Organic matter mineralization and the effects of petroleum pollution in a shallow-marine sediment - a case study from Århus Bugt, Denmark

JØRGEN A. BOJESEN-KOEFOED

Bojesen-Koefoed, J. A. 1995: Organic matter mineralization and the effects of petroleum pollution in a shallow-marine sediment - a case study from Århus Bugt, Denmark, *Nor. geol. unders. Bull. 430*, 117-127.

Organic geochemical analyses of core samples from the Station 6 site in Århus Bugt, Denmark, show systematic changes with depth below the sediment-water interface. Over the upper 6-7 centimetres, corresponding to the deposits of the last 25-30 years, mineralization of organic matter is manifest in decreasing TOC, increasing C/N and Hydrogen Index, changes in pyrolysate compositions, and in fatty acid distributions. Calculated losses of organic carbon due to microbial sulphate reduction show a close correspondence to measured values, supporting the important role of this process in organic matter mineralization. Below 6-7 cm, steady state sedimentation apparently has been disturbed, probably due to the excavation of a nearby navigation channel in the 1960-ties. Analyses of saturated hydrocarbons, including triterpane and sterane biological markers, point to a mixed origin for this group of compounds, comprising a dominant contribution from anthropogenic petroleum pollution, and a minor contribution from indigenous organic matter.

Jørgen A. Bojesen-Koefoed, GEUS, Geological Survey of Denmark and Greenland, 8 Thoravej, DK-2400 Copenhagen NV, Denmark.

Introduction

Since the early work by C. G. J. Petersen and coworkers (Petersen & Jensen 1911, Petersen 1913, Blegvad 1914, Jensen 1914), which focused on the origin of 'detritus' and its importance in animal nourishment, numerous papers have addressed various aspects of organic matter deposition and degradation in the marine environment, and have introduced several kinetic models (Berner 1964, Jørgensen 1979, Berner 1980, Westrich & Berner 1984, Middelburg 1989, Wiesner et al. 1990, Boudreau & Ruddick 1991).

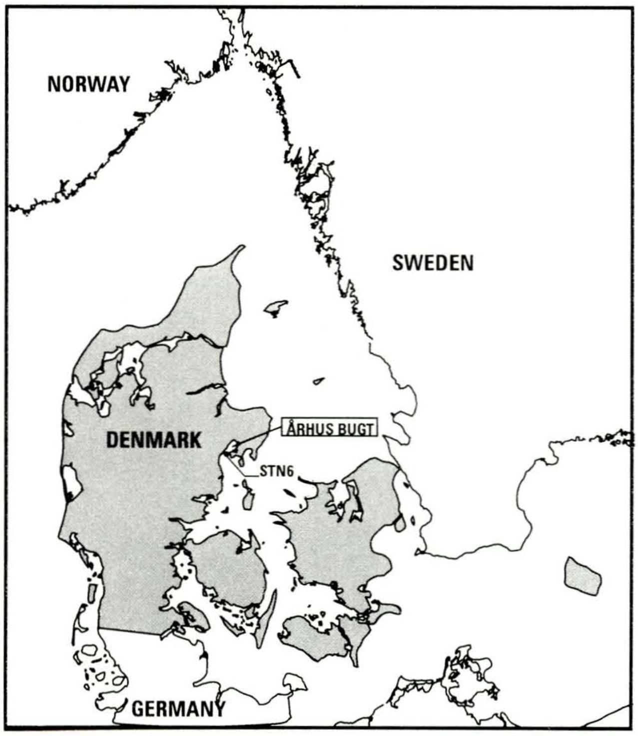

Fig. 1. Location map showing position of the Station 6 site 'STN6'

The processes of early diagenesis of sedimentary organic matter are generally microbially mediated (e.g. Fenchel & Jørgensen 1977). In coastal marine muddy sediments, the presence of oxygen is normally restricted to the upper few millimetres of sediment, and below this zone, degradation of organic matter is accomplished through the action of a community of anaerobic heterotrophic bacteria, which utilize electron acceptors other than oxygen (Fenchel & Jørgensen 1977, Fenchel & Blackburn 1979, Laanbroek & Veldkamp 1982, Reeburgh 1983, Henrichs & Reeburgh 1987). Among these anaerobic processes, microbial sulphate reduction is a very important terminal step in the mineralization of organic matter, and the process is probably responsible for approximately 50% of the oxidation of organic carbon in shallow-marine sediments (Jørgensen 1982). Sulphate is very abundant in average seawater (approximately 2.7 gkg^{-1} at a Salinity of 35 per mil), and the total oxidising capacity of sulphate, even in aerated seawater, is estimated at 200 times the oxidising capacity of oxygen (Jørgensen 1977). Furthermore, as opposed to oxic degradation, decomposition via sulphate reduction is a comparatively long-term process, as sulphate may persist to considerable depth in the sediments.

A common feature of most studies of organic matter mineralization in the sea bed is a rather poor knowledge of the overall character of the organic matter being

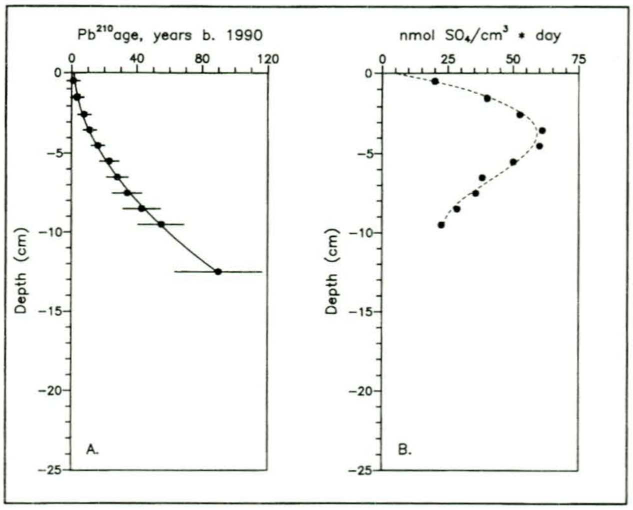

Fig. 2. A. (left) Pb^{210} dating of the Station 6 sediments (Anders Jensen, pers. comm. 1990). Note very little mixing, upper 7-8 cm roughly corresponds to the deposits of the last 25-30 years. B. (right) Microbial sulphate reduction, yearly average, calculated from the data of Jørgensen et al. (1991), see text. Broken line indicates 'best fit', average peak sulphate reduction is observed at approximately 4 cm. The depth of peak sulphate reduction intensity varies considerably with the season.

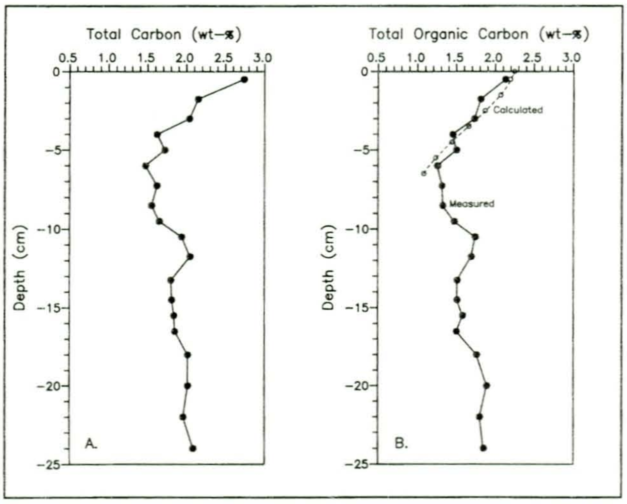

Fig. 3. A. (left) Total carbon (TC) content versus sediment depth, in weight-% (dry sediment). B. (right) Total organic carbon (TOC) content versus sediment depth, in weight-% (dry sediment), measured values (curve labelled 'Measured') and calculated from compaction data by A. Jensen (pers. comm. 1990) and sulphate reduction data of Jørgensen et al. (1991), assuming an initial value of 2.25% TOC (broken curve labelled 'Calculated'). See text for further discussion.

degraded and the changes in gross composition, which occur as a consequence of microbial attack. The present work demonstrates a number of changes in the sedimentary organic matter composition, which occur as a consequence of microbial degradation in a shallow-marine sediment. The study is based on the assumption that, provided the natural sedimentary environment has not been subjected to major disturbances, the overall degradative state of the organic matter will increase with depth.

Study location, samples and methods

The study was undertaken on samples from the 'Station 6' site, Århus Bugt, Denmark (56°09.10N, 10°19.20E: Fig. 1). The site is well sheltered from both wind and waves, and the water depth is approximately 15 metres.

Analyses were performed on horizontally sliced sediment cores obtained by means of a 'HAPS' bottom corer (Kanneworf & Nicolaisen 1973). Sediment slices were stored in airtight metal containers, frozen within a few hours of collection, and subsequently freeze dried. The methods applied include: Total Carbon (TC) and Total Organic Carbon (TOC) determinations using a Leco induction furnace; determination of C/N ratios by means of a Hewlett-Packard HP185B CHN-analyser; and Rock-Eval pyrolysis using a Delsi Rock-Eval II instrument (Espitalié et al. 1985a,b).

Organic extracts were prepared by extracting sediment with dichloromethane/methanol (93+7%) in a 'soxtec' apparatus (boiling 1h in solvent, followed by 5h rinsing). Extracts were fractionated by means of column chromatography (activated silica, Merck 100, sequential elution with n-heptane, dichloromethane and methanol), and the saturated fractions were subsequently analysed using Gas Chromatography (GC) (Hewlett-Packard 5890 GC, and 25m 0.22mm i.d. HP-1 WCOT column) and combined Gas Chromatography-Mass Spectro- metry (GC/ MS) using selected ion monitoring (SIM) (Hewlett-Packard 5890 Series II GC, 25m 0.22 i.d. HP-5 WCOT column, coupled to a Hewlett-Packard 5971A Mass Selective Detector). In one instance, GC/MS peak identification was checked by comparison with Selected Metastable Ion Monitoring (SMIM) traces obtained by from a VG-7070E Mass Spectrometer. Pyrolysis-Gas Chromatography (Py-GC) was carried out, using a custom-made pyrolysis unit coupled to a Newtronic TP96 temperature control unit and a Hewlett-Packard 5890 gas-chromatograph fitted with a 50m Chrompack WCOT column (CP-SIL-8CB, 0.22mm i.d.). The method applied is very similar, though not identical, to the method described by Horsfield (1989). Fatty acids were extracted and converted into methyl-esters, following the procedures outlined by Metcalfe et al. (1966), and analysed by GC/MS.

Results

The sediments at the Station 6 site consist of slightly sandy muds. Grain-size distributions are not available, but macroscopical examination of the individual subsamples revealed no changes in lithology with depth. The colour of the sediments graded from dark grey with an olive greenish-brownish tinge in the uppermost part of the core to dark grey/black with olive and bluish grey mottles in the deeper parts. No well-defined colour-transition was noted, but the change appeared to occur at a depth of 6-8 centimetres, coinciding with the initial occurrence of sulphide in the porewaters (B. Thamdrup,

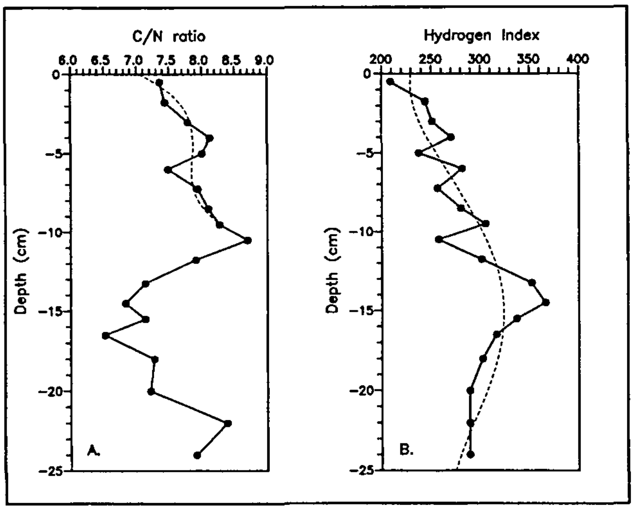

Fig. 4. A. (left) C/N ratio versus depth, broken curve indicates a tentative 'best fit'. Note the overall increasing trend over the upper part of the core. See text for further discussion. B. (right) Rock-Eval Hydrogen Index, broken curve indicates tentative 'best fit'. Note increasing trend over the upper part of the core, and trend reversal or stabilisation at greater depth. See text for further discussion.

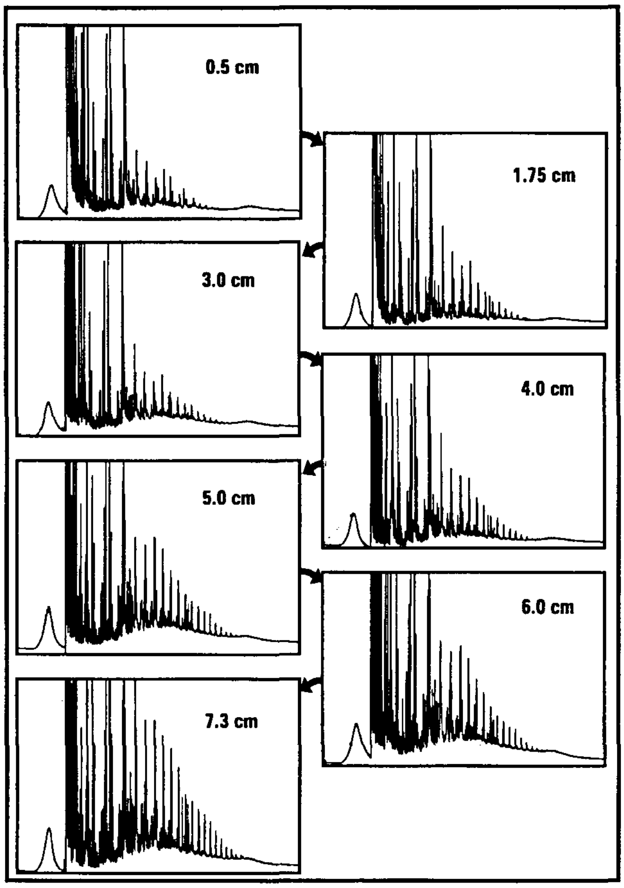

Fig. 5. Pyrolysis-gas chromatograms from analyses of samples from the upper c. 7 cm of the sequence, sample depths are posted. Note gradual changes in pyrolysate composition with increasing sediment depth. Near the sediment-water interface, pyrolysates are dominated by low molecular weight aromatic/phenolic compounds and unknown, probably functionalised, compounds (irregularly spaced tall peaks, left of centre of chromatograms). With increasing depth below the sediment-water interface, high H/C compounds like n-alkanes/alkenes become increasingly prominent (regularly spaced peaks right of centre of chromatograms). See text for further discussion.

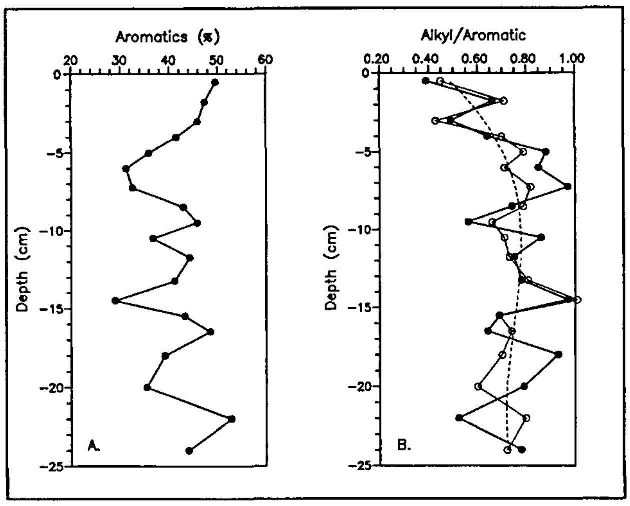

Fig. 6. A. (left) Sum of benzene, toluene, xylenes, cresols, xylenols, naphtalene, methylnaphtalenes and dimethylnaphtalenes in pyrolysates, as percentage of resolved C_{6+} fraction of pyrolysates. Note steady decrease over the upper part of the core in response to elimination of unsaturated and functionalised organic moieties with a pronounced affinity for aromatization upon pyrolysis. Random variation or perhaps a slight increase is observed in the deeper portion of the sediment. B. (right) Bold line, filled symbols: ratio of n-alkyl (alkanes and alkenes) to aromatic/phenolic compounds listed above, in C_{6+} fraction of pyrolysates. Fine line, open symbols: n-octene/m+p-xylene ratio, broken curve indicates tentative 'best fit'. Note increasing proportions of n-alkyl moieties with depth in the upper part of the sequence.

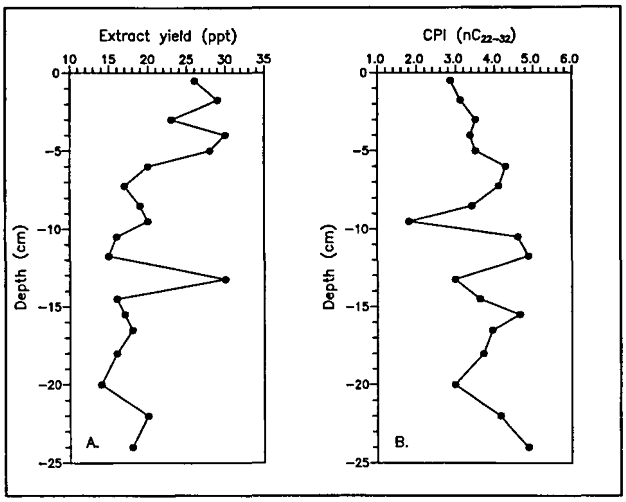

Fig. 7. A. (left) Extract yield in milligram soluble organic matter per gram organic carbon. B. (right) Carbon Preference Index (CPI), calculated for the nC_{22-32} carbon number range.

pers. comm. 1990). A strong sulphide odour was noted when the core was extruded from the liner.

Pb^{210}-dating indicates a moderate to high sediment accumulation rate (884 $gm^{-2}yr^{-1}$) and very little sediment mixing (A. Jensen, pers. comm. 1991), rendering the locality well suited for this type of study (Fig. 2a).

The bottom water oxygen concentration is low, and the benthic macrofauna is accordingly very scarce (B. Kruse, pers. comm. 1991). In situ measurements show oxygen to be exhausted within the upper 1-2 millimetres

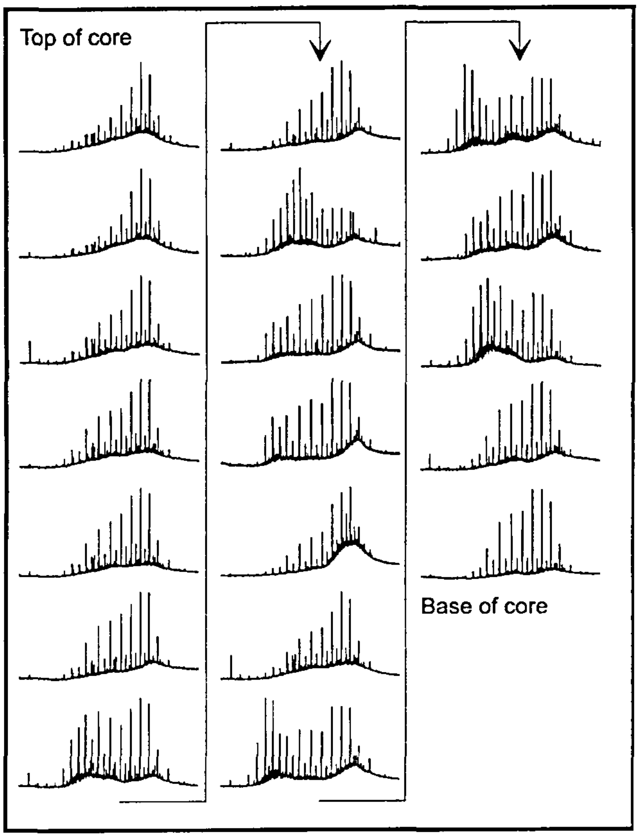

Fig. 8. Gas chromatograms of saturated extract fractions. See text for discussion.

of sediment (J. Gundersen, pers. comm. 1990).

Measurements of the rate of sulphate reduction using radioactive tracer techniques were carried out every two weeks over a ten-month period (Jørgensen et al. 1991). Both the sulphate reduction rate and the depth of peak microbial activity varies through the year. Fig. 2b shows an average sulphate reduction rate profile for the study site.

The total carbon (TC) and total organic carbon content (TOC) both display steadily decreasing trends over the upper part of the section (Figs. 3a & 3b, curve labelled 'measured'). The inorganic carbon fraction remains constant and the trend is attributed more or less exclusively to changes in organic carbon content.

C/N ratios are somewhat variable, but rather low. In the upper part of the core, an irregular increase with depth is observed, whilst in the central and basal parts, a significant decrease followed by renewed increase is observed (Fig. 4a). The hydrogen index (HI) increases significantly over the upper part of the core (Fig. 4b).

Pyrolysis-gas chromatography reveal notable changes in pyrolysate composition with depth (Fig. 5). The sum of the relative abundance of a number of aromatic and phenolic pyrolysate components in the C_{6+} pyrolysate fraction decreases markedly over the upper portion of the core (Fig. 6a). In addition, the proportion of n-alkyl moieties in the pyrolysate increases markedly with depth, as does the largest observed chain length of these compounds (Figs. 5 & 6b).

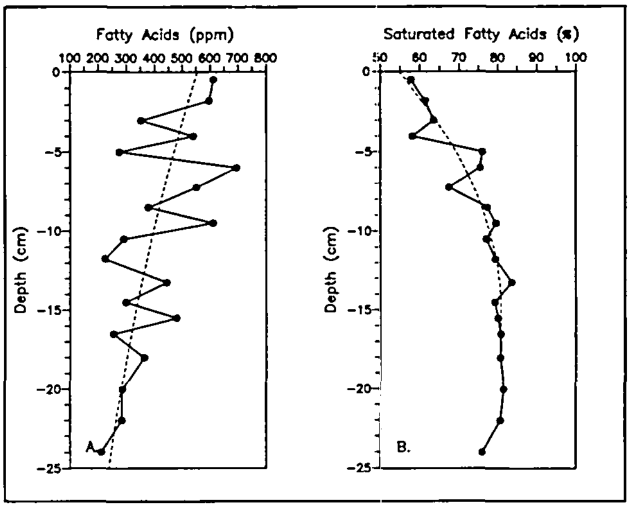

Fig. 9. A. (left) Free fatty acid yield relative to organic carbon versus depths below sediment water interface. Broken line indicates tentative 'best fit'. B. (right) Saturated fatty acids, in percent relative to total free fatty acids versus depth below sediment-water interface.

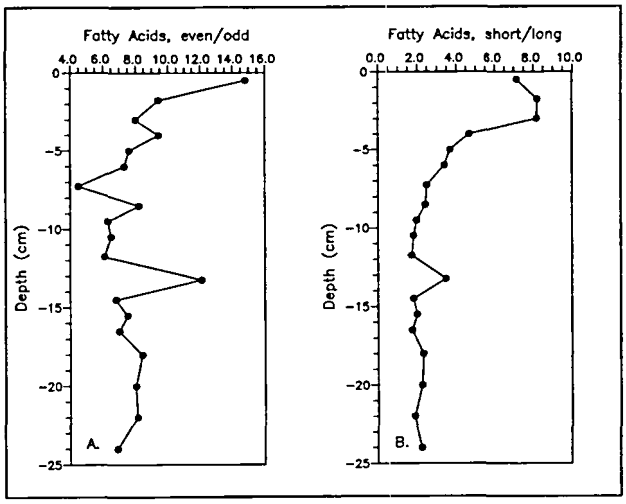

Fig. 10. A. (left) Ratio of even carbon number fatty acids to odd numbered linear fatty acids in the C_{14-19} range versus depth below sediment-water interface. B. (right) Ratio of short-chain fatty acids (C_{14-19}) to long-chain fatty acids (C_{20-28}) versus depth below sediment water interface.

Solvent extract yields are comparatively low, generally less than 30 mg per gram organic carbon, and a notable decrease is observed through the upper portion of the core (Fig. 7a). The extract yield seems to reach a stable level of 15-20 mg per gram organic carbon from a depth of c. 7 cm, although higher values are recorded at 9.5 cm and 13.25 cm. Off-trend values at these particular depths are recurring in both CPI and biomarker data (see below).

In the upper part of the core, gas chromatograms of the saturated fraction of solvent extracts show unimodal normal alkane distributions, centred around nC_{29}, having a strong preponderance of odd-numbered compounds

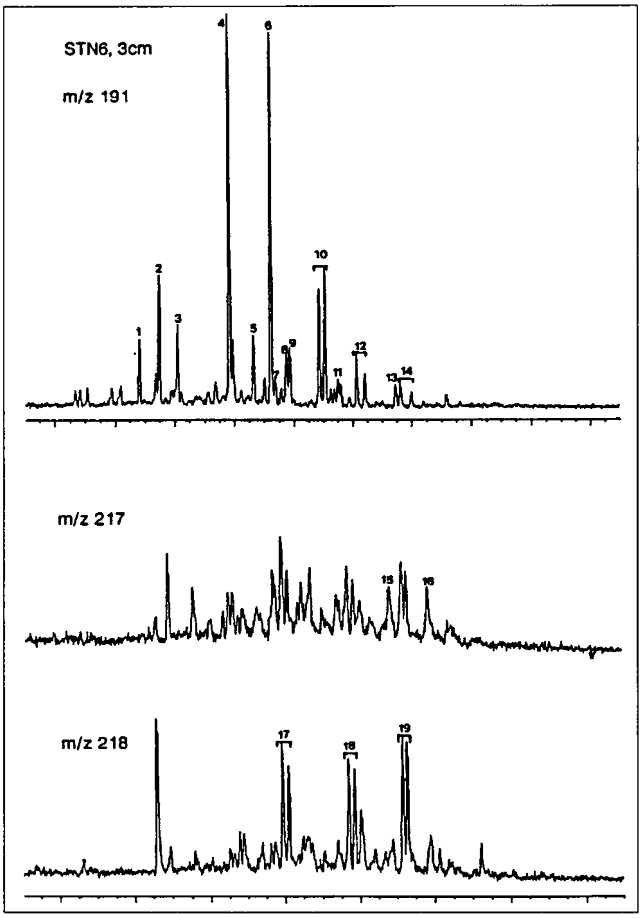

Fig. 11. Ion fragmentograms m/z 191, 217 and 218, sample STN603, 3 cm below the sediment-water interface. Peak identification: 1. Ts; 2. Tm; 3. 17β(H)-trisnorhopane; 4. norhopane; 5. normoretane; 6. hopane; 7. hop-17(21)-ene; 8. 17β(H)21β(H)-hopane; 9. moretane; 10. homohopane (22S & 22R); 11. 17β(H)21β(H)22R-homohopane; 12. bishomohopane (22S & 22R); 13. 17β(H)21β(H)22R-bishomohopane; 14. bishomohopane (22S & 22R); 15. 5α(H)14α(H)17α(H)20S-ethylcholestene; 16. 5α(H)14α(H)17α(H)20R-ethylcholestene; 17. 5α(H)14β(H)17β(H)-cholestenes (20R & 20S); 18. 5α(H)14β(H)17β(H)-methylcholestenes (20R & 20S); 19. 5α(H)14β(H)17β(H)-ethylcholestenes (20R & 20S).

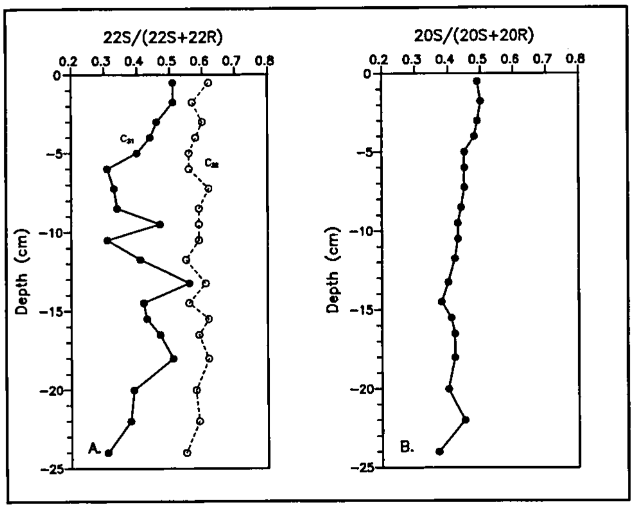

Fig. 12. A. (left) Homohopane (filled symbols, solid line, labelled 'C_{31}') and bishomohopane (open symbols, dashed line, labelled 'C32') 22S/(22S+22R) epimerization ratio. B. (rigth) C_{29}-regular sterane 20S/(20S+20R) epimerization ratio.

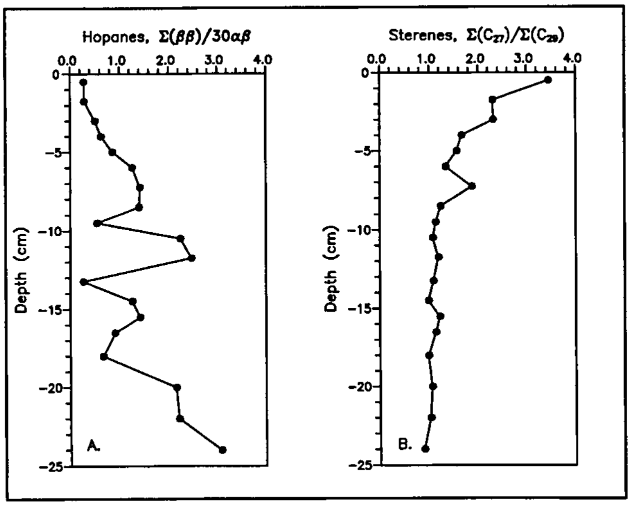

Fig. 13. A. (left) Ratio of the sum of C_{27-32} 17ß(H)21ß(H)-hopanes to 17α(H)21ß(H)-hopane. B. (right) Ratio of C_{27}-sterenes to C_{29}-sterenes as given by the m/z 215 ion fragmentogram.

and high proportions of 'Unresolved Complex Mixture' (UCM). Below a depth of c. 7 cm n-alkane distributions tend to become more variable, occasionally characterised by a higher abundance of lower carbon number compounds, less pronounced odd-number predominance, and even bimodal distributions (Fig. 8). Acyclic isoprenoids are generally scarce, and pristane and phythane can hardly be detected. A steady increase in the Carbon Preference Index, CPI, with depth (Bray & Evans 1961, Cooper & Bray 1963) is observed over the upper part of the sequence (Fig. 7b). In the deeper part a few prominent excursions towards low CPI are observed, and to some extent these may coincide with the occurence of 'anomalous' n-alkane distributions and increased extract yields. For instance at 9.5 cm (sample 9) an nC_{21}-centred n-alkane distribution is observed, coinciding with low CPI and slightly increased extract yield, and at 13.25 cm (sample 12) increased extract yield and decreased CPI coincide with a very pronounced, unresolved 'biomarker-hump' in the gas chromatogram (cfr. Figs. 7a, 7b & 8).

The amounts and distributions of fatty acids also change with depth. Although the trend is somewhat irregular, an overall decrease in total free fatty acids with depth is observed (Fig. 9a). The distribution of fatty acid types shifts towards increased proportions of saturated compounds at the expense of unsaturated compounds (Fig. 9b). Branched chain fatty acids are largely unaffected. In addition, the fatty acid distribution shifts with depth in favour of long-chain and odd-numbered compounds (Figs. 10a & 10b).

The m/z 191 ion fragmentogram reveals the presence of a series of 17α(H)21ß(H) hopanes, ranging from C_{27} to C_{34} (occasionally C_{35}), as well as a series of 17ß(H)21ß(H) hopanes. In addition, small amounts of hop-17(21)-enes may be traced (Fig. 11). Calculation of the 17α(H) 21ß(H) bishomohopane 22S/(22S+22R) epimer ratio yields values close to 0.6, suggesting that the isomerisation has reached equilibrium. Calculation of the same ratio based on 17α(H)21ß(H) homohopane yields subequilibrium values, and a notable decrease is observed over the upper part of the core. Sharp increases are noted at 9.5 cm and 13.25 cm, coinciding with increased extract yields and minimum CPI-values (Fig. 12a). In the upper part of the core, the C_{29} 14α(H)17α(H) sterane 20S/(20S+20R) epimer ratio is close to 0.5, suggesting equilibrium. Towards the base of the core, a slight, but steady decrease is noted (Fig. 12b). The ratio of the sum of the ßß-hopanes to C_{30} aß-hopane increases significantly with depth over the upper part of the sequence (Fig. 13a). In the deeper part, prominent excursions towards low values are noted at 9.5 cm and 13.25 cm, again coinciding with anomalies in other parameters (see above), and the trend is an almost perfect mirror image of the homohopane epimerization trend (cfr. Fig. 12a). The normalised distribution of C_{27-29} steranes given by the m/z 218 ion fragmentogram roughly equals 29%-33%-38%, and shows little variation through the core. Notable quantities of diasteranes are present in all samples.

The presence of small amounts of C_{27}, C_{28} and C_{29} sterenes is noted in the m/z 215 ion fragmentogram. The ratio of C_{27} to C_{29} sterenes decreases regularly through the core (Fig. 13b).

Discussion

From the preceeding section, it is clear that a number of parameters show systematic trends from the sediment-water interface to a depth of 6-7 centimetres. Below this depth, the trends tend to become irregular or absent. According to Pb^{210}-data, the sediments at 6-7 cm were laid down in the period 1965-1970, when a major power plant was constructed on the coast in the northern part of Århus Bugt, and a navigation channel was excavated in the vicinity of the study site. Since no apparent changes in lithology, except for a gradual colour-change, have been observed at 6-7 cm, it is tempting to attribute the break in a number of parameter trends to some unknown disturbance of the sedimentary environment, related to the activities mentioned above. However, it should be noted that the sediments themselves were probably not disturbed; rather, the conditions of deposition were, which is why the disturbance is not manifest in all parameters. In the following, emphasis will be placed on data from the upper part of the sequence, although samples from deeper parts of the sediment are also discussed.

The regular decrease in TOC observed over the upper part of the core may be related to organic matter mineralization. The decrease in organic carbon content due to oxidation by sulphate reduction can be estimated from the data of Jørgensen et al. (1991) combined with the sedimentation rate and compaction data of Jensen (pers. comm. 1991):

(1) The yearly average sulphate reduction in cm-intervals throughout the section is calculated (in mmole sulphate/cm^3yr) from the data of Jørgensen et al. (1991). The results have been extrapolated to cover a one-year period, which may be done without introducing serious errors, since the missing data are from the winter months when microbial activity is minimal.

(2) Residence time (in years) of organic matter in each cm-interval is calculated from the Pb^{210}-profile.

(3) Average yearly sulphate reduction rate is multiplied by the residence time to yield total mmol sulphate reduced per cm^3 sediment in each interval.

(4) Assuming a stoichiometric relationship between the amounts of carbon oxidised and sulphate reduced of 2:1, multiplication by 2 yield mmol carbon oxidised per cm^3 sediment.

(5) Recalculation from 'wet' to 'dry' sediment using the water-content data of Jensen (1991 pers. comm.) yield mmol carbon per gram dry matter. Multiplication by 12 (= molecular weight of carbon) yields mg carbon per gram dry matter.

(6) Carbon-losses through the core are summed for each cm-interval.

(7) Mg carbon lost per gram dry matter due to sulphate reduction is recalculated to wt.% TOC, using a density of solids = 2.5 g/cm^3.

(8) Assuming an initial TOC-content of 2.25 wt. %, a 'calculated' TOC-profile of the upper part of the core can be constructed by plotting (2.25% - wt% carbon lost) at the midpoint of each interval (Fig. 3b, curve labelled 'calculated'). Despite the crude approach and method of calculation, the fit of the calculated values of TOC to the measured data is surprisingly good (r=0.94, n=7), supporting a prominent role for sulphate reduction in organic matter degradation in this case. The measured TOC-trend shows a largely exponential decrease with depth, whilst the calculated trend is more linear. This may be explained by fuelling of the sulphate reduction processes by small amounts of methane, diffusing upward from deeper parts of the sediment. The occurrence of anaerobic methane oxidation is established (e.g. Devol & Ahmed 1981, Reeburgh 1983, Iversen & Jørgensen 1985), although the exact relationship to sulphate reduction remains unclear (see Skyring 1987 for discussion).

The C/N-ratio is expected to rise with increasing degradation of the sedimentary organic matter. Although the C/N-ratio trend is very irregular, the tentative 'best fit' curve shown on Fig. 4a may suggest a decreased rate of rise over the 4-6 cm depth interval. Since this interval is roughly equivalent to the zone of peak sulphate reduction, this may be explained by selective incorporation of nitrogen into the bacterial biomass (e.g. Fenchel & Harrison 1976, Fenchel & Blackburn 1979, Kristensen & Blackburn 1987), which thus contains a major part of the organic nitrogen in the sediments, while constituting but a very minor fraction of the total carbon content

(Hylleberg & Riis Vestergaard 1984). Unfortunately, no biomass data are available. The decrease observed in the central part of the core may record disturbance of the conditions of sedimentation as mentioned above. The increasing trend in the deepest part may represent a 'subfossil' analogy to the trend observed in the uppermost part of the core.

The Rock-Eval Hydrogen Index (HI) is a measure of the hydrogen relative to carbon content of the organic matter analysed, and the increasing trend observed over the upper part of the core indicates the presence of increasingly hydrogen-rich organic matter with depth. This can be explained by a combination of hydrogenation reactions (elimination of double bonds) (e.g. Tissot & Welte 1984), preferential degradation of highly functionalised organic matter such as sugars/polysaccharides (e.g. Tegelaar et al. 1989), and removal of functional groups from the sedimentary organic matter during bacterial degradation, eventually leading to a relative hydrogen enrichment in the remaining organics. Increasing proportions of C and H in sedimentary organic matter with progressive degradation was also noted by Bordovskiy (1965). Preferential removal of functional groups is well established; for instance, Huc & Durand (1974) showed that during very early diagenesis, various nitrogen-containing groups are readily eliminated, while oxygen-containing groups are largely unaffected, eventually causing relative increases in aliphatic and carboxylic compounds. Elimination of nitrogen from humic acids was reported by Brown et al. (1972), and similar effects are expected for phosphorus, which is depleted very rapidly (Hartmann et al. 1973). Early elimination of functional groups has also been demonstrated by carbon isotope studies (e.g. Galimov 1980, Schidlowski 1986). The reversal of the HI-trend in the deeper part of the core is explained by condensation reactions, which lead to decreasing HI with further decomposition of the sedimentary organic matter (Tissot & Welte 1984).

Pyrolysis-GC data support the above interpretation of Rock-Eval data. Pyrolysis of high H/C organic matter will yield pyrolysates rich in high H/C components, i.e. n-alkyl compounds, whilst organic matter rich in heteroatoms tends to yield pyrolysates rich in heteroatomic/oxidised compounds and H_2O, CO_2, NO_x, H_2S, etc. Hence, increasing proportions of n-alkyl compounds with depth point to the presence of increasingly hydrogen-rich organic matter with depth over the upper part of the core, whereas the decreasing trend in the deeper part may be indicative of condensation reactions. Although minor discrepancies between HI and Alkyl/aromatic ratio are present, e.g. at 5 cm, and the Pyroysis-GC data generally show more scatter than the Rock-Eval data, the overall increasing-decreasing depth-trends are very similar. Upon pyrolysis, aromatic components may be generated from ligno-cellulosic kerogens or from mature or oxidised kerogens (e.g. Baker 1974, Larter 1984, Horsfield 1989), but the abundance of low molecular weight aromatic moieties is also linked to the abundance of unsaturated compounds in the organic matter being pyrolysed. By heating recent marine sediments, Erdman (1961) and Mulik & Erdman (1963) showed the generation of light aromatic compounds from carotenoids and unsaturated fatty acids. Thermolytic generation of light aromatic moieties from unsaturated fatty acids via alkylcyclohexanes by heating in a sealed vessel in the presence of a catalyst was reported by Hoffmann et al. (1987). Clay may be assumed to catalyze the pyrolytic formation of aromatics from carotenoids, unsaturated lipids, sugars, certain proteins, etc. (e.g. Meuzelaar et al. 1982, Larter 1984). Hence, the decrease in pyrolysate 'aromaticity' may result from decreased abundance of unsaturated and heteroatomic components, and changes in pyrolysate composition with depth are explained in terms of preferential removal of highly functionalised organic matter and functional groups leading to the presence of increasingly hydrogen-enriched organic matter with depth over the upper part of the core. Conversely, reversal of trend in the deeper parts may be explained by selective preservation of resistant ligno-cellosic compounds, and by condensation reactions.

The decreasing extract yields are explained by preferential elimination of readily degradable low molecular weight components, leading to enrichment in resistant and less soluble organic matter types. Furthermore, insolubilization reactions may contribute to the trend observed (Leenheer & Meyers 1983, Tissot & Welte 1984). High, off-trend values recorded at 9.5 cm and 13.25 cm may record random contributions of excess soluble organic matter, perhaps derived from minor oil-spills. This interpretation is supported by other data (see below).

High CPI, unimodal, heavy-end centred n-alkane distributions are generally indicative of terrigenous lipids, and high proportions of UCM are commonly found in recent sediments close to urban areas, and represent background anthropogenic contributions of degraded petroleum (e.g. Barrick et al. 1980). Small quantities of normal alkanes are present in most biological material. In the range C_{12}-C_{36}, the distribution of n-alkanes is generally dominated by odd-numbered compounds, although this predominance may be more or less pronounced. In marine algae, the predominance is often, albeit not always, rather slight, while in epicuticular waxes of terrestrial higher plants, the predominance may be very strong (Cooper & Bray 1963, Clark & Blumer 1967, Eglinton & Hamilton 1967, Han & Calvin 1969, Tissot & Welte 1984, Lichtfouse et al. 1994). In contrast, fatty acids, primary alcohols, and aldehydes in biological tissue are almost exclusively of even carbon number, resulting from the fact that these compounds are synthesized by the organisms from acetate. Although exceptions do occur (e.g. Welte & Ebhardt 1968, Nishimura & Baker 1986, Kennicutt & Brooks 1990), organic extracts of recent sediments generally display n-alkane distributions dominated by odd-numbered compounds (e.g. Bray & Evans 1961, Clark & Blumer 1967, Hunt 1974). In contrast, crude oils in general show little or no odd-predominance. Increasing

CPI with depth may have several causes: elimination of terminal functional groups from even-numbered alkanoic acids may take place through decarboxylation reactions, which are known to occur during the degradation of amino-acids (e.g. Schlegel 1976, Frey 1988), and may lead to the accumulation of long-chain normal alkanes of odd carbon number. Decarboxylation reactions have been invoked by numerous authors as a mechanism of formation for normal alkanes in sediments (e.g. Cooper & Bray 1963, Jurg & Eisma 1964, Kvenvolden & Weiser 1967, Han & Calvin 1969, Simoneit 1974, Peake et al. 1974, Fenchel & Blackburn 1979, Tissot & Welte 1984, Lichtfouse & Collister 1992). Moreover, this interpretation conforms both to the observations of Leenheer & Meyers (1983), who showed increasing absolute concentrations of hydrocarbons with depth in recent sediments, and to the results of Foree & MacCarty (1970), indicating low lipid utilisation among the sulphate-reducing community. Increasing CPI with depth in recent sediments was also noted by Wade & Quinn (1979), and by McCaffrey et al. (1991). Wade & Quinn (1979) attributed the phenomenon to gradually increasing anthropogenic input of hydrocarbons with low odd-predominance through time. Thus, the natural high odd-predominance was assumed to decrease in response to increasing input of anthropogenic hydrocarbon pollutants with low odd predominance over the period represented by the study, leading to decreasing CPI towards the top, rather than increasing CPI with depth. A 'background' contribution of normal alkanes from human activities is present, and this mechanism possibly contributes to the observed pattern. However, such high CPI (i. e. >2) is not encountered in petroleum, and the scarcity of acyclic isoprenoids and n-alkanes in the lower carbon-number range do not seem to agree with a dominant petroleum source. McCaffrey et al. (1991) suggested increasing CPI with depth to be caused by selective degradation of low-CPI marine material. This may be a feasible hypothesis, but considering the hydrocarbon distribution in marine algae (e.g. Clark & Blumer 1967, Han & Calvin 1969), this implies very high contributions of marine organic matter, compared to terrigenous organics, which does not seem to agree with the setting of the station 6. Moreover, due to comparatively higher proportions of 'heavy' n-alkanes in terrestrial organic matter, these tend to dominate the CPI (Tissot & Welte 1984). Finally, changing provenance of organic matter (i.e. organic matter type) supplied to the sediments may contribute to changes in CPI. In summary, it is suggested that increasing CPI with depth in the present case primarily arises in response to elimination of terminal functional groups, with the associated carbon atom, from long-chain, even numbered biological compounds. In addition, changes in anthropogenic petroleum input probably also contribute to the trend (see below). In the deeper part of the core, off-trend low values of CPI that are recurring as anomalies in other data (see below) possibly record random oil spills in the past.

From the ratio of even- to odd-numbered C_{14}-C_{19} fatty acids, it appears that compounds containing an even number of carbon atoms are preferentially eliminated (Fig. 10a). The data also suggest that short-chain fatty acids are more easily degraded than are long-chain species (Fig. 10b). Very similar observations have been made by numerous authors. Rapid changes with depth in fatty acid abundance and distribution were noted by Matsuda & Koyama (1977). Elimination of unsaturated species was shown by Rhead et al. (1971), Johnson & Calder (1973) and Leenheer & Meyers (1983). Preferential removal of short-chain fatty acids was noted by Matsuda & Kyoama (1977), and by Leenheer & Meyers (1983). The observations conform to the results of Green & Allmann (1968), who showed enzymatic activity to be related to fatty acid chain length.

The biological marker distributions are dominated by compounds which are not indigenous, in the sense that they are generally not derived from recent organic matter. These biological markers are polycyclic terpanes and steranes, which are not easily degraded, and which tend to survive while less refractory compounds, such as n-alkanes are destroyed. The presence of notable quantities of these compounds is thus indicative of erosion of ancient sediments containing these compounds (e.g. Kennicutt et al. 1987) and/or anthropogenic background contributions of petroleum-derived hydrocarbons.

The presence of comparatively labile compounds such as hopenes, sterenes and 17β(H)21β(H)-hopanes, as well as the discrepancies between homohopane and bishomohopane epimerization ratios point to a mixed origin of the biomarker distributions. Both the sterenes, hopenes and the 17β(H)21β(H)-hopanes (for compounds with more than 30 carbon atoms 17ß(H)21ß(H)22R) are probably largely indigenous, originating from defunctionalisation and hydrogenation of sterols, and bacterial cell membrane hopanoids during very early diagenesis (e.g. Ensminger et al. 1974, van Dorsselaar et al. 1974, Gaskell & Eglinton 1974, Philp, 1985, Simoneit 1986, Peters & Moldowan 1993).

Hence, the observed biomarker distributions record mixing of an indigenous biomarker compound fraction, the composition of which shows only minor diagenesis-related changes with depth, and a petroleum-derived biomarker distribution, which becomes increasingly prominent towards the top of the core, corresponding to increasing anthropogenic petroleum input through time. This is particularly well illustrated by the relative abundance of 17β(H)21β(H)-hopanes and of the homohopane epimerization ratio (Figs. 12a & 13a). At several levels, previously noted for increased extract yields and low, off-trend CPI, the depth trends of these parameters also show prominent excursions conformable with the expected effects of random oil-spills in the past. Sterane and bishomohopane epimerization ratios are unaffected (Figs. 12a & 12b), and these compounds can thus be assumed to be supplied more or less exclusively from petroleum. Futhermore, the effect of mixing is not clearly manifest in n-alkane distributions, since petroleum-derived n-alkanes probably are largely eliminated due to evaporation and oxic degradation en route to the locale of sedimentation.

The distribution of C_{27}-C_{29} steranes is often used as an indicator of the origin of hydrocarbons (Huang & Meinschein 1979). A dominance of C_{27} steranes is held to indicate an origin primarily from marine plankton, while a predominance of C_{29} steranes indicates a higher landplant or cyanobacterial origin. Although the validity of these assumptions has been debated, sterane ratios may at least serve as a rough indicator of changes in sedimentary environment (see reviews by Volkman 1986, 1988).

The sterenes are indigenous, being formed rapidly from the steroids of various organisms (e.g. Gaskell & Eglinton 1974; Peakman & Maxwell 1988), and provided the rates of formation of the various sterenes from their biological precursors are identical, the sterenes may be used analogous to the steranes as an indicator of changes in organic matter provenance in the present sedimentary environment. The proportion of C_{27}-sterenes, assumed to be indicative of marine plankton, clearly decreases with increasing sediment depth (Fig. 13b). Nishimura (1978) found that C_{27} stenols were converted into stanols more rapidly than the C_{29} homologs. Stanols are held to be more stable than sterols (de Leeuw & Baas 1986). Whether similar effects are valid for the conversion into sterenes and steranes remains unclear. Furthermore, degradation of C_{28}- and C_{29}-steroids may lead to the formation of C_{27}-steroids, and alter the relative proportions of $C_{27\text{-}29}$-steroids in favour of C_{27}-compounds (Conte et al. 1994). However, the action of such mechanisms will influence the relative proportions of sterenes adversely to what is actually observed.

The overall importance of primary production with respect to the amount and character of the organic matter incorporated into marine sediments has been much debated (e.g. Demaison & Moore 1980, Tyson 1987, Stein 1990, Pedersen & Calvert 1990, Tyson 1995), but in shallow-water sediments the primary production in the overlying water masses is necessarily of considerable importance.

In the light of the preceeding discussion, the observed increase in abundance of C_{27}-sterenes towards the top of the sequence may indicate a steadily growing input of algal organic matter over at least the last 20-30 years. This is probably a product of the increasing eutrophication of the sea, leading to a shift in the composition of the sedimentary organic matter in favour of autochthonous matter, i.e. planktonic microalgae.

In summary, the bulk organic matter analyses (TOC, Rock-Eval, C/N, Pyrolysis-GC) as well as the fatty acid analyses primarily seem to record changes in organic matter composition related to microbially mediated decomposition. Conversely, the changes observed by hydrocarbon analyses seems to record the cumulative response to a number of factors including microbial organic matter degradation, eutrophication, and anthropogenic contributions of petroleum hydrocarbons.

Conclusions

Organic geochemical investigations performed on a depth sequence of samples from the Station 6 site in Århus Bugt have shown the effects of microbial mineralization of organic matter in the sediments, as well as human impact on the sedimentary environment.

- Over the upper 6-7 centimetres, roughly corresponding to the deposits of the last 25-30 years, a number of parameters show systematic changes.
- In deeper parts of the sequence, indications of disruption of steady state sedimentation, probably due to the excavation of a nearby navigation channel in the 1960-ties, are observed.
- Over the upper part of the sequence, organic matter mineralization is manifest in significant decreases in organic carbon contents.
- Calculation of organic carbon lost due to microbial sulphate reduction yields a close correlation with measured values, supporting a prominent role for microbial sulphate reduction at the study site.
- Changes in bulk organic matter composition are evident from HI and C/N data, showing preferential elimination of highly functionalised and unsaturated organic matter, leading to increasing values of both C/N and HI with depth.
- These results are supported by pyrolysis-GC data, showing decreasing proportions of heteroatomic and pyrolytic aromatic/phenolic compounds and increasing proportions of high H/C n-alkyl compounds with depth.
- Analyses of free fatty acids show preferential elimination of short-chain, even-numbered and unsaturated fatty acids.
- Analyses of saturated hydrocarbons show the presence of high proportions of UCM, indicative of background anthropogenic petroleum pollution.
- Sterane and triterpane biomarker distributions suggest a mixed origin for these compounds, featuring a prominent contribution from anthropogenic petroleum pollution, and a minor contribution from indigenous organic matter.
- Changes in relative proportions of C_{27}- and C_{29}-sterenes suggest changes in sedimentary organic matter composition through time, probably in response to increasing eutrophication over the last few decades.
- Vestiges of fortuitous oil-spills in the past are recorded as off-trend values of extract yield, CPI and biomarker ratios.

Acknowledgments

The assistance of D. Postma, J. M. Hansen and H. P. Nytoft, B. Larsen, E. Thomsen, H. Fossing, J. Gundersen, B. Thamdrup and B. B. Jørgensen is gratefully acknowledged. A. Jensen provided Pb^{210} data. Metastable ion analyses were carried out by A. S. Steen. N. J. Anderson and D. J. Jutson improved the English language of the text. Useful comments, corrections and suggestions by the reviewers L. Leith and M. G. Wiesner are gratefully acknowledged. The study received financial support from The Danish Research Academy and the Danish Environmental Protection Agency.

References

Baker, B. L. 1974: Generation of alkane and aromatic hydrocarbons from humic materials in arctic marine sediments. *Advances in Organic Geochemistry 1973*, 137-152.

Barrick, R. C, Hedges, J. I. & Peterson, M. L. 1980: Hydrocarbon geochemistry of the Puget Sound region - I. Sedimentary acyclic hydrocarbons. *Geochim. et Cosmochim. Acta 44*, 1349-1362.

Berner, R. A. 1964: An idealized model of dissolved sulfate distribution in recent sediments. *Geochim. et Cosmochim. Acta 28*, 1497-1503.

Berner, R. A. 1980: A rate model for organic matter decomposition during bacterial sulfate reduction in marine sediments. Colloques internationaux du Centre National de la Recherche Scientifique N° 293: Biogeochemistry of organic matter at the sediment water interface. *Éditions du Centre National de la Recherche Scientifique, Paris*, 35-44.

Blegvad, H. 1914: Undersøgelser over Næring og Ernæringsforhold hos Havbundens invertebrate Dyresamfund i danske Farvande. *Beretning til Landbrugsministeriet fra Den danske biologiske Station 22*, 37-124. (in Danish)

Bordovskiy, O. K. 1965: Accumulation and transformation of organic substances in marine sediments. *Marine Geol. 3*, 3-114.

Boudreau, B. P. & Ruddick, B. R. 1991: On a reactive continuum representation of organic matter diagenesis. *Amer. Jour. Sci. 291*, 507-538.

Bray, E. E. & Evans, E. D. 1961: Distribution of n-paraffins as a clue to recognition of source beds. *Geochim. et Cosmochim. Acta 22*, 2-15.

Brown, F. S., Baedecker M. J., Nissenbaum A. & Kaplan, I. R. 1972: Early diagenesis in a reducing fjord, Saanich Inlet British Columbia - III Changes in organic constituents of sediment. *Geochim. et Cosmochim. Acta 36*, 1185-1203.

Clark Jr., R. C. & Blumer, M. 1967: Distribution of n-paraffins in marine organisms and sediment. *Limnology and Oceanography 12*, 79-87.

Conte, M. H., Madureira, L. A. S., Eglington, G., Keen, D. & Rendall, C. 1994: Millimeter-scala profiling of abyssal marine sediments: role of bioturbation in early sterol diagenesis. *Org. Geochem. 22*, 979-990.

Cooper, J. E. & Bray, E. E. 1963: A postulated role of fatty acids in petroleum formation. *Geochim. et Cosmochim. Acta 27*, 1113-1127.

Demaison, G. J. & Moore, G. T. 1980: Anoxic environments and oil source bed genesis. *Bull. Amer. Assoc. Petrol. Geol. 64*, 1179-1209.

Devol, A. H. & Ahmed, S. I. 1981: Are high rates of sulphate reduction associated with anaerobic oxidation of methane? *Nature 291*, 407-408.

van Dorsselaer, A., Ensminger, A., Spyckerelle, C., Dastillung, M., Sieskind, O., Arpino, P., Albrecht, P., Ourisson, G., Brooks, P. W., Gaskell, S. J., Kimble, B. J., Philp, R. P., Maxwell J. R. & Eglinton, G. 1974: Degraded and extended hopane derivatives (C_{27}-C_{35}) as ubiquitous geochemical markers. *Tetrahedron Letters 14*, 1349-1352.

Eglinton, G. & Hamilton, R. J. 1967: Leaf epicuticular waxes. *Science 156*, 1322-1335.

Ensminger, A., van Dorsselaer, A., Spyckerelle, Ch., Albrecht P. & Ourisson, G. 1974: Pentacyclic triterpenes of the hopane type as ubiquitous geochemical markers: Origin and significance. *Advances Org. Geochem. 1973*, 245-260.

Erdman, J. G. 1961: Some chemical aspects of petroleum genesis as related to the problem of source bed recognition. *Geochimi. Cosmochi. Acta 22*, 16-36.

Espitalié, J., Deroo G. & Marquis, F. 1985a: La pyrolyse Rock-Eval et ses application, première partie. *Revue de l'Institut Français du Pétrole 40*, 563-579.

Espitalié, J., Deroo G. & Marquis, F. 1985b: La pyrolyse Rock-Eval et ses application, deuxième partie. *Revue de l'Institut Français du Pétrole 40*, 755-784.

Fenchel, T. & Blackburn, T. H. 1979: *Bacteria and Mineral Cycling*. Academic Press, London, 225 pp.

Fenchel, T. & Harrison, P. 1976: The significance of bacterial grazing and mineral cycling for the decomposition of particulate detritus. *In* Anderson, J. M. & Macfadyen, A. (eds.): *The role of terrestrial and aquatic organisms in decomposition processes.* Blackwell Scientific Publications, London, 285-299.

Fenchel, T. & Jørgensen, B. B. 1977: Detritus food chains of aquatic ecosystems: The role of bacteria. *In* Alexander, M. (ed.): *Advances in microbial ecology, 1.* Plenum Press, New York, 1-58.

Foree, E. G. & McCarty, P. L. 1970: Anaerobic decomposition of algae. *Env. Sci. Tech. 4*, 842-849.

Frey, P. A. 1988: Structure and function of coenzymes. In Zubay, G. (ed.): *Biochemistry, 2nd edition.* Macmillan Publ. Co., London & New York, 347-389.

Galimov, E. M. 1980: C^{13}/C^{12} in kerogen. In: Durand, B. (ed.): *Kerogen, insoluble organic matter from sedimentary rocks.* Éditions Technip, Paris, 271-299.

Gaskell, S. J. & Eglinton, G. 1974: Short-term diagenesis of sterols. *Advances Org. Geochem. 1974*, 963-976.

Green, D. E. & Allmann, D. W. 1968: Fatty acid oxydation. *In* Greenberg, D. M. (ed.). *Metabolic pathways 2*, Academic Press, London, 1-36.

Han, J. & Calvin, M. 1969: Hydrocarbon distribution of algae and bacteria, and microbial activity in sediments. *Proc. Nat. Acad. Sci. 64*, 436-443.

Hartmann, M., Müller, P., Suess E. & van der Weijden, C. H. 1973: Oxydation of organic matter in recent marine sediments. *'Meteor' Forschungs-Ergebnisse, C 12*, 74-86.

Henrichs, S. M. & Reeburgh, W. S. 1987: Anaerobic mineralization of marine organic matter: rates and the role of anaerobic processes in the oceanic carbon economy. *Geomicrobiol. Jour. 5*, 191-237.

Hoffmann, C. F., Foster, C. B., Powell T. G. & Summons, R. E. 1987: Hydrocarbon biomarkers from Ordovician sediments and the fossil algae *Gloecapsomorpha prisca Zalessky* 1917. *Geochim. Cosmochim. Acta 51*, 2681-2697.

Horsfield, B. 1989: Practical criteria for classifying kerogens: Some observations from pyrolysis-gas chromatography. *Geochim. Cosmochim. Acta 53*, 891-901.

Huang, W. Y. & Meinschein, W. G. 1979: Sterols as ecological indicators. *Geochim. Cosmochim. Acta 43*, 739-745.

Huc, A. Y & Durand, B. M. 1974: Étude des acides humiques et de l'humine des sédiments récents considérés comme précurseurs des kérogènes. *Advances Org. Geochem. 1973*, 53-72.

Hunt, J. M. 1974: Hydrocarbon geochemistry of Black Sea. *Amer. Assoc. Petrol. Geol. Memoir 20*, 499-504.

Hylleberg, J. & Riis-Vestergaard, H. 1984: *Marine Environments; the fate of Detritus, Biologiske Studier 5.* Akademisk Forlag, København, 288pp.

Iversen, N, & Jørgensen, B. B. 1985: Anaerobic methane oxidation rates at the sulfate-methane transition in marine sediments from Kattegat and Skagerrak (Denmark). *Limnology and Oceanography 30*, 944-955.

Jensen, P. B. 1914: Studier over Havbundens organiske Stoffer. *Beretning til Landbrugsministeriset fra Den danske biologiske Station 22*, 3-36. (in Danish).

Johnson, R. W. & Calder, J. A. 1973: Early diagenesis of fatty acids and hydrocarbons in a salt marsh environment. *Geochim. Cosmochim. Acta 37*, 1943-1955.

Jurg, J. W. & Eisma, E. 1964: Petroleum hydrocarbons: Generation from fatty acids. *Science 144*, 1451-1452.

Jørgensen, B. B. 1977: The sulfur cycle of a coastal marine sediment (Limfjorden, Denmark). *Limnology and Oceanography 22*, 814-832.

Jørgensen, B. B. 1979: A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments. II Calculation from mathematical models. *Geomicrobiol. Jour. 1*, 29-47.

Jørgensen, B. B. 1982: Mineralization of organic matter in the sea bed - the role of sulphate reduction. *Nature 296*, 643-645.

Jørgensen, B. B., Fossing H. & Thamdrup, B. 1991: Sulfidoxidation og jern/mangan-kredsløb i havbunden. *Statusrapport, havforskningsprogram 90, projekt nr. 3.17.* (in Danish).

Kanneworf, E. & Nicolaisen, W. 1973: The 'Haps', a frame supported bottom corer. *Ophelia 10*, 119-128.

Kennicutt II, M. C., Barker, C., Brooks, J. M., de Freitas, D. A. and Zhu, G. H. 1987: Selected organic matter source indicators in the Orinoco, Nile, and Changjiang deltas. *Org. Geochem. 11*, 41-51.

Kennicutt II, M. C. & Brooks, J. M. 1990: Unusual normal alkane distributions in offshore New Zealand sediments. *Org. Geochem. 15*, 193-197.

Kristensen, E. & Blackburn, T. H. 1987: The fate of organic carbon and nitrogen in experimental marine sediment systems: Influence of bioturbation and anoxia. *Jour. Marine Res. 45*, 231-257.

Kvenvolden, K. A. & Weiser, D. 1967: A mathematical model of a geochemical process: Normal paraffin formation from normal fatty acids. *Geochim. Cosmochim. Acta 31*, 1281-1309.

Laanbroek, H. J. & Veldkamp, H. 1982: Microbial interactions in sediment communities. *Phil. Trans. Royal Soc. London B297*, 533-550.

Larter, S. R. 1984: Application of analytical pyrolysis techniques to kerogen characterization and fossil fuel exploration. *In* Voorhees, K. J. (ed.): *Analytical pyrolysis - techniques and applications*. Butterworth, London, 212-275.

Leenheer, M. J. & Meyers, P. A. 1983: Comparison of lipid compositions in marine and lacustrine sediments. *In* Bjorøy, M. et al. (eds.): *Advances Org. Geochem. 1981*, 309-316.

de Leeuw J. W. & Baas M. 1986: Early-stage diagenesis of steroids. *In* Johns, R. B. (ed.): *Biological Markers in the Sedimentary Record.* Methods in geochemistry and geophysics 24, Elsevier, Amsterdam, 101-123.

Lichtfouse, É. & Collister, J. W. 1992: Tracing biogenic links of natural organic substances at the molecular level with stable carbon isotopes: n-alkanes and n-alkanoic acids from sediments. *Tetrahedron Letters 33*, 8093-8094.

Lichtfouse, É., Derenne, S., Mariotti, A. & Largeau, C. 1994: Possible algal origin of long-chain odd n-alkanes in immature sediments as revealed by distributions and carbon isotope ratios. *Org. Geochem. 22*, 1023-1027.

Matsuda, H. & Koyama, T. 1977: Early diagenesis of fatty acids in lacustrine sediments - I. Identification and distribution of fatty acids in recent sediment from a freshwater lake. *Geochim Cosmochim. Acta 41*, 777- 783.

McCaffrey, M. A., Farrington J. W. & Repeta, D. J. 1991: The organic geochemistry of Peru margin surface sediments: II. Paleoenvironmental implications of hydrocarbon and alcohol profiles. *Geochim. Cosmochim. Acta 55*, 483-498.

Metcalfe, L. D., Schmitz, A. A. & Pelka, J. R. 1966: Rapid preparation of fatty acid esters from lipids for gas chromatographic analysis. *Anal. Chem. 38*, 514-515.

Meuzelaar, H. L. C., Haverkamp J. & Hileman, F. D. 1982: Pyrolysis mass spectrometry of recent and fossil biomaterials - compendium and atlas. *Techniques and instrumentation in analytical chemistry 3*, Elsevier, Amsterdam, 293 pp.

Middelburg, J. J. 1989: A simple rate model for organic matter decomposition in marine sediments. *Geochim. Cosmochim. Acta 53*, 1577-1581.

Mulik, J. D. & Erdman, J. G. 1963: Genesis of hydrocarbons of low molecular weight in organic rich aquatic systems. *Science 141*, 806-807.

Nishimura, M. 1978: Geochemical characteristics of the high reduction zone of stenols in Suwa sediments and the environmental factors controlling the conversion of stenols into stanols. *Geochim. Cosmochim. Acta 42*, 349-357.

Nishimura, M. & Baker, E. W. 1986: Possible origin of n-alkanes with a remarkable even-to-odd predominance in recent marine sediments. *Geochim. Cosmochim. Acta 50*, 299-305.

Peake, E., Casagrande, D. J. & Hodgson, G. W. 1974: Fatty acids, chlorins, hydrocarbons, sterols, and carotenoids from a Black Sea core. *Amer. Assoc. Petrol. Geol. Memoir 20*, 505-523.

Peakman, T. M. & Maxwell, J. R. 1988: Early diagenetic pathways of steroid alkenes. *Advances Org. Geochem. 1987*, 583-592.

Pedersen, T. F. & Calvert, S. E. 1990: Anoxia vs. Productivity: What controls the formation of organic carbon-rich sediments and sedimentary rocks. *Bull. Amer. Assoc. Petrol. Geol 74*, 454-466.

Peters, K. E. & Moldowan, J. M. 1993: *The biomarker guide. Interpreting molecular fossils in petroleum and ancient sediments.* Prentice Hall Englewood Cliffs, New Jersey, 363 pp.

Petersen, C. G. J. 1913: Havets Bonitering II. Om Havbundens Dyresamfund og om disses Betydning for den marine Zoogeografi. *Beretning til Landbrugsministeriet fra Den danske biologiske Station 21*, 110 pp. (in Danish)

Petersen, C. G. J. & Jensen, P. B. 1911: Havets Bonitering I. Havbundens Dyreliv, dets Næring og Mængde (Kvantitative Studier). *Beretning til landbrugsministeriet fra Den danske biologiske Station 20*, 78 pp. (in Danish)

Philp, R. P. 1985: *Fossil fuel biomarkers. Application and spectra.* Elsevier, Amsterdam, 294 pp.

Reeburgh, W. S. 1983: Rates of biogeochemical processes in anoxic sediments. *Ann. Rev. Earth Planet. Sci. 11*, 269-298.

Rhead, M. M., Eglinton, G., Draffan, G. H. & England, P. J. 1971: Conversion of oleic acid to saturated fatty acids in Severn Estuary sediments. *Nature 232*, 327-330.

Schidlowski, M. 1986: $^{13}C/^{12}C$ ratios as indicators of biogenicity. In Johns, R. B. (ed.): *Biological markers in the sedimentary record*, Elsevier, Amsterdam, 347-362.

Schlegel, H. G. 1976: *Allgemeine Mikrobiologie, 4. auflage*. Georg Thieme Verlag, Stuttgart, 480 pp.

Simoneit, B. R. T. 1974: Organic analyses of Black Sea cores. *Amer. Assoc Petrol. Geol. Memoir 20*, 477-498.

Simoneit, B. R. T 1986: Cyclic terpenoids of the geosphere. In Johns, R. B. (ed.): *Biological Markers in the Sedimentary Record.* Methods in geochmistry and geophysics 24, Elsevier, 43-99.

Skyring, G. W. 1987: Sulfate reduction in coastal ecosystems. *Geomicrobiol Jour. 5*, 295-374.

Stein, R. 1990: Organic Carbon Content/Sedimentation Rate Relationship and its Paleoenvironmental Significance for Marine Sediments. *Geo-Marine Letters 10*, 37-44.

Tegelaar, E. W., de Leeuw, J. W., Derenne S. & Largeau, C. 1989: A reappraisal of kerogen formation. *Geochimi. Cosmochim. Acta 53*, 3103-3106.

Tissot, B. P. & Welte, D. H. 1984: *Petroleum Formation and Occurrence, 2nd ed.* Springer Verlag, Berlin, 699 pp.

Tyson, R. V. 1987: The genesis and palynofacies characteristics of marine petroleum source rocks. *In* Brooks, J. & Fleet, A. J. (eds.): Marine Petroleum Source Rocks. *Geol. Soc. Special Publ. 26*, 47-67.

Tyson, R. V. 1995: *Sedimentary organic matter.* Chapman & Hall, London, 615 pp.

Volkman, J. K. 1986: A review of sterol markers for marine and terrigenous organic matter. *Org. Geochem. 9*, 83-99.

Volkman, J. K. 1988: Biological marker compounds as indicators of the depositional environments of petroleum source rocks. *In* Fleet, A. J., Kelts, K. & Talbot, M. R. (eds.): Lacustrine Petroleum Source Rocks. *Geol. Soc. Special Publ 40*, 103-122.

Wade, T. L. & Quinn, J. G. 1979: Geochemical distribution of hydrocarbons in sediment from mid-Narragansett Bay, Rhode Island. *Org. Geochem. 1*, 157-167.

Welte, D. H. & Ebhardt, G. 1968: Distribution of long-chain n-paraffins and n-fatty acids in sediments from the Persian Gulf. *Geochim. Cosmochim. Acta 32*, 465-466.

Westrich, J. T. & Berner, R. A. 1984: The role of sedimentary organic matter in bacterial sulfate reduction: The G-model tested. *Limnology and Oceanography 29*, 236-249.

Wiesner, M. G., Haake, B. & Wirth, H. 1990: Organic facies of surface sediments in the North Sea. *Org. Geochem. 15*, 419-432.

Manuscript received March 1995; revised version accepted January 1996