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The biological degradation of acetaldehyde in coastal seawater

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ABSTRACT

To assess how fast acetaldehyde can be removed in seawater, acetaldehyde loss was measured in filtered and unfiltered seawater collected from Pacific Ocean waters at a coastal site in Orange County, California, USA between January and June 2014. Samples were injected with fully deuterated acetaldehyde, and concentrations measured periodically by purge and trap isotope dilution GC/MS. For unfiltered seawater, measured first-order rate constants ranged from 3.3×10^{-4} min^{-1} to 5.4×10^{-3} min^{-1}, with an average of $2.0 \pm 0.1 \times 10^{-3}$ min^{-1}. This suggests an acetaldehyde turnover in these waters ranging from 185 min to ~3000 min with an average of 500 min. Loss rate constants measured in seawater filtered through 0.2 μm filters (attributed to chemical degradation) were negligible relative to those for unfiltered seawater (attributed to abiotic or biotic particles). First order rate constants in filtered seawater were on average 4 ± 2% of those measured in unfiltered seawater. Unfiltered rate constants increased during regional rainfall events and were positively correlated with aerobic bacterial counts. The correlation was stronger in the wetter first half of the experiment ($R^2 = 0.873$ vs. 0.685). Correlations with bacteria levels and activation/deactivation experiments suggest that the loss in unfiltered seawater samples is driven by biotic particles rather than abiotic particles. Acetaldehyde degradation rate constants are higher than acetone degradation rate constants measured previously at the same site. Comparison with estimated photochemical production rates suggests that these waters are a source of acetaldehyde to the atmosphere.

1. Introduction

Oxygenated hydrocarbons, ubiquitous in the atmosphere, are an atmospheric source of both hydrogen oxide radicals (HO_X) and ozone (O_3) (Singh et al., 1995; Finlayson-Pitts and Pitts, 1999; Naik et al., 2010; Singh et al., 2004; de Gouw et al., 2005; Dufour et al., 2007; Millet et al., 2008; Millet et al., 2010). Reacting rapidly with hydroxyl radicals (OH) in the gas phase, they are also a significant hydroxyl radical sink (Singh et al., 2001; Singh et al., 2004). Oxygenated hydrocarbons therefore have a direct impact on the oxidative capacity of the atmosphere. The role of the oceans in cycling oxygenated hydrocarbons into or out of the atmosphere is believed to be important, and while significant recent progress has been made (Read et al., 2012; Beale et al., 2013; Yang et al., 2014; Beale et al., 2011) in general the oceans remain the largest source of uncertainty in budget calculations (Naik et al., 2010; Millet et al., 2008; Millet et al., 2010).

Acetaldehyde is an atmospheric source of O_3, peroxyacetyl nitrate (PAN) and HO_x (Singh et al., 1995; Millet et al., 2010). It is also classified as a hazardous air pollutant by the Environmental Protection Agency (EPA) (Millet et al., 2010). The primary sink for atmospheric acetaldehyde is reaction with OH radicals (188 Tg/yr; Millet et al., 2010); wet and dry deposition (3 Tg/yr) and direct photolysis (22 Tg/yr) are relatively minor sinks. There have been two recent attempts to inventory acetaldehyde sources and analyze atmospheric budgets in the literature (Singh et al., 2004; Millet et al., 2010). Both agree that atmospheric production via the photodegradation of alkenes, alkanes, isoprene and ethanol, net oceanic emissions and terrestrial plant growth and decay are the primary sources and biomass burning and anthropogenic emissions are minor sources. However, there is significant discrepancy in estimated magnitudes of the atmospheric production and net oceanic emission sources. Singh et al. (2004) suggest that the oceans are the dominant source (125 Tg/yr) while Millet et al. (2010) propose atmospheric production is the dominant source (128 Tg/yr). Singh et al.'s (2004) estimate is based largely on atmospheric measurements as only one or two seawater datasets were available at the time. Millet et al. (2010) attempted to calculate an in situ photochemical production rate from ocean absorbance, used as a proxy for CDOM, and a photochemical production rate measured by Kieber et al. (1990). These efforts are hindered by the limited database of ocean mixed layer acetaldehyde measurements and a limited understanding of the processes that control these levels in seawater. More measurements of ocean mixed layer acetaldehyde levels, production rates and quantum yields, and degradation rates leading to improved

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in situ assessments of the turn-over rate of acetaldehyde would clearly aid budget calculations.

In theory acetaldehyde can be produced in seawater via chemical, photochemical, and/or biological processes. The primary production mechanism is believed to be photochemical (Mopper and Stahovec, 1986; Kieber and Mopper, 1987; Kieber et al., 1990; Zhou and Mopper, 1997; de Bruyn et al., 2011; Beale et al., 2015). Biological production of acetaldehyde in seawater is believed to be negligible relative to photochemical production (Mopper and Stahovec, 1986). There is also no evidence of the chemical production of acetaldehyde in surface seawater in the literature. Similarly it is possible that acetaldehyde can be lost via chemical, photochemical, and/or biological pathways. Chemical and photochemical processes are believed to be minor or negligible and biological pathways are believed to be the primary loss pathway (Beale et al., 2015). Dixon et al. (2013) suggest that microbial oxidation controls acetaldehyde concentrations in the surface waters of the Atlantic Ocean. However, overall there are limited direct measurements of the biological consumption of acetaldehyde in seawater. Mopper and Stahovec (1986) made a single measurement of acetaldehyde degradation in waters off the west coast of Florida. More recently acetaldehyde microbial oxidation rates have been measured in the Atlantic (Dixon et al., 2013) and in shelf waters off the coast of Plymouth (Beale et al., 2015). There have been no measurements in the Pacific Ocean.

In this paper, we report measurements of acetaldehyde degradation in filtered and unfiltered Pacific Ocean waters at a coastal site in Southern California, USA, over a six-month period. The difference between the filtered and unfiltered first order rate constants represents a particle mediated rate constant, which could be a result of either biological processes or loss processes taking place on very small abiotic particles. Additional activation/deactivation experiments and comparisons with bacterial counts suggest that the loss is due to biological degradation pathways, specifically bacterial consumption. The data is compared to the limited database in the literature and to the photochemical production rate estimated from measured absorbance data.

2. Methods

2.1. Site and sample preparation

Water samples (1 L) were collected between January and June 2014 in Pacific Ocean coastal waters at Huntington State Beach (HSB) (33°37′ 32″ N; 117°57′01″ W) at the Santa Anna River mouth (SAR) in Orange County, Southern California, U.S.A. The SAR drains a watershed of approximately 2600 mile^2 in Southern California with the Prado Dam separating upper and lower basins (Izbicki et al., 2004). There are a number of tributaries and different geographic areas within the watershed and water flow is complex and very controlled (Izbicki et al., 2004). During the dry summer months, the dam is open and most of the water flowing in the system is treated wastewater which is fed back into aquifers and reused. During the wet winter months the dam is used to control water flow to the aquifer diverter system. During the summer months very little water reaches the mouth of the river and the river mouth acts as a tidally flushed system, filling on a flood tide and draining on an ebb tide. It is only during rain events in the wet winter months when water flow exceeds the aquifer diverter system that water flows down the river and out the mouth to the Pacific Ocean. Because of the size of the basin and the complexity of the controlled flow there is often a delay in increase in stream gauge flow relative to rainfall if the rain is localized in the watershed above the dam. During the wet months, during storm events flow out the mouth generally increases and with it, bacteria levels, inorganic particles and dissolved organic matter. This is a relatively well studied site (Ahn et al., 2005; Ahn and Grant, 2007; Grant et al., 2001; Boehm et al., 2002) with ongoing long term monitoring (http://ocbeachinfo.com/data) by various state agencies and is relatively representative of Southern California coastal waters.

Water samples were collected weekly for the six-month period, mostly in the morning for logistical reasons. Samples were collected using a 6 ft. Teflon scoop from the shoreline and immediately transported in the dark back to the laboratory in 1 liter brown glass bottles for analysis within 1 h. Samples were not temperature controlled during the 30–45-minute transit. Work carried out by Ahn and Grant (2007) identified three size modes in particles in waters off this site; a dinoflagellate mode centered around 40–50 μm in diameter, an inorganic particle mode associated with storm water runoff with maxima in the size distribution at ~10 μm and <5 μm; and a large biological particle mode (10–100 s μm). A portion of the sample was immediately gravity filtered through a coarse 20–25 μm filter (Double rings; 12.5 cm diameter; 101 Qualitative) to remove large plant debris, zooplankton debris, dinoflagellate particles, and larger inorganic particles leaving fine inorganic particles, bacteria, and some plankton, and analyzed immediately. Periodically a second portion of the water sample (about 200 mL) was also filtered through 0.2 μm membrane filters (Durapore; 3.5 in diameter; Millipore/Sigma Aldrich) twice to remove fine particles, plankton and bacteria and analyzed within 24 h. Relatively light throttled house vacuum (0.3 to 0.5 atm) was used to filter the 0.2 μm sample. The ambient acetaldehyde peak was monitored pre and post filtration to determine if there was any contribution to ambient acetaldehyde due to cell rupture; none was observed. Throughout the manuscript we refer to the first coarse filtered portion as the unfiltered sample and the second 0.2 μm filtered portion as the filtered sample. All glassware was cleaned with ultrapure water (Barnstead Genpure UV Xcad Plus; >18 MΩ cm; <5 ppb TOC). Prior to incubation the syringes were cleaned in hot ultrapure water (~90 °C) to minimize any persistent bacteria carryover.

2.2. Ancillary measurements

The temperature, salinity and pH of the samples were measured in situ with a handheld Hanna Instruments Multiparameter probe (HI9828) designed for environmental water quality measurements. The pH probe was calibrated using three points: pH 4.01 ± 0.01 (Hanna: HI7004); pH 7.01 ± 0.01 (Hanna HI7007); and pH 10.01 ± 0.01 (Hanna HI 7010). The pH probe has a reported accuracy of ±0.02 pH. Conductivity and salinity were calibrated against a 1413 μS/cm standard (HI7031); the reported accuracy of the salinity measurement is ±2% of the reading. The reported accuracy of the temperature measurement is ±0.15%°C. Bacteria levels were estimated using Petrifilm Aerobic Count Plates (ACP; 3 M Corporation). The Petrifilm ACP system is a sample ready culture medium system containing nutrients, gelling agent, and tetrazalium indicator developed for the food industry (Tan et al., 2014) and used more recently in environmental aquatic studies (Harmon et al., 2014). While we refer to these measurements as bacteria counts it is important to realize that this measurement is only a measurement of culturable colonies and clearly underestimates the total population. Bacteria measurements (culturable colony forming units; CU) were made immediately on arrival in the laboratory. One mL of a 1:100 dilution of the sample in artificial seawater (premium seawater aquatic aquarium mix) was plated and incubated at 37 °C for 48 h, after which the number of colony forming units were estimated from a visual examination of the plates. Bacteria counts are reported as colony forming units per ml (CU/ml). The absorbance was also measured immediately on arrival back in the laboratory to assess the optical properties of the colored dissolved organic matter in the sample. Florescence and absorbance spectra were measured with a Horiba Aqualog spectrofluorometer in a 1 cm quartz cell using an ultrapure water blank. The instrument is a CCD based fast response spectrofluoremeter that measures both fluorescence and absorbance spectra simultaneously. Instrument specifications give a wavelength accuracy of ± 1 nm, stray light <1% at 230 nm, and photometric stability < 0.002 AU/h. The instrument uses a reference detector to correct for

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