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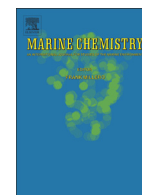

Annual study of oxygenated volatile organic compounds in UK shelf waters

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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

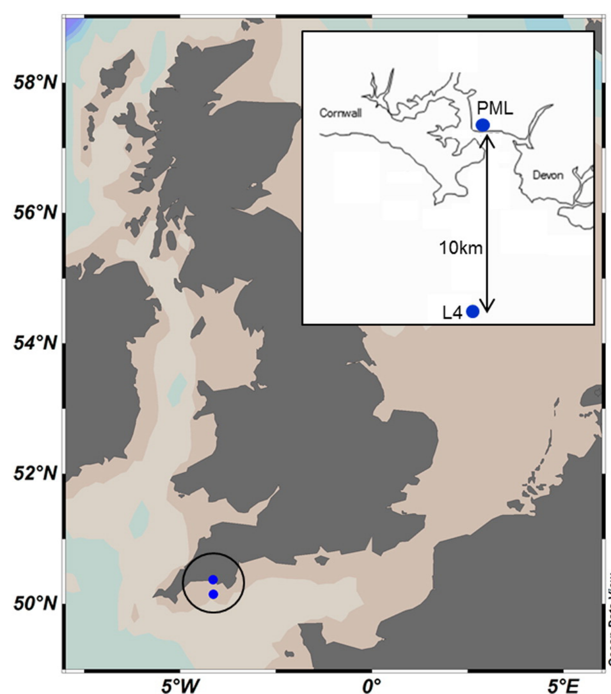

Fig. 1. Location of station L4 in the Western English Channel.

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

concentration measurements. A radiochemical technique was employed using the addition of ^{14}C-labelled OVOC to seawater samples in order to determine the microbial conversion to carbon dioxide (CO_2) (Dixon et al., 2010, 2014). Note that oxidation measurements were made using surface water only.

OVOC analysis was accompanied by surface nutrient analysis (phosphate, nitrate, nitrite, silicate and ammonia as per Woodward and Rees, 2001) and CDOM absorbance (January to July 2011 data only) which was measured spectrophotometrically (Kitidis et al., 2006). Phytoplankton abundance was determined via flow cytometry for prokaryotes (synechococcus and heterotrophic bacteria) and eukaryotes (pico- and nano-eukaryotes) (Tarran et al., 2006) and via microscopy for larger cells (>20 μm) including counts of diatoms, dinoflagellates, coccolithophores, phytoflagellates, zooplankton flagellates and ciliate numbers (Widdicombe et al., 2010). Chlorophyll concentration was determined for surface seawater by Turner fluorometry (Welshmeyer, 1994). Additionally, an autonomous buoy (Smyth et al., 2010b) positioned at L4 was equipped with sensors to record sea surface temperature (SST), salinity, wind speed and direction and optical properties such as Photosynthetically Active Radiation (PAR) and Ultra-Violet (UV) irradiance via a Satlantic hyperspectral radiometer. Net shortwave radiation was calculated as a function of date and position according to Smyth et al. (2014).

3. Results

We were unable to sample every week due to inclement weather and boat/instrument maintenance; in total, OVOC data were collected from 33 time-points over January 2011–March 2012 at depths of 5, 10, 25 and 50 m. Fig. 2(a–c) shows the monthly mean OVOC surface concentrations measured over the time-series and additional environmental variables at L4 over the period of study (d–f). Fig. 3 illustrates the variability of OVOCs with depth throughout 2011.

The sea surface temperature (SST) at station L4 in 2011 (for those time points we sampled) reached a minimum of 8.4 °C in February and a maximum in August of 16.9 °C (Fig. 2f). In 2011, chlorophyll peaked in March, as SST started to climb, and monthly means remained high (>1.3 mg m^{-3}) until September (Fig. 2d). Nitrate and phosphate levels declined from the end of March and remained low until September (Fig. 2e). CDOM showed a general increase in absorption over January to July with a maximum measured at 1 m^{-1} (at a wavelength of 300 nm). This seasonality creates a dynamic environment that has

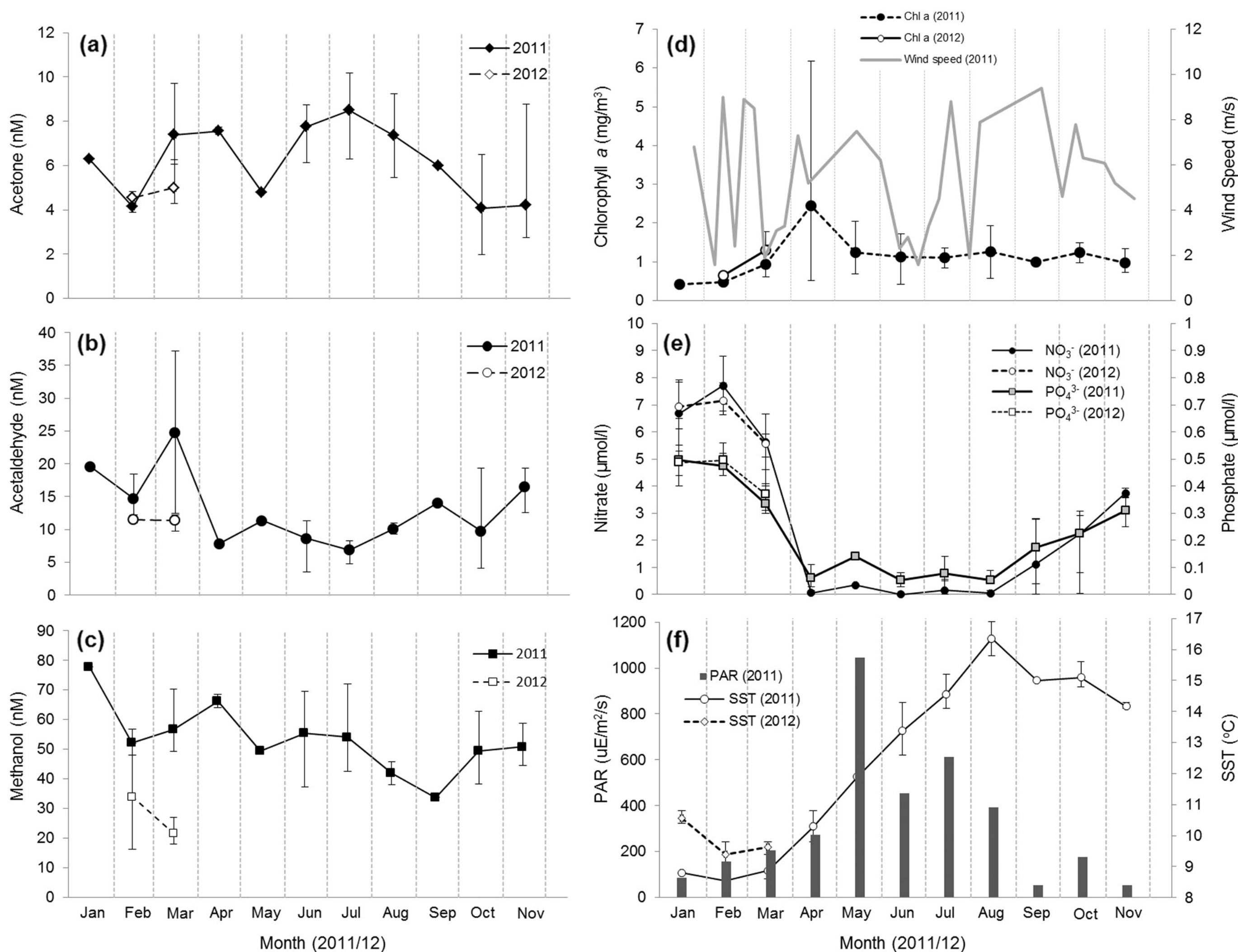

Fig. 2. Monthly averaged 5 m concentrations for January 2011–March 2012 at L4 for (a) acetone, (b) acetaldehyde, (c) methanol. Error bars for OVOC data represent the range of concentrations measured during each month (no error bars are shown for May and September 2011, as only one sampling point was made during these months). Also plotted are (d) monthly chlorophyll-*a* levels at the sea surface (2011 and 2012; error bars represent monthly range in values) and wind speed (2011), (e) Monthly nitrate (NO_3^-) and phosphate (PO_4^{3-}) levels in surface waters in both 2011 and 2012 (error bars represent monthly range in values; only one data point taken in May 2011) and (f) average monthly Photosynthetically Active Radiation (PAR) levels (2011) and Sea Surface Temperature (SST) (2011 and 2012 with error bars representing range of temperature for each month) (NB. Only one data point in January, May and September 2011 for PAR).

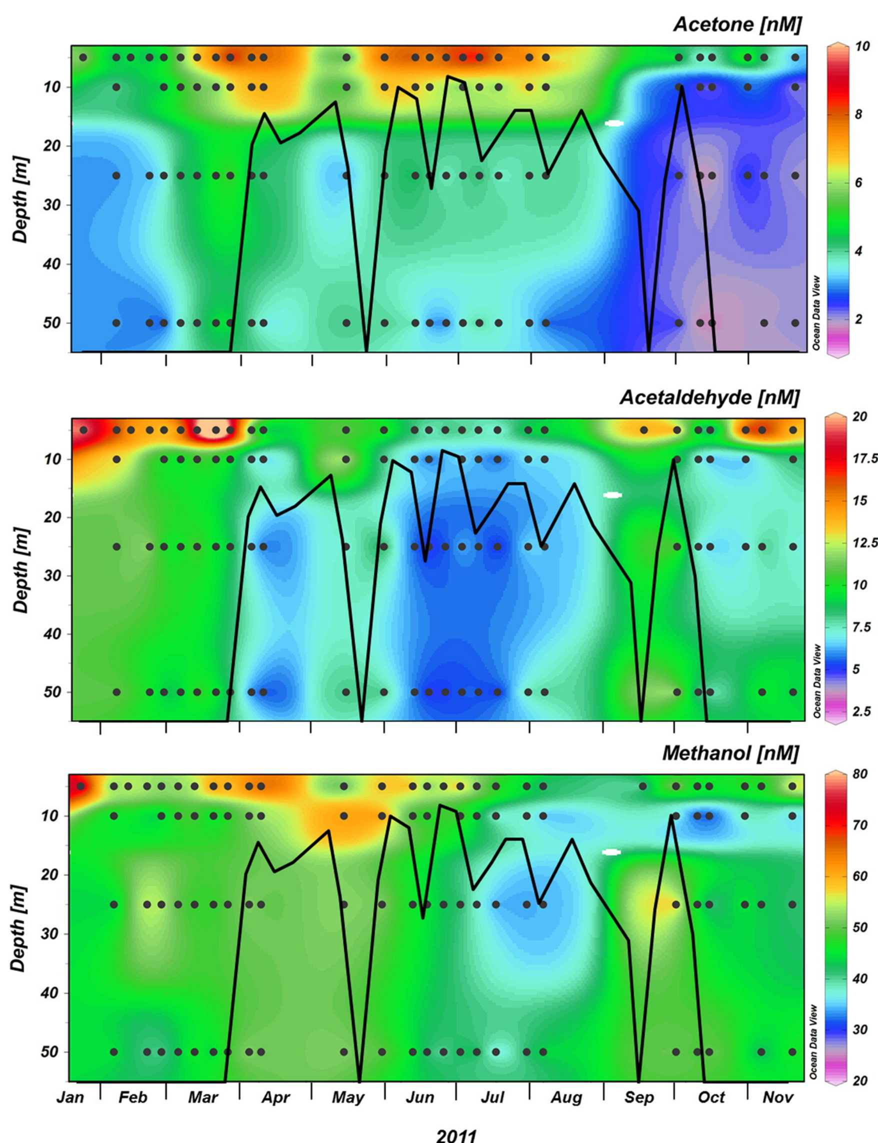

Fig. 3. Contour plot of all OVOC measurements during 2011 time-series for (a) methanol, (b) acetaldehyde and (c) acetone. Mixed layer depth (MLD) is represented by the black line and is calculated as the point at which the temperature change exceeds 0.5 °C from the surface value during the depth profile (Levitus, 1982). MLD data includes weekly values.

previously been shown to exert a strong influence on the concentrations of other biogenic gases (e.g., Archer et al., 2007).

The range of concentrations observed for acetone in surface waters (5 m) over the study period was between 2–10 nM (Fig. 2a) with a 2011 average of 6 nM. We consistently observed higher acetone concentration at the surface and declining levels with depth, as shown in Fig. 3a. We report average (± standard deviation) concentrations of 5 (±2), 4 (±1) and 3 (±1) nM for 10, 25 and 50 m depths respectively during 2011. Samples taken from L4 during February to March in 2011 and 2012 are comparable; average acetone concentrations were 6 (±2) and 5 (±1) nM respectively.

Acetaldehyde surface concentrations from Jan 2011–March 2012 ranged between 4–37 nM (Fig. 2b). We observed an average concentration of 13 (±7) nM for 5 m samples, 8 (±3) nM for 10 m, 8 (±3) nM for 25 m and 8 (±3) nM for 50 m (Fig. 3b). Surface concentrations were therefore consistently higher than the water column below, which typically appeared to be well mixed with respect to acetaldehyde. In contrast to acetone, there is some evidence of inter-annual variability in acetaldehyde concentrations as surface values from February to March in 2011 were higher (18 ± 8 nM) than in 2012 (11 ± 1 nM), but these differences are not statistically significant (at the 95% confidence level).

Surface methanol concentrations varied between 16–78 nM at L4 during the period of 2011–2012 (Fig. 2c). Thus methanol, is the dominant OVOC measured in these shelf waters. There was some variability in methanol concentrations at 5 m compared to the rest of the water column throughout the year (Fig. 3c). However, over the whole period of study there was no significant difference (at the 95% confidence level) in methanol concentration with depth; averages were 49 (±15), 44 (±11), 46 (±9) and 45 (±7) nM for 5, 10, 25 and 50 m respectively during 2011. Methanol values showed evidence of strong inter-annual variability; Concentrations averaged 55 (±7) and 27 (±15) nM for February and March in 2011 and 2012 respectively. These results are significantly different when a two-tailed *t*-test is applied to the data ($t(4) = 4.0, p = 0.05$).

4. Discussion

4.1. Surface OVOC data at L4

Shelf seas are usually characterised by seasonal high productivity, and hence often represent significant sources of biogenic gases; enhanced concentrations of halocarbons (Archer et al., 2007) and DMS

(Archer et al., 2009) have been observed previously at L4. Further, low molecular weight carbonyl species, such as acetone and acetaldehyde, are thought to be produced via the UV degradation of CDOM (Mopper and Stahovec, 1986; Kieber et al., 1990). The proximity of the L4 site to the S W England coastline (Fig. 1) suggests that the terrestrial component of the CDOM pool should be enhanced compared to the open ocean, providing a larger substrate for chemical transformations.

It is therefore perhaps surprising that our L4 surface acetone concentrations are lower than observations made in the oligotrophic northern Atlantic gyre (Beale et al., 2013), in the Pacific Ocean (Kameyama et al., 2010; Marandino et al., 2005) and in the equatorial North Atlantic (Williams et al., 2004) (Table 1). Our L4 surface data in October 2011 are, however, in agreement with measurements made at similar latitudes to L4, but in the North Atlantic, during October 2009 (Beale et al., 2013) and October 2012 (Yang et al., 2014). Acetone values similar to ours (Table 1) have also been reported in bulk seawater taken close to the Bahamas (Zhou and Mopper, 1997), perhaps indicative of lower acetone values in coastal and other high productivity regions.

In contrast to acetone, our acetaldehyde data, with a mean of 13 nM, are higher than most published datasets (Table 1). Indeed, the maximum concentration of 37 nM we observed on 22nd March 2011 represents the highest published value for marine waters. Acetaldehyde measurements at L4 are greater than observations from the Atlantic and Pacific Oceans, but are in reasonable agreement with values off the coast of Florida (Mopper and Stahovec, 1986), indicating that coastal regions may be an important source of acetaldehyde to the atmosphere.

Methanol concentrations in L4 surface waters are, similarly to acetone, lower than data from a north to south transect of the Atlantic Ocean (Beale et al., 2013), the tropical Atlantic (Williams et al., 2004) and the North Pacific Ocean (Kameyama et al., 2010) (see Table 1). However, methanol concentrations at L4 in October 2011 (50 ± 12 nM) are comparable to observations (71 ± 18 nM) from a similar latitude in the North Atlantic in October 2009 (Beale et al., 2013). Chlorophyll a levels at L4 in October 2011 were approximately 1.1 mg m^{-3} compared to 0.1–0.3 mg m^{-3} in the North Atlantic (49–44°N) in 2009 and were below 0.1 mg m^{-3} in the northern Atlantic oligotrophic gyre (35°N) where a highest published methanol concentration of 361 nM was observed (Beale et al., 2013). However, we observed no significant relationship throughout this L4 time series between methanol and chlorophyll *a*. Our observation of reduced methanol concentrations in 2012 compared to 2011 indicates there may be significant interannual variability in levels of this volatile, an observation supported by the difference in methanol concentrations reported from similar transects of the Atlantic Ocean in 2009 (Beale et al., 2013) and 2012 Yang et al. (2013b, 2014) (Table 1).

4.1.1. Seasonal variability of OVOC concentrations in surface waters

This work was primarily conducted to determine whether OVOCs exhibit seasonal variability in concentrations in shelf waters similar to that of other dissolved gases previously studied at L4; Dimethyl sulphide (DMS) (controlled mainly by specific phytoplankton and bacterial communities), halocarbons (which are directly influenced by light and some particular species of micro-organisms) and carbon dioxide (CO_2) (controlled by both biology and temperature).

Previous work at L4 has shown that DMS levels (over 2003–2004), were low from October through to February, peaked in April–May and reached a maximum in June/July in response to seasonal phytoplankton succession (Archer et al., 2009). Concentrations varied by about two orders of magnitude over the year. Iodomethane levels were at a minimum at L4 in winter months, showed a broad maximum from July–September and then declined during the autumn (Archer et al., 2007). Chloroiodomethane, however, showed three sharper maxima in April, June and in September, probably linked to production by successive groups of discrete phytoplankton. These shelf waters acted as a source of both DMS and iodocarbons throughout the year. For comparison, the seasonal CO_2 dynamics at L4 are in part driven by changes in water temperature (characteristic of 2011, Fig. 2(f)) and hence solubility. Once the effect of SST was removed, CO_2 levels showed winter maxima and July minima mostly due to net biological consumption in the spring and summer (Kitidis et al., 2012).

We observed evidence of a seasonal cycle (Fig. 2a) for acetone in surface waters, with higher concentrations in spring (defined here as March–May 2011) and summer (June–August 2011) compared to autumn (September–November 2011) and winter (December–February 2011). Statistical analysis (performance of a two-tailed *t*-test at the 95% ($p = 0.05$) confidence level here and thereafter) shows that there was no significant difference between the surface acetone concentrations measured in spring and summer, neither between those in autumn and winter, but that spring and summer are statistically different to autumn and winter (summary of the significantly different *t*-test results: $t(4–6) = 2.8–4.8$, $p = 0.05$). Monthly mean concentrations are approximately twice as high in spring/summer as in autumn/winter. We had no prior expectation of likely acetone concentrations or possible temporal cycle in these coastal shelf waters. The reduced amplitude of the seasonal signal, compared to those observed previously for DMS and VICs, suggests that production and consumption of acetone may be relatively tightly coupled. The maxima observed in the acetone seasonal cycle are perhaps 'muted' compared to DMS; we observed a difference of 8 nM over the study in surface waters, not two orders of magnitude. This might suggest that acetone concentrations are not influenced by the seasonal succession of phytoplankton groups, unlike DMS and VICs, and hence production may not be limited to particular plankton classes.

A positive correlation (via regression analysis) was observed between acetone and net shortwave radiation ($p < 0.001$, $r^2 = 0.6$, $n = 28$) for 2011. The latter term includes light from the visible, infra-red and UV regions of the spectrum. We also observed a positive relationship between UV-A (sum of 348–398 nm wavelengths over the cast time; 6–9 am) and acetone concentration ($p = 0.002$ (99.8%), $r^2 = 0.4$, $n = 19$). It is unlikely that there was direct UV-A photoproduction of acetone from CDOM as Kieber et al. (1990) reported that carbonyl production is restricted to the UV-B (280–320 nm) region of the spectrum where the energy provided is sufficient to cleave the carbon–carbon bonds within the humic component of the CDOM pool.

Table 1
Summary of published OVOC in-situ surface measurements.

Location	Acetone (nM)	Acetaldehyde (nM)	Methanol (nM)	Reference
West coast Florida	–	2–30	–	Mopper and Stahovec (1986)
Bahamas, USA[a]	3 ± 0.2	1 ± 0.1	–	Zhou and Mopper (1997)
North Atlantic Ocean	18 ± 8	–	118 ± 42	Williams et al. (2004)
Tropical Pacific Ocean	15 ± 13	–	–	Marandino et al. (2005)
North Pacific Ocean	12 ± 3	–	–	Marandino et al. (2005)
Pacific Ocean	19 ± 4	<6	159 ± 33	Kameyama et al. (2010)
Atlantic Ocean	2–24	3–9	48–361	Beale et al. (2013)
Atlantic Ocean	5–36	4–9	15–62	Yang et al. (2014)
UK Coastal shelf waters	2–10	3–37	16–78	Beale et al., this data

[a] Bulk water results, not microlayer.

Furthermore, we observed no significant correlation between our acetone levels and CDOM absorbance over January to July 2011 at any of the following wavelengths (spanning both UV-A and UV-B light); 275, 300, 315, 325, 350, 365, 375, 400 nm.

Another source of acetone to surface waters at L4 may be deposition from the atmosphere. This too may be driven by changes in light and we discuss this further in Section 4.4.

Thus overall, our observations support results from previous incubation experiments using open ocean surface waters that suggested the production of acetone in the North Atlantic was principally controlled by light (Dixon et al., 2013a).

A comparison of acetone concentrations with other environmental variables at L4 found few other significant relationships. We did find a positive correlation between acetone and autotrophic nanoeukaryote numbers ($p = 0.012$ (98.8%), $r^2 = 0.3$, $n = 24$) in surface waters. Either these autotrophs were producing acetone or it could be that the numbers of these organisms are governed by light intensity, thereby generating a similar cycle to our acetone concentrations at L4.

We determine microbial oxidation rates for acetone in L4 surface water over the 2011 seasonal cycle (Dixon et al., 2014). Oxidation of acetone to CO_2 rates during the time-series ranged between 0.001–0.38 nM hr^{-1} (equivalent to 0.03–9.2 nM d^{-1}). We observed periods of faster uptake in the first half of 2011 (January–May) with rates between 0.001–0.38 nM hr^{-1}, with a smaller range of 0.001–0.006 nM hr^{-1} reported for the remainder of 2011. There was not a significant relationship between the oxidation data and surface acetone concentrations. These acetone oxidation rates imply turnover times (calculated as concentration divided by microbial oxidation rate) in the range of 0.4–327 days at L4. Slower rates occurred during summer (average of 165 days) and the fastest turnover rates were in winter (average of 6 days), in qualitative agreement with our observations of reduced acetone concentrations in winter and autumn. This suggests that in summer, when there is a likely abundance of carbon sources, marine microbes will not favour acetone but that in winter, when there may be less labile carbon available, acetone will be consumed faster (Dixon et al., 2014).

Surface acetaldehyde concentrations over the seasonal cycle were opposite in trend to that observed for acetone, ie higher acetaldehyde levels during autumn and winter that decreased over spring and summer (Fig. 2b). Statistical analysis of the acetaldehyde data by season shows no significant differences other than when winter (16 ± 3 nM) is compared to summer (8 ± 3 nM) ($t(4) = 4.3$, $p = 0.05$).

The seasonality in acetaldehyde concentrations at L4 is rather similar to that of CO_2, the cycle of the latter being controlled largely by solubility, biological uptake during the spring and summer, and vertical mixing in autumn (Kitidis et al., 2012). However, neither temperature nor biological productivity correlated with surface acetaldehyde concentrations at L4. Although acetaldehyde concentrations did appear to track nitrate levels (Fig. 2e), ie higher values at the start of the year, depletion during spring and summer and replenishment during winter, no significant relationship was observed. Indeed, none of the ancillary data from L4 correlated with surface acetaldehyde concentrations.

Given that photochemistry was thought to be the principal marine source of acetaldehyde (Zhou and Mopper, 1997), it was surprising to observe a decrease in surface concentrations throughout the summer when longer days, coupled with higher intensity sunlight, would have been expected to result in enhanced levels of acetaldehyde. A comparison between acetaldehyde concentrations and UV levels gave a negative relationship ($p = 0.03$ (97%), $r^2 = 0.26$, $n = 19$) suggesting that the days when UV levels were higher corresponded to lower acetaldehyde concentrations. However, as acetaldehyde is not thought to be significantly photolysed in seawater (Kieber et al., 1990), this may not be causal. Another possibility is that due to the timing of the sampling (typically 9 am and not when solar insolation would be strongest), the photochemical enhancement of the acetaldehyde signal was missed (no samples were taken at solar noon from station L4 during 2011). However, this would require rapid loss of acetaldehyde in seawater otherwise there should have been a gradual increase in concentration during summer. Furthermore, Beale et al. (2013) report no statistical difference in acetaldehyde concentrations from samples taken at pre-dawn compared to solar noon throughout a transect of the Atlantic Ocean.

We also found significant negative relationships ($p > 95\%$) between acetaldehyde concentration and each of the 8 wavelengths extracted for CDOM absorbance (spanning both UV-A and UV-B light, listed above). The strongest relationship was found with CDOM absorbance at 275 nm (a_{275nm}) ($p = 0.009$ (99.1%), $r^2 = 0.38$, $n = 17$). This implies that as the magnitude of the CDOM absorption increased (an indication of increasing CDOM in surface waters at L4), concentrations of acetaldehyde decreased, ie. the opposite to the trend we expected.

Mechanistic approaches to the photochemical production of low molecular weight carbonyls in natural waters suggest that acetone and acetaldehyde differ in their production routes from CDOM (de Bruyn et al., 2011). Acetone shows higher production rates via CDOM reactions with both OH and O_2 whereas acetaldehyde is favoured when direct photolysis of CDOM occurs. The authors also report that the production efficiency is likely to vary with location, age of CDOM and the presence of photosensitizers. Our results indicate that acetaldehyde concentration is highest when CDOM absorption (a_{300nm}) is lowest during 2011; coincident with January–April. April was a critical month in the seasonal cycle at L4 in 2011. SST and PAR increased, nutrients significantly decreased and phytoplankton communities were thriving. It is likely that the biological and terrestrial components of CDOM were different before and after April.

We therefore calculate the slope of the natural log-transformed absorption spectra over two band widths; 275–295 and 350–400 nm^{-1} as per Helms et al. (2008). We then determined the ratio of these slopes (S_R) which provide an indication of CDOM molecular weight at L4. We calculate an S_R range of 1.3–2.0. Generally, the lower the S_R value the more indicative it is of terrestrial CDOM (Helms et al., 2008) with a higher molecular weight (~0.7). Therefore our values are appropriate for near-shore waters with a marine influence. Over January–April and May–July we calculate slope ratios in the range of 1.4–1.8 and 1.3–2.0 respectively. Thus, there was a larger variation in the size of the CDOM in the latter study period, perhaps suggestive of a change in CDOM sources.

Alternatively, the decrease in acetaldehyde in the summer could be due to faster microbial oxidation rates. The radiochemical technique, based upon the addition of ^{14}C-labelled acetaldehyde to seawater, was therefore utilised to determine the microbial conversion of acetaldehyde to CO_2. Microbial acetaldehyde oxidation rates, coincident with in-situ sampling, were observed to be between 5–31 nM hr^{-1} (117–756 nM d^{-1}) during 2011. These rates are likely to exceed photochemical production by a possible factor of 10 (likely to be between 3–8 nM h^{-1}, Zhou and Mopper, 1997). Oxidation rates were at a maximum in October and November. Knowledge of microbial oxidation rates and surface concentrations allowed us to estimate that the turnover of acetaldehyde at L4 ranged between 0.01–0.13 days. The slowest turnover was in spring (mean 0.08(±0.04) days) and the fastest was in the autumn (mean 0.05(±0.04) days). These data indicate that microbial oxidation of acetaldehyde represents a major sink for this compound in these shelf waters. However, there was no correlation between microbial uptake rate and surface acetaldehyde concentrations during 2011.

There is no clear seasonal cycle of methanol (Fig. 2c) when compared to either acetone or acetaldehyde, and any of the biogenic gases determined at L4 so far e.g., CO_2, DMS and VICs (Kitidis et al., 2012; Archer et al., 2007, 2009). Applying a two-tailed t-test ($p = 0.05$) to the methanol surface data (Fig. 2c) indicates there is no significant difference between seasons.

A positive relationship was observed ($p = 0.006$ (99.4%), $r^2 = 0.3$, $n = 24$) between surface methanol concentrations and heterotrophic nanoeukaryotes which may indicate a possible methanol production pathway in the surface waters at L4. No other significant correlation

between surface methanol and any other environmental variable at L4 was observed.

The seasonal cycle of methanol is the most complex of the three OVOCs measured here to interpret. We know that methanol is used as a source of microbial carbon in seawater for both energy and growth (e.g., Dixon et al., 2010). Surface microbial oxidation rates of methanol at L4 during 2011–2012 (for when we have corresponding water concentrations) ranged between 1–11 nM hr^{-1} (16–257 nM d^{-1}). Rates generally increased throughout the time series. Oxidation rates were similar to a limited number of earlier measurements from the North East Atlantic Ocean in October 2009 (Dixon et al., 2011). Methanol turnover rates varied between 0.1 and 4.5 days during 2011. The shortest lifetime (0.1 days) was observed in February 2012, in agreement with our lowest surface methanol concentration measurement of 16 nM. However, we did not find a statistically significant correlation between surface methanol concentrations and microbial methanol oxidation rates over the entire dataset. Despite this, it is likely that microbial methanol consumption is a significant controlling factor on dissolved concentrations, as has been reported for oceanic waters (Dixon et al., 2013a).

Our surface methanol concentration data in February and March (Fig. 2c) were statistically lower in 2012 than in 2011 ($t(4) = 4.0$, $p = 0.05$). We cannot associate these differences to changes in ancillary variables measured at L4 (Fig. 2d–f). However, microbial methanol oxidation rates were higher in 2012 (6 ± 0.3 nM hr^{-1}) compared to 2011 (1 ± 0.1 nM hr^{-1}). Methanol concentrations do not show an equivalent 9-fold decrease but these observations indicate that (i) significant temporal variability in methanol concentrations might be expected and (ii) that there may be multiple controls on methanol concentrations that are suppressing a clear seasonal signal.

4.2. Vertical distributions of OVOCs and ancillary variables

Station L4 is seasonally stratified, typically from April through to October, although this stratification can be periodically broken down during high wind events. Mixed Layer Depths (MLD) have been determined using a criteria of the depth at which the temperature decreases by more than 0.5 °C from the surface value (Levitus, 1982) (Fig. 3). In 2011, the water column at L4 was thermally stratified during spring and summer (March–late September) with an average MLD of ~15 m. From January through to mid-March, and from mid-November to the end of 2011, the water column was completely mixed to ~55 m. Prolonged periods of high winds (Fig. 2d) resulted in short breakdowns in stratification in May and September (Fig. 3). From September onwards, SST started to drop, MLD began to increase and wind speeds remained above 4 m s^{-1} (Fig. 2d).

Fig. 4 contains data from four typical depth profiles, one for each season, and clearly shows that water column stratification also influences biological activity (as represented by total eukaryote numbers) throughout the year. Total eukaryotes are evenly distributed throughout the water column in February. However, numbers are elevated in surface waters (5 and 10 m) in April, June and October, compared to deeper samples, due to the impact of light availability. There is some evidence in April and June that total eukaryotes are highest at 10 m, presumably due to nutrient supply from beneath the pycnocline.

The highest acetone concentrations were typically observed in the shallow mixed layer during spring and summer (Fig. 3). There is no statistical difference (at 95% confidence level) in measurements from depths of between 5 m and 10 m during this period. We did observe a reduction in surface acetone concentrations (5 and 10 m) during May; this was probably due to higher winds (Fig. 2d) which caused thermal stratification to break down, as shown by a MLD of 50 m (Fig. 3a).

There was a statistically significant difference between the acetone data collected from 5 m and 10 m and depths below the mixed layer (25 m and 50 m) during spring and summer (summary of t-test results; spring: $t(6) = 2.9$–4.6, $p = 0.05$, summer: $t(7$–$8) = 5.8$–7.0, $p = 0.05$); concentrations at depth were reduced and were reasonably stable throughout April–August and from 25–50 m (Fig. 3a). We observed our lowest acetone concentrations in October 2011 at 25 m and 50 m (1 nM). There was no statistical difference in the concentrations from 5 m to 50 m in either autumn or winter, consistent with rapid vertical mixing.

Depth profiles (Fig. 4) illustrate that acetone concentrations generally follow the decline in temperature with depth, as have previously been observed for the Atlantic Ocean (Williams et al., 2004; Beale et al., 2013). Given that a positive relationship between net shortwave radiation (and UV) and acetone concentrations was observed in surface waters at L4, we suggest that acetone is being produced in surface waters and mixed down through the water column.

Acetaldehyde is generally higher at the surface than in the underlying waters at L4 (Figs. 3b and 4). There was no statistical difference between concentrations from 10, 25 and 50 m in any of the individual depth profiles sampled during the 2011 time-series. All three depths averaged 8 (± 3) nM over the 2011 time-series. However, concentrations measured at 5 m (mean 13 ± 7 nM) were consistently statistically different ($t(21$–$24) = 3.4$–3.6, $p = 0.05$) to values from below. This is somewhat surprising given that the water column was well mixed in winter and late autumn. Therefore, our acetaldehyde concentration profiles are suggestive of rapid, near-surface production and subsequent rapid consumption throughout the water column which prevents homogeneity within the mixed layer. Furthermore, the decline in acetaldehyde concentrations at 10 to 50 m from March onwards corresponds to the onset of thermal stratification (Fig. 3b) when vertical mixing is reduced. Indeed, data at 25 and 50 m are significantly different when there is a mixed layer compared to concentrations from months when the water column is well mixed (25 m: $t(10) = 3$, 50 m: $t(6) = 3.3$, $p = 0.05$). We suggest that microbial consumption in combination with reduced mixing from above could create the lower acetaldehyde levels observed below the MLD in spring and summer 2011.

Methanol concentrations were typically highest at 5 m (Figs. 3c and 4) and were, like acetaldehyde, significantly different to values in the underlying waters (summary of t-test results: $t(21$–$24) = 2.8$–3.1, $p = 0.05$). There was no significant difference between the 10, 25 and 50 m methanol datasets in 2011. There was little variability in concentrations with depth from February to mid-March synonymous with rapid vertical mixing. The higher concentrations observed in surface waters from March through to June coincided with the presence of a shallow mixed layer which would have limited transfer of methanol to the underlying waters. We observed a minimum at 10 m in October 2011 (Fig. 4d) but have been unable to find an explanation for this variability in any of the other parameters measured at L4.

Given that Dixon and Nightingale (2012) report that, in NE Atlantic water, microbial rates of methanol oxidation were not statistically different from the microlayer down to 1000 m, there must be production of methanol throughout the water column that is active above and below the mixed layer in order to maintain detectable concentrations throughout the year. There is no strong evidence from our study at L4 (or others eg, Dixon et al., 2013a) to support the photochemical production of methanol, so sources must be biological in nature (Nightingale, 1991; Heikes et al., 2002).

There is no suggestion of any enhancement in concentrations of acetone, acetaldehyde or methanol at 50 m, a depth close to the seafloor, suggesting that the sediments were not a significant source of OVOCs to the water column at L4.

4.3. Understanding OVOC loss

Analysis of dissolved gases rarely occurs immediately, particularly in coastal studies, due to transit time to the laboratory and/or relatively slow analytical methods which usually only measure one sample at a time. As a consequence, samples are likely to be subject to different storage times. We determined how sample storage

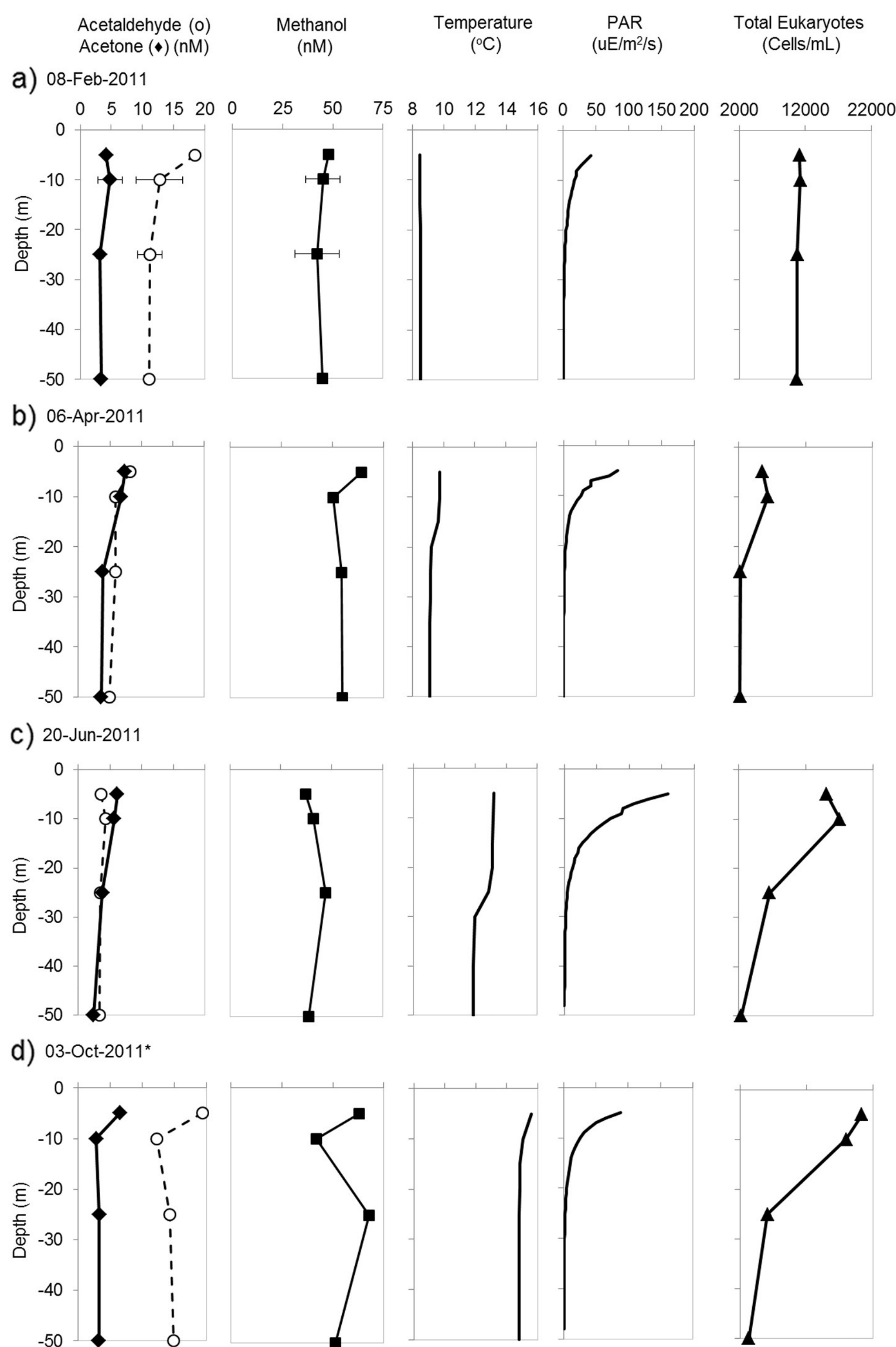

Fig. 4. Typical depth profiles of OVOC concentration at L4 with temperature, Photosynthetically Active Radiation (PAR) and total eukaryote abundance (defined as the sum of coccolithophores, cryptophytes, *Phaeocystis*, dinoflagellates and nanoeukaryote numbers by flow cytometry) in 2011 during (a) winter (08 February), (b) spring (06 April), (c) summer (20 June) and (d) autumn (03 October). *Please note that the total eukaryote numbers presented in (d) are from the 12th October, data not available for the 3rd.

might affect quantification of OVOCs in seawater at each sampling point in the time series. To the best of our knowledge we are the first to investigate sample OVOC integrity in this manner.

Our samples were stored in opaque, glass, gas-tight bottles and kept in the dark, inside a cool box at in-situ temperature, for the 3–4 h between sampling at L4 and start of analysis at PML. Previous experiments have shown that, at typical in-situ concentrations, OVOCs are stable in milliQ water for periods of up to 7 h under similar conditions (Beale et al., 2011). However, microbial OVOC oxidation rates made with our radiochemical technique during this time-series, and in the Atlantic Ocean (Dixon et al., 2011, 2014) suggest that losses during transit are possible. We did not filter our samples prior to analysis as we have previously found this to cause erroneous results, presumably due to either contamination or cell lysis/stress during the filtering process (Beale et al., 2011). We prevented OVOC production via autotrophs and direct photochemical alteration of OVOC concentrations by using opaque bottles. Therefore, any changes to OVOC concentration during storage are likely to be due to either dark chemical transformations, or biological activity by the heterotrophic community at L4.

Our sequence of analysis always began with triplicate surface samples (sample 1 (S1) to sample 3 (S3)). Each analysis lasts for approximately 30 min, thus, S3 is stored for ~1 h longer than S1. Hence, we calculate a net change in OVOC concentration with each of the 33 stations sampled in the seasonal study. On average, methanol, acetaldehyde and acetone

showed net losses of 8, 6 and 8% per hour respectively ie, close to or within our instrument precision (7%, 9% and 8% for methanol, acetaldehyde and acetone respectively, see Beale et al., 2011).

We use our microbial oxidation data to determine whether there were other unidentified losses or unknown production pathways active in the samples.

For methanol we report an average loss of 3.5($\pm$2.4) nmol/l/h for the analytical (A) and 5.3($\pm$3.4) nmol/l/h for the microbial oxidation (MO) method ($n = 9$, where n represents the number of samples where we have concurrent MO and dissolved methanol data). Applying a two-tailed t-test ($p = 0.05$) to the two datasets shows that there was no significant difference between the results, implying that microbial oxidation of methanol was the dominant loss term.

Greater losses of acetaldehyde were predicted by the MO technique, which were significantly different ($t(16) = 5.2$, $p = 0.05$) to the results of the analytical net change over time; 1.7($\pm$1.6) nmol/l/h (A) and 12.8($\pm$8.6) nmol/l/h (MO). That microbial oxidation rates were larger than net changes observed by the PTRMS suggests there may have been production of acetaldehyde in sample bottles during storage, presumably biologically-mediated.

For acetone, the PTRMS indicated average losses of 0.4($\pm$0.2) nmol/l/h, but only 0.04($\pm$0.1) nmol/l/h using the MO technique ($n = 13$). Thus we infer that there are acetone removal mechanisms that we are unable to identify. We have verified previously that acetone is not lost to glass surfaces (Beale et al., 2011) and sampling bottles were opaque, hence removal is presumably biologically-mediated.

4.4. Direction of OVOC flux at L4

We did not make concurrent air measurements at the time of L4 sampling. However, Yang et al. (2013a) made OVOC air measurements in Plymouth over the period of March–July 2012. As described previously, the close proximity of L4 to the Plymouth coast makes this the most appropriate data for estimating the likely OVOC air concentrations over the period of our time series. Including both day and night-time mixing ratios, methanol was observed over the range of 0.5–5 ppb, acetaldehyde at 0.1–0.4 ppb and acetone at 0.4–1 ppb. We use these lower and upper air concentrations (C_a) to calculate the likely saturation state of the surface waters at L4 in 2011. Water concentrations (C_w) were corrected, where appropriate, for OVOC loss/production using the analytical (A) technique described earlier to estimate in-situ surface concentrations at the time of sampling. OVOC saturation states were derived using the equation

$$[(C_w/H)/C_a] * 100$$

where H is the Henrys Law solubility (Sander, 1999) after correction for temperature and salinity.

Acetone and methanol were most likely significantly under-saturated during our seasonal cycle. For methanol, average saturations were just 17($\pm$10) % and 2($\pm$1) % for air values of 0.5 ppb and 5 ppb respectively, indicating transfer from the air to sea would have occurred. For acetone we predict saturations of 18($\pm$11) % and 7($\pm$5) % for 0.4 ppb and 1.0 ppb respectively, also indicating net air to sea transfer. Substituting the storage corrected water with measured values (presented in Fig. 2) makes little difference to the saturation state.

Read et al. (2012) measured OVOCs over 5 years at Cape Verde Atmospheric Observatory (CVAO) and report methanol and acetone over the range 0.7 $\pm$ 0.4 ppb and 0.5($\pm$0.3) ppb respectively. These measurements are therefore at the lower end of the Plymouth observations. Predictions of substantial under-saturation at L4 for methanol and acetone are in agreement with direct covariance flux measurements made in Plymouth (Yang et al., 2013b).

The range of acetaldehyde air measurements (0.1–0.4 ppb) observed in 2012 (Yang et al., 2013a) are similar to those observed during the seasonal study at the CVAO (0.2–0.6 ppb, Read et al., 2012). Use of the upper and lower values collected from Plymouth would change the direction of acetaldehyde transfer across the air–sea interface at L4 during 2011. Using lower atmospheric values of 0.1 ppb we predict surface super-saturation (298 ($\pm$236) %), hence surface waters, as expected, would be a predominant source of acetaldehyde to the atmosphere. Use of higher air values (0.4 ppb) leads to 85% of the time being under-saturated (70 $\pm$ 55%). Therefore we suggest that at times, L4 may also act as a sink for acetaldehyde.

Next we assess the importance of the atmosphere in the marine cycling of OVOCs using some simple budget calculations. We use our microbial oxidation values measured during this seasonal study. We also estimate the likely flux using the following equation;

$$F = K_t\left(\left(\frac{C_a}{H}\right) - C_w\right)$$

where K_t is the total gas transfer velocity and $1/K_t$ is equal to $1/k_w + 1/Hk_a$ which are the individual transfer velocities through liquid and air respectively (Liss and Slater, 1974). We use the parameterisations of Duce et al. (1991);

$$k_a = \frac{u_{10}}{770 + 45 * MW^{1/3}}$$

and Nightingale et al. (2000) (chosen as the 'average' k_w parameterisation);

$$k_w = \left(0.222 * u_{10}^2 + 0.333 * u_{10}\right)\left(\frac{Sc_w}{Sc_{600}}\right)^{-0.5}$$

for determination of k_a and k_w. The wind speed (u_{10}) at the time of sampling was logged via the autonomous buoy at L4, MW is the molecular weight of the gas, Sc_w is the Schmidt number of the OVOC (ratio of the kinematic viscosity (v) of seawater and the diffusivity, D, (calculated via Johnson (2010)) and corrected for both temperature and salinity) and Sc_{600} is the Schmidt number of CO_2 at 20 °C in freshwater.

For methanol we use C_a values of 0.5 and 5 ppb from March 2012 (range from Yang et al., 2013a) with an average C_w of 57 nM for March 2011. We then calculated the likely flux of atmospheric methanol to seawater and compared this to the loss of methanol via microbial oxidation. We estimate that the air–sea flux of methanol was only 2–20% of the total microbial oxidation. This implies that (i) the atmosphere is not likely to be a dominant source of methanol to L4 surface waters and (ii) that there must be in-situ production of methanol to sustain these loss rates.

Using the same approach we estimate that the flux of acetone from the atmosphere to surface waters is between 3 and 9 times greater than the microbial loss. This is in general agreement with data from Dixon et al. (2014) in the Atlantic Ocean which suggests that the oxidation rate is an order of magnitude lower than the air–sea flux of acetone. This implies that, in contrast to methanol, there may be an unknown sink for acetone that maintains a state of under-saturation in seawater and that the transfer of atmospheric acetone is likely to influence dissolved levels in seawater. Sources of acetone to the atmosphere include terrestrial and biogenic emissions as well as in-situ atmospheric production via the reaction of the hydroxyl radical (OH) with higher organics (eg, propane, monoterpenes, methylbutenol) (Singh et al., 1994; Jacob et al., 2002). The dominant route of OH production is via the photolysis of ozone (O_3) and subsequent reaction with water, therefore levels are enhanced in summer (Jaegle et al., 2001). Thus we can speculate (as we did not measure acetone in the air) that higher levels of acetone may be produced during summer when OH is more abundant. Additionally, acetone emissions from biogenic sources are also reported to be both light and temperature dependent (Seco et al., 2007 and references therein), possibly further enhancing the likely atmospheric acetone signal during summer. However, any seasonal increase to atmospheric

acetone is most likely offset by the lower wind speeds during spring/summer thereby reducing the air–sea flux.

The high acetaldehyde C_a value observed in Plymouth in March 2012 (0.4 ppb from Yang et al., 2013a) creates a state of under-saturation when combined with the average March 2011 C_w data of 22 nM. We estimate that for these conditions, the flux of acetaldehyde from the atmosphere toL4 surface waters is likely to represent 0.03% of the total microbial oxidation. Like methanol, this implies a large in-situ acetaldehyde source is still unidentified in these waters. Use of the low C_a value (0.1 ppb) creates a state of super-saturation and the ocean is then likely to be a source of acetaldehyde to the atmosphere. Thus atmospheric acetaldehyde is unlikely to significantly impact dissolved acetaldehyde levels in surface seawater at L4.

5. Conclusion

This annual study represents the first comprehensive assessment of OVOCs in shelf sea waters and their seasonal variability. We have presented data from station L4, 10 km off the Plymouth coast collected over January 2011–March 2012.

Acetone concentrations were relatively low and varied between 2 and 10 nM in surface waters. A maximum concentration was observed in summer and the lowest values were in autumn. Physical mixing in combination with a near-surface source, probably linked to photochemistry, is likely to control the surface concentrations in shelf waters. Simple budgeting calculations suggest that atmospheric deposition may be a significant source of acetone to surface waters due to slow microbial oxidation (0.001–0.38 nM hr^{-1}). Our correlations with ancillary L4 marine data show that there may be a connection between acetone production and autotrophic nanoeukaryotes but our budget also indicates that there is a substantial unknown sink that is yet to be identified to maintain the observed under-saturation in surface L4 waters.

Our research allows us to draw conclusions on the likely cycling of acetaldehyde in these shelf waters. It was surprising to observe lower acetaldehyde surface concentrations in spring and summer 2011 compared to autumn and winter. Vertical profiles show that acetaldehyde concentration is always elevated at the surface and we present here the highest published value of acetaldehyde in surface waters, at 37 nM. Throughout the annual cycle, and below a depth of 5 m, acetaldehyde concentrations are practically homogenous, despite periods of seasonal stratification. Therefore we can assume that near-surface production occurs with subsequent sub-surface loss via microbial oxidation. A negative correlation with CDOM absorbance suggests that acetaldehyde production may be reliant on a terrestrially dominant CDOM fraction, rather than that which is biologically-mediated. Our storage tests also indicate that there is a non-photochemical source of acetaldehyde and that it is most likely to be biological. We estimate that surface L4 waters are likely to be both a source and a sink of acetaldehyde to the atmosphere. However, even when the surface waters are under-saturated, we have shown that the atmosphere cannot provide enough acetaldehyde to sustain the fast microbial oxidation rates we observed during this study (5–31 nM hr^{-1}).

Methanol concentrations varied between 16 and 78 nM in surface waters, with no clear trend in seasonality. Highest concentrations were typically observed at the surface and vertical mixing rates control concentrations at depths greater than 5 m. Despite highest concentrations at the surface we estimate a consistent under-saturation with respect to the atmosphere at L4. Our simple methanol budget calculation suggests that the likely deposition from the atmosphere cannot sustain the rate of microbial oxidation, ie the dominant methanol sink (1–11 nM hr^{-1}). Therefore we can conclude that there must be an, as yet unidentified, in-situ source of methanol to sustain these loss rates. We see a positive relationship with heterotrophic nanoeukaryotes in these surface shelf waters which may provide a possible explanation. Our methanol measurements in consecutive years also show a significant difference and are evidence that large temporal changes in methanol concentrations are plausible and are likely to be controlled by multiple factors.

We have also shown that for OVOCs, even when in-situ conditions are mimicked and photochemical effects are minimised, storage time may still affect sample integrity although for these OVOCs losses are typically $<$10% per hour and close to the analytical precision. However, such possible losses are important considerations in planning future field studies.

It is clear from our work that the concentrations of OVOCs in seawater are controlled by a combination of both production and consumption mechanisms. Future targeted incubation studies should be a priority in order to determine the rates of those mechanisms in order to inform models and hence improve global budgets.

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