



# Major and trace elements in *Sphagnum* moss from four southern German bogs, and comparison with available moss monitoring data



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## ABSTRACT

In this paper, we present concentrations of an array of major and trace elements (Ag, Al, As, Ba, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Rb, Sb, Sc, Sr, Th, Tl, U, V, Zn) in living *Sphagnum* mosses from four southern German bogs and compare them with moss monitoring data of the respective regions. To do this, *Sphagnum* mosses were collected in Upper Bavaria (Oberbayern, OB) and the Northern Black Forest (Nordschwarzwald, NBF). Surfaces of *Sphagnum* carpets were marked with plastic mesh and, one year later, the annual moss production was harvested. Up to 12 samples (40 cm × 40 cm) were collected per site, and 6–10 sites investigated per bog. The concentrations of these elements were then determined in acid digests using sector field ICP-MS. Variations within a given sampling site were in the range of 2 to 3-fold for all major and trace element concentrations except for Mn (12-fold) and Tl (38-fold). For most of the elements, concentrations between bogs of a given region were significantly different and atmospheric deposition of particles seems to be considerably affected by local circumstances such as tree canopy interception and microtopography. Comparing trace element concentrations measured in *Sphagnum* mosses for 2007 with published moss monitoring data for 2005 resulted in a very good agreement for most elements. Clearly, *Sphagnum* mosses from bogs are useful biomonitors for estimating atmospheric contamination by metals. This supports the use of *Sphagnum* in atmospheric deposition monitoring especially in cases where *Sphagnum* is abundant (e.g., boreal forests). In regions with neither bogs nor forests, living *Sphagnum* moss bags could be used to the same effect.

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## 1. Introduction

During the last 50 years, the suitability of mosses to monitor atmospheric deposition of trace metals has been intensively investigated (Shotyk et al., 2015, and refs. therein). Beginning with the pioneering work of Rühling and Tyler in 1968, early results suggested that Pb is quantitatively retained from precipitation by moss, and thus, atmospheric metal deposition rates could be calculated from the annual production rate of the mosses and the measured metal concentrations (Rühling and Tyler, 1970). Mosses, in general, have unique characteristics, which make them ideal for monitoring atmospheric deposition (Tyler, 1990). To start with, the very large

surface area of a moss plant enhances interception and allows the moss surface to efficiently bind metals (González and Pokrovsky, 2014). *Sphagnum* leaves make up two-thirds of its biomass and, therefore, the surface area for the capture of airborne particles is large (Ares et al., 2012). Furthermore, because of the absence of a cuticle, ions may be retained on the surface of the moss and from here have direct access to exchange sites in the cell wall. Likewise, the moss surface has a high cation exchange capacity (CEC) (González and Pokrovsky, 2014; Carballeira et al., 2008) and ions may be adsorbed to tissues. A critical review by Aboal et al. (2010) clearly outlines the many problems and challenges in using terrestrial moss to monitor atmospheric deposition of heavy metals. Despite the various limitations, moss has a remarkable capacity to retain particles from the air, allowing them to be used to better understand spatial and temporal variations in atmospheric metal deposition.

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Further investigations revealed that trace element concentrations in *Sphagnum* moss are similar to those of forest mosses in the same area. Thus, bog mosses are not only useful for monitoring atmospheric deposition (Rühling and Tyler, 1971), but, because they grow on an organic substrate, contamination by the substrate is less problematic than in the case of forest mosses growing on mineral substrates. Moreover, in terms of morphological specificity, *Sphagna* have a particularly high CEC (Aulio, 1985) mainly due to the abundance of carboxylic functional groups (Anschütz and Gessner, 1954; González and Pokrovsky, 2014). The CEC in *Sphagnum* moss depends on the content of galacturonic acid (Knight et al., 1961; Clymo, 1963; Richter and Dainty, 1989), which varies with species (Spearing, 1972), but also on the action of the enzyme pectin methylesterase to de-esterify acid and to leave the cationic exchange sites free (Carballeira et al., 2008). Compared to forest mosses, *Sphagnum* sp. exhibit a greater density of negative surface charge and therefore a greater concentration of binding sites per unit mass and, in consequence, outstanding capacity for metal adsorption (González and Pokrovsky, 2014; González et al., 2016).

Lithogenic trace metals such as Al, Sc, and Ti, however, are present in the atmosphere almost exclusively in the form of large mineral particles derived mainly from weathering processes occurring in soils. Also, potentially toxic trace elements such as Ag, As, Bi, Cd, Cu, Ni, Pb, Sb, Tl, and Zn are mainly in the form of sub-micron aerosols derived primarily from anthropogenic high temperature combustion sources (Shotyk et al., 2015). These particles are generally not transported into the cell, but they are kept by electrostatic interactions on the cell wall. The significant difference between dissolved and particulate forms of the metals is very important for the retention process by the mosses (Aboal et al., 2010; Varela et al., 2015). For example, because very little of atmospheric Pb is in the dissolved, ionic form, ion exchange alone is insufficient to understand the mechanism of heavy metal retention by mosses (Onianwa, 2001). An additional complication is that metal bioavailability to moss from any given industrial particle may vary between elements. For example, in a study of the impact of particulate emissions from an iron smelter in Spain, it was shown that Cu bioavailability to moss exceeded that of Fe (Fernandéz et al., 2004). While metals are in general very well retained from the atmosphere by *Sphagnum* moss, this will vary from element to element, depending on the physical and chemical form of the predominant species (Shotyk et al., 2015).

In general, there are many sources of variation in respect to the chemical composition of *Sphagnum* mosses, but not only in terms of morphological specificity and growth rates. Capturing particles by natural surfaces is a complex process which is not only influenced by the physical and chemical characteristics of the particles (size, shape, aerosol chemical composition, water solubility, electric charge) and the deposition surface (roughness, wetness, leaf area index, electric charge), but also by meteorological conditions (average wind speed, annual precipitation, microclimate) (Chamberlain, 1970; Roberts, 1972; Wedding et al., 1975, 1977; Chamberlain and Little, 1981; Al-Radady et al., 1993; Zechmeister, 1994; Erisman, 1996). All these parameters may affect interception of particles by the *Sphagnum* mosses and alter the deposition of pollutants on the peat bog surface (Kempter and Frenzel, 2007, 2008). These factors should become especially evident at sites of greater pollution intensity where dry deposition of particles becomes proportionately more important. Even the formation of aerosol particles has an impact on both the deposition and distribution of elements on the peat bog surface and the retention by the *Sphagnum* mosses. Atmospheric Pb from high temperature combustion processes (anthropogenic Pb), for example, is physically incorporated into the aerosol and well retained by the *Sphagnum* mosses. Lead-210, on the other side, becomes attached onto the surface of existing aerosols (Junge, 1963) and might undergo some

detachment from the surface of the host aerosol, either in response to the low pH of bog water or the acidic pH of rainwater (Shotyk et al., 2015).

During the last decades, *Sphagnum* mosses have been successfully used to monitor atmospheric heavy metal contamination (Shotyk et al., 2015, and refs. therein). In fact, Pb has been extensively investigated along with the more abundant trace metals such as Cu, Ni, and Zn. But far fewer studies have been carried out for other elements and there is much less data for the less abundant potentially toxic elements such as Ag, As, Cd, Sb, and Tl. Our hypothesis is that many elements are efficiently retained by the *Sphagnum* mosses of ombrotrophic bogs and, therefore, *Sphagnum* may be even more valuable than currently appreciated to monitor the chemical composition of the surrounding atmosphere. Our main objective here is to present and compare concentration values of a diverse array of major and trace elements (Ag, Al, As, Ba, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Rb, Sb, Sc, Sr, Th, Tl, U, V, Zn) in living *Sphagnum* mosses from four southern German bogs and compare them with moss monitoring data of the respective regions. As part of this effort, it is of paramount importance to characterize the spatial variability within a bog, between bogs and between both investigated regions. Data presented here are coupled with previously published results from the same sites for total Pb and Ti (Kempter et al., 2010), as well as for Pb isotopes (Shotyk et al., 2015).

## 2. Experimental procedures

### 2.1. Field study

Four ombrotrophic, mostly undisturbed peat bogs (Kaule, 1974) were sampled in 2007 (Tables A.1–A.3 of Appendix 1). Wildseemoor (WI) and Hohlohseemoor (HO) are located in the Northern Black Forest (NBF), whereas Gschwender Filz (GS) and Kläperfilz (KL) are located in Oberbayern (OB); a location map is given elsewhere (Appendix 2, B.1). Further details about the studied peat bogs and methods used for this study are summarized elsewhere (Kempter and Frenzel, 2007; Kempter et al., 2010).

### 2.2. Analytical procedures

Selected major and trace elements – Ag, Al, As, Ba, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Rb, Sb, Sc, Sr, Th, Ti, Tl, U, V, Zn – were determined using sector field ICP-MS employing well established analytical procedures (Krachler et al., 2004; Rausch et al., 2005). For digestion, aliquots (~200 mg) of powdered plant samples were dissolved in a microwave autoclave (ultra-CLAVE II, MLS, Leutkirch, Germany) at elevated pressure using 3 mL high purity HNO<sub>3</sub> and 0.1 mL HBF<sub>4</sub> (Krachler et al., 2003). For quality control, the certified plant material GBW07602 (Bush Branches and Leaves, Institute of Geophysical and Geochemical Exploration Langfang, China) was used. More details are reported elsewhere (Krachler et al., 2004).

### 2.3. Statistics

The median value was used in calculating representative data because it does not use tails of the data set, is robust and unaffected by outliers. Median values are shown in Figs. 1 and 2 as well as in Appendix 2. As the shape of the sampling distribution did not always approach a normal distribution, parametric methods and their non-parametric alternatives were applied. Pearson's correlation and Spearman's rank correlation were used to test for relationships between measured and computed parameters within the data set. One-way ANOVA and Kruskal–Wallis ANOVA were used to test for differences between sites within a peat bog as well as between studied peat bogs and regions. In general, results from, for example, parametric one-way ANOVA and

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