Production of methanol, acetaldehyde and acetone in the Atlantic Ocean

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Abstract

The biogeochemistry of oxygenated volatile organic compounds (OVOCs) like methanol, acetaldehyde and acetone in marine waters is poorly understood. We report the first in situ gross production rates for methanol, acetaldehyde and acetone of 49-103, 25-98 and 2-26 nmol L^{-1} d^{-1} over contrasting areas of marine productivity, including oligotrophic gyres and eutrophic upwellings. Photochemical production estimates are mostly negligible for methanol, up to 68% for acetaldehyde and up to 100% of gross production rates for acetone. Microbial surface OVOC oxidation to CO_2 accounts for between 10-50% and 0.5-13% of the methanol and acetone losses respectively, but largely control acetaldehyde concentrations (49-100%). Biological lifetimes in a coastal upwelling vary between ≤1 day for acetaldehyde, to approximately 7 days for methanol and up to ~80 days for acetone. In open oceanic environments the lifetime of acetaldehyde ranges between 2-5 hours, compared to 10-26 days for methanol and 5-55 days for acetone.

1. Introduction

Oxygenated volatile organic compounds (OVOCs) including methanol, acetaldehyde and acetone are ubiquitous in the atmosphere [e.g. Lewis et al., 2005; Singh et al., 1995, 2003] where they affect the tropospheric ozone budget, are precursors to peroxy acetyl nitrate (PAN) and, in the remote marine environment, represent a significant sink of the hydroxyl radical and thus the oxidising capacity of the lower atmosphere [Folkins and Chatfield, 2000; Lewis et al., 2005]. In remote marine air, oceanic sources and sinks of OVOCs are assumed to be significant in controlling air concentrations [Read et al., 2012], although the magnitude and direction of the OVOC air-sea fluxes are a matter of debate [Beale et al., 2013; Carpenter et al., 2004; Heikes et al., 2002; Marandino et al., 2005; Taddei et al., 2009; Williams et al, 2004] largely as a consequence of extremely limited OVOC measurements in oceanic surface waters. Knowledge of OVOC production and loss rates, and an appreciation of the mechanisms involved in our oceans are also lacking.

The carbonyl compounds acetaldehyde and acetone are thought to be produced in surface waters by the photodegradation of coloured dissolved organic matter (CDOM) [de Bruyn et al., 2011; Kieber et al., 1990; Zhou and Mopper, 1997]. Modelling studies have suggested that there must be a large marine in situ source of methanol in the ocean mixed layer [Millet et al., 2008], which is speculated to be biological in nature. For example, methanol has been observed in the gaseous headspace above laboratory phytoplankton cultures and in water surrounding intact macroalgal cells [Nightingale, 1991, Riemer, 1998]. Bacterial consortia are also thought able to transform algal carbohydrates to methanol in the upper aerobic ocean [Sieburth and Keller, 1989].

In this paper we present results of incubation experiments conducted on seawater samples collected from contrasting regions of the Atlantic Ocean; from oligotrophic gyres to productive upwelling locations. This work was conducted to test our hypothesis that biological activity plays a significant role in controlling measured seawater concentrations and production rates of OVOCs in marine waters.

2. Experiments and Techniques

Seawater samples were collected from the Atlantic Ocean (Table 1) during two research cruises (a) SOLAS ICON (Surface Ocean Lower Atmosphere Study, UK 'The Impact of Coastal upwellings ON the production of climate active gases') aboard the RRS Discovery (D338, 15 April – 27 May 2009) and (b) AMT19 (Atlantic Meridonal Transect cruise number 19) aboard RRS James Cook (JC039, 13 October – 1 December 2009). Samples were collected with 20 L Niskin bottles deployed on a rosette equipped with a Seabird conductivity, temperature and depth sensors. The seawater was immediately transferred using Tygon tubing into acid washed quartz incubation vessels (internal diameter 20 mm, length 300 mm) with Teflon screw caps (~300 ml).

The first incubation experiment (Table 1 and Figures 1& 2a) was carried out using surface seawater and water collected from 200m depth, with parallel incubation vessels incubated under in situ light and dark conditions. The subsequent 5 photochemical incubation experiments (Table 1 and Figure 1 & 2b-d) were carried out with surface seawater only at in situ temperatures starting pre-dawn and ending after sunset. Typically each experiment had 4-6 time points from which net change in concentrations were derived. Quartz incubation vessels were placed in on deck incubators with flowing surface seawater during the natural light incubations and for dark experiments the quartz vessels were placed in temperature controlled ThermoTote incubators. Seawater concentrations of methanol, acetaldehyde and

acetone were determined at each time point using a membrane inlet system coupled to a proton transfer reaction mass spectrometer [Beale et al., 2011]. In situ initial (T_o) concentrations of OVOCs were also determined using the same analytical system (Table 1).

Microbial oxidation rates of methanol, acetaldehyde and acetone were determined using ^{14}C-labelled low nano-molar additions (<10% of in situ concentrations) and incubations of typically 1 hour either in quartz micro tubes placed in the light incubators, or in the dark [Dixon et al., 2011a]. OVOC uptake rates in nmol L^{-1} h^{-1} were calculated by multiplying the sample counts (nCi mL^{-1} h^{-1}) by the specific activity of the ^{14}C compound (methanol 57.1 mCi $mmol^{-1}$, acetaldehyde 50 mCi $mmol^{-1}$, acetone 30 Ci $mmol^{-1}$). In order to calculate the total loss of OVOCs over 24 hours due to microbial oxidation, rates were integrated over 12 hours in light and dark experiments and combined (Table 1). Microbial oxidation was assumed to be the dominant biological removal pathway [Dixon et al., 2011b] and OVOC uptake into microbial biomass was not determined during the experiments. Microbial loss rates calculated for methanol (as methanol oxidation rates) in the coastal upwelling station should be considered minimum values, as up to 57% of methanol can be assimilated into microbial biomass (rates are not known for acetaldehyde and acetone) [Dixon et al., 2012].

3. Results

Results from experiment 1 in the Mauritanian coastal upwelling region (U1) are shown in Figure 2a. Methanol showed a net production of 44 nmol L^{-1} in surface waters over 12 hours incubation in the light, but zero change under dark incubations conditions giving a daily net production of 44 nmol L^{-1} d^{-1}. Methanol showed no overall change in concentration in 200 m samples under light and dark conditions i.e. 0 nmol L^{-1} d^{-1}. Surface acetaldehyde showed net production of 7.6 in the light, but a loss of 2.7 nmol L^{-1} in the dark, giving a daily net production rate of 4.9 nmol L^{-1} d^{-1}. Acetaldehyde from 200 m when exposed to the light for

12 hours showed a net increase of 9.4 nmol L^{-1}, with no overall change in concentration in the dark resulting in a daily net production rates of 9.4 nmol L^{-1} d^{-1}. However, water sampled from 200 m would not receive any natural light, thus in situ acetaldehyde production rates are assumed to be ~ 0 nmol L^{-1} d^{-1}. Acetone always showed net production in surface waters of 18.5 and 7.5 nmol L^{-1} in light and dark incubations respectively, resulting in daily net production rates of 26 nmol L^{-1} d^{-1}. Acetone production in 200 m water was 12.8 and 3.5 nmol L^{-1} in light and dark incubations respectively, resulting in a daily net production rate of 7.0 nmol L^{-1} d^{-1} i.e. twice the 200 m dark rate. The difference in production rates between 200m water incubated in light and dark conditions of 9.4 and 9.3 nmol L^{-1} for acetaldehyde and acetone respectively suggests that these deeper upwelling waters contain acetaldehyde and acetone pre-cursors; possibly from sinking phytoplankton detritus derived from the above highly productive waters. Integrated microbial OVOC oxidation rates were not determined during experiment 1.

OVOC net production rates from experiments 2-6 are shown in Figure 2b-d. In the low chlorophyll a (<0.1 µg L^{-1}) surface waters of the Atlantic gyres and equatorial upwelling (EU, Experiments 3-5, Figure 1 and Table s1) methanol shows net daily losses of between 22-428 nmol L^{-1} d^{-1}. For higher chlorophyll stations (>1.0 µg L^{-1}) of the southern temperate region (ST) and Mauritanian coastal upwelling (U2) methanol shows net daily production rates of 89 and 93 nmol L^{-1} d^{-1} respectively. Acetaldehyde net production rates ranged between 13-35 nmol L^{-1} d^{-1} in all regions sampled, except the North Atlantic gyre (NAG), which showed no overall change in concentration over 24 hours. Acetone net daily production rates were relatively modest compared to acetaldehyde, and ranged between 2-4 nmol L^{-1} d^{-1} in open ocean low chlorophyll a regions (Experiments 3-5, Table 1). In higher chlorophyll a waters of coastal upwellings, net acetone production rates up to 26 nmol L^{-1} d^{-1} were found (Figure 2).

Daily integrated methanol loss rates due to microbial oxidation ranged between 10-18 nmol L^{-1} d^{-1} for experiments 3-6 (Table 1) and were highest in NAG. Microbial acetaldehyde oxidation rates were relatively higher at 36-65 nmol L^{-1} d^{-1} with highest loss rates in South Atlantic gyre water (SAG, Table 1). In contrast, microbial acetone oxidation rates were modest at 0.2-0.5 nmol L^{-1} d^{-1}.

4. Discussion

Methanol showed a daily net production of 44 nmol L^{-1} d^{-1} in surface waters of U1 (Figure 2a). We do not have concurrent rates of microbial methanol oxidation, but estimate that rates were ~5 nmol L^{-1} d^{-1} (based on surface water rates on 9th May 2009). Surface methanol gross production rates were therefore estimated at ~49 nmol L^{-1} day, with microbial loss processes accounting for ~10% reduction in methanol production rates at U1. Methanol production and consumption rates balanced in seawater samples from 200 m (dark and below the mixed layer). Microbial methanol oxidation rates of ~20 nmol L^{-1} d^{-1} from a day later at 200m were much larger than surface values, which suggests that gross methanol production was ~20 nmol L^{-1} d^{-1} (~ 41% of surface rates). The ICON experiment was conducted in a Lagrangian framework with SF_6 and ^{3}He measurements confirming that we sampled the same water mass on the 8th and 9th May 2009. The biological lifetime of methanol in seawater was 7 days in surface waters, and ~3 days in 200 m water from U1 (Table 1, calculated by comparing in situ concentrations (T_o) with daily integrated microbial oxidation rates).

Microbial acetaldehyde oxidation rates were much higher than for methanol at 60 and 44 nmol L^{-1} d^{-1} in surface and 200 m waters respectively (on 9th May 2009). Assuming these rates are comparable to those of experiment 1 (8th May 2009), we estimate gross surface acetaldehyde production rates of approximately 65 and 54 nmol L^{-1} d^{-1} for surface and 200 m

150 water respectively, with microbial oxidation largely controlling acetaldehyde concentrations.
151 The biological lifetime of acetaldehyde in U1 is ~6 hours in surface and 200 m water.
152
153 Microbial acetone oxidation rates (also determined on 9th May 2009) were comparatively low
154 at 0.11 and 0.05 nmol L^{-1} d^{-1} in surface and 200m water respectively. We therefore estimate
155 gross surface acetone production rates to be very similar to net rates, at fractionally over 26
156 and 7 nmol L^{-1} d^{-1}, for surface and 200 m respectively. Thus for acetone, microbial losses due
157 to oxidation are minor. The biological lifetime of acetone at U1 is >80 days in surface waters
158 and ~20 days at 200 m, where in situ acetone concentrations were relatively low at 9 and 1
159 nM respectively (Table 1). The microbial acetone loss rates reported in this study are
160 substantially lower than those of a coastal station in the Pacific Ocean, where biotic losses
161 were estimated at ~2.7 d^{-1} [de Bruyn et al., 2013], which if multiplied by our in situ acetone
162 concentrations (Table 1) suggest biologically driven loss rates between 2.7-24 nmol L^{-1} d^{-1}.
163 This large difference could represent differences in location. Alternatively, the large spike of
164 fully dueterated (d-6) acetone (4-26 nM or 44-288% of our in situ acetone surface
165 concentrations determined at station 1, Table 1) used by de Bruyn et al. [2013] may
166 overestimate losses of acetone at in situ concentrations.
167
168 The large net losses of methanol found in surface waters of NAG and EU cannot be fully
169 explained (Figure 2b). Microbial methanol oxidation accounts for 3-4% of the total daily loss
170 of methanol at these stations (Table 1). This suggests other removal mechanisms, perhaps via
171 microbial uptake of methanol (given the high surface concentrations of 272-304 nM, Table 1)
172 and subsequent excretion of overflow metabolites as other organic intermediates. However in
173 the SAG, where surface methanol concentrations are approximately 3 fold lower, measured
174 microbial losses account for ~50% of methanol loss. There is net production of methanol in

higher chlorophyll regions of the ST and U2. For ST waters integrated microbial oxidation rates were 14 nmol L^{-1} d^{-1} (Table 1). Thus gross methanol production in this biologically active region is estimated at 103 nmol L^{-1} d^{-1}, with a biological lifetime more similar to the coastal upwelling regions of 10 days. Methanol production rates in U2 can also be corrected for microbial oxidation estimated at 9.8 nmol L^{-1} d^{-1} (from 21st May 2009 in the same upwelling water mass) resulting also in methanol gross production rates of 103 nmol L^{-1} d^{-1}, which is over double the previous surface rate estimate in U1, but the biological lifetime is the same at ~7 days (Table 1). This increase in methanol production rates between U1 and U2 could be due to an increase in rates of primary and bacterial productivity of over 80% (Table s1), if the main source of methanol is either from phytoplankton cells [Nightingale, 1991, Riemer, 1998] or from bacterial breakdown of algal products [Sieburth and Keller, 1989]. It is also interesting that net production of methanol negatively correlates with surface temperature ($r=-0.854$, $P>0.05$).

Acetaldehyde net production rates can be corrected for microbial losses due to oxidation giving estimated gross production rates (assuming microbial oxidation is the major loss mechanism in seawater) of 41, 50, 98 and 87 nmol L^{-1} d^{-1} for the NAG, EU, SAG and ST waters respectively. Estimated microbial oxidation rates of acetaldehyde for U2 of 12 nmol L^{-1} d^{-1} (on 21st May 2009) result in a relatively lower gross production of 25 nmol L^{-1} d^{-1}. This is lower than observed for acetaldehyde in U1, principally due to a higher microbial acetaldehyde oxidation rate of 60 nmol L^{-1} d^{-1}. This trend between the 2 upwelling filaments i.e. U1 and U2 for acetaldehyde is opposite to that found for methanol, and could reflect decreasing microbial requirement for acetaldehyde as a preferential energy source in U2, perhaps due to an elevated range or quantity of organic sources from enhanced microbial

activity. Overall the biological acetaldehyde lifetimes in open oceanic waters are 2-5 h (experiments 3-6 Table 1), but up to 24 h in upwelling filaments.

Microbial acetaldehyde oxidation rates in surface waters are always equal to, or significantly greater than net production rates, implying strong microbial control of acetaldehyde concentrations in seawater (Table 1). High atmospheric acetaldehyde at Cape Verde in the Atlantic Ocean [Read et al., 2012] compared to the Indian [Wisthaler et al., 2002] and Pacific Oceans [Singh et al., 2003] have been attributed to high photoproduction of acetaldehyde in the biologically active upwelling regions of the West African coast. The fraction of acetaldehyde gross production attributed to photochemical production ranges between 16-68% for the coastal upwelling and NAG locations, closest to the Cape Verde (Table s2). Our results also demonstrate the significance of surface ocean microbes in reducing and controlling oceanic acetaldehyde concentrations, and could account for a lower global oceanic source of 17 Tg y^{-1} based on in situ seawater concentrations [Beale et al., 2013], compared to estimates of 57-175 Tg y^{-1} based largely on modelled air data [Millet et al., 2010, Singh et al., 2004].

In the open ocean acetone losses due to microbial oxidation (Table 1) are relatively small resulting in gross production rates approximately 9-13% higher than net rates (Table 1, assuming microbial oxidation is the dominant loss pathway). Although microbial acetone oxidation rates from U2 (on 21st May 2009) were higher at 1.2 nmol L^{-1} d^{-1} (gross production of 15.9 nmol L^{-1} d^{-1}), elevated net production rates suggest a reduced role for bacteria in removing acetone from surface seawater. Our results contrast with those from coastal Pacific experiments [de Bruyn et al., 2013] as discussed previously. Comparison of in situ acetone concentrations (T_0, Table 1) with microbial oxidation rates suggests that acetone has a

biological lifetime of ~41-55 days in the oligotrophic gyres, ~23 days in EU water, ~5 days in ST waters and 3-82 days in the highly productive coastal upwelling waters. Acetone production is always greater when exposed to light compared to dark conditions (Figure 2d) and photochemical production is estimated at 48-100% of gross production (Table s2), except in the NAG where production in the dark is approximately equal to that in the light. This could be due to elevated microbial acetone oxidation rates in the light (Table 1). Acetone oxidation rates correlate with bacterial production ($r=0.856$, $P>0.05$) and Beale et al. [2013] report a negative relationship between acetone seawater concentrations and bacterial production. Thus although acetone oxidation rates are low, these relationships suggest that as bacterial production increases so does the rate of microbial acetone oxidation, leading to a reduction in the in situ concentration of acetone. Net acetone production rates also correlate with the numbers of picoeukaryotic cells ($r=0.926$, $P>0.05$), whilst gross production rates normalised to CDOM ($\alpha_{350,}$ Table 1) explain approximately 67% of the observed spatial variability (reducing it from 9 to 3 fold). Thus we suggest that acetone production is mainly photochemical [de Bruyn et al., 2011; Kieber et al., 1990; Zhou and Mopper, 1997], and seems to be related to the UV breakdown of CDOM originating from the number of pico-eukaryotic cells.

Spatial differences in the daily UV dose, CDOM *(α_{350})* and the diffuse light attenuation coefficent K_d (340 nm) are shown in Table 1. However for methanol and acetaldehyde normalising the gross production rates by any of the aforementioned parameters in isolation or combination does not help explain the spatial variability.

Microbial oxidation rates (integrated to 1m) are compared to air-sea flux estimates from the same cruises [Beale et al.,2013: Beale, 2011] (Table s3). Comparisons suggest that for

methanol, microbial oxidation (loss) is of the same order of magnitude as the air-sea flux. For acetaldehyde the biological loss is an order of magnitude higher than the air-sea flux, and for acetone biological losses due to oxidation are an order of magnitude lower than the air-sea flux.

We conclude that in productive coastal upwelling filaments the gross production of methanol, acetaldehyde and acetone is 49-103, 25-65 and 16-26 nmol L^{-1} d^{-1} respectively. Microbial oxidation reduces net surface production rates by 10%, 50-92% and 0.5-8% for methanol, acetaldehyde and acetone respectively. Biological lifetimes vary between ≤1 day for acetaldehyde, to approximately 7 days for methanol and up to ~80 days for acetone.

In oceanic regions methanol largely showed a net loss in the incubations, of which only 3-4% could be attributed to microbial oxidation rates in the NAG and EU regions, although this increased to 50% for the SAG. Gross methanol production of 103 nmol L^{-1} d^{-1} in the ST eutrophic region (methanol biological lifetime ~10 days) was highly comparable to higher chlorophyll a waters of the Mauritanian upwelling filaments. Acetaldehyde gross production rates in open ocean environs varied between 41-98 nmol L^{-1} d^{-1} and were highest in the SAG. In agreement with coastal upwelling experiments, surface concentrations were controlled by microbial loss processes (60-100%) with a biological lifetime of 2-5 h. In contrast, acetone gross production rates were relatively low between 2.2-4.5 nmol L^{-1} d^{-1}, with microbial oxidation reducing production rates by 8-13% (Table 1). The biological lifetime of surface acetone in remote low chlorophyll a (<0.1 µg L^{-1}) regions was 23-55 days, which reduced to a minimum of 3-5 days in productive waters (chlorophyll a >0.5 µg L^{-1}).

Our results suggest that methanol photochemical production is relatively insignificant and concentrations are controlled by microbial oxidation and overflow metabolism, surface seawater acetaldehyde concentrations are largely controlled by microbial losses and photochemical production, and acetone production is mainly photochemical with relatively low microbial loss rates. We have thus highlighted the importance of the ocean in both the production and consumption of these atmospherically important OVOC compounds and have highlighted significant compound and spatial differences.

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