



A new approach for molecular characterisation of sediments with Fourier transform ion cyclotron resonance mass spectrometry: Extraction optimisation



Georgina A. McKee, Patrick G. Hatcher*

Department of Chemistry and Biochemistry, 4402 Elkhorn Avenue, Old Dominion University, Norfolk, VA 23529, USA

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ABSTRACT

Fourier transform ion cyclotron resonance mass spectrometry (FTICRMS) can begin to tease apart the molecular character of sedimentary organic matter (SOM). We therefore tested five different solvents (aqueous base, CHCl₃, MeOH, pyridine and water) for their ability to extract a representative fraction from two organic rich lacustrine sediments, Mangrove Lake, Bermuda (MLB) and Mud Lake, Florida (MLF). Following comparison using liquid state nuclear magnetic resonance spectroscopy (NMR) and negative ion mode electrospray ionization mass spectrometry (FTICRMS) we found that pyridine was the optimal solvent, extracting a more diverse (10–100× greater integration for carbonyl, amide and amine groups) and a larger number of peaks on average (1375–1450 vs. 380–1450). Comparison of the pyridine extracts between MLB, MLF and two organic poor sediments from the Mississippi River Delta and Bayou Grande (Pensacola, FL) showed that only 4.9% of the molecular formulae were common to all four and that unique formulae made up the highest proportion of the assignments. The use of pyridine for extracting immature (Holocene) SOM for FTICRMS analysis can therefore be widely applied to immature sediments and produce representative spectra.

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1. Introduction

Sedimentary organic matter (SOM) plays an integral role in global cycling of key nutrients such as C, N and S. Obtaining an in depth knowledge of its molecular composition is essential for understanding its role in global nutrient cycles. Molecular characterisation studies of SOM have been carried out for decades, identifying structures with varying levels of success (Hedges et al., 2000). Much of the difficulty in obtaining molecular information is due to the complex nature of the SOM and the lack of analytical tools for probing the entire organic pool.

One of the limiting components has been the requirement of most analytical instruments for samples to be soluble and/or volatile. Three main approaches for sample preparation and analysis have been employed to characterize SOM: (i) significantly altering the chemical nature of the sample to facilitate detailed characterization of amenable functionalities (Goñi and Hedges, 1995; del Rio et al., 1998; Challinor, 2001). (ii) Using a chemical treatment to examine certain structural entities, e.g. lipids (Marsh and

Weinstein, 1966; Sauer et al., 2001), carbohydrates (Gerchakov and Hatcher, 1972; Pakulski and Benner, 1992), lignin (Goñi and Montgomery, 2000; Dittmar and Lara, 2001) and proteins (Dauwe and Middelburg, 1998; Nunn and Keil, 2006). (iii) Relying on techniques that require little to no chemical alteration of the sediment prior to analysis, providing bulk information using methods such as nuclear magnetic resonance (NMR) spectroscopy and infrared spectroscopy (Stevenson and Goh, 1971; Niemeyer et al., 1992; Kögel-Knabner, 1997; Knicker, 2004). Although each of these approaches has its usefulness, none is able to achieve molecular characterization of sediments without significant selectivity.

The use of Fourier transform ion cyclotron resonance mass spectrometry (FTICRMS) to molecularly study natural OM provides an alternative route for the characterization of SOM. FTICRMS has been most commonly employed in the characterization of water samples, including: dissolved OM from both fresh and marine environments (Kujawinski, 2002; Hertkorn et al., 2006; Sleighter and Hatcher, 2007), porewater OM (Tremblay et al., 2007; Schmidt et al., 2009), extracted aerosols (Wozniak et al., 2008; Mazzoleni et al., 2010) and rainwater (Altieri et al., 2009). Its application to the study of solid samples requires the sample to be transformed into liquid form. Solubility based extractions have yielded detailed

* Corresponding author. Tel.: +1 757 683 6537.

E-mail addresses: gina.mckee@colostate.edu (G.A. McKee), phatcher@odu.edu (P.G. Hatcher).

information regarding the molecular character of solid samples (Kujawinski, 2002; Hockaday et al., 2006; Ohno et al., 2010, 2014). However, it seems that dissolution of solid OM samples in organic solvents is a more efficient method for evaluating the molecular character of the entire sample (Wu et al., 2003; Schmitt-Kopplin et al., 2009; Salmon et al., 2011; Zhong et al., 2011). Essential for any OM extraction of a solid sample such as a sediment is the extraction of the most extensive and representative fraction available, without disturbing the chemical character of the whole sample. Two previous studies to investigate the most appropriate solvent for solid samples concluded that polar, protic solvents such as MeOH or pyridine were the most effective (Schmitt-Kopplin et al., 2009; Salmon et al., 2011).

An investigation into the most appropriate extraction solvent for negative ion mode electrospray ionization (ESI) FTICRMS analysis of immature sediments (Holocene) had not been carried out, so we had two main objectives for this work: (i) To determine (based on number and diversity of peaks) the most appropriate solvent (out of five) for characterizing two immature sediments from organic rich anoxic environments (Mangrove Lake, Bermuda, MLB and Mud Lake, Florida, MLF). (ii) To verify that the chosen solvent was able to differentiate between organic rich and organic poor oxic (Mississippi River Delta, MD and Bayou Grande, BG) sediments, in order to demonstrate the wider applicability of the technique.

2. Material and methods

2.1. Sample collection

The well studied organic rich sediments, MLF and MLB, are primarily algal derived and were deposited under anoxic conditions (Hatcher et al., 1982; Orem et al., 1986; Filley et al., 2001, 2002; Knicker and Hatcher, 2001; McKee and Hatcher, 2010). The MLB sediments were collected in 1982 and details are included elsewhere (Orem et al., 1986). In November 2009, additional MLB sediment was collected (depth 2.8–2.85 m) and was analyzed here using 1D ¹H NMR (details given by McKee, 2011). For the MLF sample used here, collection was carried out in 1993 and is described by Filley et al. (2001). Unfortunately the amount of sample available for the study of these sediments was limited, so only two depths of the 1982 MLB sediment (1.4 and 3.0 m) and one from MLF (0 m) were available for MS analysis.

In addition to the organic rich sediments, two organic poor sediments were studied, BG and MD. BG is a tidal bayou near Pensacola (FL) of ca. 4.3 km², with OM input from both fresh (terrestrial and marine) and anthropogenic sources (Lewis et al., 2001; Simpson et al., 2005). The collection of BG sediment (0.21–0.31 m, bottom) is described by Lewis et al. (2001). Deltas comprise a major fraction of sediments globally (44% total C; Killops and Killops, 2005). The MD is one such example, with a drainage area covering 40% of the continental USA, 70–90% of its water contributing to the freshwater in the Gulf of Mexico (Turner and Rabalais, 1994; Coleman et al., 1998; Goñi et al., 1998; Gordon et al., 2001). The area of the MD collection point is in the Southwest Pass of MD (Bennett et al., 1991), previously studied for its microstructure (Bennett et al., 1977, 1991; Bennett and Faris, 1979; Bohlke and Bennett, 1980). Several studies have been directed at identifying the source of the SOM entering the Delta and, while it is agreed that the Mississippi River is the main source, there is some difference of opinion regarding whether it is terrestrial or marine in nature (Turner and Rabalais, 1994; Keil et al., 1997; Goñi et al., 1998). The identity as to the exact molecular composition of BG and MD sediment SOM was not further attempted.

2.2. Sample preparation

In order to minimize the possibility of contamination, all glassware was precombusted (to 450 °C) before use and solvents were obtained at the highest purity available (no further purification was undertaken). The following solvents were compared for SOM extraction ability: aqueous base (1 M NH₄OH, Fisher Scientific), CHCl₃ (Fisher Scientific), MeOH (Fisher Scientific), pyridine (Acros) and MilliQ water. Water and base extraction were tested since these two solvents are commonly used for sediment studies (Nunn and Keil, 2006; von Lütow et al., 2007). Different polar organic solvents were also tested to determine if increasing polarity impacted extraction efficiency. CHCl₃ has been used in a few studies to examine lipids (Worsfold et al., 2008), expected to be a major group in these immature sediments. MeOH, a polar solvent, has been successfully used in examining meteorites (Schmitt-Kopplin et al., 2009). Pyridine extraction has been employed to examine more mature sediment such as kerogen (Salmon et al., 2011), coal (Wu et al., 2003) and shale (McKay and Sterling Blanche, 1985), suggesting it might also be successful for immature sediments.

For NMR analysis (of 2009 MLB sediment), extracts were prepared by adding ca. 800 mg sediment to 16 ml of solvent. Extraction was conducted for 3 days (determined as an optimum time for maximum extraction, data not shown) using gentle shaking (orbital shaker (VWR model 57018–754) at 180 rpm) at room temperature. The extract was obtained by filtering the mixture through a low C (Kauppila et al., 2006) 0.2 μm poly(tetrafluoroethane, PTFE) filter. The pyridine extract was alternatively filtered using a glass syringe and stainless steel filter holder to limit contact with easily contaminating plastics. Extraction solvent was removed by evaporation using high purity N₂, leaving a solid extract. Samples were stored in a refrigerator (4 °C) until analysis (previous experiments determined that extracts were not altered at this temperature, data not shown). Immediately prior to NMR analysis, the solid extracts were dissolved in 600 μl dimethyl sulfoxide-*d*₆ (DMSO-*d*₆, Acros; 99.9% purity) directly in the NMR tubes.

Solvent was removed completely with a stream of N₂, followed by lyophilization, leaving the solid sediment (sediment residue) that was used for the determination of extraction efficiency. Sediment residues were weighed to determine mass loss and examined via elemental analysis. It should be noted that, despite maintaining uniform and careful extraction procedures throughout the experiment, mass measurements are subject to a certain degree of error due to the inherent difficulty in extraction by filtration. Inevitably a small quantity of unextracted sediment is drawn up through the syringe and trapped on the filter. Visual inspection of the maximum mass of sediment lost via trapping on the filter was conducted and estimated at ca. 0.5 mg sediment. This correlates with a 1% error in mass calculations, thereby not substantially altering the general conclusions presented.

For FTICRMS analysis (all samples except the 2009 MLB sample) the same sediment sample extraction protocols and experimental conditions were maintained to reduce variability and facilitate a more accurate solvent extraction comparison. Ca. 50 mg (see Supplementary Table 1 for exact quantities) of each sediment were added to 1 ml of each solvent and were extracted, filtered and stored using the same procedure as above for NMR analysis.

2.3. Total organic carbon (TOC) and total nitrogen (TN)

A ThermoFinnigan Flash EA 1112 Series elemental analyser (CE Instruments, UK), that employs a combustion approach was used. TOC and TN were determined for the sediment residues remaining after solvent extraction for NMR analysis for 2009

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