UDC: 504.5:502.521]:546.4/.8(497.751)
*Review article*

# DETERMINATION OF HEAVY METALS ON THE EARTH'S SURFACE NEAR THE JUGOHROM FACTORY BY AAS METHOD

**Emir Jonuzi[1], Dije Dehari[1], Shefket Dehari[1], Neset Izairi[2], Zulxhevat Abdija[1], Muhamet Shehabi[1]**

*1*Department of Chemistry, Faculty of Natural Sciences and Mathematics, University of Tetova, 1200 Tetovo, North Macedonia*
*2* Department of Physics, Faculty of Natural Sciences and Mathematics, University of Tetova, 1200 Tetovo, North Macedonia*
**Corresponding author e-mail: shefketd@yahoo.com*

**Abstract**

Heavy metals are potential poisons to human life and the environment. Their toxicity depends on their chemical form in the soil. Heavy metals have received special attention around the world as a result of their toxic effects even at very low concentrations. Our study aimed to determine the concentration of Pb, Cr, Cd, Ni, and Cu metals on the earth's surface by the atomic absorption spectroscopy method in the Jegunovce industrial zone in the city of Tetovo, Republic of North Macedonia.
From the obtained results, analyzing four points around the Jugohrom factory, the concentration of our metals presented in the average are: lead concentration (30.52 mg/kg), nickel concentration (28.69 mg/kg), copper concentration (49.99 mg/kg), chromium concentration (17.04 mg/kg) and cadmium concentration (3.12 mg/kg).
From the measurements that we have made, we can conclude that in the area around the Jugohrom factory, the pollution of these heavy metals was almost negligible, where only the chromium metal was with a concentration of about 0.19 mg/kg higher than the amount allowed in the soil.

*Keywords:* soil pollution, heavy metals, Tetovo, atomic absorption spectroscopy

## 1. Introduction

Soil, a major part of our world's ecosystem, is home to a large number of organisms, but at the same time, it is probably the most endangered component of our environment, open to influence from a variety of different pollutants arising from human activities (industrial, agricultural, etc.) (Bradl, 2005).
Metals serve as "technological nutrients" without which modern society can not function (Rauch et al, 2009). Heavy metals (HM) exist naturally in the environment, with changes in their concentration (Seiler H et al, 1994). Toxic heavy metals entering the ecosystem can lead to accumulation, bioaccumulation, and biomagnification (Lokeshwari et al, 2006).

Heavy metals are metals having atomic weight higher than 40.1 (exceeding that of calcium) and the soluble forms are generally ions or unionized organometallic chelates or complexes. The large concentrations of heavy metals in soil inhibit microbial activity by:

- altering enzyme conformations;
- blocking essential functional groups (sulfhydryl, amine, hydroxyl, carboxyl, imidazolyl);
- displacing other essential metal ions (deficiency effects) (Simeonov et al, 2011).

It exists around 35 metals that pose a concern because of our exposure to them in our jobs and living places. 23 of those metals are heavy metals like antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, iron, lead, etc. (Seiler H et al, 1994). The pollutants are transported to different distances, depending on the geographic area, its geology, and meteorological factors (wind, rain, fog, thermal inversions) and trophic or feeding level.

To cause any effect in a living organism, heavy metals have to come into contact with this organism. There are three principal ways, through which this might happen. The first pathway is through the atmosphere or atmospheric deposition to water and soil, the second is through drinking contaminated water or using it for cooking and crop irrigation, and the third is through accumulation in the food web (Bradl , 2005).

Human exposure to heavy metals (dietary, occupational, environmental) leads to the development of health effects: diabetes, hypertension, cancer, cardiovascular, renal, and neurological diseases. Children are much more vulnerable than adults too heavy metals exposure because of their more rapid growth rate and metabolism (Siemonov et al, 2011). The metals accumulate in the cells and tissues, interrupt cellular function, damage DNA, and slowly destroy peoples health if they are not removed from the body. The most common heavy or toxic metals are mercury, nickel, lead, arsenic, cadmium, aluminum, platinum, and copper (the metal form, not the ionic form required by the body) (Maxhuni et all, 2016). These metals have no function in the body and are hazardous to your health.

Even amounts of heavy metal exposure can negatively impact your health, but the following factors determine to what degree you will suffer:

- Nutritional status, especially anti-oxidant levels such as vitamins C, E and beta carotene, selenium, and glutathione levels.
- Strength of an individual's detoxification organs: colon, liver, kidneys, and lungs.
- Quantity and duration of the toxic exposure.
- Immune system strength.
- Other toxic exposures such as chemicals and radiation levels (Siemonov et al, 2011)

The Republic of Macedonia was involved in the UNECE ICP Vegetation – Heavy Metals in European Mosses, for the first time in 2002 (survey 2000/2001) and again in 2005 and 2010 when atmospheric deposition of trace elements was studied over the entire territory of the country using samples of terrestrial mosses Hypnum cupressiforme and Homalothecium lutescens. The results from all three studies show that the regions near the towns of Skopje, Veles, Tetovo, Radoviš, and Kavadarci were found as most affected by pollution, even the median elemental contents in the mosses in 2010 for Cd, Cr, Cu, Ni, Pb, and Zn were slightly lower than the previous surveys (Stafilov, 2014).

The purpose of this paper is to show the pollution of the soil with these heavy metals, taking into consideration that this region is generally considered as a place of high pollution with heavy metals based on some scientific works in our country in the last ten years.

## 2. Material and method

*2.1. The study area:* The study is the city of Tetovo, mainly suburbs of Jegunovce in this place is located the Jugohrom factory, which in the least years from 2014-2018 was in big public pressure for setting filters because from many analysis of air quality in this region according to their conclusion this factory was the main factor for enormous pollution of air in the city of Tetovo.

*2.2 Soil samples:* Soil samples were collected at four points. The location and coordinates of the samples are shown in the photos below (figure 1).

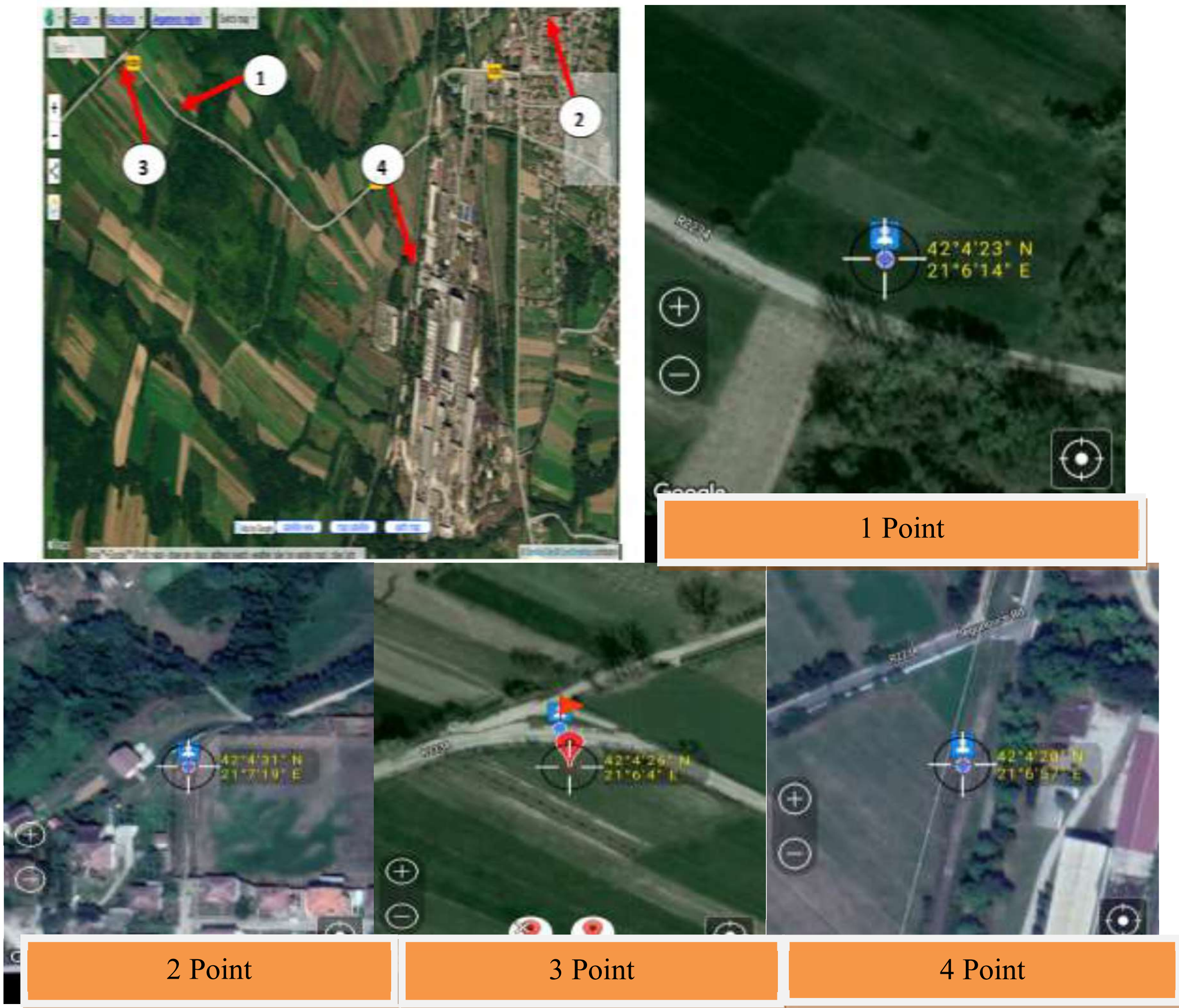


**Figure 1.** The location and coordinates of the samples

*2.3 Apparatus and reagents:* The concentration of heavy metals was determined with the atomic absorption spectroscopy method, using Nov AA400 Analytic Jena Spectrometer.

Reagents needed to carry out the experimental part are: 35% HCl, 65% $HNO_3$, 30% $H_2O_2$, distilled water, twice distilled water.

*2.4 Sample collection:* A total of four samples were analyzed, where 5 samples were taken for each point for a more comprehensive result. Samples of one point were in distance between themselves about one meter, one sample was taken in the center, and four in the corner. All the samples were taken in-depth 5 cm and for each sample, we collected around 0.5 kg of soil. After collection samples were placed in plastic bags. After that, we sent the samples to the laboratory for the experimental part.

*2.5 The treatment of soil samples:* Soil samples are cleaned from foreign materials and they have drained in the air at temperature 25-35 °C for seven days. Closely 1 gram from each sample settled in glass for digestion, there was added 20 ml (5ml $HNO_3 dhe$ $15ml$ $HCl$). Firstly, the samples left to stay quiet for 72 hours at room temperature, later they have warmed till 150 °C for one hour, after that the temperature was increased to 250 °C for two hours. After cooling the glasses, the digested material was carried out quantitatively in a volumetric vessel of 50ml, and the rest of the container was filled with redistilled water up to the mark.

*2.6 Quality control of the analysis:* Quality control for determination with AAS is based on the standard addition method.

*2.7. Statistical Analysis:* The processing of experimental results is realized through the computer program EXCEL.

## 3. Results and discussion

The concentration of heavy metals expressed in mg/kg for soil samples analyzed in the territory of the municipality of Tetova, mainly in the vicinity of the Jugohrom factory, is presented in Table 1.

**Table 1**. The concentration of metals (in mg/kg of dry weight) in soil samples in the territory of the municipality of Tetovo, mainly near the Jugohrom factory.

| samples | Pb | Ni | Cu | Cr | Cd |
|---|---|---|---|---|---|
| **1** | 21.23 | 21.47 | 22.19 | 6 | 2.42 |
| **2** | 60.8 | 30.93 | 66.45 | 11.56 | 3.19 |
| **3** | 17.53 | 17.72 | 44.63 | 40.1 | 3.88 |
| **4** | 22.53 | 44.65 | 66.7 | 10.53 | 3 |

Table 2, shows the maximum, minimum, median, and average for all soil samples analyzed**.**

**Table 2**. Statistical data of the studied points

| | Pb | Ni | Cu | Cr | Cd |
|---|---|---|---|---|---|
| **Average** | 30.5225 | 28.6925 | 49.9925 | 17.0475 | 3.1225 |
| **Maximum** | 60.8 | 44.65 | 66.7 | 40.1 | 3.88 |
| **Minimum** | 17.53 | 17.72 | 22.19 | 6 | 2.42 |
| **Median** | 21.88 | 26.2 | 55.54 | 11.045 | 3.095 |

The intensity of the concentration of heavy metals based on their average values for soil samples follows the trend Cu > Pb > Ni > Cr > Cd. The boundary values of concentration of some heavy metals in soils according to EU directives.[3]

**Table 3**. Boundary values of concentration of some heavy metals in soils according to EU directives**.**

| Metals | Border values in mg/kg |
|---|---|
| **Cadmium** | 1 – 3 |
| **Lead** | 50 – 300 |
| **Copper** | 50 – 140 |
| **Zinc** | 150 – 300 |
| **Nickel** | 30 – 75 |
| **Chromium** | - |

The results presented in Table 1, have been compared with the limit values of concentrations of some heavy metals in soils according to Council Directive 86/278/EEC of June 12, 1986, on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (figure 2).

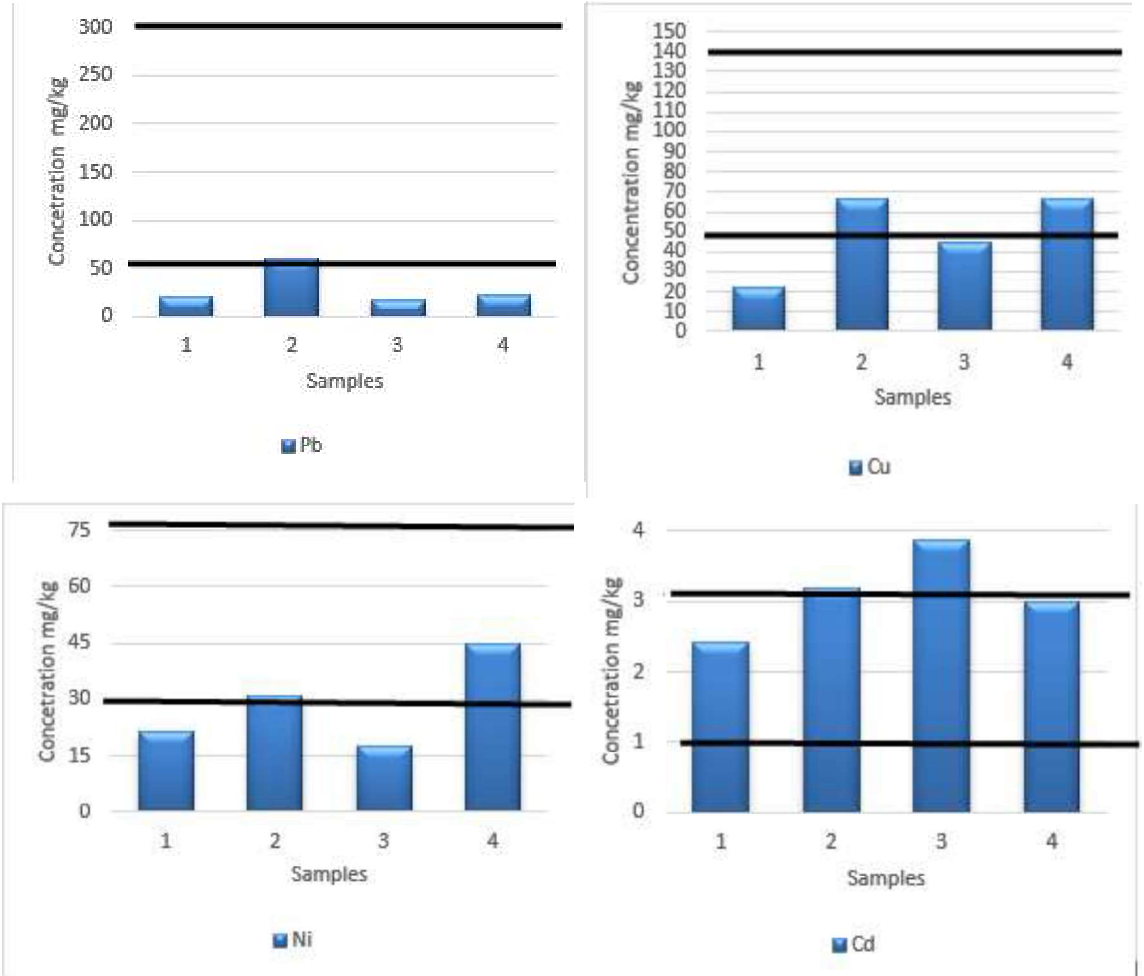


**Figure 2.** Comparison of values of concentration of some heavy metals in soils according to Council Directive 86/278/EEC

The obtained results of heavy metals show that the concentration of these metals in the analyzed samples are at permitted levels compared to the allowed values of these metals in the EU, except for the concentration of Cd in point(sample) 2 with a concentration of 3.19 mg/kg and in point(sample) 3 with a concentration of 3.88 mg/kg. However, considering allowed values of Cd in soils according to EU conditions from 0 - 3 mg/kg, we can say that this amount of 0.19 respectively 0.88 mg/kg, that has resulted to be above the allowable threshold that was 3 mg/kg, is very small and almost negligible. However, this amount of 3.88 mg/kg of Cd in point(sample) 3 was taken around the road through which road transport takes place or the concentration of 0.88 above the allowed level may be due to traffic (cars) considering that the refined oil contains a quantity of Cd, also tires and lubricating oils release a quantity of cadmium.

## 4. Conclusions

From the performed analysis and the results obtained in four points around the Jugohrom factory in the city of Tetovo, we can conclude that the soil around the factory is not polluted with heavy metals such as Cd, Pb, Ni, Cu. But we cannot conclude with certainty that soil was not polluted at all with these metals, because as we know from many studies that have been done in this, that soil composition, pH, etc. play a very big role in retaining metals or releasing them from the soil (Andersson, 1977).
In our future studies, we will analyze the composition of the soil in this region and after that, we can give a complete conclusion about pollution of the soil in this region.

## References


[1]. Andersson, A., *Heavy Metals in Swedish Soils: on their Retention, Distribution, and Amounts*, Swedish Journal of Agricultural Research, Vol.7, 1977, pp. 7-20.

[2]. Bradl H., *Heavy Metals in the Environment: Origin, Interaction, and Remediation*, Interface Science and Technology, Vol. 6, 2005, pp. 1-27.

[3]. Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture.

[4]. Lokeshwari H., Chandrappa T., *Impact of Heavy Metal Contamination of Bellandur Lake on Soil and Cultivated Vegetation*, Current Science, Vol. 91, 5, 2006, pp. 622-627.

[5]. Maxhuni, A., Lazo, P., Kane, S., Qarri, F., Marku, E., Harmens, H., *First survey of atmospheric heavy metal deposition in Kosovo using moss biomonitoring*. Environ Sci Pollut Res, Vol. 23,1, 2016, pp. 744-755.

[6]. Seiler H., Sigel A., Sigel H., *Handbook on Metals in Clinical and Analytical Chemistry*, Vol. 483, 1, 1994, p. 753.

[7]. Simeonov L., Kochubovski M., Simeonova B., *Analyses of Heavy Metal Mixtures in the Environmental Media,* Environmental Heavy Metal Pollution and Effects on Child Mental Development, Springer, 2011, pp. 159-170.

[8]. Rauch, J., Pacyna J., *Earth's global Ag, Al, Cr, Cu, Fe, Ni, Pb, and Zn cycles*. Global Biogeochemical Cycles, Vol. 23, 2, 2009, pp. 1-16.

[9]. Stafilov T., *Environmental Pollution with Heavy Metals in the Republic of Macedonia*, Contributions, Section of Natural, Mathematical and Biotechnical Sciences, MASA, Vol. 35, 2, 2014, pp. 81–119.