

Black carbon molecular marker quantification by two chromatographic methods – How do results correlate?

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Chars produced by wildfires are an important source of black carbon (BC) in the environment. After their deposition on the soil surface they can be distributed into rivers, marine waters and sediments. The analysis of benzenepolycarboxylic acids (BPCAs) as a quantitative measure for black carbon (BC) in soil and sediment samples is a well-established method (Glaser et al., 1998; Brodowski et al., 2005). Briefly, the nitric acid oxidation of fused aromatic ring systems in BC forms eight molecular markers (BPCAs), which can be assigned to BC, and which subsequently can be quantified by GC-FID (gas chromatography with flame ionization detector). Recently, this method was modified for the quantification of BC in seawater samples using HPLC-DAD (High performance liquid chromatography with diode array detector) for the determination of individual BPCAs (Dittmar, 2008). A direct comparison of both analytical techniques is lacking but would be important for future data comparison aimed at the calculation of global BC budgets. Here we present a systematic comparison of the two BPCA quantification methods. We prepared chars under well-defined laboratory conditions. In order to cover a broad spectrum of char properties we used two sources of biomass and a wide range of pyrolysis temperatures. Chestnut hardwood chips (*Castanea sativa*) and rice straw (*Oryza sativa*) were pyrolysed at temperatures between 200 and 1000°C under a constant N₂ stream. The maximum temperatures were held constant for 5 hours (Hammes et al., 2006). The BC contents of the chars have been analysed using the BPCA extraction method followed by either GC-FID or HPLC-DAD quantification. Preliminary results suggest that both methods yield similar total quantities of BPCA, and also the proportions of the individual markers are similar. Ongoing experiments will allow for a more detailed comparison of the two methods. The BPCA composition of chars formed at different temperatures and from different precursor biomass is being used for this purpose. We seek to establish a conversion factor between both methods, if required. Results show that both the GC and the HPLC method can be used for organic samples containing some silica, such as grass char. Further tests include silica-rich materials, such as soils. Ongoing methodological work aims at carbon isotope analysis (¹³C and ¹⁴C) on individual BPCAs isolated via HPLC. At present the HPLC method employs tetrabutyl ammonium bromide (TBAB) as a modifier for the liquid phase. TBAB is not volatile and contains carbon, it therefore prevents carbon isotopic analysis on isolated BPCAs.