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Annual study of oxygenated volatile organic compounds in UK shelf waters

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ABSTRACT

We performed an annual study of oxygenated volatile organic compound (OVOC) seawater concentrations at a site off Plymouth, UK in the Western English Channel over the period of February 2011–March 2012. Acetone concentrations ranged from 2–10 nM (nanomole/L) in surface waters with a maximum observed in summer. Concentrations correlated positively with net shortwave radiation and UV light, suggestive of photochemically linked acetone production. We observed a clear decline in acetone concentrations below the mixed layer. Acetaldehyde varied between 4–37 nM in surface waters with higher values observed in autumn and winter. Surface concentrations of methanol ranged from 16–78 nM, but no clear annual cycle was observed. Methanol concentrations exhibited considerable inter-annual variability. We estimate consistent deposition to the sea surface for acetone and methanol but that the direction of the acetaldehyde flux varies during the year.

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1. Introduction

The ocean can represent an important source or reservoir for oxygenated volatile organic compounds (OVOCs). Reactive gases such as acetone, acetaldehyde and methanol are a source of labile carbon to the microbial community in surface waters throughout the marine environment (Dixon et al.). However, the controls on in-situ concentrations are still poorly understood due in part to a total lack of seasonal data. Further there are no data published on OVOC concentrations in shelf seas, areas known to be high in biological productivity. Datasets with dissolved OVOC concentrations are currently limited to single field expeditions in regions of the Atlantic Ocean (Williams et al., 2004; Beale et al., 2013; Yang et al., 2014), the Pacific Ocean (Marandino et al., 2005; Kameyama et al., 2010) and the Bahamas (Zhou and Mopper, 1997). Methanol is the most abundant of these three reactive gases with concentrations as high as 361 nM reported in the northern oligotrophic Atlantic gyre (Beale et al., 2013). In comparison, acetone and acetaldehyde are rarely reported over 20 nM.

Seawater sources of OVOCs include deposition from the atmosphere and/or active in-situ production. For acetone and acetaldehyde, both low molecular weight carbonyl compounds, photochemical reactions involving Chromophoric Dissolved Organic Matter (CDOM) are thought to be the principal route of production (Mopper and Stahovec, 1986; Zhou and Mopper, 1997; de Bruyn et al., 2011). The fraction of CDOM most likely to be responsible for conversion to these biologically labile species is the humic component on exposure to UVB light (280–320 nm) (Kieber et al., 1990). A study from the Atlantic Ocean suggests that this production mechanism could account for 68% of gross acetaldehyde and potentially 100% of acetone in surface waters (Dixon et al., 2013a). Additionally, acetone has also been shown in the laboratory to be produced by a marine vibrio species of heterotrophic bacteria (Nemecek-Marshall et al., 1995) suggesting a ubiquitous biological in-situ source.

Methanol is suspected to be biologically produced in seawater via phytoplankton cultures and by the breakdown of marine algal cells (Sieburth and Keller, 1989; Nightingale, 1991; Heikes et al., 2002) but few in situ investigations have been conducted. Flux calculations in the northern Atlantic gyre suggest that the atmosphere is unlikely to deposit enough methanol to explain the concentrations measured in the sea surface, suggesting a larger, unidentified biological source (Dixon et al., 2011). Photochemical production of methanol in surface waters is thought to be insignificant (Dixon et al., 2013a).

The OVOCs represent a ubiquitous carbon source for the marine microbial community. Through oxidation to carbon dioxide (CO_2) and assimilation into cell material, microbes use these labile species for energy and growth respectively. For acetone, rates of oxidation to CO_2 in the

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Western English Channel have been measured at between 0.03–1 nM d^{-1}, with the faster rates observed during winter months (Dixon et al., 2014). Beale et al. (2013) also report possible uptake of acetone by marine heterotrophic bacteria through the Atlantic Ocean, suggesting that these organisms may be key species in the cycling of this compound.

Microbial oxidation of acetaldehyde is a dominant loss term. Uptake has been reported at 36–65 nM d^{-1} in the Atlantic Ocean, which is likely to account for 49–100% of the total acetaldehyde loss (Dixon et al., 2013a). This can be compared to rates of 2–146 nM d^{-1} for methanol in the tropical Atlantic (Dixon et al., 2011). Uptake of methanol is usually dominated by oxidation (ie used for energy) but uptake for growth has been shown to dominate (57%) in the highly eutrophic Mauritanian upwelling (Dixon et al., 2013b).

What controls the rates of in situ consumption and production in the surface ocean will inevitably influence the flux of OVOCs across the air–sea interface. The OVOCs are important in the atmosphere due to their ability to alter the global ozone budget and the oxidative capacity of the atmosphere. Methanol is primarily destroyed in the troposphere by reaction with the hydroxyl radical (OH), forming formaldehyde and reactive hydrogen radicals (HO_2) (Warneke et al., 1999). The oxidation of acetaldehyde also produces formaldehyde and hydrogen radicals as well as the stable by-product peroxyacetyl nitrate (PAN), which is involved in sequestering reactive nitrogen (Rosado-Reyes and Francisco, 2007). Acetone undergoes oxidation to form hydroperoxide, which in turn forms methyl glyoxal, acetaldehyde and formaldehyde. These reactions are also a significant source of hydrogen radicals in the mid-upper troposphere (Singh et al., 1995). Both acetaldehyde and acetone also undergo photolysis, producing carbon monoxide, acetic acid, peracetic acid, PAN and further radicals (Arnold et al., 1997).

Read et al. (2012) present the first atmospheric multiannual OVOC study from the Cape Verde Atmospheric Observatory (CVAO) showing that methanol and acetone have winter minima and pronounced peaks in September (acetone), spring (methanol) and autumn (methanol). Acetaldehyde showed no seasonal cycle. Mean mixing ratios of methanol were 742 ± 419 pptv, 546 ± 295 pptv for acetone and the lowest was acetaldehyde at 428 ± 190 pptv. Air mass trajectory analysis shows that air originating from the US and Africa is likely to control peaks in the seasonal cycles.

OVOC global budgets have been the subject of several reviews in recent years (for example, Jacob et al., 2002, 2005; Galbally and Kirstine, 2002; Heikes et al., 2002; Singh et al., 2004; Millet et al., 2008, 2010; Fischer et al., 2012). The influence of the ocean on these budgets via air–sea exchange has been highlighted as a continued source of uncertainty; largely due to a paucity of seawater measurements. In order to reduce this uncertainty, our modest understanding of OVOC marine production and loss mechanisms needs to be advanced. Here we present a time-series of OVOC seawater measurements, made over the period of February 2011 to March 2012, at station (L4) off the southwest coast of the UK. This work was conducted to investigate how seasonality influences the seawater concentrations of acetone, acetaldehyde and methanol with an aim to correlate these concentrations to other in-situ biological, chemical and physical parameters measured at L4. These data will allow progression in our understanding of what controls the concentration of these gases in shelf seas and to determine whether this location is a likely source or sink of OVOCs to the atmosphere.

2. Sampling site & methods

The L4 time-series station is located 10 km off the Plymouth coast (50°15′ N, 04°13′ W) in the Western English Channel in approximately 55 m of water (Fig. 1). A suite of biological, chemical and physical parameters have been measured routinely at the station since 1988 (Smyth et al., 2010a).

Approximately weekly sampling was conducted from the Plymouth Quest using Niskin bottles attached to a rosette sampler. Water for

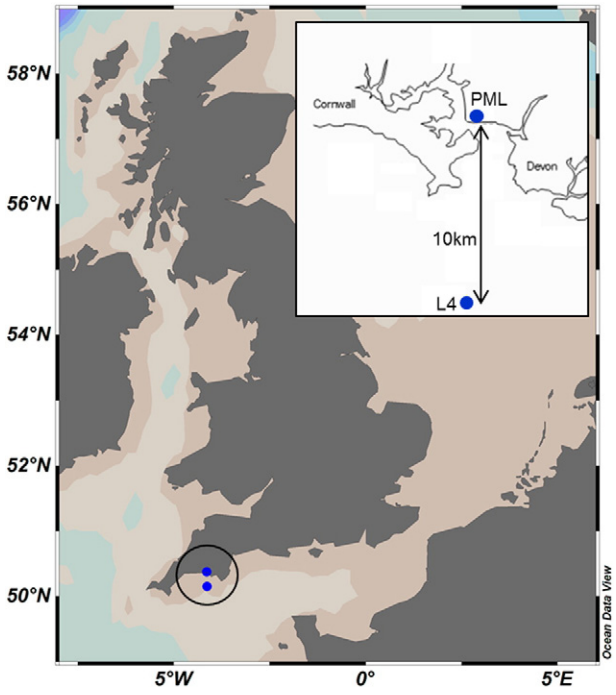

Fig. 1. Location of station L4 in the Western English Channel.

OVOC analysis was immediately transferred from Niskin bottles using Tygon™ tubing into individual brown glass sample bottles (volume of 330 mL) with gas-tight stoppers for transport back to the Plymouth Marine Laboratory in cool boxes. Depths sampled were typically 5, 10, 25 and 50 m. Sampling time was typically between 08:00–09:00 and the time between sampling and analysis of the first sample was approximately 3–4 h.

We were unable to make measurements of OVOCs in air due to difficulties sampling on the Plymouth Quest. We therefore use, where appropriate, air data collected from Plymouth in 2012 (Yang et al., 2013a). The proximity of station L4 to the Plymouth coast means that this air data represents the closest and therefore our best estimate of the likely air concentrations at the time of our water seasonal cycle.

Acetone, acetaldehyde and methanol were quantified in seawater using a membrane inlet coupled to a high sensitivity proton transfer reaction/mass spectrometer (MI-PTR/MS, Ionicon, Austria) as detailed in Beale et al. (2011). Briefly, dissolved gases in the water sample permeate through a membrane into a nitrogen gas flow linked directly into the PTR/MS where they are subsequently protonated by hydronium ions (H_3O^+) and detected by the quadrupole mass spectrometer. Following ionisation, acetone, acetaldehyde and methanol are detected at their molecular mass + 1; 59, 45 and 33 respectively. We consider the risk of interferences to mass 33 and 45 to be low in our system, ie. These masses are attributed only to methanol and acetaldehyde (de Gouw et al., 2003). Propanal and acetone are isomeric and therefore propanal represents a known potential error on mass 59 (also noted by Williams et al., 2004; Sinha et al., 2007; Marandino et al., 2005; Kameyama et al., 2010; Beale et al., 2011). Previous work has shown that acetone typically contributes between 93–98% of the mass 59 signal in seawater (Beale et al., 2013), so we assume that the data presented here represent upper limits for acetone concentration. The system was calibrated with water standards thereby allowing direct comparison of sample to standard response to provide a seawater concentration. The limit of detection of the system during the time-series was calculated (3× standard deviation of the background nitrogen response) at 13 nM for methanol and 0.5 nM for both acetaldehyde and acetone.

We also analysed L4 water to determine microbial oxidation rates for all three OVOCs during the 2011 seasonal cycle, alongside in-situ

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