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ACCUMULATION OF HEAVY METALS IN WATER, BIOTA AND SEDIMENT IN SOME ALBANIAN RIVERS

Lirika KUPE[1], Aleko MIHO[2], Alqi ÇULLAJ[2] and Pranvera LAZO[2]

1 Agricultural University of Tirana, Department of Plant Production, Kodër Kamëz.
e-mail: lirika_kupe@yahoo.com
2 University of Tirana, Faculty of Natural Sciences, Bulevardi “Zogu I”. e-mail: amiho@icc-al.org

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SYNOPSIS

In this paper are given some general consideration regarding to bioaccumulation of heavy metals in the green algae *Cladophora glomerata,* in water and sediment which were collected in some important Albanian rivers (Mati and Fani, Ishmi, Lana and Tirana, Shkumbini, Semani, Osumi and Gjanica). The sampling was done during the period May 2002-March 2004. More than 90 sampling were collected. In 28 of them are dominated by *Cladophora glomerata* which is considerate as bio-indicator of water environmental polluted by the nutrients (N & P), as well as, by the heavy metals. Beside them, additional parameters were measured, like conductivity, dissolved matter, pH, temperature, oxygen, suspended solids, nitrates, nitrites, ammonium and phosphates.

INTRODUCTION

Human destructive influence on the aquatic environment is in the form of sub lethal pollution which results in chronic stress conditions that have a negative effect on aquatic life. Heavy metals are stable in environmental contaminants of water. Heavy-metal pollution causes reduction in species diversity leading to the dominance of a few tolerant algal forms. The primary productivity also decreases after metal supplementation. *Cladophora* is part of green algae group. It is considered as one of the leading producer of the food chain in water. Due to the green color they participate actively in the photosynthesis process. In many cases heavy metal content in algae shows that they can be considered as the best indicators of aquatic ecosystems pollution. This is especially apparent for the lead contents in algae (Forster, 1982; Levkov, 2001). Also, *Cladophora* is considered as a good collector of nutrients (nitrogen and phosphorus) and heavy metals in water, (Borovitzka & Norris, 1986; Whitton et al., 1981). The aim of this study was to assess the amount of heavy metals (Zn, Mn, Fe, Pb, Cd, Cu, Cr and Ni) in biota, water and sediment. Besides heavy metals (measured in water, sediment and nitrates, nitrites, phosphates and ammonium measured in water) were measured and other parameters such as conductivity, oxygen, pH, temperature, solid waste in suspension. The main source of heavy metals in natural waters is pollution from mining areas (Miho et al., 2005).

MATERILAS AND METHODS

SAMPLING STATIONS

Monitoring was carried out in 12 stations: Mati (Shkopeti: Ma1, Milot: Ma3) with branch Fani (Rubiku: Ma2) Ishmi (Fushe-Kruja: Is3) with branch Tirana (Brari: Is1) and Lana (Kashari: Is2); Shkumbini (Labinoti: Sh1, Paperi: Sh2, Rrogozhina: Sh3) Semani (Mbrostari: Se4) with it´s branch Gjanica (Fier: Se3) and Osumi (Berati: Se1, Uravajgurore: Se2). The selection of sampling stations in the rivers of Mati, Ishmi, Shkumbini and Semani was made according to better representative's criteria of water situations, depending on the degree of human impact. In this way, the first sampling site represent the most clean or not polluted area, while other stations are located in the lower stream (west side of country), nearby industrial or urban areas. In total were carried seven expeditions: two in 2002 (May, November), four in 2003 (May, July, September and November) and one in March 2004. Based on expeditions carried out, *Cladophora* has not been always present in all seasons and all sampling stations has dominated during spring-summer, while during autumn and winter, is collected in a few sampling stations. Usually, this algae prefers clean and illuminated area (Graham et al., 1982) and appear during warm seasons (Whitton et al., 1989). From the conducted study, *Cladophora* was collected in the following stations during these periods: May ´02 (Ma1, Ma2, Ma3, Is1, Is3, Se2) Nov ´02 (Ma1, Is1), May ´03 (Ma1, Ma2, Ma3, Is1, Is3, Sh1, Sh2, Sh3, Se1, Se2, Se3) July ´03 (Ma1, Ma3, Is1, Sh1, Sh2, SH3, Se1, Se2), September ´03 (Ma1, Is1, Se1).

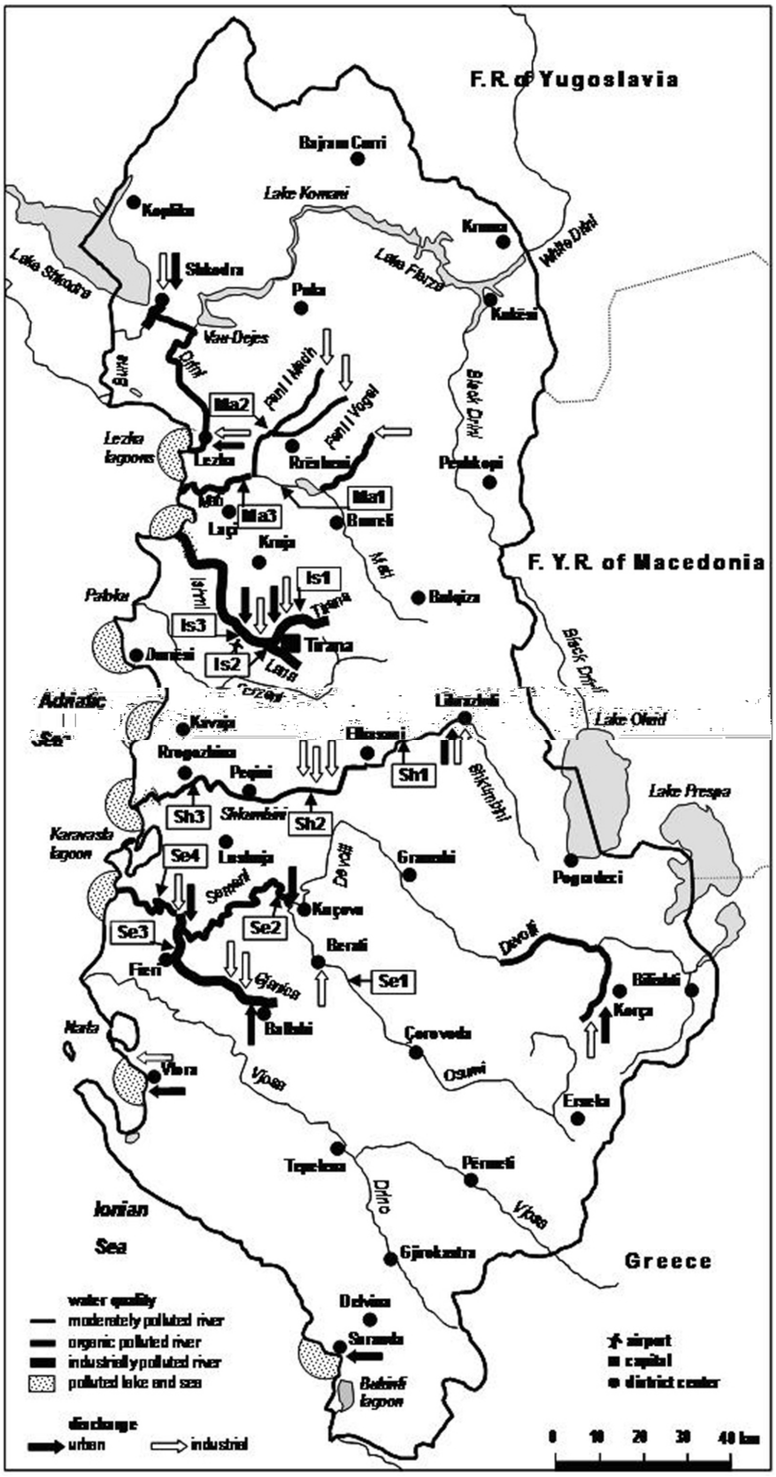


Figure 1: Hydrological map of Albania with sampling sites (UNEP, 2000).

CHEMICAL ANALYSIS

The samples of green algae (*Cladophora*) were collected in spring, summer and autumn in Layer Rivers. The samples were collected in plastic bottles, were preserved in refrigerator box (Whitton et al., 1989) and later were sent to the laboratory. Incision of plant samples and sediments were made by wet mineralization by Haswell, (Haswell, 1991). Heavy metals were analyzed by the Atomic Absorption Spectrometry (AAS) method, using Varian apparatus Specter AA 10 +. Water samples were analyzed by flame (for Fe, Mn, Zn), graffiti oven technique (for Cu, Pb, Cd, Cr, Ni) and cold steam techniques (for Hg) at the Analytical Chemistry Section, Faculty of Natural Sciences. Algae were treated in a mixture of HCl: HNO3 (3:1) in half pressure test tube. Dissolution was conducted at room temperature for 5 days, initially heated for two hours at 80-90^{o}C and then for three hours at 250^{0}C. Metals Fe, Zn, Mn, Cu and Ni were determined by the AAS (Atomic Absorption spectroscopy) system. While the metals Cr, Cd, Pb were determined by ETA-AAS (Electro-Thermal Atomic Absorption Spectroscopy atomization) system, while Hg was determined by CV AAS (Cold Vapor Atomic Absorption Spectrometry system) (Haswell, 1991). Besides heavy metals in water, biota and sediment were measured and physic-chemical parameters like: conductivity, pH, temperature, oxygen (O_2 mg-l and DO%), (TDS), suspended solids (TSS), nitrates, nitrites, ammonium and phosphates (Tab.1).

Table 1: Mean values of physic - chemicals parameters in Rivers of West Lowland.

Parameters	Ma1	Ma2	Ma3	Is1	Is2	Is3	Sh1	Sh2	Sh3	Se1	Se2	Se3	Se4
Temp.°C	15,5	16,0	16,2	115,8	17,9	19,0	15,4	15,9	17,3	16,3	16,8	20,0	19,2
pH	8,1	8,1	8,0	8,2	7,7	7,5	8,2	8,1	8,2	8,3	7,9	7,7	8,1
Cond. . µS/cm	232,9	221,6	223,2	388,0	633,1	609,4	277,3	353,4	341,9	334,8	357,1	836,3	506,3
TDS mg/l	128,0	126,2	129,1	198,4	330,2	316,4	143,6	182,6	176,4	156,2	192,8	455,3	248,6
DO .mg/l	9,6	9,0	9,4	9,0	3,0	2,2	9,5	9,3	8,6	8,7	8,3	3,2	8,1
DO .%	98,4	96,5	97,4	94,2	31,9	23,6	103,5	99,4	93,3	93,2	89,3	34,8	90,8
TSS. mg/l	37,3	34,1	53,0	73,2	117,2	84,9	114,9	137,1	143,1	141,7	142,8	111,5	286,2
NO3-N. mg/l	1,7	1,9	3,2	6,0	5,2	3,8	4,8	10,3	3,6	2,5	2,2	10,6	7,1
NO2-N. mg/l	0,0	0,0	0,1	0,1	1,6	1,1	0,1	0,2	0,2	0,1	0,1	1,1	0,1
NH4-N. mg/l	0,2	0,2	0,2	0,3	18,1	7,2	0,3	0,3	0,3	0,3	0,4	2,8	0,2
PO4-P. mg/l	0,035	0,014	0,020	0,054	2,783	1,014	0,264	0,037	0,042	0,020	0,032	0,514	0,027

Temperature, pH, conductivity, total cases and dissolved oxygen were measured with precision directly in the sampling stations, using a field camera - Multi / Parameter Meter (model 5465015 - ION156 sense). But NO_2-N, NO_3-N, NH_4-N, and PO_4-P were measured by UV-VIS Spectrophotometer, using standard methods recommended by AWWA (American Water Works Association), APHA

(American Public Health Association) and WPCF (Water Pollution Control Federation).

RESULTS AND DISCUSSIONS

Physic-chemical characteristics show that *Cladophora* is an important indicator for heavy metals monitoring in water, (Kelly & Whitton, 1995; Whitton, 2002; Whitton et al., 1981). Heavy metals such as: Fe, Mn, Zn, Cu, Pb, Cd, Ni, Cr, etc., were measured in sediments, in biota (mainly in filamentous of green algae *Cladophora*) and in water. Their average values in water, in sediments and in biota are given in tables 2 and 3.

Contents of heavy metals in water are closely associated with water quality; increase of concentration and decrease of alkalinity may risk living species and further uses of water.

The communal waste waters from the capital of Tirana, Durresi, Berati, Elbasani, Rrogozhina etc. have a great impact on the rivers that are mentioned above. This could be as a result of the huge load of organic substances, phosphates and sulfates with communal origin. The maximal values for the concentration of Fe, Cd, Pb and Zn are determined in Mati river due to the load of waste waters from the former industrial plant (Tabs. 2 & 3).

Table 2: Mean value of heavy metals (Fe, Mn, Zn) in water, biota and sediment in rivers of West Lowland (mg/l, dry weight).

Concentration of heavy metals (mg/l)	Ma1	Ma2	Ma3	Is1	Is2	Is3	Sh1	Sh2	Sh3	Se1	Se2	Se3	Se4
Fe, mg/l (Water)	0,03	0,06	0,06	0,37	0,06	0,06	0,5	0,09	0,04	0,03	0,06	0,06	0,22
Fe, mg/l (Biota)	2,7	736,1	917,4	2,4	0	3,5	2,4	3,3	1,7	3,3	2	3,1	0
Fe, mg/l (Sediment)	4,5	5,6	7,3	4,7	6,7	9,3	4	3,6	5,3	4	4,1	3,5	5,1
Mn, mg/l (Water)	0,04	0,04	0,04	0,06	0,15	0,15	0,07	0,08	0,06	0,05	0,07	0,09	0,06
Mn, mg/l (Biota)	359,1	380,3	921,7	344,5	2,9	388,6	617,7	463,8	579	341,8	329	290,4	400,6
Mn, mg/l (Sediment)	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0	0	0	0
Zn, mg/l (Water)	0,01	0,02	0,01	0,01	0,02	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01
Zn, mg/l (Biota)	9,7	39.9	25,8	16,6	0,1	29,5	13,6	23,5	1	35,9	4,9	7,8	0,1
Zn, mg/l (Sediment)	131,4	527,9	492	137,3	172,1	129,3	102,9	69,6	142,7	85,6	112,4	98	86,8

From literature, *Cladophora glomerata* is known as a species that accumulated high quantity of heavy metals in it's tissues (Borovitzka & Norris, 1986; Whitton et al., 1981). From our results of this study, that *Cladophora* is not always present during sampling periods and sampling sites. Compared to water, the sediment is considered as a good collection of heavy metal (Tabs.2 and 3) (Johnson, 1998).

Table 3: Mean value of heavy metals (Cu, Pb, Cd, Ni, Cr) in water, biota and sediment in rivers of West Lowland (µg/l, dry weight).

Concentration of heavy metals (µg/l)	Ma1	Ma2	Ma3	Is1	Is2	Is3	Sh1	Sh2	Sh3	Se1	Se2	Se3	Se4
Cu, µg/l (Water)	1,4	1,12	0,78	1,06	3,92	1,85	0,61	1,9	1,21	1,53	0,82	0,8	2,84
Cu, µg/l (Biota)	41	214,6	22,3	37,9	169,7	55	28,9	33,6	71,5	57,4	58	65,9	100,9
Cu, µg/l (Sediment)	45,7	73,4	83,7	45,3	88,7	59,8	35,9	38,6	43,5	31,8	23,3	35,4	32,4
Pb, µg/l (Water)	0,8	1,1	1	0,86	1,28	1,42	1,08	1,06	1,16	1,14	0,9	1,76	1,32
Pb, µg/l (Biota)	10,3	33	1	8,7	133	29,3	11,6	11	19,7	10,1	16,5	24,6	47,4
Pb, µg/l (Sediment)	907,8	1,1055	1,143	876	377,7	756,6	864,2	837,8	795,2	865	889	689,5	805,2
Cd, µg/l (Water)	0,21	0,52	0,12	0,15	0,15	0,09	0,13	0,26	0,14	0,1	0,76	0,39	0,1
Cd, µg/l (Biota)	206,4	455	0,3	213,8	272,5	310,7	269,9	233,7	315,6	238,7	330	418,8	979,4
Cd, µg/l (Sediment)	365,4	288,2	285,9	190,3	114,8	152,1	386,5	370,4	419,2	259,7	288	169,8	351,9
Ni, µg/l (Water)	1,86	1,36	2	3,32	4,4	3,56	4,16	4	3,62	2,46	3,2	8,18	7,52
Ni, µg/l (Biota)	120,9	147,3	26,7	75,8	92,3	116,7	220,3	177,5	184,8	127,8	189	129,4	398,8
Ni, µg/l (Sediment)	170,5	139	160,4	143,6	96	98	284,1	231,5	190,9	138,1	127	154,3	169,4
Cr, µg/l (Water)	1,94	1,86	2,18	2,03	2,75	2,03	3,08	2,28	2,44	2,56	2,46	1,78	5,3
Cr, µg/l (Biota)	102,8	83,2	21,9	74,6	128,9	193,2	156,7	139,3	120,7	138	91,9	191,5	158,6
Cr, µg/l (Sediment)	39	35	42,9	33,5	26,7	33,6	34,6	34,6	37,4	34,7	32,9	27,6	23,6

Although, their concentration in the sediment has not a good correlation with their concentration in the waters of rivers, (Verloo & Cottenie, 1985). The contents of Cu at Rubiku (Ma2) and Miloti (Ma3) stations are higher than the Mati (Ma1) station (Tab.3). This comes as a result of the impact of the metallurgical plants of copper in Rubik.

The concentration of heavy metals depends significantly from pollution sources, which is influenced by climatic conditions, wind direction and rainfall distribution (Miho et al., 2005). Their concentration decreases depending on the distance from the pollution source. Urban and industrial waste discharge in rivers cause increasing pollution within heavy metals.

The intensity of heavy metals accumulation in algae is higher than in water, as a result *Cladophora* is used as an object of monitoring. Although such monitoring may be more feasible during the spring - summer seasons but in winter the green algae are not dominating the aquatic ecosystems of rivers or are totally degraded (Levkov & Krstic, 2002), so are an unsuitable for chemical analysis. *Cladophora´s* growth is conditional by the concentration of nitrates, phosphates (Millner et al., 1982), light (Graham et al., 1982), temperature (Whitton et al., 1989), etc.

Based on the NIVA-s classification (Norwegian Institute for Water Research - NIVA), (Bratli, 2000), most of the sampling stations belong to class III and IV. Norwegian classification (Table 4), (Bratli, 2000), takes into consideration the levels of heavy metals in water and sediment. Maximum values of Cu in water (respectively 3.92 µg/l) were found in Lana (Is2) and belong to class IV.

Table 4: Classification of water quality based in heavy metals in water, biota and sediment (based in Norwegian Institute for Water Research - NIVA) (Bratli, 2000).

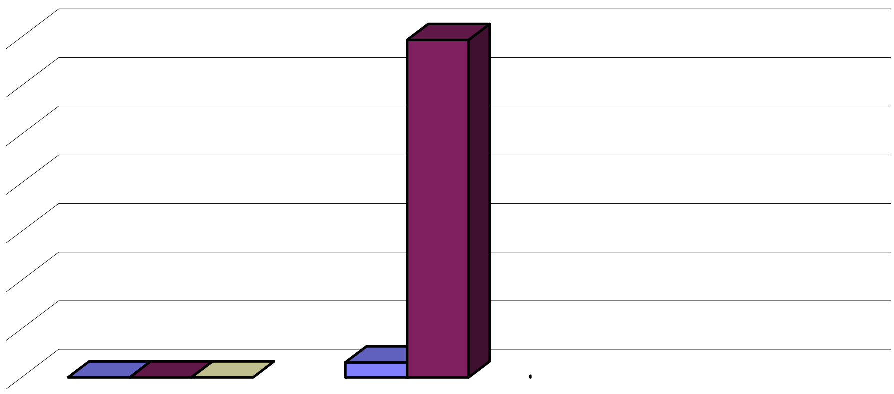
Kind of samples	Metals	Quality class of water				
		I	II	III	IV	V
		Easily polluted	Average polluted	Polluted	Heavy polluted	Very heavy polluted
Water (µg/L)	Cu	< 0,6	0,6-1,5	1,5-3	3,0-6,0	> 6
	Zn	< 5	5,0-20,0	20-50	50-100	> 100
	Cd	< 0,04	0,04-0,1	0,1-0,2	0,2-0,4	> 0,4
	Pb	< 0,5	0,5-1,2	1,2-2,5	2,5-5	> 5
	Ni	< 0,5	0,5-2,5	2,5-5	5,0-10,0	> 10
	Cr	< 0,2	0,2-2,5	2,5-10	10,0-50,0	> 50
	Hg	< 0,002	0,002-0,005	0,005-0,01	0,01-0,02	> 0,02
Sediment (mg/kg)	Cu	< 30	30-150	150-600	600-1800	> 1800
	Zn	< 150	150-750	750-3000	3000-9000	> 9000
	Cd	< 0,5	0,5-2,5	2,5-10	10,0-20,0	> 20
	Pb	< 50	50-250	250-1000	1000-3000	> 3000
	Ni	< 50	50-250	250-1000	1000-3000	> 3000
	As	< 5	5,0-25,0	25-100	100-200	> 200
	Hg	< 0,15	0,15-0,6	0,6-1,5	1,5-3	> 3

While maximum values for Pb (1.42 µg/l) were found in Ishmi (Is3) and belong to class III. Relatively high value were found for Cd (0.76 µg/l) and Ni (8.18 µg/l) in water according to NIVA-s belong to class V (Tab. 2). High values of Cd and Pb come as a result of solid waste discharge from urban and rural areas.

Accumulation of heavy metals in algae is an efficient method that allows a convenient way to determine the average pollution of waters, in a fixed period of time. However, it depends largely on the accumulative capacity of each organism.

Based on NIVA-s classification, assessment of heavy metals were analyzed and in sediment (Miho et al., 2005).

For the values of Zn, Pb and Cd most of the monitoring stations belong to the first class of NIVA-s; also for the content of Hg in waters in Shkumbini (Sh1 and Sh2) belong to the first class too. Regarding to the content of elements Cu, Ni and Hg most of the stations belong to class III and IV. Highest values of heavy metals were found in Fani (Rubik) and Mati (Ma2 respectively 527.9 mg/l and 492.0 mg/l in Ma3), (Tab. 1 and 2) that belong the class III. The content of Cu in stations Fani (Ma2 were respectively 73.4 µg/l); Mati (Ma3 were respectively 83.7 µg/l) and the peak of 88.7 µg/l was found in Lana (Is2) that is higher than in station Mati (Ma1).



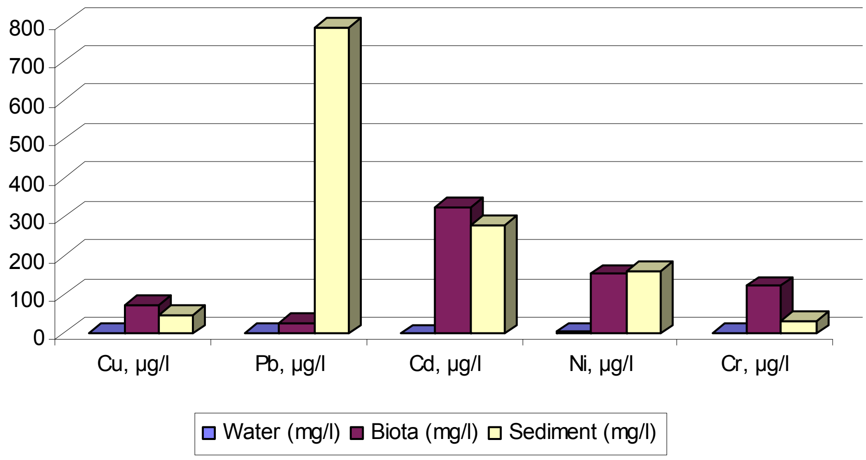


Figure 3: Average value of Cu, Pb, Cd, Ni and Cr in water, biota and sediment.

CONCLUSIONS

From this study we concluded that *Cladophora glomerata* was not collected in all stations and all sampling periods. This is a result of water eutrophication and as a result of inadequate conditions for the growing of algae (*Cladophora*). In general assessment based on the classification of NIVA-s most of the monitored rivers belong to III and IV classes. The highest values of heavy metals are measured in stations of Lana, Gjanica and Ishmi (Is2, Is3 and Se3), (Class IV), this is a result of higher values of nutrients in the water (eutrophication). Relatively high values for Pb were found in Ishmi, Lana and Osumi - May 2002, according to 2.9 mg/l, where most of the stations belong to III and IV classes. While lower values of lead are found in Ishmi river, (Lana, November 2003, respectively 0.2 mg/l). Lower values of cadmium were found in the Ishmi (Is3) 0.09 µg/l and Semani rivers (Se3) 0.10 µg/l, while the highest in the Osumi river (Se2) approximately 0.76 µg/l. The high values of Cd and Pb were caused by urban and rural discharge. In river sediments were found a high concentration of Fe, Zn, PB, Ni, Cd, Cu. The concentration of heavy metals in sediment increases in the sequence of Pb>Cd>Ni>Cu> Cr. But according to biota following the sequence Cd>Ni>Cr>Cu>Pb. Distribution of heavy metals in biota and sediment is related to the geological structure of sediment. Discharge of industrial waste waters and rivers, among other causes significant increase of pollution with heavy metals.

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