



## Comparison of methods for the characterization and quantification of carbon forms in estuarine and marine sediments from coal mining regions

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### ABSTRACT

Organic matter (OM) in sediments plays a vital role in the global carbon cycle, yet its quantification remains a major analytical challenge. The applicability of various techniques for characterizing the OM in six estuarine sediment samples from the coal-mining region of Northumbria and Tyne and Wear (UK) and three marine sediment samples from the lignite mining region of Aliveri (Greece) was tested. The techniques included wet chemical oxidation according to Walkley–Black and thermal oxidation (16 h, 375 °C), automatic carbon analysis after thermal (24 h, 500 °C) and acid treatment, organic petrography, Rock–Eval pyrolysis and thermogravimetric analysis combined with data from X-ray diffraction. The total organic carbon (TOC) content determined after HCl or thermal treatment correlated well but HCl treatment tended to record lower TOC content. Known additions showed that coal OM is partially resistant to wet chemical oxidation and does not contribute to the thermally resistant OC fraction.

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### 1. Introduction

Soil/sediment organic matter (SOM) is typically considered to play a significant role in the global carbon cycle and, on a smaller scale, in various processes mainly concerning plant growth and the buffering of the physical and chemical properties of soil and sediments (Tiessen et al., 1994). Recent studies have also demonstrated the important role of various SOM forms affecting the sorption and bioavailability of organic pollutants (e.g. Karapanagioti and Sabatini, 2000; Karapanagioti et al., 2000; Accardi-Dey and Gschwend, 2002; Jonker and Koelmans, 2002; Cornelissen et al., 2005; Werner et al., 2010). Exceptionally strong sorption and reduced pollutant bioavailability are attributed to a significant extent to the so-called 'black carbon' (BC), i.e. the carbon fraction derived from combustion, pyrolysis and/or hydrogenation of fossil fuels and biomass (Masiello and Druffel, 1998; Ghosh, 2007). Masiello (2004) and Hammes et al. (2007) attempted to further clarify the term BC, emphasizing the pyrogenic origin and the resistance to thermal or chemical degradation, not referring to the matrix but to the conditions applied in the methods of quantification. This fraction is chemically resistant, has high survival potential and represents an important sink in the global carbon cycle; thus, its accurate quantification is essential in environmental studies (Knicker et al., 2007).

Routine analysis for the quantification of SOM and the total organic carbon (TOC) in a soil/sediment usually involves oxidation at relatively low temperature and automatic elemental analysis after removal of carbonate. However, a number of other techniques have been applied for the quantification and the characterization of SOM and TOC, as well as the various OC fractions (Kögel-Knabner, 2000; Bisutti et al., 2004). Most presuppose the physical or chemical separation of inorganic matter from OM and vice versa. Particularly concerning the quantification of BC, there has been much discussion. Nguyen et al. (2004) summarized, in a comprehensive study, the methods for the quantification of BC in soils and sediments and Manning and Lopez-Capel (2009) compared techniques applied for the quantitative determination of biochar and related material. These methods were generally distinguished into four major groups including microscopic, thermal/optical and the detection of BC after chemical or thermochemical pretreatment. On the other hand, Masiello (2004) distinguished six classes, including microscopic, optical, thermal, chemical, spectroscopic and molecular marker methods. Each class/group displays advantages and disadvantages, with none able to accurately quantify the entire BC content of a soil/sediment sample. The main reason for the uncertainty in each method is the inability to precisely determine what BC is but, according to the combustion continuum inspired by Hedges et al. (2000) and later adopted by others, each technique only measures a different region within the continuum, particularly concerning size (Masiello, 2004). Gustafsson et al. (1997) suggested that the various descriptors used for this carbon fraction, such as

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char, soot, charcoal and black carbon, reflect either the functional process or the operational techniques employed for determination of the fraction. Overall, there is no unambiguous definition for the description of the highly condensed carbonaceous residue from incomplete combustion (Goldberg, 1985). In addition, a ring trial exercise (Hammes et al., 2007) conducted among 17 laboratories for the quantification of BC in 12 reference materials, enhanced the statement that one of the key factors for any discrepancy and divergence among measurements is the lack of a precise definition of BC. Pyrogenic carbon (PyC) is another term used (Preston and Schmidt, 2006) to describe incomplete combustion residues (char) and re-condensed volatile compounds (soot).

It is evident that there is broad uncertainty as to what essentially BC or pyrogenic carbon is and which carbon forms should be included under these terms. Additionally, carbon derived from unburned fossil fuel particles like coal, and particularly from “pre-combusted” compounds like inertinite (Diesel, 2010) or other forms, such as coke and tar-pitch, which derive from processes other than combustion, may exhibit the same or similar properties as the “BC fraction”. The contribution of coal, especially of medium to high rank, to the BC fraction as determined by several methods has also been pointed out in the work of Hammes et al. (2007), increasing the uncertainty as to what this term should include.

Given the importance for global carbon cycle models for understanding the role of different carbon forms, this study aimed to test and compare a range of techniques for the quantification of various carbon fractions in environmental samples obtained from two coal mining regions with intense industrial activity and serious emission sources. In the regions, SOM was expected to occur in a variety of forms originating from both natural and anthropogenic sources. The main focus was to compare the different analytical approaches, studying the coal contribution to the quantification of different organic carbon fractions. Thus, the study differs from many others, with its focus on coal mining regions and by using petrographic and mineralogical datasets in the interpretation of a wide range of analytical results.

## 2. Regional settings

The Newcastle area (Fig. 1a) has a long record of industrial activity back to medieval times. Coal mining on an industrial scale

commenced in the 12th century and reached a peak at the beginning of the 20th century: this is one reason why the whole area has been referred to as the cradle of the industrial revolution since the late 17th century. It is regarded as being heavily disturbed by human activity, such as coal mining, combustion and shipping, metal mining and smelting, ship building, railway building and trains, as well as other industrial activity associated with fossil fuel combustion. Many of these activities have been reduced during the last two decades, although coal spoil is still an important source for soil/sediment contamination, and current open pit coal mining is a possible source of airborne particulates. Additionally, the urban and industrial areas in general remain significant sources for the emission of incompletely combusted carbonaceous particles.

Geologically, the area is composed of a coal-bearing Carboniferous sandstone, siltstone and mudstone, overlain by Permian Zechstein sediments (sands, mudstone and dolomitic limestones) in the southeast (Turner and Richardson, 2004). Quaternary till and associated glaciogenic deposits (including lake sediments) cover the entire region, incised by more recent rivers with associated stream and overbank deposits. Natural erosion of coal layers occurs along the coast line and the rivers.

The Aliveri area on Evia Island (central Greece) has a shorter industrial history, starting in the first half of the 20th century, when underground mines were dug for coal exploitation. The area hosts the first power plant installed in Greece and fed with local coal until the 1980s; nowadays it is fired with oil. A cement industry also operates in the area just alongside the Gulf of Aliveri beach. The activities of the past century resulted in large dumps of mine tailings and sludge from the power plant on the Milaki Beach between the facilities of both factories (Fig. 1b). The geological setting of the area comprises successions of Mesozoic sedimentary and metamorphic rocks, whereas the coal formed in a relatively small basin of Miocene age.

The study of sediments from both sites allowed comparison of the characterization and quantification methods for both estuarine and marine environments since from the UK and Greece, respectively.

## 3. Sampling and methods

### 3.1. Sampling

Sediment samples (ca. 1 l) were collected from six estuaries on the NE coast of England and from one coastal site in central Greece.

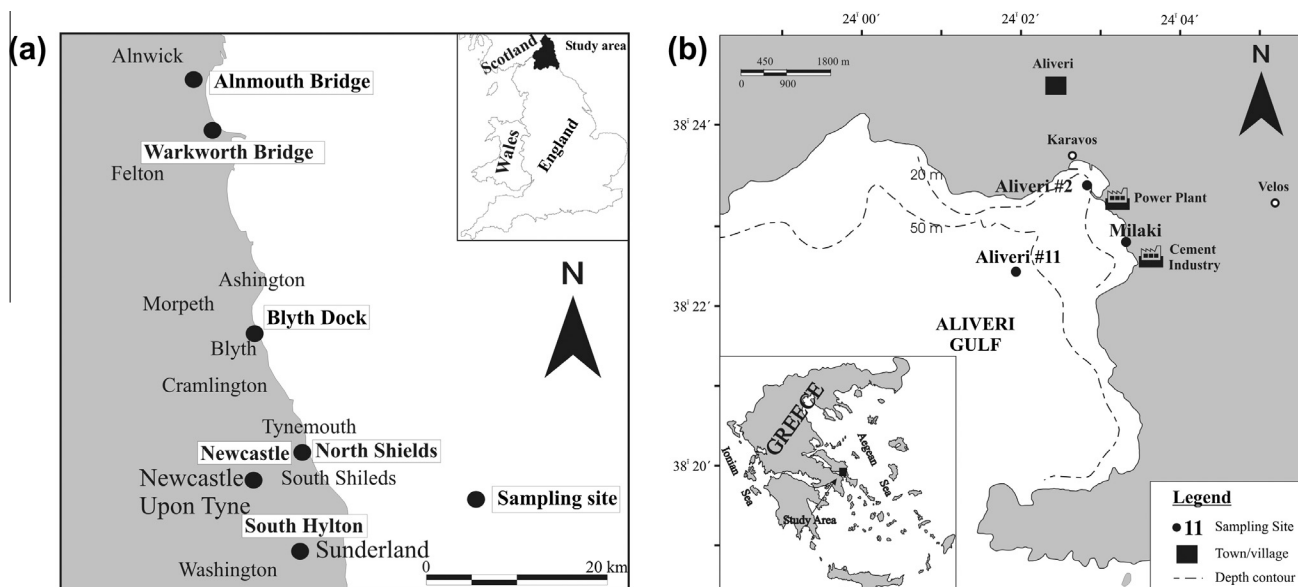


Fig. 1. Schematic maps showing sampling locations: (a) UK and (b) Greece.

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