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Status Assessment of Heavy Metals in Water of the Lepenci River Basin, Kosova

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ABSTRACT

Water represents an essential element for life and living things on earth. Aquatic ecosystems play a decisive role in the socio-economic development in urban and rural areas. In recent decades, there has been concern at the global level with regard to the deterioration of aquatic ecosystems due to the pollution, which is a product of mainly anthropogenic activity. Heavy metals pollution is worrisome for the ecological balance of the aquatic environment, affecting a variety of organisms. Therefore, the objective of this paper was to characterize the quality of water in the Lepenci River basin, to express heavy metals concentration, and to determine the surface water quality index in this basin. In order to achieve such an objective, water samples were collected at eight stations for analyzing the concentrations for heavy metals. Heavy metals were determined by means of atomic absorption spectrophotometry. A good correlation was found between Pb and Zn (r = 0.84), whereas the average negative correlation coefficient was shown between Mn and Cr (r = -0.6513). The heavy metals concentrations varied from 0.0092 to 0.1135 mg/L.The mean concentrations of heavy metals found in the river water were in the order of: Mn > Fe > Pb > Ni > Cd > Zn > Cr > Cu. The Water Quality Index varied from 57 to 81, with the average value of WQI = 68.1250, which ranks the surface water of this basin as fair. From the results we have concluded that the Lepenci River waters during the monitoring period have had low pollution from heavy metals.

Keywords: atomic absorption spectrophotometry, river water, heavy metals, WQI, quality, correlation.

INTRODUCTION

Water is an essential ingredient for the environment and its quality constitutes an issue of concern. Aquatic ecosystems, such as rivers, play an important role for rural and urban populations in many developing countries. However, in recent years, they have been subjected to various forms of degradation due to the pollution by internal waste, industrial leaks, agricultural waste, and bad fishing practices [Ndimele, 2008]. According to [Bakare et *al.*, 2003], industrialization and human activities have partially or fully turned the environment into a landfill site. Consequently, many rivers have been polluted and became harmful to the human life and the lives of other living things.

Resistant metals or metalloids with the density greater than 4.5 g/cm^3 are known as heavy metals and include lead, cadmium, mercury, iron, copper, zinc, nickel, and manganese [Anderson, 2003]. Some of them are essential elements without which the biochemical processes in living organisms would not be possible; however, when they exceed normal concentrations, they become harmful to organisms. Heavy metals pollution can cause disturbing effects on the ecological balance of the aquatic environment and affect a variety of organisms. This is of particular importance in ecotoxicology, as heavy metals are highly persistent and have the tendency to bioaccumulate and concentrate in the food chain; at higher concentrations, they become toxic to organisms. Heavy metal pollution in water can be monitored through measuring their concentrations [Senarathne and Pathiratne, 2007].

Heavy metals are of special importance to surface water pollution. Certain metals are useful, while others are harmful and toxic. Some metals, such as Ca and Mg are essential chemical elements, whereas other metals adversely affect water consumers. It was proven that Pb, Hg, and As are strong, toxic pollutants [BožoDalmacija, 2001]. The toxicity of heavy metals depends on the type of metal and compound, the amount that reaches the body and the duration of metal reaction. This group includes Hg, Pb, Cd, Cr, Cu, Ni, As and Zn.

Heavy metals are of particular importance for the environment, as they exhibit toxicity and persistence and are known for their bioaccumulation in food chains [WHO, 2000]. They cause adverse effects on plants and animals, and are dangerous to the human health. It is known that metal toxicity occurs mainly due to the presence of free metal ions.

Water quality directly affects the health of living things, reflecting the level of contamination of the aquatic ecosystem. Water quality monitoring is an important component of water management, for which the data analysis is needed to identify and characterize water quality issues. Assessment is the process through which water quality data is transformed into information. The information acquired from the monitoring is essential for assessing the water quality. Monitoring can also verify the water contamination based on which a corrective action can be undertaken. Surface waters should be monitored microbiologically, chemically, physically, and radiologicallyin order to determine the presence of pollutants. Therefore, effective monitoring and assessment of surface water quality are crucial to protecting the aquatic life and human health since wastewater consumption is one of the major causes of diseases. Thus, with a preventive approach, the quality of water can be managed.

Water quality assessment can be carried out in various ways. In 1965, Horton was the first to formulate a water quality index which was then used by many researchers for different types of water. A very powerful tool to this end is the Water Quality Index (WQI). WQI serves to sum up large amounts of water quality data in simple categories (good, bad) for management and public reporting [Durmishi et *al.*, 2012]. Researchers use different types of indices. The index aims at transforming numerous water quality data to simple, understandable, and usable information for the public. WQI represents a number from 0 to 100 where a higher value means better water quality and vice versa. The aim of the paper was to assess the level of heavy metal concentrations in water that will focus on the pollution status of the Lepenci river.

MATERIALS AND METHODS

Study area

The Lepenci river is located in the southeast of the Republic of Kosova. It originates in the Oshlak mountains at an altitude of 2212 m; its total length is 50 km and has a slope of 2.1%. Annual average flow is 8.4 m^3/s. The minimum flow of the river Lepenci 1.8 m^3/s, as shown at the Hydrometric Station in Hani i Elezit [MESP, 2010].

The Lepenci river represents the main catchment area in the southeastern region of Kosova. It has an area of 652 km^2 covering 5.98% of the territory of the Republic of Kosova. The area where the river Lepenci flows is characterized by the continental and mountain climate. The average annual rain is 861.4 mm, while the average annual temperature is 10.2°C [Kaçanik, 2011].

For realization of this work, the water samples were taken in spring, summer and autumn of 2017 in eight sampling points along the Lepenci river flow that included upper, middle and downstream. The sampling points were: SP1 (Prevallë), SP2 (Jezerc), SP3 (Brod), SP4 (Runjevë), SP5 (Nikë), SP6 (Gërlicë), SP7 (Kaçanik) and SP8 (Hani iElezit). The sample bottles were labeled with the date and source of sampling; they were kept in refrigerators at 4°C and transported under the appropriate procedure 21.

The analysis of water samples taken in river Lepenci was performed in the laboratory of the Kosova Hydro Meteorological Institute (KHMI). Heavy metals were determined by means of

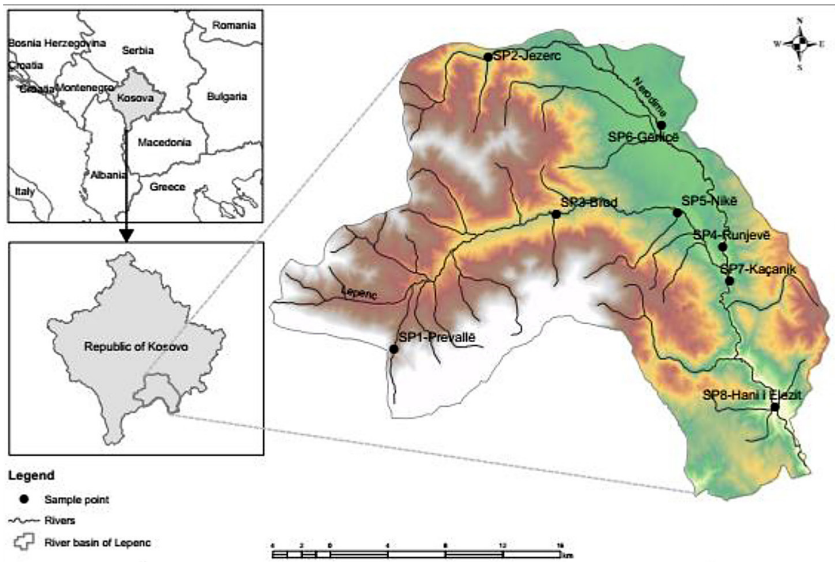

Figure 1. Map of monitoring stations

Atomic absorption Spectrophotometer of American label Perkin Elmer, type Analyst 400. The methods applied to these devices conform to standard methods such as: DIN, ISO and EN. Statistical calculations in this paper were conducted with Excel software, where the data is input and mathematical equations integrated in this program are extracted values: minimal, maximum, average, standard deviation and variation coefficient for the parameters measured for each sampling station that were shown graphically in the works. Data interpretations are performed based on the data obtained in the laboratory, their processing and comparison with the standards.

Canadian Water Quality Index

In order to assess the drinking water quality we have widely used the Water Quality Index (WQI) developed by the Canadian Council of Ministers of the Environment [CCME, 2001]. WQI consists of three measures of variance from selected drinking water quality objectives. These are: scope (F1), frequency (F2), and amplitude (F3).

The scope represents the water quality of the legal norm that does not meet the objectives during the period of interest and is expressed by the equation:

$$F_1 = \left(\frac{Number\ of\ failed\ variables}{Total\ number\ of\ variables}\right) \quad (1)$$

Frequency represents the percentage of individual tests that do not meet the objectives. It is expressed with the following equation:

$$F_2 = \left(\frac{Number\ of\ failed\ tests}{Total\ number\ of\ tests}\right) \cdot 100 \quad (2)$$

Amplitude represents the amount by which failed tests do not meet the objectives. It is expressed with the following equation:

$$F_3 = \left(\frac{nse}{0.01 \cdot nse + 0.01}\right) \quad (3)$$

where *nse* shows the normalized sum of excursions, that is, the summation by which individual tests do not meet the objectives.

WQI is then calculated according to the following equation:

$$WQI = 100 - \left(\frac{\sqrt{F_1^{\,2} + F_2^{\,2} + F_3^{\,2}}}{1.732}\right) \quad (4)$$

The number 1.732 normalizes the resulting values to an extent between 0 and 100, where 0 represents the worst water quality and 100 represents the best water quality. Water quality is then ranked in one of the following six categories (Table 1).

RESULTS AND DISCUSSION

The results of heavy metals concentrations measured in the Lepenci river water at different stations are given in Table 2 and Figures 2–9.

Table 1. Categorization of water quality according to WQI values and description.

Class	WQI value	Description
Excellent	95–100	Water quality is protected with a virtual absence of impairment; conditions are very close to pristine levels. These index values can only be obtained if all measurements meet recommended guidelines virtually all the time.
Very good	89–94	Water quality is protected with a slight presence of impairment; conditions are close to pristine levels.
Good	80–88	Water quality is protected with only a minor degree of impairment; conditions rarely depart from desirable levels.
Fair	65–79	Water quality is usually protected but occasionally impaired; conditions sometimes depart from desirable levels.
Marginal	45–64	Water quality is frequentlyimpaired; conditions often depart from desirable levels.
Poor	0–44	Water quality is almost always impaired; conditions usually depart from desirable levels

Cromium (3^+)

Cr is an essential micronutrient for animals and plants. It is considered as a relative biological and pollution significance element [Rajappa *et al*., 2010]. Generally, the natural content of chromium in water is very low except for the regions with substantial chromium deposits. The concentration of Cr can result from industrial and mining processes. Fish are usually more resistant to Cr than other aquatic organisms, but they can be affected sub-lethally when the concentration increases [Krishna *et al.,* 2014].

The results from experimental measurements for the Cr^{3+} are shown in Table 2 and Figure 2. The recommended value for the Cr^{3+} according to the Romanian standards for assessing the ecological status of surface water (GD161) is 0.025 – >0.250 mg/L. During the three-season study, the Cr^{3+} concentration varied from 0.0110 to 0.0360 mg/L. The lowest value was measured at SP3 and SP4 stations in spring and fall, whereas the highest value was measured at SP5 station in spring. The average values in spring, summer, and fall were 0.023, 0.035, and 0.012 mg/L respectively, whereas the three-season average with

Table 2. Results of metal concentration and statistics

	Heavy metals, mg/L		Prevallë	Jezerc	Brod	Runjevë	Nikë	Gërlicë	Kaçanik	Hani i Elezit	Max	Min	Aver	SD	Cv
SP	Chromium	Cr^{3+}	< 0.003	< 0.003	0.011	0.016	0.036	< 0.003	< 0.003	0.029	0.036	0.011	0.023	0.011	0.49
SA	Chromium	Cr^{3+}	<0.003	0.035	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.035	0.035	0.035	0	0
AU	Chromium	Cr^{3+}	< 0.003	< 0.003	0.011	0.011	< 0.003	< 0.003	0.018	0.008	0.018	0.008	0.012	0.004	0.34
SP	Cadmium	Cd^{2+}	< 0.001	< 0.001	< 0.001	0.084	0.042	0.104	0.082	0.089	0.104	0.042	0.078	0.023	0.29
SA	Cadmium	Cd^{2+}	0.023	0.031	0.047	<0.001	0.075	0.053	<0.001	0.084	0.084	0.023	0.052	0.023	0.45
AU	Cadmium	Cd^{2+}	< 0.001	< 0.001	0.015	0.005	0.033	0.009	< 0.001	< 0.001	0.033	0.005	0.016	0.012	0.74
SP	Nickel	Ni^{2+}	0.014	0.015	0.068	0.053	0.018	0.155	0.119	0.047	0.155	0.014	0.065	0.051	0.78
SA	Nickel	Ni^{2+}	0.069	0.066	0.027	0.025	0.118	<0.006	<0.006	<0.006	0.118	0.025	0.064	0.038	0.59
AU	Nickel	Ni^{2+}	0.054	< 0.006	< 0.006	0.002	0.012	< 0.006	0.045	0.035	0.054	0.002	0.029	0.022	0.75
SP	Zinc	Zn^{2+}	0.005	0.007	0.01	0.055	<0.0003	<0.0003	0.075	0.008	0.075	0.005	0.03	0.036	1.01
SA	Zinc	Zn^{2+}	0.078	0.03	0.018	0.035	0.031	0.04	0.036	0.011	0.078	0.011	0.036	0.019	0.54
AU	Zinc	Zn^{2+}	0.014	0.050	0.026	0.003	0.002	0.038	0.031	0.168	0.168	0.002	0.05	0.053	1.07
SP	Manganese	Mn^{2+}	<0.002	<0.002	0.136	0.285	0.117	0.151	0.242	0.433	0.433	0.117	0.23	0.12	0.50
SA	Manganese	Mn^{2+}	0.088	0.106	0.094	0.095	0.058	0.460	0.053	0.115	0.46	0.053	0.15	0.13	0.84
AU	Manganese	Mn^{2+}	3.736	0.12	1.502	1.602	0.146	0.365	0.207	0.106	3.736	0.106	1.16	1.27	1.09
SP	Copper	Cu^{2+}	0.021	0.023	0.037	< 0.002	0.001	< 0.002	0.009	0.038	0.038	0.001	0.021	-0.015	-0.7
SA	Copper	Cu^{2+}	<0.002	<0.002	<0.002	0.001	<0.002	0.010	<0.002	<0.002	0.01	0.001	0.005	0.006	1.15
AU	Copper	Cu^{2+}	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	0	0	0	0	0
SP	Iron	Fe^{2+}	0.115	0.12	0.401	0.154	0.332	0.065	0.046	0.243	0.401	0.046	0.192	0.12	0.66
SA	Iron	Fe^{2+}	0.003	<0.002	<0.002	0.229	0.034	0.175	0.081	<0.002	0.229	0.003	0.108	0.09	0.88
AU	Iron	Fe^{2+}	< 0.002	0.03	0.008	0.112	0.075	0.128	0.199	0.165	0.199	0.008	0.103	0.06	0.67
SP	Lead	Pb^{2+}	0.047	0.053	< 0.002	0.181	< 0.002	0.295	0.341	0.385	0.0385	0.047	0.21	0.14	0.67
SA	Lead	Pb^{2+}	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0	0	0	0	0
AU	Lead	Pb^{2+}	< 0.002	0.007	0.005	< 0.002	< 0.002	0.018	0.031	0.097	0.097	0.005	0.03	0.03	1.02

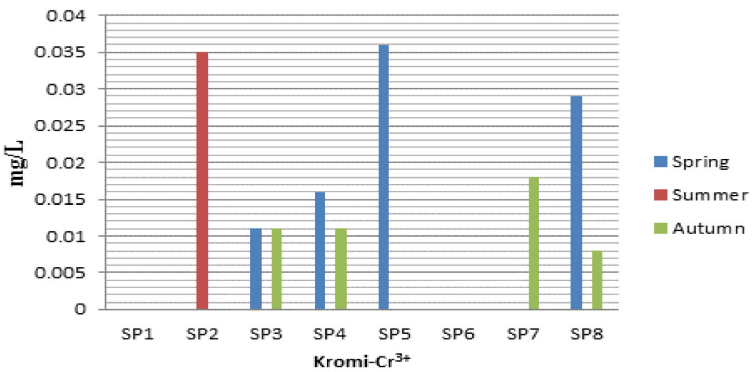

Figure 2. Variation of Cr values in water of Lepenci river

the standard deviation was 0.0233 ± 0.005 mg/L. The Cr^{3+} average concentrations at SP1-SP8 stations were 0.0030, 0.0137, 0.0083, 0.0100, 0.0140, 0.0030, 0.0080, and 0.0133 mg/L, respectively. In spring, the SP3 station showed the minimum value of 0.0110 mg/L, whereas the SP5 station showed the maximum value of 0.0360 mg/L. In summer, the SP2 station showed the minimum value of 0.0350 mg/L, whereas the SP2 station showed the maximum value of 0.0350 mg/L. In fall, SP7 and SP8 stations showed the minimum value of 0.0080 mg/L, whereas the SP7 station showed the maximum value of 0.0180 mg/L. The measurements for the Cr^{3+} in the water of Lepenc River basin were found to be within the minimum values which, if compared to the GD161 standards, were within the allowed limits, thus ranking the water of this river in the first class.

Cadmium (Cd^{2+})

Cd as pollutants in the water can reach from industrial discharges and waste ore. It is widely used in galvanization and production of batteries. Cd is chemically similar to Zn and found in water in the oxidation form +2. It occurs naturally as CdS and followed minerals of Pb and Zn. Food is the main source of Cd poisoning. The effects of acute Cd poisoning in humans are very serious, including hypertension, kidney damage, causing potential prostate cancer, etc. [Durmishi et *al.*, 2016]. The physiological effects of Zn with Cd replacement in some enzymatic reactions hampered the normal functioning of enzymes. The toxic effect of Cd in water decreases with the increasing hardness of the water, due to rising water carbonates content. Heavy metal carbonates are less soluble in water and so a part of dissolved Cd is removed . It is a non-essential element, known to have a toxic potential. Cd is highly toxic and responsible for several cases of poisoning through food. Small quantities of Cd cause adverse changes in the arteries of human kidney. It replaces Zn biochemically and causes hypertension as well as kidney damage. It interferes with enzymes and causes a painful disease called Itai-itai [Rajappa*et al*., 2010]. High concentration of Cd occurs at neutral and alkali pH.

The results from experimental measurements for the Cd^{2+} are shown in Table 2 and Figure 3. According to the Romanian standards for assessing the ecological status of surface water (GD161), the recommended value for the Cd^{2+} is 0.0005->0.005 mg/L. During the three-season study, the Cd^{2+} concentration varied from 0.0050 to 0.0840 mg/L. The lowest value was measured at SP4 station in fall, whereas the highest value was measured at SP8 station in summer. The average values in spring, summer, and fall were 0.0780, 0.0520, and 0.0160 mg/L respectively, whereas the three-season average with the standard deviation was 0.0487±0.0193 mg/L. The Cd^{2+} average concentrations at SP1-SP8 stations were 0.0083, 0.0110, 0.0210, 0.0300, 0.0500, 0.0553, 0.0280 and 0.0580 mg/L respectively. In spring, the SP5 station showed the minimum value of 0.0420 mg/L, whereas the SP6 station showed the maximum value of 0.1040 mg/L. In spring, the SP1, SP2, and SP3 stations showed the values below detection levels; water values at SP4, SP6, SP7, and SP8 stations, based on GD161 standards, resulted in classification to the fifth class, whereas the water at SP5 station belonged to the third class. In summer, the SP1 station showed the minimum value of 0.0230 mg/L, whereas the SP8 station showed the maximum value of 0.0840 mg/L. In summer, the analyzed values at SP4 and SP7 stations were below the detection levels; the water values at the SP1, SP2, and SP3 stations belonged to the third class, whereas Cd^{2+} values of water at SP5, SP6, and SP8 stations were categorized into the fifth category. In fall, the SP4 station showed the minimum value of 0.0050 mg/L, whereas the SP5 station showed the maximum value of 0.0330 mg/L. In fall, the Cd^{2+} values at SP1, SP2, SP7, and SP8 stations were under the detection levels; the water at the SP3, SP4, and SP6 stations belonged to the fifth category, whereas the water of the SP5 station belonged to the third category. According to the seasonal average at all stations, the water belonged to the fifth category.

Nickel (Ni^{2+})

Ni is an essential trace metal for several animal species, micro-organisms and plants; therefore, either deficiency or toxicity symptoms can-occur when, too little or too much Ni is taken up, respectively. Although a number of cellular effects of Ni have been documented, a deficiency state in humans has not been described [Scoott-Fordsmand, 1997]. Ni and its compounds have many industrial and commercial uses, and the progress of industrialization has led to an increased emission of pollutants into ecosystems. Although Ni is omnipresent and vital for the function of many organisms, concentrations in some areas from both the anthropogenic release and naturally varying levels may be toxic to living organisms [Diagomanol et *al.*, 2004]. Ni cause toxic effects in the respiratory tract and immune system. The exposure of the general population to Ni mainly concernedthe oral intake, primarily through water and food. It is also known to affect non-occupationally exposed individuals, especially those handling stainless steel and nickel-plated articles of everyday use, because nickel is a common sensitizing agent with a high prevalence of allergic contact dermatitis [Kitaura et *al.*, 2003].

The results from the experimental measurements for the Ni^{2+} are shown in Table 2 and Figure 4. According to the Romanian standard for assessing the ecological status of surface water (GD161), the recommended value for the Ni^{2+} is 0.01 – >0.1 mg/L. During the three-season study, the Ni^{2+} concentration varied from 0.0020 to 0.01550 mg/L. The lowest value was measured at SP4 station in fall, whereas the highest value was measured at SP6 station in spring. Average values in spring, summer, and fall were 0.065, 0.064, and 0.029 mg/L respectively, whereas the three-season average with the standard deviation was 0.0527±0.0370 mg/L. The average concentrations values of the Ni^{2+} at SP1-SP8 stations were 0.0457, 0.0290, 0.0337, 0.0267, 0.0493, 0.0557, 0.0567, and 0.0293 mg/L, respectively. In spring, the SP1 station showed the minimum value of 0.0140 mg/L, whereas the SP6 station showed the maximum value of 0.1550 mg/L. In summer, the SP3 station showed the minimum value of 0.0250 mg/L, whereas the SP5 station showed the maximum value of 0.1180 mg/L. In fall the SP4 station showed the minimum value of 0.0020 mg/L, whereas the SP7 station showed the maximum value of 0.0540 mg/L. The measurements for the Ni^{2+} in the water of Lepenc River basin were found to be within the allowed recommended values of GD161 standards, thus ranking the water of Lepenci river in the first class.

Zinc (Zn^{2+})

Zn is found in natural waters in larger quantities compared with Cu, Pb, Cd and Hg, so the industrial discharge waters containing high concentrations of it. Zn is an essential element for the life of animal and human beings. It is found in virtually all food and potable water in the form

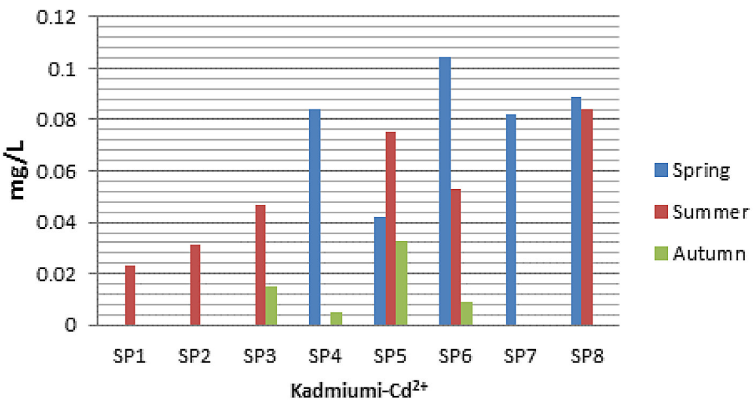

Figure 3. Variation of Cd values in water of Lepenci river

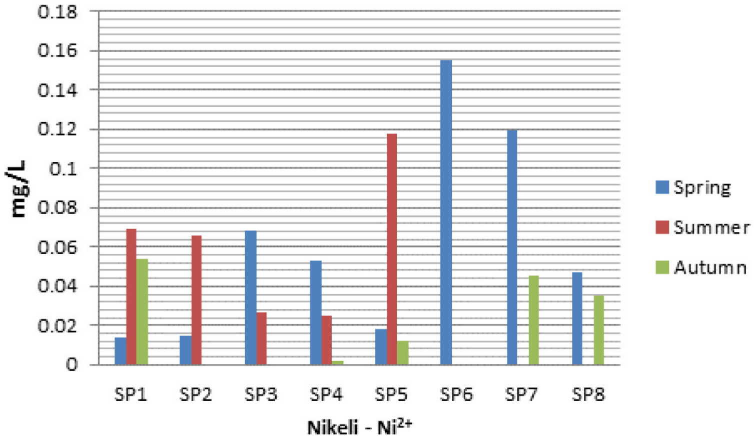

Figure 4. Variation of Ni values in water of Lepenci river

of salts or organic complexes [WHO, 2011]. The main sources of Zn pollution in the environment are zinc fertilizers, sewage sludge, and mining. Urban runoff, mine drainage, and municipal sewages are the more concentrated sources of zinc in water [Damodharan, 2013]. Zn is not accumulated in the body and it is activating enzymes. It affects bone growth, development and functioning of reproductive organs, etc. There are rare cases of Zn poisoning. Its action in the aquatic fauna depends on the hardness of water, saturated with oxygen and temperature. Salts of alkaline-earth elements reduce the toxicity of Zn, while increasing the temperature, whereas the lowering the concentration of dissolved oxygen increases the toxicity of Zn. It plays a vital role in the physiological and metabolic processes of many organisms. Other clinical signs of Zn toxicity have been reported as diarrhea, bloody urine, liver failure, kidney failure and anemia [Duruibe *et al.,* 2007].

The results from experimental measurements for the Zn^{2+} are shown in Table 2 and Figure 5. According to the Romanian standards for assessing the ecological status of surface water (GD161), the recommended value for Zn^{2+} is 0.1 – >1 mg/L. During the three-season study, the Zn^{2+} concentration varied from 0.0020 to 0.01680 mg/L. The lowest value was measured at SP5 station in fall, whereas the highest value was measured at SP8 station in fall. The average values in spring, summer, and fall were 0.030, 0.036, and 0.005 mg/L respectively, whereas the three-season average with the standard deviation was 0.0387±0.0360 mg/L. The average concentrations values of the Zn^{2+} at SP1-SP8 stations were 0.0323, 0.0290, 0.0180, 0.0310, 0.0111, 0.0261, 0.0473, and 0.0623 mg/L respectively. In spring, the SP1 station showed the minimum value of 0.0050 mg/L, whereas the SP7 station showed the maximum value of 0.0750 mg/L. In summer, the SP8 station showed a minimum value of 0.0110 mg/L, whereas the SP1 station showed the maximum value of 0.0780 mg/L. In fall, the SP5 station showed the minimum value of 0.0020 mg/L, whereas the SP8

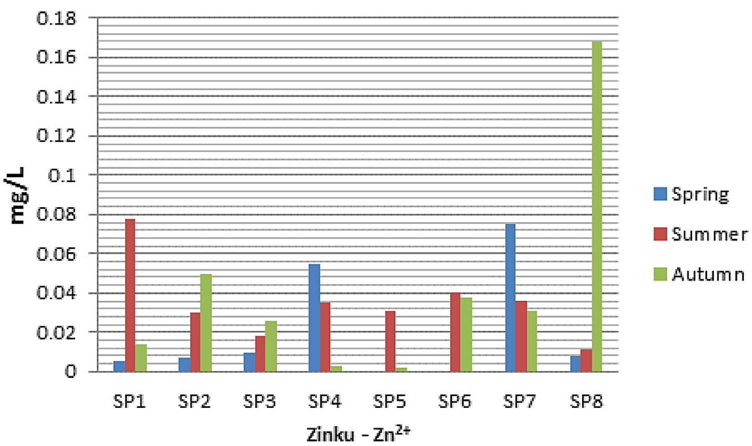

Figure 5. Variation of Zn values in water of Lepenci river

station showed the maximum value of 0.1680 mg/L. On the basis of the GD161 standards, the levels of Zn^{2+} in the water of Lepenc River basin during the three seasons were found to be within the recommended values, thus ranking the water of this river in the first class.

Manganese (Mn^{2+})

Mn is present in over 100 common salts and mineral complexes that are widely distributed in rocks, in soils and on the floors of lakes and oceans [Damodharan, 2013]. These Mn minerals include sulfides, oxides, carbonates, silicates, phosphates, arsenates, tungstates, and borates. However, the most important Mn mineral is the native black manganese oxide, pyrolusite (MnO_2). Mn is used for production of ferromanganese steels, electrolytic manganese dioxide for use in batteries, alloys, catalysts, antiknock agents, pigments, dryers, wood preservatives and coating welding rods [Bradi, 2005]. It is also used as an oxidant for cleaning, bleaching and disinfection (as potassium permanganate) and as an ingredient of various products [WHO, 2011]. Mn is an essential micronutrient present in all living organisms, because it functions as a co factor for many enzyme acticities [Suresh *et al.,* 1999]. Mn is a metal with low toxicity but has a considerable biological significance and seems to accumulate in fish [Kumar *et al.,* 2011]. According to [Krishna *et al.,* 2014], high Mn concentration interferes with the central nervous system of vertebrates; hence, the consumption of Mn contaminated fish potentially resulting in health risks to the consumers is a matter of concern. High concentration of Mn causes liver cirrhosis and also produces a poisoning called Manganese or Parkinson disease [Bradi, 2005].

The results from experimental measurements for the Mn^{2+} are shown in Table 2 and Fig. 6. According to the Romanian standards for assessing the ecological status of surface water (GD161), the recommended value for the Mn^{2+} is 0.05 – >1 mg/L. During the three-season study, the Mn^{2+} concentration varied from 0.0530 to 3.7360 mg/L. The lowest value was measured at SP7 station in summer, whereas the highest value was measured at SP1 station in fall. The average values in spring, summer, and fall were 0.2300, 0.1500, and 1.1600 mg/L respectively, whereas the three-season average with the standard deviation was 0.5133±0.5067 mg/L. The average concentrations of Mn^{2+}at SP1-SP8 stations were 1.2753, 0.0760, 0.5773, 0.6607, 0.1070, 0.3253, 0.1673, and 0.2180 mg/L respectively. In spring, SP5 station showed the minimum value of 0.1170 mg/L, whereas the SP8 station showed the maximum value of 0.4330 mg/L. The Mn^{2+} concentration in the river waters at SP1 and SP2 stations was under the detection levels; water at SP3, SP5 and SP6 stations belonged to the second class, whereas the SP4, SP7, and SP8 stations belonged to the fifth class. In summer, the SP7 station showed the minimum value of 0.0530 mg/L, whereas the SP6 station showed the maximum value of 0.4600 mg/L. Compared to GD 161 standards, the water at SP1, SP2, SP3, SP4, SP5, SP7, and SP8 stations belonged to the first class, whereas the water at SP6 station belonged to the fifth class. In fall, the SP8 station showed the minimum value of 0.1060 mg/L, whereas the SP1 station showed the maximum value of 3.7360 mg/L. Compared to GD 161 standards, the water at SP1 and SP7 stations belonged to the fifth class, the water at SP2 and SP5 stations belonged to the first class, and the water at SP3 and SP4 stations belonged to the third class.

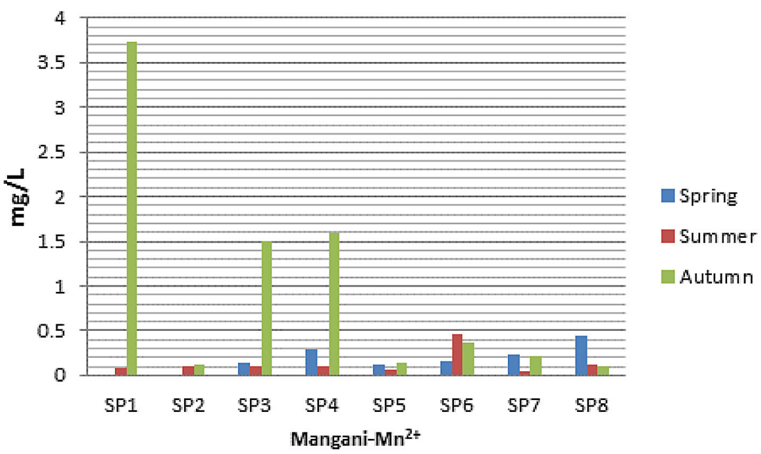

Figure 6. Variation of Mn values in water of Lepenci river

Copper (Cu^{2+})

Cu is an essential constituent of living systems and is widely distributed metal in nature. Cu can exist in aquatic environment in three forms, namely soluble, colloidal and particulate. Cu is a rare ingredient of natural waters. It is used in Cu pipes or dosing tanks with copper sulphate(II), which is used to prevent the growth of algae. It was proven that Cu is toxic to fish and other aquatic creatures, in those concentrations that do not pose a risk to man. It is known that an ion of Cu(II) is mainly poisonous chemical element. Copper is important for human life and other living things, so it plays an important role in metabolic processes, affecting a number of enzymes and hemoglobin synthesis. The toxicity of Cu in water depends on the alkalinity, pH value, the content of organic substances, etc. With the increase of these parameters, the concentration of ions of Cu(II) decreases in addition to the Cu toxicity to aquatic systems. High doses may also cause anaemia, liver and kidney damage, stomach and intestinal irritation [Tirkey *et al*., 2012]. Copper ions (Cu^{2+}) are toxic to most life forms. Cu is highly toxic to invertebrates and moderately so to mammals in trace amounts.

The results from the experimental measurements for the Cu^{2+} during the three seasons are shown in Table 2 and Figure 7. According to the Romanian standards for assessing the ecological status of surface water (GD161), the recommended value for the Cu^{2+} is 0.02 – >0.1 mg/L. During the three-season study, the Cu^{2+} concentration varies from 0.0010 to 0.0380 mg/L. The lowest value was measured at SP4 and SP5 stations in summer, whereas the highest value was measured at SP8 station in spring. The average values in spring, summer, and fall were 0.0210, 0.0050, and 0.000 mg/L respectively, whereas the three-season average with the standard deviation was 0.0087±0.0070 mg/L. The average concentrations of Cu^{2+}at SP1-SP8 stations were 0.0083, 0.0090, 0.0137, 0.0017, 0.0017, 0.0047, 0.0043, and 0.0140 mg/L respectively. In spring, the SP1 station showed the minimum value of 0.0050 mg/L, whereas SP7 station showed the maximum value of 0.0750 mg/L. When compared to GD 161 standards, the obtained measured values were found to be under the detection levels at SP4 and SP6 stations. The water at SP1, SP2, SP5, and SP7 stations belonged to the first class, whereas the water at SP3 and SP8 stations belonged to the second class. In summer, the SP8 station showed the minimum value of 0.0110 mg/L, whereas the SP1 station showed the maximum value of 0.0780 mg/L. During this season we detected only two values at two stations (SP4 and SP6) where the water belonged to the first class, whereas at all other stations, the values were under the detection levels. In fall, the SP5 station showed the minimum value of 0.0020 mg/L, whereas the SP8 station showed the maximum value of 0.1680 mg/L. In fall, the Cu^{2+} concentration values at each station were under the detection levels.

Iron (Fe^{2+})

Fe is an essential metal for most living organisms and humans. It is a constituent of proteins and many enzymes, including hemoglobin and myoglobin. Fe is usually more abundant in freshwater environment than other metals, due to its high occurrence on Earth [Forstner et *al.*, 1979]. Fe deficiency can lead to anemia and fatigue, which are usually common among children under the age of five, pregnant women and

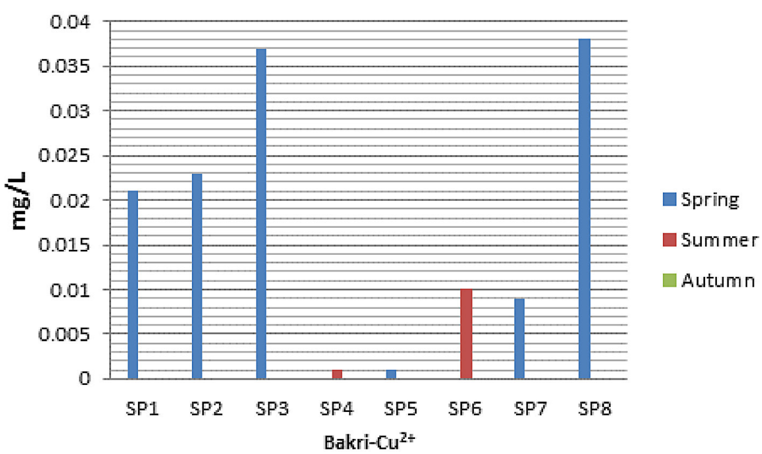

Figure 7. Variation of Cu values in water of Lepenci river

immuno-compromised individuals, thus making them vulnerable to numerous infections [Garvin, 2015]. Vuori [1995] reported that Fe has both direct and indirect effects on river ecosystems, as it affects lotic organisms by interfering with their normal metabolism and osmoregulation. He also noted that the combined effects of Fe contamination can reduce the occurrence and diversity of several aquatic organisms, including fish. High Fe concentration, together with its precipitate in aquatic ecosystems, do have negative effects on the behavior, reproduction and survival of aquatic animals [Gerhardt, 1992]. Fe is an important metal for the life of plants and animals. The soluble Fe shares two of its electrons (oxidation state +2), whereas when reacting with oxygen, it forms a rusty-brown precipitate of iron hydroxide that is insoluble. In waters rich with Fe, there is a bacterium known as "filamentous", which grows and multiplies. It has a highly negative impact on water quality, as it leads to the biomass collection in the distribution system. Fe is an essential metal of the hemoglobin structure and is used for the treatment of anemia, which is caused by the iron deficiency in the blood. It becomes toxic when used in large doses.

The results from experimental measurements for Fe^{2+}during the three seasons are presented in Table 2 and Figure 8. According to the Romanian standards for assessing the ecological status of surface waters (GD161), the recommended value for Fe^{2+} is 0.3 – >2 mg/L. During the three-season study, the Fe^{2+} concentration varied from 0.0030 to 0.4010 mg/L. The lowest value was measured at SP1 station in summer, whereas the highest value was measured at SP3 station in spring. The average values in spring, summer, and fall were 0.1920, 0.1080, and 0.1030 mg/L respectively, whereas the three-season average with the standard deviation was 0.1343±0.0900 mg/L. The average values of Fe^{2+} concentrations at SP1-SP8 stations were 0.0400, 0.0507, 0.1370, 0.1650, 0.1470, 0.1227, 0.1087, and 0.1367 mg/L respectively. In spring, the SP7 station showed the minimum value of 0.0460 mg/L, whereas the SP3 station showed the maximum value of 0.4010 mg/L. When compared to the GD 161 standards, the measured values resulted to be below detection levels at SP4 and SP6 stations. The water at SP1, SP2, SP5, and SP7 stations belonged to the first class, whereas the water at SP3 and SP8 stations belonged to the second class. In summer, the SP1 station showed the minimum value of 0.0030 mg/L, whereas the water at SP4 station showed the maximum value of 0.0030 mg/L. The values obtained at SP2, SP3, and SP8 stations were below detection levels. In fall, the SP3 station showed the minimum value of 0.0080 mg/L, whereas the SP7 station showed the maximum value of 0.1990 mg/L. In fall, the Fe^{2+} concentration values were below detection levels at all measuring stations. When compared to GD161 standard, the measured values at the three seasons resulted to be within the said standard, thus ranking the river water in the first class.

Lead (Pb^{2+})

Pb in the environment arises from both natural and anthropogenic sources. It is a natural constituent of air, water and biosphere. Pb is also a heavy metal that appears to be capable of +2 oxidation in aquatic environments and comes from various industrial sources and mines. Pb from gasoline (with tetraethyl lead), is the main source of atmospheric Pb and its large part passes in the water. Otherwise, it is rarely detected in natural waters. Pb is also a poisonous metal. In the case

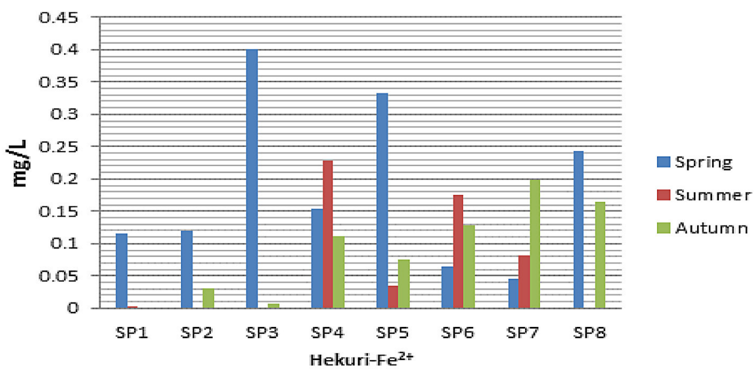

Figure 8. Variation of Fe values in water of Lepenci river

of humans, the poisoning with Pb causes disturbances in the functioning of the kidneys, reproductive system, liver and nervous system. Pb poisoning caused by the environmental exposure causes mental retardation to more children, while mild poisoning leads to anemia. The lack of Ca, Fe, Cu, Se and ascorbic acid in food conditions the accumulation of lead in the body. The largest amount of Pb accumulates is in the bones and it replaces Ca. Pb organic compounds easily reach the human body through the skin and central nervous system at risk. The toxic effect of Pb is also based on the great affinity to sulfur. Pb reduces the activity of enzymes, oxidation-reduction reactions in the cell and protein synthesis. It is known that Pb poisoning is greater in hard waters than in soft waters. Pb is a serious cumulative body poison. High levels of exposure may result in biochemical effects in humans which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system [Tirkey*et al*., 2012]. The sources include burning of lead based petroleum fuels, organic and inorganic lead compounds now used in a variety of commercial products and industrial materials including plastics, storage batteries, bearing alloys, insecticides, ceramics, cable sheathings, sheeting, radiation shields and even some paints [Mutwiri, 2001].

The measurements from experimental results for the Pb^{2+} during the three seasons are presented in Table 2 and Figure 9. According to the Romanian standards for the assessment of ecological status of surface waters (GD161), the recommended value for Pb^{2+} is 0.005 – >0.05 mg/L. During the three-year study, the Pb^{2+} concentration varied from 0.0000 to 0.0970 mg/L. The lowest value was measured at SP1 – SP8 stations in summer, whereas the highest value was measured at SP8 station in fall. The average values in spring, summer, and fall were 0.2100, 0.0000, and 0.030 mg/L respectively, whereas the three-season average with the standard deviation was 0.0800 ± 0.0452 mg/L. The average values of Pb^{2+} concentrations at SP1-SP8 stations were 0.0170, 0.0207, 0.0030, 0.0617, 0.0020, 0.1050, 0.1247, and 0.1613 mg/L respectively. The Pb values in the water of Lepenc river basin fluctuate from a minimum value of 0.0470 mg/L (SP1) to a maximum value of 0.3850 mg/L (SP8) in the spring season. At two stations (SP3 and SP5) the values were below detection levels. In summer, the values of all monitoring stations were under the detection levels. In fall, the values ranged from a minimum of 0.005 mg/L (SP3) to a maximum of 0.097 mg/L (SP8). The values at SP1, SP4, and SP5 stations were below detection levels.

Coefficients of correlation related to the concentration of metals of the river Lepenci

The coefficients of correlation related to the concentration of waters in the Lepenci river were shown in Table 3. The results show that three values of coefficients of correlation appeared to be the most significant. Pb showed high a coefficient of correlation with Zn (r=0.8488), whereas Fe and Cd showed an average coefficient of correlation (r=0.6678). A average negative coefficient of correlation was found between Mn and Cr (r = -0.6513) as well as between Ni and Cr (r= -0.5277).

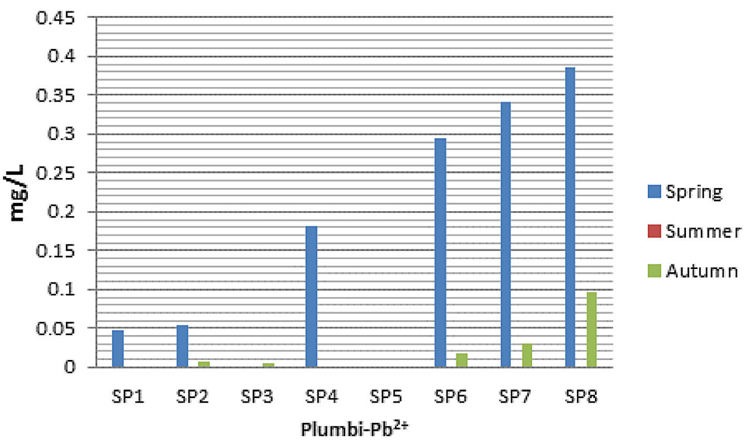

Figure 9. Variation of Pb values in water of Lepenci river

Table 3. Coefficients of correlation for metal concentrations in the Lepenci River

Correlation	Cr	Cd	Ni	Zn	Mn	Cu	Fe	Pb
Cr	1.0000							
Cd	0.1866	1.0000						
Ni	-0.5277	0.2196	1.0000					
Zn	0.0763	0.1914	-0.1559	1.0000				
Mn	-0.6513	-0.4941	-0.0573	-0.0885	1.0000			
Cu	0.0749	-0.1386	-0.4500	0.3621	0.0966	1.0000		
Fe	0.2811	0.6678	-0.1096	-0.0662	-0.3125	-0.2320	1.0000	
Pb	-0.0399	0.5742	0.1257	0.8488	-0.3152	0.0997	0.2511	1.0000

Water quality assessment of Lepenci River using WQI

The calculation of Lepenci River Water Quality Index was done using the Water Quality Index Desktop software developed by [Ramadani et *al.*, 2017]. The results for the factors F1, F2, and F3 and the WQI for the eight stations are given in Table 4, whereas the WQI values are graphically presented in Figure 10.

At SP1 station, the WQI value was found to be 80, since two parameters (Cd and Mn) did not meet the recommended value of the regulation for assessment of river water quality, and two tests failed: Cd with a value of 0.0230 mg/L in summer and Mn with a value of 3.736 mg/L in fall. At SP2 station, the WQI value resulted to be 81, since two parameters (Cd and Pb) did not meet the recommended value of the regulation for assessment of river water quality, and two tests failed: Cd with a value of 0.0310 mg/L in summer and Pb with a value of 0.0530 mg/L in spring. At SP3 station, the WQI value was 75, since two parameters (Cd and Mn) did not meet the recommended value of the regulation, and three tests failed: Cd with a value of 0.0470 mg/L in summer, Cd with a value of 0.0150 mg/L in fall, and Mn with a value of 1.5020 mg/L in fall. At SP4 station, the WQI value was found to be 65, since three parameters (Cd, Mn, and Pb) did not meet the recommended value of the regulation, and three tests failed: Cd with a value of 0.0840 mg/L in spring, Mn with a value of 1.6020 mg/L in fall, and Pb with a value of 0.1810 mg/L in spring. At SP5 station, the WQI value was 64, since two parameters (Cd and Ni) did not meet the recommended value of the regulation, and four tests failed: Cd with a value of 0.0420 mg/L in spring, Cd with a value of 0.0750 mg/L in summer, Cd with a value of 0.0330 mg/L in fall, and Ni with a value of 0.1180 mg/L in summer. At SP6 station, the WQI value amounted to 57, since three parameters (Cd, Ni and Pb) did not meet the recommended value of the regulation, and five tests failed: Cd with a value of 0.1040 mg/L in spring, Cd with a value of 0.0530 mg/L in summer, Cd with a value of 0.0090 mg/L in fall, and Pbwith a value of 0.2950 mg/L in spring. At SP7 station, the WQI value equalled 64, since three parameters (Cd, Ni and Pb) did not meet the recommended value of the regulation, and three tests failed: Cd with a value of 0.0820 mg/L in spring, Ni with a value of 0.1190 mg/L in spring, and Pb with a value of 0.3410 mg/L in spring. At SP8 station, the WQI value was 59, since two parameters (Cd and Pb) did not meet the recommended value of the regulation, and four tests failed: Cd with a value of 0.0890 mg/L in spring, Cd with a value of 0.0840 mg/L in summer; Pb

Table 4. Values obtained from the Water Quality Desktop and WQI calculation

Stations	F1	F2	F3	WQI
SP1- Prevallë	25	8.333334	20.88608	80
SP2- Jezerc	25	8.333334	17.97676	81
SP3-Brodë	25	12.5	31.23603	75
SP4-Runjevë	37.5	12.5	44.21459	65
SP5-Nikë	25	16.66667	53.10668	64
SP6-Gërlicë	37.5	20.83333	59.76530	57
SP7-Kaçanik	37.5	12.5	47.1482	64
SP8-Hani iElezit	25	16.66667	62.6401	59
			Average WQI:	68.1250

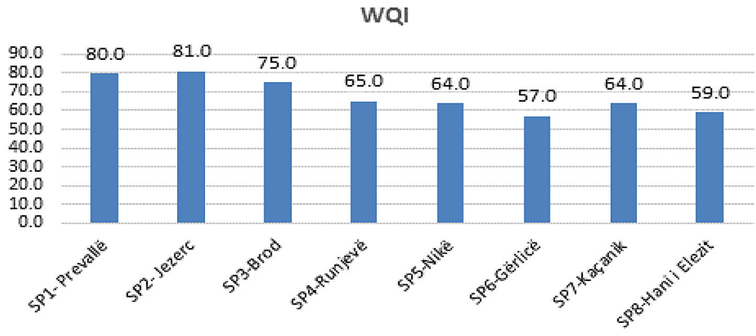

Fig. 10. WQI values at all measuring stations

with a value of 0.3850 mg/L in spring, and Pb with a value of 0.0970 mg/L in fall.

The results show that the river water at SP2 station had the best quality with a WQI value of 81 and belonged to the good category, whereas the river water at SP6 station had the worst quality with a WQI value of 57 and belonged to marginal category. Finally, based on these results, the average WQI value was calculated for the entire measurement period and it resulted to be 68.1250 which showed that the water of Lepenc River belonged to fair category.

CONCLUSIONS

Given the research conducted and the discussion of results we can draw the following conclusions:

1. Although Lepenci, being a mountain river, has a self-cleaning capability for its waters, slight heavy metals pollution was observed during the monitoring period;
2. Water pollution of Lepenci River with heavy metals assessed by the Romanian standards for the assessment of ecological status of surface waters (GD161) was low and the most severe heavy metals pollution was observed at the stations located at the bottom of the river;
3. During the monitoring period the water of Lepenci River was categorized in second-third class;
4. The sequence of average values with standard deviation of heavy metals concentrations in the water of Lepenc river expressed in mg/L was as follows: Mn (0.5133±0.5067) > Fe (0.1343±0.0900) > Pb (0.0800±0.0452) > Ni (0.0527±0.0370) > Cd (0.0487±0.0193) > Zn (0.0387±0.0360) > Cr (0.0233±0.005) > Cu (0.0087±0.0070);
5. Calculation of coefficients of correlation showed that it was the highest between Pb and Zn (r = 0.8488), average between Fe and Cd (r = 0.6678), and negatively average between Mn and Cr (r = -0.6513) and between Ni and Cr (r = -0.5277);
6. The Water Quality Index Desktop software was also used as a highly efficient tool for WQI calculation based on the guidelines of the Canadian Ministry of Environment;
7. On the basis of the WQI calculation using the Water Quality Index Desktop software, it was found that the river water at the SP2 station had the best water quality with a WQI value of 81 (the category: good), river water at SP6 station had the worst quality with a WQI value of 57 (category: marginal), whereas the average WQI for the entire measurement period was 68.1250 (category: fair);
8. Water Quality Index Desktop software has provided excellent and reasonable results;
9. We propose that the state authorities and institutions should support river water monitoring as an effective measure for examining their ecological status and protection against various types of pollution.

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