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Effects of Ethanol (E85) versus Gasoline Vehicles on Cancer and Mortality in the United States

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Ethanol use in vehicle fuel is increasing worldwide, but the potential cancer risk and ozone-related health consequences of a large-scale conversion from gasoline to ethanol have not been examined. Here, a nested global-through-urban air pollution/weather forecast model is combined with high-resolution future emission inventories, population data, and health effects data to examine the effect of converting from gasoline to E85 on cancer, mortality, and hospitalization in the United States as a whole and Los Angeles in particular. Under the base-case emission scenario derived, which accounted for projected improvements in gasoline and E85 vehicle emission controls, it was found that E85 (85% ethanol fuel, 15% gasoline) may increase ozone-related mortality, hospitalization, and asthma by about 9% in Los Angeles and 4% in the United States as a whole relative to 100% gasoline. Ozone increases in Los Angeles and the northeast were partially offset by decreases in the southeast. E85 also increased peroxyacetyl nitrate (PAN) in the U.S. but was estimated to cause little change in cancer risk. Due to its ozone effects, future E85 may be a greater overall public health risk than gasoline. However, because of the uncertainty in future emission regulations, it can be concluded with confidence only that E85 is unlikely to improve air quality over future gasoline vehicles. Unburned ethanol emissions from E85 may result in a global-scale source of acetaldehyde larger than that of direct emissions.

Introduction

In 1826, Samuel Morey (1762−1843) patented the first internal combustion engine, which ran on ethanol and turpentine. Since then, ethanol fuel has been used in all industrialized countries. Today, ethanol is being promoted as a clean and renewable fuel that will reduce global warming, air pollution, and reliance on diminishing gasoline. These reasons have been used to justify subsidies and legislation encouraging ethanol use worldwide.

Life-cycle assessments to date, though, suggest that corn ethanol's effects on equivalent greenhouse gases emissions relative to gasoline are small, with an uncertain sign (*1*−*8*). Some of the same studies have hypothesized that ethanol from cellulose may result in lower net greenhouse-gas emissions than corn ethanol. To date, though, this hypothesis has not been tested on a large scale.

With respect to air pollution, several studies have examined emission differences between gasoline- and ethanol-fueled vehicles (*9*−*19*). However, no study has examined the spatially varying effect on cancer or ozone-related illness throughout the United States that might result from a conversion to ethanol. Such a study is important because previous introductions of chemicals (e.g., tetraethyl lead, chlorofluorocarbons, DDT, dioxins) without an analysis led to damaging consequences. Air pollution (indoor plus outdoor) is also the seventh leading cause of death worldwide (*20*), so any change in fuel that could affect mortality should be examined prior to its implementation.

Here, a 3-D atmospheric computer model that treats chemical and radiative transformations, meteorology, and transport, is used with 2020 spatially resolved emissions data to calculate spatially varying chemical concentrations from gasoline and ethanol. The ambient concentrations are then combined with health effects and population data to determine health risks due to the fuels. Results are analyzed at high resolution in Los Angeles and coarser resolution in the whole United States.

Methods

The model used was the nested global-through-urban GATOR-GCMOM (*21*−*25*), described in the Supporting Information. For Los Angeles, three nested domains were treated: global (4°-SN × 5°-WE), California (0.2° × 0.15°), and Los Angeles (0.045° × 0.05°); for the U.S., two domains were treated: global and U.S. (0.5° × 0.75°). Los Angeles results are shown to test conclusions at higher resolution than in the U.S. Since Los Angeles has historically been the most polluted airshed in the U.S., the testbed for nearly all U.S. air pollution regulation, and home to about 6% of the U.S. population, it is also ideal for a more detailed study.

Simulations were run comparing future (ca. 2020) fleets fueled by gasoline and E85, where E85 contains 85% ethanol and 15% gasoline. Since ethanol, itself, contains 5% gasoline as a denaturant, E85 is really 80% ethanol and 20% gasoline. E85 was examined since the large-scale replacement of gasoline would require a fuel with high ethanol content. 2020 was examined because flex-fuel cars replacing current gasoline vehicles, most of which cannot use E85, could substantially penetrate the U.S. vehicle fleet only by 2020.

Future anthropogenic emission inventories for gasoline and E85 vehicles were prepared from the 2002 U.S. National Emission Inventory (NEI) (*26*), which treats spatially distributed point, area, and mobile onroad/nonroad emissions. Mobile emissions include evaporative and exhaust. Formaldehyde, acetaldehyde, and 1,3-butadiene result from combustion in gasoline and E85 but not from evaporation (*10*). Benzene and ethanol result from both. Non-NEI natural emissions were also treated (Supporting Information). The only emissions perturbed due to E85 were vehicle emissions since exposure in populated areas is affected far more by vehicle exhaust than production of ethanol or gasoline.

Tables 1 and S4 (where "S" refers to Supporting Information) summarize the speciated 2020 "baseline" gasoline and "Case 1" E85 emission inventories used here for Los Angeles and the U.S., respectively. The 2020 gasoline inventory was prepared by reducing NEI evaporative and exhaust mobile gasoline and nongasoline emissions by 60%, which is consistent with two independent estimates. First, D. Streets (personal communication) derived speciated 2030:2000 emission factors by sector and world region assuming IPCC SRES A1B and B1 emission scenarios. Table S2 shows the result for the U.S. transportation sector and indicates that an across-the-board 60% mobile emission reduction for 2020 assumed here is conservative since it exceeds the 2030

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TABLE 1. Summed 2020 Baseline (with Gasoline Vehicles) and Sensitivity-Test (with E85 Replacing Gasoline in Onroad and Nonroad Vehicles) Emissions in the Los Angeles Model Domain (Slightly Larger than the SCAB)[a]

species	(1) 2020 baseline onroad gasoline (t/yr)	(2) 2020 baseline nonroad gasoline (t/yr)	(3) 2020 baseline total gasoline (t/yr)	(4) percent change from gasoline to E85	(5) Case 1 E85 replacing 2020 total gasoline (t/yr)	(6) 2020 baseline and E85 non-gasoline (t/yr)
carbon monoxide	615,000	168,000	782,000	+5	821,000	285,000
nitrogen oxides as NO_2	64,400	45,400	68,900	−30	43,200	189,000
organic gases						
methane	6290	2230	8530	+43	12200	198,000
ethane	902	316	1220	0	1220	17,200
propane	342	123	465	−65	163	4890
paraffin bond group	33,400	11,300	44,720	−80	8940	115,000
ethene	2660	910	3570	−17	2960	10,100
propene	739	248	988	−65	346	1680
1,3-butadiene	1030	368	1390	−10	1250	718
olefin bond group	707	242	949	−17	787	2220
methanol	0	0	0	0	0	550
ethanol	0	0	0	*b*	69,800	4720
formaldehyde	481	169	650	+60	1040	2380
acetaldehyde	171	61.4	232	+2000	4650	631
higher aldehydes	2590	872	3460	−60	1380	4080
formic acid	0	0	0	0	0	139
acetic acid	0	0	0	0	0	246
acetone	0	0	0	0	0	2920
benzene	951	323	1270	−79	268	2550
toluene bond group	4640	1620	6260	−80	1250	26,800
xylene bond group	8570	3010	11,600	−80	2320	12,400
isoprene bond group	48.6	16.4	65	−80	13	134
unreactive	3370	1160	4540	−80	908	28,600
total organic gas (TOG)	66,914	22,969	89,883	+22	109,464	448,000
sulfur oxides as SO_2	370	103	473	0	473	22,700
ammonia	7410	20	7430	0	7430	28,900
$PM_{2.5}$						
organic matter	724	490	1210	0	1210	56,700
black carbon	242	50	292	0	292	8330
sulfate	41.3	2.8	44.1	0	44.1	3590
nitrate	1.8	3.9	5.7	0	5.7	362
other	265	76.7	342	0	342	70,600
total $PM_{2.5}$	1270	623	1900	0	1900	140,000
PM_{10}						
organic matter	1230	1140	2370	0	2370	112,000
black carbon	412	116	528	0	528	15,400
ulfate	70.2	6.5	76.7	0	76.7	6330
nitrate	3.0	9.1	12.2	0	12.2	856
other	450	178	629	0	629	298,000
total PM_{10}	2170	1450	3610	0	3610	433,000

[a] 2020 Baseline gasoline and nongasoline mobile emissions (onroad and nonroad) (Columns 1−3) were calculated as 40% of 2002 NEI emissions. Column 5 was then derived by applying Column 4 to Column 3. Column 6 includes point, fugitive, area, nonroad nongasoline, and onroad nongasoline emissions, which were held constant for both the gasoline and E85 simulations. Total emissions for the baseline gasoline simulation are the sum of Columns 3 and 6. Total emissions for the E85 Case 1 simulation is the sum of Columns 5 and 6. [b] Each "percent change from gasoline to E85" was estimated from Table 2, except that the ethanol emissions for E85 were calculated to ensure the TOG emissions from E85 divided by that from gasoline equaled 1.22 (a 22% increase, estimated conservatively from Table 2, row 1). Sensitivity test Cases 2 and 3 used the same emissions as Case 1, except that ethanol emissions were derived to ensure increases in TOG from E85 of 6% and 38%, respectively, instead of 22%. The 80% reductions of xylene and toluene were assumed since ethanol does not emit xylene or toluene but E85 contains 20% gasoline.

reductions in Table S2, interpolated to 2020, for most species. Second, Table S3 shows that the California Air Resources Board (CARB) estimates that total organic gas (TOG) emissions in the South Coast Air Basin (SCAB) may decrease 57.7% between 2002 and 2020, from 172 919 to 73 192 metric tonnes/yr. Although the 60% reduction assumed here is consistent with CARB, the CARB estimate may be optimistic since it exceeds the 2020 reduction interpolated from Table S2.

E85 vehicle emissions (Column 5) in Tables 1 and S4 were obtained by applying percent changes (Column 4) to baseline gasoline evaporative and exhaust emissions (Column 3). Ethanol emissions were then calculated as a residual (Table 1, footnote). In old E85 vehicles, only 5% of ethanol emissions are evaporative and the rest is exhaust (*27*), thus with new vehicles, ethanol emissions are closer to pure exhaust.

Percent changes in Table 1 were estimated from Table 2, which provides emission differences between E85 and gasoline or low ethanol/gasoline blends from measurements. E85 generally increased nonmethane organic gases (NMOG), methane, formaldehyde, and acetaldehyde and reduced 1,3-butadiene, benzene, and nitrogen oxides. Carbon monoxide increased in half the studies. E85 increased acetaldehyde (1250−4340%) and formaldehyde (7−240%), two important ozone precursors.

Table 3 compares 2002 NEI with 2002 CARB acetaldehyde emissions from mobile sources in Los Angeles. The NEI estimate was 36% lower (1050 versus 1630 tonnes/yr) than the CARB estimate. Table 3 also assumes 2020 acetaldehyde emissions to be 2000% of 2020 gasoline emissions, lower than the average emission difference of 2500% from six studies

TABLE 2. Measured Percentage Changes in Emissions of Gases or Groups of Gases from Vehicles or Engines Using E85 versus Gasoline or E5 (+ Indicates Higher E85 Emission)[a]

	D96	B98	N98	N99	W01	L02	M02	S05	M05	D06	G06
total organic gas (TOG)			+62				+38	+95		+43	+34
nonmethane org gas (NMOG)		+15	+48	+0	+63				+17	+31	+11
methane (CH_4)						+43		+340			+106
formaldehyde (HCHO)		+60	+228		+240		+41	+7			
acetaldehyde (CH_3CHO)	+1440	+3660	+4340		+1430		+3100	+1250			
ethene (C_2H_4)	−17										
butadiene (C_4H_6)		+0			−13						
benzene (C_6H_6)	−85	−62			−78						
carbon monoxide (CO)		+62	+32	+31			−23	+320	−33	−4	−38
NO_x (as NO_2)		−34	+13	+33			−59	−38	−33	−59	+17
PM mass								+31			
PM number								+100			

[a] D96 (*9*) Table 13, comparing gasoline and E85; B98 (*10*) comparing Limina RFG and Lumina E85; N98 (*11*) comparing flex-fuel vehicles with E85 and reformulated gasoline; N99 (*12*) comparing 1998 Taurus FFV with E85 and a 1998 Taurus gasoline vehicle; W01 (*13*) comparing conventional gasoline and E85; L02 (*14*) Section 3.4, summarizing E85 studies; M02 (*15*) comparing regular gasoline and E85 ethanol-regular blended gasoline under lean conditions − Tables 2 and 4 of that paper; S05 (*16*) average of three vehicles using E85 versus E5 at 22 °C under NEDC driving cycle; M05 (*17*) average differences between gasoline and E85 emissions from two vehicles (2005 Ford Taurus and 2005 Mercedes-Benz C 240), as determined by the California Air Resources Board on-road new vehicle and engine certification program, D06 (*18*) comparing gasoline and E85, G06 (*19*) Certification data comparison of gasoline and E85, averaged over emissions from four 2007 Chevrolet vehicles: Savanna, Avalanche, Suburban, Uplander.

TABLE 3. Comparison of Acetaldehyde Emissions (t/yr) from the California Air Resources Board Emission Inventory with Those from the U.S. National Emission Inventory for the Model Domain Used Here (Also Shown are 2020 Emission Estimates Assumed Here for a Gasoline Fleet and for an E85 Fleet)

	onroad gasoline or E85	onroad non-gasoline	total onroad	nonroad gasoline or E85	nonroad non-gasoline	total nonroad	total mobile
2002 CARB SCAB[a]			565			822	1387
2002 CARB model domain[b]			664			966	1630
2002 NEI model domain[c]	427	51.1	478	154	418	572	1050
2020 NEI model domain[d]	171	20.4	191	61.4	167	228	419
2020 E85 model domain[e]	3420	20.4	3440	1230	167	1397	4837

[a] Reference *28*. [b] The model domain is slightly larger than the SCAB. CARB emissions in the model domain were estimated by multiplying CARB emissions in the SCAB domain by 1.1756, the ratio of the populations of the model domain in 2000 (17,267,158) to that in the SCAB domain in 2000 (14,687,964) (Table 4). [c] 2002 NEI emissions for the model domain were obtained from the U.S. NEI (*26*). [d] 2020 emissions with a gasoline fleet were estimated as 40% of 2002 emissions. [e] 2020 E85 emissions were assumed to be 20 times those of onroad and nonroad gasoline emissions. E85 did not replace nongasoline emissions, which were held constant.

TABLE 4. Bottom-Up Calculation of Future Acetaldehyde Emissions from Onroad E85 Vehicles Replacing Gasoline Vehicles in the Model Domain

A	2000 population in SCAB[a]	14,687,964
B	2000 population in model domain[b]	17,267,158
C	2000 gasoline vehicle miles traveled per day in SCAB[c]	297,370,000
D	2020 estimated gasoline vehicle miles traveled per day in SCAB[c]	378,829,000
$E = D \times B/A$	2020 estimated gasoline vehicle miles traveled per day in model domain	445,351,000
F	2020 estimated new-vehicle E85 acetaldehyde emissions (mg/mi)[d]	5−15
$G=E \times F \times 365/10^9$	2020 estimated new-vehicle E85 acetaldehyde emissions (t/yr)	813−2438
H	2002 ratio of fleet average to new-vehicle HC emissions[e]	10.4:1
$I = G \times H$	2020 onroad gas acetaldehyde emissions at current fleet avg/new ratio (t/yr)	8453−25,358
J	2020 estimated ratio of fleet average to new-vehicle HC emissions	5:1
$K = G \times J$	2020 onroad gas acetaldehyde emissions at est. fleet avg/new ratio (t/yr)	4065−12,195
L	2020 onroad gas acetaldehyde emissions here (t/yr)[f]	3420

[a] Reference *29*. [b] The model domain is slightly larger than the SCAB. Population in the model domain was determined from U.S. population data at 4 km resolution from the USEPA NEI population files (*26*) (e.g., Figure 2). [c] Reference *29*. Gasoline vehicles were assumed to consist of passenger cars, light and medium-duty trucks <8500 lbs, motorcycles, and motor homes. Diesels were assumed to consist of trucks >8500 lbs, urban buses, and school buses. [d] Estimate from studies in Table 2 and accounting for future improvements. [e] Determined from Figure 1. [f] Table 3.

in Table 2. Table 4 uses an independent, bottom-up approach to show that the 2020 acetaldehyde emission estimate for onroad gasoline vehicles (3420 tonnes/yr in Table 3) may be low, thus conservative. If future emission regulations reduce acetaldehyde from E85 more than estimated here, the impacts of E85 may be lower than found here, but since unburned ethanol may be a larger source of acetaldehyde than direct emissions, control of ethanol emissions would also be needed to have a large impact.

The Table 4 analysis assumes a 2020 fleet-averaged to new-vehicle emission ratio of 5:1. Figure 1 shows that the 2003 value was about 10.4:1. The ratio exceeds unity for the following reason: Since 1984, the U.S. 50 000-mile/5-year (half useful life) total hydrocarbon (THC) emission standard for light-duty vehicles (LDVs) has been 0.41 g/mi or stricter, and that for light-duty trucks (LDTs) has been 0.8 g/mi or stricter. Figure 1, though, shows that in 2003, pre-1993 model-year LDVs and LDTs emitted >0.8 g/mi on average. Because

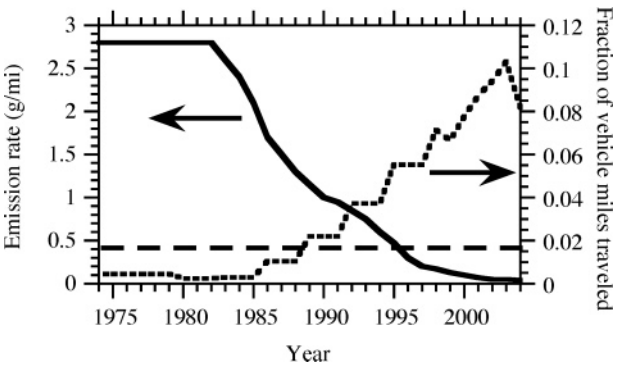


FIGURE 1. Vehicle-fleet-averaged hydrocarbon emission rate in 2003 (straight long-dashed line), determined from the frequency distribution of vehicle miles traveled versus vehicle age (*30*) and the hydrocarbon emission rate from several hundred thousand passenger vehicles and light-duty trucks in 2003 versus model year 1982−2004 (*31*). Emission rates prior to 1982 were held to the 1982 value. The ratio of the fleet-averaged emission rate (straight long-dashed line) to the 2004 model-year emission rate (last point of solid line) is about 10.4:1.

1984−1992 vehicles emitted <0.4 (LDVs) or <0.8 (LDTs) when new but more than this in 2003, such vehicles must have increased their emissions with age.

Even assuming that emissions from deterioration will decrease from 10.4:1 to 5:1 in 2020, the bottom-up acetaldehyde emissions from Table 4, 4065−12 195 tonnes/yr, still exceeds the estimate used here (3420 tonnes/yr); thus, the estimate here is conservative.

Results

Simulations results for August 2020 were used to analyze health effects. The major human carcinogens emitted during gasoline and E85 combustion are formaldehyde, acetaldehyde, 1,3-butadiene, and benzene. The U.S. Environmental Protection Agency (USEPA) and the California Office of Environmental Health Hazard Assessment (OEHHA) have assigned cancer unit risk estimates (CUREs) to these chemicals (Table 5, footnote). CURES have often been applied to emission differences (e.g., Table S5). However, emission differences translate into neither ambient differences, which also depend on chemistry, nor exposure, which also depends on population, which is why simulations of ambient pollution were needed.

Table 5 summarizes results from such simulations. It shows that E85 increased population-weighted formaldehyde and acetaldehyde mixing ratios (with population from Figure 2) but decreased those of benzene and butadiene in Los Angeles and the U.S. Whereas, one source of acetaldehyde was emission, a larger source was oxidation of unburned ethanol, which has an *e*-folding lifetime ranging from 8 h in polluted air to 8 days in the free troposphere. One study (*27*) found that E85 TOG emissions contained 73.1% unburned ethanol from exhaust and 3.7% from evaporation. Here, 64% of TOG from E85 consisted of unburned ethanol in Case 1 (Tables 1, S4). About a quarter of this ethanol oxidized to acetaldehyde during August in the U.S., providing three times more acetaldehyde than did emissions. Since most remaining ethanol eventually converts as well, future unburned ethanol may enhance global-scale acetaldehyde and ozone.

Table 5 shows that E85 increased the USEPA- but decreased the OEHHA-CURE- and population-weighted number of cancer cases relative to gasoline. For both CURES, the changes were small (+0.3, −3.5 cancers/yr in Los Angeles; +3, −29 cancers/yr in the U.S.), suggesting that E85 may result in cancer rates similar to those of gasoline (~40/yr in Los Angeles and ~430/yr in the U.S.: Table 5).

Figures 3, S1, and S5 show spatial differences in chemicals between the E85 and gasoline simulations. E85 increased unburned ethanol, acetaldehyde, and formaldehyde in the most populated area of Los Angeles by up to 20, 1.5, and 0.2 ppbv, respectively (Figure 3a−c). It decreased 1,3-butadiene and benzene by up to 0.05 and 0.2 ppbv (Figure 3d and e). Results for the U.S. were similar.

In Los Angeles, E85 increased 24 h and afternoon ozone by up to 3 and 4 ppbv, respectively (Figures 3f and S1.l). Maximum ozone increases in the high-resolution Los Angeles domain and in the coarse U.S. domain over Los Angeles were remarkably similar (3 ppbv, Figure 3e) despite the factor of 10 lower resolution in the U.S. domain. Differences for other species were generally within 0−50% between domains suggesting that the fine domain was preferable but the coarse domain provided reasonable accuracy. The population-weighted ozone increase in Los Angeles was 1.4 ppbv (Table 5, Case 1). In other words, E85 may increase 24 h ozone exposure to all 21.2 million residents in the Los Angeles domain in 2020 by 1.4 ppbv. E85 increased the U.S. population-weighted 24 h August ozone above 0 ppbv by 0.27 ppbv (Table 5).

E85 increased ozone in Los Angeles and the northeast, with some decreases in the southeast (Figure 3f). Ozone increased in the former locations because the baseline ratio of reactive organic gases (ROGs) to nitrogen oxides (NO_x) in those locations was below 8:1 (the upper triangle of the ozone isopleth in Figure S2). Under such a condition, either a decrease in NO_x or an increase in ROGs increases ozone. Since E85 decreased NO_x and increased ROGs, it increased ozone, as expected from the isopleth. Ozone decreased in the southeast because the baseline ROG/NO_x ratio there exceeded 8:1 (lower triangle of the isopleth) since isoprene

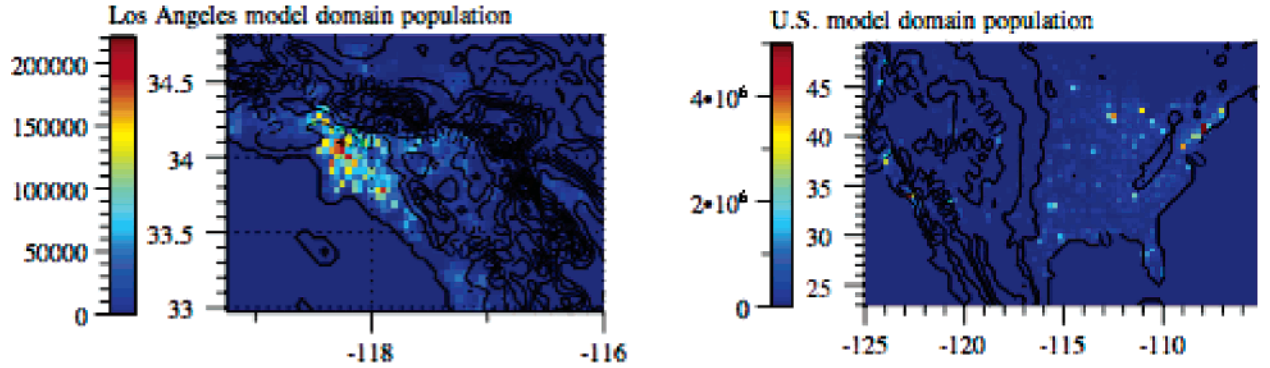


FIGURE 2. Population distributions of the (a) Los Angeles and (b) U.S. model domains (*25*, from U.S. 2000 census data). The total population in the Los Angeles domain was 17,267,158; that in the U.S. domain was 277,292,992. The California Air Resources Board estimates a population increase of 22.895% between 2000 and 2020 (*29*), giving estimated populations in 2020 in the respective domains of 21,220,474 and 340,779,223.

TABLE 5. Los Angeles and U.S.-Model Domain-Population-Weighted Values from the Case 1 E85 Simulations (w/E85) and Differences between the Five E85 Simulations (Cases 1−5) and the Gasoline Simulations (E85-gas)[a]

	Los Angeles						United States	
	Case 1 w/E85[b]	Case 1 E85 − gas[c]	Case 2 E85 − gas[d]	Case 3 E85 − gas[e]	Case 4 E85 − gas[f]	Case 5 E85 − gas[g]	Case 1 w/E85[b]	Case 1 E85 − gas[c]
formaldehyde (ppbv)	4.78	+0.0621	+0.0708	+0.0703	+0.0490	+0.0792	3.93	+0.017
acetaldehyde (ppbv)	3.00	+0.701	+0.715	+0.709	+0.658	+0.753	2.16	+0.448
1,3-butadiene (ppbv)	0.195	−0.0158	−0.0131	−0.0131	−0.0147	−0.0149	0.0819	−0.0072
benzene (ppbv)	0.480	−0.105	−0.104	−0.104	−0.105	−0.104	0.282	−0.0611
USEPA cancers/yr[i]	33	+0.315	+0.369	+0.424	+0.221	+0.481	392	+2.85
OEHHA cancers/yr[i]	50	−3.54	−3.52	−3.17	−3.52	−3.29	466	−29.3
ozone (ppbv) >0 ppbv	48.5	+1.38	+2.29	+0.291	+1.08	+1.48	33.6	+0.266
ozone (ppbv) >35 ppbv	49.5	+1.33	+2.27	+0.281	+1.02	+1.45	42.2	+0.283
ozone (ppbv) >50 ppbv	56.3	+0.785	+1.48	+0245	+0.600	+0.949	53.3	+0.647
pop (mil) expos. >35 ppbv[j]	19.826	19.826	20.984	18.885	19.507	19.507	142.10	142.10
high ozone deaths/yr >35*	1525	+140	+252	+28	+105	+150	5423	+213
med. ozone deaths/yr >35*	1320	+120	+218	+24	+91	+130	4720	+185
low ozone deaths/yr >35*	509	+47	+84	+9.4	+35	+50	1811	+71
pop (mil) expos. >0 ppbv[j]	21.220	21.220	21.220	21.220	21.220	21.220	340.78	340.78
med. ozone deaths/yr >0[k]	4719	+134	+223	+28	+105	+144	52,500	+416
ozone hospitalizations/yr[k]	7060	+645	+1170	+131	+488	+695	25,200	+988
ozone ER visits/yr[k]	8430	+770	+1390	+155	+582	+830	30,100	+1180
PAN (ppbv)	1.001	+0.0192	+0.0325	+0.0086	+0.0037	+0.0306	1.06	+0.0136

[a] Results are shown for the population-weighted 24 h averaged August near-surface mixing ratios[h] of four human carcinogens (formaldehyde, acetaldehyde, 1,3-butadiene, and benzene); the resulting number of cancer cases and changes in the number of cancer cases based on USEPA CURES and OEHHA CURES; population-weighted 24 h averaged August ozone mixing ratios and differences in mixing ratios; deaths, hospitalizations, and emergency-room (ER) visits due to ozone and ozone differences; and 24 h averaged August PAN mixing ratios and differences in mixing ratios. [b] Case 1: w/E85: E85 simulation with emissions as in Table 1 (Los Angeles) and Table S4 (United States) (TOG-E85:TOG-gasoline = 1.22 and NO_x-E85:NO_x-gasoline = 0.7). [c] Case 1: E85 minus gasoline. E85 and gasoline emissions as in Tables 1 and S4. [d] Case 2: Same as Case 1, except NO_x-E85:NO_x-gasoline = 0.55 instead of 0.70. [e] Case 3: Same as Case 1, except NO_x-E85:NO_x-gasoline = 0.85 instead of 0.70. [f] Case 4: Same as Case 1, except TOG-E85:TOG-gasoline = 1.06 instead of 1.22, with difference due to less ethanol emission. [g] Case 5: Same as Case 1, except TOG-E85:TOG-gasoline = 1.38 instead of 1.22, with difference due to more ethanol emission. [h] A population-weighted mixing ratio is the monthly averaged mixing ratio in each near-surface grid cell of a model domain, multiplied by the population in that grid cell, with the result summed over all grid cells and divided by the total population of the domain (estimated as 21,220,474 for the Los Angeles domain and 340,779,223 for the U.S. domain in 2020). A population-weighted mixing ratio difference between the E85 and gasoline simulation is the difference in the monthly averaged population-weighted mixing ratio for each simulation. [i] USEPA and OEHHA cancers/yr are determined by summing the product of individual USEPA or OEHHA CUREs (cancer unit risk assessments, which are the increased 70-year cancer risk per $\mu g/m^3$ sustained concentration change in a carcinogen) by the population-weighted mixing ratio or mixing ratio difference of a carcinogen and by air density, over all carcinogens, then dividing by 70 years. The simulation for February in Los Angeles confirms that mixing ratio changes of the carcinogens in February were similar to those in August. USEPA CURES are 1.3×10^{-5} for formaldehyde, 2.2×10^{-6} for acetaldehyde, 3.0×10^{-5} for butadiene, and 5.0×10^{-6} for benzene. The USEPA CURE for benzene ranges from 2.2×10^{-6} to 7.8×10^{-6}. The average of these numbers was used. OEHHA CUREs are 6.0×10^{-6} for formaldehyde, 2.7×10^{-6} for acetaldehyde, 1.7×10^{-4} for butadiene, and 2.9×10^{-5} for benzene. [j] The population exposed to >35 ppbv was determined from the E85 simulation for each respective case. The population exposed to >0 ppbv was the entire population of the Los Angeles or U.S. model domain in 2020. [k] The high, medium, and low ozone death rates were estimated to increase by, respectively, 1.06, 0.917, and 0.354 per year per 100,000 population per 1 ppbv increase in 24 h average ozone above 35 ppbv; the hospitalization rate (medium case only) for ozone-related respiratory problems was estimated to increase by 4.91 per year per 100,000 population per 1 ppbv increase in 24 h average ozone; the emergency-room (ER) visit rate (medium case only) due to asthma associated with ozone was estimated to increase by 5.86 per year per 100,000 population per 1 ppbv increase in 24 h average ozone (Supporting Information). Deaths/yr, hospitalizations/yr, and ER visits/yr were obtained by multiplying ozone above 35 ppbv (for w/E85 columns) or change in ozone (for E85 − gas columns) in locations where ozone was above 35 ppbv by the health effect rates listed above and by the population (given in this table) exposed to 24 h average ozone mixing ratios above 35 ppbv in either Los Angeles or the U.S, as determined from the model) The results were then divided by two to account for months of the year when ozone is lower than in August. The simulation for February in Los Angeles confirms that health effects of ozone, while greater for E85 than gasoline in February, were small, supporting the division by two. The medium ozone deaths/yr >0 ppbv was calculated as the ozone >0 ppbv multiplied by the population exposed to >0 ppbv (both given in the table) and 0.917 deaths per 100,000 per ppbv, all divided by two to account for seasonal variation.

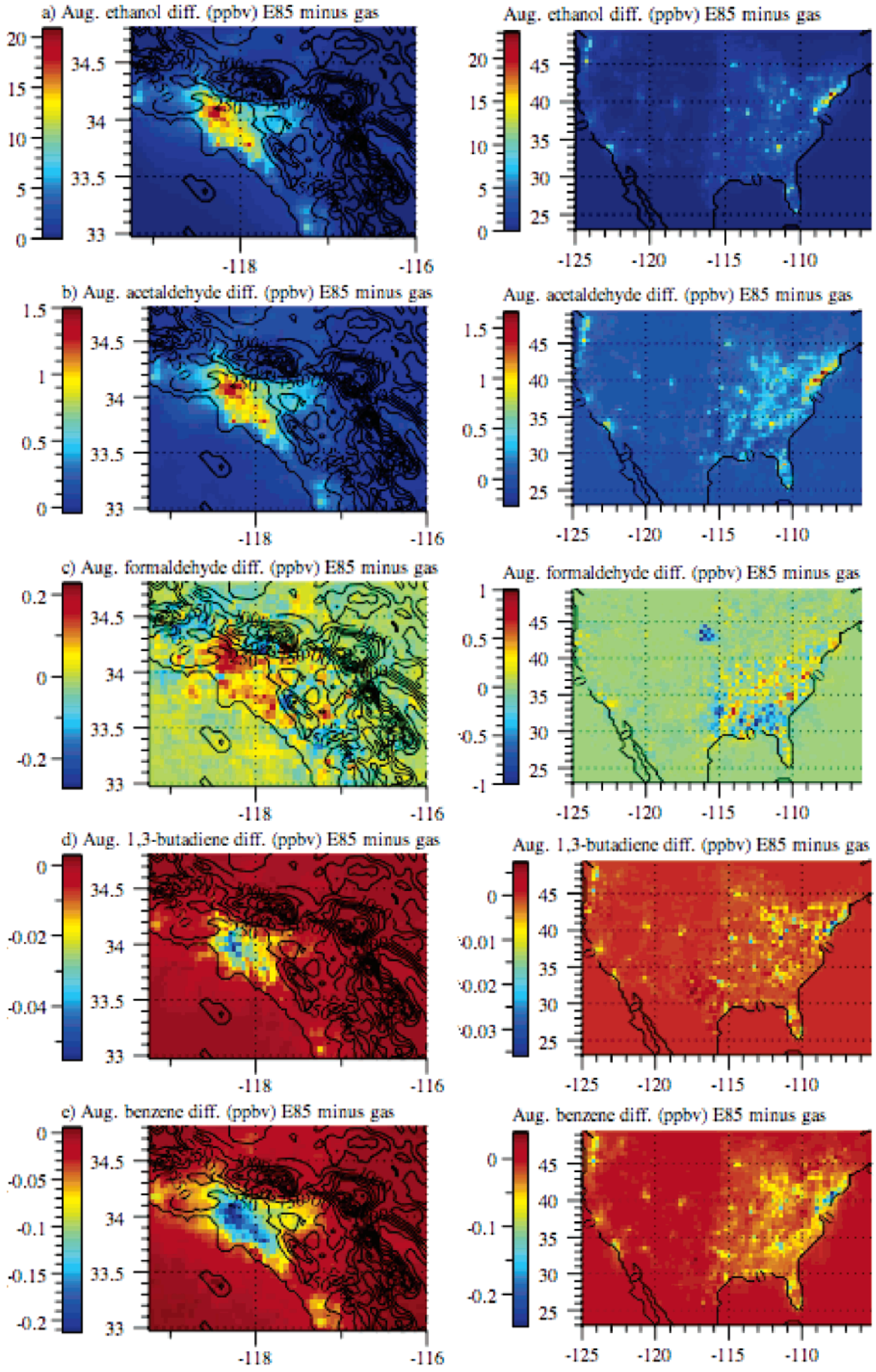
and monoterpene emissions were higher in the southeast than elsewhere (Figures S5.l and S5.m). Under such conditions, increases in ROGs have little impact on ozone but decreases in NO_x decrease ozone, as found upon conversion to E85.

Discussion

Here, the ozone health effects of E85 versus gasoline are examined. The relative risk of ozone mortality may increase above unity at about 35 ppbv (e.g., Figure 2 of *32*), the cutoff assumed here for mortality, hospitalization, and asthma. Table 5 shows the population-weighted change in annual mortality, hospitalization, and ER visits due to E85 versus gasoline and E85 alone. In the 2020 Case 1 scenario, E85 was calculated to increase ozone-related mortality by 120 deaths/yr (with a range of 47−140/yr) in Los Angeles and 185 deaths/yr (72−216/yr) in the U.S. These death rates represent an increase of about 9% in Los Angeles and 4% in the U.S. over the projected death rates with gasoline vehicles. E85 also increased hospitalization by about 650 and 990 in Los Angeles and the U.S., respectively, and asthma-related emergency-room visits by about 770 and 1200 in Los Angeles and the U.S., respectively. Some increases in health risk in Los Angeles and the northeast were offset by decreases in the southeast, but the overall health risk was greater for E85 than gasoline. E85 health effects due to ozone significantly exceeded those due to cancer.

Table 5 shows that, if ozone mortality effects occurred down to 0 ppbv rather than 35 ppbv in 2020, the change in mortality due to E85 would be about the same in Los Angeles as with the 35 ppbv threshold since most people in Los Angeles would already be exposed to >35 ppbv ozone. However, the change in the death rate in the U.S. with a 0 ppbv threshold would be about twice that with a 35 ppbv threshold.

Whereas PAN has little effect on mortality, it is an eye irritant and damages crops. E85 increased population-weighted PAN in Los Angeles and the U.S. (Table 5). PAN


a) Aug. ethanol diff. (ppbv) E85 minus gas
Aug. ethanol diff. (ppbv) E85 minus gas
b) Aug. acetaldehyde diff. (ppbv) E85 minus gas
Aug. acetaldehyde diff. (ppbv) E85 minus gas
c) Aug. formaldehyde diff. (ppbv) E85 minus gas
Aug. formaldehyde diff. (ppbv) E85 minus gas
d) Aug. 1,3-butadiene diff. (ppbv) E85 minus gas
Aug. 1,3-butadiene diff. (ppbv) E85 minus gas
e) Aug. benzene diff. (ppbv) E85 minus gas
Aug. benzene diff. (ppbv) E85 minus gas

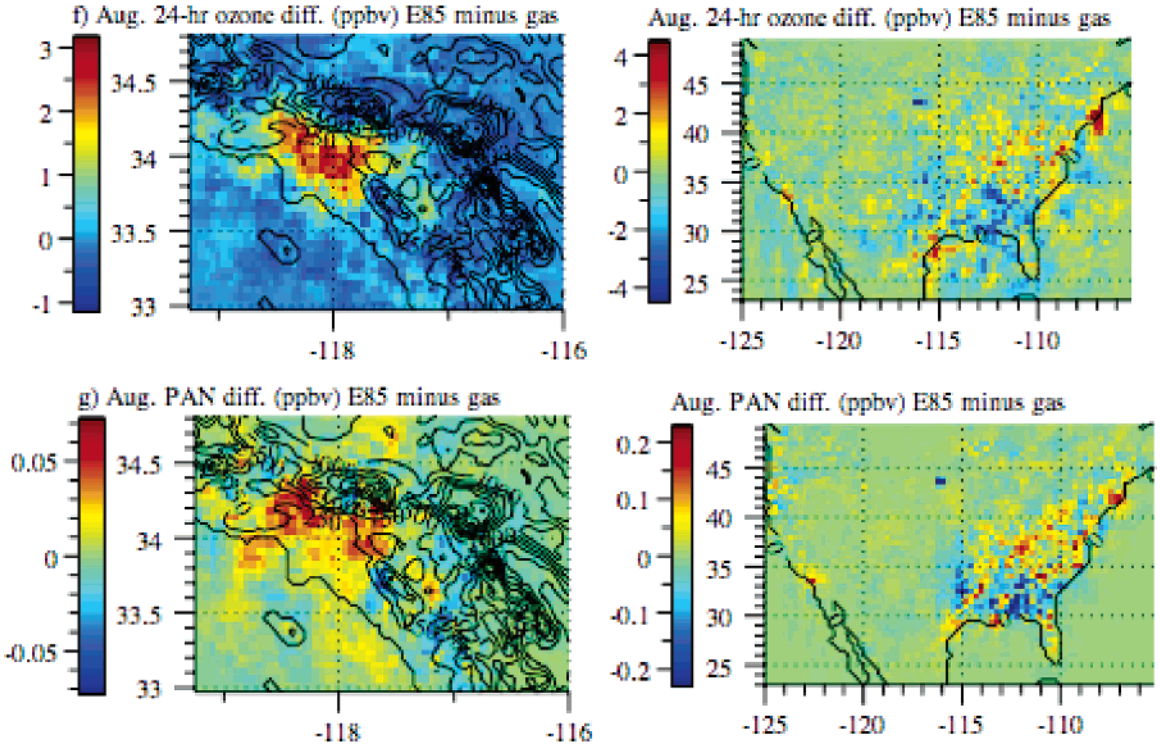


FIGURE 3. Modeled differences in the August 24-hour average near-surace mixing ratios of (a) ethanol, (b) acetaldehyde, (c) formaldehyde, (d) 1,3-butadiene, (e) benzene, (f) ozone, and (g) PAN in Los Angeles and the United States when all gasoline vehicles (in 2020) were converted to E85 vehicles under the emission assumption in Tables 1 and S4, respectively. Figures S1 and S5 gives difference plots and E85-alone plots for additional chemicals for Los Angeles and the U.S., respectively.

forms from NO_2 and the peroxyacetyl radical (CH_3CO_3), which derives from acetaldehyde. E85 increased acetaldehyde and decreased NO_2. PAN increased in Los Angeles and other highly populated areas (e.g., the northeast) where NO_x remained high even after E85 reduced its levels (Figure 3f). PAN decreased in the southeast, where nitrogen NO_x reductions due to E85 had a larger effect on it than elsewhere (Figure 3f).

Four sensitivity tests were run for Los Angeles to examine whether the conclusions reached for the baseline case would hold if the E85/gasoline emission ratio differed, due to data uncertainty, from those in the baseline case. In the respective tests, E85 NO_x was reduced 45% instead of 30% relative to gasoline (Case 2), E85 NO_x was reduced 15% instead of 30% (Case 3), E85 TOGs were increased 6% instead of 22% (by decreasing unburned ethanol) (Case 4), and E85 TOGs were increased 38% instead of 22% (Case 5). In all tests (Table 5 and Figure S3), E85 increased ozone and PAN relative to gasoline. In Cases 2 and 4 ozone increases were greater than in Case 1; in Cases 3 and 5, they were lower. The results are consistent with expectations from an ozone isopleth (Figure S2).

Another test was run to estimate the effect of converting the current, rather than 2020, Los Angeles vehicle fleet, from gasoline to E85. Although this would not be practical since most current gasoline vehicles cannot run on E85, such a test provides an upper bound of the possible effects of converting to E85. Under this scenario, baseline gasoline emissions were 150% higher than those in Table 1 (e.g., original 2002 NEI emissions were used). The percent changes in column 4 of Table 1 were then applied to 2002 NEI emissions to obtain E85 emissions. Figure S4 shows results from this test. It indicates that the peak differences (E85 minus gasoline) in daytime ozone and 24 h PAN were 275% and 500% higher than were those in the 2020 scenario (Figures S1.l and S1.m, respectively). Thus, ozone and PAN differences (E85 minus gasoline) increased superlinearly with increasing baseline emissions.

One study (Table 2) found that E85 increased particle mass and number relative to E5. Here no difference in particle emissions was assumed, to ensure a conservative result, and no effort was made to estimate the overall effect of E85 versus gasoline on particle exposure. However, E85 was found to increase sulfate (Figure S1.r) by increasing aldehydes, which increased OH (Figure S1.p), hastening sulfur dioxide oxidation (Figure S1.q). E85 also increased low-molecular-weight secondary organic mass (ethanol, acetaldehyde, and formaldehyde) dissolved in aerosol and fogwater, but it decreased nitrate (Figure S1.t) and high-molecular-weight secondary organic aerosol mass.

In sum, due to its similar cancer risk but enhanced ozone health risk in the base emission case, a future fleet of E85 may cause a greater health risk than gasoline. However, because of the uncertainty in future emission regulations, E85 can only be concluded with confidence to cause at least as much damage as future gasoline vehicles. Because both gasoline and E85 emission controls are likely to improve, it is unclear whether one could provide significantly more emission reduction than the other. In the case of E85, unburned ethanol emissions may provide a regional and global source of acetaldehyde larger than that of direct emissions.

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Supporting Information Available

Model description and emission data, and analysis of additional results. This material is available free of charge via the Internet at http://pubs.acs.org.

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