Major and trace elements biogeochemistry and C sequestration in bog soils

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Abstract

Peat soils play a crucial role in the carbon cycle as they are generally net sinks for atmospheric carbon dioxide 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 several studies have been carried out in the last decades using ombrotrophic bogs in order to reconstruct the historical trends of heavy metal pollution due to anthropogenic activities, scientific literature is still rather controversial about the role of ombrotrophic bogs as reliable record peat of past climatic and environmental changes. To answer such a nodal point, it is extremely important to better understand the process of decomposition/humification in these ecosystems. According to the most renowned theories, decomposition is a catabolic process transforming highly complex biopolymers (e.g., cellulose, lipids, tannins, polyphenols) into smaller and simpler molecules, while humification is a reconstructive process which involves all the derived molecules occurring in the medium at various stages of decomposition; those molecules are then resembled to various extents, recombined and re-polymerized to form humic substances. Consequently, understanding whether all this "information" is effectively preserved in peat deposits during humification becomes an essential aspect to be tested before using bogs as natural archives. The main goal of this research is to test if ombrotrophic bogs are reliable archives of ancient and modern metal pollution and environmental changes by studying the role of HA in preserving or affecting these records.

Key Words

Peat, humic acids, isotopic signature, natural archives.

Introduction

For at least two centuries, peat has been recognized as an excellent archive of environmental change. William Rennie (1807), for example, interpreted stratigraphic changes in Scottish bogs not only in terms of natural changes in paleoclimate, but was also able to identify environmental changes induced by humans, namely deforestation and the hydrological impacts which result from such activities. The use of bogs as archives of climate change in the early 20th century was accelerated by studies of fossil plant remains such as those by Lewis in Scotland, and by systematic investigations of pollen grains pioneered by von Post in Sweden. In Denmark, Glob outlined the remarkably well-preserved remains of bog bodies and associated artefacts (of cloth, wood, ceramic and metal) in Danish bogs. In Britain, Godwin provided an introduction to the use of bogs as archives of human history, vegetation change, and Holocene climate, with a more recent survey provided by Charman.

Recent decades have provided many mineralogical studies of peat and there is growing evidence that many silicate minerals, whether derived from the surrounding watershed or the atmosphere (soil-derived dusts and particles emitted from volcanoes), also are well preserved in anoxic peatland waters. Similarly, geochemical studies have shown that a long list of trace metals, of both natural and anthropogenic origin, also are remarkably well preserved in peat bogs. Thus, there is growing evidence that ombrotrophic (i.e., "rain-fed", Clymo 1983) peat bogs are reliable archives of atmospheric deposition of a wide range of trace elements, including conservative, lithogenic metals (e.g., Al, Sc, Ti, Y, Zr, Hf and the REE), but also the potentially toxic Class B, or "heavy metals" (e.g., Cu, Ag, Hg, Pb, Sb and Tl). When high quality measurements of these elements is combined with accurate radiometric age dating, it becomes possible to create high resolution reconstructions of atmospheric soil dust fluxes, ancient and modern metal pollution, and Holocene climate change.

But peat bog soils play a crucial role in the carbon cycle as they are generally net sinks for atmospheric carbon dioxide and net sources of greenhouse gases on a long term basis. Although several studies have been carried out in the last decades using ombrotrophic bogs in order to reconstruct the historical trends of heavy metal pollution due to anthropogenic activities (e.g., Shotyk *et al.* 1988), scientific literature is still rather controversial about the role of ombrotrophic bogs as reliable record of past climatic and environmental changes.

To answer such a nodal point, it is extremely important to better understand the process of decomposition/ humification in these ecosystems. In fact, understanding whether all these “information” are effectively preserved in peat deposits during humification becomes an essential aspect to be tested before using bogs as natural archives. Consequently, in order to better understand if bogs are consistent archives, all the information about past human activities and environmental (climatic and vegetational) changes should be recorded into the fraction of peat more recalcitrant and refractory to the degradation, i.e., into humic substances (Stevenson 1994).

Methods

A 81 cm peat core was collected in 1991 from the Etang de la Gruère bog (Jura Mountains, Switzerland), cut into 3 cm slices, and age dated; after that, humic acids (HA) were isolated from each layer according to Swift (1996). 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 and ICP-OES (for major and trace elements), Low Background γ-spectrometry (for ^{137}Cs and ^{241}Am), and Isotopic Ratio Mass Spectrometer coupled with an Elemental Analyser (for isotope ratios, δ^{13}C and δ^{15}N).

Results

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. In fact, the HA fraction accounts for 65.6 to 154.5 g kg^{-1} of bulk peat in the upper, poorly decomposed layer (from the living layer to ca. 24 cm), and for 200.5-327.3 g kg^{-1} of bulk peat in the bottom section, thus suggesting an increase of humification 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 (Figure 1a), 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 ($R^2 = 0.84$, $p<0.001$); and *iii)* most of the total Hg present in peat (66%, average value) is retained by HA molecules (Zaccone *et al.* 2009). 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 (Zaccone *et al.* 2007a).

On the contrary, other elements (e.g., Ca, Fe, Mg, Mn, Rb, Sr, Zn) showed a certain mobility along the profile (Figure 1b). Finally, Pb, although is considered a “soft” cation able to form inner-sphere complexes with the organic matter (OM), 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 (Zaccone *et al.* 2007a).

The occurrence of ^{137}Cs (Figure 1c) can be reasonably related to the 1986 Chernobyl disaster, even though its trend in the upper profile could be affected by plant uptake. The ^{137}Cs activity along the peat profile shows also additional peaks, one of which corresponding to the ^{241}Am peak, ascribed to nuclear explosions. The occurrence of ^{137}Cs in HA, although suggested a significant downward movement of ^{137}Cs along the profile, clearly remarks that the Chernobyl disaster is recorded also into the recalcitrant HA fraction (Zaccone *et al.* 2007a, b).

Finally, although big differences in the OM quality were observed along the peat profile, also isotopic ratios seem to have a certain conservative behaviour. In detail, the δ^{13}C (Figure 1d) ranges between -26.53±0.01 ‰ (in the living layer) and -24.77±0.05 ‰ (at 55-58 cm) 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 ($R^2 = 0.60$,

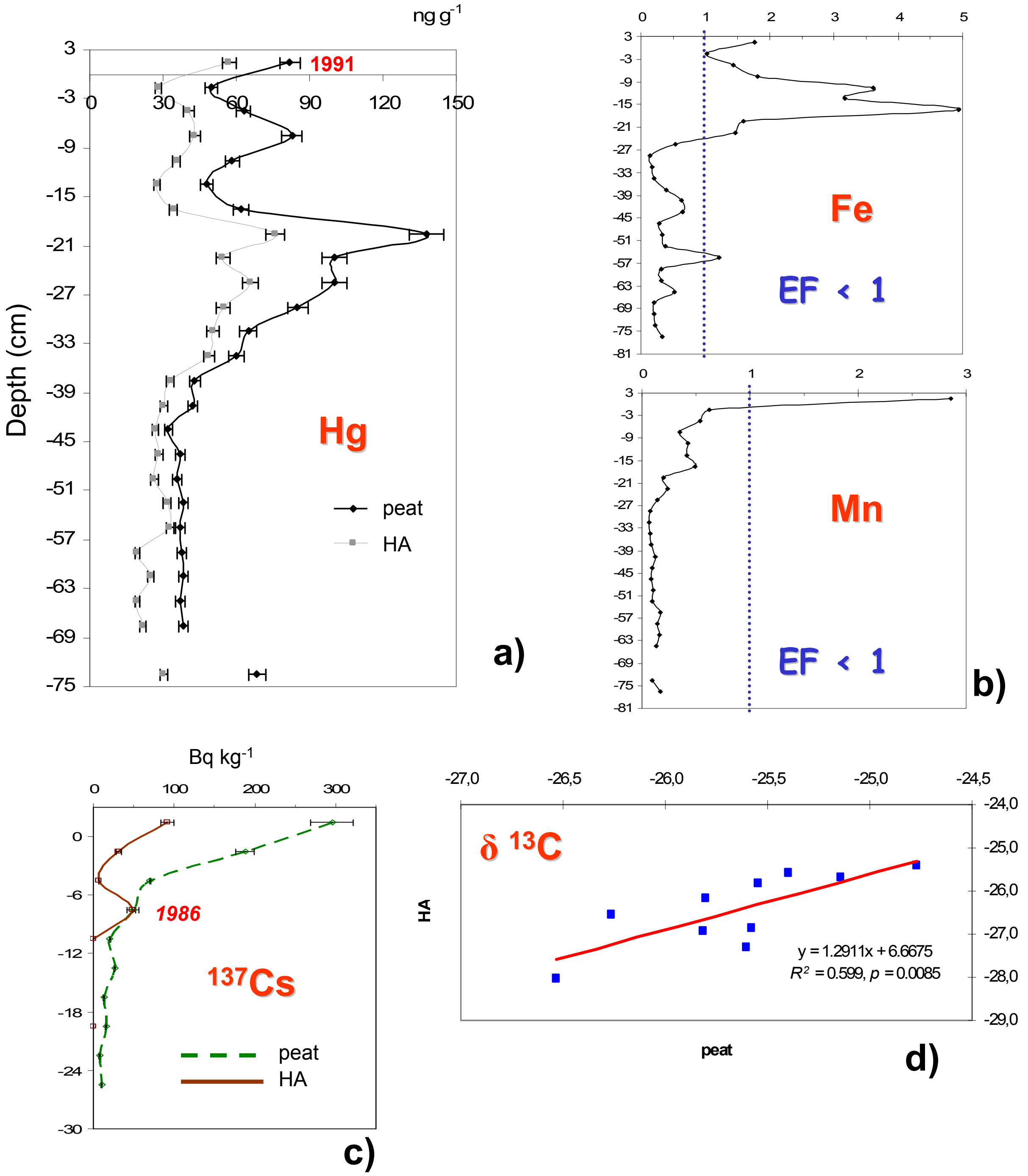

Figure 1. ***(a)*** **Mercury concentration in peat and corresponding HA;** ***(b)*** **Fe and Mn enrichment factor (EF) underlining a depletion of these elements;** ***(c)*** **^{137}Cs activity and** ***(d)*** **δ^{13}C in peat and corresponding HA samples.**

$p< 0.01$). Also the δ^{15}N features similarly in peat and HA throughout the profile ($R^2 = 0.68$, $p< 0.01$), showing values between -4.99±0.21 ‰ (in the living layer) and -2.36±0.06 ‰ (at 18-21 cm of depth) in peat samples, and between -4.15±0.05 ‰ and -1.06±0.24 ‰ in corresponding HA.

Conclusion

Can ombrotrophic bog constitute the "memory" of past human activity and environmental changes? Obviously, peat bogs cannot serve as archive of all these information. About major and trace elements, it will depend mainly on their nature and affinity for the OM in general, and for HA in particular. For example, data clearly showed that humification processes did not affect the Hg distribution along the profile. In fact, 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. The same behaviour was observed for Br. Moreover, HA are also witnesses of the Chernobyl disaster, as well as of nuclear explosions. About isotopic ratios, data apparently suggest that they are quite conservative in HA from peat, thus supporting on one hand the role of HA as recalcitrant, stable molecules with a long-term residence time, on the other hand the potential of ombrotrophic bogs to be used as “reliable archives” of climatic and vegetational changes occurring in the last 2,000 years.

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