# **Supporting Information**

Cold temperature and biodiesel fuel effects on speciated emissions of volatile organic compounds from diesel trucks

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There are 18 pages in the supporting information, including 6 tables and 4 figures. A description of VOC sampling, TO-15 VOC analysis, THC and methane analysis, TO-11A carbonly analysis, emission rate calculations and fuel change procedure is included.

Table S1A & B. VOC compound list and method detection limits

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Figure S2. Diagram of VOC emissions sampling setup

Figure S3. Average  $\Sigma$ VOCs emission rates for each test condition

Figure S4. Comparison of emission profiles from SPECIATE and this work

### **VOC** sampling

Prior to sample collection, the 6 L SUMMA canisters were cleaned in a canister cleaner (Entech Instruments Inc., Model 3100A, Simi Valley, CA, U.S.) at ~90 °C oven temperature over ten cycles of evacuation and filling with humidified N<sub>2</sub>. Canisters were evacuated to  $\leq$ 10 mTorr during the final evacuation stage. DNPH cartridges were used as is and stored in a refrigerator at 5 °C before and after use until analysis. Sampling lines from the dilution tunnel to the VOC and carbonyl sampling trains were heated to ~113 °C. A Teflon<sup>TM</sup> filter was placed in front of the SUMMA canister sampling train to minimize particle contamination. The canister pressure was recorded before and after sampling to ensure the absence of leaks. The canister vacuum was utilized to fill the canister during sampling, whereas a pump was needed to pull flow through the DNPH cartridge. Calibrated mass flow controllers were used to control and monitor the sampling flow for both sampling media. The flow rates were 1.0 sLpm for the carbonyl sampling. For VOC sampling, the flow rates were 0.90 sLpm for cold and warm start cycles and 0.25 sLpm for HD-UDDS cycles.

#### **TO-15 VOC analysis**

VOC emissions in samples collected in SUMMA canisters were analyzed by U.S. EPA Method TO-15<sup>1</sup>. Samples were analyzed within four hours of collection. VOCs collected in the canisters were quantified by sampling a volume of canister contents with an Entech Model 7500A Autosampler (Entech Instruments Inc.) and Entech Model 7150 Pre-concentrator followed by analysis with gas chromatography/mass spectrometery GC/MS. The preconcentrator adsorbed the VOCs onto two traps and removed water from the sample using a third trap. The sample was then refocused onto a cryogenically cooled single solid phase microextraction (SMPE) trap, then desorbed from the trap and injected into the GC. A constant volume of internal standard mixture was sampled by the pre-concentrator with each analytical run. A 20 ppb internal standard mixture was prepared in a canister from a 1 ppm standard mixture in a gas cylinder (The Linde Group, 5 % accuracy) containing bromochloromethane, 1,4-difluorobenzene and chlorobenzene-d5.

The GC/MS analytical system consisted of an Agilent 6890 Gas Chromatograph and an Agilent 5973N Mass Spectrometer (Agilent Technologies, Santa Clara, CA, U.S.). Helium

(Airgas, 99.9995 %) was used as the carrier gas for both the GC/MS and pre-concentrator. The GC included a Restek Rt<sub>x</sub>-1 column (Restek Corp., 60 m, 1 µm film thickness, 0.32 mm ID) with a helium carrier gas flow rate of 2.0 mL/min. GC oven temperature program was as follows: 35 °C initial temperature and hold for 5 min, ramp 5 °C/min to 130 °C, then ramp 20 °C/min to 250 °C and hold for 3 min. The GC/MS was operated in Selected Ion Monitoring (SIM) mode. The Mass Selective Detector (MSD) signal was recorded and processed by Chemstation software run on a computer that was interfaced with the GC/MS. Each chromatographic peak was inspected manually for quality control. The target compound list consisted of 79 VOCs. Acetone and acetonitrile measured by TO-15 analysis had significantly high background levels and therefore were not reported. A calibration was performed for the target compound list by sampling different volumes of a canister containing a 1 ppb and 10 ppb TO-15 calibration standard mixture. The calibration cans were prepared from 1 ppm calibration standard gas mixtures (The Linde Group, 5 % accuracy). Method detection limits were determined as outlined in the Code of Federal Regulations (CFR 136 Appendix B) by performing seven replicate measurements of a low level standard. The standard deviations of the concentrations were multiplied by 3.14, or the Student's t-value for 99 % confidence limit for seven measurements. MDLs ranged from 15 to 186 ppt and are reported for all compounds in Table S1A. Quality assurance (QA) procedures were followed as outlined in TO-15. The quantitation level (QL) for each compound was calculated as MDL $\times$ 3, where any measurement that fell below the OL was considered below detection, i.e., 0 ppb.

For quality control purposes, a blank sample canister was taken for each test condition to ensure canister cleanliness and that samples were not contaminated during the sampling process. These samples were handled like other canister samples but with no flow sampled. Blanks were filled with humidified nitrogen to ~1 atm and analyzed with total VOC concentrations of  $\leq 1.1$  ppb. Background canister samples were taken of dilution tunnel air for each test day to calculate background corrected VOC emission rates as discussed below. Total VOC concentrations in background samples were  $\leq 16$  ppb consisting of mostly ethanol (~60% of total) except for two high samples (25 and 66 ppb) where ethanol concentrations were elevated in dilution air compared to typical background levels. The background samples also contained minor amounts of propylene, isopropanol, chloromethane and dichlorodifluoromethane, which together made up another 33% of total background VOC concentration over the entire study.

#### THC and methane analysis

Non-methane hydrocarbon (NMHC) values were calculated from total hydrocarbon (THC) and methane measurements. THC was measured using a Heated Flame Ionization Detector (California Analytical Instruments, model CAI 600 HFID, Orange, CA, U.S.). Methane was measured using an identical HFID (model CAI 600 M-HFID) fitted with a methane cutter to remove all hydrocarbons except CH<sub>4</sub>.

#### **TO-11A carbonyl analysis**

DNPH cartridges (Sigma-Aldrich Corp., St. Louis, MO, U.S., LpDNPH H30) were analyzed within seven days of collection and stored in a refrigerator until analysis. The cartridges were extracted with ~6 mL carbonyl-free acetonitrile (Burdick & Jackson) with 5.0 mL final extract volume. The hydrazones were quantified according to EPA Method TO-11A<sup>2</sup> using high performance liquid chromatography (HPLC) with UV detection. In this work, an Agilent HPLC Series 1100 with Diode Array detector was used. Two C18 analytical columns were used in series and held at ~47 °C. The columns were Agilent Zorbax ODS with column size of 4.6 I.D.  $\times$ 250 mm length and 5  $\mu$ m particle size. The two mobile phases were A) 40:60 and B) 10:90 v/v water/acetonitrile, and the flow rate was 1.2 mL/min. The linear solvent program was as follows: 1) 0 to 20 min solvent B was increased from 0 to 33 %, 2) 20 to 25 min to 70 %, 3) return to 0 % from 25 to 26 min. Injection volume was 20 µL. The DAD detected absorbance of analytes was measured at the wavelength 365 nm. The analytical system was calibrated with commercially prepared derivatized carbonyl-DNPH standards from Sigma-Aldrich. Standard solution carbonyl equivalent concentrations were in the range of 0.015 to 7.5  $\mu$ g/mL in acetonitrile. MDLs and QLs were determined in a fashion similar to the VOC analysis. Minimum detection limits for formaldehyde and acetaldehyde were 5.5 and 8.8 ng/cartridge. Results from triplicate spike and recovery measurements and MDLs for all TO-11A carbonyls are reported in Table S1B. Similar to TO15 analysis described above, blank and background DNPH cartridge samples were taken, which were analyzed with the same extraction and analytical procedure as all other DNPH cartridge samples. Formaldehyde, acetaldehyde and acetone were the only carbonyls detected in the blank samples, with mean concentrations of  $0.09\pm0.06$ ,  $0.07\pm0.01$  and  $0.2\pm0.04$  ug/cartridge, respectively. These three carbonyls also represented >96% of carbonyl mass quantified in background samples. Mean background concentrations of these carbonyls are 7±4 ppb for

formaldehyde, 3±3 ppb for acetaldehyde and 6±2 ppb for acetone. Propionaldehyde and butyraldehyde were also detected in a few background samples.

#### **Emission rate calculation**

Emission rates for all VOCs and carbonyls were calculated from background-corrected concentrations or mass per cartridge and normalized by distance (mg km<sup>-1</sup>) for each driving cycle and test condition. Replicate VOC concentrations were first background-subtracted using the following equation for an example VOC compound X:

$$[X]_{e} = [X]_{de} - [X]_{d} (1 - (1/DF))$$
(1)

where  $[X]_e$  is background corrected X concentration in the diluted exhaust,  $[X]_{de}$  is the X diluted exhaust concentration, and  $[X]_d$  is the background concentration. All concentrations are in ppb. The dilution factor (DF), typically ~30, was calculated from the carbon concentrations in raw exhaust and diluted exhaust. Emission rates were calculated using the following equation:

$$ER_{x} = [X]_{e} \times G_{d} \times V_{mix} \times 10^{-9} / D$$
<sup>(2)</sup>

where  $ER_x$  is emission rate of X in mg km<sup>-1</sup>, G<sub>d</sub> is the gas density of X in mg m<sup>-3</sup>, V<sub>mix</sub> is the volume of diluted exhaust drawn through the dilution tunnel during the sampling period in m<sup>3</sup>, and D is driving distance in km. Emission factors from replicate measurements were averaged for each test cycle except for when DPF regeneration events took place. For  $\Sigma$ VOCs emission rates, errors were calculated from the propagation of the standard deviations of mean emission rates for individual VOCs. The relative standard deviations (RSD) of the propagated errors for  $\Sigma$ VOCs emission rates over replicate tests ranged from 2 to 68% (or in absolute terms 0.5 to 25 mg km<sup>-1</sup>) with mean RSD of 18% (6 mg km<sup>-1</sup>).

### Fuel change procedure

The following steps outline the actions taken to carry out fuel change:

- 1. Warm up vehicle with a 10-minute idle immediately before fuel drain. After idle, turn ignition off and bottom drain fuel tank.
- **2.** Turn vehicle ignition to RUN position for 30 seconds to allow controls and fuel level reading to stabilize. Confirm the return of fuel gauge reading to zero.

- 3. Turn ignition off. Fill fuel tank to 40% with next test fuel in sequence. Fill-up fuel must be at  $55 \pm 5$  °F.
- 4. Start vehicle, agitate the fuel by driving around the parking lot for 2 minutes, and then execute the sulfur removal procedure described in CRC E-60 Program report to purge sulfur from the catalyst. Test temperature for this step will be 68-75 °F. Side cooling fan(s) will be used to maintain air flow around the fuel tank, and the engine oil temperature will be monitored during the sulfur removal cycle.
- 5. Perform four vehicle coastdowns from 70 to 30 mph, with the last two measured. If the difference between the last two coastdowns exceeds 0.5 seconds, or their average differs by more than  $\pm$  7% from the running average for that vehicle, then the vehicle will be checked for any obvious and gross source of change in its mechanical friction. Side cooling fan(s) will be used.
- **6.** Drain fuel and refill to 40% with test fuel. Fuel temperatures will be maintained at 55±5 °F during fill up.
- Drain fuel and refill to 60% with test fuel. Fuel temperatures will be maintained at 55±5 °F during fill up.
- 8. Soak vehicle at test temperature for at least 12 hours to allow fuel temperature to stabilize to the test temperature.
- 9. Start vehicle and perform three Heavy Duty UDDS driving cycles. Following the first two prep cycles, allow the vehicle to idle in park for 2 minutes, and then shut the engine off for 2 to 5 minutes with key switch on. Following the last prep cycle, allow the vehicle to idle for 2 minutes, and then shut down the engine in preparation for the soak. Side fan(s) will be used to maintain air flow around the vehicle's fuel tank during the prep cycles.
- 10. Park vehicle in soak area at test temperature for 12 to 36 hours. During the soak period, maintain the nominal charge of the vehicle's battery using an appropriate charging device.

## References

(1) Compendium Method TO-15: Determination of volatile organic compounds (VOCs) in air collected in specially-prepared canisters and analyzed by gas chromatography/mass spectrometry (GC/MS); United States Environmental Protection Agency: Washington, DC, 1999.

(2) Compendium Method TO-11A: Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC); United States Environmental Protection Agency: Washington, DC, 1999.

Table S1A. VOC compounds and method detection limits (MDLs) quantified by TO-15 analysis with GC/MS. Compounds in red were below detection throughout the study. Highlighted compounds are mobile source air toxics.

TO15 Compaund	MDL	TO15 Commound	MDL	TO15 Compound	MDL
	ppb	1013 Compound	ppb	1015 Compound	ppb
1,1,1,2-Tetrachloroethane	0.034	Benzene	0.055	Methyl Methacrylate	0.031
1,1,1-Trichloroethane	0.061	Bromodichloromethane	0.069	Methylene Chloride	0.026
1,1,2,2-Tetrachloroethane	0.025	Bromoform	0.037	Methyl-t-Butyl-Ether	0.029
Freon-113	0.041	Bromomethane	0.086	m-Xylene	0.109
1,1,2-Trichloroethane	0.023	Carbon Disulfide	0.074	Naphthalene	0.161
1,1-Dichloroethane	0.039	Carbon Tetrachloride	0.077	n-Butyl Benzene	0.062
1,1-Dichloroethene	0.033	Chlorobenzene	0.029	n-Hexane	0.050
1,2,4-Trichlorobenzene	0.159	Chloroethane	0.074	n-Propylbenzene	0.064
1,2,4-Trimethylbenzene	0.072	Chloroform	0.073	o-Cymene	0.065
1,2-Dibromoethane	0.025	Chloromethane	0.066	o-Xylene	0.077
1,2-Dichlorobenzene	0.035	Chlorotoluenes	0.059	Propylene	0.036
1,2-Dichloroethane	0.079	cis-1,2-Dichloroethene	0.015	p-Xylene	0.053
1,2-Dichloropropane	0.024	cis-1,3-Dichloropropene	0.022	Sec-Butyl Benzene	0.059
1,3,5-Trimethylbenzene	0.062	Cumene	0.054	Styrene	0.069
1,3-Butadiene	0.090	Cyclohexane	0.049	Tert Amyl Methyl Ether	0.022
1,3-Dichlorobenzene	0.037	Dibromochloromethane	0.053	Tert-Butanol	0.117
1,4-Dichlorobenzene	0.069	Freon-12	0.083	Tert-Butyl Benzene	0.067
1,4-Dioxane	0.066	Freon-114	0.090	Tetrachloroethene	0.019
1-Ethyl-4-Methyl Benzene	0.066	Ethanol	0.147	Tetrahydrofuran	0.039
2-Butanone	0.056	Ethyl Acetate	0.064	Toluene	0.049
2-Chloroprene	0.030	Ethyl Tert-Butyl Ether	0.037	trans-1,2-Dichloroethene	0.019
2-Hexanone	0.083	Ethylbenzene	0.073	trans-1,3-Dichloropropene	0.036
3-Chloro-1-Propene	0.033	Heptane	0.040	Trichloroethene	0.031
4-Methy-2-Pentanone	0.037	Hexachlorobutadiene	0.186	Freon-11	0.095
Acrolein	0.105	Isooctane	0.048	Vinyl Acetate	0.057
Acrylonitrile	0.046	Isopropyl Alcohol	0.121	Vinyl Bromide	0.099
		-		Vinyl Chloride	0.064

Table S1B. VOC compounds quantified by TO-11A analysis with HPLC. Minimum detection limits and average spike recoveries with standard deviations in parentheses (for N = 3) are included. Compounds in red were below detection throughout the study. Highlighted compounds are mobile source air toxics.

TO11A Compounds	MDL	Spike Recovery		
TOTTA Compounds	ng/cartridge	%		
Acetaldehyde	8.8	82 (±1)		
Acetone	13.2	103 (±7)		
Benzaldehyde	31.1	85 (±1)		
Butyraldehyde	16.5	73 (±1)		
Crotonaldehyde	13.1	88 (±2)		
2,5-Dimethylbenzaldehyde	51.4	84 (±6)		
Formaldehyde	5.5	92 (±2)		
Hexaldehyde	27.8	67 (±1)		
Isovaleraldehyde	46.6	96 (±2)		
m-Tolualdehyde	31.3	80 (±2)		
o-Tolualdehyde	27.6	71 (±3)		
Propionaldehyde	12.8	77 (±1)		
p-Tolualdehyde	27.7	80 (±2)		
Valeraldehyde	19.5	93 (±5)		

Table S2. Test vehicle properties. GVWR=gross vehicle weight rating; NAC=NO<sub>x</sub> Adsorber Catalyst; DOC=diesel oxidation catalyst; DPF=diesel particle filter.

	Vehicle 1	Vehicle 2	Vehicle 3
Model Year	2011	2011	2011
Odometer / km	35,498	4,333	5,850
Engine Displacement	6.7 L	6.7 L	6.7 L
Engine Rated Power	350 Hp @3000 rpm	300 Hp @2800 rpm	200 Hp@2300 rpm
Transmission	Manual 6 spd	Auto 6 spd	Auto 5 spd
GVWR / kg	4,354	8,843	11,791
Unladen Test Weight / kg	3,369	3,851	5,868
Laden Test Weight / kg	4,215	8,323	11,191
Target A coefficient / kg	32.1	63.8	73.2
Target B coefficient / kg kph <sup>-1</sup>	0.36	0	0
Target C coefficient / kg kph <sup>-2</sup>	0.0061	0.012	0.017
Aftertreatment	NAC/DOC/DPF	SCR/DOC/DPF	SCR/DOC/DPF

Table S3. Test matrix and mean fuel consumption values. UNL=unladen weight, LAD=laden
weight. N is total number of tests conducted including tests where active DPF regeneration
occurred.

Condition	Vehicle	Weight	UNL/LAD	Fuel	Temp.	Dynam.	Ν	Fuel Consumption (kg-fuel/km)		
		(kg)			(°C)			Cold Start	HD-UDDS	Warm Start
1	1	4,215	LAD	ULSD	22	1	4	$0.28\pm0.03$	$0.158\pm0.001$	$0.217\pm0.004$
2	1	4,215	LAD	B20	22	1	3	$0.284\pm0.001$	$0.157\pm0.001$	$0.222\pm0.001$
3	1	3,369	UNL	B20	22	1	4	$0.27\pm0.02$	$0.154\pm0.002$	$0.206\pm0.007$
4	1	3,369	UNL	B20	-7	1	3	$0.35\pm0.01$	$0.167\pm0.001$	$0.228\pm0.001$
5	1	4,215	LAD	B20	-7	1	4	$0.35\pm0.02$	$0.171\pm0.001$	$0.239\pm0.002$
6	1	4,215	LAD	ULSD	-7	1	4	$0.357\pm0.008$	$0.166\pm0.002$	$0.228\pm0.001$
7	1	3,369	UNL	ULSD	-7	1	4	$0.35\pm0.004$	$0.163\pm0.002$	$0.222\pm0.006$
8	1	3,369	UNL	ULSD	22	1	4	$0.27\pm0.01$	$0.152\pm0.002$	$0.208\pm0.002$
9	2	3,851	UNL	ULSD	-7	1	3	$0.377\pm0.006$	$0.194\pm0.004$	$0.223\pm0.008$
10	2	3,851	UNL	B20	-7	1	4	$0.386\pm0.002$	$0.196\pm0.002$	$0.22\pm0.001$
11	2	3,851	UNL	B20	22	1	4	$0.278\pm0.007$	$0.171\pm0.002$	$0.201\pm0.002$
12	2	3,851	UNL	ULSD	22	1	3	$0.276\pm0.003$	$0.167\pm0.002$	$0.199 \pm 0.009$
13	3	5,868	UNL	ULSD	22	2	7	$0.34\pm0.03$	$0.211\pm0.004$	$0.275\pm0.006$
14	3	11,192	LAD	ULSD	22	2	5	$0.43\pm0.02$	$0.253\pm0.005$	$0.363\pm0.005$
15	3	5,868	UNL	B20	22	2	3	$0.33\pm0.01$	$0.218\pm0.003$	$0.283\pm0.003$
16	3	11,192	LAD	B20	22	2	3	$0.421\pm0.002$	$0.26\pm0.01$	$0.37\pm0.007$

Property	ASTM Method	ULSD	B20
Flash Point, °C	D93	85	86
Water and Sediment, vol. %	D2709	< 0.005	< 0.005
Distillation Temp., °C	D86	197.3	199.9
Viscosity at 40°C, $mm^2 s^{-1}$	D445	2.639	2.864
Ash Content, wt. %	D482	< 0.001	< 0.001
Sulfur Content, ppm	D5453	10.4	8.9
Cetane Number	D613	44.8	47
Cetane Index	D976-80	46.5	47.7
Aromaticity, vol. %	D1319-03	42.9	48.6
Cloud Point, °C	D2500	-31.7	-20.6
Ramsbottom Carbon Residue , wt. $\%$	D524	0.08	0.02
Lubricity, µm	D6079	398	245
Acid Number, mg KOH g <sup>-1</sup>	D664	NA	NA
Biodiesel Content, vol. %	D7371	0.1	20.8
Oxidation Stability, hrs	NA	NA	11.3

Table S4. Test fuel properties for ULSD and B20 fuels. NA=not applicable.

Additional Notes: Regarding the ULSD aromaticity values obtained using D1319-03, an unusual presentation of the aromatics and olefin dye zones is noted. These spread-out boundaries possibly lead to higher than normal subjectivity when assigning dye zone content margins.

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Condition #	1	2	3	4	5	6	7	8					
Vehicle	1	1	1	1	1	1	1	1					
Test Weight / kg	4215	4215	3369	3369	4215	4215	3369	3369					
Temperature / C	22	22	22	-7	-7	-7	-7	22					
Fuel	ULSD	B20	B20	B20	B20	ULSD	ULSD	ULSD					
TO11A Compounds													
Cold Start, N=	4	3	4	3	4	4	3	3					
Formaldehyde	$24 \pm 5$	$32 \pm 3$	$22 \pm 2$	$80 \pm 20$	$67 \pm 7$	$66 \pm 10$	$57 \pm 5$	$22 \pm 5$					
Acetaldehyde	24 ± 5	$26 \pm 4$	$21 \pm 1$	$50 \pm 10$	$44 \pm 5$	$45\pm 6$	$41 \pm 3$	21 ± 5					
HD-UDDS, N=	3	2	3	3	3	3	3	3					
Formaldehyde	$3.3 \pm 0.5$	$2.2 \pm 0.2$	$2.1 \pm 0.2$	$4 \pm 1$	$3 \pm 1$	$3 \pm 1$	$2.6 \pm 0.5$	$2 \pm 2$					
Acetaldehyde	$4 \pm 1$	$3.22\pm0.08$	$2.6 \pm 0.3$	$2.7\pm0.6$	$2.1\pm0.8$	$2.6\pm0.4$	$2.2 \pm 0.4$	3 ± 3					
Warm Start, N=	3	2	3	3	3	3	3	3					
Formaldehyde	$3 \pm 2$	$3 \pm 3$	$1.4 \pm 0.2$	$2.4 \pm 0.4$	$2 \pm 2$	$1 \pm 2$	$2 \pm 0.7$	$0.6 \pm 0.2$					
Acetaldehyde	$1.1 \pm 0.2$	$1 \pm 0.3$	$1.1 \pm 0.2$	$1.89\pm0.09$	$1.9\pm0.4$	$2.5 \pm 0.5$	$2 \pm 0.6$	$0.9 \pm 0.2$					
			TOI	5 Compounds									
			101	5 Compounds									
Cold Start, N=	4	3	4	3	4	4	4	4					
1,3-Butadiene	$5\pm 2$	$3.9 \pm 0.6$	$4.3 \pm 0.5$	$6 \pm 2$	$6 \pm 1$	$6 \pm 0.7$	$7 \pm 1$	$4 \pm 1$					
Acrolein	8 ± 3	$10 \pm 1$	9 ± 1	$17 \pm 5$	$16 \pm 4$	$14 \pm 4$	$21 \pm 5$	$6 \pm 2$					
n-Hexane	ND	ND	ND	ND	ND	ND	ND	ND					
Benzene	$10 \pm 5$	$5 \pm 1$	$5 \pm 0.5$	$6 \pm 1$	$6 \pm 1$	$6.8 \pm 0.9$	$8\pm 2$	$7\pm 2$					
Toluene	$3\pm 2$	$0.5 \pm 0.8$	ND	$1.1 \pm 1$	$1.1 \pm 0.8$	$1.6 \pm 0.6$	$2.7 \pm 0.8$	$1.6 \pm 0.6$					
Ethylbenzene	$0.2 \pm 0.5$	ND	ND	ND	ND	ND	$0.4 \pm 0.4$	$0.1 \pm 0.2$					
m-Xylene	$0.2 \pm 0.4$	ND	ND	ND	ND	ND	$0.5 \pm 0.6$	ND					
p-Xylene	ND	ND	ND	ND	ND	ND	$0.3 \pm 0.3$	ND					
Styrene	$0.2 \pm 0.4$	ND	ND	ND	ND	$0.3 \pm 0.2$	$0.8 \pm 0.4$	ND					
o-Xylene	$0.1 \pm 0.2$	ND	ND	ND	ND	ND	$0.4 \pm 0.5$	ND					
Naphthalene	$0.4 \pm 0.8$	ND	ND	ND	ND	1 ± 1	3 ± 3	ND					
HD-UDDS, N=	3	2	3	3	3	3	3	3					
1,3-Butadiene	$6 \pm 2$	$4.4 \pm 0.5$	$5 \pm 2$	ND	$0.19\pm0.05$	$0.4 \pm 0.1$	$0.39 \pm 0.1$	$5 \pm 2$					
Acrolein	$0.8 \pm 0.7$	ND	ND	$0.5\pm0.08$	$0.41\pm0.09$	$0.9 \pm 0.3$	$0.6 \pm 0.1$	$0.8 \pm 0.7$					
n-Hexane	ND	ND	ND	ND	ND	ND	ND	ND					
Benzene	$60 \pm 10$	$51 \pm 2$	$50 \pm 20$	ND	$0.29\pm0.05$	$0.76 \pm 0.1$	$0.68\pm0.04$	$50 \pm 20$					
Toluene	$8 \pm 2$	$6 \pm 0.2$	$5 \pm 2$	ND	$0.02\pm0.04$	$0.09\pm0.08$	$0.07\pm0.08$	$6 \pm 2$					
Ethylbenzene	$0.2 \pm 0.3$	ND	ND	ND	ND	ND	ND	$0.7 \pm 0.3$					
m-Xylene	ND	ND	ND	ND	ND	ND	ND	$0.3 \pm 0.3$					
p-Xylene	ND	ND	ND	ND	ND	ND	ND	$0.1 \pm 0.2$					
Styrene	$1.4 \pm 0.5$	ND	ND	ND	ND	ND	ND	$1.1 \pm 0.5$					
o-Xylene	ND	ND	ND	ND	ND	ND	ND	$0.2 \pm 0.2$					
Naphthalene	$1 \pm 2$	ND	ND	ND	ND	ND	ND	$1 \pm 0.9$					
Warm Start, N=	3	2	3	3	3	3	3	3					
1,3-Butadiene	ND	ND	ND	ND	$0.1 \pm 0.2$	$0.3\pm0.08$	$0.3 \pm 0.2$	ND					
Acrolein	ND	ND	ND	ND	$0.2\pm0.3$	$0.4 \pm 0.2$	$0.3\pm0.2$	ND					
n-Hexane	ND	ND	ND	ND	ND	ND	ND	ND					
Benzene	$0.02\pm0.04$	ND	ND	ND	$0.3\pm0.3$	$0.7\pm0.1$	$0.7\pm0.4$	$0.02\pm0.02$					
Toluene	ND	ND	ND	ND	ND	$0.06\pm0.04$	$0.06\pm0.06$	ND					
Ethylbenzene	ND	ND	ND	ND	ND	ND	ND	ND					
m-Xylene	ND	ND	ND	ND	ND	ND	ND	ND					
p-Xylene	ND	ND	ND	ND	ND	ND	ND	ND					
Styrene	ND	ND	ND	ND	ND	ND	ND	ND					
o-Xylene	ND	ND	ND	ND	ND	ND	ND	ND					
Naphthalene	ND	ND	ND	ND	ND	ND	ND	ND					

	Table S5. Average emission rates (in mg kg $^{-1}$ )	of air toxic compounds. $ND = not$ detected.
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### Table S5 cont.

Condition #	9	10	11	12	13	14	15	16				
Vehicle	2	2	2	2	3	3	3	3				
Test Weight / kg	3851	3851	3851	3851	5868	11192	5868	11192				
Temperature / C	-7	-7	22	22	22	22	22	22				
Fuel	ULSD	B20	B20	ULSD	ULSD	ULSD	B20	B20				
				0.000	0.000							
TO11A Compounds												
Cold Start, N=	3	4	3	3	7	5	3	3				
Formaldehyde	$114 \pm 8$	$130 \pm 20$	$28\pm7$	$27.8\pm0.5$	$7\pm2$	$11 \pm 5$	$9\pm 2$	$8 \pm 3$				
Acetaldehyde	$63 \pm 10$	$62 \pm 7$	$10 \pm 4$	$8.5\pm0.6$	$4\pm 2$	$4 \pm 2$	$4.16\pm0.09$	$4.7\pm0.8$				
HD-UDDS, N=	3	4	3	3	4	5	3	3				
Formaldehyde	$24 \pm 2$	$28.6 \pm 0.7$	$6 \pm 7$	$4 \pm 0.7$	$1.9 \pm 0.3$	$1.1 \pm 0.9$	$4 \pm 1$	$3\pm 2$				
Acetaldehyde	$13 \pm 1$	$13.9 \pm 0.3$	$2 \pm 3$	$3.2 \pm 0.8$	$0.5 \pm 0.4$	$0.2 \pm 0.2$	$0.9 \pm 0.2$	$0.3 \pm 0.2$				
Warm Start, N=	3	4	3	3	3	5	3	3				
Formaldehyde	$26 \pm 3$	$28 \pm 6$	$4 \pm 5$	$1 \pm 1$	$6 \pm 3$	$5 \pm 2$	$5\pm3$	$6 \pm 4$				
Acetaldehyde	$4.7 \pm 0.2$	$4 \pm 1$	$1.1 \pm 0.5$	$1 \pm 0.5$	$1 \pm 2$	$2 \pm 3$	$1.9\pm0.5$	$0.5\pm0.5$				
TO15 Compounds												
Cold Start, N=	3	4	4	3	4	4	3	3				
1,3-Butadiene	$0.2 \pm 0.2$	$0.3 \pm 0.2$	$0.7 \pm 0.3$	$0.5 \pm 0.4$	ND	ND	ND	ND				
Acrolein	$0.08 \pm 0.08$	$0.4 \pm 0.6$	ND	ND	$0.13 \pm 0.09$	$0.34 \pm 0.08$	$0.18 \pm 0.03$	$0.3 \pm 0.2$				
n-Hexane	ND	ND	ND	ND	ND	$0.03 \pm 0.04$	$0.01 \pm 0.01$	$0.1 \pm 0.1$				
Benzene	$7 \pm 1$	$7.7 \pm 0.6$	$3\pm 2$	$4.2 \pm 0.2$	$1.4 \pm 0.2$	$1.2 \pm 0.1$	$1.6 \pm 0.2$	$1.4 \pm 0.1$				
Toluene	$1.2 \pm 0.3$	$1.3 \pm 0.2$	$0.3 \pm 0.3$	$0.6 \pm 0.1$	$0.09 \pm 0.09$	$0.07 \pm 0.03$	$0.06 \pm 0.01$	$0.08 \pm 0.02$				
Ethylbenzene	$0.02 \pm 0.03$	ND	ND	ND	ND	$0.001 \pm 0.002$	ND	ND				
m-Xylene	$0.04 \pm 0.07$	ND	ND	ND	ND	$0.003 \pm 0.005$	ND	ND				
p-Xylene	ND	ND	ND	ND	ND	$0.001 \pm 0.003$	ND	ND				
Styrene	ND	$0.06 \pm 0.07$	ND	ND	ND	$0.002 \pm 0.003$	ND	ND				
o-Xylene	$0.03 \pm 0.05$	ND	ND	ND	ND	$0.003 \pm 0.006$	ND	ND				
Naphthalene	$0.8\pm0.7$	$0.6 \pm 0.5$	ND	ND	ND	$0.005\pm0.009$	ND	ND				
HD-UDDS, N=	3	4	3	3	2	4	3	2				
1 3-Butadiene	ND	ND	ND	ND	ND	ND	ND	ND				
Acrolein	$12 \pm 0.5$	$2.2 \pm 1$	$0.4 \pm 0.6$	ND	$0.04 \pm 0.06$	$0.03 \pm 0.02$	$0.088 \pm 0.008$	$0.06 \pm 0.04$				
n-Hexane	ND	2.2 = 1 ND	ND	ND	$0.006 \pm 0.008$	$0.002 \pm 0.002$	$0.000 \pm 0.000$	$0.000 \pm 0.001$				
Benzene	$13 \pm 03$	$1 \pm 0.2$	$0.4 \pm 0.3$	$0.34 \pm 0.07$	$0.3 \pm 0.04$	$0.11 \pm 0.08$	$0.6 \pm 0.3$	$0.17 \pm 0.02$				
Toluene	$0.11 \pm 0.1$	ND	0.1 ± 0.5	0.5 T = 0.07	$0.0 \pm 0.01$	$0.001 \pm 0.003$	$0.0 \pm 0.02$ $0.04 \pm 0.02$	$0.0061 \pm 0.0005$				
Ethylbenzene	ND	ND	ND	ND	ND	$0.0004 \pm 0.0007$	ND	ND				
m-Xvlene	ND	ND	ND	ND	ND	$0.0003 \pm 0.0006$	ND	ND				
p-Xvlene	ND	ND	ND	ND	ND	$0.0004 \pm 0.0009$	ND	ND				
Styrene	ND	ND	ND	ND	ND	$0.0002 \pm 0.0004$	ND	ND				
o-Xvlene	ND	ND	ND	ND	ND	$0.001 \pm 0.002$	ND	ND				
Naphthalene	ND	ND	ND	ND	ND	$0.001 \pm 0.002$	ND	ND				
Warm Start N-	2	4	2	2	1	4	2	2				
1 2 Dute diana	3 ND	4	3	3	I ND	4 ND	3	<u> </u>				
1,3-Butadiene	ND	ND	ND	ND	ND	ND	ND	ND				
n Havana												
Donzono	1ND			$0.02 \pm 0.02$		$0.01 \pm 0.02$	$0.01 \pm 0.01$	$0.04 \pm 0.07$				
Toluene	$5.15 \pm 0.09$ 0.37 ± 0.02	$3.3 \pm 0.4$ 0.31 ± 0.07	0.3 ± 0.4	0.227 ± 0.007	0.1	0.00 ± 0.02	$0.13 \pm 0.02$ $0.01 \pm 0.02$	0.00 ± 0.00				
Ethylbonzona	$0.57 \pm 0.05$	0.51 ± 0.07			0.000		0.01 ± 0.02					
m Vulono												
n Yylene												
p-Ayiciic Styropo												
o-Yulene												
Vanhthalanc						ND		ND				
raphinarene	IND	мD	ND	ND	ND	лD	IND	nD				

Table S6. Statistical analysis results (p-values) comparing VOC emissions (using mg/km) by driving cycle (cycle), vehicle test weight (VTW), and dynamometer temperature and fuel type (fuel) for V1, V2 and V3. Values in red are p-values  $\leq 0.05$ .

		Vehi	cle 1			Vehicle 2		Vehicle 3		
Compound	Cycle	VTW	Temp	Fuel	Cycle	Temp	Fuel	Cycle	VTW	Fuel
NMHC	<.0001	0.7117	0.3458	0.2245	<.0001	<.0001	0.7177	<.0001	0.9387	0.6286
1,1-Dichloroethene								0.3034	0.2617	0.4748
1,2,4-Trichlorobenzene								0.5786	0.3029	0.3531
1,2,4-Trimethylbenzene	0.0431	0.2053	0.2053	0.055	0.0021	0.0151	0.8826	0.6023	0.2911	0.3323
1,2-Dibromoethane								0.6382	0.2753	0.2991
1,2-Dichlorobenzene								0.6383	0.2752	0.299
1,2-Dichloropropane								0.604	0.3074	0.3022
1,3,5-Trimethylbenzene	0.4534	0.2894	0.2894	0.3308				0.6055	0.2896	0.3295
1,3-Butadiene	<.0001	0.8031	0.129	0.3625	<.0001	0.3331	0.4805			
1,3-Dichlorobenzene								0.6403	0.2744	0.2968
1-Ethyl-4-Methyl Benzene								0.6322	0.2778	0.3052
2,5-DMB					0.3735	0.3981	0.3963			
2-Butanone	<.0001	0.4806	0.0228	0.0297				0.5378	0.3595	0.3817
2-Chloroprene	0.4534	0.2894	0.2894	0.3308						
2-Hexanone	0.3759	0.3064	0.3064	0.3064				0.6015	0.3882	0.2742
3-Chloro-1-Propene								0.6388	0.275	0.2985
4-Methy-2-Pentanone								0.6033	0.2906	0.3314
Acetaldehyde	<.0001	0.6702	<.0001	0.9257	<.0001	0.0007	0.6804	<.0001	0.4531	0.4434
Acetone	<.0001	0.5912	0.0012	0.3377	<.0001	0.0004	0.6983	<.0001	0.0533	0.0231
Acrolein	<.0001	0.9197	0.0002	0.417	0.0001	0.0109	0.1141	<.0001	0.0386	0.2903
Benzaldehyde					0.3735	0.3981	0.3963			
Benzene	<.0001	0.7503	<.0001	0.5477	<.0001	<.0001	0.8623	<.0001	0.0016	0.0422
Butyraldehyde	0.0037	0.6234	0.0133	0.0061	0.3492	0.2839	0.3471	0.4966	0.4544	0.22
Carbon Disulfide	0.0988	0.3139	0.6199	0.0977	<.0001	0.0103	0.6832	0.2953	0.4823	0.4313
Carbon Tetrachloride								0.4645	0.1261	0.2731
Chlorobenzene					0.1186	0.1617	0.1111			
Chloromethane	0.2425	0.5207	0.081	0.4908	0.1293	0.1452	0.7657	0.688	0.4159	0.5532
Chlorotoluenes								0.624	0.2813	0.313
Crotonaldehyde	0.0009	0.2969	0.046	0.0044	0.1457	0.1724	0.7055			
Cumene	0.4534	0.2894	0.2894	0.3308						
Cyclohexane	0.0422	0.4145	0.423	0.0127				0.591	0.23	0.3374
Ethanol	0.0001	0.7077	0.0005	0.352	0.5461	0.1289	0.1	0.6564	0.1147	0.0875
Ethyl Tert-Butyl Ether					0.6837	0.1568	0.125			
Ethylbenzene	0.1587	0.2591	0.2004	0.0102						
Formaldehyde	<.0001	0.2506	<.0001	0.1863	<.0001	0.0003	0.3985	<.0001	0.3343	0.3918

# Table S6 cont.

		Vehi	cle 1			Vehicle 2			Vehicle 3	
Compound	Cycle	VTW	Temp	Fuel	Cycle	Temp	Fuel	Cycle	VTW	Fuel
Freon-11								0.6524	0.1625	0.1648
Freon-113					0.6718	0.1605	0.1281			
Freon-12					0.3849	0.3486	0.2824	0.4091	0.8684	0.019
Isopropyl Alcohol	0.4758	0.3113	0.2698	0.3087				0.0185	0.133	0.4816
Methyl Methacrylate								0.6469	0.2717	0.2879
Methylene Chloride	0.1033	0.8127	0.1632	0.1642				0.1612	0.0747	0.0612
m-Xylene	0.2248	0.2129	0.8379	0.043				0.4791	0.3691	0.4565
Naphthalene	0.1333	0.6158	0.4405	0.0123	0.0106	0.0359	0.7169	0.5791	0.3026	0.3527
n-Butyl Benzene	0.1149	0.0808	0.0821	0.1079	0.0108	0.036	0.591	0.6218	0.2823	0.3151
n-Hexane					0.1306	0.161	0.1595	0.237	0.1008	0.1675
n-Propylbenzene	0.4534	0.2894	0.2894	0.3308				0.6457	0.2722	0.2899
o-Cymene								0.6489	0.2709	0.2839
o-Xylene	0.231	0.1863	0.6941	0.0506				0.5553	0.3157	0.3745
Propionaldehyde	0.0001	0.7727	0.0277	0.008	0.3735	0.3981	0.3963			
Propylene	<.0001	0.8951	0.0729	0.0013	<.0001	<.0001	0.6592	<.0001	0.0937	0.0723
p-Xylene	0.3405	0.0812	0.2839	0.1007						
Sec-Butyl Benzene								0.6359	0.2762	0.3015
Styrene	0.0135	0.9566	0.2183	0.0009	0.1414	0.1755	0.2453	0.5256	0.3341	0.4037
Tert Amyl Methyl Ether	0.4006	0.0542	0.3208	0.9794	0.1721	0.9801	0.2342			
Tert-Butyl Benzene	0.4534	0.2894	0.2894	0.3308				0.63	0.2787	0.3074
Tetrahydrofuran								0.5913	0.2378	0.4536
Toluene	<.0001	0.445	0.0004	0.0475	<.0001	0.0003	0.3712	0.0002	0.1103	0.7794
trans-1,3-Dichloropropene	0.4534	0.2894	0.2894	0.3308						
Valeraldehyde					0.0448	0.0833	0.9344			
Vinyl Acetate	0.0011	0.2137	0.0073	0.0701	0.007	0.076	0.8587	0.8632	0.85	0.2657
Vinyl Chloride					<.0001	0.005	0.2628			
Sum of p<0.05	17	0	12	11	15	12	0	8	2	3



Figure S1. Test driving cycle trace. The 20 min engine off periods between the test cycles are not shown.



Figure S2. Diagram of VOC emissions sampling setup.



Figure S3. Average sum of speciated VOC emission rates (mg/km) for each test condition: A) Vehicle 1 at 22 °C, B) Vehicle 1 at -7 °C, C) Vehicle 2 at -7 and 22 °C, D) Vehicle 3 at 22 °C. Symbols in red indicate rates at 22 °C, and blue symbols represent rates at -7 °C. Error bars represent one standard deviation of propagated errors from mean emission rates of all individual VOCs. Regeneration data were excluded. UNL = unladen VTW and LAD = laden VTW.



Figure S4. Emission profiles from SPECIATE (x symbols) and this work for 22 °C tests (offset circles) from diesel engines using diesel (black) and B20 (red) fuels for individual air toxics.