

**MONITORING AND IDENTIFICATION OF HEAVY METALS
CONTENT AND SOME ION GROUPS IN SURFACE
WATERS AND SEDIMENTS IN MARITZA RIVER BASIN, BULGARIA**

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Abstract. During the year 1997, a seasonal monitoring investigation on the river Maritza and two main inflows for determination of the availability and the quantities of some heavy metals (Cu, Mn, Zn, Ni, Cd, Cr, and Pb) and other chemicals in the surface waters and water sediments has been done. Water sampling was performed from 6 points around the region of the city of Plovdiv - in the city and from the points after joining of the main inflows. The received data shows that the heavy metals content Cu, Mn, Zn, Cr, (III-VI), Ni is within the norms for ultimate levels (UL) for third category waters in Bulgaria. Above the UL are the quantities of Cd and Pb. There are no high levels of NO_3^- , N, PO_4 , SO_4 and Chemical Oxygen Demand (COD). Heavy metals content in the sediments is below the UL for Bulgaria.

Keywords: monitoring, heavy metals pollution, waters, sediments, Maritza river.

AIMS AND BACKGROUND

In Republic of Bulgaria two main water basins are formed - Black Sea and Mediterranean. The first one takes 57% of the country territory and embraces 42% of the water off-flow, which is going mainly from Danube River¹. Mediterranean water basin takes 43% of the country territory and embrace 58% of the off-flow of the country. The biggest river that flows to the Mediterranean Sea is Maritza. Its length in Bulgaria is 321 km with water basin of 21 000 km². In the region of Plovdiv and Pazardjik, some inflows are merging in Maritza river: Vacha, Tchepelarska, Topolnitza, Striama, etc. To the Mediterranean water basin also belong the rivers Struma, Mesta, Tundja, and Arda.

From the biggest city agglomerates, situated among the river Maritza main-stream, a considerable amount of waste waters (industrial and domestic) inflows to Maritza. The intensive agriculture in those regions requires the usage of considerable amounts of pesticides and artificial fertilizers. Water streams are also polluted by the surface and underground water inflows. Therefore, it is necessary to identify and quantitatively measure these substances which are contaminants to the water flows. This is a prerequisite for implementation of several measures that might decrease the ecological risk on the Bulgarian territory but also through trans-border pollution. This research aimed to determine the amounts of some toxic metals and substances in the water flows of the river Maritza and some inflows (rivers Vacha and Tchepelarska). On the points where the water samples have

been taken, a bottom sediment samples have been taken too and the heavy metals content has been determined.

EXPERIMENTAL

The water sampling was performed from 6 main points in the region around the city of Plovdiv, two times seasonally – in June and November, year 1997.

- The samples from the river water were taken in one-liter bottles from the middle of the river mainstream, from 20-50 cm depth from the water surface. The samples for determination of the heavy metals content were conserved in HNO₃, in refrigerator conditions, and were analyzed up to 48 h after their collection, in accordance with the Bulgarian State Standard 17.1.1.02-86.
- The samples from the sediments were taken from the middle of the water mainstream, from 5-10 cm depth. They were conserved in refrigerator conditions.

The analytical determination of the heavy metals content and ion groups was performed using an automatic photometer SQ-118 Merck (its software is tuned especially for determination of water samples and sediments). Merck company analytical methods that are specific for every analyzed substance were used.

The main meteorological parameters (mean month temperature and rainfall) were determined also for the months June and November when the sampling was performed. The temperature and rainfall values were compared with the climatic limits for the region of Plovdiv (Table 1).

RESULTS AND DISCUSSION

The heavy metals content that has been determined is given in Tables 2 and 3. The analyses made do not show the presence of Cu (above the susceptibility of the analytical method) in the waters of the rivers Vacha, Maritza and Tchepelarska. The Cu content is not significant in the river Tchepelarska (0.08 mg/dm³) at the analysis performed in November 1997.

The Mn content that has been determined in the water of the rivers Maritza and Tchepelarska is in considerably smaller quantities compared to UL for waters of III category (0.8 mg/dm³).

The Ni content in both sampling periods does not show considerable differences. Higher content has been determined in the river Tchepelarska (0.23 mg/dm³ in June 1997 and 0.18 mg/dm³ in November 1997). The determined contents allow those waters to be classified as the II category waters. After mixing with the water of the river Maritza the Ni content decreases.

The Zn content shows the tendency to increase along the flow of the river Maritza. The Zn content increases after mixing with the waters from the river

Table 1. Main meteorological parameters for June and November 1977

Date	June 1977		November 1977	
	Mean temperature (°C)	Rainfall (mm)	Mean temperature (°C)	Rainfall (mm)
1	16.0		5.6	
2	17.4		6.6	
3	16.3		4.6	
4	20.1	3.0	8.8	
5	21.2	7.0	2.7	
6	17.0		2.7	
7	18.4	23.0	5.2	
8	18.2	2.0	6.4	
9	20.2	2.0	12.3	
10	21.0		9.4	12.0
11	22.2	3.0	8.0	
12	24.0		9.0	
13	24.0		10.0	
14	22.2	5.3	14.6	9.2
15	24.1	5.5	8.4	
16	25.6		6.1	18.0
17	25.0		7.8	12.4
18	26.0		5.7	
19	25.8		5.0	
20	24.8		2.3	
21	26.0	2.0	5.4	1.2
22	24.5		6.2	1.5
23	25.2		5.8	
24	24.2		7.7	1.0
25	19.4		8.0	1.0
26	21.5		8.8	
27	22.8		7.2	
28	24.4		5.8	
29	24.4		7.4	
30	26.6		7.4	
Mean month.temp.	22.3	Σ = 52.8	7.0	Σ = 56.3

Tchepelarska because some industrially and surface polluted waters are delivered in there. The determined maximum content (0.54 mg/dm³ in November 1997) allows these waters to be classified as II category according to the Bulgarian State Standards.

The Cd content shows higher values after the city of Plovdiv, in the river Tchepelarska and after its mixing with the river Maritza. The determined contents are above the UL values for III category waters in the analyzed samples in November 1997.

The Cr³⁺ and Cr⁶⁺ content which show a tendency of little increase after the city of Plovdiv are lower than UL for III category waters.

The Pb content in both samples in some points is up to two-times higher compared to UL for III category waters.

The determined contents of the NO₃ - N in the waters of all points are far below UL (Fig. 1).

Table 2. Determined levels of heavy metals and some ion groups in Maritza river and flowed in it rivers Vacha and Tchepearska, measured on 17.VI.1997 (mg/dm³)

Element or group & sites	Cu	Mn	Ni	Zn	Cd	Cr	Pb	pH
"Merck" method	14 767	14 770	14 785	14 832	14 832	III-14 552 VI-14 552	14 833	
Detection limit	0.02	0.12	0.05	0.05	0.025	III-0.05 VI-0.03	0.1	
UL for water II class	0.1	0.3	0.2	5	0.01	III-0.05 VI-0.05	0.05	6-8
UL for water III class	0.5	0.8	0.5	10	0.02	III-1 VI-0.1	0.2	6-9
1. Vacha – village of Kadievo	n.d.	n.d.	0.11	0.08	n.d.	n.d.	0.3	7.42
2. Maritza river Plovdiv – 4 km	n.d.	0.01	0.08	0.17	n.d.	III-0.09 VI-0.04	0.3	7.40
3. Maritza river Plovdiv – center	n.d.	0.01	0.08	0.17	n.d.	III-0.1 VI-0.06	0.2	7.33
4. Maritza river Plovdiv – East	n.d.	0.02	0.09	0.19	0.025	III-0.13 VI-0.03	0.2	7.60
5. Tsepearska river near the outfall	n.d.	0.17	0.23	0.35	0.035	III-0.08 VI-0.05	0.3	7.30
6. Maritza river near camping "Tchaja"	n.d.	0.35	0.05	0.48	0.029	III-0.28 VI-0.09	0.3	7.39

Table 3. Determined levels of heavy metals and some ion groups in Maritza river and flowed in it rivers Vacha and Tchepearska, measured on 17.IX.1997 (mg/dm³)

Element or group & sites	Cu	Mn	Ni	Zn	Cd	Cr	Pb	pH
"Merck" method	14 767	14 770	14 785	14 832	14 832	III-14 552 VI-14 552	14 833	
Detection limit	0.02	0.12	0.05	0.05	0.025	III-0.05 VI-0.03	0.1	
UL for water II class	0.1	0.3	0.2	5	0.01	III-0.5 VI-0.05	0.05	6-8
UL for water III class	0.5	0.8	0.5	10	0.02	III-1 VI-0.1	0.2	6-9
1. Vacha – village of Kadievo	n.d.	n.d.	0.08	0.14	n.d.	n.d.	0.5	6.57
2. Maritza river Plovdiv – 4 km	n.d.	0.01	0.10	0.20	0.03	III-0.07 VI-0.05	0.3	6.76
3. Maritza river Plovdiv – center	n.d.	0.01	0.08	0.23	0.03	III-0.09 VI-0.08	0.3	6.81
4. Maritza river Plovdiv – East	n.d.	0.01	0.10	0.28	0.06	III-0.11 VI-0.04	0.3	6.99
5. Tsepearska river near the outfall	0.08	0.02	0.18	0.42	0.05	III-0.07 VI-0.08	0.4	6.53
6. Maritza river near camping "Tchaja"	n.d.	0.01	0.08	0.54	0.03	III-0.24 VI-0.08	0.4	6.75

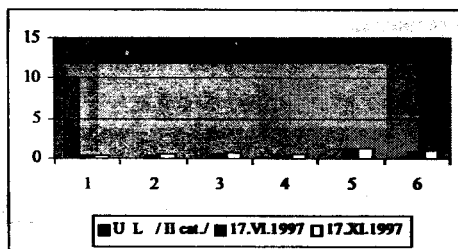


Fig. 1. Determined levels of NO₃-N (mg/l)

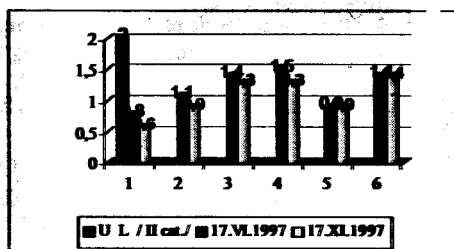


Fig. 2. Measured levels of phosphates (mg/l)

The phosphates content at both sampling do not show considerable deviation and the determined contents are below UL for ground waters (Fig. 2).

The content of sulphates is considerably lower than UL for II category waters (Fig. 3).

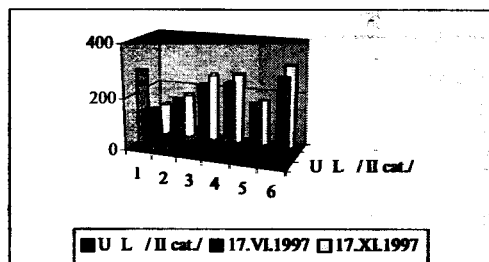


Fig. 3. Determined levels of sulphates (mg/l)

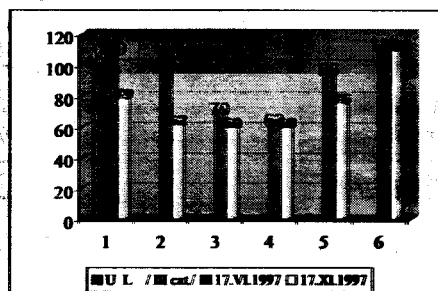


Fig. 4. Determined levels of chemical oxygen demand (mg/l)

The COD values show that surface waters of the river flow are not significantly polluted with organic and non-organic compounds. In accordance with this parameter these waters are classified as III category (according to the Bulgarian State Standards) – Fig. 4.

Concerning the pH parameter all analyzed samples are in accordance with the BG State Standards.

The heavy metals content in the sediments is shown in Tables 4 and 5.

The results of both sampling show the presence of Cu, Mn, Zn, Cd and Pb in the sediments. There have been no significant deviations in the Cd, Pb and Cu content. More significant are the changes in the Mn and Zn content in some sampling points.

The determined heavy metals contents are lower than UL for soils in Bulgaria. The pH values of the sediments are in accordance with the BG State Standards.

Table 4. Determined levels of heavy metals in the sediments from Maritza river and flowed in it rivers Vacha and Tchepelarska, June 1997 (mg/kg)

Metal & sites	Cu	Mn	Zn	Cd	Pb	pH
"Merck" method N				1290		
Detection limit	1.0	6.0	7.0	0.5	2.0	
UL (pH=6.2) for soils	230	800	300	2	75	
Sampling	June 1997	June 1997	June 1997	June 1997	June 1997	June 1997
1. Vacha – village of Kadievo	n.d.	84	107		27.5	5.62
2. Maritza river Plovdiv – 4 km	35	264	111		42.5	6.40
3. Maritza river Plovdiv – center	n.d.	747	131		20	5.71
4. Maritza river Plovdiv – East	n.d.	112	107		25	6.11
5. Tsepelarska river near camping "Tchaja"	80	147	244	0.55	37.5	6.17
6. Maritza river after camping "Tchaka"	20	164	228	0.3	20	6.32

Table 5. Determined levels of heavy metals in the sediments from Maritza river and flowed in it rivers Vacha and Tchepelarska, November 1997 (mg/kg)

Metal & sites	Cu	Mn	Zn	Cd	Pb	pH
"Merck" method N				1290		
Detection limit	1.0	6.0	7.0	0.5	2.0	
UL (pH=6.2) for soils	230	800	300	2	75	
Sampling	Nov. 1997	Nov. 1997	Nov. 1997	Nov. 1997	Nov. 1997	Nov. 1997
1. Vacha – village of Kadievo	11	55	97	n.d.	26.2	5.83
2. Maritza river Plovdiv – 4 km	26	114	106	n.d.	44.3	6.32
3. Maritza river Plovdiv – center	7	144	144	n.d.	28.6	6.20
4. Maritza river Plovdiv – East	2	136	125	n.d.	33.9	6.04
5. Tsepelarska river near camping "Tchaja"	68	138	149	0.46	42.2	6.32
6. Maritza river after camping "Tchaka"	19	145	155	0.31	94.8	6.14

CONCLUSIONS

1. The Cu, Mn, Ni, Zn, Cr³⁺ and Cr⁶⁺ contents in the surface waters in the river Maritza, Vacha and Tchepelarska are in accordance with the requirements for waters III category (in accordance with the BG State Standards).

2. Higher Cd and Pb contents are determined. There is a tendency of increase during the autumn - November. Higher values are determined in the river Tchepelarska after mixing with the waters of the Maritza river.

3. The nitrate N, phosphates, sulphates and COD values show that the waters are classified as III category in accordance with the BG State Standards.

4. The Cu, Mn, Zn, Cd and Pb values in the sediments from Maritza, Vacha and Tchepelarska rivers are lower than UL for soil in Bulgaria.

5. The results from the monitoring investigation of the surface waters of the Maritza river in the region of Plovdiv, Bulgaria, and after their assessment show that those waters can be utilised for irrigation and industrial purposes.

6. Registered meteorological parameters had no significant influence on the measured values of the ground waters and sediments for the both sampling (June and November 1997).

REFERENCES

1. I. DYADOVSKI, J. STEFANOV: Ecological Evaluation and Protection of Flowing Waters. Tiliya Ltd., Sofia, 1995.
2. N. IGNATOVA: Protection of Waters. Technika, Sofia, 1992.
3. E. KOLEVA, R. PENEVA: Climatic Reference book. The rainfalls in Bulgaria, BAS, Sofia, 1990.
4. BSS Collection: Environmental Protection. Vols 1 and 2, Sofia, 1989.
5. E. MERCK: The Testing of Water. Darmstadt, 224. 1995.
6. Methods of Chemical Analysis of Water and Waste. Method 350.1 Environmental Monitoring and Support Laboratory (EMSL). Cincinnati, OH, 1983.
7. Standard Methods for the Examination of Water and Wastewater. APHA. AWWA WPCF, 16th edition, 1985

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