

# SOIL CONTAMINATION STUDY AROUND THE BUCHIM COPPER MINE, REPUBLIC OF MACEDONIA



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## Introduction

There are many different sources of heavy metal contaminants, including mining and metallurgical industries. Copper mine with open ore pit type present a potentially emission source of heavy metals in the air, soil and water.

Here we 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 open ore body (an average of 0.3 % Cu) is approximately 500 m in diameter and 250 m in vertical extent, which actually allows direct exposure of ore particles to the atmosphere.

Ore tailings are disposed at open site near the mine, that occupies a surface of 0.8 km<sup>2</sup>. 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.



Fig. 1. Location of the soil samples around the Buchim copper mine R. Macedonia

## Materials and Methods

In total, 25 samples were collected from 25 locations, including locations near the mining center of Buchim over an area of 14.2 km<sup>2</sup>. Each sample represented 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.

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. giving us an unbiased treatment of samples and precision less than 5%.

## Results and discussion

For each sampling point sample was analyzed for a geochemical package of 20 elements (Table 1).

Table 1. Statistical data of soil samples around Buchim Mine

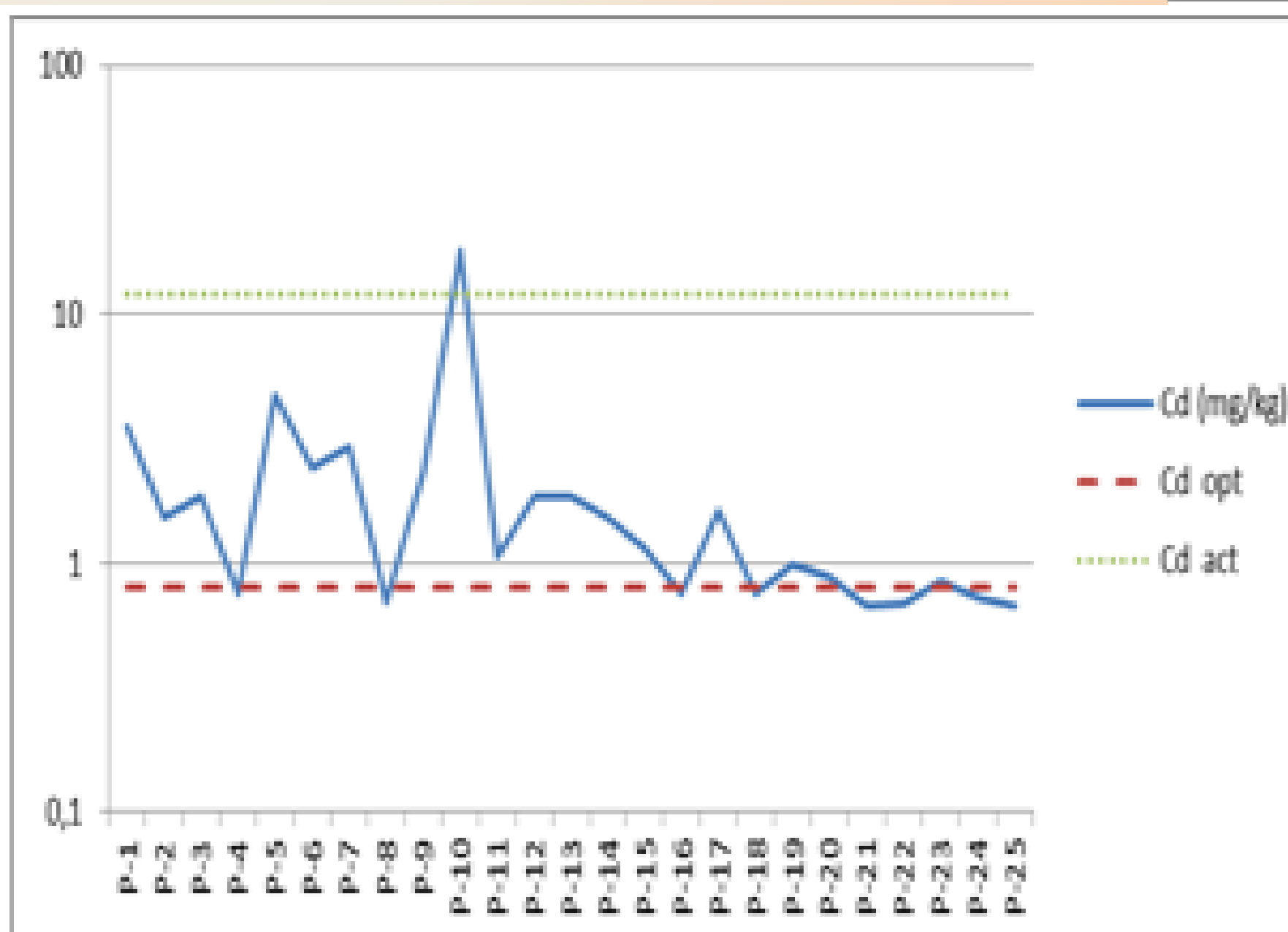
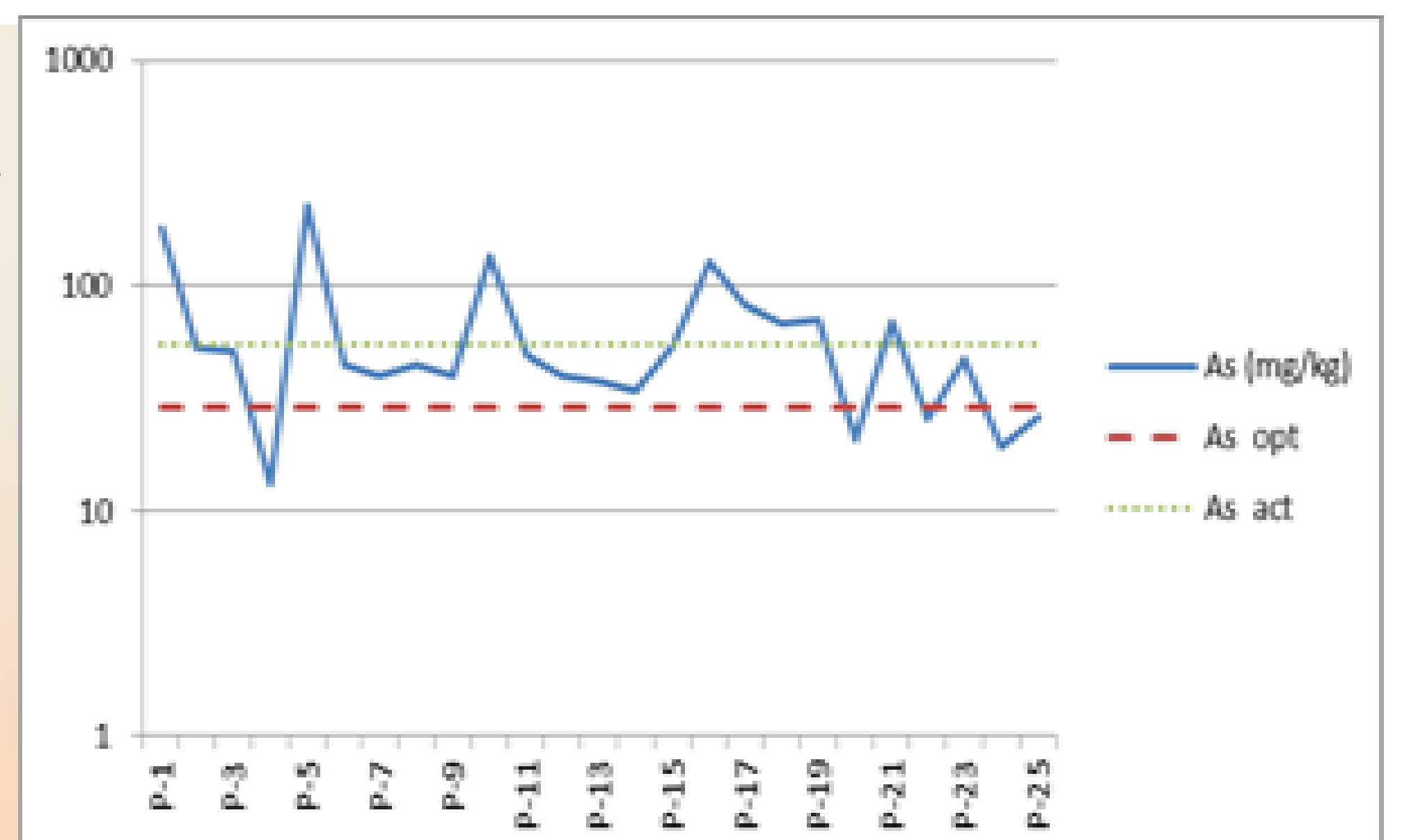
Element	min	max	average	Optimum (Dutch list)	Action (Dutch list)
Al (%)	0,72	5,9	2,8928	4,7	-
Ca (%)	0,07	4,28	1,3024	-	-
Fe (%)	0,73	5,02	3,148	1,8	-
K (%)	0,79	3,28	2,008	-	-
Mg (%)	0,12	1,97	0,9708	-	-
Na (%)	0,77	2,09	1,7624	-	-
Ag (mg kg <sup>-1</sup> )	0,1	0,1	0,1	-	15
As (mg kg <sup>-1</sup> )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

## Results and discussion

During the study of results and their statistical processing it was determined that very representative are particular elements such as **copper, arsenic, cadmium, lead and zinc** that are given in more details.

### Arsenic (As):

The average amount of As in the topsoil for the entire study area is 63.904 mg kg<sup>-1</sup>, with a range of 13.1–225 mg kg<sup>-1</sup>. 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<sup>-1</sup>) 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<sup>-1</sup>).



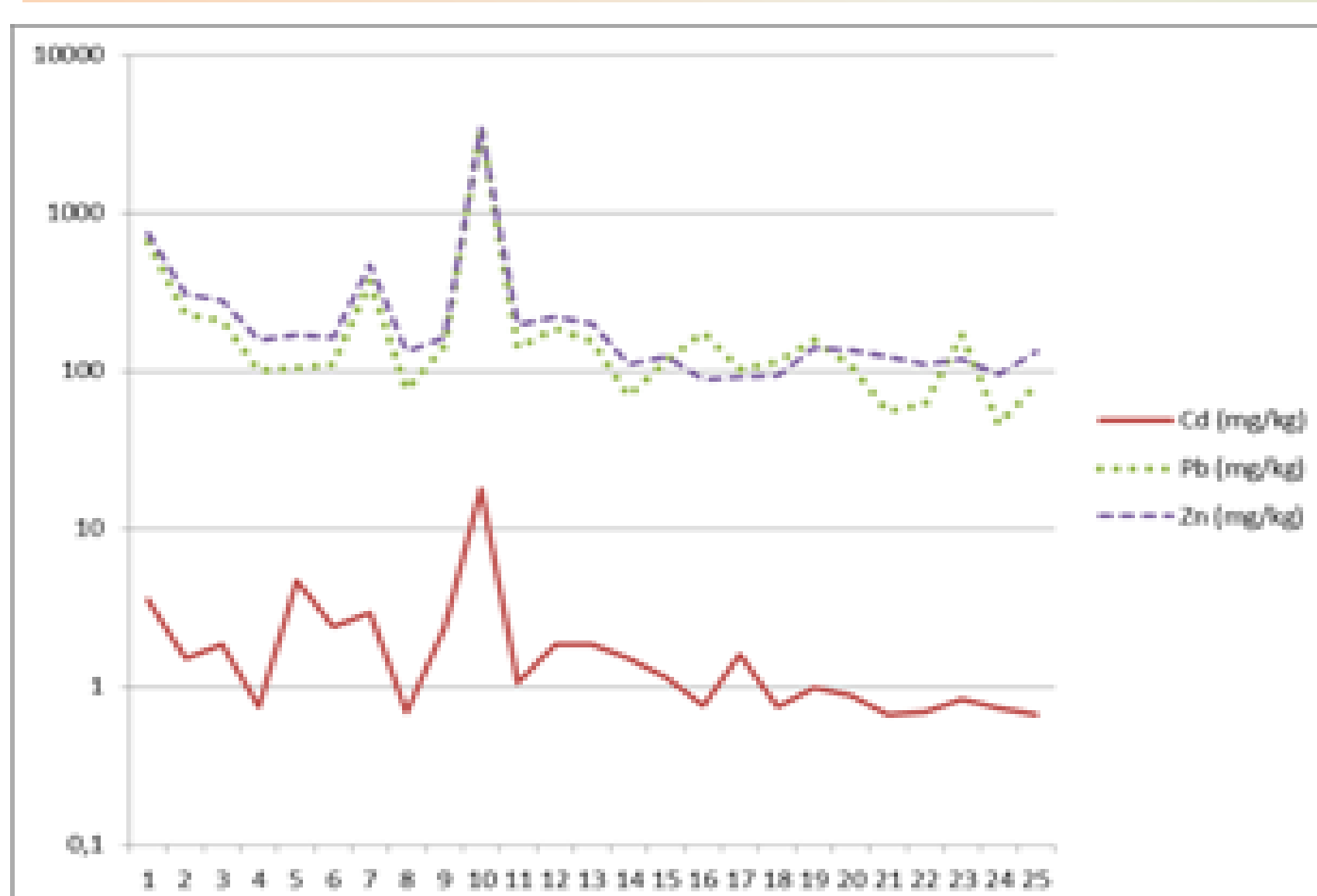
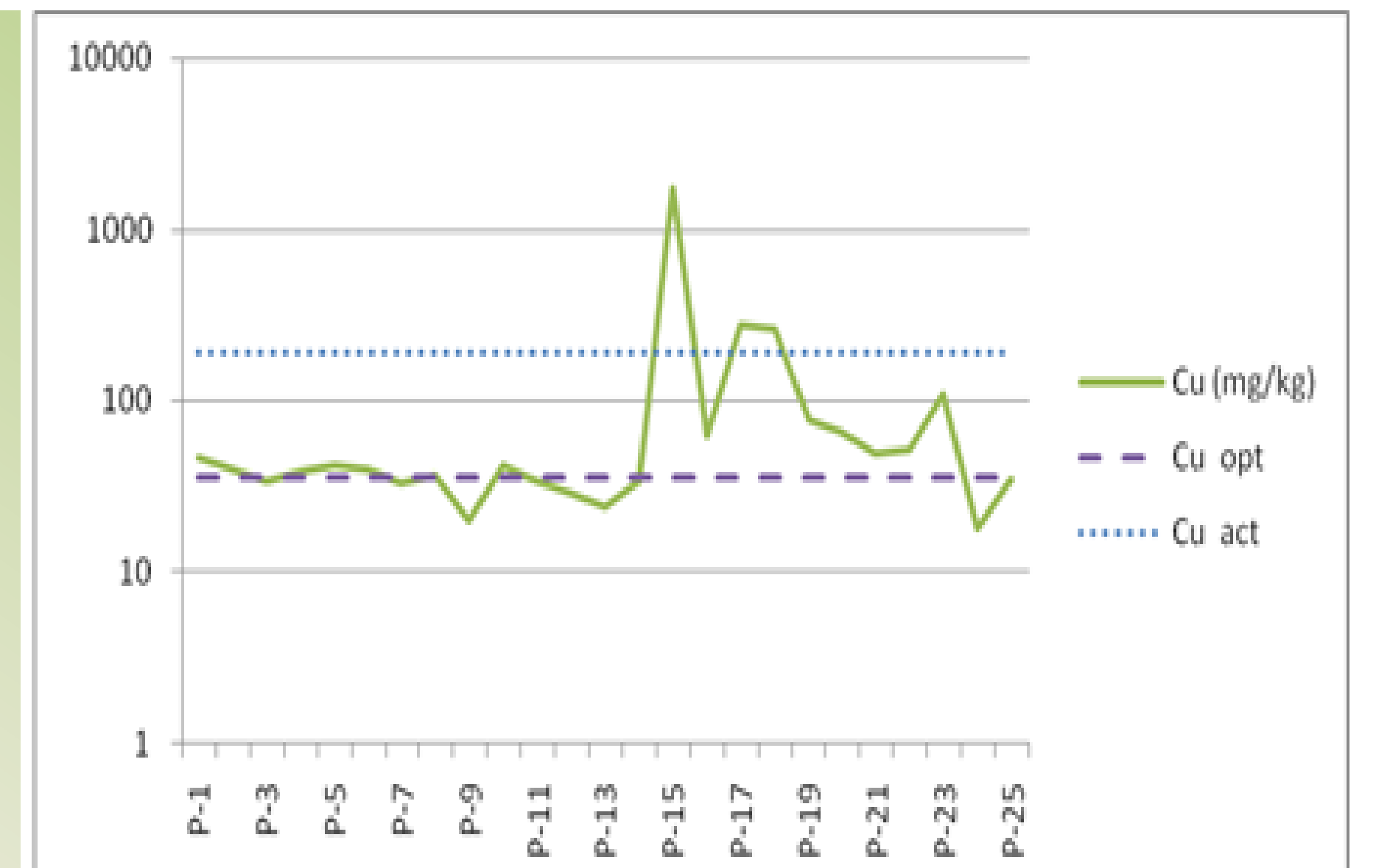
### Cadmium (Cd):

An average amount of Cd in the topsoil for the entire study area is 2.19 mg kg<sup>-1</sup>, ranging 0.67–17.9 mg kg<sup>-1</sup>. Cd. In the main polluted area, an 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<sup>-1</sup> and 0.29 mg kg<sup>-1</sup>.

Its content is very high in topsoils from the areas of the Cu mine facilities, as well as in topsoils from the flotation dam vicinity. There were determined extremely high contents of cadmium (sample No. 10 with 17.9 mg kg<sup>-1</sup> a 150-times higher than the European topsoil average of 0.12 mg kg<sup>-1</sup>).

### Copper (Cu):

The average amount of Cu in the topsoil for the entire study area is 129.064 mg kg<sup>-1</sup>, ranging 17.8–1734 mg kg<sup>-1</sup>. Obviously, there is no large difference in concentration within the studied mine and flotation areas 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.



### Correlations:

Geochemical analyses data was statistically processed and elemental correlation was obtained (Table 2).

Table 2. Statistical data of soil samples around Buchim 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

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 indicating a high elemental correlation for this suite where Zn and Cd have "historical" roots of their high correlation 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.

## Conclusion

Analytical data of the soil study around the Buchim mine displayed contamination with heavy metals on two fronts: one addressing contaminated soil around the tailing dam with 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, which coincide with the so-called rose of winds in the Buchim mine area.

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 mine.