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*Original scientific paper*

# MULTI-ELEMENT DISTRIBUTION IN ROAD AND STREET DUST IN THE BITOLA REGION, NORTH MACEDONIA

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A b s t r a c t: The results of the systematic study of the spatial distribution of trace metals in road and street dust collected from the streets in the city of Bitola and from the roads in the southern part of the Pelagonia Valley, North Macedonia, known for its coal mine and thermoelectrical power plant (REK Bitola) activities, are reported. The investigated region is covered by a sampling in the four main roads in the direction North-South and East-West. In total, 39 dust samples were collected. Inductively coupled plasma – atomic emission spectrometry (ICP-AES) was applied for the determinations of 21 elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn). Data for the elements contents were proceed using nonparametric and parametric analysis while for the data normalization the method of *Box-Cox* transformation was applied. The universal kriging method with linear variogram interpolation was applied for the construction of spatial distribution maps of each factor score and the analyzed elements. Based on the results of factor analyses, three geogenic associations of elements (factors) have been defined: F1 (Ni, Cr, Cu, Fe, Co, Mn, Zn, V and P), F2 (Ba, Al, Na and Sr) and F3 (Ca and Mg). The rest of the elements were eliminated from further analysis because they had a low share of communality or low tendency to form independent factors. Even typical potentially toxic elements, such as arsenic, cadmium, lead and zinc, are not isolated into anthropogenic geochemical associations by multivariate statistical methods still show some trends of local anthropogenic enrichment. Thus, the distributions of the arsenic, copper, lead and zinc have higher contents in the road dusts from the north and south parts of the city of Bitola and around of the REK Bitola, showing influence of the industrial and urban activities from the city indicating the distribution of fly ash from thermoelectrical power plant.

**Key words**: road dust; pollution; heavy metals; thermoelectric power plant; Bitola; North Macedonia

## INTRODUCTION

Emissions of heavy metals into the environment happen through several processes. The emission of heavy metals into the atmosphere is one of the greatest threats to human health. Large amounts of dust are generated during blasts and excavations of mining minerals, whereas they are distributed in the air by the winds. People are directly exposed to the effects of heavy metals through inhalation of airborne microparticles from atmospheric dust (Jarup, 2003; Godish, 2004). Atmospheric particles affect the human health when they enter into the respiratory system. The polluted air slows down the development of pulmonary functions in children (Gauderman et al., 2004). Senior citizens, especially those with a weakened cardio-vascular and respiratory system are a high-risk group too. Another risk group is patients with chronic pulmonary emphysema, asthma or cardiovascular diseases (Vallero, 2008).

Heavy metals in the atmosphere originated mainly from dust dispersion from metal refining, fossil fuel combustion, vehicle exhausts, and other human activities and they stay in the atmosphere until they are removed by a variety of cleansing processes (Agarval, 2009). Particular emphasis is given on ore deposits, mining, processing and flotation plants as significant anthropogenic sources of dust. Heavy metals emitted in the atmosphere by combustion processes usually have relatively high solubility and reactivity especially under low-pH

condition (Tchounwou, 2012). 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 (Athar & Vohora, 1995; Hou et al., 2005; Kabata-Pendias & Mukherjee, 2007; Longchurst & Brebbia, 2013).

Total deposited dust is commonly used as monitor for this purpose. This kind of monitoring have been performed as part of a large number of analytical studies for a long time, but their application in recent decades has taken a swing. This is due to the fact that monitoring does not require the use of expensive technical equipment. Analytical results reflect the real situation of heavy metal distribution in the investigated area. Deposited dust refers to any dust that falls out of suspension in the atmosphere. Atmospheric total deposition (deposited dust) is very useful mechanism for monitoring the fate of anthropogenic elements introduced into the atmosphere. Many investigations have focused on the chemical composition and the content of toxic substances in deposited dust (Morselli et al., 2003; Polkowska et al., 2005; Stafilov et al., 2012; Balabanova et al., 2011a, 2011b, 2017; Bačeva et al., 2011, 2012, 2015; Boev et al., 2013).

The effects on health of transport-related air pollution are among the leading concerns about transport (Keller & Lamprecht, 1995). Research in recent decades consistently indicates the adverse effects of outdoor air pollution on human health, and the evidence points to air pollution stemming from transport as an important contributor to these effects (Tiitanen et al., 1999; Krzyzanowski et al., 2005). Heavy metals in street dust may originate from anthropogenic sources such as petroleum, diesel and coal combustion, as well as industrial activities and natural geochemical processes such as weathering. Heavy metals are not biodegradable and can remain in soil and dust over long periods of time. Metal pollutants such as Cd, Cr, Ni and Pb have cumulative effects, causing growth retardation in children, kidney disease, cancer and many other adverse health effects (Kabata-Pendias & Mukherjee, 2007).

Street dust (SD) or road dust (RD) are a complex mixture of particles of natural and anthropogenic origin. Sources of natural particles are soil dusting, sea salt, volcanic ash, pollen, plant remains, forest fires, and similar. Anthropogenic particles originate from the weathering of construction materials, traffic (wear of brake pads and tires, fuel combustion, catalytic converters), high-temperature industrial combustion processes, mining, and other sources. Traffic is the biggest source of metals in street dust in large cities and their environs. The second important source of particles in street dust of a large town is the abrasion of construction materials such as asphalt, concrete, or natural stone, emissions from demolition and construction activities, soil and plant remain, dusting and sea spray. Industry can also be an important source of particles in street dust, especially in less developed countries. Even small-scale industrial activities can have a significant impact on the chemical composition of street dust. It is important to study the chemical composition of SD, because SD is a major source of inhalable PM10 and PM2.5 particles in the ambient air in urbanized environments. Chemical content of this kind of samples could also identify the eventual sources of pollution with fine dust (Khan & Strand, 2018).

The goal of this study is to follow eventual impact of the air pollution from the urban activities and from the thermo-electrical power plant REK Bitola in the Bitola region, North Macedonia, especially fly ash deposited on the fly ash damp site in the vicinity of the plant and close to the city of Bitola..

## MATERIALS AND METHODS

### *Study area*

Study area is located in southwest part of the country, in Pelagonia Valley (Figure 1). Thermoelectric power plant "REK Bitola" is a facility of strategic importance and primary installation for electricity generation in the country. This power plant is major polluter of the environment in the region and it constantly creates large amounts of waste in the form of fly ash and slag (ELEM, 2007; Stafilov et al., 2018). The biggest settlement in the study area is the city of Bitola, which is the administrative and economic centre of the region. Although Pelagonia Valley is at a distance of 155 km from the Adriatic Sea and at about 130 km from the Aegean Sea, still the Mediterranean climate influence with a temperate-continental, continental and mountainous climate are mostly felt. In this area the north wind prevails with the average speed of 2.2 m/s, the second for its constancy is the south wind with the annual average speed of 3.7 m/s and the third is the northwest wind with the average speed of 2.4 m/s (Lazarevski, 1993).

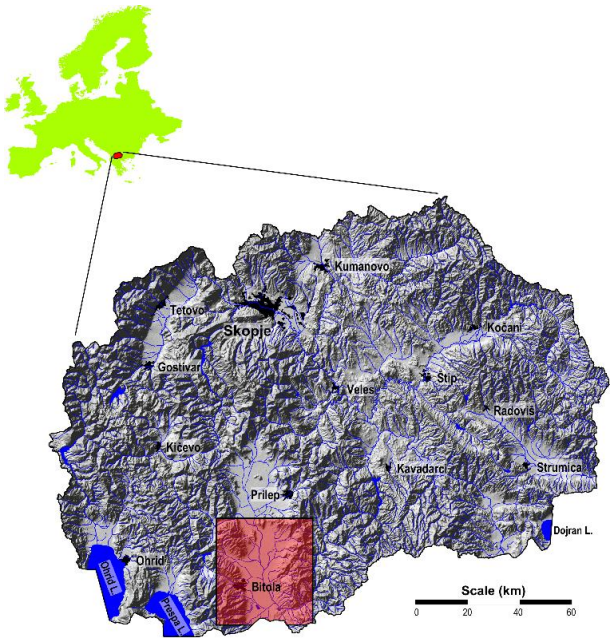


**Fig. 1.** Studying area

The study area includes parts of two large tectonic units: the Pelagonian massif and the West-Macedonian zone. The Pelagonian massif is separated from the West-Macedonian zone by a big revers Pelagonian fault, which is covered by young Quaternary deposits. The Pelagonian massif is built of Precambrian metamorphic and igneous rocks. The oldest rocks in the Western Macedonian zone are Paleozoic age and consist of low metamorphic schists and granitic rocks (Stafilov & Šajn, 2016, 2019).

*Sampling*

Sampling of the street (road) dust was conducted after several successive days without precipitation on hard surfaces like asphalt or concrete. Busy roads and areas with visible, accumulated soil or plant remains are avoided. Private parking lots, children's playgrounds, concrete roofs, bridges, or pedestrian pathways were the most suitable microlocations for the sampling. The sampling began with the removal of sand and other coarse material (free load) using a soft broom from the sampling surface. This material was not sampled. Only fixed loads electrostatically connected within pores of asphalt or concrete and which can be stripped with a hard-plastic brush were collected. Special care was taken to not sample soil or vegetation remains. A composite sample weighing at least 250 g is collected at a minimum of 10 suitable paved surfaces in an area approximately 50×50 m around the sampling point. A map of sampling locations is given in Figure 2.

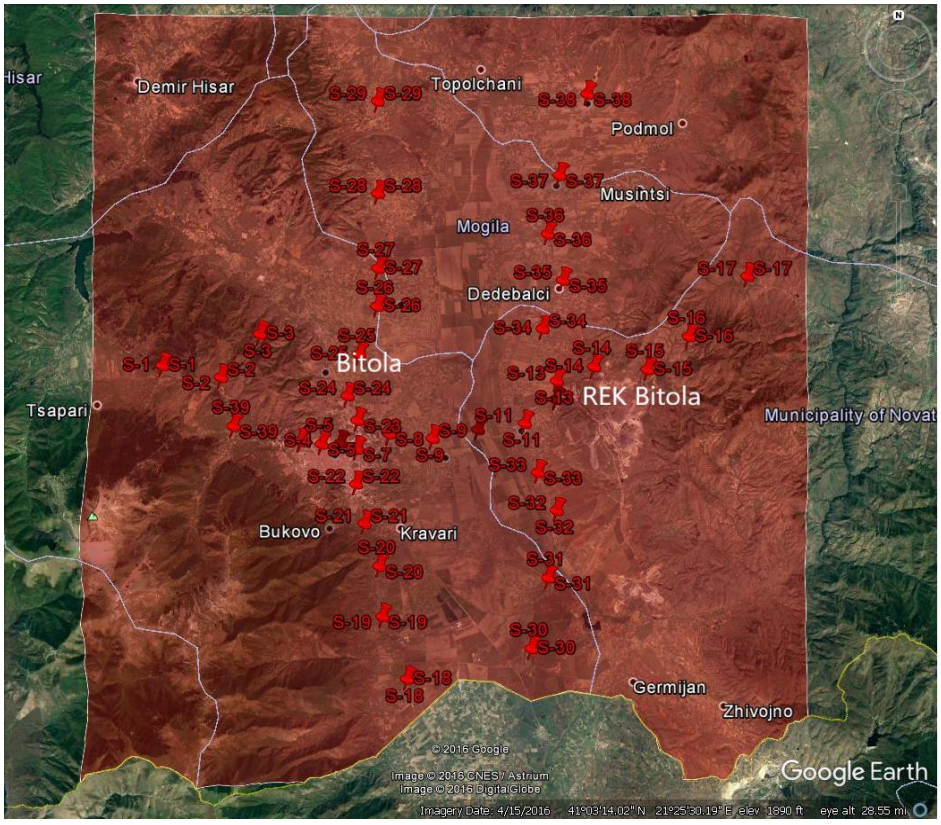


**Fig. 2**. The locations in Bitola region for road and dust sampling

*Sample preparation, digestion and analysis*

Pre-analytical preparation of the samples consisted of removing unwanted materials (stones, sand, plant remains, hair, textiles, and similar) from the material of interest (fine-grained particles deposited from the atmosphere). Samples were dried in a ventilating oven at 30°C until a constant weight had been achieved. The particle aggregates were then crushed in a ceramic mortar (when necessary). Samples were sieved through a 0.125 mm sieve, and 5 g of the material (< 0.125 mm) represented the material for the chemical analyses. The remaining sample is stored in the archives for possible future analysis.

Following the physical preparation, the samples were chemically prepared by wet digestion, applying a mixture of acids in accordance with the international standards (ISO 14869–1:2001). In this way the digested soil and sediment samples were prepared for determining the contents of the different elements using atomic emission and mass spectrometry. After the last addition of nitric acid, the dish from the hot plate was removed and cooled to room temperature before undertaking the digestion. For total digestion of inorganic components, 5–10 ml of HF were added. When the digest became a clear solution, 2 ml of $HClO_4$ were added. Perchloric acid was used for total digestion of organic matter. After cooling the vessels for 15 min, 2 ml of HCl were added for total dissolving of metal ions. Finally, the vessels were cooled and digests quantitatively transferred to 50 ml calibrated flasks.

The analysis of the digested samples was be conducted by applying atomic emission spectrometry with inductively coupled plasma (ICP-AES). For each element analyzed, previous optimization of the instrumental conditions is performed. In all samples, the contents of a total of 21 elements are analyzed: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn, in each soil sample. The quality control was performed by the analysis of certified reference soil and geological samples: soil sample JSAC 0401 (The Japan Society for Analytical Chemistry) and rock CRM samples undersaturated igneous rock SARM 3 NIM-L Lujaurite (SA Bureau of Standards, Pretoria, S. Africa), rock NCS DC71306 (GBW07114) (China National Analysis Centre).

All data for the contents of the tested elements were statistically processed using the software Stat Soft, 11.0. For all of the sediment samples as well as for the top- and bottom alluvial soil samples the basic descriptive statistical analysis of the values for the concentration of the elements was performed. By using bivariate statistics with a level of significance $p < 0.05$; $p > 0.01$, the degree of correlation of the values of the contents of the chemical elements in the samples is estimated, and the coefficients of correlation are presented in the correlation matrix.

## RESULTS AND DISCUSSION

*Data processing of the obtained results*

Data from the descriptive statistics of the measurements of 21 elements determined by ICP-AES (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) in street dust samples collected from 39 sampling locations in the Bitola region are presented in Table 1. In Table 1 the following statistical parameters are given: *n* – number of samples; X – arithmetical average; X(BC) – arithmetical average after Box-Cox method; Md – median; Min – minimum; Max – maximum; $P_{10}$ – 10$^{th}$ percentile; $P_{90}$ – 90$^{th}$ percentile; $P_{25}$ – 25$^{th}$ percentile; $P_{75}$ –75$^{th}$ percentile; S – standard deviation; $S_x$ – standard error; CV – coefficient of variation; A – skewness; E – kurtosis; BC – Box-Cox transformed values.

The values of macroelements Al, Ca, Fe, K, Mg and Na are in the following ranges: 0.22–6.8% of Al; 0.76–12% Ca; 0.23–2.5% Fe; 0.52–1.6% K; 0.042–2.0% Mg and 0.37–2.6% Na. The contents of macroelements are most frequently as result of the dominant geological formations of the area: Quaternary floodplain sediments, Quaternary swamp sediments and Quaternary younger river terraces, Pliocene and Mesozoic sediments and Paleozoic rocks.

A comparative analysis was conducted based on the data of the contents of the analyzed elements in street dust samples with those of the contents of the same elements in soil samples from the Bitola region and with data for soil for the Republic of North Macedonia (Stafilov & Šajn, 2016, 2019) (Table 2). For the comparative analysis, the median values were used as a more stable parameter.

From data presented in Table 2 it can be seen that the contents of the most of the elements are similar with those obtained for soil in the Bitola region and that they correspond in general to the lithogenic origin of the rocks from this area. However, it is visible that the median values for arsenic, cadmium, lead and zinc in road dust are high than the median of the soil from the same region, showing the influence of the urban activities and the pollution from the thermoelectric power plant due to the fly ash emission. Namely, the contents of As, Cd, Cu, Pb and Zn in fly ash is 31, 2.3, 42, 102 and 1002 mg/kg compared with their content in the surrounding soil of 18, 0.28, 20, 10 and 59 mg/kg, respectively (Stafilov et al., 2018).

T a b l e 1

*Descriptive statistics for the contents of the elements in road dust from the Bitola region (n = 39)*

| Element | Unit | X | X(BC) | Md | Min | Max | $P_{10}$ | $P_{90}$ | $P_{25}$ | $P_{75}$ | S | $S_x$ | CV | A | E | A(BC) | E(BC) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | % | 2.1 | 1.8 | 2.1 | 0.22 | 6.8 | 0.66 | 3.9 | 1.1 | 2.4 | 1.3 | 0.21 | 62 | 1.46 | 3.49 | 0.00 | 0.32 |
| As | mg/kg | 20 | 19 | 20 | 5.5 | 40 | 6.0 | 33 | 14 | 26 | 8.6 | 1.4 | 43 | 0.12 | –0.51 | –0.11 | –0.55 |
| B | mg/kg | 22 | 22 | 22 | 6.5 | 36 | 14 | 32 | 17 | 26 | 7.1 | 1.1 | 32 | –0.02 | –0.43 | –0.06 | –0.40 |
| Ba | mg/kg | 190 | 170 | 170 | 28 | 550 | 110 | 340 | 130 | 210 | 100 | 16 | 55 | 1.70 | 3.87 | 0.08 | 1.70 |
| Ca | % | 4.4 | 3.9 | 4.2 | 0.76 | 12 | 1.5 | 8.1 | 2.3 | 5.8 | 2.5 | 0.39 | 56 | 0.81 | 0.52 | –0.04 | –0.40 |
| Cd | mg/kg | 0.55 | 0.44 | 0.49 | 0.10 | 1.4 | 0.10 | 1.2 | 0.17 | 0.86 | 0.40 | 0.064 | 72 | 0.51 | –0.90 | –0.12 | –1.37 |
| Co | mg/kg | 4.0 | 3.5 | 3.3 | 1.1 | 8.9 | 1.6 | 7.4 | 2.4 | 5.8 | 2.2 | 0.35 | 54 | 0.66 | –0.62 | –0.03 | –0.89 |
| Cr | mg/kg | 33 | 33 | 33 | 5.9 | 60 | 19 | 48 | 24 | 43 | 12 | 1.9 | 36 | 0.11 | –0.24 | –0.03 | –0.14 |
| Cu | mg/kg | 20 | 18 | 20 | 1.1 | 51 | 5.4 | 44 | 12 | 26 | 12 | 1.9 | 60 | 0.94 | 0.66 | –0.00 | 0.18 |
| Fe | % | 1.2 | 1.2 | 1.1 | 0.23 | 2.5 | 0.60 | 1.9 | 0.82 | 1.6 | 0.51 | 0.082 | 42 | 0.51 | –0.28 | –0.01 | –0.13 |
| K | % | 1.1 | 1.1 | 1.1 | 0.52 | 1.6 | 0.82 | 1.5 | 0.89 | 1.3 | 0.24 | 0.038 | 22 | 0.07 | –0.30 | –0.02 | –0.22 |
| Li | mg/kg | 5.5 | 4.6 | 4.6 | 0.87 | 25 | 2.0 | 7.6 | 3.2 | 6.4 | 4.0 | 0.65 | 73 | 3.40 | 15.50 | 0.01 | 1.96 |
| Mg | % | 0.34 | 0.21 | 0.19 | 0.042 | 2.0 | 0.078 | 0.64 | 0.10 | 0.49 | 0.39 | 0.063 | 114 | 2.71 | 8.91 | 0.04 | –0.62 |
| Mn | mg/kg | 470 | 460 | 450 | 93 | 850 | 250 | 680 | 370 | 550 | 160 | 26 | 35 | 0.25 | 0.34 | 0.02 | 0.40 |
| Na | % | 1.0 | 0.93 | 0.88 | 0.37 | 2.6 | 0.55 | 1.4 | 0.79 | 1.3 | 0.43 | 0.069 | 42 | 1.64 | 4.18 | –0.01 | 0.62 |
| Ni | mg/kg | 17 | 17 | 17 | 4.8 | 31 | 7.8 | 26 | 11 | 23 | 7.0 | 1.1 | 41 | 0.14 | –0.76 | –0.10 | –0.74 |
| P | % | 0.066 | 0.060 | 0.058 | 0.015 | 0.18 | 0.037 | 0.11 | 0.044 | 0.080 | 0.033 | 0.005 | 50 | 1.66 | 3.46 | 0.01 | 1.37 |
| Pb | mg/kg | 14 | 11 | 11 | 0.93 | 67 | 4.3 | 24 | 6.0 | 19 | 13 | 2.0 | 88 | 2.64 | 8.79 | 0.03 | 1.24 |
| Sr | mg/kg | 140 | 120 | 130 | 46 | 580 | 77 | 190 | 100 | 150 | 82 | 13 | 58 | 4.25 | 22.82 | –0.10 | 3.18 |
| V | mg/kg | 53 | 50 | 49 | 14 | 100 | 28 | 93 | 39 | 67 | 23 | 3.6 | 43 | 0.57 | –0.45 | –0.02 | –0.37 |
| Zn | mg/kg | 84 | 78 | 72 | 15 | 210 | 46 | 150 | 56 | 110 | 40 | 6.3 | 47 | 1.03 | 1.40 | 0.02 | 0.53 |

X – arithmetical average; X(BC) – arithmetical average after Box-Cox method; Md – median; Min – minimum; Max – maximum; $P_{10}$ – $10^{th}$ percentile; $P_{90}$ – 90 percentile; $P_{25}$ – $25^{th}$ percentile; $P_{75}$ –$75^{th}$ percentile; S – standard deviation; $S_x$ – standard error; CV – coefficient of variation; A – skewness; E – kurtosis; BC – Box-Cox transformed values

T a b l e 2

*Comparison of the median, minimal and maximal values for the content of analyzed elements in street dust with those for soil from the Bitola region and from the Republic of North Macedonia*

| Element | Unit | Street dust | | Soil | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Bitola region (this study) | | Bitola region (Stafilov et al., 2018) | | North Macedonia (Stafilov & Šajn, 2016) | | Dutch standard | |
| | | Md | Min–Max | Md | Min–Max | Md | Min–Max | Target | Intervention |
| Al | % | 2.1 | 0.22–6.8 | 2.1 | 0.67–6.2 | 1.3 | 0.05–35 | – | – |
| As | mg/kg | 20 | 5.5–40 | 18 | 2.1–150 | 10 | 1.0–720 | 29 | 55 |
| B | mg/kg | 22 | 6.5–36 | 18 | 0.10–97 | – | – | – | – |
| Ba | mg/kg | 170 | 28–550 | 320 | 19–1500 | 430 | 6–2900 | 200 | 625 |
| Ca | % | 4.2 | 0.76–12 | 0.54 | 0.019–11 | 1.3 | 0.05–35 | – | – |
| Cd | mg/kg | 0.49 | 0.10–1.4 | 0.28 | 0.10–4.5 | 0.30 | 0.01–110 | 0.8 | 12 |
| Co | mg/kg | 3.3 | 1.10–8.9 | 8.6 | 1.20–31 | 17 | 0.5–150 | 20 | 240 |
| Cr | mg/kg | 33 | 5.9–60 | 56 | 9.3–650 | 88 | 5.0–2700 | 100 | 380 |
| Cu | mg/kg | 20 | 1.1–51 | 20 | 0.30–250 | 28 | 1.6–270 | 36 | 190 |
| Fe | % | 1.1 | 0.23–2.5 | 2.0 | 0.53–5.2 | 3.5 | 0.03–12 | – | – |
| K | % | 1.1 | 0.52–1.6 | 1.8 | 0.19–3.1 | 1.9 | 0.02–5.3 | – | – |
| Li | mg/kg | 4.6 | 0.87–25 | 13 | 1.5–93 | 26 | 1.8–210 | – | – |
| Mg | % | 0.19 | 0.042–2.0 | 0.41 | 0.003–1.3 | 0.94 | 0.12–13 | – | – |
| Mn | mg/kg | 450 | 93–850 | 540 | 170–2400 | 900 | 17–10000 | – | – |
| Na | % | 0.88 | 0.37–2.6 | 1.1 | 0.067–3.7 | 1.3 | 0.007–3.7 | – | – |
| Ni | mg/kg | 17 | 1.0–93 | 24 | 1.8–76 | 46 | 2.1–2500 | 35 | 210 |
| P | mg/kg | 0.058 | 0.015–0.18 | 0.050 | 0.012–1.9 | 0.062 | 0.011–0.39 | – | – |
| Pb | mg/kg | 11 | 0.93–67 | 10 | 1.0–1500 | 32 | 1.2–10000 | 85 | 530 |
| Sr | mg/kg | 130 | 46–580 | 70 | 3.6–420 | 140 | 21–1400 | – | – |
| V | mg/kg | 49 | 14–100 | 65 | 14–230 | 89 | 1.0–470 | – | – |
| Zn | mg/kg | 72 | 15–210 | 59 | 1.4–3500 | 83 | 8.0–10000 | 140 | 720 |

Md – median; Min – minimum; Max –maximum

The matrix of correlation coefficients between all of the analyzed elements is given in Table 3. By applying bivariate statistics, the degree of correlation between the analyzed elements in the soil samples was determined. The values for the contents of every element were correlated with the values for the contents of the other elements. All correlation coefficients between all elements are represented in the matrix of correlation coefficients (Table 3).

Table 3

*Matrix of correlation coefficients (n = 39)*

| | Al | As | B | Ba | Ca | Cd | Co | Cr | Cu | Fe | K | Li | Mg | Mn | Na | Ni | P | Pb | Sr | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Al** | 1.00 | | | | | | | | | | | | | | | | | | | | |
| **As** | 0.03 | 1.00 | | | | | | | | | | | | | | | | | | | |
| **B** | 0.13 | –0.07 | 1.00 | | | | | | | | | | | | | | | | | | |
| **Ba** | 0.81 | 0.13 | 0.17 | 1.00 | | | | | | | | | | | | | | | | | |
| **Ca** | 0.08 | 0.01 | –0.20 | 0.09 | 1.00 | | | | | | | | | | | | | | | | |
| **Cd** | –0.33 | 0.01 | 0.10 | –0.31 | –0.14 | 1.00 | | | | | | | | | | | | | | | |
| **Co** | 0.20 | –0.01 | 0.46 | 0.09 | –0.12 | 0.01 | 1.00 | | | | | | | | | | | | | | |
| **Cr** | 0.42 | –0.25 | 0.56 | 0.34 | –0.29 | 0.09 | 0.54 | 1.00 | | | | | | | | | | | | | |
| **Cu** | 0.22 | –0.19 | 0.57 | 0.20 | –0.02 | –0.06 | 0.44 | 0.71 | 1.00 | | | | | | | | | | | | |
| **Fe** | 0.55 | –0.28 | 0.61 | 0.38 | –0.32 | 0.00 | 0.61 | 0.82 | 0.64 | 1.00 | | | | | | | | | | | |
| **K** | 0.42 | 0.14 | 0.27 | 0.55 | –0.57 | –0.12 | 0.15 | 0.45 | 0.32 | 0.40 | 1.00 | | | | | | | | | | |
| **Li** | 0.56 | 0.24 | 0.46 | 0.54 | –0.01 | –0.14 | 0.40 | 0.40 | 0.43 | 0.47 | 0.55 | 1.00 | | | | | | | | | |
| **Mg** | 0.23 | 0.07 | –0.09 | 0.31 | 0.55 | –0.13 | 0.03 | –0.10 | –0.08 | –0.09 | –0.25 | 0.14 | 1.00 | | | | | | | | |
| **Mn** | 0.20 | –0.10 | 0.66 | 0.16 | –0.44 | 0.11 | 0.60 | 0.65 | 0.63 | 0.82 | 0.36 | 0.36 | –0.18 | 1.00 | | | | | | | |
| **Na** | 0.56 | 0.00 | 0.14 | 0.52 | –0.26 | –0.16 | –0.26 | 0.16 | 0.06 | 0.27 | 0.52 | 0.12 | –0.15 | 0.16 | 1.00 | | | | | | |
| **Ni** | 0.32 | –0.32 | 0.40 | 0.28 | –0.04 | –0.11 | 0.65 | 0.80 | 0.69 | 0.68 | 0.27 | 0.41 | 0.02 | 0.51 | –0.18 | 1.00 | | | | | |
| **P** | 0.15 | –0.07 | 0.50 | 0.16 | –0.44 | 0.13 | 0.48 | 0.58 | 0.47 | 0.61 | 0.44 | 0.29 | –0.38 | 0.64 | 0.14 | 0.42 | 1.00 | | | | |
| **Pb** | 0.01 | –0.43 | 0.26 | 0.22 | 0.03 | –0.04 | 0.06 | 0.23 | 0.35 | 0.12 | 0.22 | 0.05 | –0.05 | 0.06 | 0.06 | 0.30 | 0.05 | 1.00 | | | |
| **Sr** | 0.51 | –0.15 | 0.26 | 0.56 | 0.30 | 0.08 | 0.03 | 0.26 | 0.29 | 0.37 | 0.05 | 0.14 | 0.23 | 0.25 | 0.46 | 0.16 | 0.32 | 0.12 | 1.00 | | |
| **V** | 0.29 | –0.24 | 0.60 | 0.18 | –0.52 | 0.13 | 0.51 | 0.70 | 0.51 | 0.87 | 0.39 | 0.27 | –0.21 | 0.89 | 0.30 | 0.48 | 0.69 | 0.05 | 0.33 | 1.00 | |
| **Zn** | 0.18 | –0.23 | 0.32 | 0.19 | 0.32 | –0.15 | 0.37 | 0.43 | 0.66 | 0.36 | 0.13 | 0.39 | 0.13 | 0.26 | –0.11 | 0.54 | 0.37 | 0.38 | 0.30 | 0.22 | 1.00 |

In factor analysis the distribution is reduced to four synthetic variables (F1 to F4). As it can be seen from the results obtained by factor analysis (Table 4), three factors (i.e. associations of elements) were obtained F1 (Ni, Cr, Cu, Fe, Co, Mn, Zn, V and P), F2 (Ba, Al, Na and Sr) and F3 (Ca and Mg). A total of 21 elements were reduced by factor analysis to 15 elements, which had a total factor loading of 74.1% of the variability (Table 4). The rest of the elements (As, B, Cd, K, Li and Pb) were eliminated from further analysis because they had a low share of communality or low tendency to form independent factors.

T a b l e 4

*Matrix of dominant rotated factor loadings (n = 39, 15 selected elements)*

| Element | F1 | F2 | F3 | Comm |
|---|---|---|---|---|
| Ni | **0.88** | 0.06 | 0.10 | 78.1 |
| Cr | **0.82** | 0.27 | –0.21 | 78.5 |
| Cu | **0.82** | 0.13 | 0.02 | 68.2 |
| Fe | **0.79** | 0.41 | –0.32 | 89.4 |
| Co | **0.79** | –0.10 | –0.03 | 62.9 |
| Mn | **0.74** | 0.17 | –0.47 | 79.1 |
| Zn | **0.68** | 0.06 | 0.40 | 62.9 |
| V | **0.67** | 0.29 | –0.56 | 84.8 |
| P | **0.63** | 0.14 | –0.47 | 63.8 |
| Ba | 0.16 | **0.86** | 0.17 | 78.6 |
| Al | 0.23 | **0.85** | 0.10 | 78.4 |
| Na | –0.19 | **0.81** | –0.39 | 83.6 |
| Sr | 0.22 | **0.73** | 0.17 | 61.7 |
| Ca | –0.09 | 0.06 | **0.91** | 83.4 |
| Mg | –0.02 | 0.23 | **0.72** | 57.5 |
| Prp.Totl | 35.7 | 20.7 | 17.6 | 74.1 |
| Eigenvalue | 6.31 | 2.65 | 2.15 | |
| Expl.Var | 5.36 | 3.11 | 2.64 | |

F1, F2, F3 – Factor loadings; Var – Variance (%);
Com – Communality (%);
Prp.Tol – total amount of the explained system variance;
Expl.Var – particular component variance;
Eigenvalue – Eigene value

The dendrogram obtained by the application of cluster analysis is given in Figure 3. In the dendrogram the elements are divided into two major cluster and three sub-clusters according to the degree of correlation between them. The first sub-cluster includes the elements Al, Ba, Na and Sr which are included in Factor 2 of the matrix of loading of the dominant rotating factors (Table 4). The second sub-cluster is composed of Ca and Mg which belong to Factor 3 of the factor analysis (Table 4). The second cluster consists of Co, Cr, Ni, Cu, Fe, Mn, V and P belongs to Factor 1 (Table 4).

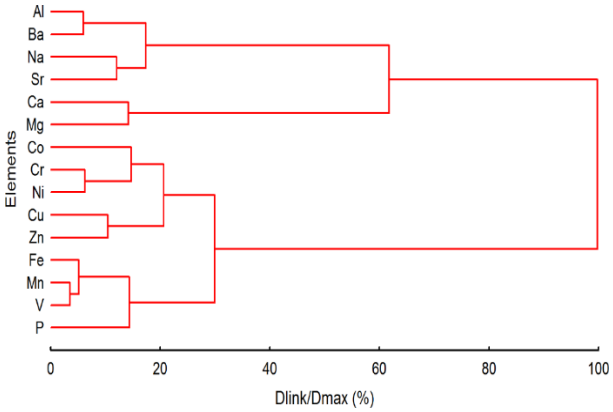


**Fig. 3.** Dendrogram from the cluster analysis of street dust analysis

**Factor 1 (Ni, Cr, Cu, Fe, Co, Mn, Zn, V and P)**. The spatial distribution map of the factor scores of factor F1 (Figure 4) shows that these elements are present in varying concentrations throughout the studied area. Spatial distribution of the factor scores of Factor 1 is presented in Figure 4. Higher contents of these elements are found in the soil samples from the central part of the study where Quaternary sediments are dominant geological formations as well as on the Baba mountain where Paleozoic schist and granites prevailed. The distributions of the copper (Figure 5) and zinc (Figure 6) from this association show their higher contents in the roads to the north of the REK Bitola, and south of the city of Bitola which is probably due to the industrial and urban activities.

**Factor 2 (Ba, Al, Na and Sr)** is typical lithogenic association. The spatial distribution map of the factor scores of factor F2 is presented in Figure 7. This map shows that these elements are present in higher contents in road dust samples from the northern and north-western part of the study from area where Paleozoic granites and schists are dominant geological formations.

**Factor 3 (Ca, Mg)** is also typical lithogenic association. The spatial distribution map of the factor scores of factor F3 is presented in Figure 8. This map shows that these elements are present in higher contents in the road dust from the central western and central eastern part of the study area. Pliocene unconsolidated sediments and Proterozoic gneisses are dominant geological formations.

Some of the analyzed elements are not included in the factor's associations (As, B, Cd, K, Li and Pb). Even typical potentially toxic elements, such as arsenic (Figure 9), cadmium (Figure 10) and

lead (Figure 11), are not isolated into anthropogenic geochemical associations by multivariate statistical methods showing trends of local anthropogenic enrichment. Thus, the spatial distribution maps show their higher contents in the road dusts from the north and south of the city of Bitola and around of the REK Bitola clearly indicating the influence of the industrial and urban activities from the city and the distribution of dust and fly ash from thermoelectrical power plant.

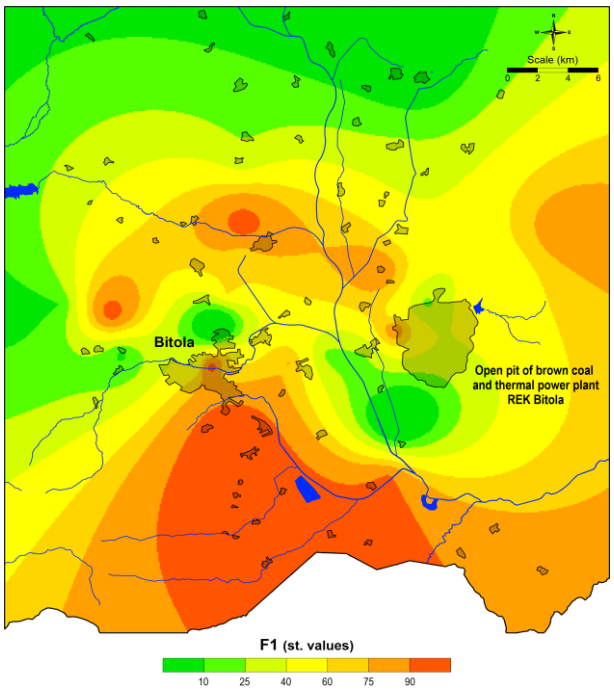


**Fig. 4**. Spatial distribution of factor scores of F1 (Ni, Cr, Cu, Fe, Co, Mn, Zn, V and P)

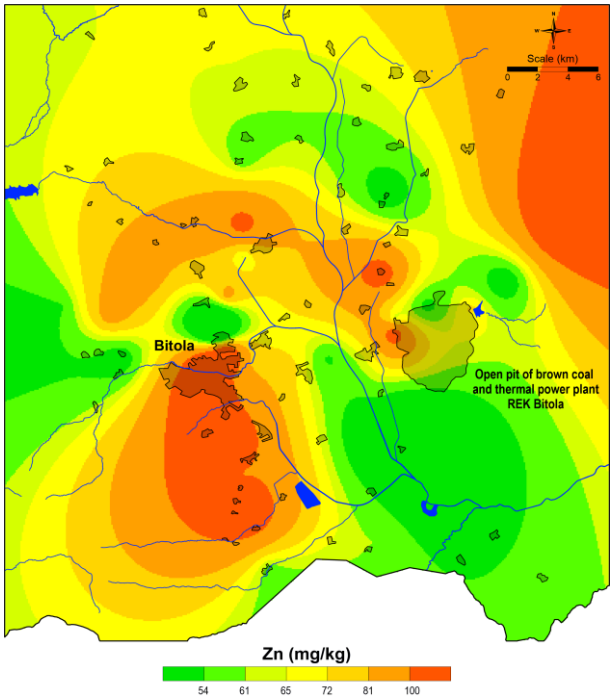


**Fig. 6.** Spatial distribution of zinc

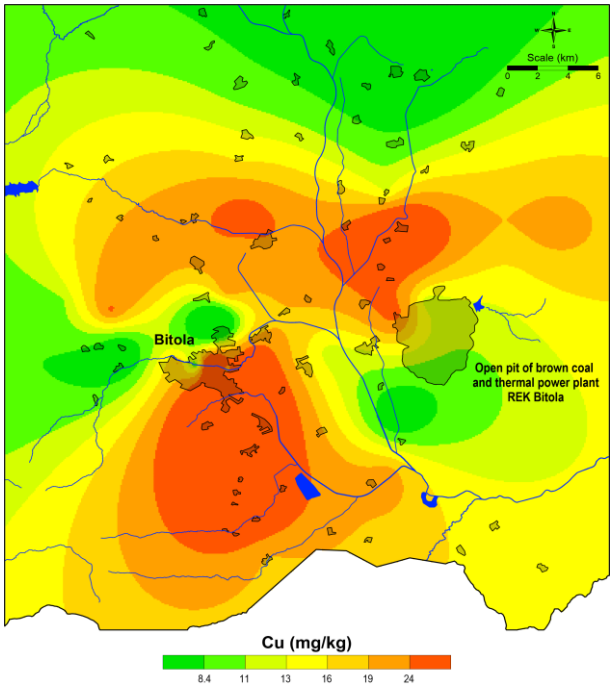


**Fig. 5.** Spatial distribution of copper

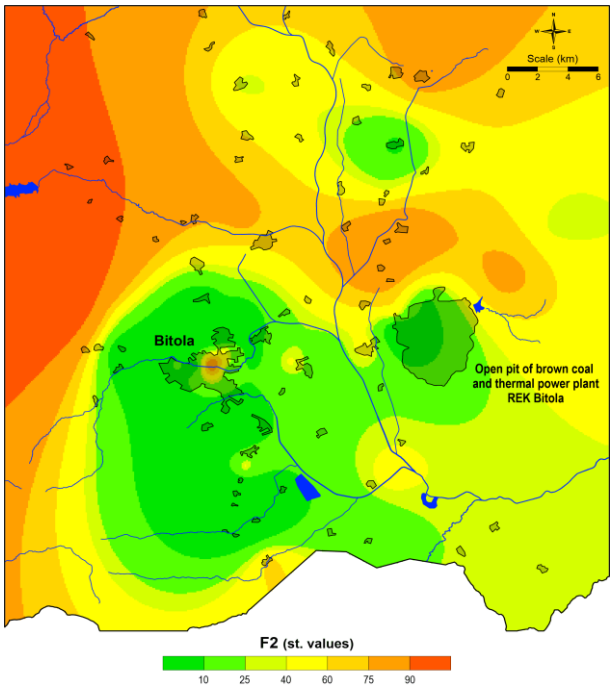


**Fig. 7**. Spatial distribution of factor scores of F2 (Ba, Al, Na and Sr)

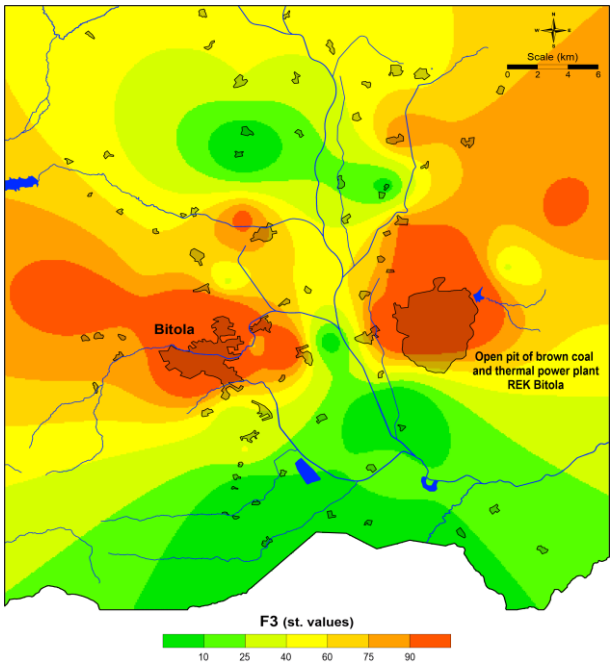


**Fig. 8**. Spatial distribution of factor scores of F3 (Ca and Mg)

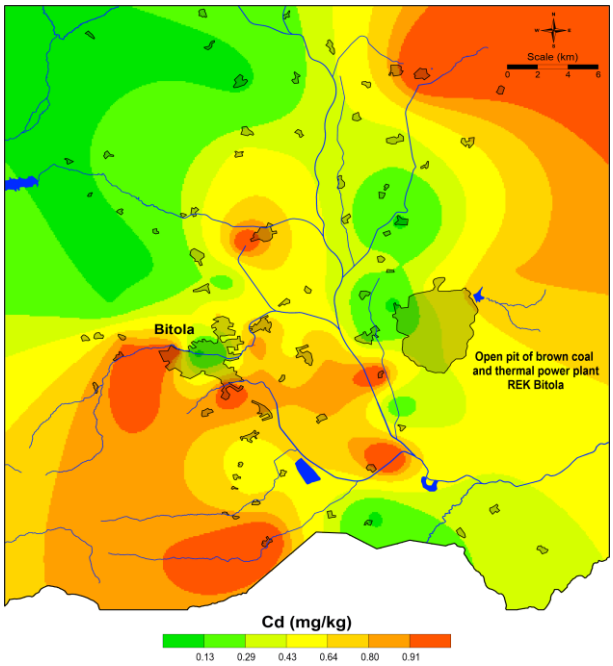


**Fig. 10.** Spatial distribution of cadmium

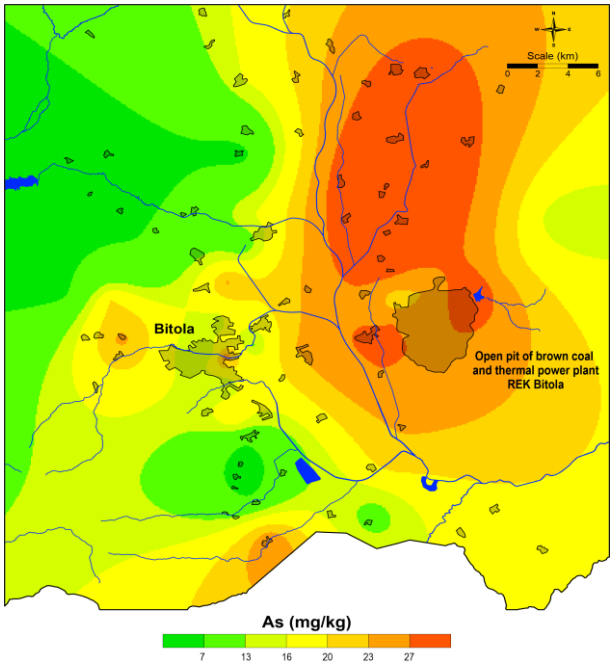


**Fig. 9.** Spatial distribution of arsenic

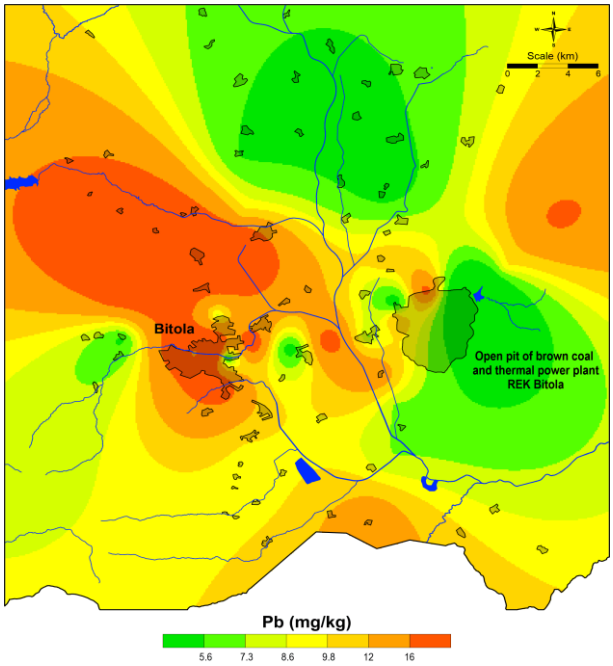


**Fig. 11.** Spatial distribution of lead

## CONCLUSION

The analyzed elements in dusts collected from the streets and roads in the Bitola region are grouped into 3 elements associations: Factor 1 (Ni, Cr, Cu, Fe, Co, Mn, Zn, V and P), Factor 2 (Ba, Al, Na and Sr) and Factor 3 (Ca, Mg). It was found that the most of the elements from Factors 1 and 2 are following the lithogenic characteristics of the region. However, the distributions of the arsenic, copper, lead and zinc have higher contents in the road dusts from the north of the city of Bitola and around of the REK Bitola showing influence of the industrial and urban activities from the city indicating the distribution of fly ash from thermoelectrical power plant.

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Р е з и м е

# МУЛТИЕЛЕМЕНТНА ДИСТРИБУЦИЈА НА ТЕШКИ МЕТАЛИ ВО ПРАВОТ ОД УЛИЦИТЕ И ПАТИШТАТА ВО РЕГИОНОТ НА БИТОЛА, СЕВЕРНА МАКЕДОНИЈА

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**Клучни зборови**: патен прав; загадување; тешки метали; термоелектрична централа; Битола; Северна Македонија

Презентирани се резултатите од систематското испитување на просторната дистрибуција на елементи во траги во примероци прав од патишта и улици емени од улиците на градот Битола и од патиштата од јужниот дел на Пелагониската Котлина, Северна Македонија, област позната по работата на термоелектричната централа (РЕК Битола) која користи јаглен. Во испитуваниот регион се земени примероци од 4 главни магистрални патишта во правец север–југ и исток–запад. Вкупно се земени 39 примероци од патен прав. За определување на 21 елемент (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V и Zn) е применета атомската емисиона спектрометрија со индуктивно спрегната плазма (ICP-AES). Обработката на добиената содржина на елементите е извршена со примена на параметриска и непараметриска анализа, додека за нормализацијата на податоците е применета трансформацијата *Box-Cox*. Универзалниот kriging-метод со линеарна вариограмна интерполација е применет за конструирање на картите за просторна дистрибуција на факторните вредности и на анализираните елементи. Врз основа на добиените резултати од факторната анализа, утврдени се три геогени асоцијации на елементи дефинирани со три фактори, F1 (Ni, Cr, Cu, Fe, Co, Mn, Zn, V и P), F2 (Ba, Al, Na и Sr) и F3 (Ca и Mg). Преостанатите елементи (As, B, Cd, Na, Pb и Zn) се елиминирани поради тоа што тие имаат мал удел во комуналноста или имаат мала тенденција да формираат независен фактор. Дури и типични потенцијално токсични елементи, како што се арсенот, кадмиумот, оловото и цинкот, не се издвојуваат во посебна антропогена геохемиска асоцијација со мултиваријантните статистички методи, иако покажуваат одреден тренд на локално антропогено зголемување на нивната содржина. Така содржината на арсенот, бакарот, олово и цинкот е повисока во правот земен од патиштата северно и јужно од градот Битола и во околината на РЕК Битола, што е резултат на влијанието на урбаните и индустриските активности во градот и укажува на дистрибуцијата на пепелта од термоелектраната.