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Comparative analysis of *black carbon* in marine sediments from a Mediterranean river influence coastal area (SW Iberia)

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Considered as uniquely generated by incomplete combustion processes such as forest fires and industrial fuel emissions [1], BC builds up a significant fraction of carbon buried in soils and sediments [2], being an useful tracer for Earth's fire history. Despite the efforts and development of multiple studies, no general agreement about a suitable unique BC estimation methodology has been achieved, resulting in a variety of protocols and accompanying values, that make it difficult to delineate the proportion of BC in sedimentary total carbon budgets [3].

In the context of growing interest in understanding and quantifying the carbon budget in the environment, this work has been developed in order to contribute to a better knowledge of one of the most important BC storages: ocean sediments. Taking into account that forest fires occur frequently during the hot and dry summers in Mediterranean ecosystems, the inner Southatlantic continental shelf of Iberian Peninsula represents an interesting location to study the contribution of refractory BC to the sediments, representing an interesting ecosystem as transition from terrestrial to marine environment.

15 Poor-OC surficial sediments (0.5-1.54 gOC/100g) collected from the Guadiana Estuary influence coastal area (Gulf of Cádiz, SW Spain) were subjected to 3 different BC estimation approaches to discuss contributions of different BC fractions to the continuum spectrum. A first chemothermal approach **(a)** consisted of acids-mixture pretreatment (HCl/HF/TFA) to remove potencial artefacts (carbonates, silicates, hydrolyzable organic matter), followed by non-BC material extraction in thermal con-

ditions (375ºC/24 h/O_2) to finally estimate the residual organic carbon (mass difference, EA), [4]. This process produced BC estimations ranging from 2-15 g/100g OC, accounting for the so called *graphitic black carbon* (GBC) within the BC spectrum. A second approach **(b)** was applied in the same way, but omiting the acidic preteatment, in order to compare both methods and discuss the effect of previous mineral removal to the BC estimation. This process was only carried out on 6 of the 15 sediments and accounted for the BC fraction called *thermal oxidation BC* [5]. A third approach **(c)** uses benzenecarboxylic acids (BPCA) as specific markers of BC [6]. This analytical method, including acid digestion, oxidation, sample cleanup, derivatization and gas chromatography, produced BPCA yields varying between 1-25 g/100g OC. Variation and systematic offsets between methods, correspondances with different fractions of the BC continuum and effects of mineral composition on BC-artefacts production will be discussed.

Keywords: incomplete combustion, carbon budgets, black carbon continuum, Mediterranean fires, graphitic black carbon, benzenecarboxylic acids.

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