



## Variability of ethanol and acetaldehyde concentrations in rainwater



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### HIGHLIGHTS

- Average concentration of ethanol and acetaldehyde in rain are 192 nM and 193 nM.
- Ethanol and acetaldehyde variability driven by temporal and air mass back trajectory.
- Ethanol results represent baseline for concentrations in North American rainwater.

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### ABSTRACT

Ethanol and acetaldehyde concentrations were measured in 52 rain events collected between January 25, 2011 and March 4, 2012 in Wilmington, North Carolina, USA. Ethanol concentrations ranged from 23 nM to 908 nM with a volume weighted average concentration of  $192 \pm 20$  nM while acetaldehyde ranged from 23 nM to 909 nM with a volume weighted average concentration of  $193 \pm 25$  nM. There was a great deal of variability in the abundance of ethanol and acetaldehyde between rain events driven primarily by temporal and air mass back trajectory influences. The ratio of ethanol to acetaldehyde was at a minimum during periods of peak solar intensity underscoring the importance of alcohol oxidation by a photochemically generated oxidant such as hydroxyl radical in the gas and/or aqueous phase. Ethanol and acetaldehyde concentrations were not strongly correlated with rain amount suggesting that gas-phase concentrations were not significantly depleted during the storm or that they were resupplied during the course of the rain event. The concentration of ethanol and acetaldehyde were correlated with nitrate and non-sea salt sulfate suggesting the importance of terrestrial and anthropogenic inputs at this location. Comparison of future ethanol and acetaldehyde concentrations in rainwater to the data presented in this study will help delineate potential consequences of these labile oxygenated volatile organic compounds (OVOCs) on the chemistry of the troposphere as the United States transitions to more ethanol blended fuels. Aqueous phase impacts of increasing ethanol concentrations will be particularly significant to the oxidizing capacity of atmospheric waters because of its reactivity with  $\cdot\text{OH}$  and  $\cdot\text{HO}_2$  radicals in solution. Increased rainwater concentrations could also have significant ramifications on receiving watersheds because of the biogeochemical lability of the alcohol.

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### 1. Introduction

Ethanol is a chemically and biologically labile compound that has received a great deal of attention recently (Kirstine and Galbally, 2012; Naik et al., 2010) because of its dramatic increase in production and use as a biofuel both in the United States and abroad (de Gouw et al., 2012; Millet et al., 2012). Current estimates indicate that 10% of the United States gasoline supply is ethanol with more than 95% of gasoline sold containing added ethanol most commonly as E10 (de Gouw et al., 2012). The use of ethanol as a fuel will most likely increase significantly with the recent approval of

E15 gasoline in light duty vehicles model year 2001 and newer by the United States Environmental Protection Agency (EPA). This upsurge in biofuel usage has significant ramifications because emission studies of vehicles utilizing ethanol-blended fuels demonstrate that significant quantities of ethanol are emitted uncombusted from tailpipes and that fuels with higher ethanol content emit higher levels of the alcohol (Pouloupoulos et al., 2001). Enhanced vehicular ethanol emissions may impact a variety of important atmospheric processes including the oxidizing capacity of atmospheric waters because of its reactions with  $\cdot\text{OH}$  and  $\cdot\text{HO}_2$  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 (Millet et al., 2012) that is a source of peroxyacetyl nitrate (PAN) and ozone (Naik et al., 2010 and references therein). Another potential unforeseen consequence

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to the increasing usage of ethanol is that it may play an important role in secondary aerosol formation (Blando and Turpin, 2000).

Despite its documented reactivity in the troposphere, virtually nothing is known regarding the abundance of ethanol in atmospheric waters. Studies of ethanol concentrations in precipitation have been limited primarily by the inadequacy of existing analytical methods. Low molecular weight saturated straight chain alcohols (C1–C4) are difficult to quantify in aqueous environmental matrices because they are in very low concentrations, structurally similar to water, have poor molar absorptivities and are hard to derivatize for spectroscopic analysis. One limited study at Creteil University 15 km from Paris, France reported <1–5  $\mu\text{M}$  ethanol measured in 7 discrete rain events by direct injection (Monod et al., 2003). The high analytical detection limit reported (1  $\mu\text{M}$ ) suggests that the data are useful primarily in comparison to highly urbanized locations but are not of adequate sensitivity to aid in the interpretation of ethanol biogeochemical cycling in precipitation collected from less urbanized locations where ethanol is produced and consumed. This study also lacked sufficient sampling frequency to allow for more detailed analysis of temporal or air mass back trajectory influences on ethanol concentrations.

The overarching goal of the research presented here is to describe in detail the processes that influence and control ethanol distributions in rainwater. Specifically we define the ranges and patterns of variation in the abundance of rainwater ethanol including such factors as the influence of season and air mass back trajectory on concentrations. We also describe patterns of correlation between ethanol and other rainwater components such as dissolved organic carbon (DOC) and inorganic ions. The manuscript contains concurrent measurements of acetaldehyde which provide important mechanistic information regarding the cycling of ethanol in precipitation.

## 2. Experimental

### 2.1. Sample collection

Wilmington rainwater samples were collected on an event basis on the campus of the University of North Carolina at Wilmington (UNCW) from January 2011 to March 2012. The 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. This area is typical of the inland coastal area of southeastern North Carolina. The site (34°13.9' N, 77°52.7' W) is approximately 8.5 km from the Atlantic Ocean. Due to the close proximity of the collection site to the laboratory, ethanol analysis or filtration and refrigeration of samples can be done within minutes of collection, which reduces the possibility of compositional changes between the time of collection and analysis. Event rain samples were collected using Aerochem-Metrics (ACM) model 301 automatic sensing wet/dry precipitation collectors containing 4 L Pyrex glass beakers that were pre-cleaned by combusting at 450 °C for 4 h to remove organic impurities. All reported samples were either collected and analyzed or filtered through a 0.2  $\mu\text{m}$  polyestersulphone filter using a Pyrex filtration apparatus and refrigerated in a 7 mL Teflon vials with within an hour after cessation of a rain event. Rainwater concentrations are reported as volume-weighted concentrations with volume-weighted standard deviations (Topol et al., 1985). This is the mathematical equivalent to mixing all rain within a specified time period together and reporting the analytical result for that composite sample.

Precipitation events were categorized using air-mass back-trajectories generated using version 4 of the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPPLIT) developed at the National Oceanic Atmospheric Administration Air Resources Laboratory (Draxler and Rolph, 2003). Trajectories were generated

using a web-based version of the model and calculated for each measured precipitation event collected at UNCW starting at the recorded end of precipitation for a 72 h hind-cast for altitudes of 500 and 1000 m.

### 2.2. Acetaldehyde and ethanol

Acetaldehyde concentrations in rainwater samples were determined by derivatization with 2,4-dinitrophenylhydrazine followed by separation and detection by HPLC (Kieber et al., 1999). Samples and standards reacted with 2,4-dinitrophenylhydrazine for one hour in the dark forming a hydrazone, which was separated from interfering substances by HPLC and quantified by UV detection at 370 nm. Derivatized samples (100  $\mu\text{L}$ ) were injected onto a reversed phase Luna 100 mm  $\times$  4.60 mm 3 $\mu$  C18 Phenomenex column with a 100 Å pore size at 10 °C. The mobile phase was a 1:1 mixture of 0.1% trifluoroacetic acid (TFA) in acetonitrile and 0.1% TFA in DIW at a flow rate of 1.00 mL min<sup>-1</sup>.

Ethanol was determined on a second aliquot by oxidation of the alcohol to acetaldehyde via alcohol oxidase obtained from the yeast *Hansenula sp.* (Kieber et al., 2013). The enzyme was prepared by dissolution of 100 units of alcohol oxidase in 5 mL of 0.1 M potassium phosphate buffer (pH 9.0). The sample (1000  $\mu\text{L}$ ) was combined with 10  $\mu\text{L}$  of buffer, 100  $\mu\text{L}$  of an enzyme working reagent (0.18 units mL<sup>-1</sup>) and allowed to react at 40 °C for 120 min before addition of 10  $\mu\text{L}$  of DNPH. The concentration of ethanol was determined after HPLC analysis by the difference in acetaldehyde concentration in samples with and without added enzyme. This method has a detection limit of 10 nM and a precision of 2% RSD. Accuracy was verified via an intercomparison study of rainwater ethanol concentrations ( $n = 26$ ) utilizing an independent method employing solid phase micro extraction (SPME). Comparison of the resulting rainwater ethanol concentrations produced a trend line with a slope of unity with a 2% deviation between analytical results demonstrating that the methods produced statistically equivalent ethanol concentrations in precipitation samples (Kieber et al., 2013).

### 2.3. Supporting analyses

Hydrogen peroxide was analyzed at the time of sample collection by a fluorescence decay technique involving the peroxidase-mediated oxidation of the fluorophore scopoletin by H<sub>2</sub>O<sub>2</sub> in rain buffered at a pH of 7 with a phosphate buffer (Mullaugh et al., 2011). Organic carbon content in rainwater samples were determined with a Shimadzu TOC 5000 carbon analyzer (Shimadzu, Kyoto, Japan) equipped with an ASI 5000 autosampler (Willey et al., 2000). Inorganic anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) were analyzed using suppressed ion chromatography. A Ross electrode with low ionic strength buffers was used for pH analysis. These supporting data were used to characterize rain events and to evaluate whether the patterns of variation observed for ethanol co-vary with any of these analytes. These supporting data also allow comparison with rain collected elsewhere.

## 3. Results and discussion

Ethanol and acetaldehyde concentrations were measured in 52 rain events collected between January 25, 2011 and March 4, 2012 in Wilmington, North Carolina. Ethanol concentrations ranged from 23 nM to 908 nM with a volume weighted average concentration of 192  $\pm$  20 nM while acetaldehyde ranged from 23 nM to 909 nM with a volume weighted average concentration of 193  $\pm$  25 nM. This sample set represents 34% of the rain events and 59% of the rain volume collected during this time period. Concentrations are reported as volume weighted averages (VWA) in order to decrease

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