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# Atmospheric ethanol in London and the potential impacts of future fuel formulations†

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There is growing global consumption of non-fossil fuels such as ethanol made from renewable biomass. Previous studies have shown that one of the main air quality disadvantages of using ethanol blended fuels is a significant increase in the production of acetaldehyde, an unregulated and toxic pollutant. Most studies on the impacts of ethanol blended gasoline have been carried out in the US and Brazil, with much less focus on the UK and Europe. We report time resolved measurements of ethanol in London during the winter and summer of 2012. In both seasons the mean mixing ratio of ethanol was around 5 ppb, with maximum values over 30 ppb, making ethanol currently the most abundant VOC in London air. We identify a road transport related source, with 'rush-hour' peaks observed. Ethanol is strongly correlated with other road transport-related emissions, such as small aromatics and light alkanes, and has no relationship to summer biogenic emissions. To determine the impact of road transport-related ethanol emission on secondary species (*i.e.* acetaldehyde and ozone), we use both a chemically detailed box model (incorporating the Master Chemical Mechanism, MCM) and a global and nested regional scale chemical transport model (GEOS-Chem), on various processing time scales. Using the MCM model, only 16% of the measured acetaldehyde was formed from ethanol oxidation. However, the model significantly underpredicts the total levels of acetaldehyde, indicating a missing primary emission source, that appears to be traffic-related. Further support for a primary emission source comes from the regional scale model simulations, where the observed concentrations of ethanol and acetaldehyde can only be reconciled with the inclusion of large primary emissions. Although only constrained by one set of observations, the regional modelling suggests a European ethanol source similar in magnitude to that of ethane ($\sim$60 Gg yr$^{-1}$) and greater than that of acetaldehyde ($\sim$10 Gg yr$^{-1}$). The increased concentrations of ethanol and acetaldehyde from primary emissions impacts both radical and $NO_x$ cycling over Europe, resulting in significant regional impacts on $NO_y$ speciation and $O_3$ concentrations, with potential changes to human exposure to air pollutants.

## 1 Introduction

The global consumption of non-fossil fuels is increasing, particularly those made from renewable biomass such as ethanol. Gasoline in the UK currently contains 5% ethanol (E5) and this is expected to rise by 2020 to 10% in order to meet EU guidelines on the use of renewable fuel sources.[1,2] These guidelines were implemented to meet two of Europe's key energy policy challenges; first, to tackle climate change by replacing fossil fuel consumption with sources of energy that on balance emit less carbon, and secondly, to ensure there are adequate local supplies of energy to reduce reliance on imported fossil fuels.[1] In the UK, there is also the Renewable Transport Fuel Obligation (RTFO), in place since April 2008. This ensures that fuel suppliers use a minimum percentage of biofuel.[1]

The term biofuel is a generic definition to describe any solid, liquid or gaseous fuel source that is derived from biomass and some liquid fuels can be used as a replacement for gasoline and diesel fuels. For gasoline, this is usually ethanol, although butanol has also been considered and for diesel, this is fatty acid

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methyl esters (FAMEs). There are a variety of feedstocks that can be used to make biofuels, and commercially available fuels are categorised as first and second generation biofuels. The former are produced from biomass that is part of the food chain such as sugar and/or starch crops, *i.e.* maize, wheat or seeds such as oil seeds or palm oil for bioethanol. The latter are made from biomass that is not part of the food chain. These biofuels can be used in two forms for the transport sector, either in a pure form or, more usually, blended with gasoline and diesel.[1] Ethanol can be blended with gasoline in a variety of mixtures, the most common in Europe is E5, in North America E10 (10% ethanol) and Brazil E85 (85% ethanol) or pure hydrous ethanol. In fact, the US and Brazil combined represent more than 90% of the world's production and consumption of bioethanol.[3,4] Although, high strength blends are used around the globe, these are generally not used in the EU. The situation in Brazil is more complex due to the introduction of flexible fuelled vehicles (FFV). These vehicles can run on normal gasoline, pure ethanol and any blends of the two using only one fuel tank. The engines in FFVs can automatically adapt and make changes to the ignition timing based on the specific fuel blend using an ethanol/gasoline sensor.[5]

Blending gasoline with ethanol has many advantages; it increases the combustive potential of the fuel,[6] improves some of the engines running processes and can decrease the emission of certain pollutants to the air.[3] The emissions of carbon monoxide (CO), tailpipe particulate matter (PM) and hydrocarbons are generally reduced, however the emissions of nitrogen oxides ($NO_x$) are more variable, with some studies suggesting a reduction,[3] while others report increases.[7] Studies of low strength ethanol blended fuels suggest that there is no consistent change in the emissions of $NO_x$ and that emissions of other regulated pollutants are decreased (CO -13 %, total hydrocarbon -5 %, benzene -12 % and 1,3-butadiene -6 %). However, there is a significant increase in the emission of acetaldehyde (+159 %), an unregulated and toxic pollutant. This large scale emission of aldehydes during combustion is the main disadvantage of using alcohol blended fuels.[1,8] Despite the increase in use of ethanol, there have only been sporadic measurements around the globe, largely focused in Brazil and the US as they use large quantities of ethanol-blended fuels.[3]

The combustion of both pure ethanol and ethanol-blended gasoline emit significant concentrations of acetaldehyde, formaldehyde, vaporized ethanol and benzaldehyde.[9,10] There have been no large-scale studies on the toxicological effects of atmospheric concentrations of these pollutants. However, acetaldehyde and formaldehyde are suspected carcinogens due to their ability to form adducts with DNA.[11] These pollutants have also been associated with respiratory irritation, asthma aggravating effects[12] and bronchitis in both outdoor and indoor environments.[3] Benzaldehyde is also a known nerve-toxin that can cause brain damage when people are exposed to high concentrations.[13] Still the main concern when using bioethanol blends remains the emission of acetaldehyde. By combining the degradation rates of acetaldehyde and its products, the exposure to ethanol combustion products can be estimated to be approximately 10 days.[3] This is a considerable time period where a large amount of the urban and rural population could be exposed, of specific concern to the increasing number of asthma and allergy sufferers present in urban areas. Depending on the local atmospheric conditions, acetaldehyde degradation can vary from 11 hours to up to 5 days.[14]

Observations of ethanol in the atmosphere are limited in number due to typically low atmospheric mixing ratios and associated measurement difficulties.[15] However, with the increased use of ethanol-blended fuels, it is expected that atmospheric concentrations will also increase. In fact, those urban areas that use ethanol-blended fuels have significantly enhanced atmospheric mixing ratios of ethanol, in some cases over an order of magnitude higher than those areas without the use of ethanol as a fuel.[15] Nguyen *et al.* (2001) compared the observed ethanol mixing ratios in Osaka, Japan (ethanol-blended fuels are not used) and Sao Paulo, Brazil (high use of ethanol-blended fuels).[16] They found that the observed mixing ratios of ethanol from Sao Paulo were enhanced by over a factor of 20.[16] Observations of atmospheric ethanol in those areas with high ethanol-blended fuel use were on average between 55-410 ppb.[16–20] However, the majority of these studies were conducted outside Europe, mainly in the United States or Brazil. There is a clear need for atmospheric measurements of ethanol in the EU and UK specifically.

The UK National Atmospheric Emissions Inventory (NAEI) currently does not include a road transport or evaporative gasoline source for ethanol,[21] rather its main source is spirit manufacture, (shown in Supplementary Figure 1). This is likely due to the fact that the volatile organic compound (VOC) source apportionment part of the emission inventory was last updated in 2002 and ethanol was first introduced in gasoline blends in 2003. An assumption is made that the VOC speciation profile of each emission source sector is unchanged each year, except for the specific VOCs benzene and 1,3-butadiene.[22] Acetaldehyde, in contrast has approximately 70% contribution from road transport to total UK emissions (Supplementary Figure 2). However, recent acetaldehyde flux measurements from London showed that the observations were approximately a factor of 6 higher than those estimated using the NAEI.[23] We believe that, not only will ethanol be underestimated given the current inventory estimates but that it is also likely that acetaldehyde will be.

The Master Chemical Mechanism degradation scheme for the reaction of ethanol with the hydroxyl (OH) radical in the presence of NOx is shown in Figure 1. Ethanol, acetaldehyde and formaldehyde are highlighted in the scheme in black, red and green boxes, respectively. This scheme shows that potentially 95% of ethanol emitted can directly form acetaldehyde through reactions with the OH radical. The degradation of ethanol also has multiple routes to form formaldehyde. In the calculations by Derwent and Jenkin (1990), ethanol shows a low photochemical ozone creation potential (POCP) value owing to its relatively slow reactivity with OH.[24] However, ethanol does show a high photochemical peroxyacetyl nitrate (PAN) creation potential (PPCP) value because it is oxidised directly to acetaldehyde, a major PAN precursor.

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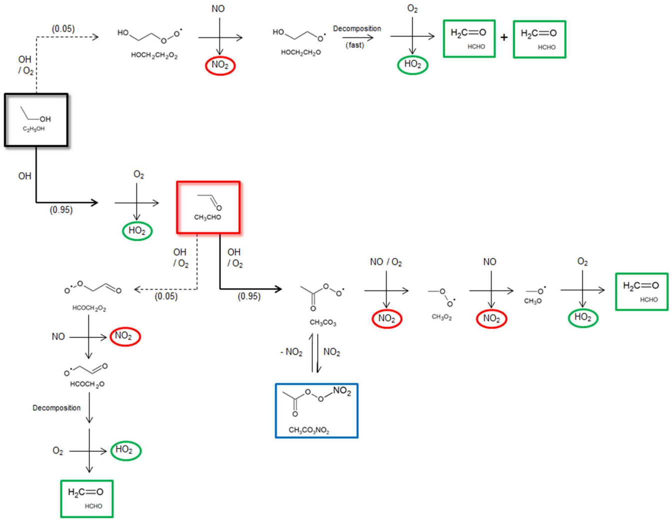

**Fig. 1** Simplified schematic mechanism for the photo-oxidation of ethanol initiated by the OH radical taken from MCM.[25] Ethanol is boxed in black, with acetaldehyde in red, PAN (peroxyacetyl nitrate) in blue and formaldehyde in green. The NO to $NO_2$ conversions, highlighted by red circles, correspond to routes to photochemical ozone formation. $HO_2$ formation (highlighted in green circles) can also lead to NO to $NO_2$ conversions.

## 2 Experimental

As part of the Clean air for London (ClearfLo) project, two 5-week intensive operating periods (IOPs) were carried out at an urban background site, North Kensington, during the winter (January and February) and summer (July and August) of 2012. For full details of the ClearfLo project and the IOP site refer to Bohnenstengel et al (2014)[26] and Bigi and Harrison (2010)[27] respectively.

### 2.1 Gas chromatography measurements

A wide range of VOCs ($C_1$-$C_{13}$) were measured using two gas chromatography (GC) instruments, a dual channel GC flame ionisation detector (DC-GC-FID)[28] and a comprehensive two dimensional GC (GC×GC-FID). These measurements have been detailed extensively in Dunmore *et al.* (2015).[29] Briefly, the DC-GC-FID has two GC columns operating in parallel. After sampling and desorption, the flow is split equally onto; one aluminium oxide ($Al_2O_3$) Porous Layer Open Tubular (PLOT, 50 m, 0.53. mm id) column for the analysis of non-methane hydrocarbons (NMHCs); and a LOWOX column (10 m, 0.53 mm id) for the analysis of oxygenated VOCs (OVOCs). The GC×GC-FID system comprised of a Markes TT24-7 (Markes International, Llantrisant, UK) thermal desorption unit, a first dimension BPX-5 (SGE, Australia, 25 m x 0.15 mm, 0.4 $\mu$m df, 50 psi) column combined with a second dimension BP-20 (SGE, Australia, 5 m x 0.25 mm, 0.25 $\mu$m df, 23 psi) column and a total transfer flow valve modulator that incorporated a 6-port, 2-way diaphragm valve (Valco Instruments, Houston, TX, USA) where actuation was achieved using a solenoid valve, controlled by 'in house' written software. The modulation period was 5 seconds, with 4.7 second sample and 0.3 second injection times.

The calibration and quantification of VOC species measured using both GC instruments was detailed in the Supplementary Information of Dunmore *et al.* (2015).[29] The two main species of interest, ethanol and acetaldehyde were measured using the LOWOX columns on the DC-GC instrument. Both species were quantified using a relative response based on an initial quantification from a certified gas standard as detailed in Hopkins *et al.* (2011).[28]

### 2.2 Details chemical modelling using the Master Chemical Mechanism

A zero-dimensional photochemical box model, based on MCMv3.2 was used to investigate the impact of current ethanol use on acetaldehyde concentrations. The MCM model was run in an analogous way as to that described in Lee *et al.* (2015).[30] Full details of the kinetic and photochemical data used as part of the model mechanism are available from the MCM website (http://mcm.leeds.ac.uk/MCM). A subset of the MCM was used in the model that treated the degradation of simultaneously measured trace VOC species, $CH_4$ and CO following oxidation initiated by OH, $O_3$ and $NO_3$, which included ~15,000 reactions and ~3,800 species. The model was constrained to *in-situ* measurements made at the North Kensington site of; NO, $NO_2$, $O_3$, HONO, CO, $CH_4$, 64 individually quantified VOC species from both GC systems, many more VOCs quantified in a grouped analysis (as detailed in Dunmore *et al.* (2015)[29]) PAN, HCHO, water vapour, temperature, pressure and photolysis rates. Model inputs were made every 15 minutes with the measured data either averaged or interpolated to 15 minute intervals if the species was measured more or less frequently, respectively. Only the summer IOP was modelled here, owing to the availability of extensive radical measurements.

### 2.3 Nested regional modelling using GEOS-Chem

To investigate the wider impacts of using ethanol blended gasoline, a regional version of the GEOS-Chem chemical transport model[31] (v10, www.geos-chem.org) was run at at 0.5°×0.666° resolution. Transport is driven by assimilated meteorology (GEOS-5) from NASA's Global Modelling and Assimilation Office (GMAO). Boundary conditions were provided by a global 4°×5° resolution simulation run for the same period. The boundary conditions are provided to the regional model from a global run that has been 'spun up' for one year. The regional model is then 'spun up' for 3 months prior to the observation period to account for interannual meteorological variability. The model uses the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) emissions (http://www.emep.int) for $NO_x$, $SO_x$ and VOCs. The base model has been extended to include a direct emission source of ethanol ('GEOS-Chem+EOH') as a simple multiplier on the $\geq$ C3 alkenes emission rate and an additional scaling on acetaldehyde emissions ('GEOS-Chem+EOH+ACET'). The nested model is run from 10th December 2011 to February 10th 2012 for the winter campaign and 20th June to 20th August 2012 for the summer campaign, with the preceding month of output to the observational

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period discarded as ‘spin up’.

## 3 Results

In terms of mixing ratio, ethanol was the most abundant VOC measured in London air during the ClearfLo campaigns. The winter and summer time series of atmospheric ethanol mixing ratios measured in London are shown in Figure 2. There were extended periods during both campaigns where very high levels of ethanol were observed (> 10 ppb). During the winter and summer IOPs, the mean and maximum ethanol mixing ratios observed were: winter mean 5 ppb, winter maximum 38 ppb, summer mean 5 ppb and summer maximum 34 ppb.

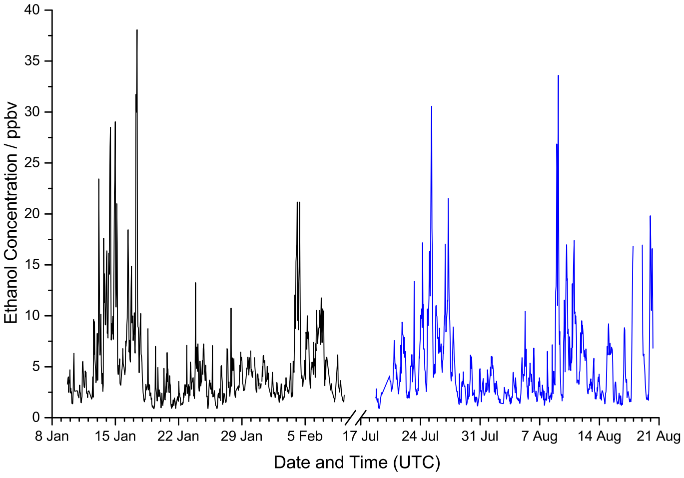

**Fig. 2** Time series of ethanol in the winter (left panel, black) and summer (right panel, blue)

The campaign average diurnal profiles of NO$_x$, CO, ethanol and acetaldehyde for winter and summer are shown in Figure 3. These profiles suggest that all four species have a dominant traffic related source given the apparent ‘rush-hour’ peaks observed in winter (left hand plots) that peak at approximately 8/9am and 5/6pm, although part of this variability is also due to changing boundary layer depth (the mean boundary layer height as measured by LIDAR increases from 441 m (06:00-10:00) to 784 m (12:00-15:00) during the day)[32]. During the summer (right hand plots) however, the average diurnals are largely influenced by meteorology (the mean boundary layer height increases from 1072 m (06:00-10:00) to 1757 m (12:00-15:00))[32] and photochemical processes. The boundary layer height observed was higher during the summer campaign,[32] leading to increased dilution of surface emissions. The ethanol winter diurnal profile (Figure 3e) shows an increase at the end of the evening (21:00-23:00) which is not seen in the diurnal profiles of the other species. It is likely that there is a background source of ethanol, (*i.e.* from brewing and distilling processes), that is more prevalent during the later evening.

A comparison of coincident mixing ratios of ethanol and acetaldehyde is shown in Figure 4. A strong linear correlation between ethanol and acetaldehyde is observed (R values = 0.89 in winter and 0.91 in summer). The data has been fitted using a least squares linear regression, with the gradient giving the ratio of the observed concentrations, (the equations of the linear regression are given on Figure 4). The approximate ratio of ethanol:acetaldehyde changes from 2:1 in winter to 1:1 in summer. This may be due to the increased production of acetaldehyde in summer due to photochemical processing of ethanol and other VOCs or due to a change in the relative emission factors between the two seasons.

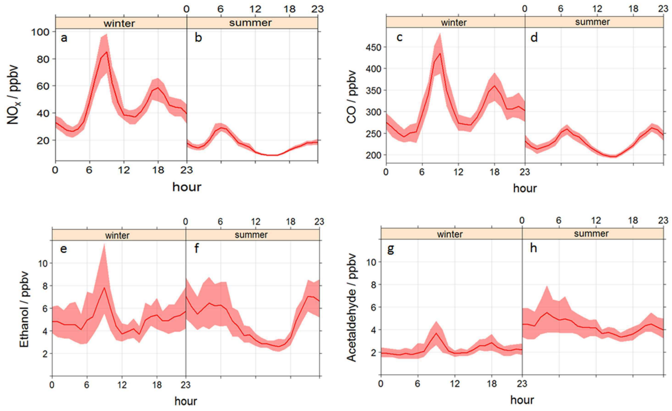

**Fig. 3** Diurnal profiles of NO$_x$ (a and b), CO (c and d), ethanol (e and f) and acetaldehyde (g and g) in winter (left-hand side of each plot) and summer (right-hand side of each plot). Each compound has the winter and summer plots on the same y-axis to aid direct comparison. This figure was constructed using the OpenAir project for R where the solid like represents the mean daily concentration and the shaded regions show the 95% confidence intervals surrounding the mean.[33–35]

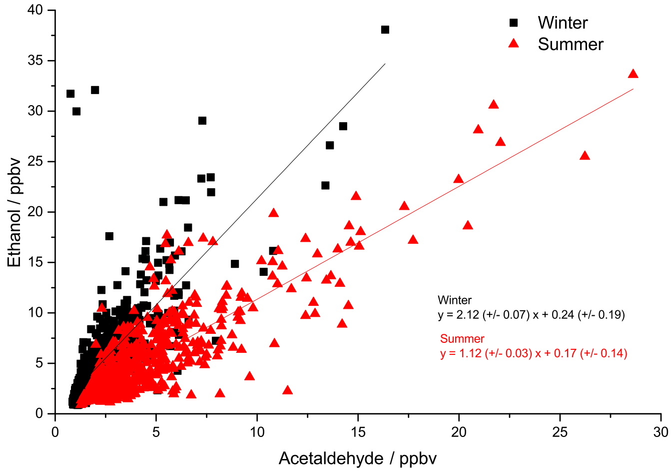

**Fig. 4** Linear regression of ethanol and acetaldehyde in the winter (black squares) and summer (red triangles) campaigns

The linear regression correlation values of the observed ethanol mixing ratios with all VOC species measured during both seasons are given in Supplementary Tables 1 and 2. During both campaigns, ethanol showed poor correlation with many of the

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other OVOC species, except acetaldehyde, likely due to the fact that ethanol has a direct anthropogenic source that is present in both seasons while the majority of the OVOCs, particularly in summer, are dominated by in-situ photochemical production. The correlation values of selected species with ethanol are shown in Figure 5, for winter (left column) and summer (right column). These species have first been ordered according to emission source, then by carbon number. In both seasons, ethanol has high correlations with gasoline related species, such as benzene, toluene, *iso*-octane (2,2,4-trimethyl pentane) and small carbon number aliphatic compounds, *n*-butane and 1,3-butadiene. Ethanol shows a stronger relationship in winter with petrol species that have a dominant combustion emission source (*n*-butane and 1,3-butadiene), whereas those with a more evaporation related emission have higher summer correlation values (benzene, toluene and *iso*-octane). The correlation between ethanol and CO, a combustion tracer, is stronger in winter than summer, but the summer value is still high (R of 0.90 and 0.83 in winter and summer respectively). Interestingly, the correlation between ethanol and isoprene is high in winter, due to a dominant traffic emission, but very low in summer when the biogenic emission source is dominant for isoprene.

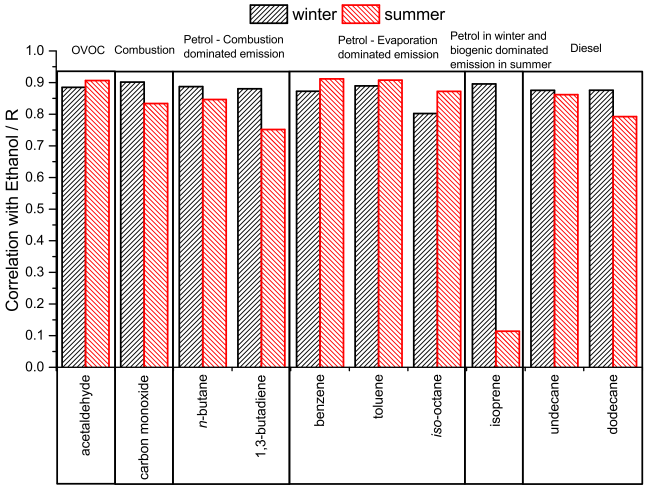

**Fig. 5** Correlation of selected compounds with ethanol in winter (left column) and summer (right column), grouped by emission source and ordered by carbon number

The most likely anthropogenic source of ethanol in London is related to gasoline use given the diurnal profiles (Figure 3) and strong correlation with other gasoline related emissions (Figure 5). The correlation between ethanol and benzene, toluene and *iso*-octane in summer are marginally higher than those in winter, which could be indicative of mutual evaporative emission from gasoline use and storage during periods of higher ambient temperatures (average summer temperature of 19.7 °C). In contrast, in winter (where temperatures are much lower, average winter temperature of 4.8 °C) a higher correlation is seen for compounds more likely to be from the combustion of gasoline, *i.e.* 1,3-butadiene and CO. This suggests that the emission of ethanol is a combination of both emission sources, with combustion of ethanol-blended fuels a larger source in winter and evaporation more important in summer.

### 3.1 Effect of ethanol content on acetaldehyde

Vasconcellos *et al.* (2005) studied the use of ethanol-blended fuels in Brazil. Generally, in urban areas there are higher observed mixing ratios of formaldehyde than acetaldehyde. However, in Brazil, where there is significant use of ethanol-blended fuels, the formaldehyde/acetaldehyde (f/a) ratio (ppb:ppb) observed was lower (in some cases less than 1), suggesting that large quantities of acetaldehyde are being directly emitted rather than formed in the atmosphere through photochemical processes.[36] Some studies use f/a ratios to suggest what the sources of these compounds are; a ratio of less than one is taken as direct emission of acetaldehyde while a ratio greater than one is representative of *in-situ* photochemical formation.[36–38] Figure 6 shows the f/a ratio from the winter (left, black) and summer (right, blue) ClearfLo campaigns in London, with the black line representing an f/a ratio of 1.

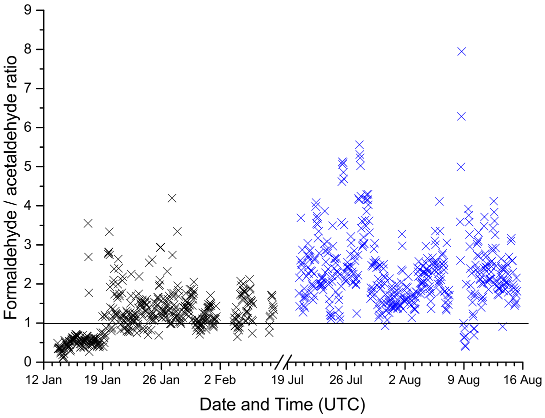

**Fig. 6** Time series of the formaldehyde/acetaldehyde ratio from the winter (left, black) and summer (right, blue) campaigns, the black line indicates an f/a ratio of 1.

The measurements from London show a mix of the two different ratio conditions, with significant periods during the winter campaign where the ratio is <1. This suggests that the use of 5% ethanol-blended gasoline in the UK is directly emitting acetaldehyde into the atmosphere. During the winter campaign, the f/a ratio is below 1 during high-pressure systems, which resulted in a shallow boundary layer and stagnant air masses, allowing the accumulation of large concentrations of acetaldehyde. However, during the summer campaign, the ratio is much larger overall with very few points below 1. Interesting, during the night of the 8th August the f/a values are also < 1. During this period, atmospheric concentrations at the North Kensington site were dominated by local emissions from London into a low boundary layer, with very low horizontal wind speeds and an unusual chemical regime, with low levels of oxidants ($O_3$, $NO_3$ and OH) leading to limited reactive chemistry. The higher ratio values in summer could suggest that the majority of acetaldehyde observed during this season is formed in the atmosphere through photochemical processing of a range of VOCs, however, this is contradicted by the lack of correlation between acetaldehyde and other OVOCs and the acetaldehyde diurnal profile observed. The higher ratios could also be due to the enhanced summer evaporative emission of ethanol from either gasoline use/storage and/or from distilling and brewing processes into the atmosphere, which then reacts with the OH radical to form acetaldehyde. It must be noted, however, that these ratios have been demonstrated to be most useful for determining the source of acetaldehyde in areas where there is a large use of high ethanol-blended gasoline, such as Brazil where the most used blend is E85. This is not the case in the UK, or London, where only E5 is used. Nevertheless, the fact that f/a ratios below 1 are observed, indicates that there is a significant direct emission of acetaldehyde into London's atmosphere.

## 3.2 Impacts of ethanol blended fuel use on air quality

### 3.2.1 Local impacts

Detailed photochemical modelling incorporating the Master Chemical Mechanism (MCMv3.2) was used to determine the local impact of road transport-related ethanol emission on secondary species such as acetaldehyde. The model was constrained to the measured concentrations of all species, except acetaldehyde. Acetaldehyde formed photochemically from ethanol in the model simulations was tagged in the resulting data, so that it could be identified as being formed directly from ethanol.

Modelling results of the impacts of measured ethanol emissions on the concentrations of atmospheric acetaldehyde in London are shown in Figure 7. On average, 6.5% of the acetaldehyde observed in London was a result of the photochemical oxidation of ethanol. Although the levels of acetaldehyde from the model degradation of ethanol (Figure 7, black filled area) are relatively consistent and show a stable diurnal pattern throughout the campaign, there are periods where ethanol produces up to 18% of the observed acetaldehyde. The profile of the total modelled acetaldehyde (black and red filled areas) shows a diurnal variation typical of photochemical production and loss, with ethanol contributing around 16% of the acetaldehyde produced in the model. However, it is clear that the detailed photochemical model simulation significantly under estimates the levels of acetaldehyde observed in London. This discrepancy is most likely due to a direct emission of acetaldehyde into the atmosphere from vehicle emissions.

A study by de Gouw *et al.* (2012) found that the ethanol emitted from the use of E10 in the US produced 20% of the acetaldehyde formed from other sources on the first day of photochemistry. They also found that on the second day this value increased to 90%, suggesting that the larger impact of ethanol emissions from fuel would be felt further away from the emission source.[4] It is worth noting that the US study only inputs 800 ppt of ethanol, while an average of 5 ppb of ethanol was observed during both ClearfLo campaigns implying that the impact of ethanol blended gasoline use in the UK could be more significant. Also worth noting is that while ethanol does not react particularly fast with the OH radical ($k$OH (298 K) = $3.2 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$)[39]

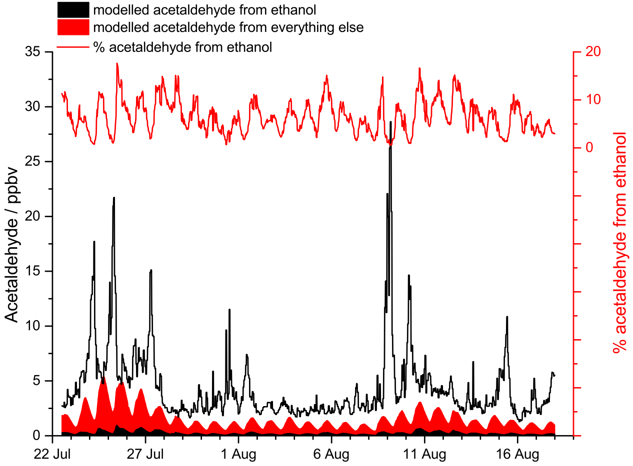

**Fig. 7** Modelling results of the impacts of current levels of ethanol observed in London. The measured acetaldehyde during the summer campaign (black), acetaldehyde formed in the model from the reaction of OH and ethanol (black filled area) and other photochemical acetaldehyde sources in the model (red filled area) are plotted on the left y axis. The percentage of the measured acetaldehyde that was directly formed from ethanol (red) is plotted on the right y axis

or produce significant quantities of $O_3$ (1.53 g $O_3$ g $VOC^{-1}$,[40] a relatively low maximum incremental reactivity (MIR) coefficient, a proxy for $O_3$ formation), the direct emission and photochemical production of large quantities of acetaldehyde (a compound which reacts rapidly with OH, $k$OH (298 K) = $15 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$,[39] and has a high MIR coefficient, 6.54 g $O_3$ g $VOC^{-1}$)[40] indicates that the impacts of the use of ethanol fuels should not be judged solely on the reactions of ethanol.[18]

### 3.2.2 Regional impacts

The wider impacts of ethanol-blended gasoline use have been investigated using a regional version of the GEOS-Chem chemical transport model. Comparisons between model and measured CO, $O_3$, ethane, propane, $\geq C_3$ alkenes, and $\geq C_4$ alkanes are shown in Supplementary Figure 3. The calculated and measured concentrations of ethanol and acetaldehyde for the summer and winter campaigns are shown in Figure 8. The base model simulation ('GEOS-Chem') does not consider ethanol, and hence is not plotted in Figure 8A. Figure 8 also shows a simulation that includes ethanol emissions ('GEOS-Chem+EOH', based on the emission of $\geq C_3$ alkenes as a proxy for vehicle emissions) tuned (multiplied by 50) to fit the observations. Appropriate ethanol degradation chemistry and deposition is included. Given the simplicity of the scaling, the model calculated ethanol concentrations appears to provide a reasonable estimate of the observations. From this simple scaling, the total annual European emissions of ethanol are equivalent to ~75 Gg $yr^{-1}$ which is ~134% of the ethane emission in the model.

The impact of the additional ethanol emission on acetaldehyde concentrations is shown in Figure 8B. Consistent with the detailed chemical box modelling, a primary ethanol emission does increase concentrations of acetaldehyde but this increase is relatively small. A simulation was also run where the acetaldehyde emissions across Europe were increased by a factor of 40 ('GEOS-Chem+EOH+ALD2'). This effectively removes the bias between the acetaldehyde observations and the model during the winter but a significant bias remains during the summer. This result suggests that there is a more significant anthropogenic source of acetaldehyde than is currently considered but there may also be a secondary (potentially biogenic) source which is currently unrepresented in the model.

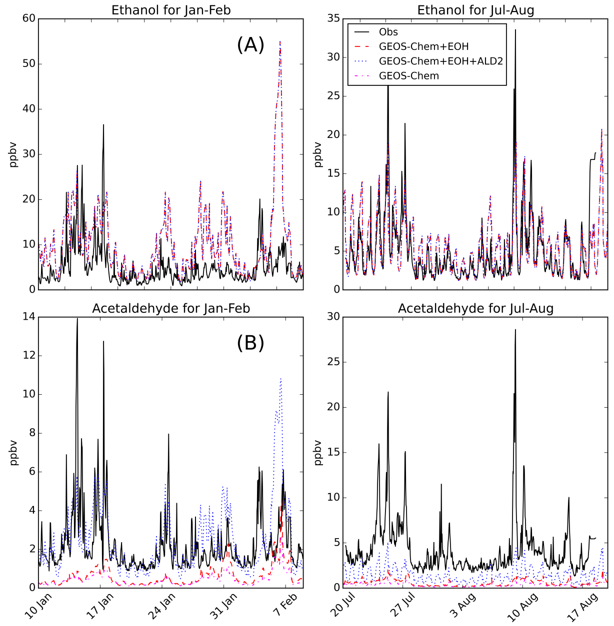

**Fig. 8** Comparison between modelled values and observed for ethanol (A) and acetaldehyde (B) for winter (left) and winter (right) observation periods. Plots show the base model simulation without increased ethanol or aldehyde emissions ('GEOS-Chem') in magenta, with added ethanol emissions ('GEOS-Chem+EOH') in red, and with both additional ethanol and acetaldehyde emissions ('GEOS-Chem+EOH+ALD2') in blue.

These changes (a primary ethanol source and an increased anthropogenic acetaldehyde source, 'GEOS-Chem+EOH+ALD2') increase the overall emissions of VOCs both for London but also across Europe. The average fractional increase in surface $O_3$ for Europe between 20th July and 20th August is shown in Figure 9. Over and downwind of major emission regions (London, Benelux, Po Valley), large increases in acetaldehyde concentrations (>1000%) are simulated which is mainly due to the increase in emission of acetaldehyde. This leads to large increases in PAN concentrations (up to 140%) downwind of the emission regions (North Sea, Mediterranean). This increase in PAN leads to local reductions in $NO_2$ concentrations of up to 10% over polluted regions (Northern Europe, North sea) but downwind from these regions the decomposition of the PAN leads to increased $NO_2$ concentrations (Mediterranean). The overall impact on $O_3$ concentration is complex. Increased OVOC emissions tend to increase $O_3$ production due to an enhanced availability of peroxy radicals. However the production of PAN leads to lower $NO_2$ concentrations close to source, reducing $O_3$ production, whilst increasing it downwind. Overall increases in surface $O_3$ are of the order of a few percent (up to 6.5%) over London and the Benelux countries. It is evident that the primary emission of ethanol and acetaldehyde can have a profound impact on the concentration of OVOCs over Europe, which in turn can impact the concentration of both $RO_x$ and $NO_x$, ultimately impacting the concentration of $O_3$.

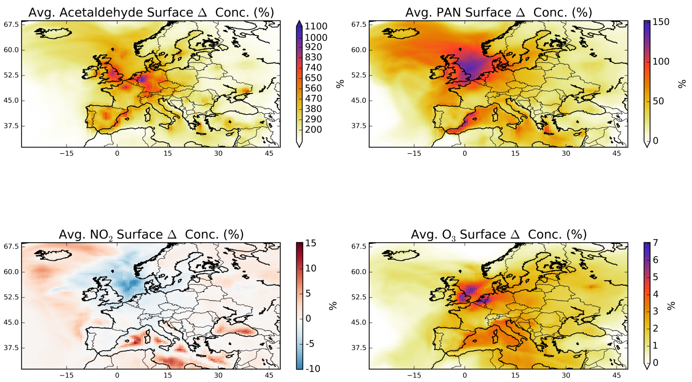

**Fig. 9** Average fractional increases in surface acetaldehyde, PAN, $NO_2$ and $O_3$ concentrations with the inclusion of both a primary ethanol emissions and an increase in acetaldehyde emissions, ('GEOS-Chem+EOH+ALD2'). Shown averaged over the summer period.

## 4 Conclusion

We have shown that ethanol was the most abundant VOC in London's atmosphere during the winter and summer ClearfLo campaigns, and significant amounts of acetaldehyde were also observed. The diurnal profiles and correlation of these two species with other VOCs have shown that their main emission source is likely to be a combination of combustion and evaporative emissions from the use of ethanol blended gasoline. Detailed photochemical MCM simulations of the local scale impacts of measured ethanol has shown that, although ethanol does not seem to produce significant local levels of acetaldehyde, the model can not accurately reproduce the observed profile of acetaldehyde, due to the presence of a direct emission into the atmosphere, with strong evidence that this is related to traffic emissions. It is clear that there are significant traffic related emissions of ethanol in urban areas and that these are not currently included in emission inventories.

In order to match the observed mixing ratios of ethanol and acetaldehyde in London, using GEOS-Chem model simulations (incorporating EMEP emissions), large additional sources were needed. This included the afforementioned unrepresented traffic related ethanol source and an increase in current acetaldehyde emissions by a factor of 40. This additional source would represent an European annual traffic-related emission of ethanol of around 75 Gg $yr^{-1}$ (c.f. annual global estimates of anthropogenic emissions of ethanol of 2-10 Tg $yr^{-1}$). This value assumes that similar scaling factors are required for all emissions inventories across Europe to match ambient concentrations. Further atmospheric observations are needed to accurately quantify the level of uncertainty in emission inventories.

Given the long lifetime of ethanol in the atmosphere, the full effects of its emission and the subsequent production of acetaldehyde may not be seen at the emission source location but rather downwind. The inclusion of previously unidentified traffic related ethanol and acetaldehyde sources in GEOS-Chem, led to increases in PAN and a reduction in $NO_2$ downwind of emission sources. The subsequent impact on photochemical $O_3$ formation is complex, but small increases were predicted across Europe compared to the base case model. The missing acetaldehyde in current inventories is likely a result of 1) an underestimate of ethanol emissions and hence secondary photochemical production of acetaldehyde, 2) a direct emission source of acetaldehyde from ethanol combustion and 3) an underestimate of acetaldehyde emissions from gasoline combustion. Although increased use of bioethanol in European fuel may help reduce net carbon dioxide emissions we would suggest that there is the potential for an inadvertent impact on air quality, which should be monitored through the transition.

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