Comparative analysis of reference materials for organic geochemical studies of black carbon

Michael W. I. Schmidt (1), Jan O. Skjemstad (2), Caroline Masiello (3), William P. Ball (4), Lloyd Currie (5), Dwight M. Smith (6) and (7) contributing parties to the comparative analysis (The Ring Trial Team)

(1) University of Zurich, Dept. of Geography, Zurich, Switzerland, (2) CSIRO Land and Water, Adelaide, Australia, (3) Rice University, Houston USA, (4) Johns Hopkins University, Ort, USA, (5) NIST, Gaithersburg, USA, (6) University of Denver, Denver USA (7) Reference materials were distributed to 24 laboratories worldwide early 2003/4 for analysis. The final list of contributing parties will become clear after January 2005.

The Black Carbon Ring Trial Team:

M.W. I. Schmidt, K. Hammes (University of Zurich, Dept. of Geography, Zurich, Switzerland), O. Gustaffson, M. Elmquist, G. Cornelissen (Stockholm University, Institute of Applied Environmental Research (ITM), Sweden), W.P. Ball, M. Fukudome, T.H. Nguyen (Johns Hopkins University Dept. of Geography and Environmental Engineering, USA), W. Amelung, S. Brodowski (Institute for Ecology, Technical University Berlin, Germany Dept. of Soil Science and Soil Geography, University of Bayreuth, Germany), G. Guggenberger, K. Kaiser, A. Rodionov (Institute for Soil Science and Plant Nutrition, Martin Luther University Halle-Wittenberg, Germany), L. Huang (Stable Isotope Laboratory, Air Quality Research Branch, Meteorological Service of Canada, Environment Canada, Canada), B.J. Huebert (Department of Oceanography, University of Hawaii, USA), C. Largeau, J.-N. Rouzaud (Laboratoire de Chimie Bioorganique et Organique Physique, Ecole Nationale Supérieure de Chimie de Paris, France Laboratoire de Géologie, Ecole Normale Supérieure, Paris, France), L. Ding (Analysis and Air Quality Division, Environmental Technology Center, Ontario, Canada), J.O. Skjemstad, R.J. Smernik (CSIRO Land and Water, Glen Osmond, Australia Department of Soil and Water, University of Adelaide, Glen Osmond, Australia), J. Song (State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, China)
Black carbon (BC) is a collective term used to describe recalcitrant organic, produced by incomplete combustion of fossil fuels and vegetation. It occurs ubiquitously in soils and sediments. BC exists as a continuum from partly charred material to highly graphitized soot particles, with no general agreement on clear-cut boundaries of definition or analysis (Hedges et al. 2000). The individual analytical BC methods rely on operational definitions with clear-cut but different boundaries and are developed for specific scientific questions whereas BC represents a continuum of materials with widely contrasting physicochemical properties. Thus, different methods may be inherently designed to analytically determine different parts of the continuum, and it is crucial to know how measurements made by different techniques relate to each other. The inherent difference can be illustrated by the results of a first comparative analysis on eight soil samples by six established methods (Schmidt et al., 2001). All methods involved removal of the non-BC components from the sample by thermal or chemical means, or a combination of both. The remaining carbon, operationally defined as BC, was quantified via mass balance, elemental composition or by exploiting benzene carboxylic acids as molecular markers or applying $^{13}$C MAS NMR spectroscopy. BC concentrations measured for individual samples vary over two orders of magnitude.

The need for intercomparison of BC methods is obvious. To address this need, a committee was formed during the 1999 Geochemical Society Meeting Goldschmidt Conference to develop representative and accessible BC reference materials for the entire environmental sciences community. It was clear from the preliminary comparative analysis that a collection of BC reference materials should be established as soon as possible i) to ensure long-term intra- and inter-laboratory data quality, and ii) to facilitate comparative analyses between different analytical techniques and scientific approaches. The final recommendations of the steering committee for Black Carbon Reference Materials included (i) five matrices containing BC (soot, charcoal, aerosol, soil, and sediment); and (ii) five materials potentially creating BC during analysis (shale, melanoidin, natural organic matter, and coal), for use in detecting methodological artifacts Schmidt et al. (2003). Further details can be found at the Web site: http://www.geo.unizh.ch/phys/bc.

Early 2003/4, these reference materials were produced and distributed and analyzed in a comparative analysis project using these reference materials to gauge how different methods can be used to interpret BC components in aerosol, soils, and sediments. The intention of the study is not to advocate a single technique; rather, such a comparative analysis will help immensely to better understand what is actually being determined by the different methods and how these results relate to one another. Reference materials were requested by 24 research groups of many disciplines, including atmospheric, environmental, marine and soil sciences. Participating research groups are currently
analyzing the materials and expected to make available all results and details of their methodology after January 2005 for discussion and eventual group publication. Summarizing, the aim of this contribution will be to present results of the comparative analysis of reference materials for organic geochemical analysis of black carbon and to stimulate discussion.

