DETERMINATION OF HEAVY METAL CONTENTS IN WATER OF LLAPI RIVER (KOSOVO). A CASE STUDY OF CORRELATIONS COEFFICIENTS

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Atomic absorption spectroscopy has been used to analyses and assesses the heavy metal content in water of the Llapi river, Kosovo. In this study, the assessment of heavy metals in water was realized in the summer period. Statistical studies have been carried out by calculating basic statistical parameters, anomalies (extremes and outliers) and correlation coefficients between different pairs of variables. The concentration of Cr, Ni, Zn, Cu and Fe in all sample stations were found to be under WHO recommended norms. But the concentration of Cd and Pb in all sample stations and concentrations of Mn at several stations were found to be above WHO recommended norms originated from mineral sources (ores) in this area. The statistical regression analysis has been found a highly significant positive relationship of Cd with Ni, Mn, Fe and Pb originated mainly of sulphide ores in this area.

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INTRODUCTION

The quality of water is an issue of significant interest for the residents of the EU.[1] In peat bogs, water flows freely in the active layer of water or acrotelm. Water storage is critical to the balance of water in peat swamps and in surrounding areas. Logging activity, agriculture, peat extraction and destruction of peat swamp drainage activity also have an adverse effect and has an unfavorable implication on the hydrology.[2]

The sources of physico-chemical contamination are numerous and include the land disposal of sewage effluents, sludge and solid waste, septic tank effluent, urban runoff and agricultural, mining and industrial practices.[3,4] Chemical contamination of drinking water is often considered a lower priority than microbial contamination by regulators because adverse health effects from chemical impurities are generally associated with long-term exposures. In contrast, the results from microbial contamination are usually immediate practices.[5] The decomposition of organic matter and pollution due to anthropogenic activity are the primary sources of pollution of water.[6] As reported by Brils,[7] adequate water quality in Europe is one of the most critical concerns for the future.

Proper management of natural and environmental waters will give results if leading institutions continuously monitor information about the ecological situation. Therefore, seeing it as a challenge for environmental chemists, our goal is to determine the amount and nature of pollutants in the environment. One could claim that the most polluted areas in the world are those with the densest population. It should, therefore, be the foremost goal of environmentalists to prevent such pollution, and to educate the community towards proper management of ecosystems.[8] Heavy metal ions can exist in several different forms.[9] The factors which determine the form of the metal ion are the extent of complexation and the oxidation state. In many samples, metal ions are present in their hydrated forms. Hydrated metal ions are usually written without the water ligands included in the chemical formula.

Determination of the concentrations of trace heavy elements in aqua systems is difficult and the results obtained often vary according to the chosen analytical technique. Atomic absorption spectroscopy (AAS) is a frequently used instrumental technique for the determination of trace heavy metal ions because of its low cost and short analysis time.[10]

Waters of Kosovo have been poorly investigated. Gashi et al. [11] performed the first step with the investigation of the rivers Drini i Bardhë, Morava e Binçës, Lepenc and Sitnica, which was of supra-regional interest. They conducted studies of mineralogical and geochemical composition and contamination status of stream sediments of mentioned rivers of Kosovo. By comparing the concentrations of toxic elements with the existing criteria for sediment quality, in that study was found that sample points in Fushë Kosova and Mitrovica of Sitnica River are significantly polluted, caused by Zn and Pb processing by flotation and Zn electrolysis factory. In Morava e Binçës River, also two sites were found to be contaminated with Cd. As Drenica River is the most important tributary of Sitnica River,[12] the next paper presents the detailed investigation and monitoring of the Sitnica river watershed, which is the most polluted river in Kosovo. Gashi et al.[13-15] performed research of ecotoxic metals: copper, lead, cadmium, zinc and manganese in waters of four main rivers (Drini i Bardhë, Morava e Binçës, Lepenc and Sitnica) of Kosovo and suggested to authorities concerned a monitoring network on main rivers of Kosovo. Also, the authors highlighted two locations in Sitnica River as very polluted with ecotoxic elements.

Study area and sampling

The Llap is a river in the north-eastern part of Kosovo and the 82.7 km long right tributary to the Sitnica river,[16] which runs through the middle of Podujevo. The source of Llapi river is considered to be the Pollata village in the Albanik Mt., where the rivers of Murgulla and Sllatina are joined. This river is wide from 9 to 12 meters and deep up to 1.2 meters. The river brings an average of 4.9 $m^3 s^{-1}$, however, there are considerable variations with the maximum going up to 25 $m^3 s^{-1}$. The Llapi river originates from Albaniku Mountain in the Prishtina region. Near the village of Stanovci i Poshtëm, the Llapi river splits and empties into the Sitnica river. The sampling process of river water was performed on August 12, 2015, to cover the river spatially, taking into account anthropogenic pressures, the different habitats, and the hydro morphological conditions of the river.

Figure 1. Study area with sampling stations.

At each sampling location, water samples were collected in polyethylene bottles. Before taking water samples, the bottles were rinsed three times with the river's water to be collected. Water samples were collected for analysis according to the recommended procedures, near the river bank at a depth of 15 cm, put into 1dm^3 bottles stored at 4° C. [17,18]

Table 1. Sampling stations (summer period) with a detailed description

Sample	Locality	Possible pollution sources
S_1	Marincë	Low probability
S_2	Sllatinë	Low probability
S_3	Pollatë	Settlement, traffic and agriculture
S_4	Bajqinë	Settlement, traffic and agriculture
S_5	Podujevë (exit)	The settlement, wastewater from Podujeva city, traffic and agriculture
S_6	Gllamnikë	The settlement, agriculture wastewater from "ABB" meat and juice factory
S_7	Llozhan	Settlement, wastewater, traffic and agriculture
S_8	Milloshevë	Settlement, wastewater, traffic and agriculture
S_9	Lummadh	Settlement, wastewater, traffic and agriculture

Preservation and experimental procedure for the water samples are carried out according to the standard methods for the examination of water Samples are preserved in refrigerator after treatment.[19-21] GPS device Extras measured geographic coordinates, "GARMIN, 12 channel," and locations were well described. The levels of heavy metals in water were compared with WHO standards for drinking water.[22] The study area with the sampling locations is shown in Figure 1 and the details about all sampling sites were presented in Table 1.

MATERIALS AND METHODS

Twice distilled water was used in all experiments. All instruments are calibrated according to the manufacturer's recommendations. All tests were performed at least three times to calculate the average value. Determination of the concentrations of trace heavy metals: Cr, Cd, Ni, Zn, Mn, Cu, Fe and Pb in environmental samples is difficult and the results obtained often vary according to the chosen analytical technique. Atomic absorption spectroscopy (AAS) is an important instrumental technique for the determination of trace/heavy metal ions because of its low cost and short analysis time. Determination of Zn (213.89 nm), Fe (371.99 nm), Mn (403.08 nm), Ni (341.48 nm), Cr (425.44 nm), Cu (327.40 nm), Cd (326.11 nm) and Pb (405.78 nm) were performed using atomic absorption spectrometer model "PERKIN ELMER 400 ANALYST".

The detection limit for analyzed heavy metals is presented in Table 2. Program statistic 6.0[23] was used for the statistical calculations in this work, such as descriptive statistics, Pearson's correlation factor and two-dimensional box plot diagrams for determination of anomalies (extremes and outliers) for solution data. Relationships between the observed variables were tested using correlation analysis, and the level of significance was set at $p < 0.05$ for all statistical analyses.

RESULTS AND DISCUSSION

The concentration of 8 heavy metals was presented in Table 2 and basic statistical parameters for 6 variables in 9 water samples are shown in Table 3. Using experimental data and box plot approach of Tukey,[24] extreme and outlier values were determined for the whole region. Two dimensional scatter box with plots diagrams are presented in Figure 2. Anomalous values (outliers and extremes) of 6 variables are shown in Table 4. The matrix of correlation coefficients (*r*) of the selected six variables was presented in Table 5.

The concentration of Cr, Ni, Zn, Cu and Fe in all sample stations were found to be under WHO recommended norms. Cadmium concentrations in unpolluted natural waters are usually below 1 μg dm^{-3}.[25] It is chemically similar to zinc and occurs naturally with zinc and lead in sulphide ores. The concentration of Cd in all sample stations was found to be above-recommended norms (WHO the highest desirable limit 0.005 mg dm^{-3}), as a possible sign of natural pollutions originated from cadmium sulphide ores in this area.

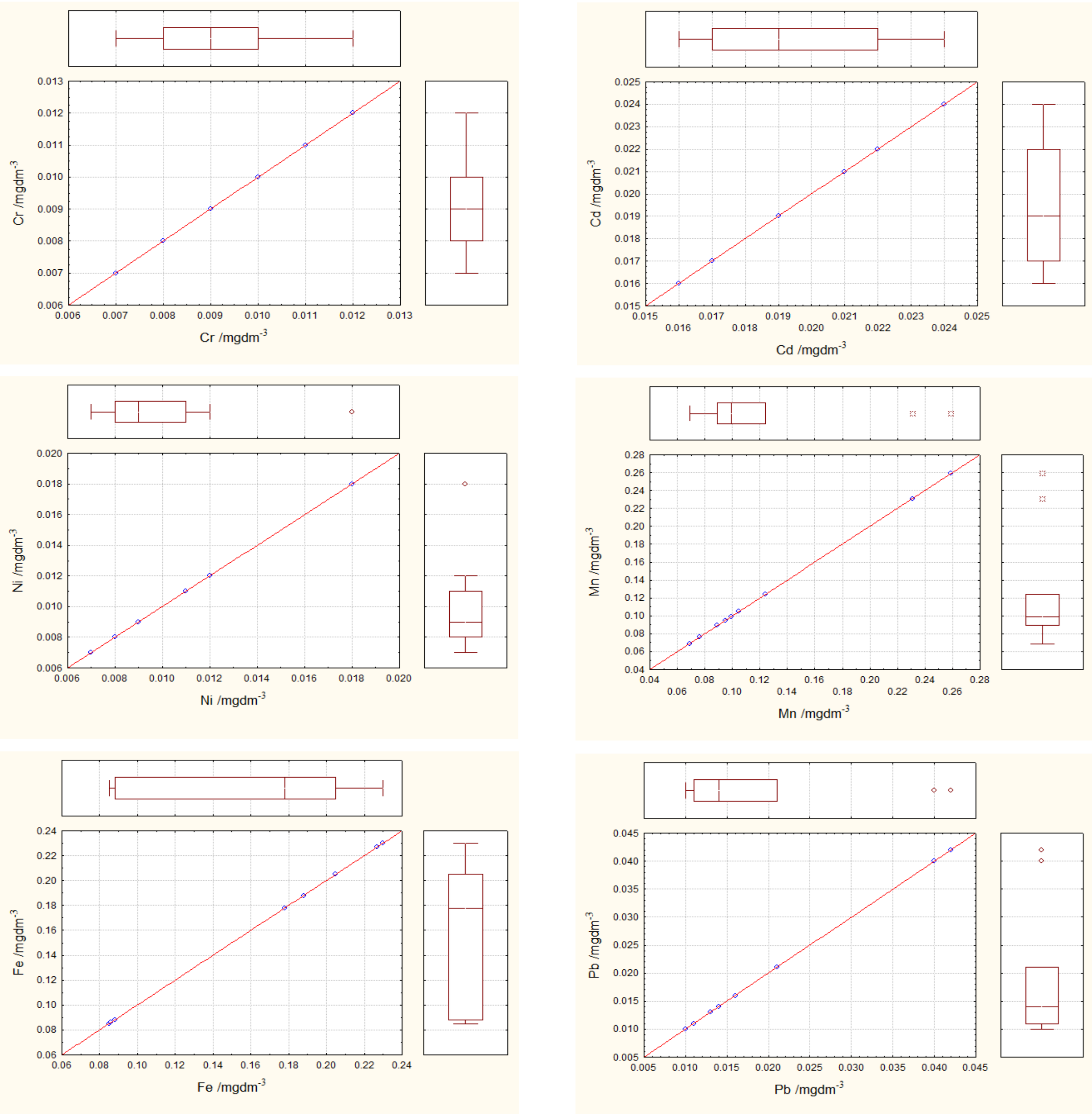

Figure 2. Scatter box plot diagrams of some selected heavy metals.

Table 2. The concentration of some metals in water sample stations

Heavy metal	Detection limit, mg dm^{-3}	WHO standard, mg dm^{-3}	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9
Cr	0.003	0.05	0.008	0.007	0.007	0.008	0.009	0.010	0.010	0.012	0.011
Cd	0.0008	0.005	0.022	0.019	0.019	0.021	0.024	0.022	0.017	0.016	0.017
Ni	0.006	0.07	0.009	0.008	0.008	0.012	0.018	0.011	0.011	0.009	0.007
Zn	0.0015	5	nd*	nd	nd	nd	nd	nd	nd	nd	nd
Mn	0.0015	0.1	0.099	0.105	0.095	0.124	0.259	0.231	0.089	0.076	0.069
Cu	0.0015	2	0.005	0.004	0.004	0.004	0.005	0.006	0.005	0.005	nd
Fe	0.005	0.3	0.205	0.178	0.178	0.188	0.227	0.230	0.088	0.085	0.086
Pb	0.010	0.01	0.011	0.010	0.010	0.021	0.040	0.042	0.016	0.014	0.013

*not detected

Table 3. Descriptive statistics of 6 variables in 9 cases

Variable, mg dm^{-3}	Descriptive statistics						
	Mean	**Geometric**	**Median**	**Minimum**	**Maximum**	**Variance**	**Std. dev.**
Cr	0.0091	0.0090	0.0090	0.0070	0.0120	0.00	0.0018
Cd	0.0197	0.0195	0.0190	0.0160	0.0240	0.00	0.0027
Ni	0.0103	0.0099	0.0090	0.0070	0.0180	0.00	0.0033
Mn	0.1274	0.1146	0.0990	0.0690	0.2590	0.00	0.0689
Fe	0.1628	0.1511	0.1780	0.0850	0.2300	0.00	0.0603
Pb	0.0197	0.0169	0.0140	0.0100	0.0420	0.00	0.0126

Table 4. Anomalous values (extremes and outliers) of 6 metals in 9 water samples

Sample	Extremes of parameters (¤)	Outliers of parameters (o)
S_1	No reg.	No reg.
S_2	No reg.	No reg.
S_3	No reg.	No reg.
S_4	No reg.	No reg.
S_5	Mn (0.259 $mgdm^{-3}$)	Ni (0.018 $mgdm^{-3}$), Pb (0.04 $mgdm^{-3}$)
S_6	Mn (0.231 $mgdm^{-3}$)	Pb (0.042 $mgdm^{-3}$)
S_7	No reg.	No reg.
S_8	No reg.	No reg.
S_9	No reg.	No reg.

Table 5. Matrix of correlation coefficients (r) of selected six variables

	Correlations, marked correlations are significant at *p* <0.05000					
	Cr	**Cd**	**Ni**	**Mn**	**Fe**	**Pb**
Cr	1.00					
Cd	-0.46	1.00				
Ni	-0.01	0.67	1.00			
Mn	-0.07	0.81	0.81	1.00		
Fe	-0.61	0.94	0.48	0.74	1.00	
Pb	0.19	0.66	0.77	0.95	0.56	1.00

Concentrations of Mn at stations S_2, S_4, S_5 and S_6 were found to be above-recommended norms (WHO the highest desirable limit 0.1 mg dm^{-3}) as a possible sign of natural pollutions originated from manganese ores in this area and uncontrolled use of fertilizers, varnish and fungicides in this area. Pb in all sample stations were found to be above WHO recommended norms from 0.01 mg dm^{-3}, originated (possible) from lead sulphide ores in this area.[26]

Basic statistical parameters (Mean, Geometric mean, Median, Minimum, Maximum, Variance and Standard deviation) for six parameters analyzed in water samples are presented in Table 3. Based on the two-dimensional scatter box plot diagrams (Fig. 2) from 6 experimental data were constructed and anomalous values (Table 4). In the sample station, S_5 and S_6 extreme values of Mn (0.259 and 0.231 $mgdm^{-3}$, respectively) were registered. The sample S_5 and S_6, the outlier value of Pb (0.040 and 0.042 $mgdm^{-3}$, respectively) was recorded.

Also, the outlier value of Ni at the sample station S_5 was registered. The statistical regression analysis has been found a highly useful technique for the linear correlating between various water parameters, and the correlation coefficient (Table 5) indicates a positive and negative significant correlation of variables with each other. A positive correlation means one parameter increase with other parameters and negative correlation means one parameter increase with other parameters decreases. In this study summer period (see Table 5). Cd showed a highly significant positive relationship with Ni, Mn, Fe and Pb originated mainly of sulphide ores in this area.[26] Ni showed a highly significant positive relationship with Mn and Pb. Manganese showed a highly significant positive correlation with Fe and Pb.

CONCLUSIONS

The concentration of heavy metals - Cr, Ni, Zn, Cu and Fe - in all sample stations were found to be under WHO recommended norms. The concentration of Cd in all sample stations were found to be above-recommended standards as a possible sign of natural pollutions originated from cadmium sulphide ores in this area. Concentrations of Mn at stations S_2, S_4, S_5 and S_6 were found to be above-recommended norms as a possible sign of natural pollutions originated from Manganese ores in this area and uncontrolled use of fertilizers, varnish and fungicides in this area. Pb in all sample stations was found to be above WHO recommended norms originated (possible) from Lead sulphide ores in this area.

Based on the two-dimensional scatter box plot diagrams in sample stations, S_5 and S_6 anomalies values of Mn and Pb were registered. Also, the outlier value of Ni at the sample station S_5 was registered. The statistical regression analysis has been found a highly significant positive relationship of Cd with Ni, Mn, Fe and Pb originated mainly of sulphide ores in this area. Ni showed a highly significant positive correlation with Mn and Pb. Manganese showed a highly significant positive relationship with Fe and Pb.

From the results, it was found out that river water quality did not fulfill the criteria set by the WHO and the distribution of pollutants (heavy metals) indicated natural pollutions and anthropogenic sources as the influence of wastewaters from the settlement, agriculture impact and wastewater from meat and juice factory.

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