Biomarker insights into a methane-enriched Holocene peat-setting from “Doggerland” (central North Sea)

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Abstract
Peats formed widespread early after the Last Glacial Maximum around the coast of the Dogger Bank, the central high of the now flooded “Doggerland” (central North Sea). Here we present biomarker and gas geochemical insights into near-surface peat cored at 43 m water depth. Based on their probable age of ~10 ka before present (BP), the peats are likely part of the so-called basal Holocene peats. Pore waters in the samples document slight methane enrichments in peat layers (up to 250 nM methane vs 60 nM above the peat layer) and δ13C-values of methane ranging between ca. −46‰ and −60‰ PDB. Ethane, propane, and n-butane were also found and may either document upward migration of thermogenic hydrocarbons in the past or, more likely, peat-specific gases, which is indicated by accompanying abundant unsaturated analogs (i.e. ethene and propene). High concentrations of elemental sulfur (up to 19 wt.%) and sulfur-specific transformation products of plant triterpenoids (Des-A-triterpenoids) point to microbial generation during and/or slightly after peat-formation as hydrocarbon source. Biomarkers indicated that peats were formed in a variable environment with high contributions from higher plant wax material. However, a C20 highly branched isoprenoid (HBI) likely records abundant diatoms typical of an oligotrophic lake environment. In addition, all samples contained a suite of bacterial hopanoids and fernenes (hop-17(21)-ene, diploptene, fern-7(8)-ene). A strongly fluctuating methane-flux and/or -turnover during peat formation is recorded in partially high 13C-depletions of <−60‰ PDB of these biomarkers. This underlines the importance of peat layers for methane generation and consumption on “Doggerland” during the Holocene.

Keywords
biomarkers, Doggerland, hopanoids, methane, methanotrophic, North Sea, peat

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Introduction/setting
The Last Glacial Maximum (LGM) represents the last major global glaciation, which caused a drop of sea level by ~130 m when global ice volumes reached their maximum (e.g. Lambeck et al., 2014). The LGM lasted from 27.5 to 23.3 ka BP (Hughes and Gibbard, 2015; Rasmussen et al., 2014) or according to Clark et al. (2009) between 26.5 and 19 ka BP. In the area of the modern central and southern North Sea (cf. Figure 1) this lowered sea level resulted in an emerged landscape, “Doggerland” (e.g. Coles, 1998), which connected the actual British Isles with the European mainland.

With the subsequent main phase of deglaciation after the LGM bracketed between 16.5 and 8.2 ka BP according to Lambeck et al. (2014), global sea level rose continuously. The interplay of these processes lead to a global increase in atmospheric methane from the escape from boreal wetlands (Fischer et al., 2008; Loulergue et al., 2008). The landscape of Doggerland that had since developed from a permafrost dominated glacial foreland into a vegetated area structured by older moraine sediments forming hills, scattered lakes, a river drainage system, and wide peat environments especially along the coastlines, slowly submerged again. The sea approached from both the North and the English Channel in the Southwest causing slowly and continuously the development of bays, peninsulas and islands in the topographic highest areas (“Dogger Island”), today’s “Dogger Bank,” in the central North Sea. A more recent reconstruction of the drowning landscape was given by Sturt et al. (2013).

Since the pioneering work of Jelgersma (1961), the reconstruction of sea level during the Holocene in the North Sea area has been further developed, but is still based on precise dating of so-called basal peats. Formation of these peats started with the rising sea level and subsequently with the rising ground water along the slowly submerging coastlines. Coastal peat formed extensively around local mean high-water level - in the landward-shifting zone (e.g. Hijma and Cohen, 2010; Krüger et al., 2017). Precise dating of peats by the radiocarbon method allowed determination of sea level index points (SIP’s) providing a framework of where and when relative sea level was located. Recent reconstructions of relative sea level development are from Vink et al. (2007) for the German Bight and from Hijma and Cohen (2010)

References
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for the Netherlands and the southern North Sea. For some sea
level reconstructions glacial-isostatic-adjustment models were
applied to compensate for effects of isostatic glacial rebound of
the foreland from the ice masses during the LGM (e.g. Sturt et al.,
2013; Vink et al., 2007).

Apart from their use as SIP’s, basal peat deposits record also
the development of the post glacial environment in the form of
pollen for example. In addition, compositions of biomarker in
peats and compound-specific (stable) carbon isotope signatures
are excellently suited to characterize their depositional environ-
ment (e.g. Pancost et al., 2000). While in the geological transfor-
mation from organic matter toward coals for example, much of
the biomarker information is blurred by chemical and physical modi-
fication reactions, the relatively immature peats still contain the
majority of primary signals. Combined biomarker studies have
therefore contributed crucially to a better understanding of peats
(and peat-derived lignites) from various geological periods in the
Cenozoic, including those covering important environmental per-
turbations like the Paleocene-Eocene Thermal Maximum (PETM;
Elvert et al., 2016; Pancost et al., 2002, 2007; Petersen et al., 2009;
Schouten et al., 2007; Venkatesan et al., 1986; Weijers et al., 2006;
Xie et al., 2000). Beside the higher plant organic matter that is
recorded mostly in mid- and long-chained odd-even predominated
n-alkanes, bacterial biomass is frequently highly abundant and
recorded in structurally different pentacyclic triterpenoids (hopanoi-
d; Dehmer, 1993; Inglis et al., 2018, 2019; Naafs et al., 2018, 2019; Quirk et al., 1984; Venkatesan et al., 1986).

Methanotrophic bacteria appear to play a crucial role for
methane turnover in peats and particularly during geological
times like the PETM. Intense terrestrial methane cycling is dem-
onstrated by relative $^{13}$C-depletions in specific hopanoids (Pan-
cost et al., 2007) and such depletions were highest during the
PETM and the Holocene after the LGM (Inglis et al., 2019).

Analysis of pollen contained in the so-called basal peats from
“Doggerland” demonstrated their origin from variable plant
communities typical for boreal settings (Krüger et al., 2017).
This confirms previous geochemical and microfacies studies of
related coastal lowlands of Northern Germany particularly seek-
ing a better understanding of floral changes (Gerdes et al., 2003;
Köller, 2002). Relatively minor studied is, however, the role
of peats for methane generation and other microbial processes in
the recent North Sea sediments. One recent publication deter-
mined the microbial methane turnover and suggested a relatively
minor role of peat-associated hydrocarbons for methane seepage
in the area (Lippmann et al., 2021).

In this study, five peat samples from three sites were taken
from mini-multicorer and gravity core sampling in the German
sector of the central North Sea. At two of the sites peat samples
from two depths (5 and 10 cm and 10 and 20 cm below seafloor
(cmsbf), respectively) were taken to obtain geochemical insights
into fluctuations during peat-forming and other processes
recorded in these samples. Also sampled and analyzed were the
recent gaseous hydrocarbon composition in peat pore waters and
the overlying bottom sea waters.

**Materials and methods**

Peat, sediment, bottom and pore water samples were taken in the
so-called “Entenschnabel” region of the German EEZ (Figure 1)
close to the border with the Dutch EEZ during cruise MSM98
with RV MARIA S. MERIAN (VARIOSEEP project) in January
2021 (Römer et al., 2021b).

**Sampling and sample preparation**

Sediment cores containing peat-rich intervals were collected dur-
ing four stations at three sites (Table 1). Peat, peat-enriched sedi-
ment, bottom and pore water samples were taken with a
### Table 1. Geochemical data of peat samples from the central North Sea taken at 43 m water depth at the three sites A and C.

| Site | Station | GeoB sample code | LIMS Latitude [N] | Longitude [E] | Sediment depth (cmbsf) | HI (mg HC/g TOC) | 13Corg (‰ PDB) | Sulfur (wt.%) | Tmax (°C) | C23/C31 | F/H | H/C31 | desAT/C31 | δcarb (MSM98) | Other remarks |
|------|---------|------------------|-------------------|---------------|------------------------|----------------|----------------|--------------|-----------|---------|------|-------|-----------|-------------|--------------|
| A    | 39-02   | 24439-02, MIC    | 55°09.1048        | 04°47.9341    | 110                    | 3.6            | −27.4          | 12.1         | 204       | 31.6   | 0.46 | 0.10 | 0.49      | −37.0       |              |
|      | 40-01   | 24440-01, MIC    | 55°09.1301        | 04°47.9389    | 114                    | 3.1            | −28.0          | 19.3         | 183       | 3.6    | 0.5  | 0.41 | 0.41      | −62.8       |              |
|      | 41-01   | 24441-01, MIC    | 55°09.1503        | 04°47.9510    | 117                    | 3.4            | −29.6          | 5.3          | 165       | 2.0    | 0.1  | 0.16 | 0.16      | −38.6       |              |

**LIMS**: BGR lab code number; cmbsf: cm below sea floor; TOC: Total organic carbon; HI: hydrogen index; HC: hydrocarbon; OI: oxygen index; F/H: Fernenes/Hopenes (m/z 191 (hop-17(21)+diploptene)); H/C31:ene (m/z 85 (n-C31)); desAT/C31: des-A-triterpenes (m/z 85 (n-C31)); C20 HBI: highly branched isoprenoids; Dip: diploptene.*Peat sample from different MUC tube or same depth in GC from same site.

**Analysis of bottom water and pore water gas geochemistry**

Concentrations of volatile compounds dissolved in bottom water samples, that were taken with a hose from the MIC liners above the sediment surface, were determined applying a headspace equilibration technique described in detail by Schloemer et al. (2018). Twenty five milliliter of the 122 ml water sample were acidified (poisoned) with 2 ml 37% HCl and stored in the dark at +5°C until processing in the home laboratory. For the compositional analyses of hydrocarbons dissolved in pore waters, sediment samples were collected with a cut-off 3 ml plastic syringe through pre-drilled holes (5 cm distance) in the MIC liners. Sediment samples were transferred into 22 ml glass vials, poisoned with 17 ml of saturated NaCl solution (resulting in a headspace volume of 2 ml) and immediately pierced with a Teflon-coated butyl rubber seal. Analysis of stable carbon isotopic compositions (δ13C) of methane from the peat pore waters could not be realized with samples from the MIC due to insufficient sample volume having remained after compositional analyses. Therefore pore waters from peats sampled in parallel with a GC (station GeoB24443-1) were taken for these investigations. For δ13C-analysis of methane, 3 ml of bulk sediment was collected with cut-off syringes from the GC and transferred into 20 ml glass vials prefilled with 5 ml of 1M NaOH, thereby creating a headspace volume of 12 ml. Subsequently, the glass vials were sealed gastight with butyl rubber stoppers and crimp caps.

With regard to primary scientific goals of the project, the sediment cores were completely processed immediately upon recovery on deck and not subjected to a detailed sedimentological description. In total, five pure peat samples were prepared from the MIC and GC liners and samples were stored frozen until further processing for geochemical and biomarker analyses in the home laboratory.

Bottom water samples were taken from the MIC liners with a flexible silicon tube. The water samples were transferred into 122 ml glass bottles allowing only minor contact with air and water turbulence and avoiding gas bubbling. The samples were acidified (poisoned) with 2 ml 37% HCl and stored in the dark at +5°C until processing in the home laboratory. For the compositional analyses of hydrocarbons dissolved in pore waters, sediment samples were taken with a mini-multicorer (MIC) and a gravity corer (GC; all at ~43 m water depth) and originate from the central North Sea close to salt dome “Britta” (Figure 1 and Table 1). Sampling was achieved in so far unexplained seafloor depressions (see for more details Römer et al., 2021a; Figure 1). Sampling was preferentially done to understand pore water gas geochemistry and geomicrobiology in those areas, and peats were incidentally recovered as well. With regard to primary scientific goals of the project, the sediment cores were completely processed immediately upon recovery on deck and not subjected to a detailed sedimentological description. In total, five pure peat samples were prepared from the MIC and GC liners and samples were stored frozen until further processing for geochemical and biomarker analyses in the home laboratory.

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Sediment samples were not treated other than equilibrating to ambient temperature. The headspace volume of only 2 ml precluded a measurement of the headspace pressure. Therefore, it is reasonable to assume a normal (ambient) pressure of 101 kPa as absolute pressure.

Headspace gas composition was measured on a Trace 1310 gas chromatograph (Thermo Fisher Scientific) with heated valve system and column switching. The system and all included sample loops were evacuated (<0.6 mbar) with a diaphragm pump via several valves. One milliliter of sample was then injected into the sample loops. The individual components were quantified in parallel on three channels.

On channel 1, pre-separation of hydrocarbons (C1 through C6) was performed on a non-polar polysiloxane polymer column (Restek MX-1, 15 m, 0.28 mm ID, film thickness 3 μm). Molecular weight components >C8 were back-flushed. Full separation...
was performed on the downstream installed 50 m Al$_2$O$_3$ capillary column (0.32 mm ID, film thickness 5 μm). Both columns were operated non-isothermally. All components were detected on a Flame Ionization Detector (FID). Carrier gas was He.

On channel 2 and 3 other gas species were determined (i.e. CO$_2$, He, Ne, H$_2$, Ar, O$_2$, N$_2$, CH$_4$, and CO). Because data from channels 2 and 3 are not reported, analytical details are not presented.

The concentrations of methane and of higher hydrocarbons dissolved in the bottom water samples were calculated using the partial pressure derived from fractional concentration and total headspace pressure, temperature of the sample, volume of headspace gas (25 ml), and remaining water (98 ml) applying the Henry’s Law constant of the gases under consideration. A correction for the salting-out effect was applied using a total salinity of 0.59 mol/l and the Setchenov constant for the analyzed components (Masterton and Lee, 1970; Morrison and Billett, 1952).

Calculation of hydrocarbons dissolved in the pore water of the sediment samples is similar, but requires additional corrections. Since the headspace gas was air, the methane concentration measured in the headspace was corrected for the methane concentration in air (1.85 ppm). Subsequently, the corrected dissolved hydrocarbon concentrations were normalized to the true pore water volume in the vial. Given that 3 ml of sediment were introduced to the vial and applying measured depth dependent porosities between 80% and 90% (see Table 2) the gas volume originated from 2.4 to 2.7 ml of pore water. The salting-out effect was calculated using a total salinity of 7 mol/l since a saturated NaCl-solution was added to the sample.

The relative error of the gas chromatographical analysis is around ±3%, and for the total analyses of waters typically ±10%. Due to the additional sources of error for the sediment samples (correction for air-derived methane, pore volume normalization), the overall error of concentrations of hydrocarbons dissolved in pore water is certainly higher, but cannot be accurately stated.

The gas chromatography-isotope ratio mass spectrometry (GC-IRMS) analyses of dissolved methane were performed using about 8 ml of 12 ml headspace of the NaOH treated 3 ml peat samples. Analytical details can be found elsewhere (Stawiarski et al., 2019). Due to the analytical procedure, which was established for (marine) samples with generally high methane concentrations, our data have a significant uncertainty. The peat-associated methane was analyzed from an air headspace, including 1.85 ppm atmospheric methane (δ$^{13}$C of ~−47‰; Ganesan et al., 2018). As total methane concentrations in the headspace were ~4 ppm (data not shown), a significant fraction of the analytes represented atmospheric methane. Assuming an about 40/60 (air methane/ sample methane) relationship, isotopic data were corrected with the atmospheric methane fraction. Uncertainties in the concentration data are, however, high and isotope corrections have thus to be taken with care.

### Peat bulk geochemistry (C/S analyses and Rock-Eval pyrolysis)

Aliquots of dried (40°C for 24 h) sediment and peat samples were crushed and ground. Total organic carbon (TOC), carbonate carbon (C$_{\text{carbon}}$), and sulfur contents were measured separately on a LECO CS-230 (Leco Instrumente, Germany). TOC was determined after decalcification (10% HCl at 80°C; dried at 40°C for 18 h) sample aliquots. Between 10 and 40 mg of each sample was combusted in a high-frequency induction furnace in an oxygen atmosphere and concentrations were determined by use of the absorption signal at the IR detector. The instrument was calibrated using commercially available standards (LECO). Reproducibility of the measurements was ±0.02%.

Rock-Eval pyrolysis was performed on a Rock-Eval 6 analyzer using a standard program described earlier (Espitalié et al., 1977; Lafargue et al., 1998): isothermal start at 300°C for 3 min, then applying a heating rate of 25°C/min up to 650°C. Initial sample weights were ~15 mg to prevent oversaturation of the FID. Hydrocarbons released isothermally at 300°C are presented as “S1” and those released between 300°C and 650°C as “S2” yields. CO$_2$ released up to 400°C is presented as “S3.” Reproducibility of the hydrocarbons and CO$_2$ determination was better than 5%. TOC-δ$^{13}$C values of the peats were determined after decalcification with HCl with an elemental analyzer coupled with a Thermo Delta V advantage IRMS.

### Biomarker compositions and compound-specific stable carbon isotopic compositions (δ$^{13}$C)

Organic compounds were extracted three times from 3 g of the ground peat samples using a 10 ml mixture of dichloromethane-methanol (DCM:MeOH, 8:2; v:v) for 15 min in an ultrasonic bath. The triplicate extracts were combined and dried under a gentle N$_2$ stream at 40°C. Elemental sulfur was subsequently removed from the extract diluted in DCM by treatment with activated (10% HCl at 60°C for ~1 h) granulated copper, before they were dried and weighed. The extracts were fractionated on chromatographic columns filled with activated silica gel (240°C for 12 h) into aliphatic, aromatic, and polar fractions using isohexane, isohexene/DCM (2:1; v:v), and DCM/methanol (2:1; v:v) as solvents, respectively. All fractions were dried under a N$_2$ stream and weighed. The distribution of compounds contained in the aliphatic fractions was determined by gas chromatograph-FID/mass.

| Site | Station no. | GeoB sample code, Tool | Type of sample | Depth | Methane (nM) | Ethane (nM) | Ethene (nM) | Propane (nM) | Propene (nM) | n-Butane (nM) | C$_1$/C$_2$ |
|------|-------------|------------------------|---------------|-------|--------------|-------------|-------------|--------------|--------------|---------------|-------------|
| A    | 39-02       | 24439-02, MIC          | Bottom water 1| −1–10 cmasf | 2.3          | nd          | nd          | nd           | nd           | nd            | 0.32       |
|      |             | 24439-02, MIC          | Bottom water 2| −1–10 cmasf | 1.7          | 0.1         | 0.1         | nd           | nd           | nd            | 20.6        |
|      |             | 24439-02, MIC          | Sediment or peat pore water | 2 cmbsf | 58.2         | 4.6         | 21.5        | 2.9          | 10.1         | 12.7         |
|      |             |                        |               | 7 cmbsf | 120.6        | 6.5         | 35.8        | 4.3          | 10.6         | 18.6         |
|      |             |                        |               | 12 cmbsf (peat layer) | 252.9       | 31.7        | 14.5        | 42.8         | 6.8          | 6.9          | 8.0         |
| B    | 40-01       | 24440-01, MIC          | Bottom water | −1–10 cmasf | 1.3          | nd          | nd          | nd           | nd           | nd            | 0.32       |
|      |             | 24440-01, MIC          | Sediment or peat pore water | 5 cmbsf (peat layer) | 98.7        | 21.8        | 3.4         | 25.3         | 3.9          | 4.5          | 4.5         |
| C    | 41-01       | 24441-01, MIC          | Bottom water 1| −1–10 cmasf | 1.4          | 0.08        | nd          | nd           | nd           | nd            | 0.32       |
|      |             | 24441-01, MIC          | Bottom water 2| −1–10 cmasf | 1.5          | 0.05        | nd          | nd           | nd           | nd            | 0.32       |
|      |             | 24441-01, MIC          | Sediment or peat pore water | 5 cmbsf (peat layer) | 155.5       | 27.5        | 10.2        | 33.4         | 10.4         | 5.6          | 5.7         |

cmasf: cm above sea floor; cmbsf: cm below sea floor; nd: not detected.
Tmax (Table 1). TOC showed a relatively slightly elevated hydrogen index (HI) and expected (peat maturity stage; Table 1). Sample 41-01 from Site −29.6‰ PDB.

δsamples from GC station no. GeoB24443-1 were available for ever, six larger gas samples (with 12 ml air headspace) from peatogen and T max values demonstrated that they are immature as analysis (tography-columns (e.g. Elvert et al., 2016). Stable carbon isotope measurements were carried out in full scan mode. Compounds were identified by comparison of mass spectra, retention times, and measurement of standard compounds (e.g. hop-17(21)-ene, hop-22(29)-ene, neo hop-13(18)-ene). Retention times of hopenes on the DB-1 column was slightly different than on other gas chromatography-columns (e.g. Elvert et al., 2016). Stable carbon isotope analysis (δ13C) of aliphatic compounds was made via gas chromatograph-C-IRMS using a coupled Trace GC Ultra, ConFlow IV, and a Delta V Advantage IRMS (all Thermo Fisher Scientific).

The gas chromatograph was equipped with a split/splitless inlet and a DB-1 column (Agilent; 30 m, length; 0.25 mm, inner diameter; 0.25 μm film thickness) coupled to the IRMS via a Combustion III interface (Thermo Fisher Scientific). Measurements were carried out in duplicate. Accuracy of the analysis was checked by replicate measurements of an n-alkane standard mixture (Mix B; Arndt Schimmelmann, Indiana) of known stable carbon isotopic ratios.

Results

Bulk geochemistry
Table 1 shows bulk geochemical and compound-specific data of the five peat samples. With the exception of the peat sample from Site C (41-01; 17.2 wt.% TOC) all samples shared TOC >30 wt.%. Sulfur was abundant in all samples (5–19 wt.%). Rock-Eval pyrolysis confirmed that samples were composed of Type III kerogen and Tmax values demonstrated that they are immature as expected (peat maturity stage; Table 1). Sample 41-01 from Site C showed a relatively slightly elevated hydrogen index (HI) and Tmax values (Table 1). TOC δ13C values ranged between −27.4‰ and −29.6‰ PDB.

Dissolved hydrocarbons in peat and sediment pore and bottom waters

Bottom waters overlying peat-rich sediments had concentrations of dissolved methane of ~2 nM. Within the sediment and peat, dissolved methane was found to be elevated compared to bottom waters and, where samples from different depths were retrieved, concentrations increased with sediment depth toward the peat layer at the bottom of the cores (Figure 2 and Table 2). Calculated concentrations of dissolved hydrocarbons were found to be highest in the peat layer. At Site A (Figure 1), changes in the sediment with depth could be studied in detail: In the peat layer, methane concentrations were ~250 nM and ethane, ethene, propane, propene, and n-butane were also observed (Figure 2). Compositions of hydrocarbons differed between all samples and highest abundances of C17+ hydrocarbons were found in the peat samples (Table 2).

Concentrations of methane in the headspaces of the studied samples were generally too low after compositional analyses for reliable δ13C analyses with the analytical setup available. However, six larger gas samples (with 12 ml air headspace) from peat samples from GC station no. GeoB24443-1 were available for δ13C of methane determinations of peat-related pore waters. δ13C values of the methane were ~−46‰ (five samples) to ~−60‰ PDB (one sample).

Composition of aliphatic biomarkers and carbon isotopic signatures
The aliphatic extract fractions were dominated by long chained n-alkanes with a strong odd-even predominance. The patterns of these plant-derived biomarkers were similar in all samples (Figure 4). Sample 41-01 from Site C and sample 39-02 from Site A (in much lower concentrations) contained a highly branched isoprenoidal hydrocarbon (HBI) with 20 carbon atoms (Figure 4). This component showed the same mass spectral characteristics as 2,6,10-trimethyl-7-(3-methylbutyl)-dodecane (C20 HBI; Yon et al., 1982), which is assumed to originate from freshwater diatoms (Muschitiello et al., 2015 and references therein). Other important aliphatic compounds were a series of des-A-triterpenes (with abundant m/z 326 and 328 ions; Figure 5; Huang et al., 2008; Regnery et al., 2013). Highest abundances of these components (relative to n-C17 alkane) were found at Site A (Table 1). Furthermore, we tentatively identified β-sitoster-2-ene (Oros and Simonetti, 2000), hopanes and hopenes as well as a suite of less concentrated fernenes (Figure 5). Ion chromatograms with m/z 243 were used to highlight fernenes. The mass spectrum of the major fernene was found to be similar to fern-7(8)-ene (Howard et al., 1984) a compound present in different aquatic sedimentary settings (see Brascell et al., 1981; Nytoft and Larsen, 2001 and references therein).

δ13C values of aliphatic biomarkers, such as n-C17, or the mean of n-C17, n-C20, and n-C22 generally ranged between ~25‰ and ~35‰ PDB (Figure 6). The highest (i.e. less negative) value was determined for the C20 HBI. Relatively low δ13C values were found for hopanes and fernenes in some of the samples, with the two samples from Site B demonstrating the most negative values (e.g. diploptene (hop-22(29)-ene) with ~62.8‰; Table 1). The tentatively identified fern-7(8)-ene and other fernenes (co-eluting with the n-C17 alkane) were also depleted in 13C (Figure 6). A relationship between the relative abundance of hopanes (vs n-C17 alkane; H/C17 in Table 1) and negativity of isotopic compositions of diolopetine during the different samples was not found.
**Discussion**

Rising temperatures during the early Holocene caused the melting of ice sheets and rise of sea level and of groundwater along the coastlines. This also caused flooding of the former “Doggerland” in the today’s central North Sea. During this interval peats were widely formed within coastal fens and the hydrological and climatological change is recorded in peats and surrounding sediments. Peats used for this study were not dated, but they were deposited between close-by 14C-dated shallow basal peat layers (samples “Dogger Bank” = Elbe palaeovalley (NY)) from Vink et al. (2007) and presumably formed at a similar age interval. Such peats were dated between 9.7 cal. ka BP (“Dogger Bank”) and 10.9–9.2 cal. ka BP (“Elbe palaeovalley (NY)”). Peats in the vicinity had similar ages and ages of the basal peats decreased toward the German coast (Vink et al., 2007). A peat sample (“RE29”; GPDN, 2013) that was taken even closer to our samples confirms that our studied peats have approximate ages of 10 cal. ka BP.

**Modern biogeochemical processes in peat-rich sediments in the central North Sea**

Recent peats host various microbial groups and this holds also for buried submarine peats like those in the North Sea, which also host microorganisms executing methane formation and oxidation (Lippmann et al., 2021). However, bottom water directly overlying the peat-containing sites, which are located a few hundreds of meters NNE of the salt dome “Britta” that were investigated in this study, was relatively poor in dissolved methane. Small amounts of ethane (and ethene; and no C2+ hydrocarbons) were also observed in one out of the two bottom water samples at station 39-02 taken near “Britta”. The relatively low methane concentrations in the bottom water – during summer 2019 concentrations were found ~10 times higher (Römer et al., 2021a) – can be best explained by a high-turbulence winter effect. During winter season a thermocline, which typically prevents methane discharging from methane-laden sedimentary pore waters into shallow water layers, is not developed. Indeed, pore waters in shallow sediments were enriched in dissolved methane compared to bottom waters (2 mM CH4) overlying the sediments. For instance, at Site A (station 39-02) CH4 concentrations were ~60 nM at 2 cmbsf and increased with depth up to ~250 nM in the peat layer at 12 cmbsf (Figure 2 and Table 2). However, methane concentrations are not elevated in comparison with marine sediments elsewhere and also with other sediments in the central North Sea. Lippmann et al. (2021) reported average CH4 concentrations of sediment pore waters of 2.1 μM at ~2 to 5 mbsf. Irrespective of the different sampling depths applied in the two studies, this difference in methane concentrations suggests that methane in the region NNE of the salt dome “Britta” is not much enriched compared to the situation in the broader area. However, CH4 concentrations in peat pore waters investigated in this study are higher than those at similar sediment depths in background cores collected 4 km SSW and 13 km NE to the sites studied herein (e.g. for core MSM98 48-01 (S5°06′46.84″N; 04°46′49.836″E) and core MSM98 49-01 (S5°15′53.19″N; 04°56′19.44″E) we observed ~10–30 nM CH4 for both cores), which were virtually devoid of peats and showed much lower TOC contents (0.1–0.2 wt.%, not shown).

In addition to the methane enrichments, higher hydrocarbons (C2–C4), although in very low concentrations, were also observed in our peat samples (Table 2). This holds particularly for ethane (and ethene). Higher hydrocarbons were also found in sediment samples overlying peat layers, but the relative abundance of methane to ethane increased slightly with decreasing depth and also concentrations differed between samples with the lowest in the bottom waters (Table 2). Because of those differences the presence of an actively gas seeping system underlying the study sites is unlikely, as this would likely lead to more uniform hydrocarbon concentrations and compositions. Further, a simple two endmember mixing (bottom waters versus pore waters from peat) cannot explain the hydrocarbon composition in the shallow sediments in between, for example, at 2 and 7 cmbsf (Station A; Figure 2). Classical thermogenic hydrocarbon formation in the peat can be excluded, because of the low thermal maturity (see Tmax in Table 1) and their depositional history including permanent shallow burial depth in relatively shallow waters. On the other hand, the hydrocarbon composition in the peat is different to what is expected in normal marine sediments as light hydrocarbons in shallow marine sediments are commonly nearly entirely composed of biogenic methane (with C1/C2 ratios >1000; e.g. Bernard et al., 1977). Unfortunately, concentrations of methane in the distinct sediment and pore water samples used for this study, which remained after compositional analyses, were too low for analyses of stable C and H isotopes. However, methane in the headspaces overlying peat samples, which were taken for other analyses during MSM98, allowed for an assessment of methane’s gas geochemical characteristics in peats sampled with a GC (station GeoB 24443-1; no further gas data available) at the same position as station A. It is therefore likely that peats in the GC and those at 12 cmbsf at station A (Table 1 and Figure 2) represent the same peat layer. However, δ13C-CH4 values ranging from ~−46‰ to ~−60‰ PDB, with the most negative value being observed in the shallowest peat sample (data not shown), points at an inconclusive origin. It can either be explained by a mixed thermogenic/biogenic, by a degraded biogenic source (Whiticar, 1999), by a (not-well understood) low-temperature thermal gas generation (Rowe and Muehlenbachs, 1999), or by a biogenic methane specific to (boreal) peats. Indeed, biogenic methane from boreal wetlands is obviously less depleted in 13C (~−53‰ to −71‰; Ganeshan et al., 2018) than methane from strictly marine sediments (Whiticar et al., 1986). Biogenic higher hydrocarbons, particularly ethane, were occasionally observed in marine sediments (Bernard et al., 2013; Hinrichs et al., 2006; Oremland et al., 1988; Pape et al., 2020; Xie et al., 2013), but the relative abundance of methane to ethane (C1/C2: ~5–20; Table 2) was much higher than the ratio which we observed in the peat samples from close to the salt dome “Britta” (C1/C2: ~5–20; Table 2). A normal, widespread marine microbial source is, however, unlikely to be the exclusive origin of the light hydrocarbons, which is also supported by the occurrences of propane for example. As pointed out, it is unlikely that the studied sediment column is currently charged with thermogenic gas even though it cannot be excluded from the geochemical data that part of the gas stems from an underlying oil-mature source rocks (e.g. the Kimmeridge clay; Müller et al., 2020). Another option would be that the gas was desorbed from charcoal, which is known to occur in basal peats at “Doggerland” (Krüger et al., 2017). We consider this process unlikely as well, because adsorption is commonly too strong to release gases by the methane desorption method applied in this study (exclusive addition of NaCl-saturated water; see method section). The occurrence of unsaturated light hydrocarbons (Table 2) additionally conflicts with a thermogenic origin. Ethene and propane are relatively abundant in our samples and are (biogenic) microbial precursors of ethane and propane, which often co-occur in sediments (Bernard et al., 2013; Kvenvolden and Redden, 1980; Kvenvolden et al., 1981; Vogel et al., 1982). The underlying microbial processes are still insufficiently understood, but ethene to methane conversion has been shown for methanogenic cultures (Xie et al., 2013).

In conclusion, the partly slightly negative δ13C values of methane (as low as ~−60‰), the co-occurrence of low molecular weight hydrocarbons with their unsaturated analogs and their enrichment in the peat layers make an origin of the hydrocarbons from the peat or peat-influenced microbial turnover most likely. The
presence of saturated/unsaturated hydrocarbon doublets in recent peats (from Pennsylvania) was previously shown (Kim, 1978) and support this interpretation.

The peat-forming environment on “Doggerland”

Four of the five peat-rich sediments jointly demonstrated relatively low HI (~150–190 mg HC/g TOC) and high OI (~110–130 mg CO₂/g TOC) values (Figure 3 and Table 1). The general narrow ranges of the HI and OI values indicate that the samples were formed in comparable terrestrial settings, which are generally characterised by Type III organic matter. However, the only patchy recovery of generally small peat samples (of few centimeters thickness) does not allow studying chronological changes on “Doggerland” in this study in detail. It, however, presents geochemical snapshots from three spatially related sites.

The peat sample from Site C (sample 41-01) had a slightly higher HI value (258 mg HC/g TOC), which corresponds to a higher Tmax value (and the relatively lowest TOC content; Table 1). As maturities of all samples are likely similar, this may be an indication of slight local differences in the paleosetting and, thus, composition of the kerogen.

All peats contain significant amounts of sulfur maximizing at ~19 wt.% (sample 40-01 from Site A) and recent microbial sulfate reduction can be excluded as driver for the sulfur formation. This is evident from the recent relatively low sulfate reduction rates (Martin Krüger; personal communication) and from the fact that peat-surrounding sediments were relatively poor in sulfur (<0.1 wt.% S; not shown). Holocene peats from lake settings in NW Germany and also from coastal environments, all in NW-Germany, were described to be partly highly enriched in (pyrite-bound) sulfur (Dellwig et al., 1998; Gerdes et al., 2003; Regnery et al., 2013). This characteristic is explained by effective sulfate-reduction after flooding of peats in the lagoon-like settings and release of H₂S, followed by the precipitation of pyrite from the H₂S and Fe, the latter being transported via rivers from the Hinterland (Dellwig et al., 2001). It is likely that the peats from “Doggerland” experienced a similar geochemical history and that the high sulfur contents are an indicator of the flooding with sea water in the aftermath of postglacial peat formation.

Indications for a changeable environment on a small spatial scale

Distributions of hydrocarbon biomarkers in companion with compound-specific stable carbon isotope signatures excellently record major peat-forming plants and related microbial processes. In accordance with other studies, we found evidence for a spatially variable boreal setting, which fostered the growth of peat-forming and other higher plants during the Late Glacial and Early Holocene as has been documented by pollen (Krüger et al., 2017) and n-alkane distributions (Gerdes et al., 2003). The majority of compounds in the aliphatic fractions of the so far unstudied Doggerland peats originated from higher plant waxes, which is documented by odd-even-predominated n-alkanes, abundant sitosterene and plant triterpenoids (Figures 4 and 5).

n-Alkane distributions were relatively uniform in all studied peats and maximize at n-C₂₇ and n-C₂₉ (Figure 4), indicating relatively similar main vegetation types in all samples. n-C₂₅, which is occasionally taken as biomarker for the contribution of the peat
bog forming *Sphagnum* species (Baas et al., 2000; Nott et al., 2000), was also found in abundance. The $n$-$C_{29}/n$-$C_{31}$ ratio may therefore record *Sphagnum* contributions to the studied organic matter, but differences in the ratio in our sample set are relatively small (Table 1) compared to other sites (Nott et al., 2000). Plant triterpenoids are represented by a series of des-A-triterpenes, which hint at a formation from terrestrial plant triterpenoids, mediated by microbial turnover in an anoxic setting (Huang et al., 2008). Such structural modifications were observed in sulfur-rich Holocene lake settings (Regnery et al., 2013) tentatively similar to those studied herein. Des-A-triterpenoids were relatively abundant at Site A (Table 1). Indeed and although a weak indicator only, highest hopane/$n$-$C_{31}$ ratios (0.27 and 0.52) suggest that bacterial turnover during peat formation might have been highest at this site. Whether the differences in des-A-triterpenoid/$n$-$C_{31}$ ratios between the two sampling depths at Site A (10–12 cmbsf: 0.71; 20 cmbsf: 0.36) is a record of varying microbial turnover or of changes in the vegetation cannot be verified by our relatively coarse biomarker study.

Bacterial hopanes and hopanoids are another important class of lipids, which are present in peats from “Doggerland” (Figure 5). While the suite of compounds with the predominating trisnorp-hop-17(21)-ene, hop-17(21)-ene and diploptene (hop-22(29)-ene) was found in all samples, relative abundances slightly differ between the samples. Fernenes of which fern-7(8)-ene was tentatively identified as major compound of the fernene compound class. Fernenes are structurally related to hopanes, are widespread in certain bacterial groups (e.g. Howard et al., 1984), and were occasionally reported from microbially influenced environmental settings (Brassell et al., 1981; Nytoft and Larsen, 2001). The very low recent methane concentrations, the stable carbon isotopic composition of methane in the recent pore waters, and the high concentrations of hopanes and fernenes in the peats, however, strongly argue against recent methanotrophy as source for these compounds. Bacterial hopanoids present in the peats are, thus, likely and among other bacteria produced by aerobic bacteria involved in the methane turnover during peat formation. Peats are settings in which methanogenesis as well as (aerobic) methanotrophy are important processes. The latter process, and the magnitude of methanotrophy and/or water table fluctuations (Huang et al., 2018) during the time of peat formation, is recorded in the stable carbon isotope signature of hopanes (Pancost et al., 2002). We observed strongly varying δ$^{13}$C values of hopanes minimizing at $\sim-63‰$ at Site B (Figure 6). Relative depletions in $^{13}$C were also found for other hopanes and the tentative fern-7(8)-ene (as negative as $-58‰$) demonstrating the role of their bacterial source organisms in the methane turnover. As demonstrated by strongest relative depletions in $^{13}$C, methanotrophic biomass is particularly abundant at Site B. Nevertheless, bacterial compounds were also slightly depleted in $^{13}$C at the other sites.

Interestingly, the isotopic composition of individual compounds at the different sites differed, whereas distributions were relatively similar. This indicates variable settings with physiologically flexible bacterial compositions responding on fluctuating methane flux and/or other factors like water table changes (Zhang et al., 2022). The calculated δ$\delta$ between hopanes (diploptene) and plant wax alkanes of $\sim30‰$ is at the lower end of other Middle-to-Early Holocene and Late Glacial peats in a global data set (Inglis

**Figure 5.** Detailed view of biomarkers extracted from sample 39-02 MIC from Site A, shown as total ion current (TIC, top) and by selected ions to highlight crucial components. *Identified by the mass spectrum from Howard et al. (1984) and the elution order published in Nytoft and Larsen (2001). Hop-17(21)-ene and diploptene were identified by comparisons with mass spectra and co-elution with authentic standards.
was a possible source organism of the C20 HBI at Site C (and in
Hepp et al., 2019), it is plausible to assume that
G. acuminatum (Muschitiello et al., 2015). Because this freshwater diatom was
originate from the freshwater diatom Gomphonema acuminatum,
ever, described from different Holocene lake settings (Aichner
studied five peat samples, their distance to each other was ~100 m
traces also in the upper sample from Site A; Table 1). As we only
lakes, and a brackish/marine overprint. Further work aiming at
of the deposition setting, which was controlled by peat-forming
plants, bacterial methane-turnover, development of freshwater
HI values argues for contributions from aquatic algae/bacteria to
the bulk organic matter. Indeed, a likely and for peat-settings
uncommon diatom-stemming highly branched isoprenoid (C20
HBI) was found in abundances that are similar to plant waxes
1995). The C20 HBI tentatively identified in this study was, how-
the bulk organic matter. Indeed, a likely and for peat-settings
uncommon diatom-stemming highly branched isoprenoid (C20
HBI) was found in abundances that are similar to plant waxes
(Figure 4). This compound was first ascribed to green algae
(Rowlant et al., 1985) and to cyanobacterial mats (Kenig et al.,
1995). The C20 HBI tentatively identified in this study was, how-
ever, described from different Holocene lake settings (Aichner
et al., 2010; Elvett et al., 2016). Recently it was suggested that
it originate from the freshwater diatom Gomphonema acuminatum,
and that high abundances reflect summer oligotrophic conditions
(Musciitiello et al., 2015). Because this freshwater diatom was
also described for the wider Holocene North Sea environment
(Hepp et al., 2019), it is plausible to assume that G. acuminatum
was a possible source organism of the C20 HBI at Site C (and in
traces also in the upper sample from Site A; Table 1). As we only
studied five peat samples, their distance to each other was ~100 m
only, and precise dating of the samples was not possible, future
studies are required to prove this relationship.

Nevertheless, our biomarker data demonstrate the variability of
the deposition setting, which was controlled by peat-forming
plants, bacterial methane-turnover, development of freshwater
lakes, and a brackish/marine overprint. Further work aiming at
extending the knowledge from our snapshot analyses and, thus,
a more detailed understanding of methane turnover in peats from
“Doggerland” should also involve polar lipid constituents, a
robust time resolution and may be accompanied by palyno-
morph data.

Conclusion
Peats were an integral part at “Doggerland” and other coastal areas
in the today’s central North Sea deposited during the Holocene
(after the Last Glacial Maximum). For the first time, biomarkers
contained in peats cored at three sites in the German Exclusive
Economic zone at ~43 m water depth were studied. Relatively high
sulfur concentrations (up to 19 wt.%) along with biomarkers spe-
cific for sulfur-driven transformation processes typify peat bulk
geochemistry and document extensive past marine sulfate reduc-
tion after flooding caused by sea-level rise. Biomarker analyses
record peat-forming plants, freshwater diatoms, and particularly
bacterial methanotrophic turnover (e.g. by 13C-depleted hopenes
and fernenes) during deposition at times, when boreal wetlands
extended, global atmospheric methane concentrations were rela-
tively high and methane became progressively 13C-depleted
(Fischer et al., 2008; Louligue et al., 2008).

Concentrations of dissolved methane in the sediment pore
waters were generally low, but slightly enriched in the peats
(~250 nM). Methane was accompanied by ethane, ethene, pro-
pane, and propene, which are most likely originate from micro-
bial/diagenetic processes as well. The exact source and the role of
peats for hydrocarbon concentrations in the water column overly-
ing peat-rich settings remains a topic for further studies in the
North Sea or at other peat-rich flooded settings.

While further investigations should focus on the changes dur-
ing geological times in more detail, our study presents novel
organic geochemical snapshots into the former methane cycle
during Holocene peat formation in the today’s North Sea.

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