPC}_{an}$; $C_{Fe} = 0.4-2.4 \text{ MPC}_{an} / C_{Fe} = 0.8-2.6 \text{ MPC}_{an}$; $C_{Mn} = 4.6-21.7 \text{ MPC}_{an} / C_{Mn} = 1.2-3.6 \text{ MPC}_{an}$; $C_{Cd} = 22.0-28.0 \text{ MPC}_{an} / C_{Cd} = 16.8-36.8 \text{ MPC}_{an}$;



 $\begin{array}{l} \textbf{Fig. 3.} \text{ HM content in benthic sediments } (C_{_{fact}}/C_{_{background}}) \text{ in } 2006-2017. \text{ Left to right: Pb, Cu, Mn, Cd.} \\ \textbf{Exceeding of background concentrations in } 2006/2017: C_{_{Pb}} = 0.2-2.9 \ / \ C_{_{Pb}} = 0.6-1.0; \\ C_{_{Cu}} = 0.2-1.6 \ / \ C_{_{Cu}} = 0.4-0.9; \ C_{_{Mn}} = 0.2-1.7 \ / \ C_{_{Mn}} = 0.4-1.9; \ C_{_{Cd}} = 0.4-10.7 \ / C_{_{Cd}} = 3.9-5.8 \end{array}$

Table 2

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	HM in sediments, total (t) and mobile (m) forms (mg/kg)													
Water body	Zn	Zn	Pb	Pb	Cu	Cu	Sr	\mathbf{Sr}	Fe	Fe	Mn	Mn	Cd	Cd
	(t)	(m)	(t)	(m)	(t)	(m)	(t)	(m)	(t)	(m)	(t)	(m)	(t)	(m)
Point T1	48.58	13.69	17.92	1.98	21.19	1.41	4.54	7.30	178.71	7.33	356.06	346.67	1.41	1.07
Point T2	51.43	3.57	19.84	2.32	15.51	0.34	2.83	5.03	63.28	0.93	657.57	430.30	1.69	0.48
Point T3	19.64	1.86	16.54	2.65	13.57	0.36	4.26	5.46	50.41	1.00	422.73	351.52	1.16	0.75
Points T4-T5	16.26	1.64	24.39	2.32	12.05	0.49	5.14	4.36	49.53	1.94	228.80	245.10	1.36	0.81
Point T6	54.50	7.97	28.82	1.74	25.26	2.38	4.18	5.31	138.08	0.76	1189.39	490.15	1.76	1.82
Points T7–T8	16.00	1.61	26.04	2.27	12.10	0.60	4.68	4.36	69.25	3.05	331.82	254.55	1.41	0.77
Point T9	51.12	13.50	18.54	1.98	27.68	2.04	2.06	6.73	171.95	4.91	373.12	309.19	1.49	1.09
$rac{\mathrm{C}_{\mathrm{background}}}{\mathrm{MPC}}$	55*	23	29	6.0	30	3.0	31	10***	6500**	_	635	500****	0.5*	0.5

Concentrations of heavy metals (total and mobile forms) in benthic sediments of Dzerzhinsky town(mg/kg) in 2017 year

Note:

* for Zn(t) and Cd(t) the MPC are given, $C_{background}$ are taken from [19];

****** according to [21];

*** by [22];

**** MPC for mobile form of Mn extracting from soddy-podzolic soils with 0.1 n H_2SO_4 solution with $pH \ge 6$ [20].

Concentrations of Zn, Cu and Sr changed insignificantly, and their content in water bodies was under $\rm MPC_{an}$

Sediments' samples were analyzed for total HM and mobile forms of heavy metals. Received data of total amount of HM compared with such data from previous research in 2006 are shown at Figure 3 (see color insert). Results of the analysis are shown in Table 2. According to received data, all benthic sediments in Dzerzhinsky town are characterized with MPC exceeding both for total and mobile form of Cd.

Also, according to resulting data, SCWPI was counted in accordance with method of Directive document RD 52.24.643-2002 [16, 17], and it has been discovered that for water bodies in Dzerzhinsky town SCWPI was 11 points, which indicates that surface waters could be classified as "strongly polluted waters".

Conclusions

In this study the estimation of surface water bodies in Dzerzhinsky town has been made. As a result of this work it was discovered, that all urban water bodies suffered from anthropogenic impact, including strongly heavy metals' pollution. HM concentrations are higher than maximum permissible concentration in water bodies to amenity needs. It's 2-5 MPC_{an} for Pb, Mn and and Fe, and nearly 37 MPC_{an} for Cd. All sediments are also characterized with concentration of Cd = 2-3.5 MPC_{an}.

Comparing these results with the research in 2006, it should be noticed, that during the previous eleven years concentrations of Pb and Mn lowered a bit, but they are still higher than MPC_{an} . At the same time, concentrations of Fe and Cd have slightly increased. In regards to HM concentrations in sediments, their dynamics changed a little.

After counting SCWPI, it was discovered, that urban surface waters could be classified as "strongly polluted waters". The critical aspect of this is that both Cd and Pb are toxicants of the first class of hazard, and their concentrations in water bodies should be minimalized.

All aforementioned data have an essential importance because of most part of urban water bodies used as the recreation zones. And if the Monastery pond (T2) and the Upper pond (T3) used only for visual recreation, without swimming (though there were some cases of fishing at the Upper pond), but the Little (T 4–5) and the Large (T7–8) sand pits used as the full-scale recreation zones with organized beaches and swimming possibility.

In accordance with this fact, it's necessary to pay the close attention at those two sand pits, including their regular cleaning and control of the pollution level under the MPC_{an} standards. Annual monitoring of their condition is also needed. In regard to the Monastery pond and the Upper pond it's also necessary to take integrated rehabilitation actions, including unwatering with the next bottomcleaning, as well as regular monitoring of the pollution level in these water bodies.

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