



Surface waters as a sink and source of atmospheric gas phase ethanol



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HIGHLIGHTS

- Fresh surface waters and estuarine waters are generally a net sink for atmospheric ethanol.
- Coastal waters can be either a sink or source of atmospheric ethanol.
- Ethanol (up to 598 nM) was found in each freshwater, estuarine and coastal sample collected.

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ABSTRACT

This study reports the first ethanol concentrations in fresh and estuarine waters and greatly expands the current data set for coastal ocean waters. Concentrations for 153 individual measurements of 11 freshwater sites ranged from 5 to 598 nM. Concentrations obtained for one estuarine transect ranged from 56 to 77 nM and levels in five coastal ocean depth profiles ranged from 81 to 334 nM. Variability in ethanol concentrations was high and appears to be driven primarily by photochemical and biological processes. 47 gas phase concentrations of ethanol were also obtained during this study to determine the surface water degree of saturation with respect to the atmosphere. Generally fresh and estuarine waters were undersaturated indicating they are not a source and may be a net sink for atmospheric ethanol in this region. Aqueous phase ethanol is likely converted rapidly to acetaldehyde in these aquatic ecosystems creating the undersaturated conditions resulting in this previously unrecognized sink for atmospheric ethanol. Coastal ocean waters may act as either a sink or source of atmospheric ethanol depending on the partial pressure of ethanol in the overlying air mass. Results from this study are significant because they suggest that surface waters may act as an important vector for the uptake of ethanol emitted into the atmosphere including ethanol from biofuel production and usage.

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1. Introduction

The use of ethanol as a fuel source has been increasing during the past decade because it is a renewable energy source and makes a smaller net contribution to atmospheric CO₂ concentrations compared to fossil fuel derived energy (www.afdc.energy.gov). The United States has experienced an exponential rise in the production and consumption of ethanol during the preceding decade with 2014 production of approximately 14 billion gallons annually (www.afdc.energy.gov). In Brazil, approximately 40% of transportation energy comes from ethanol. Emission studies of vehicles

utilizing ethanol blended fuels report significant quantities of ethanol emitted directly from tailpipes with higher emission from fuels with higher ethanol content (Poulopoulos et al., 2001). The surge in ethanol usage and its subsequent release to the atmosphere has significant environmental implications. Atmospheric ethanol impacts air quality and a variety of important atmospheric processes including the oxidizing capacity of the atmosphere because of its reactions with •OH and •HO₂ (Naik et al., 2010). 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 during smog formation events (Naik et al., 2010 and references therein; Millet et al., 2012).

In addition to fuel ethanol sources to the atmosphere, ethanol is also produced and released by natural processes in the environment (Singh et al., 2004). There could also be important natural

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sinks for ethanol such as diffusion into surface waters followed by biological transformation and mineralization (Chartrain and Zeikus, 1986; Wu et al., 1991) and/or abiotic removal (e.g. reaction with $\cdot\text{OH}$). In order to accurately assess the impact of increased fuel ethanol usage on atmospheric processes it is important to understand the relative contribution of these natural and anthropogenic sources and sinks. The relative importance of these sources and sinks has been the focus of recent modeling efforts (Kirstine and Galbally, 2012; Naik et al., 2010); however, ethanol budgets reported in these studies vary widely and contain high uncertainties especially in the magnitude of natural ethanol sources. In a recent assessment of atmospheric ethanol sources, Kirstine and Galbally (2012) concluded that the large uncertainties in global atmospheric ethanol budgets are due to the limited amount of measured fluxes available for modeling. One specific area in which there are very few measured values is surface waters. Kirstine and Galbally (2012) recognized the potential importance of surface waters on atmospheric concentrations but because there are no published values for fresh and estuarine waters and only two oceanic values their impact can only be estimated.

Ethanol concentrations in surface waters have not been determined primarily because of analytical limitations. Our laboratory has developed two different methods for determination of ethanol in aquatic systems at environmentally relevant concentrations (Kieber et al., 2013). Utilizing these new methods, this study reports the first ethanol concentrations for fresh and estuarine surface waters and greatly expands the existing database for coastal ocean waters. The specific goals of the current study were to 1) determine the range of ethanol concentrations in a variety of aquatic systems including freshwater, estuarine and coastal surface waters, and 2) determine their potential impact on atmospheric ethanol concentrations by assessing their relative state of saturation with respect to gas phase ethanol concentrations. Results of this study provide the first insight into the role surface waters play in the biogeochemical cycling of ethanol which is currently not accounted for in atmospheric ethanol budgets.

2. Methods

2.1. Gas phase measurements: condensate collection

Gas phase concentrations of ethanol were determined from aqueous samples obtained by condensation of water on the outside of glass test tubes filled with ice (Farmer and Dawson, 1982, 1984; Deforest et al., 1997). The glass tubes and all glassware used in condensate collection were carefully cleaned by extensive rinsing with deionized water followed by combustion at 450 °C for at least 4 h prior to use. Dawson and Farmer (1984) successfully used condensate collection to obtain gas phase data for water soluble gases including ethanol in Arizona, and Deforest et al. (1997) demonstrated that comparable results were obtained using either condensate collection or stripping coil gas sampling for the water soluble gas hydrogen peroxide at this site. The calculation for the conversion from condensate to gas phase concentration is discussed extensively in Farmer and Dawson (1982). In the current study, the following values were used: diffusion coefficient of water vapor in air at 25 °C $0.282 \text{ cm}^2 \text{ s}^{-1}$ and for ethanol in air at 25 °C $0.110 \text{ cm}^2 \text{ s}^{-1}$, the boundary layers for ethanol and water were assumed to be similar to each other to give a ratio of 1.0, the water vapor density at the glass cylinder surface at 0 °C was $4.84 \times 10^{-6} \text{ g cm}^{-3}$ assuming relative humidity of 100% at the surface where condensation occurs, and the ambient water vapor density was calculated as described in Farmer and Dawson (1982) using the water vapor pressure and relative humidity, pressure and relative humidity with the Ideal Gas Law. The condensate

collector used in the current study consisted of a polypropylene cylindrical tank (38.5 cm height \times 28 cm depth) constructed with six individual collecting positions. Each position contained a glass test tube (30 mm i.d., 35 mm o.d., \times 30 cm) filled with ice and placed above a glass funnel leading into a borosilicate glass sampling vial. Condensation was collected over the course of 1–2 h at ground level. Temperature and relative humidity were measured before and after sample collection using a Kestrel 3000 weather meter. Samples from the six positions in the collector were combined into a single sample. A minimum volume of 6 ml was required for triplicate analyses each requiring a volume of 2 ml. 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. Stability studies showed that ethanol concentrations were stable for at least 72 h in refrigerated filtered samples (Kieber et al., 2013).

2.2. Study sites

2.2.1. Gas phase collection sites

Collection of samples for gas phase ethanol was conducted at a variety of locations in southeastern North Carolina, USA during 2012–2013 (Fig. 1; Table 1) to provide a representative range of gas phase values. Sites were chosen based on their relative amounts and types of vegetation as well as their exposure to automobile traffic. The majority of samples ($n = 40$) were collected at one of three locations on the campus of the University of North Carolina Wilmington (Wilm), Wilmington, NC, USA located 8.5 km away from the Atlantic Ocean. The College Road site (CR) (34.13378, -77.52445) is located next to a highly traveled road, the rain site (RS) (34.13373, -77.52475) is in a secluded area on campus with minimal traffic, and the Bluethenthal Wildflower Preserve location (WFP) (34.13249, -77.52134) is in a heavily wooded area next to a small pond with moderate traffic. The predominant vegetation at these sites is representative of this region and includes the common long leaf pine and turkey oak wire grass communities. Three rural sites were also sampled in the Bladen Lakes region of eastern North Carolina, including Jones Lake (JL) (34.41009, -78.35504), Singleary Lake (SL) (34.35133, -78.27001), and White Lake (WL) (34.38416, -78.30334) which are located about 80 km northwest of Wilmington (Fig. 1). Vegetation surrounding these rural locations also includes turkey oak, long leaf pine and wiregrass as well as red bay and loblolly bay trees and evergreens such as, pond pine and Atlantic white cedar.

Gas phase sampling was also performed on Masonboro Island (34.10260, -77.49114), an uninhabited island located 7.4 km from UNCW (Fig. 1). Three collections were made between 9:30–11:30 AM during June of 2013 when winds were blowing onshore to obtain an estimate of marine air-mass ethanol concentrations.

2.2.2. Surface waters collection sites

Ethanol measurements were conducted during the same time frame as gas phase measurements from a variety of fresh surface waters located in proximity to locations where gas phase samples measurements were performed (Table 2). Samples collected on the campus of UNCW (Fig. 1) included a natural pond (WFP) (34.13249, -77.52134) and manmade retention ponds (FSC) (34.13354, -77.52202), (SRC) (34.13261, -77.52082), (RP) (43.13484, -77.53082), (CM) (34.14428, -77.52199) and a drainage ditch (CDD) (34.13284, -77.52127). Samples were also obtained from the urban location at (GL) as well as three lakes (WL, JL, SL) located in the rural Bladen lakes region described above. White Lake (WL) is a recreational lake surrounded by development and has a large

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