



## Humification processes influence on trace elements archiving along a bog profile

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Peat bogs are often used as archives of atmospheric deposition of trace elements, but the possible mechanisms by which bogs are able to preserve a historical record of these elements have undergone limited investigation. For this study, a peat core was collected from a Swiss bog (Etang de la Gruère) and humic acids (HA) isolated. Both bulk peat and HA samples were characterized using several molecular spectroscopic methods (Ft-IR, UV-Vis, DSC, Fluorescence) and elemental analysis (CHNS). Although numerous trace elements were investigated by X-ray fluorescence (i.e., As, Br, Ca, Cr, Cu, Fe, Mn, Ni, Pb, Rb, Se, Sr, Ti, Zn, and Zr), here we focus on the comparison between the abundance of Hg and Pb in peat and its corresponding HA fraction, in an effort to understand the extent to which humification may contribute to the accumulation of these two environmentally significant metals.

Lead and Hg are two “soft” cations that show a strong affinity for the organic ligands, and tend to form inner-sphere complexes. Although both are considered quite immobile along peat profiles, our data underlined completely different behaviours: Hg showed a similar trend both in peat and corresponding HA ( $R^2 = 0.84$ ,  $p < 0.001$ ), and highest concentrations in the latter fraction, while Pb, although abundant in bulk peat, was almost undetectable in the HA molecules. In detail, ca. 66% of the total Hg present in peat was strongly bound by the HA fraction, while this percentage averaged around 3% for Pb, thus suggesting that the latter element could be preferentially bound to the humin, non-humic substances and/or associated to mineral particles. In fact, while Hg is present in the atmosphere mainly in the form of a gas ( $\text{Hg}^0$ ), but can be readily washed out once it has been oxidized to the ionic form ( $\text{Hg}^{2+}$ ), Pb, in the studied bog, seems to behave similarly to Ti and Zr. Since the latter ones are known to be associated almost exclusively with dense accessory minerals (such as rutile and zircon) which are resistant to chemical reaction, even at the low pH (4) which is typical of ombrotrophic bogs, the absence of these elements in HA suggests that, during humification, the mineral phases bearing these elements are unaffected, and therefore that these metals are not available for chemical reaction. Thus, basing on the observed similarity among Pb, Ti and Zr, we assume that Pb which is deposited on the surface of the bog, whether derived from natural or anthropogenic processes, could be present in minerals or aerosols which become preserved in the peat, possibly via the formation of protective organic coatings. As a consequence, very little Pb is labile, and available for incorporation into HA molecules.

Furthermore, data clearly showed that the magnitude of changes in Hg concentrations along the studied profile cannot be attributed to the different degree of peat humification, as resulted from both the HA extraction yield and the C/N ratio. In fact, higher Hg concentrations were found in the upper layers, where a lower humification degree and higher C/N ratios occur. Consequently, because the zone of elevated Hg concentrations seen in the surface layers of the Swiss peat core corresponds to the decades of greatest industrialization, the accumulation of this element is probably the result of both natural processes as well as anthropogenic inputs, with the latter clearly dominant during the past few centuries.