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Air Quality Assessment by Moss Biomonitoring and Trace Metals Atmospheric Deposition

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ABSTRACT

Carpet-forming moss species are useful tools for monitoring the atmospheric deposition of pollutants like metals, organic compounds, nitrogen, and more recently, microplastics. Even with a dense sampling scheme, moss biomonitoring could extend the environmental study to national and/or continental scales. Moss species (Hypnum cupressiforme) was used as a biomonitor to assess the atmospheric deposition of metals in the entire territory of Albania and to identify the probable anthropogenic factors affecting the levels of the most toxic metals/metalloids (As, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, and Zn) in the current moss. Statistical analysis is used to examine the relationships between elements accumulated in moss samples, and to assess the air quality of Albania. Considering the geochemical normalized data using lithium as a normalizing element, Fe, Cr, Co, and Ni show obvious anthropogenic anomalies. GIS maps identified the local enrichment of these elements, which is stretched in the north-southeastern direction and affected mostly by anthropogenic sources. The elements Fe, Cd, Cu, Pb, and Zn look likely to be homogenously distributed by indicating a common natural origin on a national scale. It is confirmed by the association of these elements with iron which is a typical crustal element that originates mostly from lithogenic dust in sparsely vegetation regions. Fe, Cd, Cu, Pb, and Zn were mostly higher between a few regions with few obvious anomalies positioned in the center of the country with high industrial activity, in the areas with heavy traffic, and in the cross-borders of Albania with Monte Negro and Greece mostly emerging from the local contribution of anthropogenic activities, local lithology, and transboundary pollution sources. The elements Cd and Hg are linked mostly with the long-range transport of pollutants.

Keywords: Air quality, Moss biomonitoring, Toxic metals, Statistical analysis, Albania

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1 INTRODUCTION

Environmental pollution is strongly linked with the anthropogenic emissions of contaminants that show negative effects on the health of human beings and different ecosystems. For this reason, understanding and estimating the transmission, spatial distribution, and temporal trends of the pollutants in order to identify the problematic areas, their local sources, and temporal trends have been the focus of the scientists. Reviewed study done by Mamun *et al.* (2020) indicate that trace metals in atmospheric deposition revealed from diverse emission sources and environments including urban, industrial, suburban, rural, traffic, and coastal sites and are significantly affected by meteorological conditions and the size of dust particles. Generally, the crustal elements deposit at higher rates than those of the anthropogenic elements due to the larger particle sizes of crustal elements. Since metals are non-biodegradable and remain persistent in the environment for a very long time, they cannot be broken down, and remain present for an extended period in soils and sediments until they are eluted to other compartments, or can also react with other elements in the soil or sediment and form or degrade to more toxic compounds (Briffa *et al.*, 2020).

Air pollution, and especially pollution from particles containing high content of toxic metals, has serious impacts on human health by reducing life expectancy and causing many diseases (Sokhi *et al.*, 2022). Toxic and carcinogenic metals such as Cu, Fe, Cd, Cr, Ni, Hg and V, can produce reactive radicals which damage DNA, perform lipid peroxidation and depletion of protein sulphhydryls, accompanied by other health effects (Briffa *et al.*, 2020).

Road traffic is considered as a potential source of metals coming from fuel and oil combustion products, tires, brake linings, bearing con+sumption, corrosion of vehicle components, road construction materials, etc. (Richards, 2020; U.S. EPA, 2004; Kummer *et al.*, 2009; Harmens *et al.*, 2015, 2013). Old vehicles and outdated industrial technologies used in developing countries, the smoke from accidental fires and/or waste incineration (Shaman and Wheeler, 2007; Grodzinska and Szarek-Lukaszewska, 2001), have led to the increased content of different pollutants in the environment which became a serious problem in many parts of the world. Besides, different interventions in the environment without criteria have brought serious consequences linked with the growth of natural and anthropogenic emissions of various contaminants. Among them, forest degradation and forest burning, intervention in river beds, and the increase in barren land areas have increased the rate of erosion, the flooding in certain areas, the content of soil dust, fine and ultra-fine particulate matter (PM) in the air, and metal content near the emission sources. The increased level of toxic metals, Pb, Cr, As, Cd, Hg, Zn, Cu, Co, and Ni, is an inorganic chemical hazard to humans and environmental compartments (Järup, 2003). Atmospheric deposition removes pollutants from the atmosphere to natural ecosystems by causing negative effects on human health, crop yields, land, and marine ecosystems (WMO, 2019). Nowadays studies suggested that PM content in the air presents adverse effects on pulmonary and cardiovascular health by making this category of people more vulnerable to the severity of COVID-19 symptoms (Bourdrel *et al.*, 2021; Dales *et al.*, 2021; Donaldson and Mac Nee, 2001; Fang *et al.*, 2021). The data of the global COVID-19 pandemic indicate that air pollution has a direct impact on the increasing mortality among infected people (Brunekreef *et al.*, 2021; Fang *et al.*, 2021; Fattorini and Regoli 2020; Pozzer *et al.*, 2020; Zhang *et al.*, 2020). Such effects make it necessary to set strict parameters regarding air quality and develop a continuous monitoring program to control the pollution level and the effects of pollutants.

The conventional technique of monitoring requires some expensive equipment limited only to the monitoring stations. For more than 60 years, moss biomonitors have been developed and widely used as an alternative method to assess air pollution and define and characterize metal pollution sources in atmospheric deposition in European countries (Berg *et al.*, 1995; Basile *et al.*, 2008, 2009; Macedo-Miranda *et al.*, 2016; Esposito *et al.*, 2018), and more recently in Asia, Brazil, and North America (Stankovi *et al.*, 2018; Harmens *et al.*, 2015, 2013; Gjengedal and Steinnes, 1990; Steinnes, 1989). Bryophytes (particularly mosses) have been used as biomonitors for assessing metals in atmospheric deposition since the early ’60s of the last century (Tyler, 1990; Harmens *et al.*, 2015; Frontasyeva *et al.*, 2020). Biomonitors are effective species that accumulate and document the impact of different pollutants on living organisms and the impacts of different pollutants to different ecosystems (Wright *et al.*, 2018). Based on the accumulation capacity and sensibility to various chemicals, bryophytes can be used as accumulation indicators or as sensitive indicators, mainly for polluting substances (Zechmeister *et al.*, 2003). Pleurozium schreberi, Hylocomium splendens, and Hypnum cupressiforme mosses species were recommended in the experimental protocol of the European Moss Survey for assessing metals in atmospheric deposition (ICP Vegetation, 2010). The accumulation of metals in mosses varied greatly according to the type of moss species (Zechmeister *et al.*, 2003; Schröder *et al.*, 2016; Schröder and Nickel, 2019). It is important to use the same or similar moss species for passive biomonitoring of air quality because it makes it possible to compare results from different studies (Boquete *et al.*, 2020). According to Bargagli *et al.* (2002), Hypnum cupressiforme is widely used in trace element biomonitoring and in bioaccumulating studies of trace element pollution due to its wide-ranging distribution and because of the abundant data existing in the literature on this species. In such conditions, it is ideal for making comparisons with other areas of Europe. The importance of such studies is related to the fact that it can be realized both in local and intercontinental ranges and in different time periods by providing information on the spatial distribution of pollutants and the changes over time (Harmens *et al.*, 2004; Meyer *et al.*, 2014). Understanding the spatial and temporal distribution of total (wet and dry) deposition of pollutants on a global scale is critical in identifying the most vulnerable populations, ecosystems, and farmlands (WMO, 2019) a process easy doing by biomonitoring.

This paper deals with moss biomonitoring surveys in Albania, which is part of the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation). ICP Vegetation in European scale has evaluated atmospheric deposition of metals since 1990 by using moss biomonitoring at five years intervals (Rühling, 1994; Rühling and Steinnes, 1998; Harmens *et al.*, 2011, 2013, 2015; ICP Vegetation, 2010). The aim of this research is to assess the atmospheric deposition of metals in the entire territory of Albania using low-cost moss biomonitoring, to identify the most probable sources of toxic metals in the current moss, and to differentiate between their natural and anthropogenic through the use of concentration and normalized data.

2 METHODS

2.1 Sampling

The sampling process significantly affects the uncertainty of the analytical results. Thus, to guarantee the representative samples relatively free from the interference of external factors, sampling was carried out in accordance with the LRTAP Convention-ICP Vegetation protocol and sampling strategy of the European Program on Biomonitoring of Heavy Metal Atmospheric Deposition (ICP Vegetation, 2010). The moss samples (Hypnum cupressiforme (Hedv.), widely spread in Albania, were collected from 47 sampling sites (approx. 1.5 moss samples per 1000 km^2) during the relatively dry periods of October–November 2010, and June–July 2011. The locations of the sampling sites were situated at least 300 m away from main roads or buildings and 100 m from small roads and single houses, located mostly in open areas. Composite moss samples were formed by five to ten sub-samples collected within an area of 50 × 50 m^2. Disposable polyethylene gloves were used during the sampling and sample cleaning to avoid contamination of the samples. The sampling site distribution is depicted on a map of Albania (centered at 41°00′ north of the equator and 20°00′ east of Greenwich) (Fig. 1).

2.2 Moss Analysis

Moss samples were cleaned from the adhering materials and brown parts of the plant tissues. Only the green and green-brown parts of moss tissues that represent at last three years of moss growth were selected for chemical analysis. Samples were opened separately on big paper sheets

Fig. 1. The location of the sampling sites on the map of Albania position.

and then were dried at room temperature for about 72 hours. The content of metals in moss samples was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Varian, 715ES equipped with ultrasonic nebulizer CETAC (ICP/U5000AT+) for better sensitivity of the elements), and electro-thermal atomic absorption spectrometry (ETAAS, SpectrAA 640Z for Cu and Pb) after acid digestion. Around 0.5 g moss samples were digested in Teflon digestion vessels by adding 7 mL HNO_3 (69%, m/V) and 2 mL H_2O_2 (30%, m/V). Analytical grade reagents were used in this study: nitric acid, trace pure (Merck, Germany); hydrogen peroxide, p.a. (Merck, Germany); and bi-distilled water. The dried moss samples were digested with Mars, CEM, USA Microwave digestion systems with the following programme: step 1—temperature 180°C, 10 min ramp time, with power of 500 W and 20 bar pressure; step 2—temperature 180°C, 20 min hold time, with power of 500 W and 20 bar pressure (Stafilov *et al.*, 2018). Finally, the vessels were cooled and carefully opened. The digested samples were quantitatively transferred into 25-mL calibrated flasks. The ICP-AES and AAS analyses were conducted in the Institute of Chemistry, Faculty of Science, St. Cyril and Methodius University, Skopje, North Macedonia.

The digested samples with nitric acid (9:1) at half-pressure Teflon tubes were analyzed for mercury content by using the cold vapor atomic absorption spectroscopy (CVAAS) as prescribed by Lazo *et al.* (2018). Varian 10+ atomic absorber equipped with homemade Hg cold vapor system was used for Hg determination. The analysis of Hg has been performed at the University of Tirana, Faculty of Natural Sciences.

The detection limits of elements calculated as 3 SD of the lowest instrumental measurements of the blanks are as follows: 0.002 mg kg^{-1} for Zn; 0.005 mg kg^{-1} for Cd and Fe; 0.01 kg^{-1} for As, Cu; 0.05 mg kg^{-1} for Cr, Co and V; 0.25 mg kg^{-1} for Ni and Pb, and 0.002 mg kg^{-1} for Hg. The limits of quantification calculated as 10 SD of the lowest instrumental measurements of the blanks are as follows: 0.007 mg kg^{-1} for Zn; 0.02 mg kg^{-1} for Cd and Fe; 0.035 kg^{-1} for As and Cu; 0.2 mg kg^{-1} for Cr and V; 0.85 mg kg^{-1} for Ni and Pb, and 0.008 mg kg^{-1} for Hg. Three replicates per moss sample were digested and three run measurements per digest were performed.

2.3 Quality Control

The quality assurance of ICP-AES was checked by two moss reference materials, M2 and M3, prepared first for the 1995/6 European moss survey (Steinnes *et al.*, 1997). Blank samples were simultaneously analyzed with moss samples. The recovery of the investigated elements was checked by the standard addition method. It ranged between 98.5% and 101.2% for ICP-AES, and 96.9% to 103.2% for AAS.

2.4 Data Processing and Statistical Analysis

Descriptive statistics and spatial analysis were used as the first step of statistical analyses to investigate the variability and spatial distribution of the data. The concentration data (CD) were divided by their medians to standardize those at the same digit numbers. To account for natural metal variability and to highlight the anthropogenic component, the data were normalized using Li as a normalizing element (Loring and Rantala, 1992). The relationships between metals present in moss provide an indication of the factors that have influenced their distribution and origin. It is tested by Pearson correlation analysis and confirmed by the statistical significance at $p < 0.05$. Factor analysis (FA), based on the correlation matrix of concentration (CD) and normalized concentration data (NCD), may explore the hidden multivariate structures of the data (Astel *et al.*, 2008; Reimann *et al.*, 2002) and help to clarify the relationship between metals that may have similar origins or develop similar associations in moss samples. Statistical analysis was performed using the MINITAB 19 software package. The spatial distribution of the elements was visualized from the GIS maps, plotted with the Arc-GIS 10.2 system by applying the local deterministic methods and the inverse distance weighting.

3 RESULTS AND DISCUSSION

3.1 Trace Metal Concentrations in Moss Samples

The most important statistical parameters, such as the concentration range, coefficient of variation (CV%), skewness, and kurtosis are shown in Table 1.

Table 1. Descriptive statistic analysis of trace metal data (N = 47, * in mg kg^{-1}).

Elements	Range*	CV %	Sk	K^N
As	0.05–2.86	133 (124)^N	2.6 (3.5)^N	6.8 (13)^N
Cd	0.038–0.090	90 (79)^N	4.5 (1.85)^N	24.7 (3.6)^N
Cu	2.14–15.55	39 (64)^N	1.52 (1.6)^N	4.89 (2.7)^N
Hg	0.036–2.23	93 (90)^N	5.7 (2.1)^N	35.6 (5.2)^N
Pb	1.34–19.7	93 (125)^N	4.6 (5.4)^N	24.4 (33)^N
Zn	1.0–46.9	64 (82)^N	1.16 (2.2)^N	2.6 (7.6)^N
Ni	1.56–131	162 (167)^N	4.2 (4.1)^N	20.4 (20)^N
Cr	1.47–262	164 (172)^N	4.1 (4.5)^N	20.8 (24)^N
Co	0.389–7.47	87 (93)^N	2 (2)^N	3.3 (3.5)^N
Fe	469–5488	60 (32)^N	1.84 (2)^N	3.5 (5.1)^N

CV: coefficient of variation, Sk: skewness; K: kurtosis; CV: coefficient of variation; in brackets: statistical parameters of the normalized data.

The data of CDs and NCDs of As, Cd, Hg, and Ni follow the lognormal distribution model, are positively skewed, and show high variability (CV > 75%). It indicates high asymmetry in data distribution. The sequence of the CDs of elements in moss samples were similar with that of NCDs, Fe > Cr > Zn > Ni > Cu > Pb > Co > As > Hg > Cd, except Zn and Cr NCDs that changed the position between them, Zn(N) > Cr(N)). The statistical parameters that characterize the asymmetry of the elemental data differ significantly that indicate different behaviors of the elements in the study areas. Several activities were developed in different regions over the last century such as mining activity, iron, ferrochromium, nickel, and copper metallurgy, chemical and tannery industry since the early '50s till the beginning of the '90s of the last century. It could explain high variability and the enriched anomalies observed in different areas. High contents of Cr, Zn, Ni, Cu, and Pb evaluated by respective median values were followed by high variation (CV% > 75%) would suggest an effect of a polluted air mass derived from long-transport or regional air pollution. In similar way as other global regions, the data collected from this study show that the content of major elements (Fe, Ca, Mg, K, and Na), represented here by Fe, are orders of magnitude greater than those of routinely monitored anthropogenic elements (Zn, Pb, Cu, Ni, Cd, Cr) (Cheng *et al.*, 2021; Feng *et al.*, 2021; Sokhi *et al.*, 2022).

The use of mosses as a bioindicator in biomonitoring of metal atmospheric deposition is a relative method for identifying problematic areas based on the geographical fluctuation of metal concentrations. As different moss species accumulate metals in different ways, the allowed limits of metal have yet to be defined. In such conditions, the use of the same species for monitoring is recommended. To assess the extent of pollution in Albania, we compared the median values of metals in the present moss with the respective European medians, as shown in Fig. 2.

In general, the median concentration of elements in moss samples of Albania, except Cd and Zn, are higher than the respective European median values by indicating higher contamination level of these elements in atmospheric deposition of Albania, particularly for As, Cr and Ni.

3.2 Multivariate Analysis

Pearson correlation analysis was carried out to CDs and NCDs to investigate the linear relationship and the association between them. The obtained ''p'' values of Pearson correlation between CDs and NCDs ($r > 0.4$) ranged from 0.000 to 0.005 (Table S1 that meets perfectly the significance condition ($p < 0.05$) for a reliable correlation. Based on Pearson correlation data, the elements are separated into three groups: 1) the 1st group shows very strong and significant correlations ($r > 0.8$, $p \leq 0.001$) between CD-NCD data of the same element (Cr, Co, and Ni) characterized by a narrow confidence interval (CI) values (Table S1). It reflects a common chemical behavior of these metals and their common origin as mineral oxides and geochemical factors. 2) the 2nd group show strong and significant correlation ($0.6 < r < 0.8$, $p < 0.005$) between the pairs of the CDs of Cu, Cd, Zn, Pb, Hg with their respective NCDs (Table S1); 3) the 3rd group show moderate and significant correlation ($0.4 < r < 0.6$, $p < 0.01$) between the pairs of CDs of Cd, Cu, Pb, Hg, and Zn. The presence of these metals in the atmospheric deposition is mostly derived by

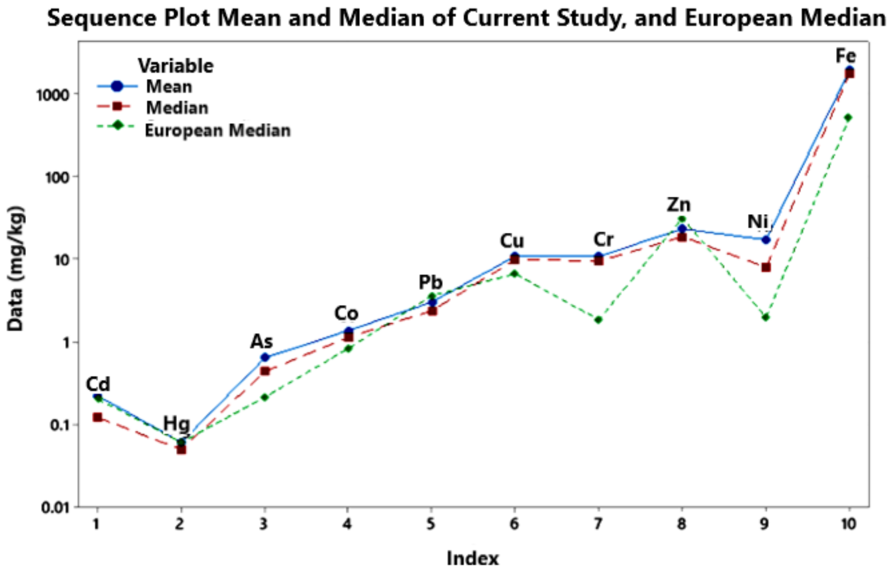

Fig. 2. Sequence plot of mean, median, and European median values (in mg kg^{-1}).

long-range transport of pollutants (Cd and Hg) from other parts of Europe (LRTP) and from local emitting sources (Cu, Cd, Zn, Pb) such as high-temperature metal processing, traffic emission, and windblown dust that represents historical waste deposition and geochemical properties of the area (Harmens *et al.*, 2015). Factor analysis (FA) was carried out to better explain the associations of the elements, to split the data into different factors based on the correlation matrix of elements in current moss, and to evaluate their probable sources in moss samples. The most important factors were extracted for an eigenvalue > 1 after varimax rotation. The associations of the elements with high loadings in the same factor (Reimann *et al.*, 2002) are assumed as similar effects or similar characteristics of the elements. Only factor loadings (FL) larger than 0.4 are used to interpret the associations of the elements at the same factor. The results of FA are shown in Table 2, and are illustrated in GIS maps of Fig. 3.

Factor analysis revealed five main factors that represent 80.9% of the total variance. The first factor, (F1), is the strongest factor representing 27.7% of the total variance. The next two strong factors (F2 and F3) represent 32.4% of the total variance, respectively 16.3 and 16.1 %. The last two weak factors (F4, and F5) represent only 20.8% of the total variance (respectively 10.4, and 10.4 %). GIS maps of each factor are shown in Fig. 3. The associations of metals within the same factor represent similar properties and similar behaviors in the environment and could be explained as follows:

Factor 1 (F1) contains high loadings of CDs and NCDs of Cr, Ni, Co, and Fe. Strong associations of Cr, Ni, Co, and Fe CDs with their respective NCDs indicate strong anthropogenic sources of these elements. Cr, and the associated elements, enter into various environmental matrices (air, water, and soil) from several natural and anthropogenic sources, and the highest releases are attributed to industrial emission sources, such as metal processing, stainless steel welding, ferrochrome metallurgical, refractory, and chemical industries (Tchounwou *et al.*, 2012), geogenic factors, and mining industry. The highest level of these elements was found in the eastern mineral belt rich with Cr, Ni, and Fe minerals. It indicates the geogenic origin of these elements. Soil dust emission is responsible for high levels of historical deposition of Cr, Ni, and Co in the soil throughout Albania. It has led to high soil concentrations of these metals, which means that the soil dust represents a major emission source of Cr, Ni, and Co in the air (Allajbeu *et al.*, 2021; Lazo *et al.*, 2019, 2021). The association of these elements with Fe, a typical crustal element, highly supports the discussion above. Arc GIS map is created to show the distribution pattern of high loading parameters of F1 (Fig. 3(a)).

The next strong factor (F2) is linked with high loadings of Cd, Zn, Cu, and Hg normalized data, obtained after the compensation of their natural variations and indicating mostly the anthropogenic fractions (Loring and Rantala, 1992). Hg and Cd are typical anthropogenic elements mostly from

Table 2. Factor Analysis of the standardized CDs and NCDs of 2010 moss survey (N = 47). Factor Analysis of the Correlation Matrix; Varimax Rotation; Sorted Rotated Factor Loadings and Communalities.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communality
Ni(N)	**0.954**					0.937
Cr(N)	**0.937**					0.883
Ni	**0.902**					0.902
Cr	**0.884**					0.877
Fe(N)	**0.846**					0.858
Co(N)	**0.830**					0.765
Co	**0.751**					0.739
Cd(N)		**0.888**				0.817
Zn(N)		**0.855**				0.795
Cu(N)		**0.788**				0.891
Hg(N)		**0.644**				0.549
Fe			**0.797**			0.886
Zn			**0.743**			0.697
Hg			**0.715**			0.630
Cd			**0.674**			0.626
Cu			**0.654**			0.705
Pb				**0.871**		0.894
Pb(N)				**0.867**		0.889
As(N)					**0.934**	0.906
As					**0.910**	0.933
Variance	5.539	3.266	3.215	2.081	2.077	16.178
% Var	0.277	0.163	0.161	0.104	0.104	0.809

Me(N) – the normalized data.

long-range transport of the pollutants, as well as from fuel combustion, waste incineration, and medical chemicals treatment indicating the possibility of anthropogenic sources (Tchounwou *et al.*, 2012). A high anomaly of F2 is found in the areas with heavy traffic, and the next in the cross-borders with Monte Negro in the North-West and Greece in the South-East. Cu and Zn are known as tracers of non-exhaust brake and tire wear, so traffic emission followed by automobile exhaust, lubricant consumption, tire wear, brake wear, and mechanical parts friction are supposed as important sources of Cu and Zn (Adamiec, 2017; Harrison *et al.*, 2003). The anomalies of Cd, Cu, Hg, and Zn NCDs in the cross border areas may indicate the effects of transboundary pollution. The lowest concentrations of these elements were found in the south. On the other hand, their distribution patterns in most parts of the territory look likely homogeneous by indicating the effects of long-range transport, as well as the effects of soil geochemistry and soil dust fine mineral particles. They may also originate from the oil-gas industry, and shipping activity in the west. Hg and Cd point also the sources of fire industrial activities, waste incineration, while the association of Cu and Zn indicates the traffic emission and atmospheric deposition sources. Hg and Cd are typical anthropogenic elements probably entrapped to soil dust fine particles. On the other hand, the association of Cd, Cu, Hg, and Zn NCDs may also indicate the geogenic factors, mining, and nonferrous metallurgy as important sources of these elements (Pacyna and Pacyna, 2001; UNEP, 2013). Although the copper mining, smelting, and processing industry in Albania had stopped since the beginning of ’90 years, and the emissions of metals such as copper, lead, cadmium, zinc, are decreased significantly, their concentrations in some parts of the country are still very high due to the historical deposition and the effects of mineral damps in the vicinity of the ex-copper industry particularly in the North (Lazo *et al.*, 2019). Arc GIS map is created to show the distribution pattern of high loadings parameters of F2 (Fig. 3(b)).

Factor 3 (*F3*) contains high CD loadings of Fe, Hg, Zn, Cd, and Cu. These elements have both natural and anthropogenic origin. The presence of Fe together with these elements under the same factor supports the natural origin of these elements. Fe is naturally distributed as a typical soil element (Rudnick and Gao, 2003) that may indicate its soil dust origin. We noticed that CDs of this group explained a homogenous distribution, and were mostly higher between a few

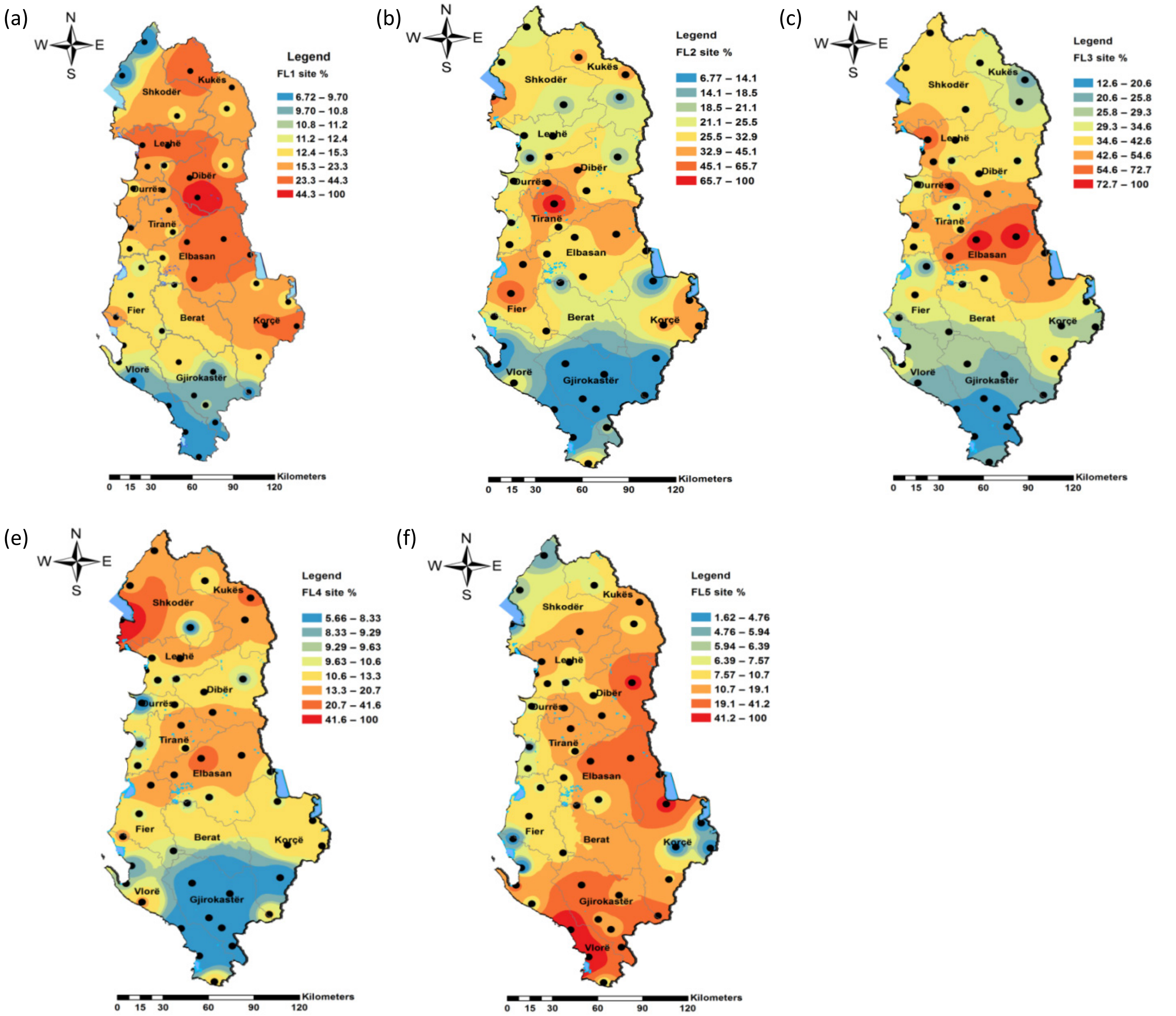

Fig. 3. Distribution pattern of the standardized average factor loadings (FL) at each factor.

regions (Fig. 3) by indicating a common natural origin on the country scale. The highest loadings of Fe, Hg, Zn, Cd, and Cu are positioned in the center of the country with high industrial activity. Arc GIS map of Fig. 3(c) shows the distribution pattern of loading parameters of this factor.

Factor 4 (*F4*) and *Factor 5* (*F5*) are associated with high loadings of Pb and Pb(N) (F4), and As and As(N) (F5). The main source of Pb is counted to be the vehicle exhaust, coal combustion, and industrial emission sources (Tchounwou *et al.*, 2012) probably explaining the Pb anomaly in the central part of Albania. The strongest Pb anomaly founded in the cross border with Monte Negro is probably affected by the transboundary pollution of metals erased from the Al and Fe processing industry in Monte Negro (Lazo *et al.*, 2018; Peck, 2004). All these findings show a strong anthropogenic origin of Pb in the current moss samples. A wide area with relatively high Pb content (13–21 mg kg^{-1}) was found in the North. It is probably originated from geogenic factors. Besides, GIS maps were created by using the local deterministic interpolation techniques that create surfaces from the measured neighboring sampling points, based on the extent of similarity of the data. The stretching of the surfaces with a similar concentration range of the elements depends on the distances between sampling points. High-density sampling points can create more accurate surfaces. Due to the conditions of the relief, the distance between sampling points in the North is relatively high, so the extension of the anomalies are relatively wide.

The highest As content is found in the South. Arsenic was used in agriculture activity as inorganic fertilizers and herbicides. It may lead to the enrichment of As in the local soils which may enter the atmosphere as fine soil dust particles, and then be re-suspended as atmospheric deposition in different distances controlled by the size of dust particles. The next area with relatively high loadings of As and As(N) belongs to the mineralized belt in the Eastern part of the country that is probably linked with geogenic factors and soil geochemistry of the area. The same as Pb, the extension of the areas with relatively high As content (11–19 mg kg^{-1}) in N–E and S–E directions were caused by the low density of sampling sites. For more accurate distribution, it is necessary to increase the density of sampling sites in different parts of the country. The distribution pattern maps of F4 and F5 are shown in Figs. 3(e) and 3(f).

4 CONCLUSIONS

The atmospheric deposition of metals was assessed in the entire territory of Albania by using moss as a bioindicator. It deals with the evaluation of the pollution level on the atmospheric deposition of trace metals at a national scale. Results showed that metal contaminations were arise from local anthropogenic activities, in particular, industry, road traffic, transboundary pollution, sea spry emission, and long-range transport of the pollutants from other parts of Europe. It is a complete research study that identified the main factors contributing to air quality in Albania. The study could contribute to other studies documenting the deposition of various elements that have been conducted in other parts of Europe by using mosses as bioindicators of trace metals atmospheric deposition under the framework of the ICP Vegetation Programme.

It is shown that moss data could provide a complementary measure of elemental deposition from the atmosphere to the terrestrial ecosystems, which makes it possible to achieve a relative comparison of the deposition data achieved at a high sampling density in national/and or continental monitoring.

The variability in the distribution pattern of the elements may identify the areas within the country with high levels of trace metals that need further investigations to determine the health and environmental risks. High concentration levels of Cr, Ni, Fe, and Co were found in the eastern part of the country, higher than the neighboring and EU countries.

The present study represents the need for more rigorous measures regarding the emission of atmospheric pollutants originating from anthropogenic sources. A continuous monitory program is necessary to control the pollution level and the effects of pollutants.

DISCLAIMER

The study was conducted by the authors under the framework of UNECE-ICP Vegetation Programme and the Doctoral Program of University of Tirana, Faculty of Natural Sciences. The survey complies the ethical rules of ICP Vegetation Programme and the Doctoral Program of University of Tirana. It does not contain any study or experiment done with human participants by the participants or the third part.

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SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version at https://doi.org/10.4209/aaqr.220008

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