



Potential and pitfalls of using solid-state ^{13}C NMR spectroscopy for the analysis of BC-containing materials

R.J. Smernik (1) and J.O. Skjemstad (2)

(1) Soil and Land Systems, School of Earth and Environmental Sciences, The University of Adelaide, Waite Campus, Urrbrae SA 5064, Australia (Email: ronald.smernik@adelaide.edu.au), (2) CSIRO Land and Water and CRC for Carbon Accounting, Glen Osmond SA 5064, Australia

The aromatic nature of black carbon (BC) enables it to be easily distinguished from most other types of organic matter by nuclear magnetic resonance (NMR). This, together with the innately quantitative nature of NMR, the minimal sample preparation required and non-destructive nature of the solid-state technique appear to mark solid-state ^{13}C NMR spectroscopy as the ideal technique for quantifying BC in soils, sediments and related materials. Oh, if only it were that simple!

In this paper we present detailed solid-state ^{13}C NMR analyses of the Ring Trial samples, highlighting the three main problems involved: (i) quantitation, (ii) sensitivity and (iii) resolution.

Whilst NMR is innately quantitative – all ^{13}C nuclei in a sample *potentially* produce the same quantum of NMR signal – this ideal situation is often not realized in the case of BC. For the most widely-used and most sensitive solid-state ^{13}C NMR technique – cross polarization (CP) – the condensed aromatic structures of BC are detected with poor efficiency compared with other types of organic matter. Using a technique known as *spin counting*, we found the *NMR observability* (C_{obs}) of BC reference materials ranged from 6% (hexane soot) to 40% (rice straw char), when the CP technique was used. Corresponding C_{obs} values for the BC-containing samples were 40% for the urban dust, 45% for the marine sediment and 50-55% for the soils. Much higher C_{obs} values were recorded for samples containing no BC – 80% for the shale, 75-85% for the melanoidins and 90-100% for the fresh plant residues. Much higher and less vari-

able C_{obs} values were recorded when the alternative direct polarization (DP) technique (otherwise known as Bloch decay or single pulse excitation) was used.

Although the DP technique is much preferable to CP in terms of quantitation, this comes at the expense of much lower sensitivity. The consequences of this in terms of the amount of sample required, the cost of analysis and precision of measurement will be discussed.

The ability to distinguish BC from aromatic carbon in other types of organic matter can also be problematic. There is no exclusive “BC region” in an NMR spectrum, and highly aromatic materials such as bituminous coal produce very similar NMR spectra to soot and charcoal. We will discuss how these materials may be distinguished using NMR parameters other than chemical shift (frequency).

Despite these limitations, solid-state ^{13}C NMR spectroscopy remains an important technique for the analysis of BC. Perhaps its most important role is in the analysis of residues of chemical extractions purported to isolate BC. We will present NMR spectra that prove the “BC” produced by some of these techniques is in fact not very aromatic.