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HEAVY AND TOXIC METALS IN THE WASTE WATERS FROM SOME INDUSTRIAL FACILITIES IN THE TOWN OF SKOPJE, REPUBLIC OF MACEDONIA

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A b s t r a c t: This paper presents the results of several months' investigations carried out on the heavy metals and toxic metals in waste waters from the town of Skopje that flow into the River Vardar. The results discovered increased amounts of arsenic, manganese and silver in the waste waters that come from the activities in industrial facilities located in and around the town

Key words: heavy metals; toxic metals; arsenic; manganese; silver

INTRODUCTION

The town of Skopje is a large urban settlement with many industrial facilities that have great influence on the character and quality of the environment. The industry and traffic carry in various kinds of materials constantly changing the environment. This has a great impact on the quality of air, water, soil, plants, wildlife and, most of all, people.

The aim of the project entitled *Heavy and toxic metals in the waste waters from some industrial facilities in the town of Skopje* was the determination of the amount of heavy and toxic metal in the waste waters from the town that flow into the Vardar River.

The destructive activities of present day life of four billion people on the earth raises the issue of the survival of the global geosystem that may lead to changes that endanger the survival of the whole population.

Natural systems on earth, expected to change in the future, will develop free of human beings. The only losers will be people. Because of this and many other reasons the protection of the environment has become an important issue.

The scientific and technological evolution, made possible by great inventions in the field of natural sciences such as Biology, Chemistry, Geology, Physics, etc., contributed to the complex relationship between man and the environment inflicting significant changes to the ecological systems and the regulation of the biosphere.

Latest scientific and technological inventions have an impact on the pollution of the environment (water, soil and air) and to a decrease in the quality of arable land and the number of animal and plant species.

The substances representing the greatest pollutants are waste waters, waste gases, dust emission coming from chemical industry, metallurgy, mining activities and other industrial facilities. They are harmful components because they carry large amounts of heavy metals and toxic materials.

The amount of heavy and toxic metals is constantly increased by erosion processes. The increased concentration, however, comes from waste waters and materials from industrial facilities.

Heavy metals are characterized by the properties that they do not decompose and cannot adhere to the river bed sediment.

Some heavy metals such as As, Se, Te and Au can be affected by biochemical transformation and change to metall-organic compounds which are several times more toxic than the inorganic ones.

When heavy and toxic metals occur in increased concentrations in soil and water they can also be found in increased concentrations in various animal and plant species. As an example one should mention their effect on the decrease in the variety and density of population in highly contaminated areas. Waste waters containing increased amounts of heavy and toxic metals cause a change in the physical conditions in natural water systems and the pH in water.

The most common heavy metals pollutants are As, Cd, Cu, Pb, Hg, Ni, Zn, Cr, etc., and the most toxic ones are Hg, Pb, Cd, As, Se and Be. The possible most poisonous metals found in high concentrations are Sn, Ni, Cu, Zn and Co.

However, with heavy and toxic metals one must bear in mind the amount that defines the limit of toxicity in certain secondary geochemical environments. It is also noteworthy that some metals are necessary for the functioning of human organs as important processes to life. Poisoning happens only when the concentrations exceed the allowed concentrations by several times.

METHOD OF WORK

Analyses of surface waters, drinking water and waste waters provide information on the better assessment of the quality of water (among which the presence of toxic elements). They are necessary for the study of

- planning and purification of surface waters,
- preparation for the study of ecological monitoring, and
- the study of the effects of trace elements on the health of people, the water biotope, etc.

Analyses include determination of the contents of major elements such as Ca, Mg, Na, K and those on the order of mg/dm^3 as well as determination of contents of microelements in concentrations on the order of $\mu\text{g/dm}^3$.

The methods of analyses are supposed to be simple, fast and delicate. Several methods are used for this kind of analyses (atomic absorption spectroscopy, UV-VIS spectrometry, etc.). However, none of the methods mentioned above complies with the conditions. Lately, the method of emission spectroscopy with inductive connected plasma or AES-ICP is used because it complies with the requirements for analyses of various kinds of water samples.

AES-ICP is used as a method of routine simultaneous determination of major and trace elements for surface water samples, drinking water, waste waters because of

- the good sensitivity (low detection limits which are lower than maximum concentrations allowed),

- multielement determination (several elements can be determined simultaneously e.g., 16 elements analyzed in this paper),

- the time necessary for one analysis is short (e.g. around three minutes are necessary for an analysis of 16 elements),

- the high linear dynamic area of concentrations and minimum matrix effects (one can analyse the contents of major elements, subordinate elements and trace elements with the same precision as they are analyzed in samples of one single element).

The contents of elements examined were determined in atomic emission spectrometer with ICP, model Liberty 110, which is in condition.

The major characteristics of the Liberty 110 model are as follows:

Spectrometer:

holographic grid,
optical construction is 0.75 Czerny-Turner,
first order resolution of 0.018 nm,
wavelength are 189 – 940 nm.

Radio frequency generator,
computer controlled thickness of 0 – 1.7 kW,
operation frequency amounting to 40.68 MHz,

Sample of introduction system,
peristaltic pump (computer controlled),
Struman-Master dispersion chamber,
glass-concentric disperser.

RESULTS AND DISCUSSION

Table 1

Values measured for the concentration of heavy and toxic metals in the waste waters that flow into the Vardar River in the area of Skopje (in ppm). Time period: September 1998

	CK-1	CK-2	CK-3	CK-4	CK-5	CK-6
pH	8.0	7.9	7.75	7.9	8.0	8.0
As	0.04507	0.06176	0.07703	0.6719	0.08806	0.08074
Ag	0.01070	0.01238	0.01595	0.01413	0.00769	0.01097
Al	0.1831	0.1439	0.01459	0.1997	0.00042	0.03268
Ni	0.01699	0.00639	0.00356	0.00157	0.01222	0.00448
Mn	0.02238	0.01755	0.02527	0.02131	0.2799	0.01622
Fe	0.04770	0.06117	0.1056	0.03343	0.09101	0.1169
Cr	0.00458	0.00526	0.01170	0.01470	0.00321	0.00429
Mg	19.14	18.15	16.44	25.06	23.02	23.44
Na	65.20	40.71	136.4	38.99	50.14	109.3
Ca	83.62	88.31	88.17	90.79	88.87	70.47
Zn	0.04247	0.03529	0.06679	0.00996	0.02165	0.02092
Cu	0.03541	0.01792	0.03804	0.03372	0.00351	0.003646
Pb	0.00784	0.00923	0.00485	0.00541	0.00679	0.01462
Cd	0.00118	0.00148	0.00026	0.000484	0.00171	0.00056
Co	0.00736	0.00726	0.00070	0.02916	0.01336	0.00071
K	10.20	11.67	14.78	12.26	7.185	3.976

Table 2

Concentrations measured (in ppm) in river runoffs in the country

Element	1 & 2 category	3 & 4 category
As	0.05	0.05
Ag	0.01	0.02
Al	-	-
Ni	0.05	0.1
Mn	-	-
Fe	0.5	1.0
Cr	0.1	0.5
Mg	-	-
Na	-	-
Ca	-	-
Zn	0.2	1.0
Cu	0.1	0.1
Pb	0.05	0.1
Cd	0.005	0.01
Co	0.2	2.0
K	-	-

Table 3

Values measured for the concentration of heavy and toxic metals in the waste waters that flow into the Vardar River in the area of Skopje (in ppm). Time period: October 1998

	SK-1	SK-2	SK-3	SK-4	SK-5	SK-6
pH	8.0	7.8	7.8	7.9	8.0	7.9
As	0.03821	0.05223	0.06733	0.06115	0.07552	0.08321
Ag	0.01230	0.01150	0.01340	0.01512	0.00951	0.01120
Al	0.1750	0.1530	0.01220	0.1850	0.1030	0.04538
Ni	0.02031	0.00428	0.00280	0.00350	0.01520	0.00630
Mn	0.03321	0.02055	0.02820	0.03351	0.3750	0.02630
Fe	0.05570	0.07180	0.1532	0.04421	0.05551	0.2031
Cr	0.00437	0.00498	0.00543	0.01102	0.00342	0.00456
Mg	18.67	17.73	14.86	19.93	20.02	22.96
Na	67.32	45.38	128.05	28.50	39.20	98.30
Ca	85.30	87.20	91.30	95.69	85.20	75.50
Zn	0.02520	0.02021	0.03525	0.02850	0.00230	0.02282
Cu	0.03821	0.02052	0.04021	0.04272	0.00521	0.00431
Pb	0.00653	0.00821	0.00550	0.00630	0.00580	0.02031
Cd	0.00151	0.00171	0.00022	0.00025	0.00231	0.00033
Co	0.00428	0.00636	0.00025	0.03315	0.0118	0.00065
K	11.30	12.50	13.60	13.70	8.235	4.531

Table 4

Concentrations of heavy and toxic metals in the waste waters that flow into the Vardar River in the area of Skopje (in ppm). Time period: November 1998

	SK-1	SK-2	SK-3	SK-4	SK-5	SK-6
pH	8.0	7.9	8.3	7.9	7.9	8.35
As	0.1572	0.05389	0.01895	0.2507	0.08126	0.03275
Ag	0.01213	0.01178	0.00793	0.00285	0.00471	0.00402
Al	0.1540	0.00835	0.00039	0.01044	0.1244	0.00839
Ni	0.01889	0.01217	0.00561	0.00546	0.01665	0.00182
Mn	0.01929	0.01286	0.01519	0.0223	0.4562	0.00244
Fe	0.04854	0.03648	0.03567	0.04192	0.04392	0.02282
Cr	0.00409	0.00128	0.00673	0.00621	0.00644	0.01482
Mg	18.62	17.07	15.16	14.36	20.76	14.53
Na	68.10	31.71	38.56	41.67	32.89	78.63
Ca	82.74	84.61	79.45	78.52	81.56	28.37
Zn	0.04419	0.01667	0.04402	0.02111	0.02398	0.02945
Cu	0.01819	0.02006	0.04230	0.01710	0.01322	0.00326
Pb	0.00167	0.00240	0.01316	0.01322	0.00409	0.01575
Cd	0.00036	0.00030	0.00096	0.00242	0.00299	0.00012
Co	0.00227	0.02036	0.00030	0.01132	0.01241	0.02827
K	11.13	10.85	16.77	12.56	5.344	4.732

Table 5

Concentrations of heavy and toxic metals in the waste waters that flow into the Vardar River in the area of Skopje (in ppm). Time period: December 1998

	SK-1	SK-2	SK-3	SK-4	SK-5	SK-6
pH	8.05	8.2	8.2	8.0	7.9	7.2
As	0.05585	0.02755	0.2068	0.01045	0.02661	0.1220
Ag	0.01461	0.02403	0.04745	0.02236	0.03491	0.0297
Al	0.1768	0.1465	0.1568	0.1600	0.1663	0.2471
Ni	0.01462	0.00738	0.00492	0.01965	0.03246	0.01551
Mn	0.01705	0.01523	0.01887	0.03414	0.5316	0.00611
Fe	0.06476	0.04473	0.05287	0.09153	0.5855	0.02935
Cr	0.00290	0.00367	0.00963	0.00067	0.00019	0.00082
Mg	20.53	19.13	16.32	19.73	22.58	21.85
Na	43.01	32.62	41.78	56.89	67.08	146
Ca	102.4	105.1	103.9	101.0	111.9	157.0
Zn	0.07375	0.04016	0.07154	0.1040	0.02889	0.00112
Cu	0.03521	0.02228	0.05704	0.02289	0.01536	0.0091
Pb	0.02134	0.00637	0.00995	0.00325	0.00323	0.00091
Cd	0.00079	0.00138	0.00008	0.00273	0.00109	0.00170
Co	0.00831	0.00762	0.00429	0.01301	0.00414	0.00794
K	9.314	8.768	16.47	14.71	12.21	4.306

Table 6

Concentrations of heavy and toxic metals in the waste waters that flow into the Vardar River in the area of Skopje (in ppm). Time period: January 1999

	SK-1	SK-2	SK-3	SK-4	SK-5	SK-6
pH	8.85	8.25	8.60	8.05	8.35	8.15
As	0.07016	0.1735	0.2314	0.1539	0.07588	0.1819
Ag	0.01051	0.00572	0.00731	0.00153	0.00026	0.00174
Al	0.04064	0.1999	0.01736	0.2592	0.00403	0.00983
Ni	0.01659	0.00095	0.00381	0.01769	0.00854	0.00376
Mn	0.01734	0.01116	0.01333	0.01866	0.2008	0.00044
Fe	0.05037	0.03033	0.04343	0.05392	0.2585	0.01024
Cr	0.00248	0.00303	0.00351	0.00357	0.00483	0.00064
Mg	16.63	16.12	14.31	13.44	11.54	18.29
Na	45.80	26.50	33.11	39.81	21.60	16.93
Ca	77.95	78.17	78.36	76.72	63.71	73.00
Zn	0.04837	0.03536	0.06689	0.04889	0.02839	0.00680
Cu	0.01046	0.00143	0.02340	0.00048	0.00461	0.00548
Pb	0.02761	0.01064	0.01718	0.03965	0.01813	0.00655
Cd	0.00005	0.00050	0.00003	0.00009	0.00098	0.00030
Co	0.00534	0.00971	0.00661	0.01060	0.00173	0.00389
K	5.111	4.468	9.855	7.668	3.964	2.244
P	2.170	2.335	5.843	5.191	1.933	1.394
N/NO ₃ ⁻	14.504	10.529	16.389	14.463	6.002	20.814

Table 7

Concentration of heavy and toxic metals in the waste waters that flow into the Vardar River in the area of Skopje (in ppm). Time period: February 1999

	SK-1	SK-2	SK-3	SK-4	SK-5	SK-6
pH	8.40	8.30	8.50	8.15	8.25	8.20
As	0.06025	0.1842	0.2521	0.1678	0.08232	0.1712
Ag	0.01125	0.00452	0.00651	0.00142	0.00015	0.00145
Al	0.05225	0.2011	0.02231	0.1552	0.00452	0.00512
Ni	0.01320	0.00331	0.00251	0.01321	0.00653	0.00313
Mn	0.01534	0.01416	0.01220	0.01750	0.2122	0.00022
Fe	0.04020	0.03530	0.04542	0.06092	0.2858	0.01320
Cr	0.00351	0.00423	0.00313	0.00363	0.00521	0.00025
Mg	15.50	17.10	13.20	14.50	12.45	18.45
Na	44.20	29.31	32.12	38.15	22.30	18.50
Ca	78.16	77.13	75.22	75.31	65.60	72.00
Zn	0.03250	0.03336	0.06898	0.04543	0.03039	0.00712
Cu	0.01150	0.00132	0.02150	0.00032	0.00411	0.00323
Pb	0.02561	0.01130	0.01650	0.03232	0.01513	0.00453
Cd	0.00031	0.00042	0.00002	0.00007	0.00052	0.00022
Co	0.00424	0.00871	0.00341	0.01130	0.00162	0.00421
K	5.155	4.321	8.621	7.530	4.250	3.250
P	2.160	2.250	5.630	5.200	2.130	1.432
N/NO ₃ ⁻	13.200	11.350	15.420	13.350	8.120	21.211

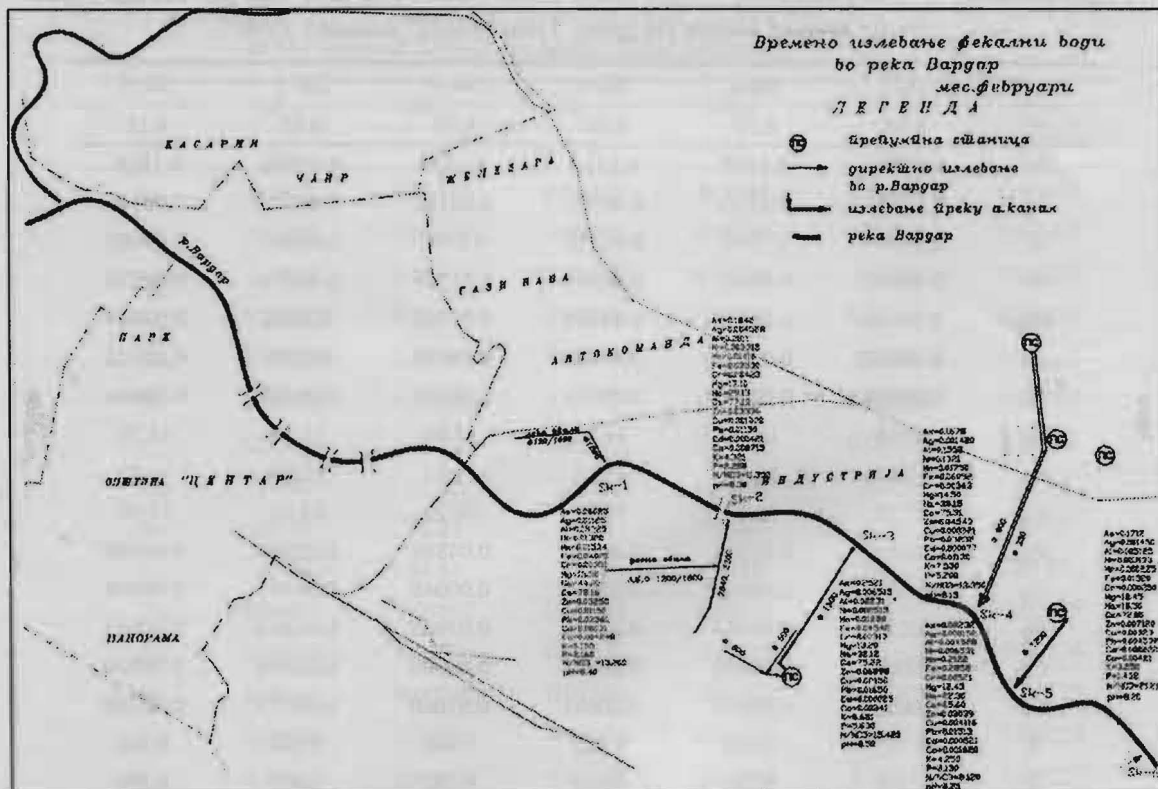


Fig. 1. Temporal faecal discharge in the River Vardar

Elements determined in all six gauging stations in Skopje are as follows: As, Ag, Al, Ni, Mn, Fe, Cr, Mg, Na, Ca, Zn, Cu, Pb, Cd, K. Based on the results obtained it can be concluded that only two elements show a continuously increased value in almost all measure sites (Fig.1). They are arsenic and silver. In one case only increased concentration of iron was found in December. In all other measure sites elements were within the allowed limits over the whole time period of survey. The increased concentration of arsenic and silver should be studied in terms of discovering the facility that causes the pollution. Most probably some industrial facilities use raw materials or semi-finished products which contain increased contents of arsenic and silver. A prompt discovery of the location of these facilities is necessary in order to take measures for solving the issue.

A comparison between these data with those obtained from investigations on the quality of water of the Bregalnica River (Boev et al., 1997) indicates that the highest values of As measured for the water of the Bregalnica along its flow through the town of Štip range from 0.12 to 0.18 ppm, whereas in the Vardar River they reach 0.25 ppm which is five times higher than the concentrations allowed for As in running water.

The As concentration in the upper course of the Bregalnica River where waste water from industrial facilities with As in the production proc-

esses flow in (reagents in waste ore) from the Sasa Pb-Zn mine are also much higher. In the lower course measurements indicate that As concentration is much lower due to its slow mobility geochemical properties (Boev, Lepitkova, 1998).

Investigations carried out in the upper course of the Kriva River show increased concentrations that are above the allowed concentrations of almost all heavy metals. This is due to increased pollution by waste waters coming from the flotation plant in the Toranica mine.

Investigations carried out in the area of the Zletovska River indicate increased concentrations in the inflowing water from the Kiselički Potok (stream) where waste waters are discharged after the processing of the Pb-Zn ore from the Zletovo mine (Boev et al., 1994, 1998) the most common being Pb, Zn and Cd. There, As occurs in increased amounts, whereas along the Zletovska River course its concentration decreases and at the mouth of the river and the Bregalnica the concentrations of As are within the limits allowed.

Comparisons with the quality of waters in other rivers in the territory of Eastern Macedonia indicate that besides As and Ag concentrations of other elements in the Vardar River are within the limits allowed. This is not the case with waters in other parts of Eastern Macedonia where increased concentrations of other heavy metals are also found.

CONCLUSION

Based on the results obtained from the investigations on the quality of waters in the Vardar River, in terms of pollution by heavy metals, it can be concluded that the amount of these concentration is within the limits allowed. Deviation were found only in the amounts of As and, in a few analyses, in the amount of Ag. Based on the comparisons with the quality of water in some rivers in Eastern Macedonia it can be concluded that the Vardar River is not highly polluted by heavy metals from waste waters coming from industrial facilities along its course through the town of Skopje. Much higher concentrations of heavy met-

als are found in other rivers. That is the result of inflow of discharged waste waters after the mineral processing of Pb-Zn ore into the river basins without any purification. This indicates that in the near future measures should be taken for the purification of waste waters from industrial facilities. This would upgrade the quality of waters in the Republic of Macedonia to I and II quality of running waters which is considered to be safe water. This would have an immediate impact on the better quality of flora and fauna that live in the waters.

REFERENCES

Boev B., Lepitkova S., 1995: *Concentration of heavy metals in the waters of river Kiselica*. 6th Balkan Conference of Mineral Processing, Ohrid.

Боев Б., Лепиткова С., Зајкова В., 1997: *Одредување на квалитетот на водите од река Брегалница и водоводот на град Штип со методата на AES-*

ICP. 15-ти конгрес на хемичарите и технолозите на Македонија, Скопје.

Боев В., Лепиткова С., Веселиновска С., 1998: *Pollution of heavy metals in part of territory of the Republic of Mace-*

donia, data on pollution of water, soils, flora and fauna. XVI Congress of the Carpathian-Balkan Geological Association, Vienna.

Резиме

ТЕШКИ И ТОКСИЧНИ МЕТАЛИ ВО ОТПАДНИТЕ ВОДИ НА ОДДЕЛНИ ИНДУСТРИСКИ ОБЈЕКТИ ВО ГРАДОТ СКОПЈЕ

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Клучни зборови: тешки метали; токсични метали; арсен; манган; сребро

Во овој труд се прикажани резултатите од повеќемесечните истражувања на проблемот на присутноста на тешките и токсичните метали во отпадните води на градот Скопје кои се влеваат во реката Вардар. Овие истражувања во основа дадоа резултати со

кои се констатираат зголемени содржини на арсен, манган и сребро во отпадните води на градот Скопје, а кои се директна последица на работата на индустриските објекти кои се лоцирани во градското подрачје.