

Dissolved methane during hypoxic events at the Boknis Eck time series station (Eckernförde Bay, SW Baltic Sea)

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Abstract. Dissolved CH₄ was measured in the water column at the Boknis Eck (BE) time series station in the Eckernförde Bay (SW Baltic Sea) on a monthly basis from June 2006 to November 2008. The water column at BE was always supersaturated with CH₄ and, therefore, CH₄ was released to the atmosphere throughout the sampling period: the mean CH₄ surface (1 m) saturation at BE was 554±317%. A pulse of enhanced CH₄ emissions occurs when the CH₄ accumulation in the hypoxic bottom layer during summer is terminated in late summer/autumn. We did not detect a straightforward relationship between periods of enhanced CH₄ in the bottom layer and hypoxic events at BE: the sedimentary release of CH₄ seemed to be mainly triggered by sedimenting organic material from phytoplankton blooms. We conclude that future CH₄ emissions from BE will be determined by the intensity of phytoplankton blooms, which in turn will be influenced by eutrophication. However, hypoxic events seem to have only a modulating effect on the enhancement of sedimentary methanogenesis and the subsequent release of CH₄ to the water column.

Rosenberg, 2008; Rabalais et al., 2009; UNEP, 2004). So-called coastal hypoxic events or hypoxia occur when [O₂] falls below ~90 μmol L⁻¹ (2 mL L⁻¹) (Diaz and Rosenberg, 2008). Anoxic conditions are defined by [O₂]=0 μmol L⁻¹ and the occurrence of dissolved hydrogen sulphide (H₂S) (Naqvi et al., 2009). The increasing number of coastal hypoxic zones is attributed mainly to increasing nutrient inputs (i.e. eutrophication) by anthropogenic activities (UNEP, 2006). The duration and actual [O₂] of hypoxia and anoxia have profound influences on both ecosystems and biogeochemical cycles in coastal zones (Diaz and Rosenberg, 2008; Malakoff, 1998). This is especially alarming in view of the fact that the microbial formation (methanogenesis) of the climate-relevant trace gas methane (CH₄) is a strictly anaerobic process which is favoured under hypoxic and anoxic conditions in the water column as well as in the sediments (Cicerone and Oremland, 1988). However, to what extent the ongoing expansion of eutrophication-induced hypoxia is going to lead to (i) an increase in [CH₄] in coastal waters and (ii) a possible enhancement of CH₄ emissions to the atmosphere is not clear (Bange, 2006; Naqvi et al., 2009).

We measured CH₄ in the water column at the Boknis Eck coastal time series station in the Eckernförde Bay (SW Baltic Sea) on a monthly basis from June 2006 to November 2008. Because of seasonally occurring hypoxic events, Boknis Eck provides an ideal natural laboratory to investigate the effects of coastal hypoxia on the distribution of dissolved CH₄.

1 Introduction

The worldwide increasing number of coastal areas with extremely (persistent or temporary) depleted dissolved oxygen (O₂) concentrations [O₂] has received considerable scientific and public attention during the last few years (Diaz and



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2 Study site description

The time series station Boknis Eck (BE) is located at the entrance of the Eckernförde Bay ($54^{\circ}31'N$, $10^{\circ}02'E$; Fig. 1) and has a water depth of about 28 m. The hydrographic setting of BE is dominated by the inflow of North Sea water through the Kattegat and the Great Belt. Seasonal stratification is associated with the development of a pycnocline at about 15 m water depth from mid of March until mid of 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 (Hansen et al., 1999). Pronounced phytoplankton blooms occur regularly in autumn (September–November) and spring (February/March) and to a lesser extent during summer (July/August) (Smetacek, 1985). The autumn and spring blooms are followed by pronounced sedimentation of organic material with >75% (autumn) and >50% (spring) of the total production being sedimented (Smetacek et al., 1984). The summer blooms can be associated with a short period of pronounced sedimentation as well, however, sedimentation during the summer months is generally lower (<25% of the total production) compared to the sedimentation events in autumn and spring (Smetacek et al., 1984).

3 Methods

Concentrations of dissolved CH_4 [CH_4] were measured with a static equilibration method: 25 mL glass vials were filled bubble-free and immediately poisoned with $HgCl_2$ (aq). The samples were usually analyzed within 24 h after sampling, however, on some occasions samples had to be stored and were measured within a few weeks after sampling. After replacing 10 mL of the water sample with helium, the samples were allowed to equilibrate for at least 2 h. A 9 mL subsample of the headspace was used to flush a 2 mL sample loop. The volume of the sample loop was then injected onto a packed stainless steel column filled with molsieve 5A for isothermal gas chromatographic separation. Detection of CH_4 was done with a flame ionization detector. Further details of the method are described in Kock (2007). Two-point calibration curves were prepared daily before and after the measurements of the samples. For the calibration we used two standard gas mixtures of 1.779 ± 0.002 and 2.543 ± 0.002 ppm CH_4 in synthetic air. The gravimetrically prepared gas standards (made by DEUSTE Steininger GmbH, Mühlhausen, Germany) were calibrated against the actual NOAA standard scale (Dlugokencky et al., 2005) in the laboratories of the Max Planck Institute for Biogeochemistry in Jena, Germany. [CH_4] in $nmol L^{-1}$ was calculated with

$$[CH_4] = x' P V_{hs} / (RT V_{wp}) + x' \beta P \quad (1)$$

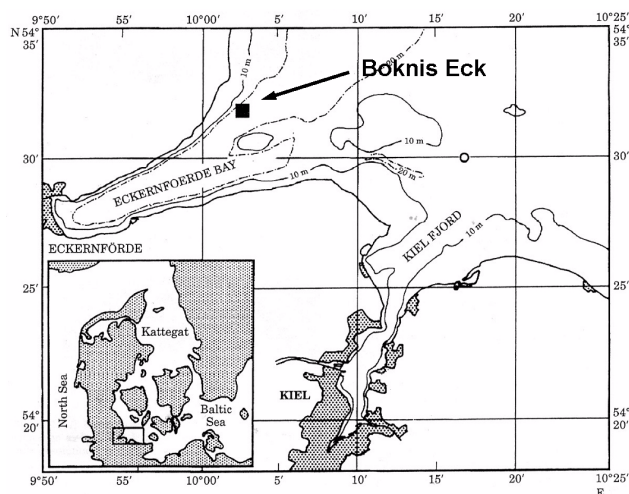


Fig. 1. Location (black square) of the time series station Boknis Eck in the Eckernförde Bay (SW Baltic Sea).

where x' is the dry mole fraction of CH_4 in the headspace, P is the ambient pressure (set to 10^5 Pa), V_{hs} and V_{wp} are the volumes of the headspace and the water phase, respectively. R stands for the gas constant ($8.31451 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1}$), T is the temperature during equilibration and β is the Bunsen solubility of CH_4 (Wiesenburg and Guinasso Jr., 1979). CH_4 saturations (Sat in %) are expressed as

$$\text{Sat} = 100[CH_4]/[CH_4]_{eq} \quad (2)$$

where $[CH_4]_{eq}$ is the equilibrium concentration calculated with the in-situ temperature and salinity at BE and an atmospheric CH_4 dry mole fraction of 1.85 ppm, which was considered to be a representative mean for the Baltic Sea region from 2006 to 2008 (Rigby et al., 2008).

Triplicate water samples for the determination of [CH_4] were taken on a monthly basis from six standard depths (1, 5, 10, 15, 20 and 25 m) with a 5 L Niskin bottle. The standard deviation was approximated with $([CH_4]_{\max} - [CH_4]_{\min})/1.91$, where $[CH_4]_{\min}$ and $[CH_4]_{\max}$ stand for the minimal and maximal CH_4 concentrations of the triplicate samples. The factor 1.91 is derived from the statistical method by David (1951). Triplicates with a standard deviation of >10% were omitted. The mean analytical error of [CH_4] was $\pm 4.7\%$.

Concentrations of dissolved O_2 and chlorophyll a were determined using standard methods (Grasshoff et al., 1999). Water temperature and salinity were taken from the monthly routine CTD measurements at BE. Water transparency was measured with a Secchi disk (~ 30 cm in diameter, white).

The CH_4 release to the atmosphere was calculated with

$$F_{ase} = k_w \cdot 60 \cdot 60 \cdot 24 \cdot (Sc_{CH_4}/600)^{-0.5} ([CH_4] - [CH_4]_{eq}) \quad (3)$$

where F_{ase} is the flux density in $\mu\text{mol m}^{-2} \text{ d}^{-1}$, k_w is the gas transfer coefficient (see below) and Sc is the Schmidt

number which was calculated as the ratio of the kinematic viscosity of seawater (Siedler and Peters, 1986) and the diffusion of CH_4 in seawater (Jähne et al., 1987). Sc_{CH_4} was calculated with the medians of the surface (1 m) water temperature (11.2°C) and salinity (16.8). For k_w we used $0.65 \times 10^{-5} \text{ m s}^{-1}$ as a lower limit and $1.51 \times 10^{-5} \text{ m s}^{-1}$ as an upper limit as recommended by Raymond and Cole (2001) for calculations of flux densities in estuaries. $[\text{CH}_4]$ was computed as the median of all measurements at 1 m depth (14.4 nmol L^{-1}) and $[\text{CH}_4]_{eq}$ was calculated as the median of the equilibrium concentrations in 1 m (3.1 nmol L^{-1}).

The data presented here are archived in MEMENTO (The Marine Methane and Nitrous Oxide Database) (Bange et al., 2009) and are available from the corresponding author upon request.

4 Results and discussion

Three hypoxic events with $[\text{O}_2] < 90 \mu\text{mol L}^{-1}$ have been observed at BE from 2006 to 2008 (Fig. 2). The most pronounced event was observed in 2007 when $[\text{O}_2]$ in the deep layer already started to drop below the threshold in May. The hypoxia in 2007 lasted until November and was most intense in September when the waters became anoxic as indicated by the occurrence of H_2S in the bottom layer (25 m). The hypoxic events in 2006 and 2008 were much shorter and less intense than in 2007: they lasted from August to November in 2006 and August to September 2008. The lowest $[\text{O}_2]$ values observed during the 2006 and 2008 hypoxia were 6.0 and $6.1 \mu\text{mol L}^{-1}$, respectively.

The fall and spring phytoplankton blooms in 2006/2007 and 2007/2008 could be easily identified by the considerably enhanced chlorophyll a concentrations, whereas the summer blooms in 2007 and 2008 showed only slightly enhanced chlorophyll concentrations (Fig. 2). The Secchi depth measurements showed a reduced water transparency of only $\sim 3 \text{ m}$ and $\sim 4 \text{ m}$ in February and March 2007, respectively, which were the lowest Secchi depths measured during the sampling period from June 2006 to November 2008. Because BE is not influenced by any river plumes, a reduced transparency could be caused only by living phytoplankton as well as dead organisms and other decaying organic material. We conclude therefore, that the sedimentation event in spring 2007 was more pronounced than the sedimentation event in spring 2008 and resulted in comparably higher O_2 consumption during remineralisation, which in turn caused the pronounced hypoxic event in 2007.

The time series of CH_4 is shown in Fig. 2. CH_4 concentrations were in the range from $6.6 \pm 0.2 \text{ nmol L}^{-1}$ ($=178\%$ saturation in 5 m in February 2008) to $235 \pm 17.4 \text{ nmol L}^{-1}$ ($=8340\%$ saturation at 20 m in October 2007). The mean CH_4 surface (1 m) saturation at BE was $554 \pm 317\%$. Our findings are in agreement with the measurements of Bussmann

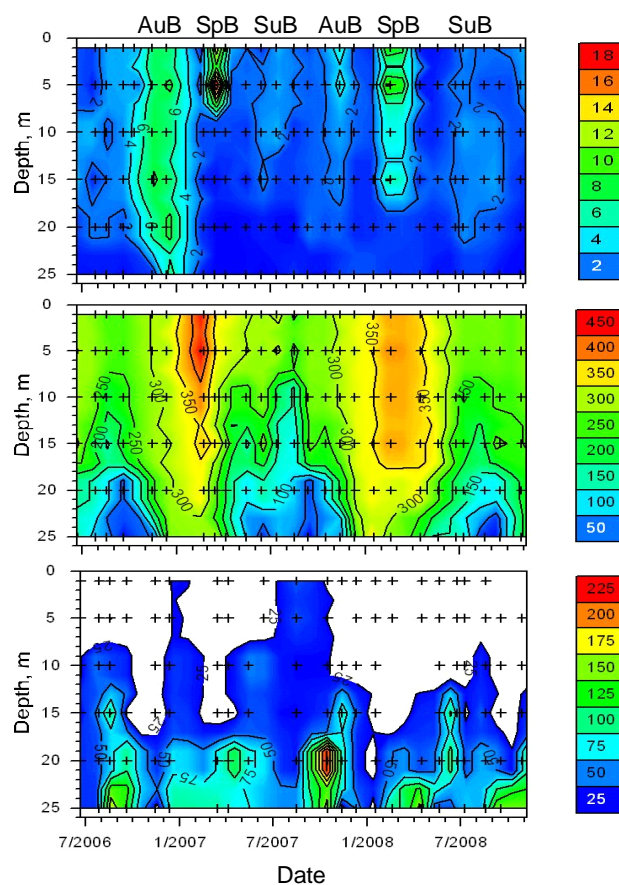


Fig. 2. Time series of chlorophyll a in $\mu\text{g L}^{-1}$ (upper panel), $[\text{O}_2]$ in $\mu\text{mol L}^{-1}$ (central panel) and $[\text{CH}_4]$ in nmol L^{-1} (lower panel) at the Boknis Eck time series station. Crosses mark the available measurements. Phytoplankton blooms are indicated: AuB, autumn bloom; SpB, spring bloom; SuB, summer bloom. On the x-axis the date is given as m/yyyy (e.g., 1/2007 stands for 1 January 2007).

and Suess (1998) at two stations in the southern part of Eckernförde Bay during February 1993 and May 1994. They found $[\text{CH}_4]$ in the surface layer (1 m) in the range from 2.1 to 2815 nmol L^{-1} . Comparable CH_4 saturations have been observed in other coastal areas of the Baltic Sea. From the Bodden Waters (southern Baltic Sea), for example, a seasonality of the CH_4 saturations in the range from 105 to 15 500% have been reported (Bange et al. 1998). CH_4 saturations in the open Baltic Sea (Baltic Proper) range from 113–395% (Bange et al., 1994) and are lower than those observed in coastal areas of the Baltic Sea. Our measurements at BE are in line with the view that the Baltic Sea is a significant regional source of atmospheric CH_4 (Bange, 2006).

The water column at BE was always supersaturated with CH_4 (Fig. 3) and, therefore, CH_4 was released to the atmosphere throughout the sampling period (for an estimate of the sea-to-air flux density see below). The seasonality of the mean monthly CH_4 surface (1 m) saturation is shown in

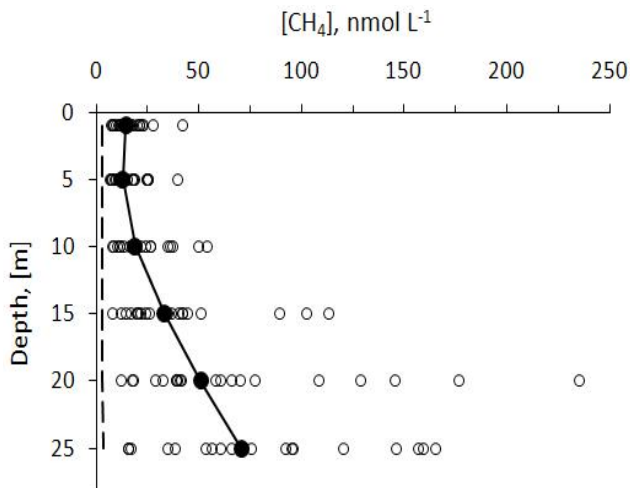


Fig. 3. Depth distribution of CH₄ at Boknis Eck (all data, open circles). The bold line indicates the mean CH₄ profile based on the median values calculated for each depth. The dashed line indicates the corresponding CH₄ equilibrium concentrations.

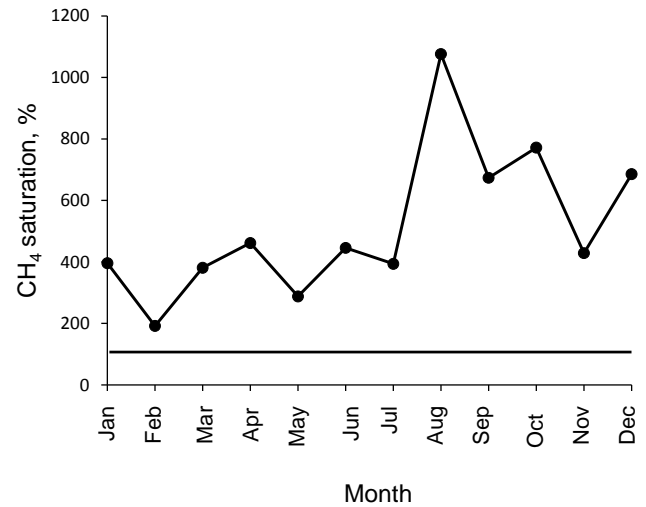


Fig. 4. Monthly mean CH₄ surface saturations at Boknis Eck. The vertical bold line indicates equilibrium with the atmosphere (i.e. 100% saturation).

Fig. 4. It is obvious that the mean CH₄ surface saturations are considerably enhanced (up to 1076%) from late summer to winter. This indicates that there is a pulse of high CH₄ emissions to the atmosphere when the accumulation of CH₄ in the hypoxic/anoxic bottom layer during summer stratification is terminated in late summer/autumn.

It is well known that the sediments of the Eckernförde Bay are sites of high CH₄ accumulation resulting from methanogenesis which, in turn, is fuelled by the high amount of organic material in the sediments (Abegg and Anderson, 1997; Treude et al., 2005; Whiticar, 2002). The CH₄ in the Eckernförde Bay sediments does not come from the underlying Schwedeneck petroleum reservoir (Whiticar, 2002). Despite the fact that at BE anaerobic CH₄ oxidation in the sediments can effectively prevent the CH₄ release to the water column (Treude et al., 2005), some of the CH₄ obviously is released via ebullition (Jackson et al., 1998). In the Eckernförde Bay CH₄ can be also released to the water column from pockmark structures during episodes of groundwater efflux (Busmann and Suess, 1998), however, the majority of the pockmarks are found in the southern part of Eckernförde Bay (Whiticar, 2002) and, therefore, a CH₄ contribution via groundwater is negligible at BE. Moreover, we did not find any signs of groundwater release in the salinity data of BE. In view of the discussion above we conclude that CH₄ in the water column of BE is dominated by its release from the sediments.

From the data in Fig. 2 it is obvious those periods with enhanced [CH₄] in the bottom layers are not correlated with the hypoxic events. This was confirmed by statistical analysis which did not reveal any statistical significant correlation between [O₂] and [CH₄]. In order to find out whether the observed variability of [CH₄] might be caused by the sea-

sonality of sedimentary methanogenesis, we focus the following discussion on the bottom layer (25 m). We detected a bimodal seasonal distribution of the mean monthly [CH₄] at 25 m with two pronounced maxima in late spring (March) and early autumn (September) (Fig. 5). The mean monthly chlorophyll a in 25 m showed a bimodal variability with maxima in autumn/spring (November–February) and summer (August) which coincide with the sedimentation events of the autumn/spring and summer blooms. The seasonal [CH₄] maxima in the bottom layer seem to be linked to both chlorophyll at 25 m and Secchi depth with a time lag of one month (Fig. 6). The correlation of [CH₄] with chlorophyll was significant at a significance level (α) of 0.05 ($r = 0.67$, $n = 10$), whereas the correlation with Secchi depth was significant at $\alpha > 0.05$ ($r = 0.56$, $n = 10$). Our results indicate that the major drivers of the seasonality of [CH₄] in the water column are the phytoplankton blooms which deliver organic material to the sediments leading in turn to enhanced sedimentary CH₄ formation (Treude et al., 2005) with a time lag of a month. Because the second (i.e. the early autumn) maximum of [CH₄] in the bottom layer is more pronounced and it is concurrent with the hypoxic event, it seems reasonable to suggest that hypoxia in conjunction with the occurrence of sedimenting organic material promotes the sedimentary CH₄ release at BE: during the hypoxic event, sedimentary methanogenesis at BE is significantly enhanced as has been shown by Treude et al. (2005). We conclude, therefore, that the hypoxic events at BE modulate (enhance) the sedimentary CH₄ release but they are not the prime cause of the CH₄ release to the water column which seems to be the sedimenting organic material.

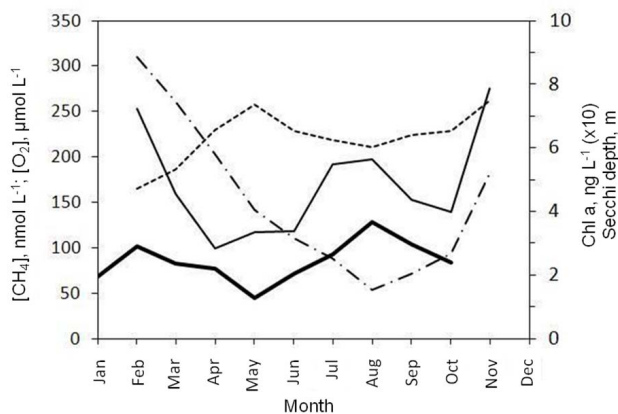


Fig. 5. Mean seasonal variability of O_2 (dashed dotted line), chlorophyll (thin black line), Secchi depth (dashed line) and CH_4 (bold line) at 25 m at Boknis Eck. The data from 2006–2008 were averaged to yield mean monthly values and smoothed with a 3-point moving average. Note that the CH_4 data were shifted back by one month.

The computed mean CH_4 flux densities for the sampling period 2006–2008 were 6.3 and $14.7 \mu\text{mol m}^{-2} \text{d}^{-1}$. This is in reasonable agreement with a rough estimate of the CH_4 ebullition flux from the sediment to the overlying water column in the range of 3 – $20 \mu\text{mol m}^{-2} \text{d}^{-1}$ (Jackson et al., 1998). Additional source or sink terms such as advection of $[CH_4]$ or aerobic CH_4 oxidation in the water column may contribute to the $[CH_4]$ distribution at BE as well, however, these processes have not been quantified at BE yet.

5 Summary

Sedimentary release of CH_4 determined the CH_4 concentrations in the water column at the Boknis Eck time series station during the sampling period from June 2006 to November 2008. The water column at BE was always supersaturated with CH_4 , and therefore, BE was a source of CH_4 to the atmosphere throughout the sampling period. Enhanced release of CH_4 to the atmosphere occurs when the CH_4 accumulated in the hypoxic bottom layer during summer is brought to the surface by mixing of the water column in late summer/autumn. We did not detect a straightforward relationship between periods of enhanced CH_4 in the bottom layers and hypoxic events. Indeed we found a bimodal seasonality of $[CH_4]$ in the bottom layer with two maxima in March and September. The sedimentary release of CH_4 seemed to be mainly triggered by sedimenting organic material from phytoplankton blooms. Therefore, we conclude that future CH_4 emissions from BE will be determined by the intensity of phytoplankton blooms, which in turn will be influenced by the future trends in nutrient inputs (i.e. eutrophication). Hypoxic events have only a modulating effect on the

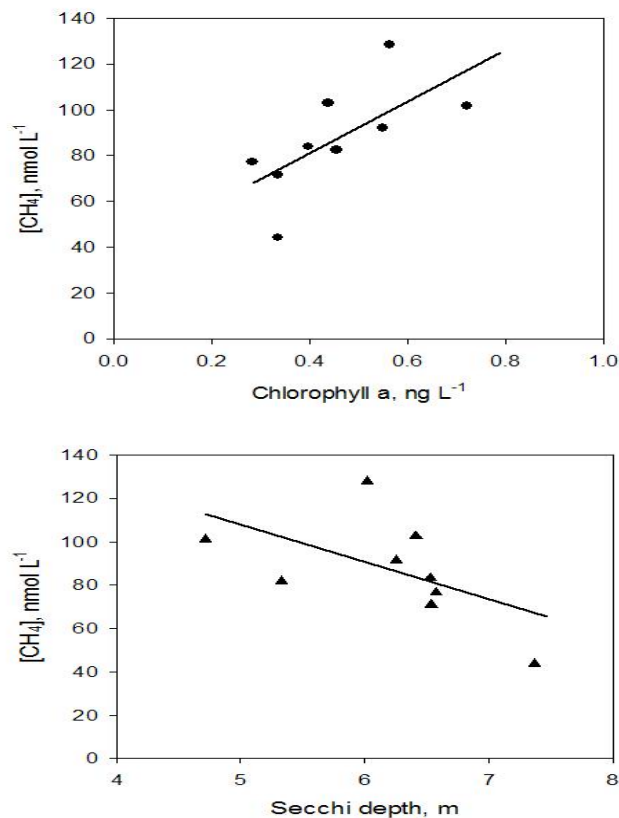


Fig. 6. Mean monthly CH_4 vs. chlorophyll (upper panel) and CH_4 vs. Secchi depth (lower panel). The mean monthly CH_4 and chlorophyll data were calculated for 25 m. Note that the CH_4 data were shifted by one month (see Fig. 4) to account for the apparent time lag of one month.

enhancement of methanogenesis in the sediments. The time series study presented here (and time series of dissolved CH_4 in other coastal regions worldwide, for example off Chile, Fariás et al., 2009) seem to be a valuable tool to monitor CH_4 emissions from coastal areas in order to infer the potential effects of eutrophication and climate change for the long-term trends of coastal CH_4 emissions to the atmosphere.

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