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.

**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.

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 peroxycetyl 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
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 •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; Deforeast 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 coal 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 cm² s⁻¹ and for ethanol in air at 25 °C 0.110 cm² 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 × 10⁻⁶ 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 × 28 cm depth) constructed with six individual collecting positions. Each position contained a glass test tube (30 mm i.d., 35 mm o.d., × 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 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), Single-tary 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 lobolly 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) (34.13484, −77.53088), (CM) (34.14428, −77.52199), and a drainage ditch (CD) (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

amount of boat traffic. JL and SL on the other hand are state parks with essentially no development or boat traffic. Additional samples were obtained from an overflow drainage ditch located adjacent to SL (SLDD) (34.35209, −78.26512). This organic-rich site contains a large amount of fresh leaf litter and pine needles.

Estuarine samples were collected on a cruise conducted on October 22, 2012 aboard the R/V Cape Fear. Salinities of samples collected during this cruise ranged from 10 to 30. Coastal ocean samples were collected during a cruise conducted on January 28–29, 2013 aboard R/V Cape Hatteras. Locations of the estuarine transect and coastal ocean samples can be found in Table 3 and Fig. 1, respectively. Samples were collected using Niskin bottles (General Oceanics) and immediately transferred to pre-combusted glass vials, poisoned with mercuric chloride (to a final concentration of 100 mg HgCl₂ L⁻¹), and sealed with no headspace for transport back to the laboratory.

Table 1
Gas phase ethanol concentrations.

<table>
<thead>
<tr>
<th>Site</th>
<th>n</th>
<th>Min (ppbv)</th>
<th>Max (ppbv)</th>
<th>Av. ± Std. Dev. (ppbv)</th>
<th>Saturation (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MI (Marine)</td>
<td>3</td>
<td>0.06</td>
<td>0.09</td>
<td>0.07 ± 0.02</td>
<td>14 ± 4</td>
</tr>
<tr>
<td>RS (Wilm)</td>
<td>23</td>
<td>0.06</td>
<td>1.25</td>
<td>0.42 ± 0.24</td>
<td>84 ± 48</td>
</tr>
<tr>
<td>CR (Wilm)</td>
<td>6</td>
<td>0.32</td>
<td>1.04</td>
<td>0.79 ± 0.27</td>
<td>158 ± 54</td>
</tr>
<tr>
<td>WFP (Wilm)</td>
<td>8</td>
<td>0.36</td>
<td>1.49</td>
<td>0.72 ± 0.38</td>
<td>144 ± 76</td>
</tr>
<tr>
<td>JL (BL)</td>
<td>2</td>
<td>0.67</td>
<td>0.81</td>
<td>0.74 ± 0.10</td>
<td>148 ± 20</td>
</tr>
<tr>
<td>SL (BL)</td>
<td>3</td>
<td>0.076</td>
<td>1.51</td>
<td>1.15 ± 0.38</td>
<td>230 ± 76</td>
</tr>
<tr>
<td>WL (BL)</td>
<td>2</td>
<td>0.57</td>
<td>3.0</td>
<td>1.8 ± 1.7</td>
<td>360 ± 340</td>
</tr>
</tbody>
</table>

* Saturation concentration is aqueous phase ethanol concentration for saturated solution based on Henry’s Law calculation.

Table 2
Ethanol concentrations in surface freshwater sites. n – number of samples.

<table>
<thead>
<tr>
<th>Site</th>
<th>Location</th>
<th>Type</th>
<th>n</th>
<th>Min (nM)</th>
<th>Max (nM)</th>
<th>Av. ± Std. Dev. (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSC</td>
<td>Wilm pond</td>
<td>29</td>
<td>5</td>
<td>142</td>
<td>55 ± 27</td>
<td></td>
</tr>
<tr>
<td>SRC</td>
<td>Wilm pond</td>
<td>28</td>
<td>5</td>
<td>146</td>
<td>56 ± 29</td>
<td></td>
</tr>
<tr>
<td>WFP</td>
<td>Wilm pond</td>
<td>50</td>
<td>5</td>
<td>598</td>
<td>117 ± 92</td>
<td></td>
</tr>
<tr>
<td>CM</td>
<td>Wilm pond</td>
<td>2</td>
<td>18</td>
<td>105</td>
<td>53 ± 61</td>
<td></td>
</tr>
<tr>
<td>RP</td>
<td>Wilm pond</td>
<td>1</td>
<td>−</td>
<td>−</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>CDD</td>
<td>Wilm pond</td>
<td>31</td>
<td>5</td>
<td>181</td>
<td>56 ± 31</td>
<td></td>
</tr>
<tr>
<td>GFL</td>
<td>Wilm lake</td>
<td>2</td>
<td>14</td>
<td>107</td>
<td>60 ± 66</td>
<td></td>
</tr>
<tr>
<td>WL</td>
<td>BL lake</td>
<td>3</td>
<td>50</td>
<td>64</td>
<td>58 ± 7</td>
<td></td>
</tr>
<tr>
<td>JL</td>
<td>BL lake</td>
<td>2</td>
<td>75</td>
<td>313</td>
<td>194 ± 168</td>
<td></td>
</tr>
<tr>
<td>SL</td>
<td>BL lake</td>
<td>2</td>
<td>62</td>
<td>89</td>
<td>76 ± 20</td>
<td></td>
</tr>
<tr>
<td>SLDD</td>
<td>BL drainage ditch</td>
<td>3</td>
<td>171</td>
<td>512</td>
<td>405 ± 328</td>
<td></td>
</tr>
</tbody>
</table>

* These minimum values were below the detection limit. A value of ½ LOD (5 nM) was used for calculation of averages.
2.3. Ethanol measurements

Ethanol measurements were performed by one of two methods described in Kieber et al. (2013) both of which produce statistically equivalent results. Freshwater samples were determined using the enzyme method whereas samples containing salt were determined using solid phase microextraction (SPME) due to salt interference with the enzyme (Kieber et al., 2013). Ethanol concentrations determined using the enzyme method were determined by high performance liquid chromatography in a two step analysis based on oxidation of the alcohol to acetaldehyde using the enzyme alcohol oxidase acquired from the yeast Hansenula sp. The initial aldehyde concentration is first determined. A second portion of sample is analyzed by oxidizing the ethanol to acetaldehyde. The increase in acetaldehyde after enzymatic conversion yields the ethanol concentration. This method has a detection limit of 10 nM and a precision of <1% RSD. The SPME method utilizes a headspace equilibration technique where aqueous ethanol is first sorbed onto a 75-μm Carboxen/PDMS SPME fiber prior to injection into a GC-FID. This method has a detection limit of 19 nM. Further details of this method can be found in Kieber et al. (2013).

3. Results

3.1. Gas phase ethanol

The majority of samples (n = 40) were collected near aquatic systems on the UNCW campus or in the city of Wilmington, N.C. Additional samples (n = 7) were obtained at one of three rural lakes 70 km inland. A more comprehensive description of these sites can be found in the methods section. Average atmospheric concentrations of the Wilmington, N.C. location ranged from 0.42 to 0.79 ppbv while values obtained in the rural Bladen Lakes region were higher with averages in the 0.74–1.8 ppbv (Table 1). These values are in the range of previously reported values of 0.05–1.9 ppbv (Naik et al., 2010) and references therein. A time series experiment was completed over a 12 h period on September 27, 2012 to determine short-term temporal variations in gas phase ethanol concentrations. The average concentration of samples obtained during this time series was 0.31 ± 0.16 ppbv and the range of gas phase concentrations was 0.09–0.61 ppbv. The high short-term variability was similar to ranges reported above for all data collected in the Wilmington area at different locations and seasons. As a result of the large short-term variations, no significant seasonal or spatial differences in gas phase ethanol concentrations were observed. Gas phase samples were also collected during onshore winds on the beach of Masonboro Island to obtain values for a marine air-mass. Ethanol concentrations were the lowest reported for this study with an average of 0.07 ± 0.02 ppbv and a range of 0.06–0.09 ppbv. These values are very similar to those reported by Naik et al. (2010) for samples collected by aircraft over the South Pacific (0.05 ± 0.03 ppbv) and North Pacific (0.14 ± 0.24).

3.2. Surface water ethanol concentrations

3.2.1. Freshwater sites

During the course of this study 153 individual measurements of ethanol were conducted on fresh surface water samples at locations in close proximity to where gas phase measurements were made (Table 2). Concentrations ranged from 5 to 598 nM and varied widely within individual sites. The relative standard deviations for individual sites where ethanol measurements were performed on more than twenty-five individual occasions were high and ranged from 49 to 78% (Table 2). Diurnal variations in ethanol concentrations performed at individual sites were large generally masking any seasonal or spatial variations (Foley 2013). There were no discernable differences between fresh surface water types.

3.2.2. Estuarine and coastal waters

Ethanol concentrations were determined along an estuarine transect of the Cape Fear River Estuary during October 2012 (Table 3). Concentrations ranged between 56 and 77 nM with lower concentrations observed at higher salinities. Ethanol displayed conservative mixing with salinity within the estuary at the surface but showed addition of ethanol at depth (Fig. 3).

A series of five ethanol concentration depth profiles were also obtained during a single cruise conducted in Onslow Bay off the coast of North Carolina between January 28–29, 2013 (Fig. 2). Concentrations ranged from 81 to 334 nM with the highest concentrations generally observed at the surface with concentrations gradually decreasing with depth. This pattern was not observed at Station 1 where a peak in ethanol was observed at 14 m depth.

4. Discussion

4.1. Ethanol concentrations and variability in surface waters

Ethanol was present in the surface waters of all sites in this study. Surface water concentrations ranged between 5 and 598 nM. The wide range in concentrations at freshwater sites where multiple measurements were made implies ethanol biogeochemical behavior in surface waters is highly dynamic. Beale et al. (2010), the only other study to report ethanol surface water concentrations, suggested that both photochemical and biological production and consumption of ethanol were responsible for the variations they observed in a limited study conducted in North Atlantic seawater. Recent work in our laboratory (Foley 2013) has confirmed these processes operate in freshwater systems as well and cause large daily fluctuations in ethanol concentrations likely resulting in the high variability reported here.

Because of the lack of temporal data for the estuarine and coastal measurements the dynamic behavior of ethanol in these systems cannot be confirmed; however, spatial variations in both in the transect data and depth profiles suggest the same processes operate in these systems as well. For example, the depth profiles obtained for Onslow Bay generally showed higher concentrations at the surface suggesting possible photochemical production or flux in from air whereas one of the profiles had a peak at depth suggesting possible biological production.

Estuarine transect data from the Cape Fear River estuary also indicated both biological and photochemical controls on ethanol
concentrations. Although variations in surface water concentration appear to be simply a mixing of two end members (Fig. 3a), differences in concentrations at the surface and depth provide further insight into possible sources and sinks. Non-conservative mixing of the samples collected at depth suggests addition of ethanol within the estuary (Fig. 3b). The Cape Fear River at these locations is highly light limited due to the elevated concentration of humic substances (Mallin et al., 1998; Shank et al., 2004) therefore the higher concentrations at depth suggest a biological source at depth possibly from the organic-rich sediments underlying the water column. Alcohols such as ethanol can be produced by byproducts of many organic matter remineralization processes in sediments, including aerobic respiration (McKinney and Jeris, 1955), denitrification (Hallin and Pell, 1998), iron reduction (Lovley and Phillips, 1988), sulfate reduction (Biebl and Pfennig, 1977), and methanogenesis (Bryant, 1979). The direction and magnitude of any benthic ethanol fluxes are likely to be highly variable because ethanol participates in multiple degradation pathways (Jin and Roden, 2011) that can co-occur in heterogeneous estuarine and coastal sediments.

A sediment grab sample collected at the lowest salinity site at the same time as overlying water samples were collected had a porewater ethanol concentration of 343 nM. Compared to the ethanol concentrations of the water collected above the sediment at this location (64 nM) a flux from the sediments to the water column is predicted. In contrast, at the higher salinity locations the surface water ethanol concentrations were similar to those measured at depth. At these locations the river water has been diluted and light penetration is much deeper possibly allowing for more photochemical production. Furthermore, sediments at these locations are sandier and contain less organic matter and likely produce less ethanol (Kieber et al., 2006; Southwell et al., 2011). A sediment grab sample at the highest salinity site of this transect had a porewater concentration of only 25 nM which was less than half the water sample collected at depth (56 nM) suggesting no sediment source at this location. These data underscore the importance of both biological and photochemical alterations to ethanol concentrations in surface waters.

4.2. Exchange of atmospheric gas phase ethanol with surface waters

One of the most significant applications of the data presented in this study is to provide the first assessment into the role surface waters play as either a source or sink of atmospheric ethanol. By using the range of atmospheric gas phase concentrations above surface waters ($P_g$) and Henry’s Law constant for ethanol at 25°C ($K_{H} = 200$ mol L$^{-1}$ atm$^{-1}$) the saturation concentration in surface waters can be predicted. This value can then be compared to the actual range of values obtained for the respective surface water types to determine their degree of saturation with respect to the atmosphere. It should be noted that we could not find any Henry’s law constant for ethanol in seawater. Because of the presence of salt this constant should be lower therefore the calculated saturation values presented in this study for estuarine and coastal waters using the Henry’s law constant for fresh water should be considered a maximum value.

The average gas phase ethanol concentrations were used to predict the saturation concentration of ethanol in these systems (Table 1). On the basis of this calculation the saturation concentration in the Wilmington N.C. region would be 84–144 nM. The observed average concentrations for all but one of the freshwater sites in this region (Table 2) fell below or at the lower range of the predicted saturation values (Table 1). A comparison of the estuarine surface water values (56–77 nM) (Fig. 3) collected in the same region also indicated undersaturation with respect to the gas phase. A similar result was obtained in the Bladen Lake region. The measured surface water concentrations (Table 2) also fall at the lower range of the predicted saturation concentrations (Table 1) with the exception of the SLDD site which is supersaturated. This
SLDD site is a leaf litter filled ditch containing mostly plant organic debris and only a shallow depth of surface water. Therefore, this site is not typical of the other sites in this study and may be more representative of wetland communities containing high organic loading. The undersaturation of the freshwater and estuarine sites in this study suggests a consumption of ethanol in these systems that generally outpaces the gas phase diffusive source of ethanol into surface waters from the atmosphere. A likely sink for surface water ethanol is conversion to acetaldehyde and acetic acid. This scenario sets up a situation where inland surface waters may act as an “ethanol pump” resulting in a significant sink for atmospheric ethanol. The most important result of the freshwater saturation comparison is the general conclusion that these systems are not likely a source of ethanol to the atmosphere but are instead a sink or have the capacity to take up any future increases of ethanol in the atmosphere.

For the coastal surface waters saturation calculation, a range of 0.11–1.9 ppbv was assumed for gas phase ethanol concentrations. These values span the range of coastal values reported by Kirstine and Galbally (2012) in their recent review of atmospheric ethanol budgets and are slightly higher to the three values obtained in recent studies. On the basis of this range of gas phase values, expected saturation concentrations for coastal waters should be between 22 and 380 nM; the Masonboro Island values extend the lower end of this range to 12 nM. Surface water values obtained in the current study for Onslow Bay ranged from 81 to 334 nM (Fig. 2) and are similar to the range of values predicted for saturation indicating that these systems can either be a source or sink of ethanol. Although surface water concentrations of the coastal samples were in the range of concentrations observed for freshwater samples, lower offshore gas phase concentrations suggest these systems at times may be a net source of ethanol to the atmosphere. Whether these systems act as a sink or source of atmospheric ethanol probably changes both temporally and spatially and is dependent on the source of the air mass above the surface waters (i.e. continental vs. marine) as well as biological and photochemical process as described above and in Beale et al. (2010).

5. Conclusions

The presence of ethanol in the majority of surface water samples collected during this study suggests that ethanol is a ubiquitous component of aquatic ecosystems. The data presented here greatly expand the previously very limited database for surface water ethanol concentrations and the potential role they play on atmospheric concentrations. Because the range of ethanol concentrations was similar in the wide variety of surface waters determined in this study; this range may be applicable to most aquatic systems, thus allowing their use in future modeling efforts. The most significant finding of this study is that fresh surface waters likely act as a net sink for atmospheric ethanol and are not a source as previously suggested. Coastal ocean surface waters may act as either a sink or a source of atmospheric ethanol depending on the concentration of ethanol in the overlying air mass. With the use of recently published methods for the determination of ethanol, future work should focus on an expansion of surface water measurements to other regions as well as open ocean measurements. Data obtained in the current study as well as future endeavors will help better delineate the fate of both natural and anthropogenic ethanol released into the environment.

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