Research Article

Evaluation of the Surface Water Quality of Lepenc Pond, with Analytical Methods, ASV and ICP-MS

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Accepted on: 14-11-2015; **Finalized on:** 31-12-2015.

ABSTRACT

In this work, we determinated physical, chemical parameters and concentration of heavy metals such as; Fe, Co, Ni, Cu, Zn, Cd, Mn, As, Pb and Cr in Lepenc river. During our fieldwork, we took samples in five sampling points that are presented with symbols L_1, L_2, L_3, L_4 and L_5. Measurement of heavy metal is made by two analytical methods AS-Voltametry and ICP-MS, and then we draw the average of the two methods. Regarding the values of physical and chemical parameters, starting from samples taken in the L_1 to L_5, we expected a gradual increase. Values of Fe have had a slight increase had it noticed a significant increase from samples taken in L_4; 460 ppm in L_5; 730 ppm, exceeding the values according to all international standards. Based on the obtained values seen in L_3 and L_4 sampling points that have values for Pb; 3.74 ppm and 3.87 ppm, values that are disturbing, if water is used for watering. During this scientific work we have followed the change of physical and chemical parameters, particularly the impact of wastewater discharged from the municipality of Sterpce, the factory "Silkapor" and factory "Sharrcem" change the value heavy metal. As expected, the minimum values are L_1-source, religion, <10 ppm, C_O; 0.006 ppm Ni; <0.3 ppm, Cu; 0.4 ppm, Zn; 0.6 ppm Cd; <0:01 ppm, Mn; 0.5 ppm, As; 0.7 ppm Pb; 0:05 ppm and Cr; <0.5 ppm.

Keywords: River Lepenc, heavy metals, water, Kaçanik.

INTRODUCTION

River Lepenc crosses the municipality of Sterpce, Kaçanik, Skopje and then flows into the Aegean Sea. The source of the Lepenc River is on the northern slopes of Mount Sharr to Oshllaku (2212 m). In the upper part of the source to the locality Brezovica formed ravine. It is one of the most attractive residential areas. From the mouth of Brod enters Sopotnic Basin, which stretches from the village to the Kaçanik, Doganaj.

The most important is the branch Nerodime. Lepenci in the territory of Kosovo is over 53 km, the basin area of 607 square kilometers, while the annual average flow rate 7.9 m^3 per second[1].

The primary importance of this study is related to the calculation of the mass concentration of heavy metals in trace: Fe (II), Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Mn (II), As (II), Pb (II) and Cr (II) and other metals, so that together with other factors may have a negative impact on crop grown efficiency along the river Lepenc.

Also, our main focus has been to analyze and assess the level of pollution of the river Lepenc with heavy metals, and the impact of this pollution in flora and fauna.

So knowing the content of heavy metals in water, it is very useful to know the quality of river water used by residents along its flow respectively from the municipality Sterpce, Kaçanik and Elez Han.

MATERIALS AND METHODS

Starting from the principle that the qualitative and quantitative composition of matter varies from place to place, determining the position of sampling in chemical terms is important. Sampling points that are selected, given the characteristic countries in which we expected pollution from anthropogenic activities. The number of site-sampling in our work is 5 and all sampling points that are sampled for determination of chemical-physical parameters. Extraction of champions and elaboration of samples were done according to standards methods for surface water[6,7]. The study area with sampling locations is shown in figure 1 and the details about all sampling sites are presented in table 1 and 2. Water from Lepenc River, marked by figures such as L_1-Oshllak, L_2-Sllatin, L_3-Nika, L_4-Kaçanik and L_5-Elez Han[1]. During the fieldwork the following parameters were: water temperature, air temperature, electrical conductivity, pH and turbidity. We have done the analysis and evaluation of water samples, the concentration of heavy metals in this environment. Samples were taken during March 2012. All required chemicals for determining the physical and chemical parameters, micro and macro pollutants analyzed, chemical purity were "pro analysis" (the highest rate of high purity). The method used for the determination of heavy metals has been methods: Anodic Stripping Voltammetry (ASV) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS)[8,9]. Samples are taken in

polyethylene bottles at sampling points that outlined high and at different depths, depending on the extent of the river, usually 25 cm below the water surface, given that flow the river at the time of sampling has been calm and normal. Water samples for analysis are taken at five sampling points (L_1, L_2, L_3, L_4 and L_5)[1 3]. The first point of sampling has been; L_1 areas-Oshllak, source river Lepenc, the type of relief rocky-mountainous, potential pollutants, natural pollution, erosion; L_2 areas - Sllatin. The type of relief are mountain, potential pollutants, waste disposal; L_3 zone -Nika, the type of flat relief, potential pollutants, the factory "Silkapor" sewage; area L_4–Kaçanik, type of relief flush pollutants potential, preparations agriculture, wastewater and areas L_5 -Elez Han, the type of relief lowlands combined polluters possible, road traffic, sewage, factory "Sharrcem" etc.

Figure 1: Sampling points marked with red dots in a square shape along the Lepenci River flow[5].

The samples are taken with special bottle of 1 dm^3. From these bottles, are divided into four cups of 100 cm^3 water samples, which are we added nitric acid HNO_3 0.1mol/dm^3 to remove anions in the form of non-metal oxides as HCl, SO_3 etc. Dry remain is dissolved again until in 100cm^3. Following further treatment with H_2O_2 samples that are evaporated in electric heater sand until complete evaporation will remove organic pollutants. Dry residue is treated with nitric acid, left for 24 hours staying (to stabilize) and then the sample is divided into four equal parts in order to determine the heavy metals. Then continually we did determination of heavy metals with anodic stripping voltammetry using internal standard techniques (VA STAND 746 Trance Analyzer, Metrohm), with three electronically system [working electrode (Hand mercury drop electrode); Referent electrode (Ag/AgCl); Auxiliary electrode (Pt) in acid nitric HNO_3 (s.p) as basic electrolyte[3]. Analytical methods to determine the elements require that samples must be in the form of aqueous solution. During digestion of the samples have been carefully digested samples quickly and completely, not for the loss of the sample by evaporation or adsorption on the walls of the container but also the elimination of sample contamination from the reagents used in the process of digestion[3].

RESULTS AND DISCUSSION

Our results are presented in table and graphical. In five different points of sampling, we determined the concentration of heavy metals (Fe, Co, Ni, Cu, Zn, Cd, Mn, As, Pb and Cr) in water.

Table 1: Water temperature, air temperature, electrical conductivity, pH and turbidity.

Sample places	Water Temperature° C	Air Temperature° C	Electrical Conductivity µs cm^{-1}	pH	Turbidity NTU
L_1	3.2	4.1	263	7.65	15.1
L_2	4.4	4.8	275	7.73	16.6
L_3	5.7	5.1	286	7.79	34.2
L_4	5.6	10.5	298	7.84	37.1
L_5	5.9	11.1	391	7.92	41.5

Table 2: Presentation values of concentration of heavy metals in water µg/dm^3.

Element µg/dm^3	L_1	L_2	L_3	L_4	L_5
Fe	<10	240	280	460	730
Co	0.006	0.417	0.654	0.903	1.96
Ni	<0.3	2.9	4.5	4.7	9.7
Cu	0.4	2.1	4.3	2.6	5.5
Zn	0.6	4.4	6.9	6.1	18.8
Cd	<0.01	0.02	0.03	0.03	0.09
Mn	0.5	34.7	51.1	96.9	119
As	0.7	0.6	0.94	1.03	1.12
Pb	0.05	0.88	3.74	1.67	3.87
Cr	<0.5	1.1	2	1.6	3.2

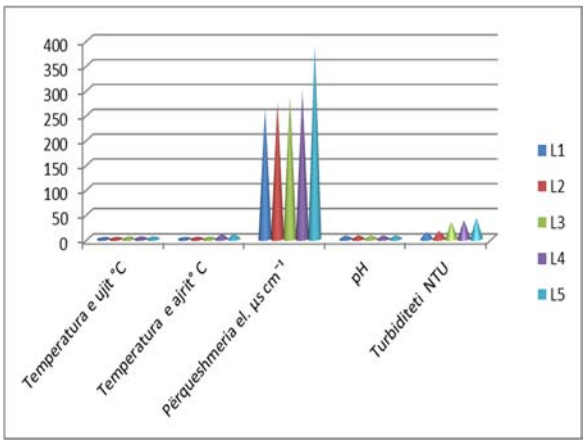

Figure 2: Graphical presentation of the results.

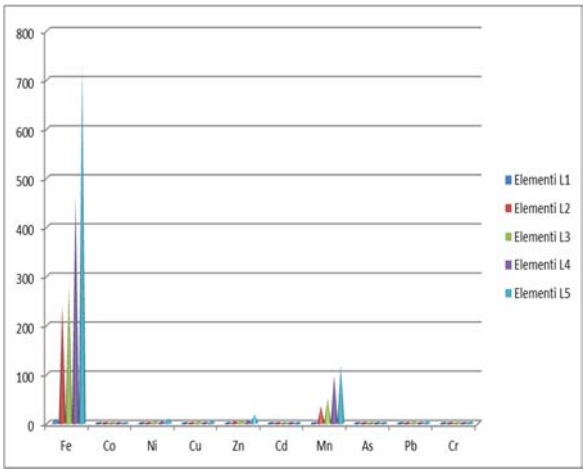

Figure 3: Graphical presentation of the results of heavy metals

From the results obtained it is noticed that the water temperature is different in intervals from 3.2 to 5.9, where in this sampling points there is a change $\Delta T = T_{max} - T_{min}$ = 5.9 °C - 3.2 °C = 2.7 °C. Electrical conductivity is increasing depending on the degree of pollution, the lowest value L_1 is sampling; 263 μS/cm^{-1} while undergoing a considerable growth in the next sampling points that reaches the maximum value and the L_5; 391 μS/cm^{-1}, this increase comes as a result of discharges of sewage and other polluting factors of the river. pH ranging in the range of 7.65 to 7.92 between weak mainly basic value that does not represent any danger to use this water. Turbidity also had an increase which is the minimum value L_1 samples taken; NTU while the maximum at 15.1 L_5; 41.5 NTU. After evaporation residue sampling L_1 is 19.8 mg/dm^3 and at L_5; 202.7 mg/dm^3, which indicates that in this sampling points that have a negative impact of the cement plant. Based on the analysis of some heavy metals with AS-Voltammetry technique and ICP-Mass Spectrometry we notice that: In sampling L_1, minimum value of Zn is 0.6 μg/dm^3 have a continuous rise to sampling L_3; 6.9 μg/dm^3 then landing L_4; 6.1 μg/dm^3 and maximum increase in L_5; 18.8 μg/dm^3, L_5. In sampling L_5, Cd maximum value 0.0032 μg/dm^3, while the minimum sampling L_1; 0.0015 μg/dm^3. In sampling L_5, Pb has a maximum value of 11.66 μg/dm^3, while the minimum is in source L_1; 0.005 μg/dm^3. In sampling L_5, Cu has a maximum value of 11.75 μg/dm^3, while the minimum is in L_1 sampling; 3.78 μg/dm^3. The minimum value is the point L_1; <0.1 μg/dm^3, while the maximum at the point L_5; 730 μg/dm^3, which means that exceeds Croatian and Slovenian standards those of which we did the comparison. Values of Ni; results are within the normal range between the minimum that <0.3 μg/dm^3 in source L_1, and it reaches a maximum of source L_5; 9.73 μg/dm^3. Mn values and Al are beyond the normal in the sampling L_5, where they brought Mn; 0.5-119 μg/dm^3 and Al; 2-842 μg/dm^3, that these two elements of the standards exceed Croatian and Slovenian standards. As values go from the minimal of 0.7 μg/dm^3 in point L_1 and L_5 and the maximal in the point L_5; 1.12 μg/dm^3, not exceeding even the EU directives EEC[2], or the WHO.

CONCLUSION

In general, based on our study regarding impact of heavy metals in the river water Lepenc, we may come to conclusions, as follows:

1. From the River Lepenc, according to the results of the analysis shows that the water has soft, hardness that ranges from 2.6 to 4.4 dH from samples taken in the L_1 to L_5, which flows because of calcareous composition of soil. Alkalinity, total hardness, electrical conductivity and turbidity are higher in the sampling points L_5, this high increase comes as a result of the discharge of wastewater from the use of agricultural land and the emissions from the cement plant "Sharrcem". Also residue after evaporation is higher in the sampling points L_4 and L_5, because the sampling L_4, join two rivers "Nerodime" and "Lepenc" increases the amount of water and discharges of wastewater from the town of Kacanik, and in the same time sampling points L_1, L_2 has had snow, less at the L_3 and L_4 and not at all at L_5.
2. Based on the analysis of heavy metals where are done with ICP-MS and AS-Voltammetry methods note that: Iron (Fe) from samples taken L_4 has a significant increase in sampling L_5, 300 μg/dm^3 to 730 μg/dm^3, this happened because at this time "Sharrcem" has been working and "Silkapor" and lime factory "Lepenc" were not in production. We can conclude that contamination above the allowed values of Fe, Cu, Zn, Pb and Cr, all these metals show an increase in the concentration of samples taken in L_1 to sampling L_3 but in sampling L_4 has a lowering of their values, and then an increase in sampling L_5. The values have a decrease in sampling L2 and then a continual increase until sampling L_5. All heavy metal values have a light increase, but we have a significant increase from sampling L_4 to L_5.

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Source of Support: Nil, **Conflict of Interest:** None.