IMPORTANT TOOLS IN AIR QUALITY STUDY: MOSS BIOMONITORING, ATMOSPHERIC DEPOSITION, TRACE ELEMENTS CONTENT AND DATA ANALYSIS

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Abstract

This study examines the spatial distribution patterns of toxic metals (As, Cd, Cr, Co, Cu, Fe, Hg, Pb, Ni, and Zn) in atmospheric deposition by using Hypnum cupressiforme (Hedv.) moss as biomonitor. Moss samples were collected from 47 sampling sites distributed over the whole territory of Albania. Moss biomonitoring made it possible to evaluate the distribution pattern of metals at national scale. High concentration levels, higher than the most European countries, were found for Cr, Ni, and Fe.

The concentrations data were statistically processed to understand their variability, the relationship between the elements, and to estimate the most likely pollution sources of the elements. The spatial distribution analysis identified the local enrichments of Cr, Ni, and Co stretched in the north-southeastern direction of Albania and affected by the soils geochemistry, mining and metal high temperature processing, and mineral deposits of the area.

Keywords: air quality, moss biomonitoring, trace metals, statistical analysis, emission inventory, ICP-AES, Albania.

1. Introduction

The increased content of different pollutants in the environment is associated with natural and anthropogenic sources. Anthropogenic emission is an important factor of environmental pollution from various pollutants, particularly from toxic metals which have adverse effects on the health of the human beings and different plants. The requirement to live in a clean air environment is fundamental to the human health and the well-being (WHO, 2000). Environmental pollution from metals is an inorganic chemical hazard, associated mainly with the increased levels of lead, chromium, arsenic, cadmium, mercury, zinc, copper, cobalt and nickel (Järup, 2003). High concentration level of metals in the air we breathe may cause adverse and undesirable effects on human beings. Metals are generally found in the air in a variety of physicochemical forms, such as solid, liquid, gaseous, or very fine particles (Richards, 2020; EPA/600/P-99/002aF, 2004).

Different monitoring methods are available to assess the level of air pollution by using traditional classic methods or different plant organisms as bioindicators of certain contaminants. The conventional technique requires expensive equipment that may cover a small area of interest. For decades, the use of mosses as bioindicator to assess air pollution, particularly the metals' pollution, was developed and widely applied in European countries

(Schröder et al. 2016; Harmens et al. 2015, 2013; Gjengedal and Steinnes, 1990; Rühling, 1994) and after in Asia, Brazil and North America (Harmens et al. 2011). The use of mosses as biomonitors is a known technique implemented as an alternative method to define and characterize the pollution sources of metals in atmospheric deposition (Stanković et al. 2018; Steiness, 1989). Due to the widespread distribution of mosses around the world, the growth in a wide-spread population group, the ability to accumulate great amounts of metals (Tremper et al. 2004; Blagnytė and Paliulis, 2010), made them widely used as bioindicators of metals atmospheric deposition.

This paper deals with 2010 moss biomonitoring survey in Albania that were conducted under the framework of the European Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops. Only the most toxic elements (As, Cd, Cr, Co, Cu, Fe, Hg, Pb, Ni, and Zn) that show negative health impact and environmental risk are included in this study. The aim of this study is the harmonization and the combination of the concepts of biomonitoring - statistical analysis – emission inventory to produce detailed information on trace metals atmospheric deposition, to assess their local emission sources and long-range atmospheric transport and to differentiate their natural and anthropogenic sources.

2. Material and methods

2.1. Sampling

Sampling process significantly affects the uncertainty of the analytical results. Thus, to guarantee the representative samples relatively free from the interferences 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 Heavy Metal Atmospheric Deposition (Harmens et al. 2010).

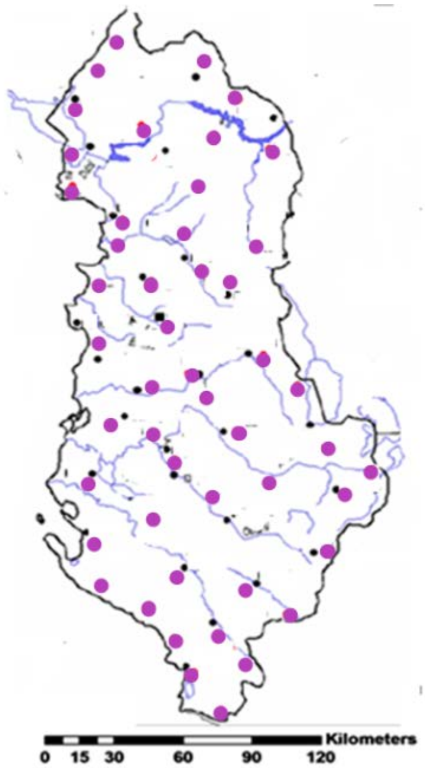

Fig. 1. The location of the sampling sites on the map of Albania position.

Moss samples (*Hypnum cupressiforme (Hedv.)* that are widely spread in Albania are collected from 47 sampling sites at relatively dry periods during October-November 2010 and June-July 2011. A systematic sampling scheme was applied using a homogeneous distribution of more or less equal densities (≈1.5 moss samples/1000 km^2). The locations of samples were situated at least 300 m away from main roads or buildings and 100 m from small roads and single houses. The distribution of the sampling sites is shown on the map of Albania (centered at the latitude 41°00′ north of the equator and the longitude 20°00′ east of Greenwich) (Fig. 1).

2.2. Moss analysis
Moss samples were cleaned from the adhering materials and the brown parts of the plant tissues were removed as died material. 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 dried at room temperature for about 72 hours.

The concentration of metals in moss was determined by instrumental neutron activation (INAA) and inductively coupled plasma-atomic emission spectrometry (ICP-AES). INAA is a non-destructive method of multi-elements analysis. It could achieve good detection limits, high accuracy and low systematic error in trace elements quantitative analysis. INAA measure the total amount of elements present in the samples of different matrixes without any pre-treatment of the sample (Salbu and Steinnes 1992). ENAA analyses were performed at the Frank Laboratory of Neutron Physics Joint Institute for Nuclear Research, Dubna, Russian Federation.

The dried samples were digested with a Microwave digestion system (Mars, CEM, USA) (Stafilov et al. 2018). The concentration of metals in moss was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Varian, 715ES) and, the electrothermal atomic absorption spectrometry (ETAAS-Varian, SpectrAA 640Z, only for Cd and As). The analysis was conducted at the Institute of Chemistry, Faculty of Science, St. Cyril and Methodius University, Skopje, Northern Macedonia. Three replications for moss samples were digested, and three replicate measurements for dissolution were made during analysis. Concentrations of metals (including mercury) are expressed in mg kg-1 dry weight.

2.3. Quality control
The quality control of ENAA results was examined by the analysis of reference materials SRMs 2710 Montana Soil (NIST), 1632b Trace Elements in Coal (NIST) and BCR 667 Estuarine Sediment (IRMM). INAA is relatively free from matrix effects and interferences that allows using standards of different compositions and physical state from the sample (Filby 1995), Frontasyeva 2011). The mean content of the elements under investigation are in good agreement with the certified data [29].

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

2.4. Data processing and statistical analysis
The variability and spatial distribution of the elements was investigated by using the statistical analysis, descriptive statistic and spatial analysis. The relationship between the elements in moss was tested by Pearson correlation analysis, confirmed by the statistical significance level, $P < 0.005$. Factor analysis (FA) was used to assess the most probable pollution sources

of the elements under investigation. FA may explore the hidden multivariate structures of the data (Astel et al. 2008; Reimann et al. 2002) and may clarify the link between the elements that tend to have similar origins or to subsequently develop similar associations on the data matrix. The associations of the elements extracted from the Pearson correlation matrix may explain the role of the factors to the group of the associated elements. Statistical analysis was performed using the MINITAB 19 software package. The spatial distribution of the elements was visualized from the distribution maps, plotted with Arc-GIS 10.2 system by applying the local deterministic methods and the inverse distance weighting. The concentration data of the elements was divided by the respective median values to standardize the data at the same digit numbers. To compensate the natural variability and to distinguish the anthropogenic variability of concentration data, the data were normalized by using Li as normalizer element (Loring and Rantala, 1992).

3. Results and discussion

3.1. Trace metal concentrations in moss samples

The most important statistical parameters, such as mean, median, minimum, maximum, coefficient of variation (CV%), skewness, kurtosis and frequency distribution, are shown in Table 1. The mean, median and the concentration range are shown in mg kg^{-1}.

Table 1. Descriptive statistic analysis of trace metal data (N=47)

Elements	Mean	Median	Range	CV %	Sk	K^N
As	0.452	0.21	0.05–2.86	133	2.6	6.8
Cd	0.146	0.11	0.038–0.090	90	4.5	24.7
Cu	6.035	5.62	2.14–15.55	39	1.52	4.89
Hg	0.206	0.136	0.036–2.23	93	5.7	35.6
Pb	3.11	2.29	1.34–19.7	93	4.6	24.4
Zn	14.49	13.9	1.0–46.9	64	1.16	2.6
Ni	13.2	5.89	1.56–131	162	4.2	20.4
Cr	26	10.9	1.47–262	164	4.1	20.8
Co	1.84	1.2	0.389–7.47	87	2	3.3
Fe	1845	1540	469–5488	60	1.84	3.5

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

The distribution of concentration data (except Pb and Zn) and the normalized data of As, Cd, Hg, and Ni follow the lognormal distribution model, and are positively skewed with high variability (CV>75%). It indicates a high asymmetry of the concentration data affected by mixed factors. The sequences of the content of elements in moss samples were Fe > Zn > Cr > Ni > Cu > Pb > Co > As > Hg > Cd. The sequence of the variability of the normalized concentrations was Ni ≈ Cr > As > Hg ≈ Pb ≈ Cd> Co > Zn > Fe > Cu. It looks likely different from the sequence of the variation in concentration data, by indicating the presence of the anthropogenic effects. The median concentrations of Cr and Ni in current moss samples is about 6 and 20 times higher than the median concentration of the European moss survey (Allajbeu et al. 2017; Harmens et al. 2015) that may indicate high anthropogenic inputs of these elements in current moss samples. High variability of the elements and wide range of the concentration revealed heterogeneous spatial distributions of the metals in moss samples by indicating high effects of the anthropogenic sources. The concentration data onto Cu, Fe and Zn are characterized by moderate variation (CV<75%) and looks likely more stable in their distribution over the territory of the country. High metal concentrations on different locations and the disparity in the distribution of the concentration data indicates that the data are affected by mixed local factors may be associated with geochemical factors and local anthropogenic sources. The skewness and kurtosis of As, Pb, Cr, Fe and Zn are higher than the respective values of concentration data The situation is similar with the variability of Cu, Pb, Ni, Cr, Co and Zn normalized data that show higher variability than the respective values of the concentration data. This behavior of the normalized and the concentration data of the elements probably indicate high anthropogenic sources of these elements in moss samples.

3.2. Multivariate analysis

Pearson correlation analysis was carried out to investigate the linear relationship and the association between the elements.

Very strong and significant correlations ($r>0.8$, $p=0$) were found between the pairs of the concentration data of As, Pb, Cr, Ni and Co, and their respective normalized data by indicating strong anthropogenic sources of these elements. Strong ($0.6<r<0.8$, $p<0.005$) and/or moderate ($r = 0.4 – 0.6$, $p < 0.01$) and significant correlations were found between the pairs of the concentration data of the group of elements Cu, Cd, Zn, Pb, Hg, as well as with their normalized data.

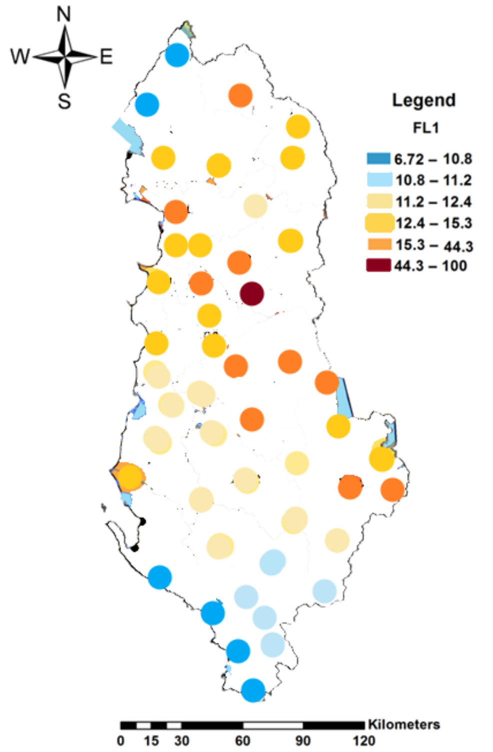

Fig. 2. Distribution pattern of factor loading FL1 linked with Cr(N), Ni(N), Ni, Co, Co(N), Fe(N) and Cr.

Moderate and significant correlations ($r = 0.4 – 0.6$, $p < 0.01$) between Cd, Cu, Pb, Hg, and Zn elements indicate their similar natural and anthropogenic origin in moss samples. The presence of these elements in atmospheric deposition is mostly derived by long-range atmospheric transport of pollutants from other parts of Europe (LRTP) and from local emitting sources such as high temperature of metal processing, traffic emission, and windblown dust that represents historical waste deposition and the geochemical properties of the area (Harmens et al. 2015).

For better explaining the association of the elements and to evaluate the probable sources of the elements in moss samples, Factor analysis (FA) was carried out.
Five main factors with 76.6% of the total variance were extracted from FA. The associations of metals within the same factor could be explained as follows:

Factor 1 (F1) is the strongest factor representing 22.2% of the total variance. It is followed by high loads of Ni(N), Cr(N), Ni, Cr, Fe(N), Co, and Co(N). These elements are anthropogenic elements mostly derived by different emission sources such as the geogenic contribution of Cr and Fe-Ni deposits, historical waste deposition, mining industry, iron, and steel and ferro-chromium metallurgy in Albania (Allajbeu et al. 2017; Qarri et al. 2014). The association of the anthropogenic fraction of Fe (represented by the Fe(N)) is highly supports the discussion above. Strong associations of the concentration data of Cr, Ni and Co with their respective normalized data indicate strong anthropogenic sources of these elements.

Factor 2 (F2) is the next strong factor representing 19.4 % of the total variance. It is linked with high loads of Cd(N), Zn(N), Cu(N) and Hg(N). The normalized concentration data of the elements come after the compensation of natural variations and indicate their anthropogenic fractions (Loring and Rantala, 1992) in moss samples. Geogenic factors, mining and nonferrous metallurgy should be important sources of these elements. Although the copper mining, smelting and processing industry in Albania had stopped since the beginning of years 1990 and emissions of metals such as copper, lead, cadmium, zinc, selenium etc., 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 vicinity of ex-copper industry particularly in the North part of the *Factor 2 (F2)* is the next strong factor representing 19.4 % of the total variance. It is linked with high loads of Cd(N), Zn(N), Cu(N) and Hg(N). The normalized concentration data of the elements come after the compensation of natural variations and indicate their anthropogenic fractions (Loring and Rantala, 1992) in moss samples. Geogenic factors, mining and nonferrous metallurgy should be important sources of these elements. Although the copper mining, smelting and processing industry in Albania had stopped since the beginning of years 1990 and emissions of metals such as copper, lead, cadmium, zinc, selenium etc., 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 vicinity of ex-copper industry particularly in the North part of the country (Lazo et al. 2019). GIS map is created to show the distribution pattern of high loads parameters of F2 (Cd(N), Zn(N), Cu(N) and Hg(N)) (Fig. 3).

Factor 3 (F3) is the next factor representing 13.8 % of the total variance. It is followed by high loads of Fe, Hg, Zn, Cd, and Cu. This group of elements is probably derived by geogenic factors that are linked with the sulfide minerals located in the North part of Albania, and other anthropogenic factors. Hg, Zn, Cd, and Cu are also typical elements for long-range transport of the chemicals, traffic emission. They may originate from oil-gas industry, shipping activity, and long-range transport of the pollutants. Hg and Cd point also the sources of fire industrial activities, waste incineration, while the association of these elements with 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. It is also verified by the presence of Fe together with these elements under the same factor. Fe is naturally distributed as a typical soil element (Rudnick and Gao, 2003) that may indicate its soil dust origin. GIS map of Fig. 4 shows the distribution pattern of high loading parameters of F3 (Fe, Hg, Zn, Cd and Cu).

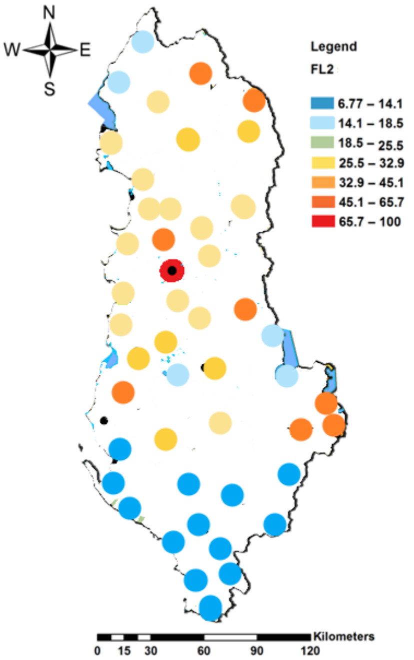

Fig. 3. Distribution pattern of factor loading FL2 linked with Cd(N), Zn(N), Cu(N) and Hg(N).

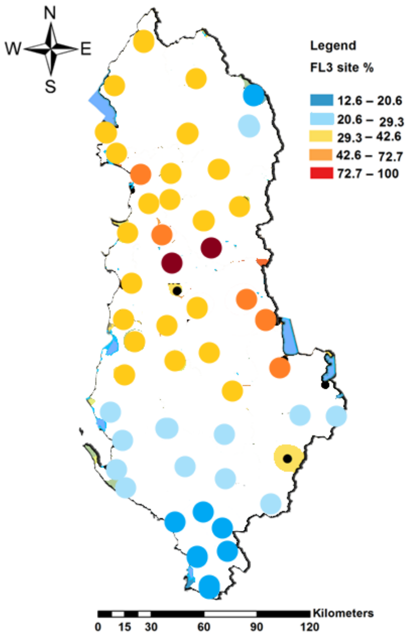

Fig. 4. Distribution pattern of factor loading FL3 linked with Fe, Hg, Zn, Cd and Cu.

Factor 4 (F4) and *Factor 5* (F5) respectively represent 11 % and 10% of the total variance. They are associated by high loads of the concentration and the normalized data of the same element, Pb and Pb(N) (F4), and As and As(N) (F5). The main sources of Pb are counted to be the vehicle exhaust and coal combustion, industrial emission sources, metallurgy of Elbasan, and geogenic factors. The strong Pb anomaly in Shkodra area is probably affected from the trans-boundary pollution of metals (Al and Fe) processing industry in Montenegro (Peck, 2004).

Arsenic is used in agriculture activity as inorganic fertilizers and herbicides. It may lead to the enrichment of As in the local soils which may enter in atmosphere as fine soil dust particles and then re-suspended as atmospheric deposition in different distances controlled by the size of dust particles. The next area with relatively high loads of As and As(N) belong 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 distribution pattern maps of factor loads FL4 and FL5 linked with Pb and Pb(N) (FL4), and As and As(N) (FL5) are shown in Fig. 5.

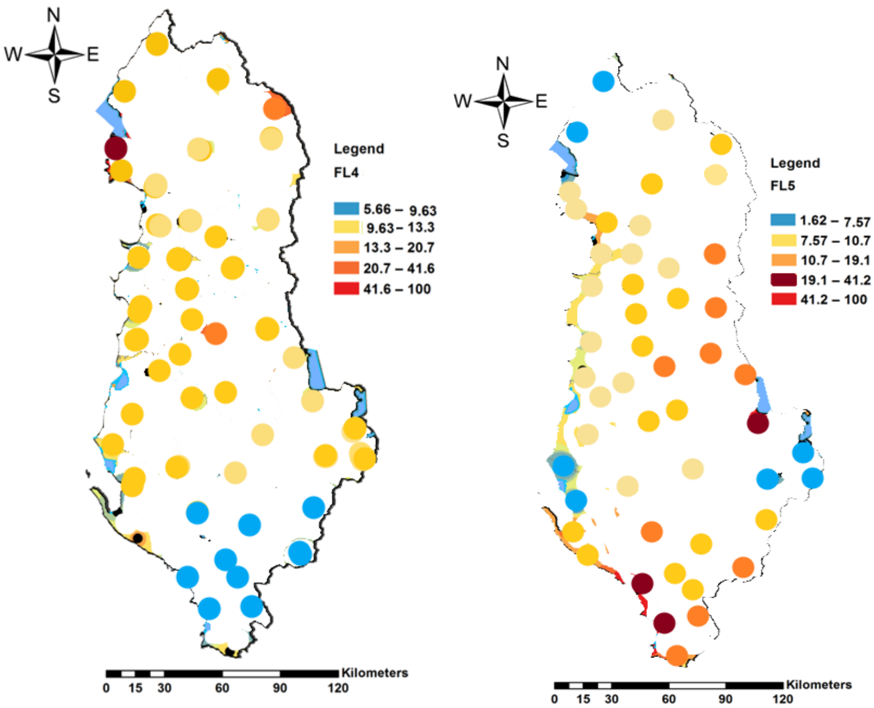

Fig. 5. Distribution pattern maps of factor loads FL4 and FL5 linked with Pb and Pb(N) (FL4), and As and As(N) (FL5).

4. Conclusions

Through this study it is clear that the biomonitoring technique by using mosses as bioindicators of metals in atmospheric deposits, combined with statistical analysis of concentration data and emission inventory gives a promising view for proper conclusions about air quality regarding the level and the presence of metals in the air.

Differentiation and the variation of metal concentrations in moss samples show strong influence of local emission sources compared to long-range atmospheric transport of the pollutants.

Higher anthropogenic level were found for Cr, Ni, Co the elements compared to the anthropogenic elements that pose high risk to human health (As, Cd, and Pb).

The results of this study represent the need for more rigorous measures regarding the emission of atmospheric pollutants originating from the mining industry, high temperature processing and smelting of metals, vehicle emissions, fertilization, pesticide spraying, waste incineration etc.

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