

## Examining the temperature dependence of ethanol (E85) versus gasoline emissions on air pollution with a largely-explicit chemical mechanism

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### ABSTRACT

The increased use of ethanol in transportation fuels warrants an investigation of its consequences. An important component of such an investigation is the temperature dependence of ethanol and gasoline exhaust chemistry. We use the Master Chemical Mechanism (MCM, version 3.1, LEEDS University) with the SMVGEAR II chemical ordinary differential solver to provide the speed necessary to simulate complex chemistry to examine such effects. The MCM has over 13,500 organic reactions and 4600 species. SMVGEAR II is a sparse-matrix Gear solver that reduces the computation time significantly while maintaining any specified accuracy. Although we use a box model for this study, we determine and demonstrate in a separate study that the speed of the MCM with SMVGEAR II allows the MCM to be modeled in 3-dimensions. We also verified the accuracy of the model in comparison with smog chamber data. We then use the model with species-resolved tailpipe emissions data for E85 (15% gasoline, 85% ethanol fuel blend) and gasoline vehicles to compare the impact of each on nitrogen oxides, organic gases, and ozone as a function of ambient temperature and background concentrations, using Los Angeles in 2020 as a base case. We use two different emissions sets – one is a compilation of exhaust and evaporative data taken near 24 °C and the other from exhaust data taken at –7 °C – to determine how atmospheric chemistry and emissions are affected by temperature. We include diurnal effects by examining two day scenarios. We find that, accounting for chemistry and dilution alone, the average ozone concentrations through the range of temperatures tested are higher with E85 than with gasoline by ~7 part per billion volume (ppbv) at higher temperatures (summer conditions) to ~39 ppbv at low temperatures and low sunlight (winter conditions) for an area with a high nitrogen oxide (NO<sub>x</sub>) to non-methane organic gas (NMOG) ratio. The results suggest that E85's effect on health through ozone formation becomes increasingly more significant relative to gasoline at colder temperatures due to the change in exhaust emission composition at lower temperatures. Acetaldehyde and formaldehyde concentrations are also much higher with E85 at cold temperatures, which is a concern because both are considered to be carcinogens. These could have implications for wintertime use of E85. Peroxy acetyl nitrate (PAN), another air pollutant of concern, increases with E85 by 0.3–8 ppbv. The sensitivity of the results to box size, initial background concentrations, background emissions, and water vapor were also examined.

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### 1. Introduction

This is a study to examine the effect of ethanol from transportation exhaust and its temperature dependence on the chemical production of ozone and other gases. Ethanol's use as a transportation fuel is growing and it is marketed increasingly as E85

(15% gasoline, 85% ethanol), which is the highest ethanol/gasoline blend that existing flex-fuel vehicles in the United States can use today. Several studies have examined the issues associated with the lifecycle of biofuels (Delucchi, 2006; Farrell et al., 2006; Patzek, 2006; Tilman et al., 2006; Crutzen et al., 2008; Fargione et al., 2008; Kammen et al., 2008; Searchinger et al., 2008; Hill et al., 2009). Other studies have examined the impact of the use of ethanol on motor vehicle engines and exhaust characteristics (Gaffney and Marley, 1990, 2009; Knapp et al., 1998; MacLean and Lave, 2000; He et al., 2003; West et al., 2007; Graham et al., 2008; Westerholm et al., 2008; Wallner et al., 2009), and a few field-based studies have linked air pollution concerns with burning ethanol in vehicles

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(Gaffney et al., 1997; Grosjean et al., 1998; Gaffney and Marley, 2000, 2001; Correa et al., 2003; Fornaro and Gutz, 2003; de Assuncao et al., 2005; Anderson, 2009). Hess et al. (2009) discuss the lifecycle implications on air quality by looking at how emissions will change. Gaffney et al. (1997) conclude that PAN levels increase when using E10 in the wintertime in Albuquerque, New Mexico. In a critical comment, Whitten (1998) criticizes the study for drawing conclusions from comparing summertime and wintertime data. He also doubts the ability to make strong conclusions from a pure field data study because other factors, like meteorology, cannot be controlled, and a model should be used to verify the results and conclusions. In our paper, we model the impact from the emissions and therefore can do an apples-to-apples comparison. We investigate emissions from E85, a higher ethanol blend than E10, therefore the resulting impact is clearer.

There have not been many studies modeling the impact of tailpipe exhaust from high ethanol content fuels like E85 on urban air pollution. Martins and Arbillá (2003) used a combination of field data and modeling to conclude that the high acetaldehyde/formaldehyde ratios measured in Rio de Janeiro are due to the use of ethanol fuels. Tanner et al. (2002) examined the effects of the higher acetaldehyde emissions from ethanol vehicles on peroxy acetyl nitrate (PAN) concentrations in Rio de Janeiro, using field data and model simulations, and found that PAN concentrations were up to 5 ppbv even with high NO. A modeling study by Jacobson (2007a) suggests that ozone (O<sub>3</sub>) levels could increase in some urban areas like Los Angeles and decrease in other urban areas in the southeastern U.S. if vehicles start using E85 instead of gasoline. The population-weighted ozone exposure over the whole U.S. would likely increase (Jacobson, 2007a). Formaldehyde and acetaldehyde concentrations also increase with E85 vehicles (Jacobson, 2007a; Graham et al., 2008).

We aim to accomplish three goals in our study. First, test the computer speed of the ordinary differential equation solver, SMVGEAR II (Jacobson and Turco, 1994; Jacobson, 1995, 1998), with respect to solving more-explicit atmospheric photochemistry and dilution alone in a three-dimensional model. Second, examine the accuracy of the mechanism, Master Chemical Mechanism (MCM, 2002), by comparing photochemical model results with smog chamber data and with results from an Adjusted Carbon Bond Mechanism (ACBM) (Jacobson, 2007b). In a separate paper, we evaluate the MCM against ambient data and for its speed in a 3-D atmospheric model (Jacobson and Ginnebaugh, in press). Finally, we use a box model that treats photochemistry and dilution only to investigate the potential impacts of ambient temperature on air pollution from vehicles using E85 versus gasoline.

### 1.1. Model description and solver evaluation

Atmospheric models must be computationally fast in order to be useful for 3-D applications. However, model speed often comes

at the expense of explicitness or accuracy. To speed solutions, many models condense a large system of chemical reactions down to a few. This can impact the gas-phase chemistry because even similar species may react differently in the atmosphere. We chose to use a large chemical mechanism with over 13,500 reactions to describe the gas-phase degradation of over one hundred typically-emitted organic gases to provide a high level of accuracy. This mechanism, the Master Chemical Mechanism (MCM), version 3.1 (MCM 2002), was integrated into a Gear-type sparse-matrix solver, SMVGEAR II (Jacobson and Turco, 1994; Jacobson, 1995, 1998).

SMVGEAR II uses sparse-matrix techniques (reordering matrices and eliminating multiplications by zero) to reduce computational requirements (Jacobson, 1998). Its speed is examined for different spatial grid dimensions and mechanism sizes and compared with the time required for an ordinary differential equation (ODE) solver that does not treat matrices as sparse or treat other optimizations. Table 1 shows the reductions in the number of multiplications in SMVGEAR II due to sparse-matrix techniques when solving the MCM v. 3.1. Since daytime and nighttime chemistry are different due to photolysis reactions during the day, the sparse-matrix reductions also differ slightly. Sparse-matrix techniques reduce the number of multiplications needed for MCM v. 3.1 during decomposition and backsubstitution by over 99.99%.

The reduction in the number of required multiplications is not linear with a change in the order of the matrix. Here we compared an older version of an Adjusted Carbon Bond Mechanism (ACBM) that had 140 species and 277 reactions, MCM v. 2 with 2325 species and 6965 reactions, and the MCM v. 3.1 with 4649 species and 13,566 reactions. The ACBM is based on the Expanded Carbon Bond IV (CBIV) mechanism (Gery et al., 1989) with updates to the inorganic reactions and with some explicit treatment of C<sub>1</sub>–C<sub>3</sub> organics. The current version has 188 species, 374 kinetic reactions, and 66 photolysis reactions (for a complete listing of the reactions, see the supplementary information in Jacobson, 2007b). Previous work done by Liang and Jacobson (2000) looked at the computational reductions when SMVGEAR II was used for an even smaller system ACBM (109 species, 233 reactions) from Table B.4 of Jacobson (1999) and MCM v. 1 (1427 species and 3911 reactions) (Jenkin et al., 1997). The results of that work plus that here (Fig. S1) shows the number of required multiplications for the first matrix decomposition for different numbers of chemical species in the model. Interestingly, sparse-matrix techniques become more efficient when the number of species increases and as grid cell quantities increase (Fig. S2) (Liang and Jacobson, 2000). For example, as model spatial dimension increases from one to 450 cells, the solver is 113 times faster per cell. Only 8.1 times more computer time is required for the MCM versus the much smaller ACBM, though the number of species and reactions in the MCM are 33 times and 49 times, respectively, that of the ACBM. On an Intel Pentium 4

**Table 1**

A summary of the number of operations using SMVGEAR II to solve MCM v. 3.1. Note: decomposition 1, 2 and backsubstitution 1, 2 refer to the first and second loops of matrix decomposition and backsubstitution, respectively.

Number of operations – MCM v. 3.1					
	Initial	After sparse-matrix reductions			
		Day	% Reduction	Night	% Reduction
Order of matrix	4649	4649	0	4649	0
No. initial matrix spots filled	21,566,736	38,016	99.82	34,859	99.84
No. final matrix spots filled	21,566,736	49,069	99.77	43,330	99.80
Decomposition 1	33,374,524,734	446,030	99.9987	92,948	99.9997
Decomposition 2	10,781,046	25,412	99.76	21,231	99.80
Backsubstitution 1	10,781,046	25,412	99.76	21,231	99.80
Backsubstitution 2	10,781,046	19,013	99.82	17,455	99.84

Extreme, a 3.2 GHz machine, 1 min of computer time is required for 24 h of model time for the MCM v. 3.1 in a box model of photochemistry alone. A larger grid with 450 cells requires only 4 min for 24 h of model simulation (excluding initialization). A 3-D model with 50,000 grid cells, which might represent a global atmospheric model ( $50 \times 50 \times 20$  layers) requires approximately 7.7 h of computer time to run one day of simulation for MCM v. 3.1 photochemistry alone. In parallel, we used the MCM in a 3-D global-through-urban climate–weather–air pollution model and found that an increase in overall computer time, accounting for photochemistry, species transport, optical properties, and other processes, was only  $\sim 3.7$  times that with a condensed mechanism despite increases in the number of species and reactions of 31 and 46 times, respectively (Jacobson and Ginnebaugh, in press).

### 1.2. Chemical mechanism evaluation

To determine the accuracy of the MCM v. 3.1, experimental smog chamber data were used to test the ability to simulate the degradation of four different organics – propene, 1-butene, m-xylene, and toluene. Details about the experimental data and the model setup for the smog chamber simulations are available in the supporting information. Results for 1-butene, toluene, and m-xylene are shown in Figs. S5, S7, and S8, respectively. The results for the propene case are shown in Fig. 1. The MCM results were compared with those from the current ACBM (Jacobson, 2007b). Although most of the species are lumped in the ACBM, toluene and propene are initially treated explicitly so their decomposition can be compared with the MCM results.

Model predictions for both mechanisms matched the smog chamber data from Hynes et al. (2005) for propene relatively well, as shown in Fig. 1. Nitric oxide and propene ( $C_3H_6$ ) model results from both MCM and ACBM were very close to the data. The model prediction for the peak of formaldehyde was high by  $\sim 40$  ppb for MCM and the trend did not decrease like the observed data did. The ACBM predicted an even higher peak for formaldehyde. The MCM captured 94% of the ozone peak, but the predicted ozone increase occurred approximately 20 min before the observed increase. The beginning of the ACBM ozone trend matched MCM's trend, but its peak was much lower. Acetaldehyde has only one data point so the accuracy of the trend cannot be evaluated. However, the MCM model over-predicts the final acetaldehyde amount by 63 ppb, which was better than was the ACBM prediction. Peroxy acetyl nitrate (PAN) and carbon monoxide are also over-predicted by both models, but the MCM again has the better trend. PAN data were sparse, so the peak could not be evaluated. Carbon monoxide's modeled peak was higher than the observed peak by a factor of 6.  $NO_2$  peaked and declined over time for both models, as expected, but the data were not available for this comparison. The hydroxyl radical (OH) and hydroperoxy radical ( $HO_2$ ) modeled results were similar trends for both MCM and ACBM but concentration was slightly higher with the MCM model. Overall, the MCM matched the observed data better than did the ACBM.

The ozone production predicted by the MCM for the toluene case (Fig. S7) was approximately twice that observed. This over-prediction is a known problem with the toluene degradation in the MCM (Wagner et al., 2002; Bloss et al., 2005a, 2005b). Suggestions to improve the mechanism have been published (Baltaretu et al., 2009) but have not been incorporated into the MCM, so we will test the sensitivity of our results to toluene. 3-D simulation using MCM compared with data shows a 2% improvement in overall ozone prediction accuracy versus ambient data in Los Angeles compared with a similar condensed mechanism as used here, giving us confidence in the MCM's overall ozone prediction accuracy (Jacobson and Ginnebaugh, in press).

## 2. Application to E85-model setup

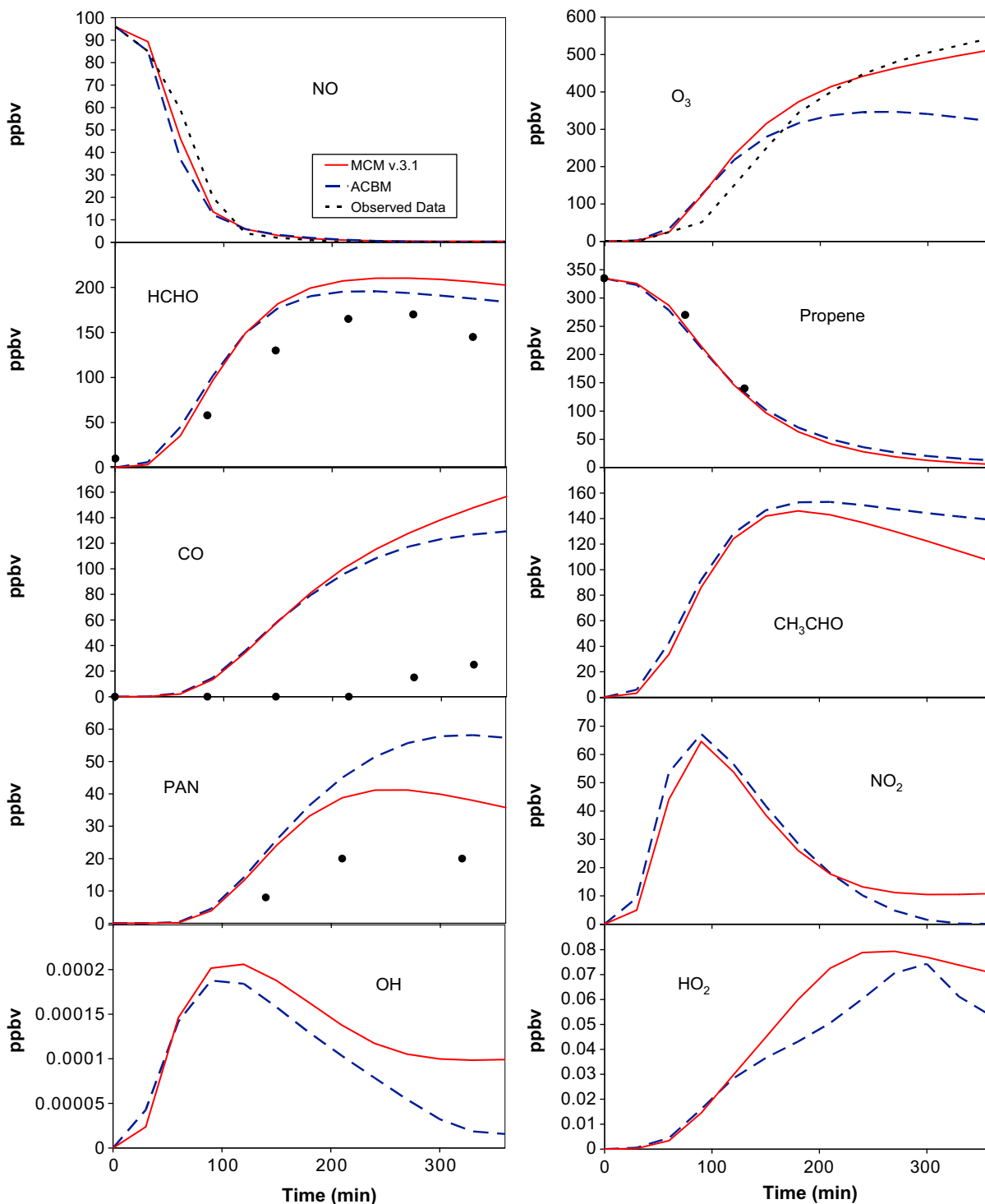
The MCM in SMVGEAR II was used in a box model to look at the impact of E85 versus gasoline on urban air chemistry for different ambient temperatures and sunlight conditions. We use a box model to isolate the sensitivity of photochemistry and dilution alone to temperature and other factors. Although results here are applied using a simple box model, the box model results for warm temperatures are similar, with respect to net ozone change, to 3-D results from Jacobson (2007a), giving us more confidence in the sensitivity tests we run for low temperatures. Further, we investigate the sensitivity of the system to changes in the box volume and to background concentrations.

The base case location chosen for this study was the South Coast Air Basin (SCAB). The warm-temperature emission data for this study were based on Table 1 of Jacobson (2007a) (Table S4). The emissions, moved forward to the year 2020, were based on 11 different studies, and included both tailpipe and evaporative emissions. They were listed for a condensed mechanism so we modified them for a more-explicit mechanism using the detailed exhaust measurement data from Black (1995–1997) (Table S5). We assumed that all vehicles were converted from gasoline to E85 for an apples-to-apples comparison of the emissions and their impact on air chemistry. The results can be applied proportionately to smaller penetrations of E85 in the vehicle fleet.

The ambient temperature impacts the exhaust emissions from vehicles in addition to affecting the chemical kinetics. The emissions from Jacobson (2007a,b) were measured under standard conditions ( $24\text{--}25^\circ\text{C}$ ). These emission data are supported by the independent review of Graham et al. (2008). Two other studies looked at the emissions from vehicles for both warm ( $22^\circ\text{C}$ ) and cold ( $-7^\circ\text{C}$ ) ambient temperatures for gasoline and ethanol fuels (Whitney and Fernandez, 2007; Westerholm et al., 2008). Westerholm et al. (2008) measured the emissions from two different flex-fuel vehicles for gasoline (E5, 5% ethanol, 95% gasoline), E70 (70% ethanol, 30% gasoline) and E85. Whitney and Fernandez (2007) measured the emissions from three different flex-fuel vehicles for gasoline (E0, 100% gasoline), E70, and E85, although they did not measure E85 emissions at the cold ambient temperatures. These two studies had similar results overall with only a few differences (Tables S8, S9 and S10). The actual emissions amounts, in  $\text{g km}^{-1}$ , differed among vehicles, but the % change from gasoline to E70 and E85 was in the same direction and of similar magnitude. The results differed among vehicles for 1,3-butadiene and benzene, where two of the vehicles saw an increase in emissions with E70 or E85 instead of a decrease. We use results from only the Volvo V50 (Westerholm et al., 2008) to represent exhaust emissions at  $-7^\circ\text{C}$  because only its emissions data were complete and included cold temperature information for E85 (Table S11). Although the cold temperature measurements did not include evaporative emissions, they are unlikely to be significant because evaporation is small at temperatures below  $0^\circ\text{C}$ .

The vehicle emissions profile used for this study followed the urban vehicle diurnal profile created by the U.S. Environmental Protection Agency for temporal allocation of emissions (USEPA, 2000). Approximately 76% of the vehicle emissions occur between 6 am and 6 pm. The model was sized to match the SCAB with a baseline height of 500 m. The sensitivity of the results to the mixing height (dilution) was investigated by examining the results for 300 m and 1 km.

The background emissions were constant and the same for the gasoline and E85 scenarios. They were also obtained from Table 1 in Jacobson (2007a), but were modified using information to separate the bond groups into explicit species (Table S14) (Carter, 2008). The background emissions include point, fugitive, area, non-road



**Fig. 1.** Observed and modeled results for propene case using the master chemical mechanism (MCM 3.1) and the adjusted carbon bond mechanism (ACBM). Note: observed data from Hynes et al. (2005).

non-gasoline, and on-road non-gasoline emissions. Initial background concentrations were set for carbon monoxide, ozone, sulfur dioxide, nitric oxide, nitrogen dioxide, methane, ethane, ethene, formaldehyde, toluene, and xylene for 6 am at the start of the model run based on measurements from the California Air Resources Board (CARB) (Tables S15–S17) (CARB, 2008). The sensitivity to these background concentrations was investigated.

The temperature was assumed to follow a sine profile throughout the day, increasing in the morning, peaking at 2 pm,

and decreasing in the evening, and was held constant during the night, following a typical temperature profile in the Los Angeles area based on temperature data from CARB (2008). We investigate the full range of low and high ambient temperature even though some temperatures do not occur in the Los Angeles area, to provide results applicable to other locations. The diurnal temperature profile was changed to target different peak temperatures (35 °C, 41 °C, etc.) (Fig. S15), which we refer to by its peak temperature. The impacts of the two sets of emissions for gasoline and E85, at 24 °C

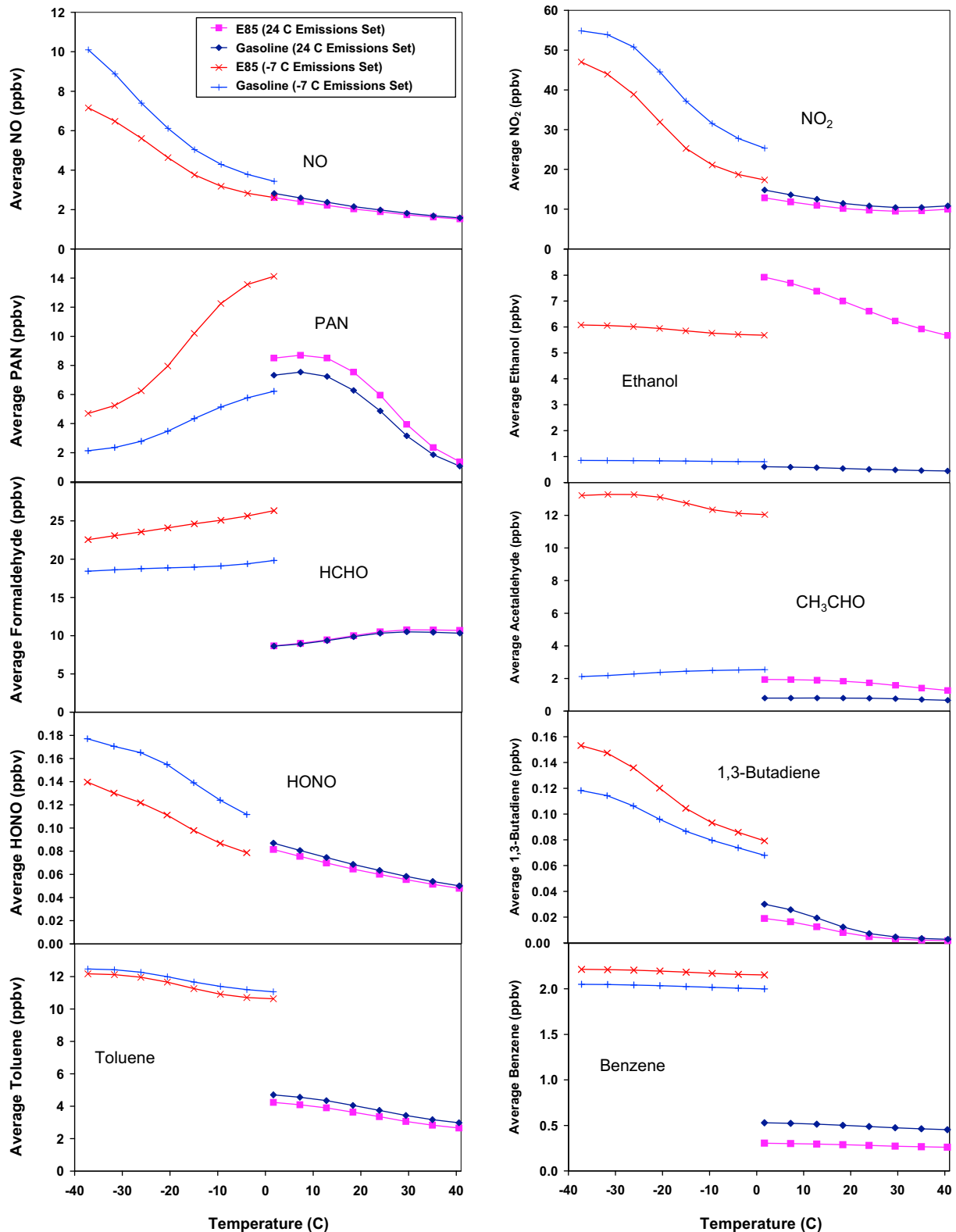


Fig. 2. Two day model results from E85 and gasoline, averaged over time, plotted versus the peak temperature using emissions data at 24 °C and at -7 °C.

and at -7 °C, were investigated over a range of temperatures – above 0 °C for the 24 °C emissions set, and below 0 °C for the -7 °C emissions set. Since the below zero temperatures would be more likely to occur in the winter, the solar profile for the model was reduced for the model runs using the -7 °C emissions set (Fig. S11).

### 3. Application – results and discussion

The time-series results from these model runs for a few species are shown in the supporting material (Figs. S18–S23). The time-series results were averaged to make comparisons easier between

the different temperature profiles. Fig. 2 shows the average concentration of select species over the two day model run for different ambient temperature profiles, referred to by the peak temperature, for each emissions data set: E85 and gasoline emissions data taken at 24 °C for model runs with the peak temperature above 0 °C; E85 and gasoline emissions data taken at -7 °C for model runs with the peak temperature below 0 °C. Since the same emissions data are used for a variety of temperature profiles, the difference in the resulting species concentrations is due to the chemical kinetic effects from the ambient temperature. The species in Fig. 2 with the steeper slopes are more impacted by the ambient temperature (such as NO, NO<sub>2</sub>, PAN, HONO, 1,3-butadiene, and O<sub>3</sub> (Fig. 3)) than the species whose concentrations do not change much with ambient temperature (ethanol, HCHO, CH<sub>3</sub>CHO, toluene and benzene). PAN in particular is very sensitive to ambient temperature.

Average NO concentrations decrease as ambient temperature increases for both gasoline and E85 (Fig. 2). NO, NO<sub>2</sub>, HONO, and toluene concentrations are higher for gasoline than for E85 at all temperatures. PAN, ethanol, formaldehyde, and acetaldehyde concentrations are all higher for E85 than for gasoline for all temperatures, which is expected due to the higher ethanol, formaldehyde, and acetaldehyde emissions from burning E85. Benzene and 1,3-butadiene concentrations are higher for gasoline for the 24 °C emissions set and lower for the -7 °C emissions set. We would expect benzene concentrations to always be higher for gasoline than for E85 because the benzene should only be present in the gasoline portion of the fuel. However, the low temperature emissions measured for the Volvo show slightly higher benzene emissions for E85 than for gasoline (0.014 g km<sup>-1</sup> and 0.013 g km<sup>-1</sup>, respectively, as shown in Table S10) (Westerholm et al., 2008). Average PAN was 0.3–7.8 ppbv higher from E85 than from gasoline. This difference started decreasing around 18 °C. At the same point, the overall average PAN concentration started to decrease for both gasoline and E85. At the warmer temperatures, the destruction dominated over the formation (Fig. 2).

The average ozone concentration for E85 was higher than the average ozone concentration for gasoline for all temperature profiles, ranging from 7.2 ppbv to 39.4 ppbv (Fig. 3), with a larger difference for the -7 °C emissions set than for the 24 °C emissions set. The average ozone concentration also increased more rapidly with ambient temperature increases for E85 than for gasoline at the cold temperatures, although for the warmer temperatures increases were similar (Fig. 3).

Although testing in a box model is not so accurate as in 3-D, the increase in average ozone concentration when using E85 for the 24 °C emissions set is very similar to the results from the study by

Jacobson (2007a), which used a 3-D global-through-urban climate–weather–air pollution model. This provides good confirmation that our box model is adequate to model this system.

At cold temperatures, where the increase in ozone concentration might be as much as 39.4 ppbv (for a two day average) and the ozone concentrations are still above 35 ppbv, the increase in premature deaths and hospitalizations is a major issue for human health considerations. Even the relatively small increases in average ozone at warm temperatures could cause an increase in mortality and hospitalizations due to ozone.

### 3.1. Model sensitivity

The sensitivity of the results to a number of parameters was tested to understand how the system would behave under different ambient conditions. The sensitivity tests were run with the 24 °C temperature profile using the 24 °C emissions and the -4 °C temperature profile using the -7 °C emissions for both E85 and for gasoline. The average ozone concentration for E85 and gasoline were then compared with those from the baseline case (Fig. 4, Figs. S23–S26). We discuss the results for the 24 °C emissions here. The similar results for the -7 °C emissions are discussed in the supplemental material.

The first parameter tested was mixing height. Setting the box height to 300 m almost doubled the difference between E85 ozone and gasoline ozone, from 7.6 ppbv to 16.1 ppbv (Fig. 4). The difference in ozone dropped from 7.6 ppbv to 1.9 ppbv when the box height was set to 1km. The average ozone concentration for both gasoline and E85 decreased with the smaller box and increased with the larger box (Fig. S25). In all three cases, E85 still resulted in higher average ozone than did gasoline.

The water vapor concentration was kept constant during the model tests. The baseline water vapor concentration was 10 parts-per-thousand (ppth) and an increase to 20 ppth and a decrease to 5 ppth were both examined. Increasing the water vapor decreased the difference in ozone from 7.6 ppbv to 5 ppbv, and slightly increased the average ozone concentrations. Decreasing the water vapor increased the difference slightly, to 8.5 ppbv, and decreased the average ozone concentrations (Fig. S25).

The initial background conditions for the baseline case are set up to represent the conditions in the Los Angeles area (Table S17). To get an idea about how the results would differ for other urban areas, it is important to investigate the sensitivity of the results to NO<sub>x</sub> and non-methane organic gases (NMOGs) because these influence ozone formation.

First, a series of model runs examined the impact of changing the initial background levels of NO<sub>x</sub> (Fig. 4 and Fig. S25). The first two sensitivity tests changed the initial NO/NO<sub>2</sub> ratio from 50/50 to 40/60 and 60/40. There was little to no change in the difference in average ozone between these cases and the baseline case.

The next four NO<sub>x</sub> sensitivity tests involved changing the initial background concentration of NO<sub>x</sub> by +20%, +10%, -10%, and -20%. The NO/NO<sub>2</sub> ratio was 50/50 for these cases. Increasing initial NO<sub>x</sub> by 20% and 10% decreased the average ozone (Fig. S25) but did not change the difference in ozone between E85 and gasoline much from the baseline case (Fig. 4). The difference in ozone between E85 and gasoline decreased by 0.2 ppbv and 0.7 ppbv for the -10% and -20% cases, respectively, compared to the baseline difference, but the average ozone increased. This suggests the system is in the upper half of the ozone isopleth (Fig. S24), where decreases in NO<sub>x</sub> can actually increase ozone formation.

Four sensitivity cases were tested for the initial background concentrations of NMOGs: +20%, +10%, -10%, -20% (Fig. 4). Increasing initial NMOGs increases average ozone concentrations for both gasoline and E85 (Fig. S25). It also decreases the difference

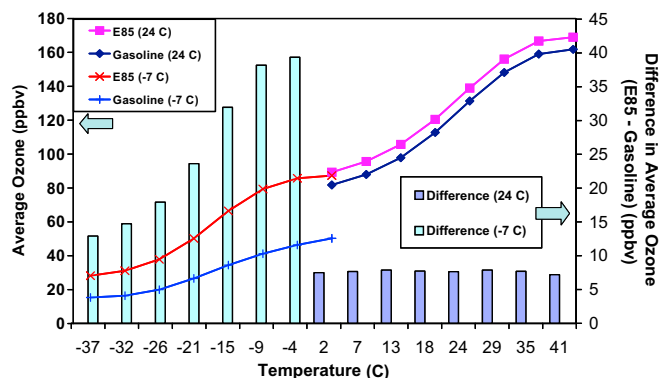
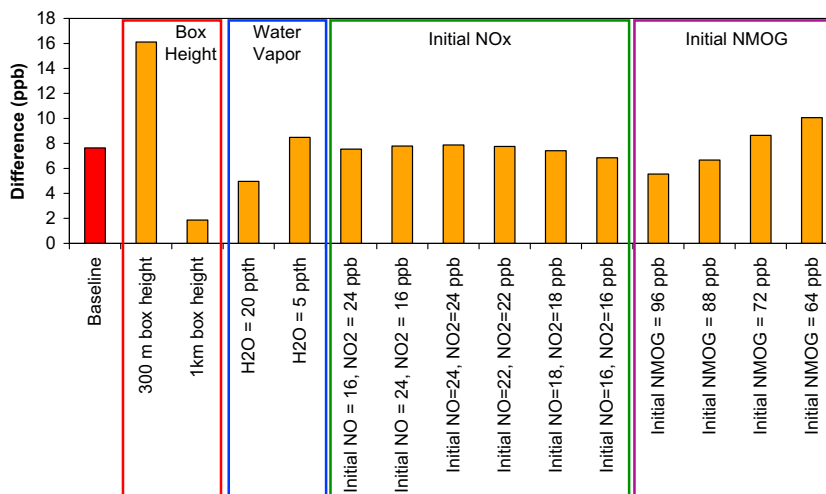


Fig. 3. Two day average ozone concentration from E85 and gasoline (left axis) and its difference (right axis) versus temperature using emission data at -7 °C and 24 °C.



**Fig. 4.** Difference in two day average ozone concentration (E85 – gasoline) to test the model's sensitivity to box height, water vapor, initial NO<sub>x</sub>, and initial NMOG, modeled at 24 °C using the 24 °C emissions set. Note: baseline has a box height of 500 m, H<sub>2</sub>O = 10 ppth, initial NO = 20 ppbv, initial NO<sub>2</sub> = 20 ppbv, initial NMOG = 80 ppbv.

between ozone for E85 and for gasoline by 2.1 ppbv and 0.9 ppbv for increases of 20% and 10%, respectively. When initial background concentrations of NMOGs were decreased, average ozone also decreased by as much as 41 ppbv. However, the difference in average ozone between E85 and gasoline increased compared to the baseline case. For these cases, the system is probably in the upper half of the ozone isopleth and therefore is sensitive to decreases in NMOGs.

The sensitivity to total background emissions, background emissions of NO<sub>x</sub>, and to toluene were also investigated (Fig. S27). Ozone concentrations were higher for E85 than for gasoline in all cases except for the case of no background emissions. Without background emissions, the average ozone concentration from gasoline was actually slightly (0.4 ppbv) higher than from E85. Changing the background emissions and the background NO<sub>x</sub> emissions by –20%, –10%, +10%, and +20% had similar results, where lower background emissions provided slightly higher average ozone concentrations and slightly smaller differences between E85 and gasoline, and the opposite was true with higher background emissions. Removing the initial background concentrations of toluene increased the difference in ozone concentration while doubling the toluene decreased the difference. This is not surprising because more toluene is emitted when gasoline is burned than with E85 and the MCM tends to over-predict ozone formation from toluene. Therefore, the bias of the model to predict higher-than-measured ozone for toluene actually makes the difference results more conservative because they increase gasoline average ozone more than they increase E85 average ozone. Removing the background emissions of toluene had very little impact on the average ozone results and only slight changes in the difference. More sensitivities are discussed in the supporting information.

#### 4. Conclusions

Ethanol use in vehicles is increasing worldwide. Here, we examined the potential impacts on urban air pollution of using E85 (85% ethanol, 15% gasoline) versus gasoline in vehicles under a variety of temperature profiles. We used four different vehicle emissions sets – two taken at 24 °C and two at –7 °C (one each for gasoline and E85) to model urban photochemistry and dilution alone in Los Angeles in 2020. In all cases, E85 emissions produced

higher average ozone concentrations than gasoline, from 7.2 ppbv to 39.4 ppbv. The E85 ozone increase was greater for cold temperatures, which could be a major concern with respect to hospitalizations and mortality resulting from ozone in cold areas using E85 although ozone levels are generally lower under cold-temperature than warm-temperature conditions. Formaldehyde, acetaldehyde, and PAN levels were all higher with E85 than gasoline and are also a concern for human health – formaldehyde and acetaldehyde as ozone precursors and possible carcinogens, and PAN as an eye and lung irritant.

We also investigated the sensitivity of the system to a variety of parameters, such as box size, background concentrations, and background emissions and in almost all cases ozone from E85 was still higher-than-gasoline. We have also shown that the MCM can be modeled with reasonable computer times in 3-D and we have examined the accuracy of the MCM versus smog chamber data, which showed an improvement in ozone prediction in all cases except for toluene. This likely led to the calculated ozone differences between E85 and gasoline to be more conservative because more toluene is emitted by gasoline than E85. In sum, the impact of biofuels, such as ethanol, on air pollution and urban health need to be considered before their use becomes more widespread.

#### Disclaimer

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#### Appendix. Supplementary information

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2009.12.024.

## References

- Anderson, L.G., 2009. Ethanol fuel use in Brazil: air quality impacts. *Energy & Environmental Science* 2, 1015–1037.
- de Assuncao, J.V., Pesquero, C.R., Bruns, R.E., Carvalho, L.R.F., 2005. Dioxins and furans in the atmosphere of Sao Paulo City, Brazil. *Chemosphere* 58 (10), 1391–1398.
- Baltaretu, C.O., Lichtman, E.I., Hadler, A.B., Elrod, M.J., 2009. Primary atmospheric oxidation mechanism for toluene. *Journal of Physical Chemistry* 113 (1), 221–230. doi:10.1021/jp806841t.
- Black, F. (1995–1997). Characterization of Alternative Fuel Vehicle Emissions Composition and Ozone Potential. EPA No. RW89936763. Annual Reports to the Department of Energy.
- Bloss, C., Wagner, V., Bonzanini, A., Jenkin, M.E., Wirtz, K., Martin-Reviejo, M., Pilling, M.J., 2005a. Evaluation of detailed aromatic mechanisms (MCMv3 and MCMv3.1) against environmental chamber data. *Atmospheric Chemistry and Physics* 5 (3), 623–639.
- Bloss, C., Wagner, V., Jenkin, M.E., Volkamer, R., Bloss, W.J., Lee, J.D., Heard, D.E., Wirtz, K., Martin-Reviejo, M., Rea, G., Wenger, J.C., Pilling, M.J., 2005b. Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons. *Atmospheric Chemistry and Physics* 5 (3), 641–664.
- CARB, 2008. California Environmental Protection Agency Air Resources Board Real-Time Query Tool AQ2MIS. <http://www.arb.ca.gov/aqmis2/paqdselect.php>.
- Carter, W.P.L., 2008. Development of an Improved Chemical Speciation Database for Processing Emissions of Volatile Organic Compounds for Air Quality Models. College of Engineering, Center for Environmental Research and Technology (CE-CERT), University of California, Riverside. <http://www.engr.ucr.edu/~carter/emitdb/>.
- Correa, S.M., Martins, E.M., Arbilla, G., 2003. Formaldehyde and acetaldehyde in a high traffic street of Rio de Janeiro, Brazil. *Atmospheric Environment* 37 (1), 23–29.
- Crutzen, P.J., Mosier, A.R., Smith, K.A., Winiwarter, W., 2008. N<sub>2</sub>O release from agro-biofuel production negates global warming reduction by replacing fossil fuels. *Atmospheric Chemistry and Physics* 8, 389–395.
- Delucchi, M.A. (2006). Lifecycle Analysis of Biofuels. ITS-Davis (Draft Manuscript).
- Fargione, J., Hill, J., Tilman, D., Polasky, S., Hawthorne, P., 2008. Land clearing and the biofuel carbon debt. *Science* 319 (5867), 1235–1238. doi:10.1126/science.1152747.
- Farrell, A.E., Plevin, R.J., Turner, B.T., Jones, A.D., O'Hare, M., Kammen, D.M., 2006. Ethanol can contribute to energy and environmental goals. *Science* 311, 506–507.
- Fornaro, A., Gutz, I.G.R., 2003. Wet deposition and related atmospheric chemistry in the Sao Paulo metropolis, Brazil: part 2 – contribution of formic and acetic acids. *Atmospheric Environment* 37 (1), 117–128.
- Gaffney, J.S., Marley, N.A., Martin, R.S., Dixon, R.W., Reyes, L.G., Popp, C.J., 1997. Potential air quality effects of using ethanol–gasoline fuel blends: a field study in Albuquerque, New Mexico. 31: 3053–3061.
- Gaffney, J.S., Marley, N.A., 1990. The search for clean alternative fuels: there's no such thing as a free lunch! *Atmospheric Environment*. Part A. General Topics 24.
- Gaffney, J.S., Marley, N.A., 2000. Alternative fuels. In: Brimblecombe, P., Maynard, R. (Eds.), *The Urban Air Atmosphere and its Effects*. Air Pollution Reviews, vol. 1. Imperial College Press, London, U.K., pp. 195–246.
- Gaffney, J.S., Marley, N.A., 2001. Comment on "Environmental implications on the oxygenation of gasoline with ethanol in the metropolitan area of Mexico City". *Environmental Science & Technology* 35 (24), 4957–4958.
- Gaffney, J.S., Marley, N.A., 2009. The impacts of combustion emissions on air quality and climate – from coal to biofuels and beyond. *Atmospheric Environment* 43 (1), 23–36.
- Gery, M.W., Whitten, G.Z., Killus, J.P., Dodge, M.C., 1989. A photochemical kinetics mechanism for urban and regional scale computer modeling. *Journal of Geophysical Research* 94, 12925–12956.
- Graham, L.A., Belisle, S.L., Baas, C.-L., 2008. Emissions from light duty gasoline vehicles operating on low blend ethanol gasoline and E85. *Atmospheric Environment* 42, 4498–4516.
- Grosjean, E., Rasmussen, R.A., Grosjean, D., 1998. Ambient levels of gas phase pollutants in Porto Alegre, Brazil. *Atmospheric Environment* 32 (20), 3371–3379.
- He, B.-Q., Shuai, S.-J., Wang, J.-X., He, H., 2003. The effect of ethanol blended diesel fuels on emissions from a diesel engine. *Atmospheric Environment* 37 (35), 4965–4971.
- Hess, P., Johnston, M., Brown-Steiner, B., Holloway, T., Andrade, J.B.d., Artaxo, P., 2009. Air quality issues associated with biofuel production and use. Biofuels: environmental consequences and interactions with changing land use. In: Howarth, R.W., Bringezu, S. (Eds.), *Proceedings of the Scientific Committee on Problems of the Environment (SCOPE) International Biofuels Project Rapid Assessment*, 22–25 September 2008, Gummiesbach, Germany. Cornell University, Ithaca, NY, USA, pp. 169–194.
- Hill, J., Polasky, S., Nelson, E., Tilman, D., Huo, H., Ludwig, L., Newmann, J., Zheng, H., Bonta, D., 2009. "Climate change and health costs of air emissions from biofuels and gasoline. *Proceedings of the National Academy of Sciences of the United States of America* 106 (6), 2077–2082. doi:10.1073/pnas.0812835106.
- Hynes, R.G., Angove, D.E., Saunders, S.M., Haverd, V., Azzi, M., 2005. Evaluation of two MCM v3.1 alkene mechanisms using indoor environmental chamber data. *Atmospheric Environment* 39, 7251–7262.
- Jacobson, M.Z., 1995. Computation of global photochemistry with SMVGEAR II. *Atmospheric Environment* 29 (18), 2541–2546.
- Jacobson, M.Z., 1998. Improvement of SMVGEAR II on vector and scalar machines through absolute error tolerance control. *Atmospheric Environment* 32 (4), 791–796.
- Jacobson, M.Z., 1999. *Fundamentals of Atmospheric Modeling*. Cambridge University Press, New York.
- Jacobson, M.Z., 2007a. Effects of ethanol (E85) versus gasoline vehicles on cancer and mortality in the United States. *Environmental Science & Technology* 41 (11), 4150–4157.
- Jacobson, M.Z., 2007b. Supplementary Information: Effects of Ethanol (E85) Versus Gasoline Vehicles on Carcinogenicity and Air Pollution in Los Angeles and the U.S. [http://www.stanford.edu/group/efmh/jacobson/es062085vsi20070219\\_033614.pdf](http://www.stanford.edu/group/efmh/jacobson/es062085vsi20070219_033614.pdf).
- Jacobson, M.Z., Ginnebaugh, D.L., The global-through-urban nested 3-D simulation of air pollution with a 13,600-reaction photochemical mechanism. *Journal of Geophysical Research*, in press.
- Jacobson, M.Z., Turco, R.P., 1994. SMVGEAR: a sparse-matrix, vectorized gear code for atmospheric models. *Atmospheric Environment* 28 (2), 273–284.
- Jenkin, M.E., Saunders, S.M., Pilling, M.J., 1997. The tropospheric degradation of volatile organic compounds: a protocol for mechanism development. *Atmospheric Environment* 31 (1), 81–104.
- Kammen, D.M., Farrell, A.E., Plevin, R.J., Jones, A.D., Nemet, G.F., Delucchi, M.A., 2008. Energy and Greenhouse Impacts of Biofuels: a Framework for Analysis. Paper UCB-ITS-TSRC-RR-2008-1. UC Berkeley Transportation Sustainability Research Center.
- Knapp, K.T., Stump, F.D., Tejada, S.B., 1998. The effect of ethanol fuel on the emissions of vehicles over a wide range of temperatures. *Journal of the Air & Waste Management Association* 48 (7), 646–653.
- Liang, J., Jacobson, M.Z., 2000. Comparison of a 4000-reaction chemical mechanism with the carbon bond IV and an adjusted carbon bond IV-EX mechanism using SMVGEAR II. *Atmospheric Environment* 34 (18), 3015–3026.
- MacLean, H.L., Lave, L.B., 2000. Environmental implications of alternative-fueled automobiles: air quality and greenhouse gas tradeoffs. *Environmental Science & Technology* 34 (2), 225–231. doi:10.1021/es9905290.
- Martins, E.M., Arbilla, G., 2003. Computer modeling study of ethanol and aldehyde reactivities in Rio de Janeiro urban air. *Atmospheric Environment* 37 (13), 1715–1722.
- MCM, 2002. Master Chemical Mechanism, vol. 3.1. University of Leeds. <http://mcm.leeds.ac.uk/MCM/home.htm>.
- Patzek, T.W., 2006. The Real Biofuel Cycles. <http://petroleum.berkeley.edu/patzek/BiofuelQA/Materials/RealFuelCycles-Web.pdf>.
- Searchinger, T., Heimlich, R., Houghton, R.A., Dong, F., Elobeid, A., Fabiosa, J., Tokgoz, S., Hayes, D., Yu, T.-H., 2008. Use of U.S. croplands for biofuels increases greenhouse gases through emissions from land-use change. 319: 1238–1240.
- Tanner, R.L., Miguel, A.H., De Andrade, J.B., Gaffney, J.S., Streit, G.E., 2002. Atmospheric chemistry of aldehydes: enhanced peroxyacetyl nitrate formation from ethanol-fueled vehicular emissions. *Environmental Science & Technology* 22 (9), 1026–1034.
- Tilman, D., Hill, J., Lehman, C., 2006. Carbon-negative biofuels from low-input high-diversity grassland biomass. 314: 1598–1600.
- USEPA, 2000. Diurnal Profile File for CAIR – Emissions Modeling Clearinghouse Temporal Allocation. <http://www.epa.gov/ttn/chief/emch/temporal/>.
- Wagner, V., Jenkin, M.E., Saunders, S.M., Stanton, J., Wirtz, K., Pilling, M.J., 2002. Modelling of the photooxidation of toluene: conceptual ideas for validating detailed mechanisms. *Atmospheric Chemistry and Physics Discussions* 2, 1217–1259.
- Wallner, T., Miers, S.A., McConnell, S., 2009. A comparison of ethanol and butanol as oxygenates using a direct-injection, spark-ignition engine. *Journal of Engineering for Gas Turbines and Power* 131 (3), 032802–032809.
- West, B.H., López, A.J., Theiss, T.J., Graves, R.L., Storey, J.M., Lewis, S.A., 2007. Fuel Economy and Emissions of the Ethanol-Optimized Saab 9–5 Biopower. 2007-01-3994. Oak Ridge National Laboratory.
- Westerholm, R., Ahlvik, P., Karlsson, H.L., 2008. An Exhaust Characterisation Study Based on Regulated and Unregulated Tailpipe and Evaporative Emissions from Bi-fuel and Flex-fuel Light-duty Passenger Cars Fuelled by Petrol (E5), Bio-ethanol (E70, E85) and Biogas Tested at Ambient Temperatures of +22 °C and –7 °C. Swedish Road Administration.
- Whitney, K., Fernandez, T., 2007. Characterization of Cold Temperature VOC and PM Emissions from Flex Fuel Vehicles Operating on Ethanol Blends. 17th CRC On-Road vehicle Emissions Workshop.
- Whitten, G.Z., 1998. Comment on "Potential air quality effects of using ethanol/gasoline fuel blends: a field study in Albuquerque, New Mexico". *Environmental Science & Technology* 32 (23), 3840–3841.