# SPATIAL DISTRIBUTION OF HEAVY METALS AND SOME LITHOGENIC ELEMENTS IN SOIL FROM COPPER CONTAMINATED AREA


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## INTRODUCTION

Monitoring with soil samples (topsoil-TS and subsoil-SS) was conducted in area with intensively exploitation of copper minerals. Topsoil samples and subsoil samples were collected in order to determine whether the potential high content of certain metals are due to anthropogenic influence in the study area, or this occurrence is due to the geology of the land. For the purpose of this study total of 40 samples were collected, 20 samples of topsoil and 20 subsoil .

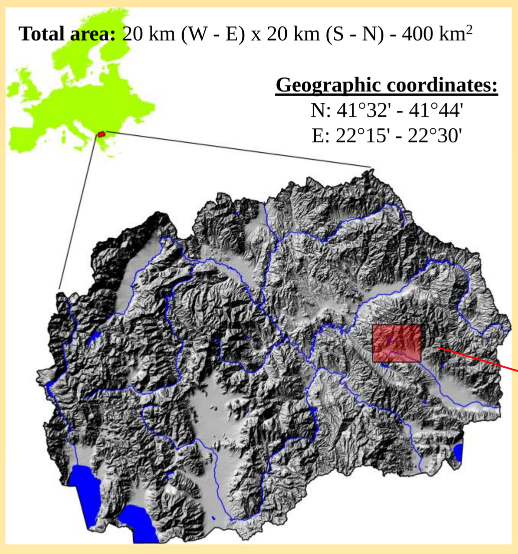



**Fig. 1.** Location of the study area

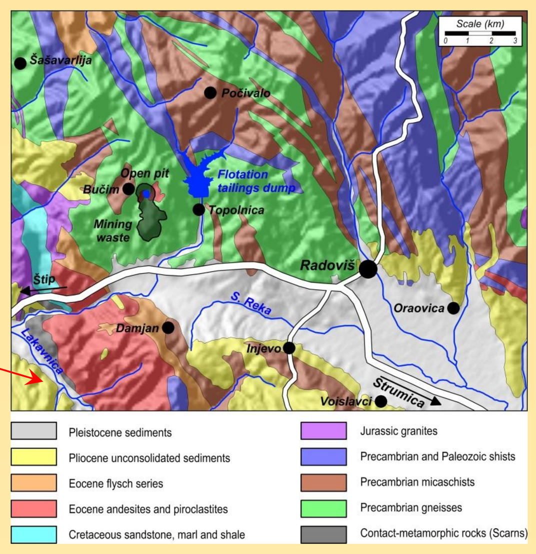


**Fig. 2.** Generalized geology of study area

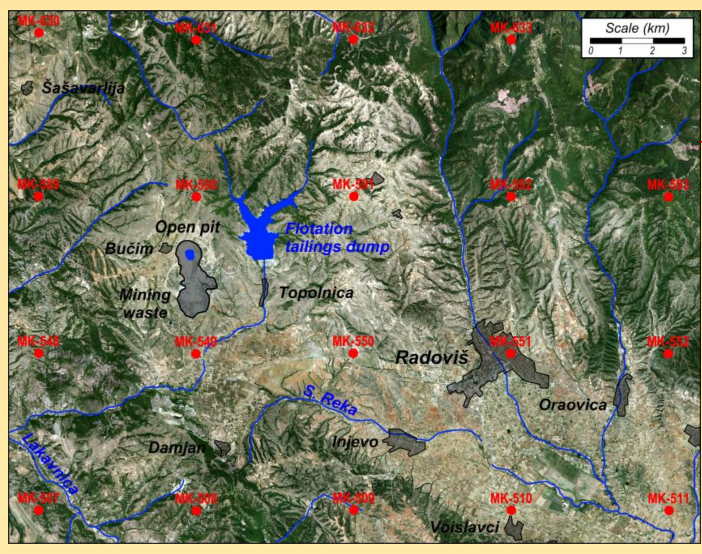


**Fig. 3.** Soil samples locations

## EXPERIMENTAL

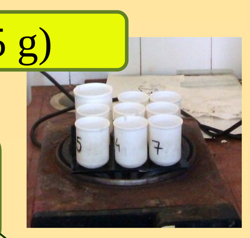
### Sampling

Soil samples were collected by a previously adapted sampling network for taking soil samples

**SAMPLING POINT.** Two soil samples were taken at each location: sample from the surface layer of soil - topsoil (0–5 cm) and deep soil layer - subsoil (20–30 cm), from the same location. Soil samples were collected according to certain standards for taking soil samples [1]. Each sample present composite of five corresponding samples collected in the area within a 10 x 10 m.

**SAMPLE PREPARATION**

Measured mass of soil samples (0.5 g)



OPEN WET DIGESTION WITH MIXTURE OF ACIDS

5 mL $HNO_3$ → 5–10 mL HF → 2 mL $HClO_4$ → 2 ml HCl, 5 mL $H_2O$

Digests quantitatively were transferred to 50 ml calibrated flasks

### Instrumentation

The analyses of digest samples were performed with an atomic emission spectrometry with inductively coupled plasma, ICP-AES, (Varian 715-ES). Total contents of 18 elements were analyzed in collected samples: Al, As, Ba, Ca, Cr, Cu, Ga, Li, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V and Zn.

## RESULTS

**Table 1**. Descriptive statistics for elements content values in soil samples

| Element | Unit | Dis. | $X_a$ | $X_g$ | Md | min | max | $P_{10}$ | $P_{90}$ | s | $s_x$ | CV | A | E |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | % | N | 2.1 | 1.8 | 1.8 | 0.59 | 5.3 | 0.77 | 3.8 | 1.2 | 0.18 | 54 | 0.79 | 0.06 |
| **As** | **mg/kg** | **Log** | **23** | **8.8** | **12** | **0.50** | **160** | **0.50** | **44** | **34** | **5.4** | **150** | **–0.21** | **–1.61** |
| Ba | mg/kg | Log | 280 | 220 | 250 | 27 | 980 | 73 | 480 | 200 | 31 | 70 | –0.76 | 1.31 |
| Ca | % | Log | 0.89 | 0.46 | 0.41 | 0.042 | 4.3 | 0.10 | 2.6 | 1.1 | 0.17 | 120 | 0.05 | –0.81 |
| Cr | mg/kg | Log | 73 | 58 | 55 | 16 | 290 | 28 | 150 | 60 | 9.4 | 82 | 0.55 | 0.57 |
| **Cu** | **mg/kg** | **Log** | **59** | **28** | **23** | **9.3** | **1200** | **11** | **54** | **190** | **30** | **320** | **2.76** | **11.9** |
| Fe | % | N | 2.6 | 2.4 | 2.6 | 0.61 | 4.7 | 1.6 | 4.1 | 0.93 | 0.15 | 35 | 0.27 | 0.59 |
| Ga | mg/kg | N | 12 | 12 | 13 | 7.2 | 20 | 10 | 15 | 2.4 | 0.38 | 19 | 0.28 | 1.25 |
| K | % | N | 1.1 | 0.93 | 0.88 | 0.32 | 2.3 | 0.50 | 1.8 | 0.56 | 0.09 | 53 | 0.03 | –0.90 |
| Li | mg/kg | N | 13 | 11 | 12 | 3.2 | 43 | 6.0 | 22 | 7.6 | 1.2 | 60 | 0.04 | 0.08 |
| Mg | % | Log | 0.76 | 0.63 | 0.71 | 0.19 | 2.6 | 0.23 | 1.2 | 0.52 | 0.08 | 68 | –0.07 | 0.15 |
| Mn | mg/kg | Log | 510 | 430 | 440 | 77 | 1800 | 220 | 820 | 330 | 53 | 65 | –0.18 | 1.28 |
| Na | % | N | 1.4 | 1.2 | 1,3 | 0.36 | 2.9 | 0.64 | 2.2 | 0.62 | 0.10 | 46 | 0.82 | 0.71 |
| Ni | mg/kg | Log | 36 | 28 | 27 | 11 | 190 | 13 | 63 | 36 | 5.6 | 99 | 1.21 | 2.45 |
| **Pb** | **mg/kg** | **Log** | **30** | **23** | **23** | **1.0** | **130** | **9.0** | **65** | **26** | **4.2** | **87** | **–1.01** | **4.03** |
| Sr | mg/kg | Log | 66 | 37 | 39 | 3.7 | 470 | 9.0 | 130 | 99 | 16 | 150 | 0.09 | 0.78 |
| V | mg/kg | Log | 73 | 53 | 59 | 0.35 | 170 | 23 | 150 | 48 | 7.6 | 66 | 0.74 | –0.71 |
| Zn | mg/kg | Log | 70 | 65 | 71 | 23 | 120 | 36 | 110 | 25 | 3.9 | 35 | 0.08 | –0.69 |

**Dis.** – distribution; $X_a$ – mean; $X_g$ – geometrical mean; **Md**–median; **min** – minimum; **max** – maximum; $P_{10}$ - percentile 10; $P_{90}$ - percentile 90; **s** - standard deviation; $s_X$ – standard error of mean; **CV** – coefficient of variation; **A** – skewness; **E** – kurtosis

Compared with average content of Cu in **World soils (30 mg kg$^{-1}$)** [2] and **European soils (17 mg kg$^{-1}$)** [3] it determinates significantly contaminated area.

Considering land use, maximum values for **Cr**, **Ni** and **Pb** were found in cultivable area (**290**, **190** and **130 mg kg$^{-1}$**, respectively).

**The median value for copper in cultivable area was 26 mg kg$^{-1}$, in the uncultivable area is 25 mg kg$^{-1}$, in the urban area 22 mg kg$^{-1}$ and in the mine environs is 19.3 mg kg$^{-1}$**

Because of the wide range values for the copper content in mine environs, the average amount was although considered, 190 mg kg$^{-1}$

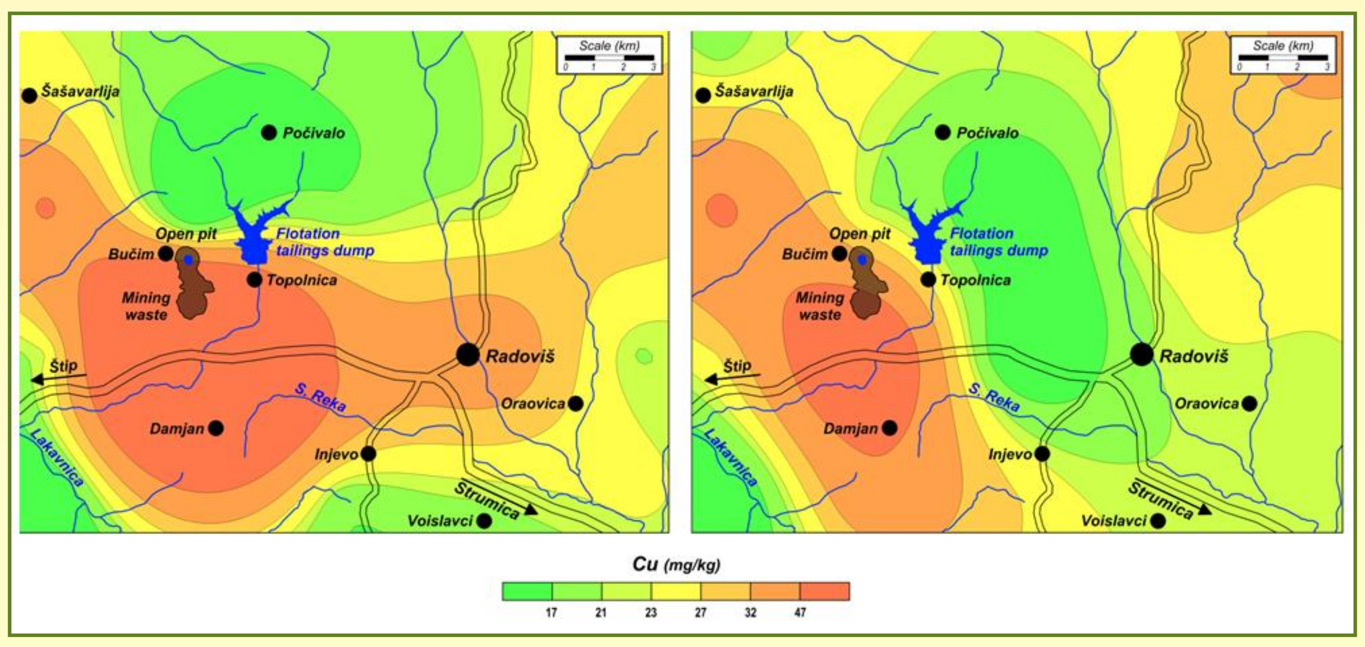



**Fig. 4.** Spatial distribution of Cu in topsoil (left) and subsoil (right)

**Four factor associations were identified (F1, F2, F3 and F4), which includes 77 % of variability of treated elements (Table 2)**

**Table 2**. Matrix of dominant rotated factor loadings (F>0.50)

| Element | F1 | F2 | F3 | F4 | Comm. |
|---|---|---|---|---|---|
| Mg | **0.92** | 0.03 | 0.09 | 0.14 | 86.7 |
| Cr | **0.85** | 0.20 | -0.24 | 0.09 | 82.0 |
| Al | **0.83** | 0.14 | 0.09 | 0.11 | 73.8 |
| Fe | **0.81** | 0.05 | 0.04 | 0.50 | 91.6 |
| Ca | **0.73** | 0.46 | 0.16 | -0.07 | 77.1 |
| Pb | 0.06 | **0.87** | 0.08 | 0.05 | 76.3 |
| Ni | 0.50 | **0.84** | 0.05 | 0.04 | 95.4 |
| Li | 0.15 | **0.80** | 0.11 | 0.23 | 73.1 |
| Mn | 0.59 | **0.63** | 0.20 | 0.14 | 79.8 |
| Ba | -0.02 | 0.04 | **0.94** | 0.17 | 91.8 |
| Sr | 0.16 | 0.06 | **0.86** | -0.17 | 80.3 |
| K | -0.06 | 0.32 | **0.60** | 0.38 | 61.0 |
| Zn | 0.25 | 0.28 | 0.05 | **0.76** | 72.3 |
| Ga | 0.24 | -0.08 | 0.20 | **0.76** | 67.5 |
| As | -0.09 | 0.40 | -0.28 | **0.50** | 49.5 |
| Var | 28.2 | 20.8 | 15.2 | 13.4 | 77.2 |

**F1, F2, F3, F4** - Factor loading; **Var** -Variance (%); **Com** – Communality (%)

**Mg-Cr-Al-Fe-Ca-Mn-Ni** (Factor 1) - their origins are related primarily to the dusting of Pliocene sediments and flysch formations (Pliocene unconsolidated sediments, Eocene flysch series).

**Pb-Ni-Li-Mn** (Factor 2) - related to volcanism E (Eocene andesite and piroclastite).

**Factor 3 (Ba-Sr-K) and Factor 4 (Zn-Ga-As-Fe)**

Their occurrence is related primarily to the enrichment of the deeper horizon (B – clay accumulated) which is particularly valid for the elements in the group F4. Empirically can considerate that these elements are related to the decomposition of rocks, especially Proterozoic micashist and schist (Precambrian and Paleozoic shists, Precambrian micaschists).

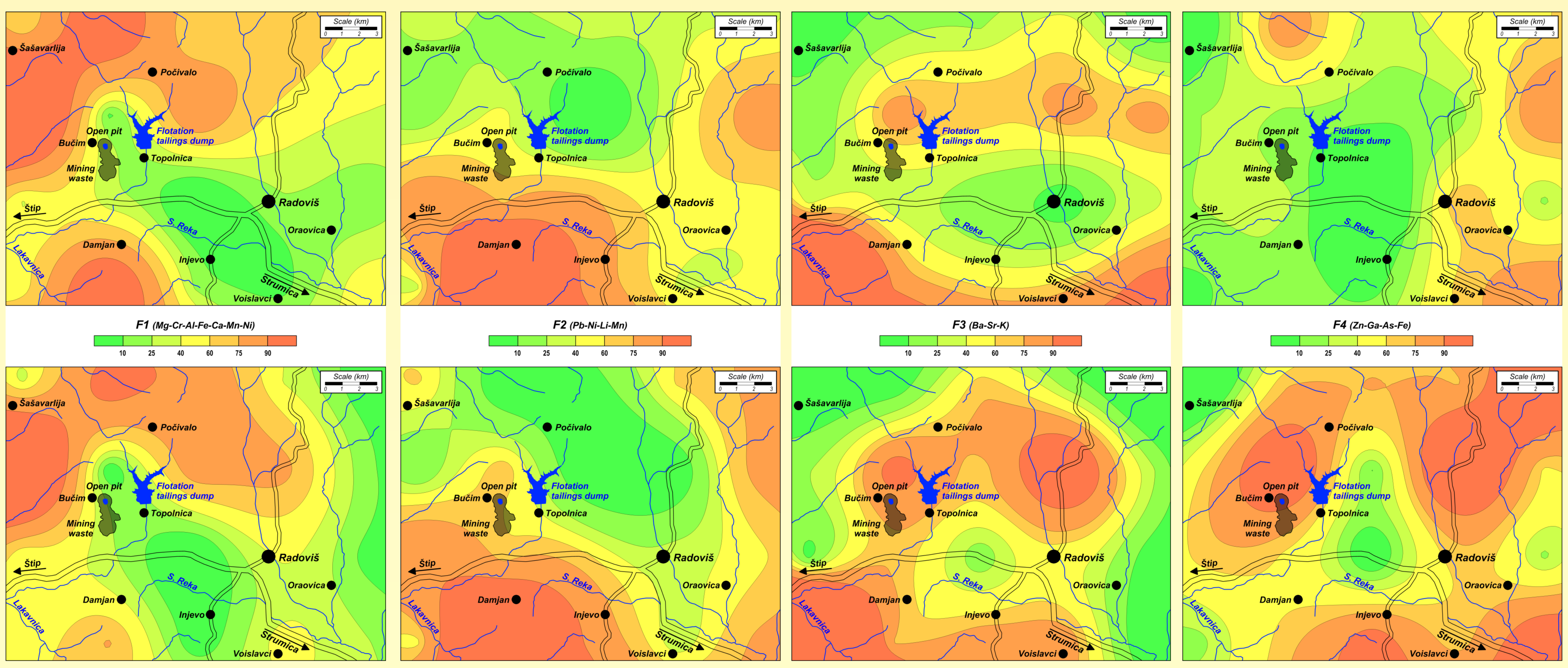


**Fig. 5.** Spatial distribution of F1, F2, F3 and F4 scores in topsoil (above) and subsoil (below)

## CONCLUSION

Conducted monitoring with soil samples (topsoil-TS and subsoil-SS) determined distribution of higher contents of some metals in area with intensively copper minerals exploitation. The enrichment factor of TS/SS for Cu was 2.8 for whole study area and ~10 for close mine environ. The lithogenic elements (Al, As, Cr, Fe, Ga, Li, Mg, Mn, Na, Ni, Sr) showed stability in the vertical direction (TS/SS); but in a across direction, variability of element contents undergoes with the geology of the region. Factor analysis singled out four geochemical associations: F1 (Mg-Cr-Al-Fe-Ca-Mn-Ni), F2 (Pb-Ni-Li-Mn), F3 (Ba-Sr-K) and F4 (Zn-Ga-As-Fe). Spatial distribution showed that higher contents of Cu (>47 mg kg$^{-1}$) are deposited in mine vicinity.


**References**

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