Spring 5-14-2015

Biological Degradation of Acetaldehyde in Southern California Coastal Waters

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Introduction

Oxygenated hydrocarbons are ubiquitous in the atmosphere with levels ranging from low ppt (acetaldehyde) to low ppb (methanol). As an OH sink and an atmospheric HO_x source, oxygenated hydrocarbons have a direct impact on the oxidative capacity of the atmosphere. The oceans are one of the largest sources of uncertainty in current atmospheric budget estimates of these species. A better understanding of the processes that produce and destroy these species in seawater would improve our understanding of the role of the oceans in cycling these species into or out of the atmosphere. Particle mediated degradation rates of acetaldehyde were measured at a southern california coastal site over a 6 month period.

Experimental Methods

Site and sample preparation Water samples (1 L) were collected between January 2014 and June 2014 in the Santa Anna River mouth (SAR) at Huntington State Beach (HSB) in Orange County, California, USA (33°37'32" N; 117°57'01" W) and immediately transported back to the laboratory for filtering and analysis. Samples were generally collected in the morning because of logistics. In the laboratory, samples were split into two 500 mL aliquots, one of which was filtered to remove particles, plankton, and bacteria through 0.2 um filters (Millipore).

Ancillary measurements . The temperature, salinity, pH, total dissolved solids, dissolved oxygen and oxidation reduction potential of the samples was measured in situ with a handheld Hanna Instruments Multiparameter probe (HI9828). Total aerobic bacteria population was determined using 3M Petrifilm Aerobic count plates. One mL of a 1:100 dilution of the sample was plated and incubated at 37 °C for 48 hours. Optical properties (absorbance and fluorescence) were also measured to characterize the organic content of the sample.

Chemical and particle-mediated degradation measurements Both the filtered and unfiltered seawater samples were spiked with fully deuterated (d-4) acetaldehyde (20-40 nM; Aldrich) and incubated in the dark in headspace-less 150 mL glass syringes in a water bath. Incubations were carried out at the temperature of the seawater measured at the time of sampling. For analyses of acetaldehyde concentration, samples were removed periodically from the syringes and analyzed by purge and trap isotope-dilution GC/MS. The unfiltered sample was analyzed immediately on arrival in the laboratory and the filtered sample within 24 hours of filtering. Acetaldehyde degradation rates were determined from the observed rate of change of acetaldehyde in the syringe.

Analytical methodology Acetaldehyde concentrations were measured by isotope-dilution purge and trap GC/MS. C-13 labeled acetaldehyde was used as the internal standard. A syringe pump was used to inject 3 mL of the sample from the incubation syringe into a glass-fritted sparger. Acetaldehyde was sparged from the sample with He at 100mL min^{-1} for 15 minutes. A cold trap (-30 °C) was used to remove water from the He stream before trapping the acetaldehyde in a glass bead cryotrap immersed in liquid nitrogen. The cold trap minimizes water reaching the liquid nitrogen trap. The trapped gases were thermally desorbed and transferred in He to a GC (Shimadzu, 14A) with a Poroplot Q column and analyzed by quadruple mass spectrometer (HP 5973). A gas loop of a 1 ppm C-13 labeled internal acetaldehyde standard (Apel-Riemer Environmental Inc, Denver, Colorado) is added to the base of the sparger, and concentrations are calculated from the ratio of the deuterated and C-13 labeled acetaldehyde peaks at m/e 48 and 46 respectively.

Results

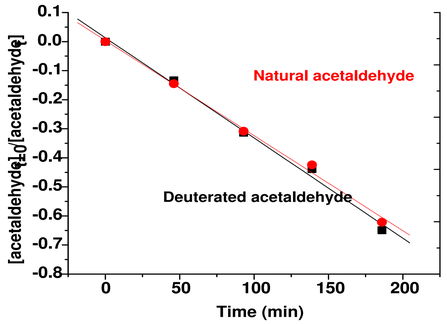

Figure 1. Acetaldehyde degradation followed first order kinetics. First order degradation plots for natural acetaldehyde and d-4 acetaldehyde in an unfiltered seawater sample carried out with a 60nM initial spike of each compound. D-4 degradation was approximately 6% faster than natural acetaldehyde.

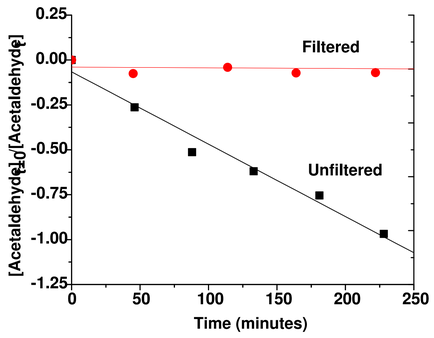

Figure 2. First order plots of the degradation of acetaldehyde for filtered (0.2 µm) and unfiltered seawater. The rate for the filtered sample represents the dark chemical loss rate (in the absence of most particles, biology or photochemistry). Particle-mediated degradation rates can then be determined from the difference between the degradation rates for the filtered and unfiltered samples. All filtered degradation rates were negligible. Unfiltered rates are therefore reported as particle mediate rates.

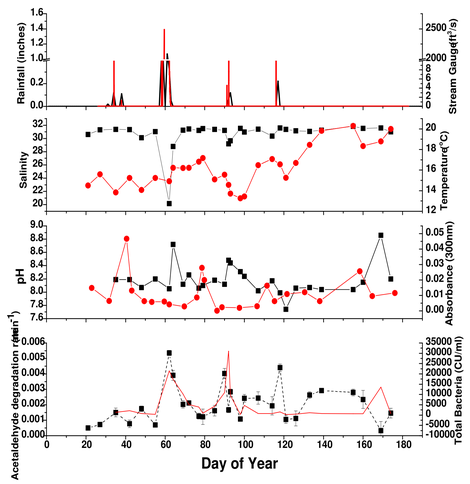

Figure 3. **A**) Rainfall for the region and stream gauge flow for the Santa Ana river during the experiment. **B)** Salinity and temperature. **C)** pH and absorbance (300nm) **D)** Acetaldehyde degradation rates and total aerobic bacteria. Rainfall events are marked by a decrease in salinity and temperature and an increase in bacteria. Acetaldehyde degradation tracks rainfall events and bacteria levels. Left axis is the black points

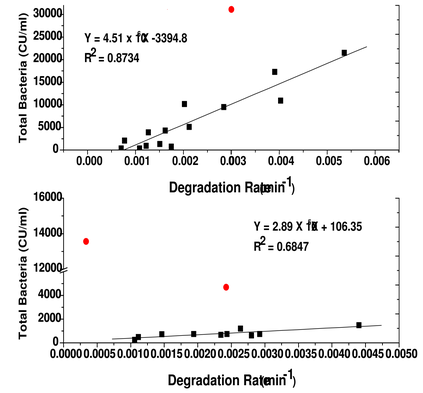

Figure 4. Correlation between total bacteria levels and acetaldehyde degradation rates for A the first half of the experiment (rainy season) and B the second half of the experiment (dry season). The red points have been excluded as outliers. The correlation is better in the rainy season.

Conclusions

- Measured particle mediated acetaldehyde degradation rates are first order.
- Chemical degradation rates are negligible on the timescale of these experiments
- Measured acetaldehyde particle mediated degradation rates track rainfall events at the Santa Ana River mouth.
- Total aerobic bacteria levels also track rainfall events. There is a correlation between total aerobic bacteria levels and measured degradation rate. The correlation is better in the rainy season. While we can't exclude contributions from abiotic particles this suggests that the primary mechanism for acetaldehyde loss is bacterial degradation.

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Acknowledgements

This work was supported by NSF award # OCE 1233091