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Can peat humic acids constitute the "memory" of past human activity and environmental changes?

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Peat soils play a crucial role in the C cycle as they are generally net sinks for atmospheric CO_2 and net sources of greenhouse gases on a long term basis. Among peatlands, ombrotrophic bogs are also considered unique archives of past environmental conditions because their genesis is directly linked to the atmospheric conditions occurring during peat formation. Although hundreds of studies have been carried out in the last decades using ombrotrophic cores, scientific literature is still rather controversial about the role of bogs as reliable records. To answer such a nodal point, it is extremely important to better understand the process of humification in these ecosystems.

A peat core was collected from the Etang de la Gruère bog (Switzerland), cut into 3 cm slices, and age dated; after that, humic acids (HA) were isolated from each layer. The whole core, corresponding to ca. 2,100 years of peat formation, and the HA samples were characterized using several molecular spectroscopic methods (Ft-IR, UV-Vis, DSC, Fluorescence). Furthermore, both peat and HA samples were analyzed by XRF (for major and trace elements), Low Background γ-spectrometry (for ^{137}Cs), and Isotopic Ratio Mass Spectrometer coupled with an Elemental Analyser (for isotope ratios, δ^{13}C, δ^{18}O and δ^{15}N).

In general, Ft-IR, UV-Vis and fluorescence results, together with main atomic ratios, suggest significant variations of the molecular composition and chemical structures of the peat samples along the profile, underlining an increase of the humification degree with depth.

Among the studied major and trace elements, Br, Cu, and Hg showed a conservative behaviour as their distribution in HA mirrored that in peat. Actually, some authors suggested that the concentration of these elements in peat increases as result of mass losses during humification. Mercury data, on the contrary, clearly underlined that: *i)* the magnitude of changes in Hg concentrations in peat samples along the profile is not directly correlated to their corresponding humification degree; *ii)* expressing both Hg concentrations per mass unit of peat, it is possible to identify a similar trend (p <0.001); and *iii)* most of the total Hg present in peat (66%, average value) is retained by HA molecules. This complexing behaviour may greatly limit the Hg mobility along the profile, thus suggesting a prevailing Hg immobilization that may reflect the different Hg deposition rates. On the contrary, other elements (e.g., Ca, Fe, Mg, Mn, Rb, Sr, Zn) showed a certain mobility along the profile. Finally, Pb 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, 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.

The occurrence of ^{137}Cs can be reasonably related to the 1986 Chernobyl disaster, even though its trend in the upper profile could be affected by plant uptake. The occurrence of ^{137}Cs in HA clearly remarks that the Chernobyl disaster is recorded also into these recalcitrant fraction.

Finally, also isotopic ratios seem to have a certain conservative behaviour. In detail, the δ^{13}C ranges between -26.53±0.01 ‰ and -24.77±0.05 ‰ in peat samples, and between -28.03±0.05 ‰ and -25.42±0.05 ‰ in corresponding HA, underling a greater "depletion" of ^{13}C in the latter fraction. Anyway, the δ^{13}C recorded both in peat and in HA samples shows a significantly similar trend with depth ($p < 0.01$). Also the δ^{15}N features similarly in peat and HA throughout the profile ($p < 0.01$), showing values between -4.99±0.21 ‰ and -2.36±0.06 ‰ in peat samples, and between -4.15±0.05 ‰ and -1.06±0.24 ‰ in corresponding HA. Compared to bulk peat, corresponding HA samples result depleted in ^{18}O. The different δ^{18}O trend between HA and bulk peat may reflect a ^{18}O depletion mainly due to a general decrease of the oxygen content in the HA fraction during the humification process.