THE SURVEY OF ATMOSPHERIC DEPOSITION OF HEAVY METAL IN ALBANIA BY USING MOSS BIOMONITORING AND ICP/AES AND NAA TECHNIQUE

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Abstract

The atmospheric deposition of As, Cd, Cu, Cr, Fe, Ni, V, and Zn in Albania was investigated by using the carpet-forming moss species (*Hypnum cupressiforme*) as bioindicators. This research is a part of the international program (International Cooperative Programme (ICP) Vegetation, UNECE) that had carried out in the most of European countries since 1987, by investigating the impacts of air pollutants on crops and natural vegetation. Sampling was carried out during the dry seasons of autumn 2010 and summer 2011 at 62 sites distributed all over Albania.
Unwashed, dried samples were totally digested by using microwave digestion, and the concentrations of metal elements were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The results reflect local emission points. The concentrations of median values were compared with other Balkan countries and to other European countries.. The median values of chromium (4.75 mg/kg, dry weight (DW)), iron (1,618 mg/kg, DW), nickel (5.85 mg/kg, DW), vanadium (3.51 mg/kg,DW), zinc (13.77 mg/kg, DW), and aluminum (6,974 mg/kg, DW) are similar to those of neighboring countries but higher than those of European countries. The certain local emitters were identified like the iron-chromium metallurgy and cement industry, oil refinery, mining industry, and transport. In addition, natural sources, such as the accumulation of these metals in mosses caused by metal-enriched soils, associated with the wind blowing soils dust particularly in the southeast direction of the country, were pointed as another local emitting factor.

Keywords: moss biomonitoring; atmospheric deposition; trace elements; ICP-AES analysis; multivariate analysis

Introduction

Air pollution is a global problem caused by anthropogenic sources such as gaseous discharges from industries and motor vehicles, and also from natural sources such as windblown soil dust and the smoke from fires. The current anthropogenic metal emissions are up to several orders of magnitude higher than their natural emissions (Chmielewska and Spiegel 2003). Numerous studies worldwide has confirmed that both long- and short-term exposures to air pollutants have a strong health effect to the people and are associated with the increases of mortality and morbidity (Dockery 2009). Several studies have indicated that different transition metals may act as possible mediators of particle induced injury and inflammation (Schaumann et al. 2004; Chen and Lippmann 2009).
Since the 1980s, many studies have been reported that used biomonitoring by analysis of mosses to assess atmospheric fallout (Fernandez and Carballeira 2001; Harmens et al. 2013).
Bryophytes are well known and widely used as bioindicators due to their specific features (Rühling et al. 1968; Markert et al. 1999; 2003): the cuticle is lacking or reduced, they have

no real root system, and leaves are only one cell layer thick so they can take up nutrients over the entire plant surface from air and precipitation.

The aims and structure of this study

Albania is a small country (28 000 km^2) with a complex geographic relief, climate, geologic setting, and characterized by high anthropogenic influence. The first study of the moss biomonitoring atmospheric deposition of metals in Albania was performed under the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops with heavy metals in Europe (UNECE ICP Vegetation) (Harmens 2010). 10 elements, such as conservative elements (Al and Fe), and trace elements, such as As, Cd, Cr, Cu, Ni, Pb, V and Zn, were measured in moss samples collected from 62 sampling sites from whole territory of Albania during the moss survey in the dry autumn and summer period of 2010 and 2011. The median concentrations of elements were compared with other European countries. The median values of chromium (4.75 mg/kg, DW), iron (1618 mg/kg, DW), nickel (5.85 mg/kg, DW), vanadium (3.51 mg/kg, DW), zinc (13.77 mg/kg, DW) and aluminium (6974 mg/kg, DW) are similar to those of neighboring countries, but higher to those of European countries. Certain local emitters were identified like, iron-chromium metallurgy and cement industry, oil refinery, mining industry, and transport. In addition, the natural sources, from the accumulation of these metals in mosses caused by metal-enriched soil, associated with wind blowing soils dust particularly in Southeast direction of the country, was pointed as another possibility of local emitting factors.
The main aims of this study is to express the spatial patterns of heavy metals distribution in mosses of 2010/11 collected in Albania and to identify the main polluted areas over the country in 2010/11.

Materials and methods

The carpet-forming mosses *Hypnum cupressiforme* and *Pseudoscleropodium purum* species were collected according to the guidelines set out in the experimental protocol for the 2010/11 survey (ICP Vegetation, 2010). The distribution of the sampling sites throughout Albania is shown in our previous publication (Qarri et al. 2013). The total digestion of moss samples is done according to the method presented by Barandovski et al. (2008). The quality control of ICP-AES results was checked by multiple analyses of samples and the certified moss reference materials M2 and M3 (Steinnes et al. 1997; Harmens et al. 2013).

Results and Discussions

The 2010 data on the concentration of 10 elements in 62 moss samples from Albania are summarized in a data matrix. Aiming to valuate the contamination level and elements distribution, the analytical results were statistically treated by using Descriptive statistics (Tab. 1) and Multivariate Analysis (Pearson Correlation, Tab. 2).

Table 1 Descriptive statistics of the data analyzes of elements (mg/kg, DW) in moss samples (N=62)

Parameters	Fe	Ni	V	Al	Cr	As	Pb	Cd	Cu	Zn
Range	469–5488	1.6–131	1.15–16.9	535–6974	1.6–31.7	0.05–2.9	1.3–19.7	0.038–0.89	2.14–16	1.0–68
Mean	1892	11.36	4.23	1958	6.38	0.541	3.28	0.17	6.07	14.06
Median	1618	5.85	3.51	1638	4.75	0.305	2.41	0.107	5.58	13.8
ST.DEV	1105	19.3	2.79	1178	5.39	0.64	3.21	0.16	2.8	11.6

The highest values of these elements were measured near the industrial centers (the central part of the country). The present median values of the elements Al, Fe, V, Cr, Ni and Zn, typically associated with air pollution are generally comparable with those presented from other neighboring countries (Qarri et al. 2013), but higher than the corresponding values from most European countries (Harmens et.al. 2013). To distinguish between lithogenic and anthropogenic origin of the elements in moss samples, correlation analysis was carried out.

Table 2 Pearson Correlation Coefficient between element concentrations in mosses in Albania.

	Cd	As	Cr	Cu	Pb	Ni	V	Zn	Al	Fe
Cd	1									
As	0.19	1								
Cr	0.46[1]	0.18	1							
Cu	0.39[2]	-0.05	0.31	1						
Pb	0.35[3]	0.08	0.26	0.45[1]	1					
Ni	0.21	-0.01	0.64[1]	0.14	0.06	1				
V	0.30	0.34[3]	**0.51[1]**	0.30	0.31	0.13	1			
Zn	0.43[1]	-0.09	0.43	**0.62[1]**	**0.52[1]**	0.21	0.34[3]	1		
Al	0.34[3]	**0.60[1]**	0.43[1]	0.11	0.12	0.08	**0.67[1]**	0.02	1	
Fe	0.43[2]	0.44[1]	**0.81[1]**	0.38[2]	0.30	**0.51[1]**	**0.72[1]**	0.39	**0.75[1]**	1

Cell Contents: P-Value: [1] P<0.001, [2] P<0.005, [3] P<0.01

Good correlations (R^2>0.5, P>0.001) were found between Fe and Cr, Ni, V, Al by explaining their lithogenic (Fe-Al, V correlation) and geogenic (Fe-Cr, Ni correlation) origin of Fe.

Arsenic, Cadmium, Cupper and Zinc

Arsenic concentrations in mosses were generally low in western part of Albania and higher in the East part of Albania, but lower than neighboring countries (Harmens et al. 2013). Cu, Cd and Zn concentrations were generally low in mosses sampled in Albania compared to many other European countries (Harmens et al. 2013). Road transport may have a considerable effect on the distribution of these elements in air pollution in Albania.

Aluminium, Chromium, Iron, Nickel and Vanadium

The background level of Al in Albanian moss samples is higher than the European 2010 moss biomonitoring survey. The highest Al concentration was found in the south and in the central part of Albania. The main contribution of Cr, Fe, Ni and V elements is coming from the Elbasan ferrochromium metallurgical plant (Lazo et al., 2013) and mining industry in Albania. The high level on wind-blow dust in the south and high level (for most metals) of industrial activity focused in the Mideast PART of Albania. The association Cr and Fe are also related to air pollution (Lazo et al. 2013). Their highest concentration is present near the iron-chromium metallurgy in Elbasan town and chromites deposits areas of Albania.

Conclusions

Moss biomonitoring provides a cheap, complementary method to deposition analysis for the identification of areas at risk from high atmospheric deposition fluxes of heavy metals.

This study demonstrates once again that, using the relatively favorable moss analysis method it is possible to fairly accurately estimate both regional differences as well as the trend in deposition over the course of time for a broad variety of metals and for nitrogen. In this way it has been possible to document the impacts of measures aimed at reducing emissions. The applied method can therefore be used for carrying out success controls in the area of environmental protection.

Based on the median distribution of Albanian data of moss survey 2010/2011 we may suggest that the elements Zn, Cd, Cu, Pb and As do not achieve high enough concentrations as a result of long-range atmospheric transport and deposition to cause adverse effects on terrestrial ecosystems. However, the elements Al, Fe, Cr, Ni and V appear the highest median values among European countries and these exceeds may result in plants' effects due to the accumulative nature of heavy metals in soils. Soil dust, industry emissions, waste incineration and road traffic were pointed as main factors causing air pollutions from heavy metals in Albania. Further measures in the future by reducing the number of sampling sites are required in Albania to reduce the relative high emissions of these elements.

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