Supporting Information

Examining the impacts of ethanol (E85) versus gasoline photochemical production of smog in a fog using near-explicit gas- and aqueous-chemistry mechanisms

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Summary
The supporting information document includes 1) a detailed description of the model used for this study, 2) additional model setup information including the tables of emissions, 3) discussion of the time-series results not included in the main paper, and 4) more sensitivity results.

1. Model Description

This air pollution box model combines a near-explicit chemical mechanism with a sparse-matrix ordinary differential equation solver.

1A. Gas-Phase Chemical Mechanism

Master Chemical Mechanism version 3.1 (MCM)

The Master Chemical Mechanism (MCM) version 3.1 was chosen for this study because it is a near-explicit chemical mechanism that has been evaluated previously. MCM v. 3.1 (updated 2005) describes the tropospheric degradation of 135 commonly-emitted volatile organic compounds (VOCs) (Jenkin et al. 1997; MCM 2002; Jenkin et al. 2003; Saunders et al. 2003; Bloss et al. 2005b). It currently incorporates over 13,500 chemical reactions and over 4,600 species.

A number of studies have looked at the accuracy of the MCM v. 3 and v. 3.1 by comparing the model results with smog chamber data, including for the species examined here (Wagner et al. 2002; Bloss et al. 2005a; Bloss et al. 2005b; Hynes et al. 2005; Pinho et al. 2005; Pinho et al. 2006a; Pinho et al. 2006b; Pinho et al. 2007). The mechanism has also been used in a number of field studies, often in conjunction with a photochemical trajectory model (PTM), to assess ozone formation in the atmosphere (Derwent et al. 2003; Derwent et al. 2005; Derwent et al. 2007; Evtyugina et al. 2007) and to look at secondary organic aerosol formation (Jenkin 2004; Johnson et al. 2004; 2005; Johnson et al. 2006a; Johnson et al. 2006b). The uncertainties associated with the MCM have also been investigated (Zador et al. 2005).

1B. Aqueous-Phase Chemical Mechanism

Chemical Aqueous Phase Radical Mechanism version 3.0i (CAPRAM)

Chemical Aqueous Phase Radical Mechanism (CAPRAM) is a chemical mechanism that includes the aqueous reactions of inorganic and organic species that are present in the atmosphere. It is available on the internet: http://projects.tropos.de/capram/. CAPRAM 3.0i has been expanded from version 2.4 (Ervens et al. 2003) to include organic species with two to six carbon atoms (Herrmann et al. 2005). The original CAPRAM was developed in 1999 to work in conjunction with RADM2 to provide a more detailed mechanism that included aqueous reactions (Herrmann et al. 1999). Today's CAPRAM 3.0i is coupled with RACM by the authors for a mechanism that deals with gas-phase and aqueous-phase reactions (Herrmann et al. 2005). We coupled CAPRAM 3.0i with MCM v. 3.1 instead of RACM because MCM is a more complete gas-phase chemistry mechanism and our ODE solver, SMVGEAR, is efficient enough to make it practical to use two large mechanisms.

CAPRAM 3.0i has the aqueous phase chemical reactions for 34 species – 13 monocarboxylic and dicarboxylic acids, 10 carbonyl compounds, 5 alcohols, 4 polyfunctional compounds, 1 ester and 1 heterocyclic compound (Tilgner and Herrmann 2007). It treats the aqueous chemistry among 390 species and 829 reactions, including 51 gas-to-aqueous phase reactions. One of the interesting results found by Hermann et al. (2005) was that the degradation of aldehydes and ketone in both the gas-phase and the aqueous-phase forms monocarboxylic and dicarboxylic compounds which build up in the aqueous phase. These results, and others, were not apparent with the previous version of CAPRAM because the chemicals dealt with in the aqueous phase were not extensive enough (Herrmann et al. 2005). CAPRAM is the most extensive aqueous phase mechanism available (Pilling 2007) and is therefore ideal for our study.

1C. Ordinary Differential Equation Solver

Sparse-Matrix Vectorized Gear Solver (SMVGEAR II)

To solve the large set of chemical equations in the MCM, we use SMVGEAR II, a sparse-matrix ordinary differential equation (ODE) solver (Jacobson and Turco 1994; Jacobson 1995; 1998). It was chosen for several reasons. First, it uses the Gear solution mechanism, which is considered a benchmark for accuracy. Second, it uses a sparse-matrix technique during matrix decomposition and backsubstitution that dramatically decreases the run times. Jacobson (1995; 1998) also describes other measures that SMVGEAR employs to decrease run time for 3D modeling, including grouping and reordering of cells. The speed of the ODE solver is very important for allowing a large mechanism such as MCM and CAPRAM to be used in urban, regional, and global 3-D models.

2. Model Setup for E85 versus Gasoline Comparisons

In this section, the setup of the box model for comparing the effect of E85 versus gasoline is described. Since the emissions data were based on data from Jacobson's study (2007), summarized in Table S1, the first step was to determine the emissions from gasoline and E85 with more explicit treatment than has been used previously. To do this, we used data from Black (1995-1997), which gives the speciated exhaust emissions for reformulated gasoline (RFG) in a Ford Taurus and for ethanol (E85) in a Ford Lumina Flex Fuel Vehicle (FFV) during the first 124 seconds of cold start. The data are summarized in Table S2.

We assumed that the speciation during a cold start is similar to that during the whole vehicle cycle, but the emission amounts differ because larger amounts of unburned emissions occur during cold start than during the whole driving cycle. The actual emissions are based on emissions data for current gasoline vehicles for the South Coast Air Basin (SCAB), moved forward to the year 2020, shown in Table S1. We assume that all of the vehicles change from gasoline to E85. The results can then be applied proportionally to any situation where a change is being made from gasoline to E85.

To start separating the emissions data from Table S1 into more explicit species, we first used the Black emissions data for RFG and E85 to determine the percent of total organic gases (TOG) for each emitted species in the Black data, shown in Table S2. Unfortunately, there were many species measured whose chemical nature was not discernable. These species were lumped together and assumed to be unreactive. There were also some species in the Black data not included in the MCM, but this was a small fraction of the total amount of species in the emissions. Even though the MCM is a near-explicit chemical mechanism, it does not describe the degradation of all organic species (that would be impractical) – it concentrates on commonly-emitted species. For the ethanol (E85) emissions, the known species from Black's data that also existed in the MCM made up a large portion (over 95%) of the TOG measured. For RFG, the known species from the data that were in the MCM made up about 75% of the TOG measured. To include more of the known species in the MCM model, information about the reactivity of species from Carter's carbon bond mechanism was used (Carter 2008).

		Emissions Data (tonnes/yr)		
Species	**In Model**	**Gasoline**	**% Change**	**E-85 Replacing All Gasoline**
CO	CO	782,000	5%	821,100
NOx		68,900	-30%	48,230
NO2	NO2	62,010		43,407
NO	NO	6,201		4,341
Methane	CH4	8,530	43%	12,198
Ethane	C2H6	1,220	0%	1,220
Propane	C3H8	465	-65%	163
Paraffin bond group	PAR	44,720	-80%	8,944
Ethene	C2H4	3,570	-17%	2,963
Propene	C3H6	988	-65%	346
1,3 Butadiene	C4H6	1,390	-10%	1,251
Olefin bond group	OLE	949	-17%	788
Methanol	CH3OH	-	0%	-
Ethanol	C2H5OH	-	0%	69,800
Formaldehyde	HCHO	650	60%	1,040
Acetaldehyde		232	2000%	4,872
Higher Aldehydes		3,460	-60%	1,384
Acetaldehyde plus higher	CH3CHO	3,692	1940%	6,256
Formic Acid		-	0%	-
Acetic acid		-	0%	-
Acetone		-	0%	-
Benzene	C6H6	1,270	-79%	267
Toluene bond group	TOL	6,260	-80%	1,252
Xylene bond group	XYL	11,600	-80%	2,320
Isoprene bond group	ISOP	65	-80%	13
Unreactive		4,540	-80%	908
Total organic gas		89,909		109,728

Table S1: Emissions Data for Gasoline and E85 (Jacobson 2007)

Note: The gasoline emissions data was brought forward to the year 2020 by calculating it as 40% of the 2002 emissions for the South Coast Air Basin, (EPA 2006; Jacobson 2007). The percent change between gasoline and E85 (where a positive change means an increase in emissions for E85) are compiled results of 12 different studies on emissions from E85 (Jacobson 2007).

Compound	Taurus RFG (ppmC)	Lumina FFV E85 (ppmC)	Taurus RFG (% of total NMOG)	Lumina FFV E85 (% of total NMOG)	**Taurus RFG (% of TOG)**	**Lumina FFV E85 (% of TOG)**	MCM species name
NMOG							
Alkanes	33.446	13.222	37%	10%	**35%**	**9%**	
Alkenes	17.281	15.07	19%	12%	**18%**	**11%**	
Aromatics	29.666	7.929	33%	6%	**31%**	**6%**	
Alkynes	3.588	2.142	4%	2%	**4%**	**1%**	
Unknowns	0.338	0.077	0%	0%	**0%**	**0%**	
Alcohols/Ethers	3.627	74.956	4%	59%	**4%**	**52%**	
Aldehydes/Ketones	2.683	14.414	3%	11%	**3%**	**10%**	
Total NMOG	**90.628**	**127.81**	100%	100%	**95%**	**89%**	
Methane	**5.025**	**15.708**			**5%**	**11%**	
CO	**393.7**	**510.117**					
TOG	**95.653**	**143.518**			**100%**	**100%**	
TOG in MCM	71.816	136.447			**75.08%**	**95.07%**	
TOG not in MCM	23.837	7.071					
Methane	5.025	15.708			**5.25%**	**10.94%**	**CH4**
Ethylene (ethene)	4.991	10.799	5.51%	8.45%	**5.22%**	**7.52%**	**C2H4**
Ethane	1.26	2.255	1.39%	1.76%	**1.32%**	**1.57%**	**C2H6**
Acetylene	3.103	1.936	3.42%	1.51%	**3.24%**	**1.35%**	**C2H2**
Propylene	3.284	1.046	3.62%	0.82%	**3.43%**	**0.73%**	**C3H6**
Iso-butane	0.022	0.02	0.02%	0.02%	**0.02%**	**0.01%**	**IC4H10**
1-Butene	0	0.294	0.00%	0.23%	**0.00%**	**0.20%**	**BUT1ENE**
Iso-Butylene	4.313	0.548	4.76%	0.43%	**4.51%**	**0.38%**	**MEPROPENE**
1,3 Butadiene	0.507	0.067	0.56%	0.05%	**0.53%**	**0.05%**	**C4H6**
N-Butane	0.338	0.969	0.37%	0.76%	**0.35%**	**0.68%**	**NC4H10**
Trans-2-Butene	0.335	0.156	0.37%	0.12%	**0.35%**	**0.11%**	**TBUT2ENE**
Cis-2-Butene	0.246	0.681	0.27%	0.53%	**0.26%**	**0.47%**	**CBUT2ENE**
3-Methyl-1-Butene	0.114	0.03	0.13%	0.02%	**0.12%**	**0.02%**	**ME3BUT1ENE**
Iso-Pentane	4.658	1.434	5.14%	1.12%	**4.87%**	**1.00%**	**IC5H12**
1-Pentene	0.135	0.044	0.15%	0.03%	**0.14%**	**0.03%**	**PENT1ENE**
2-Methyl-1-butene	0.203	0.067	0.22%	0.05%	**0.21%**	**0.05%**	**ME2BUT1ENE**
N-pentane	0.817	0.639	0.90%	0.50%	**0.85%**	**0.45%**	**NC5H12**
C5H8 TOTAL	0.147	0.044	0.16%	0.03%	**0.15%**	**0.05%**	**C5H8**
isoprene	0.122	0.022	0.13%	0.02%	**0.13%**	**0.03%**	
C5H8	0.01	0.006	0.01%	0.00%	**0.01%**	**0.00%**	
c5h8	0.015	0.016	0.02%	0.01%	**0.02%**	**0.01%**	
trans-2-pentene	0.235	0.064	0.26%	0.05%	**0.25%**	**0.04%**	**TPENT2ENE**
cis-2-pentene	0.123	0.037	0.14%	0.03%	**0.13%**	**0.03%**	**CPENT2ENE**
2-methyl-2-butene	0.103	0.063	0.11%	0.05%	**0.11%**	**0.04%**	**ME2BUT2ENE**
2,2-dimethylbutane	0.307	0.111	0.34%	0.09%	**0.32%**	**0.08%**	**M22C4**
2,3-dimethylbutane	0.882	0.28	0.97%	0.22%	**0.92%**	**0.20%**	**M23C4**
2-methylpentane	2.179	0.766	2.40%	0.60%	**2.28%**	**0.53%**	**M2PE**
3-methylpentane	1.252	0.353	1.38%	0.28%	**1.31%**	**0.25%**	**M3PE**
1-Hexene	0.081	0.036	0.09%	0.03%	**0.08%**	**0.03%**	**HEX1ENE**
N-Hexane	0.64	0.386	0.71%	0.30%	**0.67%**	**0.27%**	**NC6H14**
trans-2-hexene	0.104	0.039	0.11%	0.03%	**0.11%**	**0.03%**	**THEX2ENE**
cis-2-hexene	0.049	0.019	0.05%	0.01%	**0.05%**	**0.01%**	**CHEX2ENE**
2,3-dimethyl-2-butene	0.028	0.009	0.03%	0.01%	**0.03%**	**0.01%**	**DM23BU2ENE**
benzene	3.229	1.071	3.56%	0.84%	**3.38%**	**0.75%**	**BENZENE**
cyclohexane	0	0.023	0.00%	0.02%	**0.00%**	**0.02%**	**CHEX**
2-methylhexane	1.065	0.233	1.18%	0.18%	**1.11%**	**0.16%**	**M2HEX**
3-methylhexane	1.146	0.251	1.26%	0.20%	**1.20%**	**0.17%**	**M3HEX**
n-heptane	0.668	0.165	0.74%	0.13%	**0.70%**	**0.11%**	**NC7H16**
toluene	7.688	2.273	8.48%	1.78%	**8.04%**	**1.58%**	**TOLUENE**
n-octane	0.276	0.091	0.30%	0.07%	**0.29%**	**0.06%**	**NC8H18**
ethylbenzene	2.412	0.731	2.66%	0.57%	**2.52%**	**0.51%**	**EBENZ**
M&P-Xylene	5.868	1.621	6.47%	1.27%	**6.13%**	**1.13%**	**MXYL, PXYL**
styrene	0.455	0.079	0.50%	0.06%	**0.48%**	**0.06%**	**STYRENE**
o-xylene	2.15	0.518	2.37%	0.41%	**2.25%**	**0.36%**	**OXYL**
n-nonane	0.105	0.023	0.12%	0.02%	**0.11%**	**0.02%**	**NC9H20**
isopropylbenzene	0.108	0.031	0.12%	0.02%	**0.11%**	**0.02%**	**IPBENZ**
n-propylbenzene	0.386	0.066	0.43%	0.05%	**0.40%**	**0.05%**	**PBENZ**
1-methyl-3-ethylbenzene	1.474	0.298	1.63%	0.23%	**1.54%**	**0.21%**	**METHTOL**
1-methyl-4-ethylbenzene	0.661	0.131	0.73%	0.10%	**0.69%**	**0.09%**	**PETHTOL**
1,3,5-trimethylbenzene	0.739	0.193	0.82%	0.15%	**0.77%**	**0.13%**	**TM135B**
1-methyl-2-ethylbenzene	0.476	0.094	0.53%	0.07%	**0.50%**	**0.07%**	**OETHTOL**
1,2,4-trimethylbenzene	1.658	0.337	1.83%	0.26%	**1.73%**	**0.23%**	**TM124B**
n-decane	0.037	0.007	0.04%	0.01%	**0.04%**	**0.00%**	**NC10H22**
1,2,3-trimethylbenzene	0.008	0.063	0.01%	0.05%	**0.01%**	**0.04%**	**TM123B**
1,3-dimethyl-5-ethylbenzene	0.056	0.002	0.06%	0.00%	**0.06%**	**0.00%**	**DIME35EB**
n-undecane	0.012	0.004	0.01%	0.00%	**0.01%**	**0.00%**	**NC11H24**
n-dodecane	0.007	0.001	0.01%	0.00%	**0.01%**	**0.00%**	**NC12H26**
mtbe	3.06	0.922	3.38%	0.72%	**3.20%**	**0.64%**	**MTBE**

Compound (continued)	Taurus RFG (ppmC)	Lumina FFV E85 (ppmC)	Taurus RFG (% of total NMOG)	Lumina FFV E85 (% of total NMOG)	**Taurus RFG (% of TOG)**	**Lumina FFV E85 (% of TOG)**	MCM species name
methanol	0.229	6.684	0.25%	5.23%	**0.24%**	**4.66%**	**CH3OH**
ethanol	0.026	67.309	0.03%	52.66%	**0.03%**	**46.90%**	**C2H5OH**
2-propanol	0.312	0.04	0.34%	0.03%	**0.33%**	**0.03%**	**IPROPOL**
formaldehyde	0.605	1.528	0.67%	1.20%	**0.63%**	**1.06%**	**HCHO**
acetaldehyde	0.389	12.447	0.43%	9.74%	**0.41%**	**8.67%**	**CH3CHO**
acetone	0.461	0.121	0.51%	0.09%	**0.48%**	**0.08%**	**CH3COCH3**
propionaldehyde	0.095	0.064	0.10%	0.05%	**0.10%**	**0.04%**	**C2H5CHO**
butyraldehyde	0.063	0	0.07%	0.00%	**0.07%**	**0.00%**	**C3H7CHO**
benzaldehyde	0.255	0.088	0.28%	0.07%	**0.27%**	**0.06%**	**BENZAL**
x-butyraldehyde	0.044	0	0.05%	0.00%	**0.05%**	**0.00%**	**IPRCHO**
x-valeraldehyde	0.047	0.007	0.05%	0.01%	**0.05%**	**0.00%**	**C4H9CHO**
2-butanone	0.065	0.031	0.07%	0.02%	**0.07%**	**0.02%**	**MEK**
2,4-dimethylpentane	1.374	0.416	1.52%	0.33%	**1.44%**	**0.29%**	
2,3-dimethylpentane	2.844	0.74	3.14%	0.58%	**2.97%**	**0.52%**	
iso-octane	5.026	1.561	5.55%	1.22%	**5.25%**	**1.09%**	
methylcyclopentane	0.54	0.193	0.60%	0.15%	**0.56%**	**0.13%**	
2,3,4-trimethylpentane	1.459	0.4	1.61%	0.31%	**1.53%**	**0.28%**	
Propadiene	0.055	0.019	0.06%	0.01%	**0.06%**	**0.01%**	
Methylacetylene	0.29	0.038	0.32%	0.03%	**0.30%**	**0.03%**	
1-Buten-3-yne	0.126	0	0.14%	0.00%	**0.13%**	**0.00%**	
1-Butyne	0.021	0.105	0.02%	0.08%	**0.02%**	**0.07%**	
1,3-Butadiyne	0.028	0.003	0.03%	0.00%	**0.03%**	**0.00%**	
1,2-Butadiene	0.024	0.002	0.03%	0.00%	**0.03%**	**0.00%**	
1,4-Pentadiene	0.006	0.118	0.01%	0.09%	**0.01%**	**0.08%**	
2-Butyne	0.013	0.057	0.01%	0.04%	**0.01%**	**0.04%**	
2-Methyl-1-buten-3-yne	0.008	0.003	0.01%	0.00%	**0.01%**	**0.00%**	
3,3-dimethyl-1-butene	0.015	0.009	0.02%	0.01%	**0.02%**	**0.01%**	
trans-1,3-pentadiene	0.034	0.008	0.04%	0.01%	**0.04%**	**0.01%**	
cyclopentadiene	0.003	0.005	0.00%	0.00%	**0.00%**	**0.00%**	
cis-1,3-pentadiene	0.002	0.018	0.00%	0.01%	**0.00%**	**0.01%**	
cyclopentene	0.048	0.035	0.05%	0.03%	**0.05%**	**0.02%**	
3-methyl-1-pentene	0.167	0.065	0.18%	0.05%	**0.17%**	**0.05%**	
cyclopentane	0.072	0.043	0.08%	0.03%	**0.08%**	**0.03%**	
4-methyl-cis-2-pentene	0	0.007	0.00%	0.01%	**0.00%**	**0.00%**	
4-methyl-trans-2-pentene	0.104	0.043	0.11%	0.03%	**0.11%**	**0.03%**	
2-methyl-1-pentene	0.05	0.022	0.06%	0.02%	**0.05%**	**0.02%**	
2-Ethyl-1-Butene	0.002	0.001	0.00%	0.00%	**0.00%**	**0.00%**	
Cis-3-hexene	0.05	0.018	0.06%	0.01%	**0.05%**	**0.01%**	
trans-3-hexene	0.013	0.004	0.01%	0.00%	**0.01%**	**0.00%**	
2-methyl-2-pentene	0.056	0.034	0.06%	0.03%	**0.06%**	**0.02%**	
3-methylcyclopentene	0.034	0.014	0.04%	0.01%	**0.04%**	**0.01%**	
cis-3-methyl-2-pentene	0.035	0.021	0.04%	0.02%	**0.04%**	**0.01%**	
4-methylcyclopentene	0.018	0.009	0.02%	0.01%	**0.02%**	**0.01%**	
trans-3-methyl-2-pentene	0.053	0.031	0.06%	0.02%	**0.06%**	**0.02%**	
2,2-dimethylpentane	0.087	0.021	0.10%	0.02%	**0.09%**	**0.01%**	
2,2,3-trimethylbutane	0.041	0.023	0.05%	0.02%	**0.04%**	**0.02%**	
2,4-dimethyl-1-pentene	0.034	0.01	0.04%	0.01%	**0.04%**	**0.01%**	
1-methylcyclopentene	0.037	0.029	0.04%	0.02%	**0.04%**	**0.02%**	
4,4-dimethyl-2-pentene	0.056	0.018	0.06%	0.01%	**0.06%**	**0.01%**	
3,3-dimethylpentane	0.092	0.02	0.10%	0.02%	**0.10%**	**0.01%**	
trans-2-methyl-3-hexene	0.029	0.005	0.03%	0.00%	**0.03%**	**0.00%**	
4-methyl-1-hexene	0.019	0.006	0.02%	0.00%	**0.02%**	**0.00%**	
1,1-dimethylcyclopentane	0.039	0.024	0.04%	0.02%	**0.04%**	**0.02%**	
trans-5-methyl-2-hexene	0.024	0.008	0.03%	0.01%	**0.03%**	**0.01%**	
cis-1,3-dimethylcyclopentane	0.167	0.041	0.18%	0.03%	**0.17%**	**0.03%**	
trans-1,3-dimethylcyclopentane	0.282	0.067	0.31%	0.05%	**0.29%**	**0.05%**	
3-methyl-trans-3-hexene	0.013	0.006	0.01%	0.00%	**0.01%**	**0.00%**	
trans-3-heptene	0.042	0.014	0.05%	0.01%	**0.04%**	**0.01%**	
cis-3-methyl-3-hexene	0.097	0.037	0.11%	0.03%	**0.10%**	**0.03%**	
trans-2-heptene	0.042	0.014	0.05%	0.01%	**0.04%**	**0.01%**	
3-ethyl-2-pentene	0.041	0.007	0.05%	0.01%	**0.04%**	**0.00%**	
2-methyl-2-hexene	0.034	0.029	0.04%	0.02%	**0.04%**	**0.02%**	
1,5-dimethylcycleopentene	0.049	0.021	0.05%	0.02%	**0.05%**	**0.01%**	
2,3-dimethyl-2-pentene	0.014	0.001	0.02%	0.00%	**0.01%**	**0.00%**	
3-ethyl cyclopentene	0.006	0.003	0.01%	0.00%	**0.01%**	**0.00%**	
4-ethyl cyclopentene	0.01	0.004	0.01%	0.00%	**0.01%**	**0.00%**	
1-cis-2-dimethylcyclopentane	0.104	0.033	0.11%	0.03%	**0.11%**	**0.02%**	
methylcyclohexane	0.217	0.068	0.24%	0.05%	**0.23%**	**0.05%**	
1,1,3-trimethylcyclopentane	0.02	0.011	0.02%	0.01%	**0.02%**	**0.01%**	
2,5-dimethylhexane	0.4	0.124	0.44%	0.10%	**0.42%**	**0.09%**	
2,4-dimethylhexane	0.757	0.196	0.84%	0.15%	**0.79%**	**0.14%**	c8h18
2,2,3-trimethylpentane	0.008	0.036	0.01%	0.03%	**0.01%**	**0.03%**	
3-methylcyclohexene	0.015	0.007	0.02%	0.01%	**0.02%**	**0.00%**	
4-methylcyclohexene	0.005	0.003	0.01%	0.00%	**0.01%**	**0.00%**	
1,2,4-trimethylcyclopentane	0.073	0.027	0.08%	0.02%	**0.08%**	**0.02%**	
c,t,c-1,2,3-trimethylcyclopentane	0.025	0.01	0.03%	0.01%	**0.03%**	**0.01%**	
1-ethylcyclopentene	0	0.008	0.00%	0.01%	**0.00%**	**0.01%**	

Compound (continued)	Taurus RFG (ppmC)	Lumina FFV E85 (ppmC)	Taurus RFG (% of total NMOG)	Lumina FFV E85 (% of total NMOG)	**Taurus RFG (% of TOG)**	**Lumina FFV E85 (% of TOG)**	MCM species name
2,3-dimethylhexane	0.502	0.149	0.55%	0.12%	**0.52%**	**0.10%**	c8h18
2-methylheptane	0.339	0.111	0.37%	0.09%	**0.35%**	**0.08%**	
4-methylheptane	0.158	0.055	0.17%	0.04%	**0.17%**	**0.04%**	
3,4-dimethylhexane	0.129	0.046	0.14%	0.04%	**0.13%**	**0.03%**	
3-methylheptane	0.383	0.127	0.42%	0.10%	**0.40%**	**0.09%**	
3-ethylhexane	0.074	0.027	0.08%	0.02%	**0.08%**	**0.02%**	
1,2,4-trimethylcyclopentane	0.031	0.01	0.03%	0.01%	**0.03%**	**0.01%**	
trans-1,4-dimethylcyclohexane	0.089	0.022	0.10%	0.02%	**0.09%**	**0.02%**	
2,2,5-trimethylhexane	0.551	0.205	0.61%	0.16%	**0.58%**	**0.14%**	C9H20
1-octene	0.022	0.01	0.02%	0.01%	**0.02%**	**0.01%**	
trans-1-ethyl-3-methylcyclopentane	0.009	0.002	0.01%	0.00%	**0.01%**	**0.00%**	
cis-1-ethyl-3-methylcyclopentane	0.056	0.016	0.06%	0.01%	**0.06%**	**0.01%**	
1,1,2-trimethylcyclopentane	0.021	0.007	0.02%	0.01%	**0.02%**	**0.00%**	
1,2,3-trimethylcyclopentane	0.017	0.006	0.02%	0.00%	**0.02%**	**0.00%**	
2-octene	0	0.003	0.00%	0.00%	**0.00%**	**0.00%**	
isopropylcyclopentane	0.091	0.011	0.10%	0.01%	**0.10%**	**0.01%**	
2,3,5-trimethylhexane	0.107	0.04	0.12%	0.03%	**0.11%**	**0.03%**	
2,4-dimethylheptane	0.063	0.018	0.07%	0.01%	**0.07%**	**0.01%**	
2,6-dimethylheptane	0.067	0.019	0.07%	0.01%	**0.07%**	**0.01%**	
2,5-dimethylheptane	0.14	0.04	0.15%	0.03%	**0.15%**	**0.03%**	
3,5-dimethylheptane	0.064	0.021	0.07%	0.02%	**0.07%**	**0.01%**	
1,1,4-trimethylcyclohexane	0.009	0	0.01%	0.00%	**0.01%**	**0.00%**	
3,4-dimethylheptane	0.069	0.017	0.08%	0.01%	**0.07%**	**0.01%**	
3-methyloctane	0.179	0.045	0.20%	0.04%	**0.19%**	**0.03%**	
1-nonene	0	0.007	0.00%	0.01%	**0.00%**	**0.00%**	
n-butylcyclopentane	0	0.001	0.00%	0.00%	**0.00%**	**0.00%**	
o-methylstyrene	0.172	0.021	0.19%	0.02%	**0.18%**	**0.01%**	
2-methylpropylbenzene	0.034	0.008	0.04%	0.01%	**0.04%**	**0.01%**	
1-methylprobylbenzene	0.023	0.007	0.03%	0.01%	**0.02%**	**0.00%**	
1-methyl-3-isopropylbenzene	0.038	0.009	0.04%	0.01%	**0.04%**	**0.01%**	
p-methylstyrene	0.223	0	0.25%	0.00%	**0.23%**	**0.00%**	
2,3-dihydroindene(indan)	0.081	0.043	0.09%	0.03%	**0.08%**	**0.03%**	
1,3-diethylbenzene	0.15	0.04	0.17%	0.03%	**0.16%**	**0.03%**	
1-methyl-3-n-propylbenzene	0.33	0.034	0.36%	0.03%	**0.34%**	**0.02%**	
1,2-diethylbenzene	0.055	0.069	0.06%	0.05%	**0.06%**	**0.05%**	
1-methyl-2-n-propylbenzene	0.006	0.011	0.01%	0.01%	**0.01%**	**0.01%**	
1,4-dimethyl-2-ethylbenzene	0.059	0	0.07%	0.00%	**0.06%**	**0.00%**	
1,3-dimethyl-4-ethylbenzene	0.09	0.02	0.10%	0.02%	**0.09%**	**0.01%**	
1,2-dimethyl-4-ethylbenzene	0.116	0.02	0.13%	0.02%	**0.12%**	**0.01%**	
o-ethylstyrene	0.065	0.001	0.07%	0.00%	**0.07%**	**0.00%**	
1,3-dimethyl-2-ethylbenzene	0.051	0.035	0.06%	0.03%	**0.05%**	**0.02%**	
m-ethylstyrene	0.073	0	0.08%	0.00%	**0.08%**	**0.00%**	
1,2-dimethyl-3-ethylbenzene	0.005	0.006	0.01%	0.00%	**0.01%**	**0.00%**	
1,2,4,5-tetramethylbenzene	0.095	0.011	0.10%	0.01%	**0.10%**	**0.01%**	
1,2,3,5-tetramethylbenzene	0.025	0.016	0.03%	0.01%	**0.03%**	**0.01%**	
1-methyl-1h-idene	0.039	0	0.04%	0.00%	**0.04%**	**0.00%**	
naphthalene	0.135	0.021	0.15%	0.02%	**0.14%**	**0.01%**	
acrolein	0.04	0.013	0.04%	0.01%	**0.04%**	**0.01%**	
crotonaldehyde	0.022	0	0.02%	0.00%	**0.02%**	**0.00%**	
o-tolualdehyde	0.076	0	0.08%	0.00%	**0.08%**	**0.00%**	
m-tolualdehyde	0.173	0.029	0.19%	0.02%	**0.18%**	**0.02%**	
p-tolualdehyde	0.093	0	0.10%	0.00%	**0.10%**	**0.00%**	
2,5-dmbenzaldehyde	0.01	0	0.01%	0.00%	**0.01%**	**0.00%**	
x-dmbenzaldehyde	0.038	0	0.04%	0.00%	**0.04%**	**0.00%**	
x-acrolein	0.091	0.057	0.10%	0.04%	**0.10%**	**0.04%**	
methacrolein	0.118	0.031	0.13%	0.02%	**0.12%**	**0.02%**	
c6h10	0.01	0.005	0.01%	0.00%	**0.01%**	**0.00%**	
c6h8	0.004	0.002	0.00%	0.00%	**0.00%**	**0.00%**	
C7H12 TOTAL	0.035	0.008	0.04%	0.01%	**0.04%**	**0.01%**	
c7h12	0.014	0.005	0.02%	0.00%	**0.01%**	**0.00%**	
c7h12	0.021	0.003	0.02%	0.00%	**0.02%**	**0.00%**	
c7h14	0.105	0.066	0.12%	0.05%	**0.11%**	**0.05%**	
C8H14 TOTAL	0.108	0.041	0.12%	0.03%	**0.11%**	**0.03%**	
c8h14	0.018	0.01	0.02%	0.01%	**0.02%**	**0.01%**	
c8h14	0.046	0.018	0.05%	0.01%	**0.05%**	**0.01%**	
c8h14	0.012	0.004	0.01%	0.00%	**0.01%**	**0.00%**	
c8h14	0.032	0.009	0.04%	0.01%	**0.03%**	**0.01%**	
C8H16 TOTAL	0.254	0.07	0.28%	0.05%	**0.27%**	**0.05%**	
c8h16	0.013	0.004	0.01%	0.00%	**0.01%**	**0.00%**	
c8h16	0.072	0.018	0.08%	0.01%	**0.08%**	**0.01%**	
c8h16	0.067	0.02	0.07%	0.02%	**0.07%**	**0.01%**	
c8h16	0.021	0.006	0.02%	0.00%	**0.02%**	**0.00%**	
c8h16	0.081	0.022	0.09%	0.02%	**0.08%**	**0.02%**	

Compound (continued)	Taurus RFG (ppmC)	Lumina FFV E85 (ppmC)	Taurus RFG (% of total NMOG)	Lumina FFV E85 (% of total NMOG)	**Taurus RFG (% of TOG)**	**Lumina FFV E85 (% of TOG)**	MCM species name
C9H18 TOTAL	0.454	0.115	0.50%	0.09%	**0.47%**	**0.08%**	
c9h18	0.021	0.006	0.02%	0.00%	**0.02%**	**0.00%**	
c9h18	0.041	0.01	0.05%	0.01%	**0.04%**	**0.01%**	
c9h18	0.018	0.003	0.02%	0.00%	**0.02%**	**0.00%**	
c9h18	0.047	0.013	0.05%	0.01%	**0.05%**	**0.01%**	
c9h18	0.004	0	0.00%	0.00%	**0.00%**	**0.00%**	
c9h18	0.105	0.037	0.12%	0.03%	**0.11%**	**0.03%**	
c9h18	0.019	0.001	0.02%	0.00%	**0.02%**	**0.00%**	
c9h18	0.014	0.002	0.02%	0.00%	**0.01%**	**0.00%**	
c9h18	0.057	0.012	0.06%	0.01%	**0.06%**	**0.01%**	
c9h18	0.061	0.02	0.07%	0.02%	**0.06%**	**0.01%**	
c9h18	0.037	0.007	0.04%	0.01%	**0.04%**	**0.00%**	
c9h18	0.03	0.004	0.03%	0.00%	**0.03%**	**0.00%**	
c9h16	0.033	0.008	0.04%	0.01%	**0.03%**	**0.01%**	
C10H22 TOTAL	0.37	0.084	0.41%	0.07%	**0.39%**	**0.06%**	
c10h22	0.102	0.034	0.11%	0.03%	**0.11%**	**0.02%**	
c10h22 ?	0.03	0.006	0.03%	0.00%	**0.03%**	**0.00%**	
c10h22 ?	0.038	0.005	0.04%	0.00%	**0.04%**	**0.00%**	
c10h22 ?	0.015	0.003	0.02%	0.00%	**0.02%**	**0.00%**	
c10h22 ?	0.05	0.014	0.06%	0.01%	**0.05%**	**0.01%**	
c10h22 ?	0.026	0.005	0.03%	0.00%	**0.03%**	**0.00%**	
c10h22	0.045	0.007	0.05%	0.01%	**0.05%**	**0.00%**	
c10h22	0.064	0.01	0.07%	0.01%	**0.07%**	**0.01%**	
C10H20 TOTAL	0.186	0.055	0.21%	0.04%	**0.19%**	**0.04%**	
c10h20	0.013	0.001	0.01%	0.00%	**0.01%**	**0.00%**	
c10h20	0.025	0.012	0.03%	0.01%	**0.03%**	**0.01%**	
c10h20	0.01	0.021	0.01%	0.02%	**0.01%**	**0.01%**	
c10h20	0.008	0.005	0.01%	0.00%	**0.01%**	**0.00%**	
c10h20	0.015	0.004	0.02%	0.00%	**0.02%**	**0.00%**	
c10h20	0.024	0.01	0.03%	0.01%	**0.03%**	**0.01%**	
c10h20	0.016	0.002	0.02%	0.00%	**0.02%**	**0.00%**	
c10h20	0.075	0	0.08%	0.00%	**0.08%**	**0.00%**	
C11H24 TOTAL	0.316	0.014	0.35%	0.01%	**0.33%**	**0.01%**	
c11h24	0.011	0.002	0.01%	0.00%	**0.01%**	**0.00%**	
c11h24	0.016	0	0.02%	0.00%	**0.02%**	**0.00%**	
c11h24	0.06	0.005	0.07%	0.00%	**0.06%**	**0.00%**	
c11h24	0.129	0	0.14%	0.00%	**0.13%**	**0.00%**	
c11h24	0.087	0.002	0.10%	0.00%	**0.09%**	**0.00%**	
c11h24	0.013	0.005	0.01%	0.00%	**0.01%**	**0.00%**	
C10H12 TOTAL	0.099	0.037	0.11%	0.03%	**0.10%**	**0.03%**	
c10h12	0.018	0.008	0.02%	0.01%	**0.02%**	**0.01%**	
c10h12	0.023	0.001	0.03%	0.00%	**0.02%**	**0.00%**	
c10h12	0.018	0.01	0.02%	0.01%	**0.02%**	**0.01%**	
c10h12	0.028	0.018	0.03%	0.01%	**0.03%**	**0.01%**	
c10h12	0.012	0	0.01%	0.00%	**0.01%**	**0.00%**	
C11H16 TOTAL	0.306	0.012	0.34%	0.01%	**0.32%**	**0.01%**	
c11h16	0.007	0.001	0.01%	0.00%	**0.01%**	**0.00%**	
c11h16	0.036	0.001	0.04%	0.00%	**0.04%**	**0.00%**	
c11h16	0.01	0.003	0.01%	0.00%	**0.01%**	**0.00%**	
c11h16	0.031	0.002	0.03%	0.00%	**0.03%**	**0.00%**	
c11h16	0.038	0.001	0.04%	0.00%	**0.04%**	**0.00%**	
c11h16	0.119	0.001	0.13%	0.00%	**0.12%**	**0.00%**	
c11h16	0.04	0.001	0.04%	0.00%	**0.04%**	**0.00%**	
c11h16	0.009	0.001	0.01%	0.00%	**0.01%**	**0.00%**	
c11h16	0.003	0.001	0.00%	0.00%	**0.00%**	**0.00%**	
c11h16	0.013	0	0.01%	0.00%	**0.01%**	**0.00%**	
C11H14 TOTAL	0.036	0.001	0.04%	0.00%	**0.04%**	**0.00%**	
c11h14	0.002	0	0.00%	0.00%	**0.00%**	**0.00%**	
c11h14	0.031	0.001	0.03%	0.00%	**0.03%**	**0.00%**	
c11h14	0.003	0	0.00%	0.00%	**0.00%**	**0.00%**	
c12h26	0.068	0	0.08%	0.00%	**0.07%**	**0.00%**	
UNKNOWN TOTAL	0.339	0.079	0.37%	0.06%	**0.35%**	**0.06%**	
Unknown	0.027	0.02	0.03%	0.02%	**0.03%**	**0.01%**	
Unknown	0.042	0.013	0.05%	0.01%	**0.04%**	**0.01%**	
---unknown---	0	0.001	0.00%	0.00%	**0.00%**	**0.00%**	
---unknown---	0	0.003	0.00%	0.00%	**0.00%**	**0.00%**	
---unknown---	0.004	0.001	0.00%	0.00%	**0.00%**	**0.00%**	
Unknown	0	0.001	0.00%	0.00%	**0.00%**	**0.00%**	
---unknown---	0	0.001	0.00%	0.00%	**0.00%**	**0.00%**	
Unknown	0.006	0.001	0.01%	0.00%	**0.01%**	**0.00%**	
---unknown---	0.029	0.01	0.03%	0.01%	**0.03%**	**0.01%**	
Unknown	0.084	0.015	0.09%	0.01%	**0.09%**	**0.01%**	
---unknown---	0.002	0.001	0.00%	0.00%	**0.00%**	**0.00%**	
---unknown---	0.013	0.007	0.01%	0.01%	**0.01%**	**0.00%**	
---unknown---	0.017	0.005	0.02%	0.00%	**0.02%**	**0.00%**	
Unknown	0.115	0	0.13%	0.00%	**0.12%**	**0.00%**	
CO	393.7	510.117					

Table S2: Average Composition of Exhaust Emissions, First 124s of Cold Start (Black 1995-1997)

The Carter carbon bond characterization was determined for all of the measured reactive species that were not included in the MCM. Most of these species were then added to species that did exist in the MCM that had similar or the same reactivity. The list of the species with the Carter break-ups is shown in Table S3. The advantage of this method was to increase the amount of known species to be included in the MCM to 96% of TOG for RFG and to 99% of TOG for E85. The species used in the MCM are summarized in Table S4; the highlighted species are ones that were treated as lumped due to the addition of emission mass to them based on Carter speciation of chemicals not included in the MCM. Including these species makes modeling of secondary species like ozone more accurate without compromising the explicitness of the majority of the species.

The emissions from Table S1 were then partitioned among the individual species according to their percent of TOG from the combined Black/Carter emissions profile, for both gasoline and E85, using the TOG for each fuel from the Jacobson (2007). That study assumed the TOG emissions increase by ~22% when using E85 instead of gasoline. The TOG was then partitioned using the Black/Carter data for gasoline and E85, respectively. An alternate method would have been to split up the gasoline TOG, then use the percent change between the E85 data and the gasoline data for each species to determine the E85 emissions. This method was not used for two reasons. First, the gasoline and E85 emissions data from the Black study were taken from two different cars, which makes a percent change in emissions less useful than if the same cars were used. Also, since these data were taken from cold start emissions only and not the full cycle, emissions were higher than during the driving cycle; therefore, it only makes sense to assume the mix of organics is similar for cold start and for full cycle (full cycle includes cold start) and not the amount of emissions.

Exhaust Data from Black; Bold Species are in MCM				Carter Split for CB4											Modified Data	
Compound	Taurus RFG (ppmC)	Lumina FFV E85 (ppmC)	Formula	PAR	OLE	TOL	XYL	FORM	ALD2	ETH	ISOP	MEOH	ETOH	UNR	Taurus RFG (ppmC)	Lumina FFV E85 (ppmC)
n-dodecane	**0.007**	**0.001**	**C12H26**	**9**										**3**	**0.075**	**0.001**
c12h26	0.068	0	C12H26													
n-undecane	**0.012**	**0.004**	**C11H24**	**8**										**3**	**0.328**	**0.018**
C11H24 TOTAL	0.316	0.014	C11H24													
n-decane	**0.037**	**0.007**	**C10H22**	**8**										**2**	**0.407**	**0.091**
C10H22 TOTAL	0.37	0.084	C10H22													
n-nonane	**0.105**	**0.023**	**C9H20**	**7**										**2**	**1.354**	**0.429**
2,2,5-trimethylhexane	0.551	0.205	C9H20	7										2		
2,3,5-trimethylhexane	0.107	0.04	C9H20	7										2		
2,4-dimethylheptane	0.063	0.018	C9H20	7										2		
2,5-dimethylheptane	0.14	0.04	C9H20	7										2		
2,6-dimethylheptane	0.067	0.019	C9H20	7										2		
3,4-dimethylheptane	0.069	0.017	C9H20	7										2		
3,5-dimethylheptane	0.064	0.021	C9H20	7										2		
1,1,4-trimethylcyclohexane	0.009	0	C9H18	7										2		
3-methyloctane	0.179	0.045	C9H20	7										2		
n-butylcyclopentane	0	0.001	C9H18	7										2		
n-octane	**0.276**	**0.091**	**C8H18**	**7**										**1**	**4.764**	**1.393**
2,3,4-trimethylpentane	1.459	0.4	C8H18	7										1		
2,3-dimethylhexane	0.502	0.149	C8H18	7										1		
2,4-dimethylhexane	0.757	0.196	C8H18	7										1		
2,5-dimethylhexane	0.4	0.124	C8H18	7										1		
3,4-dimethylhexane	0.129	0.046	C8H18	7										1		
2-methylheptane	0.339	0.111	C8H18	7										1		
3-ethylhexane	0.074	0.027	C8H18	7										1		
3-methylheptane	0.383	0.127	C8H18	7										1		
4-methylheptane	0.158	0.055	C8H18	7										1		
cis-1-ethyl-3-methylcyclopentane	0.056	0.016	C8H16	7										1		
trans-1,4-dimethylcyclohexane	0.089	0.022	C8H16	7										1		
trans-1-ethyl-3-methylcyclopentane	0.009	0.002	C8H16	7										1		
isopropylcyclopentane	0.091	0.011	C8H16	7										1		
1,2,3-trimethylcyclopentane	0.017	0.006	C8H16	6.5										1.5		
c,t,c-1,2,3-trimethylcyclopentane	0.025	0.01	C8H16	6.5										1.5		
2-methylhexane	**1.065**	**0.233**	**C7H16**	**6**										**1**	**4.506**	**1.256**
3-methylhexane	**1.146**	**0.251**	**C7H16**	**6**										**1**	**4.587**	**1.274**
n-heptane	**0.668**	**0.165**	**C7H16**	**6**										**1**	**4.109**	**1.188**
2,2,3-trimethylbutane	0.041	0.023	C7H16	6										1		
2,2-dimethylpentane	0.087	0.021	C7H16	6										1		
2,3-dimethylpentane	2.844	0.74	C7H16	6										1		
2,4-dimethylpentane	1.374	0.416	C7H16	6										1		
3,3-dimethylpentane	0.092	0.02	C7H16	6										1		
1,1-dimethylcyclopentane	0.039	0.024	C7H14	6										1		
1-cis-2-dimethylcyclopentane	0.104	0.033	C7H14	6										1		
cis-1,3-dimethylcyclopentane	0.167	0.041	C7H14	6										1		
trans-1,3-dimethylcyclopentane	0.282	0.067	C7H14	6										1		
methylcyclohexane	0.217	0.068	C7H14	6										1		
2,2,3-trimethylpentane	0.008	0.036	C8H18	6										2		
2,2,4-trimethylpentane	5.026	1.561	C8H18	6										2		
1,1,2-trimethylcyclopentane	0.021	0.007	C8H16	6										2		
1,1,3-trimethylcyclopentane	0.02	0.011	C8H16	6										2		
	10.322	3.068														
2,3-dimethylbutane	**0.882**	**0.28**	**C6H14**	**6**											**0.99**	**0.3186**
2-methylpentane	**2.179**	**0.766**	**C6H14**	**6**											**2.287**	**0.8046**
3-methylpentane	**1.252**	**0.353**	**C6H14**	**6**											**1.36**	**0.3916**
N-Hexane	**0.64**	**0.386**	**C6H14**	**6**											**0.748**	**0.4246**
cyclohexane	**0**	**0.023**	**C6H12**	**6**											**0.108**	**0.0616**
methylcyclopentane	0.54	0.193	C6H12	6												
2,2-dimethylbutane	**0.307**	**0.111**	**C6H14**	**5**										**1**	**0.307**	**0.111**
Iso-Pentane	**4.658**	**1.434**	**C5H12**	**5**											**4.694**	**1.4555**
N-pentane	**0.817**	**0.639**	**C5H12**	**5**											**0.853**	**0.6605**
cyclopentane	0.072	0.043	C5H10	5												
1-Hexene	**0.081**	**0.036**	**C6H12**	**4**	**1**										**0.263**	**0.11**
3,3-dimethyl-1-butene	0.015	0.009	C6H12	4	1											
3-methyl-1-pentene	0.167	0.065	C6H12	4	1											
1,2,4-trimethylbenzene	**1.658**	**0.337**	**C9H12**	**4**			**1**								**1.658**	**0.337**
1,3,5-trimethylbenzene	**0.739**	**0.193**	**C9H12**	**4**			**1**								**0.739**	**0.193**
2-Methyl-1-butene	**0.203**	**0.067**	**C5H10**	**4**				**1**							**0.203**	**0.067**
mtbe	**3.06**	**0.922**	**C5H12O**	**4**										**1**	**3.06**	**0.922**
Iso-butane	**0.022**	**0.02**	**C4H10**	**4**											**0.022**	**0.02**
N-Butane	**0.338**	**0.969**	**C4H10**	**4**											**0.338**	**0.969**

Exhaust Data from Black; Bold Species are in MCM				Carter Split for CB4											Modified Data	
Compound (continued)	Taurus RFG (ppmC)	Lumina FFV E85 (ppmC)	Formula	PAR	OLE	TOL	XYL	FORM	ALD2	ETH	ISOP	MEOH	ETOH	UNR	Taurus RFG (ppmC)	Lumina FFV E85 (ppmC)
2,3-dimethyl-2-butene	**0.028**	**0.009**	**C6H12**	**3.5**				**0.5**	**1**						**0.028**	**0.009**
2-methyl-2-butene	**0.103**	**0.063**	**C5H10**	**3**					**1**						**0.103**	**0.063**
x-valeraldehyde	**0.047**	**0.007**	**C5H10O**	**3**					**1**						**0.047**	**0.007**
3-Methyl-1-Butene	**0.114**	**0.03**	**C5H10**	**3**	**1**										**0.114**	**0.03**
1-Pentene	**0.135**	**0.044**	**C5H10**	**3**	**1**										**0.135**	**0.044**
2-butanone	**0.065**	**0.031**	**C4H8O**	**3**										**1**	**0.065**	**0.031**
2-propanol	**0.312**	**0.04**	**C3H8O**	**3**											**0.312**	**0.04**
acetone	**0.461**	**0.121**	**C3H6O**	**3**											**0.461**	**0.121**
1-Butene	**0**	**0.294**	**C4H8**	**2**	**1**										**0.154**	**0.297**
1-Buten-3-yne	0.126	0	C4H4	2	1											
1,3-Butadiyne	0.028	0.003	C4H2	2	1											
cis-2-hexene	**0.049**	**0.019**	**C6H12**	**2**					**2**						**0.1995**	**0.094**
trans-2-hexene	**0.104**	**0.039**	**C6H12**	**2**					**2**						**0.2545**	**0.114**
4-methyl-cis-2-pentene	0	0.007	C6H12	2					2							
4-methyl-trans-2-pentene	0.104	0.043	C6H12	2					2							
cis-3-methyl-2-pentene	0.035	0.021	C6H12	2					2							
Cis-3-hexene	0.05	0.018	C6H12	2					2							
trans-3-hexene	0.013	0.004	C6H12	2					2							
1-methylcyclopentene	0.037	0.029	C6H10	2					2							
3-methylcyclopentene	0.034	0.014	C6H10	2					2							
4-methylcyclopentene	0.018	0.009	C6H10	2					2							
c6h10	0.01	0.005	C6H10													
	0.301	0.15														
butyraldehyde	**0.063**	**0**	**C4H8O**	**2**					**1**						**0.08**	**0.081**
x-butyraldehyde	**0.044**	**0**	**C4H8O**	**2**					**1**						**0.061**	**0.081**
1-Butyne	0.021	0.105	C4H6	2					1							
2-Butyne	0.013	0.057	C4H6	2					1							
	0.034	0.162														
isopropylbenzene	**0.108**	**0.031**	**C9H12**	**2**		**1**									**0.108**	**0.031**
n-propylbenzene	**0.386**	**0.066**	**C9H12**	**2**		**1**									**0.386**	**0.066**
1,3-dimethyl-5-ethylbenzene	**0.056**	**0.002**	**C10H14**	**2**			**1**								**1.211**	**0.294**
naphthalene	0.135	0.021	C10H8	2			1									
1,2-diethylbenzene	0.055	0.069	C10H18	2			1									
1,3-diethylbenzene	0.15	0.04	C10H18	2			1									
1,2,3,5-tetramethylbenzene	0.025	0.016	C10H14	2			1									
1,2,4,5-tetramethylbenzene	0.095	0.011	C10H14	2			1									
1,2-dimethyl-3-ethylbenzene	0.005	0.006	C10H14	2			1									
1,2-dimethyl-4-ethylbenzene	0.116	0.02	C10H14	2			1									
1,3-dimethyl-2-ethylbenzene	0.051	0.035	C10H14	2			1									
1,3-dimethyl-4-ethylbenzene	0.09	0.02	C10H14	2			1									
1,4-dimethyl-2-ethylbenzene	0.059	0	C10H14	2			1									
1-methyl-2-n-propylbenzene	0.006	0.011	C10H14	2			1									
1-methyl-3-isopropylbenzene	0.038	0.009	C10H14	2			1									
1-methyl-3-n-propylbenzene	0.33	0.034	C10H14	2			1									
Propylene	**3.284**	**1.046**	**C3H6**	**1**	**1**										**3.308**	**1.048**
1,2-Butadiene	0.024	0.002	C4H6	1	1.5											
cis-2-pentene	**0.123**	**0.037**	**C5H10**	**1**					**2**						**0.147**	**0.0545**
trans-2-pentene	**0.235**	**0.064**	**C5H10**	**1**					**2**						**0.259**	**0.0815**
cyclopentene	0.048	0.035	C5H8	1					2							
propionaldehyde	**0.095**	**0.064**	**C3H6O**	**1**					**1**						**0.385**	**0.102**
Methylacetylene	0.29	0.038	C3H5	1					1							
1,2,3-trimethylbenzene	**0.008**	**0.063**	**C9H12**	**1**			**1**								**0.008**	**0.063**
1-methyl-2-ethylbenzene	**0.476**	**0.094**	**C9H12**	**1**			**1**								**0.476**	**0.094**
1-methyl-3-ethylbenzene	**1.474**	**0.298**	**C9H12**	**1**			**1**								**1.474**	**0.298**
1-methyl-4-ethylbenzene	**0.661**	**0.131**	**C9H12**	**1**			**1**								**0.661**	**0.131**
ethylbenzene	**2.412**	**0.731**	**C8H10**	**1**		**1**									**2.412**	**0.731**
benzene	**3.229**	**1.071**	**C6H6**	**1**										**5**	**3.229**	**1.071**
Acetylene	**3.103**	**1.936**	**C2H2**	**1**										**1**	**3.103**	**1.936**
Ethane	**1.26**	**2.255**	**C2H6**	**0.4**										**1.6**	**1.26**	**2.255**
Methane	**5.025**	**15.708**	**CH4**	**0.01**										**0.99**	**5.025**	**15.708**
1,3 Butadiene	**0.507**	**0.067**	**C4H6**		**2**										**0.507**	**0.067**
toluene	**7.688**	**2.273**	**C7H8**			**1**									**7.688**	**2.273**
M&P-Xylene	**5.868**	**1.621**	**C8H10**				**1**								**5.868**	**1.621**
o-xylene	**2.15**	**0.518**	**C8H10**				**1**								**2.15**	**0.518**
formaldehyde	**0.605**	**1.528**	**CH2O**					**1**							**0.605**	**1.528**
Cis-2-Butene	**0.246**	**0.681**	**C4H8**						**2**						**0.246**	**0.681**
Trans-2-Butene	**0.335**	**0.156**	**C4H8**						**2**						**0.335**	**0.156**
acetaldehyde	**0.389**	**12.447**	**C2H4O**						**1**						**0.389**	**12.447**
Ethylene	**4.991**	**10.799**	**C2H4**							**1**					**4.991**	**10.799**
Isoprene	**0.147**	**0.044**	**C5H8**								**1**				**0.147**	**0.044**

Table S3: Species from Black Exhaust Data Added to MCM Species Using Carter's CB4 Reactivity Ratings (Black 1995-1997; Carter 2008)

Compound	Taurus RFG (ppmC)	Lumina FFV E85 (ppmC)	**Taurus RFG (% of TOG)**	**Lumina FFV E85 (% of TOG)**	MCM species name
TOG	**95.653**	**143.518**	**100%**	**100%**	
TOG in MCM	91.47	142.32	**96%**	**99%**	
Methane	5.025	15.708	**5.25%**	**10.94%**	**CH4**
Ethylene (ethene)	4.991	10.799	**5.22%**	**7.52%**	**C2H4**
Ethane	1.26	2.255	**1.32%**	**1.57%**	**C2H6**
Acetylene	3.103	1.936	**3.24%**	**1.35%**	**C2H2**
Propylene	3.308	1.048	**3.46%**	**0.73%**	**C3H6**
Iso-butane	0.022	0.02	**0.02%**	**0.01%**	**IC4H10**
1-Butene	0.154	0.297	**0.16%**	**0.21%**	**BUT1ENE**
Iso-Butylene	4.313	0.548	**4.51%**	**0.38%**	**MEPROPENE**
1,3 Butadiene	0.507	0.067	**0.53%**	**0.05%**	**C4H6**
N-Butane	0.338	0.969	**0.35%**	**0.68%**	**NC4H10**
Trans-2-Butene	0.335	0.156	**0.35%**	**0.11%**	**TBUT2ENE**
Cis-2-Butene	0.246	0.681	**0.26%**	**0.47%**	**CBUT2ENE**
3-Methyl-1-Butene	0.114	0.03	**0.12%**	**0.02%**	**ME3BUT1ENE**
Iso-Pentane	4.694	1.4555	**4.91%**	**1.01%**	**IC5H12**
1-Pentene	0.135	0.044	**0.14%**	**0.03%**	**PENT1ENE**
2-Methyl-1-butene	0.203	0.067	**0.21%**	**0.05%**	**ME2BUT1ENE**
N-pentane	0.853	0.6605	**0.89%**	**0.46%**	**NC5H12**
isoprene	0.147	0.044	**0.15%**	**0.03%**	**C5H8**
trans-2-pentene	0.259	0.0815	**0.27%**	**0.06%**	**TPENT2ENE**
cis-2-pentene	0.147	0.0545	**0.15%**	**0.04%**	**CPENT2ENE**
2-methyl-2-butene	0.103	0.063	**0.11%**	**0.04%**	**ME2BUT2ENE**
2,2-dimethylbutane	0.307	0.111	**0.32%**	**0.08%**	**M22C4**
2,3-dimethylbutane	0.99	0.3186	**1.03%**	**0.22%**	**M23C4**
2-methylpentane	2.287	0.8046	**2.39%**	**0.56%**	**M2PE**
3-methylpentane	1.36	0.3916	**1.42%**	**0.27%**	**M3PE**
1-Hexene	0.263	0.11	**0.27%**	**0.08%**	**HEX1ENE**
N-Hexane	0.748	0.4246	**0.78%**	**0.30%**	**NC6H14**
trans-2-hexene	0.2545	0.114	**0.27%**	**0.08%**	**THEX2ENE**
cis-2-hexene	0.1995	0.094	**0.21%**	**0.07%**	**CHEX2ENE**
2,3-dimethyl-2-butene	0.028	0.009	**0.03%**	**0.01%**	**DM23BU2ENE**
benzene	3.229	1.071	**3.38%**	**0.75%**	**BENZENE**
cyclohexane	0.108	0.0616	**0.11%**	**0.04%**	**CHEX**
2-methylhexane	4.506	1.256	**4.71%**	**0.87%**	**M2HEX**
3-methylhexane	4.587	1.274	**4.80%**	**0.89%**	**M3HEX**
n-heptane	4.109	1.188	**4.30%**	**0.83%**	**NC7H16**
toluene	7.688	2.273	**8.04%**	**1.58%**	**TOLUENE**
n-octane	4.764	1.393	**4.98%**	**0.97%**	**NC8H18**
ethylbenzene	2.412	0.731	**2.52%**	**0.51%**	**EBENZ**
M&P-Xylene	5.868	1.621	**6.13%**	**1.13%**	**MXYL, PXYL**
styrene	0.455	0.079	**0.48%**	**0.06%**	**STYRENE**
o-xylene	2.15	0.518	**2.25%**	**0.36%**	**OXYL**
n-nonane	1.354	0.429	**1.42%**	**0.30%**	**NC9H20**
isopropylbenzene	0.108	0.031	**0.11%**	**0.02%**	**IPBENZ**
n-propylbenzene	0.386	0.066	**0.40%**	**0.05%**	**PBENZ**
1-methyl-3-ethylbenzene	1.474	0.298	**1.54%**	**0.21%**	**METHTOL**
1-methyl-4-ethylbenzene	0.661	0.131	**0.69%**	**0.09%**	**PETHTOL**
1,3,5-trimethylbenzene	0.739	0.193	**0.77%**	**0.13%**	**TM135B**
1-methyl-2-ethylbenzene	0.476	0.094	**0.50%**	**0.07%**	**OETHTOL**
1,2,4-trimethylbenzene	1.658	0.337	**1.73%**	**0.23%**	**TM124B**
n-decane	0.407	0.091	**0.43%**	**0.06%**	**NC10H22**
1,2,3-trimethylbenzene	0.008	0.063	**0.01%**	**0.04%**	**TM123B**
1,3-dimethyl-5-ethylbenzene	1.211	0.294	**1.27%**	**0.20%**	**DIME35EB**
n-undecane	0.328	0.018	**0.34%**	**0.01%**	**NC11H24**
n-dodecane	0.075	0.001	**0.08%**	**0.00%**	**NC12H26**
mtbe	3.06	0.922	**3.20%**	**0.64%**	**MTBE**
methanol	0.229	6.684	**0.24%**	**4.66%**	**CH3OH**
ethanol	0.026	67.309	**0.03%**	**46.90%**	**C2H5OH**
2-propanol	0.312	0.04	**0.33%**	**0.03%**	**IPROPOL**
formaldehyde	0.605	1.528	**0.63%**	**1.06%**	**HCHO**
acetaldehyde	0.389	12.447	**0.41%**	**8.67%**	**CH3CHO**
acetone	0.461	0.121	**0.48%**	**0.08%**	**CH3COCH3**
propionaldehyde	0.385	0.102	**0.40%**	**0.07%**	**C2H5CHO**
butyraldehyde	0.08	0.081	**0.08%**	**0.06%**	**C3H7CHO**
benzaldehyde	0.255	0.088	**0.27%**	**0.06%**	**BENZAL**
x-butyraldehyde	0.061	0.081	**0.06%**	**0.06%**	**IPRCHO**
x-valeraldehyde	0.047	0.007	**0.05%**	**0.00%**	**C4H9CHO**
2-butanone	0.065	0.031	**0.07%**	**0.02%**	**MEK**
dimethyl ether	0.041	0.007	**0.04%**	**0.00%**	**CH3OCH3**
1,3-diethyl 5-methylbenzene	0.306	0.012	**0.32%**	**0.01%**	**DIET35TOL**

Table S4: Summary of Species from Exhaust Emissions from Black Data for MCM

Note: Highlighted Species Include Species not in the MCM (Black 1995-1997; Carter 2008)

The emissions we have discussed so far were all measured under standard conditions (24 to 25 C). Two studies have measured emissions under both warm (22 C) and cold (-7 C) ambient temperatures (Whitney and Fernandez 2007; Westerholm et al. 2008). Westerholm et al. (2008) measured the emissions from two different flex-fuel vehicles (Saab and Volvo), 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 (Chevrolet, Lincoln, and Dodge) for gasoline (E0), E70, and E85. The vehicles differed in type and fuel economy, as shown in Table S5. However, much of the emissions results for both warm and cold ambient temperatures were similar between the different vehicles.

					Fuel Economy (mpg)*	
Study	**Vehicles**	**Year**	**Type**	**Engine type**	**E85**	**Gasoline**
Westerholm (2008)	Saab 9-5 Biopower	2005	Wagon	L4	19	25
Westerholm (2008)	Volvo V50 1.8 F	2005	Wagon	L4		26.5
Whitney (2007)	Chevrolet Silverado	2007	Pickup Truck	5.3L V8	12	16
Whitney (2007)	Lincoln Town Car	2006	Car	4.6L V8	13	18
Whitney (2007)	Dodge Stratus	2006	Car	2.7L V6	16	21

Table S5: Vehicles Used for Emissions Studies of Ethanol Fuels at Warm and cold Temperatures.

NOTE: Fuel economy measurements are from (West et al. 2007) for the Saab, http://www.whatgreencar.com/view-car/21310/volvo-v50-1_8F_Flexifuel_2009 for the Volvo, and www.fueleconomy.gov for the Chevrolet, Lincoln, and Dodge

The emissions results are shown in Table S7 and Table S6. The actual emissions amounts differ, but the % change from gasoline to ethanol fuel are generally in the same direction and of similar magnitude. Hydrocarbons, formaldehyde, acetaldehyde, and ethanol all increased from gasoline to E70 and from gasoline to E85 for both warm and cold ambient temperatures with only a couple of exceptions (Whitney and Fernandez 2007; Westerholm et al. 2008). Hydrocarbons decreased for the Chevrolet Silverado from gasoline to E85, for the Lincoln Town Car from gasoline to E70 and for the Volvo V50 from gasoline to E85, all at the warm ambient temperature (Table S6). Another exception was the decrease in formaldehyde emission from the Lincoln Town Car for E70 at 22 C. The results for 1,3-butadiene and benzene were more mixed. For -7 C, 1,3-butadiene increased for the Chevrolet and the Volvo by 20% to 59%. It decreased for the Lincoln and Dodge by -14% and -7%, respectively (Table S7). 1,3-Butadiene decreased for all vehicles except the Volvo at 22 C by -71% to -43%. It increased by only 8% for the Volvo. At -7 C, benzene decreased for E70 for the Chevrolet, the Lincoln, and the Volvo. Surprisingly, it actually increased for E70 for the Dodge and for E85 for the Volvo (Table S7). The benzene should only be present in the gasoline portion of the fuel, so any increase in benzene emissions when switching from gasoline to ethanol fuels is unexpected. The warm temperature emissions of benzene decreased for all vehicles from gasoline to ethanol fuel, as expected (Table S6).

For the application of our model, we use the Volvo emissions data set to examine how colder ambient temperatures might impact air pollution. The Saab and Volvo vehicles were the only ones measured at -7C for E85, and the Saab has a lot of missing values in its data set. The Volvo is the most complete data set and therefore is best suited for use in our study. The complete data set for the Saab and the Volvo is shown in Table S8 (Westerholm et al. 2008).

Emissions (g/km)	Whitney et al. (2007)									Westerholm et al. (2008)									
Temp = -7C	2007 Chevrolet Silverado			2006 Lincoln Town Car			2006 Dodge Stratus			2005 Saab 9-5 Biopower					2005 Volvo V50				
Species	Gasoline (E0)	E70	% Change	Gasoline (E0)	E70	% Change	Gasoline (E0)	E70	% Change	Gasoline (E5)	E70	% Change	E85	% Change	Gasoline (E5)	E70	% Change	E85	% Change
HC*										0.30	1.20	300%	1.77	490%	0.43	1.14	165%	1.25	191%
NMHC**	0.30	0.58	96%	0.37	0.76	107%	0.26	0.77	195%										
Formaldehyde	0.00042	0.0017	300%	0.00039	0.00081	108%	0.000093	m.v.		m.v.	m.v.		0.0091		0.0008	0.0036	350%	0.0032	300%
Acetaldehyde	0.00031	0.026	8300%	0.00031	0.025	8100%	m.v.	m.v.		m.v.	m.v.		0.1229		0.0066	0.12	1702%	0.093	1314%
Ethanol	0	0.286		0	0.572		m.v.	m.v.		m.v.	m.v.		1.441		0.024	1.21	4929%	1.22	4996%
1,3-Butadiene	0.00057	0.00068	20%	0.00045	0.00039	-14%	0.00046	0.00043	-7%	m.v.	m.v.		0.0021		0.00078	0.00098	26%	0.0012	59%
Benzene	0.0081	0.0056	-31%	0.011	0.0078	-31%	0.0061	0.0071	18%	m.v.	m.v.		0.016		0.013	0.01	-19%	0.014	9%

Table S7: Vehicle Emissions Comparison for Cold Ambient Temperatures (T = -7C) ***(37,38)***

NOTE: *HC = Hydrocarbons calculated based on average gasoline carbon/hydrogen ratio and was not adjusted for ethanol fuels. **NMHC = non-methane hydrocarbons were corrected for ethanol.

Emissions (g/km)	Whitney et al. (2007)											Westerholm et al. (2008)									
Temp = 22C	2007 Chevrolet Silverado					2006 Lincoln Town Car					2006 Dodge Stratus					2005 Saab 9-5 Biopower			2005 Volvo V50		
Species	Gasoline (E0)	E70	% Change	E85	% Change	Gasoline (E0)	E70	% Change	E85	% Change	Gasoline (E0)	E70	% Change	E85	% Change	Gasoline (E5)	E85	% Change	Gasoline (E5)	E85	% Change
HC*																0.06	0.08	33%	0.07	0.05	-29%
NMHC**	0.027	0.036	31%	0.023	-14%	0.026	0.024	-9%	0.033	26%	0.022	0.026	18%	0.028	29%						
Formaldehyde	0.00022	0.00041	83%	0.00055	147%	0.00015	0.00012	-21%	0.0003	104%	0.000205	m.v.		m.v.		0.0007	0.0021	200%	0.0006	0.0016	167%
Acetaldehyde	0.000093	0.0031	3233%	0.0025	2533%	0.000062	0.0019	2900%	0.004	6400%	0.000062	m.v.		m.v.		0.0012	0.018	1367%	0.0013	0.0103	692%
Ethanol	0	0.01		0.016		0	0.0070		0.011		0	m.v.		m.v.		0.006	0.078	1200%	0.001	0.068	6700%
1,3-Butadiene	0.000065	0.00003	-54%	0.000021	-67%	0.000048	0.000014	-71%	0.000016	-67%	0.000072	0.000041	-43%	0.000025	-65%	0.00051	0.0002	-61%	0.00037	0.0004	8%
Benzene	0.00011	0.0001	-9%	0.000043	-59%	0.00014	0.000062	-56%	0.00004	-71%	0.00012	m.v.		m.v.		0.0022	0.001	-55%	0.0023	0.0002	-91%

Table S6: Vehicle Emissions Comparison for Warm Ambient Temperatures (T = 22C) ***(37,38)***

NOTE: *HC = Hydrocarbons calculated based on average gasoline carbon/hydrogen ratio and was not adjusted for ethanol fuels. **NMHC = non-methane hydrocarbons were corrected for ethanol.

	NEDC (22 C) (g/km)		NEDC (-7 C) (g/km)		From 22 C to -7 C		From E5 to E85	
	E5	E85	E5	E85	% Change E5	% Change E85	% Change 22 C	% Change -7 C
Saab - CO	0.58	1.02	1.73	4.45	198%	336%	76%	157%
Volvo - CO	0.89	0.23	4.61	6.07	418%	2539%	-74%	32%
Avg CO					**308%**	**1438%**	**1%**	**94%**
Saab - HC*	0.06	0.08	0.3	1.77	400%	2113%	33%	490%
Volvo - HC*	0.07	0.05	0.43	1.25	514%	2400%	-29%	191%
Avg HC					**457%**	**2256%**	**2%**	**340%**
Saab - NOx	0.02	0.01	0.7	0.078	3400%	680%	-50%	-89%
Volvo - NOx	0.04	0.03	0.034	0.05	-15%	67%	-25%	47%
Avg NOx					**1693%**	**373%**	**-38%**	**-21%**
Saab - PM	0.0001	0.0002	0.004	0.0047	3900%	2250%	100%	18%
Volvo - PM	0.0004	0.0002	0.0031	0.0046	675%	2200%	-50%	48%
Avg PM					**2288%**	**2225%**	**25%**	**33%**
Saab - CH4	0.008	0.019	0.022	0.13	175%	584%	138%	491%
Volvo - CH4	0.005	0.008	0.02	0.087	300%	988%	60%	335%
Avg CH4					**238%**	**786%**	**99%**	**413%**
Saab - HCHO	0.0007	0.0021		0.0091		333%	200%	
Volvo - HCHO	0.0006	0.0016	0.0008	0.0032	33%	100%	167%	300%
Avg HCHO					**33%**	**217%**	**183%**	**300%**
Saab - CH3CHO	0.0012	0.0176		0.1229		598%	1367%	
Volvo - CH3CHO	0.0013	0.0103	0.0066	0.0933	408%	806%	692%	1314%
Avg CH3CHO					**408%**	**702%**	**1029%**	**1314%**
Saab - C2H5OH	0.006	0.078		1.441		1747%	1200%	
Volvo - C2H5OH	0.001	0.068	0.024	1.223	2300%	1699%	6700%	4996%
Avg C2H5OH					**2300%**	**1723%**	**3950%**	**4996%**
Saab - NH3	0	0		0				
Volvo - NH3	0	0	0.018	0.017				-6%
Avg NH3								**-6%**
Saab - ethene	0.004	0.01		0.038		280%	150%	
Volvo - ethene	0.004	0.003	0.017	0.056	325%	1767%	-25%	229%
Avg ethene					**325%**	**1023%**	**63%**	**229%**
Saab - propene	0.0028	0.0012		0.0138		1050%	-57%	
Volvo - propene	0.0038	0.0007	0.0132	0.0159	247%	2171%	-82%	20%
Avg propene					**247%**	**1611%**	**-69%**	**20%**
Saab - 1,3 butadiene	0.00051	0.0002		0.00214		970%	-61%	
Volvo - 1,3 butadiene	0.00037	0.0004	0.00078	0.00124	111%		8%	59%
Avg 1,3 butadiene					**111%**	**970%**	**-26%**	**59%**
Saab - benzene	0.0022	0.001		0.0159		1490%	-55%	
Volvo - benzene	0.0023	0.0002	0.0126	0.0137	448%		-91%	9%
Avg benzene					**448%**	**1490%**	**-73%**	**9%**
Saab - toluene	0.006	0.003		0.056		1767%	-50%	
Volvo - toluene	0.007	0.001	0.056	0.052	700%	5100%	-86%	-7%
Avg toluene					**700%**	**3433%**	**-68%**	**-7%**

Table S8: The Tailpipe Emissions for the Saab 9-5 Biopower and the Volvo V50 flex-fuel vehicle for Ambient Temperatures 22 C (71.6 F) and -7 C (19.4 F) (Westerholm et al. 2008)

Note: *HC - Hydrocarbon data was calculated based on average gasoline carbon/hydrogen ratio and was not adjusted for ethanol fuels.

To determine the emissions data at -7 C, we first assumed the current data we have represents the emissions data at 22 C, which is a good assumption since most of the data were taken at an ambient temperature of around 24 C. We then use these data to determine the % change from gasoline (E5) at 22 C to gasoline (E5) at -7 C for the Volvo, as shown in Table S8. This % change was then applied to the gasoline emissions data for each species measured by Westerholm et al (2008). The remaining hydrocarbon emissions were calculated by breaking up the remaining % change in total hydrocarbons (not including alcohols) over the rest of the species. For example, for gasoline (E5), the following species were measured explicitly by Westerholm et al. (2008) and their % change from 22 C to -7 C can be applied directly: carbon monoxide (CO), methane, formaldehyde, acetaldehyde, ethanol, ethane, propene, 1,3-butadiene, benzene, and toluene. For CO, the Volvo % change of gasoline (E5) emissions from 22 C to -7 C was 418%. To calculate the new tonnes/year for CO emissions for -7 C in the LA area, the emissions from Jacobson (2007) for CO = 782,000 tonnes/year was multiplied by the % change,

418%, and added to the emissions from Jacobson (2007), to give 4,050,584 tonnes/year of CO at -7 C ambient temperature. To determine the % change for the hydrocarbons that were not explicitly measured by Westerholm et al. (2008), the total hydrocarbons minus the alcohols were summed for the Black/Carter emissions data, giving 85,732 tonnes/year of hydrocarbons for gasoline. The Volvo % change, 514%, of the total hydrocarbons from 22 C to -7 C from Westerholm et al. (2008) was then applied to this number, to give 526,639 tonnes/year of hydrocarbons at -7 C. The sum of the explicit hydrocarbons (methane, formaldehyde, acetaldehyde, ethane, propene, 1,3-butadiene, benzene, and toluene, which was 24,196 tonnes/year for 22 C and 127,689 tonnes/year for -7 C) was then subtracted from the total hydrocarbons. The remaining hydrocarbons were 61,536 tonnes/year for 22 C and 398,950 tonnes/year for -7 C. The % change for these remaining hydrocarbons was then calculated by dividing 398,950 by 61,536 and subtracting 1 to give 548%. This % change was then applied to all of the remaining hydrocarbons. Since methanol and 2-propanol, both alcohols, were not included in the explicit measurements and not included in the total hydrocarbons, their emissions were assumed to stay the same when the temperature decreased from 22 C to -7 C. This is a conservative assumption because the alcohol emissions likely increased substantially under colder conditions, similar to the increase seen for ethanol (2300%).

Once the emissions were known for gasoline at -7 C, the % change between gasoline and E85 at -7 C for Volvo could be used to calculate the E85 emissions at -7 C for all of the explicitly measured species. A similar system as described above was used to calculate the change in emissions for the remaining hydrocarbons. Again, methanol and 2-propanol emissions were assumed to remain the same when the temperature changed from 22 C to -7 C for E85 because there was no measured data for these alcohols. The results are shown in Table S9. The total % changes from gasoline to E85 for the different scenarios are summarized in Table S10, where a positive % means there is an increase in the emissions of that species when using E85 instead of gasoline.

	Gasoline (tonnes/yr)		E85 (tonnes/year)	
Species Name	24 C Emissions Set	-7 C Emissions Set	24 C Emissions Set	-7 C Emissions Set
CO	782,000	4,050,584	821,100	5,333,416
NOx	68,900	58,565	48,230	86,125
NO2	62,010	52,709	43,407	77,513
NO	6,890	5,857	4,823	8,613
Methane	4,723	18,893	12,010	82,184
Ethylene (ethene)	4,691	19,938	8,256	65,678
Ethane	1,184	7,678	1,724	122,358
Acetylene	2,917	18,909	1,480	105,049
Propylene (propene)	3,109	10,801	801	13,010
Iso-butane	21	134	15	1,085
1-Butene	145	938	227	16,115
Iso-Butylene	4,054	26,283	419	29,735
1,3 Butadiene	477	1,005	51	1,597
N-Butane	318	2,060	741	52,579
Trans-2-Butene	315	2,041	119	8,465
Cis-2-Butene	231	1,499	521	36,952
3-Methyl-1-Butene	107	695	23	1,628
Iso-Pentane	4,412	28,605	1,113	78,976
1-Pentene	127	823	34	2,387
2-Methyl-1-butene	191	1,237	51	3,635
N-pentane	802	5,198	505	35,839
isoprene	138	896	34	2,387
trans-2-pentene	243	1,578	62	4,422
cis-2-pentene	138	896	42	2,957
2-methyl-2-butene	97	628	48	3,418
2,2-dimethylbutane	289	1,871	85	6,023
2,3-dimethylbutane	931	6,033	244	17,287
2-methylpentane	2,150	13,937	615	43,658
3-methylpentane	1,278	8,288	299	21,248
1-Hexene	247	1,603	84	5,969
N-Hexane	703	4,558	325	23,039
trans-2-hexene	239	1,551	87	6,186
cis-2-hexene	188	1,216	72	5,101
2,3-dimethyl-2-butene	26	171	7	488
benzene	3,035	16,627	819	18,079
cyclohexane	102	658	47	3,342
2-methylhexane	4,235	27,457	960	68,133
3-methylhexane	4,311	27,951	974	69,110
n-heptane	3,862	25,038	908	64,444
toluene	7,226	57,811	1,738	53,681
n-octane	4,478	29,031	1,065	75,585
ethylbenzene	2,267	14,699	559	39,665
M&P-Xylene	5,516	35,759	1,239	87,957
styrene	428	2,773	60	4,287
o-xylene	2,021	13,102	396	28,107
n-nonane	1,273	8,251	328	23,278
isopropylbenzene	102	658	24	1,682
n-propylbenzene	363	2,352	50	3,581
1-methyl-3-ethylbenzene	1,385	8,982	228	16,170
1-methyl-4-ethylbenzene	621	4,028	100	7,108
1,3,5-trimethylbenzene	695	4,503	148	10,472
1-methyl-2-ethylbenzene	447	2,901	72	5,101
1,2,4-trimethylbenzene	1,558	10,104	258	18,286
n-decane	383	2,480	70	4,938
1,2,3-trimethylbenzene	8	49	48	3,418
1,3-dimethyl-5-ethylbenzene	1,138	7,380	225	15,953
n-undecane	308	1,999	14	977
n-dodecane	70	457	1	54
mtbe	2,876	18,647	705	50,028
methanol	215	215	5,110	5,110
ethanol	24	587	51,462	29,889
2-propanol	293	293	31	31
formaldehyde	569	758	1,168	3,033
acetaldehyde	366	1,856	9,516	26,242
acetone	433	2,809	93	6,566
propionaldehyde	362	2,346	78	5,535
butyraldehyde	75	488	62	4,395
benzaldehyde	240	1,554	67	4,775
x-butyraldehyde	57	372	62	4,395
x-valeraldehyde	44	286	5	380
2-butanone	61	396	24	1,682
dimethyl ether	39	250	5	380
1,3-diethyl 5-methylbenzene	288	1,865	9	651

Table S9: The Total Emissions for Gasoline and E85 for the SCAB in 2020 for 24 C and -7 C Emissions Sets

Note: 24 C Emissions set: Jacobson (2007), Black (1995-1997) and Carter (2008); -7 C Emissions Set: Jacobson (2007), and Westerholm et al. (2008); The alcohol emissions do not change except for ethanol because the alcohols were not measured in the Westerholm et al. data (2008)

Species	MCM Species	Jacobson (2007)	24 C Emissions Set	-7 C Emissions Set
CO	CO	5%		32%
CO2	CO2			
NOx		-30%		47%
Methane	CH4	43%	154%	335%
Ethylene (ethene)	C2H4	-17%	76%	229%
Ethane	C2H6	0%	46%	1494%
Acetylene	C2H2		-49%	456%
Propylene (propene)	C3H6	-65%	-74%	20%
Iso-butane	IC4H10		-26%	709%
1-Butene	BUT1ENE		57%	1617%
Iso-Butylene	MEPROPENE		-90%	13%
1,3 Butadiene	C4H6	-10%	-89%	59%
N-Butane	NC4H10		133%	2453%
Trans-2-Butene	TBUT2ENE		-62%	315%
Cis-2-Butene	CBUT2ENE		125%	2365%
3-Methyl-1-Butene	ME3BUT1ENE		-79%	134%
Iso-Pentane	IC5H12		-75%	176%
1-Pentene	PENT1ENE		-73%	190%
2-Methyl-1-butene	ME2BUT1ENE		-73%	194%
N-pentane	NC5H12		-37%	589%
C5H8 TOTAL	C5H8	-80%	-76%	167%
trans-2-pentene	TPENT2ENE		-74%	180%
cis-2-pentene	CPENT2ENE		-70%	230%
2-methyl-2-butene	ME2BUT2ENE		-50%	445%
2,2-dimethylbutane	M22C4		-71%	222%
2,3-dimethylbutane	M23C4		-74%	187%
2-methylpentane	M2PE		-71%	213%
3-methylpentane	M3PE		-77%	156%
1-Hexene	HEX1ENE		-66%	272%
N-Hexane	NC6H14		-54%	405%
trans-2-hexene	THEX2ENE		-64%	299%
cis-2-hexene	CHEX2ENE		-62%	320%
2,3-dimethyl-2-butene	DM23BU2ENE		-74%	186%
benzene	BENZENE	-79%	-73%	9%
cyclohexane	CHEX		-54%	408%
2-methylhexane	M2HEX		-77%	148%
3-methylhexane	M3HEX		-77%	147%
n-heptane	NC7H16		-76%	157%
toluene	TOLUENE	-80%	-76%	-7%
n-octane	NC8H18		-76%	160%
ethylbenzene	EBENZ		-75%	170%
M&P-Xylene	MXYL, PXYL	-80%	-78%	146%
styrene	STYRENE		-86%	55%
o-xylene	OXYL	-80%	-80%	115%
n-nonane	NC9H20		-74%	182%
isopropylbenzene	IPBENZ		-77%	156%
n-propylbenzene	PBENZ		-86%	52%
1-methyl-3-ethylbenzene	METHTOL		-84%	80%
1-methyl-4-ethylbenzene	PETHTOL		-84%	76%
1,3,5-trimethylbenzene	TM135B		-79%	133%
1-methyl-2-ethylbenzene	OETHTOL		-84%	76%
1,2,4-trimethylbenzene	TM124B		-83%	81%
n-decane	NC10H22		-82%	99%
1,2,3-trimethylbenzene	TM123B		541%	6912%
1,3-dimethyl-5-ethylbenzene	DIME35EB		-80%	116%
n-undecane	NC11H24		-96%	-51%
n-dodecane	NC12H26		-99%	-88%
mtbe	MTBE		-75%	168%
methanol	CH3OH		2274%	2274%
ethanol	C2H5OH	increase	210475%	4996%
2-propanol	IPROPOL		-90%	-90%
formaldehyde	HCHO	60%	105%	300%
acetaldehyde	CH3CHO	2000%	2503%	1314%
acetone	CH3COCH3	0%	-79%	134%
propionaldehyde	C2H5CHO		-78%	136%
butyraldehyde	C3H7CHO		-18%	802%
benzaldehyde	BENZAL		-72%	207%
x-butyraldehyde	IPRCHO		8%	1082%
x-valeraldehyde	C4H9CHO		-88%	33%
2-butanone	MEK		-61%	325%
dimethyl ether	CH3OCH3		-86%	52%
1,3-diethyl 5-methylbenzene	DIET35TOL		-97%	-65%
Propane		-65%		
Paraffin bond group (PAR)		-80%		
Olefin bond group (OLE)		-17%		
Higher Aldehydes		-60%		

Table S10: % Change in Emissions from Gasoline to E85 for Each Species

Now we have two sets of emissions for gasoline and E85 – at 24 C and at -7 C. These emissions sets were then investigated over a range of temperatures – above zero degrees C for the 24 C emissions set, and below zero degrees 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 modified for the model runs at low temperature. The January solar profile for the Los Angeles area was chosen as the model solar profile for these low temperature emissions. Even though the Los Angeles area does not regularly get down to these low temperatures, even in winter, the results will demonstrate how the air pollution in cold areas with sparse vegetation and large vehicle fleets is likely to change when gasoline is replaced with E85-powered flex-fuel vehicles. The sunrise was changed from 6 am to 7 am and the sunset from 6 pm to 5 pm, shortening the solar radiation over the day, as shown in Figure S1. The insolation is also decreased in the winter – in addition to the shortened day. The insolation in the Los Angeles area on a clear day in the summer is about 980 W/m^2. The insolation for a clear day in January is about 630 W/m^2, only about 64% of a clear summer day. Also, clouds are more prevalent in the winter in L.A. To account for this, the max photolysis rates were decreased by half for the winter model run, to account for lower insolation and cloud cover. This is represented by the lower insolation in Figure S1. Not unexpectedly, reducing the insolation dramatically decreases the amount of ozone produced, especially for E85.

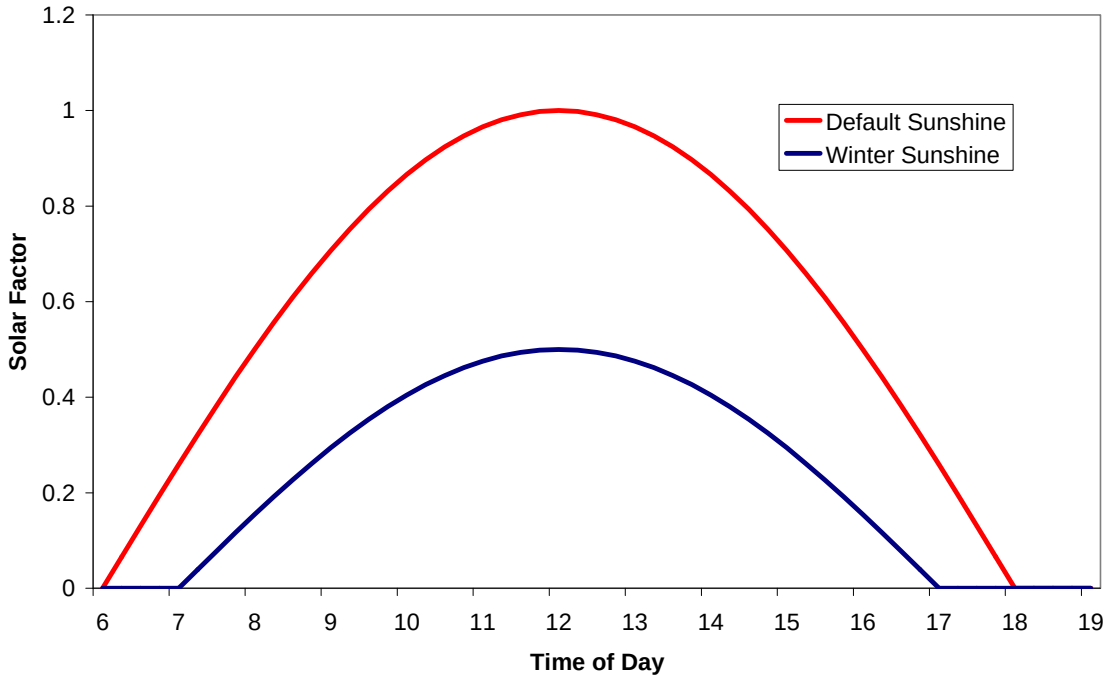

Figure S1: Representation of the Solar Intensity for 24 C Emissions (Default, or Summer, Sunshine) and -7 C Emissions (Winter Sunshine)

The ambient temperature followed a sine profile in the daytime, increasing in the morning and decreasing in the afternoon, and was constant at night. This profile was chosen based on temperature data from CARB for the SCAB (CARB 2008). The temperature was measured for many different cities/towns in the SCAB – so a representative profile was chosen

by comparing the profile of all of these different areas for a day in July, shown in Figure S2, and a day in August, shown in Figure S3. A few days in February were also examined to make sure the profile is similar in winter even though the temperatures are cooler, as shown in Figure S4.

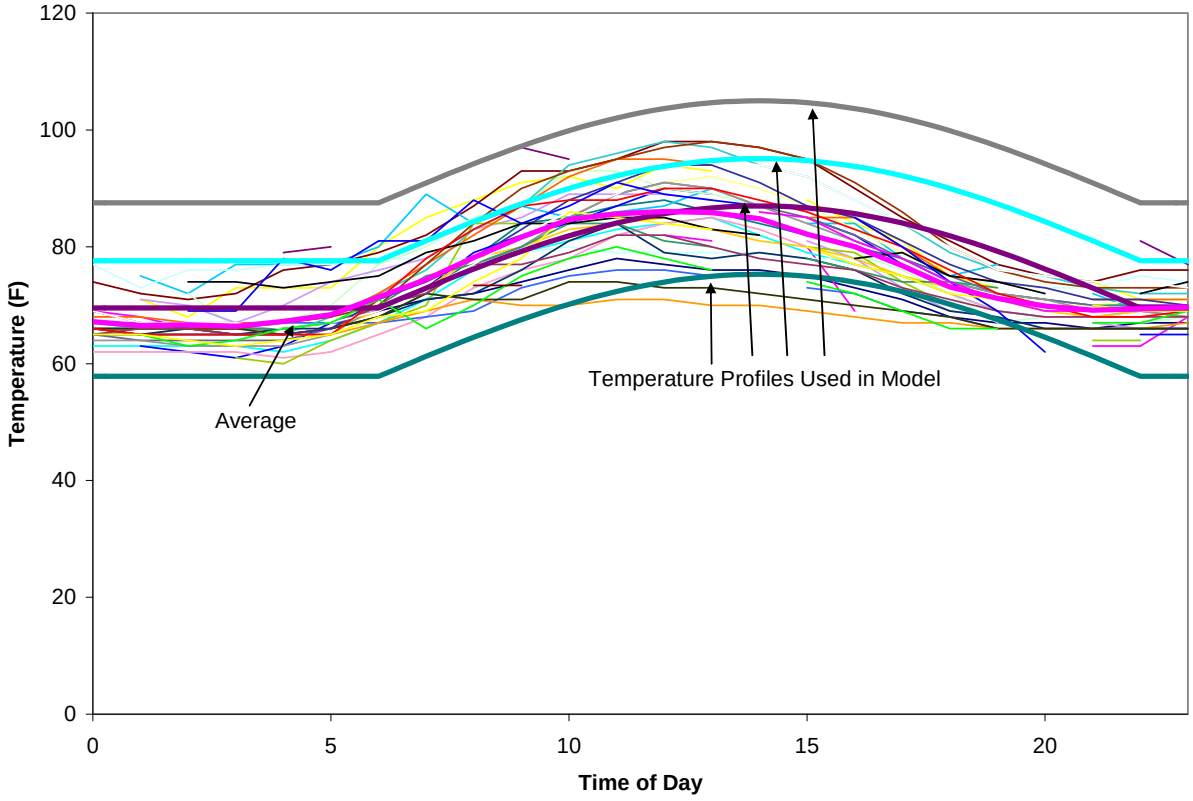

Figure S2: July 10th, 2008 Temperature Profiles for Cities in the SCAB with the Model Temperature Profiles in Bold (CARB 2008)

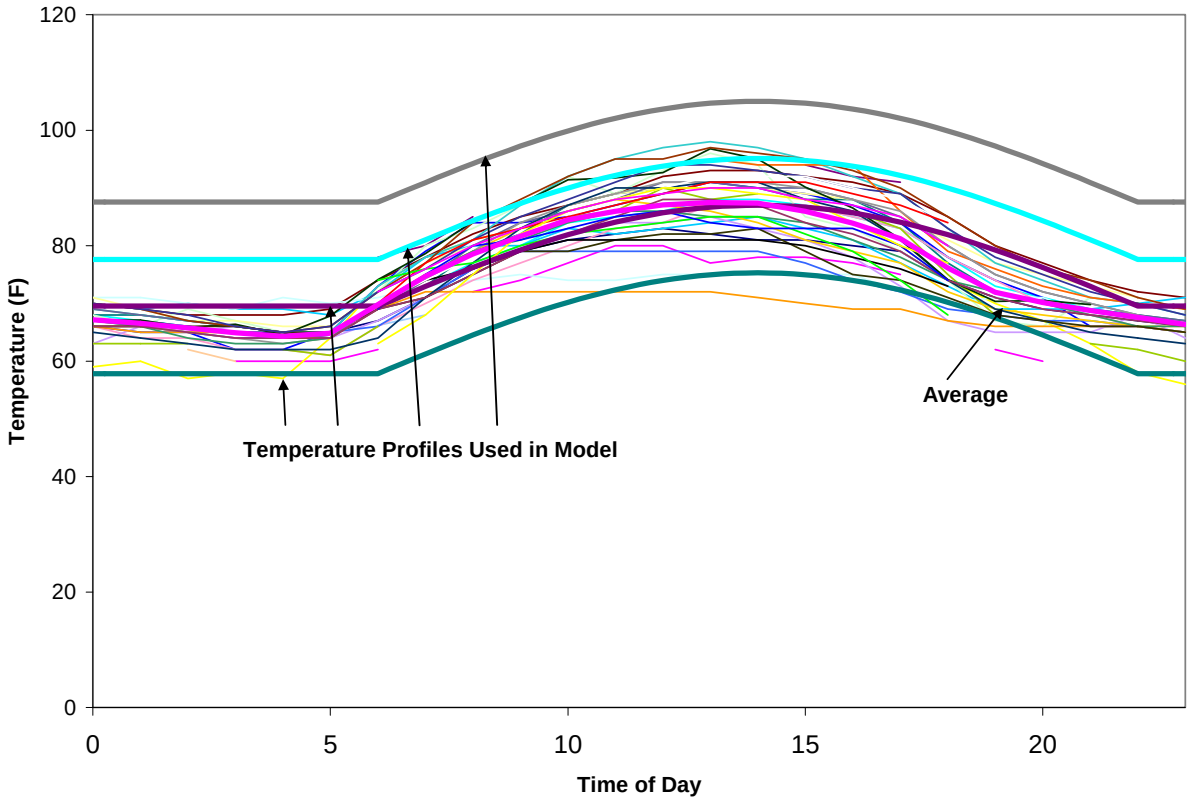

Figure S3: August 10th, 2008 Temperature Profiles for Cities in the SCAB with the Model Temperature Profiles in Bold (CARB 2008)

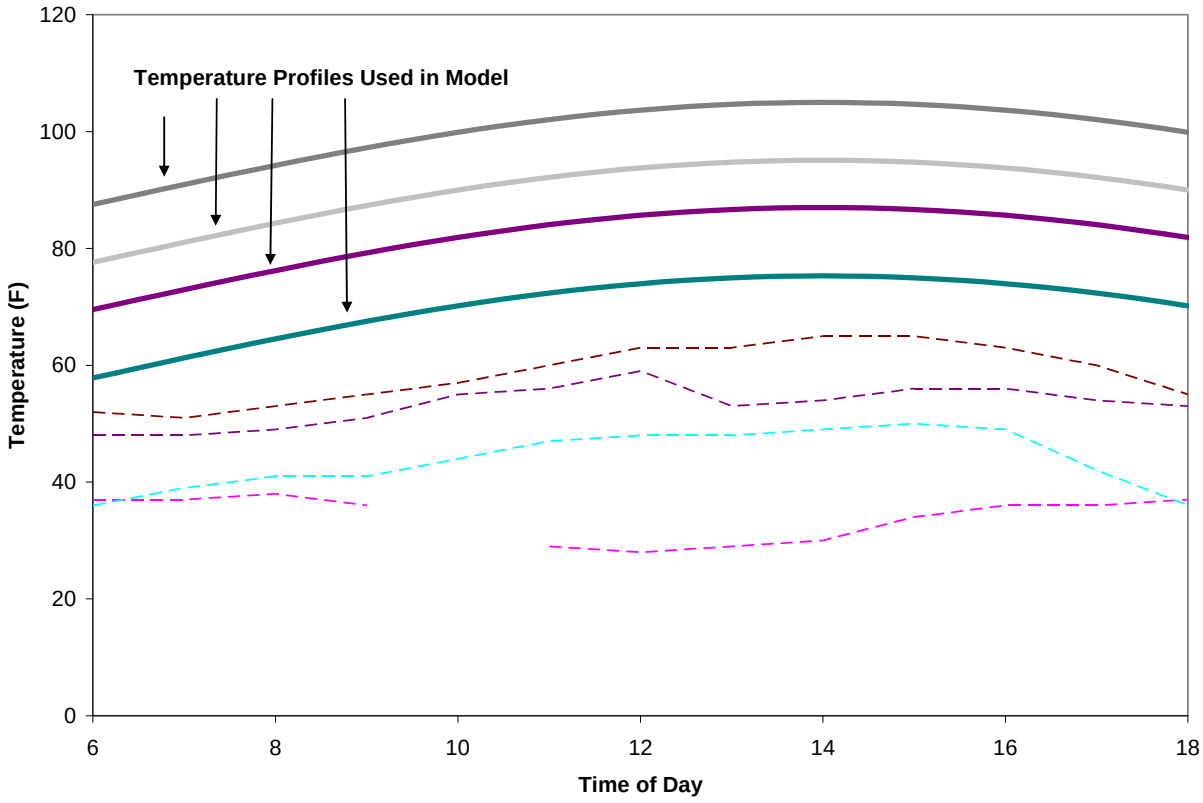

Figure S4: February 14th and 15th, 2008 Temperature Profiles for Cities in the SCAB with the Model Temperature Profiles in Bold (CARB 2008)

The temperature profile was calculated as follows. First, an average temperature profile was calculated from the temperature data for a day in July (Figure S2) and a day in August (Figure S3). The peak of this average temperature profile was 2 pm, so this was chosen as the peak for all of the temperature profiles used in the SCAB modeling study (t_{peak} = 28,000 s). A factor was chosen by trying to match the average profile (9.705555). Therefore, the temperature profile for the SCAB modeling was:

$$T = T_i + 9.705555*\sin((t*(pi/2))/28800)$$

To look at the sensitivity of the system to temperature for the system without a fog (reported in Ginnebaugh et al. (2010)), the initial temperature was changed to target different peak temperatures (35 C, 41 C, etc) as shown in Figure S5. The temperature profile will be referred to by its peak temperature in this report.

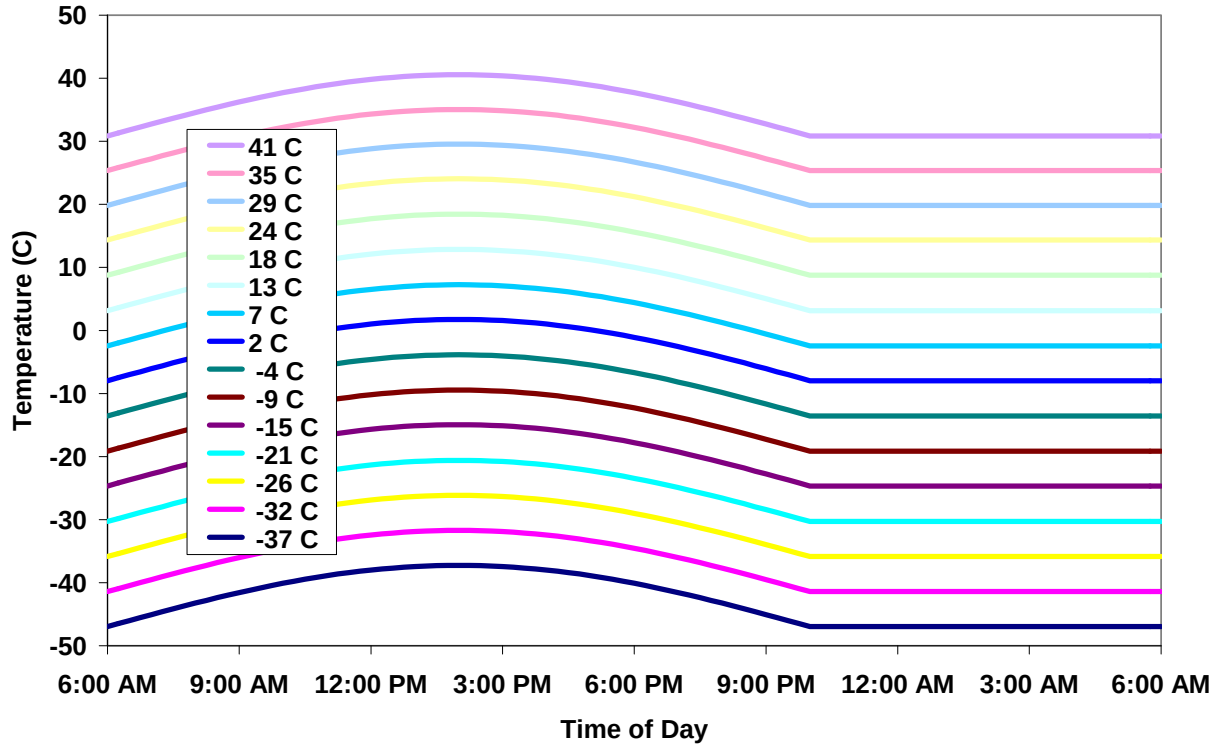

Figure S5: Temperature Profiles Used in the Model for Each Day, Labeled by their Peak Temperature, for the no fog case reported in Ginnebaugh et al. (2010). The 24 C and -4 C Temperature Profiles are used here.

Two of these temperature profiles were chosen for the fog and no fog comparison cases. For the summer scenario, the 24C temperature profile was chosen, and for the winter scenario, the -4C temperature profile was chosen. These were chosen because they are close to the ambient temperatures the two data sets were taken at.

The box model was sized to match the SCAB to make these emissions appropriate. The area of the SCAB is 6,745 mi^2 and is shown in Figure S6 (AQMD 2008). The area used for this box model was 1.5 degrees latitude by 1.1 degrees longitude, which is 6,751 mi^2, approximately the same as the SCAB. The baseline height of the box was 500 m. The sensitivity of the results to the mixing height for the no fog case was investigated by examining the results for 300 m and 1 km.

Figure S6: Map of the South Coast Air Basin (SCAB) (AQMD 2008)

The next step was to determine the emission rate for gasoline and E85 for the SCAB for each day. The vehicle emissions profile, shown in Figure S7 for a few species, describes what might happen on a typical weekday in Los Angeles. The profile is based on the diurnal profile for urban vehicles from the Emissions Modeling Clearinghouse Temporal Allocation by the U.S. Environmental Protection Agency (USEPA 2000).

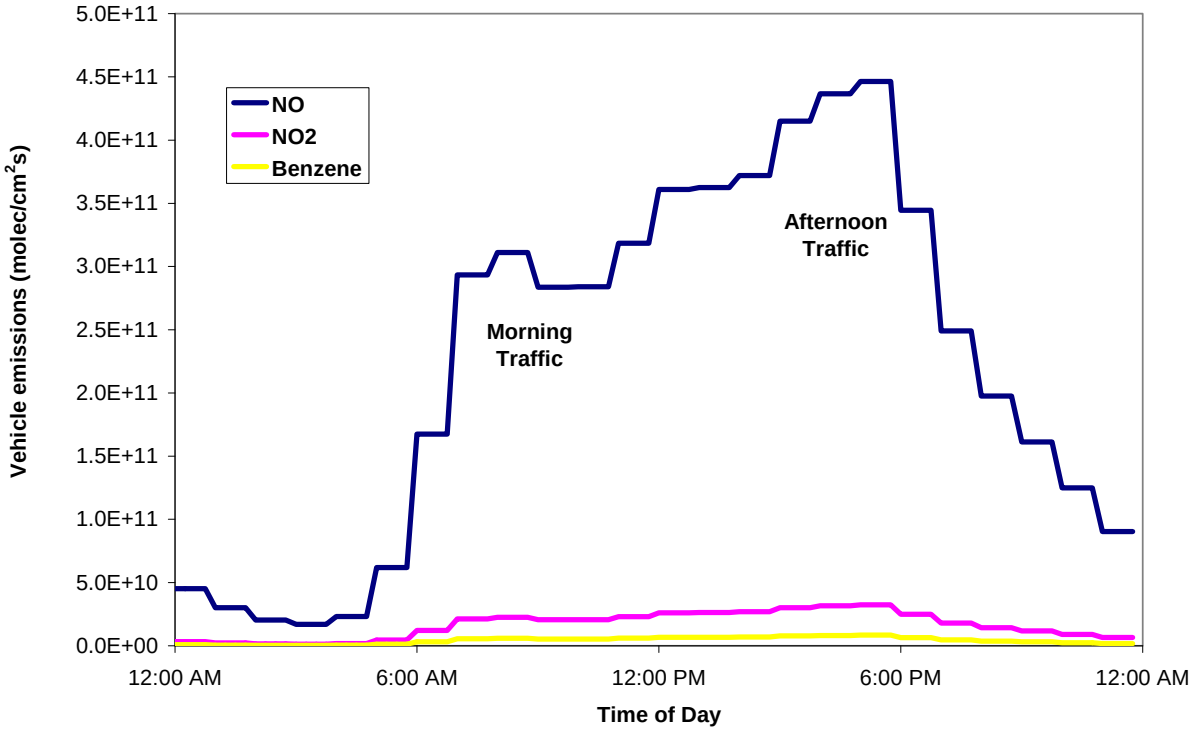

Figure S7: The Vehicle Emissions Profile for All Emitted Species, Shown for Three Example Species

In addition to vehicle emissions, the model needs the background emissions in order to more accurately calculate ozone levels. The background emissions were the same for the gasoline scenario and the E85 scenario and are listed in Table S11 (Jacobson 2007). The background emissions include point, fugitive, area, non-road non-gasoline, and on-road non-gasoline emissions. The background emissions are from Jacobson (2007) and were used in an adjusted carbon bond mechanism (ACBM), so some of the groups of species/bonds (PAR, OLE, ALD2) had to be split up and assigned to individual species in order to fit the MCM. This was done again using the Carter method for breaking up species according to their carbon bond – only this time it was done in the reverse (Carter 2008). The species that were used in place of these carbon bond categories were chosen by three criteria: 1) they did not already have background emissions listed; 2) they existed in the MCM; and 3) they were the simplest species that fit the requirements. For the Olefin bond group (OLE), 1-butene (PAR = 2, OLE =1) was used to represent all of the olefins because propene (PAR =1, OLE = 1) already was listed for background emissions. Dimethyl ether (PAR = 5, ALD2 = 1) was used to represent the higher aldehyde species (ALD2). The remaining portion of the paraffin bond group (after 1-butene and dimethyl ether were subtracted from it) was represented by an even split between iso-pentane (PAR=5) and n-pentane (PAR=5). The toluene bond group and isoprene bond group were represented by toluene and isoprene, respectively. The xylene bond group was broken up evenly and represented by m-xylene, o-xylene, and p-xylene in the MCM. The background emissions were assumed to be constant throughout the day and night.

	Background Emissions (tonnes/yr)	
Species Name	**ACBM (Jacobson 2007)**	**MCM (Carter 2008)**
Carbon Monoxide	285,000	285,000
Nitrogen Dioxide	170,100	170,100
Nitric Oxide	17,010	17,010
Methane	198,000	198,000
Ethane	17,200	17,200
Propane	4,890	4,890
Paraffin bond group (PAR)	115,000	
Iso-Pentane		9,016
N-pentane (pentane)		9,016
Ethene	10,100	10,100
Propene	1,680	1,680
1,3 Butadiene	718	718
Olefin bond group (OLE)	2,220	
1-Butene		2,220
Methanol	550	550
Ethanol	4,720	4,720
Formaldehyde	2,380	2,380
Acetaldehyde	631	631
Higher Aldehydes (ALD2)	4,080	
dimethyl ether		4,080
Formic Acid	139	139
Acetic acid	246	246
Acetone	2,920	2,920
Benzene	2,550	2,550
Toluene bond group	26,800	
Toluene		26,800
Xylene bond group	12,400	
m-Xylene		4,133
o-Xylene		4,133
p-Xylene		4,133
Isoprene bond group	134	
Isoperene		134
Unreactive	28,600	28,600
Sulfur Oxides as SO2	22,700	22,700
Ammonia	28,900	28,900

Table S11: Background Emission for SCAB for ACBM and MCM from Jacobson (2007) and using Carter (2008)

Data was taken from the California Air Resources Board (CARB) to determine what the initialized background concentrations should be for the baseline case (CARB 2008). The sensitivity to this parameter was investigated by examining a range of initial conditions because it is difficult to predict what the concentrations of these species will be in 2020, when this simulation is taking place. Looking at the sensitivity of the results to background initial conditions also provides a clue to how the results would differ in different urban areas. The data at 6 am for a week in July and a week in August in 2008 was taken from the CARB database, shown in Table S12 (CARB 2008).

		South Coast Air Basin at 6 am (ppb)														
		Carbon monoxide			Nitrogen Dioxide			Nitric Oxide			Ozone			Sulfur Dioxide		
Day	Date	Max	Min	Avg	Max	Min	Avg	Max	Min	Avg	Max	Min	Avg	Max	Min	Avg
Th	7/10/2008	1000	200	430.4	32	4	21.6	58	1	21.0	58	1	12.9	3	1	2.00
F	7/11/2008	1200	200	486.4	38	0	22.5	64	0	20.0	41	2	10.9	4	1	2.00
S	7/12/2008	1100	100	404.3	32	3	16.4	49	2	14.1	42	3	10.6	4	0	2.29
Sun	7/13/2008	1000	100	362.5	28	3	13.9	46	0	10.7	52	4	14.3	3	0	1.86
M	7/14/2008	1000	200	480.0	39	7	21.0	97	2	23.9	31	1	10.3	4	1	2.43
T	7/15/2008	1000	200	508.0	45	8	25.4	99	3	29.5	25	1	9.7	5	1	2.57
	Average			445.3			20.1			19.9			11.4			2.19
Sun	8/10/2008	1000	100	412	31	1	17.1	48	1	13.6	42	5	12.4	6	0	1.71
M	8/11/2008	1000	100	464	36	5	20.4	70	0	26.0	33	1	10.2	5	0	2.14
Tu	8/12/2008	1100	100	432	43	2	22.9	107	0	21.5	38	2	10.4	5	0	1.86
W	8/13/2008	1000	100	476	35	8	23.3	71	2	23.8	32	1	9.8	6	0	1.71
Th	8/14/2008	800	0	384	36	7	22.0	50	1	15.5	33	2	10.0	7	0	2.14
F	8/15/2008	900	100	452	51	2	24.0	105	0	26.1	36	1	9.8	6	0	2.00
	Average			436.7			21.6			21.1			10.4			1.93

Table S12: Data from CARB on the Ambient Concentration of Select Species at 6 am for the SCAB (CARB 2008)

The average concentration, in ppbv, for those two weeks was used for the baseline for the species that are measured: carbon monoxide (CO) ~ 440 ppbv, ozone (O_3) ~ 10 ppbv, sulfur dioxide (SO_2) ~ 2 ppbv, nitric oxide (NO) ~ 20 ppbv, nitrogen dioxide (NO_2) ~ 20 ppbv (see Table S14). Unfortunately, the organic species were not measured for the SCAB. To estimate the amount of methane and non-methane organic gases in the SCAB at 6 am, we used the data from the San Francisco and San Jose areas in July and August at 6 am instead, as shown in Table S13: methane (CH_4) ~ 2000 ppb, non-methane organic gases (NMOG) ~ 80 ppb. The non-methane organic gases were then broken up according to the median value from Table 3.3 in Jacobson (2005), which lists the background concentrations of different species in the polluted urban troposphere. Thus, we initialized the following NMOGs at the start of our model runs: methane (CH_4) ~ 2000 ppbv, Ethane (C_2H_6) = 11.83 ppbv, Ethene (C_2H_4) = 7.19 ppbv, formaldehyde (HCHO) = 46.61 ppbv, toluene = 7.19 ppbv, m-xylene = 2.4 ppbv, o-xylene = 2.4 ppbv, p-xylene = 2.4 ppbv. The sensitivity of the system to these parameters was investigated as discussed in detail in Ginnebaugh et al. (2010). The summary of the initial conditions are shown in Table S14.

At 6 am		San Jose (ppb)					San Francisco (ppb)
Day	Date	NMHC	CH4	CO	NO	NO2	NMHC
W	8/1/2007	30	1940	300	5	14	120
Th	8/2/2007	80	2020	400	10	19	80
F	8/3/2007						100
S	8/4/2007	230	2240	500	26	17	80
Sun	8/5/2007	0	1860	100	1	4	50
M	8/6/2007	10	1840	200	2	8	80
Tu	8/7/2007	10	1870	200	2	9	80
W	8/8/2007	80	1960	400	8	20	70
Th	8/9/2007	60	2050	300	5	16	90
F	8/10/2008	110	2190	400	27	20	90
S	8/11/2008	140	2490	400	22	18	60
Sun	8/12/2008	100	2070	300	3	12	50
Average		77.3	2048.2	318.2	10.1	14.3	79.2

Table S13: Data from CARB on the Ambient Concentration of Select Species at 6 am for San Jose and San Francisco (CARB 2008)

	Initial concentrations (ppb)				
Species	**-20%**	**-10%**	**Baseline**	**+10%**	**+20%**
Carbon Monoxide			**440**		
Ozone			**10**		
Sulfur Dioxide			**2**		
Nitric Oxide	16	18	**20**	22	24
Nitrogen Dioxide	16	18	**20**	22	24
NMOG	64	72	**80**	88	96
Methane			**2000**		
Ethane	9.46	10.6	**11.83**	13.0	14.2
Ethene	5.75	6.47	**7.19**	7.91	8.63
Formaldehyde	37.3	41.9	**46.61**	51.3	55.9
Toluene	5.75	6.47	**7.19**	7.91	8.63
o-Xylene	1.92	2.16	**2.40**	2.64	2.88
m-Xylene	1.92	2.16	**2.40**	2.64	2.88
p-Xylene	1.92	2.16	**2.40**	2.64	2.88

Table S14: The Initial Concentrations for the Model – Baseline and Variations On the Baseline Used to Test the Sensitivity of the Model Results to Initial Conditions

The fog parameters were chosen based on typical fog attributes from Jacobson (2005). The baseline fog diameter was 20 micron, with a liquid water content of 3.0×10^{-7} cm^3-water/cm^3-air. This corresponds to 72 droplets/cm^3 of air and 3.0×10^5 ug water/m^3 air. The fog duration is typical for Los Angeles (Waldman et al. 1982; Munger et al. 1983; Jacob et al. 1985; Munger et al. 1990), lasting from 10 pm the first day to 10 am the second day. The photolysis is decreased by 30% during the fog and is based on measurements of a Los Angeles fog by Lurmann et al. (1997). The fog was initialized with chlorine, iron, manganese and copper ions, as shown in Table S15, based on measurements from fogs in Los Angeles (Brewer et al. 1983; Munger et al. 1983; Jacob et al. 1985).

Initial Conditions for the Fog	
Species	**Initial Concentration (M)**
Cl^-	2.23×10^{-4}
Fe^{3+}	7.9×10^{-6}
Mn^{3+}	7×10^{-7}
Cu^+	5×10^{-7}

Table S15: Initial Species Concentrations in the Fog based on Measured Values for Los Angeles Fogs (Brewer et al. 1983; Munger et al. 1983; Jacob et al. 1985)

When the fog dissipates, aerosols are left behind with very small liquid water content (1×10^{-15} cm^3 water/cm^3 air).

A small amount of ventilation is added for the winter scenario to account for faster winds and less stagnant air in the winter. The concentrations of all species are reduced by 0.8% every 15 minutes for the ventilation.

Depositions for select species were included (Ervens et al. 2003; Herrmann et al. 2005). Their rates are listed in Table S16.

Species	Urban Depositions (1/s)
NO_2	4.00E-06
HNO_3	2.00E-05
N_2O_5	2.00E-05
H_2O_2	1.00E-05
CO	1.00E-06
O_3	4.00E-06
HCL	1.00E-05
NH_3	1.00E-05
SO_2	1.00E-05
H_2SO_4	2.00E-05
HCHO	1.00E-05
CH_3OOH	5.00E-06
HCOOH	1.00E-05
CH_3OH	1.00E-05
C_2H_5OH	5.00E-06
HOBR	2.00E-06
HOCL	2.00E-06

Table S16: Deposition Rates for Select Species

3. Results

The model was run for two ambient temperature profiles, 24C (summer scenario) and -4C (winter scenario), as shown in Figure S5, for two days for all four emissions sets (gasoline and E85, both taken at 24 C and -7 C) without a fog and with a fog. Figure S8, Figure S9, Figure S10, and Figure S11 show results from the two day model runs for a few select species for the summer scenario and the 24 C data sets. Figure S12, Figure S13, Figure S14, and Figure S15 show the same for the winter scenario and the -7 C data sets.

There are a few general conclusions to take from these time series. One is that the concentration of carboxylic acids are highly impacted by the fog (usually increased, at least after the fog). Peroxy radical concentrations also differ significantly with the fog verses no fog. Aldehydes and alcohols are not impacted as strongly by the fog as peroxy radicals and carboxylic acids.

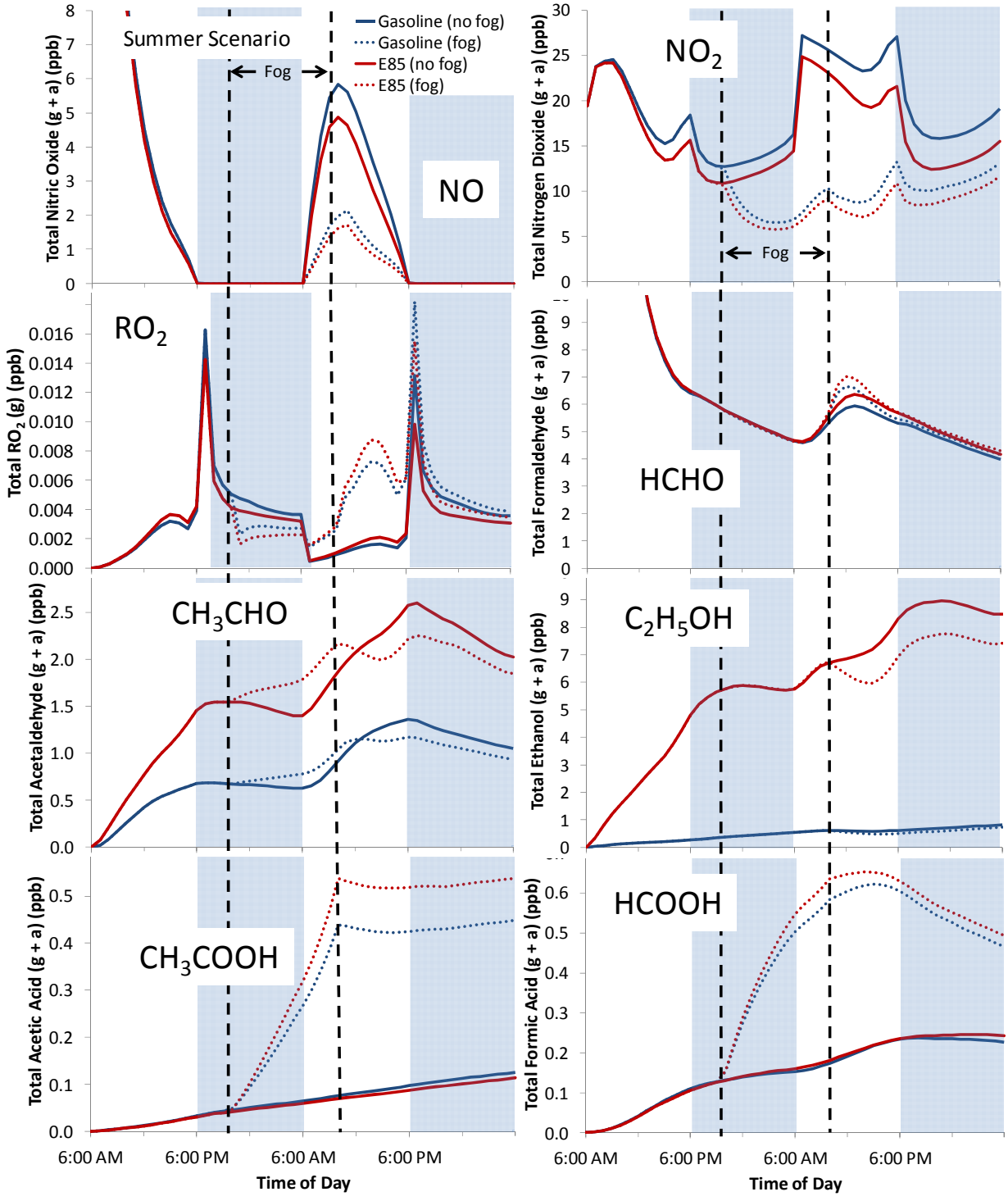

Figure S8: Two Day Model Results for Gasoline vs E85 Emissions (24 C) without a Fog and With a Fog for the Summer Scenario for Select Species (1)

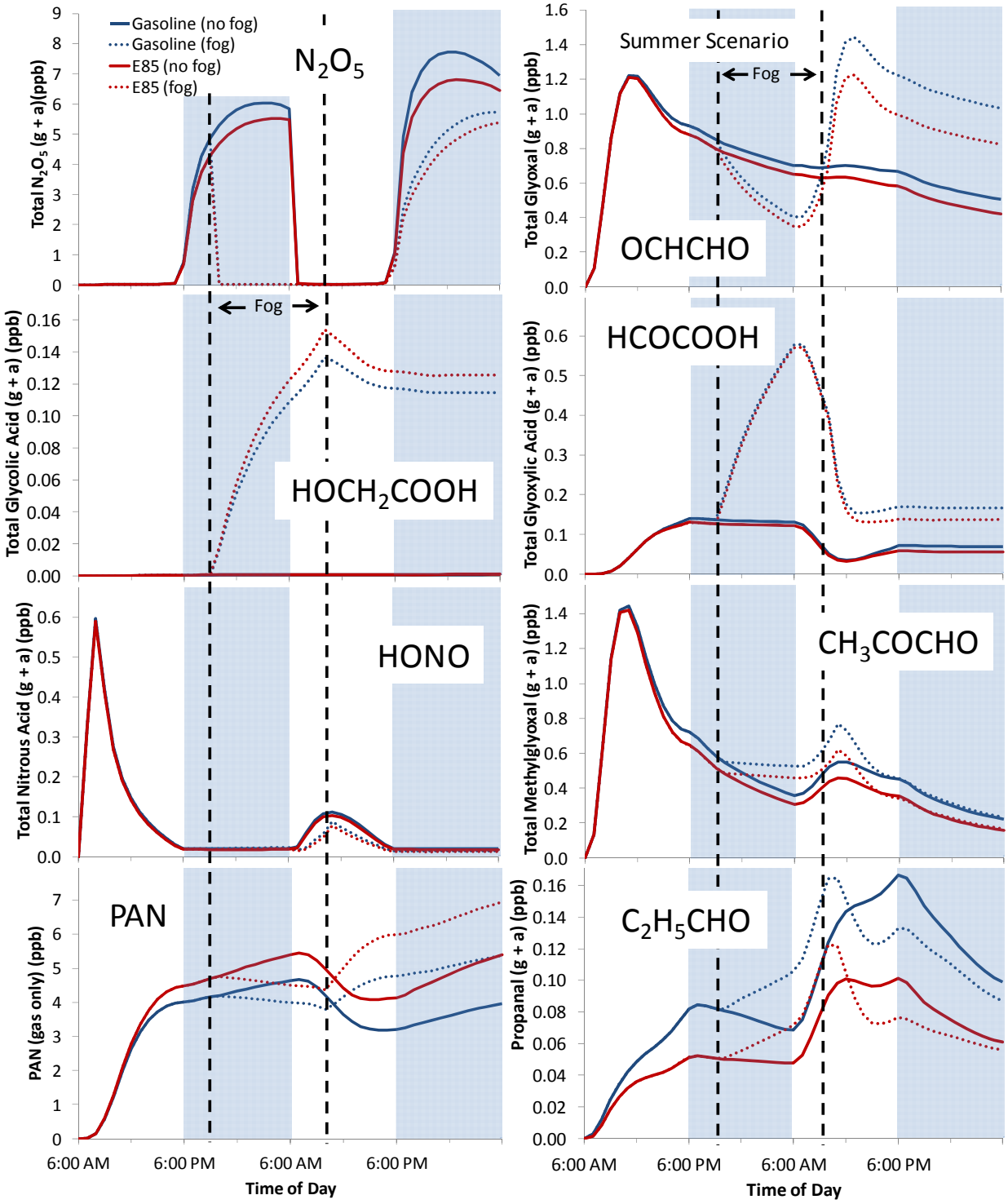

Figure S9: Two Day Model Results for Gasoline vs E85 Emissions (24 C) without a Fog and With a Fog for the Summer Scenario for Select Species (2)

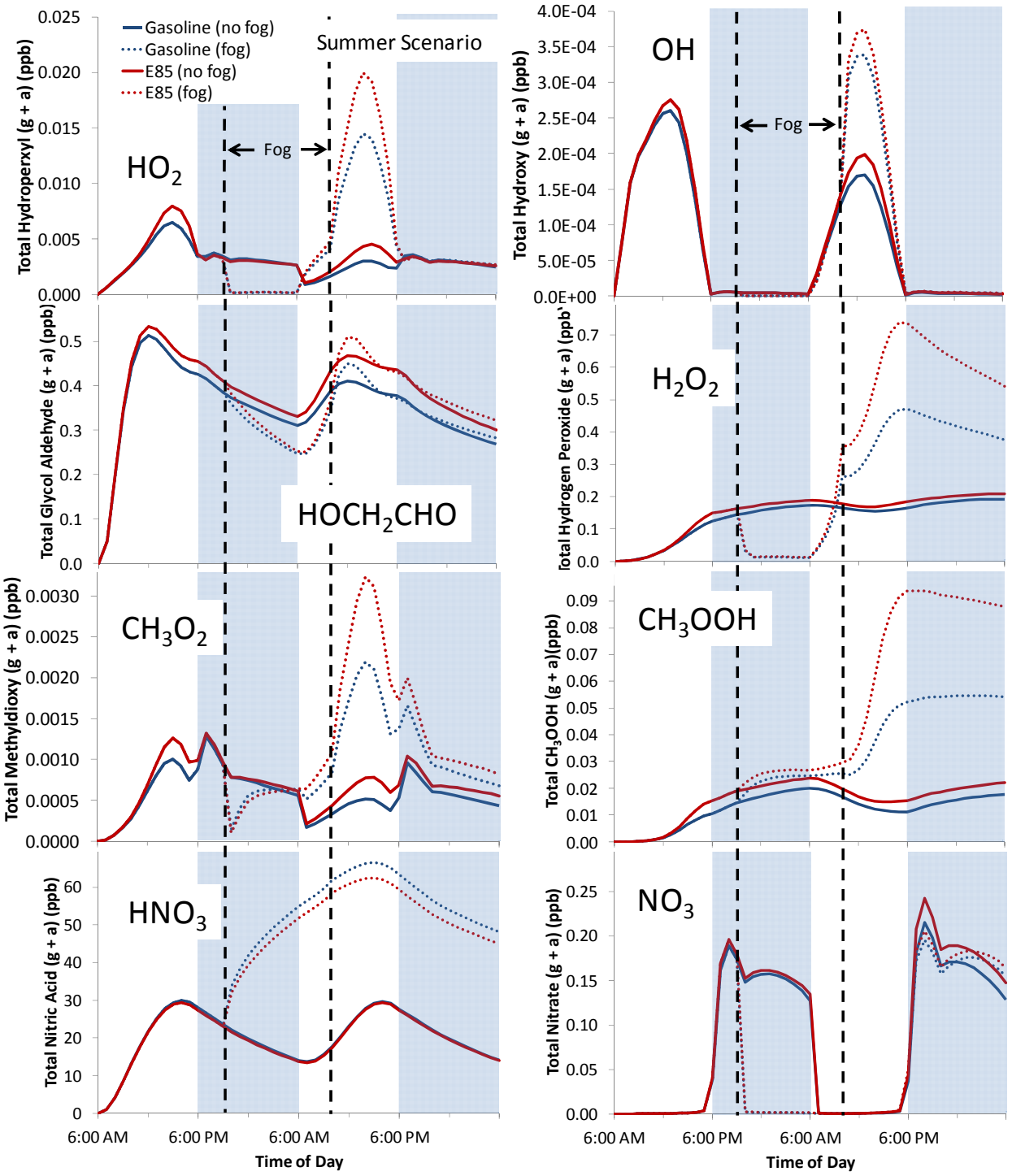

Figure S10: Two Day Model Results for Gasoline vs E85 Emissions (24 C) without a Fog and With a Fog for the Summer Scenario for Select Species (3)

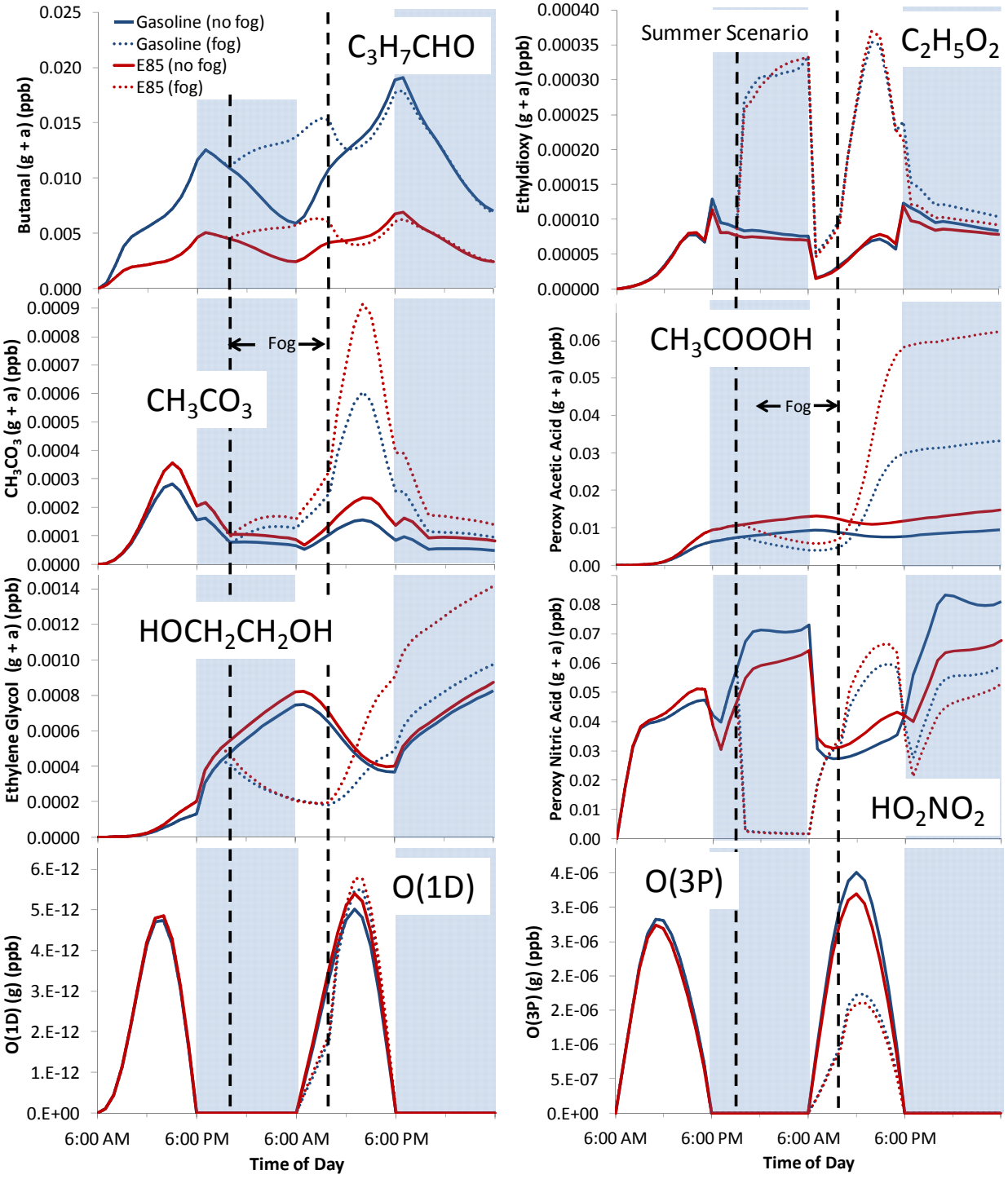

Figure S11: Two Day Model Results for Gasoline vs E85 Emissions (24 C) without a Fog and With a Fog for the Summer Scenario for Select Species (4)

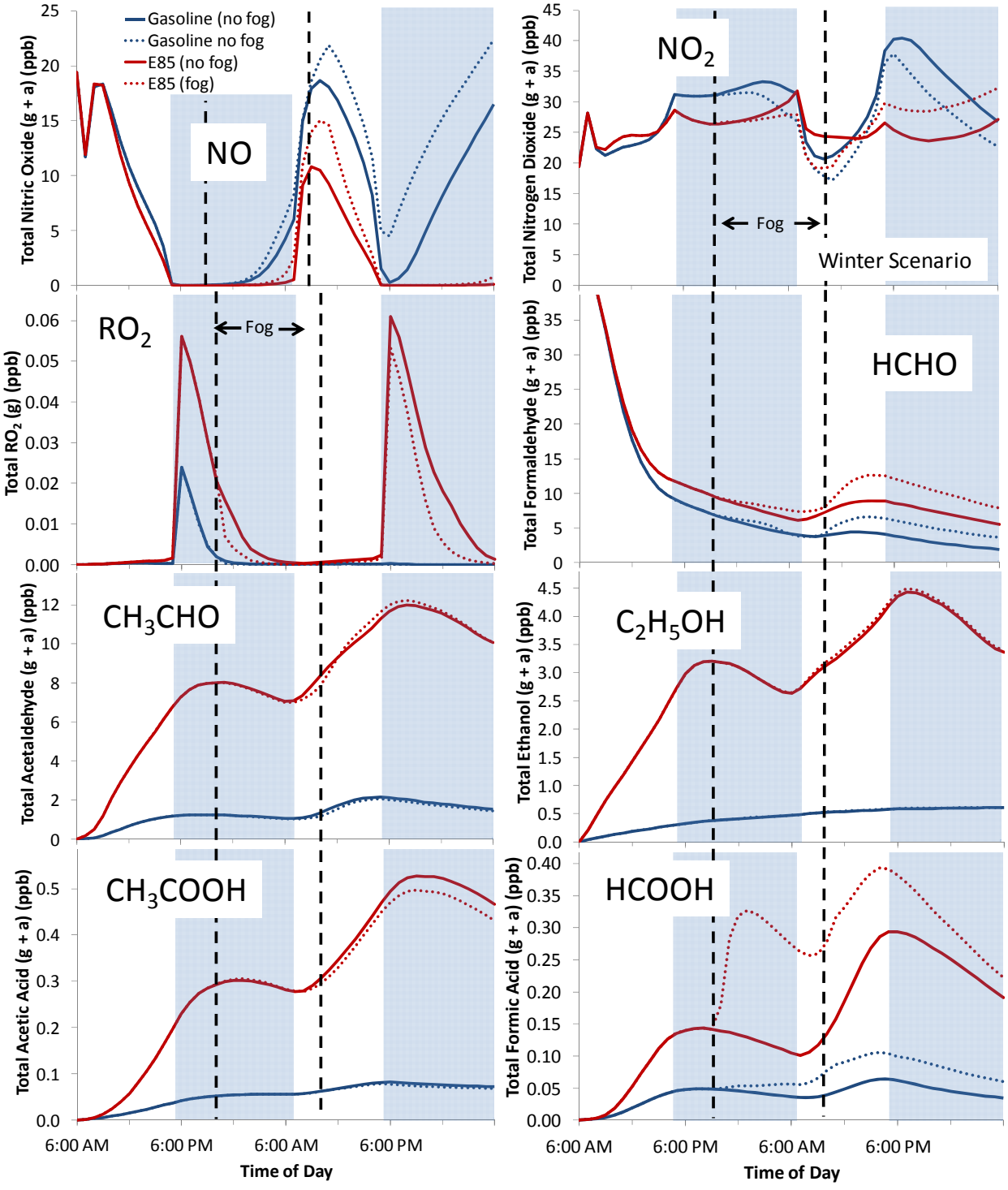

Figure S12: Two Day Model Results for Gasoline vs E85 Emissions (-7 C) without a Fog and With a Fog for the Winter Scenario for Select Species (1)

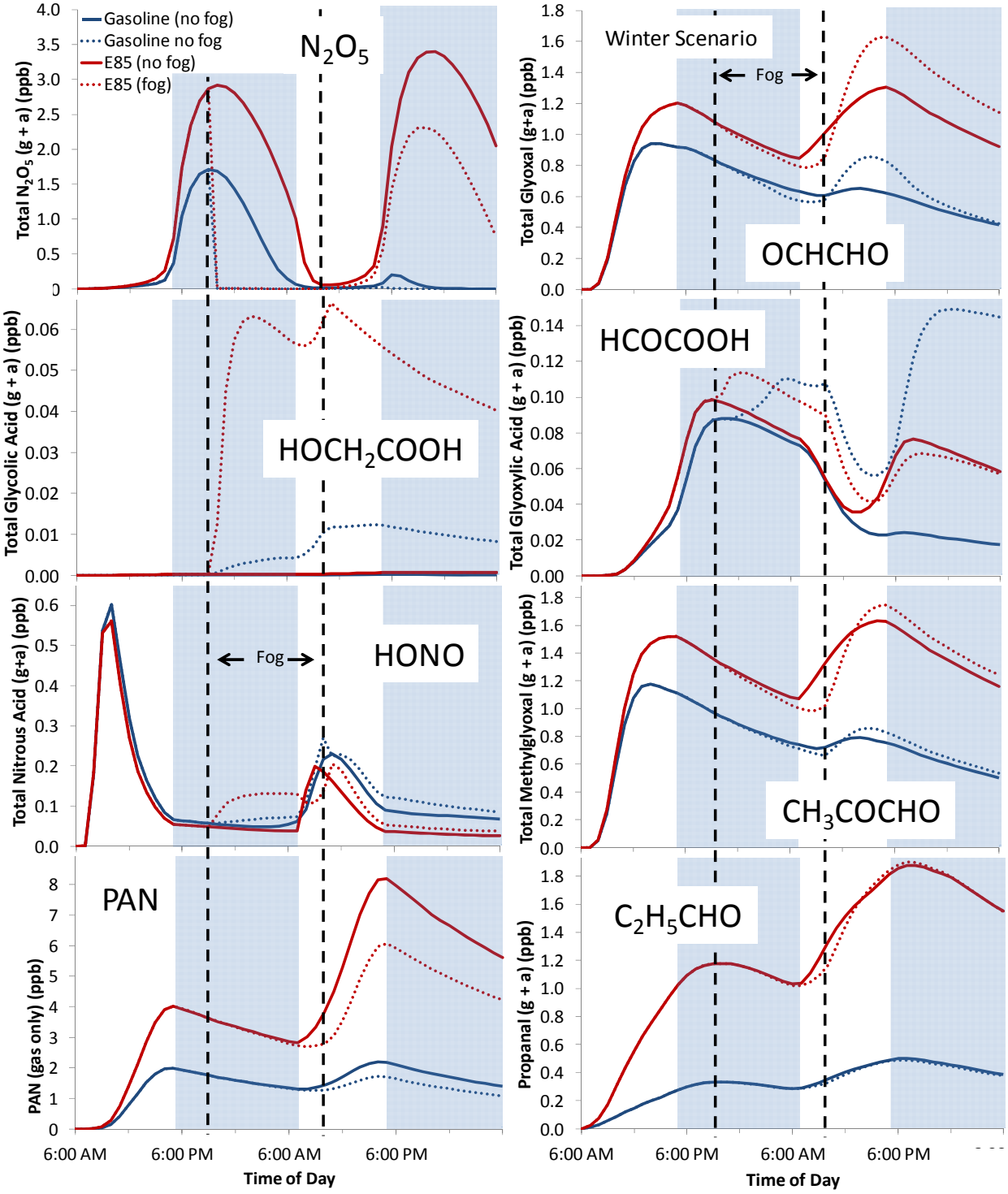

Figure S13: Two Day Model Results for Gasoline vs E85 Emissions (-7 C) without a Fog and With a Fog for the Winter Scenario for Select Species (2)

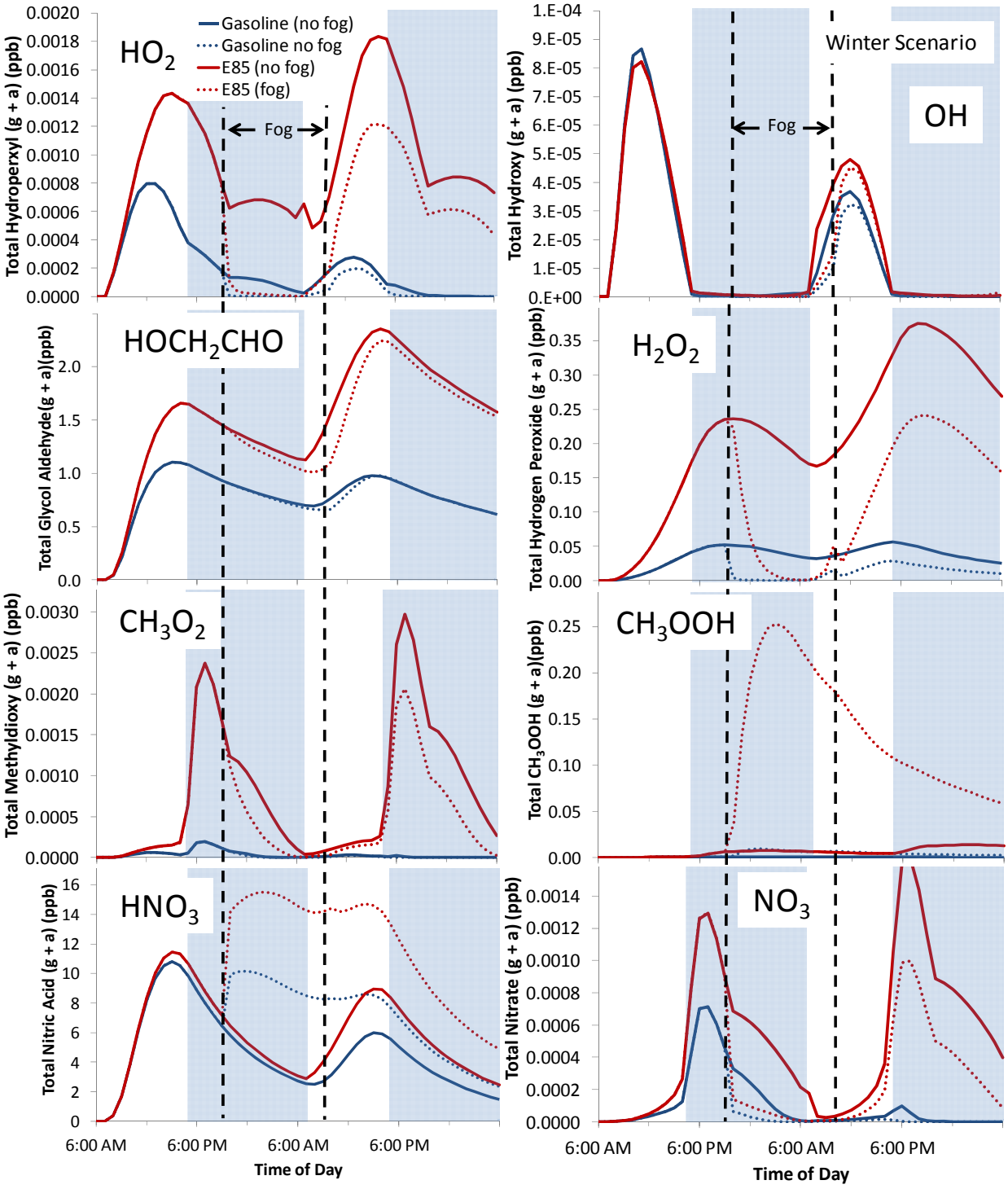

Figure S14: Two Day Model Results for Gasoline vs E85 Emissions (-7 C) without a Fog and With a Fog for the Winter Scenario for Select Species (3)

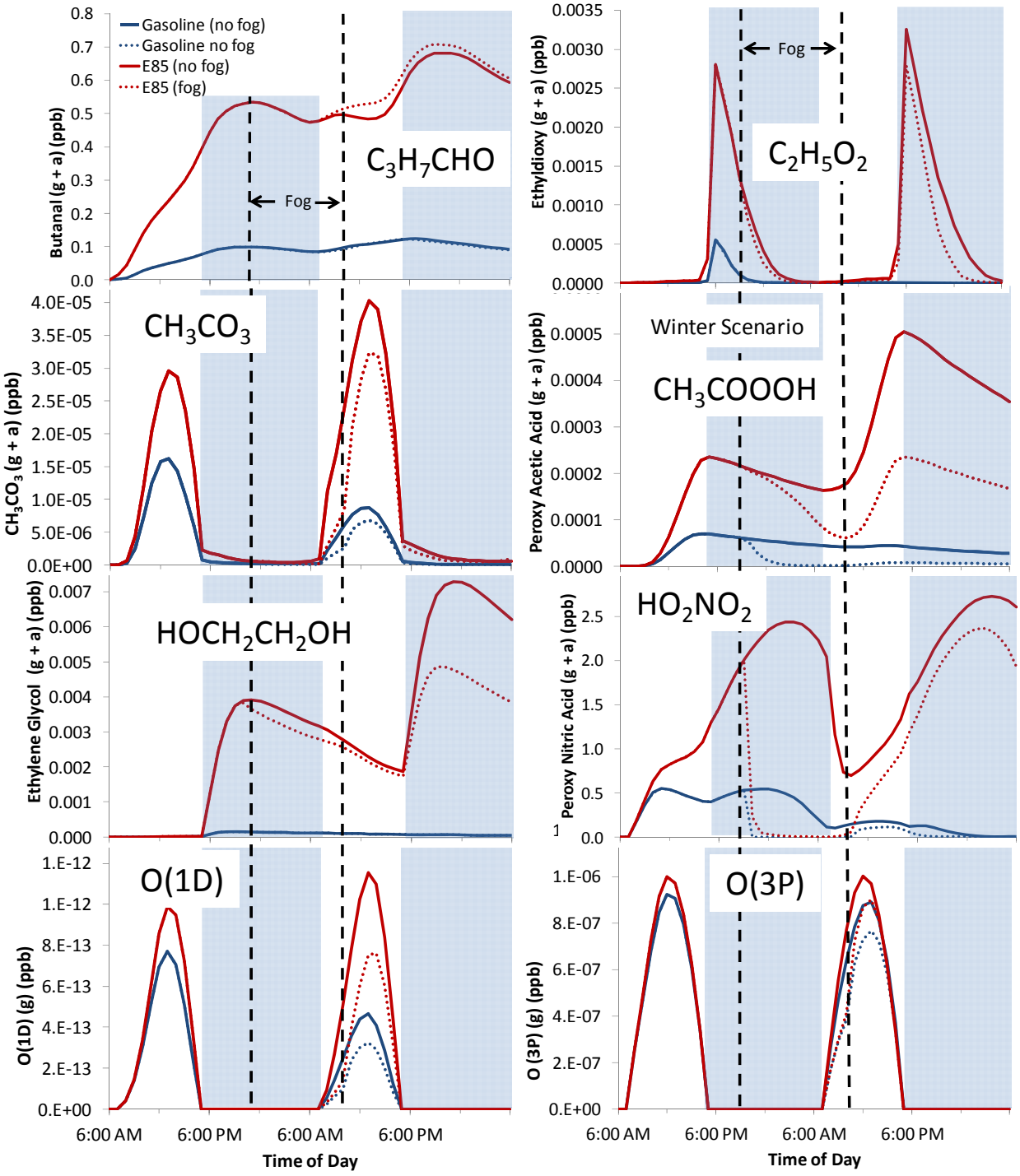

Figure S15: Two Day Model Results for Gasoline vs E85 Emissions (-7 C) without a Fog and With a Fog for the Winter Scenario for Select Species (4)

The average concentration for select species and the difference between the E85 and the gasoline case, shown in Figure S16 and Figure S17, is discussed in detail in the main paper. Figure S18 is also discussed in the main paper with the summer scenario Figure 2.

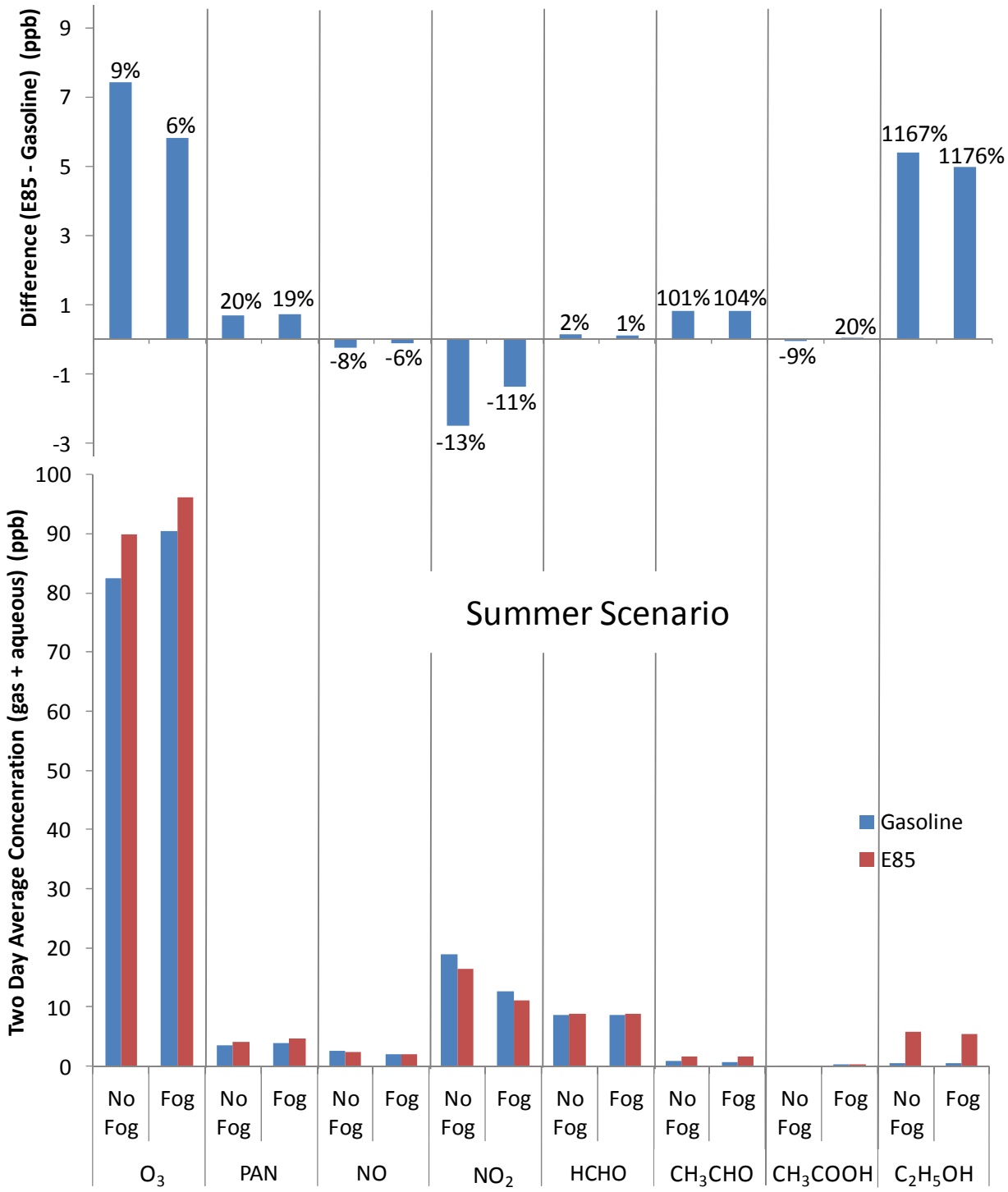

Figure S16: Difference in Two Day Average Concentration (E85 – Gasoline) (top figure) and Two Day Average Concentration (gas + aqueous) for E85 and Gasoline (bottom figure) for Select Species for the Summer Scenario

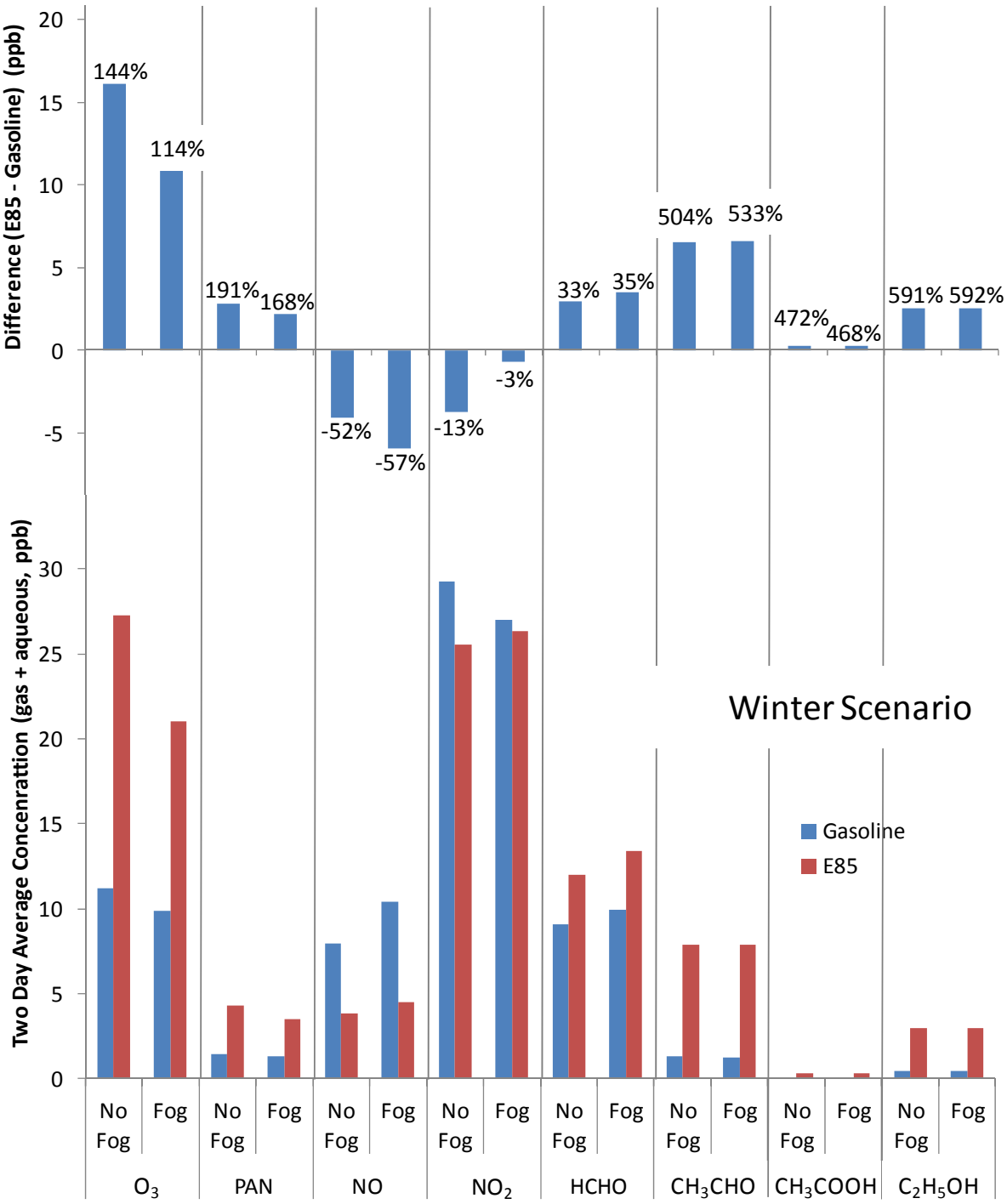

Figure S17: Difference in Two Day Average Concentration (E85 – Gasoline) (top figure) and Two Day Average Concentration (gas + aqueous) for E85 and Gasoline (bottom figure) for Select Species for the Winter Scenario

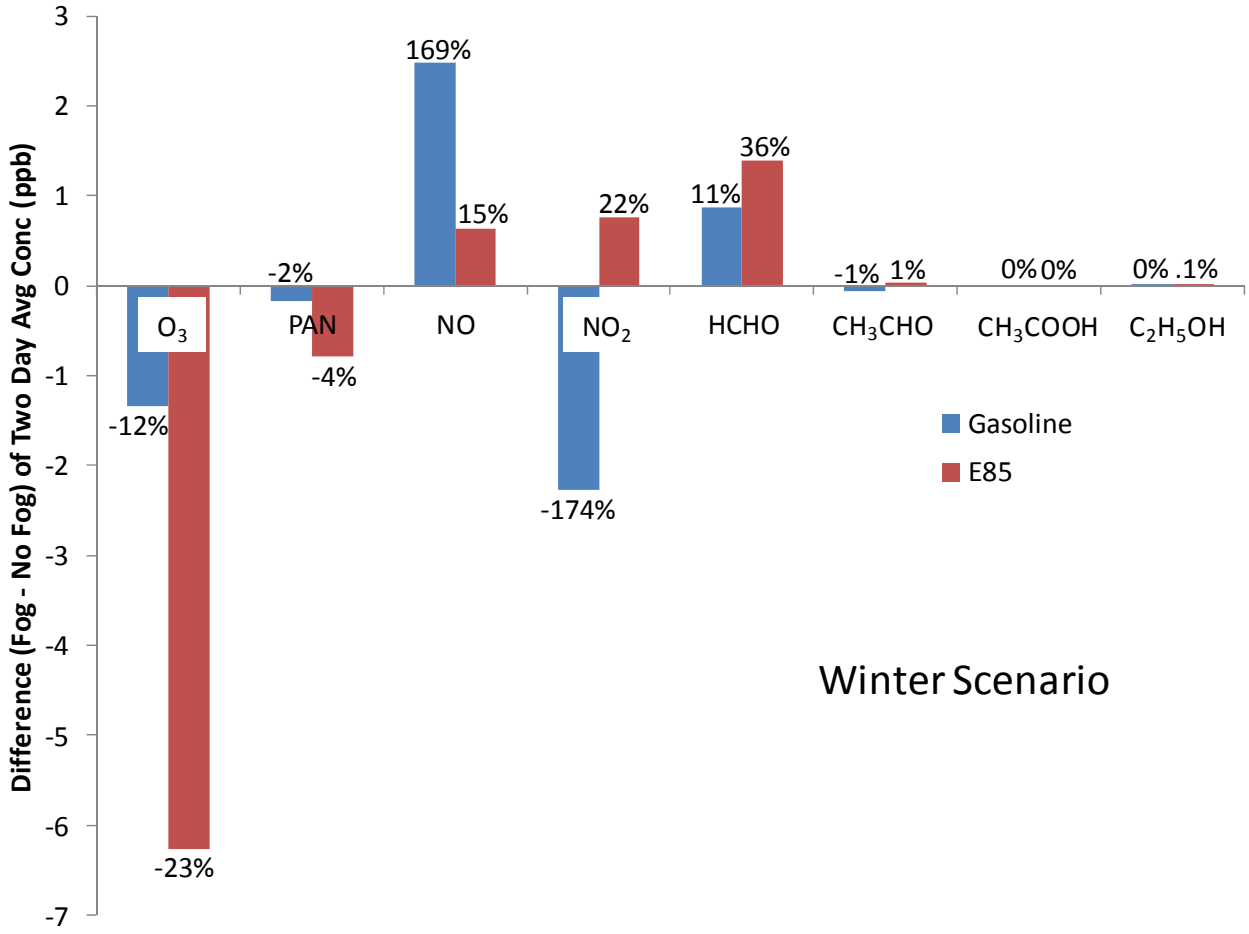

Figure S18: Difference (Fog – No Fog) and Percent Change ((Fog – No Fog)/No Fog) of Two Day Average Concentration (gas + aqueous) for Select Species for Gasoline and E85 with the Winter Scenario

Table S17 and Table S18 show the average concentration of select species during the time before the fog, during the night fog, during the day fog, during the day after the fog, and during the night after the fog. Table S17 suggests that the peroxy radical (RO_2) concentrations are the important factor in ozone production, causing ozone concentrations to actually be higher in the afternoon after the fog than in the afternoon without a fog for the summer scenario. Temperatures and photolysis are not high enough in the winter scenario for the same to occur there (Table S18).

	Time	Summer Scenario Average Concentration (ppb)				
Species	**Description**	**Before fog**	**Night fog**	**Morning fog**	**After fog, day**	**After fog, night**
NO	**Gasoline with fog**	5.6	0.0	1.3	1.2	0.0
	Gasoline no fog	5.6	0.0	**4.5**	**3.5**	0.0
	E85 with fog	5.4	0.0	1.1	0.9	0.0
	E85 no fog	5.4	0.0	**3.8**	**2.8**	0.0
NO_2	**Gasoline with fog**	18.5	7.9	9.0	9.6	11.2
	Gasoline no fog	18.5	**14.0**	**26.5**	**24.3**	**17.9**
	E85 with fog	17.1	6.9	8.0	8.0	9.6
	E85 no fog	17.1	**12.3**	**24.0**	**20.5**	**14.2**
O_3	**Gasoline with fog**	81.7	73.6	58.5	**124.7**	**103.9**
	Gasoline no fog	81.7	**74.6**	**71.7**	111.2	76.4
	E85 with fog	84.4	80.3	64.4	**131.2**	**112.6**
	E85 no fog	84.4	**81.1**	**77.4**	120.6	89.7
OH	**Gasoline with fog**	1.3E-04	3.0E-07	**8.2E-05**	**2.5E-04**	**4.7E-06**
	Gasoline no fog	1.3E-04	**3.9E-06**	7.9E-05	1.3E-04	3.5E-06
	E85 with fog	1.3E-04	2.7E-07	8.2E-05	**2.8E-04**	**5.0E-06**
	E85 no fog	1.3E-04	**4.1E-06**	**8.7E-05**	1.5E-04	4.2E-06
HO_2	**Gasoline with fog**	3.5E-03	1.5E-04	**3.0E-03**	**1.2E-02**	**3.1E-03**
	Gasoline no fog	3.5E-03	**3.0E-03**	1.2E-03	2.6E-03	2.9E-03
	E85 with fog	4.0E-03	1.6E-04	**3.4E-03**	**1.6E-02**	**3.1E-03**
	E85 no fog	4.0E-03	**2.9E-03**	1.5E-03	3.8E-03	2.9E-03
RO_2	**Gasoline with fog**	3.3E-03	3.0E-03	**2.0E-03**	**6.1E-03**	**6.2E-03**
	Gasoline no fog	3.3E-03	**4.2E-03**	6.6E-04	1.4E-03	4.9E-03
	E85 with fog	3.2E-03	2.3E-03	**2.2E-03**	**7.2E-03**	**5.3E-03**
	E85 no fog	3.2E-03	**3.6E-03**	7.5E-04	1.8E-03	4.0E-03
PAN	**Gasoline with fog**	2.6	4.1	3.9	**4.4**	**5.1**
	Gasoline no fog	2.6	**4.4**	**4.5**	3.4	3.6
	E85 with fog	2.8	4.6	4.4	**5.5**	**6.4**
	E85 no fog	2.8	**5.1**	**5.3**	4.2	4.8

Table S17: Average Concentration of Select Species During Day and Night, Fog and No Fog Segments for the Summer Scenario

	Time	Winter Scenario Average Concentration (ppb)				
Species	Description	Before fog	Night fog	Morning fog	After fog, day	After fog, night
NO	**Gasoline with fog**	8.3	**1.8**	**15.6**	**15.7**	**14.5**
	Gasoline no fog	8.3	1.1	14.4	12.1	7.9
	E85 with fog	7.7	**0.2**	**10.6**	**7.1**	**0.1**
	E85 no fog	7.7	0.1	7.7	4.7	0.0
NO_2	**Gasoline with fog**	25.8	30.5	21.2	24.2	**29.4**
	Gasoline no fog	25.8	**32.4**	**24.2**	**27.0**	34.2
	E85 with fog	25.1	27.1	21.8	24.4	**29.7**
	E85 no fog	25.1	**27.8**	**26.6**	**24.7**	24.7
O_3	**Gasoline with fog**	21.9	3.0	4.7	12.3	0.0
	Gasoline no fog	21.9	**3.3**	**8.1**	**18.5**	**0.5**
	E85 with fog	31.0	9.8	6.6	36.3	12.8
	E85 no fog	31.0	**10.8**	**15.8**	**54.5**	**23.0**
OH	**Gasoline with fog**	3.1E-05	5.0E-08	4.4E-06	2.1E-05	**5.0E-08**
	Gasoline no fog	3.1E-05	**5.6E-07**	**1.4E-05**	**2.3E-05**	1.5E-07
	E85 with fog	3.1E-05	2.9E-07	7.0E-06	3.0E-05	6.7E-07
	E85 no fog	3.1E-05	**4.7E-07**	**2.4E-05**	**3.2E-05**	**5.6E-07**
HO_2	**Gasoline with fog**	4.2E-04	1.6E-06	2.5E-05	1.5E-04	1.3E-06
	Gasoline no fog	4.2E-04	**9.9E-05**	**9.8E-05**	**2.1E-04**	**1.6E-05**
	E85 with fog	9.1E-04	2.3E-05	8.9E-05	1.0E-03	6.9E-04
	E85 no fog	9.1E-04	**6.4E-04**	**5.9E-04**	**1.5E-03**	**9.7E-04**
RO_2	**Gasoline with fog**	3.6E-03	2.5E-04	1.9E-05	1.0E-04	9.6E-07
	Gasoline no fog	3.7E-03	**3.9E-04**	**5.4E-05**	**1.3E-04**	**3.4E-05**
	E85 with fog	1.1E-02	4.0E-03	7.6E-05	8.1E-04	1.5E-02
	E85 no fog	1.1E-02	**7.1E-03**	**3.9E-04**	**1.2E-03**	**2.4E-02**
PAN	**Gasoline with fog**	1.1	1.5	1.3	1.6	1.3
	Gasoline no fog	1.1	**1.5**	**1.4**	**2.0**	**1.7**
	E85 with fog	2.1	3.2	2.7	4.8	5.0
	E85 no fog	2.1	**3.2**	**3.2**	**6.7**	**6.7**

Table S18: Average Concentration of Select Species During Day and Night, Fog and No Fog Segments for the Winter Scenario

Some aqueous species remain on the particulate matter (PM) after the fog evaporates while other species transfer into the gas phase. The aqueous species are summarized in Table S19 for the summer scenario and Table S20 for the winter scenario both during and after the fog. These tables are discussed in the main paper along with Figure 2 and Figure S19, which show the top aqueous species during the fog in the summer and winter scenarios for both gasoline and E85. Figure S20 and Figure S21 show the top aqueous species in the particulate matter after the fog.

Summer Scenario									
	Average During Fog				Average After Fog				
	Gasoline		E85		Gasoline		E85		
Species	**µg/m³**	**% of total**	**µg/m³**	**% of total**	**µg/m³**	**% of total**	**µg/m³**	**% of total**	**No. of Species**
C1	1.3	0.9%	1.4	0.9%	0.5	0.5%	0.5	0.5%	26
C2	2.9	2.0%	2.7	1.9%	2.4	2.3%	2.0	2.1%	57
C3	0.2	0.1%	0.2	0.1%	0.2	0.2%	0.2	0.2%	104
C4	0.07	0.05%	0.06	0.04%	0.1	0.1%	0.1	0.1%	91
C5	1E-17	0.0%	8E-19	0.0%	9E-15	0.0%	3E-15	0.0%	14
C6	2E-06	0.0%	2E-06	0.0%	6E-08	0.0%	2E-08	0.0%	15
Total Carbon	4.5	3.1%	4.3	3.0%	3.2	3.1%	2.8	2.9%	307
Total Chlorine	2.3	1.5%	2.3	1.6%	0.4	0.4%	0.4	0.5%	11
Total Sulfur	3.9	2.6%	4.1	2.9%	9.6	9.4%	10.2	10.5%	15
Total Copper	0.009	0.006%	0.009	0.006%	0.009	0.009%	0.009	0.01%	3
Total Mn	0.01	0.008%	0.01	0.008%	0.002	0.002%	0.005	0.005%	8
Total Iron	0.008	0.006%	0.008	0.006%	0.0002	0.0002%	0.0002	0.0002%	8
Total Nitrogen	130.7	88.8%	123.2	85.4%	88.9	87.0%	83.0	86.1%	14
Total Other Inorganics	10.3	7.0%	10.4	7.2%	0.00000002	0.0%	0.00000003	0.0%	24
Total Aqueous	**147.3**		**144.3**		**102.2**		**96.4**		375
pH	**2.69**		**2.71**		**6.75**		**6.75**		
Water Ratio	**3E-07**		**3E-07**		**1E-15**		**1E-15**		

Table S19: Summary of Aqueous Species During and After the Fog for the Summer Scenario
Note: There is some double counting in the inorganic categories due to multiple elements in a single species. However, the organic and inorganic species are counted separately.

Winter Scenario									
	Average During Fog				Average After Fog				
	Gasoline		E85		Gasoline		E85		No. of
Species	**µg/m^3**	**% of total**	**µg/m^3**	**% of total**	**µg/m^3**	**% of total**	**µg/m^3**	**% of total**	**Species**
C1	13.2	30.8%	16.2	17.9%	6.9	39.12%	9.5	31.5%	26
C2	5.2	12.2%	7.6	8.4%	2.6	14.78%	4.7	15.6%	57
C3	1.8	4.3%	2.6	2.9%	0.8	4.52%	1.3	4.4%	104
C4	0.03	0.08%	0.06	0.07%	0.003	0.017%	0.02	0.06%	91
C5	5E-23	0.0%	3E-18	0.0%	2E-16	0.0%	2E-15	0.0%	14
C6	2E-07	0.0%	9E-07	0.0%	2E-09	0.0%	7E-08	0.0%	15
Total Carbon	20.3	47.3%	26.5	29.2%	10.3	58.45%	15.5	51.5%	307
Total Chlorine	1.9	4.4%	1.9	2.1%	0.02	0.10%	0.03	0.1%	11
Total Sulfur	2.9	6.8%	8.1	9.0%	4.4	24.91%	7.2	23.8%	15
Total Copper	0.008	0.02%	0.008	0.008%	0.005	0.0259%	0.005	0.02%	2
Total Mn	0.01	0.03%	0.009	0.01%	0.009	0.0508%	0.004	0.01%	8
Total Iron	0.12	0.3%	0.09	0.1%	0.06	0.35752%	0.007	0.02%	8
Total Nitrogen	26.6	62.0%	42.5	46.9%	2.8	16.10%	7.4	24.5%	14
Total Other Inorganics	11.4	26.5%	11.5	12.7%	0.0001	0.0%	0.00007	0.0%	24
Total Aqueous	**43.0**		**90.7**		**17.6**		**30.1**		374
pH	**4.82**		**3.23**		**4.13**		**4.45**		
Water Ratio	**3E-07**		**3E-07**		**1E-15**		**1E-15**		

Table S20: Summary of Aqueous Species During and After the Fog for the Winter Scenario
Note: There is some double counting in the inorganic categories due to multiple elements in a single species. However, the organic and inorganic species are counted separately.

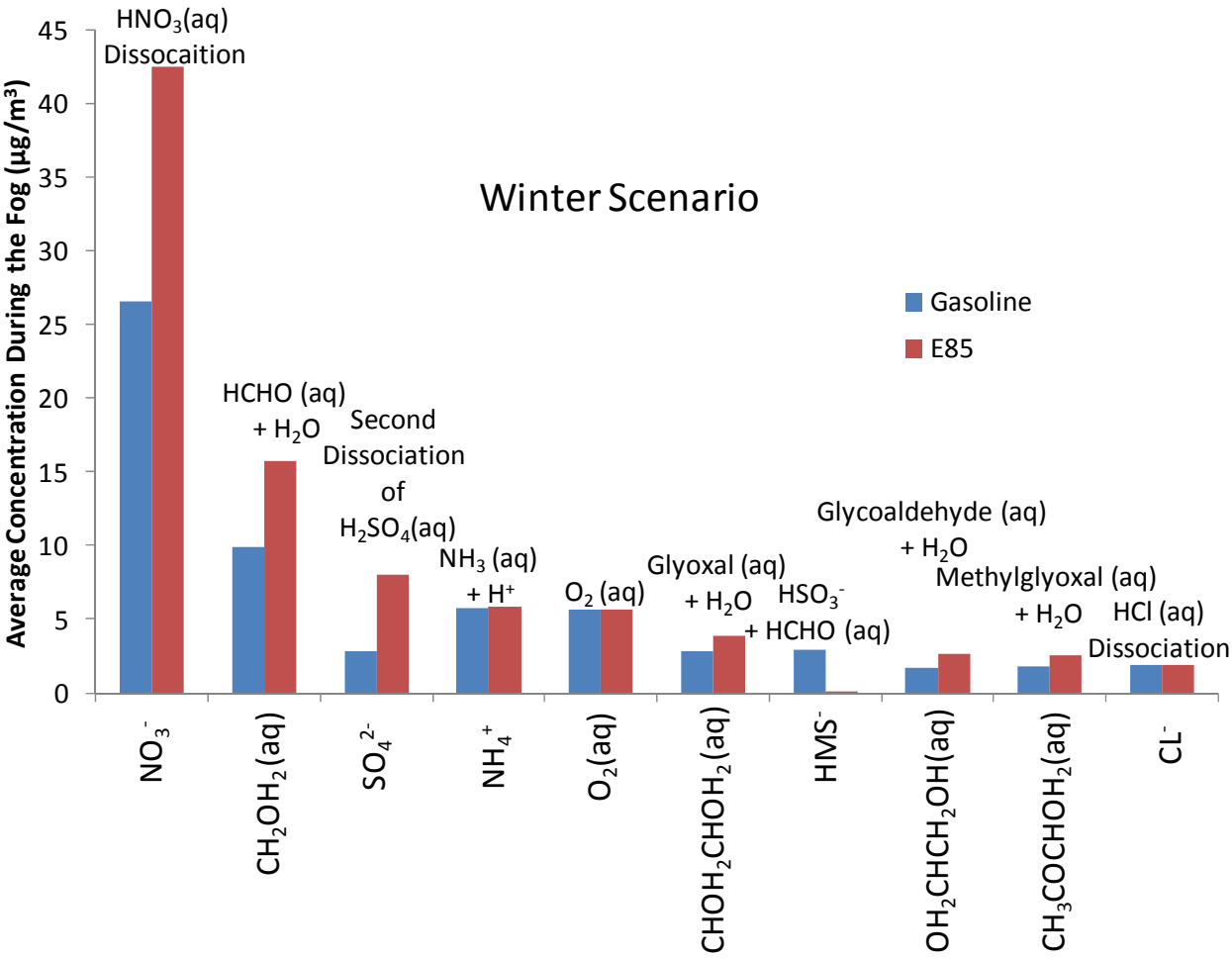

Figure S19: Average Concentration of the Top Ten Highest Concentration Aqueous Species During the Fog for the Winter Scenario

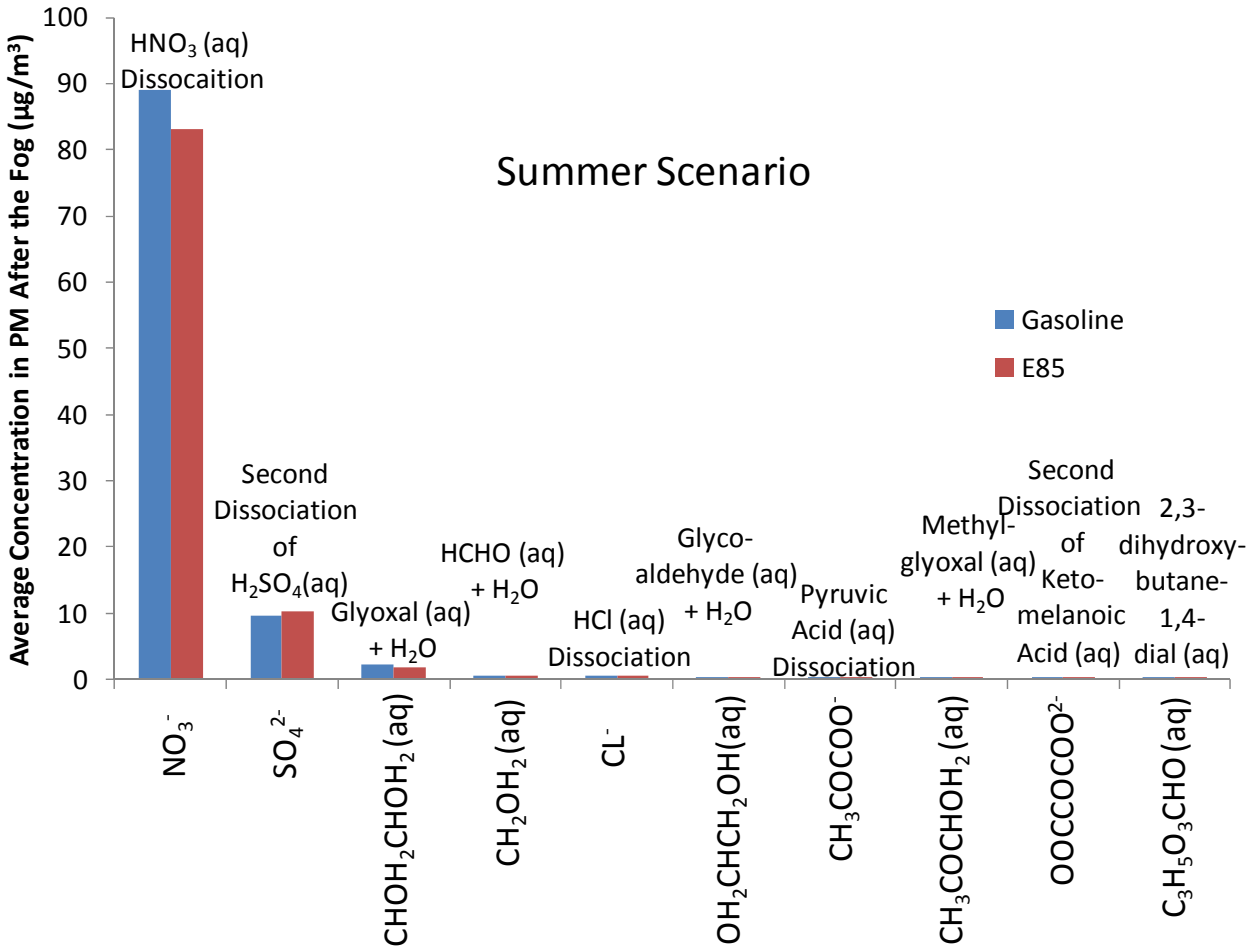

Figure S20: Average Concentration of the Top Ten Highest Concentration Aqueous Species in the Particulate Matter (PM) After the Fog for the Summer Scenario

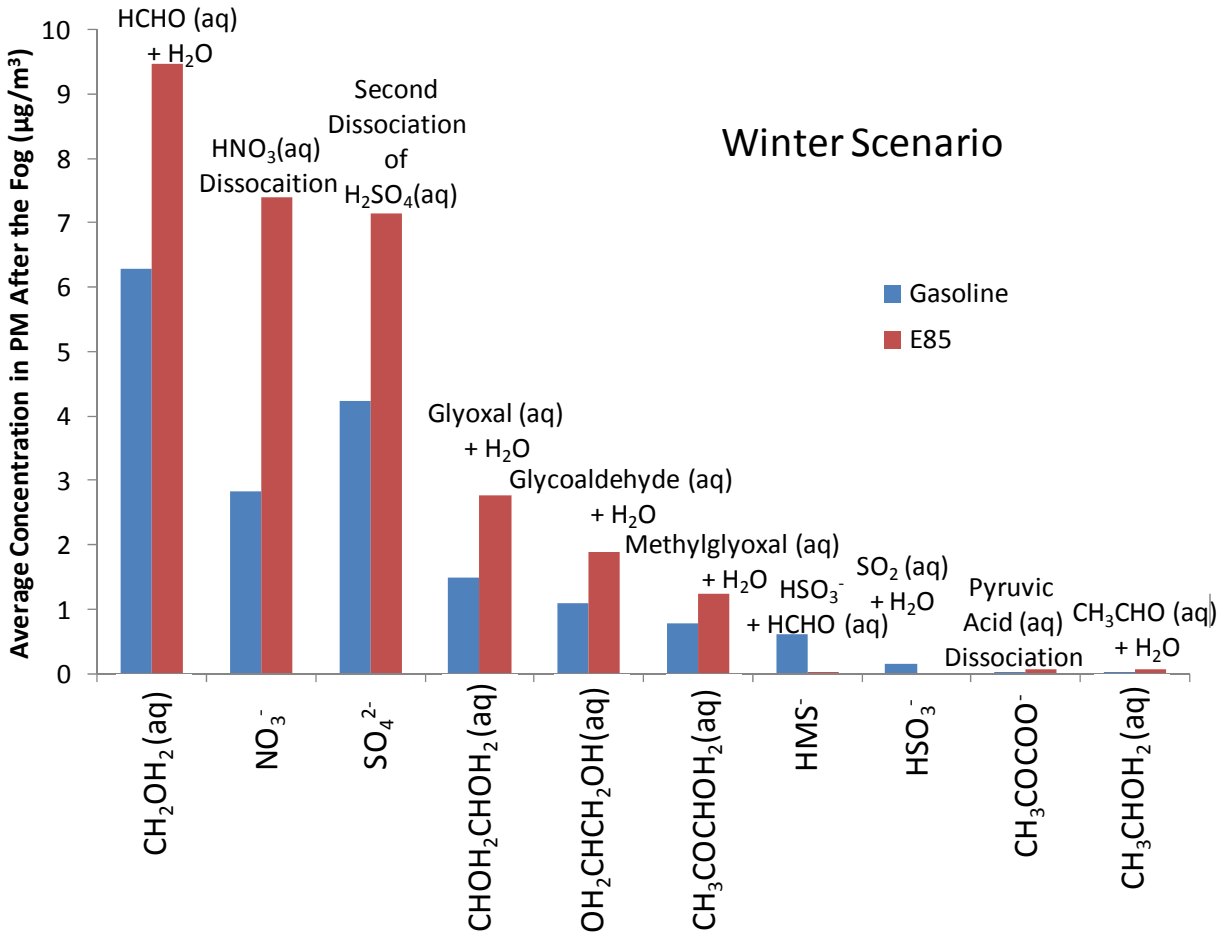

Figure S21: Average Concentration of the Top Ten Highest Concentration Aqueous Species in the Particulate Matter (PM) After the Fog for the Winter Scenario

4. Model Sensitivity

The sensitivity of the model results without a fog are discussed in Ginnebaugh et al. (2010). The sensitivity of the results to fog parameters is described in the main paper along with results for the summer scenario. The remaining results for the summer scenario and all results for the winter scenario are shown here (Figure S22, Figure S23, and Figure S24).

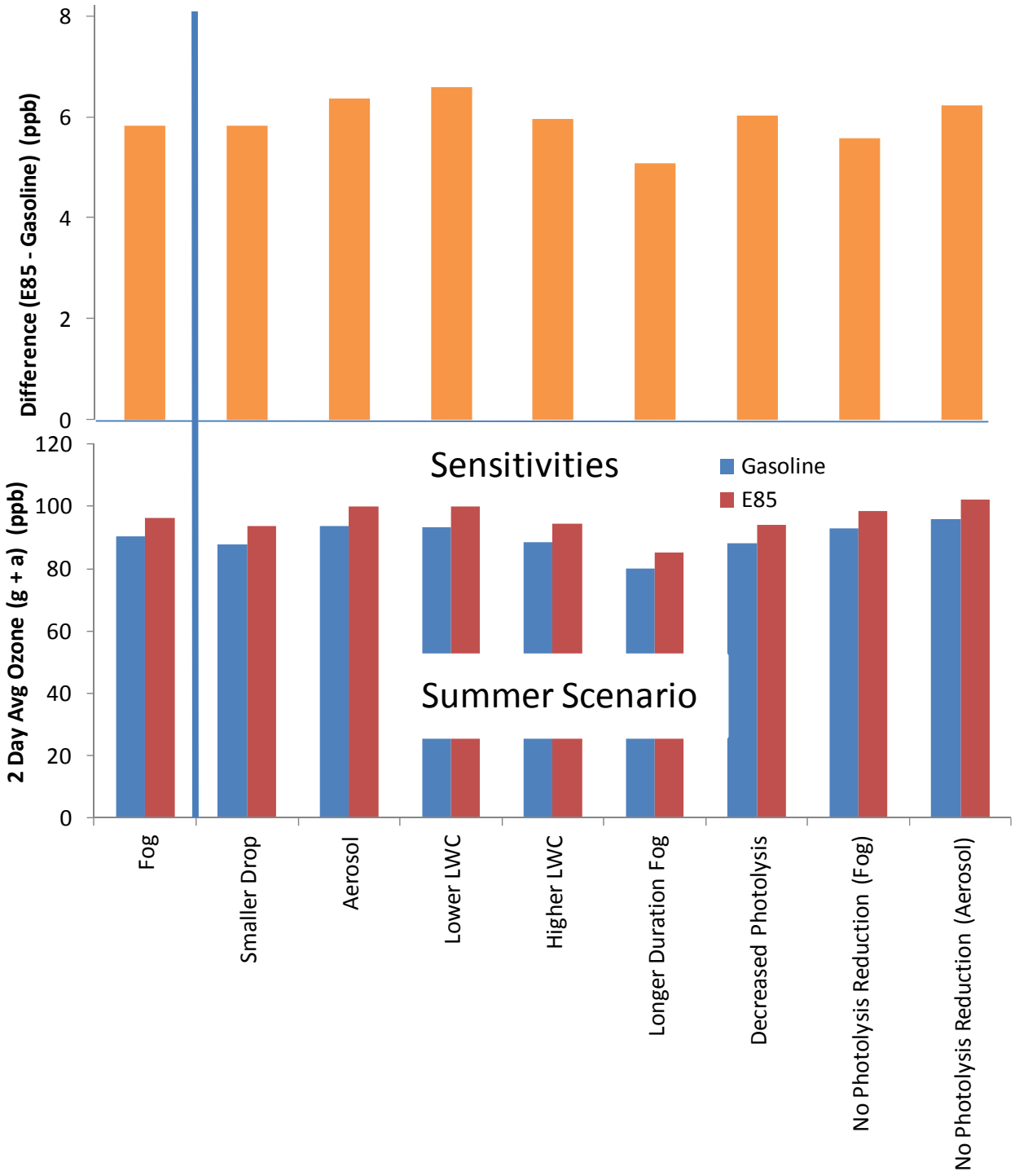

Figure S22: Difference in Two Day Average Ozone Concentration (E85 – Gasoline) (top figure) and Two Day Average Ozone Concentration for E85 and Gasoline (bottom figure) to Test the Model's Sensitivity to Fog Parameters for the Summer Scenario

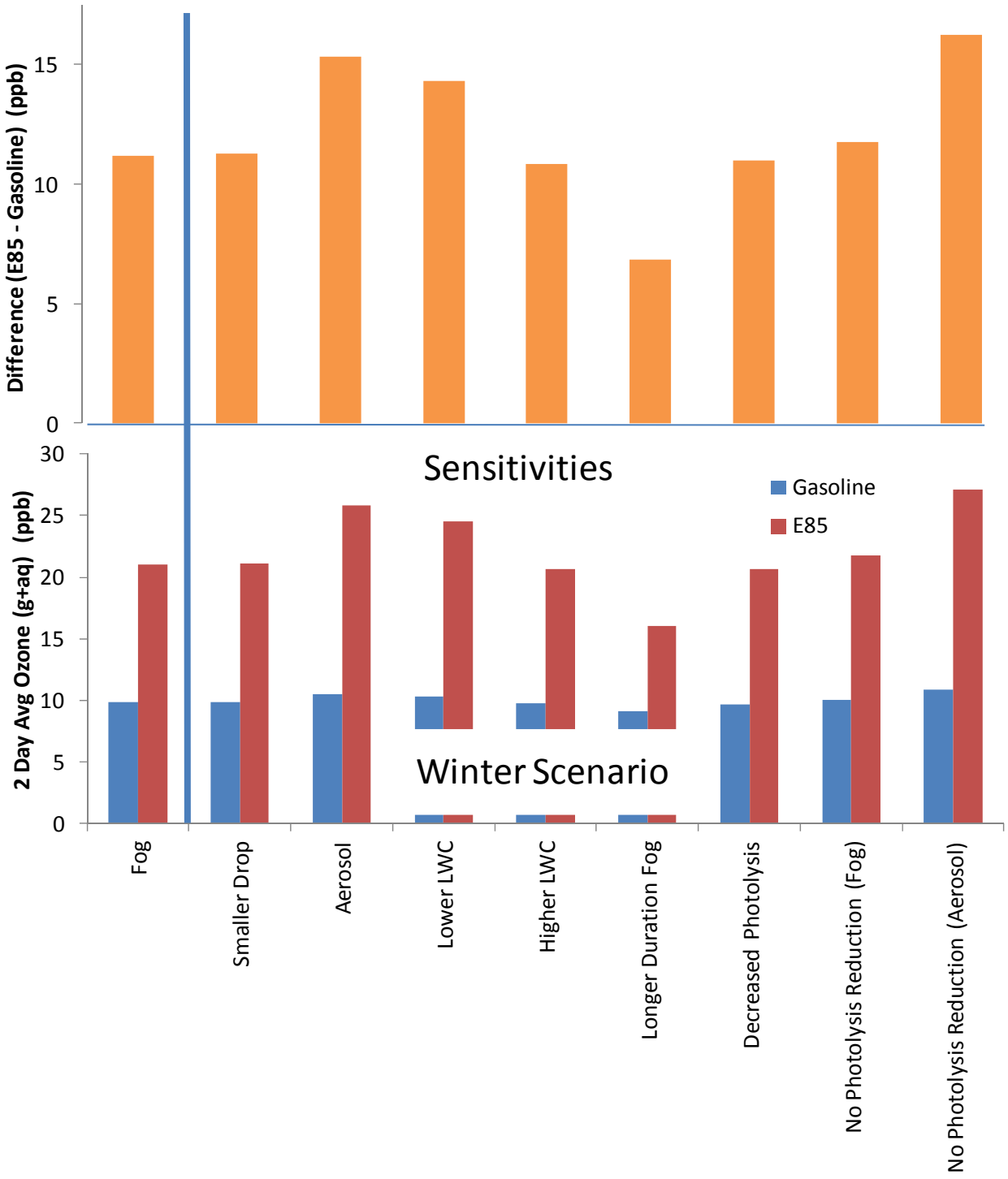

Figure S23: Difference in Two Day Average Ozone Concentration (E85 – Gasoline) (top figure) and Two Day Average Ozone Concentration for E85 and Gasoline (bottom figure) to Test the Model's Sensitivity to Fog Parameters for the Winter Scenario

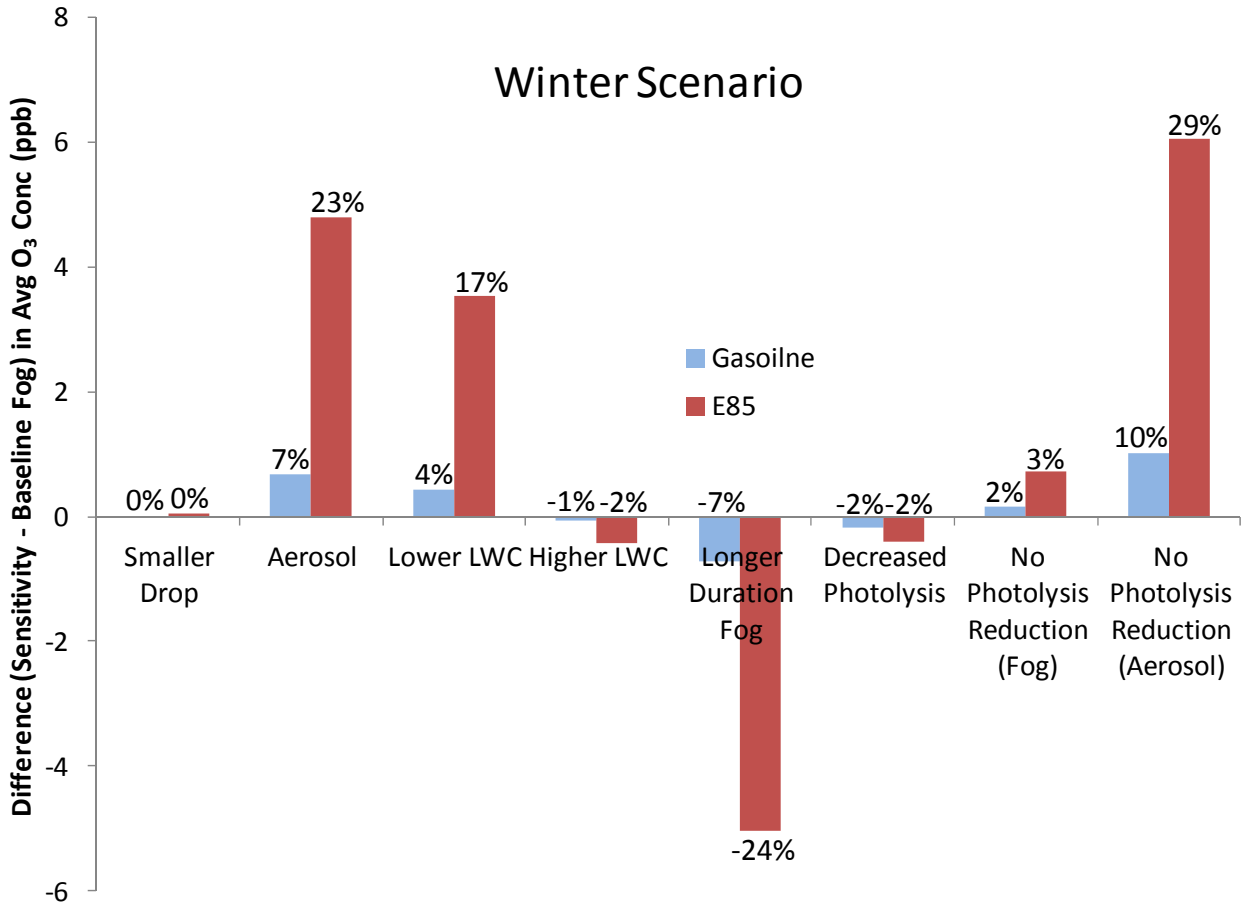

Figure S24: Difference in Two Day Average Ozone (gas + aqueous) Concentration (Sensitivity – Baseline Fog Case) and Percent Change ((Sensitivity – Baseline Fog)/Baseline Fog) to Test the Model's Sensitivity to Fog Parameters for the Winter Scenario

5. Summary

In this Supplemental Information, we have provided information on the emissions and model used for this study beyond that described in the main paper. We have shown that E85 may increase urban ozone over gasoline in a variety of scenarios. The increase is significantly greater at colder temperatures, implying a significant impact on human health during the winter when using E85. We also found that, under certain warm, summer conditions, a morning fog can increase afternoon ozone for both gasoline and E85.

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