

Characterization of Dissolved Organic Matter in Marine Pore Waters by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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. 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 analysed by GC-MS/FID for the identification and quantification of the compounds.

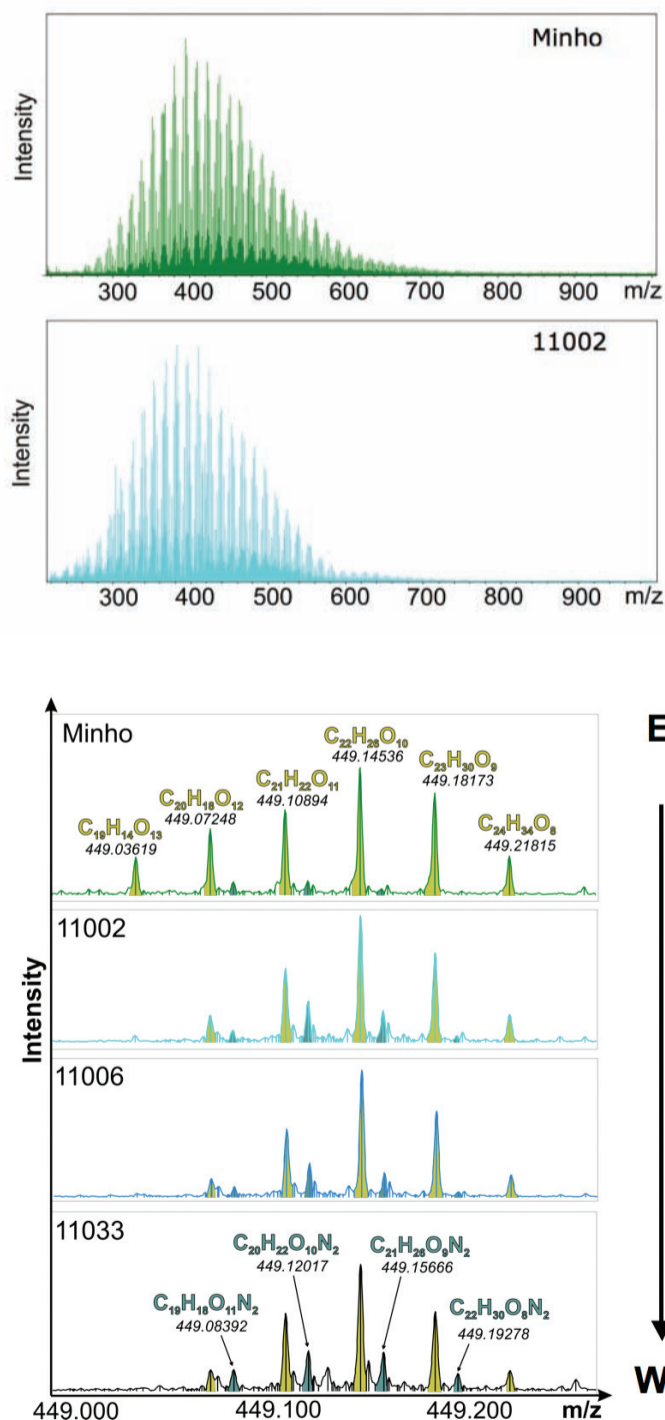


Figure 1. a) FT-ICR-MS spectrum of the Minho River and the mudbelt sample (11002) b) FT-ICR-MS spectrum of the transect samples at 449 m/z. Marine pore waters show a decrease in pure CHO-compounds and the appearance of N-containing formulas in the analytical window.

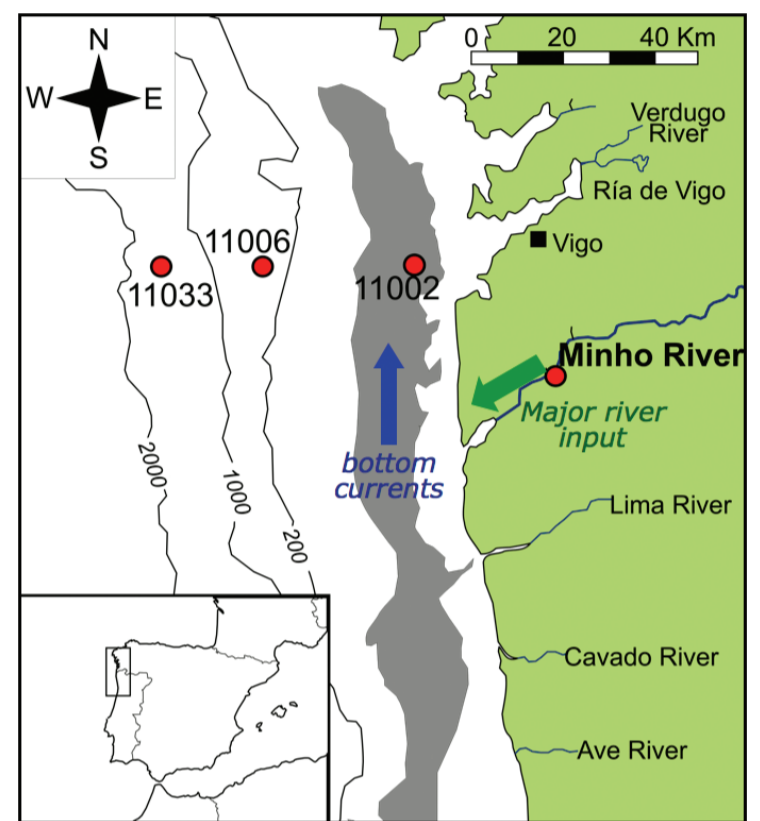


Figure 2. Sampling locations at the Galician shelf. The mid-shelf mudbelt (gray area) consists of fine grained, TOC-rich material.

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

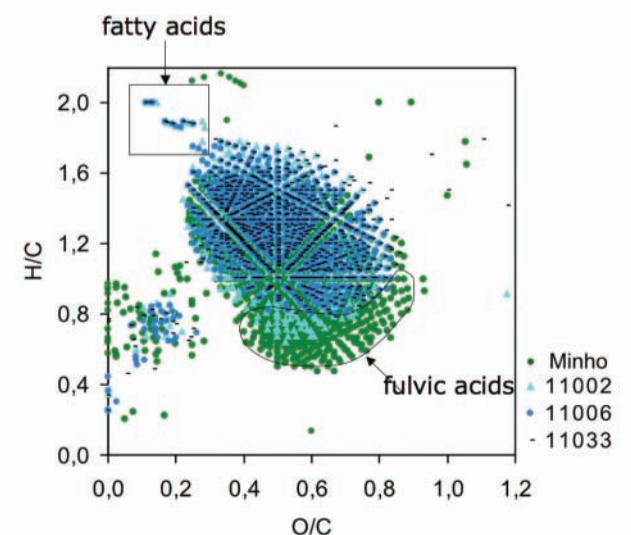


Figure 3. Van Krevelen diagram of all identified CHO-compounds ($200 < m/z < 600$, mass tolerance < 0.5 ppm). The loss of terrestrial fulvic acids and the appearance of fatty acids along the transect results in a shift to higher H/C and lower O/C ratios.

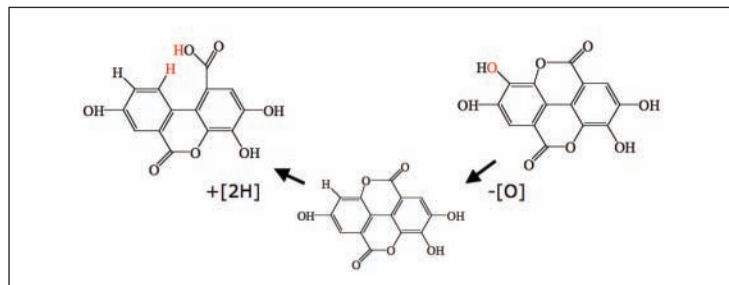


Figure 4: Artificial molecules demonstrate the change in the molecular element ratios.

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

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.

	Atlantic	11033	11006	11002	Minho
H/C	1.26	1.29	1.24	1.26	1.13
O/C	0.50	0.49	0.50	0.50	0.52
m/z	461.44	422.50	426.58	411.99	449.57
DBE	9.12	8.62	8.90	8.40	10.18

Table 1: Weighted average molecular element ratios, m/z and double bond equivalents (DBE = sum of rings + double bonds) along the transect.

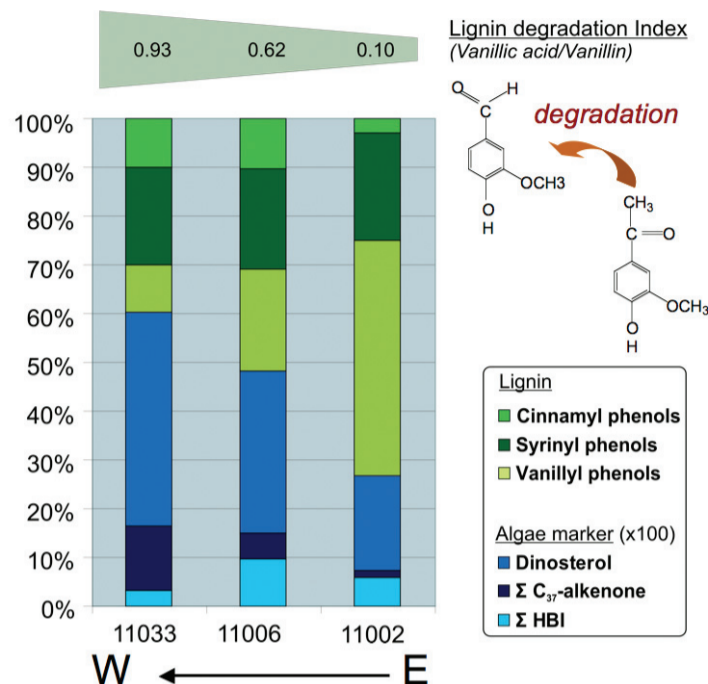


Figure 5: Relative contributions of algae markers and lignin to the POM in the marine sediment. During degradation vanillin is transformed into vanillic acid.

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Autoflush System Helps Solve Sensor Fouling Problems in the Paper Industry

Process Instruments (UK) has flushed away the problems of sensor fouling in the paper industry with a new autoflush system. Paper mills face the problem of online instruments being plagued with fouling problems. This means having to deal with a build up of fibres, particles and chemical deposits on instrument sensors.

To ensure smooth running of mill processes all this build up must be removed, which wastes considerable time and resources on cleaning and maintenance. Process Instruments has introduced an autoflush system to help sensors to stay clean without user interference. By flushing the sensor with fresh water at user defined intervals, the need for cleaning is greatly reduced and therefore overall productivity in the mill is increased.

Dr Craig Stracey of Process Instruments said: "We were constantly getting customers from paper mills telling us of the problems of sensor fouling and what a drain this was on their resources. "With our extensive experience within the industry and working closely with customers we were able to develop an autoflush system to provide a solution to these problems and enhance our existing instrumentation within the paper industry. The autoflush system continues to provide a good service to the mills we have already installed the system in and we expect it to attract new customers with similar problems."

The autoflush is suitable for use with any Process Instruments' pH, ORP, Chlorine, Ozone or Chlorine Dioxide sensors and can be customised to deal with specific problems that any mill may be experiencing. The innovative and flexible CRIUS electronics are featured within the system, which means if the autoflush needs maintaining or calibrating it can send an alarm text message or allow remote access via the internet and its GSM/GPRS modem.

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New Process Information Note for Pharmaceutical Industry

Analytical Technology (UK) announces the availability of a new technical note entitled 'Calibration of Dissolved Ozone Monitors on Ultra Pure Water Loops'. The free of charge paper, available via email on sales@atiuk.com, discusses the use of ozone for disinfection and the importance of calibration accuracy in monitors measuring dissolved ozone for pharmaceutical grade water.

There has been a significant increase in the use of ozone for the disinfection of ultra pure water systems in the pharmaceutical and medical industries. Ozone is commonly used for microbial disinfection during the sanitisation of pharmaceutical grade water which is present in process systems such as washers, autoclaves and secondary water purification systems. Analytical Technology's new application note illustrates the importance of monitoring levels of dissolved ozone at various points in the water network in order to ensure that adequate ozone levels are present during sanitisation.



Reader Reply Card no 89

New Water Quality Panel for Continuous Online Monitoring of Drinking Water Applications in Network Monitoring and Protection of Supply



Specialist electrochemical sensor manufacturer **Analytical Technology (ATI)** announces the availability of its innovative Q45WQ Water Quality Panel. This flexible system allows constant on-line monitoring of any remaining disinfectant and up to 6 other parameters in water distribution systems and moveable water treatment facilities. Without the need for expensive chemicals, reagents or buffers, the Q45WQ Water Quality Panel can be used to identify possible contaminants in the water supply, providing reliable measurements of finished water quality.

Disinfection of water is a major public health concern and it is essential to reinforce protection against microbial contaminants.

In Europe, strict regulations have been employed by the Brussels Commission to limit the amount of micro-organisms and chemical substances permitted in water. The Surface Water Treatment Rule (SWTR) adopted by the US Environmental Protection Agency (EPA) also regulates turbidity performance criteria and monitoring requirements. Analytical Technology's Q45WQ Water Quality Panel ensures that levels of disinfectant are in compliance with these legislations.

Many water companies have concerns about the possibility of deliberate contamination of the water supply. Work carried out by the US EPA (reference and report available on request) has shown that simultaneous monitoring of common water quality parameters can be used to 'fingerprint' a water supply. Many common toxic contaminants cause spikes in the data from monitors such as conductivity, pH, ORP, chlorine etc.

This new panel is capable of monitoring a number of these key parameters. A reagentless monitor measures residual chlorine. An LED or white light based turbidity monitor can cover ranges from 0-0.4NTU all the way up to 4000 NTU. The sensor is stable, offering self-adjusting electronic zero to monitor turbidity with an extensive range. Conductivity is measured by a 4 electrode sensors to cover a wide conductivity range of measurement without the need for multiple sensors. The Q45WQ Water Quality Panel is capable of offering particle count data ranges from 2-400 microns. It also can provide pH data ranges from 0-14 and ORP data between -1000 to +2000 mV.. A single combination ion selective electrode is used to measure fluoride ranges from 1000 PPM down to 0.1 PPM. Meanwhile, a rebuildable cartridge style membraned sensor is applied to measure dissolved oxygen ranges from 0-20 PPM. In addition, the panel can monitor the level of inlet pressure from 0 to 200 PSIG and sample flow rate between 0-30 GPH.

Reader Reply Card no 90

Measuring Oil/Grease Levels in Wastewater for Compliance with Permit Requirements

Determining total oil/grease levels to ensure compliance with governmental permit requirements for discharging wastewater is a worldwide problem facing numerous industries. To ensure compliance with regulations and avoid fines for exceeding permit discharge levels, more frequent wastewater measurements are necessary to determine the total oil/grease concentration. **Wilks Enterprise** (USA) manufactures portable infrared analyzers that are specifically designed for easy, on-site measurement of the oil/grease concentration.

With the InfraCal TOG/TPH Analyzer, Model HATR-T2 or the Model CVH – depending on the solvent selected for the extraction process – on-site measurement of total oil/grease concentration in the wastewater is easily and accurately determined in 10-15 minutes – including extraction process. Measurement data obtained with the Model HATR-T2 correlates to EPA Method 1664 and with the Model CVH to ASTM Method D 7066-04.

The InfraCal Analyzers currently being used for analyzing produced water on offshore oil platforms, monitoring refinery or industrial plant wastewater effluents, as well as measuring fats, oils, and greases (FOG) discharge levels into treatment centers.



Reader Reply Card no 93

Dispose of Your Used Cuvettes



Hach Lange (UK) provides a quick and easy way to dispose of your used cuvettes. From standard to high volume service. We also provide an emergency service for when speed is of the essence.

The HACH LANGE Recycling Centre is located at the company's European headquarters in Germany. The Recycling Centre facilitates recovery of toxic materials from HACH LANGE reagent tubes including, for example, COD tubes from which Mercury, Silver and Chromium are recovered. Over 70% of returned materials are either re-used or recycled.

Each of the recycling services offered by HACH LANGE includes: Pre-notification of the EA, the carrier and the waste producer within the 3 day collection period; Collection and transportation of used reagents with licensed carrier; Storage of waste at EA licensed transfer station; Documentation of waste by producer and summary statement sent to EA; Re-packing waste into UN approved cartons, palletising and storage by licensed staff; Preparation of transfrontier shipment paperwork in accordance with EA requirements when sufficient quantity collected for transfer to recycling centre; Transportation to the HACH LANGE European Recycling Centre; Paperwork sent to EA; Unpacking, sorting, recycling, re-use or treatment of waste; Certificate of recycling issued to customer.

Reader Reply Card no 94

New Electrodes Meet the Latest Environmental Compliance Standards

Mettler Toledo (UK) is proud to be the first manufacturer to bring to market RoHS (Restriction of Hazardous Substances in electrical and electronic equipment) and WEEE (Waste Electrical and Electronic Equipment) compliant electrodes.

These environmentally-friendly electrodes are ideal for nearly all applications such as pharmaceutical samples, chemicals, pure water, cosmetics and food. They are free of lead, mercury and other hazardous substances prohibited under RoHS guidelines, making them easier to dispose of at the end of their life cycle.

One of our new electrodes is the InLab® Power Pro which can be sterilised by autoclave. Thanks to the internal pressure in the reference system the sensor can easily take the external pressure from the autoclave. In addition, the rugged MultiPin™ head withstands the high temperatures of numerous sterilisation cycles.

Reader Reply Card no 91

New Data Loggers for Multi-Parameter Environmental Logging

Halma Water Management (UK) has introduced two data loggers specifically designed for multi-parameter environmental logging applications in locations such as rivers, tanks, reservoirs, pipes and open channels.

Each logger is capable of monitoring a wide range of applications including open channel level and flow, sewer overflow, rainfall, pump usage and network pressure devices.

The Vista Plus is a manual download logger with advanced specifications, a local display, multiple inputs and PDA/PC software compatibility.

The Octopus logger features multiple telemetry options with GSM and PSTN Landline, together with a switch output to drive additional equipment such as samplers to extend applications.

Rugged and fully submersible with a five year battery life, both units combine 20 years of application experience at Hydreka S.A. with the unique data logging hardware expertise of Radcom Technologies.

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