

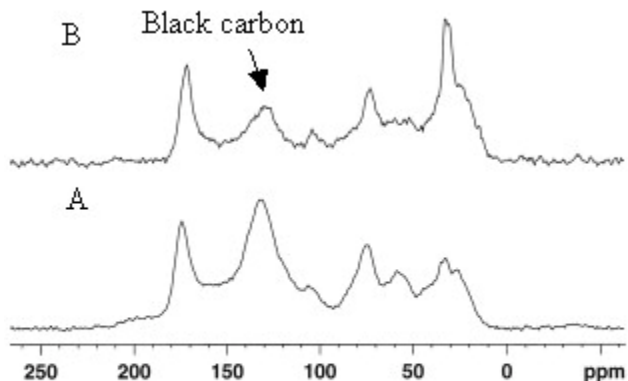
## Understanding the Role of Black Carbon in Environmental Surface Processes

Black carbon, which encompasses soot, charcoal and products of incomplete combustion, contributes significantly to the aromatic fraction of natural organic matter (NOM). Our current efforts focus on determining the bulk, molecular-level, and surface properties of black carbon, such that pollutant interactions can be understood on a fundamental level. A wide variety of natural samples have been collected which include soils, sediments, coals, and naturally charred plant and wood material. These samples were subjected to a new technique for black carbon isolation involving chemical oxidation (by sodium hypochlorite) followed by spectroscopic characterization using solid-state  $^{13}\text{C}$  NMR and FT-ICR (Fourier Transform Ion Cyclotron Resonance) mass spectrometry. The results indicate that this chemical oxidation method is excellent for removing, solubilizing and eliminating aromatic constituents found in natural organic matter (e.g., lignin and other plant-

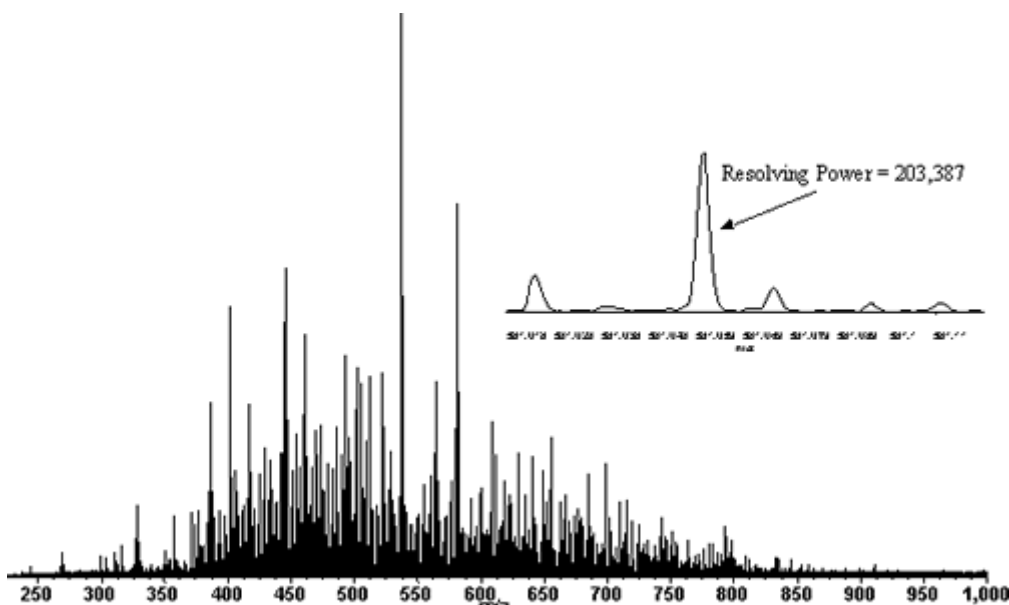
derived aromatic constituents). By measuring total carbon before and after oxidation, through integrating the NMR spectrum, and obtaining a measure of the relative amount of aromatic carbon in the oxidized residue, one can obtain a semi-quantitative value for the amount of black carbon in a given sample. This method is the first to provide a realistic measure of condensed aromatic structures in NOM; in some cases contributing a significant component of the sample. We additionally discovered that existing methods claiming to

measure black carbon will create black carbon from non-aromatic organic matter and will overestimate the amount of black carbon in a given sample. Based on our data, we hypothesize that the majority of black carbon values reported in the literature may be

an order of magnitude higher than actual values due to inherent problems of the current methodology. Such a large error in black carbon



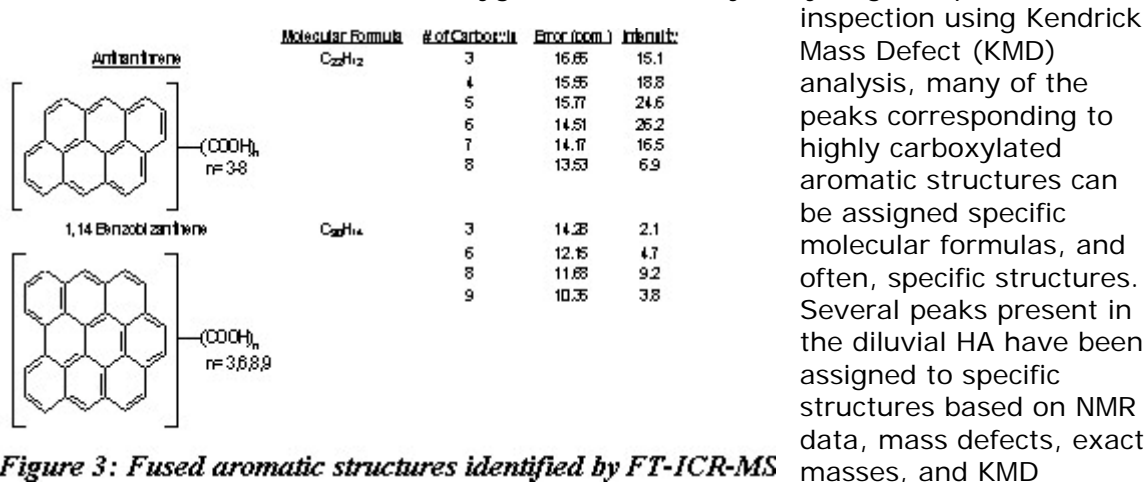
*Figure 1: Solid-state  $^{13}\text{C}$  NMR of a soil before (A) and after chemical oxidation (B)*



*Figure 2. FT-ICR mass spectrum of Diluvial humic*

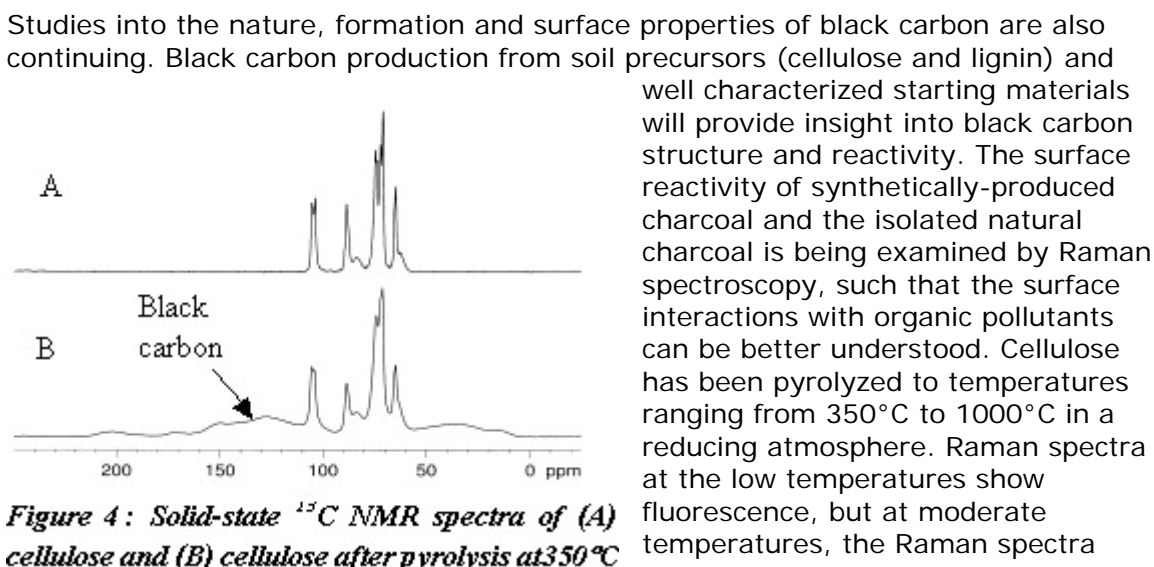
estimates is of great significance to current global carbon assessments and cycling.

We have also examined several humic materials, which are thought to have a high black carbon contents, by electrospray ionization mass spectrometry using both a Quadrupole Time of Flight mass spectrometer and a Fourier Transform Ion Cyclotron Resonance mass spectrometer (FT-ICR MS). The FT-ICR mass spectrum of the diluvial humic acid (extracted from a volcanic soil in Japan) contains almost exclusively peaks at or slightly above the nominal mass (Figure 2). Such a distribution of peaks is representative of condensed aromatic ring systems that are highly carboxylated. Highly carboxylated aromatic compounds have a low mass defect due to their abundance of oxygen and deficiency of hydrogen. Upon closer



**Figure 3: Fused aromatic structures identified by FT-ICR-MS**

analysis. An example of the structures found is displayed in Figure 3. The structures identified to date are consistent with those that would be found in a soil rich in black carbon-like material. On-going research will include the analysis of several more humic acids such that distinct structures within the black carbon consortium can be identified. To our knowledge this represents the first direct and unambiguous evidence for the existence of condensed fused aromatic ring systems in humic acids. The existence of these structures derived undoubtedly from black carbon indicates that black carbon in soil is likely to be much more mobile than previously thought, especially considering that humic acids are known to be mobilized in soil processes.



resemble graphitic carbon. Solid-state  $^{13}\text{C}$  NMR spectra of the pyrolyzed cellulose at low temperatures show the formation of black carbon as low as  $350^\circ\text{C}$ , along with intact cellulose. Future work includes using lignin as a precursor material for the pyrolysis since it is an aromatic material, in contrast to the non-aromatic cellulose. Shortly, the synthetic charcoal and the natural organic matter samples will be used in pollutant sorption studies with the intent of linking chemical and surface characteristics to the sorptive behavior of pollutants.

## **Publications and Presentations**

Kramer, R. W., E. B. Kujawinski, X. Zang, K. B. Green-Church, B. Jones, M. A. Freitas, and P. G. Hatcher. 2001. Studies of the structure of humic substances by electrospray ionization coupled to a quadrupole-time of flight (QQ-TOF) mass spectrometer. Special Publication - Royal Society of Chemistry 273(Humic Substances), pp 95-107.

Salloum, M. J., and P. G. Hatcher. Overestimates of black carbon in global carbon budgets. Submitted to Nature.

Salloum, M. J., and P. G. Hatcher. Determination of black carbon in soil and sedimentary organic matter by solid-state NMR spectroscopy after the removal of lignin by chemical oxidation. In preparation for submission to *Geochimica et Cosmochimica acta*.

Eichorst, L. and R. McCreery. A Study of Low Temperature Carbon Materials Relevant to the Environment and Molecular Electronics. Poster presentation, Department of Chemistry, Ohio State University. September 2001.

Eichorst, L. and R. McCreery. The Electronic, Structural, and Physical Properties of Pyrolytic Carbon Materials. Analytical Division Seminar, Department of Chemistry, Ohio State University, January 22nd, 2002.

Kramer, R. W. and P. G. Hatcher. The Study of Humic Substances Using Electrospray Quadrupole Time of Flight Mass Spectrometry (ESI-QqTOF MS). Analytical Division Seminar, Department of Chemistry, Ohio State University, October 9th, 2002.

Kramer, R. W., E. B. Kujawinski, and P. G. Hatcher. Characterization of a Humic Acid from a Volcanic Ash Soil in Japan by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS): Black Carbon as a Potential Source. To be presented at the International Humic Substances Society Meeting, July 21-26, 2002. Boston, MA.

Salloum, M. J., and P. G. Hatcher. Determination of black carbon in natural organic matter by chemical oxidation and solid-state NMR. To be presented at the International Humic Substances Society Meeting, July 21-26, 2002. Boston, MA.