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# Forest Soil Pollution with Heavy Metals (Pb, Zn, Cd, and Cu) in the Area of the "French Mines" on the Medvednica Mountain, Republic of Croatia

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## ABSTRACT

**Background and Purpose:** This paper deals with the results of the investigation of the selected heavy metal contents in forest soil in the region of an abandoned mine. The analysis of the forest ecosystem soil on the Medvednica Mountain was conducted in the region of the so-called "French Mines" (FM). The elements selected for analyses were cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) because of their toxicological characteristics.
**Material and Methods:** In the investigated area - five entrances of the FM - composite topsoil samples (0–5 cm) were taken. Those samples were compared to the control samples which were taken outside the area affected by mines. The soil samples were analysed for the following parameters: pH, particle size distribution, organic C content and pseudo-total mass fractions of the selected heavy metals. The heavy metals were determined by atomic emission spectrometry with inductively coupled plasma (ICP-MS).
**Results and Conclusion:** The results reveal that the soil is locally polluted, i.e. the highest mass fraction values of these four heavy metals were found in the area of the FM. Average pseudo-total fraction of Cd in the analysed topsoil samples was in the range of 0.17–4.41 $mg \cdot kg^{-1}$ (median: 0.97 $mg \cdot kg^{-1}$). Cu was found in the range of 4.54–1260 $mg \cdot kg^{-1}$ (median: 45.7 $mg \cdot kg^{-1}$). In the case of Zn, mass fraction values were found in the range of 36.8–865 $mg \cdot kg^{-1}$ (median: 137 $mg \cdot kg^{-1}$). Finally, average values of the pseudo-total fraction of Pb were found in the range of 58.4–12000 $mg \cdot kg^{-1}$ (median: 238 $mg \cdot kg^{-1}$). The results reveal that mining activities leave consequences on soil for a long time.

**Keywords:** heavy metals, soil pollution, forest soil, mining sites, Medvednica Mt.

## INTRODUCTION

There are many various environmentally hazardous substances, but researchers around the world are especially interested in heavy metals. Heavy metals are naturally occurring elements that have a high atomic weight and a density at least 5 times greater than that of water [1]. From a biological point of view, Nieboer and Richardson [2] have classified heavy metals into three groups: (i) elements essential to some organisms (V, Cr, Mn, Fe, Co, Zn, and Mo), (ii) elements necessary for growth and development of plants (Mn, Fe, Cu, Zn, Mo, and Ni), and (iii) phytotoxic elements (Cd, Hg, and Pb). World Health Organization (WHO) has classified As, Cd, Hg, and Pb among 10 groups of hazardous chemicals. Those are elements which have toxicological characteristics. Moreover, when their concentrations increase, Mn, Co, Ni, Cu, Zn, Se, Ag, Sb, and especially Cr and Ti are also considered toxic [3].

Since the pollution of soil by heavy metals is one of the possible causes of a decrease in forest ecosystem vitality and degradation of the whole habitat, there is a significant scientific interest in research of the connection of heavy metal concentration values in the environment to their degradation effect [4]. In higher concentrations heavy metals show negative influence on the environment, especially in the context of their inclusion into the biological cycle of matter [5]. Plants uptake heavy metals from soil, often as micronutrients, thus introducing them to the food chain. This way heavy metals become ready for re-distribution and dissemination in the environment [6, 7].

Several authors have already been doing research on heavy metals in the soils in the Republic of Croatia [8-15]. Generally, mass fraction values of Fe, Mn, Zn, Cu, Cr, Ni, Pb, and Cd have been determined in the surface horizon (0–5 and 5–15 cm).

The influence of mining activities on soil pollution by heavy metals is presented in a certain number of papers [16-20]. In the area of the Zrinski Mines, situated near the FM on the Medvednica Mt., there is pollution by heavy metals, primary by Hg, but also Cd and Pb [21-23]. The presence of the lead-zinc ore in Bistranska gora has been investigated in the late 18th century and in the early 19th century. During that time Count Henri Carion started to exploit this ore in pursuit of galena, with the intention of obtaining silver. However, the quantity of the found ore was too low to continue the exploitation and the mines were abandoned [24].

The hypothesis for this research was possible pollution of forest soil by heavy metals as a consequence of mining activities which were finished around 200 years ago. Therefore, the main goal of this work is to determine the extent of contamination in the forest ecosystem on the Medvednica Mt. in the area of FM. These results will give an insight into the potential ecological hazards of mining activities.

## MATERIAL AND METHODS

The research area is situated on the northern slopes of Medvednica Mt., nearly below the ski lift station in the area of FM (Figure 1). Lithological surface in the area of FM is made of parametamorphites, which originate from sedimentary rocks and were unevenly affected by regional metamorphosis. Among rocks one can distinguish quartz conglomerates and breccia conglomerates, metagraywacke, metasiltstones, recrystallized limestones and dolomites, slates, phyllites, different low-grade metamorphic schists, quartzites and marbles [25]. According to Vrbek [26], dystric cambisol are the dominant soils in the research area. The vegetation of the investigated area belongs by association to the Pannonian beech-fir forests with fescue (*Festuco drymeiae-Abietetum)* [27]. Climate of the area of the community is characterized by average annual temperatures between 6–8˚C and precipitation of 900–1200 mm [28]. Elevation of the area of FM is between 610–720 m. The orientation of the slope position is North-West, with a slope gradient between 12–35˚.

Soil sampling on the mine area were done in two occasions. On the FM sites 1–3 the regular sampling procedure (systematic statistical sample) was applied; on the regular square net 30×30 m 41 samples were taken. On the FM sites 4–5, six samples were taken by randomized sampling. Four control samples (C 1–4) out of the influence area of FM were taken with the purpose of comparison to the FM samples (Figure 1). The control samples have similar characteristics in comparison to the FM samples (similar lithological units and vegetation). The control samples were taken from grid 1×1 km within the project "Trace elements in the soil of the forest ecosystem of Medvednica Mountain". Composite samples (9 sub-samples spaced 1 m apart, and cross-scheduled) were taken from the depth of 0–5 cm by a plastic probe with an inner diameter of 80 mm. For laboratory analyses the samples were dried by air at room temperature, crushed and sieved through sieves of 2 and 0.2 mm holes [29]. The soil samples were analysed for the following parameters: pH [30], particle size distribution [31], soil organic carbon [32], and pseudo-

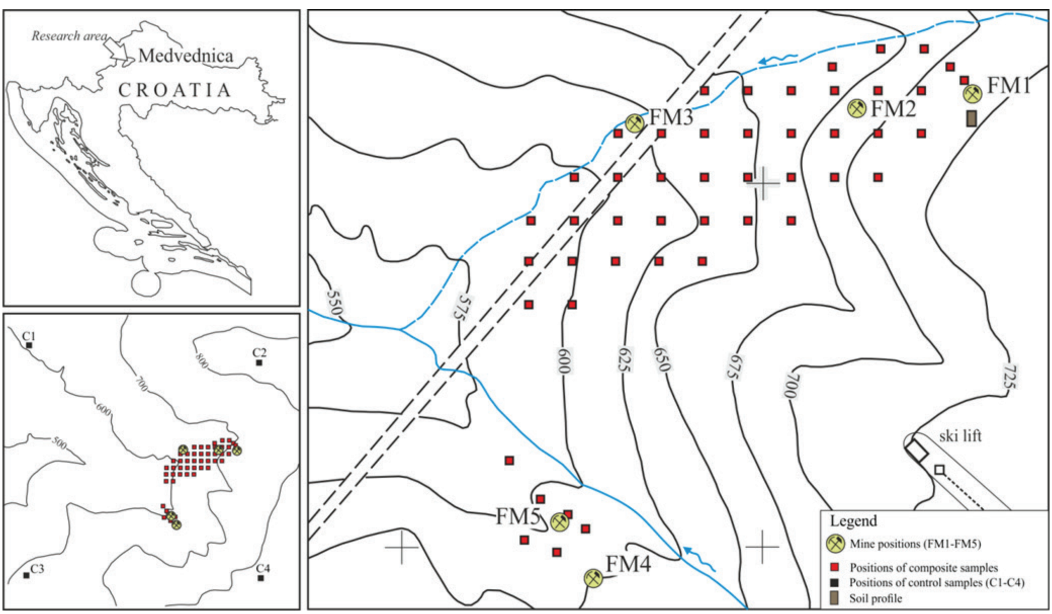


**FIGURE 1.**Geographical location of the research area with the position of composite samples and soil profile.

total mass fractions of the selected heavy metals (Cd, Cu, Pb, and Zn). The last one was determined by ICP-AES technique in aqua regia digestates of the samples; microwave enhanced digestion procedure of the soil samples was performed [33]. The main parameters of the analysis of the soil digestates by ICP-AES are given in Table 1. The samples were analysed in the laboratory of the Faculty of Forestry of the University of Zagreb.

For all analysed variables the procedures of descriptive statistics (minimum, lower quartile, median, upper quartile, maximum, mean, standard deviation, coefficient of variance, standard error, and asymmetry) were applied. In order to exclude the influence of outliers and extreme values, the median was applied as an average value. The differences between values of the analysed variables using Kruskal-Wallis non-parametric test were tested. I (α) error type of the value of 5% is considered to be statistically significant [34]. The obtained variables for the pedophysiographic characteristics of soil, as well for concentrations of th heavy metals for FM 1–3 (grid 30×30) and FM 4–5 (taken randomly) were compared to the variables determined for the control samples.

The level of contamination for the topsoil was ranked by Brüne-Ellighaus criteria [35] and Croatian Directive on the protection of agricultural land from pollution (hereinafter referred to as Directive) [36]. According to Brüne-Ellighaus criteria [35] the limit values for Cd are 2 $mg \cdot kg^{-1}$, Cu 100 $mg \cdot kg^{-1}$, Pb 150 $mg \cdot kg^{-1}$ and Zn 300 $mg \cdot kg^{-1}$. Since the soil texture class of the FM area is dominantly silt loam, according to Directive [36] maximum allowed concentrations of heavy metals are Cd 1 $mg \cdot kg^{-1}$, Cu 90 $mg \cdot kg^{-1}$, Pb 100 $mg \cdot kg^{-1}$ and Zn 150 $mg \cdot kg^{-1}$ (Table 2).

Distribution of the selected heavy metals through the investigated area is shown on prediction maps, which were created by an interpolation technique Inverse Distance Weighting (IDW) in the ArcMap programme. Geochemical maps of each element in the ArcGIS extension of Geostatistical Analyst were generated. In order to make a correct presentation of the element concentration values on

**TABLE 1.** The main ICP-AES measurement parameters

| Parameters | ICP-AES operating conditions |
|---|---|
| Instrument | Thermo Fischer iCAP6300 Duo |
| RF power | 1150 W |
| Auxiliary Ar flow | 0.5 $L \cdot min^{-1}$ |
| Sample Ar flow | 0.65 $L \cdot min^{-1}$ |
| Coolant Ar flow | 12 $L \cdot min^{-1}$ |
| Sample introduction system | – auto-sampler CETAC ASX-260 connected by peristaltic pumps<br>– concentric nebulizer with cyclonic spray-chamber |
| Peristaltic pumps rate | 45 rpm |
| Peristaltic pumps tubes | – sample: orange/white<br>– rinsing: white/white |
| Flush (take-up) time | 45 s |
| Washing time between samples | 60 s |
| Plasma view | Auto view |
| Maximum measuring time | – low wavelengths (160-230 nm): 15 s<br>– high wavelengths (230-847): 5 s |
| Lines measured (nm) | Cd-228.802; Cu-324.754; Pb-220.353; Zn-202.548 |
| Multi-elemental calibration solutions | – 0, 1, 10, and 100 µg/L (in $HNO_3$, $\psi$ = 1%) |
| System rinsing solution | Nitric acid, $HNO_3$, *supra pur*, $\psi$ = 1% |

**TABLE 2.** Criteria for determining pollution degrees according to the Brüne-Ellinghaus scale [35] and the Directive on the protection of agricultural land from pollution [36].

| Brüne-Ellinghaus, 1981 | | Directives on the protection of agricultural land from pollution, 2014 | |
|---|---|---|---|
| Pollution degree | % Lv | Pollution degree | PD (%) = HMC/MAC*100 |
| very low | 1–5 | clean | <25 |
| low | 5–10 | increased | 25–50 |
| medium | 10–25 | high contamination | 50–100 |
| high | 25–50 | contaminated | 100–200 |
| very high | 50–100 | polluted | >200 |
| above Limit value | >100 | | |

% Lv - limit value; PD - pollution degree; HMC - heavy metal content; MAC - maximum allowed content the sampling sites, the deterministic space interpolation technique Inverse Distance Weighting (IDW) was applied. In the calculation there were minimum 3 to maximum 6 neighbouring points. The calculation range was a circle of a radius of 30 m. Spatial distribution of every particular class in the map was represented as a polygon in a corresponding colour, with blue nuances for low neighbouring to red for high neighbouring [37].

## RESULTS

Average values of the analysed variables for topsoil samples (0–5 cm) in the FM area (FM 1–3 and FM 4–5) and control plots (C) are shown in Table 3.

Topsoil reaction in the FM area ranges from 4.89 to 8.09. According to Scheffer and Schachtschabel [38], pH-value in topsoil is in the range from moderately acidic to weakly basic. The pH-values determined in the samples taken in the FM area are statistically higher than the values determined in the samples collected on the control surfaces. The highest median pH-value has been found on FM 1–3 ($pH_{H2O}$=6.59; $pH_{CaCl2}$=6.09) and it has statistically higher value in comparison to the control plots ($pH_{H2O}$=4.91; $pH_{CaCl2}$=4.41). FM 4–5 have similar pH-values as FM 1–3 ($pH_{H2O}$=6.40; $pH_{CaCl2}$=5.89) and they are statistically different to those found for the control samples ($pH_{H2O}$ (H (2, N=51)=10.827; p=0.045); $pH_{CaCl2}$ (H (2, N=51)=9.860; p=0.0072) (Table 3).

Median values found for Cd were 0.70 mg·kg$^{-1}$ (FM 4–5) and 0.97 mg·kg$^{-1}$ (FM 1–3) in the area of FM and these values are higher than those found on the control plots (0.44 mg·kg$^{-1}$), but the difference is not statistically significant (Figure 2 left, Table 3).

Mass fraction values determined for Pb in topsoil are statistically and significantly different between the samples taken in the FM area and control plots H (2, N=51)=8.411; p=0.0149). The highest median mass fraction value of Pb is found for the sites FM 4–5 (273 mg·kg$^{-1}$), while on the sites FM 1–3 the median values of Pb are somewhat lower (238 mg·kg$^{-1}$). The lowest median value was found on the control plots (73.7 mg·kg$^{-1}$) (Figure 2 right, Table 3).

The determined mass fractions of Cu show similar relations as the ones determined for Pb, but no statistically significant difference between the median value determined in the samples taken on the FM area and control plots was found. The highest median mass fraction value in FM 4–5 (50.5 mg·kg$^{-1}$), and the lowest ones (26.7 mg·kg$^{-1}$) on the control plots were found. On the sites FM 1–3, the found median mass fraction value was 45.7 mg·kg$^{-1}$ (Figure 3 left, Table 3).

**TABLE 3.** Descriptive statistics for the analysed variables $pH_{H2O}$, $pH_{CaCl2}$, organic C content, Cd, Cu, Pb, and Zn in the areas of "French Mines" (FM 1–3 and FM 4–5) and control plots (C).

| Variable | | Unit | N | Minimum | Lower quartile | Median | Upper-quartile | Maximum | Mean | Std. dev. | Coef. var. | Std. errorof-mean | Skewness | *p*-values |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | FM 1-3 | | 41 | 4.89 | 6.06 | 6.59 | 7.61 | 8.09 | 6.74 | 0.93 | 13.8 | 0.14 | -0.31 | |
| $pH_{H2O}$ | FM 4-5 | | 6 | 5.86 | 5.90 | 6.40 | 6.90 | 6.94 | 6.40 | 0.49 | 7.62 | 0.20 | 0.00 | 0.0045 |
| | C | | 4 | 4.82 | 4.84 | 4.91 | 5.06 | 5.17 | 4.95 | 0.16 | 3.16 | 0.08 | 1.35 | |
| | FM 1-3 | | 41 | 4.17 | 5.38 | 6.09 | 7.19 | 7.41 | 6.19 | 0.98 | 15.9 | 0.15 | -0.39 | |
| $pH_{CaCl2}$ | FM 4-5 | | 6 | 5.27 | 5.29 | 5.89 | 6.49 | 6.63 | 5.91 | 0.60 | 10.2 | 0.25 | 0.08 | 0.0072 |
| | C | | 4 | 4.20 | 4.28 | 4.41 | 4.55 | 4.64 | 4.41 | 0.19 | 4.20 | 0.09 | 0.21 | |
| | FM 1-3 | | 41 | 36.24 | 61.82 | 92.59 | 112.65 | 158.47 | 89.12 | 29.57 | 33.18 | 4.62 | 0.05 | |
| Org C | FM 4-5 | g·kg$^{-1}$ | 6 | 91.18 | 107.65 | 115.78 | 257.41 | 309.57 | 166.23 | 92.80 | 55.83 | 37.89 | 1.06 | 0.0512 |
| | C | | 4 | 65.60 | 69.20 | 86.70 | 102.17 | 103.74 | 85.69 | 19.30 | 22.53 | 9.65 | -0.10 | |
| | FM 1-3 | | 41 | 0.17 | 0.58 | 0.97 | 1.55 | 2.75 | 1.09 | 0.70 | 64.2 | 0.11 | 0.75 | |
| Cd | FM 4-5 | mg·kg$^{-1}$ | 6 | 0.17 | 0.17 | 0.70 | 2.40 | 4.41 | 1.42 | 1.68 | 118 | 0.69 | 1.43 | 0.4117 |
| | C | | 4 | 0.23 | 0.27 | 0.44 | 0.86 | 1.15 | 0.57 | 0.42 | 73.7 | 0.21 | 1.35 | |
| | FM 1-3 | | 41 | 58.4 | 112 | 238 | 456 | 1559 | 411 | 444 | 108 | 69.4 | 1.48 | |
| Pb | FM 4-5 | mg·kg$^{-1}$ | 6 | 111 | 184 | 273 | 1594 | 12000 | 2405 | 4732 | 197 | 1932 | 2.38 | 0.0149 |
| | C | | 4 | 55.3 | 64.1 | 73.7 | 74.8 | 75.1 | 69.5 | 9.51 | 13.7 | 4.75 | -1.95 | |
| | FM 1-3 | | 41 | 4.54 | 25.1 | 45.7 | 64.9 | 1260 | 113 | 216 | 191 | 33.7 | 4.21 | |
| Cu | FM 4-5 | mg·kg$^{-1}$ | 6 | 26.8 | 37.7 | 50.5 | 130 | 798 | 182 | 304 | 167 | 124 | 2.37 | 0.2376 |
| | C | | 4 | 16.1 | 16.6 | 26.7 | 36.8 | 37.2 | 26.7 | 11.6 | 43.6 | 5.81 | 0.00 | |
| | FM 1-3 | | 41 | 36.8 | 108 | 137 | 232 | 865 | 200 | 182 | 91.2 | 28.5 | 2.19 | |
| Zn | FM 4-5 | mg·kg$^{-1}$ | 6 | 135.3 | 140 | 172 | 207 | 473 | 216 | 128 | 59.4 | 52.4 | 2.23 | 0.0983 |
| | C | | 4 | 46.3 | 57.8 | 91.8 | 125 | 136 | 91.5 | 41.1 | 44.9 | 20.5 | -0.02 | |

Similar patterns for Zn have been found too. Zinc mass fraction values which were determined in the topsoil samples taken in the FM area are not statistically and significantly different to those found on the control plots. On the sites FM 4–5, median mass fraction value is the highest one: 172 mg·kg$^{-1}$. Somewhat lower value was found on the sites FM 1–3: 137 mg·kg$^{-1}$, but the difference was not statistically significant. The lowest median mass fraction value was found on the control plots: 91.8 mg·kg$^{-1}$ (Figure 3 right, Table 3).

The median values of the soil organic carbon content ranges from 86.7 g·kg$^{-1}$ on the control plots to 115.78 on the FM 4–5 (Table 3). According to Gračanin and Ilijanić [39], soils on the FM area are very humic and thus influence the binding of Cu [36].

Twenty samples taken from the area FM 1–3 were selected for the particle size distribution analysis with the purpose of the interpretation of ‘geochemical analyses’ results in the context of Croatian Directive on the protection of agricultural land from pollution [36]. According to the particle size distribution analysis [31], soil texture class ranges from silt loam to silt clay loam [40] (Table 4).

Spatial distribution of the analysed heavy metals (Cd, Cu, Zn, and Pb) for FM (FM 1–3) is shown on the prediction maps. Red nuances indicate the highest concentration of heavy metals, and blue nuances stand for the lowest concentration [37] (Figure 4, 5, 6 and 7).

In the very vicinity of the mine the pedological profile has been opened (Figure 1 and 8). The profile reveals that there is a dystric cambisol (relatively shallow, skeletoidal) on the moderate slope; according to the previous data [26] it is the most present soil type on Medvednica Mt. The soil profile is of A-B-R type. The thickness of the A-horizon ranges from 0 to 17 cm, while for B-horizon it ranges from 17 to 43 cm. In the context of particle size distribution the investigated soil is clay loam. According to Scheffer and Schachtschabel [38], the reaction of soil is very acidic. Using the criteria of Gračanin and Ilijanić [39], this soil is very humic and richly supplied with nitrogen (Table 5).

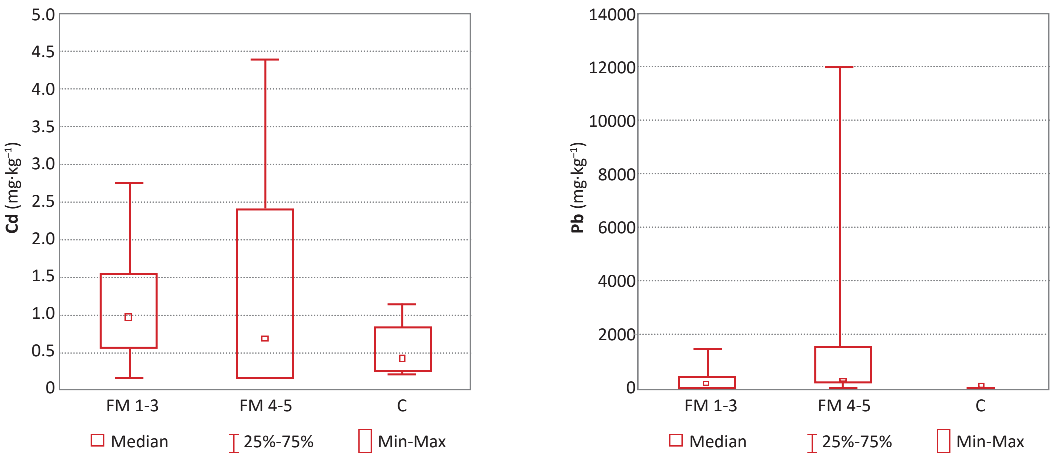


**FIGURE 2.** Average values and ranges of mass fraction of Cd (left) and Pb (right) on the research area and control plots.

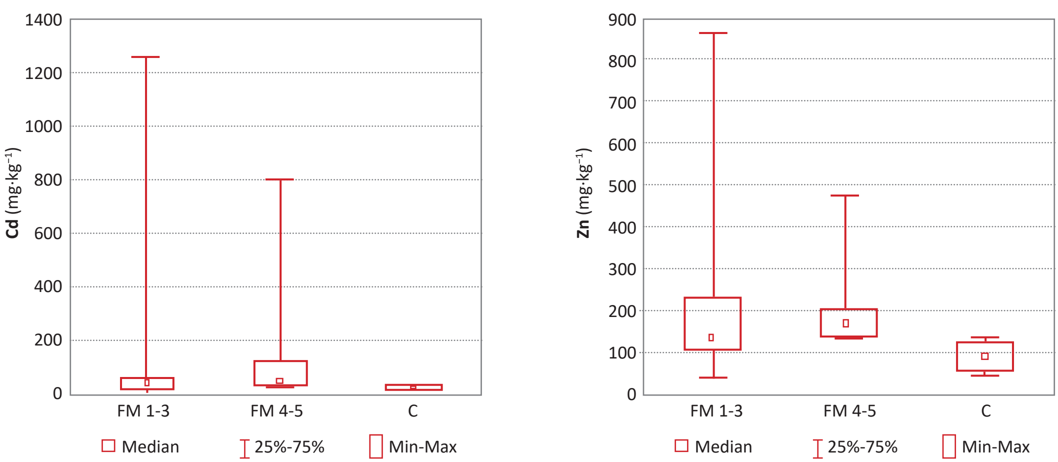


**FIGURE 3.** Average values and ranges of mass fractions of Cu (left) and Zn (right) on the research area and control plots.

**TABLE 4.** Descriptive statistics for particle size distribution of soil in the FM 1–3 area.

| Variable | Unit | N | Minimum | Lower quartile | Median | Upper quartile | Maximum | Mean | Std. dev. | Coef. var. | Std. error of mean | Skewness |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Coarse sand (0.2-2 mm) | | 20 | 11.1 | 16.1 | 18.2 | 20.9 | 31.6 | 18.7 | 4.73 | 25.3 | 1.06 | 0.87 |
| Fine sand (0.063-0.2 mm) | | 20 | 4.11 | 5.11 | 6.19 | 7.37 | 11.5 | 6.40 | 1.63 | 25.5 | 0.36 | 1.50 |
| Coarse silt (0.063-0.02 mm) | % | 20 | 16.2 | 19.8 | 22.6 | 25.3 | 37.9 | 23.2 | 5.32 | 22.9 | 1.19 | 1.25 |
| Fine silt (0.02-0.002 mm) | | 20 | 19.5 | 30.1 | 34.0 | 36.5 | 44.3 | 33.0 | 5.40 | 16.3 | 1.21 | -0.48 |
| Clay (<0.002 mm) | | 20 | 14.3 | 15.6 | 18.7 | 20.0 | 31.4 | 18.6 | 3.71 | 19.9 | 0.83 | 2.13 |

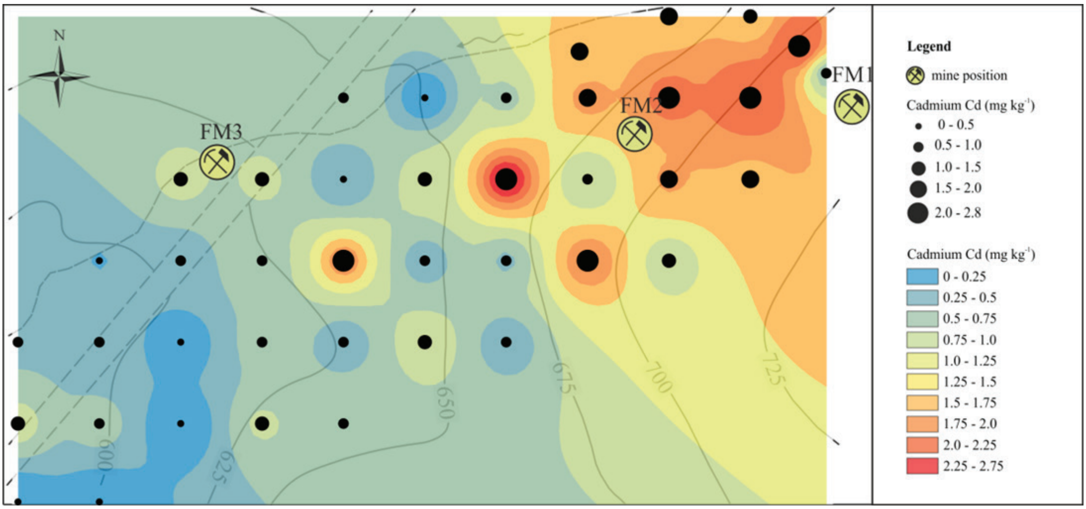


**FIGURE 4.** Cartographic presentation of the spatial distribution of Cd in the FM 1–3 area.

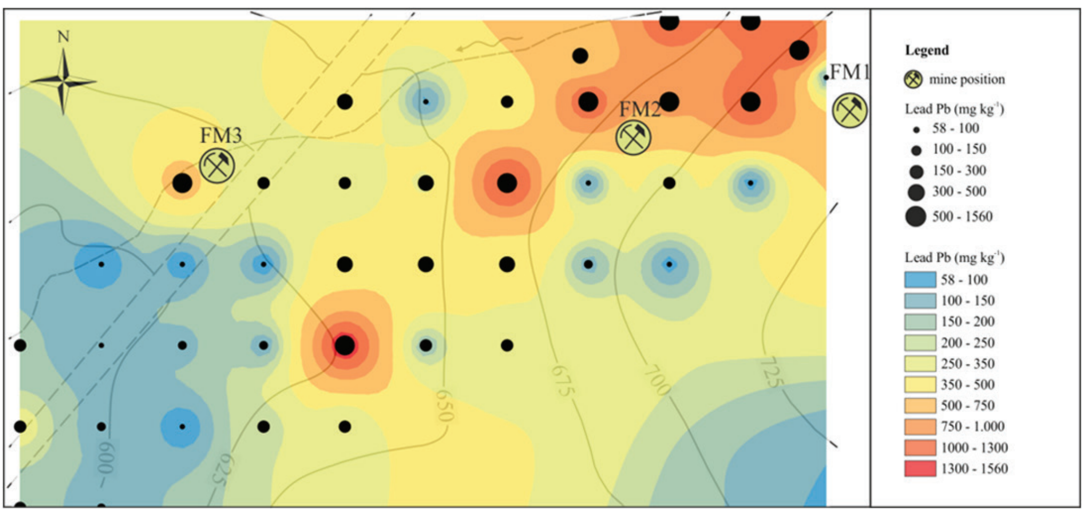


**FIGURE 5.** Cartographic presentation of the spatial distribution of Pbin the FM 1–3 area.

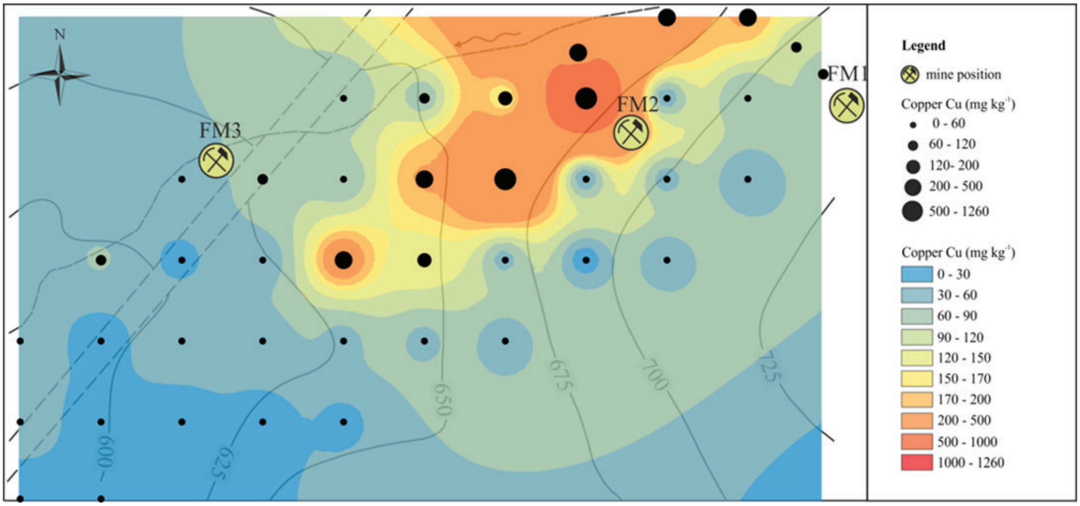


**FIGURE 6.** Cartographic presentation of the spatial distribution of Cu in the FM 1–3 area.

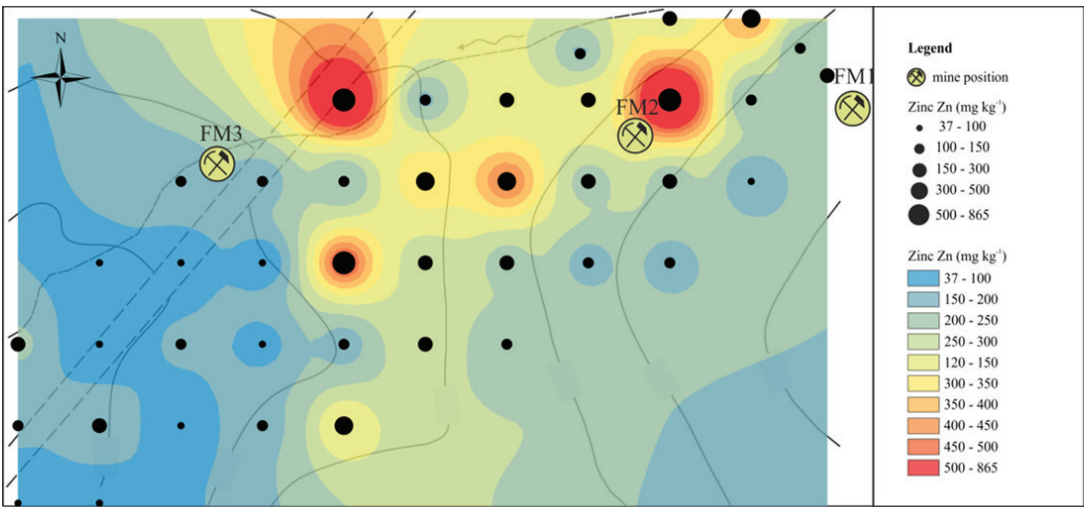


**FIGURE 7.** Cartographic presentation of the spatial distribution of Zn in the FM 1–3 area.

**TABLE 5.** Soil properties on the profile in the research area.

| Profile | Soil horizon according FAO | Thickness (cm) | | Particle size distribution (mm) | | | | | Soil texture |
|---|---|---|---|---|---|---|---|---|---|
| | | From | To | 2.0-0.20 | 0.20-0.063 | 0.063-0.020 | 0.020-0.002 | <0.002 | |
| P1 | A | 0 | 15-20 | 23.3 | 3.1 | 7.0 | 31.9 | 34.7 | clay loam |
| | B | 15-20 | 38-48 | 25.6 | 3.6 | 9.2 | 34.3 | 27.2 | clay loam |
| | | pH ($H_2O$) | pH ($CaCl_2$) | C org. $g \cdot kg^{-1}$ | N tot. $g \cdot kg^{-1}$ | Pb $mg \cdot kg^{-1}$ | Cu $mg \cdot kg^{-1}$ | Zn $mg \cdot kg^{-1}$ | Cd $mg \cdot kg^{-1}$ |
| | A | 4.64 | 4.08 | 89.73 | 7.24 | 58.1 | 29.8 | 90.2 | 0.7 |
| | B | 4.92 | 4.15 | 46.42 | 3.23 | 22.1 | 35.5 | 64.6 | 0.1 |

**FIGURE 8.** Soil profile on the research area.

## DISCUSSION

The results obtained in this study are in accordance with those in the Geochemical Atlas [37] and with the soil pollution grade according to the Brüne-Ellinghaus criteria [35] (Table 2). Croatian Geochemical Atlas is based on the analyses of composite soil samples which were taken from depth of 0–25 cm, in forest and non-forest areas, and metals by acid mixture (HCl-HF-$HNO_3$-$HClO_4$) which were extracted. At the same time, the extraction procedure using aqua regia was done and the regression models of correspondence of the two sets of results (namely, total concentrations given in the Geochemical Atlas [37] and the pseudo-total concentration values of the metals from our study) were established. Since in the Republic of Croatia there is no legislation about maximum allowed concentration of the pollutants in forest soils, the results of forest soils studies are usually compared to the guidance prescribed by Croatian Directive on the protection of agricultural land from pollution [36]. Martinović [14] claims that usual natural occurrence of the selected heavy metals in soil is as follows: Cd (<0.5 mg·kg$^{-1}$), Cu (5–20 mg·kg$^{-1}$), Pb (<10 mg·kg$^{-1}$) and Zn (10–50 mg·kg$^{-1}$). According to the Directive [36], the main "input parameters" for heavy metal determination in soil are pH, particle size distribution and mass fraction of humus.

Median of the pseudo-total mass fraction of Cd in topsoil in the FM area ranges from 0.7 mg·kg$^{-1}$ (FM 4–5) to 0.97 mg·kg$^{-1}$ (FM 1–3).These values are higher than those found on the control plots which amount to 0.44 mg·kg$^{-1}$. Halamić and Miko [37] claim that the median for Cd in soil in the central part of Croatia is 0.2 mg·kg$^{-1}$. Cd comes together with zinc in forms of sulphides and carbonates and it is usually present in fraction values that amount to about 1/200 of the values of zinc [37, 41]. Our findings are consistent with such claims. Phytotoxicity of Cd is rarely manifested, but it is well known that Cd is very toxic for humans and animals. The lower tolerance of Cd toward water stress of plantsresults in degradation of the cell wall of the conductive tissue [41]. According to the criteria given by the Directive [36] for silt loam soil (Table 3), we have detected high contamination of soil in the FM area, while according to Brüne-Ellinghaus criteria [35] the studied soil is to be classified as highly polluted with Cd (Table 2).

Median value of the pseudo-total mass fraction of Pb in soil in the area of FM ranges from 238 mg·kg$^{-1}$ (FM 1–3) to 273 mg·kg$^{-1}$ (FM 4–5), while at the control plots a statistically and significantly lower value was found (73.7 mg·kg$^{-1}$). Global average of Pb in soil is 25 mg·kg$^{-1}$ [42]. Halamić and Miko [37] found that pseudo-total fraction of Pb in the central part of Croatia ranges from 13 to 198 mg·kg$^{-1}$ with median value of 25 mg·kg$^{-1}$. These values are notably far below those found in our study of soil in the area of FM. Bioavailability of Pb in soil is, on average, less than 1% [43]. Solubility of Pb is highly correlated with pH of soil. Thus, at high pH-values precipitating of Pb in forms of carbonates, hydroxides or phosphates occurs and relatively stable lead-organic complexes can be formed [43]. In the FM area we found that median pH-values are above 6 and that suggests that Pb forms complexes with organic-mineral soil components. When fraction of Pb in soil amounts to more than 100 mg·kg$^{-1}$, such soil can be toxic for plants. In that context, speciation and bioavailability of lead has an important role. Pb toxicity is manifested as a depression in plant growth. Croatian Directive [36] set upper limit values for pseudo-total lead fraction in various soil types as 50-100 mg·kg$^{-1}$. In the context of these values, soil in the FM area is polluted with Pb, while if using the Brüne-Ellinghaus criteria [35] the studied soil is above the limit value of pollution (Table 2).

The determined pseudo-total fractions of Cu reveal that in the FM area there is a higher concentration of this metal in soil than in the soil of the control plots, but the difference is not statistically significant. Thus the median value of Cu mass fraction in the FM area ranges from 45.7 mg·kg$^{-1}$ (FM 1–3) to 50.5 mg·kg$^{-1}$ (FM 4–5), while in the soil samples taken on the control plots it is half lower (26.7 mg·kg$^{-1}$). According to Halamić and Miko [37], the median value of Cu in soil in the central part of Croatia is 16 mg·kg$^{-1}$, which is lower than the median for the entire Croatian territory, but it is still higher than the value for the whole European continent [44]. Osman [45] claims that when its fraction values in soil exceed 20 mg·kg$^{-1}$ Cu is potentially deleterious for plants. This can be manifested in terms of weak growth of roots and branches, as well as chlorosis and partially necrosis. Soils of the FM area according to the Directive [36] are to be classified as highly contaminated with Cu, while according to Brüne-Ellinghaus criteria [35] one can classify them as soils highly polluted by Cu (Table 2).

The relations similar to those for Cu, have been observed for Zn as well. In the FM 4–5 area the median mass fraction of Zn is the highest one found in the tested areas and amounts to 172 mg·kg$^{-1}$. In the area FM 1–3 median mass fraction value of Zn is 137 mg·kg$^{-1}$. On the control plots, Zn is present in the median value of 91.8 mg·kg$^{-1}$. In the central part of Croatia mass fraction values of Zn fall in the range of 27–362 mg·kg$^{-1}$, with median value of 61 mg·kg$^{-1}$. On some individual spots on the mountains Medvednica, Kalnik and Ivanšćica higher fraction values of Zn were found; this is connected to the natural ore occurrences in these mountains [37]. According to Vanmechelen *et al.* [46] the fraction of Zn in organic and mineral horizons is usually below 100 mg·kg$^{-1}$. National environment quality programmes in Europe consider that the allowable zinc fraction in soil is from 100 to 200 mg·kg$^{-1}$ [47]. Silt loam soils with pH higher than 6, such as those in the FM area, are in the context of findings by Halamić and Miko [37] to be considered as soils contaminated with zinc, while according to Brüne-Ellinghaus criteria [35] one can classify them as soils highly polluted with Zn (Table 2).

On the prediction maps for the area FM 1−3 (Figure 4, 5, 6 and 7) one can notice that the highest fraction values of the selected heavy metals are found in the area of the FM 1 and FM 2, while the lowest one is found for the FM 3. The latter result is explained by fact that the FM 3 has the lowest impact on neighbouring soil, i.e. a minimum quantity of the material (mullock) has been brought out of the mine and out of the main natural slope direction. The contamination follows the natural slope of the terrain and further studies should include a wider area of the mine, respecting the nature of the relief. The determined metals are more concentrated in the vicinities of the mines and the pollution of Medvednica Mt. has a local character. This is an obvious example that mining can locally leave consequences on soil for a long time.

On the occasion of the field work, we did not notice any changes or degradations of the ground vegetation, shrubs and trees. Kabata-Pendias and Mukherjee [43] claim that cadmium, lead, copper and zinc usually accumulate in the roots of the plants with no translocation in the higher parts and thus there are no visible symptoms. Martinović [14] gave an insight into relative indications of the toxic influences of heavy metals on flora, fauna and humans. According to the mentioned reference [14], Cd has the highest toxicological impact on flora, fauna and humans in comparison to the other three analysed elements (Cu, Pb, and Zn). Since for the area described in this paper there is no scientific knowledge about an influence of heavy metals on the flora, fauna and humans, it would be recommended to do a research with the aim of determining their possible depressive act on the vegetation and gene pool.

## CONCLUSIONS

On the basis of the results obtained in this study, we conclude as follows:

- Contamination with heavy metals in the research area is strictly local, i.e. related to the openings of the "French Mines".
- Average pseudo-total fraction of Cd in the analysed topsoil samples was in the range of 0.17–4.41 mg·kg$^{-1}$ (median: 0.97 mg·kg$^{-1}$). Cu was found in the range of 4.54–1260 mg·kg$^{-1}$ (median: 45.7 mg·kg$^{-1}$). In the case of Pb, average values of the pseudo-total fraction were found in the range of 58.4–12000 mg·kg$^{-1}$ (median: 238 mg·kg$^{-1}$), and the pseudo-total fraction values of Zn were found in the range of 36.8–865 mg·kg$^{-1}$ (median: 137 mg·kg$^{-1}$).
- Our results reveal that mining in the research area had an impact on the local soil quality in terms of pollution with heavy metals, with no visible signs on the vegetation.
- Further research in this area should be focused to the presence of heavy metals in plants, mushrooms, percolated waters and springheads with the aim of determining the possible influence of the described contamination with heavy metals on the wider area, especially in the lower parts of the terrain.

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