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Conservative behaviour of the isotopic ratios trend in peat humic acids

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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 (HS). Consequently, understanding whether all the vegetational and climatic "information" are effectively preserved in peat deposits during humification becomes an essential aspect to be tested before using bogs as natural archives. For example, pollen and macrofossil records are not always well preserved, while isotopic ratios (e.g., ^{2}H vs ^{1}H, ^{13}C vs ^{12}C, ^{15}N vs ^{14}N, ^{18}O vs ^{16}O), commonly used for paleoclimate and paleovegetation reconstruction, show complex dynamics during decomposition. In fact, as different plant macromolecules (e.g., lipids, lignin, celluloses) have distinct ^{13}C/^{12}C ratio values, a differential loss of some components during decomposition may lead to isotopic shifts. In addition, isotopic signatures in soils could be modified by dissolved organic matter vertical migration.

In order to better understand if bogs are consistent archives, all the information about climatic and vegetational changes should be recorded into the fraction of peat more recalcitrant and refractory to the degradation, i.e., HS.

Thus, a 81 cm peat core was collected 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. 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). Isotope ratios, ^{13}C/^{12}C (δ^{13}C) and ^{15}N/^{14}N (δ^{15}N), were then determined in peat and HA samples using an Isotopic Ratio Mass Spectrometer coupled with an Elemental Analyser.

In general, Ft-IR, UV-Vis and fluorescence results 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 6.6 to 15.4% of the bulk peat in the upper, poorly decomposed layer (from the living layer to ca. 24 cm), and for 20.0-32.7% of the bulk peat in the bottom section.

Although big differences in the organic matter quality were observed along the studied peat profile, isotopic ratios seem to have a certain conservative behaviour.

In detail, the δ^{13}C 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 = 0.599, $p < 0.01$). Also the δ^{15}N features similarly in peat and HA throughout the profile (R^2 = 0.681, $p < 0.01$), 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.

In conclusion, data apparently suggest that isotopic ratios 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.