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

A. Kock¹, S. Gebhardt^{1,*}, and H. W. Bange¹

¹Forschungsbereich Marine Biogeochemie, IFM-GEOMAR, Leibniz-Institut für Meereswissenschaften, Düsternbrooker Weg 20, 24105 Kiel, Germany

*now at: Atmospheric Chemistry Dept., Max Planck Institute for Chemistry, Mainz, Germany

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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 200% 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 1.6 to 2.9 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



Correspondence to: H. W. Bange (hbange@ifm-geomar.de)

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; 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 and 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 and biological 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 (see e.g. Signorini et al., 1999). On the other hand nutrient-rich upwelled water masses feed zones of high biological productivity off the Northwest African coast (Minas et al., 1982).

Upwelling events off Mauritania are characterised by a pronounced drop in the surface temperatures (here defined as the difference between the temperatures off the coast and the open ocean) of >-6.5°C (Wooster et al., 1976; Speth and Detlefsen, 1982): Surface temperatures of <17°C are typical for upwelled water masses along the coast of Mauritania (Mittelstaedt, 1986). The active upwelling occurs within a narrow (10-20 km) band along the continental margin as a consequence of offshore Ekman transport due to the trade winds along the Mauritanian 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 (\sim 15° 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; Wooster et al., 1976): On the basis of a compilation of sea surface temperature data from merchant ship observations during the period 1850-1970, Wooster et al. (1976) concluded that upwelling between 12° and 20° N takes places from January through May. With a detailed oceanographic study from 1970-1973, Schemainda et al. (1975) showed that the regional upwelling seasons last from end of November to mid of May (off Cap Vert), from October to June (off Nouakchott, $\sim 18^{\circ}$ N) and throughout the year (off Cap Blanc).

Beside the pronounced seasonal variability, the Mauritanian upwelling also shows an interannual variability caused by El Niño-Southern Oscillation (ENSO) events (Roy and Reason, 2001): During warm ENSO events upwelling is weakened and during cold ENSO events (i.e. La Niña conditions) upwelling is intensified. There is a 4–5 months time lag between the ENSO events and the resulting upwelling anomalies (i.e. wind stress and SST anomalies) off Mauritania (Roy and Reason, 2001).

Two different subsurface water masses have been identified to feed the upwelling (see e.g. Tomczak, 1982; Pastor et al., 2008): North of 21°N upwelled waters are mainly influenced by North Atlantic Central Water (NACW) while south of 21° N they show properties of South Atlantic Central Water (SACW). The temperature-salinity (T-S) characteristics of NACW and SACW are described by straight lines between the T/S points 7°C/35.0 and 18°C/36.7 (for NACW) and 5°C/34.3 and 20°C/36.0 (for SACW). This is in line with the definitions of the upper limits of NACW (18.0°C/36.38) and SACW (18.0°C/35.9) as given by Manríquez and Fraga (1982). Both NACW and SACW are found between 100 and 800 m water depth off the coast (Tomczak, 1982). SACW is advected by a poleward undercurrent into the Northern Hemisphere and is nutrient enriched compared to the NACW (Minas et al., 1982; Tomczak, 1981; Pastor et al., 2008).

During the coastal upwelling events the formation of cold water filaments (with an average length of 130 km and an average width of 30 km) have been observed off Mauritania (Kostianoy and Zatsepin, 1996). Filaments contribute significantly to the offshore export of the shelf production

(Álvarez-Salgado et al., 2007; Gabric et al., 1993).

Several attempts have been made to decipher characteristic biogeographic or oceanic provinces for the tropical Northeast Atlantic Ocean: On the basis of algal ecology, near-surface circulation patterns and chlorophyll data, Sathyendranath et al. (1995) proposed the province Canary Current (CNRY) which includes both the upwelling areas of NW Africa (off Senegal, Mauritania and Morocco) and the upwelling off Portugal. An oceanic classification was introduced by Hooker et al. (2000) on the basis of T-S data. They defined the Canary Current Upwelling Province (CCUp) from 16° N to 20° N. A more detailed classification based on bathymetry and surface circulation patterns was proposed by Hoepffner et al. (1999) who distinguished three provinces in the tropical NE Atlantic Ocean: Cap Blanc Gyre (CBgy, water depths >2000 m, Cap Blanc slope (CBsl, water depths 200–2000 m) and Cap Blanc shelf (CBsh, water depths <200 m). The two coastal provinces (CBsl and CBsh) extend from 15° N to 22° N and are therefore comparable with the CCUp province by Hooker et al. (2000) but they are not comparable with the more extended CNRY province by Sathyendranath et al. (1995).

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 ionisation 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 the 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.

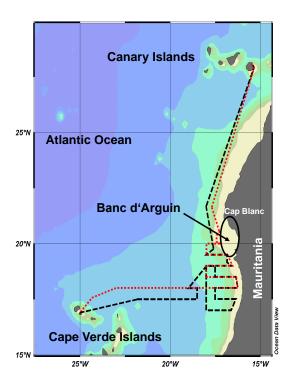


Fig. 1. Cruise tracks of P320/1 (black, March/April 2005) and P348 (red, February 2007) in the eastern tropical North Atlantic Ocean.

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 $\pm 1.1\%$. The mean relative errors of the CH₄ concentrations and saturations, were estimated to $\pm 5\%$. 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 CH_4 dry mole fraction during P320/1 in March 2005 was 1.84 ± 0.02 ppm CH_4 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 CH_4 dry mole fractions during P348 in February 2007 were highly variable and ranged from 1.79 to 2.37 ppm (Fig. 2). They are in reasonable agreement with the monthly mean CH_4 dry mole fraction of 1.836 ± 0.017 ppm measured in February 2007 at Izaña (E. Dlugokencky, personal communication). During P348 enhanced CH_4 mole fractions were found between 19° N and 21° N. This could result

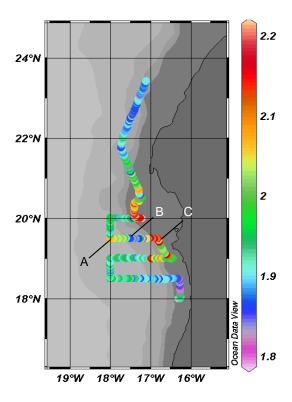


Fig. 2. Atmospheric CH₄ dry mole fraction during P348. The capital letters refer to the air mass backward trajectories shown in Fig. 3.

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 $100 \,\mu$ mol 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 μ mol h⁻¹ m⁻² (see e.g. Allen et al., 2007; Biswas et al., 2007). Unfortunately, CH₄ measurements from the inner Banc d'Arguin are not available.

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 the CH_4 source in the Banc d'Arguin area was weaker in 2005. During both cruises we did not find indications that the atmospheric values have been influenced by possible contamination due to CH_4 emissions from the ship's diesel engines (Sinha et al., 2003).

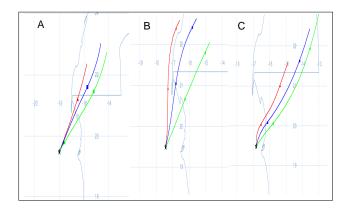


Fig. 3. Selected 12 h backward air mass trajectories. Trajectories were calculated with the NOAA HYSPLIT on-line transport and dispersion model (Draxler and Rolph, 2003). The starting points and times correspond to the ship's position as depicted with the capital letters in Fig. 2. Red trajectory, 20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

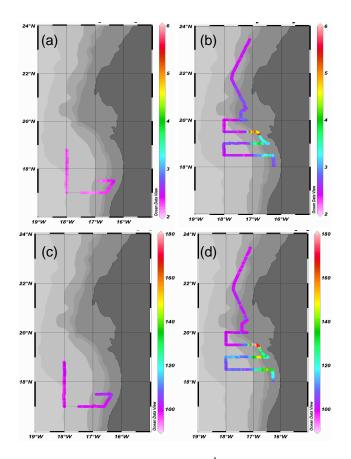


Fig. 4. CH₄ concentrations (in nmol L^{-1}) during P320/1 (a) and P348 (b) and CH₄ saturations (in %) during P320/1 (c) and P348 (d).

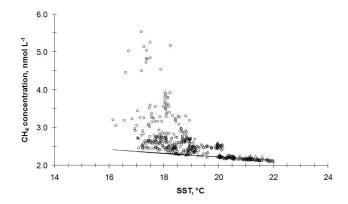


Fig. 5. CH₄ concentrations vs. SST. Open circles represent data from P348, open triangles represent data from P320/1. The solid line is the dissolved CH_4 equilibrium concentration calculated with an atmospheric CH_4 dry mole fraction of 1.83 ppm.

In March 2005 dissolved CH₄ concentrations were rather uniform and ranged from 2.1 to $2.5 \,\mathrm{nmol}\,L^{-1}$ with saturations close to the equilibrium with the atmosphere (96–106%) (Fig. 4). During P348 in February 2007 dissolved CH₄ concentrations were much more variable and ranged from 2.2 to $5.5 \,\mathrm{nmol}\,L^{-1}$. CH₄ saturations ranged from 97% to 200% (Fig. 4). The majority of low CH₄ saturations were found in the western part of the transect at $18.5^{\circ}\,\mathrm{N}$ and north of $20^{\circ}\,\mathrm{N}$, whereas significantly enhanced CH₄ saturations were mainly found close to the coast between $19^{\circ}\,\mathrm{N}$ to $19.5^{\circ}\,\mathrm{N}$ (Fig. 4).

Conrad and Seiler (1988) measured CH₄ surface saturations ranging from about 108% to about 155% during a straight transect from Cap Blanc to Cap Vert during the upwelling season in January 1979. Their data are in agreement with the data from our study (see above). Moreover, our open ocean data are in agreement with CH₄ concentrations (about $2 \text{ nmol } L^{-1}$) measured along 20° W by Rhee (2000). However, our open ocean saturations are lower than those observed by Forster et al. (2008), who found a mean CH₄ saturation concentration of $156\pm29\%$ (corresponding to a mean CH₄ concentration of $3\pm0.7 \text{ nmol } L^{-1}$) in the surface layer at three stations off Mauritania along 18° W during the non-upwelling season in September 2003. This discrepancy might results from seasonal and/or interannual differences (see section Study site description).

Figure 5 shows a plot of SST vs. CH₄ concentrations 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. The enhanced CH₄ concentrations in the upwelled water masses are most probably caused by methanogenesis in anoxic microniches of sinking organic particles and/or by methanogenesis in the shelf sediments (Rehder et al., 2002; Sansone et al., 2001) which leads to an accumulation of CH₄ before the water masses are brought to the surface. However, production of

Table 1. CH₄ emission estimate.

	Area ^a 10^{12}m^{-2}	Mean flux density ^b pmol m ⁻² s ⁻¹	Emissions ^b Gg	
			Upwelling ^c	Non-upwelling
Cape Blanc shelf	0.11	11.3/19.1	0.3/0.4	0.1 ^d /0.3 ^d
Cape Blanc slope	0.10	10.3/18.1	0.2/0.4	$0.1^{\rm d}/0.2^{\rm d}$
Cape Blanc gyre	0.37	4.55/8.47	_	$0.8^{\rm e}/1.6^{\rm e}$
Total	0.58	-	0.6/0.8	1.0/2.1

^a Areas were taken from Hoepffner et al. (1999).

CH₄ by zooplankton grazing could contribute to the CH₄ accumulation as well (De Angelis and Lee, 1994).

The hydrographic properties of the subsurface waters together with CH₄ saturations are shown in Fig. 6. All data points lie between the T/S lines of NACW and SACW (for a definition see section Study site description), 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; Tomczak, 1981) 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 $(Sc/600)^{-n}$ (n=2/3 for wind speeds ≤ 3.6 m s⁻¹ and n=0.5 for wind speeds >3.6 m s⁻¹) for LM86 and $(Sc/660)^{-0.5}$ for W92. Sc is the Schmidt number for CH₄ and was calculated using empirical equations for the kinematic viscosity of sea-

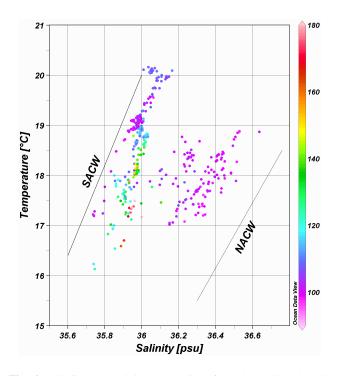


Fig. 6. T/S diagram and CH_4 saturations from the P348. The T/S curves of the predominant water masses, NACW and SACW, are shown as straight lines (Tomczak and Godfrey, 2003).

water (Siedler and Peters, 1986) and the diffusivity of CH₄ in water (Jähne et al., 1987). The measured wind speeds were normalised to 10 m height by using the relationship of Garratt (1977).

In order to estimate the CH₄ emissions from the Mauritanian upwelling we pooled our data according to the three provinces suggested by Hoepffner et al. (1999): CBgy, CBsl and CBsh (see section Study site description). For the seasonality we adopted the periods given in Wooster et

^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).

^c We assumed a mean duration of 5 months for the upwelling season (Wooster et al., 1976).

^d We assumed a mean duration of 7 months for the non-upwelling season (Wooster et al., 1976). The emissions were calculated on the basis of the mean flux densities for the Cap Blanc gyre province given in the third column.

^e Calculated for a 12 months period.

al. (1976): 5 months and 7 months for the upwelling and nonupwelling seasons, respectively (see Study Site description). Then we calculated the mean flux densities and emissions for the three provinces (Table 1). The total CH₄ emissions during the upwelling season (0.5–0.8 Gg CH₄) are comparable with the emissions from the coastal upwelling in the NW Arabian Sea (0.5–0.9 Gg CH₄, calculated for a 4 months upwelling period by Bange et al. (1998). The annual CH₄ emissions, calculated as the sum of the individual emissions during the upwelling and the non-upwelling seasons, range from 1.6 to 2.9 Gg CH₄ (Table 1) representing about 0.2-0.7% of the global open ocean emissions of 400–800 Gg yr⁻¹ (Bates et al., 1996; Kelley and Jeffrey, 2002). Thus, the upwelling area off Mauritania represents a regional hot spot but is of minor importance for the global oceanic CH₄ emissions. The emission estimates presented in Table 1, however, strongly depend on the choice of the province classification and seasonality. For example, when adopting a duration of 9 months for the upwelling season, as suggested by Schemainda et al. (1975) for 18° N, the total annual CH₄ emissions yield 1.8–3.2 Gg.

As shown by Roy and Reason (2001), the upwelling intensity off Mauritania as indicated by SST anomalies in spring/summer is positively correlated with the bimonthly multivariate ENSO index (MEI) for November/December of the preceding year: Negative (positive) MEI indicate La Niña (El Niño) conditions with intensified (weakened) upwelling (Roy and Reason, 2001). The December/November MEI for 2004 and 2006 were +0.68 and +0.97, respectively (MEI data computed by Klaus Wolter, http://www.cdc.noaa.gov/people/klaus.wolter/MEI/table.html, updated 6 May 2008). Thus, we conclude that the upwelling during the cruises P320/1 and P348 was not intensified indicating that our CH₄ emission estimate might be conservative. We speculate that CH₄ in years with intensified upwelling might be higher.

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