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Article

Pollution of Heavy Metals in the White Drin River Basin

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Abstract: Dirty water is usually a significant factor for many diseases. In Kosovo, only 9% of freshwater was used for drinking, and the rest was used in agriculture and industry. The waste from industry and agriculture was the biggest polluter of water. In this study, pollution of heavy metals in the White Drin River Basin was evaluated. Some physicochemical parameters of water samples, such as pH value, electrical conductivity, alkalinity, hardness as well as concentrations of HCO_3^- and CO_3^{2-} were measured, and concentrations of nine elements in water samples were determined by ICP-MS technique. The concentrations of Cu, Zn, Pb, Cd, Mn, As, Fe, Co and Ni were 4.05 - 22.2, 3.67 - 54.8, 2.81 - 35.1, 0.20 - 2.61, 1.60 - 38.2, 0.27 - 0.81, 22 - 77, 0.03 - 0.211 and 0.8 - 2.69 mg/L, respectively.

Keywords: heavy metals; water quality; physicochemical parameter; ICP; MS.

1. Introduction

When Homo sapiens appeared for the first time on earth 2.5 million years ago, they presented their need for human settlement construction affecting the environment. Actions from early Homo sapiens were primarily limited on environmental influences, which did little harm to the environment. However, human impacts of the modern era action in land leaved marks. As people advance in science and technology, preferring to live in urban habitats, they have impacted on the environment inadvertently, often to the points where irreversible damages are.

The discharge of a pollutant (solid, liquid or gas) into the environment has significant potential

to damage human health, living organisms, ecosystems or environment. The causes of pollution are numerous, and the most important is physical, chemical and biological contamination (Anderson and Morel, 1982; Božo, 2001; Omanović, 2001). Heavy metals may cause changes in the structure function of genetic material that are long, carried on seed and difficult to trace, as announced in subsequent generations. Some of these toxic substances can stay for a long time in the soil or water, and deposit in the body of living organisms (Omanović, 2001).

Analytical procedures are available for determining and detecting metal content more accurately. Effects of chemical environments, especially trace elements in human and animal health, have been studied (Herning, J. G., and Morel, F. M. M. (1988) . Water pollution is directly related to the degree of contamination of our environment. Streams and rivers collect dirt from the surface of the earth by discharges of sewage and industrial effluents, and these are being conducted in rivers. All man-made chemicals are eventually end up in our water supplies. These dangerous products created by agriculture, industry and other human activities go directly into rivers, lakes, and underground sources, which can contaminate drinking water. Some diseases, such as dysenteries, typhus, jaundice, cholera, and skin diseases, appear occasionally in the form of an epidemic in villages and towns, and the main cause of these diseases is bacteria and other biological and chemical pollutants in drinking water (Herning and Morel, 1988; Salomons and Foerstner, 1984; Sunda et al., 1984). The pollution and uneven water distribution of global land arises drinking water crisis which leads to a conflict among the states. In the future, it will be forgotten conflicts for gold and oil, but will appear on water (Salomons and Foerstner, 1984). Kosovo has 22 rivers to save deposits used for drinking despite weak monitoring, and the rest has been very bad quality. In Kosovo, 103 quarries are recorded, where the majority is located near the river, which have ruthlessly destroyed their beds. If this phenomenon was not prevented, the landfills infection diseases will appear within a very short time frame. The river Ibar and Sitnica pollution is large enough so that the river has lost epithets of the river, which has turned into river of dead, and fish existence is impossible without improvement because of increased eutrophication process. For over basin, sewage mainly came from previously untreated sewage and heavy launcher from the factory “Ferronikeli” and mines “Trepça”.

In major cities of Kosovo, like Pristina, air samples recorded large amount of dust 200 mg/L. Power plants and vehicular traffic release CO_2 and CO, and CH_4 from waste landfills (Knoch, 1994). Due to global warming, bee amount decreased 25% globally. Kosovo is also affected by this problem of global warming. In 1985, a beehive gave the performance of 55 kg of honey, and today at 22 kg, which reduced many wine warm and winter extreme. In Kosovo, a region previously identified one to two floods, and now is up 5 to 6 annual floods. Kosovo is currently available in 40% forests, and lost 5-7% of forest within 15 years from illegal loggers, which resulted in increased number of insects that

carry a number of diseases (Omanović, 2001; Sunda and Guillard, 1976). Trace amounts of metals and bacteria are common in the water, and these are usually harmful to our health. In fact, some metals are essential to sustain life. Calcium, magnesium, potassium, and sodium must be present for normal body functions. Cobalt, copper, iron, manganese, molybdenum, selenium, and zinc are needed for enzymatic activity as catalysts (Herning, J. G., and Morel, F. M. M. (1988). Drinking water containing high levels of these essential metals as well as toxic metals such as arsenic, aluminum, barium, cadmium, chromium, lead, mercury, and selenium, which may be harmful to our health (De Oliviera et al., 1995). In this study, pollution of heavy metals in the White Drin River Basin was evaluated.

2. Material and Methods

Sampling for analysis is made on May 20, 2012. Stations were selected based on expected pollution places, such as factories near industrial agricultural activities, traffic, settlements, etc. Çullaj, 2005; Herning and Morel, 1998). For analysis, the samples were obtained from two DM3 water. At stations set geographic location with GPS, Extrax model, "Garmin", 12 chanel, measured water temperature as well as date and time of sampling is recorded. Samples were filtered with filter paper "Selekcta" No. 589 (Germany) and subsequently pH, electrical conductivity, alkalinity, hardness as well as concentrations of HCO_3^- and CO_3^{2-} were evaluated. Water samples placed in plastic bottle (1 DM3) are divided into batches of formula of 100 cm^3 and then treated with 0.1 M HNO_3 to pH 1-2 (Korça, 2003; Smith and Martell 1981). Concentrations of elements are determined by ICP-MS technique in commercial laboratory Kosovo Polje “Agrovet”. During experiment, purity chemicals were used, and bought from “Merck”.

3. Results and Discussion

The characterization of the White Drin River Basin is shown in Tables 1 and 2. The physicochemical parameters of the water samples are given in Table 3. The concentrations of nine elements in water samples from the White Drin River Basin are determined by ICP-MS technique, and the results are shown in the Table 4 as well as Figs. 1-3. The concentrations of Cu, Zn, Pb, Cd, Mn, As, Fe, Co and Ni were 4.05 - 22.2, 3.67 - 54.8, 2.81 - 35.1, 0.20 - 2.61, 1.60 - 38.2, 0.27 - 0.81, 22 - 77, 0.03 - 0.211 and 0.8 - 2.69 mg/L, respectively. In addition, assessment of water quality with Norwegian standards is given in Table 5. Seen from Table 5, for different sampling stations, the concentration of Zn mainly belongs to Class I of Norwegian standards; Cd mainly belongs to Class IV; Pb mainly belongs to Class III; and Cu mainly belongs to Class II.

Table 1. Length, area and quantity of the White Drin River Basin

No.	Underground reservoirs	Length (Km)	Q (m^3/s)	Surface (km^2)	Annual leakage (million m^3)	Flow direction
1	White Drin	122	61.0	4.622	2.200	Adriatic Sea

Table 2. Accumulations underground water, surface, volume and capacity of White Drin River Basin

No.	Underground reservoirs	Basin (km^3)	Volume helpful (m^3)	Evaluation capacity	
				m^3/sek	In total (m^3)
1	Istog	76	12×10^6	2.8	89×10^6
2	Vrella	28	14×10^6	0.600	19×10^6
3	Peja	300	37.5×10^6	4.0	52×10^6
4	Deçani	144	33×10^6	3.5	45×10^6

Kosovo has 10098 km^2 areas with four large ponds water as a result of the use of water for irrigation, and these basins exit from the river beds during floods. Wheat, maize, potato and onions were cultivated in these parts, which are the staple foods. However, they contained high values of heavy elements because wastewater was used for agricultural irrigation. The herbicides were used to combat pests, and bees were reduced by 25% in summer and warmer winter extreme. The 1909 patients in three major cities of Kosovo under the National Health were suffering from kidney problems from the use of contaminated water, and every eighth residents in endemic regions were suffering from colon cancer because foods with high heavy elements were eaten, which is a very big concern for the citizens of Kosovo. In addition, Kosovo has suffered global warming problems as well as environmental and ecosystem decays, and the number of floods increased from two to six annual floods (Sunda, G., Klaveness, D., and Palumbo, A. V. (1984).

Table 3. Results of the analysis and some physico-chemical parameters for the White Drin River Basin

Stations	Water temperature °C	Air temperature °C	Electrical conductivity Ms/cm	pH	Turbidity NTU	Alkalinity mA	Alkalinity pA	Total hardness °D	$\gamma(CO_3^{-2})$ mg/L
A_1	7.3	16.2	1.88	7.82	2.9	28. 44	3.1	7.10	34.0
A_2	9.5	17.3	1.98	7.83	2.3	29.18	3.07	7.49	34.94
A_3	10.10	18.8	1.99	8.82	10.3	29.83	3.10	7.66	3632
A_4	11.2	20.6	2.81	8.64	20.6	27.54	3.12	7.59	39.34
A_5	11.8	21.3	2.99	8.62	30.4	28.45	3.17	7.77	36.33
A_6	12.10	23.3	2.61	7.33	24.5	25.03	4.9	8.79	35.48
A_7	12.90	20.7	2.50	7.70	26.7	26.66	3.064	7.36	37.72
A_8	13.0	24.7	2.70	8.23	24.2	27.55	3.14	7.88	37.45
A_9	14.9	23.7	2.77	8.40	22.1	9.17	3.56	8.10	38.68
A_{10}	15.8	21.8	3.40	8.32	25.3	26.12	3.45	8.12	39.70

Table 4. Concentration of elements (mg/L) in water from White Drin River Basin

Element	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	Methods setting
Mn	1.60	2.5	8.6	10.6	13.9	18.71	12.1	15.5	13.8	38.2	ICP-MS
Fe	56	25	38	46	36	45	46	77	22	58	ICP-MS
Co	0.04	0.03	0.08	0.15	0.090	0.120	0.100	0.110	0.110	0.211	ICP-MS
Ni	1.1	1.3	0.8	1.5	0.8	1.3	1.7	1.3	1.95	2.69	ICP-MS
Cu	22.2	4.80	9.58	4.44	6.54	4.45	9.46	12.4	4.05	5.87	ICP-MS
Zn	15.4	7.88	54.8	20.9	20.4	3.67	21.8	12.6	51.42	28.12	ICP-MS
As	0.28	0.39	0.27	0.38	0.4	0.45	0.69	0.67	0.70	0.81	ICP-MS
Cd	2.61	1.99	2.7	0.27	0.20	0.2	2.32	0.96	1.35	0.78	ICP-MS
Pb	26.1	35.1	14.6	5.3	2.81	4.12	24.4	9.55	9.34	5.85	ICP-MS

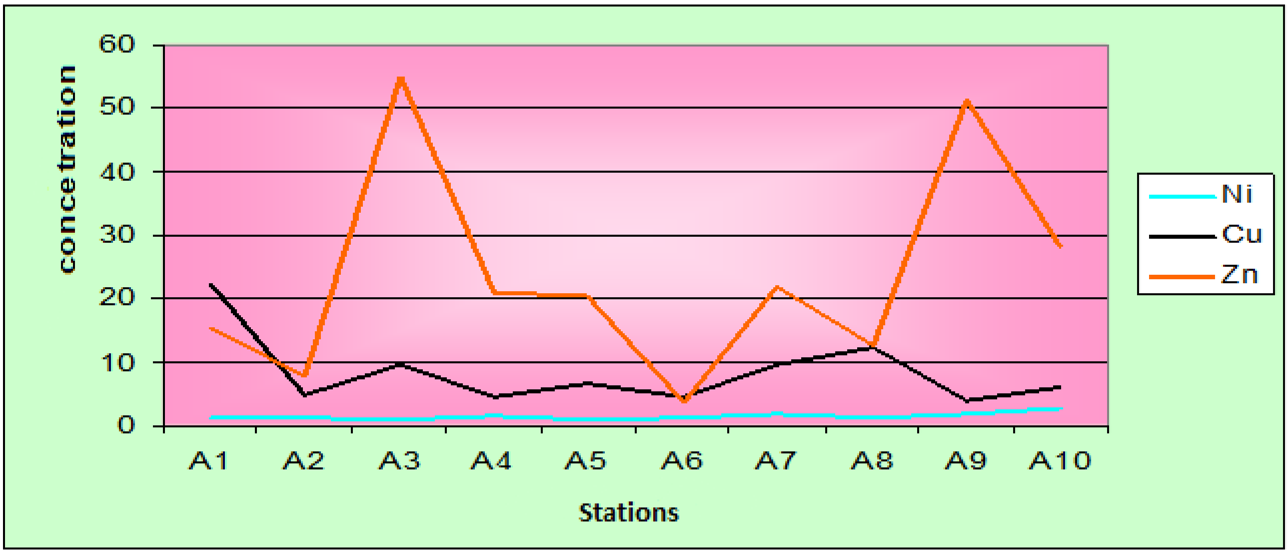

Figure 1. Graph of elements in water from White Drin River.

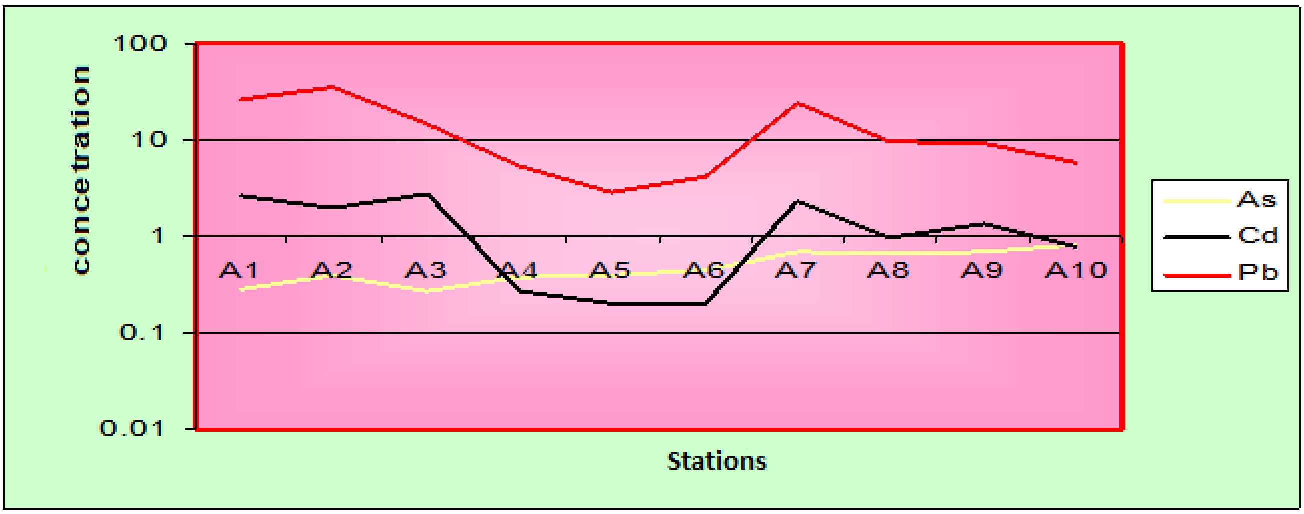

Figure 2. Graph of elements in water from White Drin River.

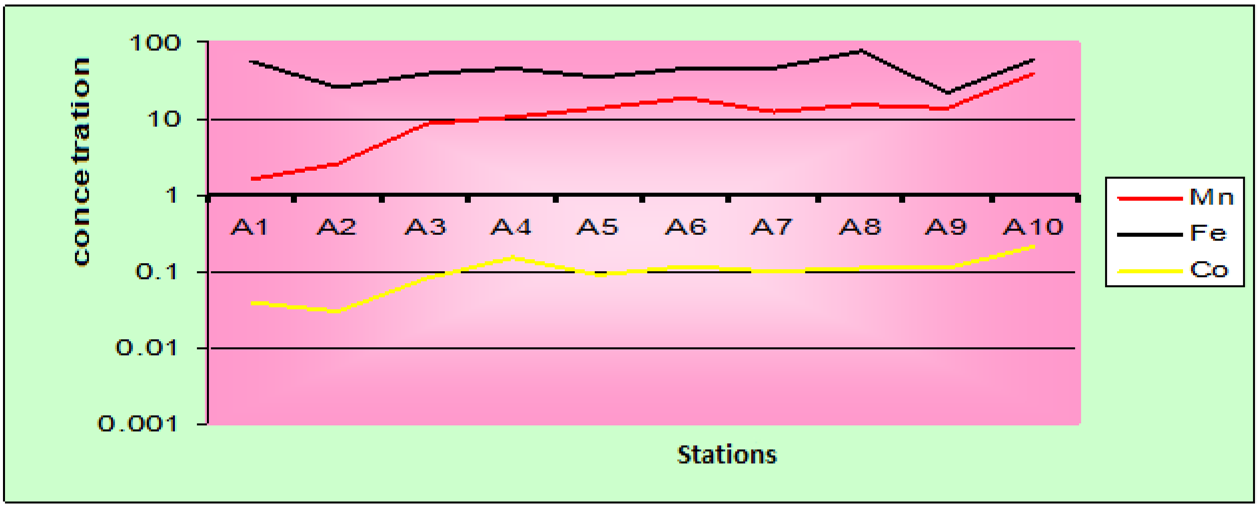

Figure 3. Graph of elements in water from White Drin River.

Table 5. Assessment of water quality with Norwegian standards

Metal	Class I	Class II	Class III	Class IV
Zn, μg/dm^3	< 30 A_1, A_2, A_4, A_5, A_6, A_7, A_8, A_{10}	30 - 60 A_3, A_9	60 - 300	> 300
Cd, μg/dm^3	< 0.2 A_5	0.2 - 0.5 A_4, A_6	0.5 - 1 A_8, A_{10}	> 1 A_1, A_2, A_3, A_7, A_9
Pb, μg/dm^3	< 1	1 - 5 A_5, A_6	5 - 15 A_3, A_4, A_8, A_9, A_{10}	15 - 40 A_1,A_2, A_7
Cu, μg/dm^3	< 3	3 - 15 A_2, A_3, A_4, A_5, A_6, A_7, A_8, A_9, A_{10}	15 - 60 A_1	> 60

4. Conclusions

The paper studied the real situation regarding water pollution in the river basins, mainly Kosovo hydrograph network and measures to be taken on the environmental impact that urban pollution discharges bring. Some physicochemical parameters of water samples, such as pH value, electrical conductivity, alkalinity, hardness as well as concentrations of HCO_3^- and CO_3^{2-} were measured, and concentrations of nine elements in water samples were determined by ICP-MS technique. The concentrations of Cu, Zn, Pb, Cd, Mn, As, Fe, Co and Ni were 4.05 - 22.2, 3.67 - 54.8, 2.81 - 35.1, 0.20 - 2.61, 1.60 - 38.2, 0.27 - 0.81, 22 - 77, 0.03 - 0.211 and 0.8 - 2.69 mg/L, respectively. For different sampling stations, the concentration of Zn mainly belongs to Class I of Norwegian

standards; Cd mainly belongs to Class IV; Pb mainly belongs to Class III; and Cu mainly belongs to Class II.

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