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Water pollution

MERCURY CONTAMINATION OF RIVER VARDAR

M. MALETIC*, AL. MALETIC

Faculty of Technology and Metallurgy, Skopje, FYROM

Abstract. The paper presents the results of investigation of mercury concentration in river water and in sediment, done in 1995, downstream of wastewater inflow. Determination of mercury concentration in river water and sediment was measured by flameless atomic adsorption spectrophotometry. Maximum concentration in river water was found at a distance of 0.1 km from chlorine alkaline wastewater inlet (5.1 μg Hg/l) and in sediment at a distance of 21 km (79.0 μg Hg/g). Downstream, mercury concentration was decreased slowly and after distance of 149 km, the concentration in river water and sediment was the same as before contamination.

Keywords: mercury, pollution, adsorption, transportation of mercury.

AIMS AND BACKGROUND

Until two years ago, the factory for chlorine-alkaline electrolysis with mercury cells used, release its waste waters into the river Vardar. Elementary mercury and mercury in ionic condition were released with the wastewaters, too. The transformation of the mercury and its compounds in water enables the transport and the distribution of this metal in the water, the sediment and the life form through the water.

This paper contains the results of the examinations taken on the sediments and the river water, downstream from the flooding channel of the factory, in 1995. The examination did not include the observation of the concentration of mercury and its compounds in the flora and fauna from the water.

EXPERIMENTAL

The characteristics of the water-flow and the choice of the measure points. Vardar is an international river that separates FYROM and R.Greece. The river flows through the west and central part of Macedonia in the length of 300 km. Treska, Lepenec, Kadina reka, Pcinja, Babuna, Bregalnica, Crna reka, Bosava and Luda Mara are the names of the tributaries that flow into this part of the river, that increase the average flow of the mean-waters from 19.37 m^3/s at Sarakinci to 135.96 m^3/s at Gevgelija.

* For correspondence.

The river flows through the following towns: Gostivar, Tetovo, Skopje, Veles, Demir Kapija and Gevgelija; many industrial capacities are located along the river, too.

All the communal and industrial wastewaters from the towns and the industry flow into the river and pollute its water.

Examinations on the sediment and the river water were taken in the period May-November 1995, from the river part Skopje – Gradec. The zero point was located on the flooding channel from the factory for chlor-alkaline electrolysis. This part of the river consists of few segments that differ in the speed of the water-flow, the free surface, the depth of the riverbed, the amount of water and the fall of the riverbed. The length of this part is 149 km.

The measuring points were selected in the parts where the river-flow is calm, which enables the deposition of the suspended substances during smaller flows and the re-suspension of the upper layers of sediments during high water-stand. The river parts with turbulent river-flow, as in the Taoric gorge and the gorge in Demir Kapija have not been examined.

Seven locations have been chosen:

1. Skopje — 0.1 km up the river from the zero point;
2. Markova reka — 0.2 km downstream from the zero point;
3. Jurumleri — 21.0 km downstream from the zero point;
4. Taor — 40.0 km downstream from the zero point;
5. Basino — 53.0 km downstream from the zero point;
6. Nogaevci — 92.0 km downstream from the zero point;
7. Gradec — 149.0 km downstream from the zero point.

The locations are shown in Fig. 1.

RESULTS AND DISCUSSION

The samples of the water and the sediment of the river Vardar were taken in May (21.05), August (27.08) and October (05.11.1995), i.e. in those periods of the year when high, minimum and average flows of the river are expected.

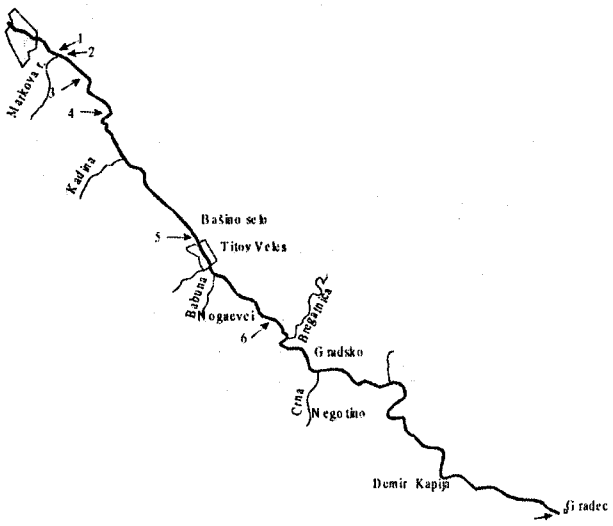

Fig. 1. The part of river Vardar Skopje – Gradec

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The examinations of the river water were taken in the terms of the following parameters: pH value, suspended matter, chemical oxygen demand through $KMnO_4$, dry residue at 105°C and 600°C and mercury concentration.

The results of the three adherent measurings are given in Table 1.

Table 1. Results of investigated parameters in river water

Location	Distace (km)	pH	Susp. mat. (mg/l)	COD (mg/l)	Dry residue (mg/l)		Hg conc. (mg/l)
					105°C	600°C	
			Measured at 21.05.1995				
Skopje	-0.1	7.20	78.00	13.58	203	132	0.0016
R. Markova	0.2	7.50	86.00	12.28	198	121	0.0051
V. Jurumleri	21.0	7.32	123.00	13.32	232	168	0.0038
V. Taor	40.0	7.39	89.00	13.07	207	140	0.0022
V. Basino	53.0	7.44	92.00	12.87	162	110	0.0017
V. Nogeevci	92.0	7.62	60.00	13.73	140	98	0.0015
Gradec	149.0	7.60	80.00	12.30	250	180	0.0012
			Measured at 27.08.1995				
Skopje	-0.1	7.13	22.00	12.08	181	108	0.0013
R. Markova	0.2	7.60	28.00	11.50	207	114	0.0050
V. Jurumleri	21.0	7.40	33.00	13.17	200	122	0.0041
V. Taor	40.0	7.52	17.00	12.86	197	136	0.0030
V. Basino	53.0	7.60	12.00	13.55	220	138	0.0023
V. Nogeevci	92.0	7.43	28.00	12.70	183	113	0.0016
Gradec	149.0	7.60	20.00	13.22	232	150	0.0014
			Measured at 05.11.1995				
Skopje	-0.1	7.25	30.00	13.17	190	112	0.0016
R. Markova	0.2	7.30	35.00	15.05	198	121	0.0042
V. Jurumleri	21.0	7.42	80.00	15.06	210	130	0.0039
V. Taor	40.0	7.35	53.00	13.60	189	114	0.0023
V. Basino	53.0	7.20	40.00	14.00	176	109	0.0016
V. Nogeevci	92.0	7.50	33.00	15.80	193	130	0.0016
Gradec	149.0	7.54	48.00	15.21	207	143	0.0014

The mercury concentration is calculated at 59 m^3/s mean flow, average year flow at Skopje.

The samples of solid specimen represent suspended material on the river bottom and are taken in the same period as the liquid specimen. Only fine fractions of the sediment, under 0.063 mm, are taken for analysis. Larger fractions, made almost of quartz and feldspat, are inert in relation of the mercury[1] and have not been analysed. The fractions under 0.063 mm are the deposited suspended substances that are characterised with large specific surface, organic substances, metal oxides and oxihydrates and their association with mercury.

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The results of the measuring of mercury concentration in the sediment[2] are given in Table 2.

Table 2. Mercury concentration in the sediment of river Vardar

Location	Distance (km)	Mercury concentration (mg/l)		
		21.05.1995	27.08.1995	05.11.1995
Skopje	– 0.1	0.0026	0.0020	0.0022
R. Markova	0.2	0.0054	0.0281	0.0026
V. Jurumleri	21.0	0.0464	0.0710	0.0712
V. Taor	40.0	0.0440	0.0690	0.0680
V. Basino	53.0	0.0161	0.0220	0.0170
V. Nogaevci	92.0	0.0130	0.0180	0.0160
Gradec	149.0	0.0020	0.0023	0.0026

The downstream changes of the concentration of mercury in the river water and the sediment are due to:

- dilution;
- sedimentation;
- ion exchange;
- biomethylation;
- evaporation.

Wastewaters from the factory for chlorine-alkaline electrolysis bring mercury into the river Vardar in elementary condition or in the form of complex compounds as: $HgCl_3^-$, $HgCl_4^{2-}$, $HgOH^-$, $Hg(OH)_3^-$, HgClOH. Maximum concentration of mercury in liquid phase is reached immediately after the industrial wastewaters have mixed with the river water, 200 m downstream from the flooding channel. As the distance from the pollution source increases, the concentration of mercury falls downstream. The reduction of the concentration in the water is not even. The fastest drop of the concentration is in the calm and non-turbulent part of the river (Jurumleri-Taor). In this part of the river largest concentrations of mercury in the sediment are registered. The calm flow of the river enables deposition of the appeared compounds of the mercury (II) with some present oxides in liquid phase like SiO_2, FeOOH, Al_2O_3, MnO_2 (Ref. 3), or for its coprecipitation with $Fe(OH)_3$ (Ref. 4).

The association of the metal ion with suspended substance can be achieved through:

- adsorption of the metal ion on the oxygen surface;
- ion exchange in the interior of the clay material;
- binding with the organic substances on the surface of the suspended particles, or
- adsorption in the kind of metal-ligand complex.

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Factors that influence the creation of these associations are the following: pH of the water environment, structure of the clay substances in the suspended particles, presence of organic substances that contain merkapto groups (–SH) and others. Hydrogen ions concentration is substantial for the creation of associations. The largest adsorption of mercury (II) appears in pH area from 7.5 to 8.2 (Ref. 5), seen from the adsorption isotherm for mercury (II) on iron (III) hydroxide, shown in Fig. 2. This pH area is normal for the river water.

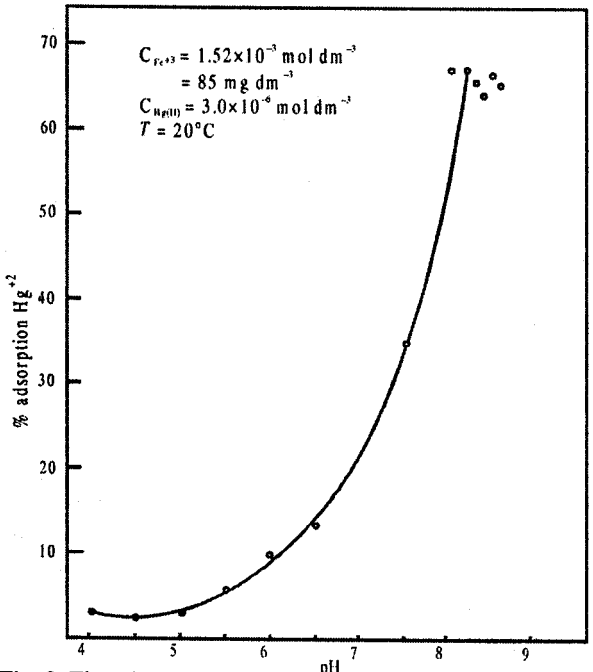

Fig. 2. The adsorption isoterm for mercury (II) on iron (III) hydroxide

When the wastewater and the water from the river have mixed, the deposition happens fast, which results in reduction of mercury concentration in liquid phase and its increase in the sediment. The maximum concentration of the mercury in the sediment is reached at 21 km downstream from the pollution of the river, and then falls through the water flow.

Microorganisms influence the desorption of mercury from deposited suspended substances. Biochemical process happens on the bottom of the riverbed and it transforms mercury in alkyl-mercury compounds: bimethyl mercury – $(CH_3)_2Hg$ and monomethyl mercury – $(CH_3)Hg^+$. This process is slow and presents a long-term source of contamination of the river with this metal even after the primary source of contamination has been removed.

Methyl-mercury goes into the atmosphere through volatilisation, while most of it accumulates in the aquatic animals. Due to its high solubility in fats and the affinity for the merkapto groups, mercury often accumulates in the brain, the central-nervous system and in the muscles of the fish[6].

CONCLUSIONS

The contamination of the river Vardar with mercury is mainly with local character. Extreme concentrations of this metal in the water and the sediment appear up

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to 21 km downstream from the point where the wastewaters empty into the river (200 m in the water and 21 km in the sediment). Then the concentration drops both in liquid and solid phase. Presence of mercury with anthropogenic character at 149 km from the factory channel is not recorded.

The pH value of the water and the type of the suspended particles have the biggest influence on the mercury distribution between water environment and the sediment.

Biomethylation processes have the biggest influence on the transport of mercury through the river. The methylation of the deposited mercury lasts many years, and with it the contamination of the water flow, too.

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