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Rapid biological oxidation of methanol in the tropical Atlantic: significance as a microbial carbon source

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Abstract

Methanol is the second most abundant organic gas in the atmosphere after methane, and is ubiquitous in the troposphere. It plays a significant role in atmospheric oxidant chemistry and is biogeochemically active. Large uncertainties exist about whether the oceans are a source or sink of methanol to the atmosphere. Even less is understood about what reactions in seawater determine its concentration, and hence flux across the sea surface interface. We report here concentrations of methanol up to 300 nM, with corresponding microbial uptake rates between 2–146 nM d^{-1}, suggesting turnover times as low as 1 day in surface waters of the oligotrophic tropical North East Atlantic. Comparisons with parallel determinations of bacterial leucine uptake suggest that methanol contributes on average 13% to bacterial carbon demand in the central northern Atlantic gyre (maximum of 54%). However, our low air to sea methanol flux estimates of 7.2–13 µmol m^{-2} d^{-1} suggest that the atmosphere is not a major source. We conclude that there must be a major, as yet unidentified, in situ oceanic methanol source in these latitudes which we suggest is sunlight driven decomposition of organic matter.

1 Introduction

Methanol is the second most abundant organic gas in the atmosphere after methane (Jacob et al., 2005), and is ubiquitous in the atmosphere (Singh et al., 2000) where it is a significant source of tropospheric CO through photochemical oxidation (Duncan et al., 2007). It plays a significant role in atmospheric oxidant chemistry where, for example, it reacts directly with hydroxyl radicals forming products that are a source of formaldehyde, hydrogen radicals, and ozone (Heikes et al., 2002). In cloud water, methanol photochemical reactions can produce formic acid contributing to cloud and rainwater acidity (Heikes et al., 2002). However, there is large uncertainty in the atmospheric methanol budget, with global sources from plant growth and decay, biomass burning, urban emissions and atmospheric production ranging between 122–350 Tg a^{-1} (Singh

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et al., 2000; Galbally and Kirstine, 2002; Heikes et al., 2002; Tie et al., 2003; Jacob et al., 2005; Millet et al., 2008). The role of the oceans as a source (Singh et al., 2000, 2001; Heikes et al., 2002; Mao et al., 2006) or sink (Heikes et al., 2002; Singh et al., 2003; Carpenter et al., 2004; Williams et al., 2004; Jacob et al., 2005; Mao et al., 2006; Sinha et al., 2007; Millet et al., 2008) of methanol is also uncertain, and has been hampered by the analytical difficulties in reliably determining methanol concentrations in seawater due to its high solubility. The first flux estimates calculated using in situ surface methanol concentrations report a mean flux of $66 \pm 267\,\mu mol\,m^{-2}\,d^{-1}$ from the atmosphere to the ocean in the tropical North Atlantic (Williams et al., 2004). Methylotrophic bacteria, who by definition, must survive on one carbon (C1) compounds like methanol (Murrell and McDonald, 2000), have been found in nearshore coastal zones (Neufeld et al., 2007, 2008; Giovannoni et al., 2008) and in oceanic regions (Dixon et al., 2011). In addition, molecular studies have suggested that a diverse range of prokaryotes and eukaryotes are thought able to use methanol for growth (Murrell and McDonald, 2000).

Methanol, and other oxygenated volatile organic carbon compounds form part of the dissolved organic carbon (DOC) pool. Dissolved organic carbon production by phytoplankton is believed to be the primary organic carbon source for marine bacteria. However for oligotrophic waters, particularly those from the tropical Atlantic, bacterial carbon demand often exceeds dissolved organic carbon produced by phytoplankton (e.g. Agusti et al., 2001; Duarte et al., 2001; Hoppe et al., 2002; Gasol et al., 2009 and references therein) indicating that additional sources are needed to sustain bacterial production in nutrient depleted areas (e.g. Morán et al., 2007; López-Sandoval et al., 2011)

We have modified a radiochemical technique to quantify microbial methanol uptake rates in seawater, and have previously reported biological methanol oxidation rates of $2.1–8.4\,nmol\,l^{-1}\,d^{-1}$ i.e. loss rate, largely in coastal and shelf areas (Dixon et al., 2011). We also previously estimated microbial methanol turnover times of 12–24 days in coastal and shelf stations (Dixon et al., 2011).

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The aim of this research in nutrient limited tropical waters of the North East Atlantic was to: (1) make the first combined measurements of microbial-mediated losses of methanol from seawater together with in situ methanol concentrations and (2) to investigate whether methanol could be a significant compound in meeting bacterial carbon demand.

2 Methods

2.1 Sampling

Sampling was mainly conducted at a series of stations in the tropical North Atlantic during two research cruises aboard the RRS James Cook (Atlantic Meridional transect, AMT19) and RRS Discovery (Surface Ocean Lower Atmosphere Study: Investigation of the near surface production of Iodocarbons, D325). For comparison purposes, stations sampled in Iberian Peninsula and European shelf waters aboard RRS Discovery (Surface Ocean Lower Atmosphere Study: Deep Ocean Gas Exchange Experiment II, D320) and from a coastal western English Channel site (L4, Western Channel Observatory) are also included (Fig. 1).

2.2 Microbial methanol oxidation and uptake into particles

We incubated surface seawater samples with nanomolar concentrations of ^{14}C labelled methanol ($^{14}CH_3OH$) and determined both uptake into particles and oxidation to CO_2 (Dixon et al., 2011), which we interpret as microbial cellular incorporation (cell growth, G) and energy use (E) respectively. For full experimental details please refer to Dixon et al. (2011). In brief, seawater samples were treated with approximately 10 nM final added concentration of $^{14}CH_3OH$, and were always <1% of the sample volume. This concentration of radiolabel was chosen as a compromise between obtaining sufficient sample counts within the linear period of label incorporation, and not wishing

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to provide excess methanol which could artificially stimulate microbial uptake or oxidation rates. An addition of 10 nM $^{14}CH_3OH$ final concentration typically represented between 3–20% of in situ concentrations. The period of linear incorporation of the labelled methanol was typically up to 18 h, and was routinely tested for uptake into particles and oxidation. Kinetic experiments typically show multiphasic behaviour for methanol uptake into particles, which suggests that for added $^{14}CH_3OH$ concentrations ≤ 20–30 nM, bacterial transport processes dominate, whereas at higher concentrations incorporation due to diffusion across cell membranes is likely to dominate (Dixon et al., 2011). We generally incubated oxidation samples for 2–3 h, and uptake onto particles for 3–9 h (to ensure sufficient counts).

The data is reported as apparent rate constants, k (h^{-1}) calculated from a ratio of the sample ^{14}C counts (from the particles on the filter or from the precipitate which contains the captured $^{14}CO_2$ as $Sr^{14}CO_3$, nCi mL^{-1} h^{-1}) divided by total $^{14}CH_3OH$ added to the sample (nCi mL^{-1}). All rate constants were corrected by subtracting killed sample (TCA, 5% final concentration) counts. Evaluation of control samples suggests that ≤1.8% of the added $^{14}CH_3OH$ is counted in the resultant precipitate (for determining oxidation) and ≤0.3% is recovered on the filters. Methanol oxidation or uptake rates were calculated from the product of k multiplied by the in situ concentration of methanol. This was determined independently by membrane inlet - proton transfer reaction mass spectrometry (MI PTR-MS), which was calibrated using spiked seawater standard additions. The relative error in k ($n = 3$) was ≤5%, and for in situ methanol concentrations was 7% ($n = 11$), giving a combined estimated error of ≤12% for methanol oxidation rates.

2.3 Community composition and chlorophyll-*a* concentraion

We also carried out parallel determinations of the concentration of chlorophyll-*a* (chl-*a*), numbers of heterotrophic bacteria (BN), *Synechococcus* (*Syns*) and *Prochlorococcus* spp. (*Pros*). The numbers of bacterioplankton cells were determined by flow cytometry on SYBR Green I DNA-stained cells from 1.8 ml seawater samples fixed in

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paraformaldehyde (5%, final concentration). Numbers of *Prochlorococcus* spp and *Synechococcus* spp were analysed on unstained samples by flow cytometry. Surface concentrations of chl-*a* were estimated using a composite Aqua-MODIS chl-*a* remotely sensed image for stations 4 and 5, as unfortunately the continuous surface fluorometer onboard the ship (D320) was not working correctly. For all other stations chl-*a* samples were determined by fluorometric analysis of acetone-extracted pigments (Holm-Hansen et al., 1965).

2.4 Primary and bacterial production

Primary production (PP) was estimated using the standard method of ^{14}C-bicarbonate incorporation (e.g. Joint and Pomroy, 1993; Dixon et al., 2006; Dixon, 2008) except that for stations 1–3 samples were incubated for approximately 6 h (between 09:00–15:00) and for stations 7–12 samples were incubated from dawn to dusk. Heterotrophic bacterial production rates were determined by measuring the incorporation of ^{3}H-leucine (20 nM final concentration) into bacterial protein synthesis on 1.7 ml seawater samples following the method of Smith and Azam (1992). The relative error based on 3 replicates was on average 7.5%.

2.4.1 Leucine to carbon conversion factors

Bacterial production (BP) was calculated from the leucine incorporation rate using an average empirically derived conversion factor of 0.73 kgC mol leu^{-1}. Published conversion factors for the surface waters of the Atlantic ocean range between 0.17–1.55 kgC mol leu^{-1} (Agustí et al., 2001; Zubkov et al., 2001; Hoppe et al., 2002; Alonso-Sáez et al., 2007; Gasol et al., 2009; Martínez-García et al., 2010), but measurements made close to our sampling locations, depths and time of year are typically in the middle of this range (Barbosa et al., 2001; Moran et al., 2002, 2004; Dixon, 2008; Calvo-Díaz and Morán, 2009).

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2.5 Bacterial carbon demand

Bacterial carbon demand (BCD) is the total amount of carbon required by bacteria for both production and respiration (Robinson, 2008). Bacterial production was determined as detailed above. Bacterial respiration (BR) was calculated from production where $BR = 3.69\,BP^{0.58}$ (Robinson, 2008). Bacterial growth efficiency (BGE) was calculated in two different ways; firstly using production (BP) and respiration (BR) estimates, and secondly using chlorophyll-*a* concentrations (Table 1). BCD was calculated by dividing bacterial production (BP) by the average of the two estimates of BGE.

3 Results

3.1 Methanol oxidation and uptake in relation to biological production parameters

3.1.1 Diel stations in the NE Atlantic

We undertook three diel experiments using drogued surface drifters in the tropical North Atlantic during November/December 2007 (Fig. 2). Hourly surface (<10 m) measurements of *G* and *E* were determined for at least 24 h at stations of contrasting microbial productivity (Stations 1–3 Tables 1 and 2). At the most oligotrophic station (Stn 1), chl-*a* and average rates of PP, BP and BN were very low. However, we found the highest average rate of microbial methanol oxidation of 5 nmol L^{-1} h^{-1} (range of 3.2–6.1 nmol L^{-1} h^{-1}, Table 2) with an estimated turnover as low as 1 day (Table 2). The corresponding microbial uptake rates into particles were low with an average *E*:*G* of 360. This suggests that more than 99% of the methanol was used by the microbes as an energy supply rather than for growth at this station. There was higher microbial activity at station 2. The average rate of methanol oxidation was approximately five fold lower, with a higher uptake into particles than station 1, giving a *E*:*G* of 32 (Table 2).

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This suggests that relatively more methanol was used here as a carbon source for microbial growth. Station 3 was located within the Cape Verde archipelago and had the highest microbial biomass and production rates of the diel experiments. The average rate of methanol oxidation was the same as Stn 2 (Table 2). Methanol turnover times for both stations 2 and 3 were on average 6–7 times longer than for the most oligotrophic station. However, the highest methanol uptake into particles was observed at station 3 resulting in an average E:G ratio of 12.

Diel patterns in methanol oxidation rates varied consistently during all experiments: typically, E was highest at or just before dawn and decreased throughout the day until dusk whereupon rates slowly increased (Fig. 2a). On average, methanol oxidation rates at stations 1 and 2 were the same during light and dark hours despite the steep decrease during the day (Fig. 2a). For station 3, average rates of methanol oxidation were twice as high during the day compared to the night. This pattern is not entirely consistent with the interpretations of Sinha et al. (2007) who deduce from atmospheric methanol concentrations (after a phytoplankton bloom during a mesocosm experiment in a Norwegian fjord) that the net flux of methanol from the atmosphere to the sea was stronger at night. Our results from station 3 show higher methanol losses from surface seawater during the day; which could invoke a higher flux into the ocean from the atmosphere, if the atmosphere was the major source of methanol.

The diel patterns are not fully understood, but it is interesting that for stations 1 and 2, statistically significant relationships were observed between methanol oxidation and numbers of *Syns* (Stn 1: $r = 0.604$, $n = 19$, $P \leq 0.01$, Stn 2: $r = 0.734$, $n = 20$, $P \leq 0.001$). Whilst this does not prove that *Syns* were oxidising methanol, it is interesting that they also uptake amino acids like methionine e.g. are not obligate phototrophs (Mary et al., 2008). Open ocean *Pros* also uptake amino acids (Zubkov et al., 2004; Mary et al., 2008) with a diel rhythmicity that has been linked to a specific cell cycle stage (Mary et al., 2008). Obvious diel trends in the microbial uptake of methanol into particles were not evident (Fig. 2b). The diel experiments may not have been truly Lagrangian, as they were tracked with drogued surface drifters. Strong wind (station 3)

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and tides/currents around the Cape Verde islands may have caused the drifters to separate from the waters we wished to follow over the experiment.

3.1.2 Iberian peninsula and european shelf

We also made surface measurements of both *G* and *E* off the Iberian Peninsula during July 2007 (station 4). Here chl, BP and BN were typical of mesotrophic waters. However, the lowest rates of methanol utilisation were found e.g. 0.12 nmol L^{-1} h^{-1} (*E*:*G* 82), resulting in the longest methanol turnover estimates of 60–83 days (Table 2).

At stations 5 and 6 on the European Shelf, (Fig. 1) where chl-*a* and BP were comparatively high (Table 2), methanol oxidation rate constants were intermediate, giving turnover times of 12 and 6 days respectively. However, the highest values of methanol uptake into particles were observed in these productive waters, resulting in *E*:*G* of 5 and 2 (Table 2). This suggests that for shelf seas, during biologically productive months, a higher proportion of microbial methanol uptake was used to support cellular biosynthesis (rather than as an energy source) compared to less productive oceanic regions.

3.1.3 Central North Atlantic gyre (methanol oxidation only)

We sampled stations 7–12a in the central North Atlantic gyre away from the influence of upwelling or continental inputs e.g. dust. The concentration of chl-*a* (see Fig. 1), PP, BP and BN (Table 2) were characteristically very low (Morán et al., 2002, 2004; Dixon, 2008). Microbial methanol oxidation was not as high as station 1, but values ranged between 0.6–1.8 nmol L^{-1} h^{-1} with corresponding turnover times of 4–15 days (Table 2). These results reinforce the earlier measurements we made at station 1 and suggest that surface methanol concentrations can be removed by the microbial community in a matter of days in the oligotrophic waters of the north Atlantic.

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3.2 Methanol contribution to bacterial carbon demand

3.2.1 Bacterial growth

Our bacterial leucine incorporation rates ranged between 1–32 pmol leu L^{-1} h^{-1} (Table 1) for oligotrophic Atlantic waters, which is not unprecedentedly low for such waters (Morán et al., 2002, 2004; Dixon 2008) that are away from continental inputs of dissolved organic matter during winter. Such low values have also been reported for temperate ecosystems during winter (Calvo-Díaz and Morán, 2009) when organic carbon from phytoplankton is often limited, and most of the carbon taken up by heterotrophic bacteria is probably respired and used for cell survival. Our average bacterial respiration of 0.23 ± 0.15 µg C L^{-1} h^{-1} ($n = 16$) compares favourably with the median open ocean value of 0.25 µg C L^{-1} h^{-1} ($n = 105$) in Robinson (2008), and with the range of 0.3 ± 0.2 µg C L^{-1} h^{-1} for the subtropical Atlantic (Obernosterer et al., 2001). Our calculated average bacterial growth efficiency (BGE) of 0.03 ± 0.01 is low, but within the range reported in the literature (Alonso-Sáez et al., 2007; Morán et al., 2007; Robinson, 2008) and reflects the low availability of nutrients and DOC, and the high energetic costs associated with growth in central gyre locations. Our BGE of 0.02–0.04, typical of warm oligotrophic stations, implies that heterotrophic bacteria respire 96–98% of the assimilated carbon, which agrees with our methanol uptake results that >99% of methanol in low chl-*a* water is respired and used as energy.

3.2.2 Methanol contribution

We wished to examine whether methanol could represent an important carbon source for marine bacteria, so we compared methanol oxidation rates with calculated BCD (Table 2). The largest contribution that methanol made to BCD was at station 1, where it averaged 54%. Maximum methanol contribution to BCD was shown either just before, or at dawn, and decreased through the day (data not shown). For all the oligotrophic gyre stations, methanol contributed on average 13% to BCD (Table 2). At the coastal

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station (L4) during summer when nutrients were depleted, average methanol contribution to BCD was also noteworthy at 6%.

4 Discussion

4.1 Significance of methanol as a microbial carbon source

When the average % contribution of methanol to BCD is plotted against chl-*a* (Fig. 3) a statistically significant power relationship is found. This suggests that for chl-*a* $\geq 0.2\,\mu g\,L^{-1}$, methanol makes very little contribution to BCD, presumably because there is enough organic carbon from phytoplankton to fuel their requirements. However, at chl $< 0.2\,\mu g\,L^{-1}$, when dissolved labile organic carbon from phytoplankton is likely to be low, bacteria look for alternative sources of organic molecules e.g. methanol and hence the contribution to BCD increases. Methylotrophic bacteria have to satisfy all their carbon and energy requirements with C1 compounds like methanol (Murrell and McDonald, 2000), and recent DNA sequencing from AMT samples has revealed that bacterial species like *Methylophaga* and *Hyphomicrobium* are commonly found throughout the Atlantic Ocean (Sargeant, personal communication, 2010), in addition to coastal locations (Neufeld et al., 2007, 2008; Giovannoni et al., 2008). Furthermore, a recent review of methylotrophy concluded that the traditional definition of methylotrophy may need to be revisited, as many organisms encoding (and expressing) their modular pathways may typically use C1 compounds like methanol in co-metabolic pathways (Chistoserdova, 2011) i.e. survival not exclusively based on C1 compounds, which ecologically makes sense in low energy environs like the oligotrophic gyres, where we now have evidence that methanol concentrations are several hundred nanomolar.

Dissolved organic carbon production by phytoplankton is believed to be the primary organic carbon source for marine bacteria. However previous results (e.g. López-Sandoval et al., 2011) have suggested that for oligotrophic waters, bacterial carbon demand often exceeds dissolved organic carbon produced by phytoplankton, indicating

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that additional sources are needed to sustain bacterial production in nutrient depleted areas. Our results suggest that under such conditions (low chlorophyll-*a* and PP) methanol could be a significant organic carbon energy source for bacteria.

4.2 Sources of methanol

There are two likely sources of methanol, supply from the atmosphere via air/sea gas transfer and in-situ production. We used the 24 h mean rate of E (Table 2), together with the daily mean depth of the surface mixed layer (data not shown), to calculate that a flux into the water column of between 2.5 mmol m^{-2} d^{-1} (Stn 1) and 130 µmol m^{-2} d^{-1} (Stn 2) is required to balance our measured loss rates. We calculated both the water-side film (k_w) and air-side transfer (k_a) via parameterisations with hourly wind speeds (Nightingale et al., 2000) at stations 1 and 2, recognising that the air-sea exchange of methanol is dominated by the k_a (Carpenter et al., 2004), as this gas is highly soluble. We have estimated net air to sea fluxes of only between 7.2 and 13 µmol m^{-2} d^{-1}, by assuming that typical values of methanol in air and seawater were 1 ppb (Jacob et al., 2005) and 100 nmol L^{-1} (Williams et al., 2004) respectively.

The estimated contribution of air/sea gas transfer to the total biological loss of methanol therefore varied between a minimum of 0.2 and 1.1% and a maximum of 4% and 28% at stations 1 and 2 respectively. The range is caused by shallowing of the mixed layer in response to solar warming during the day, and deepening due to convective mixing in the night-time. We have assumed that rates of methanol uptake are uniform with depth at these stations. Our air-sea flux estimates are an order of magnitude lower than published estimates (Sinha et al., 2007; Millet et al., 2008) probably because winds were light (3–5 ms^{-1}), and hence gas transfer rates were low at our stations.

Our flux calculations suggest that the atmosphere is unlikely to be a dominant source of methanol in the oligotrophic North Atlantic, which infers in-situ production in the ocean or lateral advection. Millet et al. (2008) concluded that, if methanol turnover was of the order of 3 days due to biotic consumption, then there must be a further

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oceanic source of 8×10^3 Tg a^{-1} in the mixed layer. Our novel observations of microbial turnover rates as low as 1 day, together with our high surface methanol concentrations of between 151–296 nM in 2009 strongly supports a large in situ oceanic methanol source. It is known that sunlight initiated reactions can decompose organic matter to form a variety of oxygenated chemicals (Zhou and Mopper, 1997), although direct evidence of methanol production from surface marine dissolved organic matter is lacking. Heikes et al. (2002) suggest that abiotic methanol production in the oceans is minor, and propose bacterial transformations of algal carbohydrates (Sieburth and Keller, 1989) and production during phytoplankton growth as probable sources. However in the open ocean gyres, where we have measured the highest concentrations of methanol and highest microbial methanol oxidation rates, PP and chl-*a* are characteristically low, indicating that production by phytoplankton like diatoms, dinoflagellates etc. is not likely unless via the numerically dominant cyanobacteria present in these latitudes.

5 Conclusions

We report the highest ever reported concentrations of methanol (up to ~300 nM) and microbial methanol oxidation rates (i.e. losses up to 6.1 nmol L^{-1} h^{-1}) for surface waters of the tropical North east Atlantic ocean, resulting in biological turnover times as low as 1 day. These results suggest that methanol, and perhaps other OVOC compounds, represent a significant labile carbon source, particularly in nutrient deplete gyre systems. Our calculations suggest that methanol could significantly contribute to the energy requirements of the oligotrophic microbial community (Del Giorgio et al., 1997; Hoppe et al., 2002; Martínez-García et al., 2010), and could thus represent a proportion of the non phytoplankton derived sources of DOC often elicited necessary in order to sustain bacterial production during oligotrophic regimes. But, contrary to current opinion (Dachs et al., 2005, Duarte et al., 2006), our results invoke in situ methanol production mechanisms (Millet et al., 2008), perhaps via photochemical degradation of dissolved

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organic carbon (Zhou and Mopper, 1997, Mopper et al., 1991) rather than air to sea transfer, as the dominant supply mechanism for methanol.

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Table 1. Bacterial production, respiration, growth efficiency and carbon demand from surface (≤10 m) waters of the eastern North Atlantic.

Sampling date (description)	No	Bacterial production (pmol Leu L^{-1} h^{-1})	BP[a] (μg C L^{-1} h^{-1})	BR[b] (μg C L^{-1} h^{-1})	BGE[c] (BP and BR)	BGE[d] (Chl-*a*)	Bacterial carbon demand[e] (μg C L^{-1} h^{-1})
North Atlantic							
12 Dec 07 (26° N 24° W)	1	2.7 (0.8–4.7)[f]	0.002	0.10	0.02	0.03	0.10
18 Nov 07 (18° N 23° W)	2	19.7 (9.9-32)[f]	0.014	0.32	0.04	0.04	0.34
29 Nov 07 (16° N 24° W)	3	64.9 (36–118)[f]	0.047	0.63	0.07	0.05	0.79
1/4/6 July 07 (42° N 16–18° W)	4	9 (3.6–14)	0.007	0.20	0.03	0.05	0.16
Shelf Break							
17 June 07 (49° N 10° W)	5	47.7	0.035	0.53	0.06	0.09	0.46
Coastal (L4)							
6 June 06 (50° N 4° W)	6	21.4	0.016	0.33	0.06	0.16	0.15
North Atlantic							
27 Oct 09 (25° N 40° W)	7	4.3	0.003	0.13	0.02	0.02	0.14
(24° N 40° W)	7a	4.8	0.004	0.14	0.02	0.03	0.13
28 Oct 09 (23° N 41° W)	8	7.9	0.006	0.19	0.03	0.03	0.19
29 Oct 09 (21° N 39° W)	9	4.8	0.004	0.14	0.02	0.03	0.13
(21° N 39° W)	9a	5.0	0.004	0.14	0.03	0.04	0.11
30 Oct 09 (21° N 39° W)	10	10.4	0.008	0.22	0.03	0.03	0.24
31 Oct 09 (19° N 38° W)	11	6.4	0.005	0.16	0.03	0.03	0.16
(18°N 37° W)	11a	3.1	0.002	0.11	0.02	0.04	0.07
01 Nov 09 (17° N 36° W)	12	10.4	0.008	0.22	0.03	0.03	0.24
(16° N 35° W)	12a	7.8	0.006	0.18	0.03	0.04	0.16

[a] Bacterial production was calculated using an empirical carbon conversion factor of 0.73 kgC mol leu^{-1} which matches with literature values for the same sampling regions and season (Morán et al., 2002, 2004; Dixon, 2008; Calvo-Diaz and Morán, 2009). [b] Bacterial respiration was calculated from bacterial production using the relationship of $BR = 3.69BP^{0.58}$ (Robinson, 2008). [c] Bacterial growth efficiency (ratio of bacterial production to production plus respiration) has been estimated using BP and BR. [d] Bacterial growth efficiency estimated from in situ concentrations of chlorophyll-*a* (BGE = 1−(1/0.727 × (chl/chl+4.08)+1.02)) (López-Urrutia and Morán, 2007). [e] Bacterial carbon demand has been calculated as BP divided by the average of BGE (BP and BR) and BGE (Chl-*a*). [f] Range found during the diel experiments where surface samples were taken approximately every hour over a 24 h period.

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Table 2. Base parameters, methanol data and estimated contribution to bacterial carbon demand in surface waters of the North Atlantic.

Sampling date (description)	No	Temp (°C)	[Chl-*a*] ($\mu g\,L^{-1}$)	Primary production ($mg\,C\,m^{-3}\,h^{-1}$)	Bacterial Numbers ($\times 10^5$ cells mL^{-1})	Bacterial carbon demand[a] ($\mu g\,C\,L^{-1}\,h^{-1}$)	Methanol concentration (nM)	Methanol Oxidation[b] ($nmol\,L^{-1}\,h^{-1}$)	Turnover Time[c] (d)	*E*:*G*[d]	% Carbon from methanol contributing to BCD[e]
North Atlantic											
12 Dec 07 (26° N 24° W)	1	22.5	0.06	0.70	3.30 ± 0.38	0.10	241[f] (154–296)	5.0 (3.2–6.1)	2 (1–3)	360 (108–1162)	54 (35–66)
18 Nov 07 (18° N 23° W)	2	25.2	0.10	1.15	7.37 ± 0.89	0.34	241[f] (154–296)	1.0 (0.7–1.3)	11 (5–15)	32 (15–105)	4 (3–5)
29 Nov 07 (16° N 24° W)	3	24.8	0.22	2.1	8.30 ± 1.20	0.79	241[f] (154–296)	1.0 (0.7–1.3)	14 (3–25)	12 (4–47)	2 (1–2)
1/4/6 July 07 (42° N 16–18° W)	4	17.8	<0.2	–	6.71 ± 1.54	0.16	70[f] (48–80)	0.12 (0.08–0.21)	83 (60–83)	82 (18–156)	1 (0.5–2)
Shelf Break											
17 June 07 (49° N 10° W)	5	15.5	0.5	–	–	0.46	70[f] (48–80)	0.24 (0.16–0.27)	12	5	1 (0.4–1)
Coastal (L4)											
6 June 06 (50° N 4° W)	6	13.5	1.23	–	–	0.15	97[f] (88–104)	0.73 (0.67–0.79)	6	2	6 (5–6)
North Atlantic											
27 Oct 09 (25° N 40° W)	7	27.1	0.03	0.07	5.92 ± 0.38	0.14	154	1.3	5	–	11
(24° N 40° W)	7a	27.2	0.07	–	5.29 ± 0.35	0.13	151	1.8	4	–	17
28 Oct 09 (23° N 41° W)	8	27.3	0.05	0.04	6.08 ± 0.21	0.19	226	0.61	15	–	4
29 Oct 09 (21° N 39° W)	9	27.4	0.09	0.10	7.41 ± 0.29	0.13	243	1.6	6	–	15
(21° N 39° W)	9a	27.4	0.10	–	7.75 ± 0.98	0.11	215	1.2	7		13
30 Oct 09 (21° N 39° W)	10	27.4	0.06	–	7.16 ± 0.59	0.24	252	1.1	10	–	6
31 Oct 09 (19° N 38° W)	11	27.2	0.08	0.14	8.24 ± 1.15	0.16	278	0.86	13	–	6
(18° N 37° W)	11a	27.3	0.11	–	8.28 ± 0.70	0.07	241	0.80	13	–	13
01 Nov 09 (17° N 36° W)	12	27.3	0.09	0.05	8.68 ± 0.17	0.24	296	1.2	10	–	6
(16° N 35° W)	12a	27.4	0.11	–	7.55 ± 0.21	0.16	153	0.57	11	–	4

[a] From Table 1. [b] Methanol oxidation to CO_2. Data in brackets show the minimum and maximum oxidation rates over a diel cycle and/or over the range in methanol concentrations used. [c] Turnover times estimated from radiochemical experiments (k^{-1}). [d] Methanol uptake into particles (G) was not determined for stations 7–12a. Values in brackets shows the minimum and maximum ratio determined over diel cycles sampling hourly, except for station 4 which shows variability over 3 days. [e] For diel stations 1–3, methanol carbon contributing to BCD is calculated for every hour using the average methanol oxidation rates (using a methanol concentration of 241 nM and in situ k) divided by the BCD. The average methanol contribution to BCD over the diel experiment in then calculated. Values in brackets use the minimum and maximum methanol oxidation rates. For stations 4–12a, minimum and maximum contributions are calculated from the range in methanol oxidation rates found. [f] Methanol concentrations were not determined. Values for stations 1–3 and 4–5 are based on the average surface concentrations measured between 16–25° N and 42–49° N respectively, during October/November 2009 transect of the Atlantic Ocean (AMT19, $n = 6$ for both average values). The concentration for station 6 is based on the average concentration determined at this station (L4) during May/June 2010 ($n = 4$). Data in brackets show the minimum and maximum concentrations.

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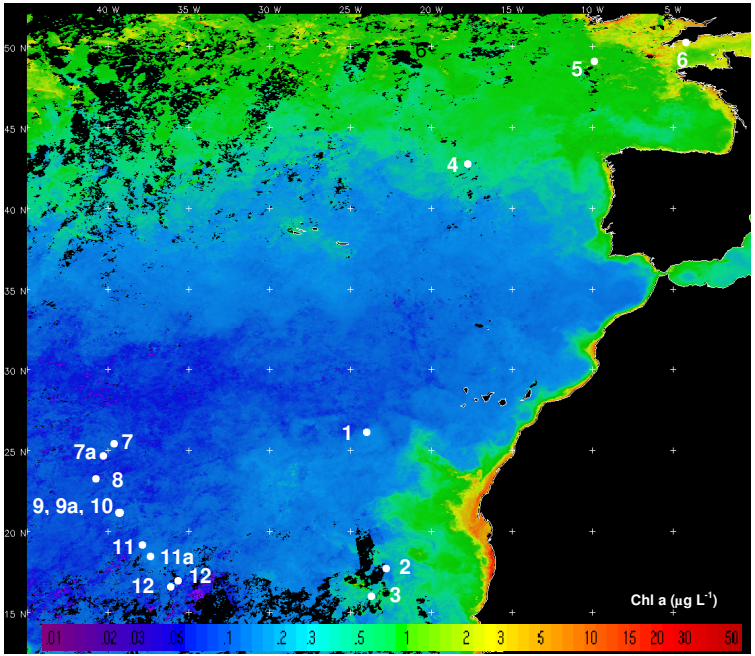

Fig. 1. Sample locations and the composite chlorophyll-*a* image for October 2009 from the modis sensor on the NASA Aqua satellite.

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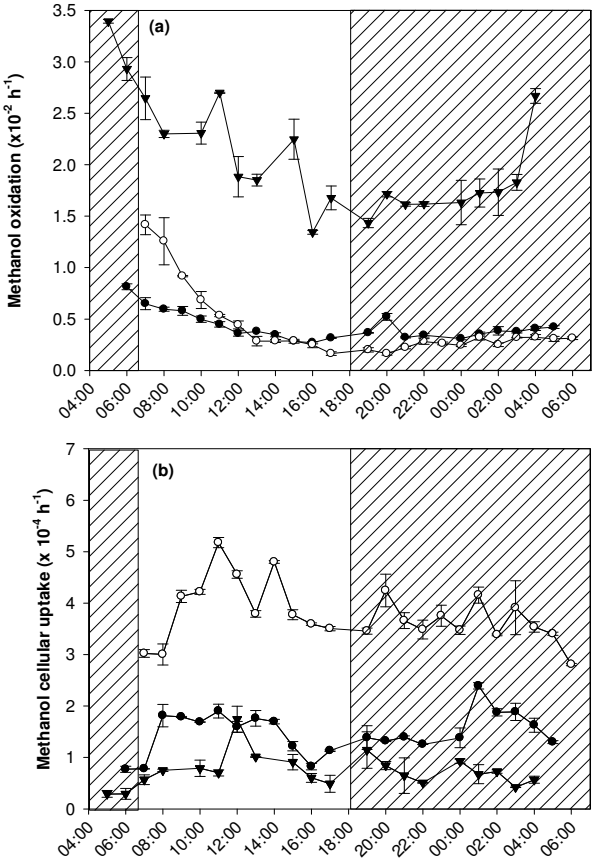

Fig. 2. Methanol oxidation **(a)** and uptake into particles **(b)** for stations 1 (▼), 2 (•) and 3. The hatched area shows night measurements.

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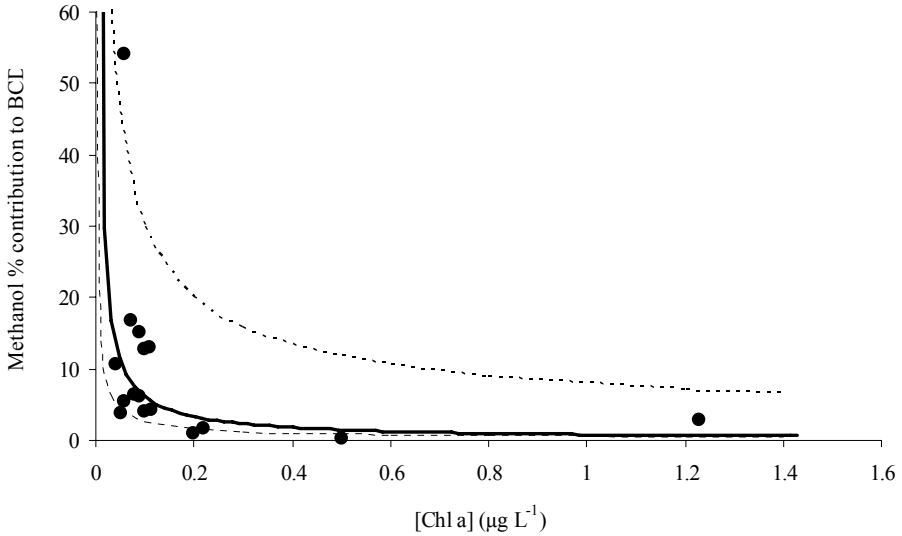

Fig. 3. Methanol contribution to BCD as a function of chlorophyll-*a* concentration. The best fit of the data is given by $y = 0.87 \times^{-0.81}$ ($n = 16$, $r = 0.640$, $P \geq 0.01$). The range shown by the dotted lines represent upper and lower limits calculated using the highest (if applicable) estimates of methanol oxidation rates divided by lowest estimates of BCD (calculated using 0.17 kg C mol leu^{-1}, Alonso-Sáez et al., 2007; Martínez-Garcia et al., 2010), and the lowest rates of methanol oxidation (if applicable) divided by the maximum estimates of BCD (calculated using 1.55 kg C mol leu^{-1}, Simon and Azam, 1989) respectively.

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