**Biogeosciences
Discussions**

Bacteriohopanepolyols record stratification, nitrogen fixation and other biogeochemical perturbations in Holocene sediments of the Central Baltic Sea

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Abstract

The Baltic Sea, one of the world's largest brackish-marine basins, established after deglaciation of Scandinavia about 17 000 to 15 000 yr ago. In the changeable history of the Baltic Sea, the initial freshwater system was connected to the North Sea about 8000 yr ago and the modern brackish-marine setting (Littorina Sea) was established. Today, a relatively stable stratification developed in the water column of the deep basins due to salinity differences. Stratification is only occasionally interrupted by mixing events, and controls nutrient availability and growth of specifically adapted microorganisms and algae. We studied bacteriohopanepolyols (BHPs), lipids of specific bacterial groups, in a sediment core from the Central Baltic Sea (Gotland Deep) and found considerable differences between the distinct stages of the Baltic Sea's history. Individual BHP structures indicate contributions from as yet unknown redoxcline-specific bacteria (bacteriohopanetetrol isomer), methanotrophic bacteria (35-aminobacteriohopanetetrol), cyanobacteria (bacteriohopanetetrol cyclitol ether isomer) and, through allochthonous input after the Littorina transgression, from soil bacteria (adenosylhopane), whereas the origin of other BHPs in the core has still to be identified. Notably high BHP abundances were observed in the deposits of the brackish-marine Littorina phase, particularly in laminated sediment layers. Because these sediments record periods of stable water column stratification, bacteria specifically adapted to these conditions may account for the high portions of BHPs. An additional and/or accompanying source may be nitrogen-fixing (cyano)bacteria, which is indicated by a good correlation of BHP abundances with C_{org} and δ^{15}N.

1 Introduction

The Baltic Sea had a variable geological and biogeochemical history after it originated 17 000–15 000 yr before present (BP; see comprehensive summary in Andrén et al., 2011). After deglaciation of Scandinavia, the closed basin of the modern Baltic Sea

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was filled with melt water and a freshwater system developed around 16 000 yr BP, the so-called Baltic Ice Lake. This oligotrophic lake setting was terminated about 11 700 yr BP by a pulse of marine water that entered the Baltic Sea via a passage through south-Central Sweden and led to a slightly brackish environment (Yoldia Sea). Freshwater

5 conditions re-established about 10 700 yr BP (Ancylus Lake), until the major marine transgression took place via the Kattegat, resulting in the establishment of the modern Littorina Sea. The onset of the Littorina Sea stage is still a matter of discussion (see, e.g. Rößler et al., 2011). Dating based on calcareous fossils revealed 8100–8000 yr BP in Great Belt (e.g. Bennike et al., 2004) and Mecklenburg Bight (Rößler et al., 2011)

10 and 7200 yr BP in Arkona Basin (e.g. Moros et al., 2002). Bulk sediment dates revealed older ages of 8500 to 8000 yr BP for the onset in Bornholm Basin (Andrén et al., 2000a) and Gotland Basin (Andrén et al., 2000b).

The ingression of marine North Sea waters led to the development of a stratified water body in the deep basins of the Central Baltic Sea, with more saline, denser

15 waters in the lower water column. Such conditions also characterize one of the deepest basins of the modern Baltic Sea, the Gotland Deep (249 m water depth). In this basin exists a relatively stable oxic-anoxic transition zone (redoxcline) at about 100 m water depth. The stratification of the Gotland Deep is only occasionally disturbed by turbulent vertical transport processes and inflows of North Sea water (Reissmann et al., 2009).

20 The stratification has major consequences on the nutrient situation of the Central Baltic Sea and the composition of pelagic micro- and macroorganisms (e.g. Labrenz et al., 2007; Schmale et al., 2012). For instance, high nutrient input with excess phosphorus loads promotes growth of nitrogen-fixing cyanobacteria (Nausch et al., 2009; Wasmund et al., 2012).

25 Numerous micropaleontological and biogeochemical studies on the Holocene in the Central Baltic Sea exist, mainly reflecting the change from oligotrophic freshwater conditions (Ancylus Lake) to a brackish-marine setting (Littorina Sea) with widespread deep water anoxia (e.g. Sohlenius et al., 1996; Bianchi et al., 2000; Brenner, 2001, 2005; Voss et al., 2001). As a result of the Littorina Sea transgression, marine diatoms

and dinoflagellates entered the Central Baltic Sea (Brenner, 2005), and cyanobacteria became increasingly important as indicated by pigment and molybdenum abundances (Bianchi et al., 2000; Kunzendorf et al., 2001; Poutanen and Nikkila, 2001; Borgendahl and Westman, 2007). Due to the lack of preservable cell remnants, however, informa-

5 tion about other microbial protagonists of biogeochemical cycling in the changeful history of the Central Baltic Sea is scarce. An organic geochemical approach was made by Nytoft and Larsen (2001), who reported changes in the composition of bacterial hopanoid hydrocarbons from the Gotland Deep and concluded that bacteria became more prominent during the Littorina Sea stage. Our study aims to specify these bacte-

10 rial contributions to the Holocene sediments of the Gotland Deep by using one of the most ubiquitous classes of lipids, bacteriohopanepolyols (BHPs). BHPs are produced by many groups of bacteria and are increasingly used for paleoreconstructions (e.g. Talbot and Farrimond, 2007; Coolen et al., 2008; Blumenberg et al., 2009). So far, only one report of BHPs from surface sediments of the Central Baltic Sea exists (Bernd-

15 meyer et al., 2012). This study focused on BHPs from methanotrophic bacteria living in the redoxcline of the modern Gotland Deep water column and demonstrated the utility of BHPs to reflect water column processes. The current study is aimed at BHPs and selected other biomarkers in deeper Holocene sediments of the Gotland Deep. Our goal is to bridge the gap between the relatively well known record of eukaryotic remains

20 and the much less understood bacteria and, by that, to get a better understanding of bacterial primary production and redoxcline-related processes in the geological history of the Central Baltic Sea.

2 Study site and core stratigraphy

During a research cruise with RV *Maria S. Merian* in summer 2010, a 11.6 m long

25 gravity core, together with a "Frahmlot" core to obtain undisturbed surface layers, were taken in the Gotland Deep (240 m water depth; station MSM 16-1 52-07; coordinates: 57° 16.998; E 20.7182°; for sampling site see Fig. 1). The cores cover sedimentary

depositions of all stages of the Baltic Sea's history. Sediment depths in the figures are composites resulting from lithostratigraphic correlation of the gravity and the Frahmlot corer. The deposits of the Baltic Ice Lake were characterised by brownish and clayish sediments with low visible organic matter content (~ 1000 to $680\,\mathrm{cm}$ below sea floor (cm b.s.f.); Fig. 2). Similarly organic-lean Ancylus Lake sediments were found between 680 to $\sim 440\,\mathrm{cm}$ b.s.f. A black color in the upper Ancyclus Lake layer is most likely due to precipitation of iron sulfide bands after downward diffusion of H_2S from sulfate reduction in the overlying Littorina Sea deposits (Boesen and Postma, 1988; Sohlenius et al., 1996; Moros et al., 2002). The brackish-marine Littorina Sea sediments start at 440 cm b.s.f. and partially show fine lamination, characterizing times of pronounced and stable deep water anoxia. Strongly laminated sediments between 60 and 90 cm b.s.f. and in the uppermost 20 cm b.s.f. most likely represent deposits of the warm stages Medieval Climate Anomaly (MCA, from $\sim$ AD 950 to 1250) and the Modern Warm Period (MoWP, since $\sim$ AD 1850), respectively, while the organic-lean sediments in between record the Little Ice Age (LIA, from $\sim$ AD 1350 to 1850; ages inferred from Kabel et al., 2012).

3 Material and methods

3.1 Sample preparation and bulk analyses (C_{org}, N, δ^{15}N, LOI)

The core was stored cool on board and in the laboratory until sampling in February 2011 (samples for biomarker and bulk analyses were then stored frozen until further analyses). The upper three samples were obtained from the accompanying Frahmlot (MSM 16-1 52-04) and data were taken from Berndmeyer et al. (2012). The samples were homogenised by grinding, and aliquots were taken for elemental analyses (C/N/S) using a Eurovector Euro EA CNS-analyser. To determine the contents of organic carbon (C_{org}), each sample was also analyzed after decarbonatization with HCl. Bulk δ^{15}N isotope analysis was carried out in duplicate using elemental analysis-isotope

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ratio mass spectrometry (EA-IRMS, Delta plus, Thermo scientific). The loss on ignition (LOI) was determined in high resolution for the upper 500 cm of the gravity core by ashing freeze-dried samples at 550 °C (3 h) and calculating the resulting mass difference (wt. %).

3.2 Extraction, column chromatography and derivatisation

About 7.5 g of the sediments was extracted three times (20 min) with 40 ml of a mixture of dichloromethane (DCM) and methanol (MeOH) (3 : 1, v : v) in a CEM Mars 5 microwave (Matthews, NC, USA) at 80 °C and 800 W. An aliquot of the combined extract was acetylated and analyzed for BHPs by liquid chromatography-mass spectrometry (LC-MS; see below). Acetylation was performed using a mixture of acetic acid anhydride and pyridine (1 : 1, v : v, 50 °C for 1 h and overnight at room temperature). The pyridine/acetic acid anhydride mixture was then dried under vacuum. Another aliquot was separated by column chromatography into a hydrocarbon (F1), a ketone and alcohol (F2), and a polar fraction (F3; details are described in Blumenberg et al., 2009). Resulting alcohols in the F2 were silylated using BSTFA (N,O-bis[trimethylsilyl]trifluoroacetamide) for 1.5 h at 80 °C.

3.3 Gas chromatography-mass spectrometry (GC-MS)

The hydrocarbon and alcohol fractions (F1, and F2) were analyzed using GC–MS (Varian CP-3800 chromatograph coupled to a 1200L mass spectrometer), and peaks were identified by comparing mass spectra and retention times with published data. The system was equipped with a fused silica column (Phenomenex Zebron ZB-5MS, 30 m, 0.25 µm film thickness, i.d. 0.32 mm). Helium was used as carrier gas and the temperature programme was 80 °C (3 min) to 310 °C at 4 °C min^{-1} (held 25 min).

3.4 Liquid chromatography-mass spectrometry (LC-MS)

Details about LC-MS analyses and quantification of BHPs can be found elsewhere (Blumenberg et al., 2010). Briefly, LC–MS was performed using a Prostar Dynamax High-Performance Liquid Chromatography (HPLC)-system interfaced with a 1200L triple quadrupole mass spectrometer (both Varian). HPLC separation was achieved using a Merck Lichrocart (Lichrosphere 100; RPC18e 5 µm column (250 × 4 mm) and a Merck Lichrosphere pre-column of the same material. Quantifications were done using external standards of BHPs with known concentrations.

4 Results

4.1 Bulk geochemical data and stratigraphy

C_{org} as well as high resolution LOI data are presented in Fig. 2. In the Central Baltic Sea, LOI [%] approximately mirrors C_{org} [%], if divided by 2.5 (Leipe et al., 2010), and this conversion factor appears to be also valid for the studied core from the Gotland Deep (see converted LOI data in Fig. 2). The high resolution of LOI data allowed a comparison with dated cores from the same area (Lougheed et al., 2012). Four maxima in C_{org} were found, the lower of which represents the establishment of the Littorina Sea (about 440 cm below sea floor (cm b.s.f.); peak at 420 cm b.s.f. ∼ 6500 yr BP), the peak at 290 cm b.s.f. represent 4500 yr BP and the peak at 70 cm b.s.f., the MCA (maximizing at ∼ 800 yr BP). The uppermost C_{org} maximum records the Modern Warm Period (MoWP) of the last 100 yr (C_{org} data from Frahmlot).

In Fig. 3, C_{org} is compared with δ^{15}N and C/N ratios. As clearly demonstrated in Fig. 3b, C_{org} and δ^{15}N are excellently negatively correlated (p-value 3×10^{-7}; excluding the surface samples). Lowest C/N ratios of about 5 were observed during the Baltic Ice Lake and Ancylus Lake stages and highest C/N values of about 10 in sediments

deposited during the Littorina stage. The maximum value of 12.9 was observed in the deepest sediment sample of the Littorina Sea stage.

4.2 Biomarkers

Figure 4 shows concentrations of selected biomarkers in the Gotland Deep sediments. Highest abundances of nonacosane (nC_{29}), a biomarker for terrestrial input, were found in Baltic Ice Lake and Ancylus Lake samples (~ 600 to 1000 cm b.s.f.; up to $150 \, \mu g \, g^{-1}$ C_{org}, Fig. 4a). Above, concentrations clearly decreased to about $20 \, \mu g \, g^{-1}$ C_{org}. In the Littorina Sea sediments, concentrations of nC_{29} were relatively stable, demonstrating low fluctuations of terrestrial plant input. Moreover, as total C_{org} abundances changed over that time period, the C_{org} increases and decreases argue for productivity-induced changes, because varying preservations should have similarly affected nC_{29} abundances in parallel to C_{org} fluctuations. In contrast to nC_{29}, abundances of dinosterol (4α,23,24-trimethyl-5α-cholest-22E-en-3β-ol), a 4-methyl steroid prominent in dinoflagellates (Withers, 1983), is positively correlated with total C_{org} (Fig. 4b).

Similar to dinosterol, the sum of bacteriohopanepolyols (BHPs) revealed highest abundances in the Littorina Sea sediments. Within this lithological unit, particularly high BHP amounts, maximizing at about $600 \, \mu g \, g^{-1}$ C_{org}, were observed in the most organic-rich layers. Whereas dinosterol increased at the establishment of the Littorina Sea stage, BHPs already went up during the late Ancylus Lake stage (after the initial Littorina transgression at about 470 cm b.s.f.). Lowest BHP concentrations were observed in the earlier Ancylus Lake and Baltic Ice Lake sediments. The Gotland Deep core contains eight distinct BHPs whose individual distributions are shown in Fig. 5. Highest amounts were found for bacteriohopanetetrol (BHT) and 32,35-anhydroBHT, with the latter showing greater abundances with increasing depth. 35-aminobacteriohopanetriol and – tetrol were prominent in sediments representing the beginning of the Littorina Sea stage. BHT cyclitol ethers (two isomers; tentatively identified by co-elutions with previously identified BHT cyclitol isomers) were first observed in sediments of the late Ancylus Lake stage and were omnipresent, although in low abundance, in the

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sediments of the Littorina Sea. In the lowermost Littorina Sea stage sample studied (at 420 cm b.s.f.) and above, an unknown BHT isomer was found, whose elution characteristics correspond with a BHT isomer found in the recent Gotland Deep water column (Berndmeyer et al., 2012).

5 Discussion

5.1 Biogeochemical changes in the Holocene as reflected by bulk geochemical parameters

The sediments from the Gotland Deep markedly reflect the establishment of the marine-brackish Littorina Sea in a steep increase in C_{org}, probably due to enhanced preservation and/or increasing primary production, and the deposition of strongly laminated sediments (Fig. 2; see discussion below). A peak in C_{org} was also observed at about 800 yr BP, most likely reflecting high organic carbon accumulation and sediment lamination during the Medieval Climate Anomaly (MCA). The sediments deposited during the subsequent cooler period (Little Ice Age; LIA) are characterized by low C_{org} and most likely oxic conditions in the bottom waters (Sohlenius et al., 1996; Andrén et al., 2000b; Fig. 2). Above, the Modern Warm Period (MoWP) and recent anthropogenic influence are reflected by a parallel increase in $\delta^{15}N$ and C_{org} (Voss et al., 2001; Struck et al., 2000). Except for the samples from the MoWP, C_{org} correlates negatively with bulk $\delta^{15}N$ (Fig. 3b). Enhanced growth of cyanobacteria capable of biological nitrogen fixation is a plausible explanation for low $\delta^{15}N$ values, a scenario which has been suggested for numerous settings (Sachs and Repeta, 1999; Kuypers et al., 2004; Blumenberg et al., 2009), including the Baltic Sea (Bianchi et al., 2000; Voss et al., 2001; Voss, 2005). The importance of cyanobacteria after the Littorina Sea transgression is supported by studies using pigment and molybdenum abundances (Poutanen and Nikkila, 2001; Kunzendorf et al., 2001; Borgendahl et al., 2007). Today, cyanobacteria contribute about 45 % to the bulk sedimentary nitrogen (Struck et al., 2004). Flourishing

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of nitrogen-fixing (cyano)bacteria is commonly promoted by phosphorus excess (lowering N/P ratios) through riverine input or release from anoxic sediments (Bianchi et al., 2000). Consequently, the establishment of a stratified, partly anoxic water body after the Littorina Sea transgression is a conceivable scenario for a decrease of N/P ratios and an increase in cyanobacterial biomass. A further reduction in the N/P ratio may have been induced by bacterial denitrification under the established anoxic conditions (Haug et al., 1998; Struck et al., 2000). Due to the high energy costs of cleaving N_2, nitrogen-fixing cyanobacteria have only an advantage over algae in waters depleted in bioavailable nitrogen (Karl et al., 2002). Hence, the good correlation between high C_{org} and low $\delta^{15}N$ argues for (i) a major role of nitrogen-fixing (cyano)bacteria during the deposition of organic-rich, laminated sediments (e.g. after the Littorina Sea transgression, and during the MCA), and for (ii) enhanced primary production under N/P ratios lower than the Redfield Ratio [C/N/P: 106/16/1 (Redfield et al., 1963)]. At the same time, cyanobacteria are known for biomass C/N ratios higher than that obtained from the Redfield Ratio (C/N = 6.6). For *Nodularia spumigena*, an important (nitrogen-fixing) cyanobacterium in the Central Baltic Sea, a C/N of 8.5 was reported (Sörensson and Sahlsten, 1987). Consequently, the observed increase in C/N in laminated sediments after the Littorina Transgression (Fig. 3a) is also in accordance with an increasing importance of cyanobacteria among the primary-producing community. Moreover, a direct temperature dependence of cyanobacterial blooming in the Central Baltic Sea was also currently reported (Kabel et al., 2012), in addition to the indirect role of high temperatures for water column stratification and, thus, a shift to low N/P ratios.

5.2 Biomarker records of biogeochemical perturbations in the Central Baltic Sea

5.2.1 Baltic Ice Lake – Ancylus Lake transition (10 700–9800 yr BP)

The resolution of samples from these intervals was low, but among the studied biomarkers the transition is not reflected in any changes.

5.2.2 Ancylus Lake – Littorina Sea transition ($\sim$ 8500–8000 yr BP)

In Ancylus Lake sediments, nonacosane (nC_{29}) was much higher in relative abundance than in Littorina Sea deposits (Fig. 4a). nC_{29} is a biomarker for higher plant waxes (Eglinton et al., 1962), and the concentration in the lower core demonstrates the high relevance of allochthonous input during the Ancylus Lake stage. This is supported by previous findings of abundant plant-derived triterpane biomarkers in Ancylus Lake sediments (Nytoft and Larsen, 2001). After the Littorina Sea transgression a substantial environmental change is reflected by a drop in nC_{29} abundance by an order of magnitude (Fig. 4a). At the same time, a biomarker for dinoflagellates, dinosterol (Withers, 1983), increased (Fig. 4b). Together, both biomarkers mirror the shift from an oligotrophic, terrestrially influenced system towards a setting controlled by brackish-marine primary producers, which fits well with micropaleontological studies (e.g. Brenner, 2001). It must be noted, however, that dinosterol contributions in the Gotland Deep sediments appear to be largely due to marine dinoflagellates of the Littorina Sea stage, whereas the high relevance of specific freshwater dinoflagellates (e.g. *Gonyaulax apiculata*) reported for the Ancylus Lake stage (Brenner, 2001; Yu and Berglund, 2007) is not reflected by this biomarker.

As a result of the Littorina Sea transgression, concentrations of BHPs increased by almost two orders of magnitude and followed a similar trend as C_{org} (Fig. 4c). The maximum BHP concentrations of up to $600 \, \mu g \, g^{-1} \, C_{org}$ were extraordinary high compared to other marine settings (e.g. 4-fold higher than in Black Sea sediments; Blumenberg et al., 2009). Similarly, diploptene, a hopanoid hydrocarbon that is produced by many bacteria along with BHP, was reported to be most abundant in the Littorina Sea stage in Gotland Deep sediments (Nytoft and Larsen, 2001). The consistently low abundances of adenosylhopane, a BHP specific of so far unknown soil bacteria (Talbot and Farrimond, 2007; Cooke et al., 2008; Fig. 5g) exclude variations in land-derived allochthonous BHP contributions as a major control on BHP patterns. Likewise, the peak in adenosylhopane in the late Ancylus Lake stage may be due to enhanced input of

soil organic matter during the flooding of land areas during the Littorina transgression (Fig. 5g).

The observed trends might be also influenced, or amplified, by enhanced lipid preservation as result of the establishment of anoxic bottom waters and sediments. Enhanced preservation is crucial for high BHP abundances in sediments as these polyfunctionalised lipid structures are prone to microbial degradation (Ourisson et al., 1982). A change in the redox environment in the course of the Littorina Sea transgression is reflected in a decrease in the relative abundance of 32,35-anhydroBHT (Fig. 5b). 32,35-anhydroBHT is a diagenetic degradation product of BHT and composite BHPs under acidic and marine sedimentary conditions (Bednarczyk et al., 2005; Schaeffer et al., 2008, 2010). Higher concentrations of this diagenetic product consequently suggest a lower preservation potential in Ancylus Lake and older sediments. In turn, the generally low amounts of 32,35-anhydroBHT in Littorina Sea deposits, with lowest abundances recorded in the organic-rich laminated sediments, may reflect a different preservational status of BHP. Apart from that, however, it is unlikely that total BHP concentrations, including the diagenetic product 32,35-anhydroBHT, are exclusively controlled by preservational issues. Studies from comparable settings demonstrated a stability of BHPs up to an age of 100 000 yr (Cooke et al., 2008; Coolen et al., 2008; Blumenberg et al., 2009, 2010). Providing additional evidence for production of BHPs as key-control for BHP abundances in the studied core, 32,35-anhydroBHT abundances are less pronounced than those of total BHPs and C_{org} trends were found to be slightly delayed to BHPs (e.g. Ancylus-Littorina transition or at the MCA; Fig. 4). This rather indicates BHPs to record pioneer organisms of these changes.

BHPs exclusively specific for cyanobacteria were not found in the Gotland Deep sediments. However, an isomer of the common BHT cyclitol ether was observed that was also found in the oxic part of the water column (Berndmeyer et al., 2012), which suggests a bacterial source from within the euphotic zone (Fig. 5f; BHT cyclitol ether were summed up as similar trend suggest the same origin). An isomer of the common BHT cyclitol ether was also reported from the cyanobacterium *Anacystis montana*

(Herrmann et al., 1996) which has, however, not been reported from the recent Baltic Sea water column. The contribution of cyanobacteria to the sedimentary BHP pool in Gotland Deep sediments therefore remains ambiguous and seemingly reflects the fact that neither all cyanobacteria produce BHPs nor that their BHP inventory, if present, must always be specific.

5.2.3 Biogeochemical variations during the Littorina Sea stage as reflected by BHPs

Despite the generally higher importance of BHP producing bacteria in the Littorina Sea stage, internal variations in this unit were also observed. 35-aminobacteriohopanetriol is, along with BHT, a ubiquitous BHP and is produced by diverse bacterial groups. Bacteria rich in 35-aminobacteriohopanetriol flourished particularly during the transition from the Ancylus Lake to the Littorina Sea where concentrations are about 4-fold higher than in all other samples studied (Fig. 5d). Which group of bacteria particularly sourced 35-aminobacteriohopanetriol is unclear, but the same maximum, at the time of the Littorina Sea transgression is revealed by a more specific BHP, 35-aminobacteriohopanetetrol (Fig. 5e), which was also particularly abundant in Black Sea sediments reflecting the marine ingression after the last deglaciation (Blumenberg et al., 2009). 35-aminobacteriohopanetetrol was reported from cultured methanotrophic bacteria (Neunlist and Rohmer, 1985; Talbot et al., 2001) as well as from sulfate reducing bacteria (SRB; Blumenberg et al., 2006, 2012b). Indeed, both bacterial groups can plausibly explain the observed trend in these individual BHP concentrations. First, the inflow of marine sulfate-rich waters during the Littorina Sea transgression, and the establishment of a stratified water column has likely strongly stimulated the activity of SRB in the upper sediments and bottom waters. Increased microbial sulfate reduction is also expressed by an increase in pyrite sulfur in the respective core section (data not shown; see also black pyrite layers from downward-diffusing H_2S in the uppermost Ancylus Lake sediments; Fig. 2). However, during the Littorina stage, SRB should have remained a stable part of the microbial community. This conflicts

with the observed decreases in 35-aminobacteriohopanetriol and – tetrol abundances after the Littorina optimum (Fig. 5d, e). Another possible source for both BHPs are methanotrophic bacteria, which were reported as members of the microbial community at the recent redoxcline of the Gotland Deep water column (Schmale et al., 2012; Berndmeyer et al., 2012). Unfortunately the analyses of $\delta^{13}C$ values to characterize the bacterial source (Hayes, 1993) and particularly to identify methanotrophy (Freeman et al., 1990) was not possible for the Gotland Deep due to low concentrations. Despite of that, we propose that both 35-aminobacteriohopanetriol and – tetrol are related to pioneer methanotrophic bacteria related to the establishment of the pelagic redoxcline.

Redoxcline processes are also reflected by another abundant BHP in Gotland Deep sediments. In the upper part of the core, we found relatively high amounts of a BHT isomer (Fig. 5c). The nature of the isomerization was not further identified, but a BHT isomer was observed to be abundant in suboxic zones of stratified marine water columns (Sáenz et al., 2011) including the redoxcline of the modern Gotland Deep water column (Berndmeyer et al., 2012), and near the redoxcline of a microbial mat (Blumenberg et al., 2012a). We therefore suggest that the consistent occurrence of the BHT isomer in the underlying sediments of the Littorina Sea stage records water column stratification. It appears, however, that the concentrations of this compound cannot directly be translated into a measure of the intensity of the stratification, because neither the strongly laminated sediments of the MCA and MoWP warm periods (intense stratification), nor the sediments of the LIA (less pronounced stratification; Zillén and Conley, 2010) show corresponding excursions in the relative abundance of the BHT isomer (Fig. 5c). Further studies are needed to corroborate the relationship of BHT isomer occurrences to redoxcline processes, as well as the identification of the biological source(s).

Apart from the ups and downs of individual BHP sources, it can be stated that the overall input of hopanoids is linked to changes in the nutrient situation (low N/P ratios with high phosphorus loads; see above) and the establishment of water column stratification. A similar scenario may explain BHP increases in Black Sea sediments

as a result of the ingression of Mediterranean waters through the Bosporus after the last glacial maximum (Blumenberg et al., 2009). The correlation between the occurrence of laminated sediments, bulk δ^{15}N and total BHPs may be taken as support for a similar relationship for the Baltic Sea (Fig. 6), but maybe also linked to the development of redoxclines and the establishment of redoxcline-specific BHP producing bacteria (Wakeham et al., 2007; Sáenz et al., 2011; Berndmeyer et al., 2012; Blumenberg et al., 2012a). For the Gotland Deep sediments it is likely that both, bacterial primary production under low N/P ratios and the presence of a redoxcline, controlled BHP abundances, but which factor prevailed is unclear. Nevertheless, the stability of the stratification is most likely an important factor as BHP abundances appear to be exceedingly high during warmer times (e.g. during the MCA and the MoWP). Future studies should focus on the identification of microbial BHP producers thriving at these biogeochemical zones, because these zones appear to be key environments for the biosynthesis of the precursors of geohopanoids, which are ubiquitous in rocks, oils and sediments.

6   Conclusions

A composite core (gravity core and Frahmlot) covering the last 9000 yr of the Central Baltic Sea history was studied for bulk geochemical parameters and selected biomarkers, with a particular focus on bacteriohopanepolyols (BHPs). Biomarker distributions and abundances in the Baltic Ice Lake (before 11 700 yr BP) and Ancylus Lake (10 700 to 8500 yr BP) sediments were similar and reflect pronounced higher plant inputs and low primary productivity. Marine dinoflagellates, as indicated by dinosterol, and BHP producing bacteria began to flourish after the Littorina Sea transgression 8500 to 8000 yr BP. In the Littorina Sea stage BHP concentrations are the highest so far reported from a marine or brackish setting. BHPs are most abundant in laminated sediments, pointing at an important role of hopanoid-producing bacteria during times of water column stratification and pronounced anoxia of the lower water column. Such

conditions characterized, for instance, the onset of the Littorina Sea transgression, the MCA and the MoWP. Whereas the discrete microorganisms that sourced the BHPs in Gotland Deep sediments still have to be identified, the structures and distributions of individual BHPs point at contributions from methanotrophic and other bacteria specific to redoxclines, as well as most likely cyanobacteria. A good correlation between BHPs, C_{org} and $\delta^{15}N$ highlights an involvement of BHP-producing bacteria in the fixation of atmospheric nitrogen and, as this process is crucial for the today's Baltic Sea, underpins their role for the entire nutrient cycle in this marginal marine basin.

Supplementary material related to this article is available online at:
http://www.biogeosciences-discuss.net/9/17139/2012/
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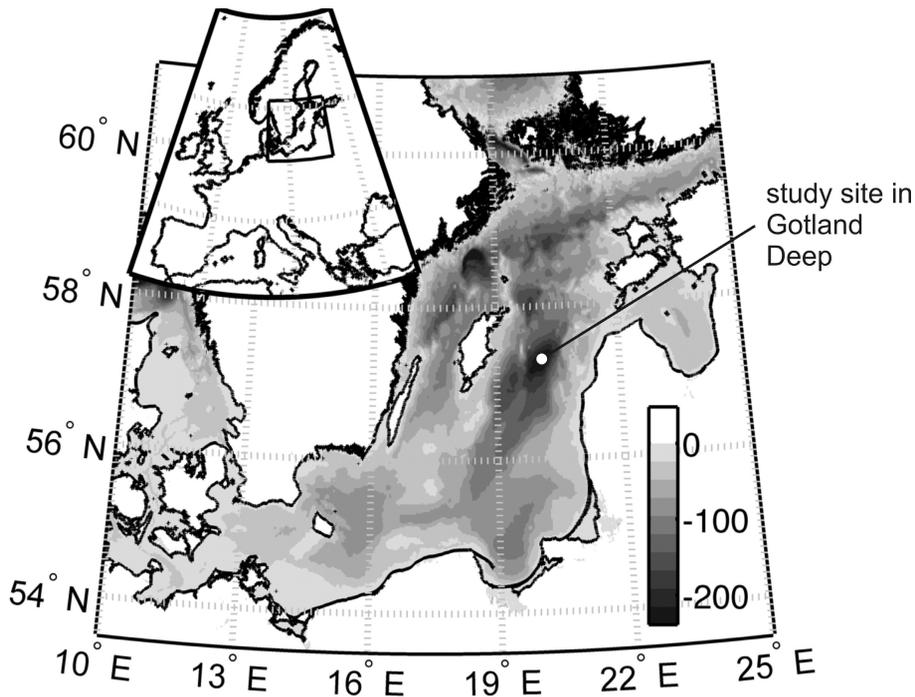
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Fig. 1. Study site (station 52-07) in the Central Baltic Sea.

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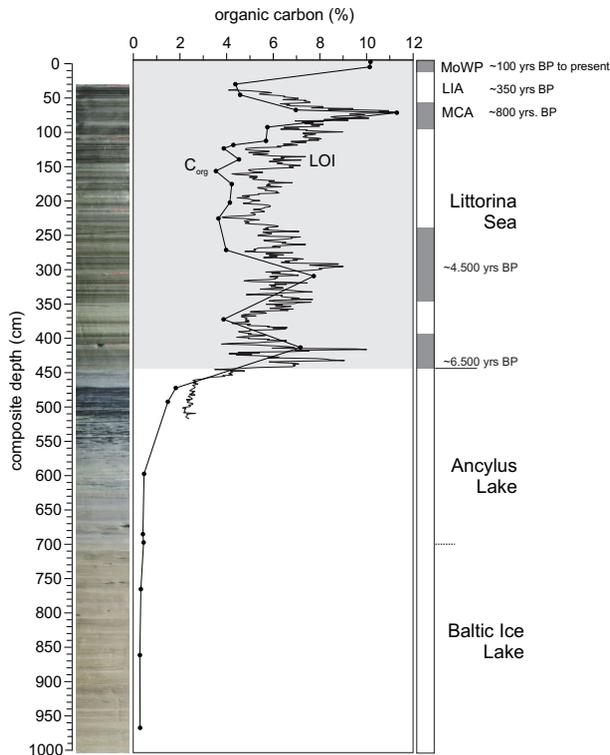
Fig. 2. C_{org} concentrations of the samples used for biomarker analyses in comparison with LOI ("loss-on-ignition") data obtained at higher resolution. Dark grey areas in the column at the right represent sediments with strong lamination and thus pronounced and stable water column stratification during the Littorina Sea stage. Layers in between lacked strong bottom water anoxia, at least for extended periods of time. Ages are inferred from correlations with the master core described in Lougheed et al. (2012). In the Central Baltic Sea, LOI have to be divided by approximately 2.5 to obtain C_{org} abundances (Leipe et al., 2010). LIA = Little Ice Age; MCA = Medieval Climate Anomaly, MoWP = Modern Warm Period.

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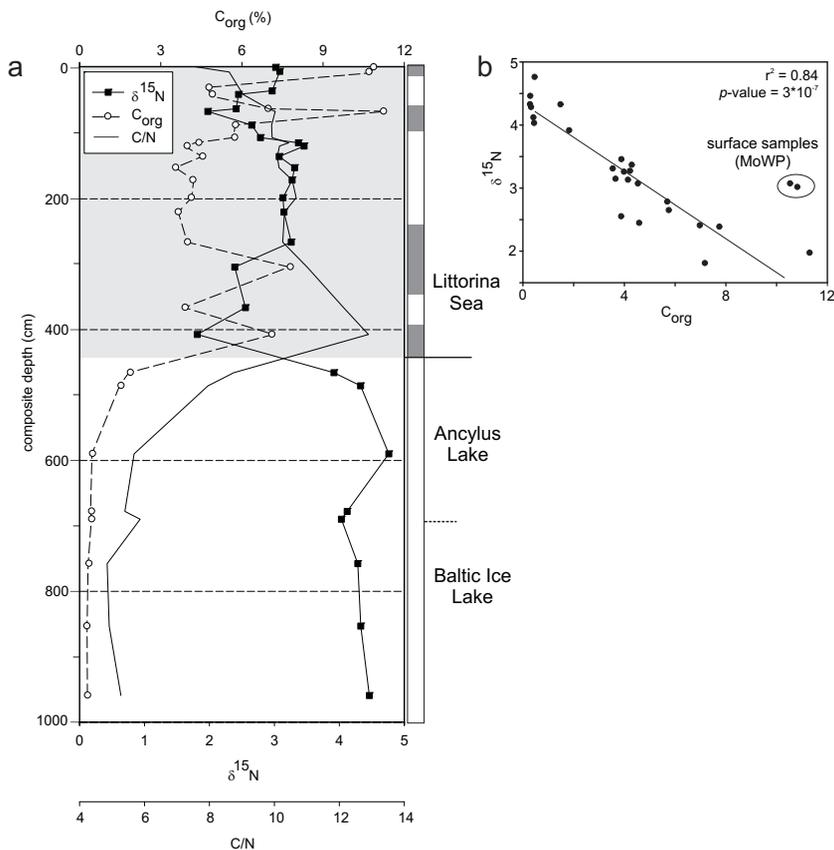
Fig. 3. (a) Concentrations and distributions of bulk geochemical data (C_{org}, $\delta^{15}N$, and C/N). Shaded areas in dark grey mark strongly laminated Littorina Sea sediment layers (see caption of Fig. 2). **(b)** Cross plot of C_{org} with $\delta^{15}N$. Surface samples were excluded from the correlation. MoWP = Modern Warm Period.
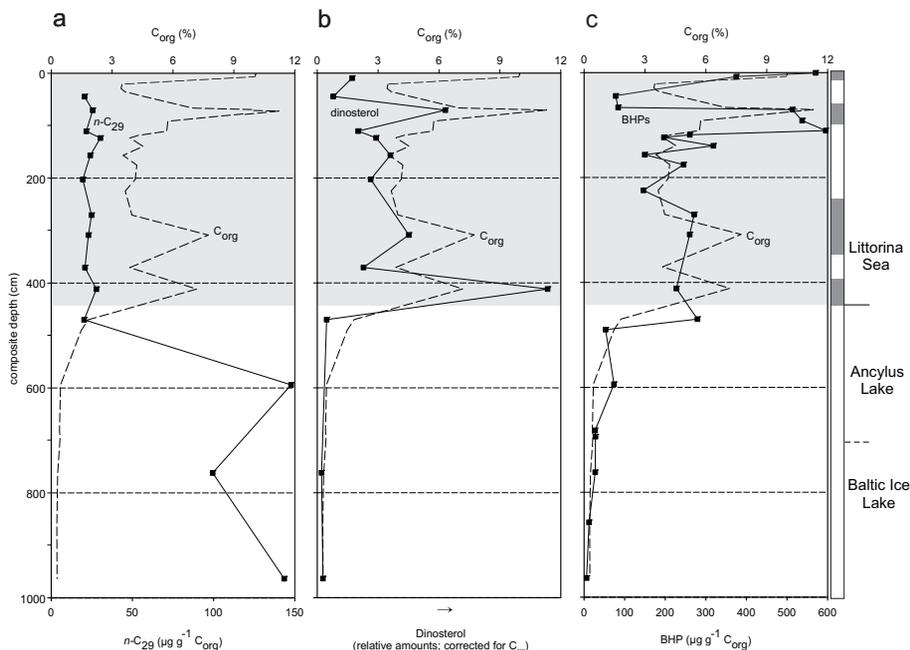
Fig. 4. Selected biomarkers in the Holocene sediments of the Gotland Deep in comparison with C_{org}. **(a)** Nonacosane (nC_{29}), representing higher plant inputs, **(b)** dinosterol ($4\alpha,23,24$-trimethyl-5α-cholest-22E-en-3β-ol), representing dinoflagellate inputs, **(c)** total BHP, representing inputs from hopanoid-producing bacteria. Shaded areas in dark grey mark strongly laminated Littorina Sea sediment layers. BHP concentrations for the surface sediment samples (0–2 and 6–8 cm b.s.f.) were taken from Berndmeyer et al. (2012).
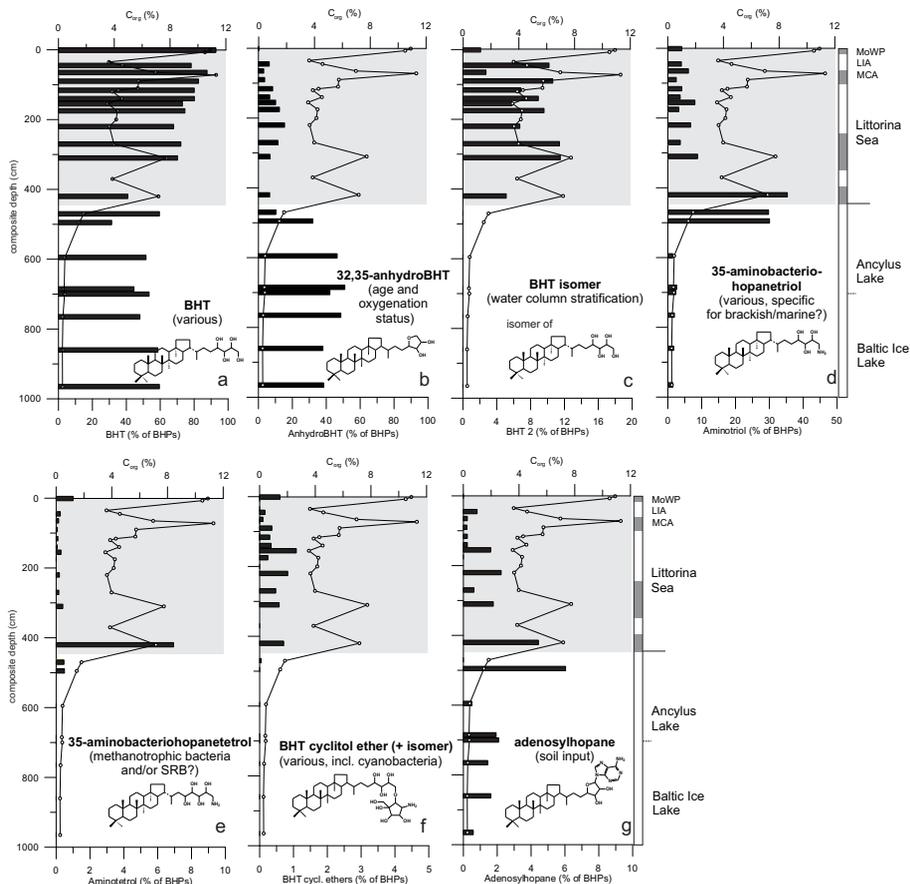
Fig. 5. Distributions of major BHPs. Note different y-axes for individual BHPs; MoWP = Modern Warm Period; LIA = Little Ice Age; MCA = Medieval Climate Optimum. Shaded areas in dark grey mark strongly laminated Littorina Sea sediment layers.

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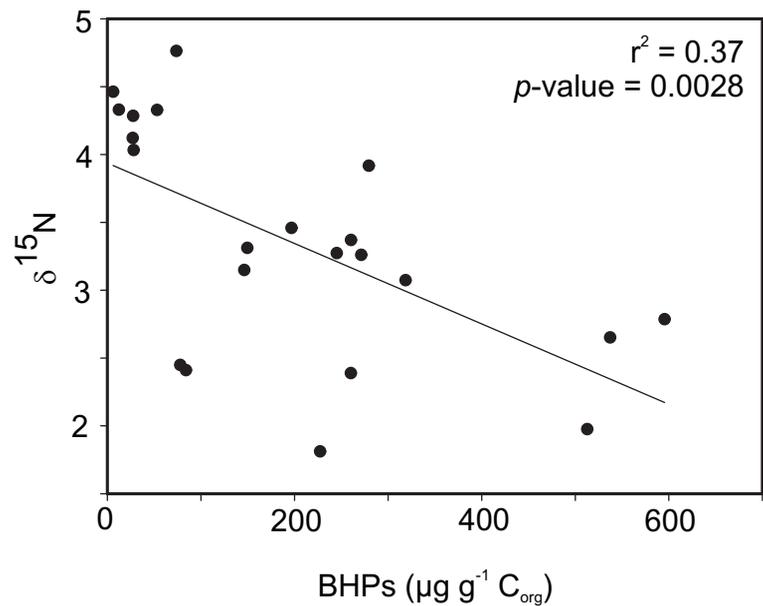
Fig. 6. Cross plot of BHP abundances with bulk $\delta^{15}N$.