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LEAD DISTRIBUTION IN SOIL DUE TO LITHOGENIC AND ANTHROPOGENIC FACTORS IN THE BREGALNICA RIVER BASIN

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A b s t r a c t: The distribution of lead, which in higher content represents hazard to the environment, causes certain unwanted consequences on human health. Therefore, the environmental monitoring not only for the lithogenic but also for the anthropogenic distribution leads to determination of the main hot spots in the environment. Bregalnica river basin in the Republic of Macedonia was selected as a study area with the presence of three potential emission sources: lead and zinc mines ("Zletovo" and "Sasa" mines) and copper mine (Bučim mine). The lead contents in alluvial and automorphic soil range from 4.4 to 46000 mg kg^{-1}. The most enriched subarea with lead in the Bregalnica river basin is the Zletovo–Kamenica region. The average Pb content in these subareas is 3100 mg kg^{-1}. Despite the anthropogenic activities in the above mentioned mines, enriched Pb deposition in soil is mainly correlated with the dominant geological formations, such as Neogene pyroclastites and vulcanites and Proterozoic gneisse and shales.

Key words: lead distribution; soil; multivariate analysis; ICP-MS; Pb-Zn mine; Bregalnica river

INTRODUCTION

The exploitation of mineral resources leads to excavation, separation, transportation and dispersion of the metals contained in the fine dust (micro-particles). In this way the metals are introduced into the environment in much higher contents than normally found in nature (Salomons, 1995). With the passage of time and the long-term activities of the human factor, the contents of certain metals have been completely and permanently changed in relation to their natural existence in the environment. These changes can have a significant influence on the physiology and ecology of the organisms adapted to survive in thus created conditions of higher metal contents or, as Van Loon & Duffy (2000) term it, *specific environment*. The distribution of the different chemical elements, including the potentially toxic metals, creates characteristic conditions for the living organisms. Taking into account that their contents in the environment are variable, it is important to identify the regions with changed contents, differing from the natural distribution of the elements in the different segments of the biosphere (Athar & Vohora, 1995; Siegel, 2002; Artiola et al., 2004). Lead is a good indicator of legacy trace metals from anthropogenic sources because of its persistence in the environment (Solt et al., 2015).

The anthropogenic activities for exploitation of natural resources and their processing through adequate technological processes and management of the waste produced by the same, represent a global problem of pollution of the environment. Republic of Macedonia does not diverge from this global framework of pollution of the environment with certain toxic metals. The studies implemented so far shows that certain areas on the territory of the Republic of Macedonia are stricken by the anthropogenic introduction of Pb in higher contents in soil (Stafilov et al., 2010a, 2010b, 2014; Balabanova et al., 2013). In order to determine the potential risk to human health of Pb contaminated soil, it is essential to gain an understanding of the universal range of Pb concentrations and how they are spatially distributed. There is a great deal of published data describing the range of Pb concentrations found in soil from both remote locations and those affected by human impact (McGrath et al., 2004).

In the region of the basin of the Bregalnica river, there are several significant emission sources of potentially toxic metals and other chemical elements in the environment, which are the following: the copper mine and flotation "Bučim" near Radoviš, the lead and zinc mines "Sasa" near Makedonska Kamenica and "Zletovo" near Probištip (Stafilov et al., 2014). The excavation of the copper minerals is carried out from an open ore pit, while in the lead-zinc mines the exploitation is underground, and the ore tailings are stored in the open air. The ore produced in the mines is processed in the flotation plants, and in the process of flotation of the relevant minerals, flotation tailings are separated and disposed on a dump site in the open.

The exposure of mining and flotation tailings, as well as the exposure of the open ore pit to the air streams, leads to distribution of the finest dust (Salomons, 1995; Athar & Vohora, 1995). On the other hand, rain waters wash the ore tailings and make water extraction of the available metals. In this way, metals and other potentially toxic chemical elements are introduced into the soil and waters (surface and underground). At the same time, the particles from flotation and mining tailings are continually distributed by the winds. These particles, depending on the weather conditions, can be distributed in the air for longer or shorter periods of time, and thus, deposited on smaller or greater distances from the emission source (Van het Bolcher et al., 2006).

Therefore, the lead distribution in soil in the Bregalnica river basin (without Ovče Pole region), Republic of Macedonia, was studied. For that purpose, top and bottom soil samples from 155 locations were collected and analyzed by inductively coupled plasma – mass spectrometry (ICP-MS).

MATERIALS AND METHODS

Geographic characterization of the investigating area

The investigated area includes the basin of the river Bregalnica which is found in the area of the east planning region of the Republic of Macedonia. The investigated area covers ~100 km (W-E) × 40 km (S-N), that is, a total of ~4.000 km^2, within the following geographic coordinates N: 41°27'–42°09' and E: 22°55'–23°01' (Fig. 1). The region of the investigated area is geographically composed of several subregions. The area is characterized by two valleys – Maleševo and Kočani valleys. The altitude varies between 290 m in the plain of the Kočani valley up to 1932 m (Kadaica) on the Maleševo mountains. The average annual temperature also varies in the different subregions. In the Kočani valley the average annual temperature is about 13°C, the warmest months in the year are July and August with average temperature of 25°C, and the coldest month is January with average temperature of about 1.2 °C (Lazarevski, 1993). In the region of Štip, the average annual temperature is about 12.9°C, with high frequency of winds (out of 365 days in the year, there are air movements on 270 days). The Berovo valley can be singled out as the coldest region, which is under direct influence of the local mountain climate with an average annual temperature of 10°C (Lazarevski, 1993).

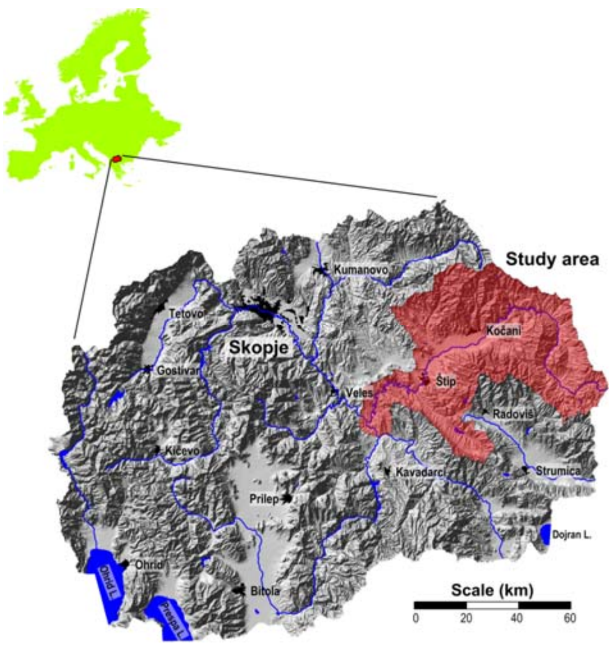

Fig. 1 The location of the study area

Most common are the winds from western direction with frequency of 199‰ and speed of 2.7 m s^{-1} and the winds from eastern direction with frequency of 124 ‰ and speed 2.0 m s^{-1}. The average annual precipitation amounts to about 500 mm with significant variations from year to year, as well as in the different subregions. The precipitation is mostly related to and conditioned by the Mediterranean cyclones (Lazarevski, 1993). During the summer period, the region is most often found in the centre of the subtropical anticyclone, which causes warm and dry summers. From the central area of the region, as the driest area, the average annual precipitation increases in all directions, because of the increase either in the influence of the Mediterranean climate or the increase in altitude.

Geological characterization of the investigated area

The investigated area that covers the basin of the river of Bregalnica lies on the two main tectonic units: the Serbian-Macedonian massif and the Vardar zone (Dumurdžanov et al., 2004). The polyphasal Neogene deformations through the insignificant movements associated with the volcanic activities had direct influence on the gradual formation of the reefs and the formation of deposits in the existing basins. From the middle Miocene to the end of the Pleistocene there were alternating periods of fast and slow landslide accompanied with variable sedimentation (Serafimovski & Aleksandrov, 1995; Serafimovski et al., 2006; Dumurdžanov et al., 2004).

The Cenozoic volcanism represents a more recent extension in the Serbian-Macedonian massif and the Vardar zone. The oldest volcanic rocks occur in the areas of Bučim, Damjan, the Borov Dol district and in the zone of Toranica, Sasa, Delčevo and Pehčevo (Serafimovski & Aleksandrov, 1995; Serafimovski et al., 2006; Dumurdžanov et al., 2004). These older volcanic rocks were formed in the mid Miocene from sedimentary rocks that represent the upper age limit of the rocks. The origin of these oldest volcanic rocks is related to the Oligocene – the early Miocene period. As volcanic rocks are categorized the following: andesite, latite, quartz-latite, dacite. Volcanism appears sequentially and in several phases forming subvolcanic areas. On the other hand, the pyroclastites are most frequently found in the Kratovo–Zletovo volcanic area, where the dacites and andesites are the oldest formations. Generalized geology of the area is produced based on the data provided by Rakićević et al. (1968) and presented in Fig. 2.

Soil samples collection

In the period between March–November 2012 samples of topsoil (0–5 cm) and subsoil (20–30 cm) were collected in the investigated area. A total of 155 locations compose the network of locations for taking samples of soil from the surroundings and the basin of the Bregalnica river (Fig. 3). The locations network is with density of 5×5 km, in order to enable mapping and specifying of the distribution of the chemical elements examined. On each location was taken a sample of topsoil, at depth of 0–5 cm, and a sample of subsoil, at depth of 20–30 cm. The collection of soil samples was undertaken in accordance with the relevant standards for collection of this type of samples from the environment (Reimann et al., 2012). The locations for collection of soil samples were previously determined by constructing a network for sample collection. Depending on the conditions on the site and the accessibility, that is, possibility of the same, the samples were collected in the surroundings of the specified locations, recording the relevant coordinates. On every location, with each sample of topsoil and subsoil, five subsamples were collected. At the specified location, a square with area 10×10 m was formed. Four samples were collected from the angles of the square while the fifth sub-sample was collected from the intersection of the square diagonals. In this way, a representative composite sample of topsoil (0–5 cm) was formed. From the same holes formed with the taking of the topsoil subsamples, the subsoil subsamples were also collected, for the formation of a representative sample of a sub-soil sample (Reimann et al., 2012).

Analytics

The soil samples brought in the laboratory were subjected to cleaning and homogenization, drying at room temperature, or in a drying room at 40°C, to a constantly dry mass. Then the samples were passed through a 2 mm sieve and finally were homogenized by grinding in a porcelain mortar until reaching a final size of the particles of 25 μm. 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 samples were prepared for determining the lead contents. Mass spectrometry with inductively coupled plasma (ICP-MS) was used for measuring the elements concentration in soil digests. The instrumental and operating conditions for each of the above mentioned techniques are given in Table 1.

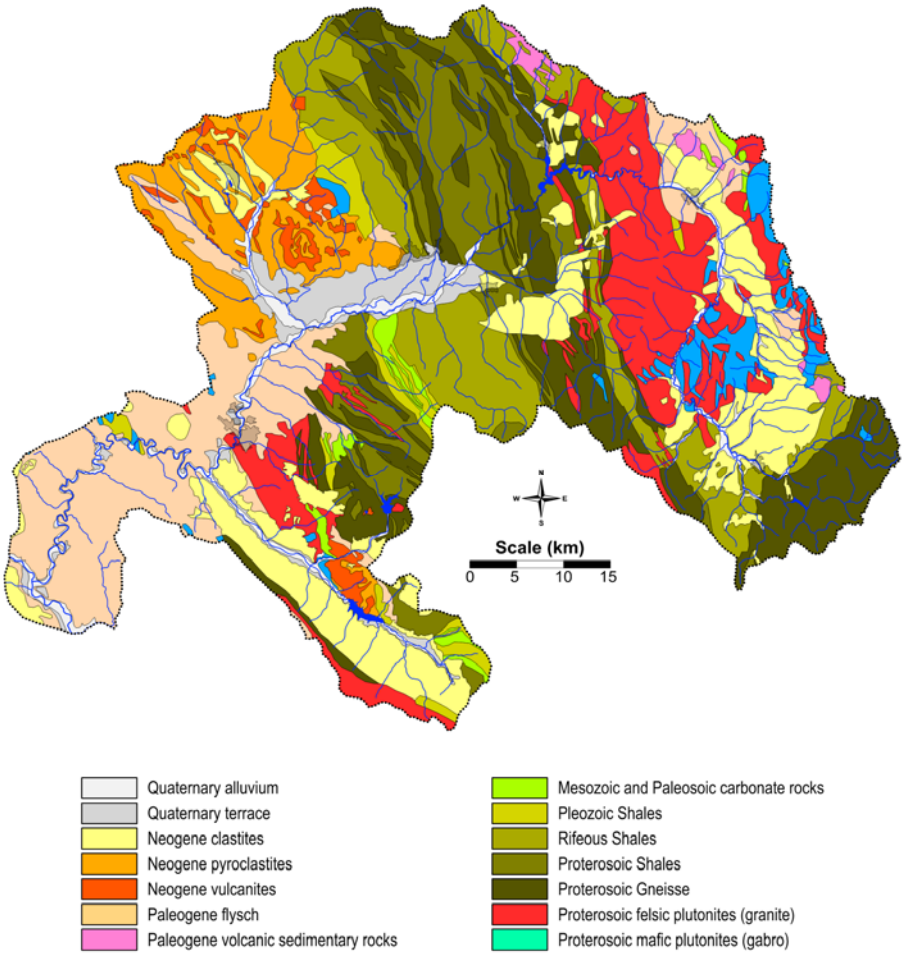

Fig. 2. Generalized geology of the investigated area

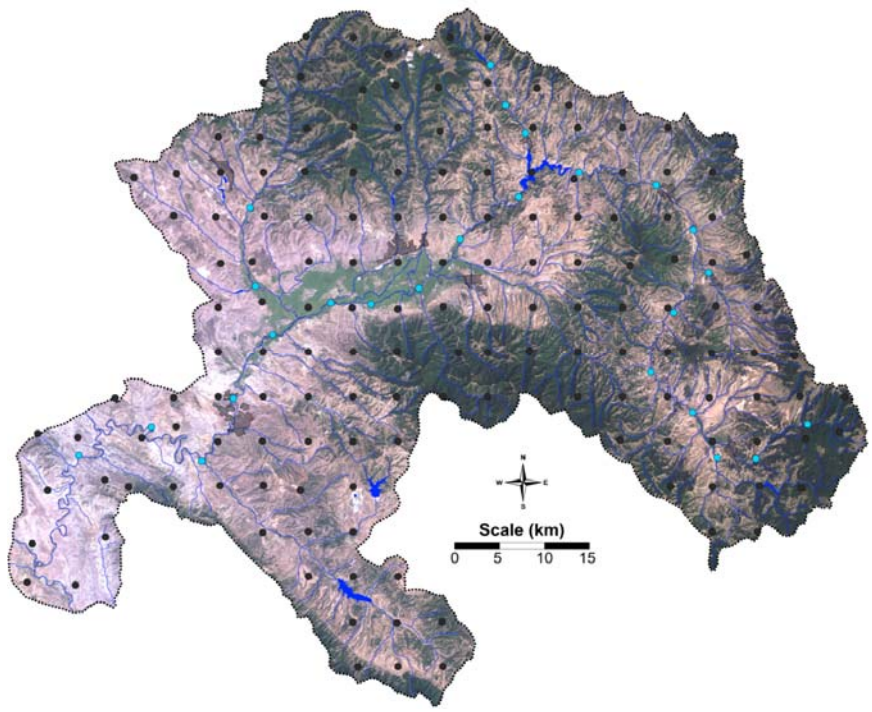

Fig. 3. Locations for collection of soil samples in the investigated area

T a b l e 1

Instrumental conditions for ICP-MS

RF Generator	
Power output of RF generator	1500 W
Power output stability	better than 0.1%
ICP Ar flow gas rate	15 l·min^{-1}
Plasma parameters	
Nebulizer	Micromist
Spray chamber	Double-pass cyclone
Cones	Platinum
Peristaltic pump	0–50 rpm
Plasma configuration	Radially viewed
Spectrometer	Echelle optical design
Total voltage (V)	0.1
Integration measurement time (ms)	0.1
Repetitions measurement	3 per point
Pb isotopes	Average: $^{206}Pb/^{207}Pb/^{208}Pb$

The limits of detection (LOD) were based on the usual definition as the concentration of the analytic yielding a signal equivalent to three times the standard deviation of the blank signal, using 10 measurements of the blank for this calculation. The calculated value for the detection limits for lead is 0.1 µg/l. Both certified reference materials (JSAC 0401) and spiked intra-laboratory samples were analyzed at a combined frequency of 20% of the samples. Recovery for spiked samples ranges from 88 to 114%. While the recovery for the certified reference material ranges from 92 to 110%.

Data processing

All data on the content of the investigated elements were statistically processed using a statistical software (Stat Soft, 11.0), by applying parametric and non-parametric analysis. Basic descriptive statistical analysis was conducted on the values of the contents of the elements in soil samples. At the same time, normalization tests were made and based on the obtained results and the visual check of distribution histograms, the distribution of data on independent variables (elements' contents) was determined. For data normalization, the method of *Box-Cox* transformation (Box & Cox, 1964) was also applied. In the making of the distribution maps the kriging method with linear variogram interpolation was applied. As area limits were considered the percentile values of the distribution of the interpolated values.

RESULTS AND DISCUSSION

The total lead content was quantified in a total of 310 samples of topsoil (TS) and subsoil (SS). The values for the elements contents were statistically processed. At the start, the distribution of the element as variable, individually, was monitored. For these reasons, comparative analysis was performed on normal and transformed values. Two statistical comparative methods were applied (T-test and F-test) to examine whether there were certain differences in the elements' distributions between the non-transformed and the transformed values. On the other hand, lithogenic distribution of different chemical elements should not significantly differ in the samples of topsoil (0–10 cm) and subsoil (20–30 cm). Box-Cox transformation was used for normalization of the values for the lead content in the soil samples. Because of the fact that no significant difference was detected in the contents, and consequently also in the distribution of the elements in the soil, the further statistical processing of the values for the elements contents in the soil refers to the mean values of their contents (the content as a mean value of the TS and the SS).

In order to determine the dependence of the lead contents between the topsoil and the subsoil, a correlation factors was calculated in all 310 samples (Table 2). The element distribution should not varies significantly between the topsoil (0–5 cm) and the subsoil (20–30 cm), except if certain destructive anthropogenic or natural processes do not contribute to the opposite (Dudka & Adriano, 1997). The correlation coefficient for the topsoil content vs. subsoil content was also examined and the value of 0.65 was obtained, which indicated on significant lithological distribution of lead in soil in the investigated area (Table 2).

The examined area lies on parts of the Kratovo–Zletovo and Toranica–Sasa ore areas, on the both sides of the Osogovo massive. Both areas lie on metamorphic and volcanic rocks originating from the Tertiary. The Pb-Zn mineralization in this area characteristically influences the distribution of lead in the wider area. The lead contents in the whole investigated area range from 4.4 to 46000 mg kg^{-1} (Table 3). The maximum content is obtained from sample located very close to the "Sasa" mine. High variability is obtained in the distribution of the data on lead, which also confirms a great difference in the values for the average (820 mg kg$_{-}^{1}$) and the median (40 mg kg^{-1}). Because of the high values for the standard deviation and the coefficient of variation, data normalization was performed using the Box-Cox transformation, and standardizing the median to the value of 26 mg kg^{-1} (Table 3).

T a b l e 2

Comparative analysis of the elements contents in topsoil and subsoil (T-test and F-test) for normal and Box-Cox transformed values (values given in mg/kg)

TS-(X)	SS-(X)	FO (X)	TS-(BC)	SS-(BC)	FO (BC)	T-test	F ratio	Sign	TS/SS
880	750	1.18	40	40	1.00	-0.03	1.40	NS	0.65

TS – top-soil (0–5 cm); SS – subsoil (20–30 cm); X – non-transformed mean values; FO – radio of TS and SS values; BC – Box-Cox transformed values, Sign. – significance; NS – non-significant difference

T a b l e 3

Descriptive statistics of the values of elements contents is samples of topsoil and subsoil (values given in mg/kg)

X	X (BC)	Md	Min	Max	P_{25}	P_{75}	S	Sx	CV	A	E	A (BC)	E (BC)
820	40	26	4.4	46000	17	75	4120	330	510	9.21	96.79	–0.19	7.64

X – -mean; X(BC) – mean of Box-Cox transformed values; Med – median; Min – minimum; Max-maximum; P_{25} – 25th percentile; P_{75} – 75th percentile; S – standard deviation; S_x – standard deviation of transformed values; CV – coefficient of variation, A – skewness; E – kurtosis; BC – Box-Cox transformed values

T a b l e 4

Distribution of the elements in the soil in different geologic formations in the examined area (values given in mg/kg)

B-1	B-2	K-Z	River terraces	River sediment	Characteristic geologic formation							F-ratio	Sign
Q)	(Q)	(Q)	(Q)	(Ng)	Pyroclastite (Ng)	Flysch (Pg)	Schist (Pz)	Schist (R)	Schist (Pt)	Gneiss (Pt)	Granite (Mz-Pt)		
20	40	3100	100	28	95	24	54	51	38	58	30	6.07	*

*Significant difference; NS – non-significant difference; B-1: upper course of the Bregalnica river; B-2: lower course of the Bregalnica river; K-Z – region of the Kamenička and Zletovska rivers; Q – Quaternary; Ng – Neogene; Pg – Paleogene; Pz – Paleozoic; R – Riphean; Pt – Proterozoic

Compared with the data provided by Salminen et al. (2005), the Pb median is 22.6 mg kg^{-1}, and there is no significant variation. For the isolated areas of the Kamenička Reka river (Sasa mine surroundings) and the Zletovska river (Zletovo mine surroundings), a median for the lead contents of 3100 mg·kg^{-1} was obtained (Table 4). Lead distribution is also related to the areas of Neogene pyroclastites, with a median of the isolated samples located on these geologic formations of 100 mg·g^{-1} (Table 4).

The values of the median for lead content in the vicinity of the Kamenička and Zletovska rivers is 3100 mg·kg^{-1} (Fig. 4) which, compared with the upper optimum values in accordance with the Dutch standards (85 mg kg^{-1}), points out to pollution. The lead contents also exceed the action value of 530 mg kg^{-1} (http://www.contaminatedland.co.uk/std-guid/dutch-l.htm).

The whole investigated area, for the further data analysis of the lead contnt in alluvial and automorphic soil was separated in zones. Dominant and specific areas for the alluvial soil were separated as upper river flow of the Bregalnica river (from the river-head to the Kalimanci accumulation), the lower river flow (from the Kalimanci accumulation to the flowing in the river of Vardar) and the Zletovska–Kamenica areas due to the anthropogenic sources in this area (Fig. 4).

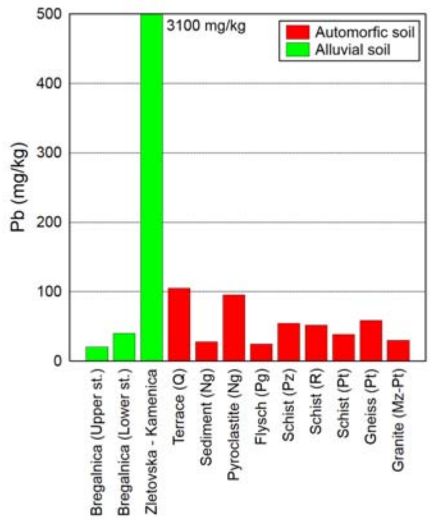

Fig. 4. Distribution across the different areas and areas with dominant geological formation

The distribution of the lead in automorphic soil was monitored in dependence with the dominant geological formation, such as: Quarternary terraces, Neogene sediments, Neogene pyroclastite, Paleogene flysch, Palaeozoic schist, Proterozoic schist, Proterozoic gneisses, Mesozoic granite. Average vaulue of lead content in alluvial soil in the Bregalnica river basin is characteristic in the area of the Zletovska and Kamenička rivers terraces (3100 mg·kg^{-1}). Those are the main tributaries that are responsible for the main introducing of lead content through the whole Bregalnica river basin. The average lead content in automorphic soils ranges from 24 mg·kg^{-1} in areas of Paleogene flysh to 95 mg·kg^{-1} in areas of Neogene pyroclastite.

The distribution map for Pb exhibits elevated concentrations near the around the central part of the Bregalnica river basin (Fig. 5). The greatest concentrations predicted by ordinary kriging occur in the central older areas of Bregalnica basin. This pattern is consistent with elevated metal concentrations in urban soils that are associated with anthropogenic sources. Several studies have demonstrated lead contamination in urban areas is a function of traffic density and age of the urban area (Mielke & Reagan, 1998; Filippelli, 2005; Laidlaw and Filippelli, 2008; Brown et al., 2008). But in the case of the present study the enrichment of the lead contents is not only correlated with the urban areas, but higher content of lead is due to the oldest geological formation in the area.

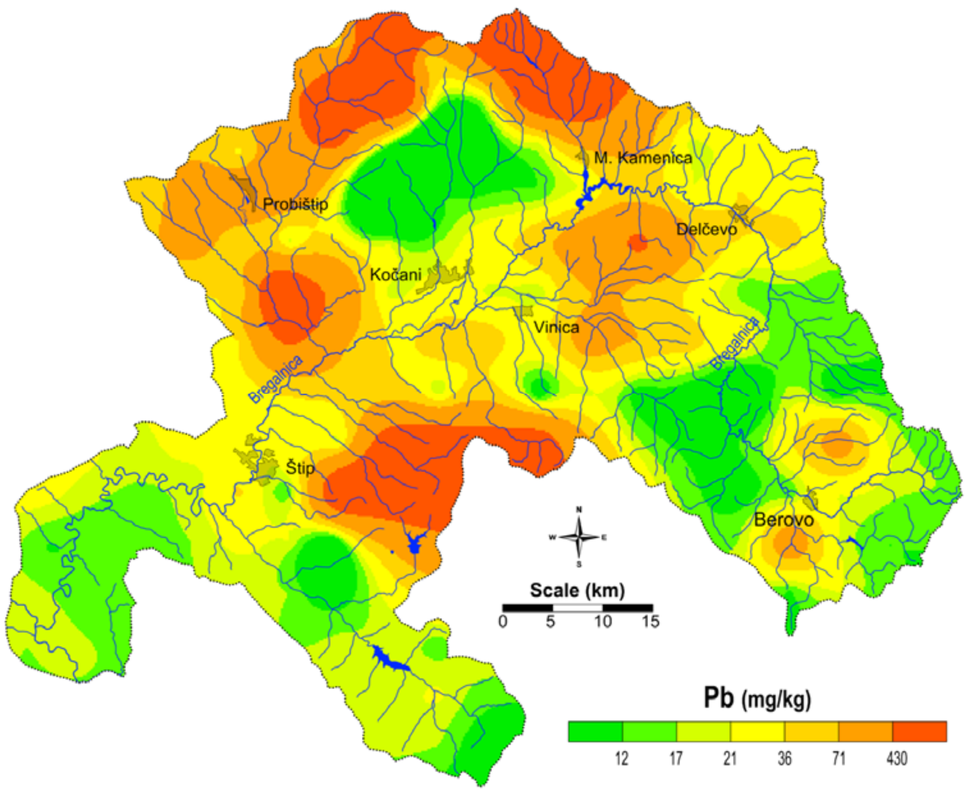

Fig. 5. Areal distribution of lead

The northern part of the area is characteristic with occurrence of the Neogene pyroclastites and vulcanites (Kratovo–Zletovo region, "Zletovo" mine) continued with the Proterozoic gneisses and shales (Kamenica subarea, "Sasa" mine). This is area where a Paleogene volcanic sedimentary rock occurs too. This natural phenomena very similar impact in the area of Cu minerals exploitation ("Bučim" mine), where as dominant geological formation occurs Proterozoic gneisses and shales. Previously investigation shows that in this area the Pb distribution is correlated with As-Cd-Cu-Zn deposition (Balabanova et al., 2013).

CONCLUSION

Detailed geostatistical analysis on lead distributions will help to gather more informations on the variability of Pb concentrations in soil in the Bregalnica river basin. Non-normal abundance distributions and geospatial correlations indicate anthropogenic origins of lead in Bregalnica river basin soils. Lead in soil, with its ability to negatively impact human health at low levels, remains a major concern. The lead content in the whole area is variable and ranges from 4.4 to 46000 mg·kg^{-1}. The enrichment of lead occurs in the areas of Pb-Zn mineralization and exploitation. Also the area of copper mineralization and exploitation correlates with the introducing of higher contents of lead in topsoil. The enrichment of lead in Zletovska–Kamenička rivers area is with average values of 3100 mg kg^{-1}. Comparisons with the values from Dutch standards show enrichments of 6 times. This knowledge can aide in determining possible sources of lead contamination which, in turn, will better allow for the protection of human health.

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Р е з и м е

ДИСТРИБУЦИЈА НА ОЛОВО ВО ПОЧВИТЕ КАКО РЕЗУЛТАТ НА ЛИТОГЕНИТЕ И АНТРОПОГЕНИТЕ ФАКТОРИ ВО РЕГИОНОТ НА СЛИВОТ НА РЕКАТА БРЕГАЛНИЦА

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Дистрибуцијата на оловото во почви, што во повисока содржина претставува опасност за животната средина, предизвикува некои несакани последици по здравјето на луѓето. Затоа мониторингот не само на литогената туку и за антропогената дистрибуција овозможува утврдување на главните жаришта во животната средина. Сливот на реката Брегалница во Република Македонија беше избран како испитуван регион поради присуството на три потенцијални извори на емисија на олово: олово-цинкови рудници (рудниците „Злетово“ и „Саса“) и рудник за бакар (рудникот „Бучим“). Содржината на олово во алувијалните и автоморфните почви во ова подрачје се движи од 4,4 до 46.000 mg·kg^{-1}. Најмногу збогатени почви со олово во сливот на реката Брегалница има во регионот Злетово–Каменица. Просечната содржина на Pb во почвата во оваа област е 3100 mg на kg^{-1}. И покрај антропогените активности во горенаведените рудници, присуството на оловото е во корелација и со доминантните геолошки формации како што се неогените пирокластити и вулканити и протерозојски гнајсеви и шкрилци.