324
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SPATIAL DISTRIBUTION OF ZINC IN SOIL FROM THE CITY OF SKOPJE AND ITS ENVIRONS, REPUBLIC OF MACEDONIA

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A b s t r a c t: The results of the spatial distribution of zinc in topsoil (0–10 cm) over the city of Skopje, Republic of Macedonia, are reported. The soil samples from 233 previously defined locations in the study area were collected. Inductively coupled plasma – atomic emission spectrometry (ICP-AES) was applied for the determination of zinc. Data analysis and construction of the map were performed using the Statistica (ver. 9), AutoDesk Map (ver. 2008) and Surfer (ver. 9) software's. It was found that the median content of zinc in the topsoil for the entire study area is 100 mg/kg (with a range of 23–18000 mg/kg) which exceeds the estimated Macedonian and European zinc median contents in topsoil by a factor of 1.2 and 1.9, respectively. It is evident that the content of zinc is high in the topsoils from the industrial areas (156 mg/kg) exceeding the target value of Dutch standards (140 mg/kg) which is a result of contamination, mainly by dust from the iron and steel works.

Key words: zinc; soil; spatial distribution; Skopje; Republic of Macedonia

INTRODUCTION

Zinc is the 22[nd] most abundant element in the Earth's upper continental crust, with an estimated abundance of 75 mg/kg. The global average amount of Zn in soils is 90 mg/kg (Bowen, 1979) and in European topsoil is 68 mg/kg. Zinc occurs in oxidation state +2 and has five naturally occurring stable isotopes. Many naturally occurring Zn minerals exist of which sphalerite (ZnS), smithsonite ($ZnCO_3$), zincite (ZnO), vurcite (ZnS), ganite ($ZnAl_2O_4$) and hemimorfite [$Zn_4(OH)_2Si_2O_7\cdot H_2O$] are a few examples. Zinc is present as an accessory element in many common minerals, such as pyroxene, amphibole, mica garnet, sulphides and magnetite (Stafilov & Šajn, 2016). Zinc typically exhibits elevated concentrations in mafic rocks (in basalt about 100 mg/kg) and lower values in felsic rocks (in granite about 50 mg/kg). Most sediment rocks contain between 20 and 100 mg/kg Zn (shale and schist have the highest values) (Stafilov & Šajn, 2016).

The most important anthropogenic sources of Zn are the metallurgy industry, burning of fossil fuels, mines and Zn ore processing. Most Zn is used in car industries, alloys and galvanzation procedures, the colour industry, lacquers and ointments. Zinc is employed to form numerous alloys with other metals. Zinc is also used extensively to galvanize other metals such as iron, to prevent corrosion. Zinc oxide is widely used in the manufacture of paints, rubber products, cosmetics, pharmaceuticals, floor coverings, plastics, printing inks and soap etc. Therefore, Zn is often present in urban regions where it is mostly generated from industrial activities and traffic (Adriano, 1986- Šajn et al., 1998; Crnković et al., 2006; Stafilov et al., 2009, 2010).

Zinc is an essential element for most living organism with important role in enzymes processes and cellular metabolism (Sandstead, 1994), in immune function, protein synthesis, DNA synthesis, and cell division (Prasad, 1995). Even the toxicity of Zn is relatively low there are cases when poisoning with Zn can occur in both acute and chronic forms. Acute adverse effects of high zinc intake include nausea, vomiting, loss of appetite, abdominal cramps, diarhea and headaches. The chronic effects are expressed as low copper status, altered iron function, reduced immune function, and reduced levels of high-density lipoproteins (Rink & Gabriel, 2000) or in raising the possibility that chronically high intakes of zinc adversely affect some aspects of urinary physiology (Johnson et al., 2007).

Previously Jančev et al. (2010, 2014) have published data for the contents of several elements in soils from the Skopje Valley including Zn (Pb, Zn, Cu, Ni, Cr, Ba, Y and As) determined by ESA method (emission spectral analysis) with very high calculated average and median values for most of these elements, which is as a result of the analytical technique applied. Therefore the results present in this work are the first detailed data about the content of zinc in the soil of the city of Skopje. Thus, the purpose of this work is monitoring and determination the distribution of zinc in the soil in the city of Skopje, Republic of Macedonia, and its immediate surroundings. From the investigated region topsoil samples (0–10 cm) were taken from 233 locations. The content of zinc was analyzed using atomic emission spectroscopy with inductive coupled plasma (ICP-AES). All data about the content of zinc were statistically processed and from the obtained results distribution map was prepared.

STUDY AREA

Skopje, the capital and the largest city in the Republic of Macedonia, occupies the northern part of the Republic of Macedonia. The Skopje region covers an area of 1815 km^2 with a width of 10 km and in a length of 25 km from which the urban area covers an area of about 225 km^2 (Figure 1). The region is clearly defined from the natural surroundings by mountain massifs. To the south the Mt. Jakupica separates it from the Pelagonia Valley; to the east the hill of Gradeški Rid separates it from Ovče Pole, to the north-east it is open to Kumanovo Valley through the Romanovce Downhill, and to the north the Mt. Skopska Crna Gora separates it from the Kosovo Valley. To the west the mountain of Žeden separates the Skopje Valley from the Polog Valley (MOEPP, 2009). The city of Skopje has 550,000 inhabitants.

Geographical location and orographic characteristics are the major modifiers of the climate in Skopje Valley: there is no direct influence of the Mediterranean climate and it is directly affected by continental influences, while a typical mountain climate prevails in the higher mountains (Lazarevski, 1993; MOEPP, 2009).

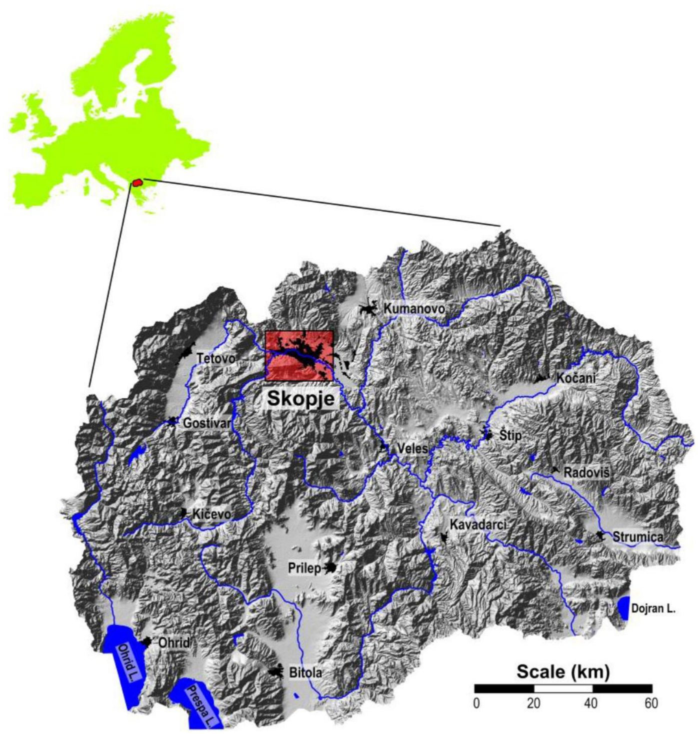

Fig. 1. Location of the investigated area in the Republic of Macedonia

The Skopje Valley is built of Neogene-Quaternary sediments, and its mounts and hilly parts consist of rock masses of various ages (Figure 2). Precambrian rocks are present in the southern part of the valley in various petrographic varieties (gneiss, mica, leptinolites, cipolines and marbles). Magmatic granite rocks are embossed in these rocks in the spots and today are quite changed (i.e. highly metamorphosed). Precambrian rocks are mostly found on the mounts of Kitka and Suva Planina and they penetrate under the Neogene sediments to the valley of the Markova Reka river. In structural view these areas belong to the peripheral part of the Pelagonian horst-anticlinorium and on the mountains of Osoj and Vodno they are in tectonic contact with Paleozoic schists (MOEPP, 2009).

Paleozoic rocks are found in the northern and western brim of the valley, in the mountains of Osoj and Vodno, along the river of Fuš, the mounts of Žeden and Skopska Crna Gora and also near Katlanovo. More petrographic varieties appear (marbles, low crystalline schists, quartzites and granites). From a structural point of view these terrains are part of the Western Macedonian zone, which reaches a deep fault along the Vardar zone. Mesozoic rocks are mainly found in the south, north and north-west of Skopje Valley. The Skopska Crna Gora mountain is mainly built of Paleozoic rocks, and belongs to the Vardar zone (Stafilov & Šajn, 2016). Cenozoic rocks are represented by conglomerates and flysch sediments deposited in older terrains on the flat southern parts of the valley.

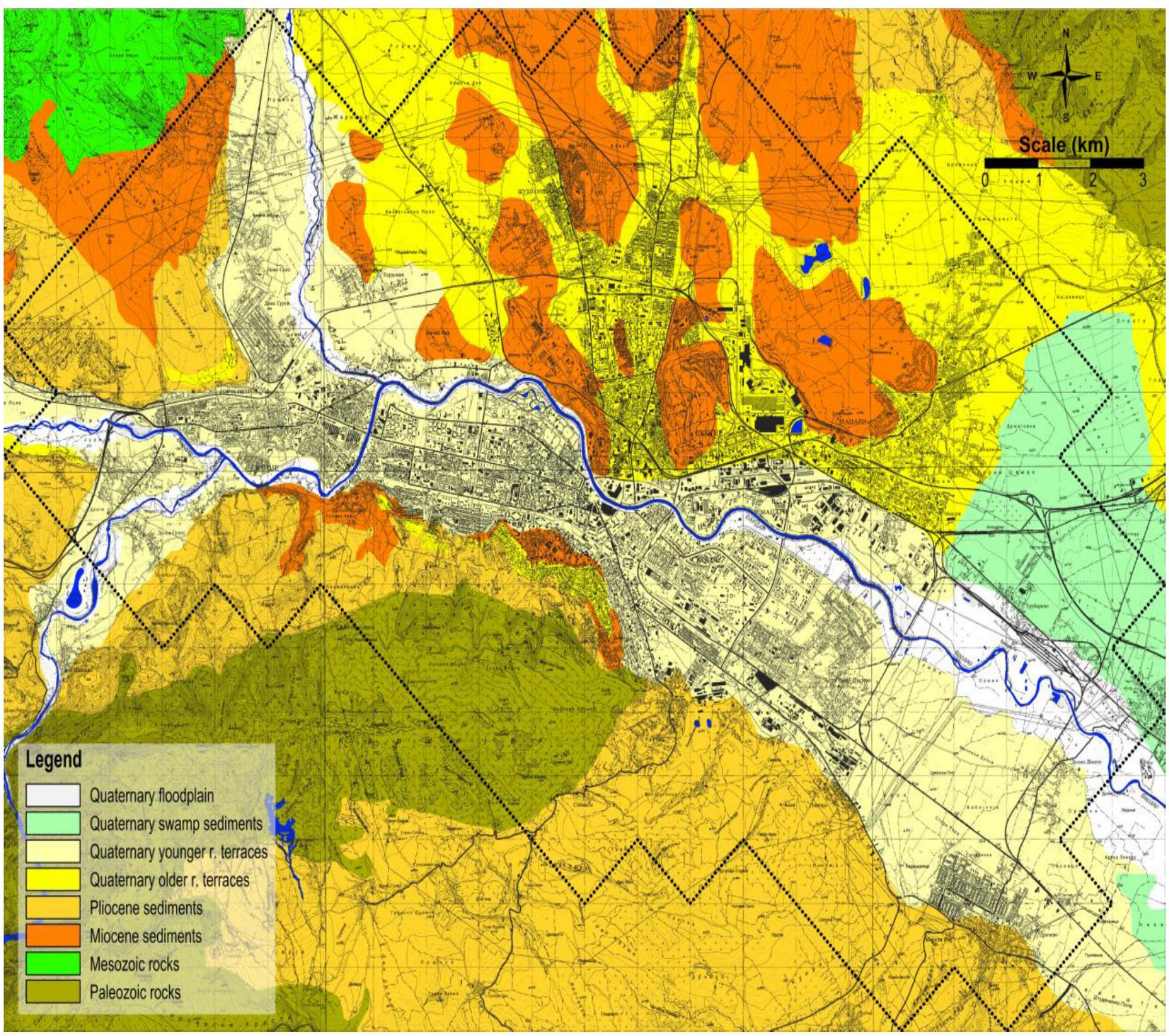

Fig. 2. Geological map of the investigated area

The bottom of the valley mainly consists of Neogene and Quaternary sediments. Neogene sediments are mostly found in the basin of Markova Reka river, between Katlanovo and Taor, near the villages of Brazda, Glumovo and Nerezi; Quaternary sediments and conglomerates are mostly found in the southern part of the valley, while glacial and moren forms are found in the southern basin of the river of Markova Reka, among other places. The most widespread alluvial and proluvial sediments are found at the bottom of the valley from 220 to 240 m (MOEPP, 2009).

A geological map of the investigated area was prepared acording to the Geological Map of the Republic of Macedonia from 1976 (Pendžerkovski & Hadži-Mitrova, 1977) (Figure 2). It can be seen Quaternary floodplain sediments, Quaternary swamp sediments and Quaternary younger river terraces are present along the Vardar, Treska and Lepenec rivers. The mountain Vodno in the south is built mostly of Pliocene sediments and Paleozoic rocks, with some Miocene sediments and Quaternary older river terraces at the foot of the mountain close to the city. Pliocene and Miocene sediments compose the western part of the study area, while the northern part is mostly composed of Quaternary older river terraces and Miocene sediments. Quaternary swamp sediments are present in the eastern part of the study area.

In pedological structure of the Skopje region the following types of soils could be found: vertisols, red soil (terra rossa), cambisols, solonetzes, alluvial soils and skeletal soils. The most prevalent soil type in the Skopje Field are alluvial soils which cover an area of about 10,000 ha, mostly on the right side of the Vardar river and along the lengths of the major Vardar, Treska Lepenec, Pčinja and Markova Reka rivers (MOEPP, 2009). Vertisols appear at all altitudes and they are ranked as relatively fertile soils and are suitable for growing cereals (Stojmilov, 2002). Red soils, present on the Skopska Crna Gora, Jakupica and Žeden mountains in the eastern part of the valley, among other locations, are the oldest soils in the valley. The lower slopes of Mt. Skopska Crna Gora are under deluvial soils. Terra rossa soils appear on the higher hills while cambisols originate from deluvial and alluvial soils. Most of them are present in the north-west part of the area (MOEPP, 2009).

MATERIALS AND METHODS

Sampling, sample preparation and analyses

Samples of surface soil (0–10 cm) were collected for analysis from 233 previously defined locations in the study area (Figure 3). All samples were collected in accordance with specific standards for collecting soil. Each sample must be representative, which means each sample should be a mixture of five samples collected in an area of 10 × 10 m. It is important to collect the sample at each defined coordinate. Figure 3 presents a map showing the soil sampling locations in the city of Skopje and its surroundings. The soil samples were packed in polyethylene bags marked with a code and sample number.

The soil samples brought to the laboratory were cleaned and homogenized and dried at room temperature or in a drying oven at 40°C. Subsequently, they were passed through a 2 mm sieve and ground in a porcelain mortar until reaching a final particle size of 125 μm. For decomposition of soil samples, a wet process of decomposition was applied via the addition of a mixture of acids. In PTFE vessels, 5 ml of concentrated HNO_3 was added to 0.2500 g of fine-ground sample; the process was repeated until brown vapours appeared. Then, 2 ml of $HClO_4$ and 5–10 ml of HF were added. When the soil samples are completely dissolved, 5 ml of H_2O and 1 ml of HCl were added. This is performed once or twice, depending on whether the soil was completely dissolved. Finally, dissolved sample was filtered and transferred to a 25 ml calibrated flask and made up to the mark with redistilled water.

The prepared solutions were analyzed by atomic emission spectrometry with inductively coupled plasma (ICP-AES) according to the instrumental conditions previously given by Balabanova et al. (2011).

Data processing and preparation of distribution maps

From the obtained results descriptive statistics were prepared and multivariate factor analyses by R-method were applied in order to identify the associations of the chemical elements (Reimann et al., 2002). Spatial distribution maps were prepared for each factor using universal kriging method with a linear variogram interpolation.

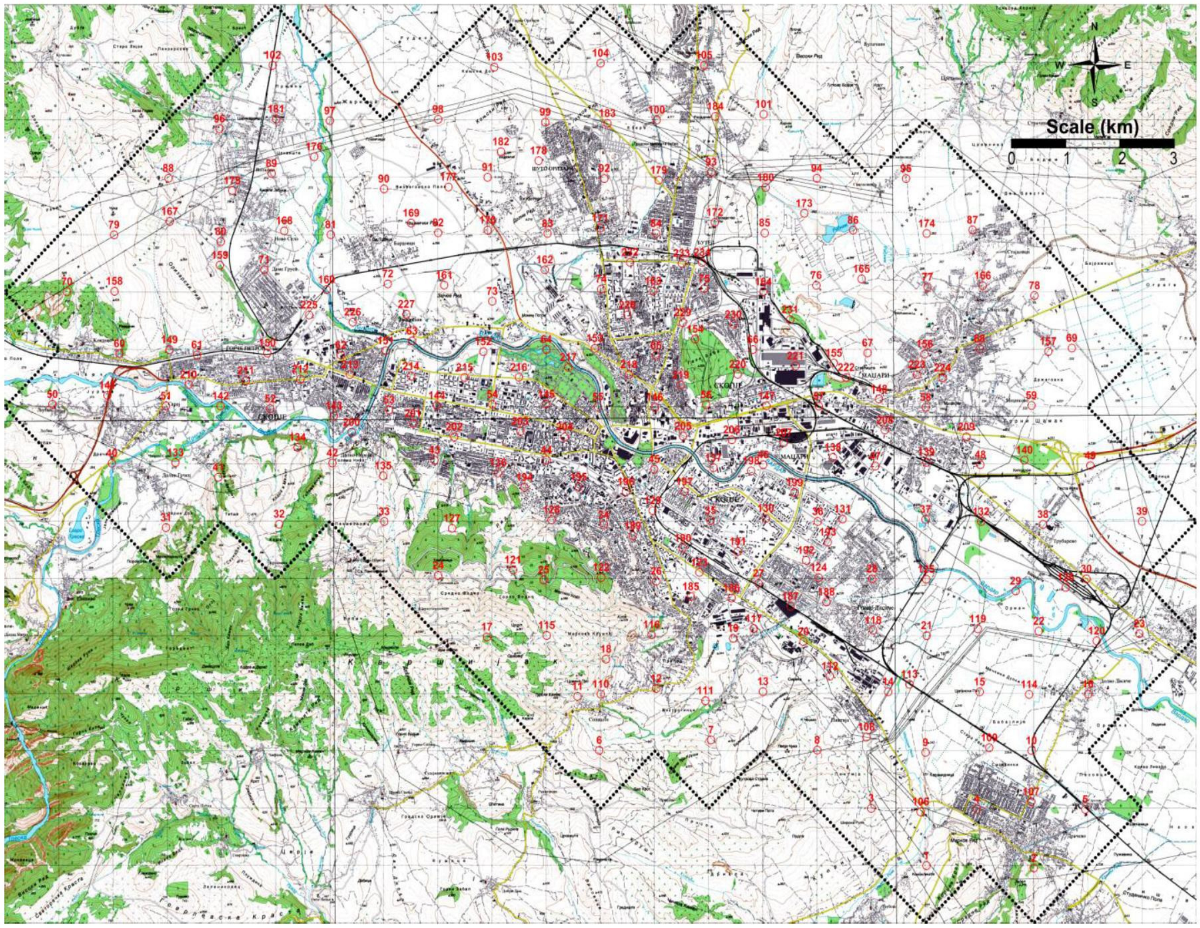

Fig. 3. Topographic map of the investigated area with the sampling locations

RESULTS AND DISCUSSION

Data from the descriptive statistics of measurements of zinc in topsoil from the city of Skopje are given in Table 1 and its spatial distribution is presented on Figure 4. The average content of Zn in soil from the investigated area is 230 mg/kg, with a minimum value of 23 mg/kg and a maximum determined content of 18000 mg/kg. The median value for the content of Zn in soil is 100 mg/kg. The highest content of Zn was found in the soil collected from the eastern part of Skopje (Madžari, eastern industrial zone and the central part of the city). A higher content of Zn was also found in the soil samples collected from the northern part (Figure 4). A higher content of Zn was also found in smaller areas in the south-eastern, southern and western parts of Skopje.

According to the geological formations, a higher content of Zn was found in the soil over the Miocene sediments and Quaternary young and old terraces (Table 2, Figures. 4 and 5). The average content of Zn according to the geological formations ranges from 79 to 118 mg/kg, with the lowest average content in soil over the Pliocene sediments (79 mg/kg) and the highest average content (118 mg/kg) in soils over the Quaternary old terraces (Table 2).

Table 1

Descriptive statistics for the content of zinc in surface soil (mg/kg)

n	X	X(BC)	Md	Min	Max	P_{10}	P_{25}	P_{75}	P_{90}
233	230	100	100	23	18000	69	82	130	200

n = number of soil samples; X = arithmetical average; X(BC) = arithmetical average after Box-Cox method; Md = median; Min = minimum; Max = maximum; P_{10} = 10th percentile; P_{25} = 25th percentile; P_{75} = 75th percentile; P_{90} = 90 percentile

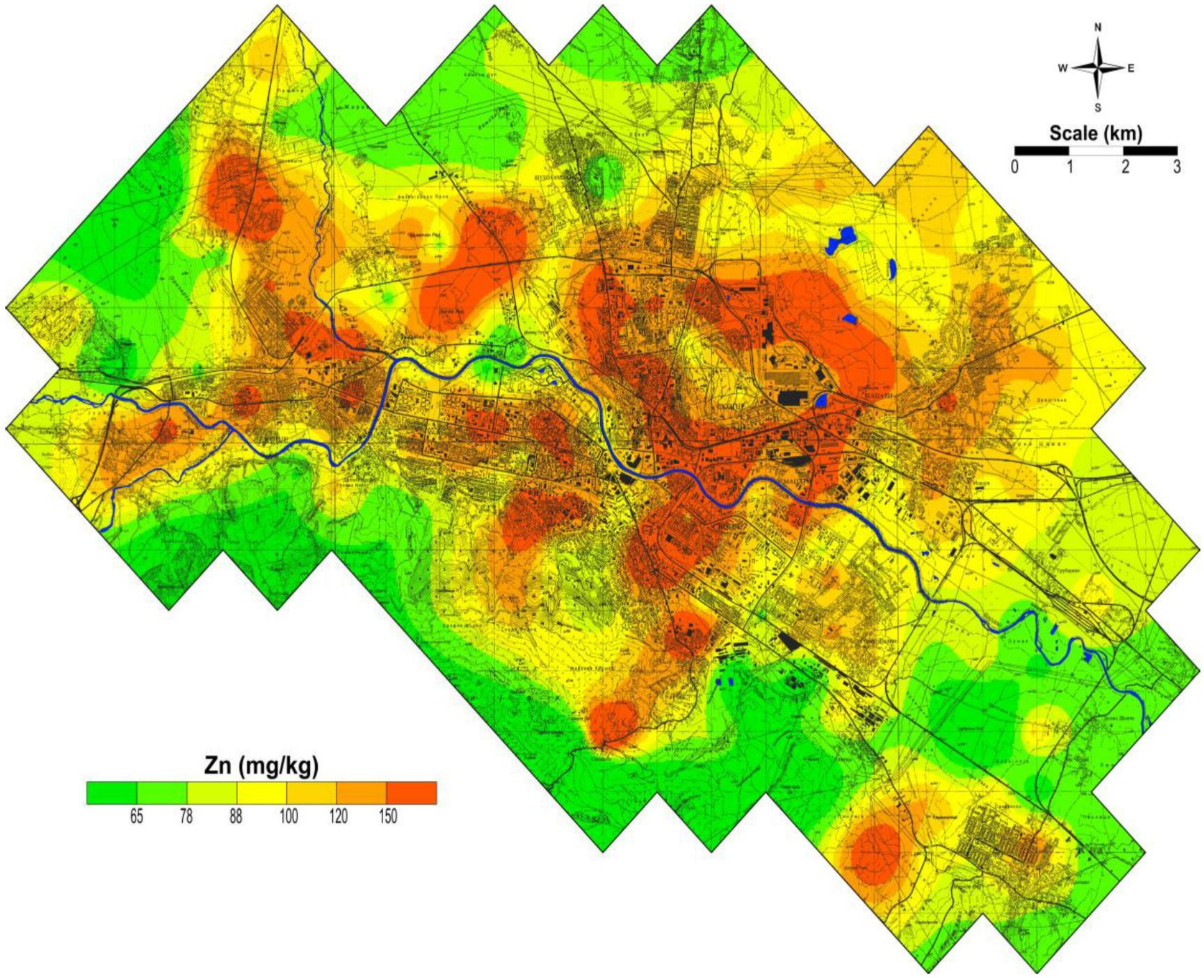

Fig. 4. Spatial distribution of the content of zinc in the soil from the city of Skopje

According to the land use, the average content of Zn ranges from 83 to 156 mg/kg. A higher average content of Zn was found in soils from the industrial areas (156 mg/kg) and the lowest average content was found in soils covered by shrubs (83 mg/kg) (Table 2, Figure 5).

From the comparison of the obtained values for Zn with Dutch standards it can be noted that the Box-Cox average content of Zn in soil from Skopje is below the target value (140 mg/kg), with the exception of its average content in soils from the industrial zone (156 mg/kg) but is consistently lower that the intervention value (720 mg/kg). The higher value of Zn in soil from the industrial zone is a result of contamination, mainly by dust from the iron and steel works. Namely, it was found that the content of Zn in filter dust from the steel production which was left on the open place for a long period is about 23 % (Stafilov, 1991, De Koning et al., 2005, Stafilov et al., 2009).

A comparative analysis was conducted based on the data of the contents of zinc in the soils in Macedonia (Stafilov & Šajn, 2016) and Europe (Salminen et al., 2005) (Table 2). For the comparative analysis, the average and median values were used from which the median value was shown as a more stable parameter. From data presented in Table 3 it can be seen that the average and median contents of zinc are higher in relation to the data for Macedonian soil for 1.6 and 1.2 times, respectively. These differences in the content of zinc in soil from Skopje and in the topsoil from the whole territory of Macedonia are due to the anthropogenic influences. The average and median contents of zinc are 3.4 and 1.9 greater in soils from Skopje than in European soils, respectively, also due to the anthropogenic influences of industry and urban activities in Skopje.

Table 2

Average contents of zinc in soil according to the geological formations and land use (mg/kg)

Geological formation	Zn	Land use	Zn
Quaternary floodplain	92	Forest	97
Quaternary swamp sediments	90	Shrub	83
Quaternary young terraces	110	Open area	110
Quaternary old terraces	118	Cultivated land	86
Pliocene sediments	79	Urban area (low buildup)	116
Miocene sediments	108	Urban area (high buildup)	134
		Industrial area	156

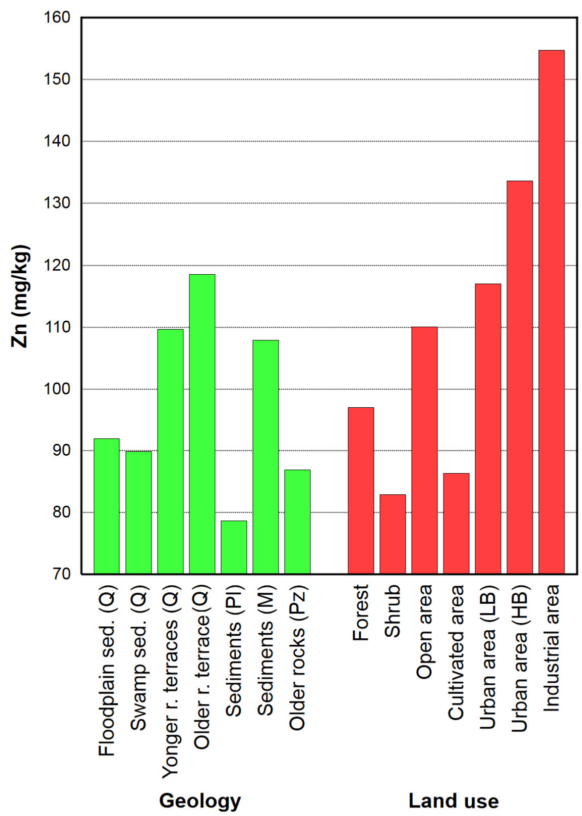

Fig. 5. Average content of Zn according to the geological formations and land use

Table 3

Comparison of the median, minimal and maximal values of zinc in soil from Skopje with those for soil from Macedonia and Europe (mg/kg)

Skopje (this work)			Macedonia (Stafilov & Šajn, 2016)			Europe (Salminen et. al., 2005)			Dutch standard	
X	Md	Min – Max	X	Md	Min – Max	X	Md	Min – Max	Target	Intervention
230	100	23 – 18000	140	83	8.0 – 10000	68	52	<3 – 2900	140	720

X = arithmetical average; Md – median; Min – minimum; Max – maximum

CONCLUSION

The results of the study of spatial distribution of zinc in topsoil (0 – 10 cm) over the city of Skopje, Republic of Macedonia, show that the arithmetical average content of Zn in the topsoil for the entire study area is 230 mg/kg, while the Box-Cox average and the median content is 100 mg/kg with a range of 23 mg/kg to 18000 mg/kg. The highest content of Zn was found in the soil collected from the eastern part of Skopje (eastern industrial zone) with the average of 156 mg/kg. From the comparison of the obtained values for Zn with Dutch standards it can be noted that the Box-Cox average content of Zn in soil from Skopje is below the target value of Dutch standards (140 mg/kg), with the exception of its average content in soils from the industrial zone of 156 mg/kg. It was found established that the higher value of Zn in soil from the industrial zone is a result of contamination, mainly by dust from the steel production.

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Р е з и м е

ПРОСТОРНА ДИСТРИБУЦИЈА НА ЦИНК ВО ПОЧВИТЕ ОД ГРАДОТ СКОПЈЕ И НЕГОВАТА ОКОЛИНА, РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: цинк; почва; просторна дистрибуција; Скопје; Република Македонија

Презентирани се резултатите од просторната дистрибуција на цинк во површинската почва (0 – 10 cm) од градот Скопје, Република Македонија. Примероците почва се земани од претходно дефинирани 233 локации. За определување на цинкот применета е атомската емисиона спектрометрија со индуктивно спрегната плазма (ICP-AES). За обработка на податоците и конструирање на картата на дистрибуција применети се софтверите Statistica (ver. 9), AutoDesk Map (ver. 2008) и Surfer (ver. 9). Утврдено е дека вредноста на медијаната на содржината на цинкот во површинските почви од целото испитувано подрачје изнесува 100 mg/kg (од 23 до 18000 mg/kg) што ги надминува пресметаните вредности на медијаната на содржината на цинк во површинските почви од Македонија и Европа за 1,2 и 1,9 пати, соодветно. Утврдено е дека содржината на цинкот е повисока во површинските почви во индустриската зона (156 mg/kg) надминувајќи ја оптималната вредност според холандските стандарди (140 mg/kg) што е резултат на загадување, главно од работата на железарницата.