

# Chemical Composition of Gas-Phase Organic Carbon Emissions from Motor Vehicles and Implications for Ozone Production

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## Supporting Information

**ABSTRACT:** Motor vehicles are major sources of gas-phase organic carbon, which includes volatile organic compounds (VOCs) and other compounds with lower vapor pressures. These emissions react in the atmosphere, leading to the formation of ozone and secondary organic aerosol (SOA). With more chemical detail than previous studies, we report emission factors for over 230 compounds from gasoline and diesel vehicles via two methods. First we use speciated measurements of exhaust emissions from on-road vehicles in summer 2010. Second, we use a fuel composition-based approach to quantify uncombusted fuel components in exhaust using the emission factor for total uncombusted fuel in exhaust together with detailed chemical characterization of liquid fuel samples. There is good agreement between the two methods except for products of incomplete combustion, which are not present in uncombusted fuels and comprise  $32 \pm 2\%$  of gasoline exhaust and  $26 \pm 1\%$  of diesel exhaust by mass. We calculate and compare ozone production potentials of diesel exhaust, gasoline exhaust, and nontailpipe gasoline emissions. Per mass emitted, the gas-phase organic compounds in gasoline exhaust have the largest potential impact on ozone production with over half of the ozone formation due to products of incomplete combustion (e.g., alkenes and oxygenated VOCs). When combined with data on gasoline and diesel fuel sales in the U.S., these results indicate that gasoline sources are responsible for 69–96% of emissions and 79–97% of the ozone formation potential from gas-phase organic carbon emitted by motor vehicles.



## INTRODUCTION

Motor vehicles are an important source of atmospheric pollutants. Direct emissions include a wide range of organic compounds in the gas phase, including volatile organic compounds (VOCs), intermediate-volatility organic compounds (IVOCs), and semivolatile organic compounds (SVOCs), which partition into the particle phase at lower volatilities.<sup>1</sup> Emissions of these compounds lead to the formation of ozone and secondary organic aerosol (SOA)—the principal components of photochemical smog.<sup>2</sup> Numerous studies have reported emission factors for gas-phase organic compounds from gasoline and diesel vehicles using a variety of methods: fuel composition-based, single vehicle dynamometer testing, and on-road measurements in roadway tunnels.<sup>3–12</sup> Emission factors vary widely as a function of fuel composition, vehicle model, age, and maintenance; on-road measurements have the advantage of sampling a mixture of exhaust from thousands of vehicles burning an average of the fuels sold in the region. Fuel composition-based assessments are also beneficial

because they allow for emissions estimates for fuel components that could not be measured in situ.

Emissions of organic compounds from motor vehicles occur via multiple pathways. These can be grouped into exhaust and nontailpipe (i.e., evaporative) emissions.<sup>13</sup> Emitted compounds originate from liquid fuels and include uncombusted hydrocarbons ( $C_xH_y$ ) and products of incomplete combustion that can be paraffinic, olefinic, or aromatic, and may include a carbonyl or other oxygenated group.<sup>4,6</sup> Previous studies over several different experiments have shown the exhaust hydrocarbon composition to be strongly correlated with the composition of liquid fuels, with the exception of products of incomplete combustion present in the exhaust.<sup>1,4,14</sup>

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The chemical composition of gasoline and diesel fuel was reported in detail in Gentner et al.<sup>1</sup> along with the calculated composition of nontailpipe (i.e., headspace vapor) gasoline emissions. Aromatics account for approximately 30% of gasoline and 20% of diesel fuel mass with the remainder composed largely of straight, branched, and cyclic alkanes. Nontailpipe gasoline vapor emissions are composed largely of straight and branched alkanes containing 4–8 carbon atoms with a sharp peak at  $C_5$ . Liquid gasoline contains 4% alkenes, while nontailpipe emissions are 7% alkenes. Both also include ethanol, which now accounts for  $\geq 10\%$  of liquid gasoline by volume. In contrast to gasoline, evaporative emissions of diesel fuel are a minor source compared to exhaust due to the relatively low volatility of diesel fuel.

The ability of gas-phase organic emissions to promote ozone formation as a byproduct of their atmospheric oxidation is determined largely by chemical composition, but also depends on atmospheric conditions and the availability of nitrogen oxides ( $NO_x$ ). The chemical structure of the individual compounds that comprise the emissions, together with the total emission rate, dictates the ozone-forming potential of a source.<sup>15</sup> Regulatory strategies in some areas that are hydrocarbon-limited have targeted and effectively reduced ozone formation by reducing the mass and also reactivity of gasoline-related VOC emissions. Wood et al.<sup>16</sup> assessed the contributions of chemical classes to ozone production from gasoline and diesel engine exhaust using previously published emission factors from the 1990s. They observed that ozone production from gasoline exhaust was predominantly due to alkenes (39%) followed by aromatics (24%), alkanes (20%), oxygenates (10%), and carbon monoxide (7%). Calculations of ozone production from diesel exhaust were limited by available measurements that focused on low molecular weight compounds rather than diesel fuel constituents. Incomplete assessments of this type found that oxygenates and CO present in diesel exhaust were responsible for 50% and 30% of ozone production, respectively.<sup>16</sup> Given the extensive reformulation of vehicle fuels and reductions in vehicle emissions that have taken place, an updated assessment is needed using new and more detailed measurements of fuel composition and vehicle emissions.

The objectives of this research are to quantify emission factors for an extensive set of compounds emitted by gasoline and diesel engines using both a fuel composition-based method and tunnel measurements of exhaust; compare these emission factors; and evaluate and compare the ozone formation potential of diesel exhaust, gasoline exhaust, and nontailpipe gasoline emissions.

## MATERIALS AND METHODS

The emission factors for individual organic compounds presented in this work are calculated by two methods. This allows comparisons of exhaust emission factors from on-road vehicles observed in a highway tunnel with expected emission factors based on detailed chemical characterization of unburned gasoline and diesel fuel samples. First, individual compound emission factors were calculated from on-road measurements made at the Caldecott tunnel in Oakland, CA during July 2010.<sup>1</sup> Second, emission factors for unburned components of the fuels were estimated using total uncombusted gas-phase organic carbon emission factors from the same study and chemically explicit characterization of fuel samples collected from across California during summer 2010.<sup>1</sup>

## Direct Calculation of Individual Emission Factors Using On-Road Measurements.

Details on the measurements of gas-phase organic compounds using a custom two-channel gas chromatograph with a mass spectrometer and a flame ionization detector are described elsewhere along with a description of the tunnel sampling site.<sup>1</sup> The study included supporting measurements of carbon monoxide (TEI infrared spectrometer model 48), carbon dioxide (LI-COR infrared absorption model LI-820), and black carbon with a  $2.5\text{-}\mu\text{m}$  cut point (Magee Scientific aethalometer model AE-16). In addition, measurements of ethene and formaldehyde were made using a quantum cascade tunable infrared laser differential absorption spectrometer (QC-TILDAS) operating at high time resolution.<sup>17,18</sup> Data were averaged to 30-min intervals for consistency with other measurements.

Emission factors were calculated using measurements of individual chemical species in mixed traffic lanes of the tunnel (bore 1) over 30-min samples. All results reported here are for vehicles driving on a 4% uphill grade. To calculate emission factors for gasoline vehicles, individual organic species concentrations were divided by background-subtracted total carbon mass (i.e.,  $CO + CO_2$ ), which is used with fuel properties to determine the amount of fuel burned.<sup>6</sup> Emission factors for diesel vehicles were similarly calculated using black carbon concentrations apportioned to diesel sources in place of total carbon. On weekdays, a mixture of gasoline and diesel vehicles were present in the tunnel with  $\sim 2000$  light-duty vehicles and 30–140 medium and heavy-duty trucks per hour. There were large decreases in the relative and absolute levels of diesel vehicle activity on the weekend, whereas light-duty passenger vehicle traffic was present at consistently high volumes on all days.<sup>19</sup> Diesel traffic was greatest on weekdays, so weekend samples were used to determine emission factors for gasoline vehicles (one weekend data point with high diesel activity was excluded from the calculation). Equation 1 summarizes this method where an arithmetic average and standard deviation are found from the concentrations of compound  $i$  ( $C_{i,t}$ ) divided by the background adjusted total carbon ( $\Delta Total C_t$ ). The result is multiplied by the fuel carbon content ( $f_c$ ) and density ( $\rho$ ) (reported in Gentner et al.<sup>1</sup>) to obtain emission factors in units of  $\mu\text{gC L}^{-1}$ . For compounds with significant background concentrations (e.g., propane), a regression method is used to obtain the ratio of compound  $i$  to total carbon, similar to methods in the Supporting Information of Gentner et al.<sup>1</sup>

$$EF_{i,gasoline} = \frac{1}{N} \sum_{t=0}^{t=0} \left[ \frac{C_{i,t}}{\Delta Total C_t} \right] f_{c,gasoline} \rho_{gasoline} \quad (1)$$

Diesel emission factors were calculated using results from weekday sampling periods, with adjustments to account for gasoline emissions. Many of the compounds measured were emitted by both gasoline and diesel sources during weekday sampling. So the gasoline contributions were subtracted to isolate diesel emissions. Diesel contributions of compound  $i$  ( $C_{i,t,diesel}$ ) (eq 2) were determined using the gasoline emission factor for each compound from eq 1 ( $EF_{i,gasoline}$ ) and total gasoline exhaust emissions determined via chemical mass balance source receptor modeling ( $SC_{t,gasoline}$ ) from recent work using Caldecott tunnel data.<sup>1</sup> The diesel emission factor was calculated using the average and standard deviation of the ratios of compound  $i$  concentrations from diesel ( $C_{i,t,diesel}$ ) over black carbon (BC) from diesel ( $BC_{i,t,diesel}$ ). Black carbon was used

Table 1. Emission Factors ( $\mu\text{g C L}^{-1}$ ) for Individual Gas-Phase Organic Compounds from Gasoline and Diesel Vehicles via Tunnel Measurements of Individual Compounds and Using Detailed Chemical Characterization of Fuel Composition<sup>a</sup>

Compound	Gasoline exhaust		Diesel exhaust	
	on-road	fuel composition-based	on-road	fuel composition-based
<b>Straight-Chain Alkanes</b>				
propane	1930 ± 250	24.4 ± 9.7		
<i>n</i> -butane	12100 ± 30300	1600 ± 540		
<i>n</i> -pentane	13200 ± 4200	9450 ± 3300		
<i>n</i> -hexane	6490 ± 2330	6520 ± 2310		
<i>n</i> -heptane	5750 ± 2250	6280 ± 2210		
<i>n</i> -octane	2290 ± 840	2700 ± 950		490 ± 412
<i>n</i> -nonane	1000 ± 380	1130 ± 400	2640 ± 1320	1070 ± 870
<i>n</i> -decane	573 ± 338	376 ± 134	4970 ± 2390	2710 ± 2110
<i>n</i> -undecane	404 ± 329	204 ± 74	5100 ± 2940	4930 ± 3040
<i>n</i> -dodecane		37.3 ± 13.8	5730 ± 1980	4470 ± 1940
<i>n</i> -tridecane		8.3 ± 2.9	3970 ± 1290	4030 ± 1470
<i>n</i> -tetradecane		3.8 ± 1.3		4330 ± 1270
<i>n</i> -pentadecane				4810 ± 1540
<b>Branched Alkanes</b>				
isobutane	1140 ± 1190	125 ± 53	13200 ± 13900	
isopentane	51400 ± 12900	32000 ± 11000		
neopentane		26.5 ± 9.1		
3-methylpentane	9840 ± 3050	10100 ± 3500		
2-methylpentane and 2,3-dimethylbutane	22200 ± 7300	21500 ± 7400		
2,2-dimethylbutane	5370 ± 2350	4950 ± 1840		
2-methylhexane	7830 ± 3250	6890 ± 2480		
3-methylhexane	7230 ± 2920	9000 ± 3170		
2,3-dimethylpentane	4520 ± 2210	7600 ± 2570		
3,3-dimethylpentane		422 ± 166		
3-ethylpentane		540 ± 209		
2,4- and 2,2-dimethylpentane	3430 ± 1030	3780 ± 1280		
2,2,3-trimethylbutane		158 ± 54		
2-methylheptane	3080 ± 1170	3710 ± 1300		327 ± 274
3-methylheptane	3450 ± 1410	1680 ± 580		307 ± 243
4-methylheptane	4700 ± 1760	4140 ± 1450		104 ± 89
2,2-dimethylhexane	234 ± 95	257 ± 93		
2,4-dimethylhexane	3880 ± 1130	2190 ± 740		30.7 ± 17.4
2,5-dimethylhexane	1940 ± 620	2070 ± 690		46.6 ± 33.4
3,3-dimethylhexane		297 ± 106		
2-methyl-3-ethylpentane		1910 ± 640		
2,3,3-trimethylpentane and 2,3-dimethylhexane	4390 ± 1530	4440 ± 1500		
2,2,4-trimethylpentane (isooctane)	15400 ± 5400	10900 ± 3700		
2,2,3-trimethylpentane	486 ± 177	554 ± 188		
2,3,4-trimethylpentane and c1,t3,c3-trimethylcyclopentane		4780 ± 1610		157 ± 117
2- and 4-methyloctane	1050 ± 500	2210 ± 780	785 ± 680	322 ± 227
3-methyloctane and 4-ethylheptane	1340 ± 500	1650 ± 580	1240 ± 1070	467 ± 353
3-ethylheptane		350 ± 124		
2,3-dimethylheptane	1110 ± 420	452 ± 155	566 ± 422	59.2 ± 44.6
2,6-dimethylheptane	739 ± 292	639 ± 228		245 ± 195
3,5-dimethylheptane	887 ± 318	1370 ± 470		163 ± 105
2,4-dimethylheptane		450 ± 156		
2,5-dimethylheptane		36.3 ± 12.7		
3,4-dimethylheptane		201 ± 70		
3,3-dimethylheptane		108 ± 40		
4,4-dimethylheptane		83 ± 29.4		
2,2-dimethylheptane		89.8 ± 32		
3-methyl-4-ethylhexane		114 ± 39		
2,3,5-trimethylhexane		662 ± 239		
2,4,4-trimethylhexane		274 ± 96		
2,2,5-trimethylhexane	4670 ± 1610	3320 ± 1240		
2,2,3-trimethylhexane		82.8 ± 41.7		
2-methylnonane		397 ± 143		

Table 1. continued

Compound	Gasoline exhaust		Diesel exhaust	
	on-road	fuel composition-based	on-road	fuel composition-based
<b>Branched Alkanes</b>				
3-methylnonane		394 ± 141		
4-methylnonane		441 ± 172		
3-ethyloctane		5.6 ± 3.2		
4-ethyloctane		164 ± 57		
2-, 3-, and 4-methylnonane and 3- & 4-ethyloctane and 2,3-dimethyloctane				2090 ± 1000
2,2-dimethyloctane		189 ± 66		
2,3-dimethyloctane		133 ± 47		
4,4-dimethyloctane		76.1 ± 27.1		
2,6-dimethyloctane	164 ± 67	41 ± 18.2	466 ± 290	201 ± 161
2,2,4-trimethylheptane	590 ± 191	98 ± 33.4		
2,2,5-trimethylheptane	383 ± 141	255 ± 90	341 ± 318	
2,3,6-trimethylheptane		222 ± 74		
2,4,4-trimethylheptane		472 ± 176		
2,4,5-trimethylheptane		81.4 ± 27.6		
2,4,6-trimethylheptane		76 ± 26.4		
2,5,5-trimethylheptane		339 ± 114		
unidentified C11 branched alkanes (13 isomers)				572 ± 147
dimethylundecane isomer #1			3010 ± 1460	1510 ± 840
dimethylundecane isomer #2			1850 ± 640	1030 ± 510
pristane				4150 ± 1270
phytane				3560 ± 1050
<b>Cycloalkanes</b>				
cyclopentane	5810 ± 2180	1770 ± 620		
methylcyclopentane	10100 ± 4100	10400 ± 3700		
ethylcyclopentane	700 ± 262	1140 ± 410		133 ± 103
<i>cis</i> -1,3-dimethylcyclopentane		2490 ± 910		
<i>trans</i> -1,3-dimethylcyclopentane		2120 ± 770		
<i>trans</i> -1,2-dimethylcyclopentane		2010 ± 730		
<i>n</i> -propylcyclopentane	293 ± 102	68.7 ± 24.5	444 ± 345	159 ± 107
isopropylcyclopentane	109 ± 40		88.5 ± 88	47.4 ± 32.5
1-methyl-1-ethylcyclopentane		273 ± 103		
<i>cis</i> -1-methyl-2-ethylcyclopentane		188 ± 71		
<i>cis</i> -1-methyl-3-ethylcyclopentane		511 ± 189		
<i>trans</i> -1-methyl-3-ethylcyclopentane		479 ± 174		
1,1,3-trimethylcyclopentane		423 ± 150		
c1,t2,c4-trimethylcyclopentane	686 ± 255	720 ± 258		75.1 ± 50.5
c1,t2,t4-trimethylcyclopentane				50.6 ± 28.7
<i>n</i> -butylcyclopentane	505 ± 298		2090 ± 990	
isobutylcyclopentane	256 ± 146			
<i>trans</i> -1,1,3,4-tetramethylcyclopentane		343 ± 126		
cyclohexane	5110 ± 3070	4990 ± 1810	3840 ± 3950	
methylcyclohexane	3390 ± 990	5170 ± 1850		577 ± 460
ethylcyclohexane	754 ± 268	509 ± 192	1730 ± 1220	758 ± 505
<i>cis</i> -1,3- and 1,1-dimethylcyclohexane	825 ± 275	872 ± 315	779 ± 611	464 ± 336
<i>trans</i> -1,2-dimethylcyclohexane	392 ± 124	358 ± 127	854 ± 572	519 ± 387
<i>trans</i> -1,3-dimethylcyclohexane	534 ± 201	611 ± 223		424 ± 285
<i>cis</i> -1,2-dimethylcyclohexane	196 ± 72	177 ± 66	310 ± 273	247 ± 147
<i>cis</i> -1,4-dimethylcyclohexane		122 ± 44		
<i>n</i> -propylcyclohexane	505 ± 298	122 ± 45	2090 ± 990	1270 ± 580
isopropylcyclohexane	83.8 ± 42.6		258 ± 146	187 ± 98
<i>cis</i> -1-methyl-3-ethylcyclohexane		209 ± 75		
<i>trans</i> -1-methyl-4-ethylcyclohexane		99 ± 36.7		
<i>trans</i> -1-ethyl-4-methylcyclohexane	137 ± 76	98.8 ± 36.6	499 ± 228	
1-ethyl- <i>cis</i> -3-methylcyclohexane	96.7 ± 48.9	209 ± 74	266 ± 130	
methylethylcyclohexane isomer #1	137 ± 76		499 ± 228	69.6 ± 26
methylethylcyclohexane isomer #2	96.7 ± 48.9		266 ± 130	
1,1,3-trimethylcyclohexane	131 ± 56	164 ± 58	389 ± 294	368 ± 274
1,1,4-trimethylcyclohexane	99.5 ± 38.1		173 ± 145	154 ± 78

Table 1. continued

Compound	Gasoline exhaust		Diesel exhaust	
	on-road	fuel composition-based	on-road	fuel composition-based
<b>Cycloalkanes</b>				
c1,c3,c5-trimethylcyclohexane	111 ± 59		356 ± 215	213 ± 137
c1,t2,c4-trimethylcyclohexane	152 ± 83		382 ± 224	479 ± 236
c1,t2,t4 and c1,t3,t5-trimethylcyclohexane		402 ± 143		83.1 ± 39.5
1,1,2-trimethylcyclohexane and isobutylcyclopentane	256 ± 146			
unidentified C10 cyclohexanes	157 ± 149		980 ± 465	807 ± 263
<i>trans</i> -1-methyl-2-propylcyclohexane		161 ± 54		
<b>Alkenes</b>				
ethene	52800 ± 3400		59000 ± 6600 <sup>b</sup>	
propyne	1480 ± 480			
propene	34600 ± 12900	0.5 ± 0.2	27700 ± 22300	
1-butene	5710 ± 1450	11.4 ± 5.0	7830 ± 6060	
<i>cis</i> -2-butene	228 ± 85	57.1 ± 24.1		
<i>trans</i> -2-butene	3150 ± 820	66.7 ± 28.2		
isobutene	14400 ± 4300	7.6 ± 4.4		
1,3-butadiene	7820 ± 2650			
1-pentene		285 ± 121		
<i>cis</i> -2-pentene	2480 ± 970	460 ± 180		
<i>trans</i> -2-pentene		959 ± 373		
2-methyl-1-butene		587 ± 241		
3-methyl-1-butene		90.3 ± 42.7		
2-methyl-2-butene		1470 ± 560		
cyclopentene	98.7 ± 81.3	160 ± 62	2140 ± 3070	
1-hexene		92.8 ± 33.9		
<i>cis</i> -2-hexene		201 ± 72		
<i>trans</i> -2-hexene		515 ± 188		
<i>cis</i> -3-hexene		272 ± 98		
2-methyl-1-pentene		293 ± 106		
4-methyl-1-pentene		126 ± 46		
<i>trans</i> -3-methyl-2-pentene		231 ± 99		
<i>cis</i> -4-methyl-2-pentene		48.4 ± 21.8		
<i>trans</i> -4-methyl-2-pentene		524 ± 207		
2-Me-2- and <i>cis</i> -3-Me-2-pentene	62.5 ± 35.5	1300 ± 500		
2-ethyl-1-butene		64.6 ± 24.3		
2,3-dimethyl-1-butene		114 ± 41		
2,3-dimethyl-2-butene		168 ± 62		
1-methylcyclopentene	195 ± 80			
cyclohexene	177 ± 67		423 ± 333	
2-methyl-2-hexene		104 ± 41		
<i>cis</i> -3-methyl-3-hexene		71.8 ± 27.8		
<i>trans</i> -3-methyl-3-hexene		44.3 ± 17		
3-ethyl-2-pentene		177 ± 67		
1-methylcyclohexene	39 ± 12		112 ± 148	
3-methylcyclopentene		74.8 ± 27.7		
4-methyl-1-heptene		158 ± 56		
<i>cis</i> -2-methyl-3-heptene		407 ± 146		
2-methyl-2-heptene		120 ± 44		
unidentified C9 cycloalkene	180 ± 101		616 ± 298	
<b>Aromatics</b>				
benzene	19500 ± 8600	2760 ± 960		
toluene	33600 ± 13400	31200 ± 10900		911 ± 688
ethylbenzene	7960 ± 2950	6370 ± 2220		529 ± 324
<i>m</i> - and <i>p</i> -xylene	30700 ± 11300	25700 ± 8900		2760 ± 1580
<i>o</i> -xylene	10400 ± 3900	9330 ± 3250		918 ± 438
styrene	1150 ± 280			
<i>n</i> -propylbenzene	2250 ± 970	2120 ± 740	578 ± 532	592 ± 251
cumene	444 ± 170	435 ± 152		187 ± 153
<i>m</i> - and <i>p</i> -ethyltoluene	10600 ± 3700	9450 ± 3290		2920 ± 1250
<i>o</i> -ethyltoluene	2140 ± 770	2320 ± 810		1100 ± 440

Table 1. continued

Compound	Gasoline exhaust		Diesel exhaust	
	on-road	fuel composition-based	on-road	fuel composition-based
<b>Aromatics</b>				
1,2,3-trimethylbenzene	2030 ± 730	2300 ± 800		1630 ± 910
1,3,5-trimethylbenzene	4140 ± 1730	3170 ± 1110		982 ± 567
1,2,4-trimethylbenzene	10400 ± 3800	10300 ± 3600		5070 ± 2640
indan	479 ± 197	1060 ± 370		1290 ± 970
indene	241 ± 76	101 ± 35	168 ± 143	
alpha-methylstyrene	19.4 ± 12.1			
<i>o</i> - or <i>m</i> -methylstyrene	156 ± 54			176 ± 136
<i>p</i> -cymene	148 ± 95	81.7 ± 29		247 ± 232
<i>m</i> -cymene	128 ± 59	272 ± 95	296 ± 384	298 ± 253
<i>n</i> -butylbenzene	245 ± 114	320 ± 117	858 ± 584	1260 ± 880
isobutylbenzene	298 ± 130	274 ± 92		69.6 ± 34.1
<i>sec</i> -butylbenzene		191 ± 67		
<i>m</i> -diethylbenzene	524 ± 227	455 ± 160	546 ± 392	5960 ± 4670
<i>p</i> -diethylbenzene	2320 ± 820	1330 ± 460		4180 ± 3300
<i>o</i> -diethylbenzene	42.5 ± 19.5		84.2 ± 54.4	317 ± 121
1-methyl-2- <i>n</i> -propylbenzene	265 ± 111	404 ± 141	506 ± 238	717 ± 330
1-methyl-3- <i>n</i> -propylbenzene	2830 ± 1220	1220 ± 430	3240 ± 1660	2470 ± 1430
1-methyl-4-propylbenzene		748 ± 262		
1,4-dimethyl-2-ethylbenzene	659 ± 276	962 ± 340	898 ± 724	1750 ± 840
1,3-dimethyl-4-ethylbenzene	726 ± 252	788 ± 275	197 ± 162	1560 ± 760
1,2-dimethyl-4-ethylbenzene	513 ± 189	1240 ± 430	225 ± 166	1120 ± 760
1,3-dimethyl-2-ethylbenzene	73.3 ± 30.3	95.3 ± 32.7	174 ± 104	642 ± 521
1,2-dimethyl-3-ethylbenzene	208 ± 75	345 ± 120	279 ± 131	498 ± 240
1,2,4,5-tetramethylbenzene	300 ± 102	659 ± 229	234 ± 144	736 ± 633
1,2,3,5-tetramethylbenzene	487 ± 181	872 ± 303	161 ± 131	1080 ± 650
1,2,3,4-tetramethylbenzene	201 ± 78	241 ± 84	327 ± 222	1630 ± 790
1-methylindan	160 ± 58	368 ± 131	265 ± 204	1470 ± 1200
2-methylindan	300 ± 110	565 ± 200	494 ± 342	2490 ± 1620
4-methylindan		15.9 ± 7.3		
trans-2-butenylbenzene	134 ± 74		234 ± 246	81 ± 44.6
1-phenyl-2-methylbutane		115 ± 39		
1-phenyl-3-methylbutane		38.6 ± 13		
1-methyl-3-butylbenzene		204 ± 73		
1,2-dimethyl-3-propylbenzene		148 ± 53		
1-methyl-3,5-diethylbenzene		115 ± 41		
1,2-dimethyl-4-propylbenzene		166 ± 57		
1,2,5-trimethyl-3-ethylbenzene		91.2 ± 32.5		
1,2,3-trimethyl-4-ethylbenzene		10.6 ± 4.0		
1,2,4-trimethyl-5-ethylbenzene		83.1 ± 28.7		
1,2,3-trimethyl-5-ethylbenzene		68.6 ± 24.3		
1,2,4-trimethyl-3-ethylbenzene		15.8 ± 5.4		
1,3,5-trimethyl-2-ethylbenzene		84 ± 28.5		
pentamethylbenzene		41.4 ± 14.3		
dimethylindans		344 ± 104		
unidentified C11 aromatics (5 isomers)				197 ± 118
naphthalene	575 ± 254	530 ± 190		295 ± 122
tetralin		5.2 ± 2.4		
1-methylnaphthalene	101 ± 43	107 ± 40	124 ± 86	395 ± 158
2-methylnaphthalene	102 ± 48	284 ± 101		708 ± 344
dimethylnaphthalenes		113 ± 41	346 ± 108	1070 ± 360
trimethylnaphthalenes				963 ± 381
<b>Alcohols and Oxygenates</b>				
ethanol		26000 ± 8900		
formaldehyde	4510 ± 740		28800 ± 14600	
acetaldehyde	9920 ± 3320			
acetone and propanal	6120 ± 3050		78700 ± 79300	
butanal	222 ± 103		785 ± 604	
hexanal	367 ± 299		1650 ± 1670	

Table 1. continued

Compound	Gasoline exhaust		Diesel exhaust	
	on-road	fuel composition-based	on-road	fuel composition-based
<b>Alcohols and Oxygenates</b>				
heptanal	259 ± 150			
total gas-phase organic carbon (mg C L <sup>-1</sup> )	550 ± 160	380 ± 110	990 ± 330	860 ± 250
total gas-phase organic carbon (mg L <sup>-1</sup> )	680 ± 200	460 ± 130	1330 ± 440	990 ± 180
carbon monoxide (g L <sup>-1</sup> )	10.7 ± 0.5 <sup>c</sup>		6.8 ± 1.0 <sup>b</sup>	

<sup>a</sup>Emission factors calculated under uphill driving conditions (see text). Blank entries are either due to no measured emissions, lack of data, or insignificant result. The number of samples used in the on-road analysis is on average  $N = 31$  for gasoline and  $N = 9$  for diesel. <sup>b</sup>Diesel CO and ethene emission factor from ref 18. <sup>c</sup>Gasoline CO emission factor from ref 30.

because 91% of emissions were from diesel vehicles, making it a robust tracer of diesel exhaust with a known emission factor. Concentrations of BC attributed to diesel were determined previously<sup>1</sup> using  $SC_{t,gasoline}$  and the gasoline BC emission factor measured at the same tunnel study (eq 3). In eq 4, the average of  $N$  samples is multiplied by the diesel BC emission factor ( $0.54 \pm 0.07$  g BC kg<sup>-1</sup>)<sup>18</sup> and fuel density to produce a diesel emission factor for compound  $i$  in  $\mu\text{g C L}^{-1}$ .

$$C_{i,t,diesel} = C_{i,t,observed} - \frac{SC_{t,gasoline}EF_{i,gasoline}}{EF_{GPOC,gasoline}} \quad (2)$$

$$BC_{t,diesel} = BC_{t,observed} - \frac{SC_{t,gasoline}EF_{BC,gasoline}}{EF_{GPOC,gasoline}} \quad (3)$$

$$EF_{i,diesel} = \frac{1}{N} \sum_N \left[ \frac{C_{i,t,diesel}}{BC_{t,diesel}} \right] EF_{BC,diesel} \rho_{diesel} \quad (4)$$

Traffic in the tunnel was typically dominated by gasoline vehicles. To improve the accuracy and sensitivity of diesel emission factor calculations, we selected samples with the largest signal from diesel traffic and relatively low gasoline emissions to reduce signal noise, which was especially important for compounds emitted from both sources. We only used the highest 20% of weekday samples with greatest diesel activity determined by BC measurements (30-min averages  $>28$   $\mu\text{g BC m}^{-3}$ ), and removed points that had large interferences from gasoline emissions. Emission factors were reported only if less than 40% of the data were excluded due to gasoline interference. On average, nine 30-min samples were used to calculate diesel emission factors over four weekdays.

**Fuel Composition-Based Approach.** Unburned hydrocarbons emitted in engine exhaust originate from liquid fuel. Emission factors can be estimated using an overall emission factor for uncombusted hydrocarbons in exhaust, in combination with detailed compositional data for unburned liquid fuels. This approach uses the total gas-phase organic carbon emission factor ( $EF_{GPOC}$ ) for uncombusted fuels, calculated previously using a chemical mass balance method and 10 tracer compounds, shown in the Supporting Information (SI).<sup>1</sup> These emission factors ( $EF_{GPOC,gasoline} = 380 \pm 110$  mg C L<sup>-1</sup>,  $EF_{GPOC,diesel} = 860 \pm 250$  mg C L<sup>-1</sup>) are multiplied by the weight fraction of compound  $i$  in each fuel ( $WtC\%_i$ ) as shown in eq 5. Reported uncertainties are a combination of uncertainties in overall hydrocarbon emission factors together with uncertainty in fuel composition profiles. The Supporting Information in Gentner et al.<sup>1</sup> includes the detailed chemical speciation of gasoline and diesel fuels used to calculate emission

factors for uncombusted hydrocarbons originating in the liquid fuels. Although 52 fuel samples were collected across California, samples from Berkeley were chosen for calculating emission factors in this study, consistent with the San Francisco Bay Area location of Caldecott tunnel measurements. Within California, minor inter-regional differences exist in fuel composition for individual organic compounds, and can affect emission factors in other locations. Other work examines these differences using the comprehensive chemical speciation data for gasoline and diesel.<sup>1</sup>

$$EF_{i,source} = \frac{1}{100} WtC\%_{i,source} EF_{GPOC,source} \quad (5)$$

**Ozone Production Potential.** We assessed the ozone production potential of diesel exhaust, gasoline exhaust, and nontailpipe gasoline emissions. The ozone production potential for each emission category was determined using the chemically speciated composition of each source and reactivities for those components as calculated by Carter<sup>15</sup> using the SAPRC-07 mechanism. The maximum incremental reactivity (MIR) and maximum ozone incremental reactivity (MOIR) are specified in units of g O<sub>3</sub> g<sup>-1</sup>. They describe the potential of an incremental addition of a specified organic compound or group of structural isomers to form additional ozone in the atmosphere. MIR describes ozone forming potential under high-NO<sub>x</sub> conditions where ozone formation in the base mixture is maximally sensitive to incremental additions of VOCs. In contrast, MOIR is calculated under conditions with lower NO<sub>x</sub> along the ridgeline of the ozone isopleth diagram.<sup>20</sup> Ozone formation is still sensitive to VOC emissions under these conditions, but absolute increments in ozone formation are typically smaller under MOIR conditions for the same incremental addition of VOCs. The primary objective of the calculations in this work is to provide a robust comparison of the sources rather than absolute values. Emerging work based on the newer SAPRC-11 mechanism suggests increases of 1–3% and 3–16% for MOIR and MIR of aromatics, respectively, and a 0.3% increase for nonaromatic compounds.<sup>21</sup> These relatively minor changes in MOIR values are not expected to affect the conclusions of this analysis within existing uncertainties. SI Tables S1 and S2 show the MOIR and MIR values used to characterize the ozone formation potential of gas-phase organic carbon present in diesel exhaust, following the framework of Gentner et al.<sup>1</sup> where emissions are described as a function of carbon number and chemical class.

Products of incomplete combustion (e.g., alkenes and oxygenated VOCs) tend to have high ozone formation potentials and are thus included in the estimates for exhaust. Equation 6 describes the calculation of the overall normalized

**Table 2. Fuel Composition-Based Emission Factors for Gas-Phase Compounds from Diesel by Carbon Number and Chemical Class (mg C L<sup>-1</sup>)<sup>a</sup>**

carbon number	straight-chain alkanes	branched alkanes	cycloalkanes (single straight alkyl chain)	cycloalkanes (branched or multiple alkyl chain(s))	bicycloalkanes	tricycloalkanes	single-ring aromatics	polycyclic aromatic compounds
7			1.29				1.81	
8	0.86	1.46	1.63	3.61			6.28	
9	1.81	1.72	2.24	3.01			17.4	
10	4.30	13.8	3.011	16.1	11.9	0.95	20.5	0.26
11	5.16	19.5	2.49	16.3	15.7	1.81	16.4	1.55
12	4.73	16.3	1.72	16.9	15.1	2.92	15.7	2.58
13	4.39	15.6	1.46	15.0	11.2	3.78	12.6	2.75
14	4.39	17.7	1.29	12.0	8.60	4.21	10.1	4.21
15	4.82	16.3	1.29	10.5	7.40	3.87	8.86	4.82
16	4.99	14.6	1.20	9.80	6.36	3.78	8.51	4.39
17	5.50	11.6	1.03	9.03	5.59	3.35	7.65	4.30
18	5.33	13.3	0.86	9.12	5.33	3.18	7.22	3.87
19	4.30	16.3	0.69	8.08	4.90	2.92	6.28	3.61
20	3.70	14.0	0.52	7.05	4.30	2.58	5.25	2.75
21	2.92	8.86	0.43	6.02	3.61	2.15	4.56	0.69
22	2.15	6.28	0.086	5.07	2.84	1.81	3.87	0.52
23	1.38	5.16		3.27	2.24	1.46	3.01	
24	0.95	2.92		2.67	1.81	1.20	2.41	
25	0.52	0.34		2.15	1.38	0.95	1.89	

<sup>a</sup>Uncertainties are  $\pm 30\%$  based on the total uncombusted diesel fuel emission factor. Emission factors calculated under uphill driving conditions (see text).

reactivity for a source ( $MOIR_{source}$ ) as an emissions-weighted average ( $Wt\%_{i,source}$ ) of ozone reactivity values for individual organics ( $MOIR_i$ ).

$$MOIR_{source} = \frac{1}{100} \sum_i [Wt\%_{i,source} MOIR_i] \quad (6)$$

## RESULTS AND DISCUSSION

**Emission Factors.** Chemically speciated emission factors for both gasoline and diesel exhaust are shown in Table 1 along with carbon monoxide emission factors calculated from coincident tunnel measurements.<sup>1,18</sup> The suite of compounds reported for gasoline and diesel is more detailed than in previous studies. In situ measurements of all isomers were not possible in the tunnel, so several emission factors are estimated by the fuel composition-based method only. Some minor components present in exhaust emissions are not included to keep Table 1 concise, but their abundances in unburned fuel are available elsewhere.<sup>1</sup>

The emission factors represent a 2010 vehicle fleet in California operating under loaded mode operating conditions (steady speed of  $\sim 80$  km h<sup>-1</sup> on a 4% uphill grade). Changes in driving conditions may affect both the overall gas-phase organic carbon mass emission rate and the relative abundance of unburned fuel versus incomplete combustion products present in the exhaust. Another recent on-road emission study reports increases in running evaporative emissions on hot days, but those conditions were not observed in the present study.<sup>9</sup> Fuel samples and tunnel measurements were collected during the summer, and emissions of the most volatile components of the fuel (e.g., *n*-butane) vary seasonally due to deliberate adjustments to fuel composition. The volatility range of measurements in this study is more aligned with gasoline than diesel fuel, so the compound-specific factors in Table 1 appear to be more gasoline focused. Omitted emission factors

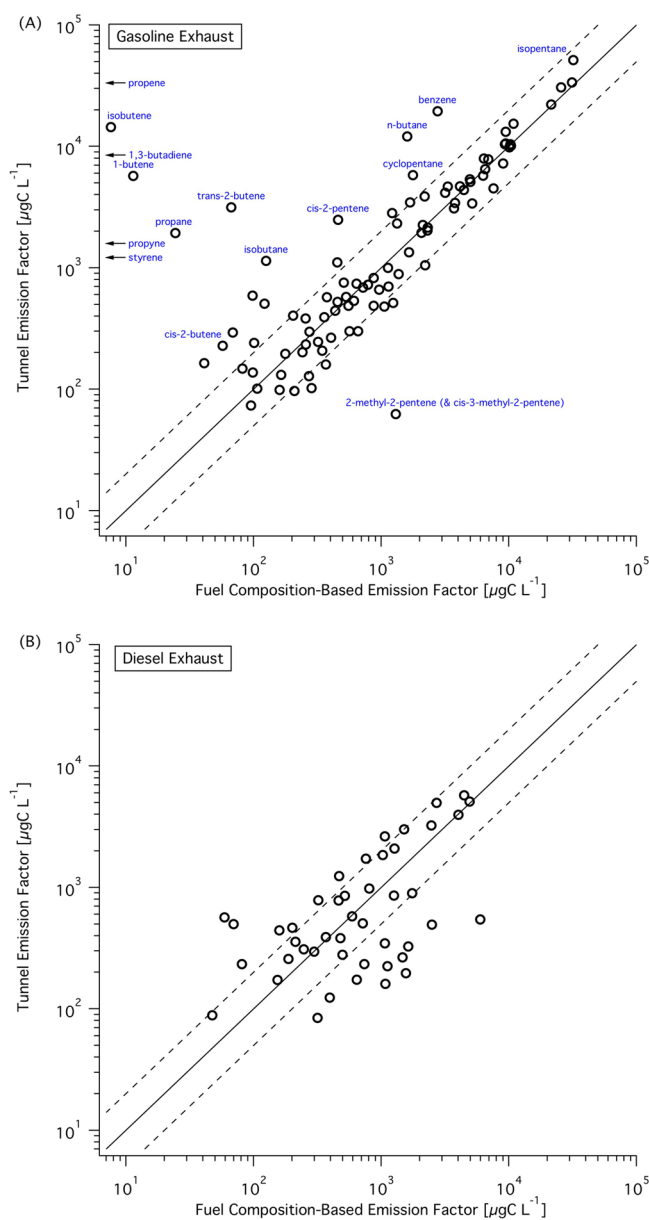
in Table 1 are either due to there being no measurements for a particular compound, the absence of emissions, or no statistically significant result. There are large reported uncertainties for a few of the on-road emission factors in Table 1; in these cases we report the emission factors, but recommend that readers remain aware of the potential for high variability in emissions when using these values.

Diesel fuel and exhaust emissions include over 1000 compounds, with an increasing number of possible isomers as the number of carbon atoms increases. As a result, it is helpful to describe diesel emissions in terms of structural isomers rather than trying to list all individual compounds.<sup>22</sup> Table 2 summarizes emission factors for diesel exhaust as a function of carbon number and compound class using the fuel composition-based method. These emission factors do not include contributions from motor oil, which would increase emission factors in the SVOC range.

Emission factors calculated via the two methods agree well (Figure 1) with the exception of products of incomplete combustion, which are present in the exhaust, but not in fuels. In combining the emission factors for products of incomplete combustion with the total uncombusted fuel emission factor, it was found that  $32 \pm 2\%$  of gasoline exhaust emissions (on a mass basis) is due to products of incomplete combustion. A smaller fraction of diesel exhaust is from incomplete combustion products ( $26 \pm 0.5\%$ ), but inclusion of other previously measured oxygenated species will increase this value.<sup>6</sup> The total exhaust emission factors, adjusted to include products of incomplete combustion, are  $550 \pm 160$  and  $990 \pm 330$  mg C L<sup>-1</sup> for gasoline and diesel vehicles, respectively, which are equivalent to  $680 \pm 200$  and  $1330 \pm 440$  mg L<sup>-1</sup> when associated hydrogen and oxygen mass is included.

Some components of the liquid fuels can also be formed as products of incomplete combustion. To check for contributions from products of incomplete combustion to prominent compounds in unburned fuel, we compared emission factors





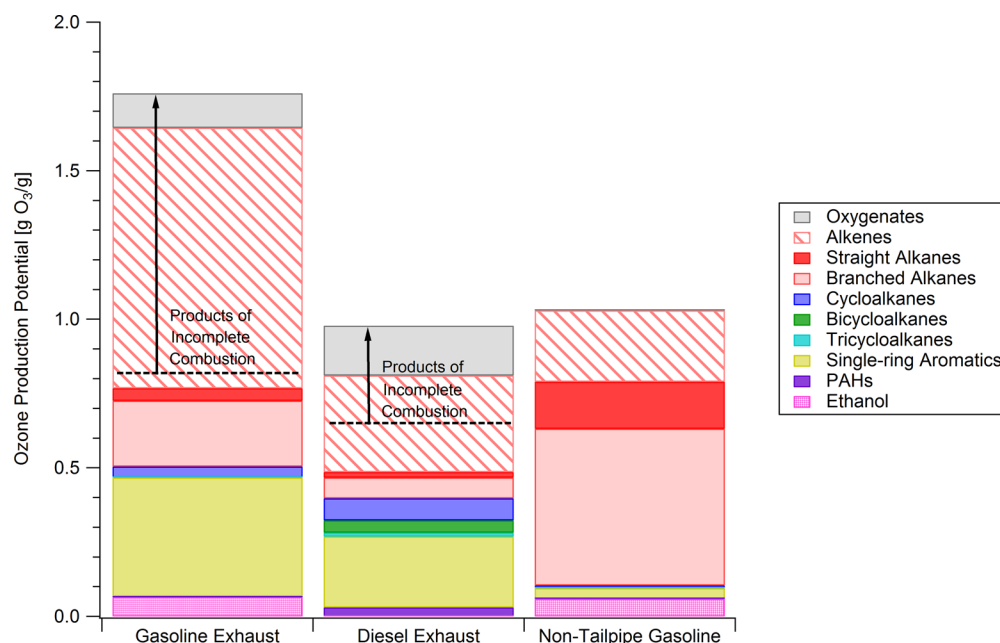
**Figure 1.** Comparison of gasoline and diesel exhaust emission factors from two methods show good agreement with the exception of products of incomplete combustion. Values are shown with 1:1 and 2:1 lines. Uncertainties in both methods are  $\pm 40\%$  and  $\pm 60\text{--}70\%$  on average for gasoline and diesel, respectively (shown in Table 1). Outliers and compounds of interest are labeled in A, and outliers in B are  $C_{10+}$  aromatics, which may be lower limits in the method that uses tunnel measurements due to sampling losses. The 2- (and *cis*-3-) methyl-2-pentene outlier in A is anomalous and is not expected to translate to other studies.

from the two methods. Cyclopentane emissions at the Caldecott tunnel were higher than expected based on the abundance of cyclopentane in liquid gasoline. Emissions of cyclopentane in gasoline exhaust due to formation from other fuel components (e.g., ethylcyclopentane) were equivalent to those from cyclopentane present in unburned fuel, such that doubling the fuel composition-based emission factor of cyclopentane accurately represents emissions in the tunnel study. We did not observe any significant emission enhancement for cyclohexane. A large enhancement was reported for benzene in gasoline exhaust in the late 1980s and mid 1990s,

with 1.6–5.5 times more benzene from fragments of other compounds than fuel-based benzene.<sup>4,14</sup> In this study, benzene emissions due to formation from other fuel precursors were 6.1 times greater than emissions of benzene due to benzene in liquid gasoline, and accounted for 86% of benzene emissions. This increase in the fraction of benzene from products of incomplete combustion versus benzene present in the uncombusted fuel can be attributed to the regulation of benzene in liquid gasoline, such that more of the benzene emissions are now coming from the dealkylation of larger aromatics or potentially formation from other smaller fragments.

With the exception of changes in oxygenates (e.g., MTBE, ethanol), the overall composition of emissions from gasoline and diesel vehicles has remained similar over the past 20 years likely due to similarities in fuel composition.<sup>3,5,6,10,11</sup> The ratio of toluene to benzene in gasoline exhaust (used in photochemical clocks) is similar in our work ( $1.5 \text{ mol mol}^{-1}$ ) to the mid-1990s in California ( $1.2\text{--}1.4$ ).<sup>3</sup> However, the original work by de Gouw et al. featured a higher value of  $3.7 \text{ mol mol}^{-1}$  in the Northeastern U.S.<sup>23</sup> Kirchstetter et al. reported  $24 \pm 2\%$  of gasoline emissions from products of incomplete combustion in a 1994 study that measured fewer compounds, and is therefore lower than the value of  $32 \pm 2\%$  reported in this work.<sup>3</sup> While fuel composition has remained similar, exhaust emission factors for gasoline engines have decreased by an order of magnitude since previous work done at the same tunnel site in 1994.<sup>3</sup> This decrease can be attributed to the nearly universal adoption of catalytic after-treatment of exhaust from on-road gasoline engines. Whereas diesel emission factors have decreased only modestly compared to the 1990s.<sup>5</sup> A comparison of our emission factors to diesel exhaust factors from Schauer et al.<sup>5</sup> using dynamometer tests in the 1990s shows similarities in composition to their mileage-based emission factors (e.g.,  $\mu\text{g C km}^{-1}$ ). There are marginal increases for some compounds (*n*-alkanes, light alkenes, formaldehyde), decreases for acetone and larger aldehydes, and relatively similar emissions for many aromatic species. A comparison to more recent diesel emissions data from the Caldecott tunnel in 2006 shows a minor decrease in formaldehyde and butanal emission factors (20–25% within reported uncertainties).<sup>6</sup> Our reported formaldehyde emission factor for diesel traffic is similar to the emission factor calculated using individual truck plumes at the 2010 Caldecott tunnel study.<sup>18</sup> Emissions of carbonyls in gasoline exhaust from the 2006 study were similar within reported uncertainties with the exception of acetaldehyde, acetone + propanal, and hexanal, which were all greater in our more recent measurements.<sup>6</sup> Ambient concentrations of ethanol have been increasing with its use in gasoline in the U.S.,<sup>24</sup> which is consistent with the large ethanol emission factor reported in this work.

Not all emissions from gasoline vehicles occur via tailpipe exhaust. Emission factors reported in this work represent running exhaust, and additional analyses and data are needed to account for emissions during engine ignition and from nontailpipe (evaporative) emissions. Overall, 25% of gasoline-related emissions in the tunnel were due to evaporative sources, which is similar to the range of ambient observations in urban areas (17–40%).<sup>1,13,25</sup> Exhaust emission factors from the tunnel (Table 1) include some of these nontailpipe emissions for smaller, more volatile compounds in liquid gasoline that are especially prone to evaporation (e.g., *n*-butane, *n*-pentane, isopentane, and other  $C_5\text{--}C_6$  hydrocarbons). In the case of these compounds, the fuel composition-based exhaust emission



**Figure 2.** Ozone production potential for gasoline and diesel sources. The fraction from products of incomplete combustion is denoted for the exhaust sources and excludes carbon monoxide. Tabular data can be found in SI Table S3.

factors are more representative of tailpipe emissions. Exhaust emissions during the ignition of gasoline vehicles (i.e., cold start emissions) were not measured in the tunnel. These emissions may increase total exhaust emissions by 60–90% depending on location and season, according to estimates from the California Air Resources Board EMFAC model.<sup>26</sup> The regional effect of these emissions requires further assessment due to the uncertainties associated with current measurements and estimates. These additional emissions need to be considered when assessing inventories and potential impacts on air quality.

The array of compounds presented in this work includes all gas-phase species measured using our instrumentation, but is not fully comprehensive. Previous studies have reported emissions of other products of incomplete combustion (e.g., acids), and further work is necessary to characterize these emissions.<sup>5,6</sup>

**Ozone Production Potential.** Both gasoline and diesel emissions contribute to ozone formation through emissions of reactive organic carbon and NO<sub>x</sub>. In terms of reactive organic precursors, gasoline exhaust was found to have the greatest ozone production potential, followed by nontailpipe gasoline emissions and diesel exhaust. The ozone production potential for fresh unaged reactive organic emissions from these three sources determined using MOIR values are 1.8, 1.0, and 0.98 g O<sub>3</sub> g<sup>-1</sup> for gasoline exhaust, nontailpipe gasoline, and diesel exhaust, respectively (Figure 2). Corresponding values obtained using higher MIR rather than MOIR values were 4.5, 2.0, and 2.5, respectively. Without inclusion of products of incomplete combustion, gasoline and diesel exhaust had ozone-formation potentials that were ~40% lower: 1.2 and 0.63 g O<sub>3</sub> g<sup>-1</sup>, respectively. Including carbon monoxide emissions increases the ozone formation potential of both gasoline and diesel exhaust by 35% and 20%, respectively, in MOIR conditions. This increase is smaller under MIR conditions where inclusion of CO emissions increases the ozone formation potential by 20% and 11%, respectively. When considering all vehicle-related emissions, the additional ozone-forming potential of nontailpipe emissions reduces the impact of including CO

emissions. Disagreements in the CO contribution to ozone between this paper and previous work by Wood et al.<sup>16</sup> are attributed to differences in the emission factors used in the calculations.

The fuel components that dominate the ozone-forming potential of vehicle emissions are similar to previous work by Kirchstetter et al.<sup>4</sup> Our work includes more measurements of oxygenates, but the similarities in hydrocarbon reactivity reflect stability in the hydrocarbon composition of gasoline over time. The ozone produced from gas-phase organic compounds in gasoline engine exhaust comes predominantly from its olefinic and aromatic content, while ozone from nontailpipe emissions is due to its olefinic and paraffinic content. Over half of the organic precursors to ozone from diesel exhaust come from alkenes (i.e., olefins) and oxygenates, followed by aromatics. Recent work has shown that structure activity calculations for high molecular weight compounds may be different from the estimates developed using data on C<sub>10</sub> and smaller compounds.<sup>27,28</sup> These advancements are likely to affect MOIR and MIR values, but these differences, once resolved, should not substantially affect the assessment of ozone production from diesel exhaust using the values presented here. Furthermore, since the values presented here are normalized combinations of the individual components, modeling and laboratory tests of the complex organic mixtures are recommended to further elucidate the ozone production potential of these sources.

Given the lower ozone formation potential for diesel emissions of gas-phase organic carbon, and the fact that less diesel fuel is used than gasoline in the U.S.,<sup>1</sup> we conclude that gasoline emissions (both exhaust and nontailpipe) are responsible for the majority of ozone formation due to organic emissions from on-road motor vehicles. In urban areas where gasoline accounts for a range of 73–90% of total on-road fuel use,<sup>1</sup> gasoline sources are responsible for 69–96% of reactive organic carbon emissions and 79–97% of organic precursors to ozone from motor vehicles in the U.S. These estimates include uncertainties and reflect differences in emission factors between engine types, and also include cold start and nontailpipe

contributions to gasoline emissions at levels equivalent to 60–90% of running exhaust emissions and 33–67% of total exhaust from gasoline engines, respectively. Yet, emissions of nitrogen oxides (NO<sub>x</sub>) from mobile and stationary combustion sources remain a critical part of ozone mitigation strategies, particularly in NO<sub>x</sub>-sensitive areas. Diesel vehicles are now responsible for most of the mobile source NO<sub>x</sub> emissions (74% in California as of 2010), so control of both gasoline and diesel emissions remains an important priority for air quality improvement at urban to national scales.<sup>29</sup>

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Supplementary tables (S1–S3) referenced in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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