THE CONTENT OF As, Pb AND Cd IN ENVIRONMENTAL SAMPLES IN MUNICIPALITY OF KIJEVO

Aida Šapčanin[1], Zahida Begović [2], Amna Kukić [2], Farzet Bikić[2]
[1]University of Sarajevo-Faculty of Pharmacy, Zmaja od Bosne 8, 71000 Sarajevo, Bosnia and Herzegovina
[2]Faculty of Engineering and Natural Sciences, University of Zenica, Fakultetska 3, 72000 Zenica Bosnia and Herzegovina
Corresponding author: Aida Šapčanin, aida.sapcanin@ffsa.unsa.ba

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ABSTRACT
Toxic metals like arsenic (As), lead (Pb)and cadmium (Cd) are the major indicators of environmental pollution that have serious impact to human health as well as the environment. Measurement of these metals were done in the samples of: selected plants, Željeznica river, and agricultural soil in the municipality of Kijevo near Sarajevo city; by using the conventional methods of GFAAS. Results showed potential concern to plants and human population posed to long-term exposure to identified heavy metals.Therefore, bioremediation could be an effective and sustainable method for treating toxic metals contaminated areas that has many advantages over conventional treatment technologies. It is very important that all necessary measures are taken to avoid contamination of the environment. Emissions of heavy metals and other pollutants would have to be harmonized with the capacity (degree sensitivity) of soil and other environmental components for their safe reception.

1.INTRODUCTION

Nowadays, due to urbanization, industrialization and increased production, environmental pollution is becoming a pressing issue. A large part of land and water is in a state of high degree of pollution with various toxic substances. Among them, heavy metals stand out due to their negative and toxic effects. Continuous monitoring of concentrations and permitted values of substances in water, air and soil is an important and indispensable part of the preservation of all habitats. According to the Amendment (NN 72/19), heavy metals (Cd, Cr, Cu, Hg, Ni, Pb, Zn, Mo, As, Co) and potentially toxic essential elements (Zn and Cu), organic chemical substances, radionuclides are considered pollutants. and pathogenic organisms [1]. All those substances that reach the environment from various sources, are usually introduced into the soil and in some way seriously impair the quality of the environment and/or human health are considered pollutants [2,3]. Accumulation of pollutants burdens the production capacity of the ecosystem [4]. Heavy metals represent a group of chemical elements with specific properties and a relative density greater than 5 g/cm^3. In the biological sense, these are metals and metalloids that, even at low concentrations, can be toxic to living organisms. Heavy metals can be essential (Cu, Fe, Mn, Zn and Mo) i.e. they are necessary for the development of living organisms and if their values are in deficit certain problems arise. The remaining part of heavy metals has no physiological significance and is considered toxic (Pb, Cd, As and Hg) because they cause various changes in the body. Heavy metals are extremely toxic because they accumulate in the body without the possibility of excretion [5]. They enter the air, soil and water due to erosion and volcanic activity, the action of watercourses and atmospheric precipitation. They are naturally found in the soil, and are formed as a result of the weathering of parent rocks and the influence of external factors, primarily anthropogenic. It is estimated that the retention of heavy metals in the soil lasts from 150 to 5000 years.

They also represent the most common inorganic pollutants in the soil of Europe and it is estimated that about 2.5 million soils in Europe are contaminated with heavy metals [5]. When they reach the soil, they remain passively in the pores or actively bind to colloidal complexes. They reach the plant from the soil via the root system, and are later distributed to the leaves through transpiration. The absorption of heavy metals into plant roots depends on the pH value of the soil, the content of water and organic matter. Heavy metals can enter humans in different ways: ingestion, inhalation and dermal route. When heavy metals are introduced into the human body, they bioaccumulate in the system. Therefore, they are classified as dangerous [6]. They act on organisms by slowing down the function of oxidoreductive enzymes and thus cause increased formation of reactive oxygen species (ROS). They then react with proteins and other non-enzymatic molecules and cause inhibition of metabolic processes and oxidative stress [7]. They inhibit physiological metabolic processes such as growth, photosynthesis, ion and water exchange and nitrate assimilation. One of the most common symptoms of stress caused by heavy metals is leaf chlorosis. It occurs as a result of a decrease in the concentration of chlorophyll [8]. Arsenic (As), cadmium (Cd) and lead (Pb) are on the priority list of heavy metals dangerous to the environment and living organisms. As is considered a carcinogenic element due to its extreme toxicity even at low levels of exposure. Acute exposure to its compounds can cause nausea, vomiting, stomach pain, muscle cramps, and diarrhea, while chronic exposure is associated with peripheral nerve damage it causes [9]. Cd is released into the atmosphere as a result of natural phenomena or anthropogenic activities, and animals and humans can be exposed to it in different ways. Water system Cd pollution occurs through absorption, industrial waste and surface runoff into soil and sediments [10]. Cd is known to be toxic even at low concentrations and is also considered carcinogenic. Cd can also result in bone fracture, kidney dysfunction, hypertension and even cancer. Arthritis, diabetes, anemia, cardiovascular disease, cirrhosis, reduced fertility, headaches, and stroke are some of its unusual long-term effects [9]. Pb is a biodegradable metal that is available in nature and is found in relatively small amounts. However, levels of Pb in the atmosphere are continuously increasing due to human activities, including manufacturing, mining and burning of fossil fuels. Pb is toxic to the human body when exposed to amounts greater than optimal. Children are exposed to a greater risk of Pb poisoning than adults [10]. Pb is also considered a probably carcinogenic element. It causes kidney tumors and also disrupts the normal functioning of the kidneys, joints, reproductive and nervous systems [10]. In order to reduce the concentration of heavy metals in the most exposed environmental sample - the soil, measures are taken to decontamination of heavy metals through soil remediation. Remediation should bring the soil to a natural state that corresponds to the natural content of heavy metals and other elements necessary for the smooth growth of plants. In fact, the main goal of soil remediation is to reuse the soil for agricultural purposes. Soil decontamination can be done by mechanically removing the surface layer of the soil, and then by adding nutrients and organic matter, which reduces the content of heavy metals to a minimum. However, this procedure is limited to smaller areas and is usually very extensive and expensive. In the last decades, the process of soil phytoremediation using certain plant species that have the ability to hyperaccumulate heavy metals has been used more and more in the world for soil decontamination. Phytoremediation as a term comes from the Greek word "phito" which means plant and the Latin word "remedium" which means re-establishing balance, i.e. healing. In addition to the fact that this technique is very economical, because the costs of this method of removing contaminants are lower compared to some traditional methods of decontamination, it also has the advantage of being the least destructive method, due to the use of a natural method of removal with minimal environmental destruction. The US Environmental Protection Agency (EPA) defined phytoremediation as a technology that uses plants and their rhizospheric microorganisms to remove, degrade or retain harmful chemical substances found in the soil, underground and surface waters and the atmosphere [11]. Different techniques are used to determine heavy metals. The conventional AAS technique is used to obtain reliable data on the content of heavy metals in environmental samples. Atomic absorption spectrometry (AAS) is a quantitative method of metal analysis that is suitable for the determination of elements using three techniques (flame, graphite furnace technique, hydride technique). AAS measures the concentration of metals such as As, Cd, Pb, by transmitting light (of a certain wavelength) from a radiation source [12]. The main goal of this study was to identify and quantify the most toxic elements such as As, Pb and Cd in the water of Željeznica river, selected agricultural soil and most commonly grown edible plants in the weekend settlement of Kijevo area. Determining the content of heavy metals in soil is a basic indicator for determining the degree of contamination and suitability of soil for plant production. The bioaccessibility and bioaccumulation of heavy metals in plants is directly related to their content and mobility in the soil.

2. MATERIAL AND METHODS

2.1. Sampling area

Kijevo (43°45′33″N 18°24′41″E) is a village in Trnovo municipality, Istočno Sarajevo, Republika Srpska, Bosnia and Herzegovina. Kijevo is south of Sarajevo on the road M-18 Sarajevo-Trnovo-Foča-Trebinje. The closest airport is Sarajevo International Airport, located 9.7 km north west of Kijevo. The Željeznica river is one of the Kijevo's chief geographic features. It flows through the town and municipality from south through the center of Trnovo, Kijevo and East Sarajevo to west part of Sarajevo eventually meets up with the Bosna river. On the grassy areas that stretch along the river, there are different types of medicinal plants. The most famous among them are: *Colchium autumenale*, *Hypericum perforatum*, *Equisetum arvense*, *Mentha piperita*, *Matricaria chamoilla*, *Atropa belladona*, *Genitiana lutea*, *Achillea millefollum*, *Thymus serpyllum* and others. From early spring until autumn at the latest, many types of mushrooms, most of which are edible, grow in forests, meadows, and arable land. In this regard, it can be stated that the area in question, which is rich in forest communities, has a positive effect on the absorption capacity of the environment, because the greatest values of forests are indirect, which are the result of their ecological functions (they affect the global circulation and accumulation of carbon in nature, thus mitigating greenhouse effect and climatic extremes; they protect the soil from erosion; they are a reservoir of genetic information and a refuge for rare organisms; they protect watercourses and their living world oxygen, etc.).

The sampling area (the satellite view) is presented in Figure1.

Legend: blue circle- water sampling point; brown circle- soil sampling point and green circle-plant sampling point.

Figure 1. Sattelite view of sampling area in Kijevo, Republika Srpska (Google maps)

2.2. Sample collection

Representative water samples were collected from selected locations of river Željeznica in Kijevo area. (Fig.1.) four times during 2024. in the different season (winter, spring, summer, and autumn) and analysed by using an GFAAS [13]. Soil and plant material samples were analyzed for the total content of heavy metals (As, Pb, Cd) using the GFAAS method. Edible leafy plants like: beet, sprout, spring onion, lettuce and leek were collected directly from the land. After collection, the plant samples were cleaned of impurities and damaged parts and then subjected. The leaves of samples were cut into small pieces after thoroughly washing with tap water and deionised water. Drying was carried out in a dark and airy place at room temperature. After drying, samples were milled and sieved (1 mm stainless-steel mesh) for wet digestion. 1.00 g of the dried sample was transferred into polytetrafluoro- ethylene (PTFE) vessels, and then 30 mL of 65% HNO_3 was added. After evaporating the nitrogen oxides, the vessels were closed and allowed to react for 18 h at 90 °C. The digest was cool to room temperature, filtered, transferred to a volumetric flask of 50 mL, and filled up with redistilled water up to the mark. A GFAAS was used to measure the concentrations of As, Pb, and Cd. The standard solutions were prepared by dilution of 1000 mg/L stock single-element atomic absorption standard solutions and used to develop calibration curves. The analysis was based on analytical-grade chemicals and reagents. The mean value was obtained by subtracting the value of the blank procedural probe. The accuracy and precision of the analysis were evaluated using the standard reference material and the obtained results were in the range of the reference material [14,15,16].

3. RESULTS AND DISCUSION

In the municipality of Trnovo, waste water, rainwater and sewage, as well as from part of the septic tanks, is discharged without treatment directly into the nearest watercourses or the ground. The sewage system is incomplete, partially designed and built. The percentage of residents covered by the sewage system is below 50%. The stormwater network is insufficient. The water treatment plant was destroyed during the war and after the division of the municipality it belonged to Trnovo FBiH, so that the wastewater is now discharged into the Željeznica river. That's why the investigated heavy elements such as As, Pb and Cd were identified and quantified in the river water samples as it shows in the Figure 2.

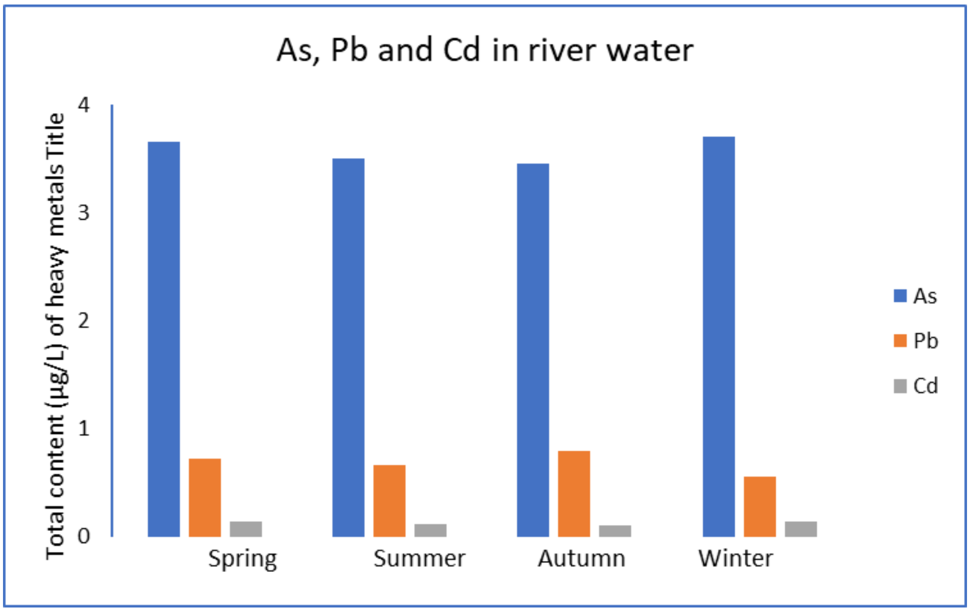

Figure 2. The content of heavy metals in investigated river water samples during the different seasons.

According to the pedological map of the Republic of Srpska (Amendments to the Spatial Plan of the Republic of Srpska until 2025), the examined area includes anthropomorphic soils - the most common are: a chalcomelansol - chalcocambisol mosaic [1]. Anthropomorphic soils are soils where human intervention is considered the main pedogenetic factor [17]. The content of heavy metals in investigated soil samples is presented in Figure 3.

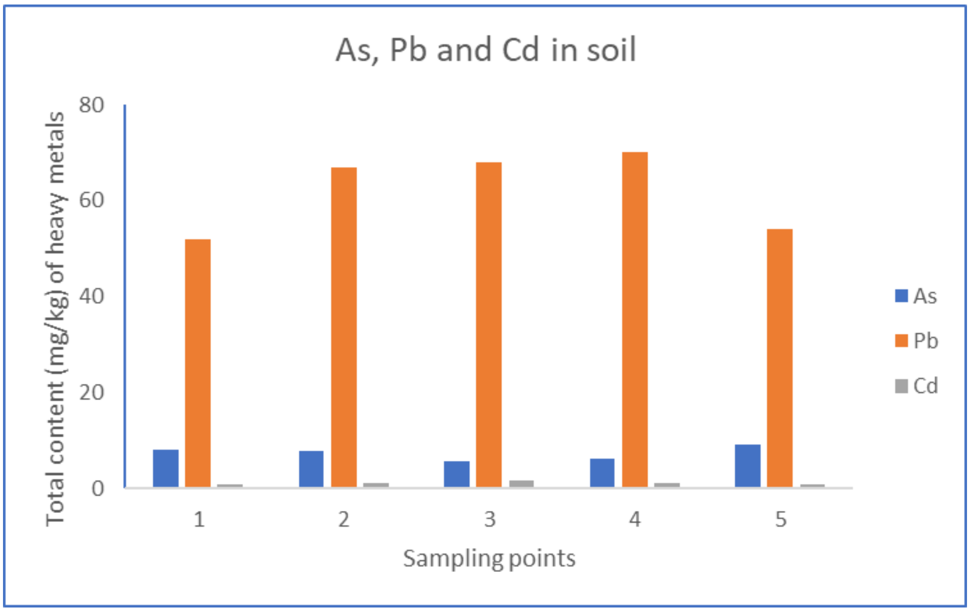

Figure 3. The content of heavy metals in investigated soil samples

Heavy metals have the ability to bioabsorb and bioaccumulate. The absorption and accumulation of heavy metals in plants depends on the bioavailability and content of heavy metals in the soil, the genetic characteristics of the plants, edaphic and other ecological factors. Figure 4. shows the content of heavy metals in the tested plants in the zone 50-150 m distance from the river Željeznica.

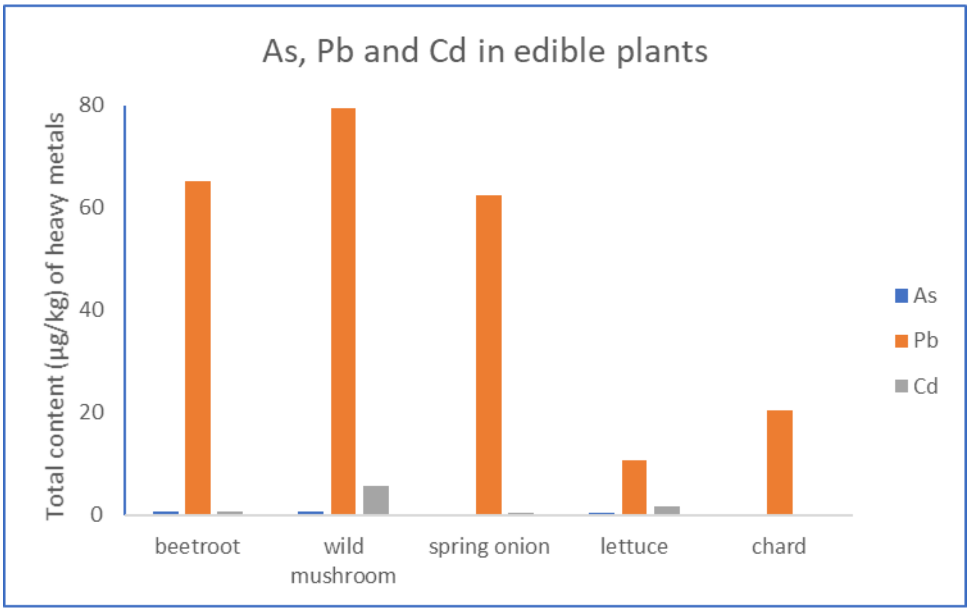

Figure 4. The content of heavy metals in investigated edible plants

The total content of heavy metals in analysed leafy plants decreases as follows: content of As: wild mushrooms > beetroot > lettuce > chard > spring onion; content of Pb: wild mushrooms > beetroot > spring onion > chard > lettuce; and content of Cd: wild mushrooms > lettuce > beetroot > spring onion chars > chard. Similar research results have been published, showing that green leafy plants generally accumulate heavy metals more than non-leafy plants [16]. The study area's high concentrations of heavy metals in the plant samples are most likely the result of anthropogenic activities like mining and car exhaust pollution. Some mushrooms species, however, can accumulate high concentrations of toxic metals such as cadmium, lead and arsenic. The results from various studies have shown that these elements can be identified and quantified in significant concentrations, even when mushrooms are picked from unpolluted areas [18, 19, 20]. Foreign studies have shown that mushrooms can also serve as bioaccumulators of Cd. There were differences between studied wild mushroom species due to metal contents, but it should be stated that the metal content of each species is dependent of the accumulation of these metals from their local surroundings and absorbance capacity. The highest total metal content was determined in wild mushroom species and the plants of this family can be used for phytoremediation to clean heavy metal-contaminated areas [21,22].
The content of lead and cadmium in fruit and vegetables (except leafy vegetables) meets the maximum permitted values prescribed by the provisions of the Ordinance on Maximum Permitted Quantities of Certain Contaminants in Food [21]. The maximum permitted values for lead are 0.10 mgPb/kg and 0.05 mgCd/kg for vegetables and fruits, 0.20 mgPb/kg for green vegetables and 0.30 mgPb/kg for leafy vegetables, and 0.05 mgCd/kg for cadmium for vegetables and fruits and 0.20 mg Cd / kg for leafy vegetables [21].
The correlation between content of heavy metals in water, soil and plants was calculated and presented in Table 1.

Table 1. Correlation diagram for As, Pb and Cd content in water(w), soil(s) and tested edible plants(p).

	As w	As s	As p	Pb w	Pb s	Pb p	Cd w	Cd s	Cd p
As w	1								
As s	0.213021	1							
As p	0.363809	0.258589	1						
Pb w	-0.70595	-0.1281	-0.57952	1					
Pb s	-0.29662	**-0.78573**	0.044716	-0.3131	1				
Pb p	-0.70066	-0.01646	0.362682	0.671212	-0.00429	1			
Cd w	**0.950654**	0.500216	0.616948	-0.70553	-0.43196	-0.47335	1		
Cd s	**-0.90222**	-0.66636	-0.33683	0.556305	0.674711	0.451361	**-0.97964**	1	
Cd p	-0.23476	0.064811	**0.77525**	-0.39713	0.451493	0.463957	-0.01304	0.20318	1

Pearson coefficient values that indicate a very good to excellent correlation between the examined variables (0.75 to 1 or from –0.75 to –1) are shown in the table and are bolded. A signifcant relationship was noticed particularly regarding As and Cd content in river water and soil. Some mushrooms species, however, can accumulate high concentrations of toxic metals such as cadmium, lead and arsenic. The results from different studies showed that these elements can be identified and quantified in significant concentrations even if mushrooms have been picked from unpolluted areas [15,18,19,20]. Foreign studies showed that mushrooms could serve as bioaccumulators of Cd, too. There were differences between studied wild mushroom species due to metal contents, but it should be stated that the metal content of each species is dependent of the accumulation of these metals from their local surroundings and absorbance capacity. Strong positive and negative correlation between measured metals was also noted [22]. Residents in the investigated areas can be afected by pollutants in diferent ways, and one signifcant concern is heavy metal long term exposure through the food.

Additionaly, our obtained results also shows that all analyzed samples had a Hazardous Risk Index (HRI) for As, Pb and Cd values below 1 [16, 22]. This means that the presence of these heavy metals didn't pose a risk of investigated metals toxicity to individuals in the sampling area of Kijevo.

4. CONCLUSION

No significant sources of emissions have been identified in the immediate vicinity of the investigated area. The characteristic of this area is the absence of industrial pollutants. All this indicates that the quality of the environment at the examined location and in its surroundings is at a fairly high level. The most significant source of emissions currently at the location in question is the main road M18 Sarajevo-Trnovo-Foča. This road is also a source of noise and air pollution in this area, which are caused by the friction of moving parts of the vehicle and the road surface, as well as the result of the operation of internal combustion engines. Also, as sources of pollution in the narrower area of Kijevo, a waste dump, located on the left side of the bank of the Željeznica river, a quarry and a dam of a hydropower plant, located at a distance of about 300 meters upstream, were identified.

The greater presence of heavy metals in the soil than natural values affects their greater bioaccumulation in plants. That is why it is necessary to provide monitoring of heavy metals in the soil and plants in the goalmonitoring the state of environmental quality, population health

protection and the effects of implementing measures for reduction of dust and heavy metal emissions from the road, as well as transfer from the Željeznica river and underground water.
It is very important that all necessary measures are taken to avoid contamination of the environment. Emissions of heavy metals and other pollutants would have to be harmonized with the capacity (degree sensitivity) of soil and other environmental components for their safe reception.

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