

Characterization of dissolved organic matter in marine pore waters by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

Frauke Schmidt,¹ Boris P. Koch,² Marcus Elvert,¹ Matthias Witt,³ Kurt Haag,⁴ Kai-Uwe Hinrichs¹

¹ Marum-Center for Marine Environmental Science, Bremen, Germany

² Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany.

³ Bruker Daltonik GmbH, Bremen, Germany.

⁴ Bruker Daltonics, Manning Park Billerica, USA

Introduction

Recently, the application of ultrahigh resolution Fourier transform ion cyclotron mass spectrometry (FT-ICR-MS) has been extended to the characterization of dissolved organic matter (DOM) in natural environments. We used FT-ICR-MS to elucidate the fate of organic matter (OM) shortly after deposition on a continental shelf. Although OM in shelf sediments plays an essential role in the global carbon cycle, sources and transformation processes within the sediment are poorly understood. In this study, we analyze for the first time small volumes of marine pore water DOM using FT-ICR-MS and compare the results to the lipid biomarker composition in particulate organic matter (POM) of the associated sediment.

Methods

50 ml of pore water was obtained from the surface sediment by rhizon sampling. DOM was extracted from the pore water and the river water by solid phase extraction (Varian, PPL). Samples were ionized by negative electrospray ionization and detected with a 9.4 T FT-ICR mass spectrometer.

Unequivocal molecular formulas were determined on the base of exact masses. Lipid biomarkers were microwave extracted with DCM/MeOH (2:1) and analyzed by GC-MS/FID for the identification and quantification of the compounds.

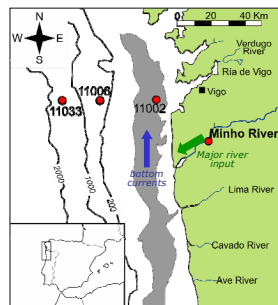


Figure 2. Sampling locations at the Galician shelf. The mid-shelf mudbelt (gray area) consists of fine grained, TOC-rich material.

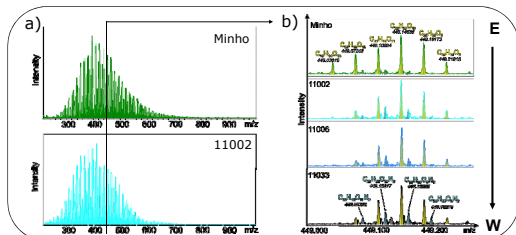


Figure 1. a) FT-ICR-MS spectrum of the Minho River and the mudbelt sample (11002) b) FT-ICR-MS spectrum of the transect samples at 449 m/z. Marine pore waters show a decrease in pure CHO-compounds and the appearance of N-containing formulas in the analytical window.

Results

We identified distinct molecular changes from the river to the pore water DOM and linked them to either source variations or transformation processes.

River DOM:

- High O/C and low H/C values (Fig. 3b)
- ↳ source signal: higher complexity and oxygenation of terrestrial OM

Pore water DOM:

- Higher abundance of N-containing molecules and compounds with lower m/z (Fig. 1)
- ↳ source signal
- Progressive loss of fulvic acids and first appearance of compounds with high H/C ratios (Fig. 3a) along the transect
- ↳ source signal

- Weighted average m/z & DBE compared to the marine and river water column (Fig. 3b)
- ↳ transformation of DOM induced by a higher microbial activity in the sediment

Within the pore water DOM the transformation strength seemed to be linked to sediment properties (e.g. grain size, TOC (data not shown)) and, therefore, potential substrate for microbes.

Contrariwise **POM** shows a decrease of terrestrial markers (lignin) and a higher degradation along the transect (Fig.4)

- ↳ Lipids in POM represent a more stable organic matter pool and degradation is a factor of the residence time

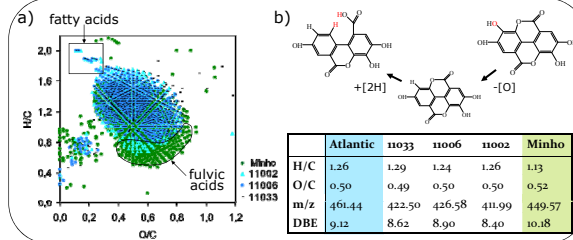


Figure 3. a) Van Krevelen diagram of all identified CHO-compounds ($200 < m/z < 600$, $ppm < 0.5$). The loss of terrestrial fulvic acids and the appearance of fatty acids along the transect results in a shift to higher H/C and lower O/C ratios. b) Weighted average molecular element ratios, m/z and double bond equivalents (DBE = sum of rings + double bonds) along the transect. Artificial molecules demonstrate the change in the molecular element ratios.

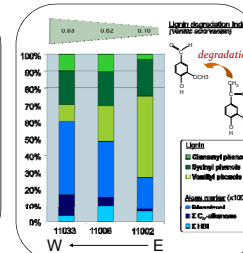


Figure 4. Relative contributions of algae markers and lignin to the POM in the marine sediment. During degradation vanillin is transformed into vanillic acid.

ASMS 2008, Poster TPD 105

Summary

➤ The molecular compositions of DOM in marine sediment pore water and of river DOM was determined by FT-ICR-MS.

➤ Molecular variations in DOM could either be linked to a change in source (O/C, H/C) or to transformation processes (m/z, DBE) within the sediment.

➤ At least a certain proportion of the analyzed DOM represents a rather labile pool, whereas the majority of lipids in POM is more stable and probably preserved in the sediment; degradation of lipids becomes more important during longer transport and residence times.

Conclusions

The study demonstrates that FT-ICR-MS is able to resolve the molecular composition of DOM, extracted from sediment pore water even in a volume as small as 50 ml. The observed variations can be linked to environmental processes and are an important contribution to the basic understanding of the organic matter cycle at continental shelves.