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ATMOSPHERIC DEPOSITION OF CADMIUM IN CROATIA STUDIED BY USING MOSS BIOMONITORING TECHNIQUE AND ICP-AES

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A b s t r a c t: Croatia participated for the first time in moss survey in 2005, in the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops with heavy metals in Europe (UNECE ICP Vegetation) when different species of moss samples (*Hypnum cupressiforme, Pleurozium schreberi, Brachythecium rutabulum* and *Homalothecium sericeum*) were collected from 96 locations evenly distributed over the country. An additional 27 new sampling sites were added for the investigation in 2010. Moss samples were collected during the summer and autumn of 2010. Collected moss samples were air dried, cleaned and totally digested by using microwave digestion system. Digests were analyszd for cadmium by atomic emission spectrometry with inductively coupled plasma (ICP-AES). The results for cadmium were compared with the results obtained in previous investigations in Croatia and some other neighboring countries and Norway as a pristine area. The content of cadmium ranges from 0.10 mg kg^{-1} to 1.42 mg kg^{-1}. It was found that the median value of cadmium (0.38 mg kg^{-1}) is 1.41 times higher than the value obtained in the study performed in 2005. Compared to the other countries, Croatia shows insignificantly higher median value. Highest contents of cadmium were found in the Podravina region (1.14 mg kg^{-1} and 1.42 mg kg^{-1}) where cadmium inputs as a result of anthropogenic origin from Slovenia and Austria (Pb and Zn mines and smelter plants). High levels of cadmium were also found in moss samples collected at some industrialized areas in northern parts of Croatia as a result of anthropogenic influence as well as in samples collected in the Coastal region where high levels are a result of geological origin.

Key words: atmospheric deposition; cadmium; moss biomonitoring; ICP-AES; Croatia

INTRODUCTION

Biomonitoring is a technique using organisms or biomaterials to obtain quantitative information on certain characteristics of the biosphere (Wolterbeek, 2002). Monitoring of air pollution using bioindicators is emerging as a potentially effective and more economical alternative performing than direct ambient air measurements. This is especially relevant for monitoring large areas (Rühling and Tyler, 1968). Mosses have been used as biomonitors, in most cases, of trace-element atmospheric pollution. They possess many properties that make them suitable biomonitors for air pollutants. Bryophytes are excellent biomonitors of pollution because of their differential ability to accumulate a wide range of metals (Fernandez et al., 2000; Saxena, 2006). They do not have real roots so they obtain nutrients from wet and dry deposition and nutrient uptake from the atmosphere is promoted by their weakly developed cuticle. Other advantages are: slow growth rate that lets them accumulate pollutants over a larger time period, undeveloped vascular bundles allow better adsorption than vascular plants, they have minimal morphological changes during moss lifespan, they are widely distributed and can be easily collected (Onianwa, 2001; Zeichmeister et al., 2003). The accumulation of pollutants in mosses occurs through a number of different mechanisms: (1) as layers of particles, (2) entrapment on the surface of the cells, (3) incorporation into the outer wall of cells through ion exchange processes and (4) metabolically controlled passage into the cells (Brown and Bates, 1990).

Cadmium is a heavy metal that is dispersed throughout the modern environment mainly as a result of pollution from a variety of sources (Bhattacharyya et al., 2000; Järup et al., 1998). Cadmium and cadmium compounds are, compared to other heavy metals, relatively water soluble. They are therefore also more mobile in e.g. soil, generally more bioavailable and tend to bioaccumulate. The major natural sources for emission to air are volcanoes, airborne soil particles, sea spray, biogenic material and forest fires. Cadmium is produced mainly as a by-product from mining, smelting, and refining sulphide ores of zinc, and to a lesser degree, lead and copper. The metal has no known beneficial biological function and prolonged exposure to this element has been linked to toxic effects in both humans and animals (Zadorozhnaja et al., 2000). The largest potential sources of cadmium intoxication for humans are food, drinking water, and cigarette smoke (Koller, 1998). Tobacco is an important source of cadmium uptake in smokers, as tobacco plants like other plants accumulate cadmium from the soil. Data from experimental animals and humans have shown that absorption via lungs is higher than gastrointestinal absorption (via the stomach). Up to 50% of the inhaled cadmium may be absorbed (WHO 1992). Liver and kidneys have been considered the major target organs for cadmium toxicity. These tissues have been used as standards for delimiting metal toxic concentrations (Satarug et al., 2003). Human exposure to this metal is associated with increased incidences of several cancer types and other diseases (Satoh et al., 2002). Cadmium exposure can also result in low bone mass and a high risk of osteoporosis and bone fractures in humans and experimental animals (Wang et al., 2003; Jin et al., 2004; Brzoska et al., 2005). It is well known that cadmium can act as an endocrine disruptor strongly affecting the reproductive organs (Henson et al., 2004). It has been demonstrated that cadmium stimulates free radical production, resulting in oxidative deterioration of lipids, proteins, and DNA, and prompting various pathological conditions in human and other animals (Waisberg et al., 2003).

The first extensive moss survey was carried out in Scandinavia at the end of the 1960s, and then the first survey at a national level was carried out in Sweden, Norway and Denmark at the turn of the 1970s and 1980s (Steinnes, 1977). During the 1980s, the survey expanded to cover all the Nordic countries, and in the 1990s, to most of the countries in Europe (Buse et al., 2003). Since then on, the method of moss biomonitoring is used every 5 years on a national basis to evaluate the level of heavy metal pollution in European countries. Croatia participated in this kind of survey for the first time in 2005 in the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops with heavy metals in Europe (UNECE ICP Vegetation) (Špirić et al., 2012).

Results in the present work are part of the moss survey in 2010. The aim of this investigation is to present the contents of cadmium analyzed in 121 moss samples collected in summer and autumn in 2010 from the whole territory of Croatia. These results will be compared with the results from previous investigation in 2005 in order to follow the trend of atmospheric pollution over the last five years. Additional comparison will be made with the results for this element evaluated in investigations in some neighboring countries and Norway as a pristine area. The map of distribution will show the sites of the country with higher levels of cadmium and the main anthropogenic and geological sources of this element will also be identified.

STUDY AREA

The Republic of Croatia is located between Bosnia-Herzegovina and Serbia in the east, Slovenia in the west, Hungary in the north and Montenegro and the Adriatic Sea in the south (Fig. 1). The territory of Croatia covers an area of 87.677 km^2 of which 56.610 km^2 is landmass. It is Central European and Mediterranean country that lies mostly between 13.5° and 19.5° eastern longitudes and 42.5° and 46.5° northern latitudes extending from the vast Pannonian plain across the narrow Dinaric mountain range to the Adriatic coast. Zagreb is the capital city of Croatia. The Croatian landscape includes mountains and highlands, areas of karst (limestone), plains, rugged coastline and islands. The main rivers are the Sava, Drava and Danube. Croatia is naturally divided into three large, geographical entities: half of its territory belongs to the Pannonian-Peripannonian region (54%), one third to the Adriatic part (31.6%), while the rest belongs to the Dinaric region (14%). Most of Croatia has moderately warm and rainy continental climate as defined by the Köppen climate classification. The prevailing winds in the interior are light to moderate northeast or southwest. In the coastal area, the prevailing winds are determined by local area features. Higher wind velocities are more often recorded in cooler months along the coast, generally as Buras or less frequently as Siroccos. The climate ranges from continental temperate to the north to Mediterranean climate along the coastline and in the adjacent hinterland. Temperatures increase from west to east while precipitation varies reversely with temperatures (Halamić et al., 2012).

Within the area of the Republic of Croatia, two geologically specific and different areas are notable. Clastic sedimentary rocks and metamorphic and magmatic rocks are found dominantly in the area of north Croatia, or the Pannonian part, while carbonate rocks are mostly found in the mountainous and coastal part of the country (Halamić & Miko, 2009).

Since 1990, air emissions of the main pollutants from stationary and mobile sources in Croatia have decreased as a consequence of the overall economic recession, the economic reform, and the war. Croatia protects 6.7 percent of its total land area in parks and other reserves – a higher percentage than any of the country's eastern European neighbors, yet much lower than many western European countries. Industrial pollution is the major cause of environmental problems in Croatia, as it is in the rest of Eastern Europe. Heavy industry, light industry, metallurgy, chemical, steel, and textile industry are mostly developed in larger cities like Zagreb, Sisak, Kutina, Osijek, Split, Šibenik and their vicinity.

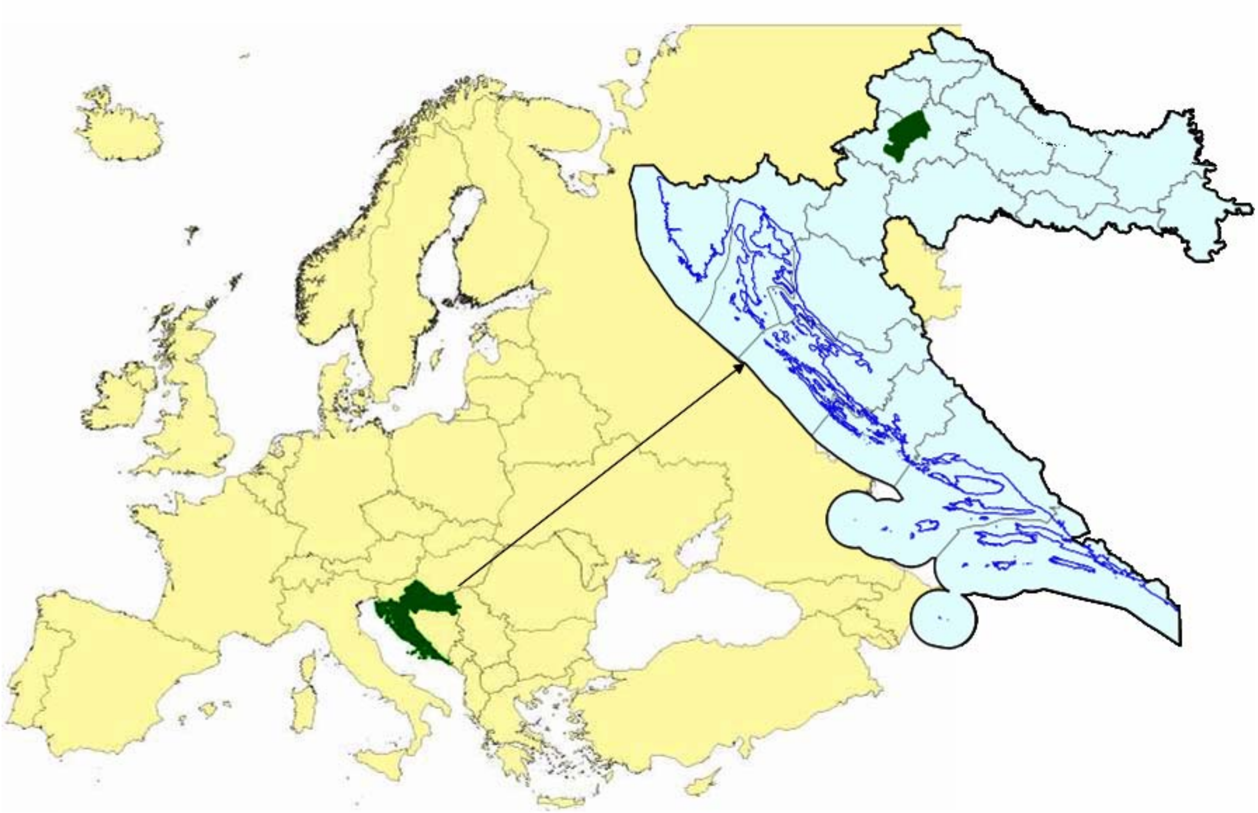

Fig. 1. Geographical position of Croatia

EXPERIMENTAL

Sampling

Moss samples were collected from 121 sampling sites during the summer and autumn of 2010 (Fig. 2). Sampling was carried out according to the guidelines of UNECE ICP Vegetation. The moss species that were collected in this study area were *Hypnum cupressiforme, Pleurozium schreberi, Homalothecium sericeum* and *Brachythecium rutabulum.* The most dominant species found in more than half of the moss samples is *Hypnum cupressiforme*. Samples were collected on a distance at least 300 m from main roads, 100 m from local roads and 200 m from villages. In order to make the moss samples representative for a reasonably large area, each sample was composed of five to ten sub-samples collected within an area of 50 × 50 m. A separate set of polyethylene gloves was used for the collection of each sample. Collected samples were stored in paper bags.

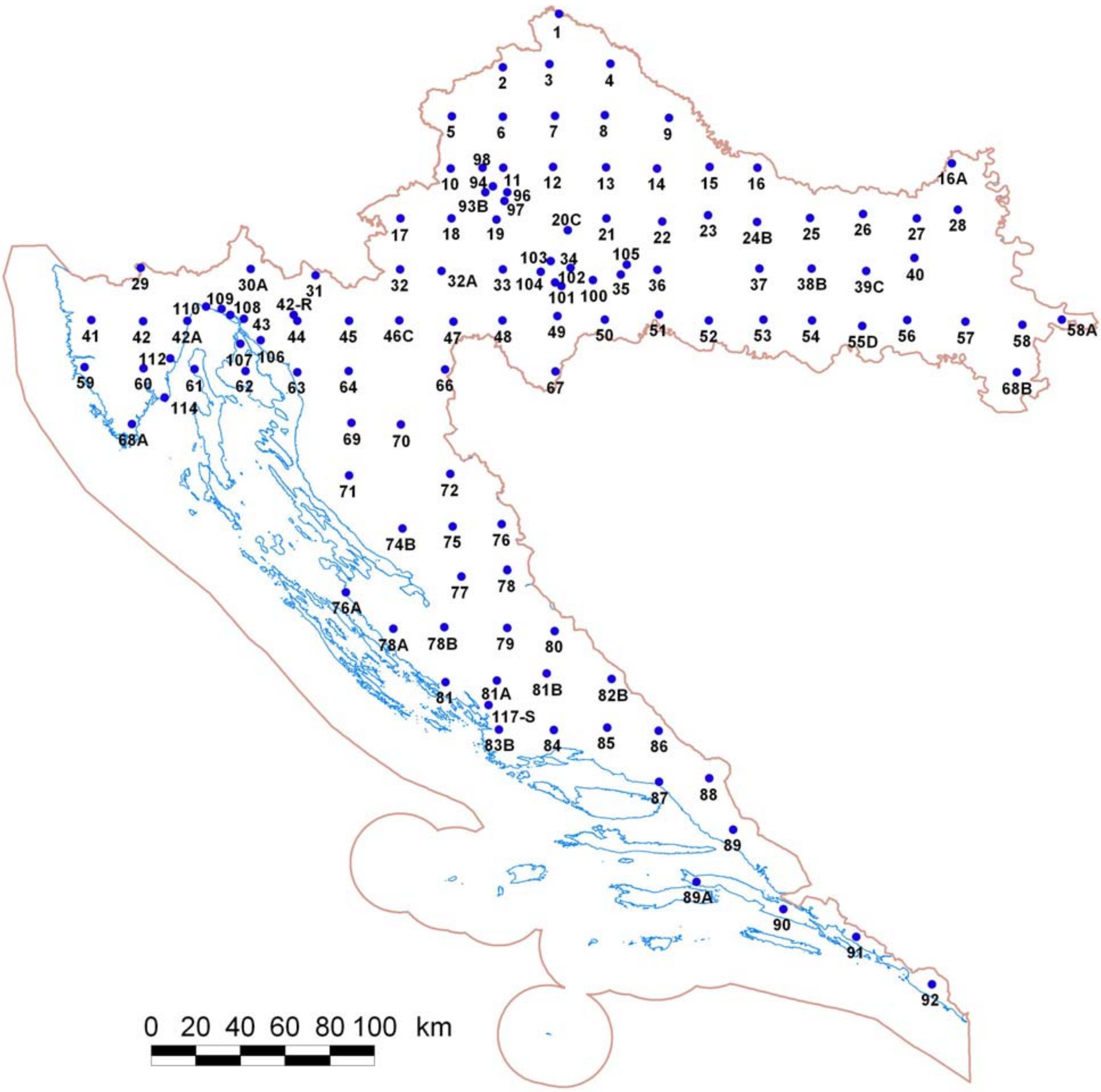

Fig. 2. Locations of sampling points

Sample preparation

Moss samples were air dried and then cleaned from other plant species and soil particles. Only the last three years growths of cleaned moss samples were separated, homogenized and powdered by hands using nylon gloves. Moss samples were digested by applying microwave digestion system (Mars, CEM, USA). From powdered material about 0.5 g were measured in specialized Teflon digestion vessels. Samples were totally digested with 7 ml of concentrated HNO_3 and 2 ml of H_2O_2 (30%) in a microwave digestion system. Digestion was carried out in two steps. In the first (ramp) step, the temperature increases to 180 ˚C for a period of 20 minutes with 400 W power and pressure of 20 bars. The second step is the holding step which holds the temperature of 180 °C for 10 minutes, on 400 W power and pressure of 20 bars. Then, the system was cooled down. Vessels were carefully opened, and digests were quantitatively transferred to 25 ml calibrated flasks, prepared for additional analyses.

Reagents and standards

The reagents used for the preparation of the moss samples were with analytical grade: nitric acid, trace pure (Merck, Germany), hydrogen peroxide, p.a. (Merck, Germany), and redistilled water. Solution used for preparing standard solutions was with concentration of 1000 mg l^{-1} (Merck, ICP-Multielement standard solution IV).

Instrumentation

For analyzing the content of cadmium in moss samples an atomic emission spectrometer with inductively coupled plasma, AES-ICP (Varian, 715ES) was used. Optimal operating instrument parameters are given in Table 1.

T a b l e 1

Instrumentation and operating conditions for ICP-AES system

RF generator			
Operating frequency		40.68 MHz free-running, air-cooled RF generator	
Power output of RF generator		700–1700 W in 50 W increments	
Power output stability		Better than 0.1 %	
Introduction area			
Sample nebulizer		Ultrasonic nebulizer CETAC (ICP/U-5000AT^{+})	
Spray chamber		Double-pass cyclone	
Peristaltic pump		0–50 rpm	
Plasma configuration		Radially viewed	
Spectrometer			
Optical arrangement		Echelle optical design	
Polychromator		400 mm fo cal length	
Echelle grating		94.74 lines/mm	
Polychromator purge		0.5 l min^{-1}	
Megapixel CCD detector		1.12 million pixels	
Wavelength coverage		177 nm to 785 nm	
Wavelength for Cd measurement		226.502 nm	
Conditions for program			
RFG power	1.0 kW	Pump speed	25 rpm
Plasma Ar flow rate	15 l min^{-1}	Stabilization time	30 s
Auxiliary Ar flow rate	1.5 l min^{-1}	Rinse time	30 s
Nebulizer Ar flow rate	0.75 l min^{-1}	Sample delay	30 s
Background correction	Fitted	Number of replicates	3

RESULTS AND DISCUSSION

Data from the descriptive statistics obtained from the analyses of cadmium in moss samples are given in Table 2 and the map of distribution is presented on Fig. 3.

Table 2

Descriptive statistics for the results of Cd obtained in moss samples

n	X_a	X_g	Md	min	max	P_{10}	P_{90}	Var	s	A	E
121	0.43	0.37	0.38	0.10	1.42	0.19	0.74	0.06	0.24	1.27	1.94

n – number of moss samples; X_a – aritmetical mean; X_g – geometrical mean; Md – median; min – minimum; max – maximum; P_{10} – 10 percentile; P_{90} – 90 percentile; Var – variance; s – standard deviation; A – skewness; E – kurtosis

The median value of cadmium content is 0.38 mg kg^{-1}. Content of cadmium vary between 0.10 mg kg^{-1} and 1.42 mg kg^{-1}. In the Podravina region the highest contents of cadmium were found at sampling sites 4 (1.14 mg kg^{-1}) and 6 (1.42 mg kg^{-1}). According to the Geochemical atlas of the Republic of Croatia (Halamić & Miko, 2009), there is an abnormal distribution of cadmium in this region. The content of cadmium in soils from this region ranges from 0.2 mg kg^{-1} to 7.1 mg kg^{-1}. Anomalous contents of cadmium have been registered in soils in flood plain sediments of the Drava River and a part of the Mura River. These higher contents of cadmium in moss samples are the result of anthropogenic origin where cadmium inputs from Slovenia (Mezica Pb-Zn mine) and Austria (Pb and Zn mines with Cd) (Šajn et al., 2011).

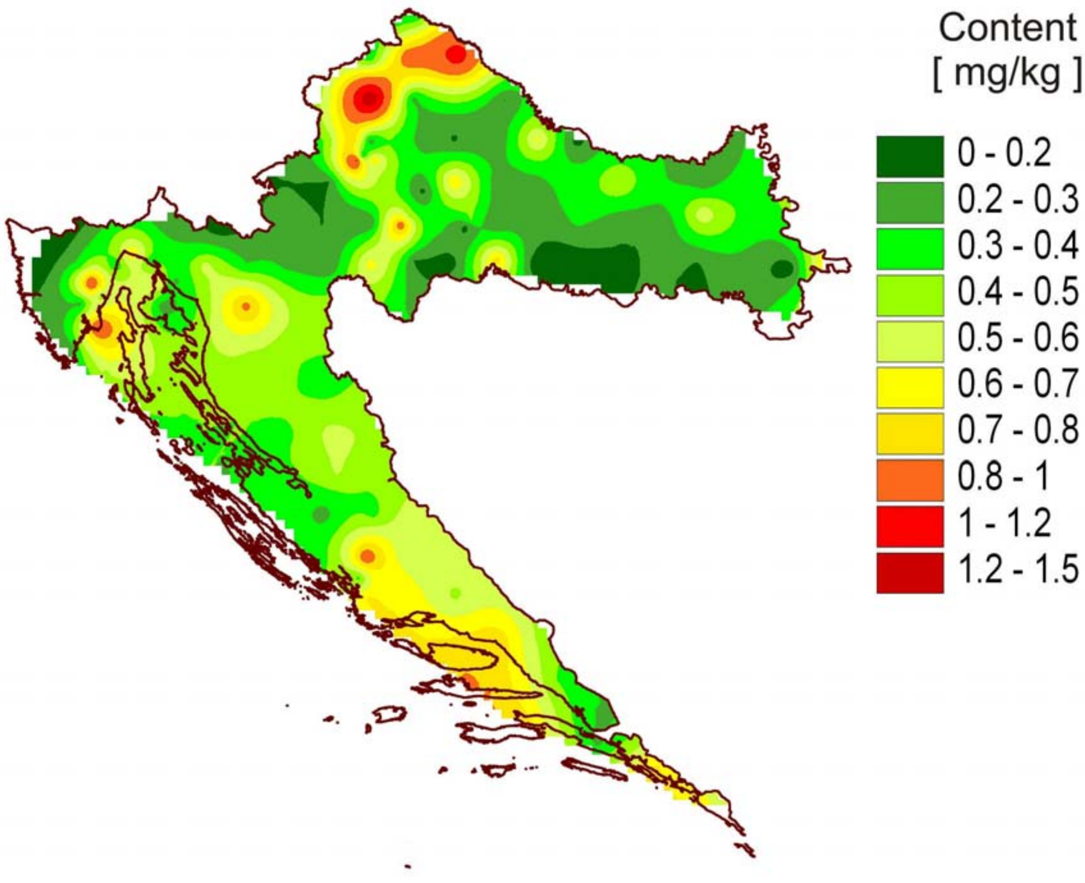

Fig. 3. Distribution of Cd in moss samples

In Central Croatia the reason for higher values for cadmium are industrial activities. Iron and steel metallurgy are developed in Sisak, and the chemical industry in Zagreb, which are probably anthropogenic sources of air pollution with cadmium. Higher values of cadmium in moss samples were found in/near Zagreb and Sisak at sampling sites 93B (1.04 mg kg^{-1}) and 104 (0.91 mg kg^{-1}).

Soils of the greater part of Coastal Croatia are loaded with cadmium content higher than in the other regions. The median is doubled in this region and amounts to 1.1 mg kg^{-1} (Halamić & Miko, 2009). According to this, high contents of cadmium in moss samples collected from this region generally have a natural origin.

Median values and ranges for cadmium contents were compared with those obtained in previous investigation in 2005 (Špirić et al., 2012). Additional comparison was made with the median values and ranges of cadmium obtained in similar studies in the neighboring (Slovenia, Serbia and Hungury), some other Balkan countries (Macedonia and Bulgaria), and Norway as pristine area. These comparisons are shown in Table 3.

Table 3

Comparison of median values and ranges obtained in the present study with those obtained in the previous study in 2005, in neighboring, other Balkan countries, and Norway as pristine area

	No. of samples	Median (mg kg^{-1})	Range (mg kg^{-1})
Croatia (Present work)	121	0.38	0.10–1.42
Croatia, 2005 (Špirić et al., 2012)	94	0.27	0.07–1.9
Slovenia, 2005 (Harmens et al., 2008)	56	0.33	0.13–1.21
Serbia, 2005 (Harmens et al., 2008)	193	0.26	0.04–1.11
Hungary, 2000 (Buse et al., 2003)	32	0.55	0.31–1.48
Macedonia, 2002 (Barandovski et al., 2008)	73	0.16	0.016–2.95
Macedonia, 2005 (Barandovski et al., 2012)	72	0.29	0.015–3.0
Bulgaria, 2005 (Harmens et al., 2008)	213	0.31	0.1–5.23
Norway, 2010 (Steinnes et al., 2011)	464	0.081	0.009–1.87

From the results presented in Table 3 it can be seen that the median value of cadmium (0.38 mg kg^{-1}) increased 1.4 times in the last five years. This result is probably caused by influence of high industrial activities in larger cities, public electricity and heat production which became the major sources of cadmium across Europe (Ilyin et al., 2007), as well as smelter and mining activities in Slovenia and Austria. In comparison with neighboring countries, it can be noted that Croatia has 1.46 times higher median value for cadmium compared to Serbia (0.26 mg kg^{-1}), Slovenia has a very similar median value (0.33 mg kg^{-1}) (Harmens et al., 2008) while Hungary has 1.45 higher median value for cadmium (0.55 mg kg^{-1}) (Buse et al., 2003). From other Balkan countries it can be observed that Macedonia is less polluted with cadmium which is seen from median values obtained in previous investigations in 2002 (0.16 mg kg^{-1}) (Barandovski et al., 2008) and 2005 (0.29 mg kg^{-1}) (Barandovski et al., 2012). Croatia has 4.7 times higher median value for cadmium than Norway (0.081 mg kg^{-1}) (Steinnes, 2011) which leads to the opinion that Croatia is relatively polluted with cadmium. But it should be emphasized that, except for Norwegian study, results for other countries are obtained in investigations undertaken a few years ago, which means that the situation with air pollution has probably changed during those years.

CONCLUSION

Moss biomonitoring technique and atomic emission spectrometry with inductively coupled plasma (ICP-AES) were applied for analysis of cadmium content in moss samples collected all over the territory of Croatia. The highest contents of cadmium were found in the Podravina region as a result of anthropogenic origin from mining activities in Slovenia and Austria. Higher contents of this element were also found in moss samples collected in the regions of Central Croatia (near Zagreb and Sisak) as a result of industrial activities, and Coastal Croatia as a result of geological origin. Median value of cadmium is insignificantly increased during the last five years. By comparing median value of cadmium with data obtained in some other neighboring and Balkan countries, it can be observed that in most cases Croatia has a slightly higher value.

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Р е з и м е

ОПРЕДЕЛУВАЊЕ НА АТМОСФЕРСКАТА ДЕПОЗИЦИЈА НА КАДМИУМ ВО ХРВАТСКА СО УПОТРЕБА НА БИОМОНИТОРИНГ СО МОВ И ICP-AES

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Клучни зборови: атмосферска депозиција; кадмиум; биомониторинг со мов; ИСП-АЕС; Хрватска

Хрватска за прв пат учествуваше во Меѓународната програма за ефектите на загадувањето на воздухот со тешки метали врз вегетацијата и земјоделските култури во Европа (UNECE ICP Vegetation) во 2005, од 96 локации соодветно распределени на целата нејзина територија беа собрани различни видови примероци од мов (*Hypnum cupressiforme, Pleurozium schreberi, Brachythecium rutabulum* и *Homalothecium sericeum*). Во 2010 година за истражувањето се вклучени нови 27 локации. Примероците од мов беа собрани во текот на летото и есента во 2010 година. Собраните примероци беа исушени, исчистени и целосно растворени со употреба на микробранов систем. Содржината на кадмиумот во овие раствори беше анализирана со примена на атомска емисиона спектрометрија со индуктивно спрегната плазма (ICP-AES). Добиените резултати беа споредени со резултатите добиени во претходните истражувања во Хрватска и во некои соседни земји, како и во Норвешка како најмалку загадена област. Содржината на кадмиум во испитуваните примероци од мов се движи од 0,10 mg kg^{-1} до 1,42 mg kg^{-1}. Вредноста на медијаната (0,38 mg kg^{-1}) е за 1,41 пати повисока од вредноста добиена во истражувањето спроведено во 2005 година. Споредено со другите земји, Хрватска има незначително повисока вредност на медијаната. Највисоки вредности за содржината на кадмиум се најдени во примероците собрани од регионот на Подравина (1,14 mg kg^{-1} и 1,42 mg kg^{-1}), каде што кадмиумот има антропогено потекло како резултат на екстракцијата од рудниците за олово и цинк во Словенија и Австрија. Повисоки вредности на кадмиумот се забележуваат и во примероците собрани во околината на индустриските центри во северните делови на Хрватска, како резултат на човековите активности, и во примероците собрани во приморскиот дел каде што кадмиумот е застапен како резултат на геолошко влијание.