RESEARCH ARTICLE

Airborne measurements of the atmospheric emissions from a fuel ethanol refinery

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Abstract Ethanol made from corn now constitutes approximately 10% of the fuel used in gasoline vehicles in the U.S. The ethanol is produced in over 200 fuel ethanol refineries across the nation. We report airborne measurements downwind from Decatur, Illinois, where the third largest fuel ethanol refinery in the U.S. is located. Estimated emissions are compared with the total point source emissions in Decatur according to the 2011 National Emissions Inventory (NEI-2011), in which the fuel ethanol refinery represents 68.0% of sulfur dioxide (SO_2), 50.5% of nitrogen oxides ($NO_x = NO + NO_2$), 67.2% of volatile organic compounds (VOCs), and 95.9% of ethanol emissions. Emissions of SO_2 and NO_x from Decatur agreed with NEI-2011, but emissions of several VOCs were underestimated by factors of 5 (total VOCs) to 30 (ethanol). By combining the NEI-2011 with fuel ethanol production numbers from the Renewable Fuels Association, we calculate emission intensities, defined as the emissions per ethanol mass produced. Emission intensities of SO_2 and NO_x are higher for plants that use coal as an energy source, including the refinery in Decatur. By comparing with fuel-based emission factors, we find that fuel ethanol refineries have lower NO_x, similar VOC, and higher SO_2 emissions than from the use of this fuel in vehicles. The VOC emissions from refining could be higher than from vehicles, if the underestimated emissions in NEI-2011 downwind from Decatur extend to other fuel ethanol refineries. Finally, chemical transformations of the emissions from Decatur were observed, including formation of new particles, nitric acid, peroxyacyl nitrates, aldehydes, ozone, and sulfate aerosol.

1. Introduction

Since the early 2000s, a growing fraction of gasoline in the U.S. has consisted of E10, a fuel blend of 10% ethanol in gasoline [*de Gouw et al.*, 2012]. Fuel ethanol in the U.S. is made almost entirely from corn, and ~40% of this crop is now grown for fuel production according to data from the U.S. Department of Energy [*Hill et al.*, 2009; *Wright and Wimberly*, 2013]. Fuel ethanol is produced from corn in approximately 200 fuel ethanol refineries across the nation. Quantification of atmospheric emissions from these refineries is essential for determining their impact on air quality and climate and is the subject of this work. Most of the fuel ethanol refining capability is located in the Midwestern states, where corn is grown (Figure 1). The production of fuel ethanol grew rapidly until 2011. At that point, the market acceptance of E10 was almost complete and further increases in ethanol production and use can only occur if E15 (a fuel blend of 15% ethanol in gasoline) was approved as a fuel in standard gasoline vehicles or if the market share of E85 (a fuel blend of 85% ethanol in gasoline) flex-fuel vehicles was to increase.

There has been significant research on the net effects of fuel ethanol use on greenhouse gas emissions. It has been argued that corn ethanol does contribute to reductions in CO_2 emissions, but that larger reductions require the development of cellulosic ethanol [*Farrell et al.*, 2006; *Hill et al.*, 2009; *Wang et al.*, 2012], which is currently only produced in small amounts [*Peplow*, 2014; *Service*, 2014]. Other studies pointed out that any reductions in CO_2 emissions could be partially or completely offset by the carbon release associated
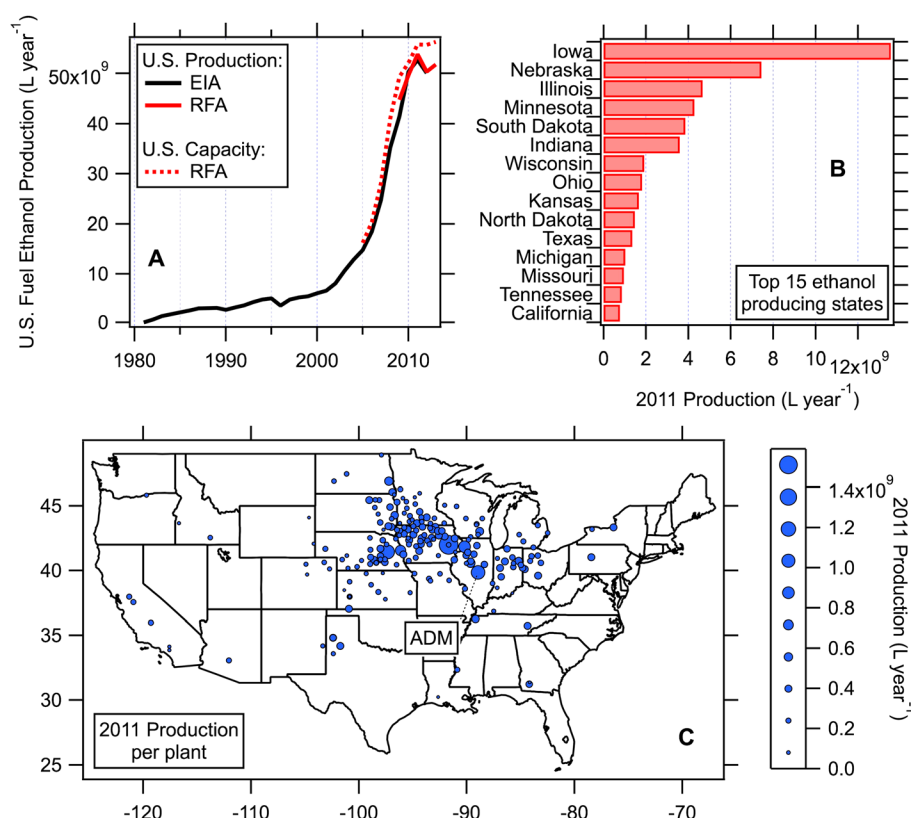
Figure 1. Fuel ethanol production in the U.S. (a) The total production and capacity according the Energy Information Administration (EIA) and Renewable Fuels Association (RFA). (b) Top 15 ethanol-producing states in 2011. (c) The location of all fuel ethanol refineries in the U.S. sized by their 2011 production. The location of the Archer Daniels Midland (ADM) plant in Decatur, Illinois, studied in this work, is indicated in Figure 1c.

with land use changes [*Fargione et al.*, 2008; *Searchinger et al.*, 2008] or by increases in emissions of the greenhouse gas N_2O associated with fertilization [*Crutzen et al.*, 2008; *Smith et al.*, 2012].

Several studies have looked at the effects of fuel ethanol use on air quality [*Hill et al.*, 2009; *Tessum et al.*, 2014]. Measured emissions from motor vehicles that use ethanol fuel blends depend strongly on the fuel blend and on the vehicle model and year. As a general trend, the emissions of nitrogen oxides ($NO_x = NO + NO_2$) tend to be lower for ethanol blends in comparison with gasoline, whereas emissions of volatile organic compounds (VOCs) such as aldehydes tend to be higher [*Graham et al.*, 2008; *Salvo and Geiger*, 2014]. A modeling study indicated that widespread use of E85 fuel in urban areas could lead to increases in acetaldehyde, ozone, and peroxyacetyl nitrate at the surface [*Jacobson*, 2007]. An observational study showed that the atmospheric burden of ethanol in the U.S. has increased over the last decade, but also, that effects on air quality have been overshadowed by the large reductions in motor vehicle emissions that occurred over the same period [*de Gouw et al.*, 2012]. A recent study from Brazil provided evidence that a higher fraction of fuel ethanol use, and therefore reduced NO_x emissions, could lead to higher ozone pollution in urban air [*Salvo and Geiger*, 2014]. There are still many uncertainties about the atmospheric chemistry of ethanol in general [*de Gouw et al.*, 2005; *Naik et al.*, 2010; *Giebel et al.*, 2011; *Millet et al.*, 2012]. For example, ethanol may have large natural sources in addition to the man-made source from fuel ethanol use. These uncertainties limit the predictive capability on the effects of fuel ethanol use.

Several recent studies quantified the emissions of reactive trace gases from various processes associated with ethanol production and their effect on air quality. A few recent papers looked at the emissions of volatile organic compounds (VOCs) from growing biofuel crops [*Eller et al.*, 2011; *Graus et al.*, 2013]. The emissions of VOCs from corn are relatively low compared to those from tree species, but nevertheless, per volume of ethanol produced, the integrated emissions from growing biofuel crops can be of the same order of

Table 1. Measurements On board the NOAA WP-3D Aircraft Used in This Analysis

Measurement	Method	Reference
NO, NO_2, NO_y, O_3	Chemiluminescence	*Pollack et al.* [2010]
CO	Vacuum ultraviolet resonance fluorescence	*Holloway et al.* [2000]
CO_2, CH_4	Infrared laser absorption	*Peischl et al.* [2012]
SO_2	Pulsed UV fluorescence	NA (not applicable)
HNO_3	Chemical ionization mass spectrometry	*Neuman et al.* [2002]
NH_3	Chemical ionization mass spectrometry	*Nowak et al.* [2007]
Aromatic and oxygenated VOCs	Proton-transfer-reaction mass spectrometry	*de Gouw and Warneke* [2007]
Hydrocarbons, ethanol	Whole air sampling–GC-MS analysis	NA
Formaldehyde	Laser-induced fluorescence	*Cazorla et al.* [2014]
Glyoxal	Cavity-enhanced absorption spectroscopy	*Washenfelder et al.* [2008]
Peroxyacyl nitrates	Chemical ionization mass spectrometry	*Slusher et al.* [2004]
Aerosol size distribution	Optical and condensation particle counters	*Brock et al.* [2000]
Aerosol size and composition	Time-of-flight aerosol mass spectrometer	*Canagaratna et al.* [2007]
Black carbon aerosol	Single-particle soot photometer	*Schwarz et al.* [2008]

magnitude as fuel-based VOC emission factors from motor vehicles [*Graus et al.*, 2013]. Other biofuel crops such as hybrid poplars are isoprene emitters [*Eller et al.*, 2012], and their widespread use could have more significant impacts on air quality, crop yields, and mortality [*Ashworth et al.*, 2012, 2013].

In this work, we report airborne measurements of atmospheric emissions downwind from Decatur, Illinois, where the third largest producer of fuel ethanol in the U.S. (Archer Daniels Midland) is located. The measurements are used to estimate the emissions of various trace gases including nitrogen oxides, sulfur dioxide, and VOCs. The results are compared with the 2011 National Emission Inventory (NEI-2011) from the U.S. Environmental Protection Agency, which has not been evaluated in detail for fuel ethanol refineries. Also, we briefly discuss the chemical transformations in the plume using airborne transects at different distances from the source. The analysis is extended to all other fuel ethanol refineries in the U.S. Figure 1 summarizes the U.S. production of fuel ethanol according to the Energy Information Administration (EIA) as well as the Renewable Fuels Association (RFA). By combining the NEI-2011 database with the RFA production numbers, we calculate the atmospheric emissions per mass of ethanol produced for all fuel ethanol refineries in the U.S. and compare these numbers to fuel-based vehicle emission factors. These comparisons give insight into the relative contribution from different important processes in the life cycle of fuel ethanol to the total atmospheric emissions.

2. Aircraft Measurements

Measurements were made from the NOAA WP-3D research aircraft during the NOAA Southeast Nexus project in June and July of 2013 (http://www.esrl.noaa.gov/csd/projects/senex/). The aircraft was operated out of the Smyrna/Rutherford County airport in Smyrna, Tennessee. The NOAA WP-3D was outfitted with a suite of instruments to characterize the chemical composition of gas- and aerosol-phase species, as well as the size distribution, radiative, and cloud-nucleating properties of the aerosol. The measurements that are used in this analysis are summarized in Table 1. Additional measurements on board the NOAA WP-3D that are not used in this analysis have been omitted from this table.

Whole air samples (WASs) were collected in-flight and analyzed postflight for VOCs using a newly developed gas chromatography–mass spectrometry system. The airborne canister sampling system was designed based on the advanced whole air sampler that was developed for the research aircraft operated by the National Center for Atmospheric Research. Up to 72 canisters could be collected in-flight either at predetermined time intervals or under manual control. The fill time at low altitude was typically 4–5 s. The analytical system consists of a two-channel gas chromatograph with a single Agilent 5975C mass spectrometric detector. The system is similar to an instrument that was used for in situ VOC measurements over the last decade [*Gilman et al.*, 2010], but uses a Stirling cooler (Sunpower Cryotel GT) to provide the cryostatic temperatures required for trapping VOCs, as opposed to liquid nitrogen in the previous system. Measurements are generally accurate within 10% but can be affected by losses in the canisters for some higher hydrocarbons. Measurements of ethanol were made from the whole air samples, and results are
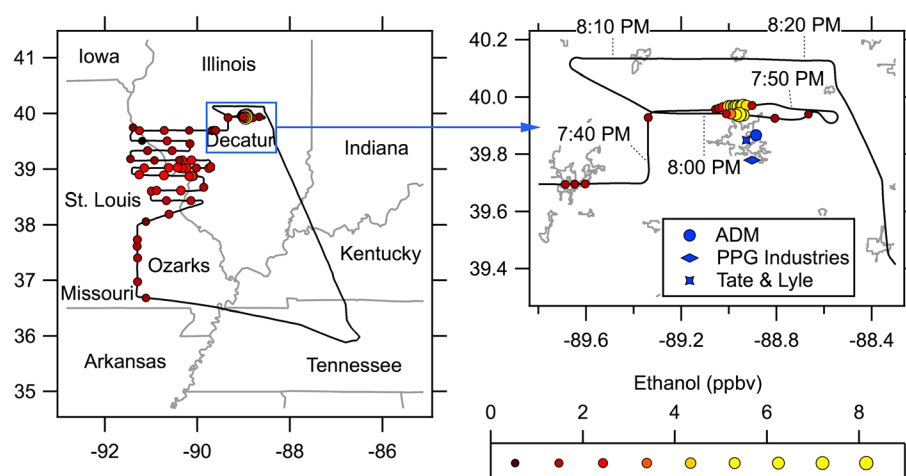
Figure 2. Flight track of the NOAA WP-3D research aircraft on 5 July 2013. The canister sampling locations are indicated by circles and color coded by the measured mixing ratio of ethanol. The gray lines indicate (left) state boundaries and (right) urban boundaries.

included in this study. After the project, the recovery of ethanol from the sampling canisters was investigated in the laboratory. The results of these tests showed that ethanol can be quantitatively retrieved from the canisters (Figure S1 in the supporting information).

3. Measurement Results

Figure 2 shows the flight track of the NOAA WP-3D on 5 July 2013. The aircraft took off from Smyrna, Tennessee, and flew at low level over the Ozarks toward St. Louis, Missouri. Several flight legs upwind, overwind, and downwind from St. Louis were made, before the aircraft transited to Decatur, Illinois. Two passes at 500 m altitude above ground were made shortly downwind from Decatur (12 and 9 km), and one further downwind (30 km), before the aircraft returned to Smyrna.

The circles along the flight track in Figure 2 indicate the locations where whole air samples were collected and the circles are size and color coded by the measured mixing ratio of ethanol in the samples. Modest enhancements of ethanol downwind from St. Louis were consistent with a motor vehicle source (Figure S2 in the supporting information) [de Gouw et al., 2012]. Much higher enhancements were observed directly downwind from Decatur. Unfortunately, no sample canisters were left for the furthest downwind transect.

The three blue symbols in the right of Figure 2 indicate the locations of the three largest point sources of NO_x, SO_2, and VOCs in Macon County, where Decatur is located, according to the NEI-2011. The emissions from these three sources as well as other point sources in Macon County are summarized in Table 2. The Archer Daniels Midland (ADM) plant that includes the fuel ethanol refinery has the highest emissions for all species in Table 2. In addition to fuel ethanol, the ADM plant in Decatur also produces a range of food, animal feed, and industrial products from corn, oilseeds, wheat, and grains. Figure S3 in the supporting information shows the different processes that contribute to the total emissions of different trace gases from the ADM plant. The Tate & Lyle plant in Decatur produces a range of food products and industrial ingredients from corn and is a

Table 2. Emissions of NO_x, SO_2, Total VOCs, and Ethanol From Point Sources in Macon County From the 2011 National Emissions Inventory

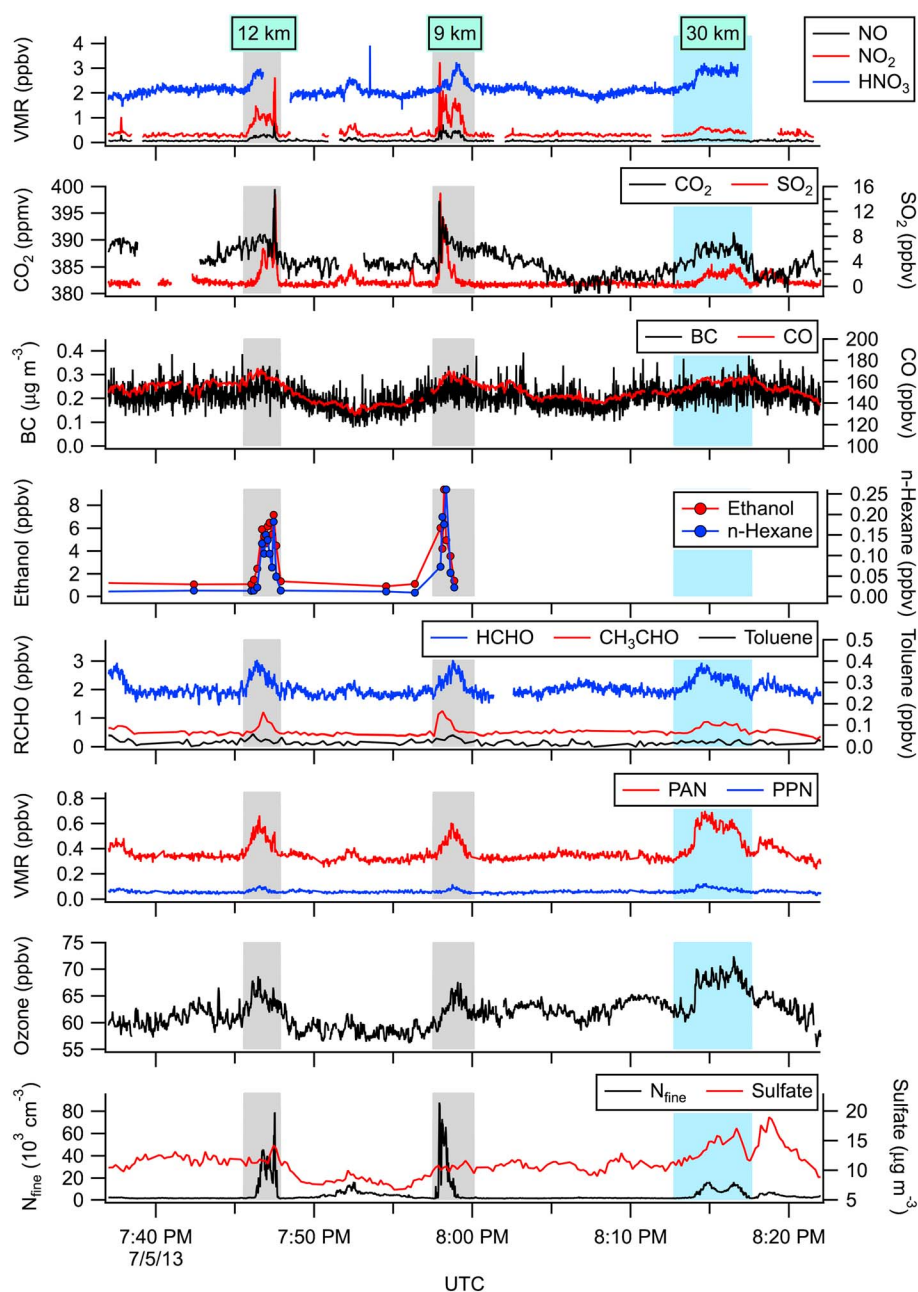|	SO_2		NO_x		VOCs		Ethanol	
	kg h^{-1}	%	kg h^{-1}	%	kg h^{-1}	%	kg h^{-1}	%
ADM	907	68.0	241	50.5	324	67.2	37.7	95.9
Tate & Lyle	414	31.0	38.9	8.1	122	25.2	1.37	3.5
PPG Industries	12.4	0.9	173	36.4	2.27	0.5	0.0354	0.1
Other	1.52	0.1	23.7	5.0	34.1	7.1	0.220	0.6
Total	1335		476		482		39	

Figure 3. Time series of measurements made from the NOAA WP-3D downwind from Decatur, Illinois. The gray shaded areas indicate plume intersects nearest to Decatur. The blue shaded area indicates the plume intersect furthest from Decatur. VMR stands for volume mixing ratio. RCHO stands for aldehydes.

significant emitter of SO_2 and VOCs but not ethanol. The PPG Industries plant to the south of Decatur manufactures flat glass for use in residential and commercial markets. The plant is a significant emitter of NO_x but not VOCs and ethanol. Because these three sources (ADM, Tate & Lyle, and PPG Industries) are very close, their emissions were not separately observed from the aircraft. Therefore, the observations downwind from Decatur will be compared with the total emission estimates for these three sources in the following analysis.

The time series of several measurements downwind from Decatur are shown in Figure 3. The two peaks on the left, during the gray shaded periods, were obtained directly downwind from Decatur (12 and 9 km), whereas the broader structure on the right, during the blue shaded period, was observed further downwind (30 km). The species that showed clear enhancements immediately downwind from Decatur included NO, NO_2, nitric

acid (HNO_3), CO_2, SO_2, ethanol, n-hexane, formaldehyde (HCHO), acetaldehyde (CH_3CHO), peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN), and the number concentration of fine particles (N_{fine}).

The ADM and Tate & Lyle plants use coal as an energy source (Figure S3 in the supporting information), which explains the presence of NO_x and SO_2 downwind from Decatur. Black carbon aerosol and carbon monoxide were correlated during this part of the flight, consistent with an influence from motor vehicle emissions, but were not strongly enhanced downwind from Decatur. Toluene, one of the more abundant VOCs in motor vehicle emissions, was also not strongly enhanced during this part of the flight. These observations show that the strong enhancements in most trace gases and aerosol species must be attributed to emissions from the industrial sources in Table 2 rather than to motor vehicles.

Since ethanol is produced in bulk quantities at the ADM plant in Decatur, the emission of ethanol could be expected. The emission of n-hexane was higher than that of the other alkanes. Fuel ethanol refineries use either a dry or wet milling process (http://www.ethanolrfa.org/pages/how-ethanol-is-made). In the wet milling process used at the ADM plant, corn is first soaked in water and dilute sulfurous acid. Subsequently, the corn germs are separated from the corn slurry. Corn oil, one of the valuable by-products from corn ethanol production, is extracted from the germs using n-hexane as a solvent, which likely explains the presence of n-hexane downwind from Decatur.

The presence of formaldehyde, acetaldehyde, PAN, and PPN downwind from Decatur is explained by a combination of direct emissions and chemical transformation in the atmosphere. Other products from the chemical transformation of emissions in the plume are shown in the bottom of Figure 3 and include ozone and sulfate aerosol. These observations will be discussed in more detail below. The number concentration of fine particles was strongly enhanced directly downwind from Decatur and correlated well with the mixing ratio of SO_2. These enhancements are caused by new particle formation in the plume. Further downwind, the number concentration of fine particles had decreased due to dilution and coagulation.

4. Discussion

4.1. Emission Estimates and Comparison with NEI-2011

Emission fluxes were estimated from the measurements in the two plume transects nearest to Decatur. The method involves integrating the enhancements in mixing ratios across the plume and multiplying the integral with the orthogonal wind speed and depth of the boundary layer [*White et al.*, 1976; *Ryerson et al.*, 2011]. Results are presented in Figure 4 and Table S1 in the supporting information. The following values and assumptions were used in the calculations:

1. The boundary layer depth was estimated to be 1175 m with an uncertainty of 20%, as estimated from the measured wind direction and speed, potential temperature, CO, CO_2, and O_3 data during two altitude profiles made before and after the plume transects near Decatur.
2. The average orthogonal wind speed was 4.1 m s^{-1} with an uncertainty of 10% due to the variability in the wind field.
3. Enhancements in mixing ratios are defined as the mixing ratio or mass loading in the plume minus the background measured outside the plume. The backgrounds determined here are given in Table S1 in the supporting information.
4. Measurements of species that were not measured continuously such as the proton-transfer-reaction mass spectrometry (1 data point every 15 s for each species) and WAS (several discrete samples across the plume) were interpolated onto a 1 s time basis for the integration across the plume. For the WAS data, this was only done for the first plume intercept, as the second plume was undersampled.
5. The uncertainty in the fluxes is estimated to be 50% due to the uncertainties in the plume integrals, boundary layer depth, the orthogonal wind speed, and in particular the assumption of uniform vertical mixing [*de Gouw et al.*, 2009; *Ryerson et al.*, 2011].
6. Several species did not show clear enhancements downwind from Decatur (methane, NH_3, propane, butanes, isoprene, ethyne, benzene, methanol, glyoxal, and methylethylketone). For these species, the measurements are used to define an upper limit to the fluxes.

The estimated emissions are compared in Figure 4 with those from the NEI-2011 database. Estimated emissions of SO_2 and NO_x agree with NEI-2011 within the uncertainty. This agreement could be fortuitous
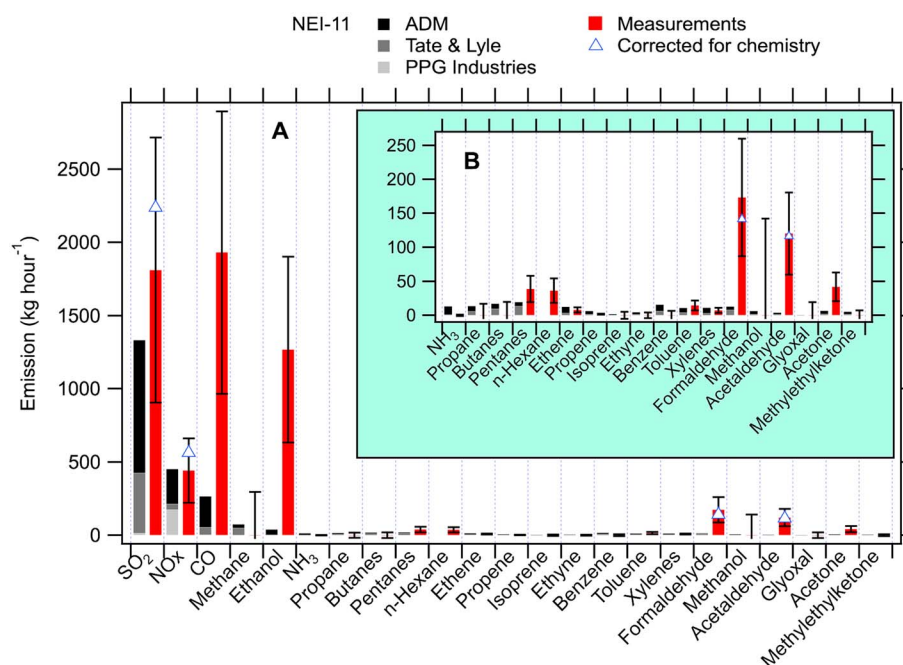
Figure 4. Comparison of the emissions downwind from Decatur, Illinois, between the three largest sources in the National Emissions Inventory in that area and the measurements from the NOAA WP-3D aircraft. (a) All compounds and (b) the compounds from ammonia (NH_3) onward on a smaller scale. The blue triangles show the possible effects of chemical transformations in the plume on the estimated emissions as discussed in section 4.2.

as fluctuations in the emissions do occur, and our measurements only provide two snapshots. However, a strong disagreement would not be expected since the point source emissions of SO_2 and NO_x in NEI-2011, including for many fuel ethanol refineries, are based on continuous emission measurements at the stack. It should be noted that the total SO_2 emissions from the ADM plant in Decatur (7950 t) are not small. For comparison, one of the largest SO_2 point sources in the U.S. is the Homer City electric power plant in Pennsylvania, which emitted 104,000 in 2013 (http://ampd.epa.gov/ampd/), i.e., only about a factor of 13 higher.

In contrast to SO_2 and NO_x, estimated emissions of several VOCs, notably ethanol, formaldehyde, and acetaldehyde, are significantly higher (factors of 10–30) than the NEI-2011 emissions, which is well outside the 50% uncertainty in the flux estimates. As discussed below, some of the formaldehyde and acetaldehyde may have been formed chemically in the plume, but this does not explain the difference with the NEI-2011 emissions. Examination of the SO_2 and ethanol time series obtained downwind from Decatur (Figure S4 in the supporting information) provides further evidence for the issues with the NEI-2011 reported here. Measured enhancements in SO_2 and ethanol were very similar downwind from Decatur, and the emission ratio derived from the measurements was 0.70 kg kg^{-1} (Table S1 in the supporting information). In contrast, the ratio from the emission inventory is only 0.029 kg kg^{-1}. The inventory is therefore inconsistent with the measurements, regardless of the uncertainties associated with estimating absolute fluxes from the measurements. Figure S3 in the supporting information shows the different processes that contribute to the emissions of total VOCs, ethanol, formaldehyde, and acetaldehyde from the ADM plant according to the NEI-2011. The largest fraction of total VOC emissions is attributed to a generic profile (Food and Agriculture: not specified) that is unlikely to be accurate for this specific source. It should also be noted that severe underestimates in VOC emissions from industrial sources are not unprecedented and were observed downwind from petrochemical plants near Houston, TX [*Ryerson et al.*, 2003; *de Gouw et al.*, 2009], and in an oil and gas production region [*Petron et al.*, 2012].

4.2. Chemical Transformation of the Emissions

The emissions intercepted at 30 km from Decatur (blue shaded period in Figure 3) were chemically more processed than the emissions intercepted at 12 and 9 km from Decatur (gray shaded periods in Figure 3).
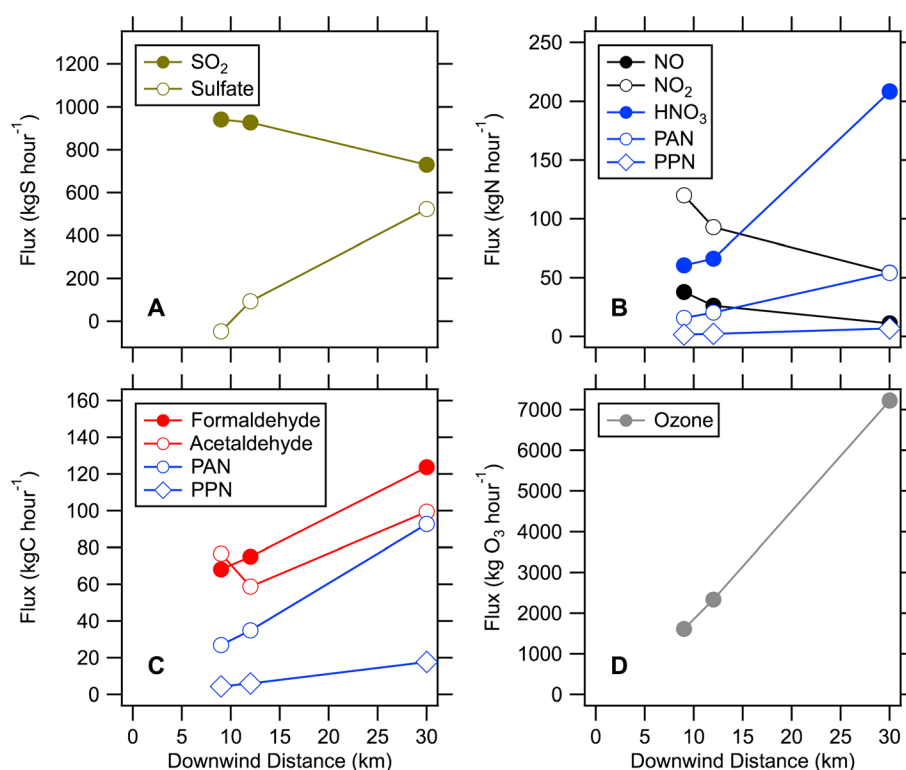
Figure 5. Estimated fluxes of (a) sulfur, (b) nitrogen, (c) organic carbon species, and (d) ozone as a function of distance and transport time from the ADM plant in Decatur. The uncertainties in the estimated fluxes are ±50%.

In Figure 5, the fluxes of various sulfur, nitrogen, and organic carbon species, as well as ozone, are shown as a function of the distance from the sampling location to the ADM plant. Fluxes were determined by the same method as used for the emissions. The plume intercept furthest from Decatur does not include the sulfate enhancement shortly before 08:20 P.M. This particular air mass was observed further east and did not have enhancements in other species such as aldehydes, PANs, and ozone. Based on the measurement location, back trajectories, and plume composition, this plume likely originated from a source further upwind than Decatur and was not included in the data shown in Figure 5.

At the downwind plume intercept, a significant fraction of the SO_2 had been converted into sulfate aerosol. Sulfate showed weak enhancements directly downwind and stronger enhancements of 6–8 $\mu g\,m^{-3}$ further downwind. Total sulfur was conserved within the 50% uncertainty of the flux estimates (albeit ~30% higher downwind). It is possible that the SO_2 emissions derived in the previous section reflect an underestimate because of this chemical removal, although sulfate concentrations were not measurably enhanced at 9 km downwind.

Figure 5b shows the chemical transformations of nitrogen oxides in the plume from Decatur. As the emissions moved downwind, NO and NO_2 reacted to form HNO_3, PAN, and PPN. As in the case of the sulfur species, total nitrogen was not perfectly conserved (~20% higher downwind) but stayed constant within the 50% uncertainty. Nitric acid is formed from the reaction between NO_2 and OH radicals. PAN and PPN are by-products from hydrocarbon oxidation in the presence of nitrogen oxides. Extrapolating the fluxes for these three species back to a zero distance gives values close to a zero flux, suggesting that, indeed, the presence of HNO_3, PAN, and PPN can be fully explained by chemical formation. It should be noted that the "kink" seen in the HNO_3 flux as a function of distance is not significant due to the 50% uncertainties. While some of the uncertainties, like wind speed and boundary layer depth, affect all the fluxes in the same manner, the largest uncertainty is due to the assumption of homogeneous vertical mixing, which cannot be assumed to affect the different data points in the same direction.

Figure 5c shows the fluxes of four organic carbon species. Formaldehyde and acetaldehyde fluxes increased downwind, suggesting that photochemical production of these species occurred in the plume. For

acetaldehyde, the relative increase is similar in magnitude as the relative increases in total sulfur and total nitrogen, indicating that acetaldehyde formation cannot be ascertained with complete certainty. These aldehydes can be intermediate products of the same chemistry that formed PAN and PPN. Efficient precursors of formaldehyde and acetaldehyde, such as ethene, propene, and isoprene, were not detected in large amounts downwind from Decatur. Ethanol itself can also be a precursor of acetaldehyde. At an estimated OH concentration of 5×10^6 molecules cm^{-3}, the loss of ethanol would be 11% in the 2 h transport time for the 30 km downwind distance. A simple calculation that takes into account the formation of acetaldehyde from ethanol with a yield of 90%, and a loss of acetaldehyde itself to OH, shows that 50 kg C h^{-1} of acetaldehyde may have been formed from ethanol in this plume, which is in the range of the observations in Figure 5c. A significant fraction of the aldehydes may also have been directly emitted from industrial sources. Consistent with this, extrapolating the formaldehyde and acetaldehyde fluxes back to a zero distance suggests that there are nonzero fluxes, i.e., direct emissions, at the source.

Ozone can be formed from the photooxidation of VOCs in the presence of NO$_x$. Data in Figure 5d show that the ozone flux steadily increased with downwind distance. The ozone production efficiency [*Ryerson et al.*, 2001; *Neuman et al.*, 2009] was estimated from a scatterplot of ozone versus NO$_z$ (=NO$_y$ − NO$_x$) for the downwind transect. The resulting value for the ozone production efficiency was 6, suggesting that six molecules of ozone were formed for every NO$_x$ molecule removed. This value is in the range of ozone production efficiencies observed in urban air but somewhat higher than what is observed downwind from power plants [*Ryerson et al.*, 2001; *Neuman et al.*, 2009]. The likely explanation is the coemission of VOCs with the NO$_x$ from these industrial sources. In these plumes, however, the VOC reactivity is dominated by oxygenated species, in contrast with urban plumes and those from petrochemical industries. From the product of their respective emission fluxes times the rate coefficients for the reaction with OH [*Atkinson and Arey*, 2003], we estimate that ethanol represents 42%, formaldehyde 26%, and acetaldehyde 20% of the total OH reactivity for all observed VOCs (Figure S5 in the supporting information).

As mentioned above, the chemical transformations observed downwind from Decatur may imply that the emissions estimated above were too low for SO$_2$, NO$_x$, and others and too high for the aldehydes that were formed photochemically downwind. To investigate the possible magnitude of this effect, we linearly extrapolated the fluxes of SO$_2$, NO$_x$, formaldehyde, and acetaldehyde back to a zero distance. This was done after downscaling the fluxes at 30 km downwind by 25% to account for the nonphysical increase in total sulfur and nitrogen fluxes. The resulting corrected fluxes are shown by the blue triangles in Figure 4 and are well within the uncertainties of the flux estimates. We conclude that chemical transformations downwind from Decatur do not significantly affect our previous conclusions of the comparison between estimated emissions and the NEI-2011 database.

4.3. Emission Intensities of Fuel Ethanol Refineries

Fuel ethanol production numbers from the Renewable Fuels Association (RFA) for 2011 (Figure 1) were combined with emissions from the NEI-2011 database to calculate emission intensities for SO$_2$, NO$_x$, VOCs, and ethanol, defined as the pollutant emissions per amount of ethanol produced:

$$\text{Emission Intensity} \left(\text{g kg}^{-1}\right) = \frac{\text{Pollutant Emission} \left(\text{g yr}^{-1}\right)}{\text{Ethanol Production} \left(\text{kg yr}^{-1}\right)}$$

Results are shown as distributions in emission intensities in Figure 6. Out of 215 fuel ethanol refineries listed by the RFA for 2011, we found matching entries in the NEI-2011 databases for 139 plants. Matches were based on names, locations, and the emission description in the NEI-2011 database. Fuel ethanol refineries without a matching entry in the NEI-2011 database were mostly confined to smaller plants. We assume here that the 139 plants with a matching entry in the NEI-2011 database are representative for all U.S. fuel ethanol refineries. The descriptions of the emissions from the NEI-2011 database were also used to distinguish between plants that use coal versus natural gas as an energy source. Out of the 139 plants, 12 plants use coal and are shown separately by the black bars in Figure 6. Four of the plants that use coal are in the top six of ethanol producers; the other eight are more average in terms of ethanol production.

An implicit assumption in the calculation of emission intensities is that all of the emissions from the NEI-2011 database are associated with the fuel ethanol-refining process. However, some plants such as the ADM plant studied here produce other food and animal feed products in bulk quantities from corn, oilseeds, wheat, and
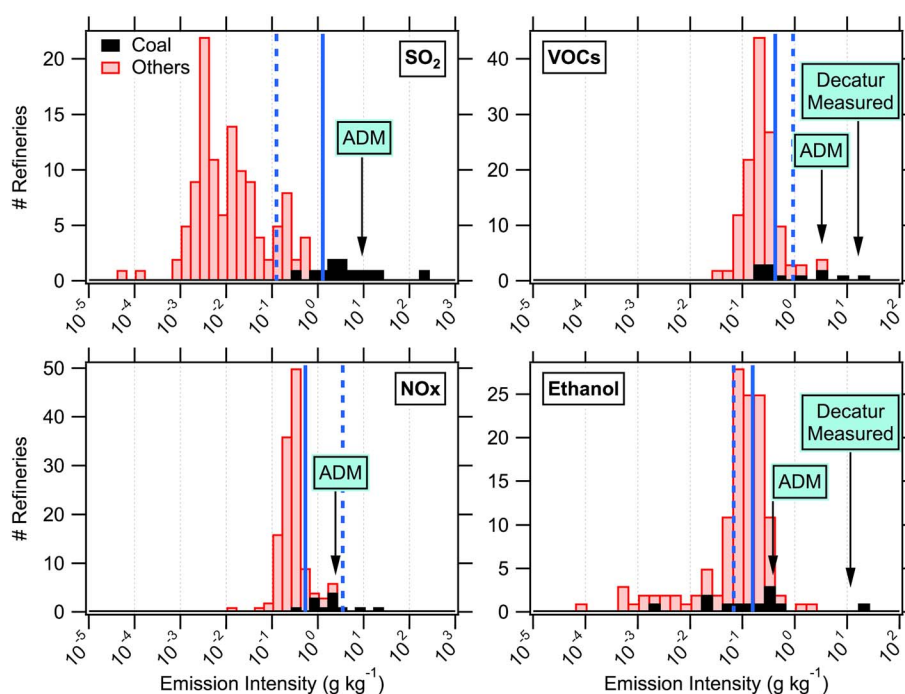
Figure 6. Emission intensities of SO_2, NO_x, VOCs, and ethanol from fuel ethanol refineries derived from combining the 2011 National Emissions Inventory and ethanol production numbers reported by the Renewable Fuels Association. Note that the *x* axes are on logarithmic scales. Average emission intensities (total emissions divided by total production) are shown by the solid blue lines. Plants that use coal are indicated in black, all others in red. Emission intensities for the ADM plant calculated from the NEI-2011 and estimated from the measurements downwind from Decatur here are shown by the arrows. For comparison, fuel-based emission factors from gasoline vehicles are shown by the dashed blue lines.

grains. Attributing all of the emissions to ethanol production is therefore an overestimate. Based on the available information, we cannot separate the emissions into the fraction that is associated with fuel ethanol production only.

The calculation of emission intensities facilitates the comparison with fuel-based emission factors from vehicles and other important processes in the life cycle of corn ethanol. Fuel ethanol is mostly used as E10 in gasoline vehicles. Fuel-based emission factors for NO_x, SO_2, and VOCs from gasoline vehicles that are averaged across a representative vehicle fleet are available from roadside and tunnel studies [*Burgard et al.*, 2006; *Bishop and Stedman*, 2008; *Bishop et al.*, 2012; *McDonald et al.*, 2012; *Gentner et al.*, 2013]. To estimate the vehicle emissions per liter of ethanol, we have to multiply the emissions from 10 L of E10 times the fraction of the emissions that is associated with ethanol only. The latter fraction is not well known, and we assume here that it scales with the volume fraction of ethanol (10%). The two factors of 10 cancel, and thus, we can compare the emission intensities for fuel ethanol refineries with fuel-based emission factors for gasoline vehicles in this section.

4.3.1. Sulfur Dioxide

Emission intensities for SO_2 are shown in the top left of Figure 6. Most plants have emission intensities below 0.04 g SO_2 kg^{-1} of ethanol, but the distribution has a very long tail. Plants that use natural gas have emission intensities up to 1 g SO_2 kg^{-1} of ethanol, whereas plants that use coal emit up to 100 g SO_2 kg^{-1} of ethanol. The solid blue line indicates the average emission intensity (1.3 g SO_2 kg^{-1} of ethanol), calculated from the total emissions divided by the total production.

Recent roadside measurements put the average SO_2 emissions from motor vehicles in 2005 at ~0.125 g SO_2 kg^{-1} of gasoline [*Burgard et al.*, 2006], indicated by the dashed blue line in Figure 6. Emissions in 2011 were likely even lower because of the tightening of the gasoline sulfur standard in 2006 to 30 ppm by weight and the continued turnover of the vehicle fleet. In comparison with the fuel-based SO_2 emission factor, the average SO_2 emission intensity from fuel ethanol refineries (1.3 g SO_2 kg^{-1} of ethanol) is higher. This shows that over the life cycle of ethanol fuel, more SO_2 is emitted from the fuel

refinery process than from the fuel use. Two comments need to be attached to this finding. First, most fuel ethanol refineries have SO_2 emission intensities that are well below 0.1 g SO_2 kg^{-1} of ethanol; i.e., a limited number of high emitters including those plants that use coal as an energy source are responsible for most of the SO_2 emissions associated with fuel ethanol refining. Second, SO_2 emissions from highway vehicles (17 kt in 2011) are very small compared to emissions from power plants in the U.S. (4529 kt in 2011) (http://www.epa.gov/ttn/chief/trends/index.html), and therefore, fuel ethanol refining is still a small source nationally.

4.3.2. Nitrogen Oxides

Emission intensities for NO_x are indicated in the bottom left of Figure 6. Most fuel ethanol refineries have NO_x emission intensities between 0 and 0.4 g NO_x kg^{-1} of ethanol. The average, defined as total emissions divided by total production, is at the high end of this range (0.53 g NO_x kg^{-1} of ethanol) as a result of the presence of several high emitters, including the ADM plant in Decatur, that use coal as an energy source.

Fleet-averaged, fuel-based emission factors for NO_x from gasoline vehicles have been determined using tunnel and roadside measurements [*Bishop and Stedman*, 2008; *Bishop et al.*, 2012; *McDonald et al.*, 2012]. From a tunnel study in 2010, an average NO_x emission of 3.5 ± 1.5 g NO_x kg^{-1} of gasoline was determined for gasoline vehicles using mostly E10. This number is 4–10 times higher than the average NO_x emission intensity from fuel ethanol refineries, which shows that the NO_x released from fuel ethanol refining is a smaller but nonnegligible source of NO_x emissions over the life cycle of this fuel.

4.3.3. Volatile Organic Compounds and Ethanol

Emission intensities for VOCs and ethanol are shown in the right of Figure 6. The blue lines indicate the average emission intensities for VOCs (0.42 g VOCs kg^{-1} of ethanol) and for ethanol (0.16 g ethanol kg^{-1} of ethanol). For VOCs, the distribution is relatively narrow with the emission intensities from most plants below 0.6 g VOC kg^{-1} of ethanol. For ethanol, the distribution has a tail toward small emission intensities. Most of the NEI point sources with the lowest ethanol emission intensities did not report ethanol emissions from ethanol/methanol production directly, in contrast to those sources with an ethanol emission intensity greater than 0.01 g ethanol kg^{-1} of ethanol. Several had ethanol emissions assigned only to grain handling and drying, which has a low ethanol/VOC partitioning profile. Several others were assigned VOC profiles for beer production, which also has a small ethanol/VOC ratio within the NEI. It thus seems likely that remaining disparities in the RFA ethanol production database and the emission database are responsible for the long tail toward very low values. Unlike for SO_2 and NO_x, plants that use coal do not appear to have systematically higher emission intensities for VOCs and ethanol than plants that use natural gas. The ADM plant in Decatur has relatively high emission intensities for VOCs and ethanol; it is possible that other production processes than fuel ethanol refining contribute significantly to the total emissions, although for ethanol itself, this may be less likely.

Emissions of VOCs from gasoline vehicles were quantified in detail in a 2010 tunnel study [*Gentner et al.*, 2013]. The emissions of all VOCs that were quantified, including hydrocarbons and oxygenated species, added up to 0.93 g VOC kg^{-1} of gasoline (from 0.68 g L^{-1} using an E10 density of 0.735 kg L^{-1}). Emissions of ethanol in that study were 0.068 g VOC kg^{-1} of gasoline (from 0.026 g C L^{-1} using the same E10 density and after conversion from carbon into ethanol mass). For total VOCs, this fuel-based emission factor is at the high end of emission intensities for VOCs in Figure 6. For ethanol itself, this fuel-based emission factor is lower than most emission intensities from ethanol refineries in Figure 6. These comparisons indicate that fuel ethanol refining could be a significant source of VOCs and, in particular, ethanol compared to vehicle emissions.

In section 4.1, it was shown that VOC and ethanol emissions from the point sources in Decatur exceeded the NEI-2011 emissions by factors of 5 for total VOCs to 30 for ethanol. It is not exactly known to what extent the emissions from the ADM plant contribute to these underestimates. It is likely that the ADM plant plays a significant role in the underestimate of ethanol emissions, since it is the only and a large producer of ethanol in the area. In addition, since ethanol represents a large fraction of total VOC emissions (Figure 4 and Table S1 in the supporting information), it is also likely that the underestimate in total VOC can be attributed significantly to the ADM plant. If emissions of VOCs and ethanol from fuel ethanol refineries are underestimated in general, then the VOC and ethanol emissions due to fuel ethanol refining could actually be higher than those from the fuel use. To illustrate this point, the VOC and ethanol emissions observed downwind from Decatur were divided by the ethanol production from the ADM plant and added to Figure 6.

The suggested emission intensities are well outside the distributions for fuel ethanol refineries calculated from the NEI-2011 and more than an order of magnitude higher than the emission factors from vehicles.

5. Conclusions

Over the past decade, the use of fuel ethanol produced from corn has increased significantly in the United States, and the volume of fuel ethanol is now approximately 10% of the volume of gasoline used. This ethanol is produced in over 200 fuel ethanol refineries in the country, particularly in several of the corn-producing states in the Midwest. In this work, we made atmospheric measurements downwind from Decatur, Illinois, where the third largest fuel ethanol refinery in the U.S. is located. Emissions of SO_2 and NO_x were in agreement with those reported in the 2011 National Emissions Inventory (NEI-2011). However, emissions of VOCs and ethanol were a factor of 5 for VOCs and 30 for ethanol higher than those included in the NEI-2011. Emissions from all fuel ethanol refineries in the U.S. were analyzed by combining emissions from the NEI-2011 with the ethanol production numbers from the Renewable Fuels Association. It is shown that fuel ethanol refining is a smaller source of NO_x and a larger source of SO_2 compared with the emissions from the use of fuel ethanol in motor vehicles. Emissions of VOCs from ethanol refining are similar to those from the use of ethanol in motor vehicles and could be much higher if the underestimates in emissions for the fuel ethanol refinery studied here extend to other refineries.

References

Ashworth, K., G. Folberth, C. N. Hewitt, and O. Wild (2012), Impacts of near-future cultivation of biofuel feedstocks on atmospheric composition and local air quality, *Atmos. Chem. Phys.*, *12*, 919–939, doi:10.5194/acp-12-919-2012.

Ashworth, K., O. Wild, and C. N. Hewitt (2013), Impacts of biofuel cultivation on mortality and crop yields, *Nat. Clim. Change*, *3*, 492–496, doi:10.1038/nclimate1788.

Atkinson, R., and J. Arey (2003), Atmospheric degradation of volatile organic compounds, *Chem. Rev.*, *103*, 4605–4638.

Bishop, G. A., and D. H. Stedman (2008), A decade of on-road emissions measurements, *Environ. Sci. Technol.*, *42*, 1651–1656, doi:10.1021/es702413b.

Bishop, G. A., B. G. Schuchmann, D. H. Stedman, and D. R. Lawson (2012), Multispecies remote sensing measurements of vehicle emissions on Sherman Way in Van Nuys, California, *J. Air Waste Manage.*, *62*, 1127–1133, doi:10.1080/10962247.2012.699015.

Brock, C. A., F. Schroeder, B. Kaercher, A. Petzold, R. Busen, and M. Fiebig (2000), Ultrafine particle size distributions measured in aircraft exhaust plumes, *J. Geophys. Res.*, *105*, 26,555–26,567, doi:10.1029/2000JD900360.

Burgard, D. A., G. A. Bishop, and D. H. Stedman (2006), Remote sensing of ammonia and sulfur dioxide from on-road light duty vehicles, *Environ. Sci. Technol.*, *40*, 7018–7022, doi:10.1021/es061161r.

Canagaratna, M. R., et al. (2007), Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer, *Mass Spectrom. Rev.*, *26*, 185–222.

Cazorla, M., G. M. Wolfe, S. A. Bailey, A. K. Swanson, H. L. Arkinson, and T. F. Hanisco (2014), A new airborne laser-induced fluorescence instrument for in situ detection of formaldehyde throughout the troposphere and lower stratosphere, *Atmos. Meas. Tech. Discuss.*, *7*, 8359–8391.

Crutzen, P. J., A. R. Mosier, K. A. Smith, and W. Winiwarter (2008), N_2O release from agro-biofuel production negates global warming reduction by replacing fossil fuels, *Atmos. Chem. Phys.*, *8*, 389–395.

de Gouw, J. A., and C. Warneke (2007), Measurements of volatile organic compounds in the Earth's atmosphere using proton-transfer-reaction mass spectrometry, *Mass Spectrom. Rev.*, *26*, 223–257.

de Gouw, J. A., et al. (2005), Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, *J. Geophys. Res.*, *110*, D16305, doi:10.1029/2004JD005623.

de Gouw, J. A., et al. (2009), Airborne measurements of ethene from industrial sources using laser photo-acoustic spectroscopy, *Environ. Sci. Technol.*, *43*, 2437–2442.

de Gouw, J. A., et al. (2012), Increasing atmospheric burden of ethanol in the United States, *Geophys. Res. Lett.*, *39*, L15803, doi:10.1029/2012GL052109.

Eller, A. S. D., K. Sekimoto, J. B. Gilman, W. C. Kuster, J. A. de Gouw, R. K. Monson, M. Graus, E. Crespo, C. Warneke, and R. Fall (2011), Volatile organic compound emissions from switchgrass cultivars used as biofuel crops, *Atmos. Environ.*, *45*, 3333–3337.

Eller, A. S. D., J. A. de Gouw, M. Graus, and R. K. Monson (2012), Variation among different genotypes of hybrid poplar with regard to leaf volatile organic compound emissions, *Ecol. Appl.*, *22*, 1865–1875.

Fargione, J., J. Hill, D. Tilman, S. Polasky, and P. Hawthorne (2008), Land clearing and the biofuel carbon debt, *Science*, *319*, 1235–1238.

Farrell, A. E., R. J. Plevin, B. T. Turner, A. D. Jones, M. O'Hare, and D. M. Kammen (2006), Ethanol can contribute to energy and environmental goals, *Science*, *311*, 506–508.

Gentner, D. R., D. R. Worton, G. Isaacman, L. C. Davis, T. R. Dallmann, E. C. Wood, S. C. Herndon, A. H. Goldstein, and R. A. Harley (2013), Chemical composition of gas-phase organic carbon emissions from motor vehicles and implications for ozone production, *Environ. Sci. Technol.*, *47*, 11,837–11,848, doi:10.1021/es401470e.

Giebel, B. M., P. K. Swart, and D. D. Riemer (2011), New insights to the use of ethanol in automotive fuels: A stable isotopic tracer for fossil- and bio-fuel combustion inputs to the atmosphere, *Environ. Sci. Technol.*, *45*, 6661–6669.

Gilman, J. B., et al. (2010), Ozone variability and halogen oxidation within the Arctic and sub-Arctic springtime boundary layer, *Atmos. Chem. Phys.*, *10*, 10,223–10,236.

Graham, L. A., S. L. Belisle, and C.-L. Baas (2008), Emissions from light duty gasoline vehicles operating on low blend ethanol gasoline and E85, *Atmos. Environ.*, *42*, 4498–4516, doi:10.1016/j.atmosenv.2008.01.061.

Graus, M., A. S. D. Eller, R. Fall, B. Yuan, Y. Qian, P. Westra, J. A. de Gouw, and C. Warneke (2013), Biosphere-atmosphere exchange of volatile organic compounds over C4 biofuel crops, *Atmos. Environ.*, *66*, 161–168.

Hill, J., S. Polasky, E. Nelson, D. Tilman, H. Huo, L. Ludwig, J. Neumann, H. Zheng, and D. Bonta (2009), Climate change and health costs of air emissions from biofuels and gasoline, *Proc. Natl. Acad. Sci. U.S.A.*, *106*, 2077–2082.

Holloway, J. S., R. O. Jakoubek, D. D. Parrish, C. Gerbig, A. Volz-Thomas, S. Schmitgen, A. Fried, B. Wert, B. Henry, and J. R. Drummond (2000), Airborne intercomparison of vacuum ultraviolet fluorescence and tunable diode laser absorption measurements of tropospheric carbon monoxide, *J. Geophys. Res.*, *105*, 24,251–24,261, doi:10.1029/2000JD900237.

Jacobson, M. Z. (2007), Effects of ethanol (E85) versus gasoline vehicles on cancer and mortality in the United States, *Environ. Sci. Technol.*, *41*, 4150–4157.

McDonald, B. C., T. R. Dallmann, E. W. Martin, and R. A. Harley (2012), Long-term trends in nitrogen oxide emissions from motor vehicles at national, state, and air basin scales, *J. Geophys. Res.*, *117*, D00V18, doi:10.1029/2012JD018304.

Millet, D. B., E. Apel, D. K. Henze, J. Hill, J. D. Marshall, H. B. Singh, and C. W. Tessum (2012), Natural and anthropogenic ethanol sources in North America and potential atmospheric impacts of ethanol fuel use, *Environ. Sci. Technol.*, *46*, 8484–8492.

Naik, V., et al. (2010), Observational constraints on the global atmospheric budget of ethanol, *Atmos. Chem. Phys.*, *10*, 5361–5370.

Neuman, J. A., et al. (2002), Fast-response airborne in situ measurements of HNO_3 during the Texas 2000 Air Quality Study, *J. Geophys. Res.*, *107*, 4436, doi:10.1029/2001JD001437.

Neuman, J. A., et al. (2009), Relationship between photochemical ozone production and NO_x oxidation in Houston, Texas, *J. Geophys. Res.*, *114*, D00F08, doi:10.1029/2008JD011688.

Nowak, J. B., J. A. Neuman, K. Kozai, L. G. Huey, D. J. Tanner, J. S. Holloway, T. B. Ryerson, G. J. Frost, S. A. McKeen, and F. C. Fehsenfeld (2007), A chemical ionization mass spectrometry technique for airborne measurements of ammonia, *J. Geophys. Res.*, *112*, D10S02, doi:10.1029/2006JD007589.

Peischl, J., et al. (2012), Airborne observations of methane emissions from rice cultivation in the Sacramento Valley of California, *J. Geophys. Res.*, *117*, D00V25, doi:10.1029/2012JD017994.

Peplow, M. (2014), Cellulosic ethanol fights for life, *Nature, 507*, 152–153.

Petron, G., et al. (2012), Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study, *J. Geophys. Res.*, *117*, D04304, doi:10.1029/2011JD016360.

Pollack, I. B., B. M. Lerner, and T. B. Ryerson (2010), Evaluation of ultraviolet light-emitting diodes for detection of atmospheric NO_2 by photolysis-chemiluminescence, *J. Atmos. Chem.*, *65*, 111–125.

Ryerson, T. B., et al. (2001), Observations of ozone formation in power plant plumes and implications for ozone control strategies, *Science, 292*, 719–723.

Ryerson, T. B., et al. (2003), Effect of petrochemical industrial emissions of reactive alkenes and NO_x on tropospheric ozone formation in Houston, Texas, *J. Geophys. Res.*, *108*(D8), 4249, doi:10.1029/2002JD003070.

Ryerson, T. B., et al. (2011), Atmospheric emissions from the Deepwater Horizon spill constrain air-water partitioning, hydrocarbon fate, and leak rate, *Geophys. Res. Lett.*, *38*, L07803, doi:10.1029/2011GL046726.

Salvo, A., and F. M. Geiger (2014), Reduction in local ozone levels in urban São Paulo due to a shift from ethanol to gasoline use, *Nat. Geosci.*, *7*, 450–458, doi:10.1038/ngeo2144.

Schwarz, J. P., et al. (2008), Coatings and their enhancement of black carbon light absorption in the tropical atmosphere, *J. Geophys. Res.*, *113*, D03203, doi:10.1029/2007JD009042.

Searchinger, T., R. Heimlich, R. Houghton, F. Dong, A. Elobeid, J. Fabiosa, S. Tokgoz, D. Hayes, and T. Yu (2008), Use of U.S. croplands for biofuels increases greenhouse gases through emissions from land-use change, *Science, 319*, 1238–1240.

Service, R. F. (2014), Cellulosic ethanol at last?, *Science, 345*, 1111.

Slusher, D. L., L. G. Huey, D. J. Tanner, F. M. Flocke, and J. M. Roberts (2004), A thermal dissociation-chemical ionization mass spectrometry (TD-CIMS) technique for the simultaneous measurement of peroxyacyl nitrates and dinitrogen pentoxide, *J. Geophys. Res.*, *109*(D19), D19315, doi:10.1029/2004JD004670.

Smith, K. A., A. R. Mosier, P. J. Crutzen, and W. Winiwarter (2012), The role of N_2O derived from crop-based biofuels, and from agriculture in general, in Earth's climate, *Philos. Trans. R. Soc. London, Ser. B, 367*, 1169–1174.

Tessum, C. W., J. D. Hill, and J. D. Marshall (2014), Life cycle air quality impacts of conventional and alternative light-duty transportation in the United States, *Proc. Natl. Acad. Sci. U.S.A.*, *111*, doi:10.1073/pnas.1406853111.

Wang, M., J. Han, J. B. Dunn, H. Cai, and A. Elgowainy (2012), Well-to-wheels energy use and greenhouse gas emissions of ethanol from corn, sugarcane and cellulosic biomass for U.S. use, *Environ. Res. Lett.*, *7*, 045905.

Washenfelder, R., A. O. Langford, H. Fuchs, and S. S. Brown (2008), Measurement of glyoxal using incoherent broadband cavity enhanced absorption spectroscopy, *Atmos. Chem. Phys.*, *8*, 7779–7793.

White, W. H., J. A. Anderson, D. L. Blumenthal, R. B. Husar, N. V. Gillani, J. D. Husar, and W. E. Wilson Jr. (1976), Formation and transport of secondary air pollutants: Ozone and aerosols in the St. Louis urban plume, *Science, 194*, 187–189.

Wright, C. K., and M. C. Wimberly (2013), Recent land use change in the Western Corn Belt threatens grasslands and wetlands, *Proc. Natl. Acad. Sci. U.S.A.*, *110*, 4134–4139.