

## Contamination of Environment with the Heavy Metals Emitted from a Cement Factory, Kosovo

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### ABSTRACT

The environment and its components have been severely contaminated over the years due to massive pollution. The multiple use of heavy metals in industrial, domestic, agricultural, medical and technological applications have led to their wide distribution in the environment. Different studies implied that the primary contribution to the ecological risk index, originated from various anthropogenic influences such as industrialization and urbanization. This has compromised the ability of the environment to foster life and render its intrinsic values due to the heavy usage of these elements. This research illustrates the assessment of heavy metals in waste, water, sludge and soil. Monitoring was performed in vicinity of a cement factory on the southern Kosovo, where the sampling and measurements were performed in the autumn season of 2018. With the use of atomic absorption spectroscopy technique (AAS), the elements determined in this study were Pb, Zn, Cu, Ni, Fe, Mn, and Al. The findings of this study revealed a little change in the concentrations of these elements in the environment samples, especially in water, apart from that there is slight pollution of the environment with heavy metals in this zone.

**Keywords:** Sharrcem, cement factory, heavy metals, water.

### INTRODUCTION

The ancient sign of the existence of life in earth, is the presence of water. Even though the issue of water and its purity is problematic today, living without clean and sufficient water is impossible (Kilaru et al., 2019). Soil is considered an important natural resource of pollution, due of its capability to act as a geochemical reservoir for various contaminants, including heavy metals, resulting from the aerosol deposition through urban and manufacturing activities (Liu et al., 2014; Nagajyoti et al., 2010). Soil can also act as a natural buffer and therefore can control the dispersal of chemical contaminants in the air, water and biological components. (Lutts et al., 2015). Numerous studies have shown that soil contamination with heavy metals in soils also result in the contamination of food cultivated in those agricultural

soils (Jusufi et al., 2017a; Prabhat et al., 2019; Jusufi et al., 2017b).

The anthropogenic activities such as construction, energy production, industrial mining, fossil fuel combustion and waste disposal, resulted in the uncharacteristic deposition of heavy metals in urban soil resulting in severe environmental pollution (Demaku et al., 2020; Demaku et al., 2019; Wekpel et al., 2019; Jusufi et al., 2016; Boateng et al., 2019). The industries involved in cement production are also an enormous source of environmental pollution due to the emission of dust that contains toxic chemicals, which vary according to the raw materials used (Isikli et al., 2003, Isikli et al., 2006).

Many of the heavy metals produced also as a byproduct of cement industrial activities are known to be toxic for living organisms, even in minimal concentrations. This study is based on

the heavy metal contamination in the vicinity area of the “Sharrcem” cement factory in Kosovo. The results are presented in figures and statistical analysis.

## MATERIAL AND METHODS

### Study Area

Elez Han is a town and municipality located in the Ferizaj District of Kosovo. This region of the country is also known as an industrial zone due to the cement factory located in this area. Figure 1 shows the map of Kosovo with the study area (near the Sharrcem factory).

### Treatment of water sample

In each sampling point, two samples of water were taken in 2l glass bottles. Initially, the water samples were filtered, before placing them into a Teflon vessels. The samples were then treated with 1 mL of HCl and 5 mL of HNO<sub>3</sub> as well as digested in a BERGHOF-Speed Wave microwave (Canbay et al., 2016)

### Treatment of soil, waste and sludge samples

The solid samples (soil, waste and sludge) were prepared according to the (Kadhun et al, 2015), weighting 3.5 gram of solid sample and

placed them in Teflon vessels. The samples were then treated with 10 ml of aqua regia and digested in a microwave. After the microwave digestion was finished, the samples were filtered, diluted to 100 ml using distilled water (USEPA Method 3050B 1996)

### Instrumentation

All chemicals needed for the determination of elements were of the “pro analysis” chemical purity. Atomic Absorption Spectroscopy (AAS) was used to measure the concentrations of heavy metals. For each group of analytical samples, two spiked blanks and two method blanks were simultaneously processed.

## RESULTS AND DISCUSSION

In order to assess the concentration of heavy metals, four different components (water, sludge, waste and soil) were determined at three sampling points. The results are presented in mg/kg content, respectively mg/l for water.

### Waste results

The risk that could come as a result of heavy metal discharging without prior treatment, can be enormous. Vongdala et al. (2018), reported that the waste dumping with high concentration

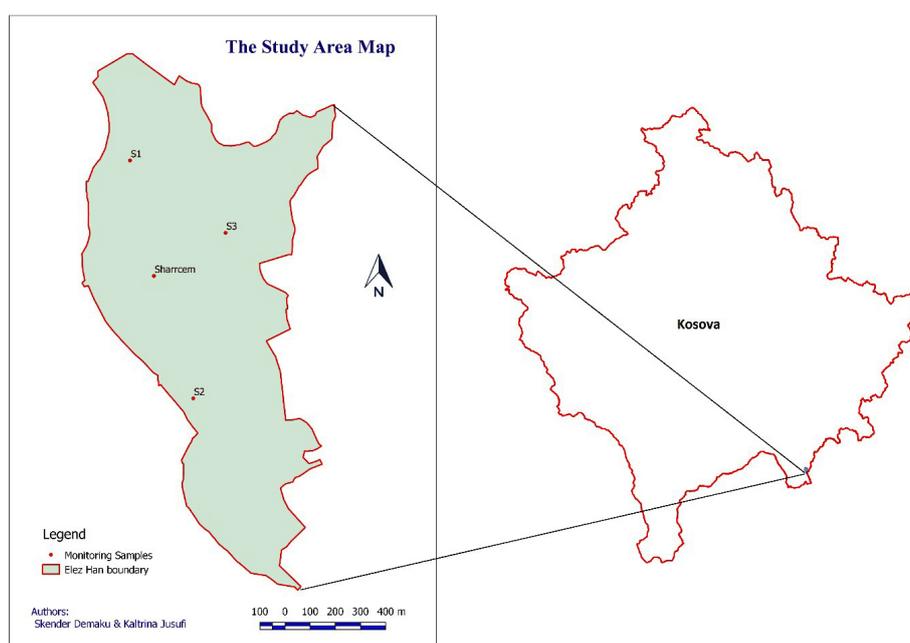


Figure 1. Map of Kosovo and the studied area near “Sharrcem” cement industry

of these elements, resulted in an increase of this contamination in soil, water or even in plants that were grown in those areas. Figure 2 shows the graphical results of these elements in the waste samples given in mg/kg of their mass.

If the results presented above are considered, as a remaining part of a solid *substance*, compared with the EU standard recommended (EU Directive 2018/852, 2018), it can be seen that the concentration of elements did not exceed the amount allowed. The higher concentration of the elements was observed in sampling point number 3 (S3), with the maximum Al concentration of 1.991 mg/kg, Fe of 1.895 mg/kg, Mn of 1.748 mg/kg and Ni of 1.095 mg/kg. As far as the concentration of copper, zinc and lead is concerned, lower values were recorded in this monitoring zone. Figure 3 shows the distance distribution dendrogram of these elements (Pb, Zn, Cu, Ni, Fe, Al and Mn) in the analyzed samples of waste.

From the results obtained in Figure 3, it can be seen that there is a high similarity of the elements in general. Al, Fe and Cu are presented separately as elements. In all the cases, these elements showed high percentage of resemblance. In the case of Al for example, its similarity is about 77% with Pb and Ni group and in the right side of the diagram, Fe showed resemblance with the Mn and Ni groups with around 99% similarity. Cu in the right side of the dendrogram was presented separately from the other elements, with the resemblance to iron of 97%.

If all the results presented in the figure 3 are compared, high percentage of similarity of element can be seen. From these results, it can

be concluded that the source of contamination with these metals comes from the Cement Factory waste (Skoczylas and Rucińska, 2020, Tahri et al., 2005).

### Soil results

Heavy metals are substances with the odd properties. Due to their ubiquity, toxicity at a trace level, bioaccumulation and persistence and so on, these elements have been attracting much attention worldwide. Furthermore, heavy metals that have been accumulated in soils can infiltrate to other ecosystems: water, rivers, crops and so on. Figure 4 shows the graphical results of these elements in the soil samples given in mg/kg of their mass.

The concentration of heavy metals in agricultural areas in three sampling points is different and it varies depending on the concentration of the element in an increasing order  $Ni < Fe < Al$ . The highest concentration of nickel was observed in sample number 2 (S2) with 1.074 mg/kg and the lowest reached 0.151 mg/kg. The concentration of iron varied in the range of 0.984–1.283 mg/kg. Aluminium had the highest concentration in the S2 1.432–0.993 mg/kg. If the results are compared with the Dutch list for soil standards (Dutch target and Intervention Values, 2000), none of the elements exceeded the maximum amount allowed according to this list. Moreover, the concentration of other elements measured (Cu, Zn, Pb and Mn) were below the maximum amount allowed compared to the Dutch list for soils. Figure 5 shows the

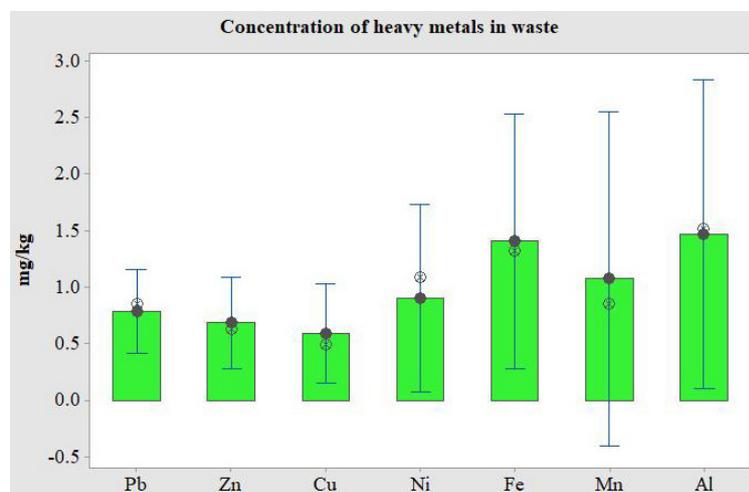


Figure 2. Concentration of heavy metals in waste, expressed in mg/kg.

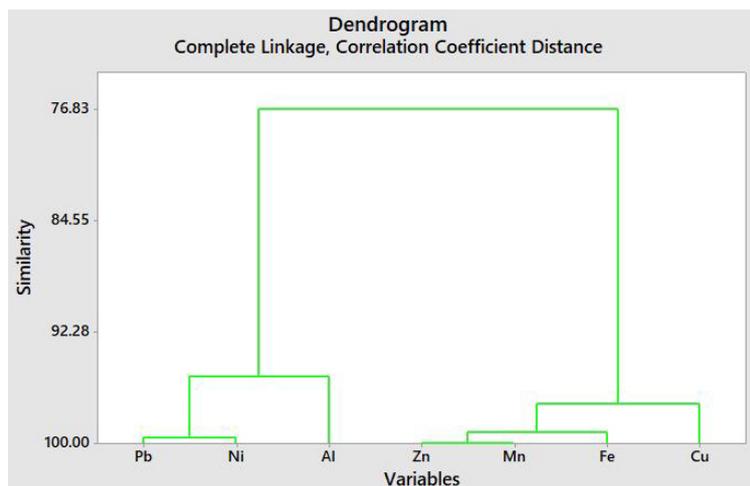


Figure 3. Distribution dendrogram of Pb, Zn, Cu, Ni, Fe, Al and Mn in the analyzed samples of waste

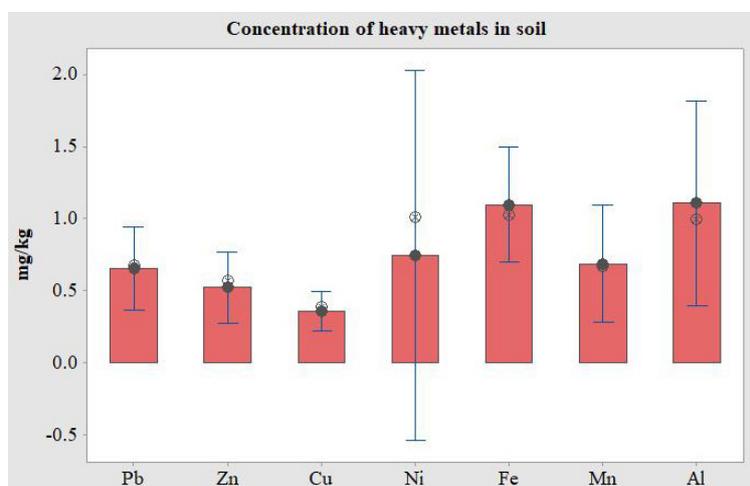


Figure 4. Concentration of heavy metals in soil, expressed in mg/kg

distance distribution dendrogram of these elements (Pb, Zn, Cu, Ni, Fe, Al and Mn) in the analyzed samples of soils.

In figure 5 presents the elements divided into three main groups of elements, according to their distribution similarity. The first group is between the Pb and Mn with almost 90% of similarity, group 2 Cu and Ni close to 100% of resemblance and the third group is between Fe and Al with the percentage of 98%. Zinc is presented alone with the similarity to the second group (Cu and Ni) of about 95%.

The case of the similarity of these elements distributed in the soils in the vicinity of cement factory, a very high similarity percentage of these elements in soils can be seen. Thus, it can be conclude that they came from the same source.

### Sludge results

The high amount of sludge in the environment comes as a result of industrial overload. However, another concern that may arise from this high urbanization, is that the sludge has a high concentration of pollutants that are deposited in there. Figure 6 shows the graphical results of these elements in the sludge samples given in mg/kg of their mass.

Wang et al. 2015 reported that the concentrations of heavy metals in sludge are higher especially after the atmospheric rain in the river and its shore. The highest concentration observed for lead is 0.898 mg/kg, for nickel is 0.997 mg/kg and for Al – 1.621mg/kg. In turn, the concentrations of copper, manganese and zinc are lower. If these results are compared, it can be see that in every case the concentration of these elements in

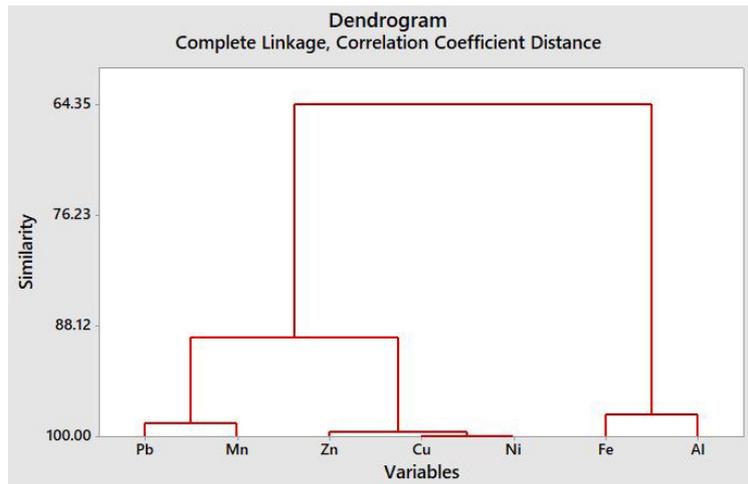


Figure 5. Distribution dendrogram of Pb, Mn, Zn, Cu, Ni, Fe, and Al in analyzed soil samples

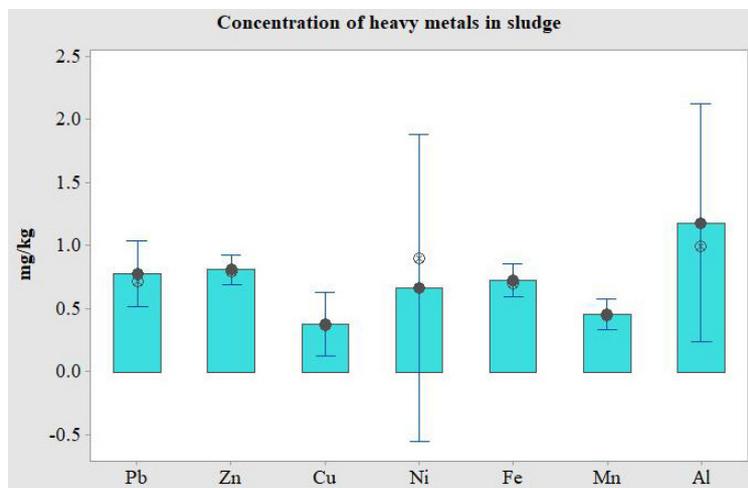


Figure 6. Concentration of heavy metals in sludge expressed in mg/kg.

sludge is lower than compared to the Dutch list for soils. (Dutch Target and Intervention Values, 2000). Figure 7 shows the distance distribution dendrogram of these elements (Pb, Zn, Cu, Ni, Fe, Al and Mn) in the analyzed samples of sludge.

Figure 7 shows the similarity of the elements based on their distribution in the sludge samples near the cement factory in Kosovo. According to the results presented in this figure, the highest similarity is presented between Pb, Al and Fe with over 99%, while in the another group of elements, Cu, Mn and Zn have a percentage of about 99%. Nickel in this diagram is presented as the only element with a high resemblance to both groups of compared elements.

### Water results

Water pollution is one of the greatest concerns of the century. It is very easy from the

atmospheric and soil pollution to infiltrate to water. From water, all kinds of free contaminants can end up in the food chain. Figure 7 shows the graphical results of these elements in the water samples given in mg/l.

The concentration of heavy metals that were determined in the river Lepenc are as followed: for Ni the highest concentration found is 0.098 mg/l, Cu ranges from 0.163–0.189 mg/l, Zn varies from 0.17 to 0.198 mg/l and the maximum amount for Fe is 0.588 mg/l. The results presented for Mn and Pb are lower than the other elements. The concentration of lead varies from 0.06 to 0.099 mg/l, while for manganese, the lowest concentration is 0.04–0.068 mg/L. Aluminium was also found in lower concentrations, ranging from 0.654–0.878 mg/l. If the results are compared according to the sampling points found, it can be see that the higher concentrations of these elements in water were found in

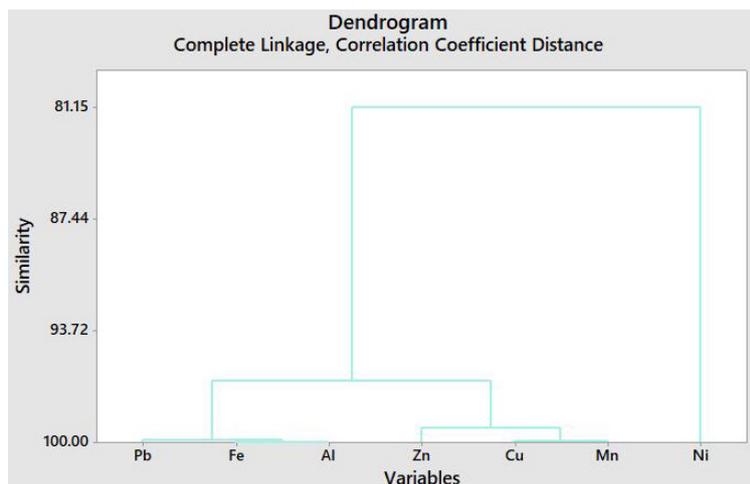


Figure 7. Distribution dendrogram of Pb, Mn, Zn, Cu, Ni, Fe, and Al in the analyzed sludge samples.

the second sampling point (S2). Figure 9 shows the distance distribution dendrogram of these elements (Pb, Zn, Cu, Ni, Fe, Al and Mn) in the analyzed samples of water.

The dendrogram presented above, represents the similarity percentage of lead, nickel, manganese, zinc, copper, iron and aluminum in the water samples. From the results obtained, it can be seen the high similarity between Zn, Ni and Mn with almost 100%. There is also high percentage of similarity of lead with this group of elements (more than 98%). On the other side of dendrogram, there is similarity of Cu and Fe reaching around 100%. Aluminum is presented alone with high similarity to both these groups of elements (around 90%). From the results obtained, it can be concluded that the source of these elements in water comes from the Cement Factory in this region.

### Statistical data

The following analysis and tables show the statistical data of pollution and distribution of these elements in water, soil, sludge and waste samples. If the results are compared with the literature and standards, it can be seen that in most of the cases the concentration of these elements is below the limits provided by these results.

**Copper** in drinking and pure water can be very low in concentrations (only a few mg/L), but plumbing can result in an increased concentration (WHO, 1993). The results of this element in this study in sludge samples is around 0.28–0.48 mg/kg and in every sample presented, the results are below the maximum amount allowed compared to the EU standards in sludge. Similarly, for soil samples, copper is lower than 36 mg/kg (according to the Dutch list) as a target value in soils.

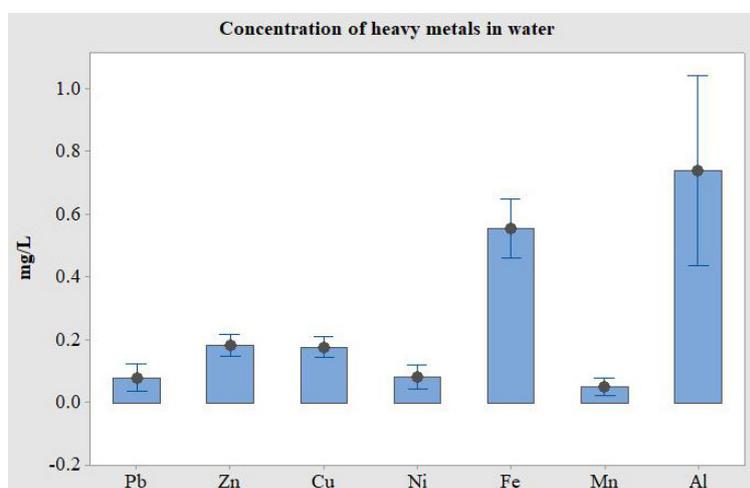


Figure 8. Concentration of heavy metals in water expressed in mg/l

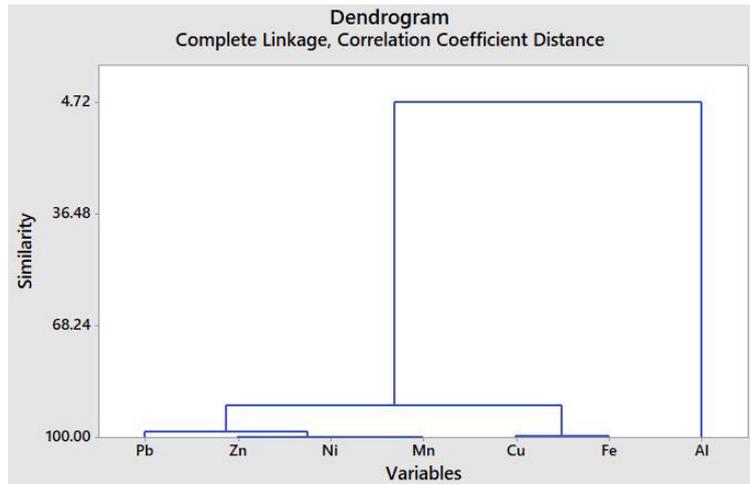


Figure 9. Distribution dendrogram of Pb, Mn, Zn, Cu, Ni, Fe, and Al in the analyzed water samples

**Lead** is widely used as a lead-acid batteries, allows etc. Most lead in drinking water can come from plumbing in buildings (WHO, 1993).

From the results observed from our measurements it can be seen that lead concentration is from 0.614–0.889 mg/kg in the waste samples. In soil, it varies from 0.531 to 0.758 mg/kg, in the sludge samples 0.711–0.898 mg/kg and in the water samples, the lowest concentration reached the value of 0.071, while the highest – 0.099 mg/L. In all the measured samples, it can be see that there are lower concentrations than those recommended from relevant standards for maximum amount allowed values (Table 2). In the case of soil samples, lead has a lower value than 85 mg/kg which is the target value according to this standard. When it comes to the results of lead in the water samples, it ranges from 0.071 to 0.099 mg/L. Environmental Protection Agency (EPA) gives the maximum amount allowed for Pb around 15 µg/L, so in most of the considered samples, it exceeded the maximum amount allowed than EPA recommends.

**Zinc** is an essential trace element found in a lot of foods and potable water in the form of salts or organic complexes. Although the levels of zinc in water normally do not exceed 0.01–0.05 mg/l, the concentrations in tap water can be much higher as a result of dissolution of zinc from pipes. The concentration of Zn in the investigated soil samples is from 0.408–0.586 mg/kg, while the value for soil standard (Dutch List) is around 140 mg/kg, so this measured element in soil is under the maximum amount allowed. Moreover, in the water samples, this element is below the allowed limits as compared with the EPA standards which recommend that Zn should be less than 5 mg/l.

**Nickel** showed lower value than the Dutch standards for soils (36 mg/kg). In the considered soil samples, the maximum concentration was 1.074 mg/kg. In the water samples the concentration of this element is higher than compared with drinking water standard (Table 1). In the studied water samples, nickel is five times higher

Table 1. Ranging results of elements in the samples of waste, soil, water and sludge

Elements	Waste mg/kg	Soil mg/kg	Sludge mg/kg	Water mg/l	Soil <sup>1</sup> mg/kg	mg/kg	Water <sup>2</sup>
Pb	0.614–0.889	0.531–0.758	0.711–0.898	0.071–0.099	85		10 µg /l
Zn	0.559–0.87	0.408–0.586	0.772–0.865	0.17–0.198	140	>90*	5 mg/l <sup>2</sup>
Cu	0.485–0.798	0.298–0.397	0.286–0.486	0.163–0.189	36	>25*	2 mg/l
Ni	0.515–1.095	0.151–1.074	0.106–0.997	0.079–0.098	35	>20*	20 µg/l
Fe	0.998–1.895	0.984–1.283	0.689–0.786	0.513–0.588			200 µg/l
Mn	0.624–1.748	0.531–0.859	0.414–0.511	0.04–0.063			50 µg/l
Al	0.897–1.991	0.993–1.432	0.933–1.621	0.654–0.878			200 mg/l

<sup>1</sup> Dutch List (Intervention Values for soils, 2000), <sup>2</sup> European Communities (Drinking Water) Regulations 2007, <sup>3</sup> EPA (Environmental Protection Agency), \* non polluted sludge.

than the recommended value for this element as the maximum of 20 µg/l. Additionally, in the sludge samples, it can be seen that the samples are non-polluted, comparing the value of lower than 20 mg/kg which can be considered as non-polluted sludge.

From the obtained results, it can be noticed that the pollution is not severe. In most of the cases, the elements presented did not exceed the maximum amount allowed, excluding Ni and Pb in the samples of water. However, these comparative values were made with drinking water, and the samples taken for analysis were from the river Lepenci which is not used directly as drinking water.

## CONCLUSION

According to the results obtained from the measurement of Pb, Zn, Cu, Ni, Fe, Mn and Al, it can be seen that the concentration of these elements are within the allowable limits. On the assumption of water sample, some of the elements were higher than drinking water standards. From different perspectives of the current study, the average of ecological risk potential is described as a region with low polluted zone with heavy metals due to the cement factory. In order to verify the results, and to keep the area under control due to the cement factory that can release a greater amount of pollution, it is advisable to keep the continuous monitoring and analysis of the region.

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