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Pre- and post-industrial environmental changes as revealed by the biogeochemical sedimentary record of Drammensfjord, Norway

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Abstract

The biogeochemical sedimentary record of the anoxic Drammensfjord, Norway, was investigated on a decadal to centennial time scale over the last millennium, in order to reconstruct the pre-industrial fjord environment and ecosystem and human-induced environmental changes. The sediments were dated by a combination of ^{14}C and ^{210}Pb analysis and varve counting. Analysis of the bulk sedimentary parameters and of the biomarker distribution revealed that the sedimentary organic matter of the fjord is primarily of terrigenous origin, indicating that the fjord was oligotrophic or mesotrophic. The fjord's bottom water has been continuously euxinic since at least 1000 AD, but photic zone euxinia occurred only irregularly in the fjord. The organic matter flux and composition remained virtually invariable until the 18th century. After that time, the flux of material derived from coniferous trees started to increase, indicated by elevated concentrations of dehydroabietic acid and related compounds, but also by raising levels of C_{24} *n*-alcohols and fatty acids. This marked the onset of sawmill activities in the hinterland. After the beginning of the industrial revolution, around 1850, the flux of organic waste from sawmills and paper mills increased substantially. It is suggested that slow bacterial degradation of this relatively nutrient-poor organic waste caused a gradual eutrophication trend, which is reflected in substantial increased bacterial and moderately increased other aquatic biomarker accumulation rates. After the industrial revolution, this trend accelerated and was possibly enhanced by a growing population of the area with accompanying agricultural and domestic waste. This promoted primary productivity and changed the phytoplankton composition in the fjord.
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1 Introduction

Coastal areas harbour important and intricate ecosystems representing a large part of the world's

biodiversity, due to their fertility and dynamic nature. Not accidentally, coastal areas are also the most heavily populated in the world and they are of high agricultural and economic importance. In the last century, visible environmental deterioration of many coastal areas pressed the need for environmental monitoring, often initiated by governments after public concern (e.g. http://www.epa.gov; http://www.rivm.nl; http://www.environment.no), in order to gain insight into ecosystem dynamics and the effects of human activities. However, continuous and comprehensive monitoring started in general only after natural ecosystems were severely affected in the last century (Nixon, 1990; Rosenberg et al., 1990; Johannessen and Dahl, 1996; Gowen et al., 1999; Skei et al., 2000) and there is not much information about unaffected coastal environments neither in populated areas, nor on early anthropogenic effects in pre- and
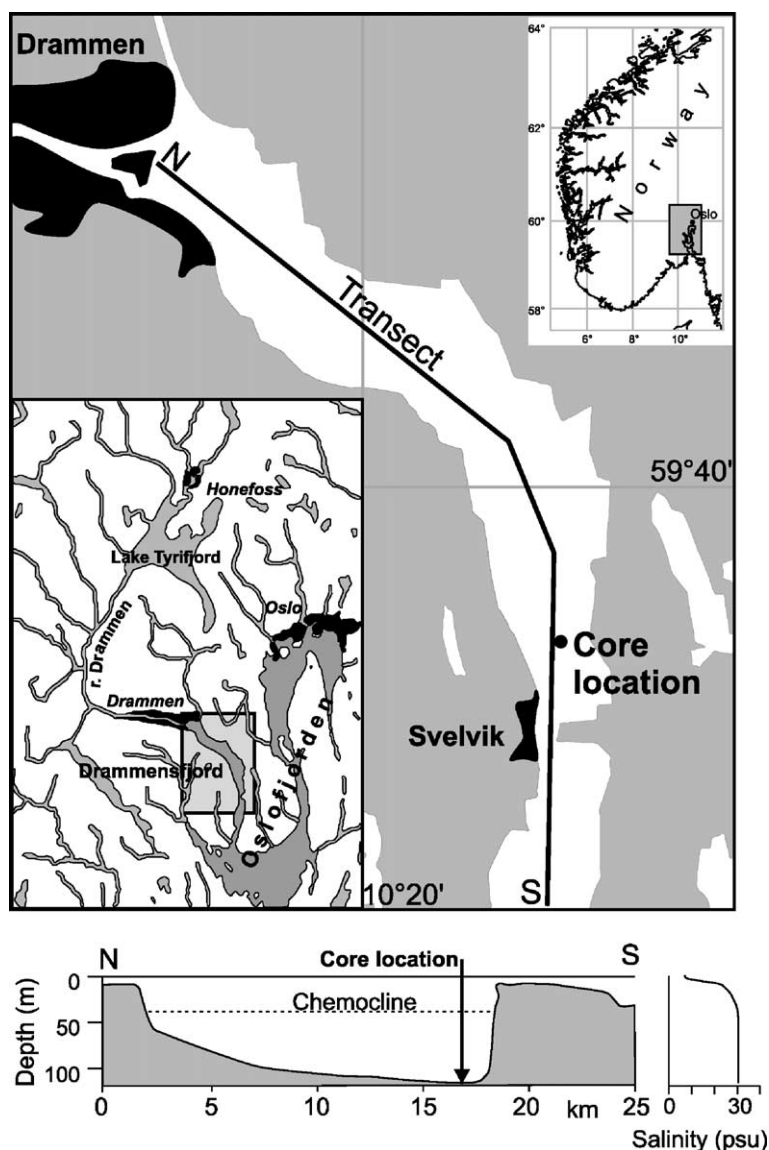

Fig. 1 Map and vertical profile of the Drammensfjord. The location of the sediments used in this study is indicated, as well as the salinity gradient as measured with a CTD during the cruise.

post-industrial times. Furthermore, large-scale factors like climatic variability and variations in oceanic currents may also affect environments (e.g. Broecker, 1995; Hulme et al., 1999; Cullen et al., 2001; Mikalsen et al., 2001; Moy et al., 2002).

Examination of sediment cores from populated coastal regions can increase our knowledge about past environmental change, whether naturally or anthropogenically caused (e.g. Alve, 1991; Zimmerman and Canuel, 2000; Pellatt et al., 2001; St-Onge and Hillaire-Marcel, 2001). Assemblages of palynomorphs, e.g. dinoflagellate cysts (Dale et al., 1999), or other microfossils like diatoms (Andrén, 1999) or foraminifera (Alve, 1990) are often used as proxies for recent environmental change. Biogeochemical studies of recent sediments which include biomarkers for the same purpose are less common (e.g. Ficken and Farrimond, 1995; Zimmerman and Canuel, 2000; Pinturier-Geiss et al., 2002; Gerdes et al., 2003; Smittenberg et al., 2004b), even though this is a widely used method in paleoceanographic research (e.g. Brassell et al., 1986). An advantage of the use of biomarkers is that this allows deconvolution of the various organic matter sources and their variability, thereby revealing information about past physical and chemical conditions, microbial and algal communities and the vegetation of the surrounding area, thus allowing a comprehensive view of the total ecosystem. Determination of the fluxes of various biomarkers gives more insight into the relative importance of various organic matter sources, as well as the response of various organisms to a changing environment.

The sediments of the currently anoxic and polluted Drammensfjord, a side-arm of the greater Oslofjord, Norway (Fig. 1), were investigated by Alve (1991) to reconstruct both natural and human-induced environmental alterations over the last 1500 years, for which sediment characteristics, foraminiferal assemblages and pollen grains were used. In a similar way, eutrophication of the inner Oslofjord was investigated by Dale et al. (1999), who used dinoflagellate cyst assemblages to track anthropogenic eutrophication, while Pinturier-Geiss et al. (2002) used the abundance of various lipid classes and some biomarkers for the same purpose. These studies revealed that eutrophication started in the area in the first half of the 19th century, and was related to population growth and the

industrial development. The study described in this paper aimed to provide more insight into the various organic matter sources and the natural, pre-industrial ecology of the Drammensfjord and into the early effects of human activities, by analysing the sediment cores, focusing on the biomarker distributions and their accumulation rates.

2 Setting

The Drammensfjord has a length of 20 km and a width of 1.6–3.0 km (Fig. 1). It is separated from the greater Oslofjord by a sill at Svelvik, which was dredged around 1900 from 6 to 8 m depth, and to 10 m in 1951 (Alve, 1990). Before that time, the ongoing isostatic uplift of Fennoscandia, a result of the deglaciation, caused the sill depth to decrease at a rate of 3–4 mm/year in the second half of the Holocene (Pirazzoli, 1991). Mixing of fresh water of the river Drammen, which enters at the head of the fjord, leads to a brackish surface water layer (salinity 1–10‰, depending on the season) that is separated from saline bottom water (30.5‰) below 40 m water depth (Fig. 1) (Alve, 1990). River water regulations have smoothed the annual fresh water supply to the fjord in the last 60 years, reducing the effect of spring flooding and increasing the winter supply. This has changed the minimum fresh water supply from winter to late summer, thus increasing the residence time of the surface water during summer. The shallow sill prevents the exchange of bottom waters with the open ocean, and degradation of organic matter, partly by sulphate reducers, leads to euxinic conditions. Oxygen depletion was first detected in 1899, and the presence of H_2S in June 1933 (Öztürk, 1995 and references therein). Incursion of oceanic waters occurs currently once every 3–5 years, mainly between November and May, displacing parts of the euxinic bottom waters upwards (Richards, 1965; Alve, 1995). The anoxic bottom water conditions prohibit infauna, resulting in the preservation of the laminated sedimentary structure.

It is known from historical records that since at least 1750 the fjord has been increasingly affected by sawdust and wood-chips from sawmills along the river Drammen and upstream fresh water bodies (Alve, 1990, 1991 and references therein). After 1870, a number of paper and pulp mills were

established, causing a substantial increase in the amount of fibrous material to the fjord. In the 20th century, the supply of organic matter to the fjord increased even more, but during the first half of the 1970s most of the paper industry was closed down. During the last century, domestic and agricultural waste also increased drastically (Richards and Benson, 1961; Alve, 1991).

3 Sampling and methods

3.1 Sediment collection and subsampling

The sediments used for this study were selected from a suite of box, gravity and piston cores that were recovered from the Drammensfjord, Norway, during a cruise in October 1999 with the R/V *Pelagia*. Several surface sediment cores from the depocenter of the fjord (59°37′ 99″ N, 10°25′ 39″ E) (Fig. 1) were obtained by taking subcores from a box core. From one of these subcores, subsamples of known volume were taken from the centre of the core after slicing the core in two halves, in order to determine the bulk density. Another subcore was sliced into 0.5 cm thick horizontal slices, including the edges of the core, immediately after recovery for geochemical analysis. The slices were stored on board at −20 °C and later freeze-dried in the laboratory. Sections of a piston core (coded D1G), obtained from the same location, were sliced into two halves and stored at 4 °C before subsampling. The upper part was photographed for grey-scale analysis. One half of the upper section, with a length of 95 cm, was subsampled into sections of 0.5–7 cm (Fig. 2), depending on sediment colour and laminae thickness, and the subsamples were subsequently freeze-dried. The sides of the core were avoided in the sampling procedure. Approximately half of these subsamples, evenly distributed over the core, were ground to a fine powder and analysed. From the other half of the upper piston core section, subsamples of known volume were taken for bulk density measurement, as well as for microscopic analysis.

3.2 Sedimentological and bulk geochemical analysis

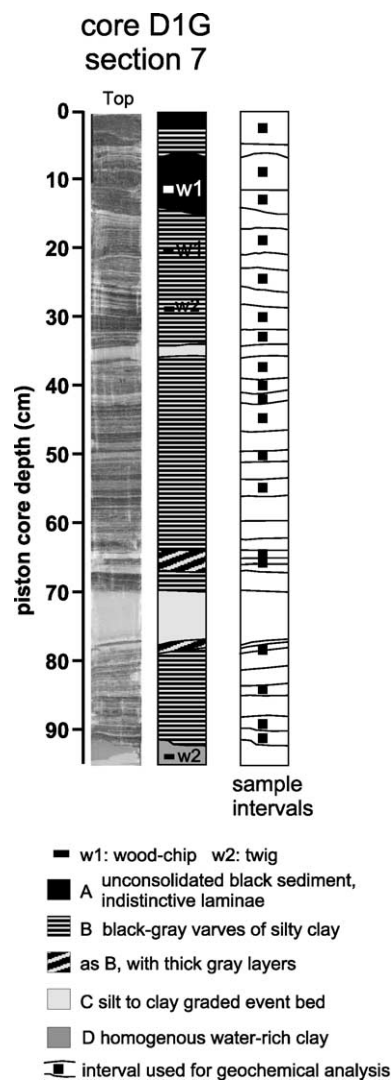In order to perform varve counting, parts of the piston and gravity cores were photographed, which

Fig. 2 Photograph and sedimentological graphic of the investigated piston core. The subsampling intervals used for biogeochemical analysis are indicated by black squares.

after development were digitised for computerised grey-scale analysis in a similar way as described by Nederbragt et al. (2000). A backscatter electron image (BSEI) was taken from a thin section made from a varved interval at around 190 cm of one of the piston cores (code D1L), corresponding to the varved interval at around 175 cm depth of core D1G (Fig. 2), in order to assess the composition of the varves. A number of smear slides made from sediment subsamples of the upper 2 m of core D1G were analysed using a normal light microscope. Total organic carbon

contents (TOC) and nitrogen (TN) contents were determined on acid-treated (1 N HCl, 12 h) sediment subsamples using a LECO Element Analyzer. Bulk stable carbon isotopic compositions were determined on a Carlo Erba 1112 series Flash Element Analyzer coupled to a Finnigan DELTA[PLUS] isotope-ratio-monitoring mass spectrometer and are reported in standard delta notation relative to the VPDB standard, with a standard deviation of 0.1‰. Five freeze-dried 0.5 cm thick box core slices were analysed with Rock-Eval 6 (version 3.02×05) at the University of Utrecht (Netherlands) to obtain hydrogen (HI) and oxygen indices (OI) of the sedimentary organic matter.

3.3 Dating

For dating purposes, ^{210}Pb, ^{137}Cs and [226]Ra radio activities of a selection of the 0.5 cm thick freeze-dried box core slices were determined, as well as the ^{210}Pb activities of sediment subsamples from 0–5, 7.5–12 and 85.5–88 cm piston core depth. To determine the ^{210}Pb activity, the sediment samples were spiked with [209]Po and digested with 5 ml concentrated HNO_3 and 5 ml concentrated HF in a microwave oven for 3 h. Subsequently, 2 ml 3.5% $HClO_4$ was added and the acids were removed by evaporation. The resulting precipitate was re-dissolved in 40 ml 0.5 M HCl, followed by spontaneous electrochemical deposition of the Po-isotopes onto silver in 0.5 M HCl at 80 °C for 4 h. The activity of ^{210}Pb was measured via its α-particle emitting grand-daughter isotope [210]Po with a Passivated Implanted Planar Silicon detector (Canberra A-600-23-AM). Counting time was 48 h, and the counting error 3–7%. The level of ^{137}Cs was measured using a high-purity germanium γ-ray well-detector (Canberra GCW 2522) with 25% relative efficiency. Counting time was 1–3 days, resulting in a counting error of 5–10%. The gamma detector was calibrated with a QCY48 standard mixed with sediment (Zuo et al., 1991; de Haas et al., 1997). The [226]Ra activity was measured after an equilibrium time of 1 month, using the same detector as used for [137]Cs. The activity was calibrated against a dilution series of the IAEA Uranium RGU-1 standard.

Two pieces of wood remains obtained from the upper part of the piston core sediment were radio-carbon-dated following standard procedures. Radio-carbon ages were converted to calendar ages using the atmospheric calibration curve of Stuiver et al. (1998). Compound-specific radiocarbon analyses were performed on several isolated glycerol dialkyl glycerol tetraethers (GDGTs), following the procedure described in Smittenberg et al. (2002). The selected GDGTs were isolated from the uppermost (0–10 cm) and lowermost (25–35 cm) part of the sliced and freeze-dried box core sediment and furthermore from subsamples from 0–7.5 and 85–92 cm piston core depth. [14]C analysis was performed at Woods Hole Oceanographic Institution (WHOI) as described by Eglinton et al. (1996) and Smittenberg et al. (2004a).

3.4 Biomarker analysis

3.4.1. Extraction and fractionation

For biomarker analysis, part of the freeze dried sediment subsamples from the studied piston core were extracted with a dichloromethane–methanol (DCM–MeOH, 9:1 v/v) mixture using an Automated Solvent Extractor (Dionex, Sunnyvale, CA, USA), deployed over three static cycles of 5 min of 100 °C and 1000 psi. To remove salts, the extracts were washed with double-distilled water against DCM in a separatory funnel, and dried over Na_2SO_4. The bulk of the solvent was removed by rotary evaporation and the remaining solvent under a stream of nitrogen. The residues were taken up into DCM and stirred overnight with activated Cu(s) to remove elemental sulfur. For quantification, a known amount of deuterated *anteiso* C_{22} alkane was added as an internal standard to weighed aliquots of the total lipid extracts. The aliquots were subsequently methylated with diazomethane (CH_2N_2) in diethyl ether to convert fatty acids into their corresponding methyl esters. To remove very polar material, the aliquots were eluted with ethyl acetate over a small column filled with silica. The ethyl acetate was removed under a stream of nitrogen, after which the residues were dissolved in 25 μl pyridine to which 25 μl bis(trimethylsilyl)trifluroacetamide (BSTFA) was added. This mixture was heated at 60 °C for 20 min to convert alcohols into their corresponding trimethylsilyl ethers. The derivatized fractions were diluted to 1 mg/ml in ethyl acetate and analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS).

For analysis of glycerol dialkyl glycerol tetraethers (GDGTs) by high performance liquid chromatography-mass spectrometry (HPLC/MS), aliquots of the total lipid extracts were separated into two fractions by column chromatography over activated Al_2O_3 with n-hexane–DCM (9:1 v/v; 4 column volumes; apolar fraction) and DCM–MeOH (1:1 v/v; 3 column volumes; polar fraction) as eluents. The solvents of the polar fractions were removed as described above, and the residues dissolved by sonication (10 min) in n-hexane/iso-propanol (99:1; v/v). The resulting suspensions were centrifuged (1 min, $2300 \times g$) and the supernatants were filtered through a 4-mm-diameter PTFE filter (0.45 μm pore size) to produce fractions suitable for analysis by HPLC.

For carotenoid analysis, ca. 5 g of the freeze-dried sediment subsamples were three times ultrasonically extracted with acetone for 3 min each, under continuous cooling with ice. The combined extracts were then rotary evaporated towards a small volume and dried under nitrogen. The residues were subsequently taken up in DCM and eluted over a small column filled with silica, dried under a stream of nitrogen and dissolved into a known volume of acetone. To avoid degradation, extracts were stored at -20 °C and measured the same day. Direct light and heat exposure was avoided as much as possible during the work-up procedure and analysis.

3.4.2. Gas chromatography and gas chromatography-mass spectroscopy

Gas chromatography was performed with a Hewlett-Packard 5890 gas chromatograph equipped with an FID detector and a fused silica column (25 m×0.32 mm) coated with CP Sil 5 (film thickness=0.12 μm). The carrier gas was helium. The samples, dissolved in ethyl acetate, were on column injected at 70 °C. Subsequently, the oven was programmed to 130 °C at 20 °C/min, then at 4 °C/min to 320 °C at which it was held for 25 min.

Individual lipids were identified by gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard 5890 gas chromatograph interfaced to a VG Autospec Ultima mass spectrometer operated at 70 eV with a mass range of m/z 50–800 and a cycle time of 1.7 s (resolution 1000). The gas chromatograph was equipped and programmed as described

above. Compounds were identified by comparison of mass spectra and retention times with those reported in the literature. Quantification of selected compounds was performed by integration of peak areas of one or more diagnostic mass fragments of the different compounds and comparing these with that of the internal standard. The areas of the diagnostic mass fragments were corrected for their relative intensity compared to that of the total ion current using a response factor.

3.4.3. High performance liquid chromatography-mass spectrometry (HPLC/MS)

For GDGT analysis, high performance liquid chromatography-mass spectrometry (HPLC/MS) was performed using an HP 1100 series HPLC/MS equipped with an auto-injector, single quadrupole mass detector, and Chemstation chromatography manager software, following the method as described by Hopmans et al. (2000). Quantification was performed by integration of peaks in the summed mass chromatograms of $[M+H]^+$ and $[M+H]^+ + 1$ and comparison with a standard curve obtained using a dilution series of a known amount of a GDGT-0 standard.

For carotenoid analysis, the same HPLC system was used as described above, following the method described by Menzel et al. (2002), except that only a photo diode array detector was used and no mass detector.

4 Results and discussion

4.1 Sedimentology

The upper part of sediment from the depocenter of the Drammensfjord consists of black, unconsolidated material. Distinctive mm-scale black and grey laminae or varves become increasingly visible down core, and prevail until 92 cm piston core depth (Fig. 2). The sediment layers and laminations are often not horizontally oriented (Fig. 2). Microscopic analysis of smear slides taken at various depths revealed that the laminated sections were dominated by clay and silt-sized mineral material, though with a substantial contribution of diatoms, other microfossils and structured and amorphous organic matter. In the

non-laminated sections, the contribution of biogenic material appears to be lower.

Backscatter electron image (BSEI) analysis of a laminated section of core D1L revealed that the varves are generally composed of four layers, all dominated by quartz and feldspar. The layers vary from each other by the average grain size, clay content, and the amount of structured and amorphous organic matter, as discussed in more detail by Smittenberg (2003). In short, the differences between the layers can be related to a yearly cycle of varying strengths of the fresh water input and of primary productivity, and are interpreted as annual. The black colour in the laminated sections of the sediment is most likely caused by iron sulphides (FeS), as earlier suggested by Alve (1990). After exposure to oxygen, the colour of the black laminae turned slowly into brown-red, and subsequently to the same grey as the neighbouring grey laminae. The alternation of black and grey laminae suggests a yearly cycle in the deposition or preservation of iron sulphides (black) and iron disulphides (grey), which is ruled by the availability of decomposable organic matter, the reactivity of detrital iron minerals, and the extent of the euxinic circumstances (Berner, 1984). In analogy with anoxic sediments of Orca basin (Sheu and Presley, 1986), it can be argued that the thickness of the black laminae is related to the extent of the yearly water mixing in the fjord. The black-grey laminae observed under normal light compare only roughly with the layers visible with BSEI, which must be due to the different mechanisms of deposition. However, the number of black-grey lamina pairs and the number of BSEI-counted varves are the same, which justifies counting of the black-grey laminae as a means of varve dating. The near absence of grey layers in the upper part of sediment (Fig. 2) may be explained by a larger degree of euxinia in the fjord, leading to a higher production of black FeS minerals that are not completely converted to FeS_2 during times of mixing.

Microscopic analysis of the grey-coloured layers of 70–77 and 35–37 cm piston core depth (Fig. 2) revealed a fining upwards sequences from silt to clay with a lower diatomaceous contribution and with a lower TOC content than the sediment above and below. This indicates that these horizons are turbidites, presumably originating from the steep side of the fjord.

The dry bulk density increases from 0.25 g cm^{-3} at 3 cm box core depth to around 0.7 g cm^{-3} at 25 cm (Fig. 3B), while the dry bulk densities measured on the piston core sediments are 0.8 ± 0.08 g cm^{-3}.

4.2 Dating and sediment accumulation rates

The ^{210}Pb profile obtained from the box core sediment does not reflect a clear exponential decrease (Fig. 3A) as was observed for another location in the fjord (Zegers et al., 2003), even when plotted against cumulative dry mass (not shown). Possibly the upper box core sediments were somewhat disturbed during sampling. Furthermore, the ^{226}Ra activity, which determines the background ^{210}Pb activity, varies between 60 and 70 Bq kg^{-1} (Fig. 3A), while the ^{210}Pb activity at 85 cm piston core depth, which should also reflect the background value, is 70 ± 5 Bq kg^{-1}. These constraints made an exact dating using the ^{210}Pb radio isotopes somewhat uncertain. However, the maximum in the ^{137}Cs activity at 7.5 cm box core depth (Fig. 3A) indicates that at that depth the sediment was deposited in 1986, when the Chernobyl nuclear power plant accident happened. Below 11 cm box core depth no ^{137}Cs activity is detected, pointing towards sediments from before the first atmospheric nuclear weapons testings in the early 1950s. Because of these unambiguous sediment ages, it can be argued that at the ^{210}Pb background value at 15 cm box core depth (Fig. 3A) is a sedimentary disturbance or artefact, and that the above-background ^{210}Pb values below that depth are likely to be true. These values can be correlated with the ^{210}Pb values at 0–5 and 7.5–12 cm piston core depth, which are slightly above background. This indicates that at 7.5–12 cm the piston core sediments are from around 1850, while the sediment between 0 and 5 cm is likely from after 1900.

The radiocarbon age of the wood chip recovered from 11 to 12 cm is 240 ± 45 ^{14}C years BP (Table 1). Calibration towards calendar age resulted in three possible calendar ages, namely 1940, 1790 ± 25 and 1660 ± 25. Taking the ^{210}Pb results into account, the calibrated ^{14}C age of 1790 for the piece of wood recovered from 11 to 12 cm piston core depth seems to be the most probable, as the other two possible dates are either regarded too old (1660), or too young (1940). However, 1790 also does not correspond well
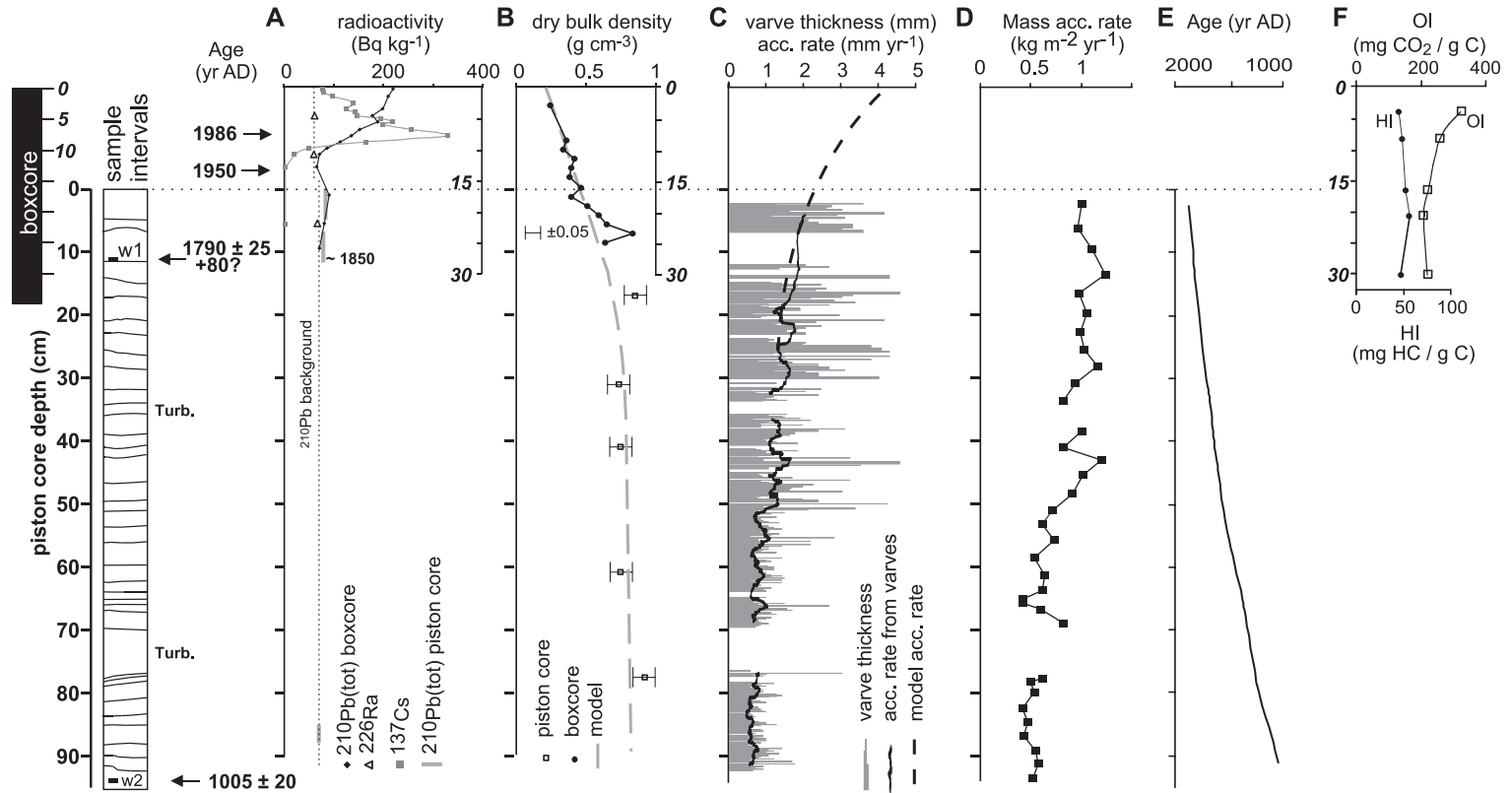
Fig. 3 ^{210}Pb, ^{137}Cs and [226]Ra data (A), dry bulk density (B) and varve thickness (C) and mass accumulation rate (D) of the sediment of Drammensfjord, as determined on subsamples of a box core (depth indicated in italics) and the upper meter of a piston core recovered from the depocenter of the fjord. The sampling intervals re indicated, as well as ages determined by radiometric analyses. The varve thicknesses in C are the combined thicknesses of a black and a grey lamina. Varves >5 mm are considered to be >1 year and are not plotted. The accumulation rate (C, black line) was based upon the varve thickness data. The dashed lines in plots B and C represent a fitted model based on the data. Sediment accumulation rates (D) were calculated based upon the fitted bulk density model and the accumulation rates based upon the varve thickness data. Plot E displays the age/depth scale for the piston core. In the upper right, oxygen and hydrogen indexes (OI and HI, respectively) measured on box core sediment samples are plotted (F).

Table 1
$\delta^{13}C$ values and radiocarbon ages of two organic macrofossils and a suite of isolated GDGTs from the depocenter of the Fjord

Compound	Core	Depth (cm)	$\delta^{13}C$ (‰)	^{14}C age (years BP)	calibrated age (years AD±1σ)	Sediment age (years AD)[a]	Res. age[b]
Wood-chip	P	11–12	−25.3	240±45	1657; 1788; 1940±25	1870±30	
Twig	P	94	−27.5	1030±35	1008±20		
GDGT-0	B	0–10	−24.7	<0	>1950 AD	1998–1990	
Crenarchaeol	B	0–10	−23.9	<0	>1950 AD	1998–1990	
GDGT-0	B	25–35	−25.7	440±90		1880–1820	325
Crenarchaeol	B	25–35	−24.8	385±60		1880–1820	270
GDGTs F+G+H	B	25–35	−28.4	1610±35		1880–1820	1495
GDGT-0	P	0–7.5	−25.2	520±75		1930–1890	420
Crenarchaeol	P	0–7.5	−24.5	860±120		1930–1890	760
Crenarchaeol	P	85–92	−24.5	1020±240		1140–1040	90
GDGTs F+G+H	P	85–92	−28.6	1050±80		1140–1040	120

Core: P=piston core; B=box core.
[a] Sediment ages as derived from the age model described in the text.
[b] Reservoir age=measured ^{14}C age minus atmospheric ^{14}C age.

with a sediment age of ca. 1870, the age inferred from the ^{210}Pb profile, but this may be explained by pre-aging of the wood-chip. As indicated by its angular appearance, it is likely a piece of wood derived from a full-grown tree that was cut for commercial use, which can easily have been ca. 100 years old. The calibrated age of 1008±20 years of the twig at 94 cm piston core depth (^{14}C age 1030±35 years BP) is considered unambiguous, which means that the laminated sediments above 92 cm piston core depth were deposited after that date.

The number of varves counted between 0 and 94 cm depth by grey-scale analysis was 735. However, in the upper black, relatively unconsolidated part of the sediment no varves could be determined. Furthermore, at times with a higher degree of euxinia or less mixing, some years may not exhibit grey laminae, as is especially the case in the upper part of the sediment. To correct for this, all unusually thick varves within the sequence were attributed to multiple years. The sediments between 70–77 and 35–37 cm depth (Fig. 2) were identified as redeposited sediment beds (turbidites), and it is likely that at the bottom of these beds some laminated sediment was eroded. After these corrections, a moving average of the varve thicknesses was used to determine sediment accumulation rates (Fig. 3C). Using the sediment ages determined by radiometric analysis as a framework, this allowed an age determination for the individual sediment sections used in this study (Fig. 3E). The decreasing varve thickness and accumulation rate with

time (Fig. 3C) can mainly be attributed to compaction. To estimate the accumulation rates of the upper part of the sediment, a logistic model, describing the development of the dry bulk density due to compaction, was fitted with both the measured dry bulk density data and the accumulation rates of the lower part of the core (Fig. 3B and C). Combination of the bulk density data with the sediment accumulation rate lead to a gradually increasing mass accumulation rate (Fig. 3D), which increases from approximately 0.5 towards 1.0 kg m^{-2} year^{-1} over the last millennium. This increase may be due to the slow decrease of the sill depth due to the isostatic uplift of the Scandinavian continent at 3–4 mm/year (Pirazzoli, 1991), resulting in a gradually increasing containment of the sediment by the shallow sill.

4.3. Bulk organic matter sources

The accumulation rate (AR) of the total organic carbon (TOC) of the Drammensfjord sediment gradually increases from 5 to 10 g m^{-2} year^{-1} during the period 1000–1800 (Fig. 4), while the total nitrogen (TN) AR shows approximately the same profile (Fig. 4). These ARs correlate with the gradual increase in the mass accumulation rate until that time (Fig. 3). This suggests that most organic matter is also terrigenous, because the sediment is predominantly of a terrigenous origin. The $\delta^{13}C_{TOC}$ content increases slightly from −27.6‰ at 1100 to −26.7‰ around 1850 (Fig. 4), values which are comparable with the
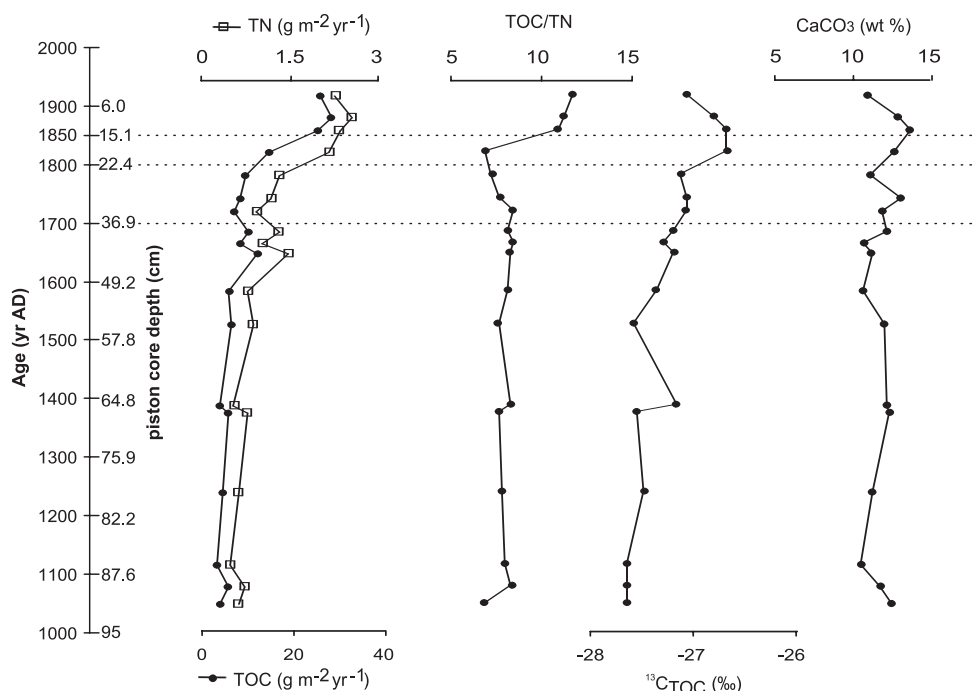
Fig. 4 Age/depth profiles of accumulation rates of total organic carbon (TOC) and total nitrogen (TN), TOC/TN ratio, $\delta^{13}C_{TOC}$ values and CaCO$_3$ contents.

two $\delta^{13}C$ values obtained from the two pieces of wood used for radiocarbon dating, −25.3‰ and −27.5‰ (Table 1). This corroborates with the earlier interpretation of a predominantly terrigenous origin of the organic matter. The observed gradual $\delta^{13}C_{TOC}$ increase may stem from a gradual relative increase of marine derived organic matter, as this generally exhibits lower $\delta^{13}C$ values than terrigenous organic matter (Deines, 1980; Tyson, 1995), but a gradual change in the composition of the terrigenous organic matter is equally possible. Taking the different $\delta^{13}C$ values of the wood pieces and the invariable TOC/TN ratio into consideration, as well as biomarker distributions as discussed below, we favour the latter interpretation. The Rock-Eval hydrogen and oxygen indices, respectively, ca. 50 mg HC/g C and 200–300 CO$_2$/g C (Fig. 3F), obtained for the upper sediments of the fjord, also indicate a predominantly terrestrial origin of the organic matter (type IV, e.g. Whelan and Thompson-Rizer, 1993), especially when the anoxic conditions in the fjord are considered. The invariable TOC/TN ratio (g/g) of ca. 8, until 1800, is similar to many anoxic fjord sediments receiving riverine

particulate organic matter (Tyson, 1995). In the 18th century the ARs of TOC and TN (Fig. 4) start to increase substantially to 30 g m^{-2} year^{-1} for TOC and 2.5 m^{-2} year^{-1} for TN around 1900. This is likely related to the increasing sawmill activities in the region of the fjord, resulting in an increased flux of organic waste to the fjord. In the first part of that period, the TOC/TN ratio decreases gradually from 8 to 7, when the TN AR increase lags the TOC AR increase (Fig. 4), with a sudden increase to 12 around 1850. The increase is likely related to industrialisation of the saw- and paper mill industry after 1850, leading to the deposition of large amounts of fibrous organic matter, which generally exhibit high C/N ratios (Tyson, 1995). The initial decrease is enigmatic, but may be related to the stimulation of bacterial activity by the initial slow increase of the organic matter load.

4.4 Biomarker composition of the sediments

4.4.1. Long-chain alkyl compounds

The lipid extracts of the sediments are dominated by vascular-plant-derived long-chain *n*-alkanes, *n*-

fatty acids and *n*-alcohols, with the typical strong odd-over-even or even-over-odd distributions (Kolattukudy, 1980) (Fig. 5; Table 2), while generally less abundant terrigenous biomarkers like alkan-2-ones and wax-esters (e.g. Volkman et al., 1981; Smittenberg et al., 2004b) were also detected (Table 2). This biomarker distribution is in agreement with the dominance of terrigenous organic matter to the fjord as determined by bulk parameters. Furthermore, a suite of even carbon numbered ω-hydroxy fatty acids (C_{22}–C_{30}) and (ω-1)-hydroxy fatty acids and (C_{24}–C_{30}) were observed in the Drammensfjord sediments (Fig. 5; Table 2), compounds that are not very commonly reported in literature. Long-chain ω-hydroxy fatty acids have been reported as minor components in suberin (Kolattukudy et al., 1973) but unlike in the Drammensfjord sediments they are in that case, however, accompanied by much higher abundances of the C_{16} and C_{18} homologues, which makes suberin an unlikely source in this instance. There are several reports of long-chain ω-hydroxy

fatty acids in, mainly decomposing, eelgrass species within intertidal sediments (Nichols et al., 1982; Volkman et al., 1980; de Leeuw et al., 1995), and they are generally attributed to microbial oxidation of alkyl chains. Microbial oxidation can also produce (ω-1)-hydroxy fatty acids (Miura and Fulco, 1975), which has in most instances been assumed to be their most likely source in sediments (e.g. Boon et al., 1977; Goossens et al., 1989; Wakeham, 1999), a conclusion that can also be drawn from the data presented by Huang et al. (1996) for largely unoxidised Miocene lacustrine sediments. Methanotrophic bacteria are an unlikely source for (ω-1)-hydroxy fatty acids in the Drammensfjord sediments, because of the absence of other diagnostic compounds (cf. Skerratt et al., 1992). It is, however, remarkable that the scarce reports of these compounds in sedimentary biomarker essays are all from anoxic or low oxygen-sediments of lacustrine or estuarine signature. Possibly, these compounds are produced through incomplete oxidation of alkyl compounds by, e.g. nitrate or
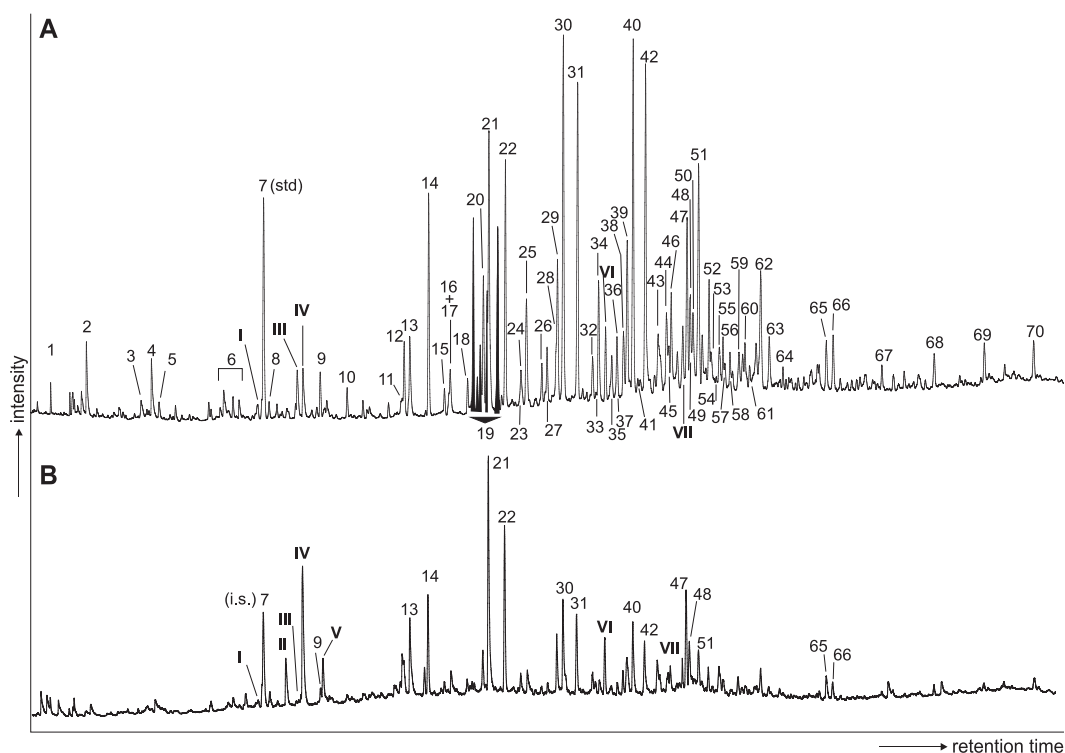

Fig. 5 Gas chromatograms of total lipid fractions of extracts derived from 50 to 52 cm core depth (A) and from 5 to 7.5 cm core depth (B). The peak numbers and lettering refer to compounds listed in Table 2. Roman numerals refer to structures shown in Appendix A.

Table 2
List of compounds identified in Drammensfjord sediment extracts

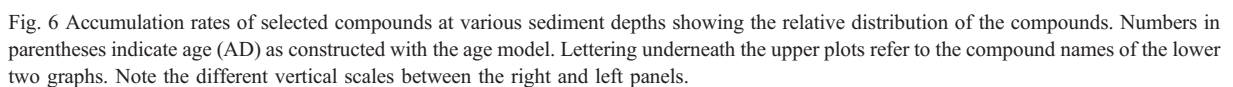|			
1	C_{14} FA	VI	tetracosane-2,23-diol
2	Loliolide	35	C_{27} OH
3	$C_{16:1}$ FA	36	ω-OH C_{24}FA
4	C_{16} FA	37	cholest-5-en-3β-ol
5	Norabietane	38	C_{29} alkan-2-one
6	$C_{18:2}$+$C_{18:1}$+C_{18} FAs	39	C_{31} *n*-alkane
I	pimaric acid	40	C_{28} FA
7	6-D_2-3-methylheneicosane (i.s)	41	hop-22(29)-ene
8	phytol	42	C_{28} OH
II	isopimaric acid	43	24-methylcholest-5-en-3β-ol
III	1-phenanthrene carboxylic acid	44	24-ethylcholesta-5,22-dien-3β-ol
IV	dehydroabietic acid	45	(ω-1)-OH C_{26} FA
9	C_{23} *n*-alkane	46	C_{29} FA
V	abietic acid	VII	hexacosane-2,25-diol
10	C_{20} OH	47	24-ethylcholest-5-en-3β-ol
11	C_{23} alkan-2-one	48	24-ethylcholestan-3β-ol
12	C_{25} *n*-alkane	49	ω-OH C_{26} FA
13	C_{22} FA	50	4,23,24-trimethyl-5α-cholest-22-en-3β-ol
14	C_{22} OH	51	C_{30} FA
15	C_{26} *n*-alkane	52	C_{30} OH
16	C_{23} FA	53	4,23,24-trimethyl-5α-cholestan-3β-ol
17	C_{16} monoglycerol ester	54	lanosta-8,24-dien-3β-ol
18	C_{23} OH	55	tetrahymanol
19	$C_{32–34}$ mono- and bicyclobotyococcenes	56	diplopterol
20	C_{27} *n*-alkane	57	(ω-1)-OH C_{28} FA
21	C_{24} FA	58	C_{31} FA
22	C_{24} OH	59	octacosane-2,27-diol
23	C_{18} monoglycerol ester	60	C_{31} OH
24	C_{28} *n*-alkane	61	ω-OH C_{28} FA
25	C_{25} FA	62	C_{32} FA
26	C_{25} OH	63	C_{32} OH
27	ω-OH C_{22} FA	64	ω-OH C_{30} FA
28	C_{27} alkan-2-one	65	17β,21β(*H*)-bishomohopanoic acid
29	C_{29} *n*-alkane	66	17β,21β(*H*)-bishomohopanol
30	C_{26} FA	67	C_{38} wax-esters
31	C_{26} OH	68	C_{40} wax-esters
32	C_{30} *n*-alkane	69	C_{42} wax-esters
33	(ω-1) C_{24} FA	70	C_{44} wax-esters
34	C_{27} FA		

The Arabic and Roman numbers refer to the peaks indicated in Fig. 5. The structures of the compounds numbered with Roman numerals are given in Appendix A.
FA=fatty acid; OH=alcohol; i.s=internal standard.

sulphate reducing bacteria, which are likely abundant just below the chemocline (Cole and Pace, 1995). Taken the observations lined out above, it can also be argued that the (ω-1)-hydroxy fatty acids are early oxidation products within plant debris which are protected from further degradation once they encounter anoxic conditions, while they would normally disappear from the sedimentary record under oxygenic conditions.

Tetracosane-2,23-diol (**VI**, see Appendix A) and hexacosane-2,25-diol (**VII**) and, to a lesser extent, docosane-2,21-diol and octocosane-2,27-diol (i.e. even carbon numbered C_{22}–C_{28} β,(ω-1)-diols), are abundant compounds within the lipid extracts of the Drammensfjord sediments. The distribution of these diols is similar to that of the *n*-alcohols and *n*-fatty acids, with the AR of the C_{24} homologue increasing substantially in the upper part of the core (Figs. 5

and 6). These diols have only scarcely been reported in the literature (Versteegh et al., 1997) and they have, to the best of our knowledge, never been detected in any identified organism. The same diols were detected in the sediments of the anoxic and monomictic Ace Lake, Antarctica (Schouten et al., 2001). This lake does not receive any vascular plant material, and is dominated by prokaryotic, aquatic organisms (Volkman et al., 1986), implying that the β,(ω-1)-diols may be attributed to an aquatic source. They were also detected in lipid extracts of an anoxic wastewater treatment plant (unpublished results, cf. Schmid et al., 2003). In contrast, the remarkable similarity between the distributions of the n-alcohols and the β,(ω-1)-diols suggests a direct relationship with those n-alcohols, i.e. either the diols are oxidation products of terrigenous alkyl compounds, or they share a similar source. The origin of these compounds remains thus inconclusive, although the prevalence of anoxic conditions in both in Ace lake, the wastewater treatment plant and in the Drammens-

Fig. 6 Accumulation rates of selected compounds at various sediment depths showing the relative distribution of the compounds. Numbers in parentheses indicate age (AD) as constructed with the age model. Lettering underneath the upper plots refer to the compound names of the lower two graphs. Note the different vertical scales between the right and left panels.

fjord suggests at least a relationship of the occurrence of β,(ω-1)-diols with anoxia.

4.4.2. 'Coniferous' biomarkers

A major compound in especially the upper core section was dehydroabietic acid (**IV**, see Appendix A) (Fig. 5). Its precursor abietic acid (**V**), and diagenetic product norabietane (Simoneit et al., 1985), and the related compounds pimaric acid (**I**), isopimaric acid (**II**) and their hydrogenated counterparts (**III**) were also found, albeit sometimes in trace amounts. These lipids or their precursors are major compounds in the resins of coniferous trees (e.g. Otto and Simoneit, 2002) and have previously been detected in abundance in sediments influenced by paper-mill waste (Simoneit, 1986). They have also been observed in the sediments of the inner Oslofjord (Pinturier-Geiss et al., 2002).

4.4.3. Glycerol dialkyl glycerol tetraethers

Other biomarkers present in the Drammensfjord sediments are glycerol dialkyl glycerol tetraethers crenarchaeol and GDGT-0 (Fig. 7A and D). Until recently, crenarchaeol was attributed solely to non-thermophilic marine crenarchaeota (e.g. Sinninghe Damsté et al., 2002), but has recently also been found in lakes (Powers et al., 2004), rendering this compound a biomarker for marine or lacustrine crenarchaeota. GDGT-0 is a more general archaeal lipid that is

also produced by, e.g. methanogenic terrestrial archaea (Schouten et al., 2000 and references therein), and the same holds for the less abundant GDGT-1 and GDGT-2 (Fig. 7B and C). The similarity in the AR profiles of these isoprenoidal GDGTs (shown for A and D in Fig. 8), increasing from the early 18th century onwards, suggests that they are all derived from the same crenarchaeotal source.

Besides the isoprenoidal DGDTs, branched non-isoprenoidal GDGTs were detected (Fig. 7F–H). These compounds have so far only been found in peats, soils and coastal sediments (Sinninghe Damsté et al., 2000), and are currently attributed to a terrigenous prokaryotic source (Schouten et al., 2000). Their ARs remain virtually constant throughout the core (Fig. 8). The combined non-isoprenoidal GDGTs from 25 to 35 cm box core depth show a radiocarbon age of 1610 ± 35 years (Table 1), pointing towards either extensive pre-ageing of these lipids in the soil (Trumbore, 2000) before transportation to the fjord sediment, or towards a use of old or fossil carbon derived from, e.g. dissolving rock carbonates or slowly degrading organic matter (Heier-Nielsen et al., 1995). Enigmatically, the combined non-isoprenoidal GDGTs from 85 to 92 cm piston core depth have an ^{14}C age of 1050 ± 80 years BP, which is close to the sediment age, suggesting a carbon source that is in equilibrium with atmospheric CO_2.
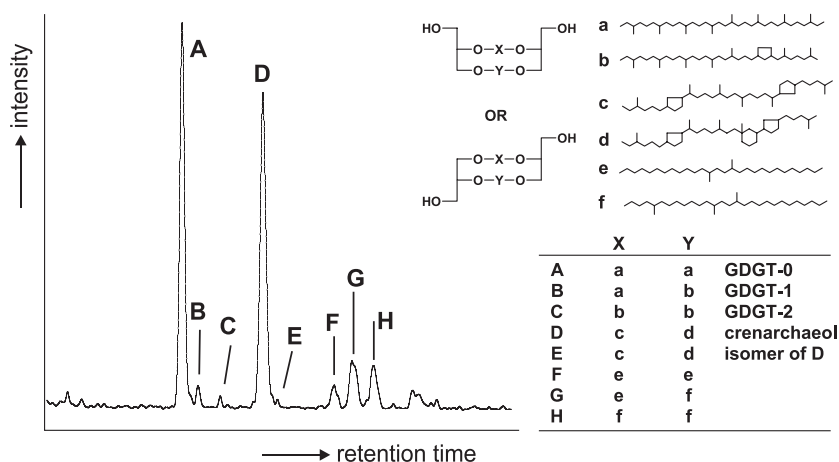

Fig. 7 HPLC base peak chromatogram of the polar fraction of the sediment extract from 32.5 to 35.5 cm piston core depth showing the GDGTs detected in the Drammensfjord. Chemical structures are given, with lettering as used in the text.
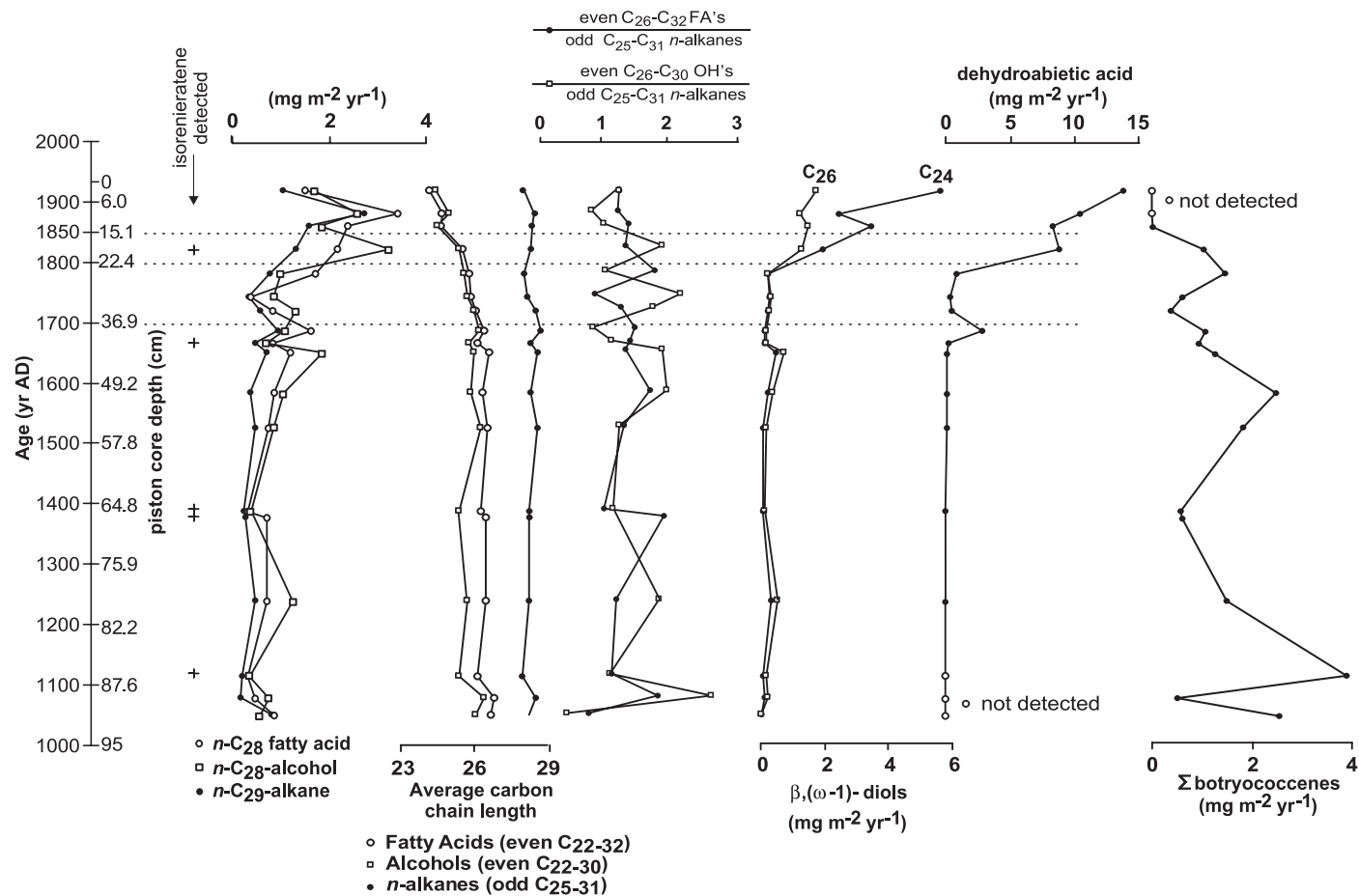
Fig. 8 Age/depth profile of ratios of the accumulation rates of odd long-chain *n*-alkanes, the average carbon chain lengths of the long-chain *n*-alkyl compounds, the ratios between the *n*-fatty acids, *n*-alcohols and odd *n*-alkanes, the accumulation rates of the C_{24} and C_{26} β,(ω-1)-diols, dehydroabietic acid and the sum of all botryococcenes. The samples in which isorenieratene was detected are also indicated.

4.4.4. Sterols

A few sterols were identified in the Drammensfjord sediments, but because the biomarker analysis was limited to that of the total lipid extracts, it is likely that a number of sterols with lower abundances remained undetected. The most abundant sterol was sitosterol (24-ethylcholest-5-en-3β-ol) (Fig. 5). Sitostanol (24-ethyl-5α(*H*)-cholestan-3β-ol), cholesterol (cholest-5-en-3β-ol), campesterol (24-methylcholest-5-en-3β-ol) and stigmasterol (24-ethylcholest-5,22-dien-3β-ol) were also detected in the total lipid extracts (Table 2). All these Δ^5 sterols are commonly found in vascular plants, and they are often the dominant ones in sediments with a high contribution of terrigenous organic matter. Cholesterol is also a dominant sterol in seawater, while all other detected sterols have also been found to be produced to some extent by algae (Volkman, 1986). However, based upon the high abundance of vascular plant material in the Drammensfjord, it is anticipated that the various sterols are primarily of terrigenous origin.

In contrast to the Δ^5 sterols, the source of dinosterol (4,23,24-trimethyl-5α(*H*)-cholest-22-en-3β-ol, Table 2) and dinostanol (4,23,24-trimethyl-5α(*H*)-cholestan-3β-ol) is almost undoubtedly aquatic, as these biomarkers are primarily produced by dinoflagellates (e.g. Boon et al., 1979; Kokke et al., 1982).

Lanosterol (lanosta-8,24-dien-3β-ol, Table 2) was detected in part of the sediment extracts. This sterol is a precursor compound in the biosynthesis of sterols in animals, fungi and most dinoflagellates (Giner et al., 1991), and therefore it is normally only present in relatively low abundances in living organisms compared with other sterols. Higher plants do not produce this compound, while it is also readily degradable. Therefore an aquatic source is inferred, with dinoflagellates as the most likely candidates.

4.4.5. Other biomarkers

A dominant group of compounds in the lower part of the investigated core are monocyclo- and bicyclobotryococcenes (Fig. 5), which can be attributed to the alga *Botryococcus braunii* (Kützing), as discussed in Smittenberg et al. (2005). This alga has commonly been reported in oligotrophic, humus-rich Scandinavian lakes (e.g. Rosén, 1981; Tyson, 1995), and has been present in the fresh water bodies in the Oslo region until the early 20th century (Huitfeldt-Kaas, 1917; Printz, 1914). However, *B. braunii* may also have thrived in the fjord itself (Smittenberg et al., 2005). The AR of the botryococcenes decreases on average throughout the core (Fig. 6), and they are entirely absent after 1850.

Isorenieratene, a carotenoid produced by strictly anaerobic photosynthetic green sulphur bacteria (Hartgers et al., 1994 and references therein), was detected in trace amounts (ca. 10 ng/g sediment) in a number of sediment samples throughout the core (Fig. 8), suggesting that euxinic bottom water conditions have prevailed over the last millennium, irregularly extending into the photic zone.

Loliolide is an anoxic degradation product of fucoxanthin (Repeta, 1989), a carotenoid predominantly found in diatoms (Wahlberg and Eklund, 1998), and present throughout the core (Fig. 6). The detection of loliolide agrees with both the presence of diatoms, as already noticed from the presence of their frustules in the sediments, and with the prevalence of anoxic bottom water conditions over the last millennium.

The general bacterial biomarkers 17β,21β(*H*)-bishomohopanol and 17β,21β(*H*)-bishomohopanoic acid (Taylor, 1984; Rohmer et al., 1992) are present throughout the core (Fig. 6). Tetrahymanol (gammacer-3β-ol) exhibits approximately the same profile (Fig. 6). Although this compound can be produced by the photosynthetic purple bacteria *Rhodopseudomonas palustris* (Kleemann et al., 1990; Harvey and McManus, 1991), it is also indicative for the presence of extensive grazing by bacterivorous ciliates of the genus *Tetrahymena* under anoxic conditions when their diet contains no sterols (Harvey and McManus, 1991; Sinninghe Damsté et al., 1995 and references therein).

4.5 Anoxic water conditions and organic matter preservation

The preservation of varves and the presence of iron sulphides within the Drammensfjord sediments indicate that the present-day euxinic conditions in the fjord's bottom water prevailed over the last millennium, at least in the deepest part. The detection of isorenieratene in some of the extracts (Fig. 8) indicates that the upper limit of the euxinic zone

(the chemocline) occasionally overlapped with the lower part of the photic zone. Currently, the chemocline lies at around 30 m water depth, but due to a high turbidity of the water the photic zone extends only a few meters below the surface. This prevents the growth of photosynthetic green sulphur bacteria, even though they can thrive in very low light conditions (Montesinos et al., 1983). Using foraminiferal assemblages, Alve (1991) showed that in the last 150 years the chemocline shallowed. Thus, before 1850 the chemocline must have been below 30 m depth, while at the same time the photic zone must have been reaching approximately the same depth. It can therefore be argued that the fjord waters were much clearer before the 18th century. However, a photic zone extending to a depth of over 30 m also suggests relatively oligotrophic conditions with limited phytoplankton abundance, as can also be inferred from the relatively low ARs of planktonic/aquatic biomarkers (Fig. 6), except those for *B. braunii*. The variance of the chemocline depth, as suggested by the intermittent detection of isorenieratene in the core, is in settings like that of the Drammensfjord for a large part dependant on the frequency and strength of bottom water renewals (Anderson and Devol, 1987).

The stable and radiocarbon isotopic composition of biomarkers may give insight into the extent to which the bottom waters are renewed. In settings with stagnant water conditions, carbon recycling can have a significant effect on the carbon isotopic composition of DIC (Fry et al., 1991; Goericke and Fry, 1994; Hartgers et al., 2000): DIC formed upon degradation of sinking ^{13}C-depleted primary produced organic matter or terrigenous derived DOC (del Giorgio and Peters, 1994) is retained in the water column and not exchanged with atmospheric CO_2. This δ^{13}C-depleted DIC can, after partial mixing back into the photic zone, be sequestered again by primary producers. This results in lower δ^{13}C values of marine biomass compared with well-mixed open ocean circumstances. Crenarchaeol appears to record the carbon isotopic composition of DIC rather accurately. Produced upon uptake of bicarbonate by marine crenarchaeota (Wuchter et al., 2003), its open ocean δ^{13}C values are almost invariably measured around −21‰ (Hoefs et al., 1997; Schouten et al., 1998; Pearson et al., 2001), suggesting a constant biosynthetic isotopic

fractionation not affected by environmental conditions. Here, the δ^{13}C values of crenarchaeol and GDGT-0 vary between −23.9‰ and −25.2‰ (Table 1), which is much more negative than the open ocean values, indicating that recycling of CO_2 is an important factor in the fjord waters.

Crenarchaeol and GDGT-0 from sediments deposited after 1950 clearly exhibit ^{14}C contents influenced by atmospheric nuclear weapons testing (Table 1), while those from before 1950 both exhibit a ^{14}C age of around 400 BP. This would imply a marine DIC reservoir age of approximately 300 ^{14}C years (Stuiver et al., 1998), which would be in agreement with a mixture of 3/4 Eastern North Atlantic ocean water, that exhibited a reservoir age of 400±50 years over the last 2000 years (Bondevik et al., 1999; Reimer et al., 2002), with 1/4 well-mixed ^{14}C-enriched fresh water from either the Scandinavian coast or from riverine water, i.e. the river Drammen. In contrast, the ^{14}C ages and calculated reservoir ages of crenarchaeol and GDGT-0 from the upper part of the piston core sediment are somewhat higher (Table 1), while the ^{14}C age of crenarchaeol isolated from 85 to 92 cm piston core depth shows only a minor difference with the sediment age, resulting in a low reservoir age (Table 1). These differences may lie in a varying contribution of fresh water and oceanic water to the fjord, as previously observed in Danish fjords (Heier-Nielsen et al., 1995), where dissolution of mineral, and thus fossil, $CaCO_3$ may also play a role. To further deconvolute the varying factors that determine the ^{14}C content of the GDGTs, which would allow more insight into the source of DIC in the fjord, a larger data set is necessary.

The permanently anoxic condition of the Drammensfjord sediments, combined with the relatively high sediment AR, results in ideal circumstances for the preservation of organic matter (Harvey and Macko, 1997; Hartnett et al., 1998). Degradation of organic matter and biomarkers, however, also occurs under anoxic conditions (Cole and Pace, 1995), with functionalised lipids being in general the most susceptible ones and saturated hydrocarbons the least (Cranwell, 1981; Sun and Wakeham, 1994). If (preferential) degradation of functionalised lipids would be prevalent, a changing ratio between the long-chain *n*-alkanes, *n*-alcohols and *n*-fatty acids would be expected. However, this is not case (Fig. 8),

which suggests that degradation of specific bio-markers does not play an important role in this setting.

4.6 Pre- and post-industrial biogeochemical changes

The ARs of the all long-chain n-alkanes, the n-fatty acids and n-alcohols increase slightly throughout the core until around 1750 (Figs. 6, 8). This is concurrent with the MAR (Fig. 3), and consistent with the interpretation that they make part of the riverine transported terrigenous material that makes up the bulk of the sediment. After 1750 the fatty acid and alcohol homologues $>C_{26}$ increase approximately 3-fold (Fig. 9), in line with the increase in the TOC content of the sediment (Fig. 4). Furthermore, the C_{24} and C_{22} n-fatty acids and n-alcohols start to become relatively more important around 1700, which is reflected in the average carbon chain lengths (Fig. 8), and their ARs start to rise steeply after 1800 (Fig. 9). The coniferous biomarkers dehydroabietic acid and related compounds also start to increase just before 1700 (Fig. 8), and become so abundant after 1800 (Fig. 9) that they become dominant lipids in the sediment extracts (Figs. 5 and 6). This is especially the case for the precursor compounds isopimaric acid and abietic acid (**II** and **V**), which are virtually absent before 1800 (data not shown). The AR of the terrigenous non-isoprenoidal GDGTs remains virtu-ally constant throughout the core (Fig. 9).

These variations in the terrestrial biomarker record indicate that after 1700 the nature of the terrigenous derived organic matter started to change, with an ever increasing flux of coniferous material to the fjord sediment. The overall 3-fold increase of the TOC and the 3- to 5-fold increase of the initially most dominant terrigenous biomarkers (i.e. the n-alkanes, the $>C_{26}$ n-fatty acids and n-alcohols) is in line with historical reports of sawmills that were present in the middle 18th century along the river Drammen (Alve, 1991 and references therein), and with the finding of several wood chips and twigs in the upper part of the sediment (Fig. 2). After 1800, the dramatic increase in the ARs of the C_{22} and C_{24} n-fatty acids, n-alcohols and diols, but especially of the 'coniferous' biomarkers points towards a heavily increased input of conifer-derived organic matter, while the 'background' organic matter input increased only moderately. The clear shift in the TOC/TN ratio from 8 to 12 around 1850 (Fig. 4)

and the decreasing $\delta^{13}C_{TOC}$ values in the upper 20 cm of the piston core (Fig. 4) are both as expected from a higher relative contribution of woody tissue to the TOC (Tyson, 1995). This shift marks the start of industrial saw- and paper mill activities where the flux of fibrous, nitrogen-poor organic matter increased substantially, while before that time the organic waste produced from pre-industrial saw mills mimicked TOC/TN ratios of naturally occur-ring terrigenous organic matter. A higher input of sawmill and paper mill derived organic matter is also likely the cause for the increase in the AR of sitosterol (Fig. 9) and other Δ^5 sterols. Leeming and Nichols (1998) found that all Δ^5 sterols reported above, except cholesterol, were major compounds in pulp-fibre pollution in a Tasmanian estuary. As discussed above, these sterols likely have a primary terrigenous source and may actually be dominant in paper and pulp waste. However, the increase could also, maybe partly, be related to an increase in the algal contribution of sterols.

In comparison with the terrigenous biomarkers, the aquatic biomarkers (dinosterol, loliolide, tetrahyma-nol, hopanoids, isoprenoidal GDGTs) are in general much less abundant (Figs. 5 and 6), except for bo-tryococcenes. This indicates that the pre-industrial state of the Drammensfjord was oligotrophic or mesotrophic, as could also already be inferred from the apparent clear waters before 1800, discussed above. A high trophic state would likely have resulted in a larger contribution of aquatic biomarkers [cf. Saanich Inlet, (Smittenberg et al., 2004a), Framvaren fjord (Ficken and Farrimond, 1995), Kyllaren fjord (Smittenberg et al., 2004b)]. The occurrence of *B. braunii* also fits within this reasoning, as this alga can thrive in relatively low trophic conditions (Tyson, 1995). The ARs of the aquatic biomarkers do not significantly change compared to that of the terrige-nous biomarkers during 1000–1700 (Figs. 8 and 9).

Striking is the 8- to 30-fold increase of the ARs of the bacterial biomarkers $17\beta,21\beta(H)$-bishomohopa-noic acid and -hopanol after 1800 (Fig. 9), as well as those of the bacterivorous biomarker tetrahymanol (Fig. 9), after a modest increase between 1700 and 1800. The sharp increase in the bacterial ARs concurs with the overall AR increase of organic matter and virtually all biomarkers, but especially with the 'coniferous' biomarker ARs (Fig. 9). This supports
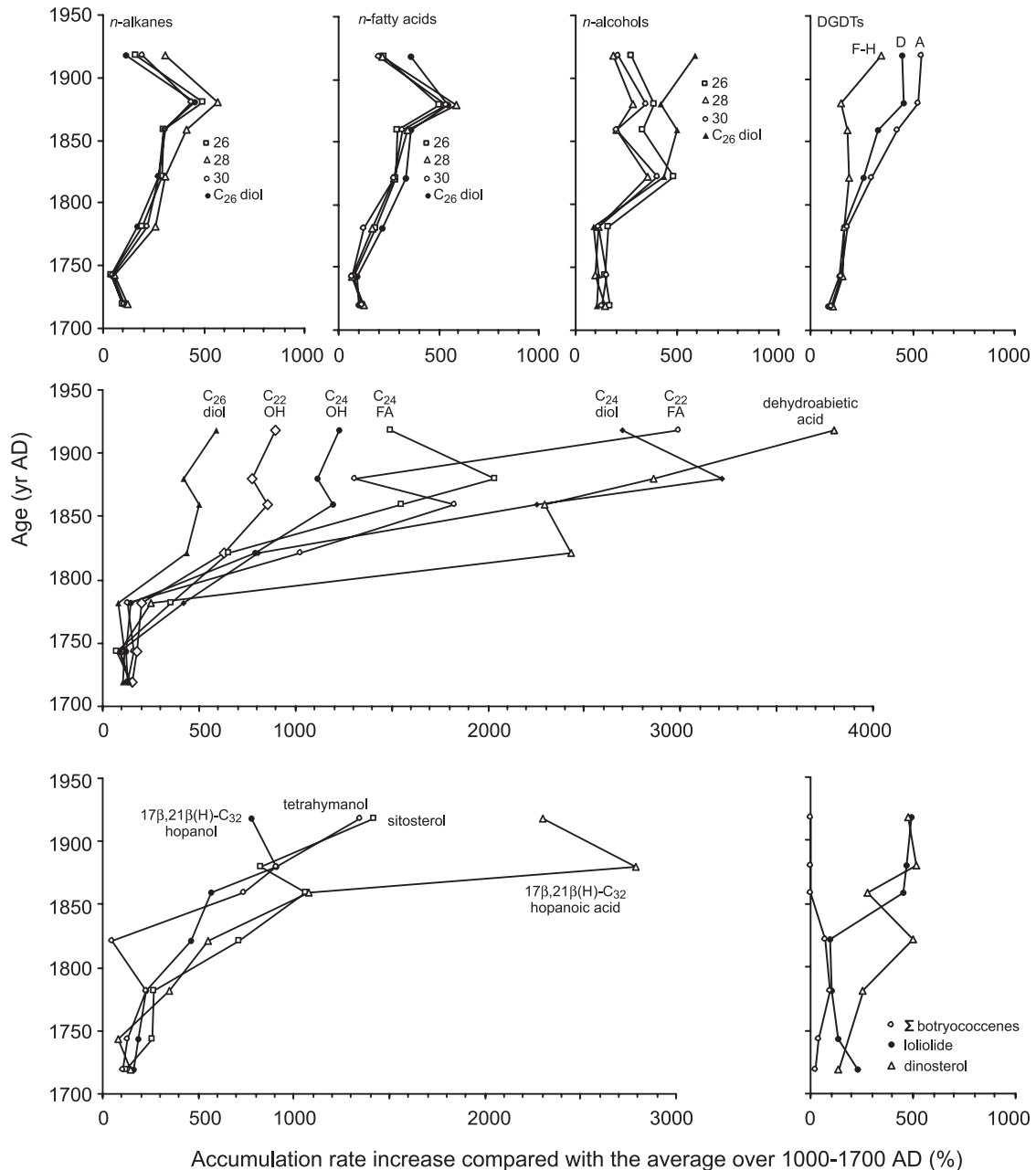
Fig. 9 Relative increases in accumulation rates of various biomarkers, compared to the average accumulation rates of 1050–1700. All horizontal scales are the same.

the theory of Alve (1991) that the relatively nutrient-poor fibrous organic waste, including DOC, from the early paper mills is slowly degraded by bacteria (del Giorgio and Peters, 1994). Indeed, a higher turbidity, combined with a shallower chemocline, can promote bacterial degradation (Cloern, 1987; Cole and Pace, 1995). The same factors may limit photosynthesis, but bacterial breakdown of nutrient-poor organic matter,

resulting in higher nutrient availability for phyto-plankton, may well offset these limitations (Cloern, 1987). Indeed, the ARs of dinosterol, loliolide, crenarchaeol and GDGT-0 increased approximately 5-fold in the last two centuries, which is a little more than the AR increase of the 'background' terrigenous biomarkers (Fig. 9). Thus, the increase of terrigenous organic matter input likely stimulated microbial degradation, which in its turn gave rise to an increase of the trophic state of the fjord, resulting in increased primary production by archaea, foraminifera, dino-flagellates and bacterivorous plankton, and likely a suite of other organisms. Besides this cascade of nutrient enrichment via bacterial degradation of saw- and paper mill waste, population growth and increas-ing agricultural activity in the fjord area was also likely responsible for some eutrophication (Dia, 2001), as has been shown for the last century (Alve, 1991 and references therein). Coprostanol, an indica-tive biomarker for faeces (e.g. Leeming and Nichols, 1998), was not detected in the sediments, which suggests that the fjord remained more or less unaffected by direct eutrophication from sewage waste.

With respect to eutrophication, part of the AR increase of sitosterol and other Δ^5 sterols may partially be derived from an algal source. The lagging of the diatom-sourced loliolide AR increase compared to the other aquatic biomarkers (Fig. 9) may be because diatoms thrive especially well under eutrophic con-ditions (Round et al., 1990), and their more abrupt increase suggests that before 1850 the trophic state of the fjord was not yet sufficient to induce larger diatom blooms. One algal species that did not profit from increased nutrient availability is *B. braunii*, as indicated by the absence of botryococcenes after 1850 (Figs. 6, 9). The changing environment with higher turbidity and nutrients, resulting in competition from other algal species that can take advantage of higher nutrient levels, like foraminifera and diatoms, likely led to the demise of this alga within the fjord, as discussed elsewhere (Smittenberg et al., 2005).

5 Conclusions

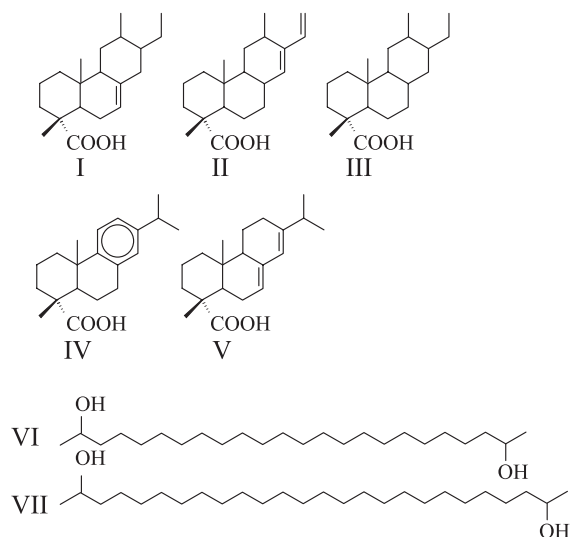The sedimentological and organic geochemical analyses of the sediments deposited in the depocenter of the presently anoxic Drammensfjord, Norway, revealed a number of environmental changes that occurred especially during last three centuries. Since 1000 AD, euxinic conditions prevailed in the fjord bottom waters, leading to the preservation of near-annually deposited varves, predominantly composed of terrigenous silt- to clay-sized mineral grains. The biogeochemical record indicates that the fjord used to be oligotrophic or mesotrophic and relatively clear, and the organic matter input to the sediments was mainly of terrigenous origin. It is inferred from relatively low $\delta^{13}C$ values of crenarchaeol that the ^{13}C content of DIC is depleted compared to normal oceanic water, which can be attributed to a high contribution of degraded terrigenous organic carbon and carbon recycling within the fjord. From 1000 to 1700, a gradual increase in the mass accumulation rate and, directly related to that, also an increase in the total organic carbon accumulation rate occurred. This may be attributed to the slow shoaling of the sill depth due to the isostatic uplift of Scandinavia, leading to a more efficient trapping of sediment in the fjord. From 1700 to recent times (1950), the organic matter accumulation rate increases approx-imately 3-fold, together with most both terrigenous and aquatic biomarkers, and this can be attributed to the development of saw mill activities in the fjord's hinterland. Indicative biomarkers for this are 'coniferous' biomarkers: dehydroabietic acid and related terpenoid compounds. However, straight-chain C_{24} and C_{22} fatty acids, -alcohols, and -hydroxy fatty acids also appeared to be closely related to saw mill waste. The accumulation rates of these bio-markers increase dramatically after 1800. These changes are attributed to an increasing load of coniferous fibrous material from industrialised paper mills, while the 'background' terrigenous organic matter flux to the fjord kept on increasing gradually. It is argued that the increasing organic matter load stimulated bacterial activity, resulting in increasing amounts of nutrients into the stagnant fjord waters. Although this was profitable for phytoplankton growth, the concurrent increase in turbidity and shoaling of the chemocline also likely provided a negative feedback. This study indicates that the baseline ecology of the fjord was already being affected in pre-industrial times when sawmill activ-ities in the hinterland started, but that with the onset

of industrial times the fjord's environment was affected dramatically.

Acknowledgements

Appendix A

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