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Biological Degredation of Acetaldehyde in Southern California Wetlands

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Biological degradation of acetaldehyde in Southern California wetlands

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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. A better understanding of the processes that produce and destroy these species in natural water would improve our understanding of the role that these systems play in cycling these species into or out of the atmosphere. These species can be lost to chemical, photochemical, and partical mediated (abiotic and biotic) processes in natural waters. Chemical loss and photochemical loss are believed to be negligible. Chemical and particle mediated degradation rates of acetaldehyde were measured in a southern california coastal wetland over a 3 month period. Corrolation between partical mediated rates and bacteria levels suggest that loss is primarily due to bacterial consumption. It was hypothesized that the bacteria present in the wetlands would consume the acetaldehyde in the water.

Experimental Methods

Site and sample preparation: Water samples (1 L) were collected between September 2014 and March 2015 in the San Diego Creek (SDC) at Newport Back Bay (NBB) in Orange County, California, USA (33º39'3.8" N; 117º51'58" W) and immediately transported back to a laboratory at Chapman University for filtering and analysis. All samples were collected in the morning between 8-9am. 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 ºC 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 ºC) 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 Poraplot Q column and analyzed by quadrupole 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

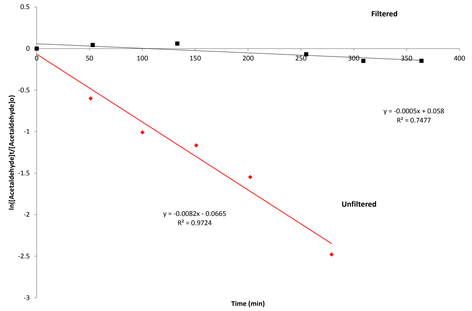

Figure 1. First order plots of the degradation of acetaldehyde for filtered (0.2 µm) and unfiltered water. The rate for the filtered sample represents the dark chemical loss rate (in the absence of most particles, biology or photochemistry). Particle-mediated degradation rates can then be determined 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.

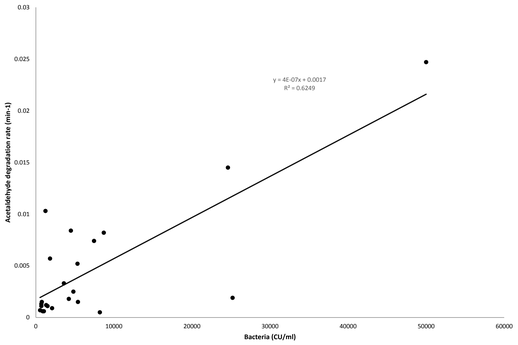

Figure 3. Correlation between total bacteria levels and acetaldehyde degradation rates.

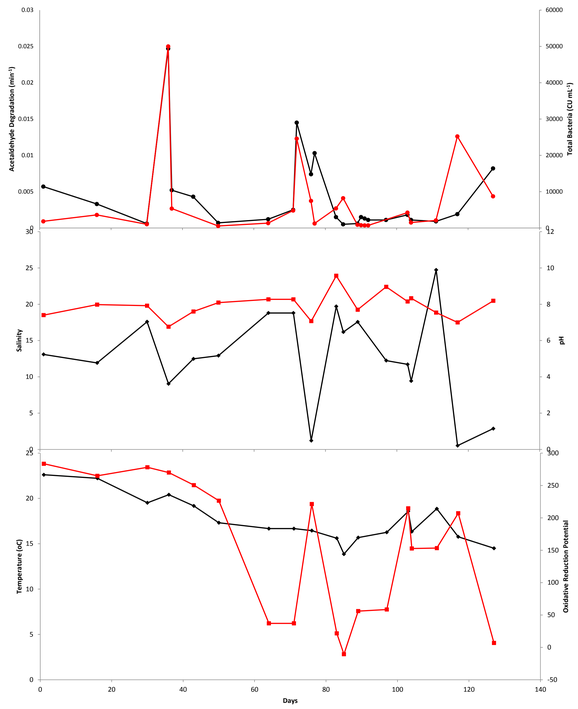

Figure 2. **A**) Rate of acetaldehyde degradation and total bacteria **B)** Salinity and pH. **C)** Temperature and oxidation reduction potential. Rainfall events are marked by a decrease in salinity and temperature and an increase in bacteria. Acetaldehyde degradation tracks rainfall events and bacteria levels. Left axis is the black points.

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 Newport Back Bay.
- Total aerobic bacteria levels also track rainfall events. There is a correlation between total aerobic bacteria levels and measured degradation rate. While we can't exclude contributions from abiotic particles this suggests that the primary mechanism for acetaldehyde loss is bacterial degradation.

Acknowledgements

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