

1 **Seasonal methane accumulation and release from a gas emission site in the central North Sea**

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13

14 **Abstract**

15 We investigated dissolved methane distributions along a 6 km transect crossing active seep sites at
16 40 m water depth in the central North Sea under conditions of thermal stratification in summer (July
17 2013) and homogenous water column in winter (January 2014). Dissolved methane accumulated
18 below the seasonal thermocline in summer with a median concentration of 390 nM, whereas during
19 winter, methane concentrations were typically much lower (median concentration of 22 nM). High
20 resolution methane analysis using an underwater mass-spectrometer confirmed our summer results
21 and were used to document prevailing stratification over the tidal cycle. We contrast estimates of
22 methane oxidation rates (from 0.10 to 3.99 nM day⁻¹) using the traditional approach scaled to
23 methane concentrations with microbial turnover time values, and suggest that the scaling to
24 concentration may obscure the ecosystem microbial activity when comparing systems with different
25 methane concentrations. Our measured and averaged rate constants (k') were on the order of 0.01
26 day⁻¹, equivalent to a turnover time of 100 days even when summer stratification leads to enhanced
27 methane concentrations in the bottom water. Consistent with these observations, we could not
28 detect known methanotrophs and *pmoA*-genes in water samples collected during both seasons.
29 Estimated methane fluxes indicate that horizontal transport is the dominant process dispersing the
30 methane plume. During periods of high wind speed (winter), more methane is lost to the
31 atmosphere than oxidized in the water. Microbial oxidation seems of minor importance throughout
32 the year.

33

34 **1 Introduction**

35 Methane is, after water vapor and CO₂, the most important greenhouse gas. Its concentration has
36 increased by a factor of 2.5 since preindustrial times, from 722 ppb in 1750 to 1800 ppb in 2011
37 (IPCC, 2013). The total global emission was estimated to be ~550 Tg (methane) yr⁻¹ with an
38 anthropogenic contribution of 50 to 65%. Geological sources, which were not considered in IPCC
39 reports previously, are suggested to account for up to 30% of total emissions. These include
40 anthropogenic emissions related to leaks in the fossil fuel industry as well as natural geological seeps
41 both terrestrial and marine (IPCC, 2013). An improved emission estimate from marine seeps suggests
42 that these sources contribute ~20 Tg methane yr⁻¹, i.e., 4% of the global emissions, to the
43 atmospheric methane (Etiope et al., 2008).

44

45 In general, oceans are a minor source of methane to the atmosphere, accounting for 2-10% of the
46 global emissions (Bange et al., 1994). The main oceanic source (75%) is thought to originate from
47 estuaries, shelf and coastal areas (Bange, 2006; Bange et al., 1994). The European coastal areas were
48 found to emit 0.46-1 Tg yr⁻¹, but this value may underestimate the coastal input, since fluxes from
49 estuaries and shallow seeps have not been adequately represented (Bange, 2006).

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51 Although continental margins account for only 10% of total ocean area and 20% of total ocean
52 primary production (Killops and Killops, 1993), more than 90% of all organic carbon burial occurs in
53 sediments deposits on deltas, continental shelves, and upper continental slopes (Bernier, 1989). At
54 these locations, which are also characterized by high sedimentation rates, organic carbon is rapidly
55 buried beneath the sulfate reduction zone and becomes available to methanogens (e.g. Cicerone and
56 Oremland, 1988). Methane is also generated by thermal breakdown at high temperature and
57 pressure. A significant fraction of the methane is oxidized in anaerobic and aerobic sediments (e.g.
58 Boetius et al., 2000; Jørgensen and Kasten, 2006; King, 1992; Niewöhner et al., 1998). At cold seep
59 sites, methane escaping microbial oxidation may be transported into the overlying water either
60 dissolved in upwardly advecting pore waters or in case of oversaturation, in the form of gas bubbles.
61 Because methane is undersaturated in seawater, rising methane bubbles partially dissolve during
62 ascent through the water column (McGinnis et al., 2006), where the dissolved methane may be
63 further consumed by microbial oxidation. Only if this methane survives transport to the mixed layer,
64 it may be transferred to the atmosphere.

65

66 Because of processes consuming methane in the water column, shallow seeps are more likely to
67 contribute to the atmospheric methane pool. However, even at shallow sites, density stratification
68 may limit vertical transport. For example, at the 70 m deep Tommeliten area in the North Sea, a
69 summer thermocline constrains methane transport to the atmosphere, such that during this season

70 less than ~4% of the gas initially released at the seafloor reaches the mixed layer (Schneider von
71 Deimling et al., 2011). Here we examine the seasonal cycle of methane in the North Sea by chemical
72 and microbiological analyses of water samples collected in a region of shallow seepage during
73 summer (July 2013) and winter (January 2014). For the case of expected seasonal stratification; we
74 further consider whether the methane trapped in bottom waters is significantly consumed by
75 microbial oxidation during summer, thus limiting the fraction that can be released at the onset of
76 storm events in fall.

77

78 1.1 Study Site

79 The study site is situated in an area of active gas venting above a shallow gas reservoir in the central
80 North Sea south of Dogger Bank, a sandbank that is 20 m shallower than the surrounding (Fig. 1). The
81 gas vents are located in the Netherlands sector, license block B13 in a shallow (< 45 m) and flat
82 region that lacks any morphological expression typical of seep structures (Schroot et al., 2005). The
83 seeps are likely sourced from a biogenic methane reservoir ($\delta^{13}\text{C}$ values of -80‰ VPDB) of Pliocene to
84 Pleistocene age, which lies 600-700 m below the seafloor. Patches of gas saturated sediments
85 between the gas reservoir and the seafloor have been imaged in seismic surveys. These data, plus
86 observations of discreet bubble streams in the water column and rapidly decreasing methane
87 concentrations in cores with distance from the vent site, led Schroot et al. (2005) to describe our
88 study area as a leaking gas reservoir with laterally discontinuous seepage.

89

90 In this region, water masses from the north (Atlantic Water) and south (Straits of Dover) meet
91 (Kröncke and Knust, 1995) and the general anticlockwise circulation along the coasts of the North Sea
92 becomes weak and varied (Fig. 1, Howarth, 2001). Tides have the strongest influence on the currents
93 in this region, with wind forcing becoming secondary (Howarth, 2001; Otto et al., 1990; Sündermann
94 and Pohlmann, 2011).

95

96 Seasonal temperature stratification, common to this and other shelf seas, separates high-light and
97 low-nutrient surface water from low-light and high-nutrient bottom water. Even though in some
98 shelf areas, the tidal energy is sufficient to overcome stratification, Pingree and Griffiths (1978) and
99 Holt and Umlauf (2008) have shown that our study area is situated east of the tidal front that
100 bifurcates Dogger bank. Consequently, the water column above the Dogger sandbank is well-mixed
101 throughout the year, whereas the deeper waters that surround the bank become stratified during
102 spring and summer through the course of a tidal cycle.

103

104 2 Methods

105 All data used in this study was collected during two cruises with *RV Heincke*. The first cruise (HE406)
106 was conducted during summer 2013 (20.-24. July), the second cruise (HE413) during winter 2014
107 (13.-22. January).

108

109 2.1 EM710 flare imaging

110 Hydroacoustic data was collected only during the winter cruise, using a Kongsberg EM710 multibeam
111 echosounder to map active gas emissions (Fig. 2). For the precise localization of individual flares, i.e.,
112 bubble streams in an echogram, the water column data were post-processed using the Fledermaus
113 tools FMMidwater, DMagic, and the 3D Editor (© QPS). The origin of individual flares was identified
114 as the point of highest amplitudes near the seafloor. The coordinates of these points were extracted
115 using the FMGeopicker and subsequently plotted on top of the bathymetry using ArcGIS 10.2
116 (©ESRI).

117

118 For visualization of flare deflections and bubble rising heights, selected flares were extracted from
119 the water column data as point data and edited using the 3DEditor of DMagic. The processed flares
120 were plotted over the bathymetry data in a 3D-view (Fig. 2).

121

122 2.2 Water column sampling

123 To identify the size and magnitude of the dissolved methane plume generated by the bubble
124 discharge, seawater was sampled along a hydrocast transect that crossed the active gas emission
125 sites (Fig. 2). The transect extends 3 km to the east and 3 km to the west from the main bubbling
126 location denoted as cluster 1 in Fig. 2A and 2C (4°5.44'N, 55°18.36'E). [To better capture the methane
127 plumes and minimize tidal current changes, the station transect was oriented in direction of tidal
128 water movement.](#) The stations were sampled both in summer 2013 and in winter 2014; in both
129 cases, the eastern sector (5 stations) was sampled on one day (~3 h) and the western sector (5
130 stations) on another day (~3 h), so that the station directly above cluster 1 was sampled twice.

131

132 We used a rosette equipped with twelve 5 L Niskin bottles mounted on a frame that holds a Sea-Bird
133 SBE 911 plus CTD, and an SBE 43 oxygen sensor for online monitoring of salinity, temperature,
134 pressure, and dissolved oxygen. The data are archived in PANGAEA (doi:10.1594 / PANGAEA.824863
135 and doi:10.1594 / PANGAEA.832334). Twelve different water depths were sampled at each station
136 for quantification of the methane concentration and 5 water depths for methane oxidation rates.
137 Additional casts were conducted to recover sufficient water for molecular analyses.

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139 2.2.1 Methane concentration

140 For methane concentration analysis, samples were collected in 60 ml crimp-top glass bottles, flushed
141 with 2 volumes of water and filled completely to eliminate bubbles. Bottles were immediately
142 capped with butyl rubber stoppers and crimp sealed. After adding 0.2 ml of 10 M NaOH to stop any
143 microbial activity, a 5 ml headspace of pure N₂ was introduced into each bottle as described in
144 Valentine et al. (2001) and the samples were stored at 4 °C. One to two aliquots of the headspace
145 were analyzed to determine methane concentrations using a gas-phase chromatograph equipped
146 with a flame ionization detector. [The methane concentrations were calculated as detailed in Magen
147 et al. \(2014\).](#) Analyses were performed both on board and post cruise. Replicate analyses of samples
148 yielded a precision of ± 5%.

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150 2.2.2 Methane oxidation rates

151 Methane oxidation (MOx) rates were determined from ex situ incubations of water samples in 100
152 ml serum vials. Sample collection and incubation were performed as described in Mau et al. (2013).
153 Briefly, duplicate samples were collected and 50 µl of ³H-labeled methane (160–210 kBq) in N₂ were
154 added to each sample. After shaking the bottles to equilibrate the tracer with the water, the samples
155 were incubated in the dark for 24 h, those collected in summer 2013 were incubated at 10 °C and
156 those from winter 2014 at 9 °C. After incubation, the total activity (³H-CH₄ + ³H-H₂O) in an 1 ml
157 aliquot was measured by wet scintillation counting; the activity of ³H-H₂O was measured after
158 sparging the sample for >30 min with N₂ to remove excess ³H-CH₄, so that the net amount of ³H-CH₄
159 consumption can be estimated.

160

161 MOx rates were calculated assuming first-order kinetics (Reeburgh et al., 1991; Valentine et al.,
162 2001):

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$$164 \text{MOx} = k'[\text{CH}_4] \quad (1)$$

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166 where k' is the effective first-order rate constant calculated as the fraction of labeled methane
167 oxidized per unit time, and [CH₄] is the in situ methane concentration. To verify first order kinetics we
168 conducted time series incubations and measured the tracer consumption after 1, 2, 3, and 4 days.
169 The MOx values were corrected for differences between in situ and incubation temperatures
170 (Supplementary Material 1).

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172 In addition, control samples were frequently taken and poisoned immediately after the addition of
173 the tracer. The mean (\bar{x}) and standard deviation (s) of all controls sampled during a cruise were
174 calculated and the limit of detection (LOD) was set as:

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$$LOD = \bar{x} + 3s \tag{2}$$

The *LOD* was 0.02 nM day⁻¹ and 0.09 nM day⁻¹ for the summer 2013 and winter 2014 surveys, respectively.

2.2.3 Analysis of bacterial communities

The composition of the bacterioplankton assemblages was examined using denaturing gradient gel electrophoresis (DGGE) based on the 16S rRNA gene as described in Mau et al. (2013). In short, immediately after sampling, 8 L of water were filtered and the bacterial cells were concentrated on Nuclepore filters (0.2 μm pore size). The filters were stored on board at -20 °C and at -80 °C post cruise. DNA was extracted by an UltraClean Soil DNA Kit (MoBio Laboratories, USA). 16S rRNA gene specific PCR was conducted using the forward primer GM5 plus GC-clamp and the reverse primer 907RM (Muyzer et al., 1993) under conditions described by Gerdes et al. (2005). The PCR products (ca. 500 bp) were analyzed by DGGE according to the protocol of Muyzer et al. (1993). Clearly visible bands of the DGGE gels were excised from the gel. The DNA was reamplified by PCR (Gerdes et al., 2005) and sequenced. The 16S rRNA gene sequences were taxonomically assigned by SILVA Online Aligner (Pruesse et al., 2012).

The presence of methane-oxidizing bacteria was checked by searching for genes encoding the particulate methane monooxygenase (*pmoA*), a key enzyme of methanotrophs (McDonald et al., 2008). The *pmoA*-gene-specific PCR reaction was conducted by using the primer set “*pmoA*” and amplification conditions described in McDonald and Murrell (1997).

2.3 Methane concentration analysis by underwater mass-spectrometry (UWMS)

In addition to the conventional methane analysis, in situ methane concentrations were quantified with an UWMS during the summer 2013 cruise (Inspectr200-200, Bell et al., 2007; Gentz et al., 2013; Schlüter and Gentz, 2008; Short et al., 2001; Wenner et al., 2004). The fast sampling frequency (≤ 2 s) of the UWMS allows mapping of methane concentrations at much higher resolution than the commonly used CTD/rosette-sampling technique. The instrument consists of a membrane inlet system (MIS), an Inficon (Bad Ragaz, Switzerland) Transpector CPM 200 quadruple mass spectrometer, a Varian (Palo Alto, USA) turbo pump, a roughing pump, a peristaltic pump (KC Denmark), an embedded PC, and a microcontroller. The UWMS was partly redesigned to include a cooling system (Ricor, K508), which lowers the detection limit for methane to 16 nM. The cooling system and the improvement of the detection limit are described in detail by Gentz and Schlüter

210 (2012) and Schlüter and Gentz (2008). For reproducible gas permeation through the MIS, water is
211 constantly heated to a steady temperature of 50°C and pumped at a flow rate of 3 ml min⁻¹ along the
212 membrane by an external peristaltic pump.

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214 The UWMS was deployed above the central gas seeps (cluster 1, Fig. 2) on 21.07.2013 (16:31 – 22:32
215 UTC) at five different water depths: just above the seafloor, 35 m, 28 m, 25 m, and 10 m. When the
216 system had reached the respective depth, the research vessel moved slowly along a rectangular track
217 (~125 m S-N, ~150 m E-W, Fig. 2C) surrounding the flares of cluster 1 and towed the UWMS, which
218 continuously measured the methane concentrations. Each of the 5 tows (Fig. 2C) took approximately
219 one hour and recorded 400-800 methane concentration values.

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221 2.4 Estimation of methane fluxes

222 Advection, horizontal and vertical turbulent diffusion, sea-air flux, and microbial oxidation rates were
223 quantified for the upper (0-30 m) and lower water column (30-40 m) during summer stratification
224 (July 2013) and for the entirely mixed water column (0-40 m) in winter (January 2014).

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226 The advective flux (*ADV*) was calculated by multiplying methane concentration (*C*) and current
227 velocity (*v*):

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$$229 \quad ADV = vC \quad (3)$$

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231 Methane concentrations were averaged above and below the thermocline from the summer survey,
232 averages throughout the water column were calculated from the winter data. Current velocities refer
233 to the resultant velocities calculated from the *u* and *v* component of the velocity vectors
234 (Supplementary Material 2 and 3) and were averaged over the time period of sampling. The current
235 data were provided by the *Bundesamt für Seeschifffahrt und Hydrographie* (BSH)
236 (www.bsh.de/de/Meeresdaten/Vorhersagen/Vorhersagemodelle/index.jsp), who model currents
237 using wind and air temperature forecasts.

238

239 If advective transport were to be uniform, then it would simply displace methane, but differences in
240 current velocity and direction with depth lead to turbulent mixing, i.e., eddy diffusion. The strength
241 of small-scale motions that act to smooth out concentration gradients can be parameterized by the
242 eddy diffusivity κ , such that mass transport is proportional to the mean concentration gradient
243 (Largier, 2003; Roberts and Webster, 2002):

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245 $Diff = \kappa \left(\frac{\partial C}{\partial x} \right)$ (4)

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247 where κ is the horizontal or vertical diffusion coefficient in $m^2 s^{-1}$. $\delta C/\delta x$ is the spatial concentration
248 gradient in $nM m^{-1}$, estimated between the center and the outermost stations in the case of
249 horizontal diffusion calculation, and the concentration gradient between the lower and upper water
250 column in the case of vertical diffusion (Mau et al., 2012), calculated only for summer 2013.

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252 κ_y , the horizontal diffusion coefficient, can range between 0.1 and $1000 m^2 s^{-1}$ (Largier, 2003;
253 Sundermeyer and Price, 1998) depending on the proximity to land. κ_y exponentially increases with
254 distance from the shore: κ_y is on the order of $1-10 m^2 s^{-1}$ if $y \sim 0.1 km$, $\sim 100 m^2 s^{-1}$ if $y \sim 10 km$, and on
255 the order of $1000 m^2 s^{-1}$ or greater if $y \sim 100-1000 km$. As the study area is located more than 230 km
256 from shore, we used a κ_y of $1000 m^2 s^{-1}$ for our calculations. The vertical turbulent diffusion
257 coefficient (κ_z) can vary between 10^{-3} and $10^{-6} m^2 s^{-1}$ depending on the energy in the water column
258 (wind, tides, etc.) and stratification (Denman and Gargett, 1983; Wunsch and Ferrari, 2004). κ_z was
259 estimated according to the equation by Osborn (1980):

260

261 $\kappa_z = \Gamma \frac{\epsilon}{N^2}$ (5)

262

263 where Γ is the efficiency of mixing and assumed to be a constant of 0.2. We used published
264 dissipation rates of turbulent kinetic energy (ϵ) in stratified shallow shelf seas (Palmer et al., 2008;
265 Thorpe et al., 2008) and calculated the buoyancy frequency (N) from the available CTD-profiles. The
266 results indicate that κ_z is in the order of 10^{-4} to $10^{-6} m^2 s^{-1}$ during stratification. This rough
267 approximation neglects hourly changes, which can vary by an order of magnitude. For example,
268 Palmer et al. (2008) observed and calculated κ_z to range between 10^{-4} and $10^{-5} m^2 s^{-1}$ over a tidal
269 cycle. We used $10^{-4} m^2 s^{-1}$, which is a common cited value across the thermocline, in order to not
270 underestimate the vertical eddy diffusion. This diffusion was estimated for all vertical profiles (all 10
271 CTD-stations).

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273 The sea-air flux was calculated as:

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275 $SAF = k_w(C_w - C_a)$ (6)

276

277 where k_w is the gas transfer velocity in $cm h^{-1}$, C_w is the measured concentration of methane and C_a
278 is the methane concentration in atmospheric equilibrium, both in nM. We calculated k_w , which

279 depends on wind speed and the temperature-dependent Schmidt number of the gas, using
280 parameterization developed by McGillis et al. (2001). Wind speed was recorded 22 m above sea level
281 onboard and corrected to the standard height of 10 m. C_A was derived using the mean atmospheric
282 methane concentration of Ocean Station M, Norway at 66°N and 2°E, in 2009 (1.874 ppm,
283 <http://www.esrl.noaa.gov/gmd/dv/data/>), the Bunsen solubilities given by Wiesenburg and Guinasso
284 (1979) and measured ocean temperature and salinities. The sea air flux was calculated for surface
285 water samples of all 10 stations sampled in summer 2013 and winter 2014.

286

287 The oxidative loss (OL) was calculated by depth integration of the MOx rates:

288

$$289 \quad OL = \bar{x}_{MOx} z \quad (7)$$

290

291 where \bar{x}_{MOx} is the averaged MOx rate in nM day⁻¹ over the depth interval z in m. The depth interval
292 is defined by the water stratification in the case of summer 2013 and covers the entire water depth
293 in the case of winter 2014. Integration was done for all vertical profiles.

294

295 3 Results

296 3.1 Seep locations

297 Echosounder data collected during the winter survey indicate bubble emission in the area of the
298 sampled transect (Fig. 2). The center station was located at a known gas bubble emission site or flare
299 cluster, where several bubble streams occur in close proximity to each other. We observed an
300 additional four flare clusters near the western sector of the transect, similar in seepage intensity as
301 those from the central seep denoted as cluster 1 (Fig. 2A and C). In contrast, no additional flares
302 were found in the area of the eastern sector. Although echosounder data point to bubbles rising to,
303 or close to, the sea surface, no bubbles were visually identified at the sea surface due to rough sea
304 state. Seepage intensity showed no obvious variation related to tidal cycles, i.e., pressure variations
305 due to high or low tides. The seeps were found to be active during all survey crossings. No
306 echosounder data were collected in summer 2013, nonetheless, surfacing gas bubbles were visually
307 documented when the sea was calm.

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309 3.2 Oceanographic setting

310 In summer (July 2013) a seasonal thermocline separated surface (0-30 m) from bottom waters (30-42
311 m; Fig. 3). The surface water consisted of a 10 m thick mixed layer below which the temperature
312 decreased stepwise from 17.5 to 7°C in 30 m. Lower salinity was observed at 15 and 25 m depths,
313 which departed from the general value of 34.55. The stepwise decrease in temperature and the

314 salinity variations indicate the successive development of several pycnoclines driven by increasing
315 sea surface temperatures and less wind activity in spring and summer. The oxygen concentrations
316 increased from 220 μM at the surface to 240 μM at 30 m. In contrast to the surface water, the
317 bottom water had a homogeneous temperature of 7°C, a salinity of 34.63 and contained less oxygen
318 (190 μM).

319
320 In winter (January 2014) the entire water column was mixed (Fig. 3). The water had a temperature of
321 7°C, a salinity of 34.85, a density of 27.3 kg m^{-3} , and oxygen concentrations of 280 μM .

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323 Modeled regional current data provided by the BSH indicate a dominant north-west transport
324 throughout the water column with surface velocities ranging between 0.06 and 0.27 m s^{-1} (resultant
325 velocity). In summer, the eastern part of the transect was sampled when currents were directed to
326 the north-west with an average velocity of 0.24 m s^{-1} and the western part was sampled when
327 currents turned from north-west to south-west with an average velocity of 0.19 m s^{-1} . In winter, the
328 eastern part of the transect was sampled when water moved north-east turning north-west with an
329 average velocity of 0.22 m s^{-1} and the western part was sampled when water also turned from north-
330 east to north-west, but with an average velocity of 0.1 m s^{-1} . Water velocity and direction plots are
331 given in Supplementary Material 2 and 3.

332

333 3.3 Methane concentrations

334 Consistent with the two layer structure observed on the hydrographic data, the methane
335 concentration in summer 2013 also show a two layer distribution, with higher values in the bottom
336 water (Fig. 4A, [Supplementary Material 4](#)). Methane concentrations in the surface water range from
337 3.9-517.8 nM with a median of 32.5 nM. Methane concentrations in the bottom water range
338 between 39.7 and 1627.7 nM with a median of 390.6 nM. Highest concentrations in the surface
339 water were found near cluster 1 (170 nM) and generally decreased towards the outermost stations
340 (to the west to 96 nM and to the east to 13 nM). Similarly, in the bottom water the highest methane
341 concentrations were found at cluster 1 (600-700 nM), and concentrations decreased unevenly
342 towards the outmost stations (200-300 nM). In both layers the methane concentrations exceed the
343 background concentration of ~ 20 nM as measured at a reference station located 32 km to the south-
344 east of cluster 1 (Supplementary Material 5), and those reported by Grundwald et al. (2009). Even
345 this regional background value is supersaturated with respect to the atmospheric equilibrium
346 concentration of 2.3-2.9 nM (at the relevant T/S conditions, Wiesenburg and Guinasso, 1979).

347

348 Much lower methane concentrations were found in winter 2014 (Fig. 4B, [Supplementary Material 4](#)).
349 Highest values were observed only at one station near cluster 1 with concentrations reaching 656.6
350 nM. Such elevated values decreased rapidly horizontally (within 1 km) and were not encountered
351 during repeated hydrocasts at the same location. The median of all methane concentration
352 measurements along the transect was 22.4 nM, which is only slightly above the regional background
353 concentration. In general, methane concentrations indicate a patchy distribution as expected in an
354 active seep area.

355

356 3.4 UWMS methane concentrations

357 The UWMS was deployed in the vicinity of flare cluster 1 in summer 2013 covering an area of 125 m
358 by 150 m during instrument tow (Fig. 2C). Therefore, the hydrocast data (described in section 3.3)
359 cover a much larger spatial scale sampled during the UWMS-tows. When the UWMS was towed close
360 to bubble streams, it recorded methane concentrations ranging over three orders of magnitude,
361 from <16 nM (the detection limit, which is recorded as 0) to 2127 nM in surface waters (transects in
362 10 m, 25 m, 28 m), but values > 500 nM were only recorded during a period of ~11 min of the ~30
363 min tow at 25 m and ~4 min of the ~60 min tow at 28 m (Fig. 5). During bottom transects (30 m and
364 42 m) methane concentration are generally higher, ranging from 259 to 2213 nM. The median values
365 of the records from the 10 m, 25 m, and 28 m water depth tows were <16 nM, 133 nM, and 158 nM,
366 respectively, while the median in 30 m and 40 m depth were 508 and 679 nM.

367

368 The UWMS tows were conducted during ebbing tides, when water levels fell from 0.18 to -0.27 m,
369 whereas hydrocast samples were collected during rising tides, when sea level height increased from -
370 0.21 to 0.06 m and from 0.04 to 0.16 m ([Supplementary Material 6](#)). The general pattern of lower
371 concentrations in the surface and higher ones in the bottom water was apparent in all stations, even
372 though methane data were obtained using different techniques and samples were collected during
373 different tidal phases.

374

375 3.5 Methane oxidation

376 Similar to the distribution of methane and co-located oceanographic data, the MOx rates calculated
377 using equation (1) show a two layer pattern in summer 2013, but are uniform throughout the water
378 column during the winter 2014 survey (Fig. 6A). In summer, MOx-rates in surface waters ranged
379 between 0.04 and 9.17 nM day⁻¹ with a median of 0.10 nM day⁻¹ and in the bottom water between
380 1.60 and 840.93 nM day⁻¹ with a median of 3.99 nM day⁻¹. The total range of both layers (0.04-
381 840.93 nM day⁻¹) exceeds the range of MOx-rates observed during the winter survey (0.09-8.72 nM
382 day⁻¹). The median of all MOx-rates measured in January 2014 was 0.24 nM day⁻¹.

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3.6 Microbial communities

Molecular samples taken in summer 2013 show also a difference between surface and deep waters, whereas winter 2014 samples indicate a homogeneous distribution of microorganisms (Fig. 7, Tab. 1). In summer 2013, different DGGE banding patterns reveal changes in microbial communities with depth. The surface water samples showed two strong bands (Fig. 7, bands 6, 7) that could be affiliated to the *Rhodobacteraceae* and two bands that could be assigned to the *Cyanobacteria* / *Synechococcus* clade (8, 9). The middle and bottom water samples were characterized by a strong chloroplast band (2), but also showed bands affiliated to the *Rhodobacteraceae* (5, 6). In the bottom water samples of the central station, we found an additional band, assigned to *Pseudoalteromonas* (10). The gel pattern of the winter samples showed no significant bands. The sequences of the faint bands excised were of low quality. Only two of the bands could be assigned to the *Rhodospirillaceae* (12, 13).

Neither the summer nor the winter bacterial communities exhibited known methanotrophic bacteria, even though the samples originate from an actively gas venting area. The absence of methanotrophic bacteria was further supported by the negative results of the *pmoA*-PCRs that targets a methanotroph molecular marker gene.

4 Discussion

The echosounder and visual observations at the central North Sea sites document gas emissions that in some cases reach the sea surface. This fraction of methane that is transported directly to the atmosphere by bursting bubbles might be crucial, as was shown for example at the shallow seep field Coal Oil Point in California (<70 m) where about half of the methane is directly emitted to the atmosphere via bursting bubbles and the other half is injected in the water (Clark et al., 2000). However, we focus on the dissolved methane fraction that remains in the in the ocean and can be microbially oxidized.

4.1 Distribution of methane in summer and winter

Our highest dissolved methane concentrations, measured in the bottom water during the summer survey, reach magnitudes similar to those observed at other shallow seep sites (Tab. 2). Our highest value of 1627.7 nM is comparable to measurements near the Coal Oil Point seep field (up to 1900 nM, Mau et al., 2012), and it is higher than methane concentrations reported for seep locations in the Tommeliten, North Sea (268 nM, Schneider von Deimling et al., 2011), and offshore Svalbard, west of Prins Karls Forland (524 nM, Gentz et al., 2013).

418

419 Even though gas bubbling was observed at the sea surface during the summer survey, the dissolved
420 methane appears trapped beneath the seasonal thermocline (Fig. 4A). This observation is similar to
421 those at the Tommeliten site, where the dissolved methane plume was sequestered beneath the
422 seasonal thermocline (Schneider von Deimling et al., 2011) although gas flares were imaged to rise
423 within 10 m of the sea surface. Elevated methane concentrations at other vent sites have also been
424 reported beneath a thermocline or halocline that hamper further ascent of dissolved methane to the
425 mixed layer. The dissolved methane plume originating from the 245 m deep seeps offshore Prins
426 Karls Forland was confined to water depths beneath a local halocline (Gentz et al., 2013). In the Baltic
427 Sea, summer stratification also leads to accumulation of methane below the thermocline (Gülzow et
428 al., 2013). At all these sites, an enhanced release of methane to the atmosphere is thought to occur
429 upon erosion of stratification. In contrast, the dissolved methane plume originating from seeps
430 situated between 5 and 70 m at the Coal Oil Point is dispersed within the mixed layer above the
431 thermocline (Mau et al., 2012), and as such it is not controlled by seasonal stratification patterns.

432

433 Trapping and accumulation of dissolved methane beneath a thermocline is also well documented in
434 lakes and freshwater reservoirs, where thermal stratification separates methane-poor, surface water
435 from the methane-rich, but anoxic, bottom water in e.g. a shallow floodplain lake in south-eastern
436 Australia (Ford et al., 2002), in a polyhumic lake in southern Finland (Kankaala et al., 2007), in the
437 subtropical Lake Kinneret in Israel (Eckert and Conrad, 2007), and in 8 freshwater reservoirs in India
438 (Narvenkar et al., 2013). The accumulated methane is released to the atmosphere at the onset of
439 water column mixing in response to enhanced wind forcing and lower temperatures.

440

441 Our results show that in a seasonal stratified system, no methane accumulation occurs in winter,
442 when the water column is well mixed (Fig. 4B). Methane concentrations were found to deviate only
443 due to bubble ascent and were otherwise low and constant throughout the water. The median
444 winter concentration of 22 nM is similar to the background values of 20 nM reported by Grunwald et
445 al. (2009) for the German Bight, but is elevated relative to water originating from the Atlantic Ocean,
446 which carries 2.5-3.5 nM of methane (Rehder et al., 1998) and to the methane background
447 concentrations of <5 nM at Tommeliten (Niemann et al., 2005; Schneider von Deimling et al., 2011).

448

449 The observed difference between summer and winter dissolved methane concentrations may also be
450 due to changes in seepage rate. The visual observation of gas bubbles during the summer, Schroot et
451 al.'s (2005) sub-bottom profiler recording of gas plumes in the water column in August 2002, and our
452 acoustic records of gas flares in the winter (Fig. 2B) indicate that seepage occurred during both

453 seasons. Notwithstanding these observations, we recognize that we do not have enough temporal
454 data coverage and that bubble release frequency, bubble size and initial methane content could still
455 have been different between our surveys causing the difference in overall methane concentrations
456 (Greinert and McGinnis, 2009; Leifer and Clark, 2001; McGinnis et al., 2006). However, even when a
457 change in seepage regimes could affect the overall methane concentration, it would not explain the
458 difference in the methane profiles observed between summer and winter surveys.

459

460 Discrete sampling bias and currents variability may also explain the difference observed between
461 summer and winter dissolved methane concentrations. The currents had a strong westward
462 component during summer sampling with small north/south deviation throughout the water column
463 (Supplementary Material 2), and thus the easternmost profiles are likely to be less influenced from
464 direct bubble seepage (Fig. 4A). However, the profiles still show elevated methane concentration in
465 the bottom water and lower concentrations in the shallow samples, consistent with methane
466 trapping below the seasonal thermocline. We considered whether the low observed concentrations
467 during winter may be due to the fact that during this survey we only partially sampled isolated
468 plumes. Although the east-west-transect directly crust the cluster 1 flares (Fig. 2) and was oriented in
469 direction of the tidal movement in that area, the stronger northward component of the current in
470 winter (Supplementary Material 2 and 3) displaced methane plumes more rapidly than in summer.
471 The elevated methane concentrations at the central seep site and along the western transect
472 (although with much lower methane concentrations) suggest that we indeed sampled methane
473 plumes (Fig. 4B). We note that the horizontal concentration gradient in surface water were 0.01 to
474 0.02 nM m⁻¹ during summer and winter, respectively. As a first order approximation we take the
475 highest concentration measured (39 in summer and 73 nM in winter) and a general current speed of
476 0.2 m s⁻¹ to estimate a plume size of ~4 km in diameter that would take ~5 h to cross our sampling
477 transect. Since we always sampled 5 stations in ~3 h for the eastern or western segments of the
478 transect, it seems rather unlikely that we completely missed a methane plumes.

479

480 To summarize, even when methane concentrations may appear biased by discrete sampling, current
481 differences, and seepage rate, our data analyses suggest that the seasonal differences are real. Even
482 if the total magnitudes may be questioned, we are confident that the methane distribution pattern is
483 the result of seasonal stratification.

484

485 4.2 Interpreting methane oxidation rate data

486 Measured MOx-rates at our study site (Fig. 6A) lie at the upper end of MOx-rates previously reported
487 at sites elsewhere, which span over six orders of magnitude from 0.001-1000 nM day⁻¹ (Tab. 2 and

488 summarized in Fig. 1 in Mau et al., 2013). The rates measured in deep water samples during summer
489 (median 3.9 nM day⁻¹, up to 840 nM day⁻¹) equal those observed in the Gulf of Mexico after the
490 Deepwater Horizon event (median 10 nM d⁻¹, up to 820 nM day⁻¹) (Valentine et al., 2010). Even in
491 winter time, the estimated rates are high in comparison to those measured in the Eel River Basin, an
492 area of documented gas hydrate dissociation (Valentine et al., 2001) and match rates of the Coal Oil
493 Point seep field in the Santa Barbara Basin (Mau et al., 2012; Pack et al., 2011).

494

495 In spite of the reported high MOx values, our data reveal an overall low activity of methane oxidizing
496 microorganisms based on the values obtained for the rate constant k' , which provides an indication
497 of the relative activity in a water sample (Koschel, 1980). This is a first-order constant if the reaction
498 is solely dependent on the methane concentration and biomass does not increase during incubation.
499 Our experiments yielded similar k' values over a wide range of methane concentrations spanning
500 from 4 to 728 nM (Fig. 6C). Furthermore, the good correlation between methane oxidation rates and
501 methane concentration (Fig. 6D) indicate that the biomass did not increase during incubation, thus
502 validating our inferences on microbial activity based on k' values. Based on 116 (out of 123)
503 measurements we calculate an average value for k' of 0.01 day⁻¹, i.e., a turnover time of 100 days
504 (Fig. 6B). This value matches the value k' derived from our time series incubation results (0.01 day⁻¹,
505 $n=4$), which show that only 5-6% of the added ³H-methane tracer was consumed by microbial activity
506 after 4 incubation days (Supplementary Material 7). The time series show a linear increase of tracer
507 oxidation and the function derived from Fig. 6D that yield a first-order relationship between methane
508 oxidation rates and methane concentration with $k'=0.01$. If we use the average k' and methane
509 concentrations that span 4-728 nM, the resulting oxidation rates (Eq. 1) range between 0.04-7.28 nM
510 day⁻¹. Thus relatively high MOx-rates here reflect primarily high methane concentrations, and must
511 not be taken as indication of a high microbial turnover.

512

513 We note that 7 data points collected in summer near flare cluster 1 (stations 12 and 13) had k' values
514 ranging from 0.08 to 0.64 day⁻¹, significantly higher than the rest of the measurements. These high
515 values multiplied with high corresponding methane concentrations gave the highest MOx-values
516 measured during this study. These elevated k' values may indicate an increase in biomass and/or an
517 increase in activity of the methane oxidizing community in the water sample during incubation.

518

519 The general low activity of methane oxidizing microorganisms is further supported by molecular
520 analysis of filtered matter from seawater. Consistently, DGGE and *pmoA* analysis did not reveal the
521 presence of any known methanotrophic bacteria or *pmoA*-genes. Either methanotrophs were only
522 present in low numbers and/or poorly matched to the used PCR primers and, thus, were not

523 detected (Hansman, 2008). We also note that although no canonical methanotrophs were detectable
524 in shallow marine waters (< 200 m) in the Pacific, Atlantic, and the Gulf of Mexico, further analyses of
525 these samples revealed sequences closely related to those coding for methane monooxygenase
526 (Elsaied et al., 2004; Tavormina et al., 2008; Tavormina et al., 2013; Valentine, 2011; Wasmund et al.,
527 2009), an enzymatic hallmark of aerobic methanotrophs. We recognize that not having detected
528 methanotrophs in our samples does not preclude their presence in the water column.

529

530 Even though during summer stratification methane is trapped beneath the seasonal thermocline, the
531 resulting higher methane concentrations do not appear to enhance the activity of methane oxidation
532 microbes. The residence time of central North Sea water is about 1.5-2 years (Prandle, 1984; Ursin
533 and Andersen, 1978) and thermal stratification prevails for 4 months, which may provide sufficient
534 time to establish a methanotrophic community. However, microbial turnover times in bottom water
535 samples are consistently low and we were not able to identify methanotrophic organisms in the
536 water column. Doubling times of planktonic marine methanotrophs are not known to the authors,
537 but if we assume a doubling time of ~10 h as known from cultured methanotrophs (Baani and
538 Liesack, 2008; Khadem et al., 2010) or a doubling time of 3.5 days estimated after the Deep Water
539 Horizon incident in the Gulf of Mexico (Kessler et al. (2011)), a methanotrophic community could
540 potentially develop in the central North Sea during the 4 months where stratification leads to
541 enhanced methane content in the bottom water. Even if the doubling time of methanotrophs in the
542 field was longer than in culture as nutrients and substrates can be limiting, the residence time of the
543 water would permit growth. Possible limitations may be a lack of essential trace elements or that the
544 methane oxidizing microorganisms are facultative methanotrophs (Tavormina et al., 2013), i.e., not
545 necessarily depending on methane.

546

547 In summary, even though total MOx rates are necessary to constrain overall methane budgets and
548 carbon cycles, to better characterize microbial activity among different ecosystems it is necessary to
549 also report data on the microbial turnover rates at each site. The low turnover rates measured here
550 are consistent with molecular analyses that failed to identify methanotrophic bacteria or *pmoA*-
551 genes. Enhanced methane concentrations do not appear to foster higher turnover rates.

552

553 4.3 Methane transport in the North Sea is faster than oxidation

554 When methane enters the water column, either directly from the seep or by dissolution/gas
555 exchange from ascending bubbles, it is transported by ocean currents and spreads by horizontal and
556 vertical eddy diffusion. Methane oxidizing microorganisms can consume dissolved methane in the

557 water column, and methane will be transferred into the atmosphere if its concentration in the mixed
558 layer is higher than saturation.

559
560 As a first order evaluation of the relative importance of these transport and loss processes, we
561 estimated the advective transport, the horizontal and vertical eddy diffusion, sea-air flux, and
562 integrated the MOx-rates (see methods and Mau et al., 2012). Summer fluxes for the bottom (30-
563 43m) and surface waters (0-30 m), were estimated using data collected in July 2013, and winter
564 fluxes were derived for the entire unstratified water column (0-42m) using data from January 2014.
565 All fluxes were estimated in units of $\text{nmol m}^{-2} \text{s}^{-1}$. These flux estimates may vary by up to one order of
566 magnitude due to measurement errors, assumed diffusion coefficients and parameterization of the
567 gas transfer velocity. A detailed discussion of the uncertainties associated with the calculations is
568 given by Mau et al. (2012).

569
570 The results shown in Fig. 8 revealed that in both summer and winter seasons, horizontal advection
571 and eddy diffusion are the dominant processes transporting and diluting the emitted methane. The
572 loss processes, i.e., sea air flux and microbial oxidation, are more than 4-orders of magnitude lower
573 than physical horizontal transport processes.

574
575 Vertical mixing due to internal waves resulting from proximity to the elevation of the Dogger Bank
576 cannot be ruled out. Estimates of κ_z for the shelf break range in the order of $0.5\text{-}0.7 \cdot 10^{-4} \text{ m}^2 \text{ s}^{-1}$
577 (Palmer et al., 2008). Our vertical fluxes based on $\kappa_z = 10^{-4} \text{ m}^2 \text{ s}^{-1}$, thus include the enhanced mixing by
578 internal waves that support increased transport across the seasonal thermocline.

579
580 Sea-air flux estimates depend on variations in the atmospheric methane concentration. We don't
581 have data on atmospheric methane variations directly over our study site; however, if we consider
582 published variations at other seep sites (e.g. 1.71-3.83 ppm above seeps in the northern Gulf of
583 Mexico, Hu et al., 2012), our estimates are correct within the order of magnitude range stated as our
584 uncertainty. Not surprisingly, the sea-air flux removes more methane from the water column during
585 winter due to increased wind speed. More unexpectedly, our flux estimates revealed that in summer
586 the amount of methane that is transported via vertical diffusion into the surface water is of similar
587 magnitude than the loss by oxidation in the bottom water, even water stratification leads to
588 enhanced methane concentrations at depth. In summer, when lower wind speeds prevail, methane
589 oxidation was estimated to be of similar magnitude as the gas transfer to the atmosphere.

590

591 Our findings are similar to those reported by Scranton and McShane (1991) for the Southern Bight of
592 the North Sea. They conclude that methane oxidation constitutes a relatively small sink for methane
593 ($0.00023\text{-}0.3\text{ nM day}^{-1}$), relative to methane losses to the atmosphere ($0.00026\text{-}7.5\text{ nM day}^{-1}$), which
594 are highest during periods of high wind speed. Similarly, estimates for the shallow Coal Oil Point
595 methane plume in the Santa Barbara Basin (Mau et al., 2012) show that at this location 0.05 mol day^{-1}
596 ¹ are oxidized in the surface water and 0.03 mol day^{-1} are transferred to the atmosphere.

597

598 5 Conclusions

- 599 1. Observations at a shallow gas seep site in the central North Sea document methane
600 accumulation below the thermocline during summer stratification, but no methane
601 accumulation in the winter when water column is well mixed.
- 602 2. At our study site, physical transport processes always outcompete microbial methane
603 oxidation. Horizontal advection and diffusion of methane are consistently higher than
604 vertical transport, even within order of magnitude uncertainties. During periods of high wind
605 speed (fall and winter), more methane reaches the atmosphere than is oxidized in the water;
606 in summer the loss to the atmosphere and the oxidation terms are of similar magnitude.
- 607 3. We show that MOx rates alone cannot be used to characterize the ecosystem microbial
608 activity, as these values are scaled to the methane concentration. We instead propose to
609 include interpretation of k' values as an indicator of microbial activity. Averaged k' values
610 generate a more realistic parameter than values based solely on replicate samples as further
611 documented by our work-intensive time series incubations.
- 612 4. Our results demonstrate that trapping of methane below a seasonal thermocline does not
613 necessarily lead to enhance microbial oxidation. Further research is needed to elucidate why
614 stratification over a summer season of 4 months does not enhance methanotrophy enough
615 to significantly hamper methane release to the atmosphere upon water column mixing.

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626 Author contribution
627 S. M. designed study, measured methane concentrations and methane oxidation rates, calculated
628 the fluxes, wrote the manuscript
629 T.G., R. M., and M.S. deployed the UWMS and post-processed the data
630 J.-H. K., M. R., H. S., and P. W. collected and post-processed hydroacoustic data
631 M. T. interpreted methane oxidation rate data, edited manuscript
632 E. H. implemented and interpreted molecular analyses
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870 Tables

871 Tab. 1 Classification of partial 16S rRNA gene sequences (Fig. 7) to bacterial taxa performed with the
872 Silva classifier (Pruesse et al., 2012). The confidence value (0–1) for assignment at the level of class
873 and genus is given in parentheses.

No.	Class	Family
1	Alphaproteobacteria (0.4)	<i>SAR11 clade</i> (0.2)
2	Cyanobacteria (1)	<i>Chloroplast</i> (1)
3	Alphaproteobacteria (1)	<i>Rhodobacteraceae</i> (1)
4	Bacteroidetes incertae sedis (0.43)	<i>Marinifilum</i> (0.4)
5	Alphaproteobacteria (1)	<i>Rhodobacteraceae</i> (1)
6	Alphaproteobacteria (1)	<i>Rhodobacteraceae</i> (1)
7	Alphaproteobacteria (1)	<i>Rhodobacteraceae</i> (1)
8	Cyanobacteria (1)	<i>Synechococcus</i> (1)
9	Cyanobacteria (1)	<i>Synechococcus</i> (1)
10	Gammaproteobacteria (1)	<i>Pseudoalteromonadaceae</i> (1)
11	Proteobacteria (0.36)	
12	Alphaproteobacteria (1)	<i>Rhodospirillaceae</i> (0.8)
13	Alphaproteobacteria (0.91)	<i>Rhodospirillaceae</i> (0.7)

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891 Tab. 2 Comparison of highest methane concentrations, methane oxidation rates, and sea-air fluxes from different locations

Location	Methane concentration <i>up to nM</i>	MOx-rate <i>nM day⁻¹</i>	SAF <i>nmol m⁻² s⁻¹</i>	Reference
Seep sites				
central North Sea	1628	0.04-840	0.02-8.3	this study
Coal Oil Point, Santa Barbara Basin	1900	0.02-30	1.8	Mau et al., 2012; Pack et al., 2011
Tommeliten, North Sea	268		10.8*	Schneider von Deimling et al., 2011
west of Prins Karls Forland, Svalbard	524	up to 0.8		Gentz et al., 2013
Eel River Basin	300	0.002-0.8		Valentine et al., 2001
Deepwater Horizon event				
Gulf of Mexico	180000	up to 820		Valentine et al., 2010
Gulf of Mexico	1000000	up to 5900		Crespo-Medina et al., 2014
Overall areas				
Baltic Sea	38		0.008-0.2	Gülzow et al., 2013
Southern Bight of the North Sea	372	0.0002-0.3	0.07-7	Scranton and McShane (1991)
general European shelf estimate	21		0.11-0.24	Bange, 2006
Lakes				
floodplain lake in south-eastern Australia	50000		8.3-2700	Ford et al., 2002
polyhumic lake in southern Finland	150000	30-14400	0.5-695	Kankaala et al., 2007
the subtropical Lake Kinneret in Israel	450000			Eckert and Conrad, 2007
freshwater reservoirs in India	156000			Narvenkar et al., 2013

*direct transport via bubbles

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894 Figures

895 Fig. 1: Location of the study area in the central North Sea. The main currents are shown following
896 Howarth (2001). The map was drawn using GeoMapApp with 40 m contours.

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898 Fig. 2: A) Overview of gas flares mapped in January 2014 and CTD stations sampled in July 2013 (S12-
899 S21) and January 2014 (W2-W12). Flares cluster in 5 distinct areas (cluster 1-5) and reach to 6 m
900 from the sea surface (e.g. cluster 2 (B)), which corresponds to the echosounder's transducer depth.
901 Hence, most likely the gas transport extends to the sea surface. Cluster 1 corresponds to the gas seep
902 area investigated by Gentz (2013) (C).

903

904 Fig. 3: Depth profiles of potential temperature, salinity, density (sigma theta), and oxygen for all
905 stations in both summer and winter field programs.

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907 Fig. 4: A-B Contour plots of the dissolved methane concentrations measured in the water column in
908 July 2013 and January 2014. The 6 km transect was divided into an eastern (positive numbers) and
909 western part (negative numbers) starting from the center station at 0 km. Note the different
910 methane concentration scales, which are necessary to properly display the different concentration
911 ranges. The black dots indicate the sampled water depths.

912

913 Fig. 5: Methane concentrations recorded by UWMS on 21.07.2013 in the vicinity of flare cluster 1
914 (Fig. 2C) at different water depth. The detection limit of the instrument is 16 nM, all measurements
915 below this value are recorded as 0. Apart from temporal and spatial elevations most likely due to
916 bubble streams, the background value is elevated throughout the recording time in 30 and 42 m
917 water depth.

918

919 Fig. 6: Methane oxidation rates versus water depth measured with ³H-methane in July 2013 and in
920 January 2014 (A). B The first order rate constant k' of summer and winter samples indicating the
921 relative activity of the water. C k' versus methane concentration illustrate similar k' values over a
922 wide range of methane concentration. D Methane oxidation rates versus methane concentrations
923 shows for most of the data a first order function: $MOx=0.01[CH_4]^1$ (function with R^2 of 0.92 derived
924 from winter data and with R^2 of 0.85 from summer data).

925

926 Fig. 7: DGGE profile of 16S rRNA gene fragments of samples from different depth and stations in the
927 central North Sea. Numbers on the lines indicate excised and successfully sequenced DGGE bands,
928 whose phylogenetic assignment is listed in Tab. 1.

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930 Fig. 8: Sketch of transport and loss terms estimated for the study area in $\text{nmol m}^{-2} \text{s}^{-1}$.

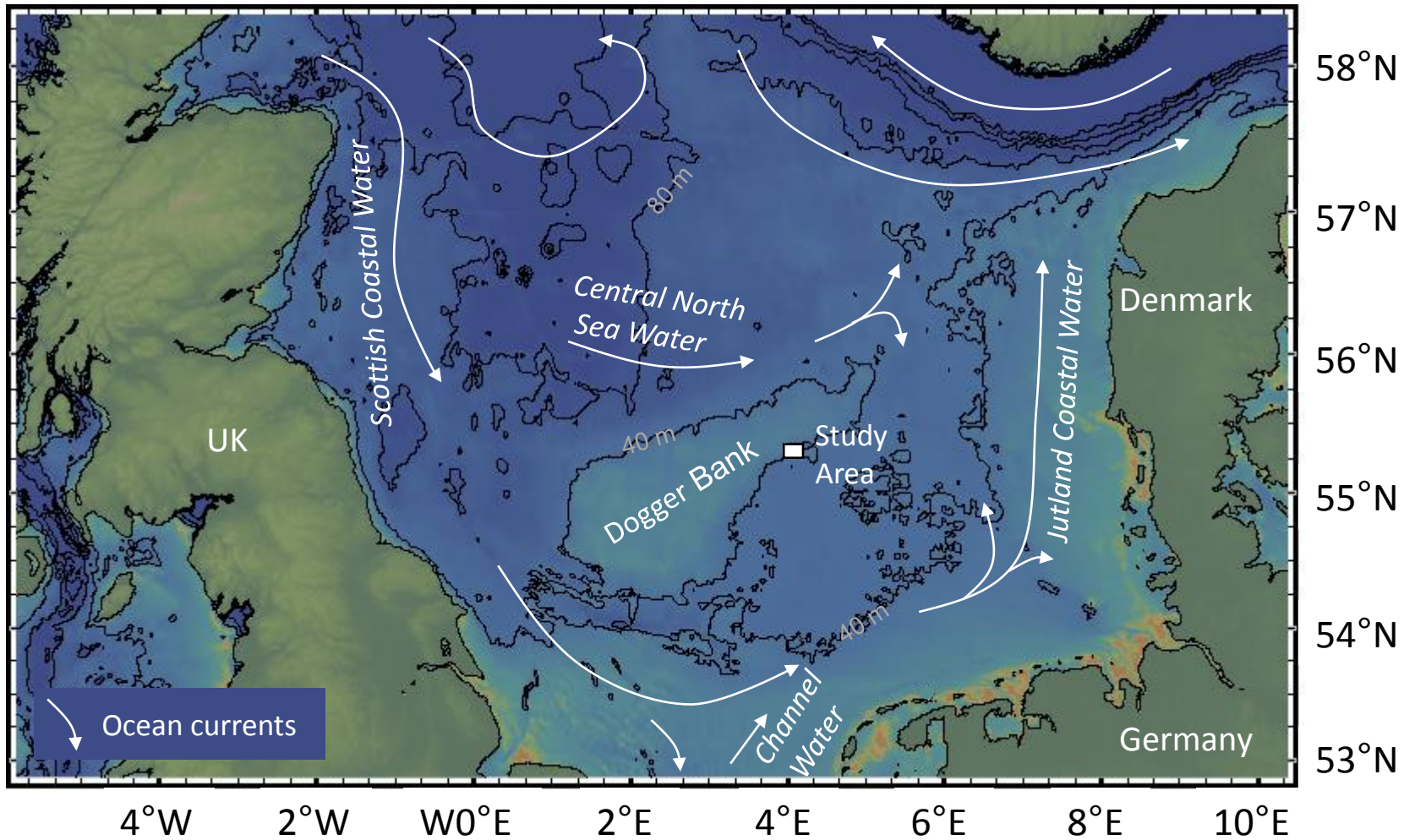


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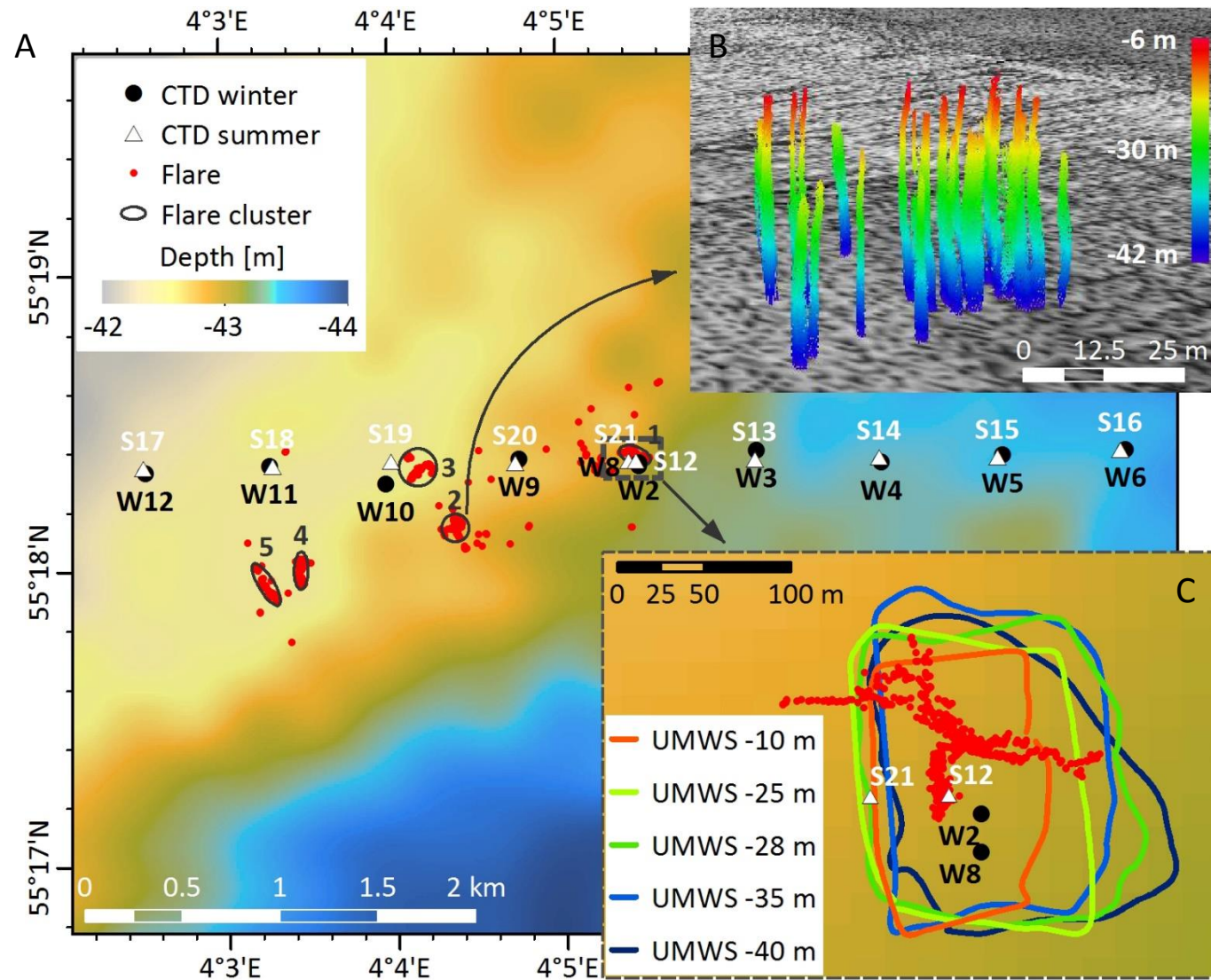


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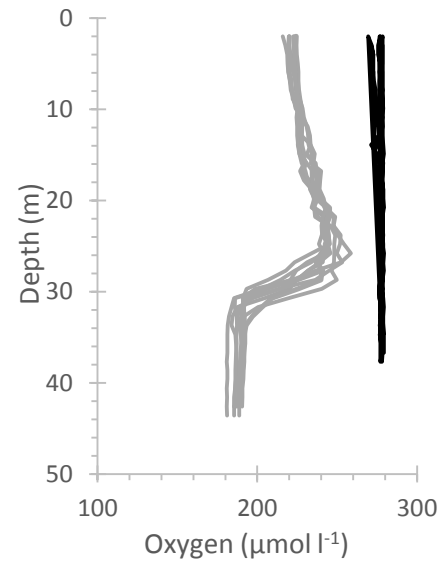
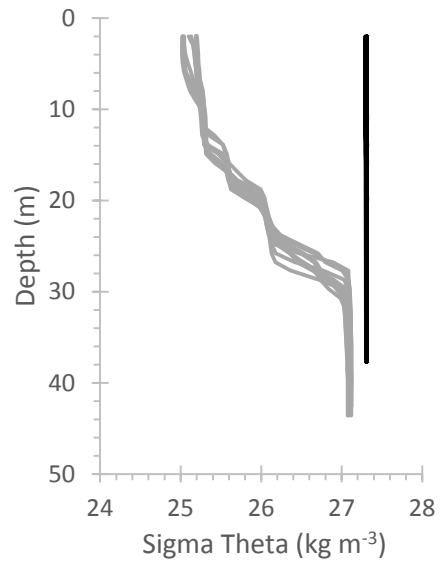
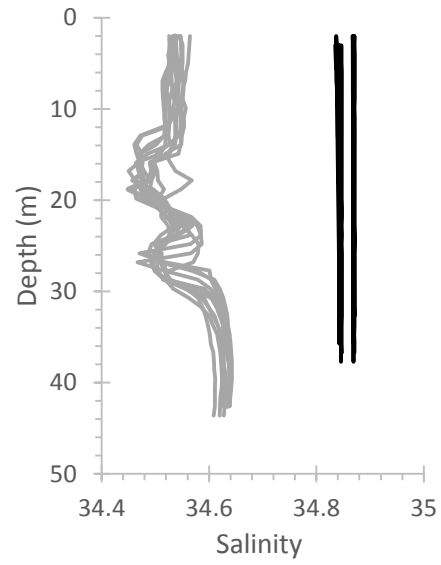
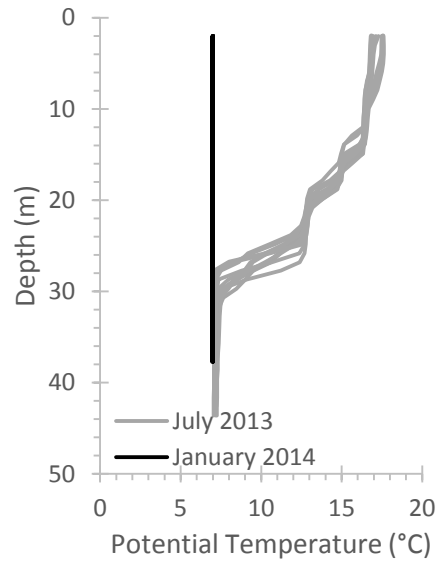


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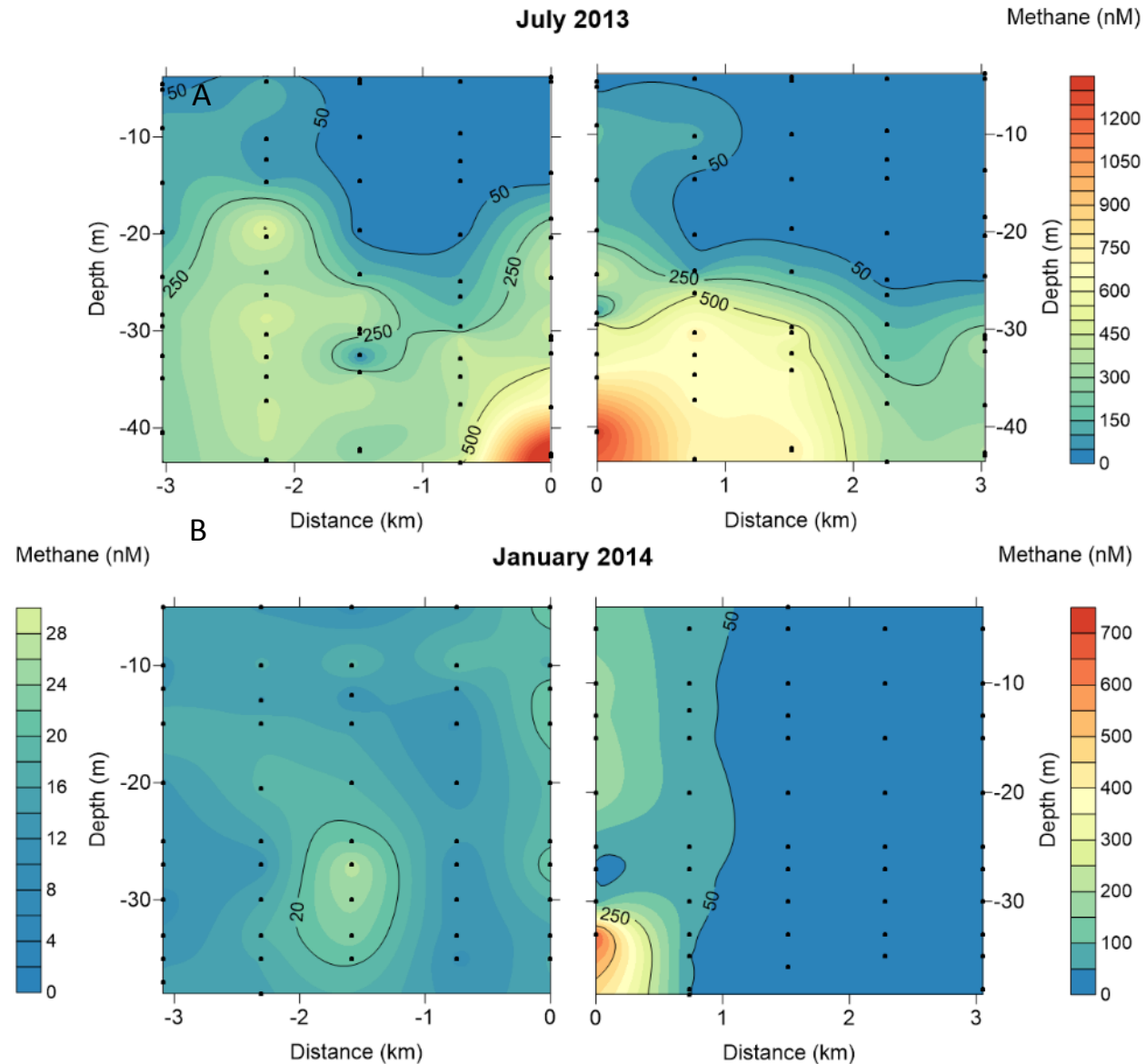


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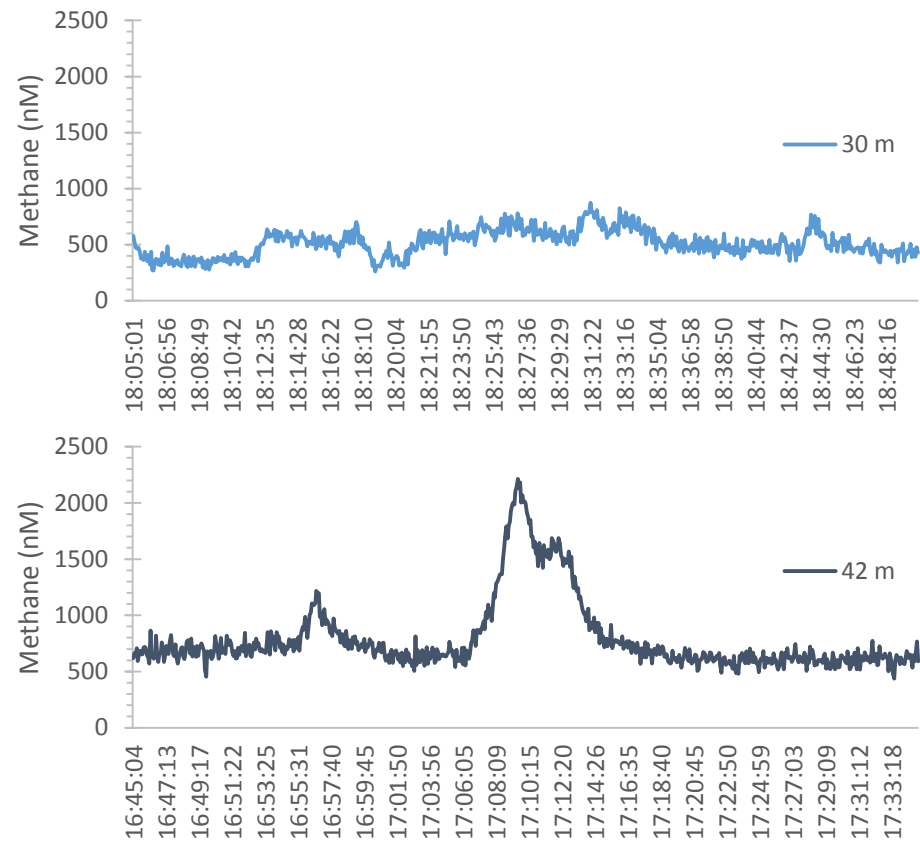
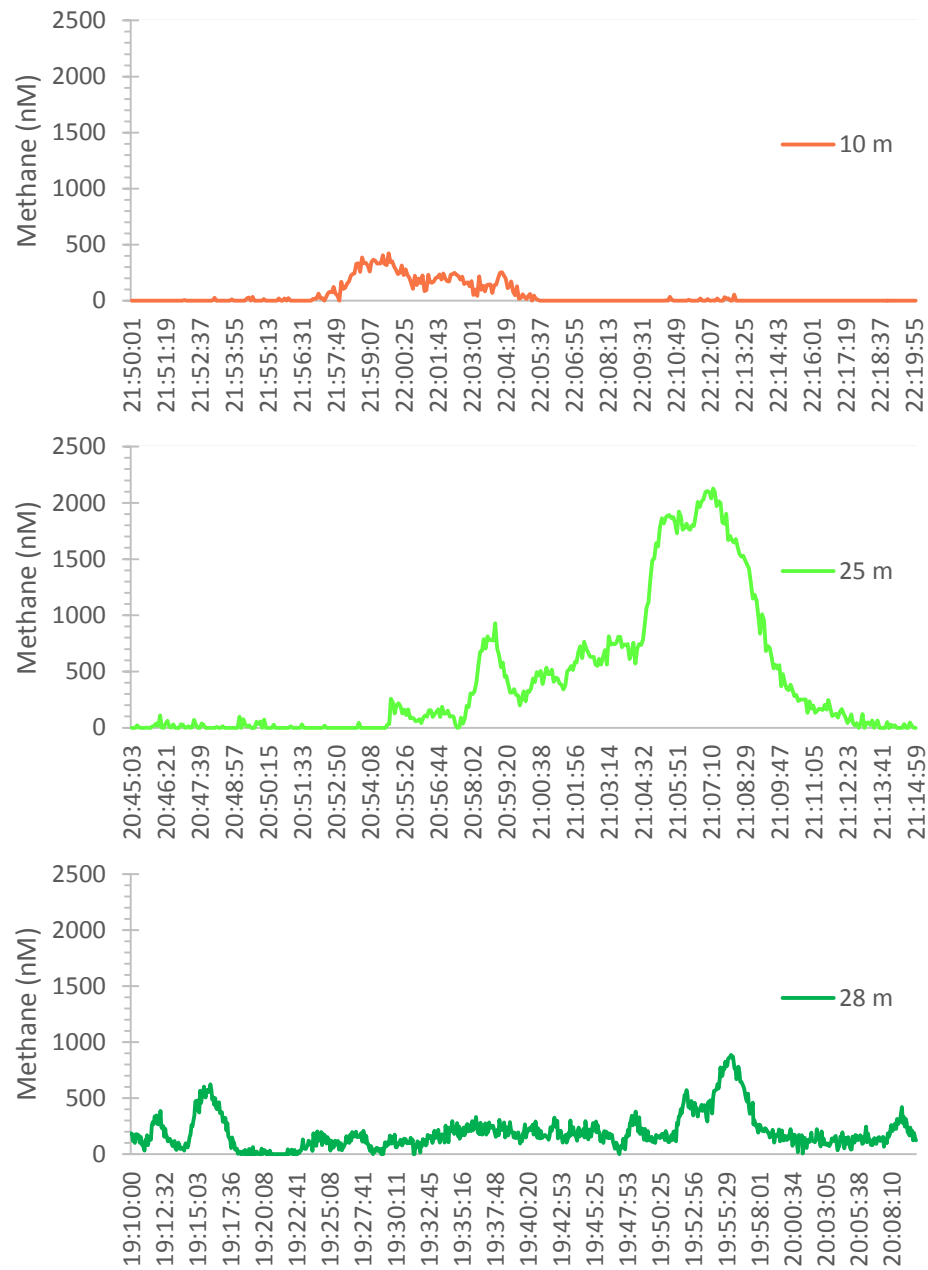


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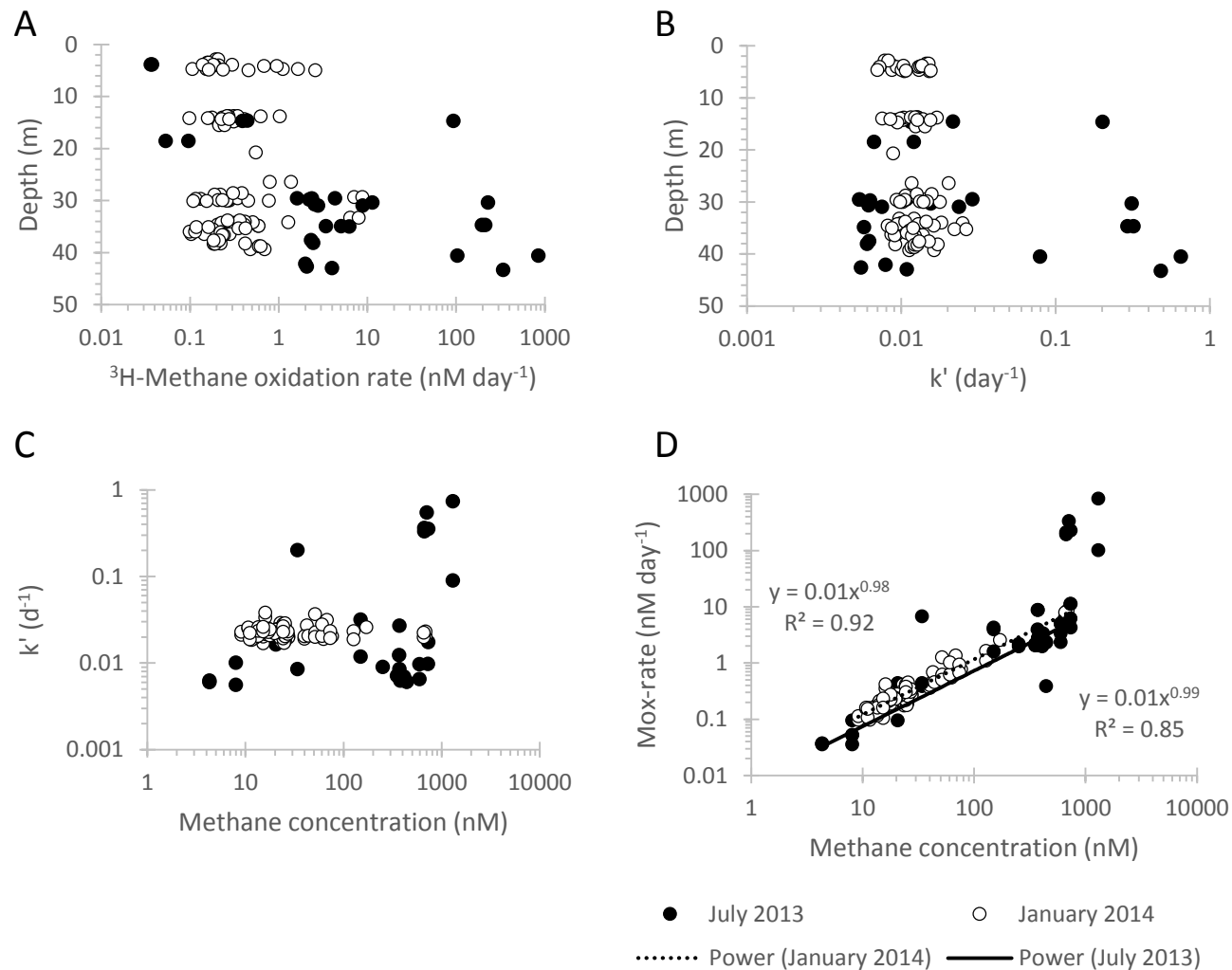


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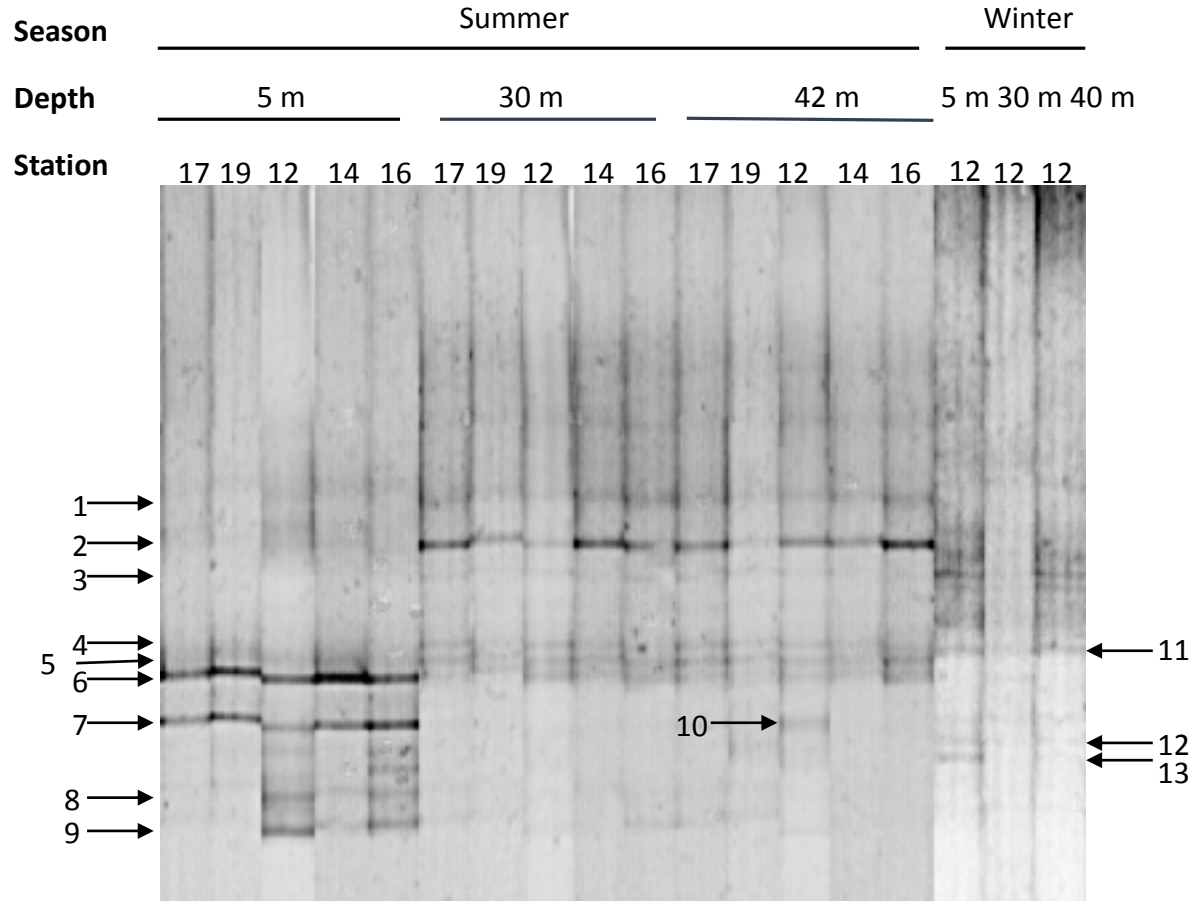
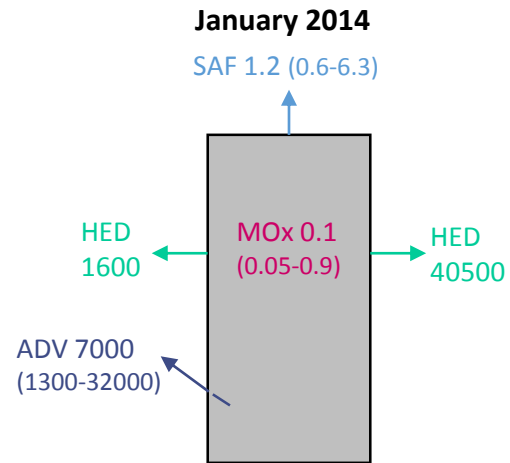
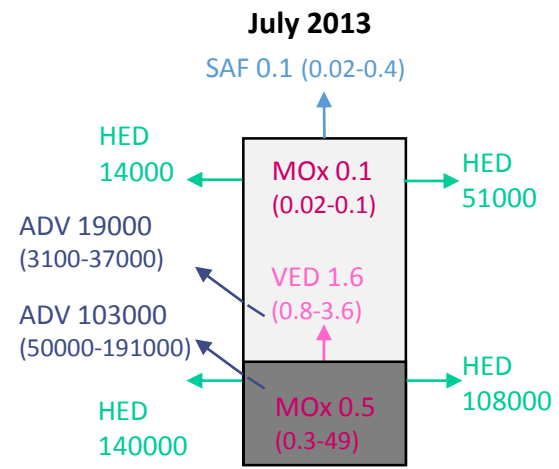


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SAF – Sea Air Flux
 MOx – Methane Oxidation rate
 VED – Vertical Eddy Diffusion
 HED – Horizontal Eddy Diffusion
 ADV – Advection
 Median of estimates (range of estimates)

Fig. 8: Sketch of transport and loss terms estimated for the study area in $\text{nmol m}^{-2} \text{s}^{-1}$.