ORGANIC GEOCHEMISTRY OF RIBETEHILO PEAT BOG (DOÑANA N.P., SW-SPAIN)

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Introduction
Sediment cores encompass information about past environmental changes, fire history and conditions of organic carbon deposition. The information is provided for a range of research fields such as global climate change, pollution assessment and conservation (González-Vila et al., 2003). During the last 30 years, a varied array of modern analytical techniques to assess the molecular composition of sedimentary organic C (OC) has been developed (Rothwell and Rack, 2006).

Material and Methods
In this work shifts in down-core molecular composition of the organic matter of a 85 cm peat bog from the Ribetehilo lagoon (Doñana National Park, SW-Spain) 37°730.81T; 6°37.16N is studied (Fig. 1). In less than 50 years, the area occupied by peat bogs in the Gulf of Cádiz has been reduced drastically by more than 90% (Sousa and García Murillo, 1999). Therefore, this peat bog may well be considered as relict and one of the last and more meridional still in existence. For this work, 6 samples taken at different depths were analyzed in detail (0–10, 25–30, 45–50, 65–70 and 80–85 cm) using Solid State NMR (CP-MAS 13C RMS), analytical pyrolysis (Py-GC/MS) and ultra-high resolution mass spectrometry (ESI/FT/ICR/MS), the latter was performed in humic extracts because solubility is required. The detected compounds were grouped into 6 main biogenic families: lipids, unspecific aromatic compounds, polyphenols, proteins, carbohydrates and condensed compounds.

Results
Both, NMR and pyrolysis analyses give complementary and similar results. For the shallow layer (0–10 cm) the organic carbon (OC) composition was dominated by carbohydrate and polyphenol compounds (40% and 20%, respectively), whereas down core the OC composition was gradually dominated by lipids and unidentified aromatic compounds (until 40%, and from 16% to 39.7%, respectively) (Fig. 2A & 2B). At the same time, a conspicuous depletion of labile compounds and a complete disappearance of polyphenolic compounds in the deepest sub-sample was observed. These results suggest that while shallow OC reflects the molecular signature of a more or less fresh material, OC in deeper bog samples underwent higher chemical alteration produced by either higher microbial activity or chemical transformations also occurring in an anoxic environment. The latter is supported by a lower soil conductivity and basic pH values (0.49 µS cm−1 and −8, respectively) as well as a 13C depleted isotopic composition (δ13C < −29‰ VPDB) found at depth (Fig. 3). In addition, an enrichment of condensed organic compounds is observed from the middle of the core sample to the bottom layer. This may be due either to the existence of older wildfires or to a transport of highly humified OC from upper layers. More than 8700 unique formulas were detected by ultra-high resolution mass spectrometry of alkaline extracts of the peat. Van Krevelen diagrams for more than 2500 chemical compounds, made up of only C, H and O-containing formulas are depicted in Fig. 2C & 2D. Again, for the shallow sample the OC composition was found dominated (larger bubble size) by oxidized compounds (carbohydrate and polyphenols) and almost negligible contribution of hydrogen-rich compounds (lipids and proteins). In addition, this sample displayed a relatively high amount of condensed compounds not observed by Py-GC/MS. Bottom OC composition (Fig. 2D) was characterized by a lower chemical diversity of total compounds (4125 vs. 6374 in shallow sample) and C, H, O compounds (1863 vs 2317 in shallow sample) and a relatively high contribution of recalcitrant compounds with a lower O/C ratio and a conspicuous contribution of microbial compounds with high H/C ratio (proteins and lipids). In addition, in line with the pyrolysis results, this bottom sample (80–85 cm) showed also a contribution of condensed aromatic compounds. This can be better depicted in the C-D subtraction shown in Fig 2E whereas blue colors are compounds preferentially found in shallow sample whereas red are these more abundant in depth.

Conclusions
The results obtained by the techniques used were similar, showing as shallow OC composition was dominated by fresh material from upper vegetation cover, while more transformed and humified material was accumulated in the bottom layers. This may be due to i) intense microbial activity combined with large fluctuations of the water table occurring during the year; and ii) anaerobic processes. In general, this lack of peat preservation at depth is probably a sign of bog degradation processes, probably linked with climate changes since Mediterranean wetlands are especially responsive to such a perturbation.

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References


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