Characterization of pyrogenic organic matter by 2-dimenstional HETeronucleus CORelation solid-state 13C NMR (HETCOR) spectroscopy

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During the last years, increasing evidences are provided that the common view of charcoal as a polyaromatic network is too much simplified. Experiments with model compounds indicated that it represents a heterogeneous mixture of thermally altered biomacromolecules with N, O and likely also S substitutions as common features. If produced from a N-rich feedstock, the so called black nitrogen (BN) has to be considered as an integral part of the aromatic charcoal network. In order to study this network one-dimensional (1D) solid-state nuclear magnetic resonance (NMR) spectroscopy is often applied. However, this technique suffers from broad resonance lines and low resolution. Applying 2D techniques can help but until recently, this was unfeasible for natural organic matter (NOM) due to sensitivity problems and the high complexity of the material. On the other hand, during the last decade, the development of stronger magnetic field instruments and advanced pulse sequences has put them into reach for NOM research.

Although 2D NMR spectroscopy has many different applications, all pulse sequences are based on the introduction of a preparation time during which the magnetization of a spin system is adjusted into a state appropriate to whatever properties are to be detected in the indirect dimension. Then, the spins are allowed to evolve with the given conditions and after their additional manipulation during a mixing period the modulated magnetization is detected. Assembling several 1D spectra with incrementing evolution time creates a data set which is two-dimensional in time (t1, t2). Fourier transformation of both dimensions leads to a 2D contour plot correlating the interactions detected in the indirect dimension t1 with the signals detected in the direct dimension t2. The so called solid-state heteronuclear correlation (HETCOR) NMR spectroscopy represents a 2D technique allows the determination which protons are interacting with which carbons. In the present work this technique was used for monitoring the chemical changes occurring during charring of biomass derived from model compounds, fire-affected and unaffected NOM. The 2D 13C HETCOR NMR spectrum of the fire- unaffected soils revealed that most of the carboxyl C occurs as ester or amide. Aside from cross peaks typically seen in spectra of NOM, the spectrum of the respective fire-affected counterpart shows additional signals assignable to PyOM.