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Atmospheric Pb and Ti Accumulation Rates from *Sphagnum* Moss: Dependence upon Plant Productivity

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The accumulation rates of atmospheric Pb and Ti were obtained using the production rates of *Sphagnum* mosses collected in four ombrotrophic bogs from two regions of southern Germany: 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 production of plant matter was harvested. Metal concentrations were determined in acid digests using sector field ICP-MS employing well established analytical procedures. Up to 12 samples (40 × 40 cm) were collected per site, and 6–10 sites were investigated per bog. Variations within a given sampling site were in the range 2.3–4× for Pb concentrations, 1.8–2.5× for Ti concentrations, 3–8.3× for Pb/Ti, 5.6–7.8× for Pb accumulation rates, and 2.3–6.4× for Ti accumulation rates. However, the median values of these parameters for the sites (6–10 per bog) were quite consistent. The mosses from the bogs in NBF exhibited significantly greater productivity (187–202 g m^{-2} a^{-1}) compared to the OB peat bogs (71–91 g m^{-2} a^{-1}), and these differences had a pronounced effect on the Pb and Ti accumulation rates. Highly productive mosses showed no indication of a "dilution effect" of Pb or Ti concentrations, suggesting that more productive plants were simply able to accumulate more particles from the air. The median rates of net Pb accumulation by the mosses are in excellent agreement with the fluxes obtained by direct atmospheric measurements at nearby monitoring stations in both regions (EMEP and MAPESI data).

Introduction

During the past decades there have been many retrospective studies of atmospheric deposition of trace metals such as Pb using peat cores from ombrotrophic bogs (*1–7*). Not only are these bogs supplied with trace metals exclusively from the atmosphere, but a growing number of studies have shown that Pb is well-preserved in the acidic, anoxic waters, and not subject to postdepositional migration (see ref *4* for a list of recent publications). It has become apparent that Pb is so well preserved in peat profiles that reliable archival studies are more dependent upon careful site selection, sampling and sectioning of the cores, handling and preparation of the samples, and accurate age dating, than they are on the diagenesis of Pb subsequent to its deposition from the atmosphere (*8*). However, legitimate concerns have been raised about the principle issue of variation in Pb accumulation rates within a given bog and whether a single core can yield a representative historical record of atmospheric deposition (*9*, *10*).

In Central European ombrotrophic peat bogs, *Sphagnum* mosses are the basis of peat growth and represent the interface where exchange processes between the atmosphere and the bog surface take place. Thus, before undertaking further studies of peat core records of atmospheric trace metals, it may be important to better understand the extent of variation in metals concentrations within *Sphagnum* mosses on the bog surface. Variations in the chemical composition of *Sphagnum* mosses may be partly due to preferential uptake of essential plant nutrients such as Mn, Cu, or Zn. However, in the case of trace metals such as Pb which has no physiological function, or Ti which is found primarily in effectively insoluble, soil-derived minerals, variations in their abundance are likely to appear because of physical differences in the bog surface. Parameters such as canopy height, topography, structure of the surrounding vegetation (*Pinus mugo* stands, dwarf shrubs), exposure to the predominant winds, average wind speed, and annual amount of precipitation all can affect the deposition of particles. Moreover, it can be expected that the efficiency of the *Sphagnum* layer in trapping the metals deposited depends on such parameters as wetness, or the relative abundance of pools of open water, roughness and microhabitats such as hummocks and hollows, and the surface area of leaves; all of these may affect interception and alter the deposition of pollutants on the peat bog surface (see refs *3 and 9)*. Studies of forest mosses (*11*) showed that *Hylocomium splendens*, for example, is more effective at trapping of dust particles compared to *Pleurozium schreberi* simply because of its greater surface roughness. It is reasonable to expect, therefore, that variations in the shape and density of the *Sphagnum* mosses might significantly affect the roughness of the bog surface and influence its ability to serve as a receptor of atmospheric particles and aerosols. Most *Sphagnum* species show a loose and lax growth form in wetter conditions and the availability of moisture generally has a distinct effect on the compactness of the plants (*12*, *13*). Additionally, annual production of a given species of *Sphagnum* moss may be affected by site conditions such as depth to water table, surface water flow pattern, and capillarity which, in turn, varies with density.

Studies of the geochemistry of peat mosses found that Ti concentrations within a peat bog varied considerably at different sites even within the same species (*3*, *9*). These studies, however, employed a uniform sampling thickness (5 cm) and given the lack of control on the age of the samples, no information could be obtained about spatial variations in atmospheric fluxes. Thus, it is not yet clear to what extent the variations in Ti concentrations (*3*, *9*) were the result of differences in the duration of exposure to atmosphere or a reflection of differences in moss productivity. Clearly, calculations of net element accumulation rates in *Sphagnum* mosses require an accurate knowledge of the ages of the collected moss samples.

The purpose of this investigation was to precisely determine the variation in Pb and Ti concentrations as well as net metal accumulation rates in *Sphagnum* mosses within a given

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peat bog and between peat bogs of two regions. To do this, variation in Pb and Ti concentrations and accumulation rates were investigated by harvesting and analyzing the annual *Sphagnum* production of defined parcels. Lead was selected not only because of its environmental relevance, but also because it is known to be immobile in peat bogs and has been studied more than any other trace metal (summary in refs *1−7*). Thus, there is an extensive data set of published Pb deposition rates for other regions, and other periods of time, for comparison. Titanium was also studied because of its conservative geochemical behavior, its occurrence almost exclusively in effectively insoluble soil-derived particles, and its lack of physiological relevance (*14, 15*).

Experimental Procedures

Field Study. In total, four ombrotrophic peat bogs were studied (see Table S1 and Figure S1 of Supporting Information). Wildseemoor (WI) and Hohlohseemoor (HO) are situated in the Northern Black Forest (NBF) and Gschwender Filz (GS) and Kläperfilz (KL) are situated in Oberbayern (OB). All studied peat bogs are mostly undisturbed (*16*). Further details and literature are summarized elsewhere (*3*). In April 2007 plastic nets (ca. 40 × 40 cm, surface area 1680 cm^2, 1.5 cm mesh) were placed on the peat bog surface and fixed with plastic anchors to mark the surface of the mosses. This approach has the important advantage of being able to determine exactly the annual production of plant material, to be sure that all collected material is the same age and has been exposed to atmospheric deposition for the same duration. Each net represents a single sample, and up to 12 nets were installed at each sampling site; between 6 and 10 of these sites were established on the surface of each bog (SI, Tables S2 and S3). While maintaining a representative distribution of the sampling locations, preference was given to open sites least influenced by trees, dwarf shrubs, or hummocks which are known from measurements of ^{210}Pb to affect interception (*17*). Focus was placed on *Sphagnum* lawns, whereas large hummocks and hollows were excluded from the study (see refs *3* and *9*). One year later, sedges and dwarf shrubs were first removed from the parcels and all moss material above the plastic net was cut away with stainless steel scissors and packed into labelled polyethylene bags. All sites were extensively described (e.g., coordinates, parcel, and surrounding vegetation) at the beginning and at the end of the experiment. The identification of *Sphagnum* species was first determined in the field and confirmed at the lab following the *Sphagna* key (*18*). Moreover, notes were made concerning any exceptional habits of the peat mosses or exceptional colours. At GS and KL the entire area of each sample (40 × 40 cm) was harvested, whereas at WI and HO only half this amount (40 × 20 cm) was harvested; the remainder was left undisturbed to allow one more year of growth and exposure; these were harvested in April 2009 and the results will be presented elsewhere. Because of the poor growth of moss in the peat bogs in Oberbayern not all marked samples could be harvested after the period of one year. These samples were left to be exposed for another year. At KL, for example, *Sphagnum* growth was generally so poor that only the samples with good growth could be selected. In total, for this study, 230 samples which had been exposed to atmospheric deposition during the period of one year (April 2007 to 2008) were selected for analysis. All of the collected moss material was stored in a freezer (−18 °C) immediately upon arrival at the lab.

Preparation of Samples. To avoid any possible contamination of the *Sphagnum* material, a considerable effort was invested to carefully remove all other plant material with pincers. Although time-consuming, this made it possible to remove stems and leaves of *Oxycoccus palustris*, *Andromeda polifolia*, and *Calluna vulgaris*, but also parts of *Cyperacea* (mostly *Eriophorum vaginatum*). If samples were not dominated by a single species and provided that there was sufficient material, in particular the sites from WI and HO, individuals of *S. magellancium* and *S. rubellum* were separated to allow possible differences between *Sphagnum* species to be determined; this amounted to 27 additional samples. All of the foreign plant matter was removed after the samples had been defrosted, but prior to drying. After drying the material at 40 °C, dry weights were determined and samples were milled with an agate ball mill (Fritsch, Planetenmühle Pulverisette 5, Idar Oberstein, Germany).

Analytical Procedures. A diverse range of trace metals, including Pb and Ti, was determined using sector field ICP-MS employing well established analytical procedures (*19, 20*). For digestion, aliquots (∼200 mg) of powdered peat and plant samples were dissolved in a microwave autoclave (ultraCLAVE II, MLS, Leutkirch, Germany) at elevated pressure using 3 mL of high-purity HNO_3 and 0.1 mL of HBF_4 (*21*). For quality control, the certified plant material GBW07602 Bush Branches and Leaves (see ref *19* for details) Institute of Geophysical and Geochemical Exploration, Langfang, China was used.

Statistics

Statistical Procedures. The median was used in calculating representative data because it does not use data in tails of the data set, is robust and unaffected by outliers (see also SI). Pearson's product correlation was used to test for relationships between measured and computed parameters within the data set. One-way analysis of variance (ANOVA) was used to test for differences between *Sphagnum* species and between sites within a peat bog as well as between studied peat bogs and regions. The level of confidence was set to $P < 0.01$. Statistics were done using STATISTICA 8 (*22*).

Pb Concentrations. Single outliers with up to 20-fold concentration differences occurred at WI (7 out of 93) and at HO (3 out of 60). All of the statistical analyses were undertaken twice, with outliers and without. However, the results and interpretation presented here represent the data set without outliers; the corresponding analyses with outliers included is given elsewhere (see SI).

Calculation of Annual Production [g m^{-2} a^{-1}]. The yield of dry plant matter from the marked surface area (ca. 1680 cm^2 at GS and KL, ca. 840 cm^2 at WI and HO) was extrapolated to one square meter as follows: Annual production [g m^{-2} a^{-1}] = dry weight [g] × 5.95 (×12 for WI and HO).

Calculation of Net Metal Accumulation [mg m^{-2} a^{-1}]. To differentiate between the atmospheric deposition rate which is commonly estimated using wet-only or bulk collectors, the term "net metal accumulation" rate has been used in studies of metal deposition using peat cores from bogs (*23*); this latter approach was selected, with the net accumulation rate for one year calculated as follows (see also SI): Net metal accumulation rate [mg m^{-2} a^{-1}] = annual production [g m^{-2} a^{-1}] × metal concentration [μg g^{-1}]/1000.

Correction of Net Metal Accumulation Rates. In some cases, mostly in the bogs from Oberbayern, part of the net area was not penetrated by the moss individuals at all. Thus, the plant growth rates, and therefore also the net metal accumulation rates, had to take into account the percentage of defined surface (1680 cm^2) actually occupied by living plants. Using the photographs taken before cutting the annual production, the number of units of mesh still visible could be counted and the total surface penetrated by the mosses was estimated. Net metal accumulation rates calculated this way differed only slightly from the uncorrected data, and more importantly showed the same correlations with other parameters (SI, Figure S7 and Tables S41−S45). In these cases,

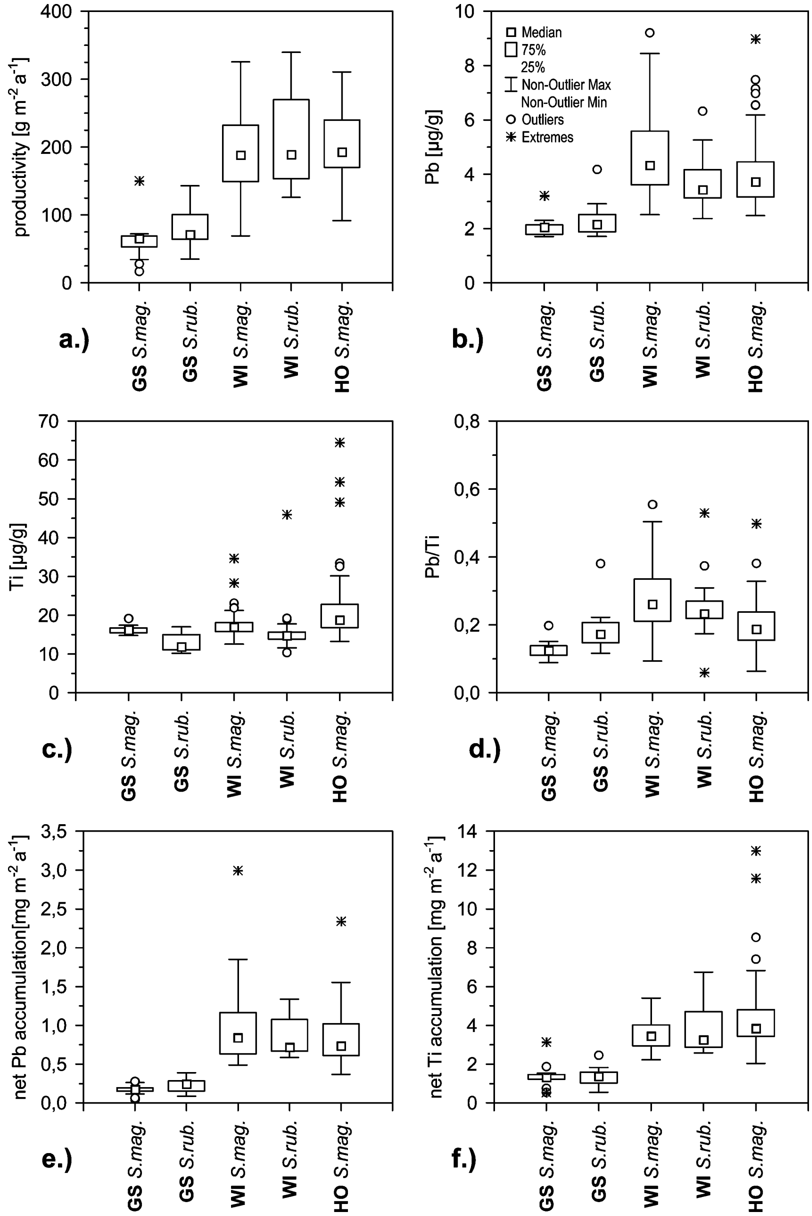

FIGURE 1. Between-species variation: (a) annual production, (b) Pb concentration, (c) Ti concentration, (d) Pb/Ti ratio, (e) corrected net Pb accumulation, (f) corrected net Ti accumulation.

corrected net metal accumulation rates were used for further interpretation.

Pb/Ti Ratio. Part of the variation in Pb concentrations may be natural, and due mainly to differences in the amount of mineral material supplied to the mosses from soil dust particles. To take this into account the possible importance of mineral material Pb concentrations were normalized to Ti (*24*).

Results

Between-Species Variation. Given the large surface area represented at each collection site, it was generally difficult to find samples consisting of or dominated by a single species. Thus, differences between species could only be studied at WI and GS with comparably few samples. Whereas at HO nearly all studied samples were dominated by *S. magellancium*, at KL mostly samples of mixed species were found. However, both moss species (*S. magellancium* and *S. rubellum)* reveal quite similar values for all studied parameters (Figure 1a−f). Although significant differences for some parameters (Pb concentration at WI, Ti concentration and Pb/Ti ratio at GS) were indicated when applying ANOVA (SI, Tables S9, S12, S15), it is clear that differences between species of *Sphagnum* mosses are minor compared to the variation within a site, within a given bog, or between regions. Thus, it is not important to collect and analyze individual species of *Sphagnum*, but sampling should certainly be restricted to the common lawn species.

Within-Bog Variation. Within the living moss layer found at the surface of a given peat bog, on the scale of a sampling site there are considerable variations in annual production (2−4 times, up to 10-fold), concentrations of Pb (see Figure 2a−d, 2.3−4 times) and Ti (1.8−2.5 times), Pb/Ti ratio (3−8.3 times), as well as the net accumulations of Pb (up to a 7.8 fold) and Ti (2.3−6.4 fold). The sources of these variations stem from natural variability in the growth of the moss species and may reflect a number of factors related to small but important differences in site conditions. Similarly, there are small-scale variations in Pb and Ti accumulation rates, primarily as a result of differences in the annual production

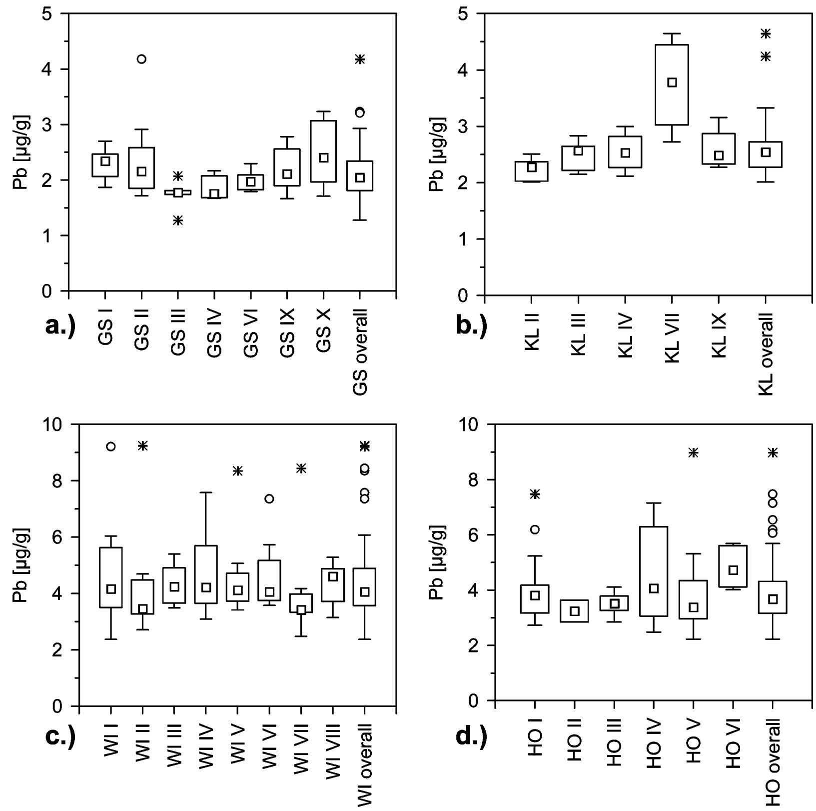

FIGURE 2. Within-bog variation of Pb concentration: (a) Gschwender Filz (GS), (b) Kläperfilz (KL), (c) Wildseemoor (WI), (d) Hohlohseemoor (HO).

of the *Sphagnum* mosses themselves. Thus, small differences in atmospheric accumulation rates, whether contemporary or from the past, have to be interpreted carefully, bearing these variations, and the causes to which they are due, in mind.

In contrast, the median Pb and Ti concentrations, the corresponding accumulation rates, and Pb/Ti ratios for a given peat bog are, in general, quite consistent. Significant differences between sampling sites within a peat bog are mostly due to single sites with especially high or low values (see SI, Tables S8−S19). However, small scale variations and observations of single sites with elevated or diminished values illustrate the necessity of collecting an adequate number of samples, to be sure that the results obtained are truly representative.

Between-Bog and between-Region Variation. Annual production of *Sphagnum* (Figure 3a) in the studied regions showed remarkable differences with far more annual production (ca. 2.5 times), at the NBF peat bogs (WI 187 g m^{-2} a^{-1} and HO 202 g m^{-2} a^{-1}) compared to the OB peat bogs (GS 71 g m^{-2} a^{-1}, KL 91 g m^{-2} a^{-1}). In fact, at KL, only a limited number of samples could be selected for study because of poor growth and many were not representative of annual production. Within the NBF region annual production at WI and HO was similar, and no significant differences could be found. While the NBF peat bogs clearly yielded a significantly greater production of *Sphagnum* than the OB peat bogs, it is not clear why. However, the productivities of *Sphagnum* reported here are consistent with those measured two decades earlier by Wandtner (*25*) in the same NBF peat bogs.

Pb concentrations (Figure 3b) were significantly higher (1.8 fold, ANOVA see SI, Table S28) at the NBF peat bogs (WI 4.1 μg/g, HO 3.7 μg/g) compared to the OB peat bogs (GS 2.1 μg/g, KL 2.6 μg/g). This was also found by Wandtner (*25*) during his studies in the 1970s (OB 22 μg/g, NBF 35 μg/g), by Kempter and Frenzel during the 1990s (estimated OB 7 μg/g, NBF 14 μg/g), and by the moss monitoring network (*26*) where the data from 2005 show OB <5 μg/g and NBF 5−10 μg/g. Moreover, atmospheric deposition monitoring sites at OB measured by governmental institutions during the 1980s and 1990s also revealed higher values compared to the NBF sites (summarized in *3*). The present study, therefore, is the fifth study to show significantly greater Pb concentrations in the mosses from NBF compared to OB. All of these data, including the moss monitoring data, are consistent and also show that the Pb concentrations in peat mosses decreased sharply during the last three decades. Although this trend is certainly a positive development, the Pb concentrations in the mosses today, even in the OB peat bogs, are still a factor of 10 greater than the "natural background" (0.28, 0.40 μg/g) obtained from peat cores predating the onset of industrialization in Germany and Switzerland (*27, 28*). Lead concentrations found in the bogs of a given region correspond quite well with one another even though if ANOVA found a significant difference between OB peat bogs (SI, Table S26).

Of considerable interest and broader significance is the finding that a high annual production of *Sphagnum* mosses was rarely combined with low Pb concentrations. In other words, there is no "dilution effect" of Pb concentrations by high moss production rates. This phenomenon was already reported by Wandtner (*25*) as well as by Kempter and Frenzel (*3, 9*). To confirm this finding, Pearson's Product Correlation Coefficients were applied to all measured parameters within each bog and for all peat bogs (SI, Tables S41−45). The results fail to reveal a significant negative correlation between annual production and Pb concentration. In fact, in general a positive correlation was found between annual production and Pb concentration. The consistent findings from these studies indicate that productive mosses are able to adsorb and retain more particles onto their surface than less productive mosses are. Wandtner (*25*) suggested that increased biomass, all other

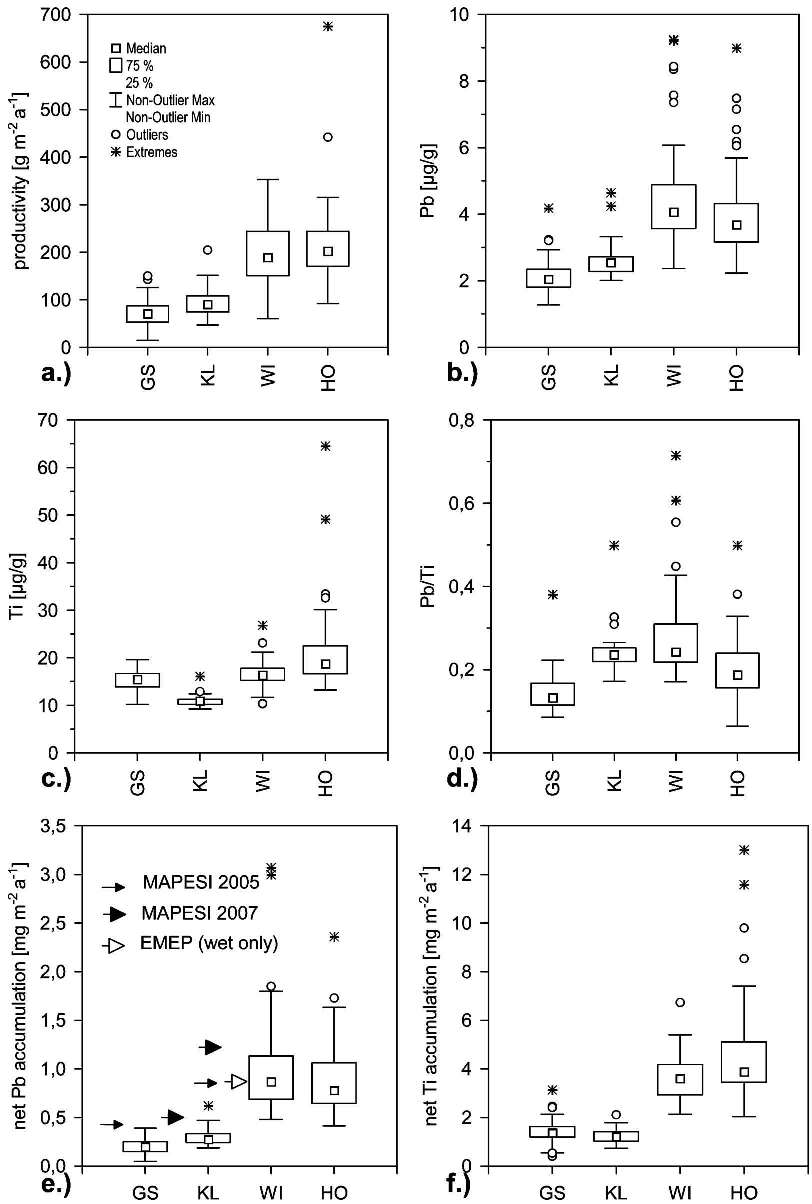

FIGURE 3. Between-bog variation: (a) annual production, (b) Pb concentration, (c) Ti concentration, (d) Pb/Ti ratio, (e) corrected net Pb accumulation, (f) corrected net Ti accumulation.

parameters being equal, provides an increased number of sites on the surface of the leaves for accumulation of elements from the air.

Ti concentrations, unlike those of Pb, showed only minor differences (WI 16.5, HO 18.7, GS 15.5, KL 10.9 μg/g Ti, Figure 3c) supporting the use of Ti as a reference element for Pb. In all cases the Ti concentrations are interpreted as reflecting the concentrations of dust particles, mainly derived from soils. Again, it is remarkable that there is no "dilution effect" of the Ti concentrations in the NBF bogs where the mosses exhibit much greater productivity. The Ti concentrations reported here are consistent with the data from moss monitoring in 2005 (*26*). All four studied peat bogs are situated in well sheltered forested areas. However, the NBF bogs are situated on the very top of the main ridge of the Black Forest and both are exposed to strong westerly winds from the Upper Rhine Valley. These characteristics may help to explain the slightly greater Pb concentrations, and more variable concentrations of both Pb and Ti, compared to the OB bogs from the Pre-Alpine Region. In addition, the pools and ponds on the surface of the NBF peat bogs often flood the bog surface after heavy rainfall, and this might be an additional source variation in metal concentrations.

Pb/Ti ratios (Figure 3d) were not distinctly higher in the NBF peat bogs (WI 0.24, HO 0.19) compared to those of OB (GS 0.13, KL 0.24) even if one-way ANOVA reveals significantly different Pb/Ti ratios within the peat bogs of one region as well as between the two studied regions (SI, Tables S32−S34). To put these values into perspective, however, the Pb/Ti ratio of approximately 0.20 reported here is still very far removed from the "natural background" ratios (0.008) found in peat from Étang de la Gruère (Swiss Jura Mountains, *28*) dating from 6k to 9k BP, as well as from the ratio in crustal rocks (0.006, *29*). Thus, the aerosols supplied to these bogs today are still significantly enriched in Pb from anthropogenic activities.

Net Pb accumulation (Figure 3e) at WI and HO (ca. 0.85 mg m^{-2} a^{-1}) was up to 4-fold higher than at GS and KL (ca.0.25 mg m^{-2} a^{-1}). However, the median Pb concentrations are only around 1.8 times higher in the NBF compared to OB. Thus, a large part of the difference in net Pb accumulation rates might be primarily due to the differences in moss production rates which were a factor 2.5 higher at the NBF compared to OB. This interpretation is supported by the Pearson's Product Correlation revealing a significant correlation between annual moss production and net Pb accumulation (SI, Tables S41−S45). Clearly, productive *Sphagnum* mosses are able to accumulate more particles from the air.

The net rates of atmospheric Pb accumulation obtained from the *Sphagnum* mosses from the NBF peat bogs (WI 0.89 mg m^{-2} a^{-1} and HO 0.78 mg m^{-2} a^{-1}) agree well with the direct measurements of atmospheric Pb reported by the EMEP (European Monitoring and Evaluation Programme) monitoring station "Schauinsland" (wet deposition from 0.95 mg m^{-2} a^{-1} in 2004 to 0.75 mg m^{-2} a^{-1} in 2007, see Figure 3e, SI, Table 46) which is situated around 100 km to the south of the studied peat bogs. Moreover, the latest available data (from 2005 and 2007) on total Pb deposition for the studied peat bogs (MAPESI Modeling of Air Pollutants and Ecosystem Impact, *31*, see Figure 3e, SI, Table S47 and S48) reveal similar rates of atmospheric Pb deposition using direct measurements and *Sphagnum* not only for the region of the NBF (MAPESI 2005 ca. 0.81 mg m^{-2} a^{-1} and 2007 ca. 1.22 mg m^{-2} a^{-1}, *Sphagnum* ca. 0.85 mg m^{-2} a^{-1}) but also for OB (MAPESI 2005 c. 0.34 mg m^{-2} a^{-1} and 2007 0.51 mg m^{-2} a^{-1}, *Sphagnum* 0.20 mg m^{-2} a^{-1} and 0.34 mg m^{-2} a^{-1}). Despite the significant within-bog variation (up to 7.8 fold), the median net rates of net Pb accumulation obtained from the *Sphagnum* mosses in this study reflect very well the best current estimates of atmospheric Pb deposition. However, it is also clear that an adequate number of samples must be measured to ensure that the data obtained are representative. We suggest that at least 5 samples should be taken per sampling site, and 5 sampling sites investigated per bog.

Compared to the "natural background" rate of atmospheric Pb deposition thousands of years ago at Étang de la Gruère (0.01 mg m^{-2} a^{-1}, *32*), or at Kohlhütte Moor (Black Forest, 0.02 mg m^{-2} a^{-1}, *27*) net Pb accumulation rates reported here are a factor of 20−80 times higher.

Net Ti accumulation (Figure 3f), too, was significantly elevated (2.9 fold) at the NBF peat bogs (WI 3.6 mg m^{-2} a^{-1}, HO 3.9 mg m^{-2} a^{-1}) compared to GS (1.4 mg m^{-2} a^{-1}) and KL (1.2 mg m^{-2} a^{-1}). The median Ti concentrations, as noted above, were only slightly greater. As it is true of the net Pb accumulation rate, the differences in net Ti accumulation rates are partly due to the 2.5 times higher annual production of the peat mosses growing at WI and HO (NBF) compared to the OB peat mosses. In fact, because the median Ti concentrations are nearly the same at all sites, the differences in net Ti accumulation rates between the regions might be almost exclusively due to the different rates of moss production. Unfortunately, there is neither EMEP nor MAPESI Ti data available for comparison.

The finding of single greatest importance for both historical reconstructions using peat cores and studies of contemporary deposition using mosses is simply that the net metal accumulation rates are strongly dependent on the annual production of dry matter by the mosses. Highly productive mosses even within a sampling site on the same bog yield similar concentrations of Pb and Ti compared to those of low productivity, revealing a remarkable ability to accumulate more particles onto their surfaces. Thus, rates of atmospheric metal deposition are not exclusively reflected by their concentrations in the *Sphagnum* mosses, but rather strongly dependent on the moss production rates. Metal accumulation in *Sphagnum* mosses clearly reflects the mass of particles these simple plants were able to accumulate within a given period of time. Although the ratio of Pb/Ti might offset to some extent the problem created by variable moss production rates, it appears that Pb may be more affected by differences in plant production rates than Ti (Figure 3b, c). Given that the mean diameter of Pb-bearing aerosols from combustion processes is 0.5 μm (*33*) whereas most of the Ti-bearing minerals in atmospheric dusts derived from soils are in the range of 5−50 μm (*34*), the ability of the mosses to remove metals from the air may be also depend on the size of metal-bearing particles. The efficiency of the *Sphagnum* layer in trapping metals may be more pronounced at sites of greater pollution where dry deposition of aerosols is more important, thus the spatial variability in moss chemistry might be less expressed at background sites.

While the variations in metal concentrations and accumulation rates reported here have clear implications for monitoring studies employing mosses, the significance for retrospective studies using peat cores is less apparent simply because an individual peat slice provides an average of several, or perhaps even many, years of moss accumulation.

Acknowledgments

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Supporting Information Available

This information concerning the sites and bogs described here, several figures not presented in the manuscript, data tables, and statistical results (ANOVA, Pearson's Product Correlation) of all studied parameters, is available free of charge via the Internet at http://pubs.acs.org/.

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