Sources and effects of short-term environmental changes in Gullmar Fjord, Sweden, inferred from the composition of sedimentary organic matter

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Dissertations in Geology at Lund University,
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Cover Picture: *R/V Skagerak* in Gullmar Fjord during the DISCO 3 cruise in October 2015 (Bernhard Viehweger)

Abstract

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Viehweger, B., 2015: Sources and effects of short-term environmental changes in Gullmar Fjord, Sweden, inferred from the composition of sedimentary organic matter. *Dissertations in Geology at Lund University*, No. 460, 30 pp., 45 hp (45 ECTS credits).

Abstract: In this study I will assess sources and effects of short-term environmental changes on the sedimentary organic matter in Gullmar Fjord. To achieve this, a high resolution sediment core (sedimentation rate 0.7 cm yr^{-1}) was retrieved from the deepest part in the fjord and analyzed with multiple geochemical methods, targeting bulk organic matter and biomarker composition. The distribution of *n*-alkanes did not display any major changes for the terrestrial fraction in the investigated time frame from 1954 until 2014. Marine organic matter was found to be the dominant source of sedimentary organic matter in the fjord, though it is most likely produced remotely in the Skagerrak. Sea surface temperature (SST) reconstructions based on long-chain alkenones do not show any general increase during the studied interval, as observed from the hydrographic data set available for Gullmar Fjord. Temperatures of 14.1 to 21.1°C (mean 16.4 ± 1.6) were reconstructed, so the haptophyte blooms producing the long-chain alkenones occurred most likely during summer to early autumn. However, they would also fit to temperatures and blooming seasons reported for the Skagerrak. Even though Gullmar Fjord is considered to be free from industrial pollution, we found indications which could be interpreted as a slight contamination of the sediments by petrogenic hydrocarbons. Lower oxygen minimum concentrations observed in the bottom water since the 1980s are thought to be caused by changes in the North Atlantic Oscillation (NAO) and were related with a possibly ongoing eutrophication in previous studies. Signs for an ongoing eutrophication in the fjord were not visible in our sedimentary organic matter record, suggesting that most marine organic matter is produced in the Skagerrak, or that there is no ongoing eutrophication in the fjord since the 1950s.

Keywords: Gullmar Fjord, Skagerrak, biomarker, organic matter, n-alkane, sea surface temperature, alkenone, eutrophication, deoxygenation, sources, terrestrial, marine

Supervisors: Helena Filipsson and Petra Schoon

Subject: Quaternary Geology

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Svensk sammanfattning

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Sammanfattning:

Den här studien undersöker källor och effekt av kortsiktiga miljöförändringar genom studier av sedimentärt organiskt material (OM) i Gullmarsfjorden. En sedimentsekvens (sedimentationshastighet 0.7 cm år^{-1}) från den djupaste delen av fjorden analyserades i hög upplösning med flera olika geokemiska metoder applicerat på OM med fokus på komposition av biomarkörer. Fördelningen av *n*-alkener uppvisade inga större förändringar i den terrestra fraktionen under den undersökta tidsperioden mellan 1954 och 2014. Marint OM visade sig vara den dominerande källan av sedimentärt OM i fjorden, dock är det troligt att att produktionen skett längre ut i Skagerrak. Rekonstruktioner av havsytans temperatur baserat på långa kedjor av alkenoner uppvisar ingen generell ökning av temperaturen under den undersökta tidsperioden. Samma slutsats kan dras från hydrografiska data från Gullmarsfjorden. Temperaturer mellan 14.1 till 21.1°C (medel 16.4 ± 1.6) uppmättes vilket tyder på att blomningarna av fästalger (Haptophyta) som producerar långa kedjor av alkenoner troligtvis ägde rum under sommar till tidig höst. Temperaturspannet anstår emellertid också blomningstider och temperaturer rapporterade för Skagerrak. Även om Gullmarsfjorden anses förskonad från industriella föroreningar så fanns indikationer till en ringa förorening av petrogena kolväten. Tidigare studier har föreslagit att de syre-minima som observerats sedan 1980-talet kan vara beroende av den nordatlantiska oscillationen (NAO) vilket även har kopplats till den pågående eutrofieringen av fjorden. I denna studien fanns inga tecken på en pågående eutrofiering i fjorden utifrån det sedimentära organiska materialet, antingen på grund av dominansen av organiskt material från Skagerrak över terrestert alloktont kol alternativt bevis för avsaknaden av en pågående eutrofiering sedan 1950-talet och framåt.

Nyckelord: Gullmarsfjorden, Skagerrak, biomarkör, organiskt material, n-alkaner, havsytetemperatur, alkenoner, eutrofiering, syrebrist, källor, terrester, marin

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1 Introduction

During the past decades a global decrease in dissolved oxygen concentrations is observed in the world's coastal ocean areas (Rabalais et al., 2009 and 2010). The increased use of fertilizers as well as a large industrial and urban pollution are the main causes of this deoxygenation in coastal areas (Doney, 2010, Carstensen et al., 2014). Additionally, lower oxygen gas solubility in the oceans is the result of a steady warming trend observed in the last years. It is the main cause of deoxygenation in the open ocean and, to some extent, is also important in the coastal areas. Low oxygen concentrations in the water column greatly affect the sedimentary organic matter (OM), as less OM can be remineralized during sedimentation leading to increased carbon burial rates. Therefore, it is important to understand the effects of deoxygenation on carbon cycle processes in coastal settings. In my project I will focus on the definition of sedimentary OM sources and to what extent short-term environmental changes affect the composition of OM in fjord environments.

Fjord systems are a special class of continental margin environments, which account for 11% to 12% of the global organic carbon burial in the oceans (Nuwer and Keil, 2005, Smith et al., 2015). Furthermore, fjords are excellent systems to study recent environmental changes (e.g. Smittenberg et al., 2004, Filipsson and Nordberg, 2010, Sepúlveda et al., 2011, Faust et al. 2014). This is mainly because: [1] they act as a natural sediment trap with high sedimentation rates, allowing ultra-high (sub decadal) resolution studies on sediment cores. [2] limited deep-water exchange, small basin size and stratification enforce environmental changes faster than in open marine systems, in particular in areas with little tidal effects and - [3] due to their proximity to the coast, they are under severe pressure by anthropogenic activities, such as agricultural runoff and pollution.

The macro-, meio- and micro-fauna in fjords are strongly influenced by the climate and the environmental conditions. After death, their organic remnants and the microorganisms grazing and decaying them, make excellent targets to study the local carbon cycle. One objective of my study is to identify and quantify the contributions from terrestrial and marine sources of sedimentary OM accumulated in the Gullmar Fjord (Fig. 1). The other objective is to evaluate, if sedimentary OM is affected by short-term environmental changes observed in the fjord, such as hypoxia. Thus, my study contributes to gain a better understanding of the effects of those changes on carbon cycle processes in the poorly ventilated Gullmar Fjord.

Therefore, several methods and proxies for bulk sedimentary OM were applied in high-resolution to achieve an understanding of the overall OM composition and its properties. In addition, biomarker analyses were performed in lower resolution to create a more detailed overview of the specific OM sources and a better understanding of the carbon cycle interactions. Possible links of OM composition to the recently more frequently occurring low oxygen events (Fig. 4) will be investigated along with the effects of other documented environmental changes in the Gullmar Fjord area.

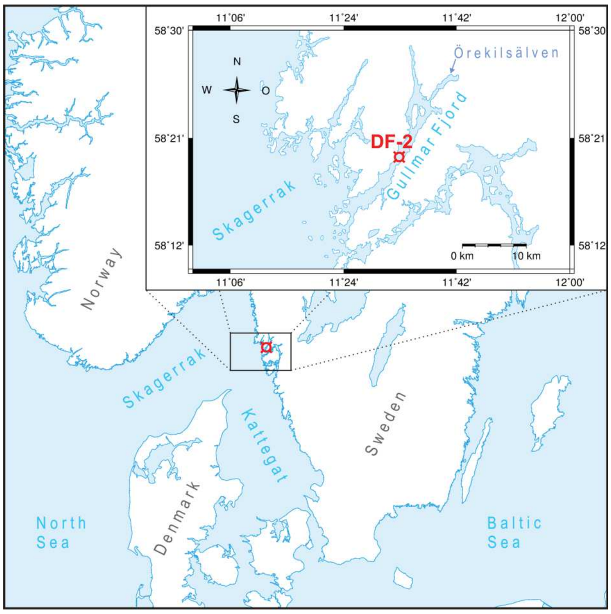

Fig. 1. Map of the sampling site DF-2 (58.316°N/11.540°E) in the Alsbäck Deep in Gullmar Fjord, Sweden. The fjord is 120 m deep, connected by a 42 m deep sill to the adjacent Skagerrak and highly stratified. The Örekilsälven is the main fresh water supply to the fjord. The base map was created with the open source software Generic Mapping Tools (GMT).

1.1 Background

1.1.1 Organic matter deposition

In general, OM concentrations in marine environments decrease from the photic zone, the main site of primary production (PP), to the sediment (Fig. 2). A large amount of OM derived from the PP is remineralized during sinking. The longer the OM is exposed to oxygen during and after deposition, the higher is the remineralization. Resuspension and redeposition of sediment at the basin slopes are processes leading to longer oxygen exposure times. Obviously, water depth, sinking velocity (related to particle size) and oxygen availability influence oxygen exposure time as well (Meyers, 1997).

1.1.2 Organic matter sources

Organic matter in coastal settings is a mixture of marine, terrestrial and anthropogenic sources, each with varying reactivity (Meyers, 1994, Zonneveld et al., 2010).

The majority of OM in continental margin sediments derives from phytoplankton blooms followed by fluvial input of land plant detritus (Meyers, 1997).

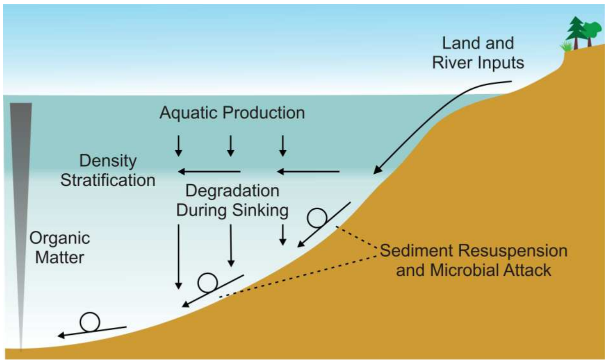

Fig. 2. General remineralization mechanisms for OM in marine environments during transport and deposition (modified from Meyers, 1997).

Terrestrial OM transported by wind represents only a small fraction of the total organic matter in marine sediments, while fluvial derived OM is the main transport mechanism of terrestrial OM to the marine realm (Meyers, 1997). Microorganisms utilize and degrade OM from PP, resulting in microbial derived OM which can represent a major portion of the total OM. Most primary OM produced in the surface water is respired by microorganisms during sinking with the extent of respiration being strongly dependent on multiple factors mentioned in the previous paragraph (see also Fig. 2) (Meyers, 1997). Even though microbial biomass in the water column can be high, the portion exported to the sediment is, due to small particle size, thought to be low. However, if it aggregates, bigger particle sizes and therefore higher sinking velocity could increase the importance of it in the total OM of marine sediments. In contrast, microbial activity in the sediments can yield a significant portion of microbial biomass in the total OM (Meyers, 1997). In-situ microbial activity in marine sediments is usually dominated by bacteria. As a result, PP in the water column and microbial *in-situ* growth are the two major and very distinct sources of marine OM in marine sediments. OM derived from zooplankton and animals is present as well, though usually less abundant (Meyers, 1997).

Thus, separating different sources of OM is important to identify the local controls on OM sedimentation and composition and therefore to be able to interpret variations in total organic carbon (TOC) content and its stable carbon isotope signature as actual changes in climate and environment.

C/N ratios are one of the most widely applied proxies to separate autochthonous from allochthonous OM (e.g. Sepúlveda et al., 2011; Faust et al., 2014). Marine derived OM usually has C/N ratios from 4 to 6 (Table 1), whereas terrestrial derived OM has usually a C/N ratio of over 20 (Meyers, 1994; Meyers 1997). The differences are caused by the general protein-rich (i.e. nitrogen-rich) composition of marine algae and microorganisms compared to the cellulose-rich (i.e. carbon-rich) composition of terrestrial plants. Stable carbon ($\delta^{13}C$) and stable nitrogen ($\delta^{15}N$) isotopes on TOC and total nitrogen (TN) are other proxies commonly used (e.g. Sepúlveda et al., 2011). Marine organisms produce $\delta^{13}C$ signatures of -20‰ to -22‰ (Meyers, 1994) and marine phytoplankton $\delta^{15}N$ signatures of 4‰ to 8‰ (Peters et al., 1978). Terrestrial OM derived from plants using the C_3 pathway yields $\delta^{13}C$ signatures of -27‰ (O'Leary, 1981) and an average $\delta^{15}N$ signature of 0.4‰ (Peters et al., 1978). The differences of both pathways are a result of the different carbon sources used for biosynthesis. Terrestrial plants use atmospheric CO_2 whereas marine phytoplankton utilizes dissolved inorganic carbon, mainly in the form of CO_2. So, an initial $\delta^{13}C$ fractionation of -7‰ of atmospheric CO_2 towards dissolved CO_2 in the oceans (Hayes, 1993 and 2001), leads to generally lower $\delta^{13}C$ values in terrestrial OM synthesized via the C_3 pathway.

A combination of multiple bulk parameters is a much more powerful tool to define the OM sources (see e.g., Sepúlveda et al., 2011). Nevertheless, C/N and stable isotope signatures of bulk OM have substantial drawbacks. One of them is that fjords are mixed systems and the application of a linear two end-member mixing model and its assumptions make it difficult to draw definitive conclusions (Perdue and Koprivnjak, 2007). Other drawbacks are end-member definition, effects of transport on OM, the assumption of TN being equal to total organic nitrogen (TON) in marine settings and low source specificity.

On the other hand, compound specific isotope analysis on specific biomarkers and their relative abundances are much more powerful tools, enabling one to assign compounds directly to different sources, thus avoiding the above mentioned limitations. Biomarkers are fossil chemical compounds, which have a biological origin and can be related to a specific group of organisms or to their metabolic pathways (Peters et al, 2005).

Biomarkers investigated in this study can be separated in three different categories: [1] straight-chain hydrocarbons, [2] isoprenoids and [3] triterpenoids.

Straight chain hydrocarbons are synthesized from acetyl-CoA and malonyl-CoA precursors. The most common examples are *n*-alkanes, *n*-alcohols and *n*-fatty acids. In nature, the latter two show a predominance of even numbered carbon chains over the odd numbered ones. After death, the start to degrade and lose their carboxyl and hydroxyl group, respectively,

Table 1. Stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) as well as C/N ratio ranges for different environments and sources of organic matter.

environment/source	**$\delta^{13}C$**	**$\delta^{15}N$**	C/N	references
marine phyto- and zooplankton	-22‰ to -19‰	-8‰ to -3‰	4 - 6	Meyers 1997
freshly deposited marine	-22‰ to -19‰	-8‰ to -3‰	8 - 10	Meyers 1997
C3-plants (= terrestrial	-32‰ to -26‰	ca. 0.4‰	20 - 50	Meyers 1994 & 1997
riverine OM	-35‰ to -25‰	ca. 5‰	11-13	Meyers 1997, Keil 1994
lacustrine algae	-30‰ to -25‰	ca. 0.4‰	5-10	Meyers 1994 & 1997

leading to an odd over even dominance of *n*-alkanes. Short, 12 to 24 carbon bearing *n*-alkanes are considered to be of bacterial and eukaryotal origin, whereas long, 25 to 33 carbon bearing *n*-alkanes are predominantly derived from terrestrial plant leaf waxes (Poynter and Eglinton, 1991). They reach the marine system by aerial and fluvial transport from land. Isotope signatures of long chain *n*-alkanes are often used as a terrestrial proxy (e.g. Sepúlveda et al., 2011; Mead et al, 2004; Sánchez-García et al, 2008). The most diverse group of straight-chain hydrocarbons are the *n*-fatty-acids. They can have multiple sources within the domains of bacteria and eukaryotes as they are main building blocks of their cell membranes, being linked with ester bonds to the glycerol backbone of cell membrane lipids. They do not occur in archaea as their cell membranes have ether instead of ester bonds to the glycerol backbone and cleaving them off, does not result in fatty acids but alcohols. Fatty acid compositions and their stable carbon isotope signatures are highly specific for different types of (microbial) metabolism or their source organism. Unfortunately we were not able to investigate fatty acids in this study.

Another important compound class for marine geochemical studies are alkenones. They are long-chain ketones with the keto-group on the second carbon atom and several double bonds in the carbon chain. The ratio of di- and tri-unsaturated alkenones with 37 carbon atoms ($C_{37:2}$ and $C_{37:3}$) was found to be linked to the sea surface temperature, making the $U^{K'}_{37}$ (Prahl and Wakeham, 1987) one of the most widely applied proxies in oceanography (e.g. Eglinton and Eglinton, 2008, Kaiser et al., 2015, van Dongen et al., 2008). Coccolithophores, which are unicellular, calcareous phytoplankton, were found to be the biological source of these long-chain alkenones. In present times, the main coccolithophore species producing the long-chain alkenones is called *Emiliana huxleyi*. Though the source is known, the biological function of long-chain alkenones is still under discussion (Eglinton and Eglinton, 2008). The temperature dependence of the unsaturation is a result of adaption to colder or warmer environments. Relative abundance of the tri-unsaturated $C_{37:3}$ alkenone is hereby increased in colder environments. As coccolithophores are calcareous organisms and therefore depend on high carbonate and salt concentrations, they almost exclusively occur in marine environments and not in fresh-water environments.

Isoprenoids are synthesized by polymerization of isoprene. Examples of isoprenoids are pristane and phytane. The latter is also found in archaeal cell membrane lipids but in non-extreme environments, such as fjords, it is mainly regarded as a product of anaerobic degradation of phytol. Both are degradation products of phytol which is a side chain of the chlorophyll macromolecule. Phytol is assumed to represent marine phytoplankton (algae and bacteria) but especially in settings with high terrestrial input it can also originate from plant chlorophyll. In settings with high primary production and strongly reducing conditions, pristane and phytane can also originate from α-tocopherol (Vitamin E) degradation (Peters et al., 2005, Rontani and Bonin, 2011).

Triterpenoids are synthesized via squalene or oxidosqualene, and are tetracyclic (steroids, eukaryotal) or pentacyclic (e.g. hopanoids, bacterial) (Volkman, 2005). With very few exceptions (Elvert and Niemann, 2008), both are very specific biomarker for their domain of life. Their biological function is stabilizing their respective cell membranes (e.g. Rontani and Bonin, 2011, Volkman, 1986).

In general, steroids are markers of eukaryotes and are especially widespread in planktonic organisms, e.g. diatoms (Hudson et al., 2001). Steroids with intact hydroxyl functional groups are called sterols and are very diverse. One prominent example of sterols is cholesterol. It is not very specific in regards of taxonomy, but it is widespread in eukaryotes and therefore, represents them very well as an entire community. In contrast, other sterols such as dinosterol, which originates from dinoflagellates, has very specific and valuable taxonomic information. This can be very useful when evaluating the role and the effect of a certain organism on the carbon cycle or to reconstruct OM sources in a detailed manner. Sterols derived from marine plankton have $\delta^{13}C$-values of -20‰ to -22‰. A detailed review on sterol synthesis and diversity can be found in Volkman (1986 and 2005).

Hopanoids are bacterial markers. Their stereochemistry and composition are often used as proxies for maturation of OM matter, including thermal degradation and early diagenesis of the sediment. Biologically produced hopanoids have a certain stereochemical configuration which is altered when exposed to temperature and pressure (Peters et al., 2005). For

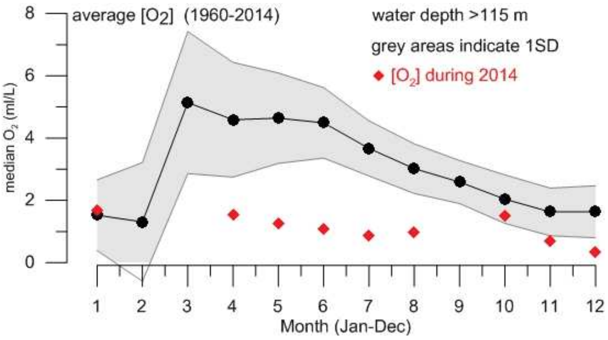

Fig. 3. Annually stacked median oxygen concentrations ($[O_2]$, black dots) in the bottom water of Gullmar Fjord from 1960-2014 compared to the year 2014 (red dots). The usual yearly bottom water renewal is visible by the sharp increase in median $[O_2]$ during February to March. It is followed by a slow decrease in median [O2] for the other months, representing the oxygen consumption in the bottom water. The data for 2014 did not show the regular bottom water renewal during early spring which resulted in sustained hypoxia for this year (figure from Filipsson, unpubl., based on SMHI's database SHARK).

studies on OM sources they can provide valuable ecological and chemotaxonomic information (Elvert and Niemann, 2008).

1.2 Sampling site

Gullmar Fjord on the Swedish west coast is 28 km long, about 1-2 km wide and stretches south-west to north-east (Fig. 1). The 120 m deep and roughly 5 km long fjord basin is separated by a 42 m deep sill from the Skagerrak. The top layer of the water column is mostly formed by the river run-off of Örekilsälven and other smaller rivers discharging in the fjord area. It is highly variable in thickness and time. For example, in October 2014 it had a thickness up to 2 m after massive rainfall and flooding whereas it was absent during the sampling in June 2014. Below the very fresh surface layer, a brackish surface water layer can be found down to 15 m and has salinities of 24-27. It is associated with the northward directed flow of brackish surface water from the Baltic Sea (Lindahl et al., 1998). The residence time is estimated to be 20-38 days (Arneborg, 2004). The intermediate layer has salinities of 32-33 and extends from 15-50 m water depth. This layer is more stagnant with residence times of 29-62 days and has similar properties as the adjacent Skagerrak water mass (Lindahl et al., 1998). The bottom water layer stretches down to the deepest parts of the fjord and has salinities of 34-35. The temperature is between 4-8°C and usually the water exchanges once a year during the early spring. The deep water originates as North Sea surface water. The stagnant conditions lead to increased stratification and low oxygen concentration of <2 mL L^{-1} before the exchange occurs between January and April. However in 2014 there was no exchange of the bottom water (Fig. 3). This has not occurred since the late 1990s and resulted in more severe hypoxia (<2 mL L^{-1}) with concentrations <1 mL L^{-1} (Fig. 4). In general, the stratification intensity and the water column properties highly depend on the extent and frequency of deep water exchange with the Skagerrak.

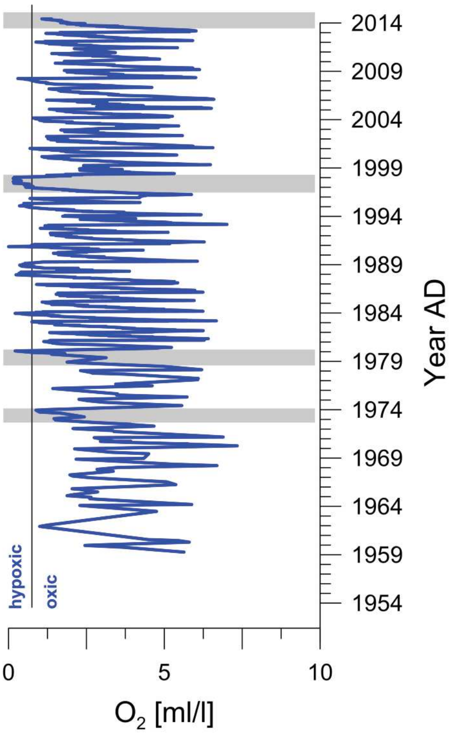

Fig. 4. Bottom water (>110 m) oxygen concentrations from 1959 till 2014. Periods of sustained hypoxia are marked by grey boxes. Generally lower minimum oxygen concentrations were observed from 1980. (data from SMHI's database SHARK)

Gullmar Fjord is an intensively monitored system (smhi.se) where several studies focused on the effects of changing oxygen conditions on the macro- and meiofauna (e.g. Dando and Spiro, 1993, Filipsson and Nordberg, 2004, Gustafsson and Nordberg, 2001, Nordberg et al., 2000). Benthic foraminifera showed a shift in 1979/80 from a Skagerrak-Kattegat fauna to a domination of the low oxygen tolerant benthic foraminifera *Stainforthia fusiformis* (Nordberg et al., 2000; Filipsson et al., 2004; Polovodova et al., 2011). Changes in dinoflagellate cyst assemblages during the 1970s were related to variations in hydrography, North Atlantic Oscillation (NAO) and eutrophication (Harland et al., 2006 and 2010). A $\delta^{13}C$ record of the benthic foraminifera *Cassidulina laevigata* showed ~2‰ variation during the last 2400 years and a major drop in the 1970s (Filipsson and Nordberg, 2010). However, the origin of the more negative $\delta^{13}C$ values after 1970 has not been fully resolved. The inorganic carbon pool, and therefore the isotope chemistry of foraminifera, is also influenced by the remineralization of OM. A focus on the OM will help to further explain the observed changes and will deepen our understanding of the carbon cycling in Gullmar Fjord.

2 Methods

During the DISCO 2 Cruise on the *R/V Skagerak* in June 2014, a GEMAX-corer was used to retrieve several sediment cores from the Alsbäck Deep in Gullmar Fjord at station DF-2 at a water depth of 120 m (58.316°N/11.540°E) (Fig. 1).

2.1 Water column parameters

Water column parameters were obtained by conductivity, temperature and depth (CTD) measurements from station DF-2B, Gullmar Fjord in June 2014. Dissolved O_2-concentrations and chlorophyll fluorescence were measured with additional sensors mounted on the CTD unit. Water depth and salinity were calculated from measured pressure and conductivity respectively. Salinity is hereby given in practical salinity units (psu).

2.2 Sediment sampling

A 43 cm long sediment core (DF-2B) was selected and sliced in 0.5 cm intervals directly after recovering and transferred to pre-cleaned glass jars, which were stored at -20°C prior to analysis. All samples were freeze-dried and homogenized. The analysis followed a dual

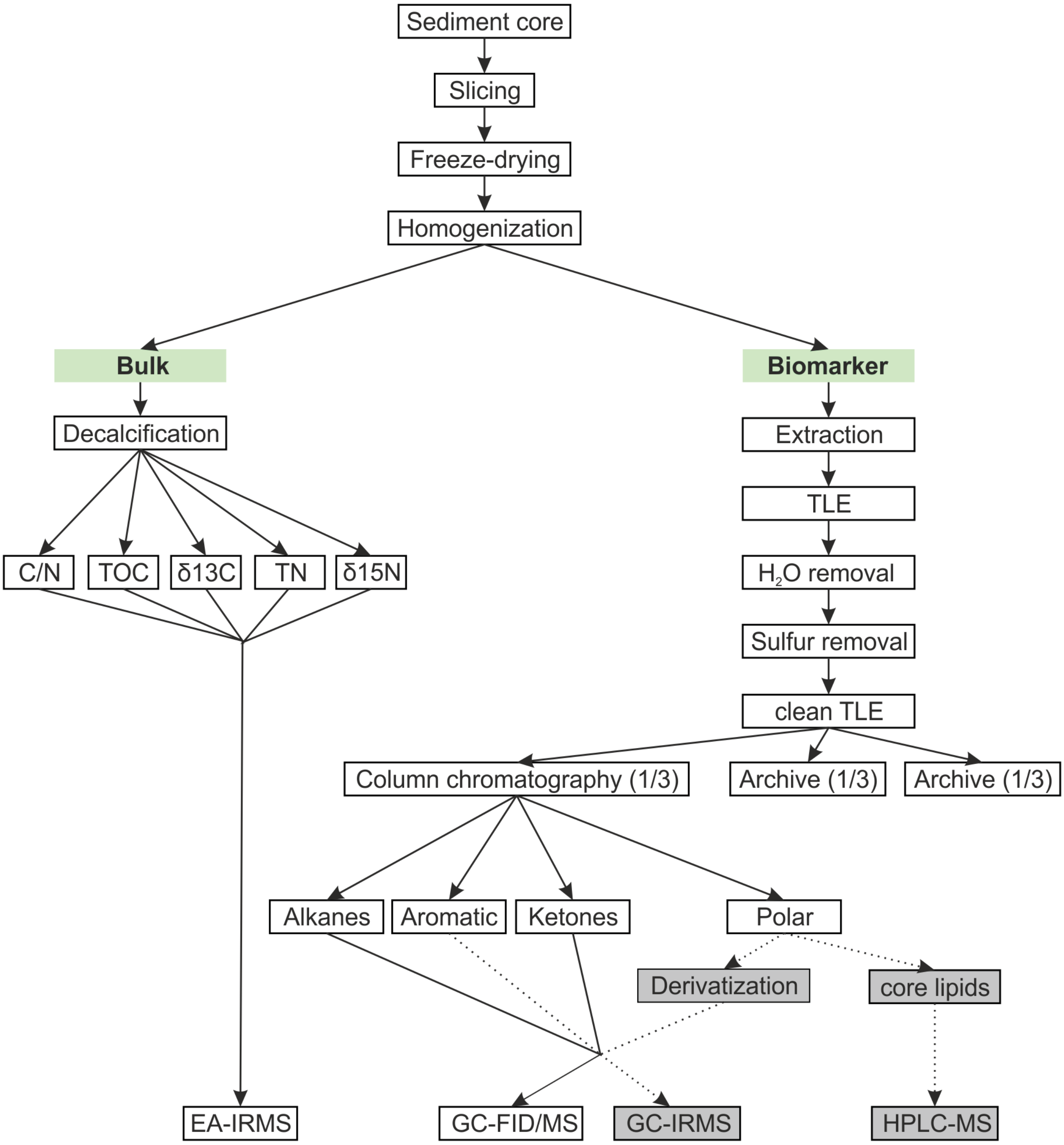

Fig. 5. Experimental approach of this study focusing on bulk organic matter and biomarker (green boxes). Dotted lines and grey background represent steps which were not carried out in this project but were performed by Petra Schoon or are planned for future work.

approach to evaluate sediment bulk and biomarker properties (Fig. 5). An amount of 1 g of dried sediment was used for bulk analysis, whereas the rest was stored for biomarker analysis.

2.3 Bulk organic matter analysis

All 83 samples were used for analyses of the following bulk parameters: total organic carbon (TOC), total nitrogen (TN) and their stable isotope values. Prior to analysis 8 mg of sediment were weighed in to silver capsules and decalcified. Decalcification was achieved following the "capsule method" described in Brodie et al. (2011a and 2011b). In short, 10 µL of ultra-pure water was added before the addition of 10 µL of 2N HCl to prevent splashing, and placed on a hot plate at 55°C. Subsequently, 20, 30 and 3x 50 µL of 2N HCl was added stepwise to ensure removal of inorganic carbon. Complete removal of inorganic carbon was guaranteed by visual inspection under the microscope for absence of bubbling after the last acid addition. Finally, all samples were dried in an oven at 40°C for 16 h.

After decalcification each sample in a silver capsule was placed in a tin capsule to improve combustion efficiency (Brodie et al., 2011a). Analysis was performed on an elemental analyzer coupled to an isotope mass ratio spectrometer (EA-IRMS). Stable isotope values are given in the delta notation and normalized to the Vienna Pee Dee Belemnite (V-PDB) standard for carbon ($\delta^{13}C$) and the atmospheric air for nitrogen ($\delta^{15}N$).

2.4 Biomarker analysis

Biomarker analysis was performed on selected samples with an 0.5 cm interval for the first 9 cm and a coarser resolution for the rest of the core.

2.4.1 Biomarker extraction

For each sample, two-thirds of the sediment stored for biomarker analysis were transferred to a pre-extracted cellulose thimble. All samples were soxhlet extracted with a Büchi B-811 extraction system at ~35°C for 72 cycles using a 200 mL solvent mixture of dichloromethane and methanol (DCM/MeOH, 7.5:1, v/v). Total lipid extracts (TLEs) were transferred to round bottom flasks and evaporated close to dryness with a Heidolph vacuum rotation evaporator (Rotavap). Sodium-sulfate columns were used to remove remaining water. Sulfur removal was done by adding sufficient amounts of activated copper to the TLEs. DCM was added to cover the samples and ensure contact of the TLEs and the copper for the overnight reaction to copper-sulfide. To clean the TLEs from the copper-sulfide, all samples were transferred to short sodium-sulfate columns and collected in pre-weighed 4 mL vials. The TLEs were then split into three equal aliquots; one for column chromatography and two for archive (Fig. 5).

2.4.2 Column chromatography

A standard mixture of 20 µL 5α-cholestane and squalene with 0.5 mg mL^{-1} concentration was added. The aliquot was transferred on a pre-rinsed column packed with combusted cotton wool and 0.75 g, 5% deactivated silica gel. Separation in four fractions was achieved by stepwise addition of ~4 mL solvent and solvent mixtures with increasing polarity. Solvents used were: [1] n-hexane (Hex, 100%), [2] hexane/dichlormethane (Hex:DCM, 9:1, vs/vs), [3] Hex/DCM (1:1, vs/vs)) and [4] DCM/MeOH (1:1, vs/vs) to split the TLE's in apolar, aromatic, ketone and polar fractions, respectively. Each fraction was collected in a pre-weighed 4 mL vial, left in the fume hood to evaporate to dryness, weighed again (see App. A) and stored at 4°C until further treatment.

2.4.3 Gas chromatographic analysis

All samples were analyzed on an Agilent 7890B Gas chromatograph connected to a flame ionization detector (GC-FID) equipped with a 25 m long CP-Sil 5 CB column (Agilent) with a diameter of 0.32mm and a solid film thickness of 0.12 µm. An auto sampler was used for cool on-column injection with a column flow rate of 2.4078 mL min^{-1}. The system was later switched to a HP 5 column (Agilent) with the same measures as the CP-Sil 5 CB and a splitless injection port. Inlet temperature was set to track the GC oven program and septum purge flow equal to 15 mL min^{-1}. Initial GC-oven temperature was set at 70°C, which was held for 1 min before increased to 130°C by a rate of 20°C min^{-}1, and subsequently followed by an increase to 320°C by a rate of 4°C min^{-}1, which was held there for 20 min. The FID detector was set to 300°C and quantification was achieved by integration of peak areas and by comparison to a standard of known concentration.

Identification of compounds was performed with a Shimadzu GC-2010 Plus gas chromatograph connected to a Shimadzu QP2010 mass spectrometer (GC-MS) equipped with a CP-Sil 5 CB column. Hand injection on a splitless inlet system was used to transfer the samples to the column. Resulting mass spectra were compared to known fragmentation patters and retention times for identification of biomarker.

2.5 Age model

The age model applied in this study was taken from Filipsson and Nordberg (2004). The authors used the ^{210}Pb methodology in combination with a constant rate of supply (CRS) model and biostratigraphy for the dating of a 60 cm long sediment core (GA113 2A) from a station nearby the Alsbäck depth in Gullmar Fjord. A sedimentation rate (SR) of 0.7 cm yr^{-1} of this core was chosen as it was applied for a similar time range from 1915 to 1999 by Filipsson and Nordberg (2010). All results from this study are plotted using the same age model and SR, including a linear extrapolation from 1999 to the year 2014.

2.6 Mixing model

A simple linear two end-member mixing model was used to separate terrestrial and marine sources (Thornton and McManus, 1994)

$$F(t) = \frac{X - X(m)}{X(t) - X(m)}$$

(Eq. 1)

In which F(t) is the terrestrial fraction and X, X(t) and X(m) are referring to the sample, the marine end-member and the terrestrial end-member.

2.7 Calculations for biomarker ratios

The calculations for the more complex biomarker ratios are displayed. Information about the application and purpose are given in the result and discussion section below.

Average chain length (ACL)

$$ACL = \frac{25*C_{25}+27*C_{27}+29*C_{29}+31*C_{31}+33*C_{33}}{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}$$

(Eq. 2)

Carbon preference index (CPI)

$$CPI = \frac{1}{2} * \left(\frac{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}{C_{24}+C_{26}+C_{28}+C_{30}+C_{32}} + \frac{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}{C_{26}+C_{28}+C_{30}+C_{32}+C_{34}} \right)$$

(Eq. 3)

Terrestrial alkane ratio for hydrocarbons (TAR_{HC})

$$TAR(HC) = \frac{C_{27}+C_{29}+C_{31}}{C_{15}+C_{17}+C_{19}}$$

(Eq. 4)

3 Results

3.1 Water column parameters (CTD)

The temperature in the surface water in June 2014 was around 18°C with a drop to ~10°C at the thermocline, located at ~12 m water depth (Fig. 6). Temperature declined further between 12 m and 55 m to ~7°C and remained constant at this value down to the bottom water at 115 m water depth. Salinity 1 m below the water surface was ~20 followed by a rapid increase to ~32 at the halocline at 12 m water depth (Fig. 6). Salinity continued to slightly increase between 12-55 m and reached a constant level of ~35 below 55 m. Chlorophyll fluorescence had a value of ~1 mg m^{-3} in the surface water at 1 m water depth. At 11 m it showed a distinct peak with a maximum value of ~4 mg m^{-3} followed by a rapid decline to almost 0 mg m^{-3} below 30 m (Fig. 6).

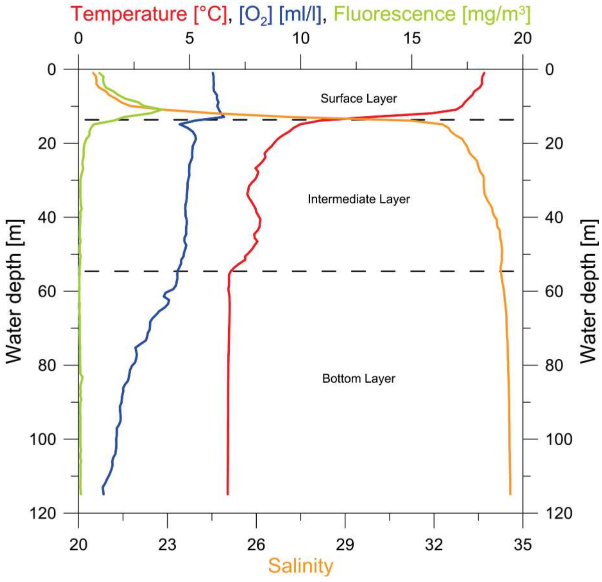

Fig. 6. Water column parameters determined by conductivity, temperature and depth (CTD) measurements at the sampling site DF-2 during the DISCO 2 cruise in June 2014. The stratification were clearly visible and the interfaces of the three main layers were drawn in (dashed lines).

Oxygen concentrations were constant at ~6 mL L^{-1} in the upper 12 m of the water column followed by a sharp drop at 12 m to just under 5 mL L^{-1} (Fig. 6). Values returned to ~5 mL L^{-1} at ~19 m and then started to decrease again slightly below 5 mL L^{-1} at ~50 m. The gradient of the decline was enhanced in between 50-90 m. Below 90 m the gradient returns to about the same as seen between 19-50 m, where oxygen concentrations reached their lowest values of ~1 mL L^{-1}.

3.2 Oxygen time series

A time series of oxygen concentrations in the Alsbäck Deep at water depths of 110 m and below is available from Swedish Meteorological and Hydrographical Institute (SMHI, smhi.se) (Fig. 4). After 1967, data was collected several times a year, but less frequent before that date. Overall one can see a saw-tooth pattern from 1980 until 2014 (Fig. 4). This pattern did not exist before 1980, being a result of lower measuring frequency. So, the data before 1980 is no sufficient to display the seasonal variation of the oxygen concentrations and will not be described further. Focusing on the time series from 1967 until 2014, one can see that the annual saw-tooth pattern (Fig. 4) was interrupted in some years, indicating longer periods of low oxygen concentrations. The first low oxygen period occurred in 1973/1974 with oxygen concentrations below 2 mL L^{-1} and a minimum of 0.88 mL L^{-1}. The second one took place from 1978 until 1980 with similar low concentrations. However, at one point in 1979 there were higher oxygen levels of 3.13 mL L^{-1} and a much lower minimum in 1980 of 0.21 mL L^{-1}. The third event of sustained oxygen concentrations occurred from 1996 until 1998 and is the most extensive one in the time series. Oxygen levels were below 2 mL L^{-1} for almost the entire 2 years and below 1 mL L^{-1} for almost 1.5 years. Repeating minima with oxygen levels below 0.2 mL L^{-1} occurred during the entire low-oxygen event. The fourth and most recent event of sustained low oxygen concentrations started in the winter 2013/2014 and might still be ongoing. Unfortunately, since winter of 2015 SMHI terminated their hydrographic monitoring in the Alsbäck Depth station. Recorded oxygen

Table 2. Ranges and mean values for all bulk and biomarker parameters. Analytical precision was estimated by double measurement of one sample on both instrumental settings (see 2.4.3) used for analysis.

parameter	range	mean	analytical prec.
TOC	2.0-2.9	2.6 ± 0.2	n.a.
TN	0.24-0.34	0.28 ± 0.02	n.a.
C/N	7.7-10.6	9.2 ± 0.6	n.a.
$\delta^{13}C_{TOC}$ (‰)	-30.4 to -22.2	-23.9 ± 1.6	n.a.
$\delta^{15}N_{TOC}$ (‰)	5.5 to 6.9	6.3 ± 0.3	n.a.
Σn-alk (µg/g TOC)	114-310	178 ± 41	17
ACL	28.6-29.2	29 ± 0.1	0.1
CPI	2.1-3.7	3.0 ± 0.4	0.2
Pr/Ph	1.6-3.7	2.4 ± 0.5	0.05
C_{31} ratio	0.44-0.52	0.49 ± 0.02	0.005
TARHC	3.0-7.9	5.6 ± 1.1	0.3
Hop/Ster	13-243	35 ± 48	n.a.
$SST_{UK'37}$ (°C)	14.1-21.1	16.4 ± 1.6	n.a.

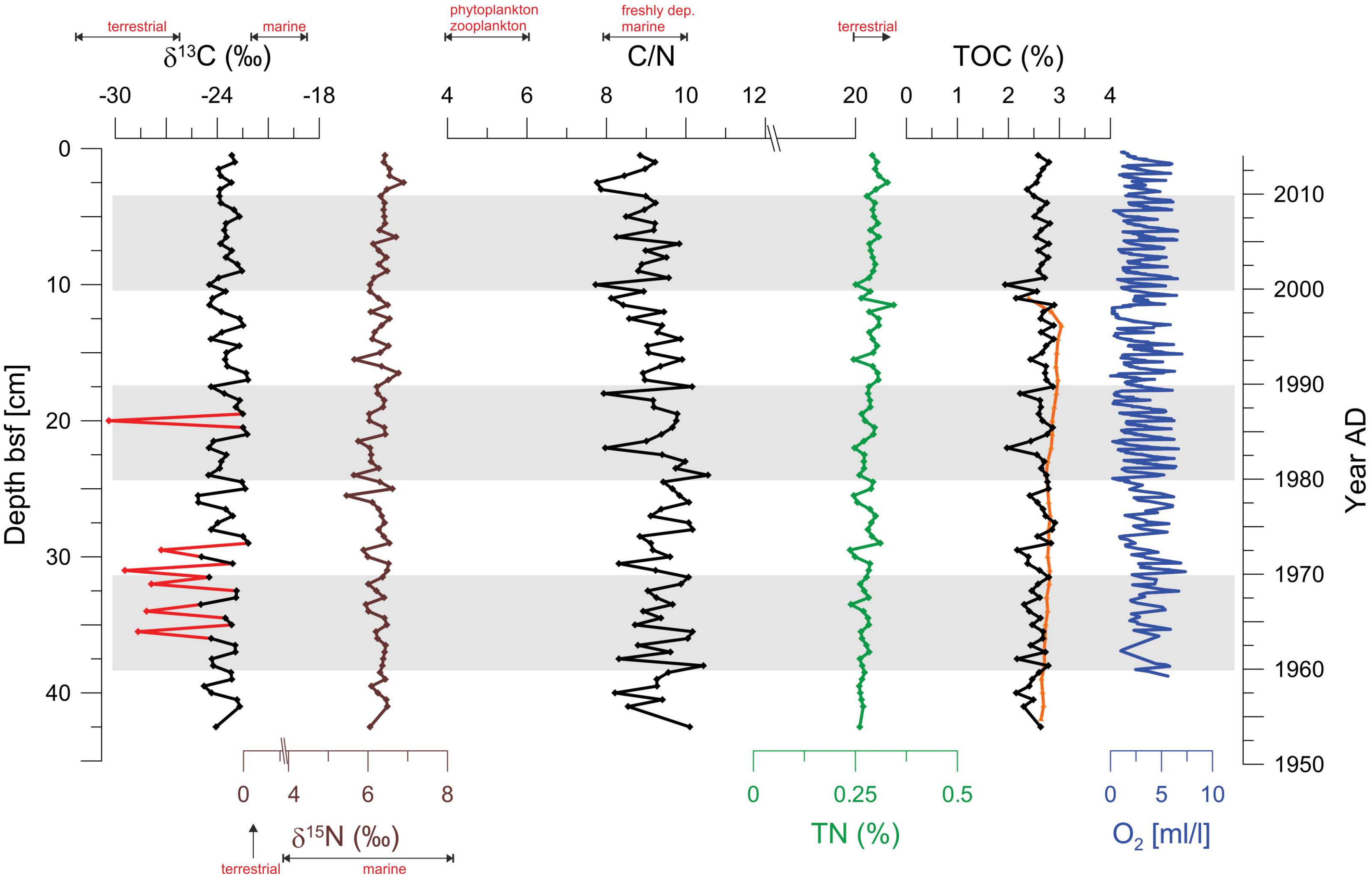

Fig. 7. Bulk organic matter variations plotted over depth below sea floor (bsf) and corresponding years AD (^{210}Pb dating, Filipsson and Nordberg, 2004). Total organic carbon (TOC) and total nitrogen (TN) abundances from this study and their ratio (C/N) are shown. TOC content from a previous study from Filipsson and Nordberg (2010) is displayed as well (orange line). Stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) are shown in the common delta notation and were normalized to the Vienna Pee Dee Belemnite (V-PDB, for carbon) and atmospheric nitrogen (for nitrogen) standard, respectively. Notably lower d13C data points were marked red and grey boxes in the background were inserted for better readability. Oxygen concentrations from figure 4 were drawn in for an easier, visual comparison with bulk data.

levels in the bottom water from winter 2013 until winter 2014 are all below 2 mL L^{-1} for depths greater than 110 m.

3.3 Bulk organic matter analysis

Bulk sediments were analysed for TOC, TN (=TON), $\delta^{13}C_{TOC}$ as well as $\delta^{15}N_{TN}$ and are plotted in Fig. 7 against both depth and calendar years. Additionally, C/N-ratios, an oxygen concentration record for the last 50 years (smhi.se) and the TOC data from Filipsson and Nordberg (2010) are shown in Fig. 7. By assuming a SR of 0.7 cm yr^{-1} for core DF-2B a time coverage from 1954 until 2014 was achieved.

TOC values remained constant around a mean value of 2.6% ± 0.2 for the entire 50 years (Fig. 7, Table 2). However, minima were present in 1958, 1961, 1973, 1983, 1999 and 2000 TOC concentrations below 2.2%. The TOC maxima were recorded in 1975 and 1998, both with values of 2.9%. TN concentrations were constant over the entire core with a mean value of 0.28% ± 0.02, a recorded minimum of 0.24% in 1967 and a recorded maximum of 0.34% in 1998 (Fig. 7, Table 2). Because both the TOC and TN records showed little variation, this pattern was also reflected in the C/N ratios (Fig. 7). The mean C/N ratio was 9.2 with minima and coincided with the low TOC concentrations. The absolute minimum ratio of 7.73 was recorded in the year 2000 and the maximum of 10.44 in 1960.

Stable nitrogen isotopes ($\delta^{15}N_{TN}$) displayed little variation for the time period from 1954 until 2014 (Fig. 7). The mean $\delta^{15}N_{TN}$-value was 6.3‰ ± 0.3 (Table 2).The minimum of 5.5‰ occurred in 1978 and the maximum of 6.9‰ in 2011.

Stable carbon isotopes ($\delta^{13}C_{TOC}$) showed the most prominent variations of all bulk records (Fig. 7). An obvious feature was the significantly lower $\delta^{13}C_{TOC}$ -values in the lower half of the core. Whereas all other values were in the range of -22.2‰ to -25.1‰, six data points ranged between -27.3‰ and -30.4‰ for the years 1964, 1966, 1969, 1970, 1973 and 1995. The mean $\delta^{13}C_{TOC}$-value was -23.9 ± 1.6‰ (Table 2) including all data points and -23.5 ± 0.8‰ (App. B), excluding the six distinct ones.

3.4 Apolar hydrocarbons

3.4.1 *n*-alkanes

A prominent odd-over-even predominance of the carbon chain length was displayed by a mean carbon preference index (CPI) of 3.0 ± 0.4 (range 2.1 to 3.7) (Fig. 8, Table 2). Even though the major *n*-alkanes varied between C_{29} to C_{31} throughout the entire core, the $C_{31}/(C_{31} + C_{29})$ ratio (C_{31} ratio), an index for terrestrial OM source variation (e.g. Kim et al., 2006), displayed little variation of 0.44-0.52 (mean 0.49 ± 0.02) (Fig. 8, Table 2). Total *n*-alkane concentrations were high with a range of 114-310 µg g^{-1} TOC (mean 178 ± 41) (Table 2) with the maximum at the sediment surface (Fig. 8). Some variation can be observed between 1954-1974 and 2003-2014. Little variation and generally low concentrations occurred between 1974 and 2003. The *n*-alkane average chain length (ACL), a weight-averaged index of the odd numbered *n*-alkanes (C_{25}-C_{33}) (Eq. 2) associated with higher plants (e.g. Poynter and Eglinton, 1990), was constant around a mean value of 29.0 ± 0.1 (range 28.6-29.2) (Fig. 8, Table 2). The ratio of terrigenous to aquatic *n*-alkanes (TAR_{HC}) (Meyers, 1997) was one of the most variable parameters with a range of 3.0-7.9 (mean 5.6 ± 1.1) (Fig. 8, Table 2). Highest values were reached in 1963, 2003 and 2013. Minima were present in the 1960s, the early 1990s and the mid 2000s.

3.4.2 Pristane/phytane ratio

The pristane/phytane ratio (Pr/Ph) (Fig. 8) can be used to investigate potential petrogenic sources of hydrocarbons or oxic conditions during deposition (Peters et al., 2005, Kaiser et al., 2014). Pr/Ph showed some variation with a mean value of 2.4 ± 0.5 (range 1.6 – 3.7) (Table 2). High ratios above 2.9 were present in six different years (1956, 1968, 1986, 1992, 1997 and 2014) throughout the record. No long phase of high ratios was observed. Most of the time, ratios were below 2.9 with values around 2. Such a phase is especially prominent in the upper part of the core from the late 1990s until 2012. A major drop in Pr/Ph ratio from 3.7 to 1.7 can be seen in the late 1990s.

3.4.3 Triterpenoids

Triterpenoids were analysed for half the samples and detected only in minor amounts. A different column and injection method was used for the other half complicating a reliable identification of the same compounds with the available mass spectra. Only one sterane compared to several hopanes and one hopene was detected, resulting in high hopanoid-to-steroid ratios of 13-243 (Table 2).

3.5 Sea surface temperatures

The $U^{K'}_{37}$ index used to calculate the sea surface temperatures (SST) is based on the relative abundances of two long chain ketones, called alkenones, where $U^{K'}_{37} = [C_{37:2}]/([C_{37:2}] + [C_{37:3}])$. The global core top calibration SST = $(U^{K'}_{37} - 0.039)/0.034$ (Prahl et al., 1988) was applied to convert $U^{K'}_{37}$ values to SST. The validity of the calibration was confirmed by Müller et al. (1998).

Reconstructed SSTs showed no trend throughout the 60 year period (Fig. 8). The mean temperature was 16.4 ± 1.6°C and a range of 14.1 to 21.1°C (Table 2). The maximum of 21.1°C in 2003 is very pronounced in the record and more than 2°C higher than any other reconstructed SST in our record. Observed variability matched the one observed in instrumental records.

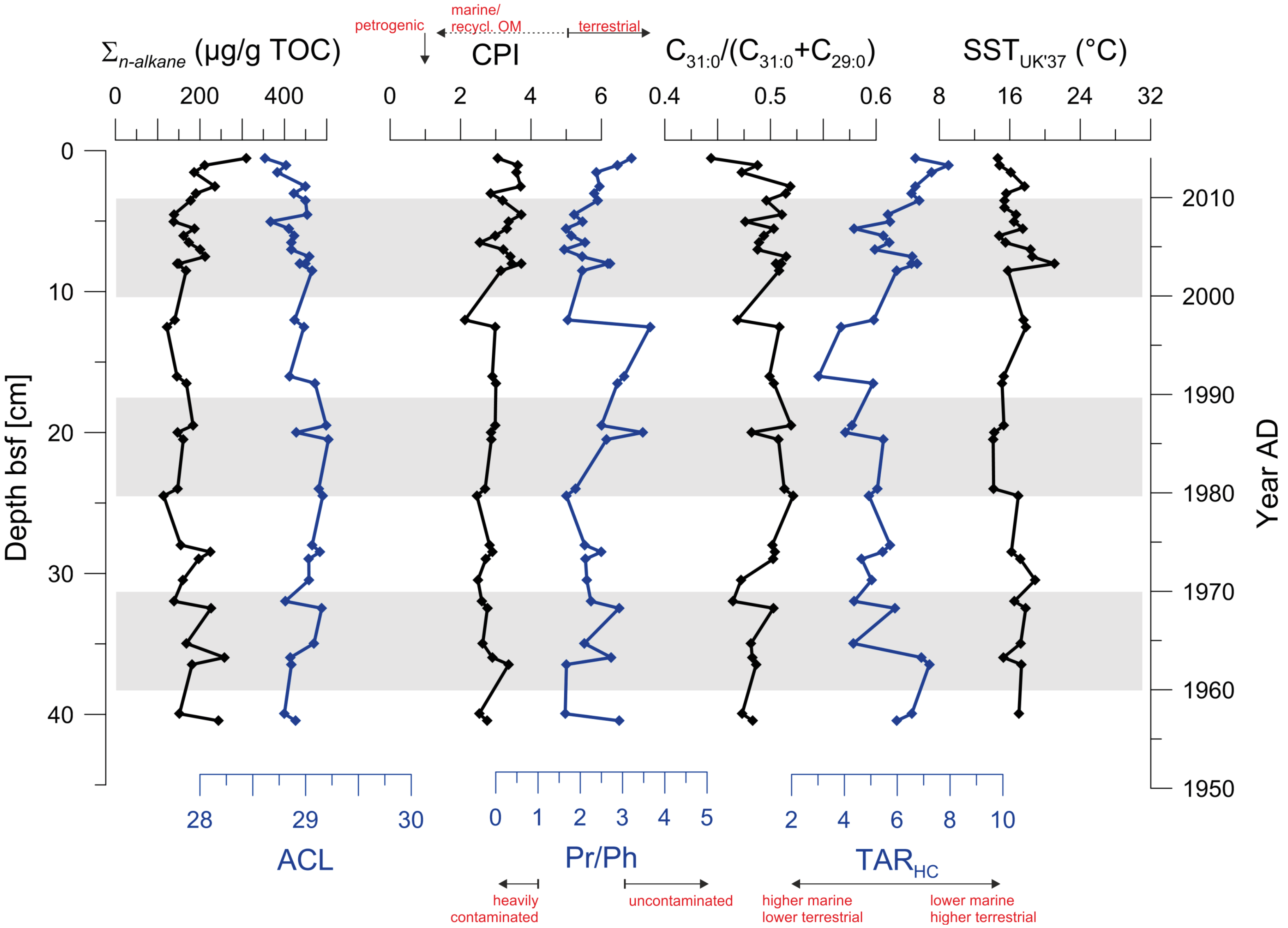

Fig. 8. Biomarker results plotted over depth below sea floor (bsf) and corresponding years AD (^{210}Pb dating, Filipsson and Nordberg, 2004). Total sum of *n*-alkane concentrations ($\Sigma_{n\text{-alkane}}$), average chain length (ACL), carbon preference index (CPI), pristane to phytane ratio (Pr/Ph), major n-alkane ratio (C_{31}/(C_{31}+C_{29}), terrestrial alkane index (TAR_{HC}) and sea surface temperatures (SST) reconstructions, based on an long-chain alkenone ratio($U^{K'}_{37}$) are displayed. Grey boxes and annotations were added for better readability and understanding.

4 Discussion

The following discussion is divided into three major parts. Firstly, I will focus on the applied age model and the implications on the interpretation of our data. Secondly, the sources and the composition of the OM will be evaluated based on the bulk and biomarker results. Thirdly, short-term environmental changes and possible links between the low oxygen events and the OM will be investigated. Please note that the comparisons of the observed relative changes in OM will not be affected by the applied age model and sedimentation rate (SR) (as discussed in 4.2). However, linking those changes to the environmental development and to the time series of low oxygen events recorded in Gullmar Fjord (as discussed in 4.3) heavily relies on the accuracy of the applied age model and sedimentation rate.

4.1 Age model

The age model from Filipsson and Nordberg (2004) for sediments from the Alsbäck Depth resulted in coverage for the years 1915-1999 and a SR of 0.7 cm yr^{-1}. As the core of this study was taken in 2014, the SR was linear extrapolated for the top 15 years. This assumption is supported by a new age model based on ^{210}Pb data (unpubl. Results from Stefanie Müller, pers. com.), which results in very similar sedimentation rates from 1986 until 2013.

Signs of bioturbation in sediments of Alsbäck Depth were observed by Dando and Spiro (1993), which can seriously affect the age model. They investigated the bivalves in relation to sulphur concentrations in the sediment for the autumns 1986 to 1988 and the summer 1989. The bivalve species' they investigated reached a length of 12 mm and could theoretically burrow itself up to nine times of their length. The resulting tunnels and therefore the bioturbation could reach depths down to 20 cm. For 1986 they report elevated sulphur concentrations down to 10 cm, most likely caused by bioturbation. It was shown that the deoxygenation of the bottom water in 1988 to 1989 led to high faunal mortality and the abundance of the investigated bivalve species was reduced dramatically afterwards. However, the core used in this study showed no clear signs of massive bioturbation as described by Dando and Spiro (1993). Additionally, the ^{210}Pb data did not suggest any clear evidence of bioturbation (Stefanie Müller, pers. com.). Also water content gradually decreased from top to bottom of the sampled core (App. A), indicating no major interruption of sediment deposition by bioturbation (see also Filipsson and Nordberg, 2004). Even though the sampling interval of 0.5 cm is slightly lower than the assumed annual SR of 0.7 cm yr^{-1}, one cannot assume a sub-annual signal in our data. If we exclude any form of mixing after deposition, such as bioturbation, we would still have only one data point per year. A denser sampling interval would not help to address this, as bioturbation in the surface is most likely present. However, fast oxygen consumption and the observed change to anoxic conditions within the first centimetres of the core (colour change and H_2S smell) should effectively limit bioturbation of benthic fauna to the sediment surface. To conclude, our data points should be regarded as an, at least, annual average.

4.2 Organic matter sources and composition

4.2.1 Bulk organic matter

The $\delta^{15}N_{TOC}$ values are all well within in the range of marine OM (Table 1) and mostly well above the ~5‰ of river OM. The lowest values could also be interpreted as derived from river OM, but in context with the other values of the record it seems unlikely. This assumption is supported by the lack of evidence for riverine OM in the other bulk parameters. Applying the mixing model (Eq. 1), with 0.4‰ as terrestrial end-member and 8‰ as marine end-member, results in a marine fraction of at least 78% the TN (Table 3).

The $\delta^{13}C_{TOC}$ values with a mean of -23.9 ± 1.6‰ are, beside the six very negative values, well in between the marine (-20 to -22‰) and terrestrial (-26 to -32‰, C_3 plants) end-members (Tab. 3). Waite et al. (2005) reported $\delta^{13}C_{TOC}$ values of -19‰ for sediment trap samples during diatom spring blooms in Gullmar Fjord, possibly providing a more precise marine end-member for Gullmar Fjord. However, diatoms are not the only blooming algae occurring in Gullmar Fjord and the adjacent Skagerrak (Egge et al., 2015, Harland et al., 2010), making it difficult to decide on a marine end-member value without further investigations. Therefore, a linear mixing model (Eq. 1) was applied for both extremes of the marine end member of -19‰ and -22‰ (Table 3).

Six data points were more negative than the theoretical average of -27‰ of terrestrial OM (Meyers, 1994), suggesting an important change in the total OM composition. However, they show no peculiar values in the other bulk parameters (Fig. 7). As all bulk parameter were analysed simultaneously on the same sample, it is almost certain that those are real $\delta^{13}C_{TOC}$ values and not outliers caused by an analytical error. Regarding the obviously different nature, the mixing model was applied separately for the mean

Table 3. End-member values used for the linear mixing model (Eq. 1). Measured means for $\delta^{13}C$ were split to the values in the regular range (mean -23.5‰) and to the six which clearly showed more negative values (mean -28.6‰).

	TOC: terrestrial vs. marine						TN: terrestrial vs. marine		
	$\delta^{13}C$ (‰)				N/C		$\delta^{15}N$ (‰)	C/N	
End-member terr.	-32	-32	-32	-32	0.05	0.05	0.4	20	20
End-member mar.	-22	-19	-22	-19	0.17	0.125	8	6	8
Mean measured	-28.6	-28.6	-23.5	-23.5	0.11	0.11	6.3	9.1	9.1
Terr. [%]	66	74	15	35	50	20	22	22	9
Mar. [%]	34	26	85	65	50	80	78	78	91

values of the six more negative values (-28.6‰ ± 1.1) and the rest (-23.5‰ ± 0.8) (Table 3). As the lowest $\delta^{13}C_{TOC}$ value was -30.4‰ around the year 1986, a value -32‰ was chosen as the most plausible terrestrial end-member.

The mixing model suggests that the majority of the time from 1954 until 2014, the marine contribution to the TOC (TOC_{mar}) seems to have been between 50 to 85% (Table 3). During the short pulses of more $\delta^{13}C$ depleted TOC, the terrestrial fraction (TOC_{terr}) seems to have dominated the OM with a range from 66 to 74% (Table 3). Those pulses could result from [1] a larger input of terrestrial plant OM, [2] from high input of riverine OM, which has similar $\delta^{13}C$ values compared to terrestrial plant OM, [3] a reduced aquatic production or [4] from bacterial and archaeal methanotrophs and sulphate reducers.

The first could be explained by massive rainfalls, increased surface runoff and therefore a higher fluvial input of terrestrial OM. However, such a massive change should result in higher C/N ratios as well. The same argument would be valid when considering a reduced aquatic production. Remineralisation of OM by bacterial and archaeal methanotrophs and sulphate reducers could have a major impact on the OM $\delta^{13}C$ signature, as they can reach $\delta^{13}C$ values of -70‰ to -110‰. Nonetheless, a more precise evaluation of their appearance and their effect on the entire OM is not possible without confirmation from compound-specific isotope analysis on e.g. hopanoids, fatty acids and archaeal lipids. This leaves the increased input of riverine OM as an explanation for the more negative $\delta^{13}C$ values. It could have been caused by flood events coupled to a major resuspension of river sediments. C/N ratios of 11-13 of riverine OM are reported to be close to freshly deposited marine OM (8-10, see Table 1). Therefore a major change in $\delta^{13}C$ values can be achieved through a high fraction of riverine OM being washed in the fjord without considerably affecting the C/N ratios. Investigating historical flood reports was not done but would clearly be beneficial for future work.

Combining $\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$ with N/C ratios (Fig. 9), illustrates along with tables 1, 2 and 3 the end-member ranges and mixing lines (see also tables 1, 2 and 3). N/C ratios were used for the figure instead of C/N ratios to reach a graphical linear relation of the isotope values to the TOC values used in the ratios (Perdue and Koprivnjak, 2007). C/N ratios are with an average of 9.2 in the range of freshly deposited marine OM (8-10‰) (Meyers, 1997). Considering the lower range limits of the terrestrial and marine C/N ratios of 20 and 6, one reaches TOC_{mar} and TN_{mar} contributions of 50% and 78%, respectively. Yet, fast degradation of N-rich proteins of phyto- and zooplankton can lead to a fast increase in C/N ratios from 4-6 to 8-10 during sedimentation (Meyers, 1997). Thus, using a higher C/N ratio than 6 for the marine end-member is justified, despite some values being slightly lower than 8. Applying the lowest C/N ratio of freshly deposited OM of 8 results in TOC_{mar} and TN_{mar} contributions of 80% and 91%, respectively (Table 3).

It should be noted that one should use the N/C ratio again instead of the C/N ratio to apply the linear mixing model (Eq. 1) and in order to obtain the TOC_{mar} following the argumentation of Perdue and Koprivnjak (2007). One has to consider that for calculating the end-members only the lowest C/N ratio for terrestrial plants was used. Increasing the value to >20, which is quite common for terrestrial plants, would give an even higher marine contribution. The higher abundance of fast degrading compounds containing nitrogen in the phyto- and zooplankton, causing a bias towards terrestrial C/N ratios, could have been counterbalanced by my use of a higher C/N ratio for the marine end-member. Overcompensation cannot be ruled out entirely if compared to the total range of the $\delta^{13}C_{TOC}$ derived TOC_{mar} contributions of 65 to 85% (Table 3). Nevertheless, it suggests that the higher marine end-member estimate of 8 for the C/N ratio might be more accurate as it favours a largely marine source too.

To summarise, defining the appropriate end-member values for the model has been proven difficult. A proper end-member sampling and analysis would have been essential to assign reliable values of source contributions. The mixing model is very sensitive to the end-member input and our estimates can lead to variable results. However, most of the applied combinations show a dominant to very dominant marine source of the OM.

4.2.2 Biomarkers

Unfortunately, the aquatic and sedimentary marine source could not be divided in eukaryotic, bacterial and archaeal sources. Firstly, due to time restrictions and analytical challenges, the polar fraction could not be investigated. For example, some very source specific sterols, hopanols and fatty acids would have provided detailed information on bacterial and eukaryotic origin of the OM and would have helped greatly to get a more complete picture. Secondly, compound specific isotope analysis on those compounds would have been beneficial to investigate remineralisation of OM in the water column and sediment. Thirdly, hopanes and steranes could only be analysed for approximately half of the samples. As mentioned, a change in analytical conditions on the GC-FID led to a shift in retention times and therefore to a shift in the peak pattern, making it impossible to identify the triterpenoids for the second half. The low concentrations of them further complicated the identification of individual triterpenoids for the second batch. Only the Hop-17(21)-ene could be assigned by name, inhibiting the use of the homohopane index (Peters and Moldowan, 1991) as an indicator for anoxia during sedimentation.

The high ratio of hopanes to steranes (range 13 to 243) (Table 2) would indicate a higher bacterial than eukaryotic/algal fraction, but were generally low

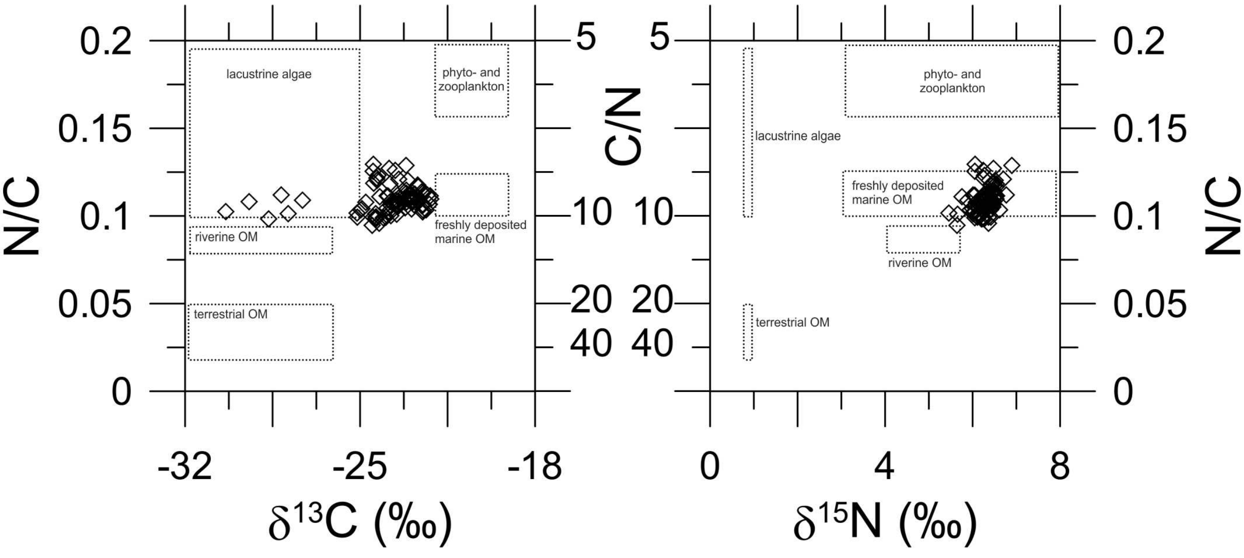

Fig. 9. Correlation of stable isotope values ($\delta^{13}C$, $\delta^{15}N$) to total organic carbon and total nitrogen ratio (C/N). Possible end-member sources and their ranges are drawn in for better understanding (boxes with dotted contour). Marine and terrestrial contributions of total organic carbon (TOC) and total nitrogen (TN) were calculated separately along the x– and y-axis, respectively (Table 3), indicating a dominant marine contribution for TOC and TN.

in total abundance. Especially, the minor appearance of steranes, associated with algae and other eukaryotes, appears to be contradictory to the observed increasing eutrophication in Gullmar Fjord (Lindahl et al., 1998, Rosenberg et al., 1996) and Norwegian fjords adjacent to the Skagerrak (Aure et al., 1996) and the haptophyte-derived, high long-chain alkenone abundances in Gullmar Fjord in this study. Steranes and hopanes are diagenetically very stable degradation products of sterols and hopanols (Volkman 1986). However, sterols and hopanols are quite stable as well and regarding the short time interval of only 60 years we cover in this study, degradation and (thermal) maturation should not have occurred extensively. So, the hopane to sterane ratio (Hop/Ster), often used in much more mature sediments or for the characterization of crude oil (e.g. van Dongen et al., 2008), could not be applied in our study.

The biomarker analysis focused on *n*-alkanes, which provide details on the terrestrial fraction of the OM and more precisely on vascular plant waxes. Biomarker represent only a minor fraction of the total OM, but it has been shown that they represent it extremely well (Eglinton and Eglinton, 2008, Meyers, 1997, Poynter and Eglinton, 1991). Long chain *n*-alkanes (C_{24}-C_{33}) with an odd-over-even predominance originate from terrestrial higher plants. This pattern them can be found, so to speak as a fingerprint, in coastal marine sediments, which are generally considered to have a relevant terrestrial input of OM (e.g. Eglinton and Eglinton, 2008).

A means to measure the above described odd-over-even predominance for the long chain *n*-alkanes is the CPI (Eq. 3). A heavy contamination can be excluded as the CPI range obtained was 2.1-3.7 opposed to ~1.0 for petrogenic carbon (Farrington and Tripp, 1977, Jeng 2006). They were also clearly outside of the reported terrestrial range of 5.0-10.0 (Rielley et al, 1991). They best fit values associated with high input of marine microbial OM and/or recycled OM (Kennicutt et al., 1987, Meyers and Ishiwatari, 1995), leading to a shift from the terrestrial range to values closer to 1.0. Alternatively, they could represent a minor contamination with petrogenic carbon, as about half the values are below the reported values of ≥ 3.0 for uncontaminated sediments (Farrington and Tripp, 1977). Without considering a possible contamination, the CPI values are in accordance with bulk results, indicating a mixed source of OM but with a higher marine than terrestrial contribution.

Recycling of OM is especially dominant in systems with intense stratification such as lakes. Such a stratification is also a characteristic for Gullmar Fjord (Arneborg, 2004, Filipsson and Nordberg, 2004), with a strong and shallow thermocline in summer, as seen during the sampling campaign at ~12 m in June 2014 (Fig. 6). The effects of variable stratification intensity will be discussed in the next section, including a discussion of the influence of the reported seasonal varying oxygen concentrations during deposition. Higher CPI values, mostly occurring after the year 2000, may be an indication for a reduced algal contribution, higher terrestrial input or a change in the terrestrial source. The TAR_{HC} (Eq. 4) also indicates changes in either less aquatic (algal) or more terrestrial contribution to the OM from the early 1990s and onward (Fig. 8). However, the pattern is very different to the CPI, therefore it seems unlikely that the observed changes in both are the result of the same cause. Also, the increasing eutrophication reported for the region (Lindahl, 1993 and 1998, Rosenberg et al., 1996) would be expected to have the opposite effect. Eutrophication and other environmental changes and their effects on OM sedimentation will be discussed in more detail in the next section.

Another indicator for petrogenic contamination of marine sediments and its implications is the Pr/Ph index (Steinhauer and Boehm, 1992 and references within). There is no clear evidence for a heavy contamination, as no Pr/Ph ratio is below 1 (Fig. 8). However, almost all are below the threshold of ≥ 3, associated with uncontaminated sediments (Kaiser et al., 2014, Steinhauer and Boehm, 1992 and references therein), which might show a slight contamination of the sediments by petrogenic carbon. The Pr/Ph index was proposed to be a proxy for redox conditions during sedimentation but is heavily doubted or even rejected (Rontani and Bonin, 2011, Sinninghe Damsté et al., 1987).

The ACL of long-chain alkanes (C_{25}-C_{33}) (Eq. 2) can basically be seen constant in our record for a number of reasons. The analytical precision for a duplicate has been shown to be ± 0.1 covering already a third of the 0.6 difference between all ACLs obtained. Although not experimentally proven by duplicate extractions, it can be assumed that the uncertainty of the extraction and the column chromatography increase the total precision error further. All variations from data point to data point were below 0.4, being close to the analytical precision of ± 0.1 (Table 2). Furthermore, Poynter and Eglinton (1990) state a constant ACL for coastal marine sediments for shorter timescales, as no, or no major changes in latitude, fluvial vs. eolian input and humidity (Schefuß et al., 2003) would be expected.

ACLs of 29 to 31 are typical for terrestrial vegetation with the latter being associated with grassland and the former with other C_3-plants, such as trees (Eglinton and Eglinton, 2008, Nott et al., 2000, Rommerskirchen et al., 2003). *Sphagnum* moss dominated peat bogs are amongst the most common terrestrial ecosystem in the Northern hemisphere and have a significant higher contribution of the C_{25} *n*-alkane in their leaf wax distribution (Kulichevskaya et al., 2007, Nott et al., 2000). As all values narrowly cluster around an ACL of 29 ± 0.1, a relevant contribution of *sphagnum* moss derived, C_{25} *n*-alkane (Nott et al., 2000) to the Alsbäck sediments can be excluded.

The C_{31} ratio used by Kim et al. (2006) is, like the ACL, an indicator for changes in the terrestrial OM source. Compared to the ACL, it can show variations from grassland to other C_3-plants more clearly, by focusing on the major chain length (C_{29} and C_{31}) associated with them. The ACL has shown that C_{25} *n*-alkane is not relevant which is also supported by the very similar pattern of ACL and C_{31} ratio. To conclude, there is no evidence for changes in the terrestrial vegetation in the overall catchment area.

Shorter *n*-alkanes have multiple sources and are not very specific in its own. However, the occurrence of C_{17} *n*-alkane, as observed in this study, is commonly associated to be of algal origin (Meyers, 1997). In every sample, the peak was higher than any of the neighbouring, odd numbered *n*-alkanes, indicating a clear algal contribution to the OM. Variations in the aquatic (e.g. algal) and terrestrial contribution to the OM can be displayed by the TAR_{HC} (e.g. Meyers, 1997). While we already discussed the positive trend in the upper part earlier, we will have a closer look on the slight negative trend for the lower part until the early 1990s. Changes in terrestrial source material could play a role, though we have already shown in the previous paragraph that those changes are negligible (ACL, C_{31} ratio).

So, the lower part represents either an increased aquatic production or a decreased terrestrial contribution. The latter is unlikely, as neither CPI nor the bulk data indicate major shifts in terrestrial OM supply. While a higher export of aquatic derived OM to the sediment cannot be ruled out, an opposite trend after closing down a sulphite pulp mill in 1966 (Rosenberg, 1996) would be anticipated. However, Lindahl et al. (1998) showed that there is ongoing eutrophication in Gullmar Fjord until the mid 1990s, despite the elimination of waste water and industrial sewage (Harland et al., 2006), possibly related to a large proportion of yacht tourism in summer. The change in trends we see in the early 1990s might be the elimination of the sewage finally taking effect. Nevertheless, the intense yacht tourism and the ferry operating close to the sampling site might still have a relevant effect on the pollution of the fjord. Further investigations of aromatic compounds would be beneficial to evaluate a possible contamination, as they derive predominantly from burning of fossil fuels and are a good indicator of anthropogenic impact on the environment (e.g. Wakeham et al, 1980).

4.3 Effects of short-term environmental changes and North Atlantic Oscillation

In the previous section I have already started to evaluate the pollution history of Gullmar Fjord and its effect on the OM composition. The closing of a herring cannery in Lysekil, a paper and a sulphite pulp mill as well as the installation of water treatment facilites in the 1960s eliminated industrial and anthropogenic sewage to the fjord. The fjord is considered free from local pollution since the 1970s (Harland et al., 2006, Lindahl et al., 1998). Despite the major efforts, no positive response to the elimination of local pollution was observed and eutrophication is still ongoing according to Lindahl et al. (1998).

Since the 1960s, an increased drainage of sewage and agricultural fertilizers to the North Sea, Skagerrak, Kattegat and Baltic Sea has been reported (Aure et al, 1996, Rosenberg et al., 1996). The Gullmar Fjord water masses are closely connected to those, as the surface layer is largely supplied by the brackish Baltic surface water flowing northward along the Swedish west coast, whereas the deeper water masses in the fjord are exchanged with the high saline Skagerrak water (e.g. Lindahl et al., 1998). So, even if no local pollution is present anymore since the 1970s, more and more nutrient rich, polluted water reaches the fjord every year, enhancing the primary production (PP) and may alter the algal composition (Harland et al., 2006).

Higher PP and therefore more degradable OM in the surface layer, leads to a higher oxygen consumption while sinking. As a result, oxygen deficiency in the bottom water and benthic fauna mortality increases (Harland et al., 2006, Meyers, 1997). Faunal shifts in benthic foraminifera (early 1980, Filipsson and Nordberg, 2010) and dinoflagellates (mid 1970s, Harland et al., 2006 and 2010) along with a decoupling from the Skagerrak faunal assemblages were observed. The former being associated with the extensive low oxygen event occuring at the same time, establishing a low oxygen tolerating benthic foraminiferal fauna (Filipsson et al., 2004).

Since the 1970s, extensive and more frequent periods of hypoxia (<2 mL L^{-1}) were observed (Fig. 4) (Filipsson and Nordberg, 2010). They are the result of no or only a partial exchange of bottom water with the Skagerrak during the winter or early spring. The precise mechanism leading to the less frequent water renewals is still not fully understood. Nordberg et al. (2000) proposed that the North Atlantic Oscillation (NAO) and the wind regime, along with the fjord morphology are the reason for this. Modelling results, based on geostrophic winds, indicate lower upwelling intensities during the summers after 1963 (Björk and Nordberg, 2003). While they found a link between NAO index and winter upwelling, summer upwelling was decoupled from the NAO index. Less upwelling during summer leads to a stronger stratification and more intense deoxygenation of the bottom water in the fjord (Björk and Nordberg, 2003), hence, notably affecting the marine environment. Nonetheless, the water renewal occurs during winter, where upwelling is generally strong.

A declining trend in the overall upwelling was observed between 1950 and 1990 (Björk and Nordberg, 2003), possibly explaining the more frequent extensive hypoxic conditions in the bottom water. Erlandsson et al. (2006) found a 50% increase in oxygen consumption in Gullmar Fjord whereof 40% of the increase was caused by physical factors, mainly by the NAO variation and timing of oxygen renewal of the stagnant bottom water. They did not account for the higher bottom temperatures which have been observed since the 1980 (Filipsson and Nordberg, 2010). As warmer water has a lower oxygen solubility (Rabalais et al., 2009), parts of the 50% increase in oxygen consumption should result from the higher bottom water temperatures in the fjord. However, the surface temperature did not show an increase since the 1950s in neither the hydrographic data nor the reconstructed SSTs from long-chain alkenones (Fig. 8).

Overall, the bulk OM and biomarker data do not display any obvious trends for the investigated time between 1954 and 2014 (Fig. 7). This means that the sewage reduction in Gullmar Fjord did not affect the OM composition. Furthermore, marine and terrestrial contributions of OM did not change notably. Despite there is overall more OM remineralised in the water column with increasing eutrophication, more excess OM is exported to the sediment which should result in a more dominant algal signal in the bulk and biomarker records. To conclude, the ongoing eutrophication reported by e.g. Lindahl et al. (1998) and Rosenberg et al. (1996) is not evident in our data. The TAR_{HC} even indicates a trend to lower aquatic fraction in the OM after 2005 (Fig. 8), though it is not supported by the other biomarker proxies. Whereas the instrumental records showed no change in the physical and chemical surface water properties for the 1954 to 1986 period (Harland et al., 2006), the bottom water clearly had lower summer oxygen concentrations since 1980 (Fig. 4) (Filipsson and Nordberg, 2010). Assuming them as signals for higher eutrophic levels since the 1980s, how can they not have affected the OM?

Extensive remineralisation of OM in the sediment by microorganisms, preferentially bacteria could be an explanation. Implying that most of the more labile aquatic marine OM (Killops and Killops, 2005) of the PP is utilized and converted to secondary OM, the original aquatic marine signal might be overprinted. However, our data is not sufficient to evaluate this hypothesis and further investigations of algal and bacterial biomarker would be required.

Another possible explanation would be that most aquatic marine production is not local to Gullmar Fjord but transported into the fjord from the adjacent Skagerrak. So, local aquatic production possibly affected by eutrophication is only a minor part of the aquatic marine OM, thus not altering the OM composition significantly. This is also concluded by another study (Erlandsson et al., 2006), where they propose that most of the particulate organic matter (POM) is produced remotely in the Skagerrak. We compared

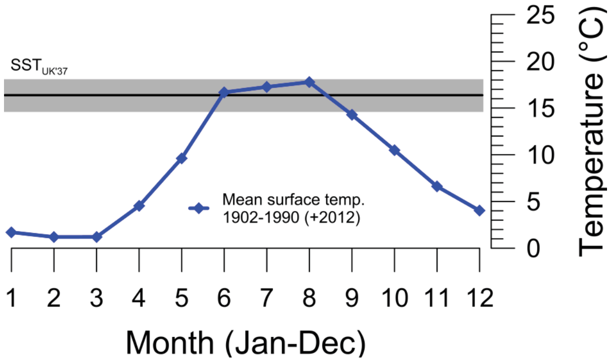

Fig. 10. Stacked mean surface water temperatures (<5 m) of Gullmar Fjord for the years 1902 to 1990 and the year 2012 (blue line) in comparison with the mean value from long-chain alkenone based sea surface temperature ($SST_{UK'37}$) reconstructions (black line, standard deviation marked with grey box). Reconstructed mean $SST_{UK'37}$ of 16.4°C ± 1.6 suggested a summer to early autumn bloom of haptophyte algae, the source of long-chain alkenones.

SST reconstructed, haptophyte (*E. huxleyi*) derived long-chain alkenones, to stacked instrumental temperature data from 1902 until 1990 plus the year 2012 (see Fig. 10) (smhi.se). Reconstructed temperatures range between 14.1-21.1°C with a mean of 16.4 ± 1.6° C presumably representing a summer to early autumn signal. $U^{K'}_{37}$ derived SSTs in the northern Skagerrak seem to be lower between 11-12°C (van Dongen et al., 2000). Nonetheless, instrumental data for the Skagerrak shows summer temperatures around 15°C for the Skagerrak (Rueda et al., 2009), making it realistic that the SSTs found in Gullmar Fjord could represent an exported signal from there. While the spring blooms in the Skagerrak are dominated by diatoms, dinoflagellate and haptophyte blooms occur afterwards (Egge et al., 2015). Blooms for most of the calcifying coccolithophores were observed from summer to early winter. *E. huxleyi* grows there all year round, but is prominently peaking in summer to early autumn (Egge et al., 2015). Hence, it is possible that reconstructed SSTs were derived from haptophytes growing in the Skagerrak and were not locally produced in the fjord. This is strongly supported by Erlandsson et al. (2006) who concluded that most of the POM in Gullmar Fjord is produced in the Skagerrak and washed into Gullmar Fjord. Only the strong, local spring blooms of diatoms in the fjord were suggested to have a significant export to the sediment (Erlandsson et al., 2006).

As previously mentioned, our sedimentary OM data should be regarded as an, at least, annual average. So links between it and the oxygen time series are difficult to establish. Seasonal variability of 5-6 mL L^{-1} is much higher than the overall change to lower summer oxygen concentrations (Fig. 4) of < 2mL L^{-1}, so a record with several data points per year would be essential to display seasonal effects on the sedimentary OM. Sampling particulate organic matter (POM) in sediment traps during different seasons could overcome this obstacle for the present day, but can obviously not be applied for a palaeo-study.

So, the only possible links between oxygen and OM that could be established would be the shift to lower oxygen concentrations in summer since the 1980s and the low oxygen events. The former was already addressed above and we proposed that it did not affect the sedimentary OM. To the latter; four events with sustained low oxygen concentrations for longer than a year are marked with grey boxes in figure 4. Due to their refractory nature, the investigated, mainly terrestrial derived apolar hydrocarbons are unlikely to display those events. Also the sampling interval below 9 cm is too coarse to record them as an isolated signal. Even though it would be sufficient for the upper 9 cm, only the most recent, still ongoing event is covered. Some of the more prominent variations of, e.g. the C_{31} ratio or the Pr/Ph ratio occur in the very top. Nevertheless, linking those to the effects of low oxygen concentrations would be highly speculative as it would be solely based on one event.

Looking for links between the consistently denser sampled bulk data and the low oxygen events seems more promising. Filipsson and Nordberg (2010) reported a decrease in TOC concentration in the late 1990s for their surface sediments (Fig. 7). Our record showed low TOC concentrations during the same period with just a slight delay of ~2 years. Such a shift is well within the error of the ^{210}Pb dating, so it is safe to assume that both represent the same time interval. Interestingly, the onset of the decrease in TOC showed by Filipsson and Nordberg (2010) occurred at the same time as the most extensive and sustained low oxygen event (1996-1998) (Fig. 7). Though this relation is counter-intuitive, as phases of sustained hypoxia should allow a higher export of OM to the sediment and aerobic degradation by detrivores (decomposer) should be decreased (Killops and Killops, 2005), which would mean lower relative remineralisation of OM to CO_2 and finally a higher sedimentary TOC content. Furthermore, TOC content did not decrease during all the other extensive low oxygen events. Altogether, the observation of sustained hypoxia and a decrease in TOC content seems to be coincident. TN, C/N, $\delta^{15}N_{TOC}$ and $\delta^{13}C_{TOC}$ did not show any change during the phases of longer bottom water hypoxia (Fig. 7). This could be due to the fact that bacterial degradation, which is largely unaffected by oxygen availability (Killops and Killops, 2005), is dominant.

5 Conclusions

Two end-member mixing models for several bulk parameters showed a dominant marine source of the sedimentary OM in Gullmar Fjord for the entire time between 1954 and 2014. However, a proper end-member sampling and analysis would allow for much more precise model results. Biomarkers, especially *n*-alkanes did not indicate any major change in the terrestrial source material. A slight contamination of the sediments by petrogenic hydrocarbons might be present, but further investigations of aromatic compounds would be beneficial. The cause of the more negative $\delta^{13}C_{TOC}$ excursions observed remains unclear. One possible explanation is the increased resuspension of large amounts of riverine OM and transport to the fjord basin. Furthermore, biomass with extremely low $\delta^{13}C$ values, derived from bacterial and archaeal sulphate reducers and methanotrophs, could be another explanation. However, additional biomarker and compound specific stable carbon isotopes would be necessary to evaluate it.

Despite reports of ongoing eutrophication in Gullmar Fjord (Lindahl et al., 1998, Rosenberg et al., 1996) and other fjords adjacent to the Skagerrak (Aure et al., 1996), I could not find signs for this in the OM composition. Assuming an intensified eutrophication, the absence of evidence in our records could be the result of a large portion of remotely produced marine OM being washed in from the Skagerrak, which is strongly supported by the study of Erlandsson et al. (2006). Long-chain alkenone based reconstructions of

SSTs from haptophytes indicate a blooming season from summer to early autumn for Gullmar Fjord, but would also match with the blooming season and temperatures reported for the Skagerrak (Egge et al., 2015, Rueda et al., 2009). Links between the extensive low oxygen events reported for Gullmar Fjord (Fig. 4) and the OM were not observed.

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Appendix

A

depth (cm)	dry weight (g)	water content (%)	inweigh bulk (g)	extr. sediment (g)	TLE (mg)	Apolar (mg)	Aromatic (mg)	Ketone (mg)	Polar (mg)
0.5	4.65	80	1.00	11.52	13.3	1.2	-0.3	1.0	7.0
1.0	12.55	76	1.00						
1.5	13.30	75	1.00	8.91	12.2	1.2	0.1	0.6	3.1
2.0	16.12	74	1.00	10.80	14.3	1.2	0.6	0.6	4.0
2.5	12.69	73	1.01	11.66	17.2	1.1	-0.1	0.5	5.2
3.0	4.71	72	1.00						
3.5	13.17	71	1.00	8.82	10.1	1.2	0.0	0.3	2.9
4.0	15.90	71	1.00	10.65	8.1	1.2	0.1	0.9	3.8
4.5	20.39	70	1.00	13.66	13.6	0.9	0.0	0.5	4.1
5.0	17.25	69	1.00	11.56	10.5	0.4	0.3	0.5	3.0
5.5	16.05	68	1.00	10.75	11.9	0.2	-0.5	0.2	2.4
6.0	16.04	68	1.01	10.75	10.6	0.3	0.4	0.7	2.4
6.5	17.30	66	1.00	11.59	11.1	1.7	0.0	0.8	3.1
7.0	16.18	66	1.00	10.84	10.6	1.3	0.5	0.6	2.8
7.5	19.92	66	1.00	13.35	13.2	1.5	0.2	0.6	3.5
8.0	20.27	66	1.00	13.58	15.1	1.2	0.3	0.2	4.3
8.5	15.77	66	1.00	10.57	9	1.0	0.9	0.1	2.6
9.0	18.51	66	1.00	12.40	10.6	0.8	0.8	1.2	2.7
9.5	18.49	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
10.0	13.99	67	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
10.5	15.53	67	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
11.0	20.95	65	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
11.5	13.89	65	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
12.0	19.31	65	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
12.5	14.13	65	1.00	9.47	7.8	1.0	0.3	1.0	2.2
13.0	13.04	67	1.00	8.74	8.5	0.6	0.4	0.6	1.7
13.5	19.92	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
14.0	18.00	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
14.5	20.25	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
15.0	20.12	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
15.5	15.64	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
16.0	18.77	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
16.5	15.29	66	1.00	10.24	11.5	1.3	0.7	0.3	2.7
17.0	16.38	66	1.00	10.97	9.4	0.5	-0.2	0.5	1.8
17.5	19.99	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
18.0	18.47	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
18.5	17.98	65	1.01	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
19.0	20.04	65	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
19.5	15.44	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
20.0	17.61	65	1.00	11.80	19.1	1.6	1.5	1.7	3.4
20.5	19.63	65	1.00	13.15	11.2	0.8	-0.1	0.4	2.4
21.0	18.85	65	1.00	12.63	11.3	1.2	0.0	0.8	2.5
21.5	18.63	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
22.0	12.88	65	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
22.5	18.51	65	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
23.0	16.72	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
23.5	19.30	67	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
24.0	16.45	67	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
24.5	14.21	67	1.00	9.52	8.3	0.5	-0.2	0.5	1.9
25.0	15.35	67	1.00	10.28	8.5	0.6	0.0	0.2	1.5
25.5	14.89	67	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
26.0	18.86	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
26.5	17.71	65	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
27.0	16.83	65	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
27.5	17.71	68	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
28.0	14.69	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
28.5	16.51	66	1.00	11.06	9.7	0.4	-0.1	0.3	2.8
29.0	16.90	66	1.00	11.32	11.4	1.0	0.0	0.6	3.4
29.5	19.98	66	1.00	13.39	23.4	1.4	1.6	2.2	3.5
30.0	14.21	70	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
30.5	15.27	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
31.0	13.24	66	1.00	8.87	16.2	2.0	1.7	2.0	1.9
31.5	16.79	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
32.0	14.87	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
32.5	14.31	66	1.00	9.59	7.6	0.2	0.3	-0.7	1.5
33.0	18.40	66	1.00	12.33	10.7	1.2	0.0	0.1	2.5
33.5	12.19	67	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
34.0	16.10	67	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
34.5	15.23	67	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
35.0	16.90	68	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
35.5	13.78	68	1.00	9.23	16.4	1.7	1.3	1.3	3.1
36.0	14.54	68	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
36.5	15.05	67	1.00	10.08	12	1.9	-1.0	-0.4	2.6
37.0	19.76	67	1.00	13.24	12.9	1.3	-0.3	-0.6	3.5
37.5	16.66	67	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
38.0	14.27	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
38.5	16.34	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
39.0	17.21	66	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
39.5	17.53	65	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
40.0	18.17	65	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
40.5	21.01	64	1.00	14.08	14.5	0.2	-0.5	0.0	1.8
41.0	16.97	64	1.00	11.37	10	0.5	-0.2	-0.3	2.0
42.5	29.13	65	1.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

B

depth (cm)	Dec. year (AD) (SR 0.7cm/yr)	$\delta^{13}C_{TOC}$ (‰)	$\delta^{15}N_{TN}$ (‰)	TOC (%)	TN (%)	C/N	N/C
0.5	2013.7	-23.1	6.4	2.58	0.29	8.8	0.11
1	2013.0	-23.0	6.4	2.80	0.30	9.2	0.11
1.5	2012.3	-23.9	6.5	2.67	0.30	9.0	0.11
2	2011.6	-23.8	6.5	2.60	0.31	8.4	0.12
2.5	2010.8	-23.2	6.9	2.55	0.33	7.8	0.13
3	2010.1	-23.8	6.5	2.36	0.30	7.9	0.13
3.5	2009.4	-23.9	6.3	2.50	0.28	9.0	0.11
4	2008.7	-23.8	6.4	2.75	0.30	9.2	0.11
4.5	2008.0	-23.0	6.4	2.62	0.29	9.0	0.11
5	2007.3	-22.7	6.4	2.51	0.30	8.5	0.12
5.5	2006.6	-23.5	6.4	2.82	0.31	9.2	0.11
6	2005.8	-23.6	6.3	2.64	0.29	9.2	0.11
6.5	2005.1	-23.5	6.7	2.54	0.31	8.3	0.12
7	2004.4	-23.8	6.1	2.80	0.28	9.8	0.10
7.5	2003.7	-23.1	6.3	2.59	0.29	9.0	0.11
8	2003.0	-23.5	6.5	2.78	0.29	9.5	0.11
8.5	2002.3	-22.8	6.3	2.65	0.30	8.9	0.11
9	2001.6	-22.5	6.5	2.59	0.29	8.8	0.11
9.5	2000.8	-23.9	6.2	2.71	0.28	9.6	0.10
10	2000.1	-24.5	6.1	1.94	0.25	7.7	0.13
10.5	1999.4	-23.5	6.1	2.56	0.29	8.9	0.11
11	1998.7	-24.3	6.3	2.15	0.26	8.1	0.12
11.5	1998.0	-24.5	6.5	2.90	0.34	8.4	0.12
12	1997.3	-23.8	6.1	2.68	0.28	9.4	0.11
12.5	1996.6	-22.7	6.5	2.63	0.31	8.6	0.12
13	1995.8	-22.5	6.3	2.89	0.31	9.4	0.11
13.5	1995.1	-23.7	6.2	2.64	0.28	9.3	0.11
14	1994.4	-24.4	6.1	2.89	0.29	9.9	0.10
14.5	1993.7	-22.7	6.5	2.74	0.30	9.0	0.11
15	1993.0	-23.5	6.3	2.66	0.29	9.1	0.11
15.5	1992.3	-23.5	5.7	2.43	0.25	9.9	0.10
16	1991.6	-23.4	6.3	2.74	0.29	9.4	0.11
16.5	1990.8	-22.3	6.8	2.72	0.30	8.9	0.11
17	1990.1	-22.2	6.5	2.74	0.31	9.0	0.11
17.5	1989.4	-24.4	6.2	2.88	0.28	10.2	0.10
18	1988.7	-23.6	6.2	2.23	0.28	7.9	0.13
18.5	1988.0	-22.7	6.4	2.62	0.29	9.2	0.11
19	1987.3	-22.9	6.4	2.64	0.29	9.2	0.11
19.5	1986.6	-22.5	6.0	2.60	0.27	9.8	0.10
20	1985.8	-30.4	6.0	2.67	0.27	9.8	0.10
20.5	1985.1	-22.5	6.4	2.87	0.30	9.7	0.10
21	1984.4	-22.2	6.4	2.76	0.29	9.4	0.11
21.5	1983.7	-24.2	5.8	2.44	0.27	9.0	0.11
22	1983.0	-24.5	6.1	1.97	0.25	8.0	0.13
22.5	1982.3	-23.5	6.1	2.56	0.27	9.4	0.11
23	1981.6	-23.8	6.1	2.70	0.27	10.0	0.10
23.5	1980.8	-23.9	6.3	2.64	0.27	9.7	0.10
24	1980.1	-24.5	5.6	2.74	0.26	10.6	0.09
24.5	1979.4	-22.5	6.3	2.76	0.29	9.4	0.11
25	1978.7	-22.4	6.6	2.79	0.29	9.7	0.10
25.5	1978.0	-25.1	5.5	2.42	0.25	9.8	0.10
26	1977.3	-25.1	6.1	2.57	0.25	10.1	0.10
26.5	1976.6	-23.5	6.3	2.68	0.29	9.4	0.11
27	1975.8	-23.1	6.3	2.73	0.30	9.1	0.11
27.5	1975.1	-24.0	6.4	2.91	0.29	10.1	0.10
28	1974.4	-24.4	6.3	2.85	0.28	10.2	0.10
28.5	1973.7	-22.5	6.4	2.57	0.29	8.8	0.11
29	1973.0	-22.2	6.5	2.84	0.31	9.1	0.11
29.5	1972.3	-27.3	5.9	2.17	0.24	9.2	0.11
30	1971.6	-24.9	6.0	2.39	0.25	9.6	0.10
30.5	1970.8	-23.1	6.5	2.37	0.29	8.3	0.12
31	1970.1	-29.4	6.5	2.61	0.28	9.2	0.11
31.5	1969.4	-24.5	6.4	2.79	0.28	10.1	0.10
32	1968.7	-27.9	6.0	2.58	0.26	9.9	0.10
32.5	1968.0	-22.9	6.2	2.46	0.27	9.0	0.11
33	1967.3	-22.9	6.4	2.62	0.28	9.3	0.11
33.5	1966.6	-25.0	5.9	2.31	0.24	9.7	0.10
34	1965.8	-28.2	6.0	2.41	0.27	8.9	0.11
34.5	1965.1	-23.5	6.4	2.63	0.28	9.4	0.11
35	1964.4	-23.2	6.5	2.47	0.28	8.7	0.11
35.5	1963.7	-28.7	6.2	2.68	0.26	10.2	0.10
36	1963.0	-24.4	6.2	2.67	0.27	10.0	0.10
36.5	1962.3	-22.9	6.4	2.44	0.28	8.8	0.11
37	1961.6	-22.9	6.4	2.73	0.28	9.6	0.10
37.5	1960.8	-24.3	6.4	2.17	0.26	8.3	0.12
38	1960.1	-24.2	6.4	2.78	0.27	10.4	0.10
38.5	1959.4	-23.2	6.3	2.60	0.27	9.6	0.10
39	1958.7	-23.1	6.4	2.47	0.27	9.3	0.11
39.5	1958.0	-24.8	6.1	2.41	0.26	9.3	0.11
40	1957.3	-24.3	6.2	2.15	0.26	8.2	0.12
40.5	1956.6	-22.8	6.5	2.49	0.26	9.4	0.11
41	1955.8	-22.7	6.5	2.30	0.27	8.5	0.12
42.5	1953.7	-24.1	6.1	2.63	0.26	10.1	0.10
	mean	-23.9	6.3	2.59	0.28	9.2	0.11
	sd	1.6	0.24	0.21	0.02	0.6	0.01

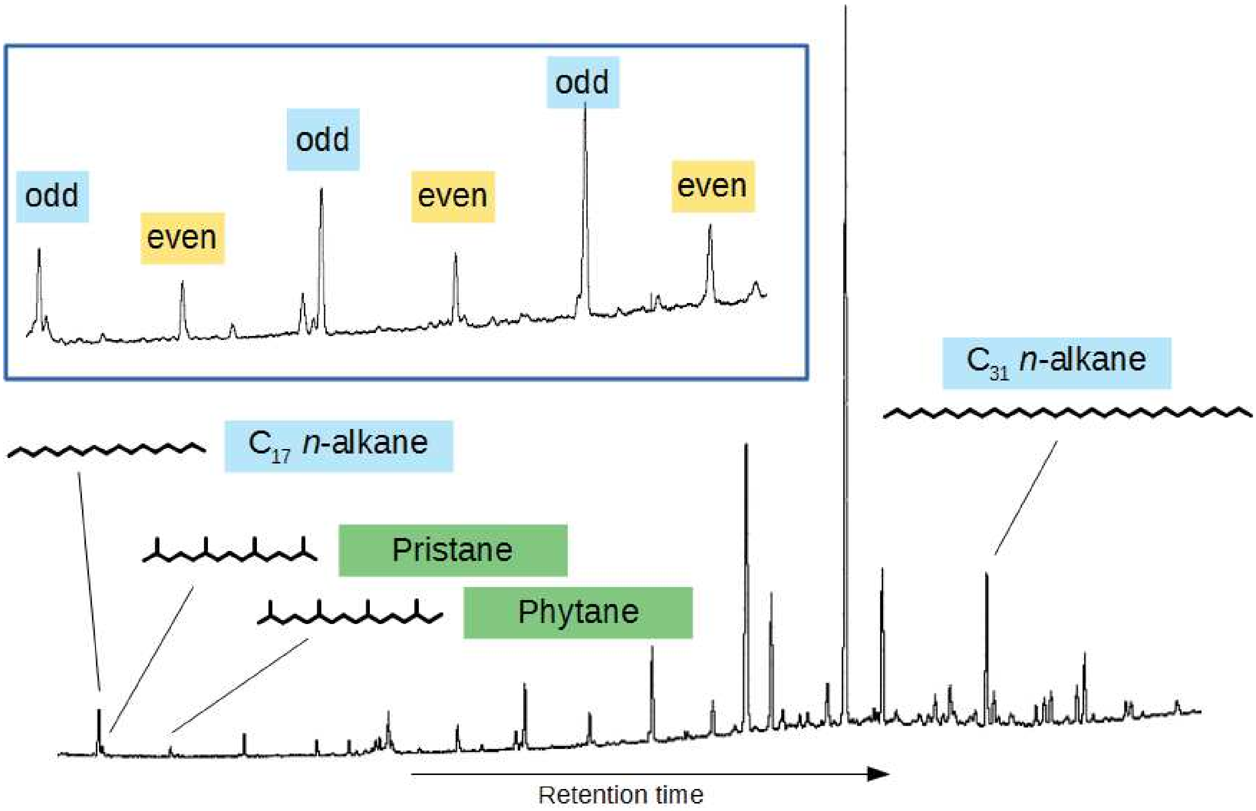
C

depth (cm)	Dec. year (0.7 cm/yr)	SST (°C)	$\Sigma_{n\text{-}alk}$ (μg/g TOC)	ACL	CPI	TAR_{HC}	Pr/Ph	C_{31} ratio	Hop/Ste
1	2014.0	14.6	310	28.6	3.1	6.7	3.2	0.44	21
1.5	2013.3	14.8	211	28.8	3.6	7.9	2.9	0.49	24
2.0	2012.6	16.1	186	28.7	3.6	7.3	2.4	0.47	30
3	2011.1	17.7	235	29.0	3.7	6.7	2.5	0.52	22
3.5	2010.4	15.6	191	28.9	2.9	6.5	2.3	0.51	35
4	2009.7	15.4	178	29.0	3.2	6.8	2.4	0.50	19
4.5	2009.0	15.4							21
5	2008.3	16.7	139	29.0	3.7	5.7	1.9	0.51	14
5.5	2007.6	16.5	138	28.7	3.4	5.7	2.1	0.48	24
6	2006.9	17.5	187	28.8	3.3	4.4	1.7	0.50	16
6.5	2006.1	14.8	161	28.9	3.0	5.5	1.8	0.49	22
7	2005.4	15.5	173	28.9	2.5	5.7	2.1	0.49	22
7.5	2004.7	18.4	200	28.9	3.2	5.2	1.6	0.49	21
8	2004.0	18.6	212	29.0	3.4	6.6	2.0	0.51	19
8.5	2003.3	21.1	150	29.0	3.5	6.5	2.7	0.51	13
8.5	2003.3		147	28.9	3.7	6.8	2.7	0.51	n.a.
9	2002.6	15.8	167	29.1	3.2	6.0	2.0	0.51	14
12.5	1997.6	17.5	140	28.9	2.1	5.1	1.7	0.47	17
13	1996.9	17.8	122	29.0	3.0	3.9	3.7	0.51	n.a.
16.5	1991.9	15.3	146	28.8	2.9	3.0	3.0	0.50	n.a.
17	1991.1	15.1	168	29.1	3.0	5.1	2.9	0.50	n.a.
20	1986.9	15.3	184	29.2	3.0	4.3	2.5	0.52	n.a.
20.5	1986.1	14.2	147	28.9	2.9	4.0	3.5	0.48	n.a.
21	1985.4	14.1	161	29.2	2.9	5.5	2.6	0.51	n.a.
24.5	1980.4	14.2	147	29.1	2.7	5.3	1.9	0.51	20
25	1979.7	17.0	114	29.2	2.5	4.9	1.7	0.52	20
28.5	1974.7		155	29.1	2.8	5.7	2.1	0.50	52
29	1974.0	16.2	225	29.1	2.9	5.4	2.5	0.50	n.a.
29.5	1973.3	17.2	197	29.0	2.7	4.7	2.1	0.50	n.a.
31	1971.1	18.9	160	29.0	2.5	5.0	2	0.47	n.a.
32.5	1969.0	16.5	139	28.8	2.6	4.4	2.3	0.46	n.a.
33	1968.3	17.8	226	29.2	2.8	5.9	2.9	0.50	n.a.
35.5	1964.7	17.2	168	29.1	2.6	4.3	2.1	0.48	n.a.
36.5	1963.3	15.3	258	28.9	2.9	6.9	2.7	0.48	n.a.
37	1962.6	17.3	181	28.9	3.4	7.2	1.7	0.49	243
40.5	1957.6	17.0	152	28.8	2.5	6.6	1.6	0.47	74
41	1956.9		244	28.9	2.8	6.0	2.9	0.48	n.a.

D

month	T (°C)	sd
January	1.70	2.08
February	1.20	1.69
March	1.20	1.51
April	4.52	1.73
May	9.62	2.09
June	16.68	2.25
July	17.26	1.75
August	17.78	1.64
September	14.28	1.55
October	10.49	1.86
November	6.61	1.88
December	4.02	1.99

E


odd
even
odd
even
odd
even
C$_{17}$ n-alkane
Pristane
Phytane
C$_{31}$ n-alkane
Retention time

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