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## ASSESSMENT OF WATER QUALITY OF THE LEPENC RIVER IN KOSOVO THROUGH PHYSICO-CHEMICAL PARAMETERS

Water is a very important resource of vital importance to humans and other organisms. In this study, we investigated the water quality in the Lepenc River in the Republic of Kosovo, using various physico-chemical parameters. A total of 15 parameters were analyzed at six different locations: temperature, pH, electrical conductivity (*EC*), total dissolved solids (TDS), total organic carbon (TOC),  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , Cr, Cu, Fe, Mn, and Zn. Heavy metals were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Statistical analysis (basic statistics, Pearson correlation, and principal component analysis) was performed to better explain the data of different parameters. The concentration of chromium (range from 0.07 to 0.108 mg/dm<sup>3</sup>) in all water samples exceeds the permitted level for drinking water, while the concentration of iron (1.45 mg/dm<sup>3</sup>) exceeds the permitted value at some locations. The median value for ammonium (0.81 mg/dm<sup>3</sup>) and phosphates (0.80 mg/dm<sup>3</sup>) exceeds the permitted level for drinking water. The pollution of the river water has mainly occurred due to anthropogenic factors, because the former ferronickel mine is located in this area, and the use of agricultural lands and the discharge of wastewater from settlements located along the river's course.

### 1. INTRODUCTION

Water resources are very important for animal and plant life and the economic development of countries, but unfortunately, freshwater is limited, and the lack of water causes many problems [1, 2]. Water is a strategic asset because it drives the growth, development,

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and survival of life on Earth. Population growth is a key driver of water scarcity, as rising populations drive increased water demand. Consequently, the annual amount of available freshwater per person has declined by more than 20 percent in the last two decades [3]. Rapid population growth, progressive urbanization, industrial development, and the growth of intensive agriculture have contributed to surface water pollution [4]. Today, the contamination of rivers and sediment with different pollutants presents a complex long-term environmental problem, particularly in areas with high anthropogenic pressure [5]. Heavy metals are one of the most serious environmental pollutants due to their toxic effects, persistence, and abundance that can accumulate in aquatic ecosystems [6].

Kosovo is a country surrounded by high and medium altitude mountains, but there are river valleys created by the geological activities that enable the connection of Kosovo with neighboring countries [7]. Kosovo does not have abundant water resources, and the use of river and lake water in agriculture and various industrial branches causes these waters to be polluted with potentially toxic metals, various inorganic, organic, and bacteriological pollutants. Recently, many authors in Kosovo have investigated the impact of industry, traffic, and agriculture on food, soil, and air pollution [8–10], as well as investigated the physicochemical parameters of waters and sediments in Kosovo's rivers and lakes [4, 5, 11–15].

The purpose of this investigation is to evaluate the physicochemical parameters and water quality of the Lepenc River in the territory of the Republic of Kosovo, from the source of the river to the border with the Republic of North Macedonia. A total of 15 physicochemical parameters (temperature, pH, electrical conductivity, total dissolved solids, total organic carbon  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , Cr, Cu, Fe, Mn, and Zn) were analysed to assess the impact of anthropogenic and geogenic factors on the water quality of the Lepenc River. Statistical analysis (Pearson's Correlation and Principal Component Analysis) was used as a tool to find the correlation between these parameters as well as the main pollution sources.

## 2. EXPERIMENTAL

*Study area.* Kosovo is located at the top of the Balkan Peninsula, influencing surface waters to be autochthonous waters (created within the territory of Kosovo) and transboundary rivers. Kosovo's surface waters flow into 3 seas: the Black Sea, the Adriatic Sea, and the Aegean Sea [7]. The river Lepenc is located in the southeast of the Republic of Kosovo, originating in the Oshlak mountains at an altitude of 2212 m. The total length in the territory of Kosovo is 50 km and flows to the Vardar River in North Macedonia [6]. The river Lepenc represents the main catchment area in the southeastern region of Kosovo, and it has an area of 652 km<sup>2</sup>, while the average annual flow is 7.9 m<sup>3</sup> per second [6, 7].

*Samples.* Sampling was done according to water sampling standards. All samples were taken along the river at depths of 20–40 cm. Samples were collected in six different

locations through the flow of Lepenc River: W1 (Kovaqec), W2 (Kaçanik) and W3 (Gajre), W4 (Pustenik), W5 (Hani i Elezit), and W6 (Seqishte-near the border of North Macedonia), presented in Fig. 1. The physical-chemical characteristics were taken by placing the samples in clean polyethylene bottles. The parameters that are directly measured in the locality are: water temperature (WT), pH, and electrical conductivity (EC). Other physical and chemical parameters were analysed in the laboratory of the Kosovo Hydro-Meteorological Institute, such as: total dissolved solids, nitrates, nitrites, ammonium, sulphates, phosphates, and total phosphorus, and total organic carbon according to standard methods [16]. The concentration of heavy metals Cr, Fe, Mn, and Zn were determined with ICP-MS, in Agrovet Institute in Fushë Kosova.

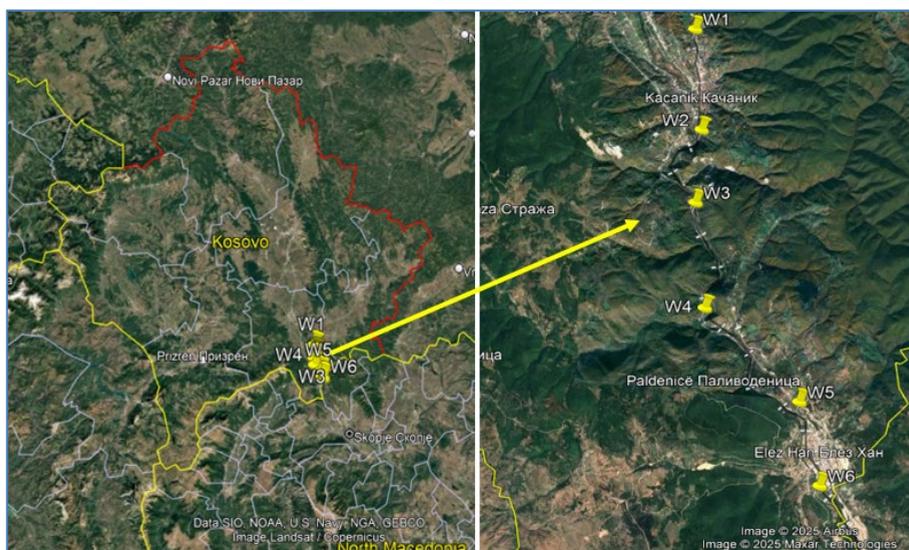


Fig. 1. Map of sampling locations W1–W6 with the coordinates:

|    |                 |                  |    |                  |                  |
|----|-----------------|------------------|----|------------------|------------------|
| W1 | 421°4' 24.68" N | 21° 15' 12.34" E | W4 | 42° 10' 37.84" N | 21° 15' 44.14" E |
| W2 | 42° 13' 3.92" N | 21° 15' 25.75" E | W5 | 42° 9' 26.86" N  | 21° 17' 26.30" E |
| W3 | 42° 12' 3.09" N | 21° 15' 26.27" E | W6 | 42° 8' 21.30" N  | 21° 17' 52.66" E |

*Statistical analysis.* The software PAST 4.11 was used for basic statistical analysis (minimum, maximum, mean, median, standard deviation, 25th and 75th percentile, skewness, and kurtosis), Pearson correlations, and principal component analysis (PCA).

### 3. RESULTS AND DISCUSSIONS

The results for water samples from six different locations in the Lepenc River, analysed for physical and chemical parameters, are presented in Table 1, and compared with

World Health Organization (WHO) standards [17]. The temperature ranged from 19 to 22.5 °C, pH ranged from 7.06 to 8.5. These parameters were within the standards for drinking water of the WHO. The electrical conductivities (290–436  $\mu\text{S}/\text{cm}$ ) were lower compared to those for the water of the Drenica River in Kosovo (420–798  $\mu\text{S}/\text{cm}$ ) presented by Gashi et al. [14], but higher than those for the water of the Batllava Lake [4]. These values were within the permitted limits of WHO, and water with EC between 250 and 750  $\mu\text{S}/\text{cm}$  considered to have low salinity and is also suitable for various uses [2]. Total dissolved solids ranged from 10 to 22.6  $\text{mg}/\text{dm}^3$ , and were within permitted limits of WHO [17], lower than for water of the Drenica River [14], but higher than for the Batllava Lake [4]. The lowest value for total organic carbon (TOC) was recorded 1.0  $\text{mg}/\text{dm}^3$  while the highest was 6.5  $\text{mg}/\text{dm}^3$ . Total phosphorus (0.13–0.39  $\text{mg}/\text{dm}^3$ ) and sulfates (7–16  $\text{mg}/\text{dm}^3$ ) were also within the permitted limits for drinking water.

Table 1

Descriptive statistics for the content of physicochemical parameters in water ( $n = 6$ )

| Variable                                     | Min   | Max   | Mean   | St. dev. | Median | Percentile |        | Skewness | Kurtosis | WHO standard [17] |
|--|-------|-------|--------|----------|--------|------------|--------|----------|----------|-------------------|
|  |       |       |        |          |        | 25th       | 75th   |          |          |                   |
| $T, ^\circ\text{C}$                          | 19    | 22.5  | 20.37  | 1.15     | 20.15  | 19.75      | 20.93  | 1.38     | 3.33     | 25                |
| pH   | 7.06  | 8.5   | 7.81   | 0.47     | 7.87   | 7.49       | 8.09   | -0.29    | 1.53     | 6.5–8.5           |
| EC, $\mu\text{S}/\text{cm}$                  | 290   | 436   | 391.83 | 53.45    | 398.50 | 367.25     | 435.25 | -1.75    | 3.59     | 1000              |
| TDS, $\text{mg}/\text{dm}^3$                 | 10    | 22.6  | 15.82  | 4.94     | 15.20  | 11.05      | 21.03  | 0.33     | -1.41    | 500               |
| TOC, $\text{mg}/\text{dm}^3$                 | 1     | 6.5   | 3.22   | 1.97     | 2.90   | 1.68       | 4.70   | 0.86     | 0.50     | –                 |
| $\text{NO}_3^-$ , $\text{mg}/\text{dm}^3$    | 1.8   | 9.6   | 5.50   | 3.04     | 5.30   | 2.48       | 8.63   | 0.19     | -1.41    | 50                |
| $\text{NO}_2^-$ , $\text{mg}/\text{dm}^3$    | 0.35  | 3.33  | 1.46   | 1.01     | 1.25   | 0.85       | 2.02   | 1.49     | 3.19     | 3                 |
| $\text{NH}_4^+$ , $\text{mg}/\text{dm}^3$    | 0.47  | 1.67  | 0.95   | 0.43     | 0.81   | 0.65       | 1.34   | 0.95     | 0.37     | 0.5               |
| $\text{PO}_4^{3-}$ , $\text{mg}/\text{dm}^3$ | 0.4   | 1.2   | 0.80   | 0.26     | 0.80   | 0.63       | 0.98   | 0.00     | 1.53     | 1                 |
| TP, $\text{mg}/\text{dm}^3$                  | 0.13  | 0.39  | 0.27   | 0.09     | 0.28   | 0.21       | 0.32   | -0.25    | 1.41     | 60                |
| $\text{SO}_4^{2-}$ , $\text{mg}/\text{dm}^3$ | 7     | 16    | 10.50  | 3.02     | 10.00  | 8.50       | 12.25  | 1.31     | 2.80     | 250               |
| Cr, $\text{mg}/\text{dm}^3$                  | 0.07  | 0.108 | 0.09   | 0.02     | 0.10   | 0.07       | 0.11   | -0.72    | -1.87    | 0.05              |
| Fe, $\text{mg}/\text{dm}^3$                  | 0.122 | 1.45  | 0.41   | 0.51     | 0.23   | 0.14       | 0.55   | 2.39     | 5.78     | 0.3               |
| Mn, $\text{mg}/\text{dm}^3$                  | 0.03  | 0.064 | 0.04   | 0.01     | 0.04   | 0.03       | 0.06   | 0.33     | -2.11    | 0.08              |
| Zn, $\text{mg}/\text{dm}^3$                  | 1.93  | 2.983 | 2.49   | 0.43     | 2.48   | 2.08       | 2.96   | -0.05    | -1.53    | 5                 |

The results for anions are presented in Table 1 and Fig. 2. Concentration of nitrate increased from samples W1 (1.8  $\text{mg}/\text{dm}^3$ ) to W6 (9.6  $\text{mg}/\text{dm}^3$ ) through the flow of river. The values were within permitted limits (50  $\text{mg}/\text{dm}^3$ ) for drinking water [17], but there

are higher than for the Oued Fez River of Morocco [1]. Also, the concentration of nitrite increased through the flow of river, with the maximum value of  $3.33 \text{ mg/dm}^3$  in the location W4. Nitrite concentrations were within the permissible value ( $3 \text{ mg/dm}^3$ ) of WHO drinking water standards, except for the location W4, which exceeded the permissible value of WHO [14]. Ammonium concentration ranged from  $0.47$  to  $1.67 \text{ mg/dm}^3$ , and it decreased from location W1 to W6. The median value for ammonium was 1.6 times higher than the allowed value ( $0.5 \text{ mg/dm}^3$ ). Increasing levels of nitrogen (nitrates, nitrites, and ammonium) resulted from agricultural activities and wastewater discharged from settlements [2]. The median value for phosphates was very close to the WHO standard, but the maximum measured value exceeded the allowed value ( $1 \text{ mg/dm}^3$ ), as a result of wastewater and urban discharges [1, 2].

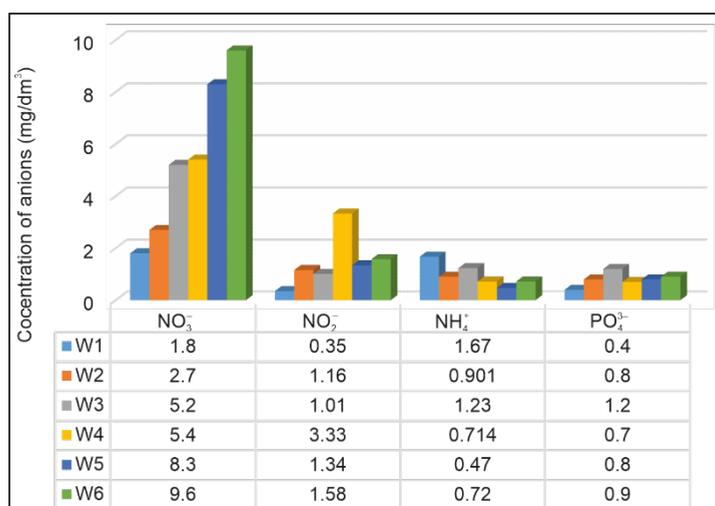


Fig. 2. Concentration of anions in water samples of the Lepenc River ( $n = 6$ )

The concentrations of chromium (Table 1 and Fig. 3) ranged from  $0.07$  to  $0.108 \text{ mg/dm}^3$ , with median values 2 times higher than permitted limits for drinking water [17]. Chromium concentrations in water of the Lepenci River were higher than in other studies for waters of lakes and rivers in Kosovo [4, 5, 14], and have geogenic origin because this area is located near former nickel mines [6]. Iron concentrations in water ranged from  $0.122 \text{ mg/dm}^3$  to the maximum value of  $1.45 \text{ mg/dm}^3$ , in location W4, as a result of anthropogenic factors of former nickel factory of Ivaja [6]. The maximum value for iron was 5 times higher than allowed value of WHO standards [17], and much higher than lake and river waters in Kosovo [4, 14]. Manganese concentrations in water were ranged from  $0.06$ – $0.064 \text{ mg/dm}^3$  and were within the permitted limits for drinking water ( $0.08 \text{ mg/dm}^3$ ), but much higher than in water of the Drenica River [14]. The minimum value of zinc in water ( $1.93 \text{ mg/dm}^3$ ) was higher than the maximum value ( $0.086 \text{ mg/dm}^3$ ) for water of the

Drenica River [14], but lower than the maximum value (7.994 mg/dm<sup>3</sup>) for the Trepça and Sitnica Rivers [5].

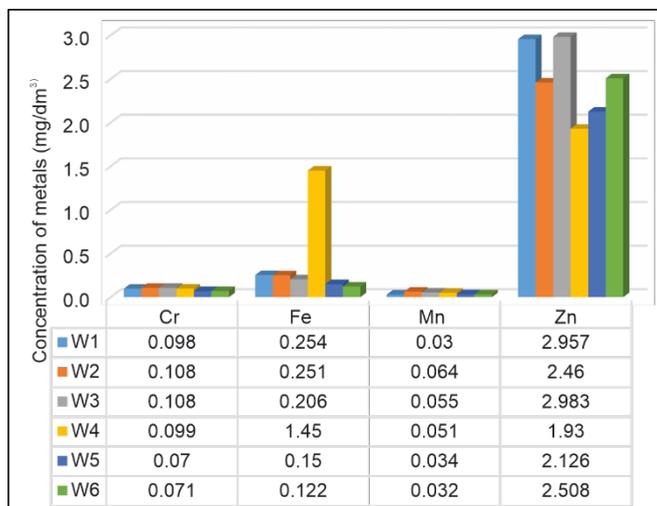


Fig. 3. Concentration of metals (Cr, Fe, Mn and Zn) in water samples of the Lepenc River ( $n = 6$ )

The Pearson correlation coefficient ( $r$ ) and their significance level ( $p$ -values) for the examined parameters are presented in Table 2. The absolute value between 0.50 and 0.70 presents a good correlation, and from 0.70 to 1.00 – a strong correlation [10, 18]. Temperature had strong positive correlations with pH (0.921),  $\text{NH}_4^+$  (0.799) and Zn (0.716), but strong negative correlations with EC (–0.959),  $\text{NO}_2^-$  (–0.826) and TOC (–0.778). Electrical conductivity had strong positive correlations with  $\text{SO}_4^{2-}$  (0.756) and TOC (0.704) and strong negative correlations with  $\text{NH}_4^+$  (–0.891), pH (–0.817) and Zn (–0.731). pH had strong positive correlations with Zn (0.809) and  $\text{NH}_4^+$  (0.743) and strong negative correlations with  $\text{NO}_2^-$  (–0.968), TOC (–0.818) and Fe (–0.727). TDS had good positive correlations with  $\text{SO}_4^{2-}$  (0.661), Mn (0.606) and TOC (0.507) and also good negative correlation with  $\text{NH}_4^+$  (–0.535). TOC had strong positive correlations with  $\text{NO}_2^-$  (0.868) and Fe (0.811) and also strong negative correlation with Zn (–0.849). Nitrates had good positive correlations with  $\text{SO}_4^{2-}$  (0.516) and TP (0.503), and also strong negative correlations with Cr (–0.830) and  $\text{NH}_4^+$  (–0.740). Nitrites had strong positive correlation with Fe (0.872) and strong negative correlation with Zn (–0.809). Ammonium had strong positive correlation with Zn (0.843) and strong negative correlation with  $\text{SO}_4^{2-}$  (–0.773). Phosphates had very strong positive correlation with TP (0.989). Chromium had strong positive correlation with Mn (0.752). Based on data from Table 2, in total shown 50 associations with absolute values between 0.5 and 0.989, where 13 of them had significance level below 5% ( $p < 0.05$ ).

Table 2

Pearson correlation coefficients between physicochemical parameters in water ( $n = 6$ ) of the Lepenc River

| Variables          | $T$           | EC            | pH            | TDS    | TOC           | $\text{NO}_3^-$ | $\text{NO}_2^-$ | $\text{NH}_4^+$ | $\text{PO}_4^{3-}$ , | TP           | $\text{SO}_4^{2-}$ | Cr           | Fe           | Mn     | Zn           |
|--------------------|---------------|---------------|---------------|--------|---------------|-----------------|-----------------|-----------------|----------------------|--------------|--------------------|--------------|--------------|--------|--------------|
| $T$                |               | <b>0.003</b>  | <b>0.009</b>  | 0.404  | 0.068         | 0.268           | <b>0.043</b>    | 0.056           | 0.249                | 0.224        | 0.244              | 0.836        | 0.283        | 0.383  | 0.110        |
| EC                 | <b>-0.959</b> |               | <b>0.047</b>  | 0.237  | 0.118         | 0.186           | 0.132           | <b>0.017</b>    | 0.226                | 0.171        | 0.082              | 0.622        | 0.516        | 0.486  | 0.099        |
| pH                 | <b>0.921</b>  | <b>-0.817</b> |               | 0.749  | <b>0.047</b>  | 0.297           | <b>0.002</b>    | 0.091           | 0.611                | 0.599        | 0.445              | 0.732        | 0.102        | 0.631  | 0.051        |
| TDS                | -0.423        | 0.570         | -0.169        |        | 0.305         | 0.955           | 0.866           | 0.274           | 0.603                | 0.508        | 0.153              | 0.827        | 0.911        | 0.203  | <b>0.391</b> |
| TOC                | -0.778        | 0.704         | -0.818        | 0.507  |               | 0.931           | <b>0.025</b>    | 0.203           | 0.988                | 0.947        | 0.363              | 0.768        | 0.050        | 0.292  | <b>0.032</b> |
| $\text{NO}_3^-$    | -0.540        | 0.624         | -0.514        | -0.030 | 0.046         |                 | 0.522           | 0.093           | 0.372                | 0.309        | 0.294              | <b>0.041</b> | 0.823        | 0.438  | 0.415        |
| $\text{NO}_2^-$    | <b>-0.826</b> | 0.687         | <b>-0.968</b> | 0.089  | <b>0.868</b>  | 0.330           |                 | 0.201           | 0.898                | 0.896        | 0.581              | 0.907        | <b>0.024</b> | 0.641  | 0.051        |
| $\text{NH}_4^+$    | 0.799         | <b>-0.891</b> | 0.743         | -0.535 | -0.605        | -0.740          | -0.607          |                 | 0.549                | 0.449        | 0.072              | 0.232        | 0.713        | 0.899  | 0.035        |
| $\text{PO}_4^{3-}$ | -0.558        | 0.581         | -0.266        | 0.272  | 0.008         | 0.449           | 0.068           | -0.311          |                      | <b>0.000</b> | 0.627              | 0.921        | 0.666        | 0.386  | 0.817        |
| TP                 | -0.584        | 0.640         | -0.274        | 0.341  | 0.035         | 0.503           | 0.069           | -0.387          | <b>0.989</b>         |              | 0.451              | 0.958        | 0.640        | 0.443  | 0.920        |
| $\text{SO}_4^{2-}$ | -0.563        | 0.756         | -0.389        | 0.661  | 0.456         | 0.516           | 0.287           | -0.773          | 0.254                | 0.385        |                    | 0.350        | 0.952        | 1.000  | 0.163        |
| Cr                 | 0.110         | -0.258        | 0.181         | 0.116  | 0.156         | <b>-0.830</b>   | -0.062          | 0.576           | 0.053                | -0.028       | -0.468             |              | 0.599        | 0.084  | 0.465        |
| Fe                 | -0.526        | 0.335         | -0.727        | -0.060 | 0.811         | -0.119          | <b>0.872</b>    | -0.194          | -0.227               | -0.245       | 0.032              | 0.274        |              | 0.596  | 0.205        |
| Mn                 | -0.440        | 0.358         | -0.252        | 0.606  | 0.518         | -0.395          | 0.244           | -0.067          | 0.437                | 0.391        | 0.000              | 0.752        | 0.277        |        | 0.890        |
| Zn                 | 0.716         | -0.731        | 0.809         | -0.433 | <b>-0.849</b> | -0.414          | -0.809          | <b>0.843</b>    | 0.123                | 0.053        | -0.649             | 0.374        | -0.603       | -0.073 |              |

Values in bold are different from 0 with a significance level alpha equal to 0.05.

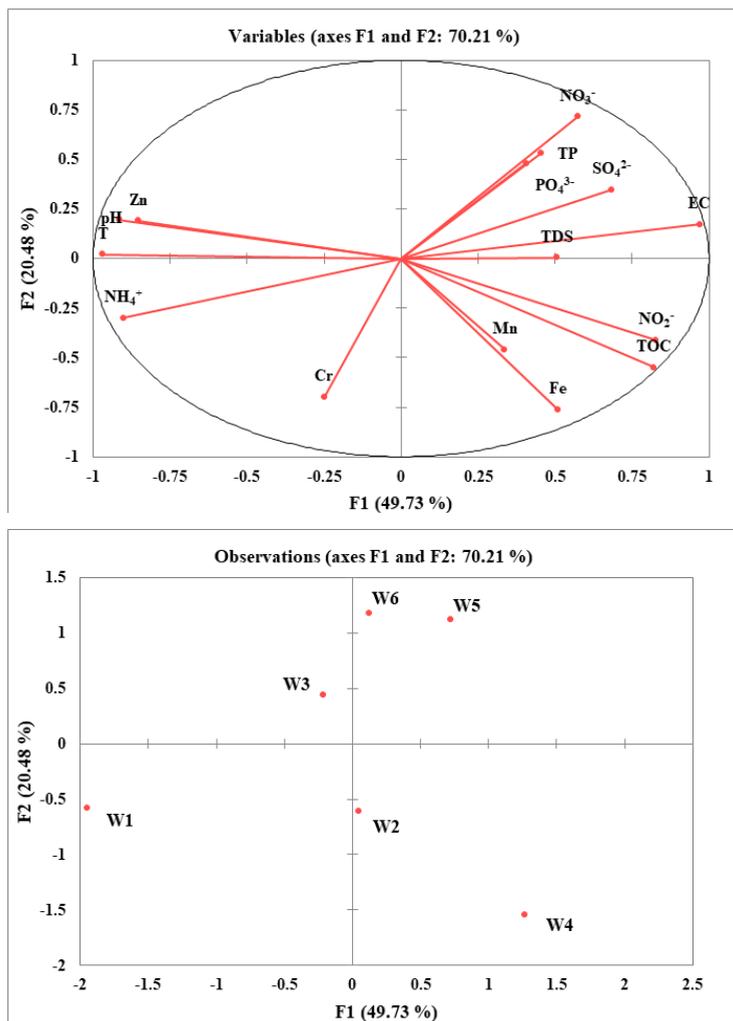


Fig. 4. Principal component analysis of physicochemical parameters (upper), and locations (lower)

In Figure 4, it is shown that PC1 contributed to 49.73% and PC2 with 20.48% of total variables (70.21%). Location W4 has a large vector in PC1 and PC2 and was affected by anthropogenic factors, because there is a former ferro-nickel factory in Ivaja which polluted the water with iron. Locations W5 and W6 have high vector in PC1 and PC2 and influenced by anthropogenic factors; agricultural activities, wastewater and industrial discharged from cement factory in Hani i Elezit and former asbestos factory, had impacted in increasing levels of EC, TDS,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$  – in these locations. Chromium has a vector orientation in the opposite direction and may have a mixed geogenic and anthropogenic origin.

#### 4. CONCLUSIONS

In this work we investigated 15 physicochemical water parameters in the Lepenc River. Based on the World Health Organization drinking water guidelines, five chemical parameters exceeded the permitted values at one or more locations. Ammonium exceeded permitted value in all water samples, nitrites in location W4 and phosphates in W3 exceeds permitted values of WHO. Chromium exceeds allowed values in all water samples and the median value was 2 times higher than permitted value of WHO. Iron exceeds 5 times the allowed value for drinking water of WHO in location W4 as a result of industrial discharged of former ferro-nickel factory in Ivaja (Kaçanik).

The Pearson correlations identified 50 associations with strong and good (positive and negative) correlations between physicochemical parameters, where 13 of associations had significance below  $p < 0.05$ .

Principal component analysis identified the contributions of 15 physicochemical parameters at different locations. Location W4 mostly influenced by anthropogenic factor of former ferronickel factory in Ivaja (Kaçanik). Locations W5 and W6 affected in pollution by wastewater of settlements, agricultural activities and industrial discharged from cement factory in Hani i Elezit. Chromium has a uniform distribution throughout the River and can have mixed geogenic and anthropogenic origins.

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