Supporting Information for:

Investigation of the effect of mid- and high-level ethanol blends on the particulate and the mobile source air toxic (MSAT) emissions from a GDI flex fuel vehicle

Jiacheng Yang, Patrick Roth, Thomas D. Durbin, Kent C. Johnson, Akua Asa-Awuku, David R. Cocker III, Georgios Karavalakis*

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Number of Figures: 2

Number of Tables: 3

* Corresponding Author. (Georgios Karavalakis) Email: gkaraval@cert.ucr.edu

Fuel Change Protocol.

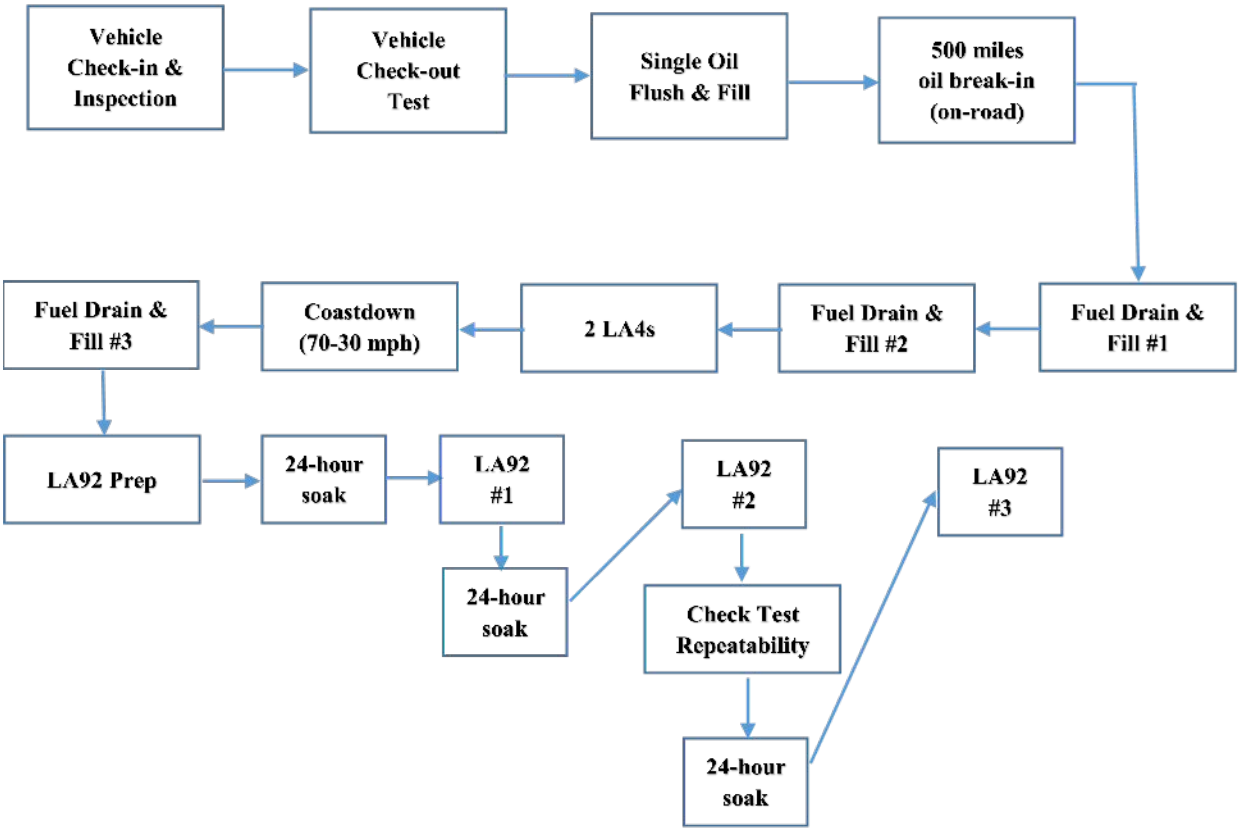


Figure S1. Fuel change procedure flowchart

Emissions Analysis.

PM measurements were made on both a mass and number basis. PM mass samples were collected cumulatively over the entire length of the LA92 cycle, with one sample collected for each test. Total PM mass samples were collected using 47-mm polytetrafluoroethylene (PTFE) filters (Whatman) and weighed with a 1065-compliant microbalance in a temperature and humidity controlled clean chamber meeting 1065 requirements. Buoyancy corrections for barometric pressure differences were also made for the PM filter weights as per CFR 1065.

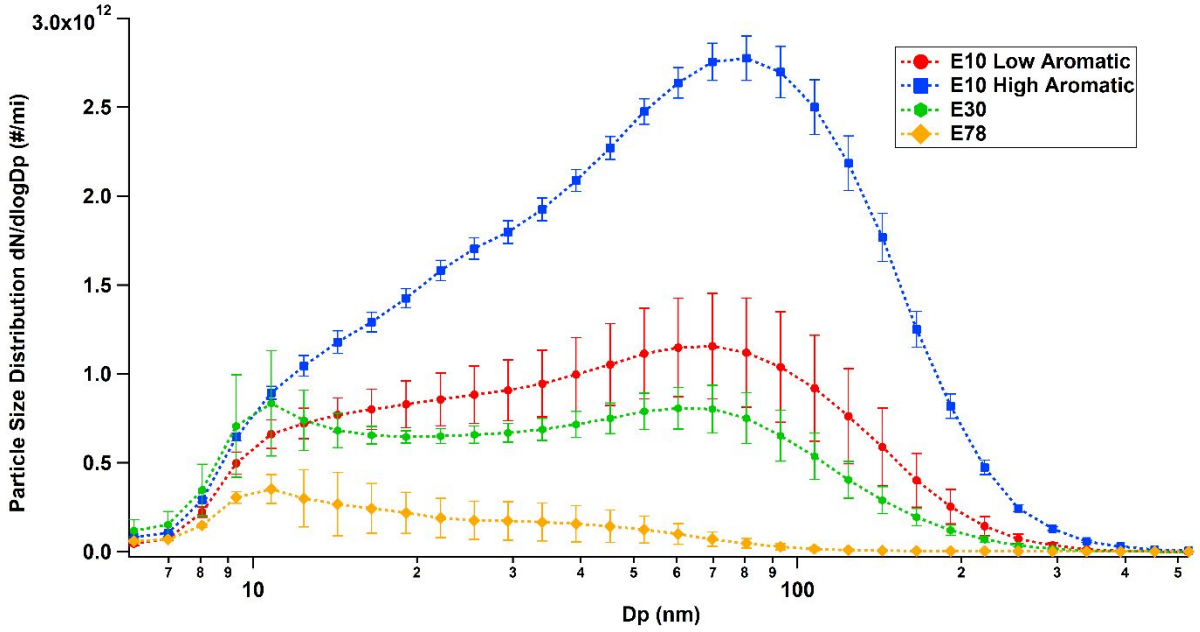
Total particle number was measured using a TSI 3776 ultrafine-Condensation Particle Counter (CPC) with a 2.5 nm cut point. The instrument operated at a flowrate of 1.5 L/min. Solid particle number counts were measured with the use of a catalytic stripper. The catalytic stripper both vaporizes volatile species and oxidizes them, and hence more efficiently removes volatiles from the sample than thermal treatment alone. For this study, the catalytic stripper used was 40 mm long with a diameter of 17 mm and was based on a cordierite monolith with a 400 cpsi cell density and a 6 mils substrate thickness. It had both oxidation and sulfur storage capability, but its exact chemical composition was unknown. The particular unit was characterized according to the protocol outlined by Amanatidis et al. [1] and was deemed appropriate for the measurements of this study. The particles were counted downstream of the catalytic stripper with a TSI 3776 ultrafine CPC at a flow rate of 1.5 L/min. An ejector diluter was used to collect particle number samples from the CVS tunnel for the GDI vehicles.

Real-time particle size distributions were obtained using an Engine Exhaust Particle Sizer (EEPS) spectrometer. The EEPS (TSI 3090, firmware version 8.0.0) was used to obtain real-time second-by-second size distributions between 5.6 to 560 nm. Particles were sampled at a flow rate of 10 L/min, which is considered to be high enough to minimize diffusional losses. They were then charged with a corona charger and sized based on their electrical mobility in an electrical field. Concentrations were determined through the use of multiple electrometers. In this study, the measured electrometer currents over 22 electrometers were inverted to particle size distributions into 32 bins using two inversion matrices, known as Default Matrix or Soot Matrix.

Real-time soot or black carbon emissions were measured using an AVL Micro-Soot Sensor (MSS). The MSS is an instrument that measures soot mass concentration at a frequency of one

Hertz basis using a photo acoustic detection technique, where the light-absorbing PM components (such as soot particles) are exposed to laser light that is periodically modulated at the acoustical resonant frequency [2]. The instrument is designed to measure soot concentrations down to ~5μg/m^3, and operates at a flow rate of 2 L/min.

A



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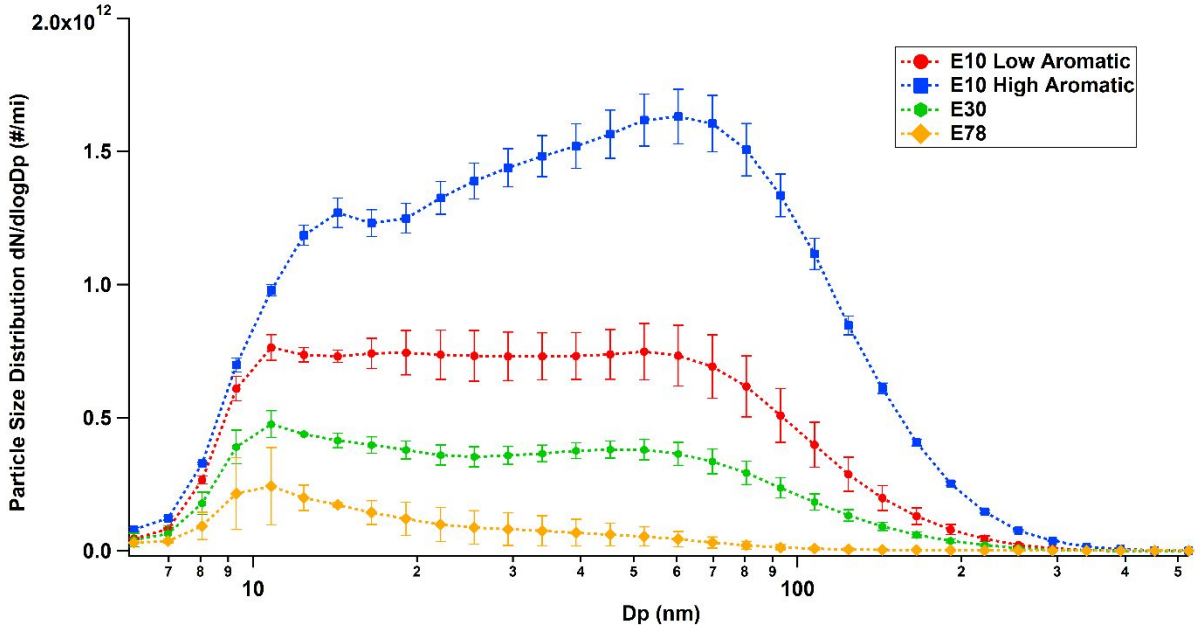

Figure S2. Particle size distributions over the cold-start LA92 (top panel A) and hot-start LA92 (bottom panel B)

Table S1. Monoaromatic and other VOCs emitted during the cold-start and hot-start LA92 cycles

	Cold-start LA92				Hot-start LA92			
	E10	E10HA	E30	E78	E10	E10HA	E30	E78
Ethylene	23290.3±142.6	22843±11	23093±22.3	22977.3±22.9	23218.7±32.5	22896.7±21.5	23125.3±26.7	22988±38.2
Acetylene	149.97±0.03	152±0.14	148.65±0.66	151.91±0.43	149.32±0.86	151.83±0.68	149.1±0.87	152.38±0.75
Ethane	11.06±0.018	11.037±0.09	11.09±0.023	11.082±0.009	11.085±0.014	11.092±0.014	11.055±0.03	11.092±0.013
Propylene	1.675±0.477	1.998±0.01	1.73±0.115	2.467±0.041	1.002±0.036	0.769±0.023	0.572±0.014	0.412±0.024
Propane	0.467±0.215	0.851±0.097	0.546±0.013	1.323±0.081	0.073±0.019	0.07±0.015	0.012±0.004	0.019±0.017
Isobutane	1.045±0.229	1.371±0.05	0.977±0.035	1.358±0.045	0.886±0.037	1.153±0.025	0.657±0.022	0.681±0.092
1-Butene	1.224±0.5	1.657±0.015	1±0.027	0.503±0.007	0.775±0.003	0.735±0.016	0.388±0.025	0.126±0.02
1,3 Butadiene	0.054±0.138	0.331±0.065	0.126±0.021	0.084±0.138	-0.025±0.032	0.192±0.106	0.038±0.007	0.639±0.778
n-Butane	-0.023±0.013	0.931±0.02	0.022±0.001	-0.003±0.006	-0.015±0.001	0.551±0.046	0.01±0.001	-0.004±0.017
trans-2-Butene	0.22±0.089	0.304±0.009	0.147±0.016	0.07±0.013	0.089±0.005	0.133±0.002	0.048±0.014	0.025±0.003
cis-2-Butene	0.2±0.115	0.254±0.074	0.171±0.007	0.07±0.003	0.125±0.03	0.13±0.003	0.061±0.002	0±0
Isopentane	0.968±0.244	0.562±0.008	0.775±0.083	0.101±0.02	0.755±0.146	0.383±0.019	0.432±0.029	0.074±0.047
1-Pentene	0.067±0.041	0.103±0.002	0.062±0.001	0.03±0.001	0.048±0.001	0.05±0.002	0.028±0	0±0
n-Pentane	0.049±0.028	0.075±0.002	0.046±0.002	0.029±0.004	0.036±0	0.037±0.002	0.021±0	0±0
Isoprene	0.991±0.507	0.938±0.031	1.024±0.074	0.14±0.008	0.678±0.005	0.586±0.028	0.558±0.002	0.091±0.04
trans-2-Pentene	0.055±0.022	0.065±0.001	0.056±0	0.026±0.001	0.036±0	0.037±0	0.03±0.006	0.014±0.001
cis-2-Pentene	2.331±0.473	2.854±0.172	1.953±0.159	0.669±0.084	1.251±0.02	1.321±0.057	0.983±0.023	0.327±0.028
2,2-Dimethylbutane	0.062±0.046	0.032±0.015	0.061±0	0.025±0.002	0.045±0.029	0.05±0	0.014±0	0±0
Cyclopentane	0.025±0.016	0.044±0	0.024±0.002	0.015±0.002	0.009±0.013	0.024±0.001	0±0	0±0
2,3-Dimethylbutane	0.012±0.017	0.026±0	0.017±0.001	0±0	0±0	0.014±0.001	0±0	0±0
2-Methylpentane	0.645±0.136	0.029±0.001	0.4±0.02	0.263±0.03	0.273±0.026	0.025±0	0.225±0.007	0.146±0.009
3-Methylpentane	0.888±0.137	0.021±0.001	0.553±0.044	0.353±0.047	0.334±0.036	0.007±0.01	0.242±0.002	0.142±0.009
1-Hexene	0.058±0.027	0.117±0.006	0.055±0.005	0.03±0	0.031±0.003	0.066±0.002	0.031±0.004	0.019±0.006
n-Hexane	0.305±0.106	0.643±0.038	0.276±0.013	0.128±0.009	0.156±0.015	0.317±0.01	0.137±0.006	0.066±0.015
Methylcyclopentane	0.3±0.077	0.635±0.0	0.276±0.0	0.114±0.00	0.158±0.01	0.288±0.01	0.138±0.00	0.065±0.00

		45	3	8	4	5	2	8
2,4-Dimethylpentane	0.72±0.285	1.52±0.132	0.569±0.024	0.155±0.027	0.182±0.017	0.247±0.009	0.124±0	0.034±0.002
Benzene	0.581±0.075	1.107±0.076	0.467±0.021	0.206±0.02	0.26±0.014	0.491±0.018	0.219±0.004	0.099±0.015
Cyclohexane	0.224±0.019	0.417±0.035	0.168±0.007	0.071±0.003	0.093±0.006	0.186±0.002	0.077±0.006	0.036±0.01
2-Methylhexane	0.085±0.037	0.163±0.023	0.078±0.008	0.035±0.001	0.042±0.004	0.09±0.002	0.028±0.002	0.009±0.012
2,3-Dimethylpentane	1.092±0.451	1.824±0.025	0.986±0.07	0.599±0.001	0.899±0.008	0.972±0.031	0.471±0.05	0.151±0.02
3-Methylhexane	0.03±0.005	0.065±0.003	0.025±0.001	0.02±0	0.007±0.01	0.04±0	0.007±0.01	0.008±0.011
2,2,4-Trimethylpentane	0.133±0.051	0.371±0.026	0.13±0.007	0.052±0.003	0.065±0.007	0.175±0.007	0.054±0.004	0.023±0.007
n-Heptane	0.07±0.018	0.147±0.003	0.072±0.018	0.034±0.007	0.03±0.003	0.079±0.003	0.03±0.002	0.018±0.007
Methylcyclohexane	0.105±0.05	0.367±0.029	0.105±0.007	0.034±0.008	0.056±0.004	0.163±0.008	0.046±0.006	0.019±0.007
2,3,4-Trimethylpentane	2.829±0.585	1.264±0.096	2.404±0.004	1.128±0.128	1.411±0.177	0.613±0.029	1.201±0.009	0.536±0.029
Toluene	0.011±0.015	0.174±0.015	0.027±0.002	0.026±0.001	0.007±0.01	0.082±0.003	0.015±0.002	0.011±0.016
2-Methylheptane	0.054±0.042	0.08±0.003	0.063±0.002	0.028±0.003	0.031±0.004	0.042±0.001	0.027±0.003	0.008±0.012
3-Methylheptane	0.469±0.118	0.774±0.065	0.416±0.005	0.13±0.014	0.216±0.034	0.339±0.016	0.186±0.001	0.057±0.006
n-Octane	1.798±0.671	2.912±0.22	1.654±0.071	0.628±0.027	0.908±0.017	1.014±0.014	0.509±0.041	0.127±0.034
Ethylbenzene	0.071±0.049	0.075±0.006	0.081±0.001	0.023±0.002	0.044±0.007	0.035±0.002	0.035±0	0±0
m/p-Xylenes	0.049±0.033	0.052±0.004	0.058±0	0.017±0.002	0.03±0.005	0.026±0.001	0.025±0	0±0
Styrene	0.22±0.129	0.191±0.015	0.243±0.003	0.059±0.005	0.128±0.015	0.09±0.005	0.102±0.002	0.024±0.003
o-Xylene	0.311±0.132	0.519±0.055	0.281±0.026	0.104±0.008	0.152±0.001	0.187±0.006	0.092±0.002	0.027±0.003
Nonane	0.656±0.383	1.344±0.058	0.682±0.047	0.211±0.033	0.366±0.009	0.509±0.001	0.183±0.005	0.043±0.008
Isopropylbenzene	0.03±0.043	0.118±0.023	0.07±0.011	0.016±0.002	0.018±0.026	0.048±0.003	0±0	0±0
n-Propylbenzene	0.2±0.07	0.364±0.028	0.217±0.005	0.075±0.012	0.106±0.011	0.141±0	0.056±0.004	0.021±0.002
m-Ethyltoluene	0.153±0.024	0.119±0.022	0.138±0.004	0.051±0.004	0.075±0.007	0.065±0.001	0.058±0.001	0.022±0.001
1,3,5-Trimethylbenzene	0.035±0.017	0.073±0.01	0.037±0.002	0.018±0.002	0.018±0.002	0.027±0.001	0.006±0.009	0±0
o-Ethyltoluene	0.146±0.067	0.326±0.038	0.16±0.005	0.07±0.006	0.082±0.015	0.129±0.001	0.041±0.001	0.022±0.001
1,2,4-Trimethylbenzene	0.051±0.022	0.145±0.013	0.065±0.014	0.038±0.001	0.033±0.003	0.061±0.001	0.017±0.001	0.014±0.001
n-Decane	0.067±0.048	0.159±0.021	0.073±0.002	0.038±0.005	0.044±0.013	0.07±0.005	0.019±0.003	0.015±0.001
1,2,3-Trimethylbenzene	0.026±0.037	0.097±0.022	0.036±0.007	0.024±0.004	0.009±0.012	0.036±0.003	0±0	0±0
m-Diethylbenzene	0.126±0.085	0.271±0.072	0.129±0.001	0.064±0.006	0.084±0.043	0.121±0.002	0.035±0.004	0.021±0
p-Diethylbenzene	0.048±0.023	0.004±0.015	0.048±0.004	0.019±0.002	0.036±0.003	0±0.01	0.028±0.002	0.012±0

Table S2. Emission rates for emission pollutants and fuel economy over both LA92 cycles

Cold-start LA92				
	E10	**E10HA**	**E30**	**E78**
THC (g/mi)	0.037 ± 0.009	0.042 ± 0.001	0.034 ± 0.002	0.032 ± 0.001
NMHC (g/mi)	0.027 ± 0.007	0.033 ± 0.001	0.024 ± 0.002	0.015 ± 0.001
CH_4 (g/mi)	0.011 ± 0.002	0.011 ± 0.001	0.011 ± 0.000	0.020 ± 0.001
CO (g/mi)	1.183 ± 0.285	1.210 ± 0.038	0.943 ± 0.028	0.767 ± 0.027
NOx (g/mi)	0.031 ± 0.011	0.034 ± 0.006	0.026 ± 0.003	0.020 ± 0.001
CO_2 (g/mi)	263.6 ± 13.0	290.1 ± 3.8	261.0 ± 2.1	273.5 ± 3.1
Fuel Economy (mpg)	32.4 ± 1.7	29.8 ± 0.4	30.2 ± 0.2	23.5 ± 0.3
PM Mass (mg/mi)	2.82 ± 1.49	8.97 ± 0.70	2.12 ± 0.02	0.51 ± 0.24
BC (mg/mi)	2.16 ± 0.92	7.26 ± 0.54	1.27 ± 0.16	0.23 ± 0.12
TPN (#/mi)	7.5E+12 ± 1.3E+12	1.4E+13 ± 3.2E+11	n/a	2.2E+12 ± 7.0E+11
Solid PN (#/mi)	5.0E+12 ± 1.1E+12	9.6E+12 ± 3.0E+11	3.3E+12 ± 3.7E+11	6.4E+11 ± 2.2E+11
Formaldehyde (μg/mi)	9.132 ± 0.046	5.555 ± 1.835	10.512 ± 0.873	8.080 ± 0.076
Acetaldehyde (μg/mi)	8.806 ± 1.612	6.872 ± 2.550	21.012 ± 0.063	47.774 ± 1.379
Benzene (mg/mi)	1.092 ± 0.451	1.824 ± 0.025	0.986 ± 0.070	0.599 ± 0.001
Toluene (mg/mi)	1.798 ± 0.671	2.912 ± 0.220	1.654 ± 0.071	0.628 ± 0.027
Ethylbenzene (mg/mi)	0.311 ± 0.132	0.519 ± 0.055	0.281 ± 0.026	0.104 ± 0.008
m/p-Xylenes (mg/mi)	0.656 ± 0.211	1.344 ± 0.366	0.682 ± 0.509	0.211 ± 0.183
o-Xylene (mg/mi)	0.200 ± 0.075	0.364 ± 0.106	0.217 ± 0.141	0.075 ± 0.056
1,3-butadiene (mg/mi)	0.200 ± 0.115	0.254 ± 0.074	0.171 ± 0.007	0.070 ± 0.003
Hot-start LA92				
	E10	**E10HA**	**E30**	**E78**
THC (g/mi)	0.027 ± 0.001	0.028 ± 0.001	0.022 ± 0.001	0.017 ± 0.001
NMHC (g/mi)	0.017 ± 0.001	0.019 ± 0.001	0.013 ± 0.001	0.005 ± 0.001
CH_4 (g/mi)	0.011 ± 0.000	0.011 ± 0.000	0.010 ± 0.001	0.014 ± 0.000
CO (g/mi)	1.164 ± 0.062	1.142 ± 0.172	0.815 ± 0.072	0.579 ± 0.069

NOx (g/mi)	0.037 ± 0.002	0.033 ± 0.002	0.030 ± 0.004	0.020 ± 0.002
CO_2 (g/mi)	260.0 ± 3.7	281.7 ± 3.8	248.9 ± 13.5	260.2 ± 2.0
Fuel Economy (mpg)	32.8 ± 0.5	30.7 ± 0.4	31.7 ± 1.8	24.7 ± 0.2
PM Mass (mg/mi)	1.30 ± 0.20	3.27 ± 0.06	0.57 ± 0.06	0.44 ± 0.13
BC (mg/mi)	0.71 ± 0.13	2.33 ± 0.13	0.36 ± 0.04	0.12 ± 0.05
TPN (#/mi)	5.7E+12 ± 5.2E+11	1.0E+13 ± 4.9E+11	3.2E+12 ± n/a	1.2E+12 ± 4.0E+11
Solid PN (#/mi)	3.4E+12 ± 5.4E+11	6.4E+12 ± 3.1E+11	1.7E+12 ± 2.8E+11	3.2E+11 ± 2.2E+11
Formaldehyde (µg/mi)	3.196 ± 1.507	0.000 ± 0.000	2.749 ± 0.186	0.169 ± 0.034
Acetaldehyde (µg/mi)	3.111 ± 0.667	1.848 ± 0.072	5.958 ± 0.516	8.041 ± 2.214
Benzene (mg/mi)	0.899 ± 0.008	0.972 ± 0.031	0.471 ± 0.050	0.151 ± 0.020
Toluene (mg/mi)	0.908 ± 0.017	1.014 ± 0.014	0.509 ± 0.041	0.127 ± 0.034
Ethylbenzene (mg/mi)	0.152 ± 0.001	0.187 ± 0.006	0.092 ± 0.002	0.027 ± 0.003
m/p-Xylenes (mg/mi)	0.366 ± 0.043	0.509 ± 1.000	0.183 ± 0.420	0.043 ± 0.245
o-Xylene (mg/mi)	0.106 ± 0.021	0.141 ± 0.282	0.056 ± 0.133	0.021 ± 0.073
1,3-butadiene (mg/mi)	0.125 ± 0.030	0.130 ± 0.003	0.061 ± 0.002	0.000 ± 0.000

n/a: not available

Table S3. *P* values for emission results; Bolded values indicate marginally statistically significant or statistically significant results

p-value	Cold-start LA92			Hot-start LA92		
	E10HA	E30	E78	E10HA	E30	E78
THC (g/mi)	0.373	0.538	0.392	**0.096**	**0.003**	**0.000**
NMHC (g/mi)	0.273	0.449	0.037	**0.077**	**0.006**	**0.000**
CH_4 (g/mi)	0.993	0.956	**0.003**	0.172	**0.040**	**0.000**
CO (g/mi)	0.877	0.221	**0.066**	0.843	**0.003**	**0.000**
NOx (g/mi)	0.723	0.455	0.153	**0.086**	**0.074**	**0.000**
CO_2 (g/mi)	**0.028**	0.754	0.267	**0.002**	0.245	0.919
Fuel Economy (mpg)	**0.055**	**0.081**	**0.001**	**0.003**	0.355	**0.000**
PM Mass (mg/mi)	**0.034**	0.577	0.164	**0.006**	**0.008**	**0.036**
BC (mg/mi)	**0.001**	0.177	**0.023**	**0.000**	**0.036**	**0.002**
PN (#/mi)	**0.001**	n/a	**0.003**	**0.000**	n/a	**0.000**
Solid PN (#/mi)	**0.002**	**0.063**	**0.002**	**0.001**	**0.026**	**0.001**
Formaldehyde (µg/mi)	0.110	0.155	**0.004**	**0.095**	0.717	0.105
Acetaldehyde (µg/mi)	0.460	**0.009**	**0.001**	0.117	**0.041**	**0.095**
Benzene (mg/mi)	0.149	0.774	0.262	**0.087**	**0.007**	**0.000**
Toluene (mg/mi)	0.156	0.792	0.133	**0.020**	**0.006**	**0.001**
Ethylbenzene (mg/mi)	0.177	0.776	0.157	**0.013**	**0.001**	**0.000**
m/p-Xylenes (mg/mi)	0.128	0.934	0.243	**0.002**	**0.002**	**0.001**
o-Xylene (mg/mi)	**0.092**	0.767	0.131	**0.044**	**0.025**	**0.008**
1,3-butadiene (mg/mi)	0.633	0.761	0.251	0.853	**0.092**	**0.027**

n/a: not available

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