



Variability of ethanol concentration in rainwater driven by origin versus season in coastal and inland North Carolina, USA

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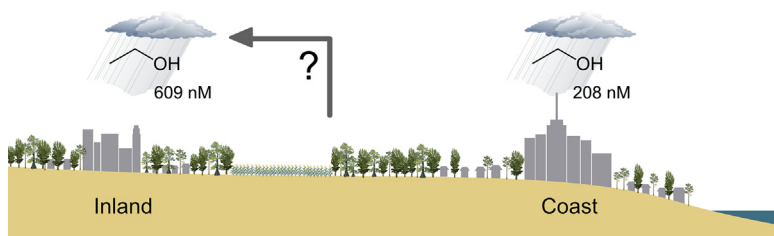
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HIGHLIGHTS

- Drivers of variable ethanol concentrations in rainwater was explored in two sites.
- Storm origin – terrestrial vs. marine was a major control in the coastal site.
- Seasonality by biogenic emission or photooxidation was found in the inland site.
- Rapid supply of locally emitted ethanol to rainwater was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

Rainwater ethanol concentrations were measured for one year (June 2013–May 2014) in central (Elon, NC) and coastal (Wilmington, NC) North Carolina, allowing for a comparison of the effects of coastal and marine rain on ethanol concentration and deposition both at the coast and 250 km inland. Rain samples were collected on an event basis and analyzed using enzyme oxidation and headspace solid-phase microextraction (HS-SPME). The volume-weighted average ethanol concentration at Elon (609 ± 116 nM) was higher than at Wilmington (208 ± 21 nM). Rainfall influenced by air masses originating over the Atlantic Ocean has previously been observed to be lower in ethanol concentration than terrestrial rain at the Wilmington location, and this was true during this study as well. Lower-ethanol marine and coastal air masses did not affect the concentration of ethanol in Elon rain, 250 km from the coast. This is likely due to the rapid supply of locally emitted ethanol to air masses moving over the land. No difference in rainwater ethanol concentrations was observed for Elon rain based on air mass back trajectories, most likely because all the rain was impacted by both anthropogenic and biogenic terrestrial sources typical of most inland areas. Seasonal variation in ethanol concentrations was significant in the inland location with elevated ethanol concentrations observed in fall; no seasonal variation was observed in coastal location rain. This study presents for the first time the different drivers for ethanol concentrations in rainwater from a coastal and a proximal inland location.

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1. Introduction

Ethanol is a chemically and biologically labile compound that has received a great deal of attention recently as a renewable energy source (Naik et al., 2010; Kirstine and Galbally, 2012). Ethanol biofuel production and usage has dramatically increased (24 times since 1985) in the United States and abroad (Renewable Energy Production and Consumption by Source, 2017). 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 10% ethanol in gasoline (E10) (de Gouw et al., 2012). As a consequence of biofuel usage, uncombusted ethanol is emitted through car exhaust to the atmosphere (Poulopoulos et al., 2001). The enhanced evaporative and exhaust emissions from automotive sources and increases in this biofuel usage likely have elevated anthropogenic ethanol emission to the atmosphere (de Gouw et al., 2012). The atmospheric gas phase ethanol concentrations in São Paulo, Brazil, where approximately half the automotive fuel used is ethanol, were 10–100 times higher than in Los Angeles (Colón et al., 2001; Anderson, 2009). The USA and Brazil have increased their production of ethanol by ~3 and ~1.5 times respectively in the last decade (Industry Statistics, 2015).

In addition to the agricultural production of corn and sugarcane to produce ethanol for use as a biofuel, ethanol is also naturally produced by many types of vegetation (MacDonald and Kimmerer, 1993; Fukui and Doskey, 1998; Rottenberger et al., 2008). It is removed primarily through oxidation by the hydroxyl radical to acetaldehyde which in turn increases the concentration of the secondary pollutant peroxyacetyl nitrate (PAN), a component of smog (Naik et al., 2010; Hubbard et al., 2014; Salvo and Geiger, 2014; Suarez-Bertoa et al., 2015). Because of its high water solubility, approximately 10% of atmospheric ethanol is removed by wet deposition (Naik et al., 2010; Kirstine and Galbally, 2012; Felix et al., 2017). The atmospheric residence time of ethanol is approximately 3 days (Naik et al., 2010; Mellouki et al., 2015).

A recent study examined the occurrence and variability of ethanol concentrations in Wilmington, NC, USA rainwater (Kieber et al., 2014). Ethanol concentrations ranged from 23 nM to 908 nM with a volume weighted average concentration of 190 ± 20 nM for rain collected in 2011–2012. The variability in concentration between rain events was driven largely by air mass back trajectory; rain events that originated over land had significantly higher ethanol concentrations than those originating over the Atlantic Ocean. The high ethanol levels in terrestrially derived storms were attributed to a combination of biogenic emissions and vehicular exhaust. The goal of the research presented here is to provide for the first time a comparison of ethanol concentrations in rainwater collected at an inland location (250 km from the NC coast) with that of rainwater collected on the coast in order to determine the relative importance of long range transport as indicated by the air mass back trajectory over three days vs. more localized sources of rainwater ethanol.

2. Methods

2.1. Sample collection, preservation, and storage

Rainwater samples were collected in an open field (Loy Farm) adjacent to the campus of Elon University (36.101 °N, 79.491 °W) in accordance with the National Atmospheric Deposition Program recommendations for collection of wet deposition (Bigelow, 1984) from June 19, 2013 through May 16, 2014. Rain was also collected on the University of North Carolina Wilmington campus (34.227 °N, 77.858 °W) during this period and from 2011 to 2014 for additional comparison with a larger data set. Both studies collected rain on an

event basis using an Aerochem-Metrics model 301 automatic sensing wet/dry precipitation collector containing a 4 L Pyrex glass beaker. All glassware used for rain collection, filtration, storage, and analysis was rinsed with Milli-Q Plus Ultra pure deionized water (resistivity $\geq 18 \text{ M}\Omega \text{ cm}^{-1}$) and then combusted at 450 °C in a muffle furnace for at least 4 h to remove organic contaminants. Rainwater samples were recovered from the collector within an hour after it stopped raining between 8 a.m. and 8 p.m. after each rain event. When it continued to rain through 8:00 p.m., rainwater samples were recovered by 8:30 a.m. next morning. Samples were filtered within minutes under low vacuum through 0.2- μm Gelman Supor polysulfone filters in a glass filtration apparatus. A 40-mL aliquot of the sample was preserved with HgCl_2 (Alfa Aesar, >98%) to a final concentration of 100 mg L^{-1} to eliminate biological activity such as microbial degradation or production of ethanol and stored in the dark at 4 °C in a glass vial with minimal headspace until analysis within 158 days. A previous study demonstrated that the concentration of ethanol in samples preserved with HgCl_2 did not significantly change after 158 days of storage (Kieber et al., 2013).

2.2. Ethanol concentration analysis

Ethanol concentrations were determined by either enzyme oxidation or head-space solid-phase microextraction (HS-SPME). The ethanol concentrations measurements by these two analytical methods produce statistically equivalent results (Kieber et al., 2013). The enzyme method was performed for Wilmington samples. In this method, ethanol is oxidized to acetaldehyde via alcohol oxidase from yeast *Hansenula* sp. (Sigma-Aldrich), then reacted with 2,4-dinitrophenylhydrazine (Sigma-Aldrich) and analyzed by using high-performance liquid chromatography; the ethanol concentration is determined by the difference between initial acetaldehyde and acetaldehyde concentration after oxidation (Kieber et al., 2013). HS-SPME was used for the samples collected in Elon. The HS-SPME method also followed the procedure described in Kieber et al. (2013). Briefly, a 12.0-mL aliquot of a sample was added to a glass vial containing 3.5 g NaCl (MilliporeSigma, ACS grade), 400 μL of a succinic acid buffer (Aldrich, pH 4.5), and a magnetic stir bar. The solution was stirred (750 rpm) until the salt dissolved (~1 min) and then was heated in a water bath to 50 °C with stirring for 10 min. A 75- μm Carboxen/Polydimethylsiloxane fiber (Supelco) fiber was then introduced to the headspace of the sample for 20 min with stirring continued throughout the extraction. The fiber was then thermally desorbed for 1 min in the injection port of gas chromatograph with flame ionization detector (GC-FID; HP 6890). The GC was equipped with an Equity-5 fused silica capillary column (Supelco, 30 m by 0.53 mm i.d., 5 μm film thickness). The oven temperature began at 35 °C and was ramped to 60 °C at $5 \text{ }^\circ\text{C min}^{-1}$ where it was held for 1 min and then increased to 200 °C at a rate of $60 \text{ }^\circ\text{C min}^{-1}$ and then held for 2 min. The FID was operated at a temperature of 250 °C with a hydrogen flow rate of 45 mL min^{-1} and an air flow rate of 400 mL min^{-1} . All samples were run in triplicate, except when limited rainfall did not provide enough volume for triplicate analysis.

2.3. Data compilation and statistical analyses

The volume weighted average concentration of ethanol in rainwater in Elon from June 2013 to May 2014 is published in Felix et al. (2017). Rainwater data for Wilmington were compiled using the same date range as the Elon study to allow direct comparison between the two sites during the same period. Wilmington data were also compiled from January 1, 2011 through December 31, 2014 to have a multi-year data set for comparison. A portion of

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