274
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DISTRIBUTION OF LEAD AND ZINC IN SOIL OVER THE BITOLA REGION, REPUBLIC OF MACEDONIA

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Abstract: Data for the distribution of lead and zinc in topsoil and subsoil over the Bitola region, Republic of Macedonia, known for its coal mine and thermoelectric power plant are presented. The study area (1400 km^2) is covered by a sampling grid of 5×5 km with a total of 58 spots. The samples were collected at two depths: topsoil (0–5 cm) and subsoil (20–30 cm). The samples were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The obtained results of these two elements were statistically processed and maps of areal distribution were prepared. It was assumed that the higher contents of Pb and Zn are connected with the anthropogenic influence by the fly ash from the thermoelectric power plant deposed on the open as well as the influence of the high frequency traffic near the city of Bitola.

Key words: soil; lead; zinc; Bitola; Republic of Macedonia

INTRODUCTION

Urban pollution with heavy metals is a global problem initiated by the world technology progress and human exploitation of natural resources and this becomes a subject to many studies. The regional contamination of soil occurs mainly in industrial regions and within centres of large settlements, where factories, motor vehicles and municipal wastes are the most important sources of trace metals (Kabata-Pendias & Pendias, 2001). The level of the environmental pollution will depend on proper control of anthropogenic activities as well extraction, concentration and separation of waste at the open (Qin et al., 2012). The above mentioned factors indicate global problem of environmental pollution.

Republic of Macedonia has the same problem with global pollution by heavy metals. Recent years the results obtained from previous studies, suggest that the most important emission sources are mines and drainage systems and smelters near the towns of Veles, Tetovo, Kavadarci and Radoviš, and some uranium deposition patterns were described by the activity of power plants using lignite coal as fuel (Stafilov et al., 2010a, 2010b; Barandovski et al., 2012; Balabanova et al., 2010, 2011; Bačeva et al., 2012). The purpose of this research was to detect the level of soil contamination with heavy metals in the Bitola region, Republic of Macedonia. This was done to see the impact of thermoelectric power plant “Bitola” situated near the city of Bitola, as well as traffic and industrial facilities in the city and its environ. Soil samples (topsoil and subsoil) were taken according to network and prepared for the analysis.

Zinc is an essential element and is commonly found in nutritional supplements. However, taking too much zinc into the body can affect your health. Zinc compounds are widely used in industry. Zinc oxide is also used in producing rubber. Zinc enters the air, water, and soil as a result of both natural processes and human activities. Most zinc enters the environment as the result of mining, purifying of zinc, lead, and cadmium ores, steel production, coal burning, and waste burning. These activities can increase zinc levels in the atmosphere. Waste streams from zinc and other metal manufacturing and zinc chemical industries, domestic waste water, and run-off from soil containing zinc can discharge zinc into waterways. The level of zinc in soil increases mainly from disposal of zinc wastes from metal manufacturing industries and coal ash from electric utilities. Sludge and fertilizer also contribute to increased levels of zinc in the soil. In air, zinc is present mostly in fine dust particles which eventually settle over land and water (Buchauer, 1973). Inhaling large amounts of zinc dust or fumes from smelting or welding can cause a specific short-term disease called metal fume fever. However, very little is known about the long-term effects of breathing zinc dust or fumes. Ingesting high levels of zinc for several months may cause anemia, damage the pancreas, and decrease levels of high-density lipoprotein cholesterol. Consuming food containing very large amounts of zinc caused many health effects (Bothwell et al., 2003).

Lead is a heavy, low melting, bluish-gray metal that occurs naturally in the Earth's crust (Budavari et al., 1996). However, most of the high levels found throughout the environment come from human activities. Environmental levels of lead have increased more than 1,000-fold over the past three centuries as a result of human activity (Hamilton et al., 1994). Lead can enter the environment through releases from mining lead and other metals, and from factories producing and processing lead, lead alloys, or lead compounds. Lead is released into the air during burning coal, oil, or waste. Sources of lead in dust and soil include lead that falls to the ground from the air, and weathering. Landfills may contain waste from lead ore mining, ammunition manufacturing, or other industrial activities such as battery production. Disposal of lead-containing products contribute to lead in municipal landfills. Past uses of lead such as its use in gasoline are a major contributor to lead in soil, and higher levels of lead in soil are found near roadways. Most of the lead in inner city soils comes from old houses with paint containing lead and previous automotive exhaust emitted when gasoline contained lead. Once lead falls onto soil, it sticks strongly to soil particles and remains in the upper layer of soil (Hamilton et al., 1994). Lead exposure has been associated with increased risk of lung, stomach and urinary-bladder cancer in diverse human populations (Fu and Boffetta, 1995; Steenland and Boffetta, 2000; NTP, 2003). Gastrointestinal absorption of lead is higher in children than in adults (Hammad et al., 1996).

The purpose of this research was to detect the level of soil contamination with heavy metals like Pb and Zn in the Bitola region, Republic of Macedonia. This was done to see the impact of thermoelectrical power plant “Bitola” situated near the city of Bitola, as well as traffic and industrial facilities in the city and its environ. Soil samples (topsoil and subsoil) were taken according to network and prepared for the analysis. Lead and zinc were determined by the application of inductively coupled plasma-atomic emission spectrometry (ICP-AES).

MATERIALS AND METHODS

Study area

The study area is located in southwest part of the Republic of Macedonia, with largeness of 35 km (W-E) × 40 km (S-N), total 1400 km^2 (Fig. 1). The Mining and thermoelectric power plant “Bitola” is located in the periphery of Pelagonia plain near the village of Novaci. The plant which basic activity is the production of electricity and coal is the biggest in the system of the Macedonian electric power plant and consists of mine “Suvodol” and thermoelectric power plant. Other industries that could be considered air pollutants in the region are Renosil, the factory produces quartz, and the industry for metal processing "Metalec". 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 general description of the study area was given previously (Dimovska et al., 2013).

Sampling and sample preparation

The investigated area covers 1400 km^2 with 58 sampling locations (Fig. 1). From each location 2 samples were taken: sample from the surface layer of soil – topsoil (0–5 cm), and deep soil layer – subsoil (20–30 cm). Soil samples were collected according to certain standards for taking soil samples (Stafilov et al., 2010a). Every sample must be representative, which means mix of 5 corresponding samples collected in the area within a 10×10 m. Soil samples were air dried at room temperature, and then they were gently crushed and grind to become fine dust. For digestion of soil samples, wet digestion with mixture of acids was applied. At first mass of dust samples (0.5 g) was placed in teflon vessels. After this 5 ml concentrated HNO_3 was added, until the brown vapors came out from the vessels. Then 5–10 ml of HF were added for total digestion of inorganic components. When all of this became a solution for total digestion of organic matter, 2 ml of $HClO_4$ were added. After cooling the vessels, 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 (Balabanova et al., 2011).

Instrumentation

The obtained solutions of soil samples were analyzed with the application of atomic emission spectrometer with inductively coupled plasma Varian 715ES. Standard solutions of the analyzed elements were prepared by dilution of 1000 mg l^{-1} solutions (11355-ICP multi Element Standard). In all of this samples Zn and Pb were detected. Instrumental parameters and quality control are given in our previous work (Balabanova et al., 2011).

Mapping

Universal kriging with the linear variogram interpolation method (Davis, 1986) was applied for the construction of maps showing the spatial distribution of Zn and Pb. The basic grid cell size for interpolation was 500×500 m. For class limits, the percentile values of distribution of interpolated values were chosen. Four classes at the following percentiles were selected: 0–25, 25–50, 50–75, and 75–100.

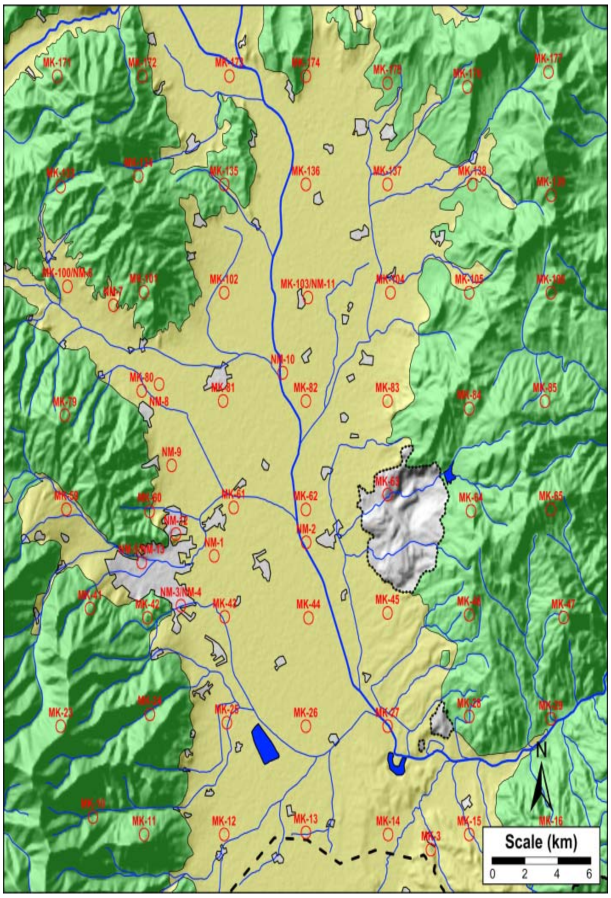

Fig. 1. Land-use map with location of sampling sites

RESULTS AND DISCUSSION

Descriptive statistics and maps of areal distribution of Pb and Zn were prepared from data obtained with analyses of these elements in soil samples. Basic descriptive statistics include: data for arithmetical and geometrical mean, median; minimal and maximal content, 10- and 90-percentile standard deviation, coefficient of variation, skewness and kurtosis. Because of the significant difference between the median and arithmetical mean, logarithm of values was use for the normalization. Data from the descriptive statistics are given in Table 1 and the maps of distribution are presented on Figs. 2 and 3.

Table 1

Basic descriptive statistical parameters (n = 71)

	Unit	Dis	X_a	Md	X_g	Min	Max	P10	P90	s	s_x	CV	A	E
Pb	mg/kg	Log	14	11	9.8	2.1	130	2.8	24	16	1.9	115	0.00	–0.14
Zn	mg/kg	Log	40	26	27	3.4	220	6.1	81	39	4.6	97	–0.22	–0.36

n – number of moss samples; Dis – distribution; X_a – arithmetical mean; X_g – geometrical mean; Md – median; Min – minimum; Max – maximum; P10 – 10 percentile; P90 – 90 percentile; s – standard deviation; s_x – standard error of mean; CV – coefficient of variance; A – skewness; E – kurtosis

The content of Zn in soil samples from the territory of Bitola and its environs vary between 3.4 mg kg^{-1} and 220 mg kg^{-1} with the median value of 26 mg kg^{-1}, and for Pb vary between 2.1 mg kg^{-1} and 130 mg kg^{-1} with the median value of 11 mg kg^{-1}.

From the results presented in Figs. 2 and 3 it can be noticed that the element contents undergoes with the geology of the region. However, it can be also concluded that these two elements have anthropogenic influence from the thermoelectric power plant and high frequency traffic and industrial activities in the town of Bitola. Thus, higher content of Pb and Zn is visible around the town Bitola and thermoelectric power plant (Figs. 2 and 3). Probably the influence of Pb in the city center is conducted with traffic and some activities in the town (Fig. 2). From Fig. 2 it can be also seen the influence of thermoelectric power plant, because in this areola lead has high concentrations. It should be added that the content of Pb in top soil is 1.4 time higher than in the subsoil.

In this study the maximum value for Pb 130 mg/kg (Table 1) is 1.5 times higher than target value (85 mg kg^{-1}) from the new Dutch list (http://www.contaminatedland.co.uk/std-guid/dutch -l.htm) for soil and 4 times lower than the intervention value (530 mg kg^{-1}). This maximal value for the content of Pb was found in the soil from the city center, at sampling point MN13. Also this point gives the highest concentration for Zn of 220 mg kg^{-1}. The same behaviour has Zn, it's maximum value of 220 mg kg^{-1} is 1.6 times higher than the target value (140 mg kg^{-1}) and 3.3 times lower than the intervention value (720 mg kg^{-1}). This confirms that pollution with Pb and Zn comes from traffic and activities in the city center and fly ash from the thermoelectric power plant. Higher values of zinc appear also on the south-western part of the studied area which is probably due to the lithogenic origin of higher content of zinc in the Paleozoic granatoides (Waker, 2013).

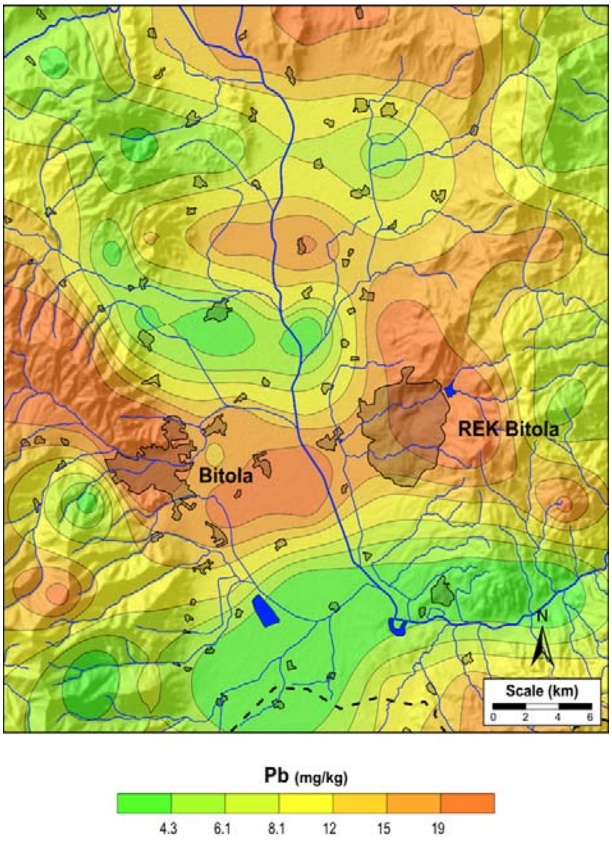

Fig. 2. Spatial distribution of lead

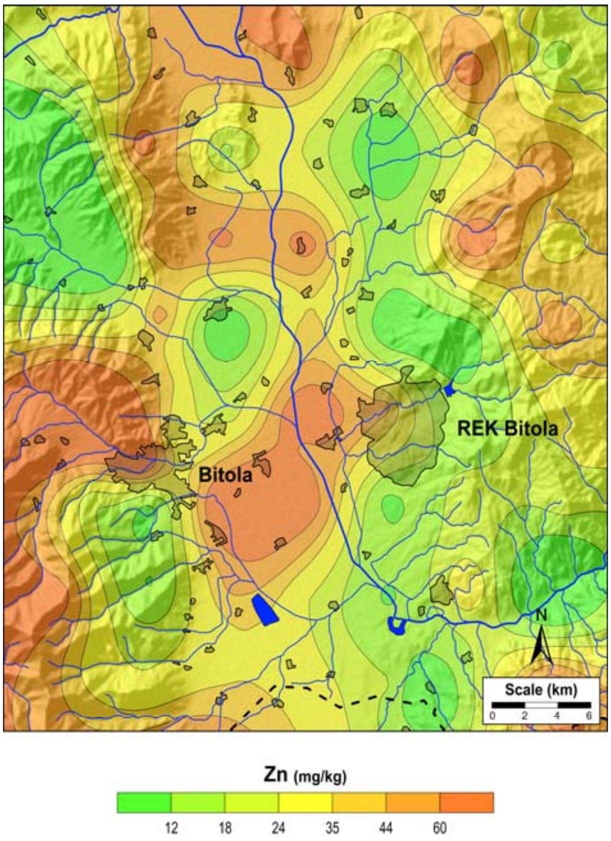

Fig. 3. Spatial distribution of zinc

CONCLUSION

Following the results of analysis for soil, anthropogenic impact of Zn and Pb has been defined. It could be concluded that the element distribution undergoes with the geology of the region. However it was also assumed that the higher contents of Pb and Zn are connected with the anthropogenic influence by the fly ash from the thermoelectric power plant deposed on the open as well as the influence of the high frequency traffic and industrial activities in the city of Bitola.

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Резиме

ДИСТРИБУЦИЈА НА ОЛОВО И ЦИНК ВО ПОЧВАТА ВО ГРАДОТ БИТОЛА И НЕГОВАТА ОКОЛИНА, РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: почва; цинк; олово; Битола; Република Македонија

Во трудот се презентирани резултати од испитувањето на дистрибуцијата на олово и цинк во површинска и длабинска почва во регионот на Битола, Република Македонија, познат по рудникот за лигнит и термоелектричната централа. Истражуваната област (1400 km^2) е покриена со мрежа точки со оддалеченост од 5×5 km, од кои се земени примероците од почвата; вкупно 58 локации. Почвите беа собрани од две длабочини: површинска (0–5 cm) и длабинска (20–30 cm). Примероците беа анализирани со примена на атомска емисиона спектрометрија со индуктивно спрегната плазма (ISP-AES). Добиените резултати за двата елемента беа статистички обработени и беа подготвени карти на нивната просторна дистрибуција. Се покажа дека повисоките содржини на Pb и Zn се поврзани со антропогено влијание, односно потекнуваар од пепелта од термоелектричната централа, како и од високата фреквенција на сообраќајот во градот Битола и неговата непосредна околина.