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Dissolved methane during hypoxic events at the Boknis Eck Time Series Station (Eckernförde Bay, SW Baltic Sea)

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Abstract

Dissolved CH_4 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 CH_4 and, therefore, CH_4 was released to the atmosphere throughout the sampling period. A flux estimate indicates that the atmospheric CH_4 emissions are balanced by the CH_4 flux from the sediment. We did not detect a straightforward relationship between periods of enhanced CH_4 in the bottom layer and hypoxic events at BE: The sedimentary release of CH_4 seemed to be mainly triggered by sedimenting organic material from phytoplankton blooms. We conclude that future CH_4 emissions from BE will be determined by both the occurrence and the intensity of phytoplankton blooms, which in turn will be influenced by eutrophication. However, hypoxic events seem to have only a modulating effect in the way that they enhance sedimentary methanogenesis.

1 Introduction

The worldwide increasing number of coastal areas with extremely (persistent or temporary) depleted dissolved oxygen (O_2) concentrations [O_2] has received considerable scientific and public attention during the last years (Diaz and Rosenberg, 2008; Rabalais et al., 2009; UNEP, 2004). So-called coastal hypoxic events or hypoxia occur when [O_2] falls below $\sim 90\,\mu mol\,L^{-1}$ ($2\,mL\,L^{-1}$) (Diaz and Rosenberg, 2008). Anoxic conditions are defined by $[O_2] = 0\,\mu mol\,L^{-1}$ and the occurrence of dissolved hydrogen sulphide (H_2S). The increasing number of coastal hypoxia is attributed mainly to increasing nutrient inputs (i.e. eutrophication) by anthropogenic activities (UNEP, 2006). The duration and actual [O_2] 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 alerting in view of the fact that the microbial formation (methanogenesis) of the climate-relevant trace gas methane (CH_4) is a strictly

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anaerobic process which is favoured under hypoxic and anoxic conditions in the water column as well as in the sediments (Cicerone and Oremland, 1988). Therefore, on the one hand, it was speculated that an expansion of eutrophication-caused hypoxia might lead to an increase in the accumulation of dissolved CH_4 and thus lead to increasing coastal CH_4 emissions to the atmosphere (Bange, 2006). On the other hand, Naqvi et al. (2009) concluded that an expansion of hypoxic areas not necessarily would lead to an increase in CH_4 emissions.

We measured CH_4 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 CH_4.

2 Study site description

The time series station Boknis Eck (BE) is located at the entrance of the Eckernförde Bay (54°31′ N, 10°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 via 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).

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 $HgCl_2$

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(aq). After replacing 10 mL of the water sample with helium, the samples were allowed to equilibrate for at least 2 hours. 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 took place with a flame ionization detector. Further details of the method are described in Kock (2007). Two-point calibration curves were measured 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

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

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 m^3 Pa K^{-1} 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 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

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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 ±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 routine CTD measurements at BE. Water transparency was measured with a Secchi disk (~30 cm in diameter, white).

4 Results and Discussion

Three hypoxic events with [O_2] <90 μmol L^{-1} have been observed at BE from 2006 to 2008 (Fig. 2). The most pronounced event was observed in 2007 when [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 intensive in September when the waters became anoxic in the bottom layer (25 m). The hypoxic events in 2006 and 2008 were much shorter: They lasted from August to November in 2006 and August to September 2008. The lowest [O_2] observed during the 2006 and 2008 hypoxia were 6.0 and 6.1 μmol L^{-1}, respectively. The pronounced hypoxic event in 2007 was resulting from an intensive phytoplankton bloom which is clearly visible in both the enhanced chlorophyll a concentrations from November 2006 until March 2007 (Fig. 2) and a reduced water transparency (Secchi depth) of only ~3 m and ~4 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, the reduced transparency was caused only by living phytoplankton as well as dead organisms and other decaying organic material. The intensive bloom led to enhanced sedimentation of organic material which, in turn, resulted in enhanced O_2 consumption during remineralisation and the development of 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

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6.6±0.2 nmol L^{-1} (=178% saturation in 5 m in February 2008) to 235±17.4 nmol L^{-1} (= 8340% saturation in 20 m in October 2007). 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). Our findings are in agreement with the measurements of Bussmann and Suess (1998) at two stations in the southern part of Eckernförde Bay during February 1993 and May 1994. They found [CH_4] in the surface layer (1 m) in the range from 2.1 to 2815 nmol L^{-1}.

It is well known that the sediments of the Eckernförde Bay are sites of high CH_4 accumulation resulting from in situ 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 CH_4 in the Eckernförde Bay sediments does not come from the underlying Schwedeneck petroleum reservoir (Whiticar, 2002).) Despite the fact that at BE anaerobic CH_4 oxidation in the sediments can effectively prevent the CH_4 release to the water column (Treude et al., 2005), some of the CH_4 obviously is released via ebullition (Jackson et al., 1998) or methanogenesis in the upper sediments (Treude et al., 2005). In the Eckernförde Bay CH_4 can be also released to the water column from pockmark structures during episodes of groundwater efflux (Bussmann and Suess, 1998), however, the majority of the pockmarks are found in the southern part of Eckernförde Bay (Whiticar, 2002) and, therefore, a CH_4 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 CH_4 in the water column of BE is dominated by its release from the sediments.

From the data in Fig. 2 it is obvious that periods with enhanced [CH_4] in the bottom layers are not correlated with the hypoxic events. This was confirmed by statistical analysis which did not revealed any statistical significant correlation between [O_2] and [CH_4]. In order to find out whether the observed variability of [CH_4] may be caused by the seasonality of sedimentary methanogenesis, we focus the following discussion on the bottom layer (25 m). We detected a bimodal seasonal CH_4 distribution in 25 m with

two pronounced maxima in spring and fall (Fig. 4). The seasonal [CH_4] maxima in the bottom layer seem to be linked to both chlorophyll in 25 m and Secchi depth with a time lag of one month (Fig. 5). The correlation of [CH_4] 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 $\alpha > 0.05$ ($r = 0.56$, $n = 10$). We conclude that the major drivers of the seasonality of [CH_4] in the water column are the phytoplankton blooms which deliver organic material to the sediments leading in turn to enhanced sedimentary CH_4 formation (Treude et al., 2005) with a time lag of a month. Because the second (i.e. the fall) maximum of CH_4 in the bottom layer is more pronounced and it is concurrent with the hypoxic event, it might be reasonable to suggest that hypoxia in conjunction with the occurrence of sedimenting organic material emphasise the sedimentary CH_4 release at BE: During the hypoxic event in Fall, sedimentary methanogenesis at BE is significantly enhanced as has been recently shown by Treude et al. (2005). Therefore, the hypoxic events at BE modulate the sedimentary CH_4 release but they do not trigger enhanced CH_4 release to the water column.

The CH_4 release to the atmosphere was calculated with

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

where F_{ase} is the flux density in $\mu mol\,m^{-2}\,d^{-1}$, 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). For k_w we used $0.65\times10^{-5}\,m\,s^{-1}$ as a lower limit and $1.51\times10^{-5}\,m\,s^{-1}$ as an upper limit as recommended by Raymond and Cole (2001) for calculations of flux densities in estuaries. [CH_4] was computed as the median of all measurements in 1 m depth ($14.4\,nmol\,L^{-1}$) and $[CH_4]_{eq}$ was calculated as the median of the equilibrium concentrations in 1 m ($3.1\,nmol\,L^{-1}$) (see Fig. 3). The resulting mean CH_4 flux densities for the sampling period 2006–2008 were 6.3 and 14.7 $\mu mol\,m^{-2}\,d^{-1}$. 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 $\mu mol\,m^{-2}\,d^{-1}$ (Jack-

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son et al., 1998). Therefore, we conclude that the CH_4 release from the sediments is sufficient to balance the CH_4 release to atmosphere. Additional source or sink terms such as advection or aerobic CH_4 oxidation in the water column seem to be negligible at BE.

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. A rough flux estimate indicates that the CH_4 release to the atmosphere is balanced by the CH_4 flux from the sediments and no further sink or source processes are required to explain the CH_4 water column distribution. We did not detect a straightforward relationship between periods of enhanced CH_4 in the bottom layers and hypoxic events. Indeed we found a 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 both the occurrence and intensity of phytoplankton blooms, which in turn will be influenced by the future trend in nutrient inputs (i.e. eutrophication). Hypoxic events have only a modulating effect in the way that they enhance 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; Farías et al., 2009) seem to be a valuable tool to monitor CH_4 emissions from coastal areas in order to decipher 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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Boknis Eck time series station is run by the Forschungsbereich Marine Biogeochemie of the IFM-GEOMAR, Kiel: www.ifm-geomar.de/index.php?id=bokniseck.

References

Abegg, F. and Anderson, A. L.: The acoustic turbid layer in muddy sediments of Eckernfoerde Bay, western Baltic Sea: Methane concentrations, saturation and bubble characteristics, Mar. Geol., 137, 137–147, 1997.

Bange, H. W.: Nitrous oxide and methane in European coastal waters, Estuarine, Coast. Shelf Sci., 70, 361–374, 2006.

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, 1998.

Cicerone, R. J. and Oremland, R. S.: Biogeochemical aspects of atmospheric methane, Global Biogeochem. Cy., 2, 299–327, 1988.

David, H. A.: Further applications of range to analysis of variance, Biometrika, 38, 393–409, 1951.

Díaz, R. J. and Rosenberg, R.: Spreading dead zones and consequences for marine ecosystems, Science, 321, 926–929, 2008.

Dlugokencky, E. J., Myers, R. C., Lang, P. M., Masarie, K. A., Crotwell, A. M., Thoning, K. W., Hall, B. D., Elkins, J. W., and Steele, L. P.: Conversion of NOAA atmospheric dry air CH_4 mole fractions to a gravimetrically prepared standard scale, J. Geophys. Res., 110, D18306, doi:10.1029/2005JD006035, 2005.

Farías, L., Fernández, C., Faúndez, J., Cornejo, M., and Alcaman, M. E.: Chemolithoautotrophic production mediating the cycling of greenhouse gases N_2O and CH_4 in an upwelling ecosystem, Biogeosci.Discuss., 6, 6205–6247, 2009.

Hansen, H. P., Giesenhagen, 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. Suppl., 56, 65–71, 1999.

Jackson, D. R., Williams, K. L., Wever, T. F., Friedrichs, C. T., and Donelson Wright, L.: Sonar evidence for methane ebullition in Eckernförde Bay, Cont. Shelf Res., 18, 1893–1915, 1998.

Jähne, B., Heinz, G., and Dietrich, W.: Measurements of the diffusion coefficients of sparingly soluble gases in water, J. Geophys. Res., 92, 10767–10776, 1987.
Kock, A.: Methane measurements in selected ocean areas: Eastern tropical North Atlantic Ocean and southwestern Labrador Sea, Diploma thesis, Kiel University, Kiel, Germany, 106 pp., 2007.
Malakoff, D.: Death by suffocation in the Gulf of Mexico, Science, 281, 190–192, 1998.
Naqvi, S. W. A., Bange, H. W., Farías, L., Monteiro, P. M. S., Scranton, M. I., and Zhang, J.: Coastal hypoxia/anoxia as a source of CH_4 and N_2O, Biogeosci. Discuss., 6, 9455–9523, 2009.
Rabalais, N. N., Díaz, R. J., Levin, L. A., Turner, R. E., Gilbert, D., and Zhang, J.: Dynamics and distribution of natural and human-caused coastal hypoxia, Biogeosci. Discuss., 6, 9359–9453, 2009.
Raymond, P. A. and Cole, J. J.: Gas exchange in rivers and estuaries: Choosing a gas transfer velocity, Estuaries, 24, 312–317, 2001.
Rigby, M., Prinn, R. G., Fraser, P. J., Simmonds, P. G., Langenfels, R. L., Huang, J., Cunnold, D., . M., Steele, L. P., Krummel, P. B., Weiss, R. F., O'Doherty, S., Salameh, P. K., Wang, H. J., Harth, C. M., Mühle, J., and Porter, L. W.: Renowed growth of atmospheric methane, Geophys. Res. Lett., 35, L22805, doi:10.1029/2008GL036037, 2008.
Siedler, G. and Peters, H.: Properties of sea water, in: Oceanography, edited by: Sündermann, J., Landolt-Börnstein, New Series, Springer Verlag, Berlin, Germany, 233–264, 1986.
Treude, T., Krüger, M., Boetius, A., and Jørgensen, B. B.: Environmental control on anaerobic oxidation of methane in gassy sediments of Eckernförde Bay (German Baltic), Limnol. Oceanogr., 50, 1771–1786, 2005.
UNEP: The nitrogen cascade: Impacts of food and energy production, in: Global Environment Outlook Year Book 2003, edited by: UNEP, UNEP, Nairobi, Kenya, 55–60, 2004.
UNEP: Marine and coastal ecosystems and human well-being: A synthesis report based on the findings of the Millennium Ecosystem Assessment, UNEP, Nairobi, 76, 2006.
Whiticar, M. J.: Diagentic relationship of methanogenesis, nutrients, acoustic turbidity, pockmarks and freshwater seepages in Eckernförde Bay, Mar. Geol., 182, 29–53, 2002.
Wiesenburg, D. A. and Guinasso Jr., N. L.: Equilibrium solubilities of methane, carbon monoxide, hydrogen in water and seawater, J. Chem. Eng. Data, 24, 356–360, 1979.

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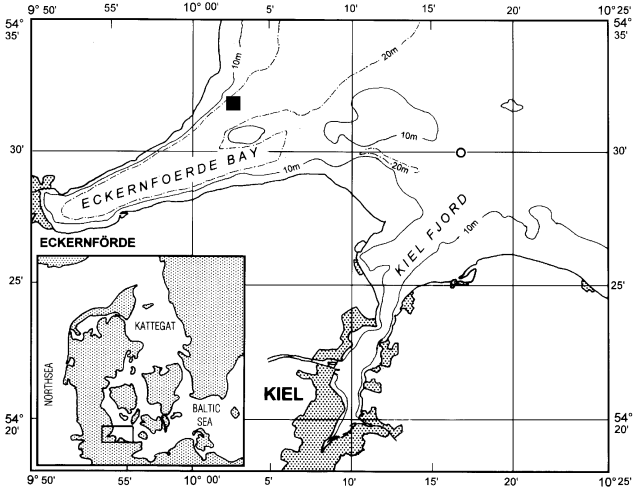

Fig. 1. Location (black square) of the time series station Boknis Eck in the Eckernförde Bay (SW Baltic Sea).

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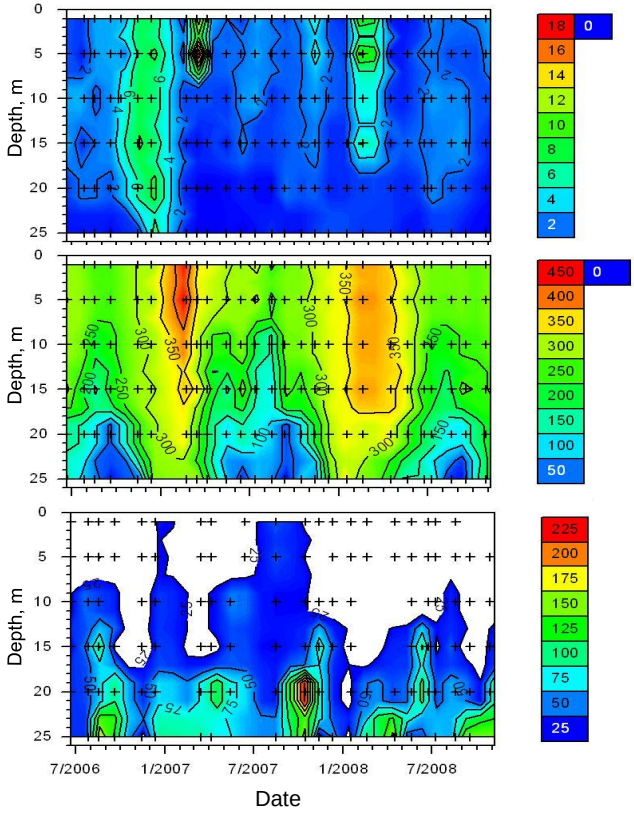

Fig. 2. Time series of chlorophyll a in $\mu g\,L^{-1}$ (upper panel), $[O_2]$ in $\mu mol\,L^{-1}$ (central panel) and $[CH_4]$ in $nmol\,L^{-1}$ (lower panel) at the Boknis Eck time series station. Crosses mark the available measurements.

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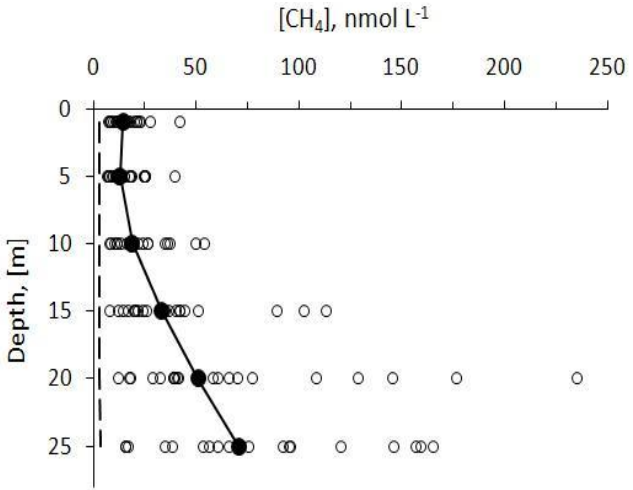

Fig. 3. Depth distribution of CH_4 at Boknis Eck (all data, open circles). The bold line indicates the mean CH_4 profile based on the median values calculated for each depth. The dashed line indicates the corresponding CH_4 equilibrium concentrations.

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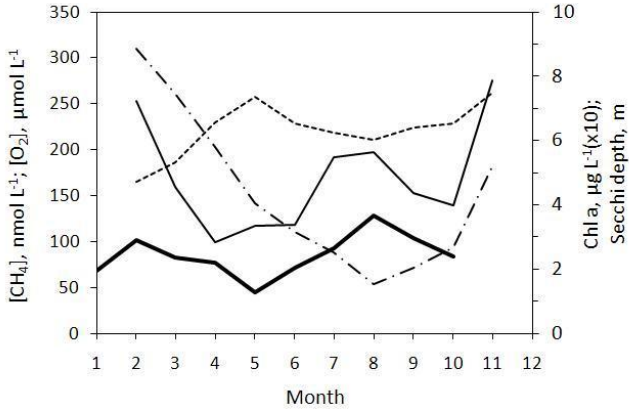

Fig. 4. Mean seasonal variability of O_2 (dashed dotted line), chlorophyll (thin black line), Secchi depth (dashed line) and CH_4 (bold line) in 25 m at Boknis Eck. The data from 2006–2008 were averaged to yield mean monthly values and smoothed with a 3-point moving average. Please note that the CH_4 data were shifted back by one month.

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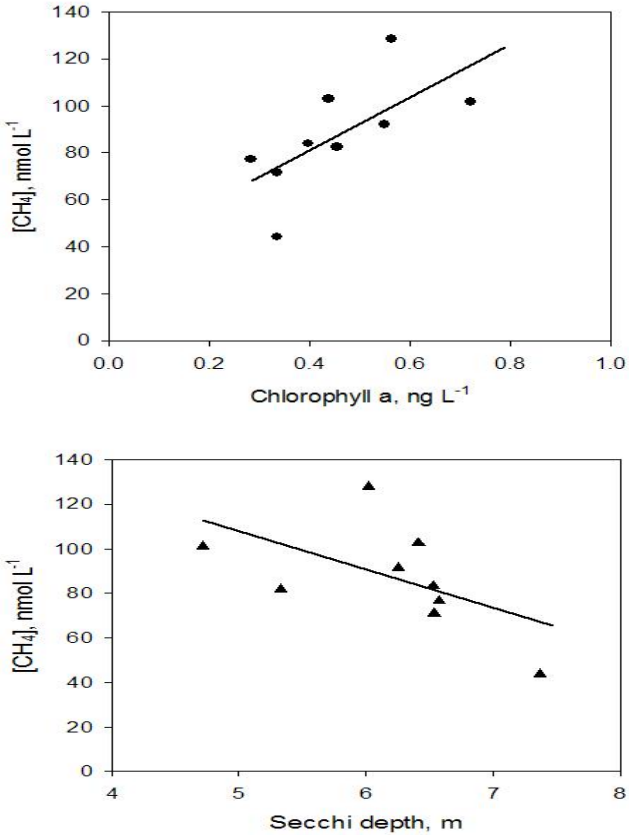

Fig. 5. Mean monthly CH_4 vs. chlorophyll (upper panel) and CH_4 vs. Secchi depth (lower panel). The mean monthly CH_4 and chlorophyll data were calculated for 25 m. Please note that the CH_4 data were shifted by one month (see Fig. 4) to account for the apparent time lag of one month.

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