

A decade of methane measurements at the Boknis Eck Time-series Station in the Eckernförde Bay (Southwestern Baltic Sea)

Xiao Ma¹, Mingshuang Sun¹, Sinikka T. Lennartz^{1,2}, and Hermann W. Bange¹

¹ GEOMAR Helmholtz Centre for Ocean Research Kiel, Düsternbrooker Weg 20, 24105 Kiel, Germany

5 ² now at ICBM, University of Oldenburg, Oldenburg, Germany

Correspondence to: Xiao Ma (mxiao@geomar.de)

Abstract. Coastal areas contribute significantly to the emissions of methane (CH₄) from the ocean. In order to decipher its temporal variability in the whole water column, dissolved CH₄ was measured on a monthly basis at the Boknis Eck Time-series Station (BE) located in the Eckernförde Bay (SW Baltic Sea) from 2006 to 2017. BE has a water depth of about 28 m and dissolved CH₄ was measured at six water depths ranging from 0 to 25 m. In general, CH₄ concentrations increased with depth, indicating a sedimentary release of CH₄. Pronounced enhancement of the CH₄ concentrations in the bottom layer (15–25 m) was found during February, May–June and October. CH₄ was not correlated with Chlorophyll *a* or O₂ over the measurement period. Unusually high CH₄ concentrations (of up to 696 nM) were sporadically observed in the upper layer (0–10 m) (e.g. in November 2013 and December 2014) and were coinciding with Major Baltic Inflow (MBI) events. Surface CH₄ concentrations were always supersaturated throughout the monitoring period, indicating that the Eckernförde Bay is an intense but highly variable source of atmospheric CH₄. We did not detect significant temporal trends in CH₄ concentrations or emissions, despite of ongoing environmental changes such as warming and deoxygenation in the Eckernförde Bay. Overall, the CH₄ variability at BE is driven by a complex interplay of various biological and physical processes.

1. Introduction

20 Methane (CH₄) is an atmospheric trace gas which contributes significantly to global warming (IPCC, 2013) and the evolution of stratospheric ozone (WMO, 2018). Atmospheric CH₄ mole fractions have been increasing by about 150 % since the industrial revolution (IPCC, 2013).

The oceanic release of CH₄ to the atmosphere plays a minor role for the global atmospheric CH₄ budget (Saunois et al. 2016). However, coastal areas have been identified as hot spots of CH₄ emissions (see e.g. Bange et al., 1994; Upstill-Goddard et al., 2000; Borges et al., 2016). Dissolved CH₄ in coastal waters is mainly resulting from the interplay of (i) sedimentary sources such as anaerobic methanogenesis during the decomposition of organic matter (Xiao et al., 2018; Dale et al., 2019) or seepage from oil and natural gas reservoirs (Bernard et al., 1976; Hovland et al., 1993; Judd et al., 2002) and (ii) microbial CH₄ consumption which occurs under oxic conditions in the water column and under anoxic conditions in the sediments (Pimenov et al., 2013; Steinle et al., 2017; Egger et al., 2018). Only recently, Weber et al. (2019) estimated the

30 global oceanic CH₄ emissions to range from 6 to 12 Tg yr⁻¹, of which about 0.8–3.8 Tg yr⁻¹ were attributed to coastal waters. Occasional studies of the CH₄ production and consumption pathways in coastal waters and the associated CH₄ emissions to the atmosphere have received increasing attention during the last decades (Bange et al., 1994; Reeburg 2007; Naqvi et al., 2010). However, time-series measurements of CH₄ which would allow identifying short- and long-term trends in view of the ongoing environmental changes in coastal regions (such as eutrophication, warming and deoxygenation) are still sparse. In
35 this paper we present the monthly measurements of CH₄ from a time-series station in the Eckernförde Bay (Baltic Sea) during 2006–2017.

Due to severe eutrophication, sediments in the Eckernförde Bay receive large amount of organic matter (Smetacek et al., 1987; Oris et al., 1996; Nittrouer et al., 1998) and thus are active sites of CH₄ formation (Schmaljohann, 1996; Whiticar, 2002; Treude et al., 2005; Maltby et al., 2018). Seasonal and inter-annual CH₄ variations in concentration, saturation and air-
40 sea flux density were investigated for more than a decade. The aim of this study was to assess the seasonal dynamics of and the environmental controls on CH₄ variability in the Eckernförde Bay which is affected by high nutrient concentrations, increasing water temperatures and ongoing loss of dissolved oxygen (Lennartz et al., 2014).

2. Study site

The Boknis Eck (BE) time-series station is one of the oldest continuously conducted marine time-series stations in the world.
45 The first sampling took place in 1957, and has been conducted on a monthly base with only minor interruptions since then (Lennartz et al., 2014). It is situated in the Eckernförde Bay in the southwestern (SW) Baltic Sea, with a depth of approximately 28 m (Fig. 1). The sediments in the Bay are characterized by high organic matter load and sedimentation rate (Orsi et al., 1996; Whiticar, 2002), which is closely associated with the spring and autumn algae blooms (Smetacek, 1985). The Baltic Sea has only a limited water exchange with the North Sea through the Kattegat, which makes this area very
50 sensitive to climate change and anthropogenic impacts. As a result of global warming, the increasing trend for the global sea surface (< 75 m) temperatures (SST) was about 0.11 °C per decade (IPCC, 2013), while a net SST increase of 1.35 °C was observed in the Baltic Sea during 1982–2006, which is one of the most rapid temperature increment in large marine ecosystems (Belkin, 2009). Lennartz et al. (2014) reported a warming trend of up to 0.2 °C per decade at the BE time-series station for the period of 1957–2013. Nutrients in the Baltic Sea have been increasing until 1980s as a result of the intensive
55 agricultural and industrial activities, and then started to decline due to effective wastewater control (HELCOM, 2018). However, hypoxia and anoxia have been increasing in the Baltic Sea during the past several decades (Conley et al., 2011; Carstensen et al., 2014). Similar trends in nutrients and O₂ were also detected at the BE time-series station (Lennartz et al., 2014), indicating that the Eckernförde Bay is representative for the biogeochemical setting of the SW Baltic Sea. In concert with the declining nutrient concentrations, Chlorophyll *a* concentrations at the BE time-series station were declining as well
60 (Lennartz et al., 2014).

Located close to the bottleneck of the water exchange between the North Sea and the Baltic Sea, the BE time-series station is also sensitive to hydrographic fluctuations such as inflows of saline North Sea Water. There is no riverine input to the Eckernförde Bay, and thus, the saline water inflow from the North Sea plays a dominant role in the hydrographic setting at BE. Because the inflowing North Sea water has a higher salinity compared to Baltic Sea water, a pronounced summer stratification occurs which leads to the development of a pycnocline at about 15 m water depth. The seasonal stratification occurs usually from mid-March until mid-September. During this period, vertical mixing is restricted and bacterial decomposition of organic material in the deep layer causes pronounced hypoxia and sporadically occurring anoxia during late summer (Lennartz et al., 2014). Pronounced phytoplankton blooms occur regularly in autumn (September–November) and spring (February–March) and to a lesser extent during summer (July–August) (Smetacek et al. 1985).

70 **3. Methods**

3.1 Sample collection and measurement

Monthly sampling of CH₄ from the BE time-series station started in June 2006. Seawater was collected from 6 depths (1, 5, 10, 15, 20 and 25 m) with 5 L Niskin bottles mounted on a CTD rosette. 20 mL brown glass vials were filled in triplicates without any bubbles. The vials were sealed immediately with rubber stoppers and aluminum caps. These samples were
75 poisoned with 50 µL saturated aqueous mercury chloride (HgCl₂) solution as soon as possible, and then stored in a cool, dark place until measurement. The storage time of the samples before the measurements was less than 3 months.

A static headspace-equilibrium method was adopted for the CH₄ measurements. A 10 mL Helium (99.9999 %, AirLiquide, Düsseldorf, Germany) headspace was created inside the vial with a gas-tight syringe (VICI Precision Sampling, Baton Rouge, LA). The sample was vibrated with Vortex (G-560E, Scientific Industries Inc., New York, USA) for approximately
80 20 s and then left for at least 2 h to reach the CH₄ equilibrium between air and water phases. A 9.5 mL subsample of headspace was injected into a gas chromatograph equipped with a flame ionization detector (GC-FID, Hewlett-Packard 5890 Series II, Agilent Technologies, Santa Clara, CA, USA). Separation took place on a packed column (SS, 1.8 m length, packed with molsieve 5A, Grace, Columbia, Maryland, USA). Standard gas mixtures with varying mole fractions of CH₄ in synthetic air (Deuste-Steininger GmbH, Mühlhausen, Germany and Westfalen AG, Münster, Germany) were used daily to
85 calibrate the response of FID before measurements. The concentrations of standard gases were adjusted for every measurement to make sure that the values of the samples fall in the range of the calibration curves. The standard gas mixtures were calibrated against NOAA primary gas standard mixtures in the laboratory of the Max-Planck-Institute for Biogeochemistry in Jena, Germany. Further details about the measurements and calculations of the dissolved CH₄ concentration can be found in Bange et al. (2010). The mean precision of the CH₄ measurements, calculated as the median of
90 the estimated standard errors (see David, 1951) from all triplicate measurements, was ± 1.3 nM. Samples with an estimated standard error of >10 % were omitted. Dissolved O₂ concentrations were measured with Winkler titrations, and Chlorophyll *a* concentrations were measured with a Fluorometer (Grasshoff et al., 1999). Secchi depth was measured with a white disk

(~30 cm in diameter). Sea levels were measured at Kiel-Holtenau, which is about 15 km away from the BE time-series station (<http://www.boos.org/>). A more comprehensive overview of temperature, salinity, dissolved O₂, Chlorophyll *a* as well as other parameters at the BE time-series station can be found in Lennartz et al. (2014).

3.2 Calculation of saturation and air-sea flux density

The CH₄ saturation (S_{CH_4} , %) was calculated as:

$$S_{CH_4} = 100 \times CH_{4obs} / CH_{4eq} \quad (1)$$

where CH_{4obs} and CH_{4eq} are the observed and equilibrium concentrations of CH₄ in seawater, respectively. CH_{4eq} was calculated with the in-situ temperature and salinity of seawater (Wiesenburg and Guinasso, 1979), and the dry mole fraction of atmospheric CH₄ at the time of sampling, which was derived from the monthly atmospheric CH₄ data measured at Mace Head, Ireland (AGAGE, <http://agage.mit.edu/>).

The air-sea CH₄ flux density (F_{CH_4} , in $\mu\text{mol m}^{-2} \text{d}^{-1}$) was calculated as:

$$F_{CH_4} = k \times (CH_{4obs} - CH_{4eq}) \quad (2)$$

where k (in cm h^{-1}) is the gas transfer velocity calculated with the equation given by Nightingale et al. (2000), as a function of the wind speed and the Schmidt number (Sc). Sc was computed with the empirical equations for the kinematic viscosity of seawater (Siedler and Peters, 1986) and the diffusion coefficients of CH₄ in water (Jähne et al., 1987). Wind speed data were recorded at the Kiel Lighthouse (www.geomar.de/service/wetter/), which is approximately 20 km away from the BE time-series station. The wind speeds were normalized to the height of 10 m (u_{10}) with the method given by Hsu et al. (1994).

4. Results and discussion

4.1 Seasonal variations of environmental parameters and dissolved CH₄

Seasonal hypoxia were observed every year at the BE time-series station during 2006–2017 (Fig. 2). O₂ depletion was detected in the bottom layer (~15–25m) during July–October with minimum O₂ concentrations usually occurring in September (Fig. 3). Lennartz et al. (2014) found a significant decrease in dissolved O₂ concentrations in the bottom water at the BE time-series station over the past several decades and suggested that temperature-enhanced O₂ consumption and a prolonged stratification period might be the causes of deoxygenation. Anoxia with the presence of hydrogen sulfide (H₂S, identified from the strong smell) in the period of concurrent CH₄ measurements were found in the autumn of 2007, 2014 and 2016, respectively. The anoxic event in 2016 lasted from September until November and was the longest ever recorded at the BE time-series station. In September 2017, a pronounced undersaturation of O₂ (~50%) was observed in surface water (Fig. 2). The low temperature together with enhanced salinity in the surface water in September 2017 suggests the occurrence of an upwelling event, which transported O₂-depleted and colder bottom waters to the surface. An upwelling signal was also

present in the nutrient concentrations (not shown), but less pronounced than in temperature and dissolved O₂ concentrations. Similar events were also detected in September 2011 and 2012.

Enhanced Chlorophyll *a* concentrations, which can be used to indicate phytoplankton blooms, were usually observed in spring or autumn, but not in every year (Fig. 2). Seasonal variations of Chlorophyll *a* concentrations were generally consistent with the annual plankton succession reported by Smetacek (1985). During 2006–2017, high Chlorophyll *a* concentrations were usually found in the upper layers in March (Fig. 3), which is different from the seasonality during 1960–2013 where on average, high concentrations occupied the whole water column (Lennartz et al., 2014). Another difference is that no prevailing ‘winter dormancy’ of biological activity was observed: Chlorophyll *a* concentrations usually remained high throughout the autumn–spring period. In November and December 2006 and March 2012 when high Chlorophyll *a* concentrations were observed all over the water column, nutrients and temperature were generally higher. Although the overall correlation between Chlorophyll *a* and nutrients (NO₃⁻, $r^2=0.01$, $p<0.01$, $n=674$) or temperature ($r^2=0.02$, $p<0.0001$, $n=671$) is poor, nutrients or temperature might be potential environmental controls on Chlorophyll *a* distribution. As a proxy of water transparency, Secchi depth was lowest in March indicating a high turbidity, coincident with the Chlorophyll *a* maximum. Chlorophyll *a* concentrations and Secchi depths have been decreasing over the past decades in the Baltic Sea (Sandén and Håkansson, 1996; Fleming-Lehtinen and Laamanen, 2012; Lennartz et al., 2014), but this trend cannot be identified from the median slope at the BE time-series station during 2006–2017.

CH₄ concentrations at the BE time-series station showed strong seasonal and inter-annual variability (Fig. 2, Table. 1). During 2006–2017, dissolved CH₄ concentrations ranged between 2.9 to 695.6 nM, with an average of 51.2 ± 84.2 nM. High concentrations were generally observed in the bottom layer (~15–25 m). Enhanced CH₄ concentrations were mainly observed during February, May–June and October (Fig. 3). Steinle et al. (2017) measured aerobic CH₄ oxidation at the BE time-series station and found that lowest rates occurred in winter, which might be one of the reasons for the enhanced CH₄ concentrations in February.

The CH₄ accumulation in May and June can be linked to enhanced methanogenesis fueled by organic matter from the spring algae bloom. Capelle et al. (2019) found a positive correlation between mean monthly CH₄ concentrations and Chlorophyll *a* concentrations in the upper layers of time-series measurements from Saanich Inlet. Bange et al. (2010) also reported correlations between seasonal CH₄ variation and Chlorophyll *a* or Secchi depth, albeit with a time lag of one month, at the BE time-series station during 2006–2008. Although we did not detect such relationships for the extended measurements during 2006–2017, in 2009 and 2016, when no spring algae blooms were detected, CH₄ concentrations in following summer months were lower than average (Fig. 2).

Maximum CH₄ concentrations were usually observed in October, at the end of the seasonal hypoxia (Fig. 3). Due to the long-lasting anoxic event, strong CH₄ accumulations were observed in autumn 2016 (~600 nM), which are the highest in the bottom layer during 2006–2017. Prevailing for several months, depletion of bottom O₂ concentrations exerts a strong influence on the underlying sediment. Maltby et al. (2018) detected a shoaling of the sulfate reduction zone in autumn and enhanced methanogenesis in the sediments at the BE time-series station. Reindl and Bolalek (2012) found similar variations

in sedimentary CH₄ release in the coastal Baltic Sea. In-situ production in the anoxic bottom water might be a potential CH₄ source as well (Scranton and Farrington, 1977; Levipan et al., 2007). We, therefore, suggest that the accumulation of CH₄ in the bottom water in October is caused by its release from the sediments and in-situ production in the overlying water column in combination with the pronounced water column stratification during autumn which prevents ventilation of CH₄ to the surface layer.

4.2 Enhanced CH₄ concentrations in the upper water layer

In agreement with Schmale et al. (2010) and Bange et al. (2010), we found that CH₄ concentrations generally increase with water depth, indicating a prevailing release of CH₄ from the sediments into the water column in the Baltic Sea (see Sect. 4.1). Nonetheless, unusual high CH₄ concentrations in the upper layers were detected sporadically at the BE time-series station during 2006–2017 (Fig. 2). In November 2013 and March 2014, average CH₄ concentrations in the upper waters were 187.2 ± 13.9 nM (1–10 m) and 217.8 ± 1.4 nM (5–10 m), which are about 16 and 5 times higher than those found in the bottom layers, respectively (Fig. 4). The most striking event occurred in December 2014, when CH₄ concentrations in the upper layer (1–15 m) were as high as 692.6 ± 3.4 nM (19,890 ± 115 %), whereas dissolved CH₄ in the bottom layer (20–25 m) was ~50 nM. The surface CH₄ concentration in December 2014 was the highest observed during 2006–2017. In December 2014, a major Baltic inflow (MBI) event occurred, carrying large amounts of saline and oxygenated water from the North Sea into the Baltic Sea (Mohrholz et al., 2015). Dissolved CH₄ concentrations in the surface North Sea were much lower than in the Eckernförde Bay (Bange et al., 1994; Rehder et al., 1998), and therefore a direct CH₄ contribution from the North Sea by oxygenated waters seems unlikely. We hypothesize that this inflow substituted the lower part of the water column which had high CH₄ concentration throughout the water depth before, opposite to, e.g., an in-situ production of CH₄ at the surface being responsible for the observed concentration profile anomaly. The MBI is the third strongest event ever recorded, and an unusual outflow period was detected in the Eckernförde Bay: Sea levels declined since mid-November and reached minimum on 10 December, and then began to increase with the inflow (Fig. 5). The sampling at the BE time-series station took place on 16 December, during the main inflow period. Extreme weather conditions (wind speed >15 m s⁻¹) were observed several days before the sampling date, and storm-generated waves and currents could have affected the sediment structures in the Eckernförde Bay (Oris et al., 1996). Currents across the seabed can result in pressure gradients that drive porewater flow within the permeable sediments (Ahmerkamp et al., 2015), which might be a potential CH₄ source. Sediment resuspension might also contribute to enhanced CH₄ release, but we did not observe a significant decline in Secchi depths in December 2014 (Fig. 2). The significant decrease in sea level alleviated the static pressure on the sediments. Enhanced CH₄ release from the sediments, via gas bubbles or exchange from porewater, may have led to the accumulation of CH₄ in the water column. Similar hydrostatic pressure effects were also reported in tidal systems such as mangrove creeks and estuaries (see e.g. Barnes et al. 2006; Maher et al., 2015; Sturm et al., 2017). Atmospheric pressure also contributes to the overall pressure on the sediments, but it is not recorded at the BE time-series station and thus was omitted. Although the water level fluctuation of ± 1 m (Fig. 5) seems rather small compared to the water depth (28m), it might exert a strong influence on the

sediments. Water level fluctuation, when there was no strong wind or inflow event, was approximately ± 0.2 m in the
190 Eckernförde Bay. Lohrberg et al. (2020) detected a change in water level (± 0.5 m) and air pressure (± 1500 Pa, equivalent to
approximately ± 0.15 m of water level fluctuation) during a weak storm in the fall of 2014. The fluctuation in hydrostatic
pressure induced a pronounced CH₄ ebullition event in the Eckernförde Bay, and a sedimentary CH₄ flux of $1916 \mu\text{mol m}^{-2}$
d⁻¹ was estimated (Lohrberg et al., 2020). This value is generally in good agreement with the sharp increase in the sea-to-air
CH₄ fluxes in December 2014 (see section 4.3). The outflow period of the MBI in 2014 lasted for almost a month, and bulk
195 ebullitions and supersaturated water with CH₄ could be anticipated. During the inflow period, large amounts of North Sea
water flooded into the Eckernförde Bay and presumably pushed the CH₄-enriched water to the surface. A negative
correlation was found between salinity and CH₄ concentration in the water column (Fig. 4a, $r^2=0.84$, $p=0.01$, $n=6$), indicating
that vertical CH₄ distributions were linked to the mixing of saline water in the bottom and less-saline water in the upper
layers. We suggest that CH₄ release driven by hydrostatic pressure fluctuations and the MBI-associated mixing are
200 responsible for the abnormal CH₄ profile in December 2014.

The CH₄ anomaly in November 2013 can be linked to saline water inflow as well. Nausch et al. (2014) reported the
occurrence of an inflow event from 27 October to 7 November in 2013. The sampling at the BE time-series station took
place on 5 November, and an increase in salinity was detected in the bottom water (Fig. 4b). The rapid transition from
hypoxic ($9.8 \mu\text{M/L}$, 25 m in October) to oxic condition ($239.2 \mu\text{M/L}$, 25 m in November) in the bottom layer also supports
205 the occurrence of the inflow (Fig. 2). Steinle et al. (2017) found a change in the temperature optimum of aerobic CH₄-
oxidizing bacteria (MOB) in November 2013 at the BE time-series station and linked it to a displacement of the local MOB
community as a result of saltwater injection. Although enhanced CH₄ concentrations and high net methanogenesis rates were
detected in the sediments in November 2013 (Maltby et al., 2018), the saline inflow with less dissolved CH₄ was sandwiched
between the sediments and the upper layer waters. As a result, we also found a negative salinity-CH₄ correlation in the water
210 column (Fig. 4b, $r^2=0.86$, $p<0.01$, $n=6$). This inflow event was much weaker than the MBI in December 2014, and no
obvious outflow or inflow period can be identified from sea level variations. There was no strong fluctuation in hydrostatic
pressure and thus sedimentary CH₄ release and CH₄ supersaturations in the water column were lower than in December
2014. Another difference is that the decrease in salinity and increase of CH₄ concentrations were observed between 10–20 m,
which is at shallower depths compared to the MBI in December 2014, indicating that the saline water volume in the bottom
215 layer was larger at the time of the sampling in November 2013.

The situation in March 2014 is different. We did not find any evidence for saline water inflow or hydrostatic pressure
fluctuation, and the correlation between CH₄ concentration and salinity is poor (Fig. 4c, $r^2=0.43$, $p=0.16$, $n=6$). The
occurrences of the unusual CH₄ profiles were accompanied by the enhanced Chlorophyll *a* concentrations in the upper
waters. CH₄ productions by widespread marine phytoplankton have been reported and might be potential sources of surface
220 CH₄ supersaturations (Lenhart et al, 2016; Klintzsch et al., 2019). However, spring or autumn algae blooms at the BE time-
series station were often observed without CH₄ accumulation and surface CH₄ contribution from phytoplankton remains to
be proven. Potential sources for the enhanced CH₄ in March 2014 are still unclear.

In summary, we suggest that saline water inflow and the subsequent upwelling of water are the most potential causes for the CH₄ surface accumulation in November 2013 and December 2014. Nonetheless, the occurrence of inflow does not necessarily lead to enhanced CH₄ concentrations in the upper waters. Inflow events are relatively common, for example, in 2013, besides the inflow in November, three other events with similar estimated inflow volumes were detected in January, February and April (Nausch et al., 2014), but no CH₄ anomaly was found during that period. The magnitude of the CH₄ anomalies might depend on the strength of the inflow events and other factors, such as storms and sediment resuspension. Besides, there is a high chance that the monthly sampling at the BE time-series station only captured few CH₄ pulses. Inflow events usually last days to weeks, but the accumulated CH₄ in the upper layers might last even shorter because of effective aerobic CH₄ oxidation (Steinle et al., 2017) and strong vertical mixing in winter. The occurrences of surface CH₄ accumulations at the BE time-series station might be more frequent than been observed.

4.3 Surface saturation and flux density

Surface CH₄ saturations are directly proportional to its concentrations in the surface water ($S_{CH_4}=31.40 \times [CH_4] + 10.29$, $R^2=0.9794$, $n=77$, $p<0.0001$; Fig. 6a, b), despite of the pronounced seasonal variations in temperature (Fig. 3). This indicates that the net CH₄ production at BE is overriding the temperature-driven variability of the CH₄ concentrations. Excluding the extreme value from December 2014, surface CH₄ saturations at the BE time-series station varied between 129–5563 %, with an average of 615 ± 688 %. The surface layer was supersaturated with CH₄ and thus emitting CH₄ to the atmosphere throughout the sampling period.

The coastal Baltic Sea, especially the southwestern part, is a hot spot for CH₄ emissions. Area-weighted mean CH₄ saturations for the entire Baltic Sea (113 % and 395 % in winter and summer 1992, respectively; Bange et al., 1994) were lower than at the BE time-series station. Schmale et al. (2010) extensively investigated dissolved CH₄ distributions in the Baltic Sea, and found that surface CH₄ supersaturations were stronger in the shallow western areas.

Sea-to-air CH₄ flux densities fluctuated between 0.3–746.3 $\mu\text{mol m}^{-2} \text{d}^{-1}$, with an average of $43.8 \pm 88.7 \mu\text{mol m}^{-2} \text{d}^{-1}$ (excluding the extreme value in December 2014, Fig. 6c). Comparable results in saturation and flux density were observed at the pockmark sites in the Eckernförde Bay (Bussmann and Suess, 1998). Although surface CH₄ saturations in this study are consistent with the previously published results by Bange et al. (2010) (554 ± 317 %), calculated CH₄ flux densities in this study are much higher than in Bange et al. (2010) (6.3–14.7 $\mu\text{mol m}^{-2} \text{d}^{-1}$). The discrepancy derives from different flux calculation methods. Bange et al. (2010) adopted the equations by Raymond and Cole (2001) with a lower gas transfer velocity, and they used the median of surface CH₄ concentrations for computation, which eliminated the extreme values. Our results are in good agreement with the ones reported by Bange et al. (2010) if we adopt the same method.

CH₄ emissions from coastal waters could be roughly considered as the difference between formation and oxidation of CH₄ in the water column and sediments. Although sediments are substantial CH₄ sources, most CH₄ is consumed before evading to the atmosphere (Martens et al., 1999; Treude et al., 2005; Steinle et al., 2017). Treude et al. (2005) compared the potential and field rates of anaerobic oxidation of methane (AOM) in the sediments of the Eckernförde Bay and suggested that the

AOM-mediating organisms are capable of fast response to changes in CH₄ supply. Steinle et al. (2017) reported that 70–95 % of dissolved CH₄ were effectively removed in the water column during summer stratification. Apart from MBI-driven uplift of CH₄-enriched bottom water to the surface (see below), wind-driven upwelling events can lead to a ventilation of the accumulated CH₄ to the atmosphere. For example, Gülzow et al. (2013) observed elevated CH₄ concentrations in the Gotland Basin as a result of wind-induced upwelling. The influence of upwelling at the BE time-series station, however, is more prominent due to the shallow water depth. In September 2012 and 2017, when upwelling occurred (see Sect. 4.1), sea-to-air CH₄ flux densities were 65.9 μmol m⁻² d⁻¹ and 132.3 μmol m⁻² d⁻¹, respectively, which were about 50 % and 200 % higher than the mean value.

Enhanced CH₄ saturations and associated emissions at the BE time-series station were also strongly promoted by saline inflows (see Sect. 4.2). We found very high surface CH₄ saturation and flux density in November 2013 and December 2014 (Fig. 6). In December 2014, surface CH₄ saturations were as high as 19,770 % and the calculated flux density reached 3104.5 μmol m⁻² d⁻¹. Inflows of saline waters usually occur in winter, when the well-ventilated water column, relatively low CH₄ oxidation rates and high wind speeds are all favorable for high CH₄ emissions (Wanninkhof, 2014; Steinle et al., 2017). Assuming that there was no continuous mixing or supply of CH₄ to the surface layer, it took about 3.3 days for the accumulated CH₄ to come back to equilibrium values under the calculated flux density, during which the annual CH₄ emissions from the Eckernförde Bay would increase by approximately 66 % in 2014. This is also in line with our speculation in Sect. 4.2 that the monthly sampling at the BE time-series station might have missed some of the short-lived CH₄ pulses.

Moreover, methanogenesis in the sediments of the Eckernförde Bay is sufficient for CH₄ bubble formation (Whiticar, 2002). Hydrostatic pressure fluctuations associated with saline water inflow could have triggered CH₄ seepage and gas bubble plumes from the seafloor to the atmosphere (Wever et al., 2006; Lohrberg et al., 2020). Gas ebullition sites were usually found accompanied by pockmark structures (Schneider von Deimling et al., 2011) and Jackson et al. (1998) provided sonar evidences for CH₄ ebullition in the Eckernförde Bay. However, recently Lohrberg et al. (2020) reported a widespread CH₄ ebullition event in the Eckernförde Bay and found no direct linkage between pockmarks and ebullitions. They estimated the bubble-driven CH₄ flux during a weak storm in the fall of 2014 was 1916 μmol m⁻² d⁻¹. These findings point to the fact that ebullition might be an important, but highly variable, additional CH₄ efflux to the atmosphere. However, our measurements did not capture gas bubbles and, thus, the estimate of the overall CH₄ emissions resulting from the MBI might be too low. In this case, a time-series monitoring of saline inflows and sea level variations, combined with a continuous observation of CH₄ variability, especially in winter, are essential in quantifying CH₄ emissions from the Eckernförde Bay.

4.4 Comparison with other time-series measurements

Besides this study, time-series measurements of CH₄ have also been reported from Saanich Inlet (SI), British Columbia, Canada (Capelle et al., 2019) and ALOHA station in the North Pacific Subtropical Gyre (Wilson et al., 2017).

Located in a seasonally anoxic fjord, the time-series station in SI has a similar hydrographic setting compared to BE, but a deeper water depth (230 m, Capelle et al., 2019). Surface CH₄ saturations at SI fell in the lower end of the range observed

here for BE (Fig. 7). Despite the fact that the mean surface saturation in SI was higher, CH₄ flux densities were much lower than at BE. Since the air-sea exchange approach of Nightingale et al. (2000) was used in both studies, the discrepancy is resulting from the higher wind speeds at BE. CH₄ saturations from ALOHA were only slightly supersaturated (close to the equilibrium saturation) and the flux densities were consequently low as well, which is resulting from the fact that ALOHA is a deep water (~4800 m) station located in the oligotrophic open ocean where potential strong CH₄ sources such as sedimentary release or methanogenesis under low O₂ in the water column are negligible (Wilson et al., 2017). Wilson et al. (2017) analyzed the time-series CH₄ data from ALOHA during 2008–2016 and observed a decline in the surface CH₄ concentrations since 2013. They attributed the potential decrease in CH₄ production to fluctuations in phosphate concentrations. Capelle et al. (2019) also detected a significant decline of CH₄ concentrations in the upper water column over time at SI and proposed a link with the shoaling of the boundary of the hypoxic layer. However, no significant trend was detected in CH₄ concentrations or flux densities at the BE time-series station (Fig. 6), despite of the relatively long observation period. The different situations can be explained by the shallow water depth in the Eckernförde Bay, which makes the CH₄ distribution sensitive to the variability of its sedimentary release and events such as MBI and wind-driven upwelling.

5. Conclusions

The CH₄ measurements at the BE time-series station showed a strong temporal variability and variations with depths. A pronounced enhancement of the CH₄ concentrations was usually found in the bottom layer (15–25 m) during February, May–June and October which indicates that the release from the sediments is the major source of CH₄. Organic matter and dissolved O₂ are usually considered as the main controlling factors for CH₄ production and consumption pathways, but we did not detect correlations of CH₄ with Chlorophyll *a* or O₂ during 2006–2017.

Obviously non-biological processes such as local wind-driven-upwelling and the inflow of saline North Sea waters play a significant role for the observed variability of CH₄ at BE. However, these phenomena, which occur on relatively short time scales of day or weeks, were not frequently detected; most probably due to the monthly sampling frequency. The surface layer at BE was always supersaturated with CH₄ and therefore, BE was a persistent and strong, but highly variable, source of CH₄ to the atmosphere. We did not detect significant temporal trends in CH₄ concentrations or emissions, despite of ongoing environmental changes (warming, deoxygenation) in the Eckernförde Bay. Overall, the CH₄ variability at BE is driven by a complex interplay of various biological (i.e. methanogenesis, oxidation) and physical (i.e. upwelling, inflow events) processes. Continuous observations at the BE time-series station, with an emphasis on the period when upwelling and saline inflow usually occur is therefore, of great importance in quantifying CH₄ variability and the associated emissions as well as for predicting future CH₄ variability in the SW Baltic Sea.

320 **Data availability.** Data are available from the Boknis Eck Database: <https://www.bokniseck.de> (Bange and Malien, 2020) and MEMENTO (the MarinE MethanE and NiTrous Oxide database, <https://memento.geomar.de> (Kock and Bange, 2015).

Author contributions. XM, MS, STL, and HWB designed the study and participated in the fieldwork. CH₄ measurements and data processing were done by XM, MS and STL. XM wrote the article with contributions from MS, STL and HWB.

325 **Competing interests.** The authors declare that they have no conflict of interest.

Acknowledgements. The authors thank the captain and crew of the RV *Littorina* and *Polarfuchs* as well as many colleagues and numerous students who helped with the sampling and measurements of the BE time-series through various projects. 330 Special thanks to A. Kock for her help with sampling, measurements and data analysis. The time-series at BE was supported by DWK Meeresforschung (1957–1975), HELCOM (1979–1995), BMBF (1995–1999), the Institut für Meereskunde (1999–2003), IfM-GEOMAR (2004–2011) and GEOMAR (2012–present). The current CH₄ measurements at BE are supported by the EU BONUS INTEGRAL project which receives funding from BONUS (Art 185), funded jointly by the EU, the German Federal Ministry of Education and Research, the Swedish Research Council Formas, the Academy of Finland, the Polish 335 National Centre for Research and Development, and the Estonian Research Council. The Boknis Eck Time-Series Station (www.bokniseck.de) is run by the Chemical Oceanography Research Unit of GEOMAR, Helmholtz Centre for Ocean Research Kiel. The sea level data used in this study was made available by the EMODnet Physics project (www.emodnet-physics.eu/map), funded by the European Commission Directorate General for Maritime Affairs and Fisheries.

Financial support. Xiao Ma is grateful to the financial support provided by the China Scholarship Council (grant no. 201306330056) and the BONUS INTEGRAL project (grant no. 03F0773B). 340

References

- Ahmerkamp, S., Winter, C., Janssen, F., Kuypers, M. M., and Holtappels, M.: The impact of bedform migration on benthic oxygen fluxes, *J. Geophys. Res.-Biogeo*, 120, 2229–2242, <https://doi.org/10.1002/2015JG003106>, 2015.
- Barnes, J., Ramesh, R., Purvaja, R., Nirmal Rajkumar, A., Senthil Kumar, B., Krithika, K., Ravichandran, K., Uher, G., and 345 Upstill-Goddard, R.: Tidal dynamics and rainfall control N₂O and CH₄ emissions from a pristine mangrove creek, *Geophys. Res. Lett.*, 33, L15405, doi:15410.11029/12006GL026829, 2006.
- Bange, H. W., Bartell, U. H., Rapsomanikis, S., and Andreae, M. O.: Methane in the Baltic and North Seas and a reassessment of the marine emissions of methane, *Global Biogeochem. Cy.*, 8, 465–480, <https://doi.org/10.1029/94GB02181>, 1994.

- 350 Bange, H. W., Bergmann, K., Hansen, H. P., Kock, A., Koppe, R., Malien, F., and Ostrau, C.: Dissolved methane during hypoxic events at the Boknis Eck Time Series Station (Eckernförde Bay, SW Baltic Sea), *Biogeosciences*, 7, 1279–1284, <https://doi.org/10.5194/bg-7-1279-2010>, 2010.
- Bange, H. W. and Malien, F.: Boknis Eck Time-series Database, Kiel Datamanagement Team, <http://www.bokniseck.de/>, last accessed: 23 March 2020.
- 355 Belkin, I. M.: Rapid warming of large marine ecosystems, *Prog. Oceanogr.*, 81, 207–213, doi:10.1016/j.pocean.2009.04.011, 2009.
- Bernard, B. B., Brooks, J. M., and Sackett, W. M.: Natural gas seepage in the Gulf of Mexico, *Earth Planet Sc. Lett.*, 31, 48–54, 1976.
- Borges, A. V., Champenois, W., Gypens, N., Delille, B., and Harlay, J.: Massive marine methane emissions from near-shore shallow coastal areas, *Sci. Rep.-UK*, 6, 27908, DOI: 10.1038/srep27908, 2016.
- 360 Bussmann, I., and Suess, E.: Groundwater seepage in Eckernförde Bay (Western Baltic Sea): Effect on methane and salinity distribution of the water column, *Cont. Shelf Res.*, 18, 1795–1806, [https://doi.org/10.1016/S0278-4343\(98\)00058-2](https://doi.org/10.1016/S0278-4343(98)00058-2), 1998.
- Capelle, D. W., Hallam, S. J., and Tortell, P. D.: Time-series CH₄ measurements from Saanich Inlet, BC, a seasonally anoxic fjord, *Mar. Chem.*, 215, 103664, <https://doi.org/10.1016/j.marchem.2019.103664>, 2019.
- 365 Carstensen, J., Andersen, J. H., Gustafsson, B. G., and Conley, D. J.: Deoxygenation of the Baltic Sea during the last century, *P. Natl. Acad. Sci. USA*, 111, 5628–5633, <https://doi.org/10.1073/pnas.1323156111>, 2014.
- Conley, D. J., Carstensen, J., Aigars, J., Axe, P., Bonsdorff, E., Eremina, T., and Lannegren, C.: Hypoxia is increasing in the coastal zone of the Baltic Sea, *Environ. Sci. Technol.*, 45, 6777–6783, doi: 10.1021/es201212r, 2011.
- Dale, A. W., Flury, S., Fossing, H., Regnier, P., Røy, H., Scholze, C., and Jørgensen, B. B.: Kinetics of organic carbon mineralization and methane formation in marine sediments (Aarhus Bay, Denmark), *Geochim. Cosmochim. Ac.*, 252, 159–178, <https://doi.org/10.1016/j.gca.2019.02.033>, 2019.
- 370 David, H. A.: Further applications of range to analysis of variance, *Biometrika*, 38, 393–409, 1951.
- Egger, M., Riedinger, N., Mogollon, J. M., and Jørgensen, B. B.: Global diffusive fluxes of methane in marine sediments, *Nat. Geosci.*, 11, 421–425, <https://doi.org/10.1038/s41561-018-0122-8>, 2018.
- 375 Fleming-Lehtinen, V., and Laamanen, M.: Long-term changes in Secchi depth and the role of phytoplankton in explaining light attenuation in the Baltic Sea, *Estuar. Coast Shelf S.*, 102, 1–10, <https://doi.org/10.1016/j.ecss.2012.02.015>, 2012.
- Grasshoff, K., Kremling, K., and Ehrhardt, M.: *Methods of seawater analysis*, 3rd edition, WILEY-VCH, Weinheim, Germany, 1999.
- Gülzow, W., Rehder, G., Schneider von Deimling, J., Seifert, S., and Tóth, Z.: One year of continuous measurements constraining methane emissions from the Baltic Sea to the atmosphere using a ship of opportunity, *Biogeosciences*, 10, 81–99, doi:10.5194/bg-10-81-2013, 2013.
- 380 Hansen, H. P., Giesenhausen, H. C., and Behrends, G.: Seasonal and long-term control of bottom water oxygen deficiency in a stratified shallow-coastal system, *ICES J. Mar. Sci.*, 56, 65–71, doi: 10.1006/jmsc.1999.0629, 1999.

- HELCOM: State of the Baltic Sea - Second HELCOM holistic assessment 2011–2016, *Baltic Sea Environ. Proc.*, 155, <http://stateofthebalticsea.helcom.fi/>, 2018.
- 385 Hovland, M., Judd, A. G., and Burke Jr., R. A.: The global flux of methane from shallow submarine sediments, *Chemosphere*, 26, 559–578, [https://doi.org/10.1016/0045-6535\(93\)90442-8](https://doi.org/10.1016/0045-6535(93)90442-8), 1993.
- Hsu, S. A., Meindl, E. A., and Gilhousen, D. B.: Determining the power-law wind-profile exponent under near-neutral stability conditions at sea, *J. Appl. Meteorol.*, 33, 757–765, [https://doi.org/10.1175/1520-390450\(1994\)033<0757:DTPLWP>2.0.CO;2](https://doi.org/10.1175/1520-390450(1994)033<0757:DTPLWP>2.0.CO;2), 1994.
- IPCC: Climate Change 2013: The physical science basis. Contribution of Working Group I to the fifth assessment report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, UK and New York, NY, 2013.
- Jackson, D. R., Williams, K. L., Wever, T. F., Friedrichs, C. T., and Wright, L. D.: Sonar evidence for methane ebullition in Eckernförde Bay, *Cont. Shelf Res.*, 18, 1893–1915, [https://doi.org/10.1016/S0278-4343\(98\)00062-4](https://doi.org/10.1016/S0278-4343(98)00062-4), 1998.
- 395 Jähne, B., Heinz, G., and Dietrich, W.: Measurements of the diffusion coefficients of sparingly soluble gases in water, *J. Geophys. Res.-Oceans*, 92, 10767–10776, <https://doi.org/10.1029/JC092iC10p10767>, 1987.
- Judd, A. G., Hovland, M., Dimitrov, L. I., Garcia Gil, S., and Jukes, V.: The geological methane budget at continental margins and its influence on climate change, *Geofluids*, 2, 109–126, <https://doi.org/10.1046/j.1468-8123.2002.00027.x>, 2002.
- 400 Klintzsch, T., Langer, G., Nehrke, G., Wieland, A., Lenhart, K., and Keppler, F.: Methane production by three widespread marine phytoplankton species: release rates, precursor compounds, and potential relevance for the environment, *Biogeosciences*, 16, 4129–4144, <https://doi.org/10.5194/bg-16-4129-2019>, 2019.
- Kock, A. and Bange, H. W.: Counting the ocean’s greenhouse gas emissions, *Eos (Washington DC)*, 96, 10–13, <https://doi.org/10.1029/2015EO023665>, 2015.
- 405 Lenhart, K., Klintzsch, T., Langer, G., Nehrke, G., Bunge, M., Schnell, S., and Keppler, F.: Evidence for methane production by the marine algae *Emiliania huxleyi*, *Biogeosciences*, 13, 3163–3174, doi:10.5194/bg-13-3163-2016, 2016.
- Lennartz, S. T., Lehmann, A., Herrford, J., Malien, F., Hansen, H. P., Biester, H., and Bange, H. W.: Long-term trends at the Boknis Eck time-series station (Baltic Sea), 1957–2013: does climate change counteract the decline in eutrophication? *Biogeosciences*, 11, 6323–6339, <https://doi.org/10.5194/bg-11-6323-2014>, 2014.
- 410 Levipan, H. A., Quiñones, R. A., Johansson, H. E., and Urrutia, H.: Methylotrophic methanogens in the water column of an upwelling zone with a strong oxygen gradient off central Chile, *Microbes Environ.*, 22, 268–278, 2007.
- Lohrberg, A., Schmale, O., Ostrovsky, I., Niemann, H., Held, P., and Schneider von Deimling, J.: Discovery and quantification of a widespread methane ebullition event in a coastal inlet (Baltic Sea) using a novel sonar strategy, *Sci. Rep.-UK*, 10, 4393, <https://doi.org/10.1038/s41598-020-60283-0>, 2020.
- 415 Maher, D. T., Cowley, K., Santos, I. R., Macklin, P., and Eyre, B. D.: Methane and carbon dioxide dynamics in a subtropical estuary over a diel cycle: Insights from automated in situ radioactive and stable isotope measurements, *Mar. Chem.*, 168, 69–79, <https://doi.org/10.1016/j.marchem.2014.10.017>, 2015.

- Maltby, J., Steinle, L., Löscher, C. R., Bange, H. W., Fischer, M. A., Schmidt, M., and Treude, T.: Microbial methanogenesis in the sulfate-reducing zone of sediments in the Eckernförde Bay, SW Baltic Sea, *Biogeosciences*, 15, 137–157, <https://doi.org/10.5194/bg-15-137-2018>, 2018.
- Martens, C. S., Albert, D. B., and Alperin, M. J.: Stable isotope tracing of anaerobic methane oxidation in the gassy sediments of Eckernförde Bay, German Baltic Sea, *Am. J. Sci.*, 299, 589–610, 1999.
- Mohrholz, V., Naumann, M., Nausch, G., Krüger, S., and Gräwe, U.: Fresh oxygen for the Baltic Sea—An exceptional saline inflow after a decade of stagnation, *J. Marine Syst.*, 148, 152–166, <https://doi.org/10.1016/j.jmarsys.2015.03.005>, 2015.
- Naqvi, S.W.A., Bange, H.W., Fariás, L., Monteiro, P.M.S., Scranton, M.I., and Zhang, J.: Marine hypoxia/anoxia as a source of CH₄ and N₂O, *Biogeosciences*, 7, 2159–2190, <https://doi.org/10.5194/bg-7-2159-2010>, 2010.
- Nausch, G., Naumann, M., Umlauf, L., Mohrholz, V., and Siegel, H.: Hydrographisch-hydrochemische Zustandseinschätzung der Ostsee 2013, Leibniz-Institut für Ostseeforschung Warnemünde, Germany, 2014.
- Nightingale, P. D., Malin, G., Law, C. S., Watson, A. J., Liss, P. S., Liddicoat, M. I., Boutin, J., and Upstill-Goddard, R. C.: In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, *Global Biogeochem. Cy.*, 14, 373–387, <https://doi.org/10.1029/1999GB900091>, 2000.
- Nittrouer, C. A., Lopez, G. R., Wright, L. D., Bentley, S. J., D’Andrea, A. F., Friedrichs, C. T., Craig, N. I., and Sommerfield, C. K.: Oceanographic processes and the preservation of sedimentary structure in Eckernförde Bay, Baltic Sea, *Cont. Shelf Res.*, 18, 1689–1714, [https://doi.org/10.1016/S0278-4343\(98\)00054-5](https://doi.org/10.1016/S0278-4343(98)00054-5), 1998.
- Orsi, T. H., Werner, F., Milkert, D., Anderson, A. L., and Bryant, W. R.: Environmental overview of Eckernförde bay, northern Germany, *Geo-Mar. Lett.*, 16, 140–147, 1996.
- Pimenov, N. V., Ul’yanova, M. O., Kanapatskii, T. A., Mitskevich, I. N., Rusanov, I. I., Sigalevich, P. A., Nemirovskaya, I. A., and Sivkov, V. V.: Sulfate reduction, methanogenesis, and methane oxidation in the upper sediments of the Vistula and Curonian Lagoons, Baltic Sea, *Microbiology+*, 82, 224–233, DOI: 10.1134/S0026261713020136, 2013.
- Raymond, P. A. and Cole, J. J.: Gas exchange in rivers and estuaries: Choosing a gas transfer velocity, *Estuaries*, 24, 312–317, <https://doi.org/10.2307/1352954>, 2001.
- Reeburgh, W. S.: Oceanic methane biogeochemistry, *Chem. Rev.*, 107, 486–513, <https://doi.org/10.1021/cr050362v>, 2007.
- Rehder, G., Keir, R. S., Suess, E., and Pohlmann, T.: The multiple sources and patterns of methane in North Sea waters. *Aquat. Geochem.*, 4, 403–427, <https://doi.org/10.1023/A:1009644600833>, 1998.
- Reindl, A. R., and Bolalek, J.: Methane flux from sediment into near-bottom water in the coastal area of the Puck Bay (Southern Baltic), *Oceanol. Hydrobiol. St.*, 41, 40–47, <https://doi.org/10.2478/s13545-012-0026-y>, 2012.
- Sandén, P., and Håkansson, B.: Long-term trends in Secchi depth in the Baltic Sea, *Limnol. Oceanogr.*, 41, 346–351, <https://doi.org/10.4319/lo.1996.41.2.0346>, 1996.
- Saunois, M., Bousquet, P., Poulter, B., Peregón, A., Ciais, P., Canadell, J. G., Dlugokencky, E. J., Etiope, G., Bastviken, D., Houweling, S., Janssens-Maenhout, G., Tubiello, F. N., Castaldi, S., Jackson, R. B., Alexe, M., Arora, V. K., Beerling, D. J., Bergamaschi, P., Blake, D. R., Brailsford, G., Brovkin, V., Bruhwiler, L., Crevoisier, C., Crill, P., Covey, K., Curry, C.,

- Frankenberg, C., Gedney, N., Hoglund-Isaksson, L., Ishizawa, M., Ito, A., Joos, F., Kim, H. S., Kleinen, T., Krummel, P., Lamarque, J. F., Langenfelds, R., Locatelli, R., Machida, T., Maksyutov, S., McDonald, K. C., Marshall, J., Melton, J. R., Morino, I., Naik, V., O'Doherty, S., Parmentier, F. J. W., Patra, P. K., Peng, C. H., Peng, S. S., Peters, G. P., Pison, I., Prigent, C., Prinn, R., Ramonet, M., Riley, W. J., Saito, M., Santini, M., Schroeder, R., Simpson, I. J., Spahni, R., Steele, P., Takizawa, A., Thornton, B. F., Tian, H. Q., Tohjima, Y., Viovy, N., Voulgarakis, A., van Weele, M., van der Werf, G. R., Weiss, R., Wiedinmyer, C., Wilton, D. J., Wiltshire, A., Worthy, D., Wunch, D., Xu, X. Y., Yoshida, Y., Zhang, B. W., Zhang, Z., and Zhu, Q.: The global methane budget 2000-2012, *Earth Syst. Sci. Data*, 8, 697–751, doi:10.5194/essd-8-697-2016, 2016.
- Schmale, O., Schneider von Deimling, J., Gülzow, W., Nausch, G., Waniek, J. J., and Rehder, G.: Distribution of methane in the water column of the Baltic Sea, *Geophys. Res. Lett.*, 37, <https://doi.org/10.1029/2010GL043115>, 2010.
- Schmaljohann, R.: Methane dynamics in the sediment and water column of Kiel Harbour (Baltic Sea), *Mar. Ecol. Prog. Ser.*, 131, 263–273, doi:10.3354/meps131263, 1996.
- Schneider von Deimling, J., Gülzow, W., Ulyanova, M., Klusek, Z., and Rehder, G.: Detection and monitoring of methane ebullition, *BONUS-Baltic GAS Final report WP 3.3*, 2011.
- Scranton, M. I., and Farrington, J. W.: Methane production in the waters off Walvis Bay, *J. Geophys. Res.*, 82, 4947–4953, <https://doi.org/10.1029/JC082i031p04947>, 1977.
- Siedler, G., and Peters, H.: Properties of sea water: physical properties, in: *Oceanography*, edited by: Sündermann, J., Springer, Berlin, Germany, 233–264, 1986.
- Smetacek, V.: The annual cycle of Kiel Bight plankton: A long-term analysis, *Estuaries*, 8, 145–157, 1985.
- Smetacek, V., von Bodungen, B., von Bröckel, K., Knoppers, B., Martens, P., Peinert, R., Pollehne, F., Stegmann, P., and Zeitzschel, B.: Seasonality of plankton growth and sedimentation, in: *Seawater-Sediment Interactions in Coastal Waters*, edited by: Rumohr, J., Walger, E., and Zeitzschel, B., Springer, Berlin, Germany, 34–56, 1987.
- Steinle, L., Maltby, J., Treude, T., Kock, A., Bange, H. W., Engbersen, N., Zopfi, J., Lehmann, M. F., Niemann, H.: Effects of low oxygen concentrations on aerobic methane oxidation in seasonally hypoxic coastal waters, *Biogeosciences*, 14, 1631–1645, <https://doi.org/10.5194/bg-14-1631-2017>, 2017.
- Sturm, K., Werner, U., Grinham, A., and Yuan, Z.: Tidal variability in methane and nitrous oxide emissions along a subtropical estuarine gradient, *Estuar. Coast Shelf S.*, 192, 159–169, <https://doi.org/10.1016/j.ecss.2017.04.027>, 2017.
- Treude, T., Krüger, M., Boetius, A., and Jørgensen, B. B.: Environmental control on anaerobic oxidation of methane in the gassy sediments of Eckernförde Bay (German Baltic), *Limnol. Oceanogr.*, 50, 1771–1786, <https://doi.org/10.4319/lo.2005.50.6.1771>, 2005.
- Upstill-Goddard, R. C., Barnes, J., Frost, T., Punshon, S., and Owens, N. J.: Methane in the southern North Sea: Low-salinity inputs, estuarine removal, and atmospheric flux, *Global Biogeochem. Cy.*, 14, 1205–1217, <https://doi.org/10.1029/1999GB001236>, 2000.

- 485 Wanninkhof, R.: Relationship between wind speed and gas exchange over the ocean revisited, *Limnol. Oceanogr. : Method.*, 12, 351–362, <https://doi.org/10.4319/lom.2014.12.351>, 2014.
- Weber, T., Wiseman, N. A., and Kock, A.: Global ocean methane emissions dominated by shallow coastal waters, *Nat. Commun.*, 10, 4584, <https://doi.org/10.1038/s41467-019-12541-7>, 2019.
- Wever, T. F., Lühder, R., Voß, H., and Knispel, U.: Potential environmental control of free shallow gas in the seafloor of
490 Eckernförde Bay, Germany, *Mar. Geol.*, 225, 1-4, <https://doi.org/10.1016/j.margeo.2005.08.005>, 2006.
- Whiticar, M. J.: Diagenetic relationships of methanogenesis, nutrients, acoustic turbidity, pockmarks and freshwater seepages in Eckernförde Bay, *Mar. Geol.*, 182, 29–53, [https://doi.org/10.1016/S0025-3227\(01\)00227-4](https://doi.org/10.1016/S0025-3227(01)00227-4), 2002.
- Wiesenburg, D. A., and Guinasso Jr, N. L.: Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water, *J. Chem. Eng. Data*, 24, 356-360, 1979.
- 495 Wilson, S. T., Ferrón, S., and Karl, D. M.: Interannual variability of methane and nitrous oxide in the North Pacific Subtropical Gyre, *Geophys. Res. Lett.*, 44, 9885–9892, <https://doi.org/10.1002/2017GL074458>, 2017.
- WMO: Scientific assessment of ozone depletion: 2018, World Meteorological Organization, Geneva, Switzerland, Global Ozone Research and Monitoring Project–Report No. 58, 588 pp., 2018.
- Xiao, K. Q., Beulig, F., Roy, H., Jørgensen, B. B., and Risgaard-Petersen, N.: Methylotrophic methanogenesis fuels cryptic
500 methane cycling in marine surface sediment, *Limnol. Oceanogr.*, 63, 1519-1527, <https://doi.org/10.1002/lno.10788>, 2018.

Table 1. Annual mean (arithmetic average \pm standard deviation) of water temperature, salinity, wind speed and dissolved CH₄ concentrations at the BE time-series station during 2006–2017. Water temperatures, salinity and CH₄ concentrations were averaged over the water column (0–25 m). Wind speeds were recorded at Kiel lighthouse.

year	Temperature (°C)	Salinity	Wind speed (u_{10} , m s ⁻¹)	CH ₄ (nM)
2006	9.19 \pm 5.75	20.14 \pm 3.11	7.5 \pm 2.6	39.3 \pm 38.1
2007	9.68 \pm 4.55	17.78 \pm 2.14	7.5 \pm 2.5	44.9 \pm 45.5
2008	10.11 \pm 4.20	19.14 \pm 3.43	6.2 \pm 2.1	36.9 \pm 41.9
2009	9.20 \pm 4.81	18.36 \pm 2.22	7.3 \pm 2.3	27.8 \pm 26.2
2010	8.47 \pm 5.20	17.80 \pm 3.22	5.5 \pm 2.7	34.8 \pm 39.3
2011	8.74 \pm 5.16	19.14 \pm 2.78	6.8 \pm 3.1	36.9 \pm 29.1
2012	9.47 \pm 3.89	18.67 \pm 2.63	8.7 \pm 2.1	46.4 \pm 44.3
2013	9.04 \pm 5.45	17.89 \pm 3.74	5.9 \pm 2.8	67.7 \pm 83.1
2014	10.38 \pm 4.93	19.17 \pm 2.79	7.0 \pm 3.3	101.4 \pm 183.3
2015	9.19 \pm 4.28	19.71 \pm 3.30	6.1 \pm 2.8	35.7 \pm 36.3
2016	10.09 \pm 4.71	18.80 \pm 3.19	5.9 \pm 1.7	52.6 \pm 111.4
2017	10.21 \pm 4.86	19.50 \pm 2.11	6.8 \pm 2.4	30.5 \pm 22.9

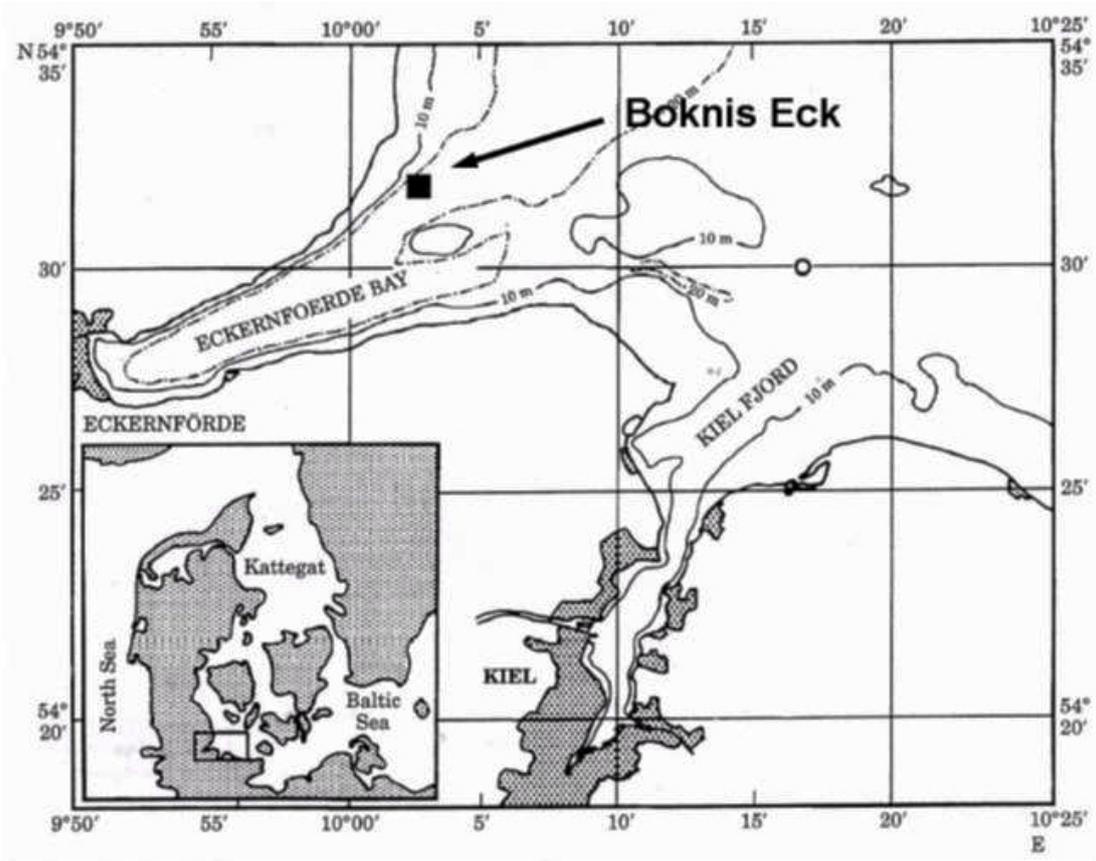
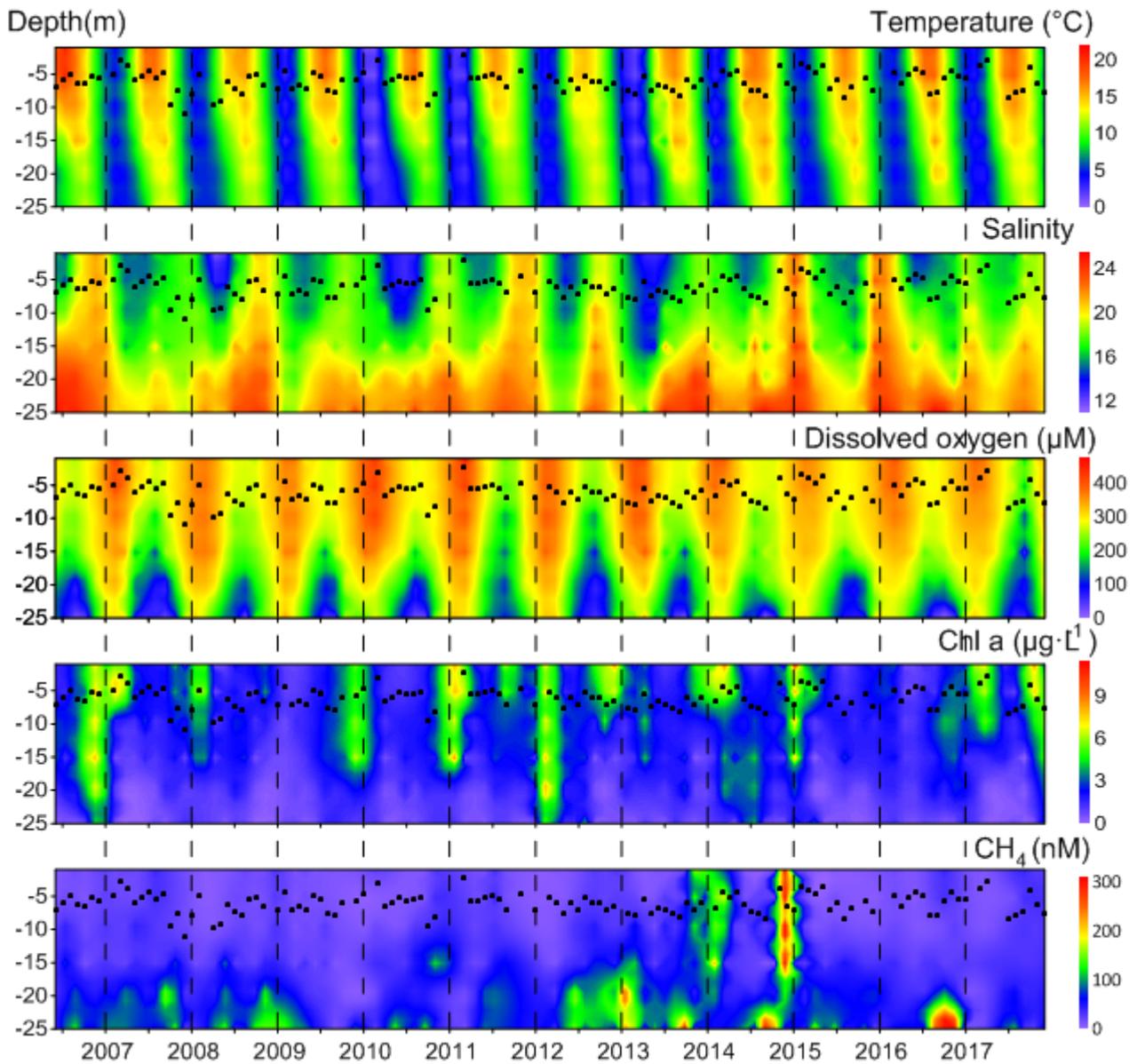
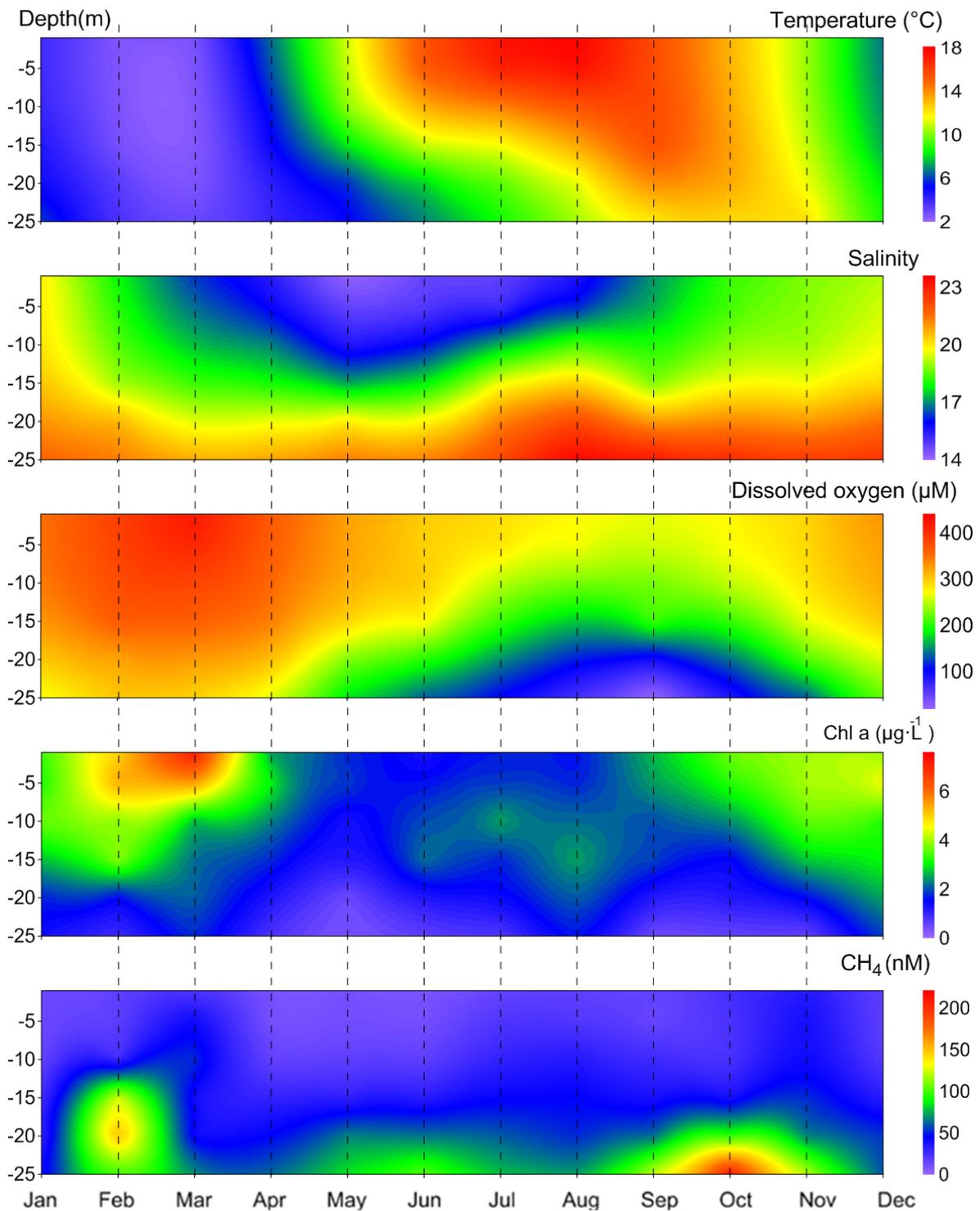


Fig. 1 Location (black square) of the Boknis Eck time-series station in the Eckernförde Bay, southwestern Baltic Sea. (from Hansen et al., 1999)



510 Fig 2. Distributions of temperature, salinity, dissolved O₂, Chlorophyll *a* and CH₄ at the BE time-series station during 2006–2017. Black dots indicate the monthly measurements of Secchi depth. To get a better visualization, the maximum color bar for CH₄ concentration is 300 nM, but some of the actual concentrations are higher (for example, in December 2014 and in autumn 2016).



515 **Fig 3.** Mean seasonal variations of temperature, salinity, dissolved O₂, Chlorophyll *a* and CH₄ at the BE time-series station during 2006–2017. CH₄ concentrations in December 2014 were excluded in plotting.

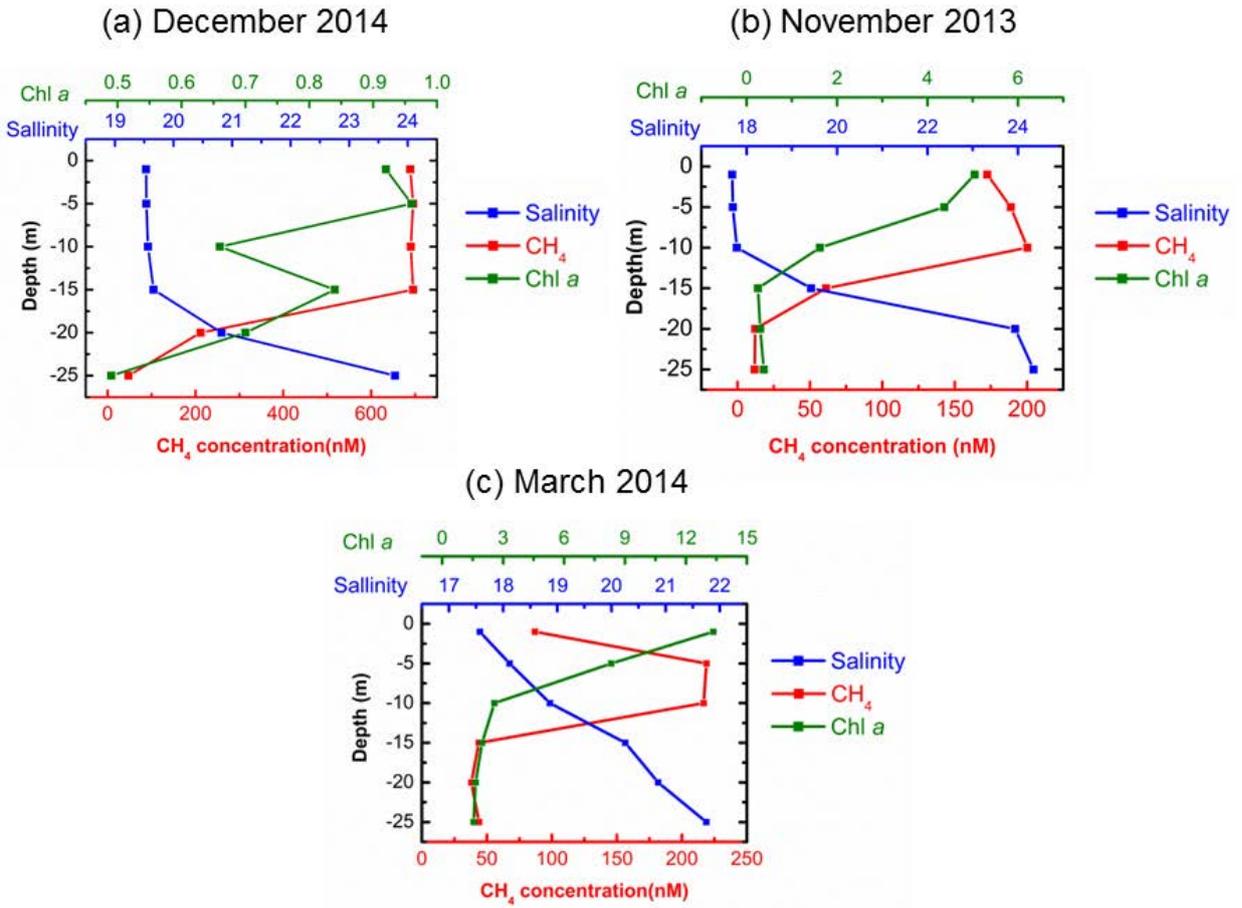


Fig 4. Vertical distribution of Chlorophyll *a*, salinity and CH₄ concentrations in the water column in December 2014 (a), November 2013 (b) and March 2014 (c).

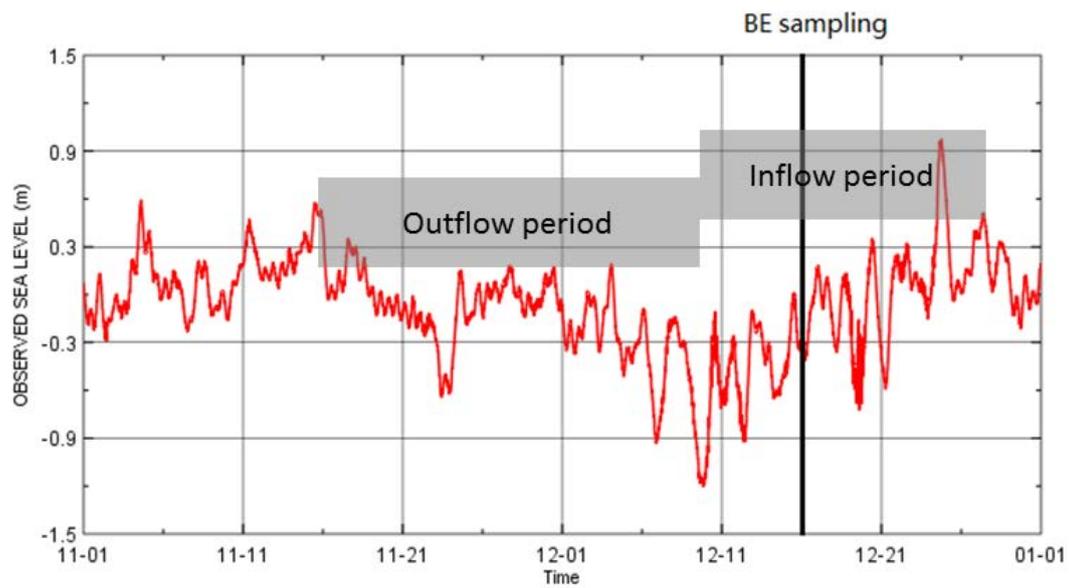
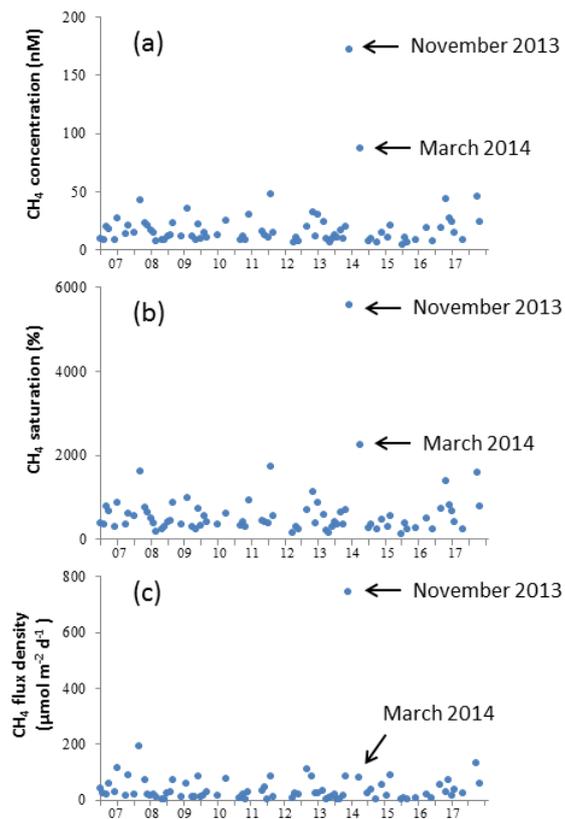
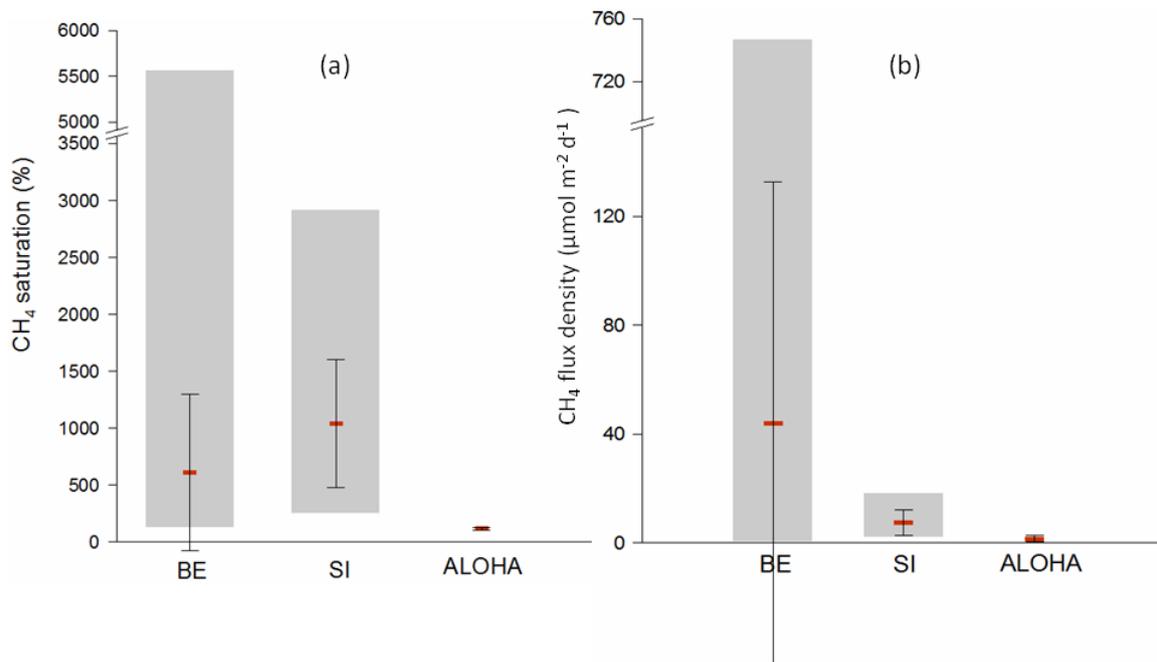


Fig 5. Sea level variations in November and December, 2014. The black line indicates the occurrence of BE sampling in December 2014.



525 **Fig 6. Inter-annual variations of dissolved CH₄ concentration (a), saturation (b) and flux density (c) at the BE time-series station during 2006–2017. Data collected from December 2014 were not shown.**



530 **Fig 7. Comparison of surface CH₄ saturations (a) and flux densities (b) from time-series stations of BE, Saanich Inlet (SI) and ALOHA. For the computation of flux density, the equations of Nightingale et al. (2000) and Wanninkhof (2014) were used for SI and ALOHA, respectively. Data in December 2014 at the BE time-series station were not included. Please note the break on the y axis for both charts.**