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HEAVY METALS MONITORING OF WATER AND BOTTOM SEDIMENTS IN DONETSK SURFACE WATER BASINS

MONITORING METALI CIĘŻKICH W WODZIE I OSADACH DENNYCH ZBIORNIKÓW WÓD POWIERZCHNIOWYCH W REJONIE DONIECKA

The investigations of water and bottom sediments of the Kalmius River, its tributaries and ponds in Donetsk were carried out concerning the heavy metals content (Cd, Pb, Cu, Mn, Fe). The necessity of these heavy metals control in the pond water was revealed. Simultaneously, water and bottom sediment biotesting was carried out with the usage of the higher vascular plant Allium Cepa. The results received have proven the negative influence of Donetsk industrial activity on water quality of the Kalmius River, gullies and ponds within the boundaries of the city.

1. Introduction

The environment of the Donetsk region has suffered from the biggest anthropogenic load among the Ukrainian regions. For the period from 2002 to 2007 years the total sewage discharge of the Donetsk region was changing insignificantly and varied in the range of 1620 – 1705 mln. m^3 per year [1]. However, in 2007 discharge of untreated and inadequately treated sewage into the river system significantly exceeded the discharge volume in 2002 – it is 7.2 and 1.3 times, correspondingly. The small rivers of the region are not only the water supply sources but the carriers of the discharged industrial, household sewage, pumped mine and open pit water as well.

In addition to everything mentioned above, it should be noted that there are more than 200 coal industrial enterprises in the region, among which there are 24 preparation plants. Therefore, the regional mine water is one of the main sources of river and basin contamination. Coal-mining enterprises annually discharge over 300 mln. m^3 of mine water in the hydrographic network. It should be mentioned that the volume of mine discharge has decreased 1.5 times in recent years due to the mine closure. All mine water is referred to the category of “contaminated”. This is caused by its high mineralization and lack of its desalination because of high prime cost of this process. In addition to this, the Donetsk region is the least provided with the water supply. The availability of general and local water resources in the region is correspondingly 1.3 and 3.1 times less than in average for Ukraine, and the availability of these resources for population is 2.6 and 5.9 times less correspondingly.

The major waterway of the Donetsk region – the Kalmius River – is the sewage receiver for mines, metallurgical plants and municipal enterprises. At the same time this river is a source of drinking, household and industrial water supply. The Kalmius River while running through the Donetsk area is the recreation area for citizens. Many urban ponds are also used for recreation purposes.

Therefore, the important problem of toxic substance investigation, especially of heavy metals contents, in water and bottom sediments of the Kalmius River and urban ponds in the boundaries of Donetsk, was raised and investigated by us.

Heavy metals (HM) are referred to non-conservative metal group, i. e. their content in water, soil, active and mixed silt depends on temperature, salt content, presence of organic and inorganic complexing agents, biological activity, season, pH factor. The plankton microorganisms accumulate copper 90000 times more, lead 12000 times more, cobalt 16000 times more than water [2, 3].

Heavy metals content in the organisms and the accumulation coefficient value are closely dependant on alkalinity, pH, organic matter content in water and other factors which regulate physical and chemical state of HM in the aqueous medium [4, 5].

HM are also mutagenic agents, they were found in animal DNA, that was noted in the research [5] (table1). The genotoxic and cytotoxic effects of HM ions are determined by their easy bonds with protein sulphur-hydric groups, what impedes macromolecular synthesis and general cellular metabolism. HM ions are significantly stronger in binding majority of organic ligands, than ions of magnum and calcium. This results in competitive relationships of these ions for the sites of binding in the active centers of many enzymes [6].

Tab. 1. Heavy metal ability to cause mutagenic changes of certain classes of organisms

Metal	**Classes of organisms**				**Presence in DNA**
	micro-organisms	**plants**	**insects**	**mammals**	
Copper	-	+	+	-	+
Lead	+	-	+	+	-
Manganese	+	+	+	+	+
Cadmium	+	+	+	+	+

2. Research object description

The Kalmius River springs from the south-west slopes of the Donetsk hilly range. The river length is 209 km, the water catchment area is 5070 km^2. The fluvial network is well developed, the river ravine density coefficient is 0.41 km/km^2. The river valley type changes from V-shaped in the city area zone to slightly marked trapezium-shaped in the lower stream. The valley width varies from 100 m to 2.2 km. The valley slopes are steep and crossed with gullies and ravines. The right slope prevails over the left one practically all over the river length. The flood plain of the river is predominately double-ended, dry, covered with meadows all over the river length. The river-bed is straight in the upstream and meandering one in the middle and lower stream. There are a lot of ponds, several reservoirs for technical and drinking water supply, industrial enterprises and hydro-electric stations on the banks of the Kalmius River and its tributaries.

The Donetsk city ponds have water capacity not more than 1 mln. m^3 . Most of them are situated near the location sites of mines and other industrial enterprises. Therefore, the pond water quality is usually determined by quality of the mine water discharge.

3. Materials and methods

The water samples from the Kalmius River, its gullies and reservoirs were being taken in January – August 2007 from five sites of the stream: the first site – where the river enters the city; the second, third, fourth sites – in the middle part of the river, the fifth site – where the river goes out from the city. The sample sites in its tributaries were the following: 6 – Ignatyevskaya gully, 7 – Kalinovaya gully, 8 – Frontier gully, 9 and 10 – Nameless gully in the source and at the point of flowing into the Kalmius River, correspondingly (fig. 1).

Also 15 water samples from the Donetsk ponds were taken during April – August 2007 (sites 11 – 25, described in the table 3). The bottom sediments were sampled only in the fifth site where the Kalmius River leaves Donetsk, and the tenth site – at the point where Nameless gully flows into the Kalmius River. The water samples in the volume of not less than 2 – 3 dm^3 were collected into plastic and glass bottles washed with diluted nitric acid and than distilled water. The bottom sediments were sampled in the quantity of 0.5 kg into glass bottles similarly treated. The sample sites are shown in the figure 1.

In the selected water and bottom sediment samples the total metal content (Cd, Pb, Cu, Mn, Fe) was analyzed by AAS method with thermal-electric atomization in conformity with the standard method [7] and recommendations [8]. The bottom sediment samples preparation was carried out according to the standard technique [9] with usage of strong nitric acid and 30 % hydrogen peroxide. Simultaneously, biotesting of samples was done with usage of the higher vascular plant *Allium Cepa* (onion common) according to the technique [10]: after 3-day onion germination in the investigated samples the length of onion roots was measured and compared with the control one, then the root inhibition coefficient was calculated (K_i). The value of inhibition coefficient allows to estimate the integral water toxicity. If the root inhibition coefficient was more than 50 %, the sample was considered to be highly toxic.

Fig. 1. Water and bottom sediments sample sites of Donetsk surface basins

4. Investigation results and their discussion

4.1. Kalmius River and its gullies

The results of the Kalmius water analysis are shown in the table 2 in the following form: *(min – max)/average*. These data show that heavy metals content tends to decrease from the first to second site of observation, than their concentration abruptly increase (for Cd – to 2.1 MPC) in the third site, and consequently increase to the last fifth site of observation (fig. 1, sites 1 – 5). Particularly, obvious tendency of the Kalmius River water pollution with copper and manganese is revealed. This situation can be explained by denser metallurgical enterprises localization towards the city outskirts ("Donetsk metallurgical plant", "Donetsk mining machine-building plant", metallurgical plants "Donetsksteel", "Istil"), the discharges of which influence the river quality.

Tab. 2. Analysis results for water and bottom sediments of the Kalmius River and its gullies

№	Site name	Heavy metal concentration, μg/l (mg/kg for bottom sediment)				K_i, %
		Cd	Pb	Cu	Mn	
			Water			
1	r. Kalmius near Scheglovsky well	0,26 – 1,67 / 0,84	< 0,5 – 47,91 / 17,6	14,23 – 40,00 / 30,42	32,83 – 194,00 / 94,72	7
2	Upper-Kalmius pond	< 0,05 – 0,84 / 0,39	< 0,5 – 9,01 / 3,63	< 0,5 – 26,49 / 10,84	3,44 – 25,16 / 16,85	6
3	Lower-Kalmius pond (1)	0,52 – 4,34 / 2,11	4,75 – 53,74 / 19,61	30,59 – 143,73 / 78,68	21,56 – 46,65 / 35,55	18
4	Lower-Kalmius pond (2)	0,84 – 1,15 / 0,99	5,06 – 14,85 / 9,82	10,85 – 111,03 / 53,96	33,33 – 75,34 / 54,04	17
5	r. Kalmius near Avdotyno bridge	0,87 – 2,22 / 1,37	3,72 – 67,79 / 30,06	16,95 – 329,76 / 163,66	36,86 – 174,64 / 95,93	45
6	Ignatyevskaya gulley	0,22 – 0,54 / 0,38	7,16 – 10,22 / 8,69	23,41 – 90,36 / 56,88	21,56 – 46,65 / 35,55	-
7	Kalinovaya gully	0,14 – 0,51 / 0,33	5,53 – 9,65 / 7,59	24,72 – 84,47 / 54,60	42,97 – 45,88 / 44,43	-
8	Frontier gully	0,32 – 0,49 / 0,41	5,61 – 248,26 / 126,94	16,53 – 73,28 / 44,91	37,62 – 43,59 / 40,61	-
9	Nameless gully in the head water	0,59 – 1,82 / 1,21	15,73 – 44,23 / 29,98	20,32 – 22,53 / 21,43	23,30 – 59,71 / 41,51	10
10	Nameless gully in the inflow point in Kalmius River	1,54 – 1,88 / 1,71	7,14 – 12,85 / 10,00	20,97 – 27,47 / 24,22	12,40 – 59,76 / 36,08	13
	Element MPC in water	1,00	30,00	1000	100,00	
			Bottom sediments			
5	r. Kalmius near Avdotyno bridge	1,4	89,4	246,6	993	-
10	Nameless gully in the inflow point in Kalmius River	0,1	4,8	18,2	345	32
	Element MPC in soil	3,0	32,0	55,0	1500	-
	Clarke	$N*10^{-1}$	20,0	100,0	800	-

It should be noted, that the water quality of gullies (fig. 2, sites 6 – 8) situated in Kalininskiy district, satisfy the established requirements [11] (except for lead content in the 8th site) due to the least quantity of the industrial enterprises which are situated there. Water of these gullies dilutes more contaminated Kalmius water in the middle part of the river section. However, Nameless gully water is more contaminated because it runs in the highly industrialized part of the city, that is confirmed by high concentration of cadmium in its water (fig. 2, sites 9 – 10). Therefore, water pollution in the Kalmius water increases to the uptown. This situation, in our opinion, is also caused by getting the untreated rain run-off from the city roads and motorways into the water basins. Significance of this factor was repeatedly marked by the authors of our country and foreign scholars [12].

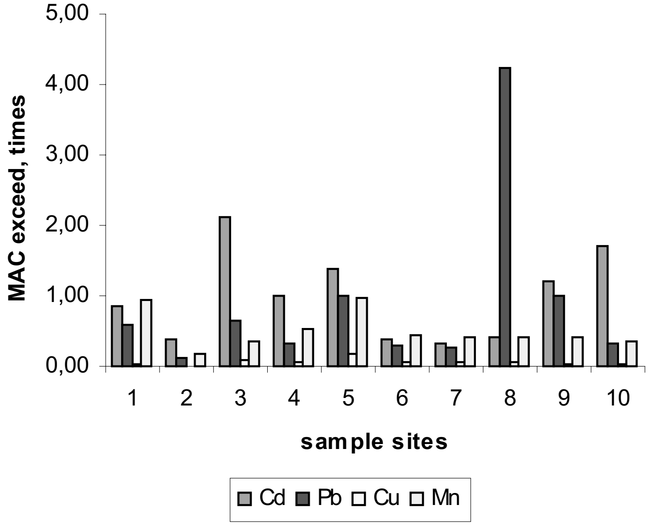

Fig. 2. Relative heavy metals content in water of Kalmius River and its gullies

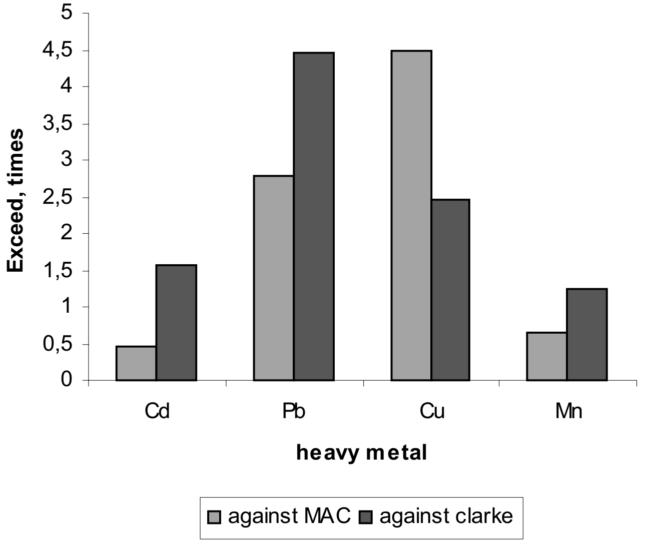

Fig. 3. Relative heavy metals content in bottom sediment of Kalmius River

Pollution of the bottom sediments with heavy metals was determined according to two criteria: MPC and clarke content of the element in soil (fig.3). According to the technique of the Institute of Soils and Agrochemistry named after N.I. Sokolovskiy, depending on the ratio of the gross form of the element to its clarke for this area, the following types of the environmental situation can be distinguished [13]:

- favorable: excess of metal content over clarke constitutes 1-2 times;
- satisfactory: excess is 2-3 times;
- pre-crisis: excess – 4-5 times;
- crisis: excess – 5-6 times;
- catastrophic: excess is more than 6 times.

According to the results of our research, there is the per-crisis situation concerning lead content in bottom sediments of the river Kalmius against this element clarke in soil. The hydrochemical research results are proven by data obtained while biotesting and testify the decrease in water quality of the Kalmius river at the point where it goes out of Donetsk that proves the negative influence of the city production activity on the hydrosystem.

4.2. Ponds

Water control of the Donetsk surface basins is implemented by Donetsk City Sanitary Station. However, from the whole list of heavy metals in water only iron content which has quite high MPC value is analyzed. The content of more toxic metals (Cd, Pb, Cu, and other) is controlled not in all water basins. Therefore, investigations of content of these metals were carried out for the purpose of establishing the necessity of their control.

The investigation results are shown in the table 3 (average values for the period under consideration) and reveal the following:

- the excess of cadmium content is observed on the levels of 1.1 – 2.4 MPC in the ponds situated in Leninskiy, Kirovskiy, Kuybyshevskiy and Kalininskiy districts; maximum is revealed in water of the Peski pond;
- the excess of lead content is registered on the levels of 1.0 – 4.2 MPC in the ponds situated in the same districts;
- copper content excess is registered only in the pond water of micro-district Shyrokiy (Kirovskiy district), and constitutes 3.9 MPC;
- manganese content varies in the range of the established normative values.

Tab. 3. Analysis results for the Donetsk pond water

№	Site name	Heavy metal concentration, µg/l					K_i, %
		Cd	Pb	Cu	Mn	Fe	
Kirovsky district							
11	Abakumovsky Pond	0,50	17,43	84,00	25,06	144,15	12
12	Pond of micro-district Shyroky	0,74	27,23	3385,90	30,07	130,14	12
13	Babakova Pond	1,57	13,89	182,26	30,11	151,13	0
14	«17-17 bis» mine Pond	1,09	36,08	159,08	26,98	147,35	24
15	Gormash settlement Pond	1,25	36,13	322,84	24,75	117,44	0
Kuybyshevsky district							
16	Pesky Pond	2,37	30,99	141,11	41,49	188,92	8
17	Pond of DPCR	1,01	24,99	103,81	31,57	107,34	0
18	Pond №2	0,61	19,91	38,53	27,00	180,64	4
19	Pond №3	0,68	22,48	27,50	26,09	210,87	8
Kiev district							
20	Putilovsky Pond	0,24	3,83	8,97	17,53	91,45	0
21	Vetkovsky Pond	0,46	8,68	40,82	27,74	76,98	0
	Voroshilovsky district						
22	City Pond №1	0,25	13,13	48,81	-	84,25	0
23	City Pond №2	0,1	13,93	47,11	-	92,54	0
Leninsky district							
24	Kirsha Pond	1,54	40,40	121,42	54,40	229,83	31
25	“Donetsk sea”	1,21	30,79	107,66	25,67	245,80	6
	MPC	1,00	30,00	1000	100,00	300,00	

In the research [14] the water forms of heavy metals were divided into 5 fractions: 1) exchangeable; 2) carbonate-bound; 3) bound with iron and manganese oxides; 4) bound with organic matter; 5) residual. The toxicity and bioavailability of heavy metals for the water organisms decrease in this list. K_i values received during biotesting of pond water prove the lack of acute and chronic toxicity, except for Kirsha pond, where the chronic toxicity was registered on the level of 31 %. This situation can be explained by the possible occurrence of heavy metals in the bounded state, that influences their bioavailability. It should be mentioned that the Donetsk region basins are notable for high natural mineralization [15, 16], in addition to this, there is high mineralization the of the mine discharge water. This factor promotes binding of heavy metals with the components which are present in water (table 4). Also the high concentrations of iron were observed in the pond water. So, it can be assumed that despite significant heavy metal content in water of the Donetsk ponds, their toxicity is weakly marked due to the mentioned factors.

Tab. 4. Water mineralization of the Donetsk ponds

№	Sample site name	Mineralization, mg/l
11	Abakumovsky Pond	2976
12	Pond of micro-district Shyroky	2236
13	Babakova Pond	2582
14	«17-17 bis» mine Pond	2109
15	Gormash settlement Pond	1927
16	Pesky Pond	2631
17	Pond of DPCR	1506
18	Pond №2	1820
19	Pond №3	1636
20	Putilovsky Pond	1257
21	Vetkovsky Pond	1924
22	City Pond №1	1193
23	City Pond №2	1205
24	Kirsha Pond	2710
25	"Donetsk sea"	2490
	MPC	1000

5. Conclusions

Water and bottom sediments investigations of the Kalmius River and its tributaries have shown the negative influence of the Donetsk industrial activity on the river water quality within the boundaries of the city. This is confirmed by increase of content for all considered heavy metals in water when the density of industrial enterprises situated in the river catchment area becomes more. It should be noted that excess of cadmium content in the river water in the middle part and at the point where the river goes out of the city is 2.1 and 1.4 times, correspondingly.

Water quality of the gullies flowing into the Kalmius River satisfies the established standards (except for Frontier gully, in which 4 time excess of lead content was revealed). This promotes improvement of the Kalmius water quality.

Our investigation results have revealed the pre-crisis situation for lead content in bottom sediments of the Kalmius River against clarke of this element in soil. The root inhibition coefficient of *Allium Cepa* while biotesting was gradually increasing from 6 % to 45 % in the sites of observation 1 – 5. Biotesting results confirm the hydrochemical analysis data and indicate deterioration of the Kalmius water quality at the point where the river goes out of Donetsk.

Excess of content for cadmium and lead was registered on the levels of 1.1 – 2.4 MPC and 1.0 – 4.2 MPC correspondingly in water of the ponds in Leninskiy, Kirovskiy, Kuybyshevskiy and Kalininskiy districts. Excess of copper was observed only in the pond of Shyrokiy micro-district and constitutes 3.9 times of MPC. The data received testify the necessity of water monitoring concerning contents of the mentioned metals.

Results of pond water biotesting have shown the lack of acute and chronic toxicity, except for water of Kirsha pond, where the chronic toxicity of 31 % was indicated. The existing situation can be explained by possible existence of heavy metals in the bounded state that influences their bioavailability.

Thus, the research results of water and bottom sediments of the Donetsk surface basins have proven the negative influence of the city industrial activity on hydro-ecosystem state. The current situation requires measures for decreasing amount of the contaminated sewage discharge into water basins and providing the constant water quality monitoring.

References

[1] Земля тривоги нашої. За матеріалами доповіді про стан навколишнього природного середовища в Донецькій області у 2006 році. / Під ред. С. В. Треьякова. – Донецьк, 2007 – 108 с.

[2] Брень Н. В. Использование беспозвоночных для мониторинга загрязнения водных экосистем тяжелыми металлами (Обзор) // Гидробиол. журн. – 1999. – №5. – С. 67–72.

[3] Брагинский Л. П., Величко И. М., Щербань Е. П. Пресноводный планктон в токсичной среде. – К.: Наукова думка, 1987. – 180 с.

[4] Воробейчик Е. Л., Садыков О. Ф., Фарафонтов М. Г. Экологическое нормирование техногенных загрязнений наземных экосистем (локальный уровень). – Екатеринбург: Наука, 1994. - 287 с.

[5] Никаноров А. М., Жулидов А. В. Биомониторинг тяжелых металлов в пресноводных экосистемах. – Л.: Гидрометеоиздат, 1991. – 312 с.

[6] Биогеохимический цикл тяжёлых металлов в экосистеме Нижнего Дона. / Под ред. П. Ф. Молодкина. – Ростов-на-Дону, 1991. – 112 с.

[7] МВИ 14 – 93. Методика выполнения измерения массовой концентрации меди, марганца, железа, свинца, стронция, алюминия, цинка, молибдена в воде. – Северодонецк, 1993. – 22 с.

[8] Алемасова А. С., Рокун А. Н., Шевчук И. А. Аналитическая атомно-абсорбционная спектроскопия. Учеб. пособие. – Донецк, 2003. – 327 с.

[9] МВВ № 081/12 – 0010 – 01. Грунти. Методика виконання вимірювань масової частки кадмію атомно-абсорбційним методом методом. – К., 2002. – 9 с.

[10] Fiskesjo, Geirid. Allium test for screening chemicals; evaluation of cytological parameters. // Plants for Environmental Studies. – 1997. – P. 308 – 333.

[11] Нормативы ПДК, утверждённые Министерством охраны здоровья для водоёмов хозяйственно-питьевого и культурно-бытового водопользования. М., 1982. – 40 с.

[12] W. Canningham, B. Saigo. Environmental science. Boston, 1995. – 612 p.

[13] Боровская Ю. И., Зубова Л. Г. Экологический анализ донных отложений р. Лугань // Матеріали VII Всеукраїнської наукової конференції студентів, магістрантів, аспірантів – Одеса, 2005. – С. 23 – 24.

[14] B. Gumgum, G. Ozturk. Chemical specitation of heavy metals in the Tigris River sediment. // Chemical speciation and bioavailability. № 13. – 2001. – P. 25 – 28.

[15] Горев Л. Н., Никаноров А. М., Пелещенко В. И. Региональная гидрохимия. – К.: Вища школа, 1989. – 280 с.

[16] Горєв Л. М., Пелешенко В. І., Хільчевський В. К. Гідрохімія України: Підручник – К.: Вища школа, 1995. – 307 с.