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Environmental implication indices from elemental characterisations of collocated topsoil and moss samples

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ABSTRACT

Pollutants, once emitted into the atmosphere, are deposited on the Earth's surface where they further accumulate in both biota and soil. It is therefore a challenge to assess pollutant distributions in different media, and define the various scaling factors to correctly assess each pollutant's environmental implications. In this study, the concentration of potentially toxic elements and their environmental implications were estimated for moss *Hypnum cupressiforme* Hedw. and the collocated topsoil (0–5 cm) samples, collected from 21 sites across the Province of Kosovo and Metohija (Serbia) during June 2016. The concentrations of Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, U, V, and Zn were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Median Ba, Cd, Cr, Co, Ni, V and maximum As, Cu, Pb, and Zn concentrations in topsoil samples from the study area were higher than prescribed limits in the national and international regulations. Furthermore, we applied and discussed different metrics to assess the pollution level (enrichment factors [EFs], geo-accumulation [I_{geo}] and pollution load index [PLI]). Different pollution scaling indicates moderate to severe environmental implications ($2 < PLI < 5$; $1 < I_{geo} < 7$, $1 < EFs < 275$) of the potentially toxic elements in the study area. The sampling sites in the northern part of the study area, well-known for their mineral resources, are particularly affected by toxic element pollution, which is likely a consequence of both the exploitation and waste disposal taking place there. More specifically, a comparison of element EFs calculated according to the Earth's crust values with those considering the topsoil background values, points toward a strong influence of (resuspended) soil component in the element enrichment of all environmental samples (i.e., in both the moss an collocated topsoil). However, the EFs of Pb, Cu, Zn, and U in the moss samples were notably higher than those calculated for the collocated topsoil, which could be an indication of a non-local pollution. Finally, both the collocated measurements and multiscale pollution assessment, performed simultaneously, testify to the strong geochemical 'signature' of the studied area.

1. Introduction

An assessment of pollutant atmospheric deposition across large areas is challenging since air quality data are highly variable and their availability is sparse, especially for remote areas. Regulatory monitoring stations are often unevenly distributed and are mainly concentrated in urban areas. The financial cost for their acquisition and technical maintenance, the provision of a reliable energy supply, and the inaccessibility of many sampling sites, represent the main limitations to regulators and their efforts to increase the number of monitoring stations.

Through bioindication or bioaccumulation of pollutants, living organisms reflect the ecological state of their particular habitat. Biomonitoring represents a complementary method to instrumental measurements since organisms can provide an integrated view of a relatively large area, either through an organism's ubiquity (plants) or ability to roam (animals), thereby overcoming the limitations of point measurements inherent to fixed instruments. Scientists worldwide have placed a particular focus on investigating the relation between biomonitors and pollutants, and associated health risks (Árvay et al., 2017;

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Fig. 1. Map of the study area (K&M province) with the locations of the moss and topsoil sampling sites on the left, and the locations of the mineral reserves shown on the right.

Aničić Urošević et al., 2017, and references therein). By definition, biomonitoring represents the systematic process of observing and tracking the temporal changes of environmental variables through living organisms (Li et al., 2010), ideally repeated over time using the same protocols. Nowadays, international programs exist that focus on the systematic use of biomonitors for the assessment of airborne pollutants and their impact on the environment. Since 1990, the European Heavy Metals in Mosses Survey has been conducted every five years, with an ever increasing number of participants of currently 36 countries (Frontasyeva et al., 2017). The idea of using mosses to measure atmospheric deposition of potentially toxic metals (risk elements) had been developed in the late 1960s (Rühling and Tyler, 1973) since mosses, especially the carpet-forming species, obtain most of their nutrients directly from precipitation and dry deposition, with only negligible metal uptake from the soil (Zechmeister et al., 2003). These ubiquitous organisms have some specific morpho-physiological adaptations, such as lacking a developed root system, a large surface area and high (cat) ion-exchange capacity of the cell membranes (González and Pokrovsky, 2014) which makes them appropriate proxies for atmospheric pollutants. However, the most elementary and mundane criterion for selecting a particular species for biomonitoring purposes is often its sheer abundance in the study area. In the framework of ICP Vegetation survey, among recommended mosses, *Pleurozium schreberi* is the most frequently sampled species in European countries (ca. 42%), followed by *Hylocomium splendens* (23.5%), *Hypnum cupressiforme* (19.6%), *Pseudoscleropodium purum* (7.7%), and other species (7.1%) (Schröder et al., 2016; UNECE ICP Vegetation, 2015). Specifically in southern and central European countries, the moss species from the *Hypnum* sp. and *Pseudoscleropodium* sp. genera are widespread and commonly used in large-scale biomonitoring studies (UNECE ICP Vegetation, 2015).

Soils are direct sinks for contaminants deposited from the atmosphere and while moss mostly uptakes nutrients/pollutants from the atmosphere, resuspension from topsoil represents a possible contamination source (Adriano, 2001; Wuana and Okieimen, 2011). While inconsistencies exist in the definition of ‘topsoil’ in the literature, it is typically considered to refer to the top 5 cm of surface soil, irrespective of the natural development of the soil horizons (Brūmelis et al., 2002). For screening studies, it is convenient to compare topsoil concentrations of pollutants with regional or local background levels (Ettler, 2016) as well as with average compositions in the Earth’s crust (Bargagli et al., 1995).

The present study was performed within the framework of the United Nations Economic Commission for Europe (UNECE) International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation) and focused on the (bio) monitoring of potentially toxic elements across the Province of Kosovo and Metohija (K&M). Although ICP Vegetation moss surveys indicated that the deposition of the majority of the studied elements has declined in many areas across Europe in recent decades, risk elements pollution still remains a problem in (South) Eastern Europe (Harmens et al.,