



A Chemical degradative analysis of BC reference materials and BC samples isolated from marine sediments

F.J. González-Vila, J.M. de la Rosa, O. Polvillo, A. Terán., J.A González-Pérez

IRNAS-CSIC, Avda. Reina Mercedes, 10, P.O. Box 1052, 41080-Sevilla, Spain

(E-mail: fjgon@irnase.csic.es)

Black carbon (BC), soot, elemental carbon and charcoal are different terms used to describe a chemically heterogeneous, biologically refractory form of organic matter remaining as residue from incomplete combustion processes. This material and due to its widespread production and stability in the environment, is ubiquitous being found in the atmosphere, ice, soils and sediments (Goldberg., 1985).

BC can contribute to the stable organic matter pool by being buried in marine sediments (Masiello and Druffel., 1998) and it has been used as a record for forest fires and fossil fuel emissions occurrence (Bird and Cali., 1998). On the other hand, BC can represent a significant sink for carbon dioxide due to the transfer of carbon from the fast biological-atmosphere carbon cycle to the long-term geological one (Gustafsson et al., 2001). Therefore, the study of BC in sediments is relevant to estimate the particulate carbon flux from the biosphere to the sediment sink. However, apparent discrepancies between BC studies exist, which are mainly due to the lack of a common terminology, common methods of analysis and a common model for BC structure (Masiello, 2004).

In this communication the chemical structure of BC materials are studied by using a series of oxidative chemical degradation methods. BC-Ring Trial (Schmidt et al) reference materials as well as BC samples isolated in our laboratory from marine sediments were analysed. The oxidizing chemical agents included potassium persulfate (a mild oxidant) followed by potassium permanganate, that were informative with respect to elucidate bound strength and molecular structural organization. Also a perborate oxidation, known for its efficiency in macromolecular depolymerisation, and a ruthenium tetroxide oxidation, especially suitable for investigating the structure of resistant aliphatic macromolecules like algaenans, cutans or suberans, were also performed. Details on the experimental procedures can be found in Vitrovic et al (1984), Almendros and Gonzalez-Vila (1987), Almendros et al. (1987), Gonzalez-Vila et al. (1994), Bajo et al. (2001), Cuypers et al. (2002). The respective digests were quantified and their composition analysed by GC-MS.

The different oxidative treatments revealed different structural features of the refractory samples studied, depending on the strength of the oxidant and the type of linkages affected. After persulfate oxidation all the samples leaves residues amounting between 40 and 80 % of the initial weights, which were further subjected to permanganate oxidation. The persulfate degradation products were in general dominated by series of aliphatic compounds (n-fatty acids, n-alkanes), whereas mainly aromatic compounds were detected among the permanganate degradation products, with alkanolic diacids and normal fatty acids detected in minor amounts. Successive sodium perborate depolymerization of the samples required different number of steps to reach a complete degradation of the samples that is dependent on the stability of the samples. The degradation products released by this procedure were similar to those observed by the above sequential degradation. Finally, ruthenium tetroxide treatments resulted in a mass sample degradation resulting in benzenepolycarboxylic as dominant degradation products acids arising from the aromatic BC network.

References:

- Almendros G. and González-Vila F.J.,1987. Degradative studies on a soil humin fraction-Sequential degradation of inherited humin. *Soil Biology and Biochemistry* 19, 513-520.
- Almendros G., Martín F. and González-Vila F.J., 1987. Depolymerization and degradation of humic acids with sodium perborate. *Geoderma* 39, 235-247
- Bajo S., Amblés A., Largeau C., Derenne S. and Vitorovic D., 2001. Precursor biostructures in kerogen matrix revealed by oxidative degradation of kerogen from estonian kukersite. *Organic Geochemistry* 32, 773-784

Bird M.I. and Cali J.A., 1998. A million-year record of fire in sub-Saharan Africa. *Nature* 394, 767-769.

Cuypers C., Grotenhuis T., Nierop K. G. J., Maneiro Franco M., De Jager A. and Rulkens W., 2002. Amorphous and condensed organic matter domains: the effect of persulfate oxidation on the composition of soil/sediment organic matter. *Chemosphere* 48, 919-931.

Goldberd E.D., 1985. *Black Carbon in the Environment*. Wiley-Interscience, New York, N.Y.

González-vila F.J., del Rio J.C., Almendros G. and Martín F., 1994. Structural assessment of humic fractions from different soils through ^{13}C NMR spectroscopy and rutheniumtetroxide oxidation. In: N. A. M. Senesi, TM (Ed), *Humic substances in the global environment and implications on human health*. Elsevier.

Gustafsson O., Bucheli T.D., Kukulska S., Anderson M., Largeau C., Rouzaud J.N., Reddy

Masiello, C.A. and Druffel E.R.M., 1998. Black Carbon in deep sea sediments. *Science* 280, 1911-1913.

Masiello, C.A., 2004. New directions in black carbon organic geochemistry. *Marine Chemistry* 92, 201-213.

Schmidt M. et al. <http://www.geo.unizh.ch/phys/bc/>

Vitorovic D., Amblés A. and Djordjevic M., 1984. Relationship between kerogens of various structural types and the products of their multistep oxidative degradation, *Organic Geochemistry* 6, 333-342.

Preference for Oral presentation