CHARACTERISATION OF ORGANIC MATTER IN SEDIMENTS FROM THE WADDEN SEA OF THE GERMAN BIGHT

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Introduction

The German Wadden Sea is a highly dynamic intertidal system with important transport, recycling, degradation and accumulation of organic matter. Settling particles in intertidal areas are resuspended several times before ultimate sedimentation (e. g. REINECK, 1980). Mixing also takes place inside the sediments by the activities of burrowing animals. Most of the early transformation and degradation processes of organic matter in the intertidal sediments are mediated by (micro-)organisms.

In NW Germany the Holocene sedimentary sequences are strongly influenced by relative sea-level fluctuations due to climatic changes. Marine sediments were deposited on 'basal' peat which had formed on Pleistocene sands. Later, during times of moderate sea-level rise and temporary regressions, peat grew relatively fast and is now intercalated with marine sediments. Therefore, sediments of the German tidal flats show a complex structure and are a composite of sand, mud and organic matter of different origins.

The aim of our study is to investigate the lipid composition of cored sediments with organic geochemical methods. On the basis of the distribution of biomarkers like *n*-alkanes, *n*-fatty acids, steroids and triterpenoids we want to distinguish different sources of organic matter like marine algae, terrestrial plants and eroded peat from the intercalated peat layers which play an important role for the composition of organic matter in the Wadden Sea sediments. Endobenthic organisms like algae, protozoa and bacteria are additional sources of sedimentary organic matter (e. g. HARVEY & MACKO, 1997). In the past, similar work was restricted to sediment layers extending to a depth of 90 cm (VOLKMAN *et al*., 2000).

Sample material

For our study, we drilled three vibrocores to a maximum depth of 6 m in the backbarrier tidal flat of Spiekeroog Island, NW Germany. The cores were taken from a sand flat, a mud flat and a mixed sand/mud flat (Fig. 1).

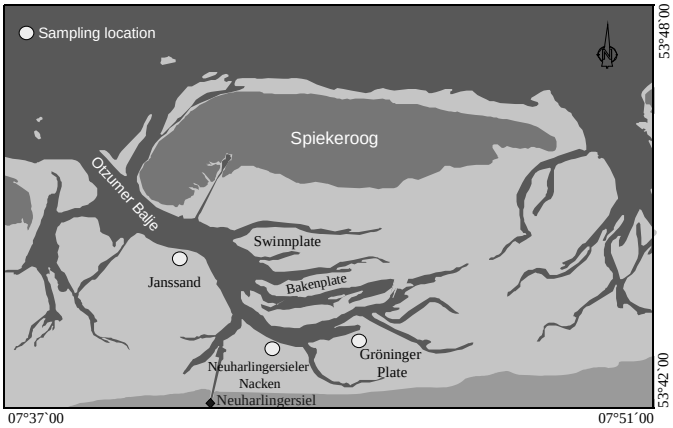

Fig. 1. Sampling locations in the backbarrier tidal flat of Spiekeroog island (NW Germany).

The vibrocore from the mud flat on the Neuharlingersieler Nacken had a length of 450 cm. Preliminary stratigraphical investigation of this core recognised the transition from tidal flat sediments to a fossil salt marsh at a depth of 300 cm. Biomarker distributions are used to illustrate the depositional changes at this site during the last approximately 3000 years. Surface sample (0-2 cm) were taken separately at all sampling stations.

The vibrocores were divided into 20 cm thick slices from 10 cm core depth downwards. Aliquots of the samples were freeze-dried, sieved (<2 mm) to remove macrofauna, shells etc., and ground before extraction. The remaining wet sediment was squeezed over a 0.4 µm polycarbonate membrane by centrifugation using teflon inserts for the centrifuge tubes similar to pore water sampling described by SAAGER *et al*. (1990).

Methods

Sediment and pore water samples

Total carbon and inorganic carbon were determined by combustion and release carbon dioxide measurement, respectively. The organic carbon content was calculated as the difference between these two values.

Salinity and the concentration of sulfate were determined by a Dionex ion chromatograph on an ion exchange column.

Extraction of sediment samples

The freeze-dried sediment (50 g) was hydrolysed under reflux and inert gas for 4h with 5% KOH solution (methanol/water, 4:1, v/v). After filtration over a membrane filter (0.45 µm) the filtrate was acidified with 2 N HCl to pH 4-5 and the residue ultrasonically extracted with a solvent mixture of dichloromethane/methanol (99:1, v/v). The aqueous phase was reextracted eight times in a separator funnel. All combined organic extracts were dried over anhydrous sodium sulfate, evaporated to dryness and stored at -20°C. Before column separation the *n*-hexane-insoluble compounds were removed by addition of an excess of *n*-hexane to the total extract dissolved in a small amount of dichloromethane. Furthermore, a mixture of internal standards (squalane, 0.1 mg/ml; erucic acid, 1 mg/ml; d_{10}-anthracene, 0.1 mg/ml; 5α-Androstan-3β-ol, 0.6 mg/ml) was added.

Column chromatographic separation

The total extract was separated on a silica gel column (16 g silica 100, 63-200 µm, dried at 180°C for 2 h and d esactivated with 5% H_2O) into three fractions by elution with the following solvents: (1) 40 ml *n*-hexane (aliphatic hydrocarbons); (2) 60 ml 10% dichloromethane in *n*-hexane (aromatic hydrocarbons); (3) 80 ml 10% methanol in dichloromethane (heterocomponents). All fractions were evaporated to dryness and stored at -20°C.

Transesterification, gas chromatography (GC-FID) and gas chromatography-mass spectrometry (GC-MS)

Aliquots of the heterocomponent fraction were transformed into their trimethylsilyl (TMS) ester derivatives using N-methyl-N-trimethylsilyltrifluoroacetamide. The TMS esters were analysed by GC-FID on a DB-5 column (30 m x 0.25 mm, 0.25 µm film thickness) and GC-MS using a Finnigan MAT SSQ 710B mass spectrometer. Double bond positions of the unsaturated fatty acids were tentatively assigned by comparison with retention times of standards and according to the relative elution order given by NICHOLS *et al*. (1989).

Results and discussion

In the Neuharlingersieler Nacken sediments, the pore-water sulfate concentartion decreases from 33 mmol/l at the surface to 0.7 mmol/l at the bottom. At a depth of 240 cm the sulfate content passes through a maximum (11.8 mmol/l). The chloride concentration decreases from 510 mmol/l at 20 cm depth to 400 mmol/l at the bottom of the core. Only at the surface a higher chloride concentration (630 mmol/l) was determined and ascribed to water evaporation at low tide.

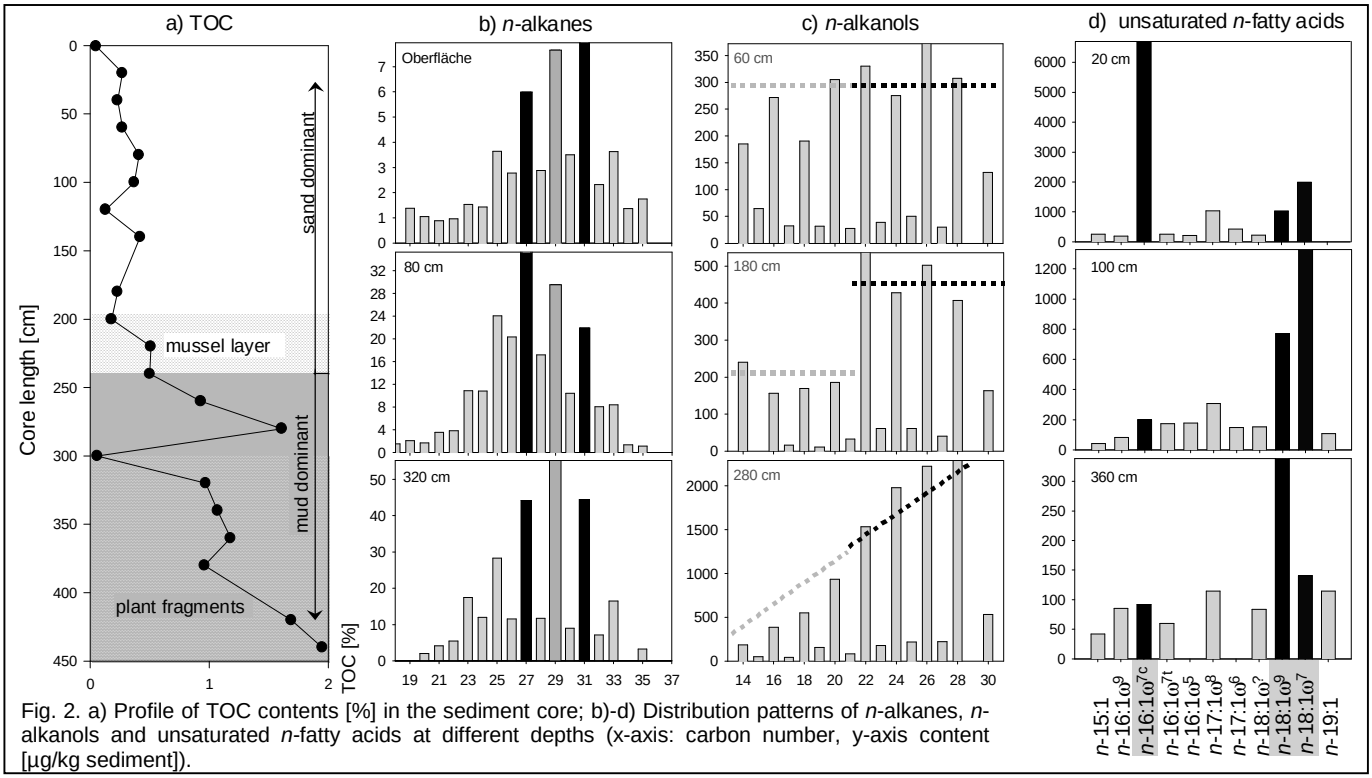

Fig. 2. a) Profile of TOC contents [%] in the sediment core; b)-d) Distribution patterns of *n*-alkanes, *n*-alkanols and unsaturated *n*-fatty acids at different depths (x-axis: carbon number, y-axis content [µg/kg sediment]).

Lithologic inspection recognised sand-dominated layers from the core top to a depth of 235 cm. Below this depth mud-dominated layers occur. These muds are homogeneous with intercalations of thin sand layers. Occasional plant stems and leaves were recognised in the mud-rich layers. From 200 cm to 235 cm depth mussel shells are common.

Our TOC data confirm the results of the lithologic inspections. Down to a depth of 240 cm TOC values were very low (between 0.1 and 0.5% dry weight). In the deeper section TOC values increase to nearly 2% with the exception of a single low value of 0.1% at 300 cm depth (Fig. 2a). The total lipid contents of nearly all detected compound classes show a depth trend almost parallel to the TOC profile.

All *n*-alkane distribution patterns exhibit the typical odd-over-even carbon number predominance of land plant waxeswith maxima at the C_{27}, C_{29} and C_{31} long-chain homologues (Fig. 2b). In most cases the C_{29} *n*-alkane is the most abundant homologue, whereas the ratio between the C_{27} and C_{31} *n*-alkanes varies. In several layers (260 cm, 280 cm, 420 cm) the C_{24} *n*-alkane is particulary enriched. The distribution patterns are characteristic of reed (*Phragmites australis*) peats (Wöstmann, unpublished results).

n-Alkanols occur with a strong even-over-odd carbon number predominance. Three types of distribution patterns were observed (Fig. 2c). They are different concerning the ratio between short- (C_{14}-C_{21}) and long-chain (C_{22}-C_{30}) alkanols.

Fatty acids are the dominant compounds in all sediment samples, and they exhibit the typical even-over-odd carbon number predominance of this compound class. Saturated and unsaturated *n*-fatty acids, *iso*- and *anteiso*-fatty acids and ω-hydroxy fatty acids were detected. Among the unsaturated *n*-fatty acids the maximum of the distribution patterns varied between $C_{16:1\omega7}$, $C_{18:1\omega9}$ and $C_{18:1\omega7}$ (Fig. 2d). Different from the others compounds, the unsaturated fatty acids decrease in their total amounts with increasing depth.

In all samples the major sterol is 24-ethylcholest-5-en-3β-ol (C_{29}). The relation between all detected C_{27}, C_{28} and C_{29} Sterols was investigated with the result that the proportion of C_{29} sterols increases with increasing depth.

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