



Extending the analytical window for water-soluble organic matter in sediments by aqueous Soxhlet extraction

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Abstract

Dissolved organic matter (DOM) in marine sediments is a complex mixture of thousands of individual constituents that participate in biogeochemical reactions and serve as substrates for benthic microbes. Knowledge of the molecular composition of DOM is a prerequisite for a comprehensive understanding of the biogeochemical processes in sediments. In this study, interstitial water DOM was extracted with Rhizon samplers from a sediment core from the Black Sea and compared to the corresponding water-extractable organic matter fraction (<0.4 μm) obtained by Soxhlet extraction, which mobilizes labile particulate organic matter and DOM. After solid phase extraction (SPE) of DOM, samples were analyzed for the molecular composition by Fourier Transform Ion-Cyclotron Resonance Mass Spectrometry (FT-ICR MS) with electrospray ionization in negative ion mode. The average SPE extraction yield of the dissolved organic carbon (DOC) in interstitial water was 63%, whereas less than 30% of the DOC in Soxhlet-extracted organic matter was recovered. Nevertheless, Soxhlet extraction yielded up to 4.35% of the total sedimentary organic carbon, which is more than 30-times the organic carbon content of the interstitial water. While interstitial water DOM consisted primarily of carbon-, hydrogen- and oxygen-bearing compounds, Soxhlet extracts yielded more complex FT-ICR mass spectra with more peaks and higher abundances of nitrogen- and sulfur-bearing compounds. The molecular composition of both sample types was affected by the geochemical conditions in the sediment; elevated concentrations of HS⁻ promoted the early diagenetic sulfurization of organic matter. The Soxhlet extracts from shallow sediment contained specific three- and four-nitrogen-bearing molecular formulas that were also detected in bacterial cell extracts and presumably represent proteinaceous molecules. These compounds decreased with increasing sediment depth while one- and two-nitrogen-bearing molecules increased, resulting in a higher similarity of both sample types in the deep sediment. In summary, Soxhlet extraction of sediments accessed a larger and more complex pool of organic matter than present in interstitial water DOM.

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1. INTRODUCTION

Organic matter in marine sediments is a major reservoir of reduced carbon on Earth and an important player in the

global carbon and nutrient cycle (Hedges and Keil, 1995). It is a highly complex and diverse organic mixture derived from marine and from terrestrial biological sources. Most of this organic matter is chemically altered during transport through the water column and sedimentation. Labile compounds are remineralized or modified and recalcitrant compounds accumulate in the sediment (Wakeham et al., 1997; Veuger et al., 2012). The buried organic matter reservoir is

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an important energy supply for microbes in subsurface sediments (Whitman et al., 1998; Parkes et al., 2000; D'Hondt et al., 2004; Biddle et al., 2006; Webster et al., 2006), which play an important role in biogeochemical element cycles (Kvenvolden, 1993; D'Hondt et al., 2002). The preservation mechanisms and availability of organic matter to microbes depends on molecular properties such as composition, size and structure (Weiss et al., 1991; Arnosti et al., 2011). For a better understanding of the biogeochemical processes in the sediment, knowledge of the molecular organic matter composition is a prerequisite, particularly of dissolved organic matter (DOM) which accumulates in interstitial water in the sediment as a result of particulate organic matter depolymerization. In the last decade, ultrahigh-resolution Fourier Transform Ion-Cyclotron Resonance Mass Spectrometry (FT-ICR MS) has extended the analytical window for organic matter characterization due to its capacity for resolving thousands of constituents with individual elemental compositions in complex DOM mixtures. FT-ICR MS provided insights into the sources of DOM in various environments (Kim et al., 2004; Koch et al., 2005; Dittmar and Koch, 2006; Hertkorn et al., 2006; Tremblay et al., 2007; Reemtsma et al., 2008; Schmidt et al., 2009; Bhatia et al., 2010; D'Andrilli et al., 2010; Lechtenfeld et al., 2013; Roth et al., 2013) and it revealed transformation of DOM related to microbial processes (Kim et al., 2006; Longnecker and Kujawinski, 2011; Schmidt et al., 2011), fungal degradation (Grinhut et al., 2011), and photochemical alteration (Kujawinski et al., 2004; Gonsior et al., 2009).

This study exploits FT-ICR MS for the characterization of interstitial water DOM (IW-DOM) and the water extractable sedimentary organic matter fraction of a 8.75-m-long sediment core from the Black Sea. IW-DOM was extracted with Rhizon samplers (Seeberg-Elverfeldt et al., 2005) from a sediment depth of down to 6 m below seafloor and compared to the organic matter (fraction $<0.4 \mu\text{M}$) that is extractable with hot water in a Soxhlet apparatus (water extractable organic matter WE-OM). Hot water extraction of organic matter has been previously applied to determine the labile organic matter fraction in soils (e.g., Sparling et al., 1998; Ghani et al., 2003; Gregorich et al., 2003; Bu et al., 2010; Xing et al., 2010; Sarkhot et al., 2011). However, to our knowledge, it has never been utilized for the molecular characterization of organic matter in marine sediments. WE-OM is one potential source for IW-DOM. We assume that not only the IW-DOM fraction is accessible to microbial attack but also the organic matter that is attached more tightly to the sediment matrix, e.g., by sorption to mineral surfaces or binding in complexes and polymeric aggregates (Keil et al., 1994; Arnarson and Keil, 2005). Conceptually, we expect this organic matter fraction to be relatively concentrated in WE-OM of marine sediments as it has been shown for soils before (Curtin et al., 2011). Hence, analysis of this pool will expand the information regarding microbially relevant organic constituents in marine sediments. Furthermore, aqueous Soxhlet extraction is a promising approach to obtain information about the DOM pool when the interstitial water volume is not sufficient for FT-ICR MS analysis,

e.g., in clay-rich sediments or consolidated sediment from great depths. It has been successfully applied for the extraction of low-molecular-weight organic acids from coal, sand- and mudstones as potential feedstock for the deep biosphere (Vieth et al., 2008).

The main goals of this study were to examine (i) the portion of “dissolved” organic matter that can be obtained by Rhizon *vs.* Soxhlet extraction; (ii) the changes in the organic matter composition related to burial depth, geochemical conditions, lithology, and provenance of the sediment; (iii) the differences in molecular composition between IW-DOM and WE-OM in corresponding samples.

2. MATERIAL AND METHODS

2.1. Sampling

Samples were taken during FS Meteor Expedition M84-1 at GeoB Station 15105 in February 2011 in the Black Sea. A gravity core and a multicore were retrieved from 1266 m water depth at latitude $41^{\circ}31'71''\text{N}$ and longitude $30^{\circ}53'07''\text{E}$. Interstitial water and sediment samples were taken from one depth of the multicore (10–12 cm) and three different depths of the gravity core (147–162, 420–435, 596–613 cm) representing different stratigraphic units. Interstitial water was sampled with Rhizons (Eijkelpamp, pore size $0.1 \mu\text{m}$). Rhizon samplers were connected to 20-ml syringes and interstitial water was sampled by applying vacuum (duration of sampling: 4–6 h). Aliquots of the interstitial water were taken for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) analyses and stored at -20°C in the dark. The main fraction of the interstitial water was stored under N_2 atmosphere at $+4^{\circ}\text{C}$ in the dark until further processing on board. Sediment was sampled in selected intervals of the open core and stored at -20°C in the dark until further processing in the home laboratory.

2.2. Soxhlet extraction of sediments

Sediments were homogenized and cryogenically ground in a cryomill (Retsch, Cryomill, Haan) cooled with liquid nitrogen. Subsequently, around 25 g of the wet sediment (including interstitial water DOM) was weighted into pre-combusted glass fiber thimbles ($30 \times 100 \text{ mm}$, Whatman) which were extracted before with distilled ultrapure water for 48 h to remove potential contaminants. 200 ml of distilled, deionized water was added to the round-bottom flask of the Soxhlet extraction unit together with boiling chips (PTFE, Roth), and the Soxhlet system was flushed with argon through a valve in round-bottom flask to create an inert atmosphere. Afterwards, the system was closed with a gas balloon that was attached to the top of the condenser unit. Extraction was carried out for 48 h in the dark to avoid photochemical reactions. After extraction, the extract solution was filtered through a GF-5 filter (Mackerey-Nagel, pore size $0.4 \mu\text{m}$) in N_2 atmosphere to avoid oxidation reactions and stored at $+4^{\circ}\text{C}$ until further preparation. Any possible effects of the different pore sizes used for Soxhlet extracts and IW-DOM on the molecular composition can be neglected due to our analytical mass

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