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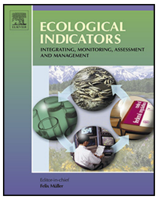

Application of the normalization process in the survey of atmospheric deposition of heavy metals in Albania through moss biomonitoring

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ABSTRACT

The present paper concerns the study of atmospheric deposition of heavy metals, using a carpet-forming-moss species (*Hypnum cupressiforme*) as a bioindicator. It provides a complementary method to evaluate elemental deposition from the atmosphere to terrestrial systems. Compared with conventional precipitation analysis, it is an easier and cheaper method that ensures a high sampling density over the monitored area. The moss samples were collected over the whole territory of the country by following, more or less, a systematic sampling scheme, which is often used in environmental studies because it is convenient to implement in field campaigns, often providing good precision and complete coverage of the target population compared with random sampling. The 2010/2011 ICP vegetation moss survey data were used in this study. The unwashed, dried samples were digested completely by the microwave digestion method. The concentration (C) of selected trace metals (As, Cr, Cu, Ni, V and Zn) and conservative metals (Al, Li and Fe) were determined by ICP-AES and AAS (Cd and As) methods. To characterize the natural and the anthropogenic pattern of heavy metal deposition throughout the whole territory, the normalization process using lithium as a normalizing element was carried out on the C data for 11 elements of 44 moss samples. The obtained data set was used to compensate the natural variability of trace metals, so that the anthropogenic metal contributors could be detected and quantified. Descriptive statistics and multivariate analyses were used for the statistical treatment of the normalized concentration (NC) data using the MINITAB 17 software package. The statistical parameters of the NC data are discussed. The level of contamination was evaluated by calculating the enrichment factors, whereas the most probable local anthropogenic emitter sources were identified. The statistical analysis of NC data demonstrated that the normalization process is useful for evaluating the relative contributions of anthropogenic and natural sources of elemental deposition from the atmosphere to terrestrial systems, when the main pollution sources are from fine dust particles.

1. Introduction

Air pollution is a global problem caused by different anthropogenic and natural emission sources such as gaseous emissions from industries, traffic emission and the smoke from fires (Grodzinska and Szarek-Lukaszewska, 2001) as well as from wind-blown fine dust detached from the sparsely vegetated areas and moving into the atmosphere (Nriagu, 1989). Dust particles have the same metallic composition as the soil composition. There is increasing awareness about fine dust particles in the atmosphere, which play an important role in climate change, biogeochemical cycles, nutrient supply to ecosystems and soil formation (Muhs et al., 2008). The dust can move through intercontinental distances (Prospero et al., 2002; Prospero and Lamb, 2003) and can influence

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Abbreviations: HM, heavy metal; ICP-ES, inductively coupled plasma emission spectrometry; BC, background concentration; C, concentration; NC, normalized concentration; EF, geochemically normalized enrichment factor; Me_i, the NC data of the metal element in the ith sample; C_{Me_i}, the C data of the metal element in the ith sample; Li_i, the C data of the Li in the ith sample; C_{HM}, the normalized mean C value of the element; C_{Li}, the normalized mean C value of lithium; BC_{HM}, the normalized background mean value of the element; BC_{Li}, the mean normalized background value of lithium.

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to irradiative transfers to the atmosphere and affect to the pollution level (Tegen, 2003).

Several methods are available to measure air pollutants, from simple methods to highly sophisticated instruments and/or monitoring stations. Attention on moss species, as an excellent biomonitor for assessing air pollution, has rapidly increased over recent decades. Mosses have been recommended as good bioindicators of metal pollution in the atmosphere since the 1960s (Rühling and Tyler, 1968). The bryophyte carpet-form moss species possesses particular properties that make it suitable for environmental studies (Onianwa, 2001). It is estimated that the absorption capacities of mosses exceed those of vascular plants by 100 times or more, owing to their ureic acid content (Winner et al., 1988). These species have no real roots and obtain nutrients directly from atmospheric depositions. The lack of a waxy layer on the leaf allows them to retain and accumulate the elements that reach them passively through both atmospheric dry and wet deposition processes. The accumulation of pollutants in mosses is controlled by different mechanisms, such as through the layers of the particles on the surface of the cells, ion-exchange processes and the metabolic process (Brown and Bates, 1990; Tyler, 1990). Low cell wall thicknesses cause the tissues to readily adsorb water, minerals and metal ions (Tyler, 1990).

The environmental compartments are subject to complex combinations of natural and anthropogenic contaminants. A key issue in environmental studies is to find the anthropogenic influence on the environment and to assess the difference between natural and the human-derived sources. As metals from natural and anthropogenic sources accumulate together in the environment, it is difficult to determine which proportion of the metal load belongs to natural pollution and which belongs to anthropogenic pollution (Loring and Rantala, 1992). The normalization process is important as an attempt to compensate the natural variability of trace metals, so that the anthropogenic metal contribution may be detected and quantified (Loring, 1991). The normalizing element must be an important constituent of one or more of the fine-grained trace metals (Loring and Rantala, 1992). Aluminum is one of the most important constituents of the alumina-silicate mineral fraction, which is often used as a normalizing element (Loring, 1991). Lithium is of equal merit, or superior importance to Al for the normalization of metal data (Wang et al., 2010).

Albania is a small country (28,000 km^2) with complex geographic relief and geologic settings, which is characterized by a large number of anthropogenic factors. The first Albanian study of atmospheric deposition was performed under the framework of the International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops (UNECE ICP Vegetation) by moss biomonitoring. Nine trace elements (As, Cd, Cr, Cu, Ni, Mn, Pb, V, and Zn) and three conservative elements (Al, Fe and Li) were measured in moss samples collected throughout the whole territory during dry autumn and summer months in 2010 and 2011 (Qarri et al., 2013). From previous studies (Qarri et al., 2013, 2014a), soil dust is known to be among the main contributors of heavy-metal content in air deposition. The main objective of this study is to explain the anthropogenic variation in trace metals after using the normalization procedure on the concentration (*C*) data from trace-metal deposition. Wang et al. (2010) suggested lithium as a conservative normalizing element, because it is not enhanced by the activity of mining, processing, smelting or agricultural activity. The Li normalized concentration (*NC*) data were used to reduce the natural variability, to determine the most probable anthropogenic pollution sources and to distinguish different environmental meanings, offering valuable information for pollution control and environmental impact assessment.

2. Materials and methods

2.1. Field sampling

The bryophyte family of moss species *Hypnum cupressiforme* was preferred for this study, because of their very dense carpet; they absorb pollutants, particularly heavy metals (HMs), directly from atmospheric deposition more effectively than other moss species (Sacharová and Suchara, 1998). Moss sampling was performed according to the guidelines set out in the experimental protocol of the 2010/11 survey (ICP Vegetation, 2010). Sampling was carried out during the dry seasons of autumn 2010 and summer 2011. The sampling points were situated 3–10 m away from the nearest projected tree (in gaps of tree canopy >3 m and forests >10 m or plantations primarily >5 m). The sampling points were located far from urban areas. In remote areas, the sampling points were located at least 300 m from main roads, villages and industries and at least 100 m away from smaller roads and houses. The moss samples were collected from the ground (soil) or on the surface of decaying stumps. Areas of grassland or areas with running water on slopes, sand and/or those occupied by ants were avoided. Smoking was forbidden during sampling. Disposable plastic, non-talcum-powdered gloves were used when picking up the moss and during the sample handling for analysis. The green or green–brown parts, representing 3–5 years of growth of the plant, were used for further analysis without washing or other treatment. The coarse contamination of moss samples such as litter, soil or animals were carefully removed.

About 1 L of fresh moss composite was prepared for each sampling point, consisting of five sub-samples of one moss species, which was collected within an area of about 50 m × 50 m. The samples were placed side-by-side in large paper bags, which were tightly closed to prevent contamination during transportation.

Owing to the high diversity of geographical and topographical features in the country, the systematic sampling scheme was used in this study with, more or less, a homogeneous distribution among 44 sampling sites with equal densities (1.5 moss samples/1000 km^2) (Harmens et al., 2010; Qarri et al., 2014b), see Fig. 1. Systematic sampling schemes are characterized as homogenous distributions of sampling points with more or less equal densities. Systematic sampling is often used in long-scale environmental studies, as these schemes provide better precision (smaller confidence intervals and smaller standard errors in population estimates) and more complete coverage of the target population compared to random sampling (EPA QA/G-5S 2002). Detailed information about the sampling points is given in our previous publication (Qarri et al., 2013, 2014b). The distribution of sampling sites is shown in Fig. 1.

2.2. Chemical analyses

The chemical analyses of moss samples were carried out at the Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Macedonia. Acid digestion for the total digestion of the moss samples, according to the method presented by Barandovski et al. (2008) and Balabanova et al. (2010), was performed on dried samples in a microwave oven (MARS, CEM, USA). All of the reagents used in this study were of analytical grade, including nitric acid, trace pure (Merck, Germany), hydrogen peroxide, p.a. (Merck, Germany), and double-distilled water.

The *C* values of the metals were determined using *inductively coupled plasma emission spectrometry* (ICP-ES) (Varian 715-ES, ICP optical emission). Optimal operating parameters and the detection limits calculated as three times the SD of the lowest instrumental measurements of the blanks were given in the previous study (Balabanova et al., 2010; Qarri et al., 2013). Electro-thermal atomic