

## ARTICLE OPEN

## Rapidly increasing ethanol concentrations in rainwater and air

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Rainwater and gas phase ethanol concentrations increased approximately fourfold between 2010 and 2017 in Wilmington, NC, USA. This 8-year study demonstrates that the gas phase and rainwater concentrations of ethanol have risen due to increased production and use of ethanol as a biofuel. Rainwater ethanol concentrations are close to equilibrium with local atmospheric gas phase concentrations and have increased in proportion to increased air concentrations. Ethanol emissions are important because they impact the oxidizing capacity of the atmosphere due to the reactivity of the alcohol towards hydroxyl radical. Gas phase ethanol contributes to air pollution through oxidation to acetaldehyde, with subsequent production of ozone, and in high NO<sub>x</sub> regions production of peroxyacetyl nitrate (PAN). However, combustion of ethanol can also lower emissions of acetaldehyde precursors such as alkenes, suggesting that the potential impact of ethanol combustion is complex. The large increase in the concentration of ethanol in both the gas and condensed phases indicates that existing sinks are not sufficient to remove the excess alcohol being added to the atmosphere from biofuel use. This suggests that the projected growth of ethanol as a biofuel will result in considerable increases in atmospheric concentrations within the next few years with direct ramifications on a host of fundamentally important atmospheric processes.

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## INTRODUCTION

The use of ethanol as a biofuel is increasing because it is a renewable transportation fuel with a potentially lower carbon dioxide atmospheric impact compared to fossil fuels. Ethanol is not completely combusted in automobile engines and hence adds to the oxygenated volatile organic compound atmospheric burden, where it can contribute to smog and ozone formation. Multiple ethanol sources and sinks have been identified, but remain poorly quantified. Because ethanol is highly water soluble, removal by rainwater and dissolution into surface waters are sinks for atmospheric ethanol. Here we show that these and other sinks for atmospheric ethanol are not sufficient to remove the excess ethanol being added to the atmosphere due to increased biofuel use, which has resulted in rapid and dramatic increases of ethanol in both air and rainwater over the last 8 years.

The use of ethanol as a transportation fuel in the USA has doubled in the last decade (<https://www.eia.gov/>, 2017). Combustion of 10% ethanol in gasoline (E10) emits less carbon monoxide<sup>1,2</sup> but usually more NO<sub>x</sub><sup>3</sup> than pure gasoline per km. However, some fuel ethanol is emitted to the atmosphere through evaporation<sup>4</sup> and from tailpipes as uncombusted ethanol by vehicle exhaust.<sup>5,6</sup> The production of ethanol through distillation also releases ethanol to the atmosphere.<sup>7</sup> Ethanol reacts with hydroxyl radical to produce acetaldehyde, which is the primary sink for atmospheric ethanol, thereby potentially contributing to ozone and smog formation including peroxyacetyl nitrate (PAN).<sup>8</sup> However, combustion of ethanol emits lower amounts of acetaldehyde precursors including aromatics and alkenes compared to gasoline,<sup>5</sup> making prediction of impacts less certain.

Because of its high water solubility, atmospheric ethanol can be removed by dissolution into rainwater<sup>9</sup> and surface waters.<sup>10,11</sup>

Although biogenic sources are thought to be the main contributor to ethanol in the global atmosphere,<sup>12,13</sup> de Gouw et al.<sup>14</sup> suggested that more than half the ethanol emitted to the atmosphere in the NE US in 2002 and 2004 and in Los Angeles, CA, USA, in 2010 was direct emissions from anthropogenic activities. Higher gas phase ethanol concentrations in Los Angeles in 2010 compared with the NE US in the earlier years were attributed to greater use of ethanol biofuel. Salvo and Geiger<sup>2</sup> used a unique opportunity in São Paulo Brazil when the price of gasoline dropped relative to ethanol to show that ozone concentrations decreased by 20% when more gasoline (75% vs. 14%) was used during the time of their study (2009–2011).<sup>2</sup> Even though in the UK gasoline contains only 5% ethanol, ethanol is the most abundant volatile organic compound (VOC) in London air.<sup>15</sup> A modeling study of the air quality impacts of the increased use of ethanol under the USA Energy Independence and Security Act<sup>16</sup> predicts a doubling of atmospheric ethanol between 2007 and 2022.

This study presents a unique 8-year data set of rainwater ethanol concentrations collected on an event basis from 2010 through 2017 collected in Wilmington, NC, USA, with comparison to km driven in North Carolina during that time. Gas phase atmospheric ethanol concentrations are also presented for diurnal experiments in July of 2011 and 2016 under similar meteorological conditions. It is imperative to understand processes that affect the concentration of ethanol in the atmosphere in order to make appropriate decisions about the future use of ethanol as a biofuel.

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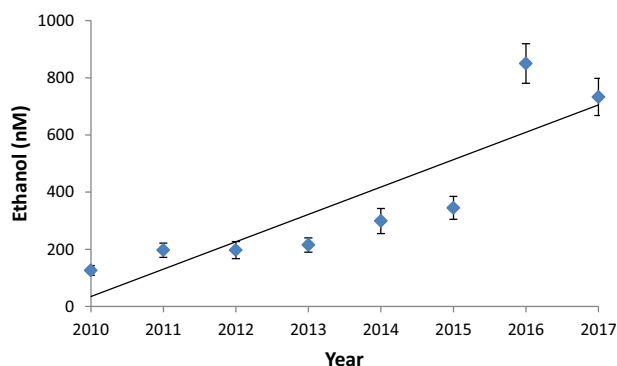
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## RESULTS

### Rainwater concentrations

The concentration of ethanol in rainwater was measured in event rain samples collected on the University of North Carolina Wilmington campus during the summer of 2010 and continuously since January of 2011. The annual volume-weighted average concentrations increased slightly from 2010 through 2013, then more extensively from 2013 through 2015, and then dramatically in 2016 (Fig. 1). The increase from 2010 to 2017 is approximately fourfold. The increasing trend (Mann–Kendall Trend Analysis) is significant (Fig. 1,  $p = 0.043$  for eight volume-weighted averages (VWA),  $p < 0.0001$  for raw data,  $n = 424$  rain samples). This trend is not dependent on the high 2016 concentration because when this point is excluded, the Mann–Kendall trend for  $n = 7$  is significant at  $p = 0.004$ , and the correlation coefficient increased from  $R = 0.8678$  ( $p < 0.01$ ) to  $R = 0.9291$  with  $p < 0.001$ . The 2016 point is not an outlier (Grubbs test,  $p = 0.4$ ); therefore, it has been included in all analyses. This increase cannot be explained by changes in temperature because the annual average temperature ( $18.4 \pm 0.8$  °C) in Wilmington did not vary in a consistent pattern over this time period. Annual rainfall amounts in Wilmington were greater in 2015 and 2016 due to excessive rain from tropical systems in the summer and autumn, and excessive rain from the 2015–2016 El Niño winter events (<https://www.weather.gov/ilm/>, 2017). Extensive flooding occurred in Wilmington and surrounding areas in September and October of 2016 due to the historic amounts of tropical rain received (<https://www.weather.gov/ilm/>, 2017). Four different tropical storms plus Hurricane Matthew delivered significant tropical rain in September and October of 2016, with subsequent flooding. Excessive dilution by the large volume of rain received (11.2 cm from Hurricane Matthew) was not observed during Hurricane Matthew because this rain had a relatively high concentration of 937 nM. Flooding during 2016 likely contributed to the high concentration observed because episodically submerged plants emit large quantities of ethanol to air.<sup>17–19</sup> The highest gas phase ethanol concentration observed in the current study was collected above submerged vegetation during flooding (>15 ppbv vs. background concentration of ethanol on a nearby undeveloped island (Masonboro Island) with marine air mass back trajectory of  $0.12 \pm 0.03$  ppbv<sup>11</sup>).

Much of the increase observed in Fig. 1 may be related to increased use of biofuel ethanol as indicated by the number of km driven by vehicles per year in North Carolina, USA where the field site is located<sup>20</sup> (Fig. 2), because of evaporation<sup>4</sup> and also the release of uncombusted ethanol in vehicle exhaust.<sup>5</sup> The amount of ethanol in gasoline in the USA has also increased from 8% in

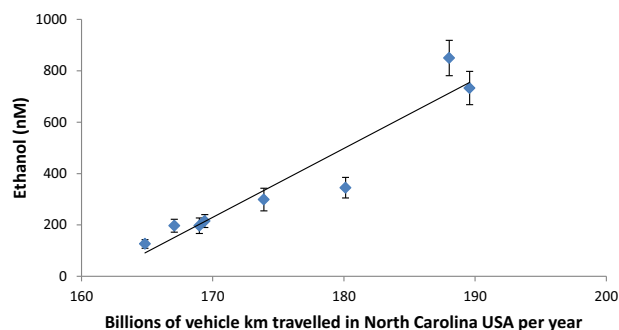


**Fig. 1** Volume-weighted annual average rainwater concentration and standard deviations for ethanol in nM vs. year for rainwater collected in Wilmington, NC, USA. The year 2010 contains summer data only ( $n = 11$ ). The Mann–Kendall Trend Analysis for these data is significant at  $p = 0.043$ ; the regression line shown has  $R = 0.8678$  and  $p < 0.01$  for  $n = 8$

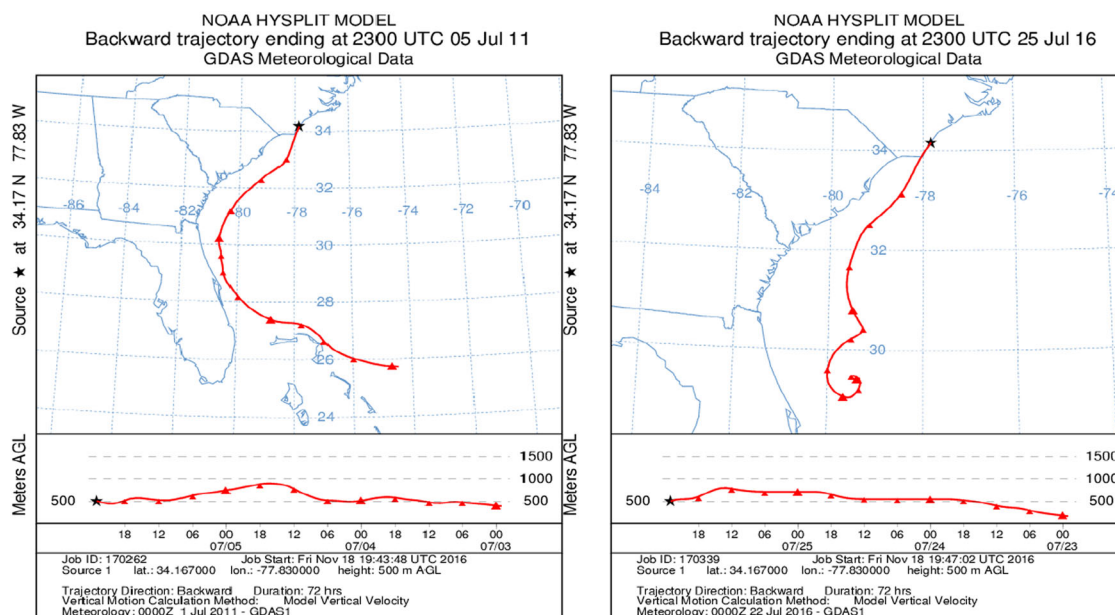
2009 to 10% in 2011 and beyond (<https://www.eia.gov/>, 2017). The Wilmington NC population (117,500 in 2016) increased by 10% from 2010 to 2016 which would also contribute to higher atmospheric ethanol concentrations in this region. However, these small changes cannot explain the magnitude or timing of the increase observed. Furthermore, compound-specific-stable carbon isotope analysis revealed that on average 59% of ethanol in rainwater ( $n = 4$ , [ethanol] >  $1 \mu\text{M}$ ) collected in Wilmington, NC, USA during 2016–2017 was sourced from biofuel ethanol,<sup>21</sup> which suggests that anthropogenic activities are dominating the biogeochemical cycling of ethanol in the southeastern USA. Even though North Carolina is not a large ethanol-producing or -consuming state, the 3-day atmospheric residence time for ethanol<sup>12,22</sup> allows for transport of ethanol from thousands of km away (Fig. 3) so the North Carolina atmosphere is affected by distant activities.

### Atmospheric concentrations

Two extensive gas phase experiments were conducted to complement rainwater measurements in the current study. Previous research at this location revealed high variations in gas phase ethanol concentrations over time periods of hours as a function of time of day;<sup>23</sup> therefore, measurements must be taken over at least a diurnal cycle to compare changes in concentrations over time. Two gas phase studies were conducted 5 years apart, both on the UNCW campus, one on July 5, 2011 and one on July 25, 2016. The air mass back trajectories for these two dates were very similar so air mass back trajectory was not a factor in the observed difference between these two experiments (Fig. 3). The results of these two gas phase studies, each of which included multiple readings over 24 h, suggest gas phase ethanol has increased over the last 5 years, perhaps by as much as fivefold (Table 1), similar to the increase observed in rainwater when comparing 2011 with 2016 concentrations (3.3 fold,  $t$  test,  $p < 0.0001$ ). This increase in atmospheric ethanol occurred over a similar time period (2011–2014, the most recent year for which data are available) when highway vehicle emissions of VOCs in North Carolina decreased by 25%, indicating that ethanol is becoming a larger proportion of total VOCs in this area.<sup>24</sup> De Gouw et al.<sup>14</sup> found a much greater increase (30×) in atmospheric ethanol when comparing atmospheric ethanol concentration in the NE US in 2002 and 2004 with that in Los Angeles in 2010 which they also attribute to greater ethanol biofuel use; the magnitude of the increase observed however probably reflects in part the two different locations used in the study as well as the temporal variability.



**Fig. 2** Volume-weighted annual average rainwater concentration of ethanol in nM with standard deviations for rainwater collected in Wilmington, NC, USA between 2010 and 2017 vs. billions of km driven by vehicles in North Carolina, USA, per year over the same time frame. For the regression line,  $R = 0.9517$ ,  $n = 8$  and  $p < 0.001$



**Fig. 3** Air mass back trajectory analyses (<https://ready.arl.noaa.gov/hypub-bin/trajtype.pl?runtime=archive>, 2017) at 500 m for the 72 h prior to the diurnal experiments shown in Table 1

**Table 1.** Average measured concentrations and standard deviations of ethanol in air over 24 h for the dates shown compared with concentrations calculated from rainwater event sample concentrations using Henry's Law during the month of July in each year in ppbv

	<i>n</i>	Average, ppbv	Method
2011			
July 5 air	12	0.78 ± 0.33	Measured
July rain	7	1.17 ± 0.81	Calculated
2016			
July 25 air	22	3.91 ± 2.58	Measured
July rain	6	5.10 ± 0.57	Calculated

*n* number of samples. Measured and calculated air concentrations are the same for each year (*t* test,  $p > 0.1$ ); however, they are significantly different between 2011 and 2016 (*t* test,  $p < 0.001$ ).

#### Air–rainwater interaction

The partitioning of ethanol between the gas and aqueous phases can be described using Henry's Law for a system at equilibrium as follows:

$$[\text{EtOH}(\text{aq})] = K_{\text{H}} P_{\text{EtOH}}, \quad (1)$$

where brackets indicate aqueous concentration of ethanol in M,  $K_{\text{H}}$  is the Henry's Law constant for ethanol at the relevant temperature in  $\text{M atm}^{-1}$ , and  $P_{\text{EtOH}}$  is the partial pressure of ethanol (atm) in the gas phase in contact with the aqueous phase. In this application, the aqueous phase is rainwater, and the gas phase is air. Using the measured ethanol concentration in rainwater, and the known Henry's Law constant for the temperature of the rain event,<sup>11,25</sup> the equilibrium atmospheric partial pressure of ethanol can be calculated.

The first diurnal experiment was conducted on July 5, 2011, with 12 air samples collected over 24 h. Even though there was substantial diurnal variation driven by photochemical production of ethanol,<sup>23</sup> the 2011 gas phase concentrations were much lower than the concentrations observed during a similar diurnal study on July 25, 2016 with 22 samples collected over 24 h (*t* test,  $p < 0.001$ ). Rainwater concentrations from individual events during

the month of July in each of the two study years were used along with the appropriate Henry's Law Constant for the ambient temperature to calculate air concentrations in equilibrium with these rainwater concentrations. The average calculated air concentrations were the same as the measured air concentrations in each year (Table 1, *t* test,  $p > 0.1$ ), which indicates rainwater is in equilibrium with gas phase ethanol at the collection location at the times of these experiments. The remarkable agreement between the predicted and measured gas phase concentrations are the first field data indicating that rainwater ethanol concentrations are in equilibrium with the gas phase at the time and location where the rain falls, which was assumed by earlier atmospheric models of ethanol cycling.<sup>12,13</sup> Therefore, atmospheric and rainwater ethanol concentrations are coupled in accordance with Henry's Law, and hence both are likely to increase in the near future.

#### DISCUSSION

Air and rainwater ethanol concentrations have increased approximately fourfold between 2010 and 2017 in response to increasing production and use of ethanol as a biofuel, and are likely to increase dramatically in the near future as ethanol biofuel use increases. The observed increase is much greater than the doubling predicted by the year 2022.<sup>16</sup> The atmospheric impacts of this increased ethanol, and the increase in acetaldehyde that accompanies it<sup>5,8,26,27</sup> are complex, and depend upon many factors including ambient<sup>28</sup> and exhaust<sup>27</sup> temperatures, and the relative concentrations of VOCs and  $\text{NO}_x$ .<sup>27</sup> Ozone concentrations are most often predicted to increase; however in certain situations ozone can decrease.<sup>16,27</sup> Both field observation and model predictions indicate that under high  $\text{NO}_x$  conditions, additional ethanol can contribute to substantial increases in the smog component PAN.<sup>8,28,29</sup> The use of ethanol as a biofuel therefore does not necessarily improve air quality relative to gasoline as a fuel.

Rainwater ethanol concentrations are close to or at equilibrium with local atmospheric gas phase concentrations suggesting that rainwater is a predictable sink for gas phase ethanol. The absolute removal of ethanol by rainwater will increase as ethanol concentrations increase in air; however, the relative magnitude

of this change compared with other sources and sinks is unknown in this dynamic system. It is clear from these data that existing sinks including rainwater are not sufficient to remove ethanol at the rate at which it is being added to the atmosphere. Because of the potential impacts of increasing ethanol on air quality, especially in high traffic urban areas, further study of this complex system is urgently needed.

## METHODS

### Rainwater collection

Rainwater was collected on the University of North Carolina Wilmington campus (34.227° N, 77.858° W) located 8.5 km away from the Atlantic Ocean. The collection site at UNCW is a large open area of approximately 0.01 km<sup>2</sup> 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. Collection was done on an event basis using an Aerochem-Metrics (ACM) 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 > 18 MΩ cm<sup>-1</sup>) and then combusted at 450 °C in a muffle furnace for at least 4 h to remove organic contaminants. Samples were filtered within minutes of collection under low vacuum through a 0.2-μm Gelman Supor polysulfone filters in a glass filtration apparatus.

### Condensate collection

Samples for gas-phase ethanol concentration studies were obtained by collecting the condensate from the outside of test tubes filled with ice. The glass tubes and all glassware used for collection and analysis were cleaned with Milli-Q DI water followed by combustion at 450 °C for a minimum of 4 h prior to use. Condensation was collected over 1–2 h at or close to ground level. Air temperature, relative humidity, and wind speed were measured before and after sample collection using a Kestrel 3000 weather meter. Gas phase ethanol was calculated from condensate concentrations using the equation for a moderately soluble gas.<sup>30</sup> Condensate was collected at the UNCW rain site and at the Bluthenthal Wildflower Preserve less than 1 km away. Collections were also done proximal to episodically flooded areas as described in the text.

### Air mass back trajectories

Air mass back trajectory analysis (<https://ready.arl.noaa.gov/hypub-bin/trajtype.pl?runtime=archive>, 2017) at 500 m for 72 h was used to indicate the origins of air masses. This 72-h time period is close to the reported atmospheric residence times of ethanol of 2.8 days<sup>12</sup> and 3.6 days.<sup>22</sup>

### Ethanol analysis

Ethanol was determined by three analytical methods during this 8-year study: enzyme oxidation (detection limit (DL) = 10 nM), solid phase micro extraction (with DL = 19 nM), and static headspace GC-MS/MS analysis (DL = 28 nM). The three methods have been described and compared extensively and produce equivalent results for the types of samples used in this study.<sup>31,32</sup> Samples for ethanol analysis (condensate and rainwater) were analyzed in triplicate when the sample volume permitted. Samples were analyzed immediately when the enzyme method was used for analysis. Other samples were refrigerated at 4 °C in glass vials with minimal headspace and preserved with 70 μL of 100 mg/mL HgCl<sub>2</sub> (Alfa Aesar, >98%) per 40 mL sample to eliminate biological activity such as microbial degradation or production of ethanol.<sup>31</sup> The concentration of ethanol in samples preserved in this way with HgCl<sub>2</sub> did not significantly change within 158 days of storage.<sup>7,31</sup>

### Data analysis

Rainwater ethanol concentrations are reported as VWA, and volume weighted standard deviations to minimize the influence of small volume rain events on concentrations.<sup>33</sup> This is equivalent to combining all samples and analyzing one representative sample. One outlier was removed from the Wilmington rainwater data: Event 1384 from January 1, 2014, 19 mm of rain with an ethanol concentration of 6020 nM ( $p < 0.0001$ , Grubbs test). Mann–Kendall Trend Analysis was performed on rainwater data using annual VWA and also on raw event concentration

data. Climatological data for Wilmington NC were obtained from the annual climate summaries (<https://www.weather.gov/ilm/>, 2017).

## DATA AVAILABILITY

The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request.

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## AUTHOR CONTRIBUTIONS

All authors researched, collated, wrote and edited this paper.

## ADDITIONAL INFORMATION

**Competing interests:** The authors declare no competing interests.

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