MOSS BIOMONITORING OF AIR POLLUTION WITH Cr AND Ni IN ALBANIA

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ABSTRACT

Moss biomonitoring and induced plasma atomic emission spectrometry (ICP-AES) was applied to study Cr and Ni atmospheric deposition in Albania. Moss samples Hypnum cupressiforme (Hedw) spp. were collected from 55 sites during the summer of 2015 in accordance with the LRTAP Convention - ICP Vegetation protocol and sampling strategy of the European Programme on Biomonitoring of Heavy Metal Atmospheric Deposition. The statistical analysis was applied to investigate the concentration level, the variation and the distribution of both elements over the entire territory of the country. The concentration level of Cr and Ni in moss samples of Albania expressed by median concentration of 55 moss samples, are compared with the respective medians of Balkan countries, and of selected European countries. The elements Cr and Ni are included in the European program of moss biomonitoring. It was found that the median values of these elements in Albania were generally higher than the respective median values observed in Europe and Balkan countries. Lower content of Cr and Ni were found in the coastline area of Albania compared with the inland area. The aim of this study is the assessment of the air quality throughout Albania and the identification of their pollution sources to produce information needed for better environmental management. The data may help the policy makers to improve the strategy for a clean environment in the country.

Keywords: moss biomonitoring; atmospheric deposition; Cromium and nickel, ICP-AES analysis, statistical analysis, Albania

INTRODUCTION

The pollutants emitted in the atmosphere from different natural and anthropogenic sources make the air we breathe hazardous to our health. Air pollution is a complex process that presents many challenges in terms of reducing the emission level of the pollutants and ensuring good air quality. Wide ranges of chemicals emitted by human activities are responsible for poor air quality which may cause several undesirable effects on humans and environmental health. It could increase the public health threats, agricultural and vegetation injury, water quality degradation, and affect the climate change. Air pollution is a global problem sourced from national and regional scales and distributed over the entire world. The transport of air pollutants depends on their physical and chemical properties, the environmental conditions, and impacts the air quality in regional and intercontinental ranges. Air pollutants could affect the human health directly through the inhalation and/or the ingestion process. The undesirable effects of air pollution to human and ecosystems health is a strong reason concern the air quality monitory. The rapid industrialization during the last decades made the human activities a major source of contaminants in the environment. 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). Metals are generally found in the air in a variety of physicochemical forms, such as solid, liquid, gaseous, or very fine particles of a wide ranges of aerodynamic size, from 2.5 nm to 1 µm of the gaseous phase, and 1 µm up to 100 µm and larger, of particle phase (Richards, 2020). Due to the high speed of sedimentation, the large particles generally remain close to the source, but the fine and ultrafine ones can spread by the wind for thousands of kilometers (Vgkevg et al. 2000). Air quality can be monitored directly by conventional techniques and/or by biomonitoring methods that use specific plant organisms as biomonitors to provide information on the quantity of the pollutants and the effects to the plants. The conventional techniques used in the classical monitoring methods require expensive equipment that may cover a small area of interest. For decades, the use of mosses as bioindicators 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). The bryophyte mosses were used for the first time in Nordic Countries since 1960. It is a good technique for air monitoring. Bryophyte moss do not posses real roots and vascular system, they obtain nutrients mostly through their entire plant surface directly from the atmosphere and the precipitation, and thus, the elements present in their tissues may reflect the presence of elements in the atmosphere (Fernandez et al. 2000; Saxena et al. 2008; Blagnytė and Paliulis, 2010). The lack of a vascular system in bryophyte moss causes a limited circulation of nutrients that lead metals to be focused on the upper two-thirds part of the moss shoots, which allows green tissues to be used as good bioindicator to assess the integrated metal deposition for a period of at last three years (Schröder et al. 2016; Harmens et al. 2015; Couto et al. 2003; Brumelis and Brown, 1997). The aim of this study is to present the content of Cr and Ni in moss samples collected from the entire territory of Albania during the moss survey of 2015. Statistical analysis is used to investigate the concentration level, the variation and the distribution of Cr and Ni over the entire territory of the country. It makes possible the identification of the sites with higher levels of these elements.

MATERIAL AND METHOD

Sampling

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). Moss samples (*Hypnum cupressiforme (Hedv.)*) that are widely spread in Albania are collected from 55 sampling sites at relatively dry periods during the summer of 2015. A systematic sampling scheme was applied using a homogeneous distribution of more or less equal densities (≈2 moss samples/1000 km2). 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. Most of the samples were collected in the open areas. Composite moss samples were formed by five to ten sub-samples collected within an area of 50×50 m2. Disposable polyethylene gloves were used during the sampling and sample cleaning to avoid the contamination of the samples. 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).

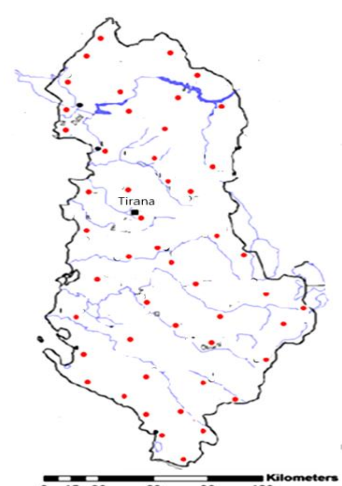

Figura 1. The location of the sampling sites on the map of Albania position

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. Moss samples were digested with a Microwave digestion system (Mars, CEM, USA). The method was presented by Stafilov et al. (2018). The concentration of metals in moss was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Varian, 715ES). The analysis was conducted at the Institute of Chemistry, Faculty of Science, St. Cyril and Methodius University, Skopje, North 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.

Quality control

The quality assurance 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 analysis.

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, $P < 0.005$. The spatial distribution of the elements was visualized from the spatial distribution graph plotted with spatial analysis performed in MINITAB 19 program.

RESULTS AND DISCUSSION

Cr and Nil concentrations in moss samples

The most important parameters, such as mean, median, minimum, maximum, coefficient of variation (CV%), skewness and kurtosis are shown in Table 1.

Table 1. Descriptive statistic analysis of Cr and Ni data (N=55)
(The mean, median and the concentration range are shown in mg kg-1)

Elements	Mean	StDev	CV%	Min	Q1	Med	Q3	Max	Sk	Ks
Cr	10.65	9.69	91	2.21	4.57	9.27	13.34	66.17	3.65	19.50
Ni	17.05	23.51	138	0.68	4.22	7.57	19.02	107.78	2.56	6.54

CV - coefficient of variation, Sk - skewness; K – kurtosis.

The sequence of the distribution of Cr and Ni in moss was Cr > Ni. They show high variability (CV>75%) followed by high values of skewness and kurtosis. It indicates a high asymmetry of the concentration data, wide spreading, strong geographical variability of the elements in moss samples, and the data are affected by different factors.

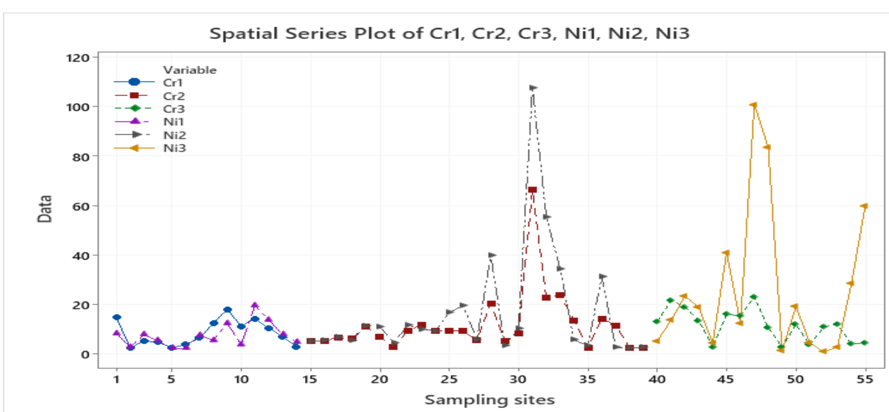

Figura 2. The distribution of Cr and Ni along sampling sites

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, characterized by high values of skewness and kurtosis, revealed heterogeneous spatial distributions of the metals in moss samples by indicating high effects of the anthropogenic sources. The geogenic factors, mining, mineral enrichment, and the industrial sites with old technology such as smelting and refining complexes (chromium, copper, iron ore, etc.), the Elbasan iron and steel plants, petroleum refineries, and chemical plants that had caused serious environmental pollution in the country (Lazo et al. 2019, 2018, Qarri et al. 2014, UNDP, 2010) can be considered the main contributors of the outlier data. The distribution of Cr and Ni along sampling sites is shown in Fig. 2 and the sites with extreme values of metal contents are summarized in Table 2.

Table 2. The sites with high contents of Cr and Ni

Sampling site	Location	Elements	Sampling site	Location	Elements
14 and 22	Milot, Gramsh	Cr,	39	Pogradec	Ni
14 and 22	Milot, Gramsh	Cr,	41	Librazhd	Cr, Ni
24	Elbasan	Ni, Cr	42	Bulqiza	Ni, Cr
27	Kruja	Cr	43	Burrel	Ni, Cr

For a correct interpretation of the results of metal content in moss, the inventory of emission sources is very important parameter to examine the origin of air pollution and to evaluate the air quality state in areas subject to anthropogenic activities (Iodice et al. 2016). It was found that the coastal line of Albania (ST 1 to ST14, Fig. 2) shows relatively low Cr and Ni content compared with the inland area. Low Cr and Ni content were also found in the south inland area (ST16 to 27, Fig. 2). High Cr and Ni content were found in the NE-SE belt that is known as Cr-Ni mineralized area and Cr-Ni mining industry zone (Lazo et al. 2019, 2018). Beside it, mining and ferrocromium industry, metal high temperature processing have negative impacts in the air quality of central inland area. Thus, the Elbasan area (ST24) resulted as the most polluted site with high content of Ni and Cr in moss samples. It is mostly *affected by the emissions from iron, steel, and ferro-chromium metallurgy, cement plant and dense traffic in the area.* The fine particles of trace metals emitted during various human activities are assumed to be the major cause of the increase in the concentration of different metals in air (*Pacyna and Pacyna,* 2001).
The highest Cr and Ni contents were found in Bulqiza, Elbasan, Burrel, Milot and Gramsh areas (ST42, 43, 24, 14 and 22) that are probably affected by anthropogenic emission from Cr-Ni mining industry, iron and ferro-chromium metallurgy. The hot-spot of Kruja (ST27), with high content of Cr, is probably affected by a strong anthropogenic effect of kiln operations of the lime stones that were using waste materials for heating like brakes and tire wear, unselected urban wastes, woods etc., during the CaO production. High Ni and Cr contents in moss samples are located in Pogradec (ST39) and Librazhd (ST41) areas that are strongly affected by geogenic factors and mining industry. The Cr and Ni concentration levels are compared with other Balkan countries and some European countries (Fig. 3).

a. b.

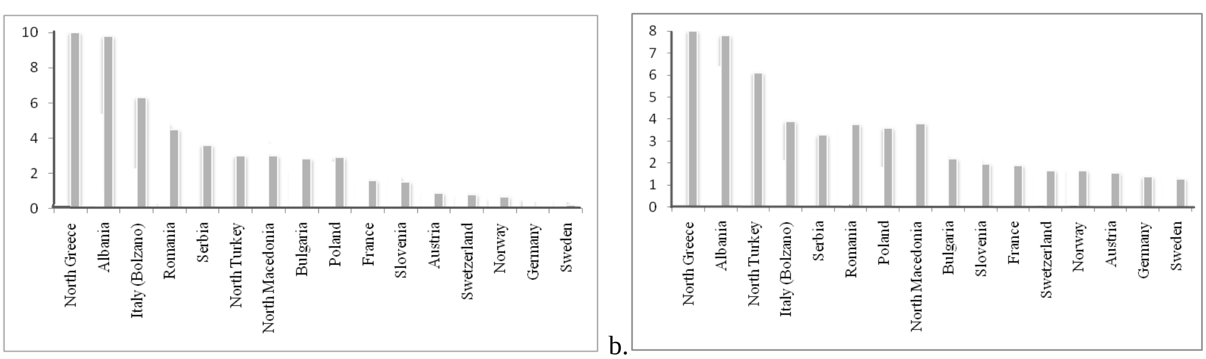

Figure 3. The comparison of Cr (a) and Ni (b) concentration levels
with other Balkan countries and some European countries.

In general, the Cr and Ni concentration levels in Balkan countries resulted higher than the European countries, particularly with North European countries. The highest content of these elements among Balkan countries were found in North Greece and Albania. It is probably affected by geogenic factors linked with Albanide-Hellenide orogenic belt rich in Cr and Ni minerals (Sacani and Tassinari, 2015, Xiong et al. 2015), mining, metal high temperature processing, ferro-nickel and chromium metallurgy in Albania (Lazo et al. 2018).

CONCLUSIONS

The following conclusions could drown from this study:

- ✓ It was found that the local emission sources and long-range atmospheric transport of the pollutants show significant contributions to atmospheric deposition of metals.
- ✓ Moss biomonitoring survey provides a unique opportunity for the assessment of metal contamination in atmospheric deposition.
- ✓ Significant variations were found in the concentration data of Cr and Ni in moss samples.
- ✓ In general, the elements considered in this study (Cr and Ni) are mostly affected by anthropogenic sources, originated from mining industry, metal high temperature processing, smelting, vehicle emissions, waste incineration etc.

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