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CH₄ off Mauritania

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Methane emissions from the upwelling area off Mauritania (NW Africa)

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Abstract

Coastal upwelling regions have been identified as sites of enhanced CH₄ emissions to the atmosphere. The coastal upwelling area off Mauritania (NW Africa) is one of the most biologically productive regions of the world's ocean but its CH₄ emissions have not been quantified so far. More than 1000 measurements of atmospheric and dissolved CH₄ in the surface layer in the upwelling area off Mauritania were performed as part of the German SOPRAN (Surface Ocean Processes in the Anthropocene) study during two cruises in March/April 2005 (P320/1) and February 2007 (P348). During P348 enhanced CH₄ saturations of up to 179% were found close to the coast and were associated with upwelling of South Atlantic Central Water. An area-weighted, seasonally adjusted estimate yielded overall annual CH₄ emissions in the range from 0.7 to 1.4 Gg CH₄. Thus the upwelling area off Mauritania represents a regional hot spot of CH₄ emissions but seems to be of minor importance for the global oceanic CH₄ emissions.

1 Introduction

Atmospheric methane (CH₄) is a greenhouse gas and plays an important role in the chemistry of the Earth's atmosphere (WMO, 2007; IPCC, 2007). The world's ocean, as a natural source of CH₄, plays only a minor role in the global budget of atmospheric CH₄. Estimates of the global oceanic CH₄ emissions differ considerably and range from 0.4–0.8 Tg CH₄ yr⁻¹ for the open ocean (Bates et al., 1996; Kelley and Jeffrey, 2002) up to 11–18 Tg CH₄ yr⁻¹ including coastal areas (Bange et al., 1994). Biologically productive coastal regions cover only a small portion of the world's ocean, but appear to be sites of significantly enhanced oceanic CH₄ emissions (see e.g. Bange, 2006). Coastal upwelling regions such as found in the NW Arabian Sea, the coast off Oregon and off Namibia (SW Africa) have been identified as sites of enhanced CH₄ concentrations and emissions, respectively (Owens et al., 1991; Rehder et al., 2002;

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Monteiro et al., 2006). CH₄ emissions from coastal upwelling areas are indirectly linked to high primary productivity which favours CH₄ formation during methanogenesis in sinking organic particles or in the sediments (Rehder et al., 2002; Sansone et al., 2001). CH₄-enriched subsurface water masses are brought to the surface during the upwelling events providing a pathway to ventilate CH₄ from the ocean to the atmosphere. The coastal upwelling area off Mauritania (NW Africa) is one of the most biologically productive regions of the world's ocean but its CH₄ emissions have not been quantified so far. Here we present the first study of CH₄ in the coastal upwelling area of Mauritania during two cruises during the upwelling seasons in 2005 and 2007. On the basis of more than 1000 measurements of atmospheric and dissolved CH₄ in the surface layer we present an area-weighted, seasonally adjusted CH₄ flux estimate for the Mauritanian upwelling.

2 Study site description

The eastern tropical North Atlantic Ocean is an area with strongly differing hydrographic properties. On the one hand, the Canary and North Equatorial Currents form the eastern part of the North Atlantic Subtropical Gyre which is a zone of low nutrient-supply and thus low primary production (Signorini et al., 1999). On the other hand nutrient-rich upwelled water masses feed zones of high biological productivity off the West African coast (Minas et al., 1986). Coastal upwelling along Mauritania occurs in consequence of offshore Ekman transport due to trade winds along the coastline (Mittelstaedt, 1986) and shows a seasonality following the shifting of the Inter-Tropical Convergence Zone (ITCZ) throughout the year (Hagen, 2001). In the region between Cap Vert (10° N) and Cap Blanc (21° N) seasonal upwelling takes place during winter/spring with the southernmost extension in February (Schemainda et al., 1975; Nykjær and Van Camp, 1994; Mittelstaedt, 1986). Two different subsurface water masses have been identified to feed the upwelling zone (Tomczak, 1980): North of 21° N upwelled waters are mainly influenced by North Atlantic Central Water (NACW) while south of 21° N they

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show properties of South Atlantic Central Water (SACW). Both NACW and SACW are found between 100 and 800 m water depth. SACW is advected by a poleward under-current into the northern hemisphere and is nutrient enriched compared to the NACW (Minas et al., 1982).

3 Methods

The measurements were performed on board the research vessel Poseidon during the cruises P320/1 and P348. The cruise P320/1 was a pilot study of the German SOPRAN (Surface Ocean Processes in the Anthropocene) project and took place from 21 March to 7 April 2005. However, CH₄ measurements were performed only from 27 March to 30 March. The cruise P348 was part of the SOPRAN study and took place from 8 to 26 February 2007. During P348 CH₄ measurements were performed in the period from 19 to 24 February. The cruise tracks are shown in Fig. 1.

CH₄ was determined using a gas chromatograph equipped with a flame ionization detector. Details of the analytical system are described in Kock (2007) and Bange et al. (1996). Seawater was pumped continuously from a depth of approximately 3 m into a shower type equilibrator developed by R. F. Weiss (Scripps Institution of Oceanography, La Jolla, CA). Concentrations and resulting saturation values were corrected for difference between the water temperature at the sea chest and the continuously recorded water temperature in the equilibrator. A series of measurements of seawater and ambient air followed by two standards (1.779±0.002 and 2.543±0.002 ppm CH₄ in synthetic air) were repeated every 26 min (P320/1) and 22 min (P348). 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.

The analytical precision, calculated for P320/1 as the ratio of the standard deviation of the atmospheric measurements to the mean atmospheric mole fraction was ±1.1%.

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The mean relative errors of the CH₄ concentrations and saturations, were estimated to ±5%. Saturation values (expressed in %, i.e., 100%=equilibrium) were calculated by applying the solubility equation of Wiesenburg and Guinasso (1979). Continuous time series of seawater temperature (SST), salinity, and wind speed were obtained from the ship's records. SST and salinity were measured by the ship's thermosalinograph and calibrated against CTD values.

4 Results and discussion

The mean atmospheric CH₄ dry mole fraction during P320/1 in March 2005 was 1.84±0.02 ppm CH₄ and is in agreement with the monthly mean of 1.821 ppm measured in March 2005 at the NOAA/ESRL atmospheric baseline observatory Izaña on Tenerife (28.3° N, 16.5° W, elevation 2300 m) (Dlugokencky et al., 2007). In contrast to P320/1, the atmospheric CH₄ dry mole fractions during P348 in February 2007 were highly variable and ranged from 1.8 to 2.5 ppm (Fig. 2). They are in reasonable agreement with the monthly mean CH₄ dry mole fraction of 1.836±0.017 ppm measured in February 2007 at Izaña (E. Dlugokencky, personal communication)]. During P348 enhanced CH₄ mole fractions were found between 19° N and 21° N. This could result from air masses, which became enriched with CH₄ while crossing the Banc d'Arguin area as indicated by air mass backward trajectories (Fig. 3). The shallow waters of the Banc d'Arguin ecosystem (water depths between 1–10 m) are very productive and, therefore, the sediments of the Banc d'Arguin should be rich in organic material and favourable for enhanced emissions of CH₄. With the assumption that an air mass at 20 m spent 6 h over the Banc d'Arguin area before being measured at the ship, the observed atmospheric increase of about 0.7 ppm requires a CH₄ surface flux of about 100 μmol h⁻¹ m⁻². This seems plausible given the fact that CH₄ fluxes from organic-rich tropical coastal environments such as mangroves can be >1000 μmol h⁻¹ m⁻² (Allen et al., 2007; Biswas et al., 2007). Unfortunately, CH₄ measurements from the inner Banc d'Arguin are not available.

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Backward trajectories for P320/1 indicated that the air masses measured during P320/1 did cross the Banc d'Arguin as well (Quack et al., 2007), however, the distance from the ship positions to the Banc d'Arguin was considerably larger compared to P348. Thus we speculate that either the CH₄ source in the Banc d'Arguin area was weaker in 2005 or that the air masses were depleted in CH₄ due to mixing or atmospheric decomposition before arriving at the ship. During both cruises we did not find indications that the atmospheric values have been influenced by possible contamination due to CH₄ emissions from the ship's diesel engines (Sinha et al., 2003).

In March 2005 dissolved CH₄ concentrations were rather uniform and ranged from 2.1 to 2.5 nmol L⁻¹ with saturations close to the equilibrium with the atmosphere (98–106%) (Fig. 4). During P348 in February 2007 dissolved CH₄ concentrations were much more variable and ranged from 2.1 to 4.9 nmol L⁻¹. CH₄ saturations ranged up to 179% (Fig. 4). The majority of low CH₄ saturations were found in the western part of the transect at 18.5° N and north of 20° N, whereas significantly enhanced CH₄ saturations were mainly found close to the coast between 19° to 19.5° N (Fig. 4).

Our open ocean data are in good agreement with CH₄ concentrations (about 2 nmol L⁻¹) measured along 20° W (Rhee, 2000). However, our open ocean concentrations are lower than those observed by Forster et al. (2007), who found a mean CH₄ concentration of 3±0.7 nmol L⁻¹ (corresponding to a mean CH₄ saturation of 156±29%) in the surface layer at three stations off Mauritania along 18° W in September 2003. The discrepancy might result from seasonal and/or interannual differences (Nykjær and Van Camp, 1994) because the measurements by Rhee (2000) and Forster et al. (2007) were performed in September/October 1998 and September 2003, respectively.

Figure 5 shows a plot of SST vs. CH₄ saturation to illustrate the role of upwelling processes. It is obvious that the enhanced CH₄ saturations during P348 were associated with low SST indicating upwelled water masses. In order to analyze the effects of mixing between open ocean and upwelled water masses during P348, we applied a simple mixing model by defining two mixing endmembers: open ocean water

masses with SST >19°C and upwelled water masses with SST <19°C and CH₄ concentrations >3.9 nmol L⁻¹. The linear correlation of these data points has a slope of -0.75±0.28 nmol L⁻¹ K⁻¹. The CH₄/SST relationship from the Mauritanian upwelling is in the range of comparable CH₄/SST relationships reported from the NW Arabian Sea upwelling area (-0.09 nmol L⁻¹ K⁻¹) (Bange et al., 1998) and from the upwelling area off Oregon (-1.5 nmol L⁻¹ K⁻¹, as estimated from Fig. 5 in Rehder et al. 2002). Thus, the potential CH₄ upwelling “efficiency” off Mauritania in February 2007 was moderate compared to the upwelling off Oregon but significantly higher than in the NW Arabian Sea.

The hydrographic properties of the subsurface waters together with CH₄ saturations are shown in Fig. 6. At temperatures <19°C, most data points lie between the T/S lines of NACW and SACW, suggesting that they were resulting from mixing of the two water masses. While the water with enhanced CH₄ saturations (i.e. those found close to Banc d’Arguin) show properties close to the SACW, water with CH₄ saturations around 100% were associated with NACW. Thus, we conclude that the observed enhanced CH₄ concentrations mainly originated from water masses with a major contribution of SACW. A possible contribution of CH₄ enriched water masses originating from the Banc d’Arguin (characterised by surface salinities of >37 (Mittelstaedt, 1986; Peters, 1976) is not visible in Fig. 6 and thus seems to be unlikely at the time of our cruises.

5 CH₄ air-sea exchange

The CH₄ exchange flux density, F in pmol m⁻² s⁻¹, can be parameterized as $F = k_w(C_w - C_a)$, where k_w is the gas transfer coefficient, C_w is the seawater concentration, and C_a is the equilibrium water concentration calculated using the corresponding atmospheric dry mole fraction. To calculate k_w , we used the tri-linear k_w /wind speed relationship from Liss and Merlivat (1986) (hereinafter referred to as LM86) or, alternatively, the quadratic k_w /wind speed relationship established by Wanninkhof (1992) (hereinafter referred to as W92). The coefficients k_w were adjusted by multiplying with

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$(Sc/600)^{-n}$ ($n=2/3$ for wind speeds $\leq 3.6 \text{ m s}^{-1}$ and $n=0.5$ for wind speeds $> 3.6 \text{ m s}^{-1}$) for LM86 and $(Sc/660)^{-0.5}$ for W92. Sc is the Schmidt number for CH_4 and was calculated using empirical equations for the kinematic viscosity of seawater (Siedler and Peters, 1986) and the diffusivity of CH_4 in water (Jähne et al., 1987). The measured wind speeds were normalized to 10 m height by using the relationship of Garratt (1977).

In order to estimate the CH_4 emissions from the Mauritanian upwelling we pooled our data into the two categories: open ocean which includes data with SST $> 19^\circ\text{C}$ and upwelling-influenced coastal data with SST $< 19^\circ\text{C}$. Then we calculated the mean flux densities and emissions for the two categories (Table 1). The CH_4 emissions from the coastal upwelling off Mauritania (0.5–0.9 Gg CH_4) are comparable with the emissions from the coastal upwelling in the NW Arabian Sea (0.5–0.9 Gg CH_4 , calculated for a 4 months upwelling period) (Bange et al., 1998). The annual CH_4 emissions, calculated as the sum of the individual emissions during the upwelling and the non-upwelling seasons, range from 0.7 to 1.4 Gg CH_4 (Table 1) representing about 0.1–0.4% of the global open ocean emissions of 400–800 Gg yr^{-1} (Bates et al., 1996; Kelley and Jeffrey, 2002).

6 Summary

Atmospheric CH_4 dry mole fractions during the cruise P348 in February 2007 were highly variable and were most probably influenced by high CH_4 emissions from the adjacent shallow waters of the Banc d'Arguin. In March 2005 (cruise P320/1) dissolved CH_4 concentrations were rather uniform whereas in February 2007 (cruise P348) dissolved CH_4 concentrations were much more variable. During P348 CH_4 saturations ranged up to 179 %. The significantly enhanced CH_4 saturations were mainly found close to the coast between 19° to 19.5° N and were associated with upwelling of SACW. The potential CH_4 upwelling “efficiency” off Mauritania in February 2007 was moderate compared to the upwelling off Oregon but significantly higher than in the NW Arabian Sea. The overall annual CH_4 emissions were estimated to range from 0.7 to 1.4 Gg CH_4 .

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Thus the upwelling area off Mauritania represents a regional hot spot but is of minor importance for the global oceanic CH₄ emissions.

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Table 1. CH₄ emission estimate.

	Area ^a , 10 ¹² m ⁻²	Mean flux density pmol m ⁻² s ⁻¹		Emissions, Gg	
		Upwelling ^b	Non-upwelling ^b	Upwelling ^b	Non-upwelling ^b
Season					
Coast	0.3	6.7/11	–	0.5/0.9	–
Open ocean	0.5	2.8/5.4	–	0.2/0.4	–
Coast + open ocean	0.8	–	2.8/5.4 ^c	–	0.04/0.09

^a We assumed a that upwelling occurs in 50 km wide band close to the coast which extends roughly from 24° N and 18° N, yielding $0.3 \times 10^{12} \text{ m}^2$. The total area of $0.8 \times 10^{12} \text{ m}^2$ is the area given by Forster et al. (2007) for the eastern (Canary) coastal province as defined by Longhurst (1998).

^b First value stands for flux densities and emissions based on Liss and Merlivat (1986), second value stands for flux densities and emissions based on Wanninkhof (1992). We assumed a mean duration of 6 months for both the upwelling and the non-upwelling seasons.

^c Adopted from the open ocean measurements during the upwelling season.

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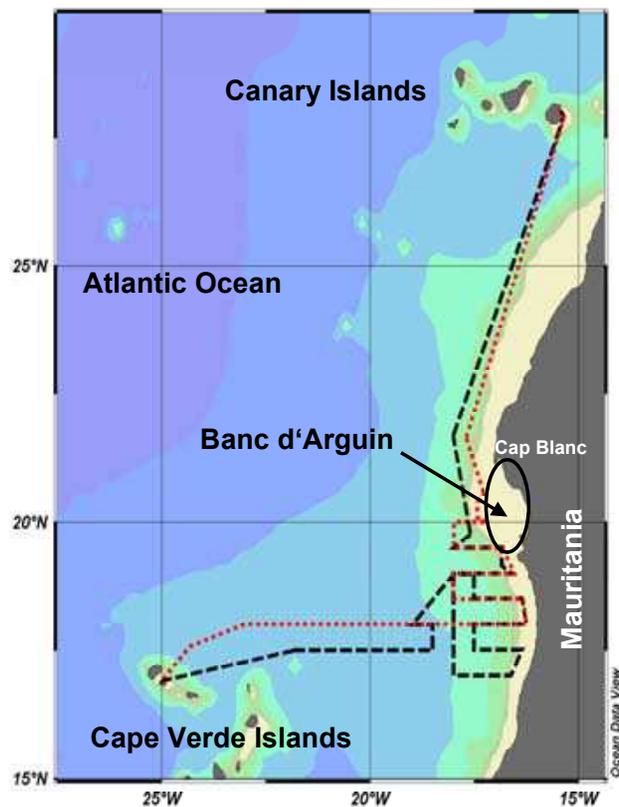


Fig. 1. Cruise tracks of P320/1 (black, March/April 2005) and P348 (red, February 2007) in the eastern tropical North Atlantic Ocean.

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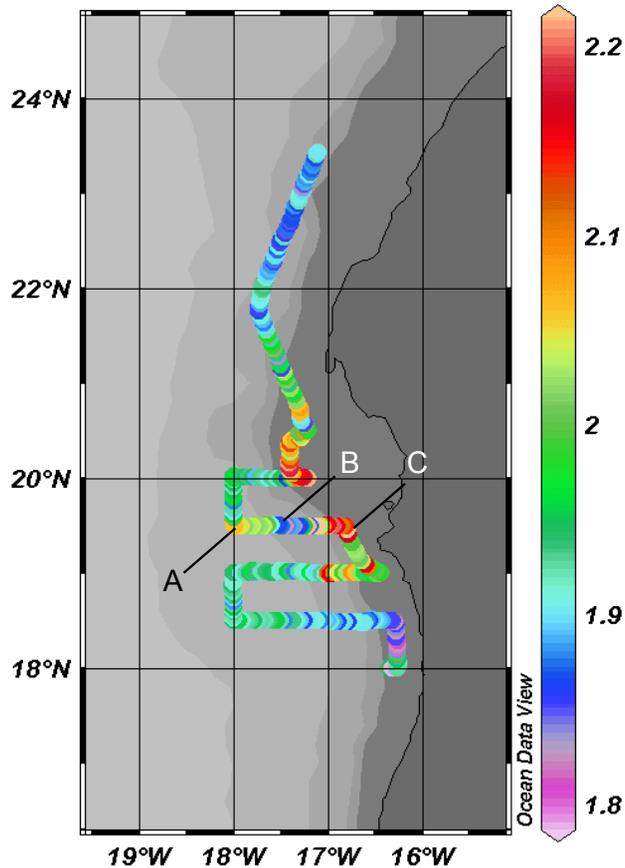


Fig. 2. Atmospheric CH₄ dry mole fraction during P348. The capital letters refer to the air mass backward trajectories shown in Fig. 3.

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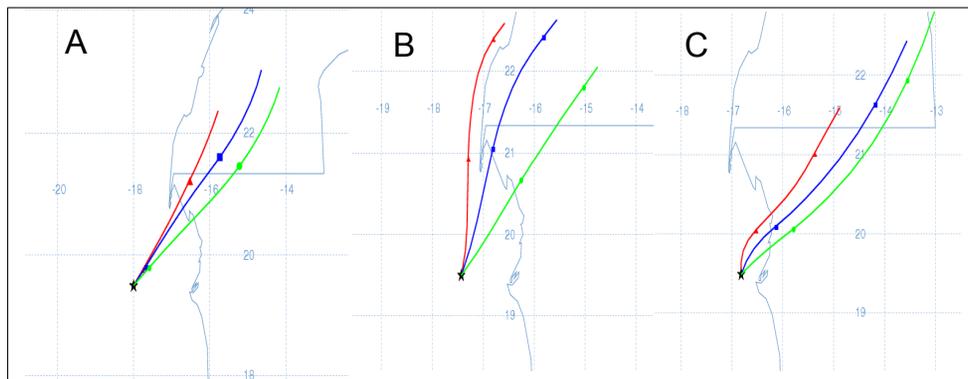


Fig. 3. Selected 12h backward air mass trajectories. Trajectories were calculated with the NOAA HYSPLIT on-line transport and dispersion model (Draxler and Rolph, 2003). The starting points and times correspond to the ships position as depicted with the capital letters in Fig. 2. Red trajectory, 20 m above sea level (a.s.l.), blue trajectory, 200 m a.s.l., and green trajectory, 500 m a.s.l.

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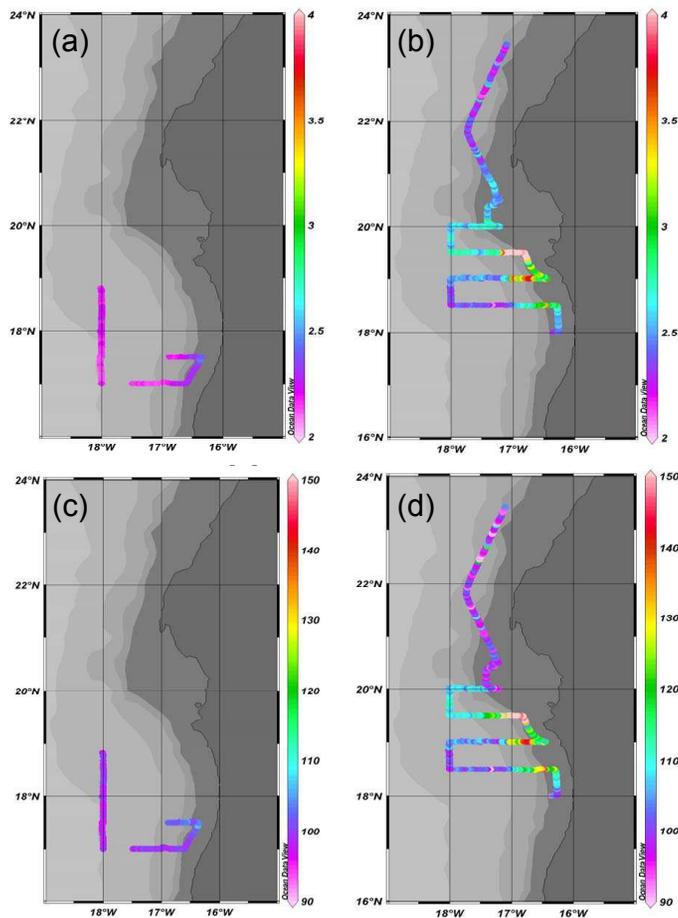


Fig. 4. CH₄ concentrations (in nmol L⁻¹) during P320/1 (a) and P348 (b) and CH₄ saturations (in %) during P320/1 (c) and P348 (d).

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CH₄ off Mauritania

A. Kock et al.

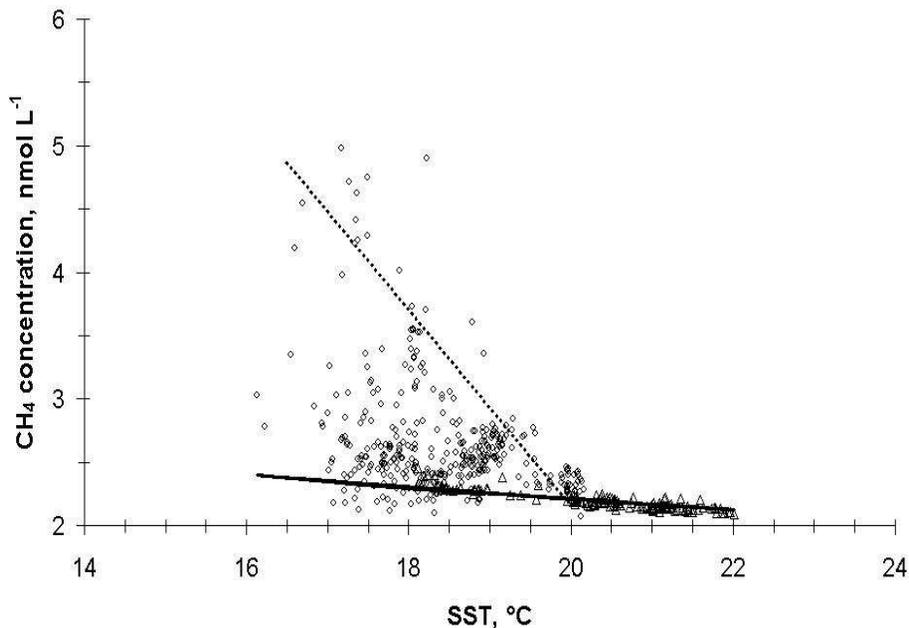


Fig. 5. CH₄ concentrations vs. SST. Open circles represent data from P348, open triangles represent data from P320/1. The solid line is the dissolved CH₄ equilibrium concentration calculated with an atmospheric CH₄ dry mole fraction of 1.83 ppm. The dashed line stands for the linear correlation between the data from the open ocean and the upwelling as defined in the text; $y = -0.752x + 17.24$ ($r = 0.923$, $n = 91$, $\alpha = 0.01$).

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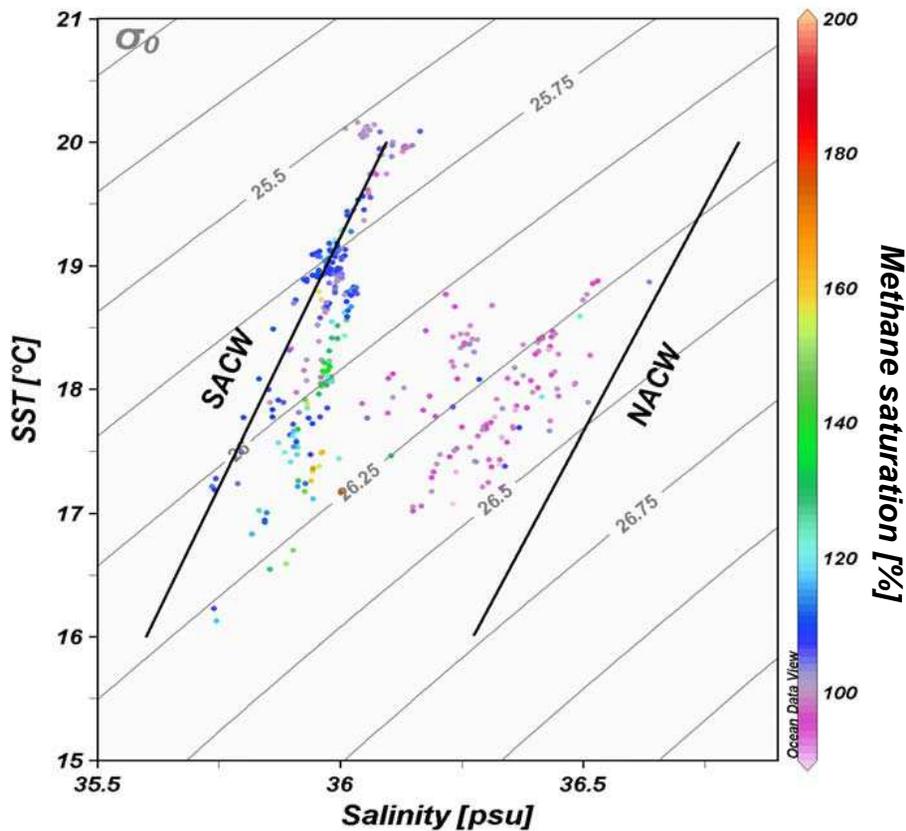


Fig. 6. T/S diagram and CH₄ saturations from the P348. The T/S curves of the predominant water masses, NACW and SACW, are shown as straight lines (Tomczak and Godfrey, 2003).

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