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Characterization and acid–base properties of fulvic and humic acids isolated from two horizons of an ombrotrophic peat bog

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Abstract

Peat humic and fulvic acids were isolated from a surface horizon (0–60 cm) and deeper horizon (>60 cm) of an ombrotrophic peat bog located in Galicia (NW Spain) and which constitutes a record of paleoenvironmental contamination. The humic and fulvic acids were characterized and compared using chemical methods and spectroscopic techniques, including ultraviolet visible (UV-vis), Fourier transform infrared (FTIR) and ^{13}C nuclear magnetic resonance (^{13}C NMR). Comparison of the E_4/E_6 ratios showed that in the deeper horizon the peat humic substances have a greater degree of aromatic condensation than in the surface horizon. The alkyl C content of the humic substances remained practically unchanged, whereas the O–alkyl–C content of humic acids decreased with depth. No variation with depth in the ionization constants of the carboxylic groups or of the phenolic groups was observed. The values of the ratios of the carboxylic/phenolic contents were similar to those reported in the available literature, with a higher content of acid groups in the humic substances isolated from the lower horizon mainly attributable to the carboxylic groups.

Keywords: Peat fulvic acid; Peat humic acid; Elemental and functional composition; FTIR spectroscopy; NMR spectroscopy; Acid properties; Soil depth effect

1. Introduction

Under the influence of the poor drainage occurring in soils of the wetlands, anaerobic decomposition prevails (Tan, 2000). Due to lack of oxygen, the decomposition process is very slow and hence contributes to the accumulation of huge amounts of organic matter. In general, peat bogs constitute authentic records of information on environmental and paleoenvironmental evolution and are thus used as references in studies of past and present patterns in global climatic change and of the impact of historical human activity in causing heavy metal contamination (Martínez-Cortizas et al., 1999). These ecosystems are therefore important sources

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of information about the carbon cycle and the processes of acid deposition and heavy metal accumulation.

Peat deposits are not limited to climatic conditions and can be found where large amounts of biomass are available and where decomposition of organic residues is inhibited. Europe's most southerly ombrotrophic peat bogs are located in Galicia (NW Spain). Plants growing on them are restricted to receiving inputs of nutrients only via atmospheric deposition, without any contribution from the substrate, and they can therefore be used to quantify the accumulation of heavy metals that has occurred as a consequence of human activity (Martínez-Cortizas et al., 1999).

In contrast to a mineral soil system where the organic matter content makes up only a small fraction, the organic matter is an integral and substantial part of peats (>80%). Humic substances are one of the most important components of soil organic matter, and the classical view states that they are macromolecular, negatively charged polyelectrolytes that contain mainly carboxylic and phenolic functional groups (Swift, 1989). Humic substances affect soil chemical properties, including cation exchange capacity, buffer capacity, acid–base reactions and metal complexation (Stevenson, 1994). Most of the information indicates that peats contain large amounts of humic acids (Kononova, 1966) although it has been reported that humic matter in peat is composed mostly of fulvic acids (Schnitzer, 1967). The elemental composition and chemical properties of peat humic substances are believed to be similar to those of humic acids in mineral soils (Mathur and Farnharn, 1985). However, Kononova (1966) was highly critical of humic matter originated from peat since the material has been formed in anaerobic conditions, completely opposite to the aerobic system present in soils. Furthermore, at the present stage of knowledge, it is not known whether the properties of the humic substances may be different in the different kinds of peat since peat from sphagnum is chemically different from peat of heath vegetation or peat formed from woody trees (Tan, 2003).

Therefore, in the present study, we characterized the humic and fulvic acid fractions isolated from two horizons of an ombrotrophic peat bog with the aims of (i) furthering knowledge of the properties of peat humic substances, (ii) analyzing the effect of horizon depth on the properties of peat fulvic and humic acids, (iii) making available the chemical and structural information necessary for interpreting the distribution of metal cations in peat bogs.

2. Materials and methods

2.1. Site description

The ombrotrophic peat bog under study is located in the Sierra del Buio (Lugo, NW Spain) on a flattened summit at a height of 640 m. The climatic conditions are typical of mountainous areas close to the sea, with an annual average precipitation of 1680 mm, an annual average temperature of 10.5 °C (5.2 °C for the coldest month, and 15.5 °C for the warmest month), a mesic thermal regime and aquic/udic hydric regime (seasonal variation). The vegetation is dominated by hidromorphous heath (*Erica umbellata, E. cinerea* and *Calluna vulgaris* and some *E. arborea*), with mossy substrate comprised of different species of sphagnum, among which *Sphagnum pilaesii* dominates. The Sierra del Buio forms part of the Galician Hercynic mountain range strongly flattened during the Mesozoic era.

2.2. Peat bog

The peat bog is an organic soil comprising fibric material in the upper third (0–60 cm) and sapric material at further depths down to 350 cm. Peat bogs as thick as 4 m have been found in the region. The soil sampled is classified as a fibric–ombric–dystric histosol (FAO-UNESCO, 1998). For the study, representative samples of the upper 60 cm (histic fibric H horizon, Hf) and of the rest of the peat bog (histic sapric H horizon, Hs) were sampled under water-saturated conditions, and their main physical and chemical characteristics are reported in Table 1.

2.3. Extraction and purification of peat humic and fulvic acids

The procedure used for the extraction of the humic acid (HA) and fulvic acid (FA) fractions was the method developed by the International Humic Substances Society (Swift, 1996). Briefly, humic substances were extracted with 0.1 M NaOH under an