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First survey of atmospheric heavy metal deposition in Kosovo using moss biomonitoring

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Abstract: Bryophytes act as bioindicators and bioaccumulators of metal deposition in the environment. The atmospheric deposition of Cd, Cr, Cu, Fe, Hg, Ni, Mn, Pb and Zn in Kosovo was investigated by using carpet-forming moss species (*Pseudocleropodium purum* and *Hypnum cupressiforme)* as bioindicators. This research is part of the European moss survey coordinated by the ICP Vegetation, an International Cooperative Programme reporting on the effects of air pollution on vegetation to the UNECE Convention on Long-range Transboundary Air Pollution. Sampling was performed during the summer of 2011 at 25 sampling sites homogenously distributed over Kosovo. Unwashed, dried samples were digested by using wet digestion in Teflon tubes. The concentrations of metal elements were determined by atomic absorption spectrometry (AAS) equipped with flame and/or furnace systems. The heavy metal concentration in mosses reflected local emission source. The data obtained in this study were compared with those of similar studies in neighboring countries and Europe (2010-2014 survey). The geographical distribution maps of the elements over the sampled territory were constructed using GIS technology. The concentrations of Cr, Ni, Pb and Zn were higher than the respective median values of Europe, suggesting that the zones with heavy vehicular traffic and industries emission input are important emitters of these elements. Selected zones are highly polluted particularly by Cd, Pb, Hg and Ni. The statistical analyses revealed that a strong correlation exists between the Pb and Cd content in mosses and the degree of pollution in the studied sites were assessed.

Key words: Air pollution, Heavy metal; Moss Biomonitoring; AAS, Contamination factor, Pollution load index, GIS technology, Kosovo

Introduction

Air pollution by harmful chemicals or biological materials is one of the serious problems in the world. This serious concern is well documented by the increasing number of publications in recent years. It is probably related with metal accumulation in the biota and vegetation and the toxicity of heavy metals which can harm public health. Different methods and models are applied in monitoring the air quality by measuring the concentration of pollutants in the air or directly in atmospheric deposits, by building different models that describe the distribution of the pollutants or by using different biomonitors (Schilling et al. 2002, Vianna et al. 2011, Blagnytė et al. 2010, Viet et al. 2010, Vukovic et al. 2013, Paoli et al. 2013). Mosses act as bioindicators as well as bioaccumulators of metal deposition in the environment (Rühling and Tyler 1968, Rühling et al. 1987, Castello 2007, Stihi et al. 2008) and the use of native terrestrial carpet-forming mosses as biomonitors is now a well-recognized technique in studies of atmospheric contamination (Fernandez and Carballeira 2002; Harmens et al. 2010, 2011, 2015). Moss biomonitoring technique is applied as a practical mode in establishing and characterizing deposition sources. Mosses have no real root system or cuticle layer (Blagnytė et al. 2010). They take nutrients directly from wet and dry deposition (Onianwa 2001; Zeichmeister et al. 2003) and the mineral adsorption occurs over their entire surface (Rühling and Tyler 1968).

Heavy metals (HMs) occur naturally in the environment, with the variations in their concentrations. They are released to the environment from a range of human and natural sources. Environmental sources of pollutants could include construction and demolition activities, mining and mineral processing, agricultural activities, sea spray, windblown dust, automobiles and transportation related activities on the road (Melaku et al. 2008). The current anthropogenic metal emissions are up to several orders of magnitude higher than their natural contents (Chmielewska et al. 2003). Atmospheric emissions tend to be of greatest concern in terms of human health, both because of the quantities involved and the widespread dispersion and potential for exposure that often ensues (Järup 2003). Numerous studies worldwide have confirmed that both long–and short–term exposure to air pollutants are associated with several health problems and the increases in mortality, particularly from bronchitis, pneumonia, nephritis and cancer (Duffus 2007, Gurgueira et al. 2002,), and morbidity (Venners et al. 2003; Dockery 2009). Different transition metals may act as possible mediators of particle-induced injury and inflammation (Dreher et al. 1997; Schaumann et al. 2004; Chen and Lippmann 2009), based on their ability to generate reactive oxygen species (ROS) in biological tissues (Øvrevik et.al 2015; Schwarze et al. 2010). At present, particulate matter (PM) and ground-level ozone (O_3) are Europe's most problematic pollutants in terms of harm to human health (Air quality in Europe — 2014). The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic (Järup 2003). Since the 1980s there have been many studies about assessing the atmospheric fallout through the biomonitoring technique by analysis of mosses (Berg et al. 1996; Faus-Kessler et al. 1999; Fernandez and Carballeira 2001; Castello 2007; Stihi et al. 2008; Harmens et al. 2015). Mosses are well known and widely used bioindicators due to their specific features (Rühling et al. 1987; Rühling, 1994; Markert et al. 1999); the cuticle is lacking or reduced.

Kosovo is situated in the Balkan Peninsula within the longitudes 41° 50’ 58’’ and 43° 15’ 42’’ and within the latitudes 20° 01’ 30’’ and 21° 48’ 02’’. The surface area of 10,900 km² is characterized by an average altitude of about 800 m above sea level. It is characterized by a complex geologic setting and high mineral activity of Pb-Zn, Cu, Ni and Cr positioned in different parts of the territory (Durmishaj 2012). The total estimated land is at 858,063 ha, and about 63.3% is agricultural land area and 35% is the forest area.

The first study of atmospheric deposition in Kosovo using mosses was performed under the framework of the UNECE International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation). The results obtained in this study have been compared with those from the investigations obtained in similar studies in some neighboring and European countries. The distribution of the elements in each sampling site identified the sites with higher levels of these elements, and the main anthropogenic and natural sources were discussed. The aim of this study was to investigate spatial trends of trace metal deposition in Kosovo by using mosses as biomonitors and to identify local sources of emissions.

Materials and methods

Sampling procedure

Moss samples were collected from 25 sampling sites evenly distributed over the territory of Kosovo during the dry period of summer 2011. The most dominant moss species in this study area were the bryophyte family of carpet-forming moss species, i.e. *Pseudoscleropodium purum and Hypnum cupressiforme*. *P. purum* was sampled at 23 sites and *H. cupressiforme* at the other two sites (ST.1 and St. 7). The locations of sampling sites were situated at least 300 meters away from main roads or buildings and 100 m from small roads and single houses. The high mountain areas, respectively at the northern, western and the southern part of Kosovo, were avoided. Most of the samples were collected in open areas. Five to ten sub-samples were collected within an area of 50 m x 50 m and mixed in one composite sample. Samples were stored in paper bags and transferred to the analytical laboratories. Samples were cleaned from extraneous material (litter and dead leaves). The green or greenish-brown parts of the plant were used for further analysis directly without washing or any other treatments. To prevent any contamination of the samples, sampling and sample handling was performed using disposable polyethylene gloves. A more detailed description of sampling procedure is given in moss survey sampling manual (Harmens et al. 2010a) and in our previous publications (Qarri et al 2013, Bekteshi et al. 2015).

The systematic sampling scheme with a homogeneous distribution among 25 sampling sites with equal densities (1.5 moss samples/1000 km^2 is recommended (Harmens et al., 2010; Qarri et al., 2014a). The positions of sampling sites are shown in Fig. 1.

Sample Preparation

Unwashed green and green-brown parts of the moss that represent 3–5 years of growth of the plant were used for analysis after cleaning from foreign materials adhered to the surface of the samples such as tree bark, lichens, soil dust and dead materials. The samples were dried to constant weight for 48 hours at 30–35 ºC. To reduce particle size and satisfy the conditions for homogeneity, the samples were hand crushed (handling was performed by using disposable polyethylene gloves) and homogenized prior to analysis.

Method of Analysis

Wet digestion of a homogeneous sub-sample was applied. About 0.5 g moss samples were transferred to the half pressure Teflon tubes and 10 ml nitric acid (9:1) was added. The closed tubes were left at room temperature for 48 hours and then were digested for 3 hours at 80-90 ºC. The temperature was then increased to 200 ºC for half an hour for further digestion. The tubes were opened and the acid was evaporated till a very small volume. After cooling, the mass was transferred to 25 ml volumetric flasks and was filled till the mark with Osmosis treated water. Heavy metals, such as Cu, Cd, Pb, Mn, Ni were determined by *atomic absorption spectrometry* (AAS) equipped with an electro thermal system by using novA400, Analytic Jena atomic absorption spectrometer (AAS). Flame AAS was used for Zn and Fe determination; cold vapor atomic absorption spectrometry (CVAAS) was used for mercury determination by using Varian 10+ instrument. The analysis was performed at the Department of Chemistry of the Faculty of Natural Sciences, University of Tirana, Albania. The solutions used for preparing standard solutions had a concentration of 1,000 mg L^{-1} (Merck Sertpur standard solutions). The range of concentrations of the elements in the calibration solutions and the detection limits (LD), equal to 3SD of the lowest instrumental measurements of the blanks were calculated. Appropriate limits of quantification were calculated as 10 LD of the lowest instrumental measurements of the blanks. The detection limits calculated as 3 SD of the lowest instrumental measurements of the blanks were: 0.007 mg kg^{-1} for Hg, 0.027 mg kg^{-1} for Cd and Zn, 0.078 mg kg^{-1} for Cu and Mn, 0.15 mg kg^{-1} for Fe, Cr and Ni. Three replicates per moss sample were digested and three replicate measurements per digest were performed.

Quality control of the analysis

The quality control of AAS results was ensured by multiple analysis of the IAEA-140/TM reference sample (Fucus; sea plant homogenate). The AAS concentration data of the elements in the reference sample, given as mean concentration ± SD, were in good agreement with the certified data (Table 1). Beside it, a control moss sample (*H.cupressiforme sp*.) collected in Albania (Alb-17, ICP Vegetation Programme, Moss survey 2010), N40 12 31; E19 35 07, was analyzed by two different methods, AAS and *inductively coupled plasma atomic emission spectroscopy* (ICP-AES) (Qarri et al. 2013). The quality control for the ICP-AES results was checked by multiple analyses of the examined samples and certified moss reference materials M2 and M3 (Steinnes et al., 1997; Harmens et al., 2010). The measured values were in good agreement with the recommended values. The certified and obtained data of the analyzed elements in certified reference moss samples M2 and M3 were reported in the previous study (Qarri et al., 2013). The AAS measured concentrations of the elements were in good agreement with the ICP-AES values (Table 1). In addition, the blanks were measured in parallel to the decomposition and the analysis of the samples.

Table 1 Metal concentration (mg/kg, DW) in reference sample (IAEA-140/TM) and moss control sample (Alb-17)

Parameters	**Zn**	**Fe**	**Mn**	**Cu**	**Cd**	**Pb**	**Cr**	**Ni**	**Hg**
IAEA-140/TM[1]	46.8±1.4	1268±38	54.8±2.1	4.87±0.46	0.553±0.033	2.23±0.31	9.78±0.94	3.72±0.44	0.036±0.012
IAEA-140/TM[2]	47.3	1256	56.1	5.05	0.537	2.19	10.4	3.79	0.038
Alb-17[1]	8.33±0.59	954±47	46.1±2.9	3.22±0.38	0.15±0.024	2.93±0.24	2.11±0.28	2.19±0.32	0.15±0.011
Alb-17[3]	7.84	985	41.7	4.62	0.15	2.98	2.32	2.33	-

[1] AAS data; [2] certified data; [3] ICP-AES data

Data processing and statistical analyses

Various statistical analysis techniques can be used on spatial distribution and multivariable data to reveal the underlying deterministic behaviors, and thus help clarify the cause and the effects of relationships in environmental problems. The Descriptive Statistics method was applied to the elemental concentration data set to explain variations in the data, or predict future data.

The analytical data of all observations were entered into a data matrix and Descriptive Statistics, exponentially weighted moving average (EWMA) chart and multivariate analysis was used to interpret the results. The application of EWMA charts in spatial distribution was described in our previous article (Qarri et al. 2014). Univariate control chart was used to investigate the moving ranges of two successive observations and to estimate variability of data. The upper and lower control limits (UCL and LCL) were computed for median moving average, by applying pooled standard deviation and the proper values of λ (the weight of EWMA, that ranges from 0 to 1). The values of European medians of each element were used as a reference line. The values of the UCL [median + 2 SDEV] were appointed as the upper limit of background variation. It was suggested as ''threshold level'' for soil cleanup goals of environmental legislation (Reimann et al. 2005) and are adopted to identify the outliers of each element (Matschullat et al. 2000, Reimann et al. 2005). The values under the UCL [median - 2 SDEV] were appointed as regional background level (BCL).

The Geographic Information System, Arc-GIS 10.2 was used to generate the maps presenting the geographical distribution of the elements. Local deterministic method combined with the radial basis functions was used for spatial interpolation. This method is able to calculate the predictions from the measured points within neighborhoods, which are smaller spatial areas within the larger study area. It provides suitable visualization of the univariate data of the element studying atmospheric deposition at each monitoring sites.

To distinguish the contamination level caused by each element, the contamination factors (CF) scales (Fernandez and Carballeira 2001) were calculated. The scale established by Fernandez et al. (2000) is based on specific approaches to terrestrial mosses and allows the categorization of the sampling sites by taking into account the method of dispersion of contaminants in the atmosphere. The scale of contamination factors is calculated as the ratio of median values of each element of the mosses of the investigated area and the median value of each element of Norway mosses, which is considered as background level. Beside it, the pollution load index (PLI) proposed by Tomlinson et al. (1980) has been used for selected metals. Two different PLIs were proposed by Tomlinson et al. (1980), site PLI (PLI_{site}) and zone PLI (PLI_{zone}). The PLI_{site} is calculated by the n-root of the product of the CF values of the metals with the highest contamination factor (Tomlinson et al. 1980), while the PLI_{zone} is calculated by the n-root of the product of the PLI_{site} values of the metals with the highest pollution loads (Tomlinson et al. 1980, Boamponsem et al. 2010):

$$PLI_{site} = \sqrt[n]{CF_1 \times CF_2 \times .... \times CF_n}$$

$$PLI_{zone} = \sqrt[n]{PLI_1 \times PLI_2 \times .... \times PLI_n}$$

The PLI_{moss} index provides a simple and comparative mean for assessing air quality (Antisari et al. 2011), but it do not provide information about health effect of the chemicals. The PLI values vary from 0 (unpolluted) to higher than 5 (extremely polluted) as follows (Zhang et al. 2011): PLI = 0 background concentration; 0 <PLI<1 unpolluted; 1 < PLI<2 moderately to unpolluted; 2 < PLI < 3 moderately polluted; 3 < PLI < 4 moderately to highly polluted; 4 < PLI < 5 highly polluted; PLI > 5 extremely polluted.

Several multivariate data analysis techniques have been applied to atmospheric data (Wiedensohler et al. 1996; Statheropoulos et al. 1998, Astel et al. 2008, Viet et al. 2010, Baceva et al. 2013). Multivariate data analysis is a powerful tool to investigate multivariate and complex data sets by revealing trends and relationships of these parameters. Factor analysis (FA) was used in the Kosovo mosses data set to identify sources of metals content and to quantify their contribution to the variation of these parameters. The numbers of the groups and the most important factors were determined and discussed. MINITAB 17 software package was applied for data processing and statistical analyses**.**

Results and discussion

The results of descriptive statistic analysis of concentration of heavy meals in the moss samples are shown in Table 2.

Table 2 Descriptive statistics of the concentration data (Hg, Cd, Cr, Cu, Fe, Ni, Pb, Mn and Zn; mg/kg, DW) in moss samples (n=25)

Parameters	**Hg**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Mn**	**Fe**
Mean±SDEV	0.055±0.008	0.37±0.05	2.7±0.38	3.1±0.42	5.9±0.76	12.1±1.47	37.8±3.83	92.7±7.2	570±45
Mean	0.055	0.371	2.72	3.12	6.6	12.1	37.4	92.7	570
Median	0.033	0.127	2.63	3.04	2.0	7.78	38.5	86.2	288
St. Deviation	0.070	0.62	0.65	0.36	11	10	15	67	259
Sample Variance	0.005	0.39	0.43	0.13	116	103	239	4,481	627
CV%	126	167.3	24.0	11.4	177.2	83.9	40.8	72.2	393,182
Kurtosis	13.5	15.3	1.5	-0.2	4.47	5.4	0.3	5.3	110
Skewness	3.4	3.65	1.07	0.46	2.46	2.08	0.63	2.03	10.6
Range	0.338	3.025	2.92	1.47	32.97	45.16	61.7	303.7	2.9
Minimum	0.009	0.028	1.63	2.46	1.22	2.62	14.3	22.3	124
Maximum	0.347	3.053	4.55	3.93	34.19	47.78	76	326	3,082

The order of the concentration of the elements in moss samples was Fe>Mn>Zn>Pb>Ni>Cu>Cr> Cd>Hg. High disparity exists in the concentrations of Cd, Hg, Fe, Ni and Pb in the moss samples. Most of elements follow lognormal distribution (P>0.05) that is characteristic for the lithogenic origin of the crustal elements (Clark and Washington 1924, Vinogradov 1962) and is reflected in atmospheric deposition from windblown soil dust. Only Ni and Cd do not follow the lognormal distribution by indicating that their distribution in moss samples is influenced by other anthropogenic factors. The coefficients of variation (CV%) (Table 2) are higher than 75% for Cd, Hg, Fe, Ni and Pb, are moderate (25–75%) for Mn and Zn and lower than 25% for Cr and Cu. CV value is the highest for Ni (177.2%) followed by Cd (167.3%), Hg (126%), Fe (105%) and Pb (84%). High values of CV(%), kurtosis and skewness for Cd, Fe, Hg, Pb and Ni explain a large range of variation of the concentration data that are positively skewned, by probably indicating the influence of complicated factors (Wang et al. 2010). The concentration level of Cd and Hg in European moss samples are quite stable for a long period of time (respectively since 2005 and 1990) (Harmens et al. 2005), their high variation values in moss samples of Kosovo are probably associated with windblown soil dust that represents historical waste deposition or originates from the mineral soil layer, and/or from industrial activity (Harmens et al. 2015). For a better interpretation of the results, the contamination factors (CF) scales were calculated (Table 3).

Table 3 The contamination factors (CF) and Contamination Classification (Fernandez et al. 2000) for metal concentrations in mosses in Kosovo.

Parameter	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
CF	2.19	4.78	0.84	1.60	0.34	1.75	6.65	1.45
Classification	C2	C3	C1	C2	C1	C2	C4	C2
Contamination	Suspected	Slightly	Non Contaminated	Suspected	Non Contaminated	Suspected	Moderate	Suspected

The CFs results indicate that the elements Cu, Mn, Cd, Fe, Ni and Zn are associated with the first two categories of contamination scales, C1 and C2, i.e. uncontaminated areas (a CF of 2 could be easily obtained from natural variation). Cr and Pb are associated with the third (C3) and the fourth (C4) category of contamination scale, described as slightly and moderately polluted scale. Even thought the complex geologic settings of Kosovo and high mineral activity of Pb-Zn, Cu, Ni and Cr positioned in different parts of the territory (Durmishaj 2012), the CF values were lower than those reported for Albania (Qarri et al. 2013). It is probably associated with the high percentage of land use (Arcotrass et al. 2006), and forest area in Kosovo, that is the main factor of decreasing the wind blowing soil dust content. To investigate the distribution of the elements in moss samples, the GIS maps are plotted as is shown in Fig. 1.

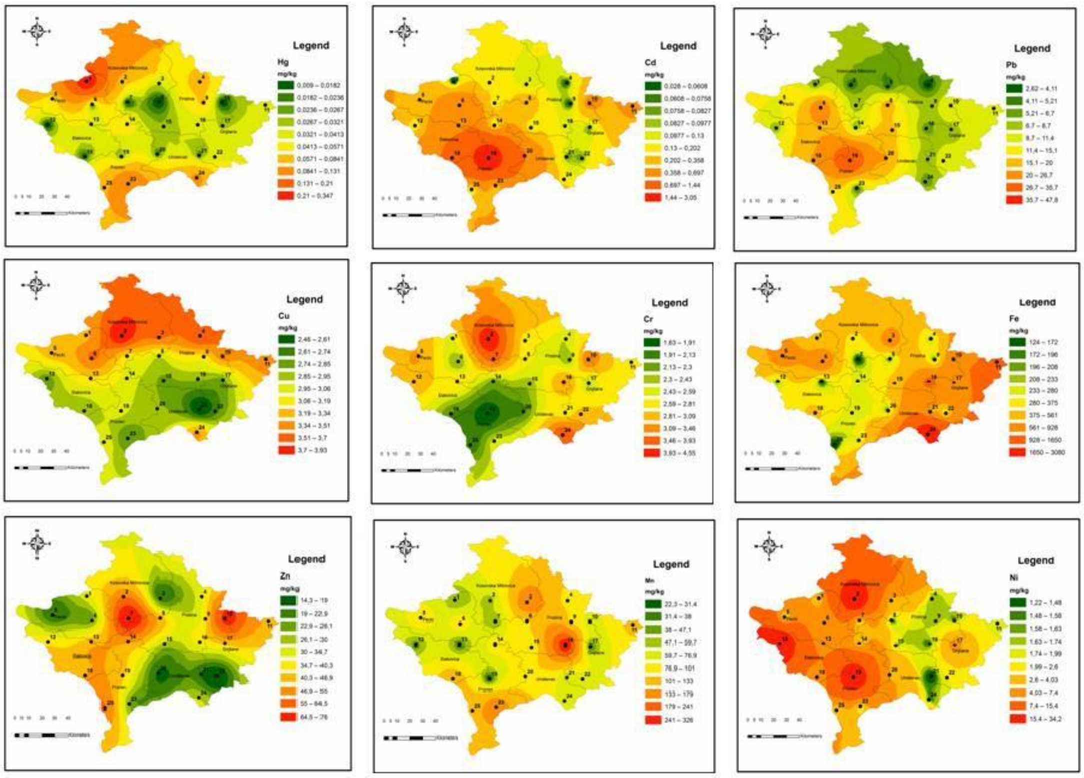


Fig. 1 The GIS maps of trace metal atmospheric deposition in Kosovo

The distribution pattern of the elements showed a regional more or less uniformity influence from the local dust particles that were entrapped by the moss and the presence of local emitting points with relatively high content of the elements.

Spatial distribution of the elements

Mercury

Mercury is quite a global pollutant, so would expect it to behave with a different distribution pattern from other metals (Harmens et al. 2015). The mercury level in Kosovo is remarkably lower in comparison to those in Albania, Macedonia and Bulgaria (Qarri et al. 2013, Harmens et al. 2015). High variability of Hg in moss (CV%=126) reflect different contamination level along the monitoring region. Hg concentrations were high in the north (site 1, 2 and 4) and the south (site 23, 24, 25) of Kosovo (Fig. 1.a and Fig. 2). The sampling sites St. 1, 2 and 4 are mainly positioned close to Pb and Zn mines of Zvecan and Zn refinery of Mitrovica, as well as to the coal fired power plants (Kosovo A and Kosovo B). Combustion facilities have been identified as the main local source of mercury emissions. Local sources that are being investigated for mercury emissions are scrap metal

processing facilities. The use of mercury in switching devices in automobiles and large appliances has led many states to believe that facilities of scrap metal processing, are probably the potentially high emission sources of mercury (Sastry et al. 2014).
The next high Hg level at the stations in the south part of Kosovo (St. 23, 24, 25, Fig 1a and Fig. 2) are probably representing the history of mercury contamination at the site. Mercury is also occurring naturally in the soil and minerals and may enter the air as windblown dust particles (WBK & Associates Inc. 2004), mostly in the form of fine particulate matters.

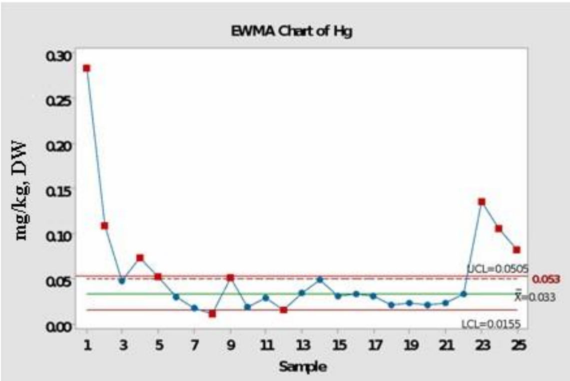
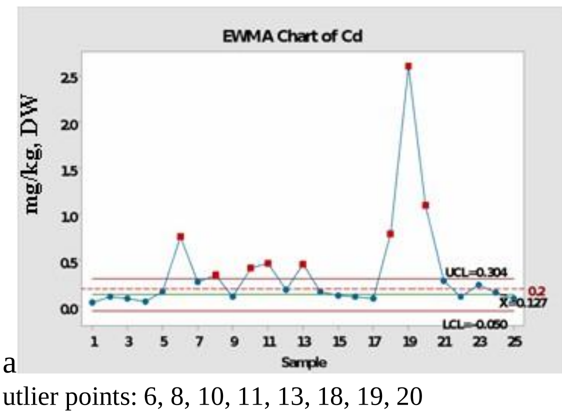
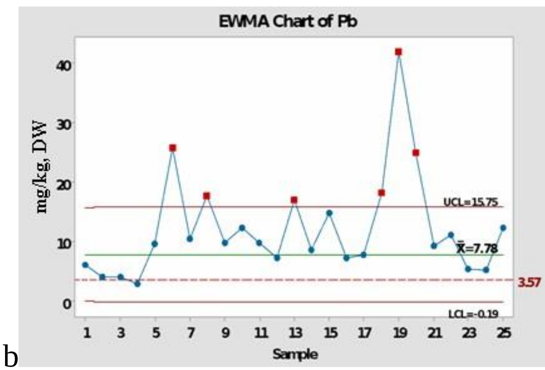


Fig. 2 EWMA charts of Hg distribution in moss samples **(**Outlier points: 1, 2, 4, 5, 9, 23, 24 and 25)
(Centre Line–Kosovo median value; dashed line–European median value; LCL - lower control limit, LCL=median-2SDEV; UCL – upper control limit, UCL=median+2SDEV)

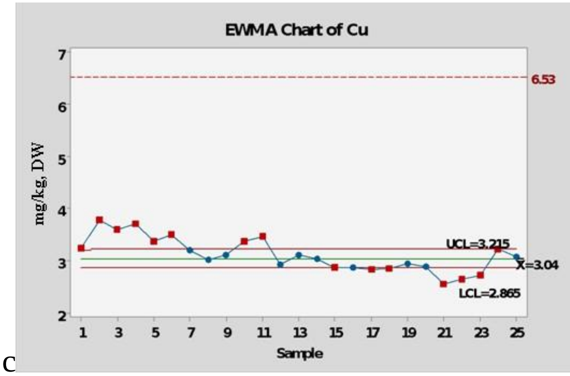
Cadmium, Cupper, Lead and Zinc
Cu concentrations were generally low in mosses sampled in Kosovo compared to the median values of other European countries (Harmens et al. 2015), while Cd, Pb and Zn content were found to be higher. Manufacturing and construction industries are the main sources of lead emission (41%), and traffic emission is a secondary source of lead emission (about 17% of total emission) (Harmens et al. 2008). Beside it, Pb and Zn are typical elements, consequences of air transport and not affected by lithological backgrounds. Pb concentrations were generally high in the south-west (sites 18, 19 and 20, Fig. 1c and Fig. 3b) and low in the north-west (Fig. 1c and Fig. 3b). The median Pb concentration in mosses was higher in Kosovo than in many of the other European countries as the use of leaded petrol has only been regulated in Kosovo since September 2012 (Kosovo - CEA, 2013). Road transport may have a considerable effect on the high content of Pb in mosses, while Pb acts as the marker element for motor vehicle emissions (Huang et al. 1994). Other sources of lead exposure in Kosovo are lead mines and their tailings that are still contaminating the air from windborne dust. The deposition of leaded particles is also a major source of lead exposure in Kosovo (Kosovo - CEA, 2013).
Zn and Cu are mostly associated with city dust, traffic exhaust, soil and resuspended road dust. Zn is present near the Zn refinery of Drenas (St. 7) and the Pd-Zn mines (St. 10). The highest Zn content was found at the station St.7 (Fig 1g and Fig. 3d), and is distinguished by the anthropogenic origin caused by the emission of two important thermal electro-power stations of Kosovo (Kosova A and Kosova B) that are positioned close to this station. The next Zn polluted areas were found around the stations St. 10 and 11 positioned close to the Pb, Zn mine of Artana.



a Outlier points: 6, 8, 10, 11, 13, 18, 19, 20

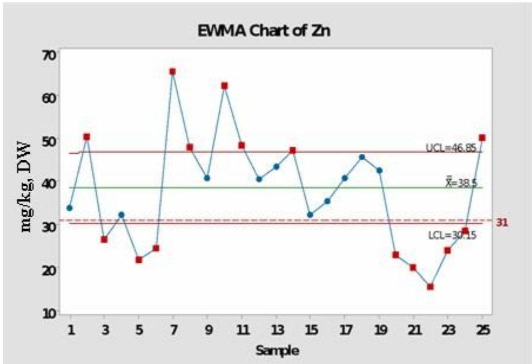


b Outlier points: 6, 8, 13, 18, 19, 20



c

Outlier points: 1, 2, 3, 4, 5, 6, 10, 11, 24



d

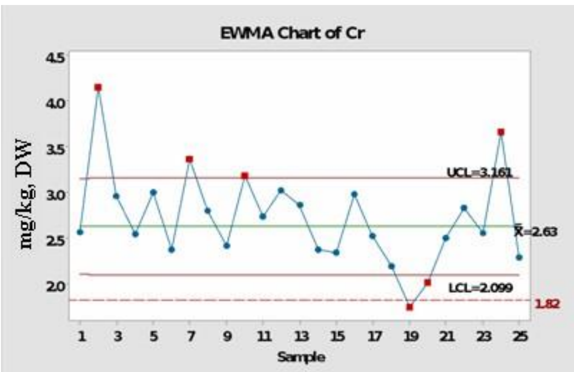
Outlier points: 2, 7, 8, 10, 11, 14 and 25

Fig. 3 EWMA charts of Cd, Cu, Pb and Zn distribution in moss samples
(Centre Line–Kosovo median value; dashed line–European median value; LCL - lower control limit, LCL=median-2SDEV; UCL – upper control limit, UCL=median+2SDEV)

Chromium, Iron, Nickel and Manganese

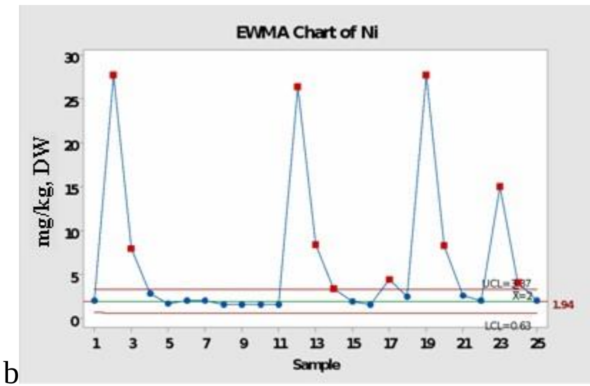
The main contribution of Cr, Fe, Ni and Mn elements probably originates from the industrial emission of the refinery of Trepca (St. 2), Cr mine (St. 7, 10 and 23) and manganese mine (St. 16). It suggested a high level of emission caused from the industrial activity focused in the middle and north part of Kosovo. The associations of these elements may be attributed to their geogenic origin (Tume et al. 2010) and industrial emissions from mineral and metal processing plants. The association of Cr and Fe is also related to air pollution (Lazo et al. 2013).

The median concentrations of Pb, Zn and Cr in mosses were higher in Kosovo than in most of the other European countries (Fig. 2b, 3d and 4a, respectively); those of Hg, Cd, Fe were lower (Fig. 2, 3a and 4c, respectively); and the median concentration of Ni and Cu in mosses of Kosovo were in the same level with many other European countries (Fig. 4b and 3c, respectively). High background level (BCL>LCL) were found for Cd, Cr, Ni, Fe and Mn (Fig. 3 and 4) that can produce high levels of exposure to these chemicals, while the BCL of Hg, Cu and Zn (Fig. 2 and 3) are lower (BCL<LCL) that is expected, the chemical does not produce a high level of exposure. The BCL is an important parameter for the calculation of PLI index that will provide low PLIs for the elements with high background level. Therefore, the chemical identified as highly toxic, i.e. Hg, Cd and Pb, are critical elements assessing health risk. The estimates of the health impacts attributable to exposure to air pollution indicate that fine particulate matter (PM2.5) concentrations in 2010 for Kosovo (Kosovo - CEA, 2013) is similar to those of European countries (Air quality in Europe — 2014). It is a reason to think that high values of concentration of Hg, Cr, Cu, Fe, and Zn at the outlier sites are probably associated with the local anthropogenic emission from mining and industrial activities. Aiming to assess air quality and to investigate the health risk from the contaminated sites the pollution load index is calculated.



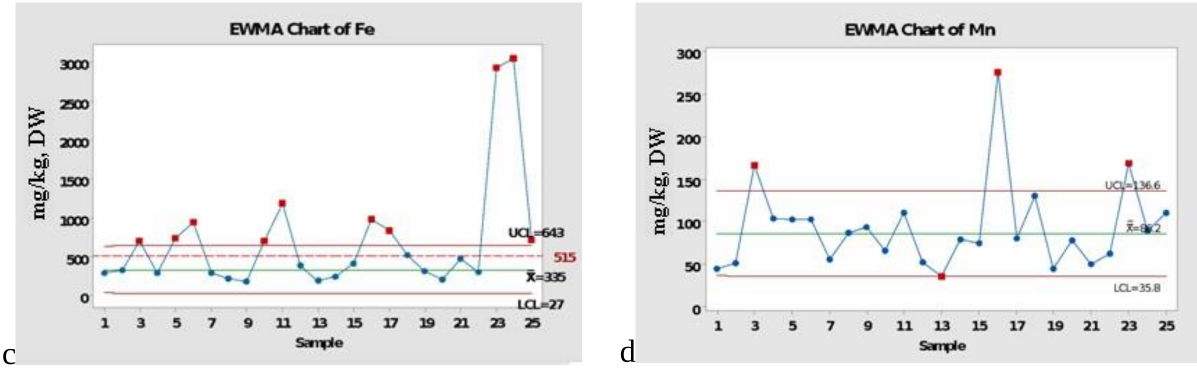
a

Outlier points: 2, 7, 10, 24



b

Outlier points: 2, 3, 12, 13, 14, 17, 19, 20, 23, 24



c Outlier points: 3, 5, 6, 10, 11, 16, 17, 23, 24, 25

d Outlier points: 3, 16 and 24

Fig. 4 EWMA charts of Cr, Fe, Ni and Mn distribution in moss samples
(Centre Line–Kosovo median value; dashed line–European median value; LCL - lower control limit, LCL=median-2SDEV; UCL – upper control limit, UCL=median+2SDEV)

Pollution load index

The pollution load index (PLI) is calculated for each sampling site taking in consideration the highest content of the selected metals like Hg, Cd, Pb, as the most toxic elements, and Fe, Ni, Zn, the elements with higher concentration values in mosses of Kosovo compare to European median.

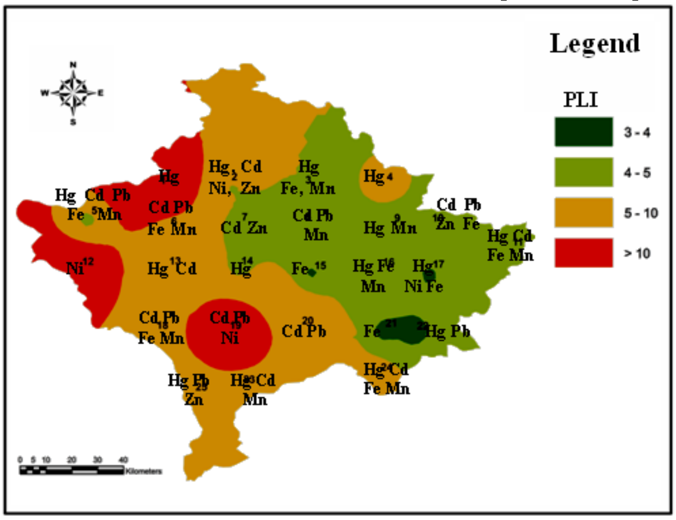


Fig. 5 The GIS map of the most polluted sites based on PLI ranges (Zhang et al. 2011) of Hg, Cd, Pb, Ni, Fe and Zn

It is shown from the map of the site PLI_{site} (Fig. 5) that the whole territory under investigation (except the sites ST.21 and 22, as moderately to highly polluted) belong to very polluted (4>PLI<5) and extremely polluted sites (PLI>5) for different elements. Based on site PLI_{site} data, the zone pollution load index is calculated for the whole territory of Kosovo. The result of zone pollution index ($PLI_{zone} = 6.3>5$) indicate that the whole territory under investigation is highly polluted from Hg, Cd, Pb, Ni, Fe and Zn. The most polluted sites are close to the most populated urban areas that will cause significant health effects. The highest risk of human exposure to individual metals might be expected in areas with the highest emission sources and concentrations of these individual metals in mosses. However, a clear relationship cannot be expected as accumulation processes in mosses and toxicity pathways in human differ, e.g. whereas elemental Hg accumulates in mosses, human health is most at risk from Hg via the accumulation of methyl Hg in the food chain (TF Health 2007). Accumulation of heavy metals in leafy vegetables can be an exposure route for humans to heavy metals; however, the risk of uptake via this route varies between metals (Harmens et al. 2005). In addition, is it difficult to distinguish between exposure to current emissions and historic emissions, as both can contribute to accumulation in mosses, latter via windblown soil dust. It is unknown which compound of particulate matter (e.g. particle size of metal compound present or metal speciation) is contributing the most to the toxicity for humans. A review by the Task Force on Health (2007) showed that cadmium exposure is associated with kidney and bone damage. Cadmium has also been identified as a potential human carcinogen, causing lung cancer. Lead exposures have developmental and neuro-behavioural effects on fetuses, infants and children, and elevate blood pressure in adults.

Multivariate analysis

To distinguish the lithogenic and anthropogenic origin of the elements in moss samples, the correlation analysis was carried out. The results of correlation analysis are shown in Table 4.

Table 4 Pearson Correlation Coefficient between element concentrations in mosses in Kosovo

Elements	**Hg**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Mn**	**Fe**
Hg	1.00								
Cd	-0.26	1.00							
Cr	-0.01	-0.42[3]	1.00						
Cu	0.22	-0.05	0.40[3]	1.00					
Ni	-0.10	0.45[3]	0.18	0.05	1.00				
Pb	-0.39	0.90[1]	-0.52[2]	-0.13	0.22	1.00			
Zn	-0.14	0.06	0.26	0.25	0.12	0.00	1.00		
Mn	-0.15	-0.17	-0.06	-0.04	-0.22	-0.23	-0.19	1.00	
Fe	0.37	-0.08	0.22	0.00	0.01	-0.24	-0.24	0.38	1.00

Cell Contents: Pearson correlation, P-Value: [1] < 0.0005; [2] < 0.001; [3] < 0.05

High and significant positive correlations (r^2 = 0.90, P=0.0001) were found between Pb and Cd in moss samples (N=25). The significant positive correlations between the concentration of Cd and Pb in mosses were found for about two thirds of the countries participating in the European moss survey since 1990 (Harmens et al., 2012). At the European scale, it is probably related to the long-range transport of air pollution (Harmens et al. 2015).

Weak positive correlations (r^2 = 0.40, P=0.005) were found between the pairs of elements Cr - Cu, and Cd – Ni. Weak negative correlations were found between the pairs of elements Cd-Cr, and Cr-Pb. For a better interpretation of the results, Factor analysis was used. Three main factors were found from the results of Factor analysis and were interpreted as source categories contributing to elements concentrations at the sampling sites. The identification of source categories was undertaken by examination of the profiles of the factors, i.e., loadings of the elements and other variables on the Varimax Rotation. The main criteria in selecting the number of optimal factors and models of major source identification, is that Eigen values are larger than 1.

Table 5 The results of the FA Analysis of the Correlation Matrix

Variable	Factor1	Factor2	Factor3	Communality
Fe	-0.005	-0.039	0.862	0.744
Cd	0.931	0.183	-0.132	0.918
Cr	-0.303	-0.794	0.126	0.737
Cu	0.009	-0.669	0.054	0.450
Hg	-0.094	-0.151	0.728	0.562
Ni	0.679	-0.421	0.137	0.656
Pb	0.817	0.346	-0.314	0.886
Zn	0.052	-0.568	-0.453	0.530
Mn	-0.284	0.306	0.459	0.385
Variance	2.179	1.848	1.841	5.868
% Var	0.242	0.205	0.205	0.652

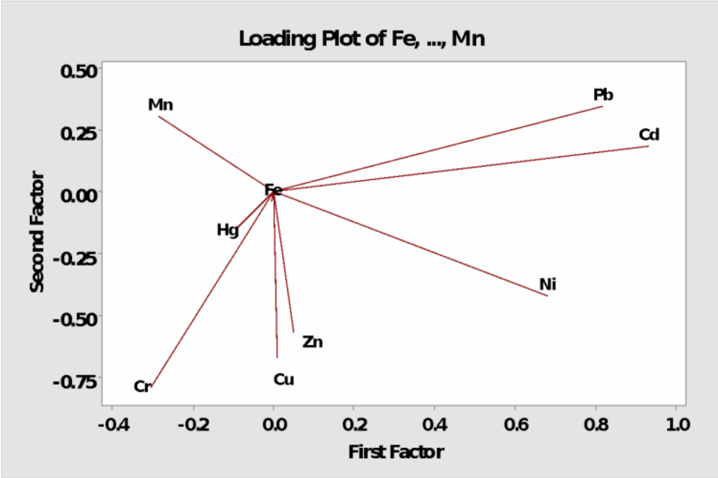


Fig. 6 The diagram of the loading plot of the elements (Factor Analysis of the Correlation Matrix; Rotated Factor Loadings and Communalities; Varimax Rotation)

From the results of Factor analysis and loading values of each element (Table 5 and Fig. 6), the association of the elements with the factors is analyzed as follows:

Factor 1 is the strongest factor representing 24.2 % of the total variance. It is influenced by high loadings of Cd, Pb and Ni and moderate negative loadings of Cr and Mn. The association of Cd, Pb and Ni with the first factor probably originates from the manufacturing (rubber production, electric batteries production, metal processing industries, and the construction activities), while Cr and Mn are probably related to the chromium processing industry. The presence of Pb and Cd in this factor indicates the long-range transport of air pollution (Harmens et al. 2015) as another probable factor contributing in high Pb loads. The negative loads of Cr and Mn are probably related to wind direction that affects the dilution of these pollutants in the air.

Factor 2 is the second strongest factor, with 20.5 % of the total variance. It is mainly influenced by weak positive loads of Pb and Mn and negative loads of Cr, Cu, Ni and Zn. The association of Factor 2 with Pb, Mn, Cr, Cu, Ni and Zn is probably related to metal industry (Trepca Metallurgical Plant and Iron-Nickel Metallurgy) and to the geochemical origin of these elements. The negative loads are probably related to the distance from the pollution sources.

Factor 3 represents 20.5% of the total variance. This factor is loaded by Fe, Hg and Mn and negatively loaded by Pb and Zn. The association of this factor with Fe, Hg and Mn is probably related to metal industry and heat production, while negative loads of Pb and Zn probably indicate a reverse tendency of desorption or a decreasing concentration of these elements when the total metal concentration increases. It is may be indicating a great influence of weather conditions, wind speed (Wehner and Wiedensohler 2002), and the amount of precipitation being the main factor (Melaku et al. 2008).

Conclusions

Moss biomonitoring combined with statistical analysis of the data provides a suitable complementary method of the spatial investigation of deposition flux for the identification of areas at risk from high atmospheric deposition of heavy metals. The differences in metals concentration in mosses between different parts of the country reflect local variation in heavy metal deposition and the location emission sources of the elements. The median concentration level of Pb, Zn and Cr in moss samples of Kosovo (2010 survey) are higher than the median concentration level of Pb in moss samples of Europe, indicating a strong effect of anthropogenic factors like traffic emission, metal processing and geogenic origin caused by wind blowing soil dust.

The pollution load index (PLI_{site}) revealed that the selected zones are highly and/or extremely polluted from Hg, Cd, Pb, Ni, Fe and Zn. The PLI_{site} results indicated that the most contaminated area is the western part of Kosovo (PLI_{zone}>5, higly polluted, see Fig. 5). It revealed that the pollution load decreases as the distance from the pollution sources increased. The most polluted sites are close to the most populated urban areas that may cause significant health effects. The result of zone pollution index (PLI_{zone}=6.3>5) indicate that the whole territory under investigation is highly polluted from Hg, Cd, Pb, Ni, Fe and Zn. For this reason, further measures are required in Kosovo for reducing the emissions of heavy metals from industry and traffic emission and reducing health risk to the people. Factor analysis proved to be a useful tool for the classification and the identification of the factors causing the air pollution. Traffic emission, industry emission and mining industry are identified as the main factors of atmospheric deposition in Kosovo.

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