The origin of sub-surface source waters define the sea-air flux of methane in the Mauritanian Upwelling, NW Africa

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Abstract

Concentrations and flux densities of methane were determined during a lagrangian study of an advective filament in the permanent upwelling region off western Mauritania. Newly upwelled waters were dominated by the presence of North Atlantic Central Water and surface CH_4 concentrations of 2.2 ± 0.3 nmol L^{-1} were largely in equilibrium with atmospheric values, with surface saturations of 101.7 ± 14%. As the upwelling filament aged and was advected offshore, CH_4 enriched South Atlantic Central Water from intermediate depths of 100 to 350m was entrained into the surface mixed layer of the filament following intense mixing associated with the shelf break. Surface saturations increased to 198.9 ± 15% and flux densities increased from a mean value over the shelf of 2.0 ± 1.1 µmol $m^{-2}d^{-1}$ to a maximum of 22.6 µmol $m^{-2}d^{-1}$. Annual CH_4 emissions for this persistent filament were estimated at 0.77 ± 0.64 Gg which equates to a maximum of 0.35% of the global oceanic budget. This raises the known outgassing intensity of this area and highlights the importance of advecting filaments from upwelling waters as efficient vehicles for air-sea exchange.

Keywords: Methane, Atlantic Ocean, Upwelling, Filaments, Air-sea exchange

1. Introduction

Methane (CH_4) is the most abundant trace organic gas in the environment [*Wuebbles and Hayhoe*, 2002] and plays an important role in the Earth's climate. It acts to limit the tropospheric oxidative capacity and is radiatively active, with a global warming potential that exceeds CO_2 by 23 times over a 100 year timescale [IPCC, 2007].

The world's oceans are a natural source of CH_4 but play only a minor role in its global atmospheric budget [*Wuebbles and Hayhoe*, 2002], contributing up to 10% of the global atmospheric emissions [*Grunwald, et al.*, 2009]. That said, marine sources are not well constrained owing to a paucity of

observations [*Forster, et al.*, 2009]. Coastal environments including estuaries are thought to account for approximately 75% of the marine source [*Bange, et al.*, 1994] and coastal upwelling areas have been shown to be particularly rich source areas [*Kock, et al.*, 2008; *Monteiro, et al.*, 2006; *Owens, et al.*, 1991]. Methanogenesis is an anaerobic process, which in oceanic waters is thought to occur either in oxygen deplete waters or in anoxic micro-environments that are associated with zooplankton guts and particulate material [*Bianchi, et al.*, 1992; *Marty et al.*, 1997; *Brooks, et al.*, 1981]. In upwelling areas CH_4 production has been indirectly linked to the high productivity of these regions and the decomposition of sinking detrital material formed therein [*Rehder et al.*, 2002; *Kock et al.*, 2008]. The association between CH_4 production and phytoplankton biomass though is not ubiquitous. Previous studies have reported both a closely coupled relationship between the two [eg. *Oudot, et al.*, 2002, *Damm et al.*, 2008], while others have found weak or no correlation at all [*Bianchi, et al.*, 1992; *Holmes, et al.*, 2000].

The NE Atlantic upwelling of the coast of Mauritania is globally one of the most biologically productive systems [*Pauly and Christensen*, 1995] and occurs as a consequence of off-shore Ekman transport due to trade winds along the coastline [*Mittelstaedt*, 1991]. Despite the high productivity of this area and the association of upwelling with positive fluxes to the atmosphere of methane [e.g. *Owens et al*., 1991, *Kock et al.*, 2008] there are relatively few studies of CH_4 in this region and those that have been performed are predominately concerned with surface waters.

During research cruise D338 on-board RRS Discovery in April 2009 we deployed the tracer SF_6 with drogued drifter buoys to track recently upwelled water and perform a lagrangian investigation [*Meunier et al*., 2012] into CH_4 concentration and its flux with the atmosphere in an area associated with active upwelling throughout the year (Fig 1).

2. Methods

A physical survey using shipboard instrumentation combined with satellite derived sea surface temperature (SST) and chlorophyll-a data of the study site was performed to identify recently upwelled water and the starting position for a lagrangian experiment. The aim was to track the evolution of an upwelling filament using a sulfur hexafluoride (SF_6) labelled patch. SF_6 deployment was made at a depth

of 5m around a central buoy [*Nightingale, et al.*, 2000] and the centre of the patch was located via on-board analysis by discrete and continuous gas chromatography, the ship was repositioned daily to the centre of the patch. Sea water samples were collected at 14 stations (Fig. 1) from Niskin bottles on a CTD rosette with clean Tygon® tubing into 1L borosilicate bottles. Samples were overfilled with three times the bottle volume to eliminate air bubbles and poisoned with 200µl of a saturated mercuric chloride solution. They were then transferred to a water bath at 25 ± 0.1 °C and temperature equilibrated for a minimum of one hour before analysis. Samples were analysed for CH_4 by single-phase equilibration gas chromatography using a flame ionisation detector similar to that described by Upstill-Goddard et al., [1996].

Air measurements were collected from the ships fore-mast whilst on station using a diaphragm pump (Charles Austen Ltd CapexL2) which was used to draw air through "Dekabon" tubing directly to the ships laboratory. The gas line was purged for 5 minutes and particulates and water were removed using quartz wool and magnesium perchlorate respectively prior to the introduction to the gas chromatograph. Seawater samples were typically analysed within 8 hours of collection. Each individual determination of dissolved and atmospheric CH_4 was calibrated against 3 certified standards 1.00, 2.04 and 3.01 ppm ± 5% (Air Products Ltd.), which were verified as such by comparison to others which are traceable to the NOAA 2004 scale for CH4 mole fractions. Instrument precision, based on measurements of the three reference gases made throughout each day (n= 5 to 10 for each standard) was better than 0.77%.

Aqueous CH_4 concentrations were calculated from the solubility table of *Wiesenburg and Guinasso*, [1979]. The CH_4 saturation in seawater was determined as the ratio of in-situ CH_4 to atmospheric samples determined on board (mean 1.84 ± 0.06ppm, compared with 1.86ppm Mace Head Ireland, 1.81 ppm Ragged Point Barbados – taken from Advanced Global Atmospheric Gases Experiment (AGAGE) data set – http://agage.eas.gatech.edu for May 2009).

The CH_4 exchange between the air and ocean, the sea-air flux density (F_{CH4}) was parameterised as:

$$F_{CH4} = (k_w(S_c/600)^{-0.5}))(C_w-C_a)$$

where K_w is the gas transfer coefficient [*Nightingale, et al.*, 2000] normalised to a height of 10m [*Large and Pond*, 1982]. C_w is the seawater concentration and C_a is the equilibrium water concentration of CH_4

calculated against the corresponding atmospheric measurement. S_c is the Schmidt number [*Wanninkhof*, 1992].

CH_4 fluxes into the surface mixed layer from deeper waters (VF_{CH4}) were estimated from:

$$VF_{CH4} = K_z \ x \ (\partial CH_4 / \partial z).$$

The mean gradients driving the flux into the surface layer were estimated by calculating the slope of a linear fit to the available data between the deep maxima (located between 100 and 350) and the bottom of the mixed layer. The values of eddy diffusivity (Kz – Fig. 2) were obtained from observations performed with a free-falling shear microstructure profiler (ISW Wassermesstechnik MSS-90). Data from MSS90 profiles were only used at depths greater than 10m, due to the potential for contamination from the motion of the ship induced by wave activity [*Lozovatsky et al*., 2006]. Values for Kz used in the calculation of VF_{CH4} were the mean of all estimates from the closest MSS90 profiles in time and covering the depth range used for calculating the methane gradient. Estimates of VF_{CH4} should be considered as conservative in part as a consequence of the low vertical sample resolution, which meant that small scale gradients in methane are likely to be larger than those used here. Similarly, the broad depth range used to determine eddy diffusivity is likely to provide underestimated values of Kz.

3. Results and Discussion

Upwelling off Mauritania is fed by two different subsurface water masses identified by *Tomczak* [1982]. Upwelling waters north of ~20°N are mainly influenced by North Atlantic Central Water (NACW) while the area south of 20°N is dominated by South Atlantic Central Water (SACW) which is generally cooler, fresher and has a higher nutrient and lower oxygen content than that of NACW [*Minas, et al.*, 1982]. The percentage of each water mass present during this analysis was determined by applying optimum multiparameter (OMP) analysis to temperature, salinity, nitrate and silicate profiles using the OMP Package for MATLAB Version 2.0 (http://www.ldeocolumbia.edu~jkarsten/omp_std). The upper 200m of the filament were dominated by NACW (50-80%) whilst SACW dominated between 200m and 500m (Fig 3). The filament was tracked for 9 days from the 21st to 29th of April 2009 over a distance of

approximately 200km though the filament may continue for approximately twice that distance [*Fischer, et al.*, 2009; *Rees, et al.*, 2011]. A full description of the physical nature of this upwelling filament can be found in Meunier et al., [2012] where it is referred to as Filament A. Surface waters of the 5 stations occupied at the most easterly section of the filament were directly influenced by newly upwelled water, which was dominated by NACW (surface temperature = 16.69 ± 0.15°C) and surprisingly had the lowest recorded concentrations of 2.2 ± 0.3 nmolL^{-1} (Fig. 3) and saturations (101.7 ± 14%) of CH_4 (Fig. 4). Kock et al [2008] also found that surface waters associated with the NACW showed lower saturations than those dominated by SACW. Although in contrast, their lowest temperatures were coincident with maximum concentrations of CH_4 of 5.5 nmol L^{-1} which were associated with the upwelling of SACW dominated waters at ~19.5°N ~17°W. The surface CH_4 concentration increased at the continental shelf break, west of ~17.6°W as CH_4 enriched SACW from intermediate depths was brought to the surface. The combination of enhanced turbulence (Fig 2.) at the shelf-break and strong diapycnal gradients in CH_4 concentration provided a strong source of CH_4 to surface waters at rates of between 170.9 µmol $m^{-2}d^{-1}$ (Fig. 4) and 876.2 µmol $m^{-2}d^{-1}$ (estimated using mean or mean +1 s.d. values of Kz respectively) Low diapycnal gradients throughout the remainder of the transect resulted in VF_{CH4} rates in the order of 1.5 ± 1.9 µmol $m^{-2}d^{-1}$. Surface concentrations increased to 4.2 nmol L^{-1}at 17.69°W and remained at this level (4.3 ± 0.3 nmolL^{-1} , 198.9 ± 15% saturation) (Fig 3, 4) until the end of the experiment as a strong westward, surface-intensified jet-like flow transported the combined NACW and SACW waters offshore [Meunier et al, 2012]. Surface temperatures increased progressively to a maximum of 17.65°C at the westernmost station, so that there was a strong positive correlation between temperature and CH_4 concentration (r^2 = 0.69, n = 14).

In the absence of methane oxidation rates for this study it is difficult to perform a realistic budget, however we have attempted this to investigate the supply of CH_4 to the surface mixed layer for the four day period between the shelf break and the end of the study. If we take our lower and upper estimates for VF_{CH4} of 170.9 µmol $m^{-2}d^{-1}$ and 876.2 µmol $m^{-2}d^{-1}$ and maintain a 50m mixed layer integrated CH_4 concentration of 215 µmol m^{-2} and losses to the atmosphere of 70 µmol m^{-2} it becomes apparent that the

lower estimate of VF_{CH4} is insufficient to maintain the water column concentrations observed. To provide a balanced budget the higher estimate of VF_{CH4} would require consumption of CH_4 in the order of 600 µmol m^{-2} $4d^{-1}$, which equates to a quite realistic rate of ~ 3 nmol L^{-1} d^{-1}, see for example Mau et al., [2013]. Whilst recognising the limitations of this exercise it would allow some confidence that the vertical flux of CH_4 from intermediate depths to the surface mixed layer is at the higher end of our estimated range.

The relationship between CH_4 production and phytoplankton biomass or productivity is inconsistent. A number of authors report a positive correlation between chlorophyll-a and CH_4, for example Damm et al., [2008], who described a strong association between a summertime phytoplankton bloom and methanogenesis. CH_4 production in other upwelling areas has been linked indirectly to enhanced productivity through the microbial degradation of sinking material at intermediate depths below the mixed layer [e.g. Rehder et al., 2002]. During the current study CH_4 showed a weak inverse relationship (r^2 = 0.43, n = 7) with chlorophyll-a as can be inferred from Fig. 4. Further to this, there was no observed difference between surface samples taken either at local noon or those collected before dawn (4.3 ± 0.28 nmol L^{-1}, 198.3 ± 12.9% compared with 4.3 ± 0.55 nmol L^{-1}, 200.2 ± 26.9% for mid-day and pre-dawn at off-shelf stations; and 2.6 ± 0.33 nmolL^{-1}, 118.7 ±14.1 compared with 2.1 ± 0.2 nmolL^{-1}, 94.9 ± 8.9% for mid-day and pre-dawn on- shelf stations). The lack of a diurnal signal in CH_4 concentration and the inverse relationship between CH_4 and chlorophyll-a suggests that CH_4 supply is largely independent of photosynthesis and zooplankton activity. This supports our contention that the elevated surface concentrations are derived from intermediate waters (maximum concentration of 7.7 nmolL^{-1} and 322.4% saturation occurring at a depth of 300m) dominated by SACW rather than from in-situ production (Fig. 3).

These surface data are in agreement with those previously published for this area (~2 nmol L^{-1} – Rhee 2000; 2.1 – 5.5 nmol L^{-1} - Kock et al.,; 2008; 3 ± 0.7 nmolL^{-1} - Forster et al., 2009;). Kock et al argue that some of the variability between datasets may be associated with seasonal and inter-annual variability. It is evident from our study that the dynamic nature of this environment and the contrasting CH_4 signature

between NACW and SACW lead to extremely heterogeneous vertical and horizontal distributions. Geographical location with respect to upwelling waters can contribute as much to the variability described as seasonal differences.

Eastern boundary upwelling regions are dominated by consistent winds which drive offshore water movement via filaments.. The average wind speed during the current study was 10.7ms^{-1} (Fig. 4) and was consistently from the north north-east which proved to be sufficient to maintain upwelling [Meunier et al., 2012] and a positive sea to air flux of CH_4 for the duration of the filament. F_{CH4} was determined using wind speed determined at the time of water collection (Fig 4). The dependence of K_W and thus F_{CH4} on wind speed becomes obvious in Fig. 4 where daily changes in wind speed at 3 stations between 17.69°W and 17.84°W of 9.5, 15.1 and 7.2 ms^{-1} result in flux densities of 14.4, 20.3 and 10.2 µmol m^{-2}d^{-1} for concentrations of 4.2, 3.9 and 4.1 nmol L^{-1} respectively. As surface CH_4 concentrations increased with progression of the filament away from the shelf-break, flux densities were found to increase by almost 8 times from 2.0 ± 1.1 µmol m^{-2}d^{-1} for the first 7 stations located over the continental shelf to 17.7 ± 4.4 µmol m^{-2}d^{-1} for the remaining 7 stations. The on-shelf flux densities are similar to those previously reported (2.31 – 4.04 µmol m^{-2}d^{-1} – Forster et al., 2009; 0.4 – 1.7 µmol m^{-2}d^{-1} – Kock et al., 2008), whilst those determined off the shelf and influenced by upwelling of SACW influenced waters are between 5.6 and 13.3 times those estimated by Forster and Kock respectively. It should be noted in any comparison, that each of these studies occupied geographically distinct areas and were at different times of the year. The current study was in the area of permanent upwelling [*Mittelstaedt*, 1991] north of 20°N in April, Forsters study (4 stations) transected the area in September , and the study of Kock was performed during February and March, largely associated with the area of seasonal upwelling [*Wooster, et al.*, 1976] south of 20°N.

The heterogeneous nature of this region with respect to CH_4 concentration and flux densities coupled with the highly complex oceanography and the inherent transcience of these advecting filaments make it difficult to extrapolate over large scales. The lagrangian approach to this study however gives us confidence in our ability to characterise the nature of sea to air flux associated with this filament. Given

that the position of the filament was north of 20°N we consider it to be in an area of persistent upwelling which allows the extrapolation of flux densities determined here over a 12 month period. In a similar approach to that taken by Kock et al [2008] we have taken our mean flux density over the whole filament of 10.17 ± 8.51 µmol $m^{-2}d^{-1}$ and using our estimate for the mean area of the filament of 1.29 $x10^4$ km^2 [Rees et al., 2011] propose an annual CH_4 emission of 0.77 ± 0.64 Gg. This compares to emissions estimated by Kock et al of 1.6 to 2.9 Gg y^{-1}, for an area 20 times larger than the filament examined here, and contributes up to 0.35% of global estimates provided by Bates et al., [1996] for an area equivalent to 0.009% of the global surface ocean.

5. Conclusion

Upwelling waters close to the Mauritanian coast in the persistent upwelling found to the north of 20°N are dominated by NACW which has a relatively low CH_4 signal of 2.2 ± 0.3 nmol L^{-1} which is comparable to offshore waters west of 20°W [*Rhee et al.*, 2009]. As upwelling filaments are advected offshore CH_4 enriched SACW is entrained into the surface mixed layer following turbulent mixing associated with the shelf break. The general uniformity of the prevailing trade winds combined with the resultant high concentrations of surface CH_4, similar to those observed in upwelling SACW south of 20°N, provide a strong source of CH_4 to the atmosphere. Short-term variability in the magnitude of the prevailing wind fields highlighted the sensitivity of density flux estimates to wind speed. The relatively small area represented by this permanently upwelling region provides a hot-spot of CH_4 emmissions relative to non-upwelling waters of the adjacent North Atlantic and these data emphasise the need to comprehensively account for the contribution of advecting upwelling filaments to global budgets.

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Figure Legends

Figure 1: MODIS – Aqua chlorophyll-a image of the Mauritanian upwelling. Station positions occupied between the 21 and 29 April 2009 are identified by black squares and direction of transit indicated by the black arrow. *Images courtesy of NEODAAS.*

Figure 2: Eddy diffusivity (Kz) determined from observations performed with a free-falling shear microstructure profiler (ISW Wassermesstechnik MSS-90) within an advecting filament in the Mauritanian upwelling during April 2009. The solid symbols and line represent the mean value from repeated profiles, whilst the dashed line indicates the positive standard deviation of this estimate. Standard deviation is not shown east of 17.5 west due to the highly turbulent nature of the on-shelf upwelling waters..

Figure 3: Contour profiles of CH_4 concentration (nmol L^{-1}) during a lagrangian study of an advecting filament in the Mauritanian upwelling during April 2009. Contoured isolines are for temperature (°C), data points indicated by ●. The dashed line indicates the approximate position of the 50:50 boundary between NACW and SACW. *Image produced using Ocean Data View (http://odv.awi.de/).*

Figure 4: The flux of CH_4 during a lagrangian study of an advecting filament in the Mauritanian upwelling relative to daily measurements of wind speed at 10m in the top panel, chlorophyll-a (bold line) and sea surface temperature (dotted line) in the middle panel. In the bottom panel F_{CH4} is shown as grey bars, VF_{CH4} as the bold line and CH_4 saturation indicated by the dashed line. The shaded area represents the bathymetric profile.

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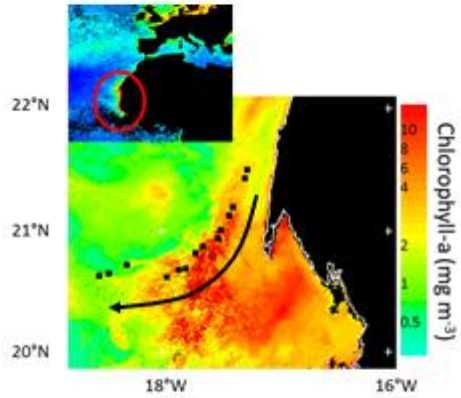
22°N
21°N
20°N
18°W
16°W
10
8
6
4
2
1
0.5
Chlorophyll-a (mg m-3)

Fig 1

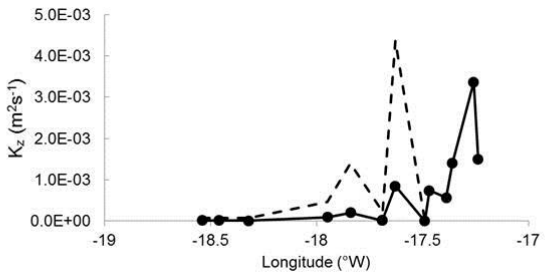
5.0E-03
4.0E-03
3.0E-03
2.0E-03
1.0E-03
0.0E+00
Kz (m2s-1)
-19
-18.5
-18
-17.5
-17
Longitude (°W)

Fig 2

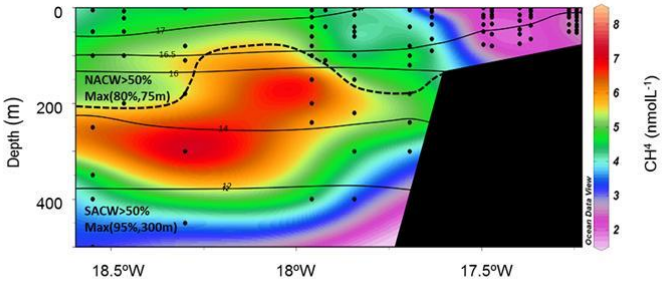
0
200
400
Depth (m)
NACW>50%
Max(80%,75m)
SACW>50%
Max(95%,300m)
18.5ºW
18ºW
17.5ºW
8
7
6
5
4
3
2
CH4 (nmolL-1)
Ocean Data View

Fig 3

366

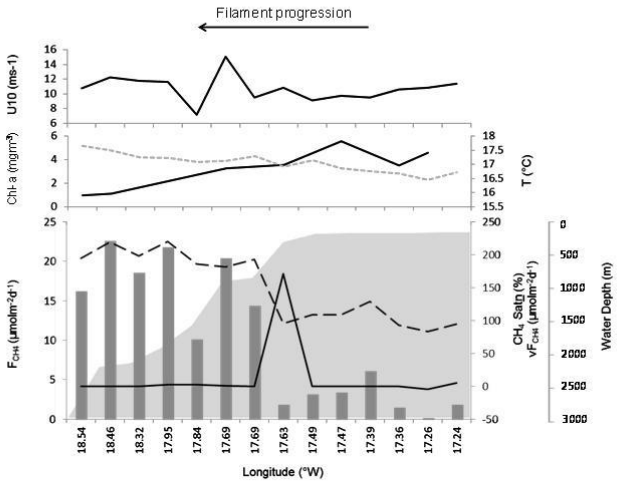
Filament progression
U10 (ms-1)
Chl-a (mgm-3)
T (°C)
F_CH4 (µmolm-2d-1)
CH4 Satg (%)
vF_CH4 (µmolm-2d-1)
Water Depth (m)
Longitude (°W)
18.54
18.46
18.32
17.95
17.84
17.69
17.69
17.63
17.49
17.47
17.39
17.36
17.26
17.24

Fig 4

367