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Productivity and Temperature as Drivers of Seasonal and Spatial Variations of Dissolved Methane in the Southern Bight of the North Sea

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ABSTRACT

Dissolved CH_4 concentrations in the Belgian coastal zone (North Sea) ranged between 670 nmol l^{-1} nearshore and 4 nmol l^{-1} offshore. Spatial variations of CH_4 were related to sediment organic matter (OM) content and gassy sediments. In nearshore stations with fine sand or muddy sediments, the CH_4 seasonal cycle followed water temperature, suggesting methanogenesis control by temperature in these OM-rich sediments. In offshore stations with permeable sediments, the CH_4 seasonal cycle showed a yearly peak following the chlorophyll-*a* spring peak, suggesting that in these OM-poor sediments, methanogenesis depended on freshly produced OM delivery. This does not exclude the possibility that some CH_4 might originate from dimethylsulfide (DMS) or dimethylsulfoniopropionate (DMSP) or methylphosphonate transformations in the most offshore stations. Yet, the average seasonal CH_4 cycle was unrelated to those of DMS(P), very abundant during the *Phaeocystis* bloom. The annual average CH_4 emission was 126 mmol m^{-2} y^{-1} in the most nearshore stations ($\sim$4 km from the coast) and 28 mmol m^{-2} y^{-1} in the most offshore stations ($\sim$23 km from the coast), 1260–280 times higher than the open ocean average value (0.1 mmol m^{-2} y^{-1}). The strong control of CH_4 by sediment OM content and by temperature suggests that marine coastal CH_4 emissions, in particular in shallow areas, should respond to future eutrophication and warming of climate. This is supported by the comparison of CH_4 concentrations at five stations obtained in March 1990 and 2016, showing a decreasing trend consistent with alleviation of eutrophication in the area.

Key words: methane; North Sea; sediments; eutrophication; dimethylsulfide; dimethylsulfoniopropionate.

INTRODUCTION

Methane (CH_4) is the second most important greenhouse gas (GHG) after CO_2 (IPCC 2013), but has a shorter residence time in the atmosphere (10 y). This means that alleviating CH_4 emissions could represent an efficient option for mitigation of climate change, because CH_4 accounts for 32% of the anthropogenic global radiative forcing by

well-mixed GHGs in 2011 relative to 1750 (IPCC 2013). This requires a full account with a reasonable accuracy of the sources and sinks of CH_4. Yet, there are large uncertainties in the quantification of natural and anthropogenic CH_4 sources and sinks (Kirschke and others 2013; Saunois and others 2016). The open ocean is a very modest source of CH_4 to the atmosphere (0.4–1.8 $TgCH_4$ y^{-1}, Bates and others 1996; Rhee and others 2009) compared to other natural (220–350 $TgCH_4$ y^{-1}) and anthropogenic (330–335 $TgCH_4$ y^{-1}) CH_4 emissions (Kirschke and others 2013). Coastal regions, and in particular estuarine zones, are more intense sources of CH_4 to the atmosphere (Scranton and McShane 1991; Bange and others 1994; Rehder and others 1998; Upstill-Goddard and others 2000; Middelburg and others 2002; Borges and Abril 2011; Upstill-Goddard and Barnes 2016) than open oceanic waters. The CH_4 emission to the atmosphere from coastal areas is sustained by riverine inputs and methanogenesis in the sediments due to high organic matter (OM) deposition (Scranton and McShane 1991; Middelburg and others 1996, 2002; Borges and Abril 2011). Additionally, natural gas seeps are sources of CH_4 leading to high dissolved CH_4 concentrations in bottom waters (from dozens of nmol l^{-1} up to several μmol l^{-1}; Mau and others 2007, 2015; Solomon and others 2009; Shakhova and others 2010; Schmale and others 2010; Schneider von Deimling and others 2011; Faure and others 2010; Gentz and others 2014; Graves and others 2015). In thermally stratified conditions, CH_4 removal by microbial oxidation and lateral physical transport leads to much lower CH_4 concentrations in surface waters (5–20 nmol l^{-1}) than in deeper waters. In contrast, in vertically well-mixed shallow coastal areas, such as the Southern Bight of the North Sea (SBNS), the CH_4 is efficiently mixed from bottom waters to surface waters, leading to high CH_4 concentrations and emissions to the atmosphere (Borges and others 2016).

Over-saturation of CH_4 with respect to atmospheric equilibrium (5–75%) is ubiquitous in the surface waters of the open ocean. This has been coined the "oceanic CH_4 paradox" (Kiene 1991), because oceanic surface waters are well oxygenated and methanogenic archaea are assumed to be strictly anaerobic. Several hypotheses have been put forward to explain this paradox, such as the occurrence of methanogenesis in anaerobic microenvironments in organic particles and aggregates (Karl and Tilbrook 1994) or in the guts of zooplankton (Oremland 1979; De Angelis and Lee 1994). More recently, CH_4 production has been linked to the transformation of methylated molecules such as methylphosphonate (Karl and others 2008; del Valle and Karl 2014; Repeta and others 2016) or dimethylsulfide (DMS), dimethylsulfoniopropionate (DMSP), dimethylsulfoxide (DMSO) and related demethylation products (methanethiol and mercaptopropionate; Damm and others 2008, 2010, 2015; Zindler and others 2013; Florez-Leiva and others 2013). Oceanic semi-labile dissolved organic matter contains methylphosphonate esters (Repeta and others 2016), whereas DMSP and DMSO are produced in large quantities by several species of phytoplankton (Keller and others 1989; Simó and Vila-Costa 2006). Yet, evidence for the formation of CH_4 from DMS(P,O) remains circumstantial and is mainly based on correlations between CH_4 and chlorophyll-a (Chl-a) or DMS(P,O) concentrations. Further, the mechanisms of CH_4 formation from DMS(P,O) remain elusive, whether abiotic (Althoff and others 2014) or biologically mediated by bacteria (Damm and others 2015) or by phytoplankton (Lenhart and others 2016). Production of CH_4 from methylphosphonate is attributed to microbial activity in phosphate-stressed oceanic regions (Karl and others 2008; Metcalf and others 2012; Repeta and others 2016). In freshwater lakes, CH_4 concentrations correlate to phytoplankton biomass and production (Bogard and others 2014) and this has been attributed to methanogenesis in aerobic conditions by methanogen archaea fixed at the surface of phytoplankton cells (Grossart and others 2011). Whatever mechanisms are responsible for the "oceanic CH_4 paradox," the CH_4 production in oxic open ocean surface waters should be linked more or less directly to primary production. In shallower waters, however, high dissolved CH_4 concentrations are frequently attributed to sedimentary methanogenesis in both coastal environments (for example, Oremland 1975; Crill and Martens 1983; Middelburg and others 1996; Martens and others 1998; Bange 2006; Egger and others 2016; Sawicka and Brüchert 2017) and inland waters (Bastviken and others 2004; Borges and others 2015; Stanley and others 2015) due to water depth in these environments, and close coupling between benthic and pelagic processes.

In this study, we report a yearly data set of CH_4 concentrations in surface waters of the Belgian coastal zone (BCZ) obtained in 2016 at nine fixed stations, at bimonthly intervals during spring and monthly intervals during the other seasons (Figure 1). This is a shallow (<30 m) and permanently well-mixed coastal area with multiple possible sources of CH_4 such as from rivers and gassy sedi-
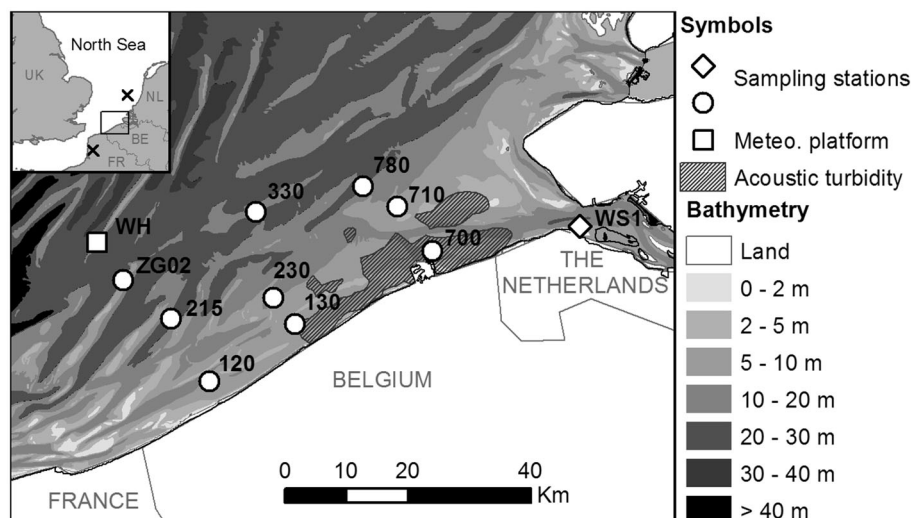
Figure 1. Bathymetry of the Belgian coastal zone and the nine stations sampled in 2016 (*circles*), station WS1 that was sampled from 2009 to 2013 (*diamond*), the platform where wind speeds were measured at sea (Westhinder, WH, *square*) and the two National Centers for Environmental Prediction (NCEP) grid points (*crosses in the inset map*). Acoustic turbidity coverage is derived from Le Bot and others (2005).

ments, and where intense phytoplankton blooms are dominated by the high DMSP producing microalgae *Phaeocystis globosa* (Lancelot and others 2005), leading to high DMSP and DMS concentrations (Turner and others 1988, 1996; Gypens and others 2014). Furthermore, the BCZ is a site of important OM sedimentation and accumulation (Mommaerts and others 1984; Verfaillie and others 2006) unlike the rest of the North Sea (de Haas and van Weering 1997).

MATERIALS AND METHODS

Data were collected in 2016 during 16 cruises of 1- or 2-day duration in the BCZ on the *RV Simon Stevin* at nine fixed stations (Figure 1). Sampling was carried out in surface waters (3 m depth) with a 4-l Niskin bottle mounted on a six-bottle rosette connected to a conductivity temperature depth (CTD) probe (Sea-bird SBE25). Sampling was only made in surface waters because we previously had shown that there are no major vertical gradients (between surface and bottom waters) of salinity, temperature and CH_4 in the BCZ which is a permanently well-mixed area due to its shallowness and strong tidal currents (Borges and others 2016). Consequently, there is no occurrence of hypoxia in the BCZ. Duplicate water samples for the determination of dissolved CH_4 concentration were collected in borosilicate serum bottles (50 ml) with silicone tubing, left to overflow, poisoned with a saturated solution of $HgCl_2$ (100 µl), sealed with a butyl stopper, crimped with an aluminum cap. Samples for total DMSP ($DMSP_t$; 10 ml of unfiltered water) were collected in borosilicate vials (20 ml) sealed with polytetrafluoroethylene (PTFE)-coated stoppers and stabilized with 50 µl of H_3PO_4 (50%;

Stefels 2009). We acknowledge that this method can lead to a substantial under-estimation of $DMSP_t$ in samples containing *Phaeocystis* due to cleavage by DMSP-lyase in acid conditions (del Valle and others 2011). The extent of under-estimation will be discussed in detail in a parallel study (Speeckaert and others unpublished); nevertheless, given the dominance in study zone of *Phaeocystis* in DMSP production compared to diatoms, and assuming a systematic bias, then the seasonal variations and spatial gradients of DMSP should be correctly captured with the present data set and sufficient for the purpose of this study (comparison of patterns of variability of DMS(P) and CH_4). Samples for DMS (30 ml of unfiltered water) were collected in borosilicate vials (50 ml) sealed with PTFE-coated stoppers. Additional samples for particulate and dissolved DMSP and DMSO were also collected but will not be presented here. Samples for the determination of Chl-*a* were filtered on Whatman GF/F glass fiber filters (47 mm diameter) and stored frozen (−20°C).

The concentration of CH_4 was determined with the headspace equilibration technique and a gas chromatograph (GC) equipped with a flame ionization detector (FID) (SRI 8610C) calibrated with CH_4:CO_2:N_2O:N_2 mixtures (Air Liquide Belgium) of 1, 10 and 30 ppm CH_4. A detailed methodological description is given by Borges and others (2016). Precision was better than ±4% based on analysis of 137 duplicate samples.

The concentrations of DMS and of $DMSP_t$ (after hydrolysis into DMS with NaOH) were determined by purge and trap in liquid N_2 and an Agilent 7890B GC equipped with a FID and a flame photometric detector (FPD), although only the data obtained with the FPD were used. A detailed

Table 1. Annual Average Air-Sea CH_4 Flux (F_{CH4}) Calculated with Wind Speeds from National Centers for Environmental Prediction (NCEP) and from the Westhinder Platform (WH) in the Belgian Coastal Zone at Nine Stations in 2016

Station	F_{CH4} (NCEP) (mmol m^{-2} y^{-1})	F_{CH4} (WH) (mmol m^{-2} y^{-1})
ZG02	3 ± 3	8 ± 8
330	4 ± 4	12 ± 13
780	23 ± 25	66 ± 66
215	6 ± 7	17 ± 17
230	8 ± 10	23 ± 27
710	28 ± 33	88 ± 116
120	14 ± 14	42 ± 42
130	47 ± 80	152 ± 274
700	61 ± 56	184 ± 176
Nearshore stations*	40 ± 60	126 ± 200
Offshore stations**	10 ± 17	28 ± 47
All stations	22 ± 41	66 ± 134

*120, 130, 700.
**ZG02, 330, 780.

methodological description is given by Borges and Champenois (2015), based on standard protocols given by Stefels (2009).

The concentration of Chl-*a* was determined on acetone (90%) extracts by fluorimetry (Holm-Hansen and others 1965) using a Kontron SFM25 fluorometer.

The air-sea CH_4 flux (F_{CH4}) was computed using the gas transfer velocity parameterization as a function of wind speed of Nightingale and others (2000), and the Schmidt number of CH_4 in seawater computed from temperature according to Wanninkhof (1992). We used two sets of wind speed data, a synthetic product from the National Centers for Environmental Prediction, hereafter referred to as NCEP, and at-sea measurements from a meteorological platform (Westhinder, Figure 1). Wind speed data from the NCEP reanalysis daily averages surface flux (http://www.cdc.noaa.gov/) were obtained at 2 grid points covering the sampled region (3.7500°E 52.3799°N; 0.000°E 50.4752°N) that were averaged. Daily wind speed data from the Westhinder platform (2.4378°E 51.3883°N) were acquired by the Meetnet Vlaamse Banken and retrieved from the Vlaams Instituut voor de Zee (VLIZ) data center (http://www.vliz.be/en/measurement-network-flemish-banks). We used a constant atmospheric value of CH_4 of 1.9 ppm, because the dissolved CH_4 concentrations were always well above atmospheric equilibrium, and the typical spatial and temporal variability of atmospheric CH_4 mixing ratios of about ±0.1 ppm will have a negligible effect on the F_{CH4} computation.

F_{CH4} was computed using daily wind speed values and values of salinity, water temperature and dissolved CH_4 concentrations that were interpolated linearly between cruises to obtain daily values. The daily F_{CH4} estimates were then averaged to obtain a yearly mean at each station (Table 1).

The georeferenced and time-stamped data set of dissolved CH_4 concentration, salinity and temperature is available in a Supplemental File.

RESULTS AND DISCUSSION

Spatial Variations of CH_4

The dissolved CH_4 concentrations ranged across all sites and all cruises from 4 to 670 nmol l^{-1} (Figure 2). The annual average dissolved CH_4 concentration showed distinct spatial gradients, with higher values nearshore, for example, 4 km away from the coast (stations 120, 130, 700) than offshore, for example, 23 km away from the coast (stations ZG02, 330, 780). There was also a longitudinal gradient with the two most eastern stations (700 and 710) showing higher values than at other stations.

This spatial pattern might have resulted from inputs of CH_4 from the nearby Scheldt estuary, as riverine–estuarine inputs have been hypothesized to be responsible for high CH_4 concentrations in the SBNS and the German Bight (Scranton and McShane 1991; Rehder and others 1998; Upstill-Goddard and others 2000). The surface salinity annual averages ranged between 30.5 at station 700 and 34.4 at station ZG02, testifying to the
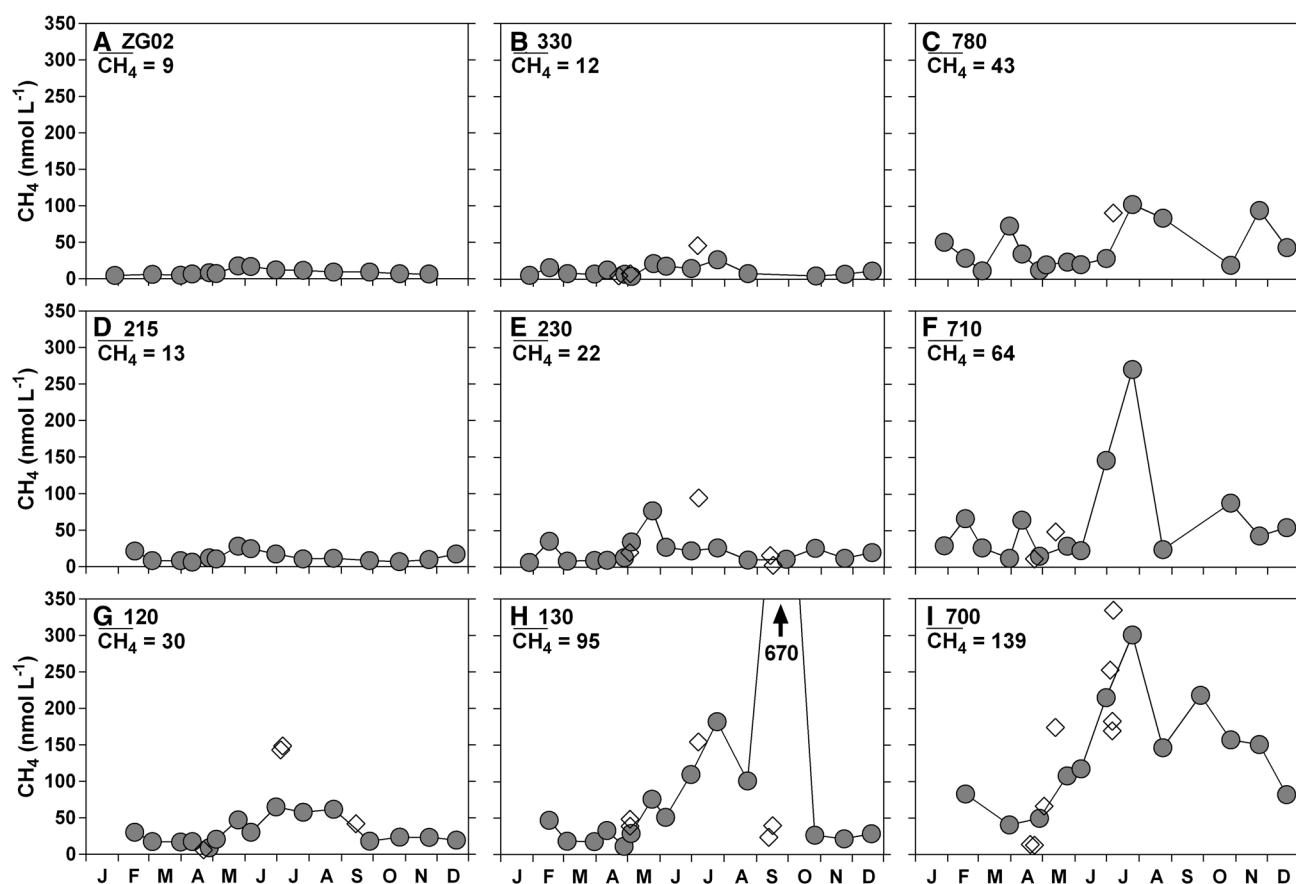
Figure 2. Seasonal variations of dissolved CH_4 concentration at nine stations in the Belgian coastal zone during year 2016 (*filled circles*) and from the more limited data set acquired in 2010–2011 (*open diamonds*, Borges and others 2016). The *plots* are arranged to correspond to the spatial distribution of the stations (Figure 1), *left* to *right* corresponding to west to east and *top* to *bottom* corresponding from offshore to nearshore. Annual average dissolved CH_4 concentration is indicated in the *top left-hand corner* of the plots.

influence of estuarine inputs in the BCZ (Borges and Frankignoulle 1999, 2002). We previously obtained a data set of dissolved CH_4 concentrations in the Scheldt estuary from 2009 to 2013 (monthly sampling, own unpublished data). For this period, the overall average at the mouth of the Scheldt (station WS1, Figure 1) was 107 nmol l^{-1} with an average salinity of 28.5 ($n = 70$). This value is lower than the average value of 139 nmol l^{-1} at station 700 with an average salinity of 30.5. Stations WS1 and 700 are located about 25 km apart, and it requires about 5 days for the water mass to travel from the mouth of the Scheldt to station 700 (Delhez and Carabin 2001). During this travel, the CH_4 will evolve as a result from the balance of sinks of CH_4 [F_{CH4} and microbial CH_4 oxidation (MOX)] and sources of CH_4 [flux from the sediments (F_{sed})]. We modeled the evolution of a water parcel with an initial dissolved CH_4 concentration of 107 nmol l^{-1} (average value at station WS1)

assuming that there was no input of CH_4 from the sediments ($F_{sed} = 0$), so that dissolved CH_4 only changed as a function of F_{CH4}, MOX and mixing with offshore water (average salinity increases from 28.5 to 30.0 between the stations WS1 and 700). The model predicts that in 5 days the dissolved CH_4 concentration decreases from 107 to 32 nmol l^{-1} (Figure 3). Although it can be argued that the parameterization of MOX we used based on the data of Ward and Kilpatrick (1990) in Saanich Inlet (British Columbia) might not be adequate for the BCZ, the model that is only based on F_{CH4} also predicts a strong decrease of CH_4 to 47 nmol l^{-1}. Hence, it is not possible to explain the high dissolved CH_4 concentrations at station 700 based only on the inputs of CH_4-rich waters from the Scheldt estuary, and an additional source of CH_4 is required, most likely from the sediments of the BCZ, in line with our analysis based on mixing curves based on an earlier CH_4 data set (2010–
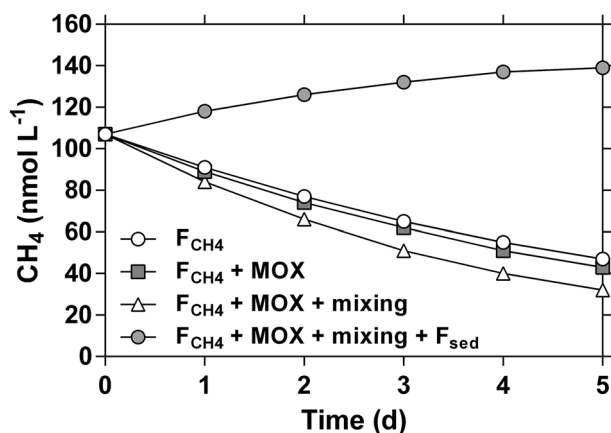
Figure 3. Modeled evolution of water parcel with an initial dissolved CH_4 concentration of 107 nmol l^{-1} corresponding to the annual average at Scheldt mouth (station WS1) from a monthly monitoring from 2009 to 2013 ($n = 70$, unpublished data). The model runs during 5 days correspond to time for the water parcel to travel from the Scheldt mouth (station WS1) to station 700. The model accounts for the exchange of CH_4 with atmosphere (F_{CH4}) computed with a constant wind speed of 5.5 m s^{-1}, a water temperature of 12.5°C (both annual average values) and assuming a depth of 9 m. The model includes methane oxidation (MOX) that was computed from a first-order parameterization derived from the data reported by Ward and Kilpatrick (1990) in Saanich Inlet (British Columbia; MOX = 0.0153* [CH_4], where MOX is in nmol l^{-1} day^{-1} and [CH_4] is in nmol l^{-1}, $r^2 = 0.63$, $n = 17$). A linear mixing between initial water parcel (salinity 28.5, average at stations WS1) and offshore water (stations ZG02, salinity 34.2, dissolved CH_4 concentration of 9 nmol l^{-1}) is used in order to attain the salinity of 30.5 at station 700 in 5 days. A simulation includes a net constant CH_4 flux from the sediments (F_{sed}) that was fitted to 309 μmol m^{-2} day^{-1} to force a model trajectory that attains after 5 days a final concentration CH_4 of 139 nmol l^{-1} corresponding to the annual average at station 700.

2011) with a lower seasonal coverage (Borges and others 2016). Indeed, it is possible to compute a model trajectory that predicts after 5 days a concentration of 139 nmol l^{-1} corresponding to the annual average at station 700, if a constant F_{sed} of 309 μmol m^{-2} day^{-1} is used. The F_{sed} value was fitted to force the model trajectory, and it is within the range of F_{sed} values reported in estuarine and nearshore coastal environments as compiled by Borges and Abril (2011), including the rates reported by Middelburg and others (1996) from intertidal sediments of the adjacent Scheldt estuary.

If we assume that the CH_4 source is not sedimentary but occurring in the water column, the corresponding volumetric source is 33 nmol l^{-1} day^{-1}. This value is higher than the rates of CH_4

production in incubations spiked with DMS(P) with samples from the Arctic Ocean (~15 nmol l^{-1} day^{-1}, Damm and others 2010) and from the Central Chile upwelling ecosystem (~2 nmol l^{-1} day^{-1}, Florez-Leiva and others 2013). The incubation with Arctic Ocean water was spiked for a final concentration of DMSP of 50 μmol l^{-1} (Damm and others 2010), three to four orders of magnitude higher than the natural abundance of DMSP (5–60 nmol l^{-1}, Damm and others 2010). The incubation with water from the Central Chile upwelling ecosystem was spiked for a final concentration of DMS of 6 nmol l^{-1}, close to natural abundance of DMS in the area (Florez-Leiva and others 2013). In natural (non-spiked) samples, reported rates of water column CH_4 production are even lower such as in aggregates of organic matter in the North Pacific Ocean (~0.05 nmol l^{-1} day^{-1}, Karl and Tilbrook 1994) or from copepods during their peak of abundance during the spring bloom in Long Island Sound (0.2–1.0 nmol l^{-1} day^{-1}, De Angelis and Lee 1994). Although we cannot exclude the possibility of CH_4 production in the water column from methylphosphonate as described by Repeta and others (2016), it would require a daily conversion of ~50% of the methylphosphonate pool. This seems unreasonably high considering that Repeta and others (2016) computed a daily cycling of 0.3% of the methylphosphonate inventory to sustain the CH_4 levels in the Pacific Ocean. We estimated the possible methylphosphonate concentration in the BCZ using an average concentration of dissolved organic phosphorus (DOP) of approximately 1000 μmol l^{-1} (van der Zee and Chou 2005), and assuming methylphosphonate represented approximately 7% of DOP based on the data given by Repeta and others (2016) in the Pacific Ocean. Finally, CH_4 concentrations in the BCZ (range 4–670 nmol l^{-1}) were much higher than those typically encountered in open oceanic surface waters, less than 4 nmol l^{-1} (Rhee and others 2009), strongly suggesting additional sources of CH_4 in the BCZ than those usually evoked to explain the ''CH_4 ocean paradox'' such as production in aggregates, in copepod guts and from the demethylation of methylphosphonate or of DMS(P).

The most likely variable that controls the spatial patterns of benthic methanogenesis is the OM content of sediments. A positive relationship was found between the average dissolved CH_4 concentration and the OM content of sediment (%OM) reported by Braeckman and others (2014; Figure 4A). The %OM content of shallow sediments depends on the deposition regime (for example, de
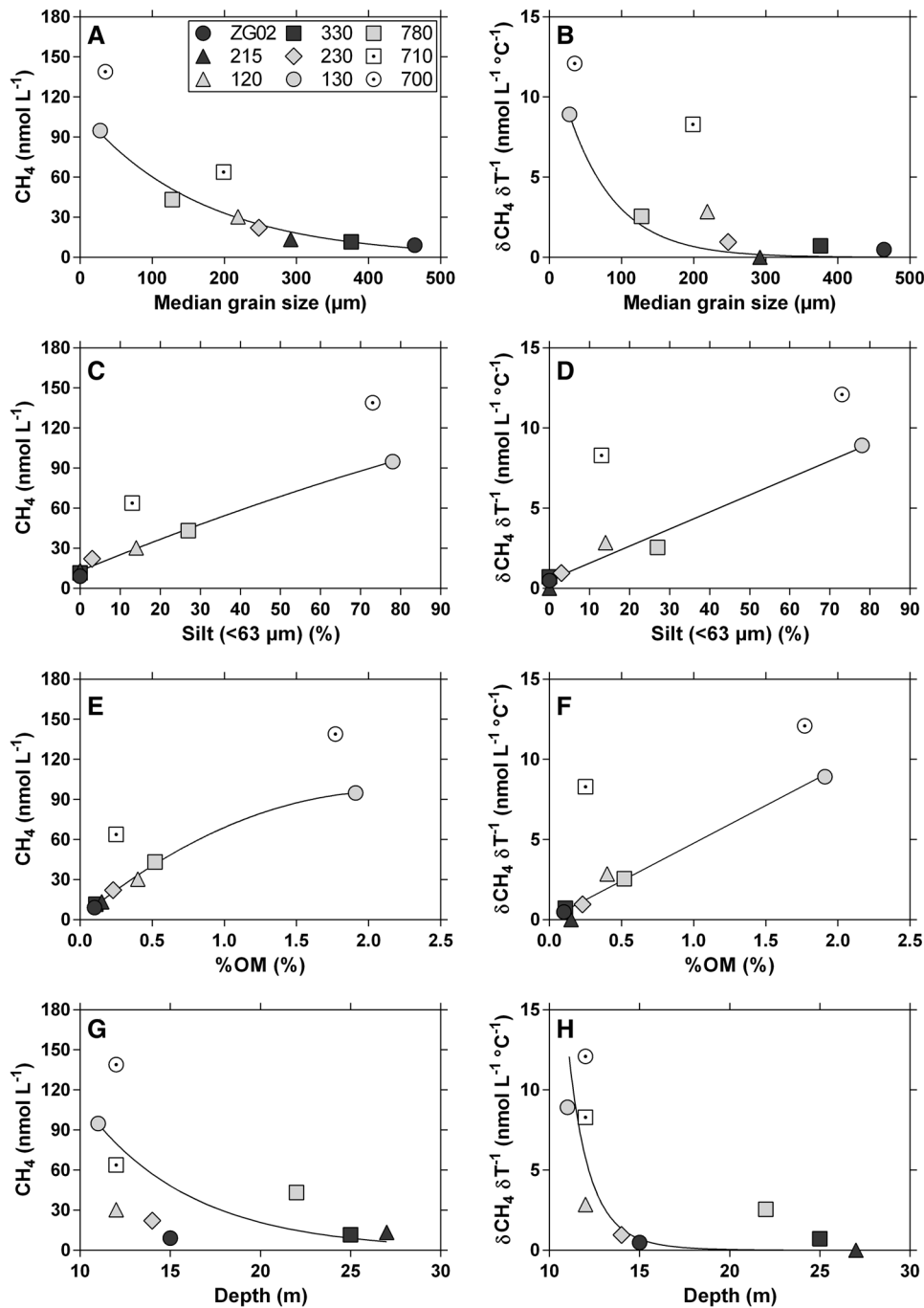
Figure 4. Annual average of dissolved CH_4 concentration and change of CH_4 with water temperature ($\delta CH_4 \, \delta T^{-1}$, computed as the slope of the linear regression of CH_4 versus temperature) at nine stations in the Belgian coastal zone in 2016 as function of sediment characteristics: organic matter content (%OM) (**A**, **B**), silt content [silt (<63 μm)] (**C**, **D**), median grain size (**E**, **F**) and depth (**G**, **H**). Sediment characteristics are annual averages obtained in 2011 reported by Braeckman and others (2014). *Solid lines* are best fit curves that provide the tendency of all stations excluding 700 and 710.

Haas and van Weering 1997); hence, a relationship was also found between average dissolved CH_4 concentration and silt content (Figure 4C) and median grain size (Figure 4D). Because the high deposition sites are located in the shallower regions, a general negative relationship was also found between dissolved CH_4 concentration and depth (Figure 4G). Stations 700 and 710 stand out from the overall patterns between average dissolved CH_4 concentration and sediment charac-

teristics (Figure 4A, C, E). Station 700 is located well inside of the region of acoustic turbidity (Le Bot and others 2005; Figure 1) that is indicative of gassy sediments most probably with high CH_4 content (Missiaen and others 2002). This could explain the deviation of the average dissolved CH_4 concentration of station 700 from the general patterns for the other stations (Figure 4A, C, E), due to additional input of CH_4 from gassy sediments, that we hypothesized to be significant in the area based
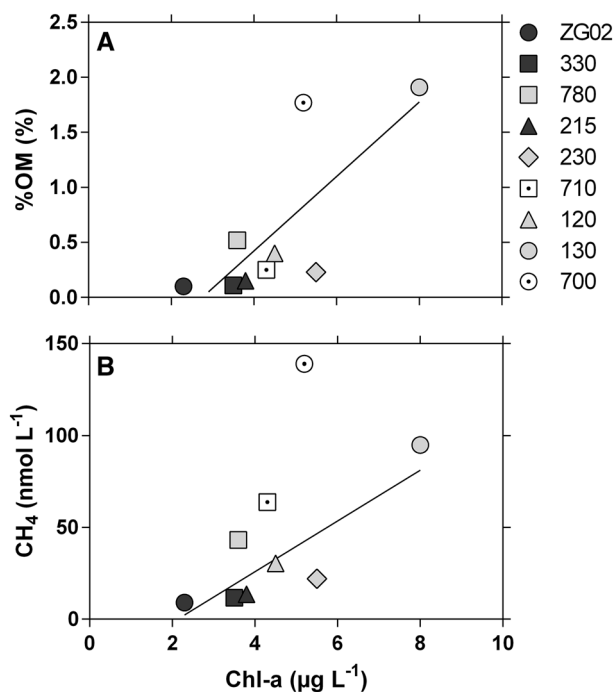
Figure 5. Relationship of annual averages of sediment organic matter content [%OM, Braeckman and others (2014)] and water column chlorophyll-a (Chl-*a*) (**A**) and dissolved CH_4 concentration and Chl-*a* (**B**) at nine stations in the Belgian coastal zone obtained in 2016. *Solid lines* are best fit curves that provide the tendency of all stations excluding 700 and 710.

on a previous data set (Borges and others 2016). The dissolved CH_4 concentration of station 710, located in the near vicinity of the mapped acoustic turbidity region (Figure 1), also deviated from the general patterns with sediment characteristics, but to a lesser extent than station 700. The general residual current direction is westward around station 700 (Delhez and Carabin 2001) so that it would be affected by the nearby surrounding gassy sediments.

There was a positive relationship between sediment %OM and water column Chl-*a* (Figure 5A) consistent with the hypothesis that OM deposition to surface sediments resulted in part from the above water productivity, but also on hydrodynamics that will determine the deposition regime. As a consequence, there was also an overall positive relationship between average dissolved CH_4 concentration and water column Chl-*a* (with stations 700 and 710 standing out; Figure 5B). However, this pattern is based on annual averages and does not necessarily imply a production of CH_4 directly related to phytoplankton through, for example, DMS(P) transformations, as suggested in some oceanic settings such as the northwestern

Barents Sea and the western Pacific Ocean (Damm and others 2008; Zindler and others 2013) or in controlled laboratory conditions (Lenhart and others 2016).

The data of dissolved CH_4 and of sediment characteristics were obtained in different years, respectively, 2016 and 2011. The comparison of the CH_4 data obtained in 2016 with the more limited data set obtained in 2010–2011 (Borges and others 2016), shows that there were inter-annual differences between data sets, more marked in the nearshore stations (for example, 700) than in the offshore ones (for example, 330; Figure 2). At stations 230 and 120, the largest differences between the 2010/11 and 2016 were observed in summer, when biological production of CH_4 was more intense (see below), and possibly more variable. The larger variability in CH_4 at station 700 is consistent with inputs from gassy sediments at this particular station since gas flaring is irregular in time (for example, Schneider von Deimling and others 2011). We tried to quantify inter-annual variations of sediment characteristics using a data set of median grain size and silt content (< 63 μm) obtained at five stations (120, 230, 330, 700, 780) once or twice a year from 2007 to 2013 (Bavo De Witte, Flemish Institute for Agricultural and Fish-
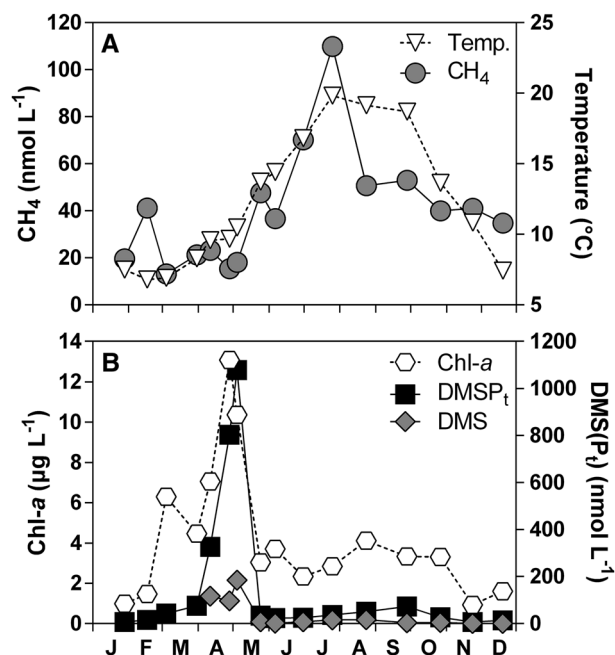

Figure 6. Seasonal variation of average values of the nine stations per cruise of dissolved CH_4 concentration, water temperature, chlorophyll-a (Chl-*a*) concentration, total dimethylsulfoniopropionate (DMSP$_t$) and dimethylsulfide (DMS) in the Belgian coastal zone during year 2016.
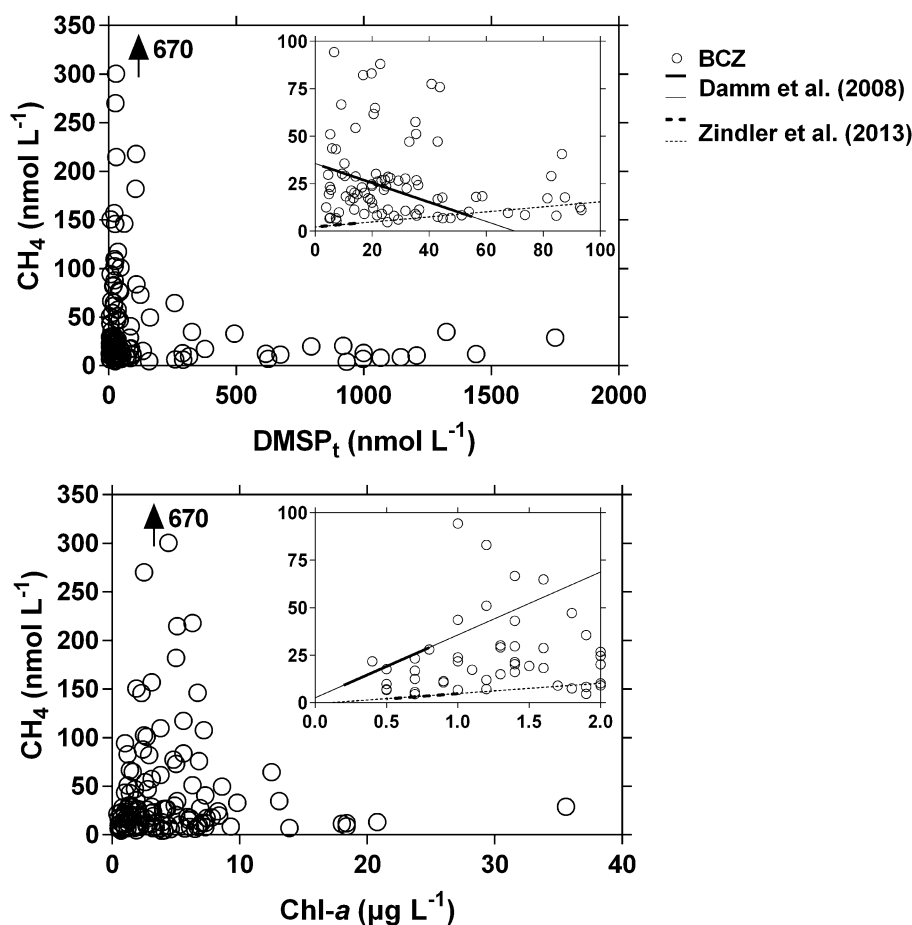
Figure 7. Dissolved CH$_4$ concentration versus total dimethylsulfoniopropionate (DMSP$_t$) and chlorophyll-*a* (Chl-*a*) in the Belgian coastal zone at nine stations during year 2016. Inset shows the relationships between CH$_4$ and DMSP$_t$ and Chl-*a* established in Storfjorden [*solid line*, Damm and others (2008)] and in the western Pacific Ocean [*dotted line*, Zindler and others (2013)]. The *thicker lines* indicate the range constrained by data to calculate the regression lines.

eries Research, personal communication). At individual stations, the median grain size showed a variance ranging between 3% (station 230) and 48% (station 700), yet, despite year-to-year variability, the differences among stations were highly significant for both median grain size and silt content (one-way Kruskal–Wallis analysis of variance test, $p < 0.0001$). We recognize that the dissolved CH$_4$ and sedimentary data sets show year-to-year variability, but the spatial gradients (differences among stations) are overwhelming higher than year-to-year variability; consequently, the conclusions based on the analysis of the spatial gradients should be robust.

Seasonal Variations of CH$_4$

The seasonal amplitude of dissolved CH$_4$ concentration at each station (computed as the difference of yearly maximum and minimum) was very variable from one station to another (Figure 2) ranging from 13 to 658 nmol l^{-1}, at stations ZG02 and 130, respectively. The overall seasonal cycle of CH$_4$ in the BCZ (average of all stations) indicated a yearly minimum in late winter and a maximum in mid-summer following the seasonal temperature cycle (Figure 6A). The seasonal variation of average Chl-*a* followed the typical cycle previously described in the area (Borges and Frankignoulle 1999, 2002; Rousseau and others 2002; Lancelot and others 2005) with a first peak in March (6.3 ± 1.7 µg l^{-1}) corresponding to the spring diatom bloom and a more intense peak in late April (13.1 ± 6.0 µg l^{-1}) corresponding to the *Phaeocystis* bloom (Figure 6B). The concentrations of DMSP$_t$ and DMS peaked during the *Phaeocystis* bloom, with maximal average values of 1079 ± 379 and 184 ± 71 nmol l^{-1}, respectively. These values
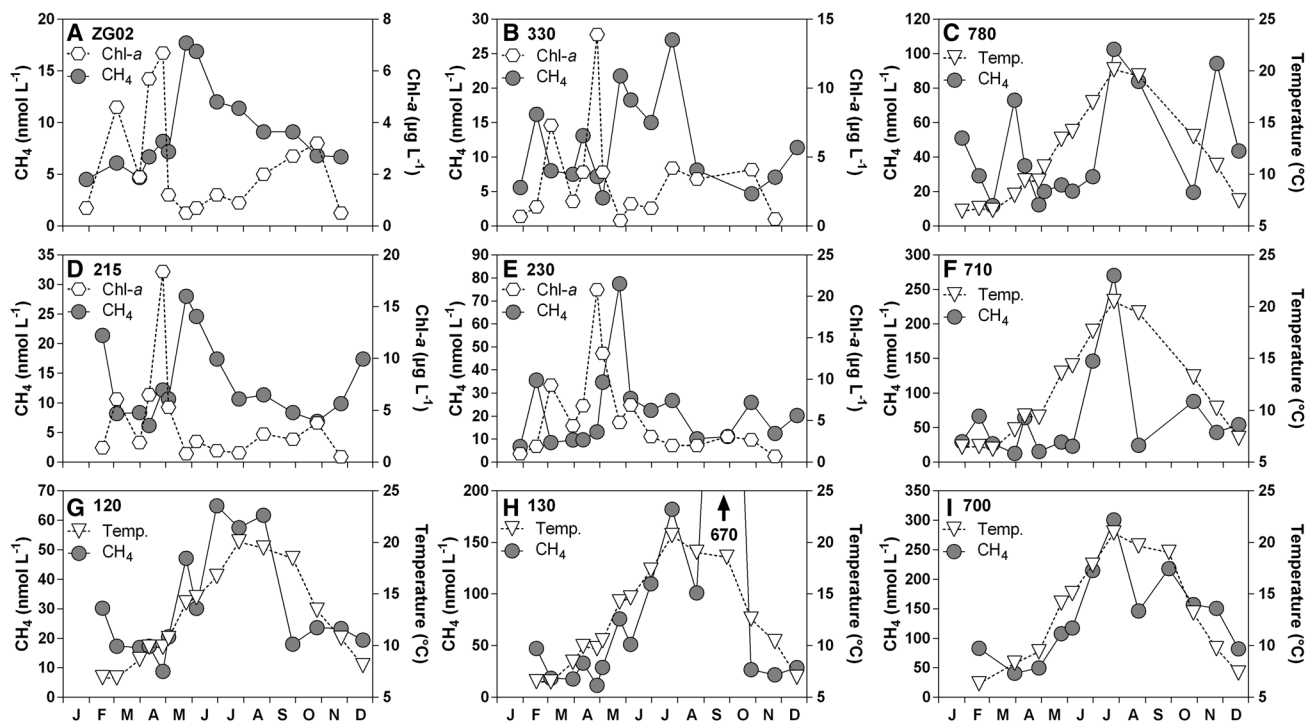
Figure 8. Seasonal variations of dissolved CH_4 concentration, chlorophyll-a (Chl-*a*) concentration and water temperature (°C) at nine stations in the Belgian coastal zone during year 2016. The plots are arranged to correspond to the spatial distribution of the stations (Figure 1), *left* to *right* corresponding to west to east and *top* to *bottom* corresponding from offshore to nearshore.

were higher than those previously reported in the SBNS (Turner and others 1988, 1996) that were compiled and summarized by Gypens and others (2014). This difference is probably related to the fact that previous data were obtained in more offshore and less productive waters, and this will be further investigated and discussed in detail in a parallel study (Speeckaert and others unpublished).

The average dissolved CH_4 concentration peaked in late July (Figure 6A), 82 days after the peak of $DMSP_t$ and DMS (Figure 6B). This would suggest that the CH_4 production in the BCZ is unrelated to DMS(P) transformations in the water column, contrary to the findings in other oceanic areas (Damm and others 2008, 2010, 2015; Zindler and others 2013; Florez-Leiva and others 2013). The latter are in part based on correlations between CH_4 and Chl-*a* or CH_4 and $DMSP_t$. In the BCZ, CH_4 was uncorrelated to $DMSP_t$ and Chl-*a* (Figure 7), and CH_4 concentrations were markedly above the regression lines of CH_4 versus $DMSP_t$ and versus Chl-*a* established in western Pacific Ocean by Zindler and others (2013). This would suggest additional sources of CH_4 in the BCZ (such as sedimentary sources) than those usually evoked to explain the "CH_4 ocean paradox." Damm and

others (2008) also reported a correlation between CH_4 and Chl-*a* and DMSP (albeit negative) in Storfjorden, although the surface CH_4 concentrations up to 40 nmol l^{-1} were higher than those typically encountered in open oceanic surface waters (< 4 nmol l^{-1}; Rhee and others 2009), possibly owing to the shallowness and coastal character of Storfjorden (~ 120 m depth). Although our findings do not invalidate the hypothesis of CH_4 formation from DMS(P) in open oceanic regions, we show that in some coastal waters where DMS(P) production is extremely intense (Figure 6B), CH_4 is mainly related to sedimentary sources that are assumed to be related to benthic methanogenesis and leakage from gassy sediments (Figure 4). This does not exclude the possibility that some of the CH_4 might originate from DMS(P) transformation in the sediments, although the turnover of these compounds is usually quite fast in the water column from a few hours to approximately 1 day (Stefels and others 2007). Copepod biomass has been reported to peak during the early spring diatom bloom in the BCZ, as these organisms are unable to ingest colonies of *Phaeocystis* (Gasparini and others 2000), so that it is also unlikely that the dissolved CH_4 concentration maximum in summer is related
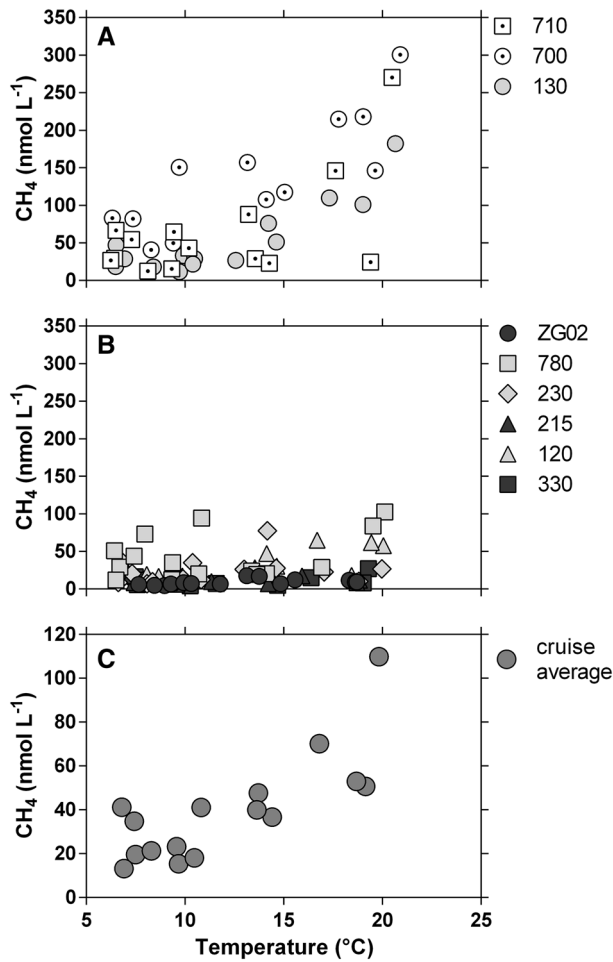
Figure 9. Relationship between dissolved CH_4 concentration and water temperature in the Belgian coastal zone at nine stations during year 2016, for nearshore muddy stations (**A**), for the other stations (**B**) and for the cruise averages (**C**).

to CH_4 production in copepod guts (De Angelis and Lee 1994).

A closer scrutiny of the seasonal cycles of CH_4 at each station allowed us to distinguish two different behaviors regarding CH_4 dynamics and their relation to sediment processes. In the nearshore stations with the highest sediment OM content (%OM > 0.4%; 120, 130, 700, 710 and 780) that were classified as muddy or fine sandy (Braeckman and others 2014), the seasonal cycle of dissolved CH_4 concentration closely followed the seasonal cycle of water temperature (Figure 8), suggesting the control of methanogenesis by temperature in these OM replete sediments. This is consistent with a temperature control of the seasonal variation of benthic remineralization (sediment oxygen demand) in a muddy station of the BCZ (Provoost and others 2013) and the seasonal variations of sedi-
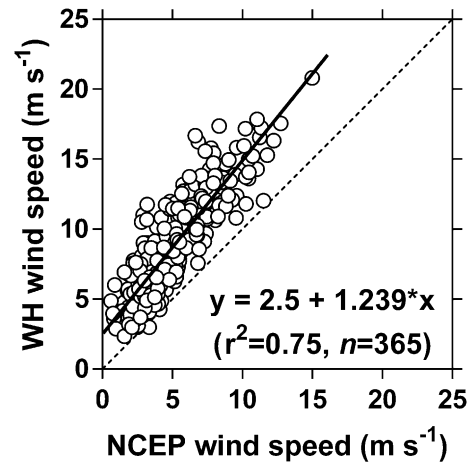

Figure 10. Comparison of daily wind speeds for 2016 measured at sea in a platform (Westhinder, WH) and from a synthetic product (National Centers for Environmental Prediction, NCEP). *Dotted line* indicates the 1:1 line, the *solid line* indicates the linear regression.
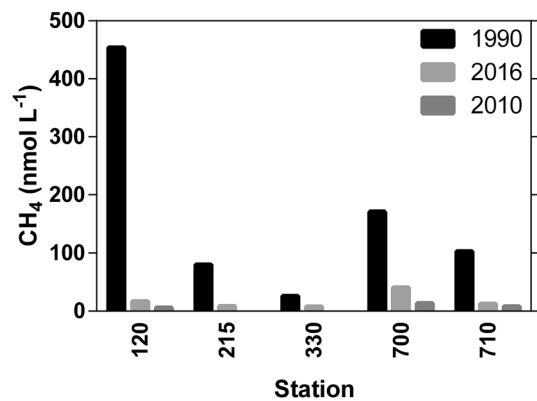

Figure 11. Comparison of dissolved CH_4 concentrations at five stations in the Belgian coastal zone obtained in March 12–14, 1990, and March 30–31, 2016, and at three stations in April 22–23, 2010 (Borges and others 2016). Data in March 1990 were measured by gas chromatography according to the protocols given by Scranton and McShane (1991).

ment-air CH_4 fluxes from inter-tidal muddy sediments in the adjacent Scheldt estuary (Middelburg and others 1996). The highest CH_4 concentration of 670 nmol l^{-1} was measured at station 130 in September 2016 that was higher than the value of September 2010 (Figure 2). Although the exact explanation for such a high value is not known, it occurred after a long spell of warm weather of nearly two months with water temperatures above 18°C. In the offshore stations with lowest sediment OM content (%OM < 0.3; 215, 230, 330, ZG02) that were classified as permeable (Braeckman and
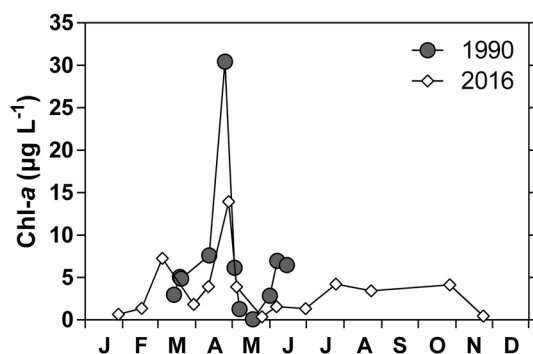
Figure 12. Comparison of chlorophyll-a (Chl-*a*) concentration at station 330 of the Belgian coastal zone in 1990 and 2016. Data were measured with the same method and protocol by the same laboratory (Laboratoire d'Ecologie des Systèmes Aquatiques). Historical data that are methodologically consistent for comparison are only available for station 330 that is located offshore, although stations closer to shore are typically more productive (for example, Borges and Frankignoulle 2002), so that the contrast between the two periods could have been even more marked at these nearshore stations.

others 2014), the seasonal cycle of dissolved CH_4 concentration was different and was marked by a yearly peak following the Chl-*a* spring peak. This suggests that, in these OM-poor sediments, methanogenesis depended on the delivery to the sediments of freshly produced organic matter, as also observed in Eckernförde Bay (Baltic Sea) by Bange and others (2010). The increase of CH_4 followed within a month of the decrease of Chl-*a* due to the shallowness of the area (< 30 m, Figure 1), leading to a transfer of OM from the surface waters to the surface of sediment that was nearly immediate. This is consistent with the seasonal variation of benthic remineralization (sediment oxygen demand) in permeable sediments of the adjacent English Channel that also peaked seasonally in response to deposition of fresh organic matter following the *Phaeocystis* bloom (Rauch and others 2008).

A positive relation between dissolved CH_4 concentration and water temperature was observed on an individual station basis for the nearshore muddy stations (Figure 9A) and also for the cruise averages (Figure 9C), but in the offshore more permeable sediments the CH_4 concentration was unrelated to temperature (Figure 9B). These patterns suggest the importance of temperature control of methanogenesis in the stations that have OM-rich sediments. The optimum temperature for methanogenic archaea is around 35–40°C, so that below those temperatures and in an environment rich in

OM, we would expect a positive relationship between methanogenesis and temperature (Zeikus and Winfrey 1976; Schulz and others 1997; Yvon-Durocher and others 2014).

This can also explain our observation that the change of CH_4 as a function of temperature (δCH_4 δT^{-1}) showed the same patterns as the dissolved CH_4 concentration [positively related to %OM and silt content (Figure 4B, D), negatively related to median grain size and depth (Figure 4F, H)]. It should be noted that higher temperature increases methanogenesis but can also enhance the flux of CH_4 from gassy sediments that we hypothesize to be important at stations 700 and 710. Indeed, the decrease of solubility of CH_4 in response to warming leads to enhanced ebullition from sediments (Martens and others 1998; Wever and others 1998). Below 10°C, the dissolved CH_4 concentration was relatively low (Figure 9A, B, C), uniform and unrelated to temperature, suggesting that CH_4 inputs from sediments were low and/or compensated by loss terms such as physical dispersion, CH_4 emission to the atmosphere and MOX, although MOX is also a temperature-dependent process (Yvon-Durocher and others 2014).

Air-Sea CH_4 Fluxes

We used two sets of wind speed data to compute F_{CH4}, one based on in situ measurements (Westhinder platform) and another modeled (NCEP), for a consistent comparison with previous estimates of F_{CH4} in the BCZ that were computed using NCEP winds (Borges and others 2016). The wind speeds from the NCEP product have been previously shown to be under-estimated (Smith and others 2001); the comparison of the two wind speed data shows that the NCEP data have an offset of 2.5 m s^{-1} compared to in situ data (Westhinder; Figure 10). This has a considerable effect on the F_{CH4} computations that were about 2.7 times higher when computed from the in situ data (Westhinder) than with the NCEP data (Table 1). The F_{CH4} values computed with the NCEP wind speed were consistent with the F_{CH4} values in the same area computed with the same wind product from a more limited CH_4 data set obtained in 2010–2011 (Borges and others 2016). Hereafter, only the F_{CH4} data computed with the in situ wind speed data (Westhinder) are discussed. The annual F_{CH4} values ranged from 8 to 184 mmol m^{-2} y^{-1} at stations ZG02 and 700, respectively (Table 1). Annual average F_{CH4} was 126 mmol m^{-2} y^{-1} in the nearshore area, that is approximately 4 km of the coastline (stations 120, 130 and 700), and

28 mmol m^{-2} y^{-1} in the offshore area, that is approximately 23 km of the coastline (stations ZG02, 330 and 780). These values are high compared to the range of global average F_{CH4} from 8 to 14 mmol m^{-2} y^{-1} in continental shelves (mostly in seasonally stratified regions; Bange and others 1994) and the global average of open oceanic waters (0.07–0.18 mmol m^{-2} y^{-1}; Bates and others 1996; Rhee and others 2009).

Comparison with Data from 1990

Dissolved CH_4 concentrations were measured at five stations in the BCZ in March 1990 (Scranton and McShane 1991) that can be compared to data acquired at the same stations in March 2016 (Figure 11). The average water temperature in March 1990 (8.7 ± 0.5°C) was similar to the one in March 2016 (8.3 ± 0.2°C), as well as average salinity (33.5 ± 1.4 in 1990 vs. 32.8 ± 2.0 in 2016) and average monthly wind speed (6.2 ± 2.4 m s^{-1} in 1990 vs. 5.5 ± 2.1 m s^{-1} in 2016). This suggests that the two cruises were comparable with regard to the seasonal biological and physical cycles. The CH_4 concentrations in March 1990 ranged between 26 and 454 nmol l^{-1} and were systematically higher than in March 2016 when they ranged between 8 and 41 nmol l^{-1}. The same spatial gradients as present day (Figure 2) were observed in March 1990 with higher concentrations in nearshore stations (120, 700 and 710) than offshore stations (215, 330). The largest difference between March 1990 and 2016 was observed at a nearshore station (26.8 times higher at station 120 in 1990 than 2016) and the lowest difference at a more offshore station (3.5 times higher at station 330 in 1990 than 2016). The differences of CH_4 concentration between 1990 and 2016 can be due to long-term trends or inter-annual variability. We do not have additional data in March of other years to evaluate inter-annual variability, but data from April 2010 (Borges and others 2016) at three stations (120, 700 and 710) are also much lower than the March 1990 values (Figure 11).

Older CH_4 data for comparison with present-day data are very rare in marine environments; hence, this comparison 26 y apart can only be made in the BCZ for a single month. The conclusions from such a comparison then need to be interpreted cautiously; nevertheless, the tendency of a decrease of CH_4 concentrations in the BCZ between 1990 and 2016 is consistent with a strong decrease in primary production in the area since the mid-1980s (Lancelot and others 2007). This is consistent with the data of Chl-*a* measured by the same laboratory and with the same protocols and instrumentation available in 1990 and 2016 for station 330, showing maximal yearly values higher in 1990 than 2016 (Figure 12). The decrease since the mid-1980s of primary production resulted from river nutrient load reduction policies and has been shown to also strongly affect the CO_2 and DMS concentrations and air-sea fluxes in the BCZ (Gypens and others 2009; Gypens and Borges 2014). A decrease of primary production would result in a decrease of OM delivery to the sediments that drives the benthic CH_4 production (Figure 4). Although the water temperature during the two cruises in 1990 and 2016 were comparable, the long-term trend in the North Sea for that period is a fast increase in temperature at a rate of 0.035°C y^{-1} (Høyer and Karagali 2017). This would imply that despite the warming of nearly 1°C from 1990 to 2016, the change primary production had a much more important effect on CH_4 concentrations in the BCZ.

The BCZ has experienced during the last decades a decrease in eutrophication that probably resulted in a decrease of CH_4 production in sediments and CH_4 concentrations in surface waters (Figure 11). The corollary implies an increase of CH_4 production and emission might be expected from eutrophication that is ongoing in numerous coastal marine areas worldwide (for example, Díaz and Rosenberg 2008). The positive relationships between dissolved CH_4 concentration and water temperature and sediment OM content we found in the study area suggest that an increase of emissions of CH_4 from coastal areas may occur in response to warming of surface waters and an increase in OM deposition due to eutrophication. Warming of superficial sediments should be more acute in permanently well-mixed continental shelves, which account for about one-third of total continental shelf areas. In addition, in permanently well-mixed continental shelves the transfer of CH_4 from bottom waters to surface waters (hence emission to atmosphere) is much more efficient than in seasonally thermally stratified continental shelves (Borges and others 2016). This scenario contrasts with the one of Naqvi and others (2010) who postulated that in open oceanic regions the CH_4 emissions should not change in response to climate warming and expanding oxygen minimum zones, because an enhancement of methanogenesis was assumed by these authors to be compensated by an increase of MOX.

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