

Increasing atmospheric burden of ethanol in the United States

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[1] The use of ethanol as a transportation fuel in the U.S. increased significantly from 2000–2009, and in 2010 nearly all gasoline contained 10% ethanol. In accordance with this increased use, atmospheric measurements of volatile organic compounds in Los Angeles in 2010 were significantly enriched in ethanol compared to measurements in urban outflow in the Northeast U.S. in 2002 and 2004. Mixing ratios of acetaldehyde, an atmospheric oxidation product of ethanol, decreased between 2002 and 2010 in Los Angeles. Previous work has suggested that large-scale use of ethanol may have detrimental effects on air quality. While we see no evidence for this in the U.S., our study indicates that ethanol has become a ubiquitous compound in urban air and that better measurements are required to monitor its increase and effects. **Citation:** 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.

1. Introduction

[2] Ethanol (C₂H₅OH) made from corn, sugar cane, switch grass and other bio-fuel crops has been promoted as a renewable transportation fuel in the U.S. and elsewhere. While the benefits of ethanol use for net carbon emissions are the subject of intense debate and are likely modest at best [Farrell *et al.*, 2006; Searchinger *et al.*, 2008; Jacobson, 2009], there has also been an increasing interest in the effects of ethanol use on air quality [Jacobson, 2007; Giebel *et al.*, 2011; Nopmongkol *et al.*, 2011]. Much of this research was done in Brazil where ethanol has been widely used as a transportation fuel for years [Grosjean *et al.*, 1998; Anderson, 2009]. A modeling study for the U.S. suggested that a widespread use of E85 (a fuel blend with 85% ethanol and 15% gasoline) could lead to significant increases in surface ozone, particularly in Los Angeles and the metropolitan areas in the Northeast [Jacobson, 2007]. Despite the increasing role of ethanol as a transportation fuel, atmo-

spheric measurements are relatively sparse and its global atmospheric sources and sinks are not understood in detail [Naik *et al.*, 2010].

[3] Vehicles that run on E85 are on the market in the U.S., but most ethanol is used in E10 (10% ethanol blended into gasoline) for regular gasoline vehicles. Fuel sale data from the Energy Information Administration of the U.S. Department of Energy show that the use of ethanol has increased significantly over the last decade (Figure 1) [Fichman, 2011]. In 2000, fuel ethanol use in the U.S. was about 1.3% of gasoline use, and this percentage increased to 9.5% in 2010; i.e., ~95% of gasoline sold in the U.S. in 2010 was E10. This widespread adoption of E10 occurred at different times in different states, with California a relatively early adopter and Massachusetts following two years later (Figure 1c).

[4] In this study, we evaluate our measurements of volatile organic compounds (VOCs) made during various intensive field missions in the U.S. over the past decade for evidence of the increased use of ethanol in the U.S. We look for trends in our data for ambient ethanol in the Northeast U.S. and in California, and also study if the increase in ethanol use led to discernable changes in ambient acetaldehyde (CH₃CHO), one of the products of ethanol oxidation in the atmosphere and a hazardous air pollutant.

2. Measurements

[5] Data used in this study were obtained during four different field missions. Measurements were made in the summers of 2002 and 2004 in the Gulf of Maine onboard the NOAA research vessel Ronald H. Brown [Goldan *et al.*, 2004; de Gouw *et al.*, 2005; Warneke *et al.*, 2007]. Airborne measurements in the Los Angeles basin were made from the NOAA WP-3D research aircraft in April–May of 2002 [Warneke *et al.*, 2007] and in May–June 2010 during the CalNex mission. Ground-based measurements in the Los Angeles basin during CalNex were made at a site in Pasadena, California [Washenfelder *et al.*, 2011].

[6] The ground and ship-based measurements of ethanol, acetaldehyde and other volatile organic compounds (VOCs) were made using an in-situ gas chromatography – mass spectrometry (GC-MS) instrument [Goldan *et al.*, 2004; Gilman *et al.*, 2010]. Onboard the aircraft, acetaldehyde and other VOCs were measured by proton-transfer-reaction mass spectrometry (PTR-MS) [de Gouw and Warneke, 2007]; ethanol measurements are not possible with this instrument. A side-by-side comparison of these two instruments was performed onboard the Ronald H. Brown in 2002 [de Gouw *et al.*, 2003a] and showed good agreement for most compounds. Ozone artifacts have been reported for acetaldehyde measurements, but are significant mostly in stratospheric air

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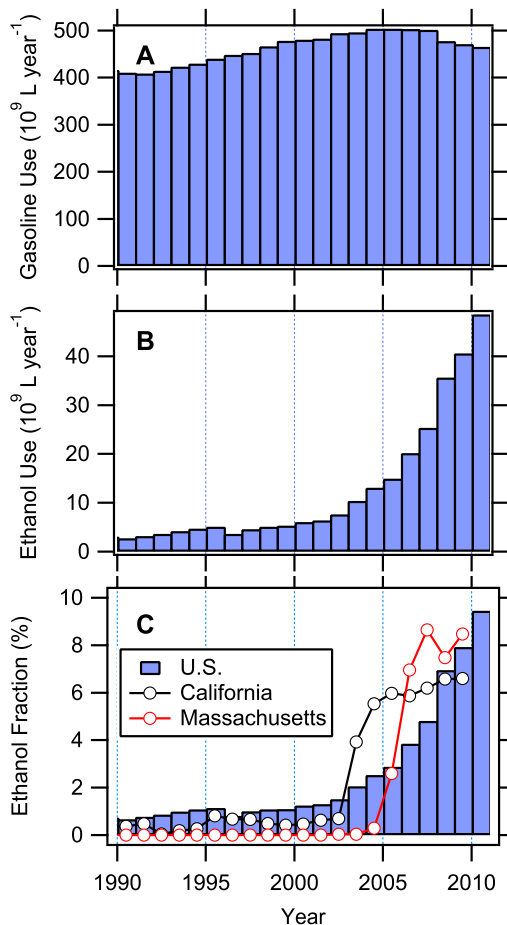


Figure 1. Total sales of (a) gasoline and (b) ethanol as motor vehicle fuel in the U.S. [Fichman, 2011]. (c) Percentage of ethanol relative to the sum of gasoline and ethanol for the U.S., and for California and Massachusetts, where NOAA conducted intensive field studies in 2002, 2004 and 2010.

with high ozone and very low VOCs [de Gouw and Warneke, 2007].

[7] Additional measurements used in this study are those of carbon monoxide (CO) and carbon dioxide (CO₂) [Chen *et al.*, 2010] made onboard the NOAA WP-3D research aircraft.

3. Results and Discussion

[8] We obtained detailed data on ethanol directly downwind from urban areas in the Northeast U.S. in 2002 and 2004, and inside the Los Angeles basin in 2010. Figure 2a compares the ethanol data between these three field studies by plotting ethanol mixing ratios versus those of the combustion tracer ethyne (C₂H₂). The highest VOC mixing ratios in the Northeast U.S. were observed when sampling at night a few km downwind from coastal cities such as Boston, Massachusetts [de Gouw *et al.*, 2005; Warneke *et al.*, 2007]. The ethanol versus ethyne plots showed similar relationships in 2002 and 2004 (Table 1). Much higher mixing ratios of ethanol were observed in the Los Angeles basin during CalNex in 2010 (Table 1). The increase in ethanol between the Northeast U.S. in 2002 and 2004 versus Los Angeles in

2010 is consistent with the increased use of ethanol between Massachusetts in 2002 and 2004, and California in 2010 (Figure 1c).

[9] Other sources of ethanol such as vegetation, biomass burning, fermenting cattle feed, bakeries and breweries do exist [Naik *et al.*, 2010; Giebel *et al.*, 2011], but are expected to be less important in the Northeast U.S. and Los Angeles data sets. Previous analyses of data from the Northeast U.S. attributed 69% of the observed ethanol to direct emissions from anthropogenic sources, 7% to biogenic sources and left 24% unattributed (a background mixing ratio that may also contain anthropogenic emissions) [de Gouw *et al.*, 2005]. In Los Angeles, the diurnal variation of ethanol was consistent with anthropogenic, traffic-related sources rather than biogenic sources. Based on the measurement of acetonitrile, a tracer for biomass burning [de Gouw *et al.*, 2003b], the contribution of biomass burning emissions in all three data sets was found to be negligible.

[10] Other than ethanol, the composition of primary, anthropogenic VOC emissions was very similar between the Northeast U.S. in 2002 and 2004, and Los Angeles in 2010. Emission ratios of VOCs versus ethyne are estimated here, by (1) defining a photochemical age based on hydrocarbon

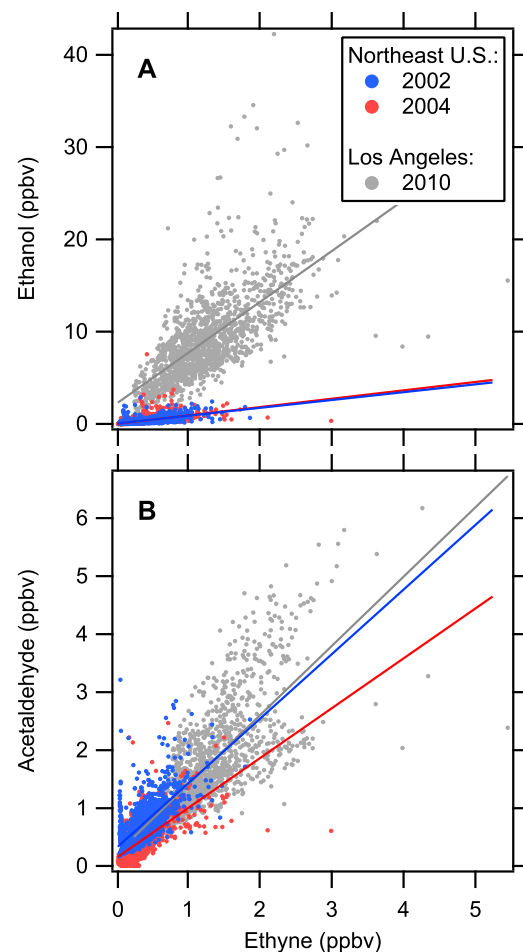


Figure 2. Correlation plots of (a) ethanol and (b) acetaldehyde versus ethyne from data obtained in the Northeast U.S. in 2002 and 2004, and in Los Angeles in 2010. Lines represent the results of linear regression fits to the data. The corresponding slopes and values of r^2 are given in Table 1.

Table 1. Average Mixing Ratios of Ethanol, and Enhancement Ratios of Ethanol and Acetaldehyde Over Ethyne From Data Obtained in the Gulf of Maine in 2002 and 2004 and in the Los Angeles Basin in 2010

	Average Ethanol (ppbv $\pm 1\sigma$)	Ethanol vs. Ethyne		Acetaldehyde vs. Ethyne	
		Slope	r^2	Slope	r^2
NEAQS 2002	0.3 ± 0.4	0.85 ± 0.03	0.415	1.12 ± 0.03	0.505
ICARTT 2004	0.3 ± 0.4	0.91 ± 0.04	0.284	0.86 ± 0.02	0.475
CalNex 2010	9 ± 5	5.4 ± 0.2	0.413	1.09 ± 0.04	0.461

ratios, and (2) calculating the VOC/ethyne ratio at zero photochemical age [*de Gouw et al.*, 2005; *Warneke et al.*, 2007]. For the Los Angeles data collected at the surface site in Pasadena, photochemical ages were determined from the measured ratio between benzene ($k_{\text{OH}} = 1.22 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [*Atkinson and Arey*, 2003]) and 1,2,4-trimethyl benzene ($k_{\text{OH}} = 32.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$); this ratio was chosen rather than benzene over toluene ($k_{\text{OH}} = 5.63 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) used in our previous work [*de Gouw et al.*, 2005; *Warneke et al.*, 2007], because of the close proximity of sources to the sampling site and the resulting smaller degree of processing. The resulting emission ratios of different VOCs versus ethyne are compared in Figure 3a with our previous results from the Northeast U.S. [*de Gouw et al.*, 2005]. Almost all emission ratios agree within a factor of 2 between the two data sets. The exception is ethanol, which was a factor of 6.1 higher in Los Angeles in 2010 compared with the Northeast U.S. in 2002.

[11] Emissions of ethanol from vehicles can occur through the tailpipe or be evaporative [*Gentner et al.*, 2009]. For either source, there are only a limited number of studies that have quantified the emissions from vehicles running on E10 [*Poulopoulos et al.*, 2001; *Graham et al.*, 2008]. A useful data set for comparison with the VOC emission ratios reported here was obtained from tunnel measurements in Wisconsin in the early 2000s [*Lough et al.*, 2005], at a time when ethanol was added to gasoline at 9–10% by volume in that state. The emission ratios obtained in Los Angeles are compared with those obtained from the tunnel study in Figure 3b. Most of the aromatics and alkenes, as well as ethanol, agree within a factor of 2 between the two data sets. Differences were larger for alkanes: ethane, propane and n-butane in particular have higher emissions in urban areas than explained by traffic, because they have sources associated with the production and use of natural and liquefied petroleum gas (LPG) [*White et al.*, 2008]. The good agreement for ethanol suggests that all ethanol in Los Angeles comes from vehicles. However, it should be noted that the uncertainties in this analysis are large, and do not rule out other significant sources of ethanol in Los Angeles.

[12] The composition of gasoline used in the Los Angeles area in 2010 was determined from 10 samples obtained from 5 different service stations in the Los Angeles area. Figure 3c compares the emission ratios for alkanes, aromatics and ethanol obtained in Los Angeles with the molar mixing ratio of these compounds in gasoline. It should be noted that the mole fraction of ethanol ($21 \pm 4\%$) is higher than its weight percent ($11 \pm 2\%$), because of its relatively low molecular mass. The C2–C4 alkanes and alkenes were excluded from the graph because they have different sources as noted in the previous paragraph. Also, the C2–C4 alkenes

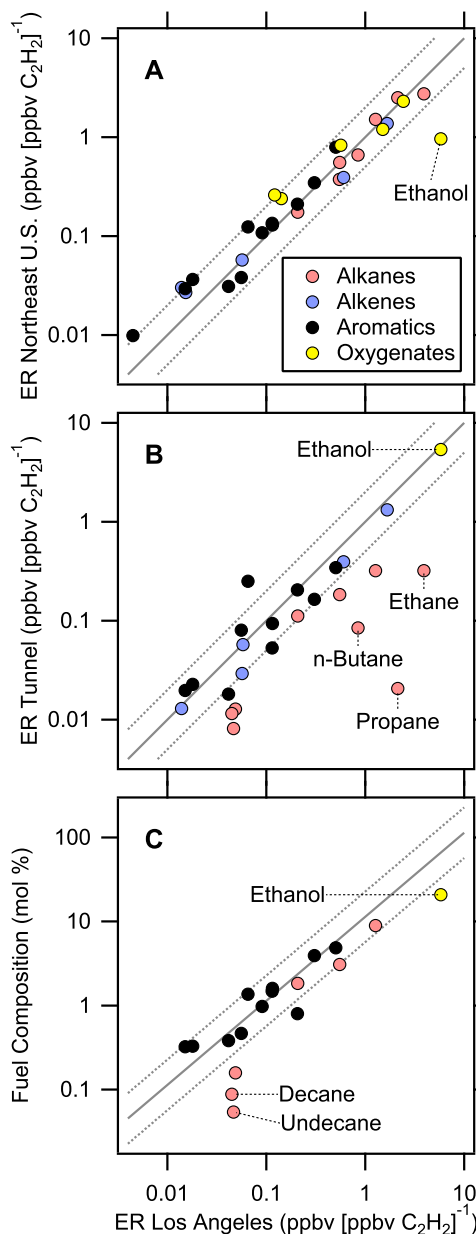


Figure 3. Emission ratios of VOCs versus ethyne from (a) the Northeast U.S. [*de Gouw et al.*, 2005], (b) a tunnel study in Wisconsin [*Lough et al.*, 2005], and (c) fuel composition in Los Angeles in 2010 versus emission ratios of VOCs derived from the data in Los Angeles. Each data point represents an individual compound, color-coded by its chemical class. Solid lines in Figures 3a and 3b represent the 1:1 relationship and dotted lines a difference by a factor of 2. The solid line in Figure 3c represents a best fit to the data, with the dashed lines a difference by a factor of 2.

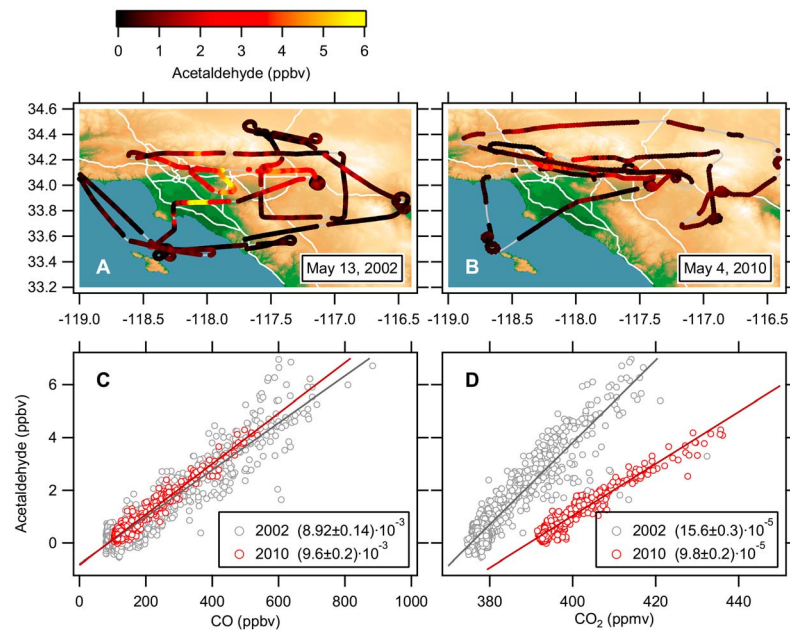


Figure 4. Flight tracks of the NOAA WP-3D aircraft in the Los Angeles basin on (a) May 13, 2002 and (b) May 4, 2010. Correlation plots of (c) acetaldehyde versus carbon monoxide and (d) acetaldehyde versus carbon dioxide for the flights in Figures 4a and 4b. The slopes of linear fits to the data are given in Figures 4c and 4d.

are partial combustion products that are not present in the fuel. The solid line in Figure 3c shows the best fit to all data included, with the dotted lines showing a difference of a factor of 2. It is seen that the composition of the selected VOCs in Los Angeles closely resembles that of gasoline. It should be noted that the emission ratio of ethanol in ambient air was a factor of ~ 3 higher than expected based on the fuel composition and the best fit to the data. This could be because of the presence of other sources of ethanol in the Los Angeles basin. However, there are also differences for the alkanes and aromatics, so it is unclear if the deviation of ethanol is significant.

[13] Combining the information in Figures 2 and 3, we conclude that the composition of anthropogenic VOC emissions was similar between the Northeast in 2002 (and 2004) and Los Angeles in 2010, with the exception of ethanol. The higher ethanol mixing ratios in 2010 are consistent with the increased use of ethanol between 2002 and 2010. In addition, the anthropogenic emission ratios estimated from the observations in Los Angeles are similar to what can be expected from a vehicle fleet that largely uses E10. These findings lead us to conclude that vehicle emissions contributed significantly to the observed ambient ethanol concentrations in Los Angeles, and that the high ethanol mixing ratios in Los Angeles are at least partially explained by the increased use of ethanol as a transportation fuel.

[14] Given the increased use of fuel ethanol, do our data sets contain any evidence for an increase of acetaldehyde, i.e., a major atmospheric oxidation product? The enhancement ratio of acetaldehyde over ethyne, determined from the slope of a linear fit to the data, was similar between the Northeast U.S. and Los Angeles (Figure 2b and Table 1). Similarly, acetaldehyde data from a rural site in New Hampshire did not show a significant trend between 2004 and 2006 [Jordan *et al.*, 2009], during a period when ethanol use in the region increased significantly (Figure 1c). While

acetaldehyde has direct emission sources, it has a lifetime of hours in the daytime atmosphere. Therefore, most of the observed acetaldehyde is formed during transport from emission sources further upwind [de Gouw *et al.*, 2005; Millet *et al.*, 2010; Sommariva *et al.*, 2011]. For that reason, the enhancement ratio of acetaldehyde to ethyne is more reflective of the enhancement ratios of the acetaldehyde precursors versus ethyne. Several studies including ours (Figure 3a) have shown that hydrocarbon emissions have very similar chemical composition in different regions of the U.S. [Warneke *et al.*, 2007; Baker *et al.*, 2008; Parrish *et al.*, 2009]. We can estimate the effect of higher ethanol emissions using the results from our previous study of acetaldehyde formation in urban air, which used the Master Chemical Mechanism and hydrocarbon emission ratios determined from the Northeast U.S. in 2002 and 2004 [Sommariva *et al.*, 2011]. Based on these model results, the additional formation of acetaldehyde from the higher ethanol emissions in 2010 can be estimated. During the first day of photochemical processing, the acetaldehyde formed from ethanol is on average 20% of the acetaldehyde formed from other sources. During the second day, this percentage increases to 90% on average. This analysis may explain why higher ethanol emissions did not cause an increase in acetaldehyde to ethyne ratios between 2002 and 2010, but does suggest that acetaldehyde could be enhanced further away from urban sources.

[15] A weakness in this study is that we do not have ethanol data from one region of the atmosphere that shows the increase in ambient mixing ratios. However, we do have acetaldehyde data from Los Angeles in 2002 and 2010, during which period the use of ethanol increased significantly in California (Figure 1c). In 2002, the NOAA WP-3D made one research flight in the Los Angeles basin on May 13 (Figure 4a). The results from this flight have been discussed elsewhere and showed a good correlation between most

measured VOCs and carbon monoxide (CO) [Warneke *et al.*, 2007]. In 2010, the NOAA WP-3D made a number of research flights in the Los Angeles basin in May and June. Figure 4b shows one of those flights, performed on May 4, which sampled the basin under conditions similar to those of the May 13, 2002 flight.

[16] During both flights acetaldehyde and CO were highly correlated (Figure 4c) with linear correlation coefficients, r^2 , of 0.888 for the 2002 data and 0.949 for the 2010 data. Three observations are made from this comparison of data between 2002 and 2010:

[17] 1. The enhancement ratio of acetaldehyde relative to CO differed by less than 8% between the two years. This difference is smaller than the calibration accuracy of the PTR-MS ($\sim 10\%$) and is therefore not significant. This finding agrees with our previous conclusion that acetaldehyde showed the same enhancement ratio in the Northeast U.S. in 2002 and 2004 vs. Los Angeles in 2010 despite strong increases in ethanol use.

[18] 2. Neither acetaldehyde nor CO reached the same high mixing ratios in 2010 that were observed in 2002. This was true for all 6 daytime flights of the NOAA WP-3D aircraft in the Los Angeles basin in 2010. While different degrees of mixing may account for differences in maximum levels observed during flights, that does not explain the much higher acetaldehyde and CO in 2002. Correlation plots of acetaldehyde versus carbon dioxide (CO₂) show distinctively different distributions between the two years (Figure 4d). The enhancements in CO₂ (the peak minus the background mixing ratios) were similar (~ 45 ppmv) for the two years, which is expected because fuel use was similar (Figure 1a). However, the slope of the correlation plot was significantly lower in 2010. Similar reductions were seen for other VOCs. We conclude that lower levels of CO and acetaldehyde in 2010 were caused by lower emissions of CO and acetaldehyde precursors in urban areas as observed elsewhere [von Schneidmesser *et al.*, 2010].

[19] 3. There was less scatter in the 2010 data as evidenced by the higher r^2 in 2010 (Figure 4c). Part of this scatter is the result of the limited ion counting statistics of the PTR-MS instrument [de Gouw and Warneke, 2007] and the reduction in noise reflects the increase in sensitivity that was accomplished by instrument improvements over the last decade [Warneke *et al.*, 2011].

4. Conclusions and Implications

[20] We have shown that ambient ethanol in California in 2010 was significantly higher, relative to other VOCs, than in the Northeast U.S. in 2002 and 2004, likely as a result of the rising use of E10 as a transportation fuel. In contrast, ambient acetaldehyde in the U.S. has decreased as a result of the introduction of cleaner vehicles. In our limited data set, we find no evidence that the increased use of ethanol has led to significant, additional sources of acetaldehyde. Other precursors such as terminal alkenes are likely the dominant precursors in the Los Angeles basin [Lewis *et al.*, 2005; Millet *et al.*, 2010; Sommariva *et al.*, 2011], but our analysis does suggest that ethanol oxidation may lead to enhanced acetaldehyde formation further downwind.

[21] Further increases in ethanol consumption can be expected in the near future, as the introduction of E15 fuel is being considered. Our current ability to monitor ambient

ethanol in urban air is very limited and should be improved to study the possible effects on air quality. In addition, different measurement techniques should be evaluated and inter-compared to warrant comparability between data sets. This would allow a much more detailed reconstruction of ethanol trends than is possible from our limited data alone.

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