Advanced Solid-State ^{13}C NMR Characterization of the Structure, Origin, and Fate of Dissolved Organic Carbon

KLAUS SCHMIDT-ROHR[1]*, XIAOYAN CAO[1]

[1]Chemistry Department, Brandeis University, Waltham, MA 02453, USA (*correspondence: srohr@brandeis.edu)

The chemical composition of natural organic matter can be analyzed comprehensively by solid-state ^{13}C NMR, better than with any other available analytical technique [1]. Through systematic chemical shifts of the resonance frequency and spectral editing, functional groups can be identified reliably, and their amounts can be quantified in terms of the peak area fraction if the experiment is performed correctly [2]. In particular, selective spectra of carbons not bonded to hydrogen often reveal distinctive structural features [3, 4]. Structural models of typical repeat units are obtained by spectral simulations that match the quantitative and selective spectra in an iterative approach [5]. The capabilities of modern NMR will be demonstrated for the example of carboxyl-rich alicyclic molecules (CRAMs) contributing to dissolved organic carbon (DOC) pools on a global scale [4, 6]. NMR shows that lignin disappears along a transect from river to ocean, which explains the reduction in the hydrophobic acid fraction of DOC, while CRAM persists and enters the ocean in large quantities [6]. Synthetic ^{13}C-enriched carboxyl-rich alicyclic molecules closely resembling natural CRAM have been produced by abiotic transformations of simple biomolecules, which suggests a source of CRAM and enables detailed structural characterization by two-dimensional ^{13}C-^{13}C NMR and spectral editing [7].

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