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**Research Article**

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# Soil contamination study around the Buchim Copper Mine, Republic of Macedonia

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Key Words:

Buchim mine, soil, copper, arsenic, contamination

## ABSTRACT

**One of the major emission sources of some metals in the eastern part of the R. Macedonia is Bucim copper mine and flotation, near the town of Radovis. Ore excavation is from open pit and the ore tailings are stored in the open, in mine vicinity. The produced copper ore from the mine is processed in the flotation plant; after the flotation of copper minerals, the flotation tailings are separated, disposed of and deposited on a dump site in an adjacent valley near the village Topolnica. During the 35 years of continuous exploitation around the Buchim Mine was created surface waste dump were have been stored more than 150 Mt and more than 100 Mt material within the hydro-tailling dam. Within this study a total content of 20 elements was determined in soil samples taken from the vicinity of the "Bucim" mine, covering an area of 14.2 $km^2$. Analyses were performed by the ICP-AES. The results have been compared to new Dutchlist and NOAA standards and the following was concluded: As values ranged 13.1÷225 mg $kg^{-1}$ with 20 samples above the optimum (29 mg $kg^{-1}$ As) and 7 above action value (55 mg $kg^{-1}$ As), in that context Cd values ranged 0.67÷17.9 mg $kg^{-1}$ with 17 values above optimum (0.8 mg $kg^{-1}$ Cd) and 1 over the action value (12 mg $kg^{-1}$ Cd), Cr with range 30.1÷171 mg $kg^{-1}$ with 6 over optimal value (100 mg $kg^{-1}$ Cr) and none above action value (380 mg $kg^{-1}$ Cr), Cu with range 17.8÷1734 mg $kg^{-1}$ with 16 over optimal value (36 mg $kg^{-1}$ Cu) and 3 above action value (190 mg $kg^{-1}$ Cu), Ni with range 9.8÷69.4 mg $kg^{-1}$ with 5 over optimal value (35 mg $kg^{-1}$ Ni) and none above action value (210 mg $kg^{-1}$ Ni), Pb with range 46÷3456 mg $kg^{-1}$ with 19 over optimal value (85 mg $kg^{-1}$ Pb) and 1 above action value (530 mg $kg^{-1}$ Pb), Zn with range 88÷3438 mg $kg^{-1}$ with 12 over optimal value (140 mg $kg^{-1}$ Zn) and 1 above action value (720 mg $kg^{-1}$ Zn), Mn with range 169÷998 mg $kg^{-1}$ with 25 over optimal value (33 mg $kg^{-1}$ Mn) and none above action value (48 mg $kg^{-1}$ Mn), Fe range 0.73÷5.02% with 21 over optimal value (1.8% Fe) and none above action value (3.2% Fe). The V, Al, Co, also, showed some increased values, but not more than optimal concentration.**

## INTRODUCTION

There are many different sources of heavy metal contaminants, including mining and metallurgical industries (Kabata-Pendias and Pendias, 2001). It is obvious from the papers published recently that mining and metallurgical activities lead to enormous soil contamination (Li et al. 2005, 2006; Wilson et al. 2005; Pruvot et al. 2006; Aryal et al. 2006; Cemek and Kizilkaya 2006; Cappuyns et al. 2006; Tembo et al. 2006). Particular emphasis is given on ore deposits, mining, processing and flotation plants as significant anthropogenic sources of dust. Copper mine with open ore pit type present a potentially emission source of heavy metals in the air, soil and water. Main processes that allow it are: minerals blasting, drilling and crushing, their loading and transportation to processing and flotation plants. From other hand, large amounts of ore waste and flotation tailings are deposited at open, continuously exposited to air flow and winds caring-out. Heavy metals emitted in the atmosphere by combustion processes usually have relatively high solubility's and reactivity's; especially under low-pH condition (Athar and Vohora, 1995; Hršak et al., 2003; Hou et al., 2005). They can be carried to places far away from the sources by wind, depending upon whether they are in gaseous form or as particulates. Metallic pollutants are ultimately washed out of the air by rain and deposited on the land (Balabanova et al., 2011b). Deposited dust refers to any dust that falls out of suspension in the atmosphere. Solid and liquid particles or dust that falls out of suspension in the atmosphere can get into the environment and lead to its contamination. Atmospheric total deposition (deposited dust) is very useful mechanism for monitoring the fate of anthropogenic elements introduced into the atmosphere (Čačković et al., 2009).

The intent of this article is to present the results of 2010 study of spatial distribution of different chemical elements in surface soil in the Buchim mine region (Figure 1), located in the eastern part of the Republic of Macedonia, known for its copper industrial activity in the last three and half decades.

The mine and the ore processing plant have been functioning since 1979 and and process 4 million tons of ore annually. It is assumed that the mine at the moment have about 40 million tons of ore reserves. The deposit is a porphyry copper type deposit and mineralization is related to Tertiary sub-volcanic intrusions of andesite and latite in a host of Pre-Cambrian gneisses and amphibolites (Serafimovski et al., 1995). The open ore body is approximately 500 m in diameter and 250 m in vertical extent, which actually allows direct exposure of ore particles to the atmosphere. The content of copper in ore is at on the average of 0.3 % Cu. Characteristic metallic minerals are chalcopyrite, pyrite, and bornite, with small amounts of galena, sphalerite, magnetite, hematite, and cubanite (Serafimovski et al., 1996; Alderton et al., 2005). Ore tailings are disposed at open site near the mine, that occupies a surface of 0.8 km$^2$. The tailing dam has about 130 million tons of ore tailings. Exposure of this great mass of ore tailings to constant air flow and wind leads to the distribution of fine dust in the air.

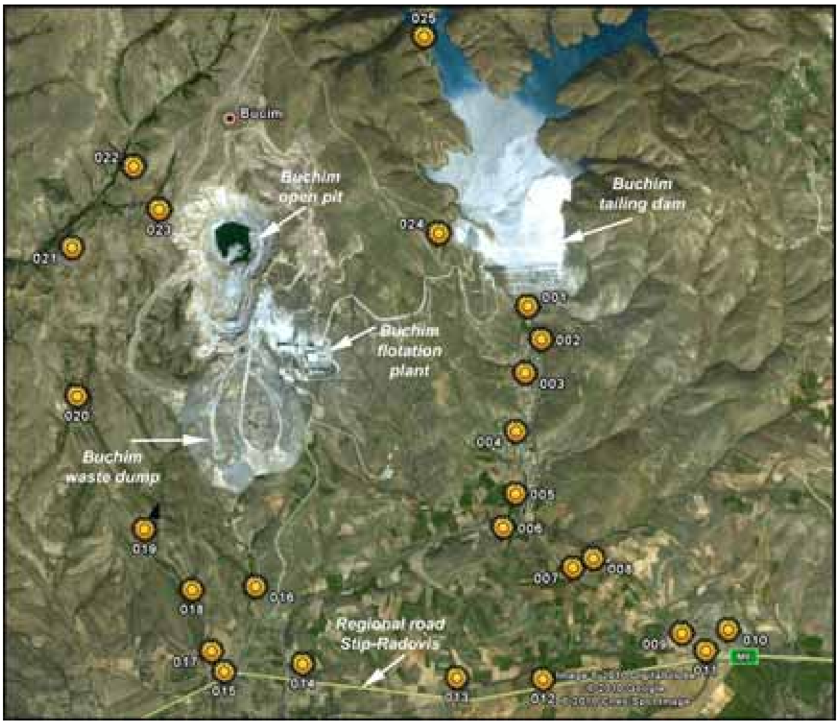


**Figure 1.** Location of the soil samples around the Buchim copper mine

## MATERIAL and METHODS

Sampling was carried out at the begining of February 2010. Soil surface samples (0 cm to 5 cm depth) were collected in around the Buchim Mine and its surrounding region (Figure 1). In total, 25 samples were collected from 25 locations, including locations near the mining center of Buchim over an area of 14.2 km$^2$. Samples were located using the Global

Positioning System (GPS), topographic maps at scale of 1:25 000 and Google Earth maps. Each sample represented the composite material collected at the central sampling point itself together with at least four points collected around a central one with a radius of 1 m towards N, E, S and W directions. The composite material of each sample (about 0.5 kg) was placed into plastic self-closing bags and brought to the Faculty of Natural and Technical Sciences, University "Goce Delcev" Stip, Republic of Macedonia, where they were prepared for atomic spectroscopy.

All of the collected soil samples were then shipped to the Institute of Chemistry at the Faculty of Natural Sciences, University "Sts.Cyril and Methodius" Skopje, R. Macedonia. Analyses were conducted using emission spectrometry with inductively coupled plasma (ICP-AES) after Aqua Regia Digestion. All samples (n=25), replicates (n=3) and geological standards (n=4) were submitted to the laboratory in a random order. This procedure assured an unbiased treatment of samples and a random distribution of the possible drift of analytical conditions for all samples. Eleven randomly selected samples were replicated for precision estimation. The precision was less than 5%.

## RESULTS and DISCUSSION

The latest study of soils around the Buchim mine complex was performed on 25 locations and for each sampling point samples were analyzed for a geochemical package of 20 elements.

**Table 1.** Statistical data from the soil samples around the Buchim copper mine

| Element | min | max | average | Optimum (Dutch list) | Action (Dutch list) | above optimum | above action |
|---|---|---|---|---|---|---|---|
| Al (%) | 0,72 | 5,9 | 2,8928 | 4,7 | - | 5 | 0 |
| Ca (%) | 0,07 | 4,28 | 1,3024 | - | - | 0 | 0 |
| Fe (%) | 0,73 | 5,02 | 3,148 | 1,8 |  | 21 | 0 |
| K (%) | 0,79 | 3,28 | 2,008 | - |  | 0 | 0 |
| Mg (%) | 0,12 | 1,97 | 0,9708 | - |  | 0 | 0 |
| Na (%) | 0,77 | 2,09 | 1,7624 | - |  | 0 | 0 |
| Ag (mg kg$^{-1}$) | 0,1 | 0,1 | 0,1 | - | 15 | 0 | 0 |
| As (mg kg$^{-1}$) | 13,1 | 225 | 63,904 | 29 | 55 | 20 | 7 |
| Ba (mg kg$^{-1}$) | 131 | 485 | 304,68 | 160 | 625 | 24 | 0 |
| Cd (mg kg$^{-1}$) | 0,67 | 17,9 | 2,1908 | 0,8 | 12 | 17 | 1 |
| Co (mg kg$^{-1}$) | 3,62 | 22,3 | 12,3884 | 9 | 240 | 22 | 0 |
| Cr (mg kg$^{-1}$) | 30,1 | 171 | 80,684 | 100 | 380 | 6 | 0 |
| Cu (mg kg$^{-1}$) | 17,8 | 1734 | 129,064 | 36 | 190 | 16 | 3 |
| Li (mg kg$^{-1}$) | 0,07 | 0,25 | 0,1264 | - | - | 0 | 0 |
| Mn (mg kg$^{-1}$) | 165 | 998 | 552,72 | 33 | - | 25 | 0 |
| Ni (mg kg$^{-1}$) | 9,8 | 69,4 | 29,548 | 35 | 210 | 5 | 0 |
| Pb (mg kg$^{-1}$) | 46 | 3465 | 288,252 | 85 | 530 | 19 | 1 |
| Sr (mg kg$^{-1}$) | 17,6 | 132 | 75,804 | - | - | 0 | 0 |
| V (mg kg$^{-1}$) | 14 | 144 | 83,612 | 42 | 250 | 22 | 0 |
| Zn (mg kg$^{-1}$) | 88 | 3438 | 319,872 | 140 | 720 | 12 | 1 |

During the study of results and their statistical processing it was determined that very representative are particular elements such are copper, arsenic, cadmium, lead and zinc that are given in more details within this paper while there are elements such are iron, manganese, chromium, vanadium, nickel, cobalt, which display slightly elevated concentrations, but without any significant impact, as well as elements such are aluminium, calcium, sodium, barium, strontium etc being direct product of geological setting and without any anthropogene enrichment (Table 1).

As it can be seen from the table above, there were analyzed 20 elements and their minimal, maximal, average and referent values according to the New Dutchlist (http://www.contaminatedland.co.uk/std-guid/dutch-l.htm), are given. Distribution of particular anthropogenically introduced elements is given as follows:

**Arsenic (As):** It is well known that an arsenic in nature usually occurs in the form of sulphides such as arsenopyrite, FeAsS, realgar, $As_4S_4$, orpiment, $As_2S_3$, and that the exposure to As by ingestion can cause problems in the digestive and nervous systems and activity of the heart while prolonged long-term exposure could result in nerve damage and may lead to lung, skin, or liver cancer (Goyer, 1996; Frumkin and Gerberding, 2007). Contamination of the environment by arsenic from both anthropogenic and natural sources has occurred in many parts of the World and is now recognized as a global problem. The principal anthropogenic sources for soil contamination by As include base metal smelters, mining of arsenic, lead and zinc, gold and other types of mines (Stafilov et al. 2010a). The average amount of As in the world's soils is 5 mg kg$^{-1}$ (Bowen, 1979), and in the European topsoil is 12 mg kg$^{-1}$ (Salminen et al., 2005). The average amount of As in the topsoil for the entire study area is 63.904 mg kg$^{-1}$, with a range of 13.1–225 mg kg$^{-1}$ (Table 1; Figure 2). .

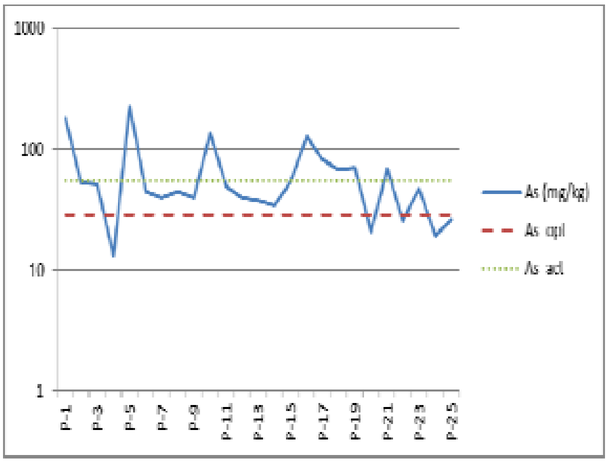


**Figure 2.** Diagram of arsenic distribution in the soil compared with optimal and action values

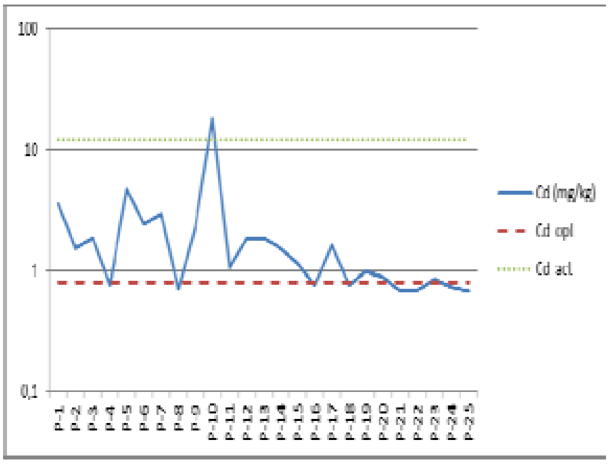


**Figure 3.** Diagram of cadmium distribution in the soil compared with optimal and action values

As it is displayed at the diagram arsenic concentration at particular sampling points were higher than optimal as well as over the action values according the New Dutchlist (http://www.contaminatedland.co.uk/ std-guid/dutch-l.htm). Also, it was found that the content of arsenic in topsoil is high in the areas of the copper mine and flotation plant, but also in the topsoil from around the flotation dam that follows the wind rose. In several anomalous areas it could be seen that the highest values are in the area closest to the outflow of flotation dam (from 51 to 225 mg kg$^{-1}$) and so-called Buchim Lake and dry riverbed draining open pit mine and in the south-western part of the area (67.4–82.8 mg kg$^{-1}$). According to this data, it is evident that the source of high arsenic in this region is directly related with processing of copper ores in the Buchim Mine. In the mineral association of the Buchim deposit it was determined one phase of low-temperature pyrites, which in its chemical composition have up to 2.5% As. During the processing of ore, probably one part of that arsenic have been released and distributed into the adjacent environment.

**Cadmium (Cd):** is a heavy metal that is dispersed throughout the modern environment mainly as a result of pollution from a variety of sources (Bhattacharyya et al., 2000; Järup et al. 1998). Cadmium is produced mainly as a by-product from mining, smelting, and refining sulphide ores of zinc, and to a lesser degree, lead and copper. The metal has no known beneficial biological function and prolonged exposure to this element has been linked to toxic effects in both humans and animals (Zadorozhnaja et al., 2000). Cadmium and cadmium compounds are, compared to other heavy metals, relatively water soluble. They are therefore also more mobile in e.g. soil, generally more bioavailable and tend to bioaccumulate.

The average amount of Cd in soils in the world is 0.35 mg kg$^{-1}$ (Bowen, 1979), in the European topsoil is 0.12 mg kg$^{-1}$ (Salminen et al., 2005). The average amount of Cd in the topsoil for the entire study area is

2.19 mg kg$^{-1}$, with a range of 0.67–17.9 mg kg$^{-1}$ (Table 1). In the main polluted area, the average concentration of Cd is more than 18-times higher than the European cadmium average and up to 7.5-13 times more than Macedonian average of 0.16 mg kg$^{-1}$ (study in 2002, Barandovski et al. 2008) and 0.29 mg kg$^{-1}$ (study in 2005, Barandovski et al. 2012). It is evident from the obtained results (Table 1; Figure 3) that the content of cadmium is very high in the topsoils from the areas of the copper mine facilities, as well as in the topsoils from the flotation dam vicinity.

In this region several topsoil samples with extremely high content of cadmium are present. It should be noted that sample No. 10 with the content of 17.9 mg kg$^{-1}$ is 150-times higher than the European topsoil average of 0.12 mg kg$^{-1}$. These higher contents of cadmium in soil samples are the result of anthropogenic origin where cadmium inputs from mine industrial complexes as it was confirmed elsewhere (Šajn et al., 2011).

**Copper (Cu):** The most important statement on Cu contamination of soils is the great affinity of surface soils to accumulate this metal. Soil contamination by Cu compounds, which has been the subject of detailed studies for several decades confirmed several significant sources: fertilizers, sewage sludge, manures, agrochemicals, industrial by-product wastes etc that have contributed to increased Cu levels. However, the highest increased levels of Cu are observed in soils surrounding Cu mines and smelters (Kabata-Pendias and Pendias, 2001). As Cu is only slightly mobile under most soil conditions elevated contents may persist for a long time. The average amount of Cu in the world's soils is 30 mg kg$^{-1}$ [Bowen, 1979], in the European topsoil is 17 mg kg$^{-1}$ (Salminen et al., 2005) and in Macedonia is 31.8 mg kg$^{-1}$ (Stafilov et al., 2010c). The average amount of Cu in the topsoil for the entire study area is 129.064 mg kg$^{-1}$, with a range of 17.8–1734 mg kg$^{-1}$ (Table 1; Figure 4).

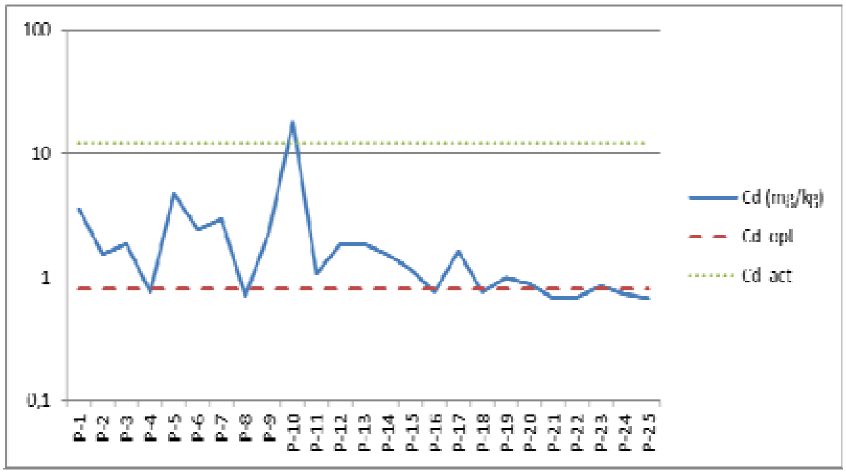


**Figure 4.** Diagram of copper distribution in the soil compared with optimal and action values

Obviously, there is no large difference in concentration within the studied mine and flotation ares (Table 1; Figure 4), except in three positions (sample 15, 17 and 18) dry riverbed draining open pit mine. In the main polluted area, the average concentration of Cu exceeds the European Cu average by a factor of 15.3 and Macedonian average for 8.2-times. The highest content of copper is present in the topsoils from the areas of the copper mine drainage dry riverbed, which is close to the mine.

**Lead (Pb):** In mining areas, Pb may be dispersed due to the erosion and chemical weathering of tailings. The severity of these processes depends on chemical characteristics, and the minerals present in the tailings (Kabata-Pendias and Pendias, 2001). In general, several observations of Pb balance in various ecosystems show that the input of this metal greatly exceeds its output. The strong Pb adsorption in soils may mean that Pb additions to soil are permanent and irreversible. The average amount of Pb in the world's soils is 35 mg kg$^{-1}$ (Bowen, 1979), in the European topsoil is 33 mg kg$^{-1}$ (Salminen et al., 2005) and in Macedonia is 44.3 mg kg$^{-1}$ (Stafilov et al., 2010c). The average amount in the topsoil for the entire study area is 288 mg/kg, with a range of 46–3465 mg kg$^{-1}$ (Table 1). Similarly to cadmium distribution, the differences between the content of lead in the studied areas are very significant (Table 1; Figure 5).

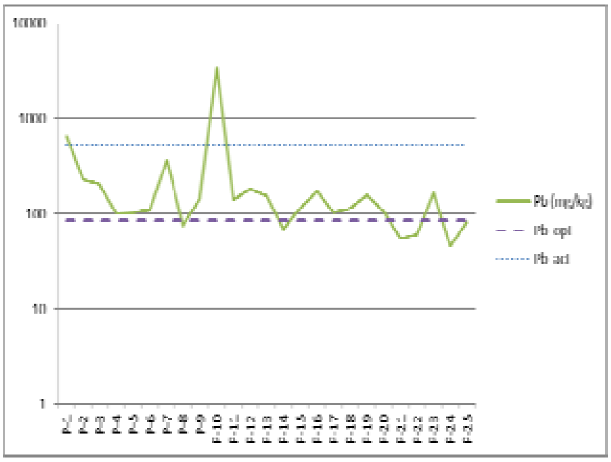


**Figure 5.** Diagram of lead distribution in the soil compared with optimal and action values

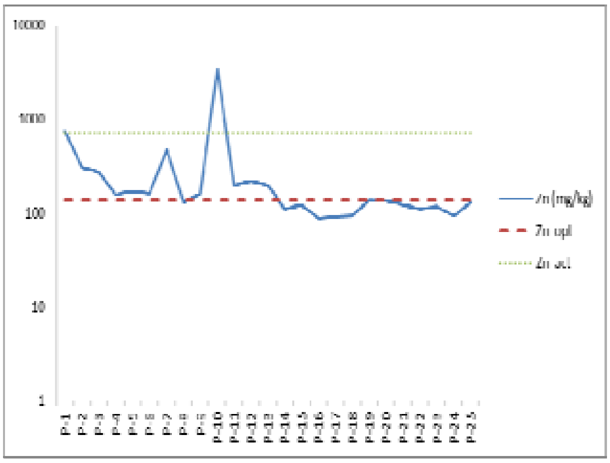


**Figure 6.** Diagram of zinc distribution in the soil compared with optimal and action values

In the main polluted area the average concentration of Pb is 8.7-times higher than the European Pb average and Macedonian average for 6.5-times. Although the average content of lead in the topsoil for the entire study area was found to be about 288 mg kg$^{-1}$, there are areas with very high contamination, as it was for example, for the main polluted area (sample 10) with content of 3465 mg kg$^{-1}$ (Table 1). The highest values for Pb content were established in the topsoils in the eastern and south-western part of an area.

**Zinc (Zn):** The most important anthropogenic sources of Zn are the metallurgy industry, burning of fossil fuels, mines and Zn ore processing (Aliu et al., 2010). Zn is an essential element for most living organism (plants, animals and humans) with important role in enzymes processes and cellular metabolism, in immune function, protein synthesis, DNA synthesis, and cell division and daily intake of zinc is required to maintain a steady state because the body has no specialized zinc storage system (Rink and Gabriel, 2000). Even the toxicity of Zn is relatively low, there are cases when poisoning with Zn can occur in both acute and chronic forms (Prasad, 1995).

The average amount of Zn in the world's soils is 90 mg kg$^{-1}$ (Bowen, 1979), in the European topsoil is 68 mg kg$^{1}$ (Salminen et al., 2005) and in Macedonia is 31.8 mg kg$^{-1}$ (Stafilov et al., 2010c). The average Zn amount in the topsoil for the entire study area is 319.8 mg kg$^{-1}$, with a range of 88–3438 mg kg$^{-1}$ (Table 1). For the main polluted area, the average concentration of Zn is 4.7-times higher than the European Zn average and Macedonian average for 10.1-times. Similarly to the findings for lead, although the average content of zinc in the topsoil for the entire study area was found to be about 319.8 mg kg$^{-1}$, there are areas with very high level of contamination (Table 1; Figure 6).

These areas are especially pronounced in the main polluted area around flotation on the east and south western parts of the area.

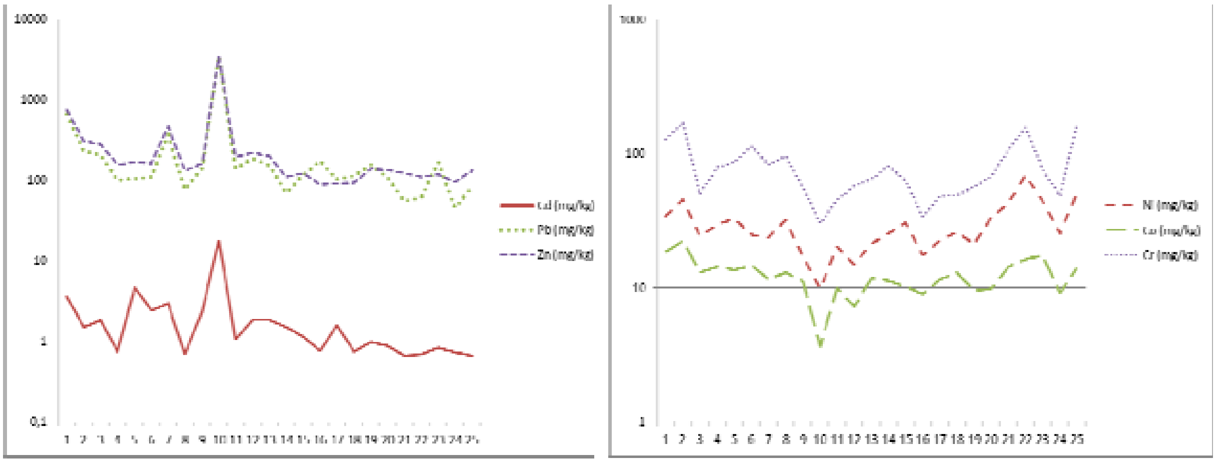
The high contents of Cu and Pb are not only due to mining works, but also the town works, traffic, industry and developed technological processes which aloud emission of higher amounts of these heavy metals in air (Balabanova et al., 2009; 2010; 2011; Stafilov et al, 2010b).

**Correlations:** Data from geochemical analyzes were statistically processed in regular Excel calculations procedure going through the Data menu where we chose Data analysis option with an array of Analysis tools where we continued with Correlation and selected data range for that particular type of data analysis. The results of correlation analysis are displayed in Table 2.

From the table above can be seen that in the whole correlation calculation where included 13 elements, which pointed out two correlation elemental suites (Figure 7). The first suite encloses Cd-Pb-Zn with correlation coefficients for Cd-Pb of 0.967, Zn-Pb of 0.998 and Zn-Cd of 0.970. These values indicate a high elemental correlation for this suite where zinc and cadmium have "historical" roots of their high correlation even in their primary sources. The second elemental suite consists of Ni-Co-Cr with correlation coefficient for Ni-Co of 0.708, Ni-Cr of 0.821 and Co-Cr of 0.773. All these correlation coefficients are relatively high and reflect the and the clear geochemical relationship of these elements, which basically belong to ultramafites or they are metals that are representative of primary mantle (oceanic crust).

**Table 2.** Matrix of correlation coefficients in soil samples (n=25) around the Buchim copper mine

| | Al | Fe | Ag | As | Cd | Co | Cr | Cu | Mn | Ni | Pb | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | 1 | | | | | | | | | | | | |
| Fe | **0,822** | 1 | | | | | | | | | | | |
| Ag | 0,000 | 0,000 | 1 | | | | | | | | | | |
| As | 0,205 | -0,041 | 0,000 | 1 | | | | | | | | | |
| Cd | -0,139 | -0,419 | 0,000 | 0,467 | 1 | | | | | | | | |
| Co | **0,774** | **0,854** | 0,000 | 0,003 | -0,415 | 1 | | | | | | | |
| Cr | **0,775** | **0,808** | 0,000 | -0,087 | -0,234 | **0,773** | 1 | | | | | | |
| Cu | -0,074 | -0,023 | 0,000 | -0,018 | -0,085 | -0,110 | -0,134 | 1 | | | | | |
| Mn | **0,825** | **0,881** | 0,000 | 0,075 | -0,327 | **0,829** | **0,656** | 0,095 | 1 | | | | |
| Ni | **0,688** | **0,836** | 0,000 | -0,163 | -0,365 | **0,708** | **0,821** | 0,008 | **0,758** | 1 | | | |
| Pb | -0,195 | -0,423 | 0,000 | 0,361 | **0,967** | -0,416 | -0,235 | -0,068 | -0,327 | -0,330 | 1 | | |
| V | **0,863** | **0,948** | 0,000 | -0,035 | -0,351 | **0,843** | **0,870** | -0,039 | **0,796** | **0,772** | -0,362 | 1 | |
| Zn | -0,170 | -0,404 | 0,000 | 0,357 | **0,970** | -0,394 | -0,201 | -0,083 | -0,316 | -0,315 | **0,998** | -0,336 | 1 |



a) b)

**Figure 7.** Correlation diagrams for the geochemical suite one Cd-Pb-Zn (a) and suite two Ni-Co-Cr (b) from the soil analytical data around the Buchim copper mine

However, here we are dealing with their anthropogenic input in soils around the Buchim mine, which clearly indicates their connection with the processing of copper ore from the mine, which in turn seems a fact that copper is the metal of oceanic crust.

## CONCLUSION

Analytical data of the soil study around the Buchim mine displayed contamination with heavy metals on two fronts. The first one regarding the contaminated soil around the tailing dam where have been determined increased concentrations of Pb, Zn, Cd and Co and the second one around the waste dump with increased concentrations of Cu, As, Cr and V. These contaminations coincide with the so-called rose of winds in the Buchim mine area and display reflection through increased concentrations of above mentioned metals in soil, air and water.

Several geochemical pairs have shown high correlation coefficients: Cd-Pb 0.967, Zn-Pb 0.998 and Zn-Cd 0.970 as well as Ni-Co 0.708, Ni-Cr 0.821 and Co-Cr 0.773 and group in two basic geochemical suites: Pb-Zn-Cd and Ni-Co-Cr. Copper did not manifested correlation with any element of the analyzed association, but however it is present in both. Increased concentration of all analyzed metals in soil around the Buchim mine implies direct correlation to the processing of porphyry copper ore in the Buchim mine, while metal deposition in soil the most frequently comes through the airborne contamination.

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