



Diurnal variability of gas phase and surface water ethanol in southeastern North Carolina, USA



R.J. Kieber*, J.P. Powell, L. Foley, R.N. Mead, J.D. Willey, G.B. Avery

Department of Chemistry and Biochemistry, University of North Carolina Wilmington, Wilmington, NC 28403-5932, USA

HIGHLIGHTS

- Gas phase ethanol and acetaldehyde variability driven by temporal influences.
- Aqueous phase ethanol and acetaldehyde also driven by temporal influences.
- Results constrain the importance of photo processes in cycling of analytes.

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ABSTRACT

Diurnal variations in gas phase and surface water concentrations of ethanol and acetaldehyde were investigated at five locations in southeastern North Carolina, USA. There were distinct diurnal oscillations observed in gas phase concentrations with maxima occurring in late afternoon suggesting that photochemical production is an important process in the cycling of these analytes in the troposphere. The rapid decrease in concentrations after the mid day maximum suggests that there is also an atmospheric photochemical sink for both analytes most likely involving photo produced hydroxyl radicals with a half-life on the order of hours rather than days at ground level. Ethanol concentrations in the surface microlayer taken at the same time as gas phase samples had a very similar diurnal profile suggesting photochemical processes, in addition to atmospheric deposition, play a role in the aqueous phase cycling of both analytes. The concentration of ethanol and acetaldehyde increased significantly in flasks containing freshwater collected from the Cape Fear River exposed to simulated sunlight for 6 h underscoring the importance of in situ photochemical production. Results of this study are significant because they represent the first simultaneous analyses of the temporal variability of ethanol and acetaldehyde concentrations in the gas and aqueous phases. These measurements are essential in order to better define the processes involved in the global biogeochemical cycling of ethanol both now and in the future as our use of the biofuel continues to grow.

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1. Introduction

Ethanol is a chemically and biologically labile compound that has received a great deal of attention recently because of its dramatic increase in production and use as a biofuel both in the United States and abroad (Kirstine and Galbally, 2012; Naik et al., 2010). Current estimates indicate that 10% of the United States automotive fuel supply is ethanol with more than 95% of gasoline sold containing added alcohol, most commonly as E10. Enhanced vehicular ethanol emissions may impact a variety of important processes including the oxidizing capacity of atmospheric and surface waters

because of its reactions with $\bullet\text{OH}$ and $\bullet\text{HO}_2$ radicals in solution (Naik et al., 2010 and references therein). Reactions of these oxidants with ethanol have also been linked to increases in ambient levels of acetaldehyde that is a source of peroxyacetyl nitrate (PAN) and ozone (Naik et al., 2010 and references therein). A more recent study suggests that surface waters may act as an important vector for the uptake of ethanol emitted into the atmosphere as a result of increasing biofuel production and usage (Avery et al., 2016). Results of this latter study are significant because they suggest that, in addition to the atmosphere, ethanol may also indirectly impact surface waters that receive added loadings of fuel alcohol.

One of the most important uncertainties relating to the global biogeochemical cycling of ethanol relates to its sources and sinks. This is a particularly important question if we are to put the

* Corresponding author.

E-mail address: Kiebert@uncw.edu (R.J. Kieber).

consequences of increasing usage of biofuel ethanol into perspective. One process that has received virtually no attention is the effect that photochemical reactions have on the fate of ethanol in environmental systems. In the first detailed publication of ethanol concentrations in rainwater, Kieber et al. (2014) observed a great deal of variability in the abundance of ethanol in precipitation driven in large part by temporal influences (Kieber et al., 2014). The authors found that the ratio of ethanol to acetaldehyde was at a minimum during periods of peak solar intensity underscoring the potential importance of alcohol oxidation by a photochemically generated oxidant such as hydroxyl radical (Kieber et al., 2014). In a related study Avery et al. (2016) determined one of the first concentration profiles of ethanol as a function of depth in Onslow Bay off the coast of North Carolina. Concentrations ranged from 81 nM to 334 nM with the highest concentrations observed at the surface, which the authors hypothesized was the result of photochemical processes.

The aim of the current study is to present a detailed examination of the photo processes that influence ethanol distributions in the atmosphere and in surface waters. Specifically, we describe the patterns observed over short-term temporal periods at several different locations and sampling dates. Selected concurrent measurements of acetaldehyde provide important ancillary data that can be used to better understand the cycling of ethanol in both the atmosphere and in surface waters. Comparison of ethanol concentrations in controlled photolysis experiments to field measurements affords additional mechanistic information regarding the role of sunlight on the fate of this biologically and chemically labile alcohol in the environment.

2. Methods

2.1. Collection sites

The majority of samples were collected at locations on the campus of University of North Carolina Wilmington (UNCW) located 8.5 km away from the Atlantic Ocean (34°13.9' N, 77°52.7' W). A freshwater pond located within the Bluethenthal Wildflower Preserve at UNCW was selected due to high dissolved organic carbon (2.7 mM) as a result of large amounts of fresh leaf litter and pine needles. The atmospheric collection site at UNCW is a large open area of approximately 1 ha and is made up of a turkey oak, long leaf pine and wire grass community typical of the inland coastal area of southeastern North Carolina. An additional site used for the photolysis experiments was located in the freshwater end member of the Cape Fear River basin (34°22'20.49"N, 77°53'59.88"W). Air mass back trajectory analysis at 500 m for 72 h was used to indicate the origin of air masses. This 72 h time period is close to the atmospheric residence time of ethanol of 3.6 days reported by Mellouki et al. (2015) and 2.8 days reported by Naik et al. (2010) (Mellouki et al., 2015; Naik et al., 2010).

2.2. Surface and microlayer water collection

Surface water samples (<5 cm) were collected by hand using combusted 1 L amber glass bottles. The surface microlayer was collected using a metal screen sampler which was dipped vertically into the water column until it was completely submerged, then drawn slowly and horizontally from the surface and drained into a 20-mL combusted borosilicate glass vial (Zhou and Mopper, 1997). All vials were capped with minimal headspace. After collection samples were either analyzed immediately or refrigerated in glass vials with minimal headspace at 4 °C and preserved with 70 µL of 100 mg/mL HgCl₂ per 40 mL sample (Kieber et al., 2013).

2.3. Gas phase collection

Gas phase concentrations of ethanol and acetaldehyde were determined using aqueous samples obtained by condensation of water on the outside of test tubes filled with ice (Avery et al., 2016). The condensate collector used in the current study consisted of a polypropylene cylindrical tank (38.5 cm height x 28 cm depth) constructed with six individual collecting positions. Each position contained a glass test tube (30 mm i.d., 35 mm o.d., x 30 cm) filled with ice and placed above a glass funnel leading into a borosilicate glass sampling vial. Condensation was typically collected over the course of 1–2 h. Temperature and relative humidity were measured before and after sample collection using a Kestrel 3000 weather meter. After collection, samples were filtered through a 0.2 µm polyethersulfone membrane using a Pyrex filtration apparatus and either analyzed immediately or refrigerated in glass vials with minimal headspace at 4 °C for a maximum time of 24 h.

The collection and analysis of atmospheric condensate was chosen primarily because of its simplicity compared to more conventional gas phase analyses which tend to be more cumbersome and fragile during field use and because no power is required allowing for much greater flexibility in sampler placement. Condensate collection is especially useful for comparing temporal differences over relatively small scales as in this study. Earlier studies have demonstrated no statistical difference between a more commonly used stripping coil method and the atmospheric condensate method for the determination of gas phase hydrogen peroxide (Deforest et al., 1997). The method has also been used to illustrate the impact of automobile exhaust on gas phase organic acid behavior at this location (Willey and Wilson, 1993) and in the study of diurnal and seasonal variations in atmospheric hydrogen peroxide concentrations at the Bermuda Atlantic Time Series Station (Kieber et al., 2001) as well as for gas phase ethanol (Avery et al., 2016).

2.4. Laboratory photochemical experiments

Controlled photolysis experiments were performed on unfiltered freshwater (salinity = 0) from the Cape Fear River (34°22'20.49"N, 77°53'59.88"W) following procedures described elsewhere (Kieber et al., 2012). River water was added to ten 10-cm long spectrophotometric quartz cells and placed in a carousel ensuring the flat, quartz end of the cells faced upwards. The carousel was placed into a thermostat controlled water bath maintained at 23 °C ± 1 °C. The carousel in which the cells were being held upright was rotated 90° every 2 h to ensure equal irradiation over the course of the irradiation experiment. Quartz cells were removed at the indicated time points and prepared for ethanol and acetaldehyde determination. Samples were irradiated using a solar simulator (Spectral Energy solar simulator LH lamp housing with a 1000 W Xe arc lamp) equipped with a sun lens diffuser and an AM1 filter to remove wavelengths not found in the solar spectrum. Light measurements at individual cell locations were made with an Ocean Optics SD2000 spectrophotometer connected to a fiber optic cable terminated with a CC-UV cosine collector. The system was calibrated with a NIST traceable tungsten lamp and data were collected with OOIrrad software. The solar simulator irradiance spectrum closely mimics the measured mid-summer solar spectrum at 40 °N latitude.

2.5. Ethanol and acetaldehyde quantification

Acetaldehyde concentrations were determined by derivitization with 2,4-dinitrophenylhydrazine followed by separation and detection by HPLC (Kieber and Mopper, 1990). Samples and standards

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