



## Heavy metals as main polluting factors in the Mirusha, Stanishor and Morava rivers in the Municipality of Gjilan, Kosovo

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**Abstract:** Pollution with the heavy metals of Kosovo's rivers has been and continues to be a serious concern not only for the population, but also for responsible institutions that deal with environmental protection in our country. Based on this fact and our doubts regarding the quality of the river waters of the Municipality of Gjilan, we were motivated to conduct a study of the quality of the Mirusha, Stanishor and Morava river waters. During our research, we have set eight monitoring points for determining the exact level of concentration of heavy metals in the river waters quoted above. The heavy metals analyzed in this study were: Pb, Hg, Mn, Cu, Fe, Ni, Cr, Cd, Zn and Ba. The analytical technique used to determine the concentration of heavy metals was ICP-OES. The obtained results show that Fe, Mn and Ba exceed the allowed level at several monitoring points of the Mirusha and Stanishor rivers and appears in the degree of pollution with these metals of Morava river waters. The presence of heavy metals in the waters of these rivers negatively affects habitat waters and indirectly human health. Therefore, the identification and then suggestions regarding elimination of polluting sources are the subject of this study.

**Keywords:** Rivers, pollution, heavy metals, ICP-OES.

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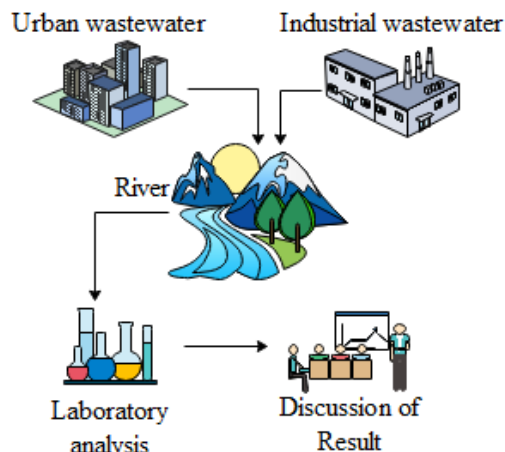
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### INTRODUCTION

Gjilan is a municipality in the Republic of Kosovo. Lastly the number of food industries has begun to grow every year and more and normally with the rise of the economy of this city the livelihood has become bigger in this city, this means that the number of inhabitants in Gjilan municipality has started to increase the population.

Gjilan has a problem of wastewater treatment due to deficiency of plants and this is the main factor of

the pollution of the Mirusha, Stanishor, and Morava Rivers. Analysis of the heavy metals of these rivers is indispensable to have sufficient chemical evidence on how the concentration of heavy metals increases each and every year in these rivers. Kosovo from the state budget allocates a lot of money on environmental issues but as a result it is not known why Kosovo as a state, namely Gjilan with a major economic development, have a problem with wastewater see Figure 1.



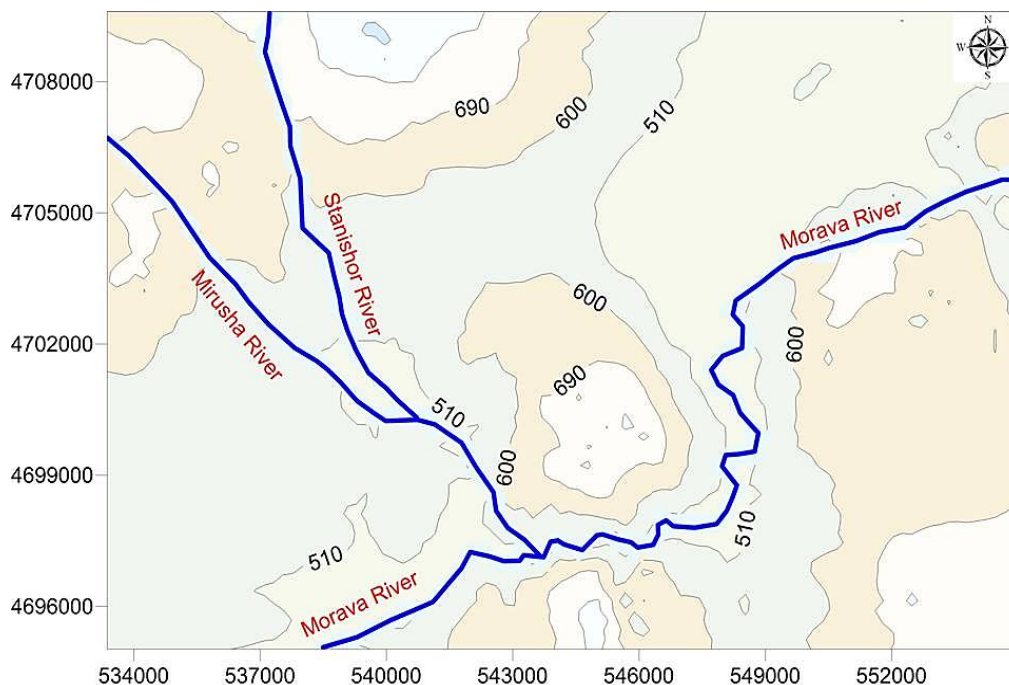
**Figure 1.** Description of the pollutant causes of rivers in Gjilan municipality, laboratory analysis of heavy metals and discussion of results.

Mirusha and Stanishor rivers are surface waters, characterized by low volumes during the summer season, while during the winter season the waters of these rivers are more voluminous. These two rivers flow into the river with a fast flow which is "Morava e Binçës". These rivers are very chemically polluted with heavy metals because domestic and industrial wastewater are discharged in these rivers as we cite above, see Figure 2. The spring of the Mirusha River is in the village of Koretisht and this spring is called church water, but the problem is that urban and industrial wastewater are discharged in this river. The Stanishor river is also a polluted river, but the spring of the Stanishor river is not contaminated with wastewater. Morava River belongs to the Black Sea basin. It also flows along the Danube River, and this is very worrying with the Morava River polluting scale. The description of the sampling place in the Mirusha, Stanishor and Morava rivers is very important to understand the degree of pollution of the heavy metals of these rivers that we have analyzed. (1).

Determining heavy metals is not an easy procedure, so we have to be careful about sample preparation and instrument work, so that there is no deviation of the results. For the determination of heavy metals, we used ICP- OES Optima 2100 DV, while mineralization of the sample is realized with BERGHOF Speedwave MWS-3 +. With the ICP-OES we have analyzed these heavy metals such as: Pb, Hg, Mn, Cu, Fe, Ni, Cr, Cd, Zn and Ba. The Republic of Kosovo, especially the Ministry of Environment, has many laws and regulations regarding the

protection of rivers in this state, but the problem is that many industries producing different products and do not follow the rules for wastewater treatment. In the past decade, the concentration of metals in the rivers of Kosovo was reported to be higher than normal and the detectable concentration of metals in some rivers was found to exceed the health standard limits.

Environmental pollution is a significant problem in modern society (2). Heavy metals are naturally occurring elements that have a high atomic weight and a density at least 5 times greater than that of water. Their multiple industrial, domestic, agricultural, medical and technological applications have led to their wide distribution in the environment; raising concerns over their potential effects on human health and the environment (3). Heavy metals are natural components of the earth's crust, and natural concentrations of heavy metals in soils tend to remain low. However, anthropogenic inputs of several heavy metals into waters greatly exceed natural inputs. This problem is more prominent in cities, since cities have a high density of anthropogenic activities and populations (4). After taking the metal from the human body, it is difficult for the metals to be completely metabolized. They may accumulate in soft tissues or in the bones, causing toxic effects. In the human body, metals can insert adverse effects on cellular organelles and components, as well as enzymes involved in metabolism, detoxification, and DNA damage repair (5).



**Figure 2.** Rivers Stanishor, Mirusha and Morava in the southeast of Kosovo in the municipality of Gjilan.

## EXPERIMENTAL

### Sampling in the area as an important step in the analysis of heavy metals

Sampling is an important part of chemical analysis and should always be carried out under the supervision of the analyst. The reliability of an analytical result depends on the accuracy of the analytical determination as well as from that sampling. It is rightly said that "a wrong sample can't be answered fairly". The water sample for chemical analysis must complement these requirements; to be representative of the water system being studied, not to suffer from contamination and loss of the sample being analyzed during transport and not to undergo chemical composition changes during storage (6). The sampling method (1669) is that of "Sampling Ambient Water for Trace Metals at EPA Water Quality".

### Preparation of samples for analysis

The samples were mineralized in a "Speedwave Four" microwave mineralizer by Berghof (7). In the experimental work phase of this research, the analysis of the samples of Mirusha, Stanishor and Morava river waters of the municipality of Gjilan was carried out at the eight sites we have taken for study see the Table 2. Sample preparation is a critical step in any analytical performance. Sample preparation means the dissolution and digestion of organic and inorganic samples in closed or open systems by applying thermal energy or radiation (UV or microwave) digestion, in the closed system, is carried out at high temperature and pressure. This technique is more efficient than digestion in the open system. Closed systems are suitable for the preparation of trace or ultraviolet elements.

The samples are immediately sent to the laboratory; acidified with  $\text{HNO}_3$  1 mL and filtered in normal

containers, after that the samples are ready to undergo the digestion-mineralization procedure or aqua regia. The method used for this performance is EPA 3015.

From the filtered solution, 50 mL of water sample is taken and discharged into Teflon® DAP 100 that was cleaned very well. This Teflon® digestion is added to 4-5 mL of  $\text{HNO}_3$  65% and 1 mL of HCl 35% (US EPA Method 3015, 1994). Teflon® dishes are placed in the positions, provide Teflon® for the rotor pipes, the Teflon® samples are closed to prevent any problem due to the high pressure used by this sample mineralization instrument. Microwave oven is started and the program for the respective method is selected (8): the first stage temperature reaches 145°C, pressure at 30 bar. This stage lasts for 5 minutes and the power is at 80%. In the second stage, the temperature rises to 170 °C, the pressure remains at 30 bar again, while the time of this stage lasts for 10 minutes and the power is at 80%. In the third stage, the temperature continues to rise to 190 °C, the pressure remains at 30 bar again, while the duration is 15 minutes and the power is at 80%. At the fourth and fifth stages, the temperature drops to 100 °C, while pressure is at 0 bar and time decreases in 10 minutes and the power is 0%.

After finishing the mineralization, the microwave switches off (BERGHOF Speedwave MWS-3+), until all data (temperature, pressure and time) are stored in the database, the Teflon® dishes are removed from the microwaves, placed in a desiccator to cool to the room temperature. Samples prepared according to the procedure described above are ready for reading at ICP-OES.

### Sampling, processing, and analysis

ICP-OES (Inductively coupled plasma - optical emission spectrometry) is a technique in which the

composition of elements in (mostly water-dissolved) samples can be determined using plasma and a spectrometer. The solution to analyze is conducted by a peristaltic pump through a nebulizer into a spray chamber. The produced aerosol is lead into an argon plasma. Plasma is the fourth state of matter, next to the solid, liquid and gaseous state. In the ICP-OES, the plasma is generated at the end of a quartz torch by a cooled induction coil through which a high frequency alternate current flows. As a consequence, an alternate magnetic field is induced which accelerated electrons into a circular trajectory. Due to collision between the argon atom and the electrons are ionized, giving rise to a stable plasma. The plasma is extremely hot, 6000-7000 K. In the induction zone it can even reach 10000 K. In the torch desolvation, atomization and ionizations of the sample takes place. Due to the thermic energy taken up by the electrons, they reach a higher "excited" state. When the electrons drop back to ground level energy is liberated as light (photons). Each element has an own characteristic emission spectrum that is measured with a spectrometer. The light intensity on the wavelength is measured and with the calibration calculated into a concentration. (9)

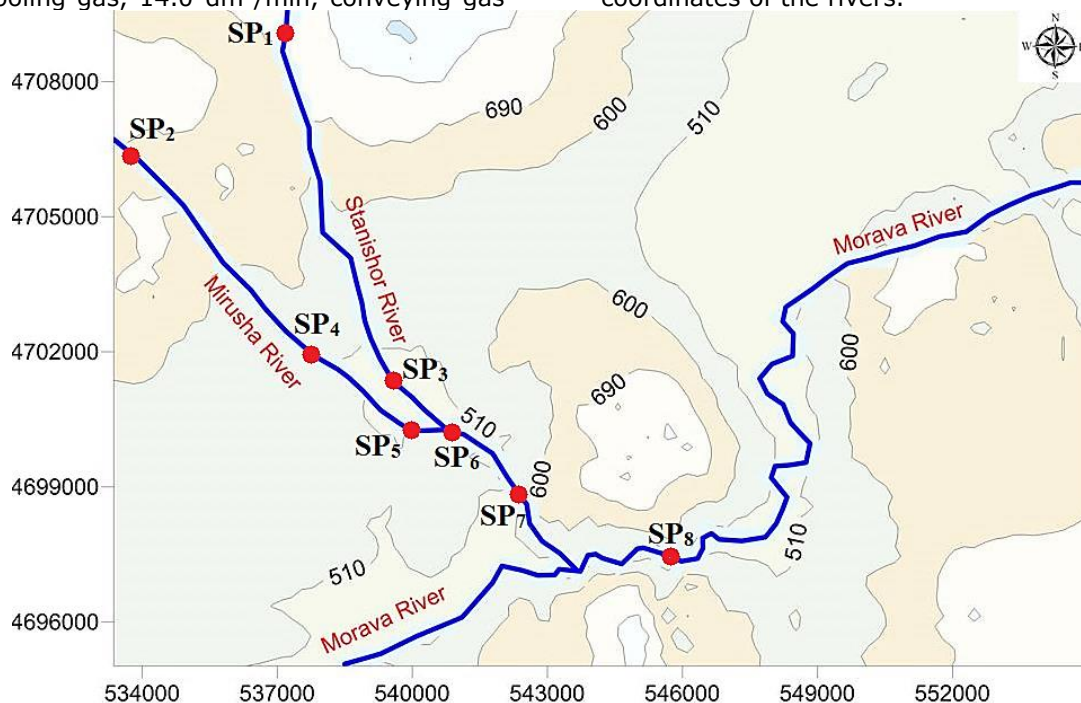
For determining the concentration of metals such as Pb, Hg, Mn, Cu, Fe, Ni, Cr, Cd, Zn and Ba, the following ICP-OES instrument was used: frequency, 27.12 MHz, power 1.1 kW, argon was used as inert gas, Ar cooling gas, 14.0 dm<sup>3</sup>/min, conveying gas

was Ar, 0.5 dm<sup>3</sup>/min and as Ar nebulizer, 1.0 dm<sup>3</sup>/min (10). This prepared sample solubility is readily available for reading at ICP-OES. We have also re-analyzed the determination of heavy metals at each point of sampling to be as confident in a conclusion in this scientific study.

**RESULTS AND DISCUSSION**

**The area of determination of heavy metals of the Mirusha River, Morava, and River Stanishor**

Surface sediment and water pollution is considered by many regulatory agencies to be one of the largest risks to the aquatic environment (2). The description of the sampling place in the Mirusha, Stanishor, and Morava Rivers is very important as to explain the network of monitoring the chemical parameters of these rivers. The SP<sub>1</sub> sample belongs to the Mirusha River spring, the SP<sub>2</sub> sample is taken after the river waters cross the Koretishta village, while the SP<sub>3</sub> sample is taken after the water has passed the municipality of Gjilan. The SP<sub>4</sub> sample includes the spring of the Stanishor river and the SP<sub>5</sub> sample is taken after crossing the Gjilan municipality, see Figure 3. The SP<sub>6</sub> sample was taken at the meeting point of two rivers, see Figures 2 and 3. The sample SP<sub>7</sub> was taken at a distant distance in compared to the sample SP<sub>6</sub> and the SP<sub>8</sub> sample belongs to the Morava River, see Figure 3. In the Table 1, the reader can see the sampling coordinates of the rivers.



**Figure 3.** Map of rivers in the municipality of Gjilan in the Republic of Kosovo (adapted 2019) (11).

**Table 1.** Coordinates of sampling in the Mirusha, Morava and Stanishor rivers

Samples	Coordinate X	Coordinate Y
SP <sub>1</sub>	42°29'27.2"N	21°25'60.0"E
SP <sub>2</sub>	42°30'21.8"N	21°27'34.3"E
SP <sub>3</sub>	42°27'13.3"N	21°29'16.0"E

SP <sub>4</sub>	42°27'57.5"N	21°28'28.8"E
SP <sub>5</sub>	42°27'18.5"N	21°29'17.7"E
SP <sub>6</sub>	42°27'41.2"N	21°28'26.1"E
SP <sub>7</sub>	42°27'21.0"N	21°29'44.0"E
SP <sub>8</sub>	42°25'33.0"N	21°31'26.4"E

**Assessment of heavy metal pollution in water**

*Discussion of results for Barium:* Ba concentrations could be toxic for marine embryos, benthic biota, and photosynthetic microorganisms (12). Ba is very widespread in nature and in the soil (13). From the measured and calculated results of the Ba concentration analysis at each site, it results high and exceeds many times the recommended amounts for the presence of this metal in the waters under Directive 75/440 / EEC which is not allowed Ba as metal heavy water in surface waters,. In the SP<sub>1</sub> sample at the source of the Mirusha River, the concentration of Ba is very high and better to say it is very dangerous if the concentration of Ba is up to 0.751 mg/L but in the SP<sub>2</sub> sample again the concentration of Ba has increased to 0.877 mg/L. In the SP<sub>3</sub> sample taken in the Mirusha River at the exit of the municipality, the amount of Ba is 1.315 mg/L, so if we compare it from the SP<sub>1</sub>-SP<sub>3</sub> samples, the amount of Ba is increasing. In the SP<sub>4</sub> sample the concentration of Ba is 0.799 mg/L and this concentration is very worrying especially for the spring of the Stanishor River. In the SP<sub>5</sub> sample the concentration of Ba is 0.864 mg/L, while in the SP<sub>6</sub> sample taken as the sampling point where the Mirusha and Stanishor Rivers join, the Ba value is 0.877 mg/L. In the SP<sub>7</sub> sample the concentration of Ba reaches up to 0.948 mg/L, while in the SP<sub>8</sub> sample of Morava River the concentration of Ba is 0.872 mg/L. The biggest concern is in the samples SP<sub>1</sub> and SP<sub>4</sub> because they are the sources of the Mirusha and Stanishor and possess a high concentration of Ba, this means is very dangerous for the inhabitants of the village if they consume it. All samples analyzed the concentration of Ba in these rivers are not in accordance with the European Union regulation, see Table 2.

*Discussion of results for Cadmium:* Cadmium (Cd) as a pollutant it can be present in water from industrial discharges and mining and or wastewater (13). Cd as heavy metal in these rivers does not display any great concentration, see Table 2. The Cd concentration in SP<sub>1</sub>-SP<sub>8</sub> samples is not more than 0.0001 mg/L. So, Cd is in accordance with Directive 75/440 / EEC, see Table 3.

*Discussion of results for Chromium:* Due to wide usage of Cr by different industries such as metal plating, paints and pigments, leather tanning, textile dyeing, printing inks and wood preservation, huge quantities of wastewater containing chromium are discharged into the environment to trivalent and hexavalent chromium ions. Hexavalent chromium compounds are toxic and carcinogenic. In contrast, toxicity of trivalent chromium is relatively low and in its trace amounts, it is not a problem for the environment. Chromium (Cr) in nature as a metal is very difficult to find in those waters, but in our case in the SP<sub>1</sub> sample the concentration of Cr is 0.004 mg/L and in the SP<sub>4</sub> sample is 0.0019 mg/L. In samples SP<sub>2</sub>, SP<sub>3</sub>, SP<sub>5</sub>, SP<sub>6</sub> and SP<sub>7</sub> it is 0.002 mg/L (<2 ppb), while in Morava river with sample SP<sub>8</sub>, see Figure 3 the concentration of Cr is 0.02 mg/L, so as seen in sample SP<sub>8</sub> the concentration of Cr is not in accordance with the other samples analyzed, see

Table 2. Cr according to Directive 75/440 / EEC are not permitted to be present in water.

*Discussion of Results for Copper:* Cu salts are used in water supply systems to control biological growth in reservoirs of the water (14). Cu as a heavy metal in most of the polluted waters is present and according to WHO is placed in the category of heavy metals that should be determined with necessity in the water because the high amount of Cu can display metabolic problems in a normal metabolism. Cu in the SP<sub>1</sub>-SP<sub>8</sub> samples does not pose a risk, so is approximately 0.0004 mg/L and this concentration is in accordance with WHO and European (Directive 75/440 EEC) water regulation, see Table 2.

*Discussion of results for Iron:* Fe, although it is the second most widespread element in the Earth, is present at relatively low amounts in natural waters. Concentration of Fe in rivers and lakes is usually below 1 mg/L (15). Fe as heavy metal in the samples analyzed as SP<sub>1</sub>-SP<sub>8</sub> has appeared contradictory to European Union (EU) and World Health Organization (WHO) rules. In the SP<sub>1</sub> sample, the spring of the river Mirusha has the concentration of Fe at 0.201 mg/L, is present compared to the EU criteria. In Mirusha River SP<sub>2</sub> sample, the concentration of Fe is 0.132 mg/L, compared to the SP<sub>1</sub> sample the concentration of Fe in SP<sub>2</sub> sample is not more than 0.069 mg/L. In the SP<sub>3</sub> sample, the concentration of Fe is 0.0137 mg/L, if compared to the SP<sub>3</sub> sample the concentration of Fe is in accordance with EU regulation, see Table 2. In the SP<sub>4</sub> sample in the Stanishor River, the concentration of Fe is 0.301 mg/L, therefore the concentration is very present compared to Directive 75/440 EEC, which is 0.1 mg/L. In sample SP<sub>5</sub> the concentration of Fe is 0.16 mg/L, we can say that it is the highest concentration of Fe, which we have analyzed in all other samples; the reader is referred to Table 2. In the SP<sub>6</sub> sample, the concentration of Fe is 0.027 mg/L, while from the SP<sub>6</sub> sample distance at the SP<sub>7</sub> sample, seen Figure 3 where the Fe concentration is 0.075 mg/L, so if we compare between sample SP<sub>6</sub> iron (Fe) in sample SP<sub>7</sub> increased to 0.048 mg/dm<sup>3</sup>. In the SP<sub>8</sub> sample to the Morava River, the concentration of Fe is 0.209 mg/L. The present concentration of Fe in these samples SP<sub>1</sub>-SP<sub>8</sub> will be divided into two groups:

- (i). In the first group including SP<sub>3</sub>, SP<sub>6</sub> and SP<sub>7</sub> samples in which the concentration of Fe is in accordance with Directive 75/440 EEC, see Table 2.
- (ii). In the second set of SP<sub>1</sub>, SP<sub>2</sub>, SP<sub>4</sub>, SP<sub>5</sub> and SP<sub>8</sub> samples in which the concentration of Fe is not in accordance with Directive 75/440 EEC, see Table 2

*Discussion of Results for Manganese (Mn):* Manganese (Mn) can be present in the environment by industries such as those involved in the production of fertilizer, petrochemicals, electroplating, tanneries, metal processing, and mining. The discharge of toxic metal effluents by various industries resulted in both land and water pollution and the destruction of mainly water flora and fauna due to intense toxicity (16). Manganese



(Mn) is not considered as a frequent element, but in nature, it is quite dispersed. In the crust of soil, it is the tenth element by dispersion in turn and has more than other metals, except iron (Fe) (16-17). Mn in the SP<sub>1</sub> sample is 0.029 mg/L, while in the SP<sub>2</sub> sample the concentration of Mn is 0.041 mg/L and in the SP<sub>3</sub> sample that is taken at the conclusion of the Mirusha River as in the Figure 3 the amount of Mn is 0.049 mg/L. As can be seen from the SP<sub>1</sub>-SP<sub>3</sub> samples, the concentration of Mn from at the point where the two flows of the Mirusha and the Stanishor Rivers join, the concentration of Mn at this point is higher compared to other sample points, see Table 2. In the SP<sub>4</sub> sample, the concentration of Mn is 0.082 mg/L is higher compared to Directive 75/440 / EEC, while in sample SP<sub>5</sub> the concentration of Mn is 0.006 mg/L, compared to the SP<sub>4</sub> sample the concentration of Mn has reduce in the SP<sub>5</sub> sample, see the Table 2. In the sample SP<sub>6</sub> at the point of joining the two rivers Mirusha and Stanishor, Mn is 0.074 mg/L. The Mn concentration in sample SP<sub>7</sub> is 0.078 mg/L. The Mn concentration in sample SP<sub>8</sub> at Morava river is 0.023 mg/L, see Table 2. The present quantity of Mn in these SP<sub>1</sub>-SP<sub>8</sub> samples will be divided into two groups:

- (i). In the first group that includes samples SP<sub>1</sub>, SP<sub>2</sub>, SP<sub>3</sub>, SP<sub>5</sub> and SP<sub>8</sub> the concentration of Mn is in accordance with Directive 75/440 EEC, see Table 2
- (ii). In the second group are included samples SP<sub>4</sub>, SP<sub>6</sub> and SP<sub>7</sub>, the concentration of Mn is not in accordance with Directive 75/440 EEC, see Table 2

*Discussion of results for Nickel:* Ni is present at the following places: industrial emission (power plants fueled by peat, coal, natural gas and oil, mining, steel production and municipal waste incineration), Motor vehicles (from petrol and abrasion of the cars' metal parts) (18). Ni as a heavy metal is not convenient in atmospheric, groundwaters and surface waters and according to Directive 75/440 EEC it is not allowed to be present in the water. The samples analyzed SP<sub>1</sub>-SP<sub>8</sub>, see Figures 2 and 3, the concentration of Ni is 0.0005 mg/L, see Table 2. The concentration of Ni does not display any high risk in Mirusha, Stanishor and Morava Rivers, compared to the other above-mentioned metals.

*Discussion of Results for Lead:* In contrast, Pb is non-essential and can be harmful even at low concentrations, and therefore should be avoided in the environment. High concentration of lead in the human body can cause anemia, diarrhea, or can induce coma as well as being carcinogenic, mutagenic, and toxic for reproduction (19). Pb according to WHO is estimated as the metal most likely to cause human metabolism after mercury. According to Directive 75/440 EEC Pb it is not essential if his concentration is very present in water and in our case, concentration are included (0.024

- 0.036) mg/L. In the SP<sub>1</sub> sample of the spring of the Mirusha river, concentration of Pb includes 0.028 mg/L, whereas in the SP<sub>2</sub> sample the concentration of Pb is 0.024 mg/L but as seen the concentration of Pb in this sample has decreased to 0.004 mg/L, also in the SP<sub>3</sub> sample as in Figure 3 the concentration of Pb is raised to 0.036 mg/L. In the SP<sub>4</sub> sample at the Stanishor River, the concentration of Pb is 0.031 mg/L, while the concentration of Pb in the SP<sub>5</sub> sample is 0.032 mg/L. In the SP<sub>6</sub> sample, concentration of Pb is 0.027 mg/L, but in the SP<sub>7</sub> sample also there is a decrease the concentration of Pb in 0.024 mg/L. In the SP<sub>8</sub> sample of the Morava river one of the most polluted rivers in the municipality of Gjilan, the concentration of Pb is 0.029 mg/L, see Table 2.

*Discussion of Results for Mercury:* Hg is a naturally occurring metal that is present in several forms. Metallic mercury is a shiny, silver-white, and an odorless liquid. Mercury combines with other elements, such as chlorine, sulfur, or oxygen, to form inorganic mercury compounds or salts, which are usually white powders or crystals. Mercury also combines with carbon to make organic mercury compounds (15). According to the Directive 75/440 EEC, Hg is allowed up to 0.0005 mg/L. In our case including the SP<sub>1</sub>-SP<sub>8</sub> samples as in Figure 3, the concentration of Hg is 0.0001 mg/L, this amount is in accordance with the European water regulations, seen in Table 3. As a conclusion for Hg, there is no great risk in these analyzed rivers, see Table 3.

*Discussion of Results for Zinc:* Zn is an essential trace element for humans, plants and animals, as it is associated with many enzymes and proteins. Large amounts of Zn are not desirable as they inhibit Cu (14). Zn, as heavy metal in the samples analyzed by SP<sub>1</sub>-SP<sub>8</sub>, (Figure 3 and Table 2) does not pose any risk because the Zn level in the samples is low. In the SP<sub>1</sub> sample of the Mirusha River source site, the Zn as heavy metal reaches approximately 0.0004 mg/L, while in SP<sub>2</sub>-SP<sub>8</sub> samples the amount of Zn is approximately 0.0002 mg/L, see Table 3. According to Directive 75/440 EEC as heavy metal such as Zn is allowed up to 0.5 mg/L. In conclusion, Zn does not present any major risk in these rivers.

*Discussion of Results for Cadmium (Cd):* Toxic heavy metals are clearly hazardous to humans. Cd is known as defective in the kidneys and bones, as well as DNA damage and mRNA(20), Cd as very dangerous heavy metal, in our case there is no high risk in Mirusha, Morava and Stanishor Rivers, see Table 3. Cd as metal in these rivers is in accordance with Directive 75/440 / EEC and this is a very important advantage for these polluted waters.

**Table 2.** The concentration of heavy metal in the rivers Mirusha, Stanishor and Morava in the Gjilan municipality. (1)

Metals	Directive 75/440/EEC	Samples							
		SP <sub>1</sub>	SP <sub>2</sub>	SP <sub>3</sub>	SP <sub>4</sub>	SP <sub>5</sub>	SP <sub>6</sub>	SP <sub>7</sub>	SP <sub>8</sub>
Ba	--	0.751	0.877	1.315	0.799	0.864	0.877	0.948	0.872
Cd	0.001	<0.1*	<0.1*	<0.1*	<0.1*	<0.1*	<0.1*	<0.1*	<0.1*
Cr	--	0.004	<2*	<2*	0.0019	<2*	<2*	<2*	0.02
Cu	0.02	<0.4*	<0.4*	<0.4*	<0.4*	<0.4*	<0.4*	<0.4*	<0.4*
Fe	0.1	0.201	0.132	0.0137	0.301	0.16	0.027	0.075	0.209
Mn	0.05	0.029	0.041	0.049	0.082	0.006	0.074	0.078	0.237
Ni	--	<0.5*	<0.5*	<0.5*	<0.5*	<0.5*	<0.5*	<0.5*	<0.5*
Pb	--	0.028	0.024	0.036	0.031	0.032	0.027	0.024	0.029
Hg	0.0005	<1*	<1*	<1*	<1*	<1*	<1*	<1*	<1*
Zn	0.5	<0.4*	<0.2*	<0.2*	<0.3*	<0.2*	<0.2*	<0.2*	<0.2*

\*The units are in mg/L.

## CONCLUSION

Such a research as analyzed in our case is very necessary to ascertain the extent to which the polluting rates of these heavy metals in the municipality of Gjilan reaches. Many states in Balkan have major problems with heavy metals in surface water due to the lack of wastewater treatment plants and this has display a major challenge for many Balkan states that are in the direction of being part of the European Union (EU). Every year the Morava, Mirusha and Stanishor Rivers are increasing the concentration of heavy metals in proportion to population and industry. The heavy metals that are present in these rivers and which are not in accordance with Directive 75/440 EEC are: Cr, Fe, Mn, and Pb. In conclusion, we have provided some theoretical and chemical explanations because some heavy metals in the rivers are present so high in these rivers. Over 95% of industries do not have wastewater treatment plants and all wastewater are discharged into the rivers and they may contain chemicals, metals and microorganisms in very high quantities.

According to many researches of different universities around the world in the field of geochemistry and water chemistry, it has been researched that in the different sources near the mines despite the naturally stems from the underground, there may be heavy metals present if close to source is a mine that is rich in minerals. In our case close to the source Mirusha and Stanishor there is the mine of Novobërd or Artana that is rich enough with Au, Zn, Fe, Cu, Cr and Pb, etc. This mine does not work since the time of the ex-Yugoslavia and today there is a high amount of water inside the mine and when the water flows into the interior of the mine, the water is in contact with different rocks and this water can be enriched with heavy metal or sand residue from the mines The lead content in the analyzed rivers is not surprising because at the time of the former Yugoslavia the battery factory produced full capacity many years ago, so that Pb as a metal may have a small amount deposited in the soil and the rivers including a not-too-large perimeter from the former Battery Factory

The presence of many heavy metals that are not in accordance with European Union directives is a problem for biotins. Wastewater treatment industry are not enough on Kosovo's territory and non-compliance with European regulations by industry is the main factor for the pollution of rivers in this area of Kosovo.

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