

DETECTION AND STRUCTURAL CHARACTERIZATION OF BLACK CARBON FROM NATURAL COMPLEX MATRICES

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Due to their well known geochemical and environmental implications, there is an increased interest in the study of the different forms of refractory organic matter (ROM) widely widespread in soils, water and sediments. Included in the refractory OM pool are kerogens, humic-like materials as well as the so-called “black carbon“ (BC). These materials might remain sequestered in soils and sediments (slow geological C cycle) from thousand to million of years, being considered as an important sink for atmospheric CO₂ (fast C cycle) and part of the “missing C” in the global C budget (Kuhlbusch, 1998).

Aiming to detect the occurrence of BC forms in natural complex matrices three set of samples including i) the reference samples recommended by an international interlaboratory research on Black Carbon (BC) (BC Ring-Trial), ii) a selection of fire affected soils and iii) a selection of marine sediments from the Southwest Atlantic coast of Spain (Gulf of Cadiz) were analysed. Bulk samples and isolated refractory forms were characterized by an array of analytical techniques including thermogravimetry (TG), TG coupled with differential scanning calorimetry (DSC), solid state ¹³C CP-MAS nuclear magnetic resonance (NMR) spectroscopy and Pyrolysis coupled with gas chromatography-mass spectrometry (Py-GC/MS).

Thermal analysis (TG, TG-DSC) provide mainly information about the proportions of labile, recalcitrant and refractory OM forms, whereas Py-GC/MS and ¹³C NMR provide complementary windows of structural information on the bulk matrices and their OM fractions (López-Capel *et al.*, 2006; Quénéa *et al.*, 2005, 2006; Knicker *et al.*, 2006).

Good agreement was observed between recalcitrant C as determined by TG analysis and the aromatic content measured by ¹³C NMR. Py-GC/MS showed an important presence of aromatic compounds in samples rich in BC like material. ¹³C NMR revealed a loss of signal intensity in the alkyl C-O region of the spectra of the BC forms compared with demineralized sediment. Several samples from marine sources revealed a high contribution of aliphatic compounds to the refractory OM fraction suggesting the relevance of alkylic moieties in the stabilization of carbonous materials in this environment.

By using analytical pyrolysis (Py-GC/MS) it was possible to directly identify, with no pretreatment, specific changes in the product of burning/charring of different materials. Several specific compounds released after pyrolysis allows a clear identification of potentially BC-interference reference materials and, in BC rich samples, compounds that could be used as markers of pyrogenic events. Other markers were also identified that provide information about the origin of the OM.

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