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MOSS BIOMONITORING OF AIR POLLUTION WITH ARSENIC IN BITOLA AND THE ENVIRONS, REPUBLIC OF MACEDONIA

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A b s t r a c t: Moss biomonitoring was applied to establishing anthropogenic influence of arsenic in city of Bitola and the environs, Republic of Macedonia. Moss samples were collected from 38 locations in the area of 1400 km^2 in summer and autumn 2010. Arsenic was analyzed by the application of inductively coupled plasma - mass spectrometry (ICP-MS). The obtained results of this element were statistically processed and the map of areal distribution was prepared. Map of arsenic distribution showed the sites with higher levels of this element. Arsenic was the element that illustrates the operation of open pit brown coal mining and thermoelectric power plant (REK "Bitola"). The obtained median for As (0.38 mg kg^{-1}) from the investigated area was compared with those for the whole territory of Macedonia and for the other Balkan countries and Europe.

Key words: air pollution; arsenic; moss biomonitoring; Bitola; Macedonia

INTRODUCTION

Environmental pollution with heavy metals is a global process initiated by the world technology progress and human exploitation of natural resources. Anthropogenic impact on environs is a danger throughout the world, mostly in the form of atmospheric pollution. Especially heavy metals were pollutants of great concern, they are nondegradable and highly toxic. Common sources of heavy metal pollution include discharge from industries such as electroplating, plastics manufacturing, fertilizer producing plants and wastes left after mining and metallurgical processes (Zouboulis et al., 2004). Heavy metals in atmosphere exist in particulate form. These particles undergoes on dry, wet and occult deposition to land or water surfaces which constitutes the first stage of accumulation of atmospheric heavy metals.

Moss biomonitoring technique was first introduced in Scandinavia and has shown to be very suitable for studying atmospheric deposition of heavy metals and other elements as well (Rühling et al., 1968, 1971). Republic of Macedonia was involved in the UNECE ICP Vegetation (United Nations Economic Commission for Europe International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops – Heavy Metals in European Mosses), for the first time in 2002 (survey 2000/2001) and then in 2005 and 2010 when atmospheric deposition of trace elements was studied over the entire territory of the country using moss samples (Barandovski et al., 2006, 2008, 2012, 2013; Harmens et al., 2003). It was found that the most important emission sources are mines and drainage systems and smelter plants.

Arsenic is ubiquitous in the air, water and soil in the form of metalloid or chemical compounds. It is used commercially in pesticides, wood preservatives, and in the manufacture of paper, glass and semiconductors (Klaassen, 2008). Many inorganic arsenic compounds are found in the environment, frequently occurring as the sulfide form in complex minerals. Arsenic compounds occur in tri- and pentavalent forms, common trivalent forms are arsenic trioxide and sodium arsenite, and common pentavalent forms are arsenic pentoxide and the various arsenates (Klaassen, 2008). Organic forms of arsenic include the metabolites: monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), and trimethylarsine oxide (TMAO). The methylated metabolites can exist for both arsenite and arsenate (Saranko, 1998). Arsenic ingestion can have number of deleterious health effects. Many mammalian species metabolize inorganic arsenic by methylation, through there is a variation in the rate and extent of methylation among human populations (Vahter, 1999). Hallmarks of chronic oral exposure to arsenic include skin lesions characterized by hyperkeratosis, hyperpigmentation and hypopigmentation (Klaassen, 2008). Contamination can also cause gastrointestinal discomfort, vomiting, diarrhea, bloody urine, anuria, shock, convulsions, coma and even death (Hughes, 2002). Potential exposure to arsenic also occurs through the consumption of drinking water contaminated with arsenical pesticides, natural mineral deposits, or arsenical chemicals that were disposed of improperly (ATSDR, 2007).

The aim of this study was establishing the level of pollution with arsenic in moss samples collected from 38 locations in Bitola, Republic of Macedonia, and its environs. Arsenic was analyzed by the application of inductively coupled plasma – mass spectrometry (ICP-MS). The obtained results were statistically processed and the map of areal distribution was prepared.

MATERIALS AND METHODS

Study area

The study area is located in southwest part of the Republic of Macedonia (Fig. 1), with largeness of 35 km (W–E) × 40 km (S–N), total 1400 km^2.

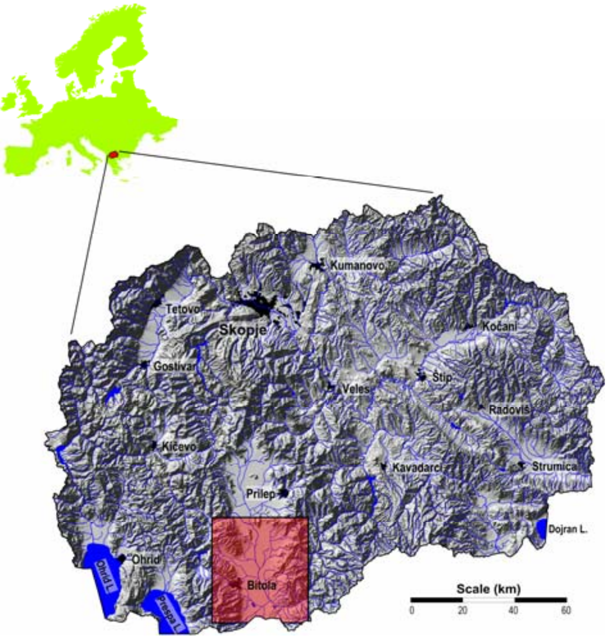

Fig. 1. Studying area

The Bitola region, as well as the whole Pelagonia Valley is rather southern positioned and due to the latitude should have an altered Mediterranean climate. However, although Pelagonia Valley is at a distance of 155 kilometers from the Adriatic Sea, and at about 130 kilometers from the Aegean Sea, still the Mediterranean climate influence isn't much felt, because of the high mountainous surrounding of the valley, and its own height above the sea level (it is between 571 and 770 meters). In Bitola the north and north-east winds prevail (Fig. 2). 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" Bitola.

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. Simplified geological map with major lithological unit is provided in Fig. 2.

The Pelagonian massif is built of Precambrian metamorphic and igneous rocks. The predominant rocks on the western Pelagonian massif are banded muscovite gneisses, but also other varieties such as the banded muscovite-biotite gneisses and augen-amydaloidal two-mica gneisses. Medium to coarse grained granodiorites, garnet-staurollite and garnet-cyanite occur as intrusive bodies in the gneiss-micaschist series. By the influence of granodioritic magmas the sourrounding rocks were felpatized and augen-amydaloidal two-mica gneisses and banded two-mica gneisses originated, the feldspatization of muscovite gneiss was weak. Some relicts of amphibolite and schistose amphibolite are present in the study area.

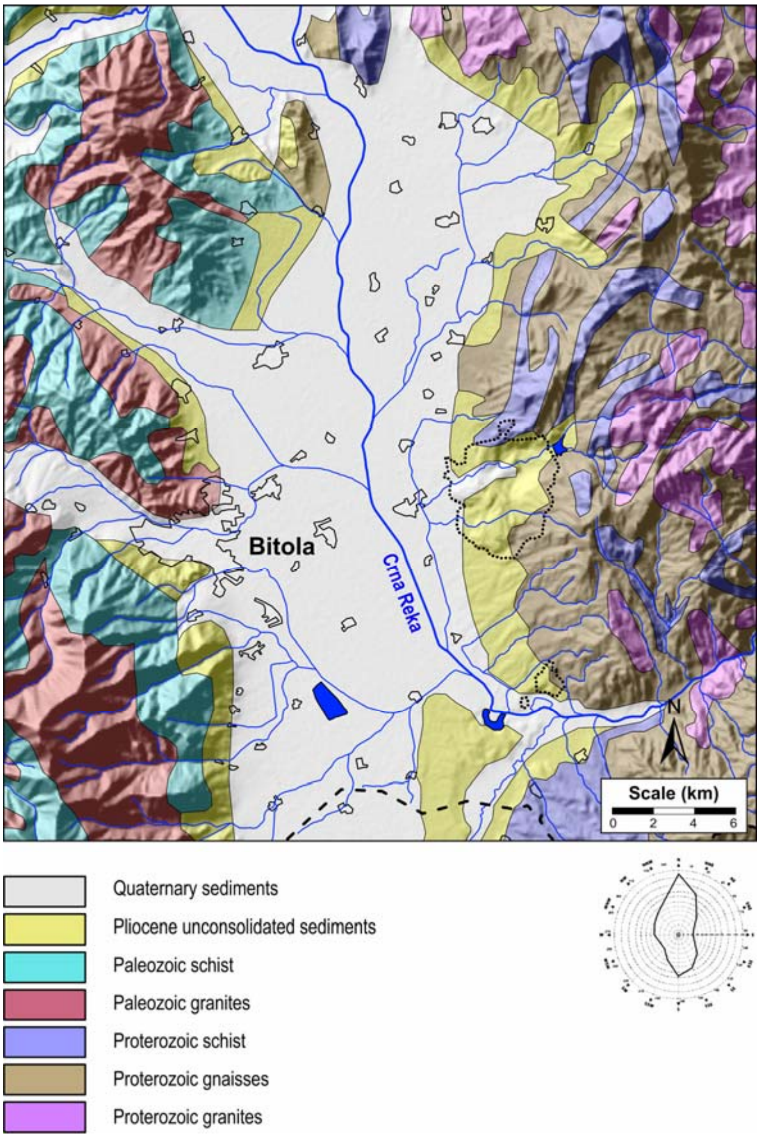

Fig. 2. Geological map of Bitola region

The oldest rocks in the Western Macedonian zone are Paleozoic age and consist of low metamorphic schists and granitic rocks. The most widespread granite is alkalic granite, extending in N–S direction. The oldest granitoides rocks are represented by biototic and amphibolitic granodiorites to which granosyenite and syenite are connected on the southern part of the Western Macedonian zone. Following the direction N-S, on left side of the map, Silurian-Devonian formation occur composed of phylite, slate, metasandstone and metaconglomerate which alter to older Paleozoic rocks. Ordovician-Silurian green shist and conglomerates with intrusions of quartz-sericite schist and schistose quartzite developed southern of Bitola.

During Pliocene and Quaternary were first deposited the lacustrine sediments in the Pelagonian depression. They begin with Middle Pliocene gravels, sands and clays with coal beds, while the upper part is composed of poorly sorted gravels, sand and silty clays. Holocene is represented by deluvial and alluvial deposits.

Sampling and sample preparation

38 samples of mosses were collected during the period from July 2010 till December 2010. The sampling network with numbered sampling sites is shown in Fig. 3. The sampling rule was: samples that were collected must be in a distance of minimum 300 m from main roads, 100 m from local roads, and 200 m from settlements. Each sample was composed of five subsamples collected within an area of 50 × 50 m. Collected material was stored in paper bags. Mosses were left to dry and cleaned.

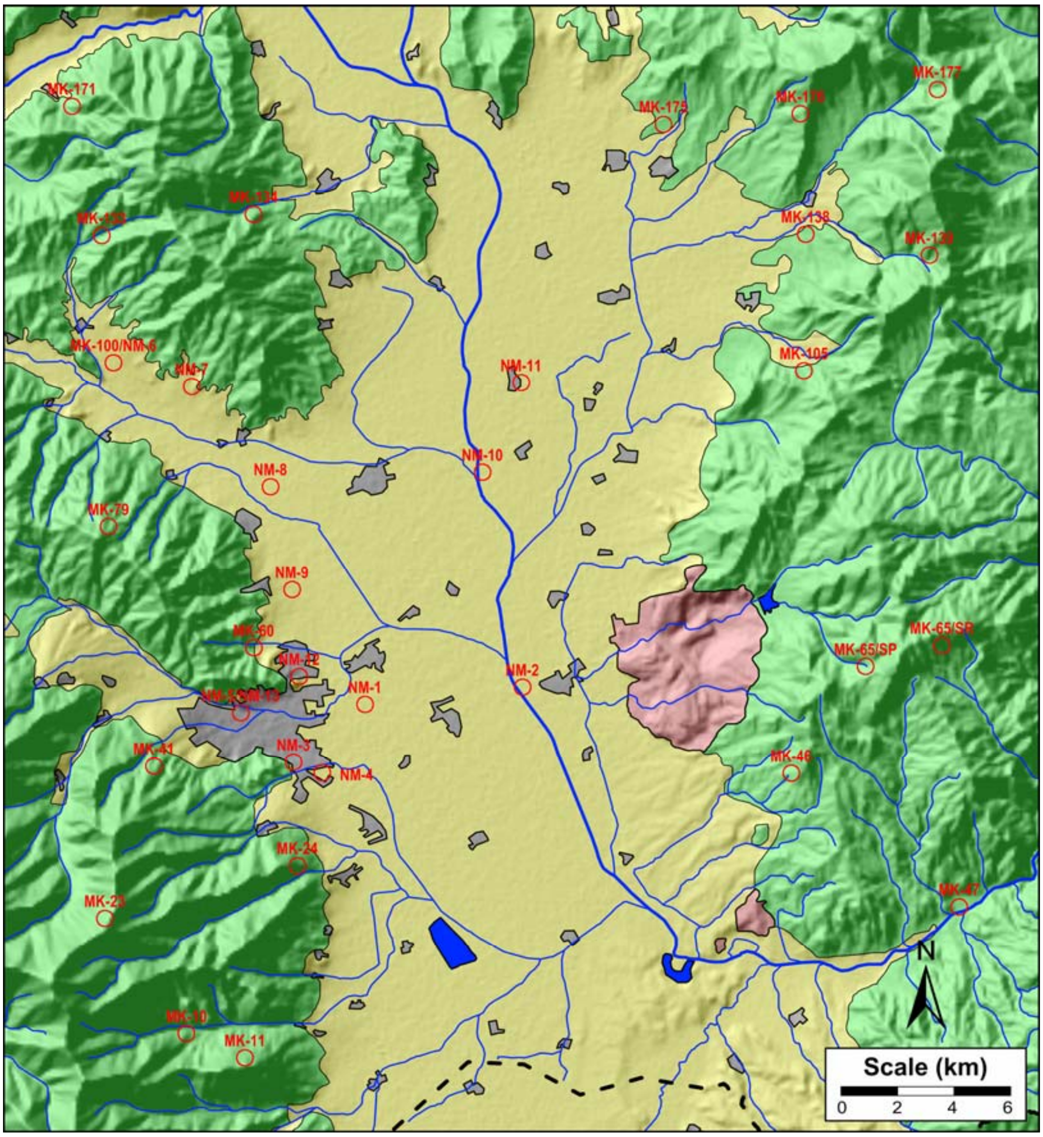

Fig. 3. Land-use map with location of sampling sites

Microwave digestion system was applied for moss samples. In teflon digestion vessels 0.5 g of moss samples together with 5 ml concentrated HNO_3 (trace pure, Merck, Germany) and 2 ml H_2O_2 (30%, $m\ V^{-1}$, Merck, Germany) were added, and the vessels were closed, tightened and placed in the rotor of a microwave digestion system (Milestone, Ethos Touch Control). After digestion and cooled samples were quantitatively transferred into 25 ml calibrated flasks.

Instrumentation

Inductively coupled plasma – mass spectrometry (ICP-MS) was applied for analyzing the content of As in moss samples. For ICP-MS measurements a SCIEX Perkin Elmer Elan DRC II (Canada) inductively coupled plasma mass spectrometer with quadruple and single detector setup was used. The instrumental parameters are given by Bačeva et al. (2012).

Mapping

Universal kriging with the linear variogram interpolation method (Davis, 1986) was applied for the construction of maps showing the spatial distribution of As, as well as map displaying the distribution of this element in soil (Beelen et al., 2005). 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.

RESULTS AND DISCUSSION

Descriptive statistics and map of distribution of arsenic was made, from data obtained from analyses of arsenic in moss samples. Data from the descriptive statistics are given in Table 1 and the map of distribution is presented on Fig. 4.

T a b l e 1

Basic descriptive statistical parameters (n = 38)

Unit	Dis	Xa	Md	Xg	Min	Max	P10	P90	Sa	Sg	CV	A	E
mg kg^{-1}	Log	0.46	0.38	0.41	0.22	1.3	0.25	0.77	0.23	0.038	51	0.67	-0.17

n – number of moss samples; Xa – arithmetical mean; Xg – geometrical mean; Md – median; Min – minimum; Max – maximum; P10 – 10 percentile; P90 – 90 percentile; Sa – arithmetical standard deviation; Sg – geometrical standard deviation; CV – coeficient of diffraction; A – skewness; E – kurtosis

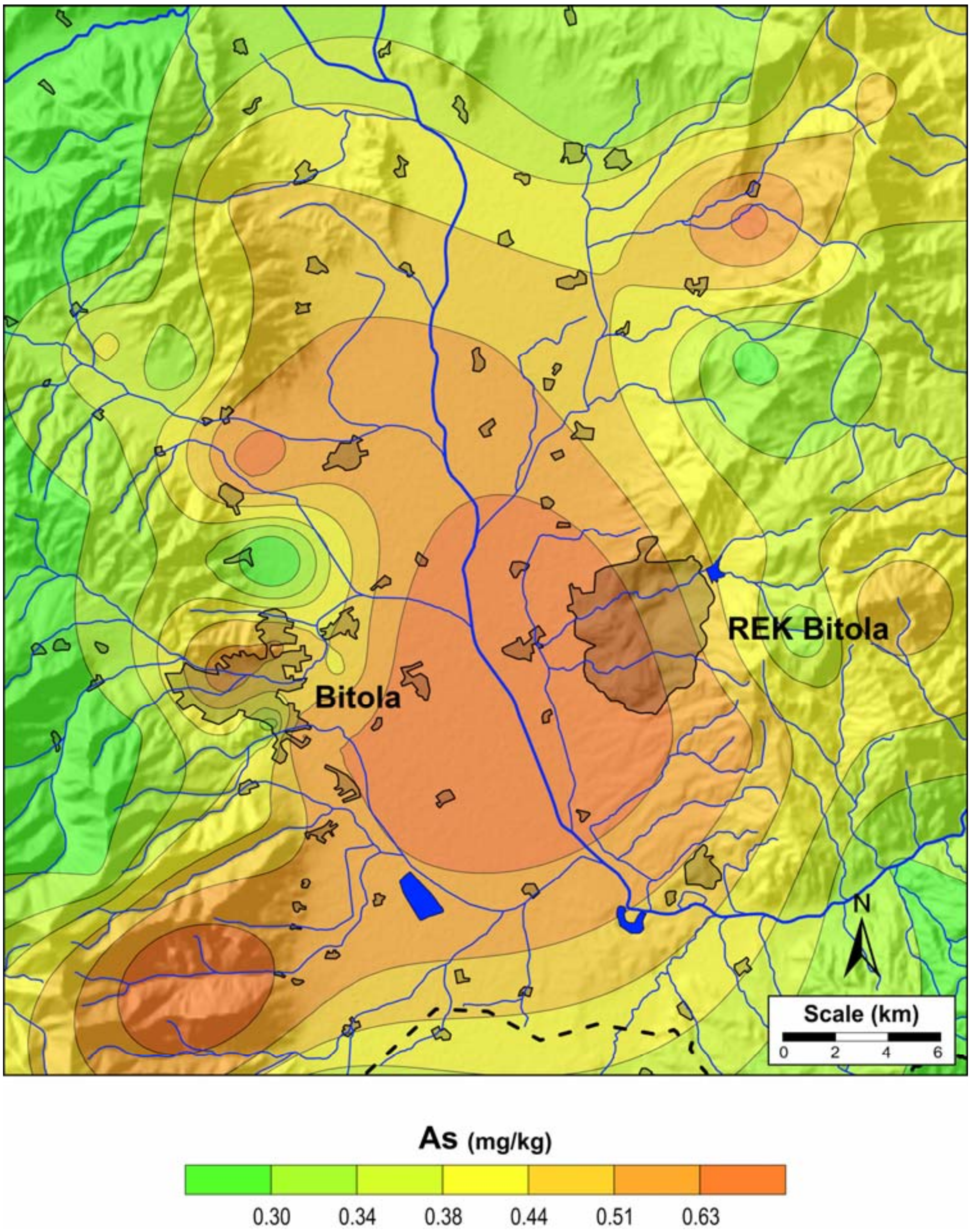

Fig. 4. Spatial distribution of arsenic

The content of arsenic in moss samples from the territory of Bitola and its environs vary between 0.22 mg kg^{-1} and 1.3 mg kg^{-1} with the median value of 0.38 mg kg^{-1}. The highest content of arsenic, 1.3 mg kg^{-1}, was found in the moss sample collected from sampling point in the vicinity of REK "Bitola" in the municipality of Novaci. This high content is a result of operation with open pit brown coal and thermoelectric power plant and was illustrated by distribution of As (Fig. 4). Arsenic can be used as a main "marker" of pollution which was consequence of coal mining activities and later to the thermoelectric power plant. Moss samples are very well established medium for biomonitoring (Barandovski et al., 2008) clearly identified the areola of As at southern part of Pelagonia. The areola has a bit elongated shape, influenced by local winds (Figs. 2 and 4). Some particularly high concentrations in the western part of study area were showing natural distribution of this element.

The obtained results were compared with those obtained for the content of arsenic in moss samples collected from the whole territory of the Republic of Macedonia and from some neighbouring countries (Albania, Bulgaria and Serbia) as well as with the median value for arsenic in moss from Europe (Table 2). Thus, the median value for As in this study of 0.38 mg kg^{-1} (ranges from 0.22 mg kg^{-1} to 1.3 mg kg^{-1}), was 1.8 times smaller then the value of 0.69 mg kg^{-1} for Macedonia from the studies in 2005 and 2010 (Barandovski et al., 2012; Harmens et al., 2013). This higher value of As content in Macedonia is due to the air pollution from mining and metallurgical activities as well as natural occurrences of arsenic in some regions in the country (Barandovski, 2008, 2012; Stafilov et al., 2010) However, the median value of As in moss samples from the studies area is very similar to the median value of arsenic in European mosses (Harmens et al., 2013). Comparing with the medians from the neighbouring countries it can be seen that the median for the studied area is higher than those in moss samples from Albania (0.24 mg kg^{-1}) confirming that it's present is due to the coal processing in the thermoelectrical power plant near Bitola, but much lower that those for Serbia (1.41 mg kg^{-1}) (Table 2).

Table 2

Comparison of median (Md), minimal (Min) and maxinmal (Max) values of arsenic obtained in the present study with those obtained in similar studies in the Republic of Macedonia, Bulgaria, Serbia, Albania and Europe (in mg/kg)

Bitola, 2010 (this work)		Macedonia, 2005 (Barandovski et al., 2005)		Macedonia, 2010 (Harmens et al. 2013)		Bulgaria, 2010/2011 (Harmens et al., 2013)		Serbia, 2005 (Harmens et al. 2008)		Albania, 2010 (Harmens et al., 2013)		European moss survery 2005/2006 (Harmens et al., 2008))	
Md	min–max	Md	min–max	Md	min–max	Md	min–max	Md	min–max	md	min–max	Md	min–max
0.38	0.22–1.3	0.68	0.18–4.3	0.69	0.08–3.30	0.63	0.15–10.8	1.41	0.22–21.6	0.24	0.04–2.20	0.42	0.10–9.36

CONCLUSION

In this study the moss biomonitoring technique was used for assessment of the arsenic distribution in the air in Bitola region. The content of arsenic in moss samples from the territory of Bitola and its environs vary between 0.22 mg kg^{-1} and 1.3 mg kg^{-1} with the median value of 0.38 mg kg^{-1}. The highest content of arsenic, 1.3 mg kg^{-1}, was found in the moss sample collected from sampling point in the vicinity of thermoelectric power plant "Bitola" near the city of Bitola. This high content is a result of operation with open pit brown coal and thermoelectric power plant and was illustrated by distribution of As. Arsenic can be used as a main "marker" of pollution which was consequence of coal mining activities and later to the thermoelectric power plant.

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Р е з и м е

БИОМОНИТОРИНГ НА ЗАГАДУВАЊЕТО НА ВОЗДУХОТ СО АРСЕН ВО БИТОЛА И НЕЈЗИНАТА ОКОЛИНА, РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: загадување на воздухот; арсен; биомониторинг со мов; Битола; Македонија

Со цел да се утврди антропогеното влијание на арсен во градот Битола и неговата околина, Република Македонија, беше применета техника на биомониторинг со мов. Примероците од мов беа собрани од 38 локации на површина од 1400 km^2 во текот на летото и есента 2010 година. Арсенот беше анализиран со примена на индуктивно спрегната плазма со масен спектрометар (ICP-МС). Добиените резултати за овој елемент се статистички обработени и врз основа на тоа е направена карта на просторна дистрибуција за арсенот. Од карти на дистрибуција може да се утврдат локациите со повисока содржина на арсен. Утврдено е дека дистрибуцијата на арсенот ја отсликува работата на рудникот за лигнит, како и работата на термоцентралата за производство на електрична енергија РЕК "Битола". Добиената вредност на медијаната за содржината на арсенот (0.38 mg kg^{-1}) во ова истражување е споредена со медијаните добиени од претходни истражувања за целата територија на Макеонија, како и за други балкански земји и Европа.