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Oxygenated Hydrocarbons in Coastal Waters

Warren J. de Bruyn, Catherine D. Clark and Lauren Pagel
School of Earth and Environmental Sciences,
Schmid College of Science and Technology,
Chapman University, Orange, California,
USA

1. Introduction

Low molecular weight (LMW) carbonyl compounds (also termed oxygenated hydrocarbons) are produced photochemically from chromophoric dissolved organic matter (CDOM) in natural waters (Kieber and Mopper, 1987; Kieber et al, 1990; de Bruyn et al., 2011). CDOM refers to the optically-active (i.e. light absorbing and hence colored) portion of dissolved organic matter (DOM). DOM is the largest organic carbon reservoir in the ocean (700×10^{15} g C), of comparable size to the atmospheric carbon dioxide (CO_2) pool (Hedges, 2002). Studying the distribution and dynamics of marine DOM is of interest to oceanographers because oceanic DOM is a significant component of the global carbon cycle, in addition to affecting the bioavailability of chemical species through absorption, contributing to the spectral properties of seawater, acting as a water source tracer and a microbial food source (Hedges, 2002). DOM is primarily derived from decaying terrestrial plant matter in fresh and coastal waters, with production in oceanic waters from marine organisms via viral or bacterial lysis, grazing and microbial degradation (Perdue, 1998; McKnight and Aiken, 1998; Hessen and Tranvik, 1998). DOM is a complex macromolecular humic-type material, which has been extensively studied by marine scientists over the last 4 decades using analytical techniques including chromatographic separation, size fractionation, radioisotopes, elemental analyses, mass spectroscopy and nuclear resonance mass spectrometry (Perdue, 1998; Benner, 2002; Sharp, 2002; Whitehead, 2008). Optical techniques like UV-VIS absorption and fluorescence spectroscopy are used to study CDOM, including the identification of components via 3 dimensional excitation-emission matrix spectroscopy (EEMs) and parallel factor analysis (PARAFAC) computational methods (see for example Yamashita et al., 2008).

CDOM absorbs sunlight to produce photo-excited states which undergo a series of primary and secondary reactions in natural waters that produce reactive species like peroxides and singlet oxygen, in addition to low molecular weight carbon-containing compounds (Miller, 1994). These photochemical processes play a significant role in the global carbon cycle through remineralization of dissolved organic carbon (DOC) to carbon dioxide (Bano et al., 1998). As a major energy source for microorganisms, LMW carbonyls also influence CO_2 levels indirectly (Clark et al., 2004). LMW carbonyls in seawater also have the potential to influence atmospheric chemistry via air-sea exchange between surface waters and the atmosphere (Zhou and Mopper, 1990; Jacob et al., 2002). Oxygenated hydrocarbons are

ubiquitous in the atmosphere (Singh et al., 2004) where they react rapidly with OH radicals (Singh et al., 2001) and produce other reactive HO_x radicals, ozone, carbon monoxide, peroxyacetyl nitrate and formaldehyde (see for eg. de Gouw et al., 2005; Dufour et al., 2007; Millet et al., 2010). As an OH sink and an atmospheric HO_x and ozone source, oxygenated hydrocarbons have a direct impact on the oxidative capacity of the atmosphere. Over the last decade there have been a number of attempts to inventory sources and analyze atmospheric budgets of these species (Singh et al., 1995; Singh et al., 2001; Jacob et al., 2002; Millet et al., 2008; Millet et al., 2010; Naik et al., 2010). While these budget calculations have improved over time, large uncertainties remain, with the role of the oceans often the largest uncertainty.

In spite of their potential significance, the database of LMW carbonyl and aldehyde measurements in seawater is extremely small. In Table 1 we show the current database for formaldehyde (CH_3O), acetaldehyde (CH_3COH) and acetone (CH_3COCH_3), the oxygenated hydrocarbons measured in this study. Previous measurements have been conducted in tropical and northern regions of the Atlantic and Pacific Oceans. The most in-depth studies have been those by Kieber and Mopper in the Atlantic Ocean, primarily in and around the southeastern coastal region of the United States (west coast of Florida, Mopper and Stahovec 1986; Biscayne Bay off Florida and Caribbean Sea, Kieber and Mopper 1990; Biscayne Bay, Sargasso Sea and Bahamas, Zhou and Mopper 1997). In general, measured ambient acetone concentrations in seawater range from 3.00 to 40 x 10^{-9} mol. L^{-3} (nM), measured acetaldehyde concentrations range from 1.38 nM to 30 nM and measured formaldehyde concentrations range from 4 to 98 nM. In general concentrations are higher at coastal sites where CDOM levels are higher. Zhou and Mopper (1997) also measured oxygenated hydrocarbon levels in the surface microlayer in the Atlantic Ocean of 54.8 and 15.7 nM for acetone and acetaldehyde respectively significantly higher than bulk levels. More recent studies have found similar levels in the North Atlantic and Pacific Oceans (Table 1).

With a photochemical production mechanism, one would expect to see well defined diel cycles in concentrations of these species if 1) the photochemical source is dominant , 2) the sinks are relatively constant over the course of a day, and 3) the photochemical precursor does not vary significantly over the diel cycle. Takeda et al. (2006) reported higher concentrations of acetaldehyde and formaldehyde in Hiroshima Bay at noon relative to midnight (by a factor of 3), consistent with a photochemically driven process. Stahovec and Mopper (1986) also report data suggesting a photochemical production mechanism, specifically diurnal fluctuations by a factor of 10 from 3 to 30 nM for acetaldehyde, and weaker fluctuations from 15 to 40 nM for formaldehyde. Similarly, Zhou and Mopper (1997) observed well defined diel cycles in acetaldehyde and formaldehyde, with midday maxima in Hatchet Bay, Bahamas. The formaldehyde and acetaldehyde cycles ranged from 15 to 30 nM and 2 to 12 nM respectively. On the other hand, Marindino et al. (2005) did not observe well defined diurnal cycles in acetone in the tropical Atlantic.

We report here ambient concentrations and diel cycling of three LMW oxygen-containing compounds (specifically acetone, acetaldehyde, and formaldehyde) measured in coastal waters of the Pacific Ocean on the southwest coast of the USA. These studies represent the first measurements of ambient concentrations of LMW compounds in this global region (near-shore Pacific waters of the western USA), where coastal waters are predominantly hydrologically linked to brackish tidally flushed salt marsh systems rather than riverine inputs (Clark et al., 2008a) as in the bulk of the prior studies on the east coast of the USA (Table 1).

Region	[CH_3COCH_3]	[CH_3COH]	[CH_3O]	Method	Source
West Tropical Atlantic	4-6	2-30	15-50	HPLC DNPH	Mopper & Stahovec, 1986
West Tropical Atlantic		4-15	10-30	HPLC DNPH	Kieber & Mopper, 1990
West Tropical Atlantic	3.00	1.38	3.88	HPLC DNPH	Zhou & Mopper, 1997
Tropical Atlantic	17.6			PTR-MS	Williams et al. 2004
Tropical Pacific	14.5			APCIMS	Marindino et al., 2005
North Pacific		7-9	31-98	HPLC DNPH	Takeda et al., 2006
North Atlantic	5.5-6.9			PFBHA SPME GC/MS	Hudson et. al. 2007
West NorthPacific	10-40	<2-10		MEM PTR-MS	Kameyama et al., 2010

Table 1. Previous measurements of acetone (CH_3COCH_3), acetaldehyde (CH_3COH) and formaldehyde (CH_3O) in seawater. All concentrations are in nM. Technique abbreviations: Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCIMS); pre-column 2,4-dinitrophenylhydrazine derivitization high performance liquid chromatography (HPLC DNPH) ; Proton Transfer Mass Spectrometry (PTR-MS); membrane proton transfer mass spectrometry (MEM PTR-MS), PFBHA derivitization solid phase micro-extraction gas chromatography mass spectrometry (PFBHA SPME GC/MS).

2. Methods

2.1 Sampling sites and procedures

Most samples were collected at Huntington State Beach (HSB), Orange County, Southern California (33.3833 N 117.5846 W), generally within a 2 h period around solar noon in January and February 2009. Other beaches sampled were Newport Beach (NB 33.3631 N 117.5542 W) and Seal Beach (SB 33.7414 N 118.104 W). This covers a 30 mile stretch of coastline in Orange County. Two Upper Newport Back Bay (UNBB 33.642243 N 117.8867235 W) estuarine source water samples were also included for comparison. The UNBB empties into the ocean at Newport Beach, down-coast from HSB (Jeong et al., 2005). Beach water samples were collected from ankle-deep surf-zone waters on an incoming wave. All samples were vacuum filtered with minimal pressure differential at the lab through glass fiber filters (GF/F; nominal pore size 0.7 μm; Whatman International Ltd) and ambient oxygenated hydrocarbon concentrations measured within 20 min to 2 h of collection. Samples were kept in sealed air-tight amber bottles during transit to the laboratory where they were derivatised and analysed by HPLC

A 28 hour diel study was conducted at Crystal Cove State Beach, Orange County, Southern California (33.574 N 117.840 W) from 8 to 9 July in 2009. Samples were collected every 2 hours and filtered as described above, but the water samples were derivatised in situ at the field site laboratory (see method described below) and extracted onto C18 Sep-Pak cartridges, stored at 4˚C and analyzed at the conclusion of the diel study (within 48 h of collection).

2.2 HPLC analysis

Formaldehyde, acetaldehyde and acetone concentrations were quantified with a pre-column 2,4-dinitrophenylhydrazine (DNPH) derivitization HPLC method (Agilent 1100; Novapak C-18 (4µm) column; UV detection at 370nm; as described by Kieber and Mopper (1990) and Zhou and Mopper (1997)). 20 mg of re-crystallized DNPH (Sigma Aldrich) was dissolved in 15 mL of a solution of concentrated hydrochloric acid (~12M; Pharmco; ACS Reagent grade), deionised water (DI) and acetonitrile (ACN) mixed in a volume ratio of 2:5:1. Any carbonyl contamination in the resultant DNPH solution was removed by 2 successive extractions with carbon tetrachloride (Sigma Aldrich Chromasolv for HPLC; 99.9%) just prior to use.

To derivatize natural water samples, 200 µL x 10^{-6} of DNPH solution was added to a 20 mL water sample in a 22 mL Teflon vial and the reaction allowed to proceed for 60 min before extraction and pre-concentration on C18 Sep-Pak cartridges (Supelco). Prior to use, cartridges were cleaned with ACN and distilled water. The derivatized sample was passed through the conditioned extraction cartridge at a flow rate of 10-15 mL min^{-1}. Excess reagent was washed off the cartridge with 25 mL of a 17% ACN (v/v) aqueous solution followed by 5 mL of DI. Carbonyl hydrazones were eluted from the cartridge with 1 mL ACN into Teflon vials.

Prior to HPLC analysis, extracts were reduced to dryness with a stream of carbonyl free nitrogen gas at room temperature and re-dissolved in 2 mL of a 10% ACN (v/v) solution in DI for a 10-fold enrichment. 2 mL of the enriched sample was injected directly onto the Novapak C-18 column (Waters). Carbonyl hydrazones were eluted using a two-solvent gradient: solvent A was 10% ACN (v/v) solution in DI adjusted to a pH of 2.6 with 10 N sulfuric acid (Sigma Aldrich); solvent B was 100% ACN. The gradient was: isocratic at 35% B for 2 min; 35% to 53% B in 4 min; isocratic at 40% B for 8 min; 40% to 80% B in 10 min; and isocratic at 100% B for 15 min. Column flow rate was 1.5 mL min^{-1}; column temperature was controlled at 25˚C.

Derivitization steps were carried out in a fume hood in a solvent-free laboratory to prevent potential contamination. A reagent blank was obtained as per Kieber and Mopper (1990) by injecting un-derivitized reagent directly i.e. the solution was treated exactly the same but the derivitization time was zero. No reagent blanks were observed for acetaldehyde and acetone. Formaldehyde had a reagent blank of 9 ± 4 nM. Based on triplicate measurements of each sample, the average precision for formaldehyde, acetaldehyde and acetone was 15, 9, and 10% respectively. Detection limits were estimated to be approximately 2, 0.5 and 0.5 nM for formaldehyde, acetaldehyde and acetone respectively.

2.3 Absorbance measurements

The absorbance of natural water samples is frequently used as a proxy for the level of CDOM (for example Green and Blough, 1994; Seritti et al., 1998; Gallegos et al., 2004), with higher absorbance corresponding to waters with higher concentrations of CDOM and organic carbon (Moran et al., 2000; Stedmon and Markager, 2003; Kowalcuk et al., 2010). Absorbance spectra were measured with a diode-array UV-visible spectrometer (Agilent Technologies 8453) from 200-700 nm in a quartz sample cell (path length = 10 cm) with a deionized water blank. Absorbance was transformed to absorption coefficient (a, in m^{-1}) by multiplying the measured absorbance at 300 nm by 2.303 and dividing by the path length in m (Hu et al. 2002). The absorption coefficient at 300 nm is commonly reported for CDOM studies for inter-comparisons (Miller 1998).

3. Results and discussion

3.1 Ambient concentrations

Seawater formaldehyde levels ranged from 7.5 to 88 nM with an average of 27 ± 25 nM. Acetaldehyde and acetone levels ranged from 2.7 to 19.9 nM and 2.7 to 12.5 nM respectively, with average levels in seawater of 9 ± 4 nM and 8 ± 2 nM respectively. Measured seawater levels for all compounds were not significantly different from the source water levels in the estuary. Overall, the ambient levels measured here in the Pacific waters of the Southwestern USA (Table 2) are consistent with the limited database of measurements in the literature for Atlantic and Pacific waters (Table 1).

Location	Date	Time	[CH_3O]	[CH_3COH]	[CH_3COCH_3]
Wetlands					
UNBB	01/16	11:00	42 ± 3	11.5 ± 0.9	12.5 ± 0.3
	02/15	11:00	10.3 ± 0.3	10.4 ± 0.2	7.5 ± 0.6
Beaches					
SB	02/10	11:00	57 ± 1	11.7 ± 0.7	6.7 ± 0.3
NB	02/11	11:00	15 ± 1	7.2 ± 0.5	12.5 ± 0.5
HSB	01/20	11:00	23 ± 13	2.7 ± 0.9	2.7 ± 1.8
	01/21	11:00	88 ± 11	9.0 ± 1.0	8.4 ± 0.6
	01/26	17:00	10 ± 1	7.2 ± 0.5	7.3 ± 0.3
	01/27	07:00	13 ± 5	9.4 ± 1.7	9.4 ± 0.6
	01/30	13:00	14 ± 1	8.1 ± 0.7	7.9 ± 0.1
	02/01	15:00	6.5 ± 0.3	7.1 ± 0.1	9.4 ± 0.1
	02/02	19:00	25 ± 1	7.5 ± 0.3	7.5 ± 0.5
	02/04	09:00	32 ± 1	19.9 ± 0.8	6.9 ± 0.3
	02/08	11:00	7.5 ± 0.8	7.4 ± 0.95	7.3 ± 0.9
Average			27 ± 25	9 ± 4	8 ± 2

Table 2. Ambient concentrations (in nM) of formaldehyde, acetaldehyde and acetone in water samples from Upper Newport Back Bay (UNBB), Seal Beach (SB), Newport Beach (NB) and Huntington State Beach (HSB) in Orange County, Southern California, USA, 2009. Concentrations are the mean of 3 measurements ± 1σ. Average values do not include the wetland samples.

In general, oxygenated hydrocarbon levels reported in the literature decrease from the coast into the open ocean as CDOM levels decrease based on decreasing absorption coefficients. Levels are also higher in the surface microlayer compared to underlying waters. The acetone levels of 8 ± 2 nM measured in this study are lower than the 30 nM reported in one coastal study in a coastal zone with significant fresh water inputs and high CDOM levels (Zhou and Mopper, 1997), and on the lower end of the range of previous ocean studies in environments with low CDOM levels. For example, Zhou and Mopper (1997) reported bulk open ocean concentrations of 3 nM , whereas Williams et al. (2004) reported open ocean acetone levels of 17 nM for the tropical Atlantic and Marindino et al. (2005) reported levels of 3-60 and 2-18 nM for the tropical and northern Pacific oceans respectively. The database of formaldehyde and acetaldehyde measurements in seawater for comparison purposes is more limited. Zhou and Mopper (1997) reported open ocean formaldehyde and acetaldehyde levels of 4

and 3 nM respectively with higher coastal levels of 15-42 nM for formaldehyde and 1-12 nM for acetaldehyde in the Atlantic. Their coastal values are consistent with the average values of 27 ± 25 nM for formaldehyde and 9 ± 4 nM for acetaldehyde we obtained in this study for coastal Pacific waters.

Although the ambient levels we measured in our study are within the range of coastal levels in the literature, it is important to note a key difference. Namely, coastal waters in this semi-arid region are dominated by inputs from tidal flushing of salt marshes for much of the year in the absence of limited and seasonal rain events (Clark et al., 2008) i.e. this is a coastal environment with low CDOM levels. Previous coastal studies focused on humic-rich coastal environments with significant freshwater riverine inputs and consequently high concentrations of CDOM. For example, Kieber et al. (1990) measured LMW concentrations for natural waters ranging from 10 to 20 m^{-1} in absorption coefficient (used as a proxy for the amount of CDOM). These absorption values are 10 to 50 times greater than the values of 0.27 to 2.4 m^{-1} we measured for these coastal waters on the Southwest coast of the USA. Given the much lower values for absorption coefficients and hence CDOM levels in our study, the similarity in ambient concentration levels suggests that there must be significant differences in production efficiencies and/or loss processes from salt-marsh derived CDOM in this study vs. the riverine CDOM in prior studies. Our previous laboratory-based study (de Bruyn et al., 2011) showed that the apparent quantum yields (i.e. efficiencies) of photochemical production for the 3 LMW carbonyls discussed here increased by an order of magnitude in going from wetland to near-shore coastal waters. These changes correlated linearly with spectral slopes, one optical measure of the aging of CDOM (Tardowski and Donaghay, 2002; Tzortziou et al., 2007; Helms et al. 2008).

3.2 Diel study

Results from the 28 hour diel study at Crystal Cove State Beach are shown in Figure 1. Relatively small concentration ranges were observed for acetone and acetaldehyde, from 6.6 to 8.5 nM for acetone and 2.0 to 10.6 nM for acetaldehyde with average levels for acetone and acetaldehyde of 5.5 ± 2 nM and 7.5 ± 0.5 nM respectively.

Both the range and average concentrations are consistent with the levels measured at the other beach sites earlier in the year (Table 1). However, formaldehyde levels exhibited a wider range of concentrations from 27.2 to 98.6 nM, with an average of 47.2 ± 25 nM which was higher than the average concentration measured at the other beach sites. Diel cycles consistent with a photochemically driven process have been previously observed for oxygenated hydrocarbons in bulk open seawaters (Zhou and Mopper, 1997) and Florida coastal waters (Mopper and Stahovec, 1986).

We observed some evidence for photochemical production of acetone and acetaldehyde, which both showed an increase in levels prior to noon followed by a decrease. For acetone, the midday maximum is the dominant feature; however there are also maxima during the night. For acetaldehyde, the midday maximum is not the dominant feature as there are 2 larger maxima during the evening and night. This contrasts with Mopper and Stahovec (1986) who observed strong diel cycling in acetaldehyde from 2 to 3 nM at night to 20 to 30 nM in early afternoon. For formaldehyde, there is no evidence of a photochemically driven process. Rather the diel cycle is dominated by a maximum of 100 nM (this abbreviation is used throughout rest of paragraph and is defined earlier) in the early morning. Mopper and Stahovec (1986) reported weak diurnal fluctuations in formaldehyde ranging from 15 to 50 nM.

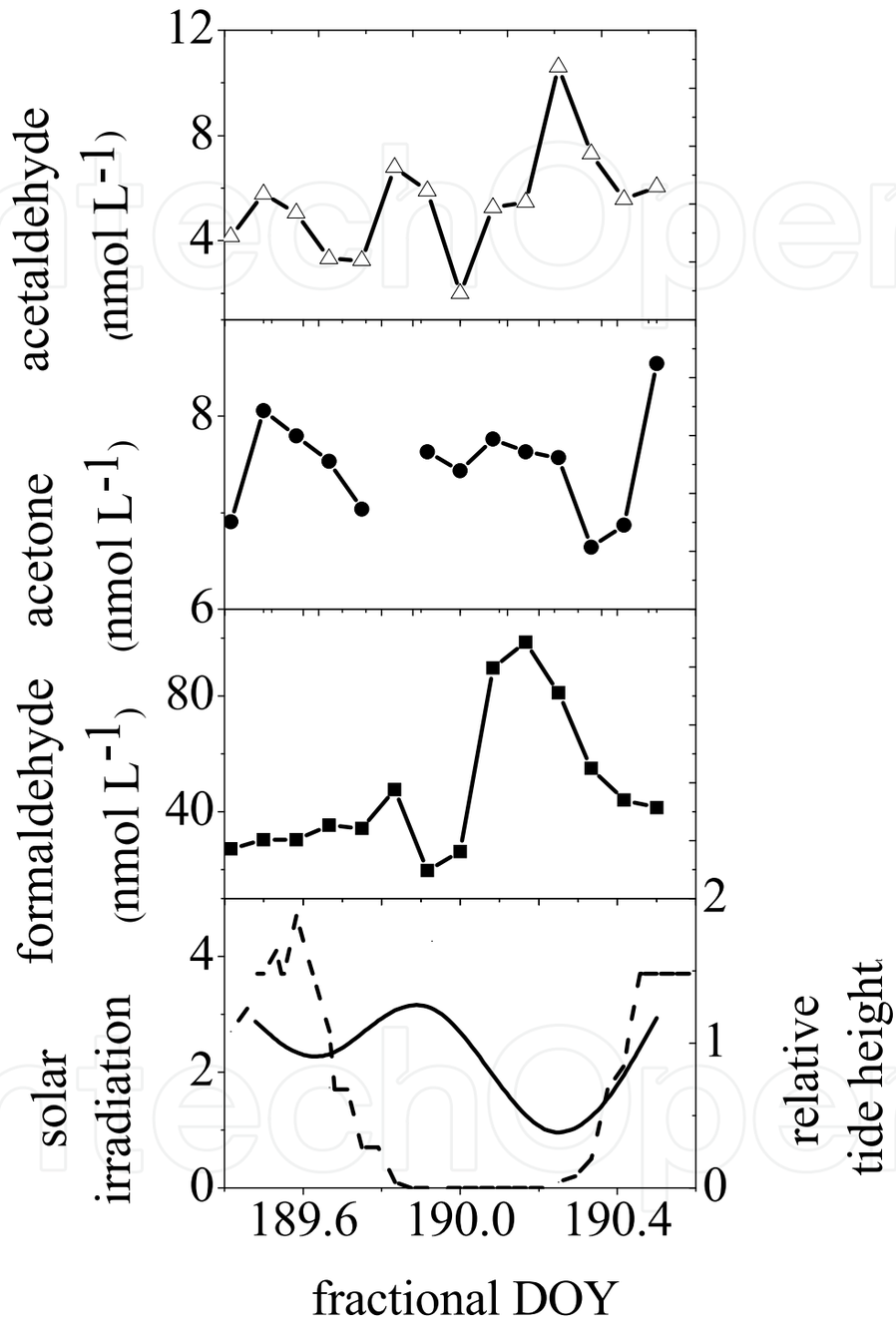


Fig. 1. A diel plot of formaldehyde (■), acetaldehyde (Δ) and acetone (●) concentrations in nmol L^{-1} (nM) as a function of local time (from 10 am 8th July to 2 pm 9th July 2009). Time on the x-axis is shown as fractional day of the year (DOY). The lower panel shows the tidal height (solid line; in m) and solar irradiation levels (dashed line; in W m^{-2}) over the same time period.

The lack of well defined photochemically-driven diel cycles in our study could be due to a combination of multiple factors: 1) additional variability in the photochemical source due to variability in the CDOM levels , 2) variability in the oxygenated hydrocarbon sinks or 3) additional non-photochemical sources.

We will discuss first factor 1, differences in CDOM levels, as a potential cause of the observed weak diel cycles. Absorption coefficient values varied by an order of magnitude over the 28 h period from 0.75 to 7.0 $.m^{-1}$, suggesting that CDOM levels varied by about the same factor during the study. Absorption coefficient variability in the surf-zone showed rapid oscillations on the time-scale of hours during this diel study (see data figures in Clark et al., 2010). This is consistent with an earlier diel study we conducted at a beach up-coast from this study site (Clark et al., 2009), where these dynamic oscillations were attributed to the passage of different parcels of water through long-shore and rip currents (Grant et al., 2005). Hydrogen peroxide (H_2O_2) was measured independently at this site over the same time period (Clark et al., 2010). This is also a photochemical product of sunlight irradiated CDOM in surface waters (Hoigne et al., 1988). By contrast to the LMW carbonyl compounds, H_2O_2 showed a well defined diurnal cycle driven by sunlight in multiple studies at this site (Clark et al., 2010). The rapid cycling in the absorption coefficients (and hence presumably CDOM levels) did not affect the regularity of the diurnal signal observed, suggesting sunlight levels were the dominant factor. The diel correlation observed for hydrogen peroxide (another CDOM photochemical product) suggests that the lack of a well defined diel cycle in oxygenated hydrocarbons observed here is not a result of the variability in CDOM levels i.e. factor 1 is not an issue.

The well-defined peroxide cycle obtained over the same time period also suggests that if we assume that peroxide and oxygenated hydrocarbon sinks are similar (both are believed to be primarily biological or particle driven (Clark et al., 2008b, and references therein)) then the limited diurnal cycle measured here is probably not due to sink variability i.e. factor 2 is not an issue. This leaves factor 3, or additional non-photochemical sources, as an explanation for the lack of well-defined diel cycles observed for the LMW carbonyls.

3.3 Additional sources

Additional non-CDOM sources for production of hydrogen peroxide in coastal waters have been suggested by Clark et al. (2009, 2010). These include photochemical production from metal species in the water and beach sediments, and non-photochemical sources from decaying plant matter in the intertidal zone. The night-time maxima observed here for the LMW carbonyls occurred at or approaching the lowest point of an ebbing tide, consistent with a non-photochemical source of oxygenated hydrocarbons in the intertidal zone. We hypothesize that this is due to senescent plant wrack releasing oxygenated hydrocarbons. Specifically, this is a marine reserve site with significant coverage by giant kelp beds in the near-shore region, which have been re-established by an aggressive reforestration program over the last decade by local environmental organizations (Orange County Coastkeeper; http://www.cacoastkeeper.org/news/kelp!-it-needs-somebody; accessed 6 June 2011). Giant kelp is a fast-growing type of brown algae (Jackson, 1977 and 1987); prior studies have shown a correlation between aldehyde levels and algal blooms and the production of aldehydes from phytoplankton (Pohnert et al., 2002; Sinha et al., 2007), suggesting biological production from kelp may be possible.

To test this hypothesis, experiments were carried out to see if kelp can produce oxygenated hydrocarbons. Fresh kelp collected from the intertidal zone at Crystal Cove State Beach was weighed and 5g immersed in 500 ml of de-ionized water for 3 hours. 20 ml samples were removed every 30 minutes, filtered, derivitized and analysed for acetone, acetaldehyde and formaldehyde. Results are shown in Figure 2. In general, the acetone and acetaldehyde concentrations increased by 8 nM from about 4 nM to 12 nM over 3 hours. Formaldehyde concentrations showed a much larger increase of about 300 nM up to a maximum of 450 nM over the same time period. The acetone and acetaldehyde levels reached after 60 minutes are comparable to the increases observed when the samples were irradiated for one hour with a low power mercury-xenon lamp system (Oriel, 150 W) with a 300 to 400 nm band pass filter (De Bruyn et al., 2011). In contrast, formaldehyde concentration changes were significantly higher than the levels of 240 nM obtained from 3 hours of irradiation.

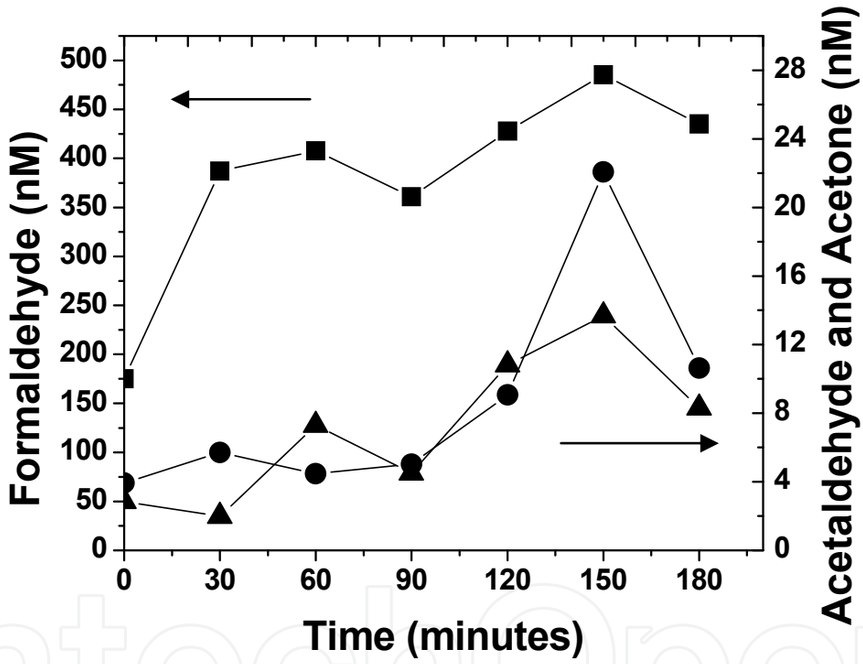


Fig. 2. Aqueous-phase concentrations of formaldehyde (■), acetaldehyde (●), and acetone (▲) in nM as a function of immersion time (minutes) for a senescent kelp sample. Note that the formaldehyde concentration axis on the left hand side covers a concentration range an order of magnitude higher (0 to 525 nM) than that for acetone and acetaldehyde on the right hand side (0 to 30 nM).

While this bench-top experiment is not the real world and does not take into consideration real oceanographic kelp mass to seawater volume ratios, it does suggest that formaldehyde leaching from kelp could be a significant source of oxygenated hydrocarbons in these waters. For formaldehyde, this source could potentially be more significant than the photochemical source.

4. Conclusions and future work

Formaldehyde, acetaldehyde and acetone concentrations were measured at a number of coastal water sites in southern California with low CDOM levels. Seawater formaldehyde levels ranged from 7.5 to 88 x 10^{-9} mol L^{-1} (nM) with an average of 27 ± 25 nM. Acetaldehyde and acetone levels ranged from 2.7 to 19.9 nM and 2.7 to 12.5 nM respectively, with average levels in seawater of 9 ± 4 nM and 8 ± 2 nM respectively. These ranges are consistent with the limited dataset of existing measurements in the literature, and are consistent with levels observed during a 28 hour diel study.

Increased concentrations were observed near solar noon, consistent with photochemical production for acetone and acetaldehyde but well defined diel cycles were not observed, most likely due to other non-photochemical sources of oxygenated hydrocarbons. Preliminary leaching experiments suggest that these compounds, particularly formaldehyde, can be produced in the dark from decaying kelp on the order of or greater than the levels that can be produced photochemically and were measured in these coastal waters. Since kelp beds are distributed globally through temperate and polar coastal regions, these could form significant LMW producers on a regional to global scale. Potentially, other near-shore biological sources like seagrass beds could also contribute to LMW production.

Future studies should focus on production from living kelp beds in situ in the near-shore region and senescent kelp in the intertidal zone, as well as contributions from other plant species. It would also be useful to extend these studies to the previously unstudied Pacific Northeast region, and also to other regions with low rainfall globally where salt marshes dominate inputs of organic matter to coastal waters, as opposed to the previous studies in riverine-dominated waters.

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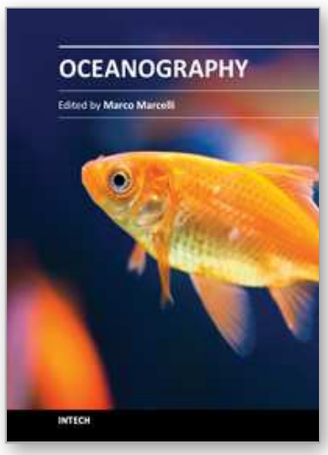
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How inappropriate to call this planet Earth when it is quite clearly Ocean (Arthur C. Clarke). Life has been originated in the oceans, human health and activities depend from the oceans and the world life is modulated by marine and oceanic processes. From the micro-scale, like coastal processes, to macro-scale, the oceans, the seas and the marine life, play the main role to maintain the earth equilibrium, both from a physical and a chemical point of view. Since ancient times, the world's oceans discovery has brought to humanity development and wealth of knowledge, the metaphors of Ulysses and Jason, represent the cultural growth gained through the explorations and discoveries. The modern oceanographic research represents one of the last frontier of the knowledge of our planet, it depends on the oceans exploration and so it is strictly connected to the development of new technologies. Furthermore, other scientific and social disciplines can provide many fundamental inputs to complete the description of the entire ocean ecosystem. Such multidisciplinary approach will lead us to understand the better way to preserve our "Blue Planet": the Earth.

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Phone: +86-21-62489820
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