Supporting information for "Comprehensive organic emission profiles for gasoline, diesel, and gas-turbine engines including intermediate and semi-volatile organic compound emissions"

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1. Comparison of three individual compounds measured using GC/MS analysis of Tedlar bag versus Tenax adsorbent samples

Figure S2(a) shows that, the most volatile of these species, *n*-pentyl-benzene, the Tedlar bags measurement averaged 5.2 times the adsorbent tubes. We attribute this difference to incomplete collection of this relatively volatile species by the adsorbent tubes or incomplete recovery of thermal desorption method. Figure S2(b) show essentially the same amount of *n*-dodecane was measured using both approaches, a linear regression yields a slope of 0.85 and R^2 of 0.9. As for naphthalene (the least volatile of these species), Figure S2(c) show the adsorbent tubes measured about 5 times more than the Tedlar bag, which we attribute to wall losses in the bag. [54]

2. Supplementing gas-turbine and diesel VOC speciation with traditional emission profiles

Given the different levels of VOC characterization, we supplemented our gas-turbine and diesel VOC data with existing speciation profiles (SPECIATE profiles 4674 and 5565).

For gas turbine exhaust, 86 individual VOCs were identified, which can be classified as 21 SAPRC groups. Meanwhile, SPECIATE profile 5565 includes 81 individual species, which can be lumped into 27 groups (not including IVOCs in the profile). Of the two grouping results, 17 groups are identified in both profiles, and 10 groups are unique only in profile 5565.

We then complement our VOC results with 10 unique groups as additional 31.9% of VOC mass (all carbonyls, 31.9% of total VOC mass in profile 5565).

For diesel exhaust, 57 individual VOCs and 11 Kovats lumped groups were identified, which can be classified as 25 SAPRC groups. SPECIATE profile 4674 includes 144 individual species, which can be lumped into 34 groups (not including IVOCs in the profile). Of the two grouping results, 22 groups are identified in both profiles, and 12 groups are unique only in profile 4674.

We then complement our VOC results with 12 unique groups as additional 10.8% of VOC mass (10.8% of total VOC mass in profile 4674).

3. Preparing NMOG and POA emission profiles from VBS version

The VBS version in Table S3(a) is designed to be applied to total organic emissions (NMOG + 1.2×OC). The VOC composition profiles in Table S3(b-f) is designed to be applied to VOC emissions. In most emission inventories, where NMOG and POA are provided separately, we recommend partition the VBS profiles into gas- and particle-phase sub-profiles for NMOG and POA emissions respectively, and then apply the VOC profiles in Table S3(b-f) to speciate VOC emissions.

Supporting Tables

Table S1 Summary of all tested engines, fuels and test cycles with complete characterization data

Source type	Category	Class / Model	Number of engines	Number of tests	Model year	Fuel	Test cycle / Thrust
Gasoline	LDGVs (on-road)	Pre-LEV	10	10	1987-1999	Commercial summertime California gasoline	Cold-start unified cycle (UC) / Hot-start
		LEV	9	10	1991-2009		
		ULEV	10	12	2003-2012		
	SOREs (off-road)	SORE-2S	2	3	2002, 2005		CARB SORE certification cycle
		SORE-4S	2	3	2004, 2005		
Gas-turbine	KC-135 Stratotanker	CFM56-2B1	1	2	/	Commercial JP-8	4% and 85%
Diesel	HDDVs (on-road)	DPF-equipped	2	8	2007, 2010	Three different ULSD fuels with varying aromatic content (9-28%)	Urban Dynamometer Driving Schedule (UDDS) / Creep and idle / High-speed cruise
		Non-DPF	1	10	2006		
	MDDV (on-road)	Non-DPF	1	1	2005	Commercial California ultra-low sulfur diesel (ULSD)	Cold-start UC
	TRU (off-road)	Non-DPF	1	2	1998		CARB procedures for engine certification

Table S2 Effect of temperature on gas/particle partitioning at equilibrium

Log (C*, T = 298K)	C* (ug/m^3)			Particle-phase fraction (X_p)			ΔH_{vap} (kJ / mol)
	T = 298K	T = 273K	T = 320K	T = 298K	T = 273K	T=320K	
Nonvolatile	n/a	n/a	n/a	1.00	1.00	1.00	n/a
-1	1.00E-01	3.14E-03	1.34E+00	0.99	1.00	0.88	96
0	1.00E+00	4.72E-02	9.85E+00	0.91	1.00	0.50	85
1	1.00E+01	7.08E-01	7.26E+01	0.50	0.93	0.12	74
2	1.00E+02	1.06E+01	5.35E+02	0.09	0.48	0.02	63
3	1.00E+03	1.60E+02	3.94E+03	0.01	0.06	0.00	52
4	1.00E+04	2.40E+03	2.91E+04	0.00	0.00	0.00	41
5	1.00E+05	3.60E+04	2.14E+05	0.00	0.00	0.00	30
6	1.00E+06	5.41E+05	1.58E+06	0.00	0.00	0.00	19

Table S4 Speciated IVOCs and their OH reaction rate constants (cm3 molec-1 s-1) and SOA yields at the OA concentration of 9 μg/m3 from Zhao et al. (2016)

Compound code	Compound name	OH reaction rate	SOA yield
1	Dodecane	1.32E-11	0.08
2	Tridecane	1.51E-11	0.21
3	Tetradecane	1.68E-11	0.28
4	Pentadecane	1.82E-11	0.34
5	Hexadecaen	1.96E-11	0.38
6	Heptadecane	2.10E-11	0.42
7	Octadecane	2.24E-11	0.42
8	Nonadecane	2.38E-11	0.42
9	Eicosane	2.52E-11	0.42
10	Heneicosane	2.67E-11	0.42
11	Docosane	2.81E-11	0.42
12	2,6,10-Trimethylundecane	1.70E-11	0.04
13	2,6,10-Trimethyldodecane	1.87E-11	0.08
14	2,6,10-Trimethyltridecane	2.01E-11	0.21
15	2,6,10-Trimethylpentadecane	2.30E-11	0.34
16	Pristane	2.44E-11	0.34
17	Phytane	2.61E-11	0.38
18	Hexylclohexane	1.76E-11	0.08
19	Heptylcyclohexane	1.91E-11	0.21
20	Octylcyclohexane	2.05E-11	0.28
21	Nonylcyclohexane	2.19E-11	0.34
22	Decylcyclohexane	2.33E-11	0.38
23	Undecylcyclohexane	2.47E-11	0.42
24	Dodecylcyclohexane	2.61E-11	0.42
25	Tridecylcyclohexane	2.75E-11	0.42
26	Tetradecylcyclohexane	2.89E-11	0.42
27	Pentadecylcyclohexane	3.04E-11	0.42
28	Hexadecylcyclohexane	3.18E-11	0.42
29	Heptadecylcyclohexane	3.32E-11	0.42
30	Naphthalene	2.30E-11	0.21
31	2-methylnaphthalene	4.86E-11	0.30
32	1-methylnaphthalene	4.09E-11	0.25
33	C2-naphthalene	6.00E-11	0.31
34	C3-naphthalene	8.00E-11	0.31

Compound code	Compound name	OH reaction rate	SOA yield
35	C4-naphthalene	8.00E-11	0.31
36	Acenaphthylene	1.24E-10	0.31
37	Acenaphthene	8.00E-11	0.31
38	Fluorene	1.60E-11	0.31
39	C1-Fluorene	8.00E-11	0.31
40	Phenanthrene	3.20E-11	0.31
41	Anthracene	1.78E-10	0.31
42	C1-Phenanthrene/anthracene	5.89E-11	0.31
43	C2-Phenanthrene/anthracene	8.00E-11	0.31
44	Fluoranthene	3.30E-11	0.31
45	Pyrene	5.60E-11	0.31
46	C1-Fluoranthene/pyrene	1.31E-10	0.31
47	Pentylbenzene	1.01E-11	0.04
48	Hexylbenzene	1.15E-11	0.08
49	Heptylbenzene	1.30E-11	0.21
50	Octylbenzene	1.44E-11	0.28
51	Nonylbenzene	1.58E-11	0.34
52	Decylbenzene	1.72E-11	0.38
53	Undecylbenzene	1.86E-11	0.42
54	Dodecylbenzene	2.00E-11	0.42
55	Tridecylbenzene	2.14E-11	0.42
56	Tetradecylbenzene	2.29E-11	0.42
57	Pentadecylbenzene	2.43E-11	0.42

Table S5a Surrogate compounds (*n*-alkanes) for OH reaction rate constants (cm^3 $molec^{-1}$ s^{-1}) and SOA yields of unspeciated IVOC bins under the IVOC-cyclic case from Zhao et al. (2016)

Bin#	OH rate constant	Surrogate compounds for SOA yields	
		Unspeciated *b*-alkanes	Unspeciated cyclic compounds (IVOC-cyclic)
B12	C12	C10	C12
B13	C13	C11	C13
B14	C14	C12	C14
B15	C15	C13	C15
B16	C16	C14	C16
B17	C17	C15	C17
B18	C18	C16	C18
B19	C19	C17	C19
B20	C20	C18	C20
B21	C21	C19	C21
B22	C22	C20	C22

Table S5b Surrogate compounds (*n*-alkanes and naphthalenes) for OH reaction rate constants (cm^3 $molec^{-1}$ s^{-1}) and SOA yields of unspeciated cyclic compounds in each IVOC bin under the IVOC-aromatics case from Zhao et al. (2016)

Bin#	OH rate constant	Unspeciated cyclic compounds (IVOC-aromatic)
B12	Naphthalene	Naphthalene
B13	C1-naphthalene	2-Methylnaphthalene
B14	C2-naphthalene	1,2-Dimethylnaphthalene
B15	C3-naphthalene	C15
B16	C4-naphthalene	C16
B17	C17	C17
B18	C18	C18
B19	C19	C19

B20	C20	C20
B21	C21	C21
B22	C22	C22

Table S6 Comparison of different estimates of IVOC fraction and overall SOA yield of NMOG emissions

	IVOC mass fraction			SOA yield		
	Gasoline	**Gas-turbine**	**Diesel**	**Gasoline**	**Gas-turbine**	**Diesel**
This work	4.6%	27.9%	54.3%	0.041	0.086	0.190
Traditional	/	/	/	0.022	0.008	0.009
ROB	1.2%	6.1%	8.0%	0.023	0.018	0.021
MUR	7.5%	39.5%	51.7%	N/A	N/A	N/A
PYE	19.9%	22.3%	6.9%	0.065	0.057	0.024
GEN	1%	N/A	62%	0.023	N/A	0.154
JAT	25%	N/A	20%	0.071	N/A	0.077

Supporting Figures

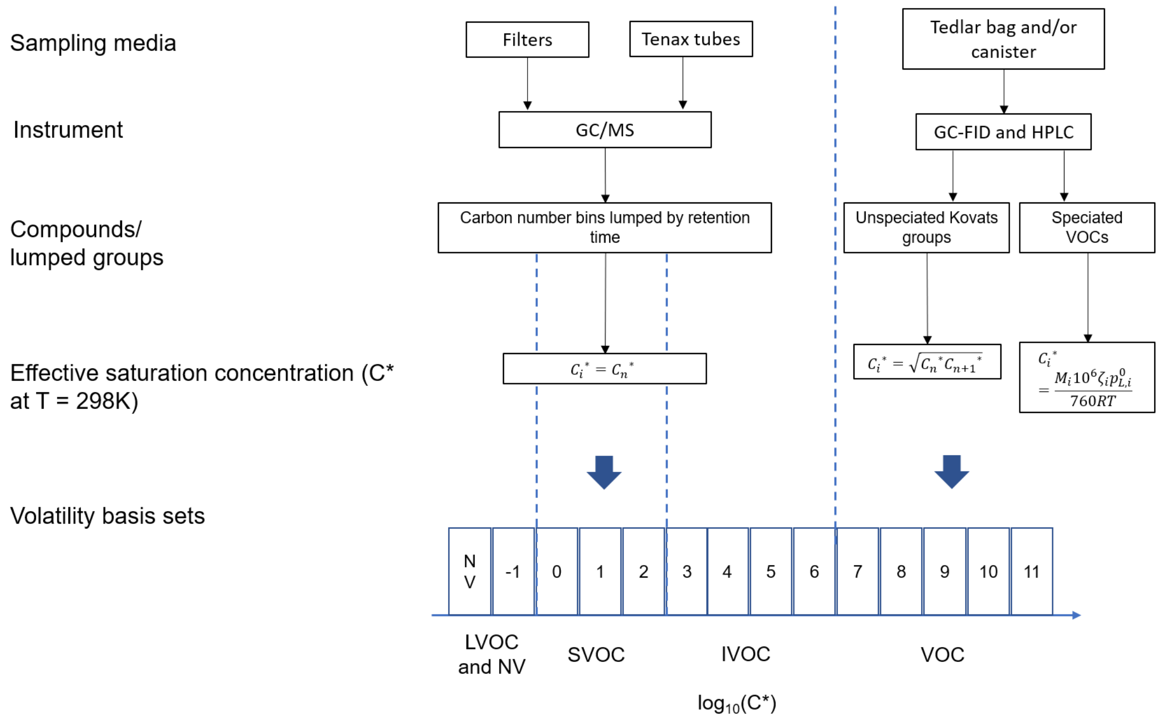
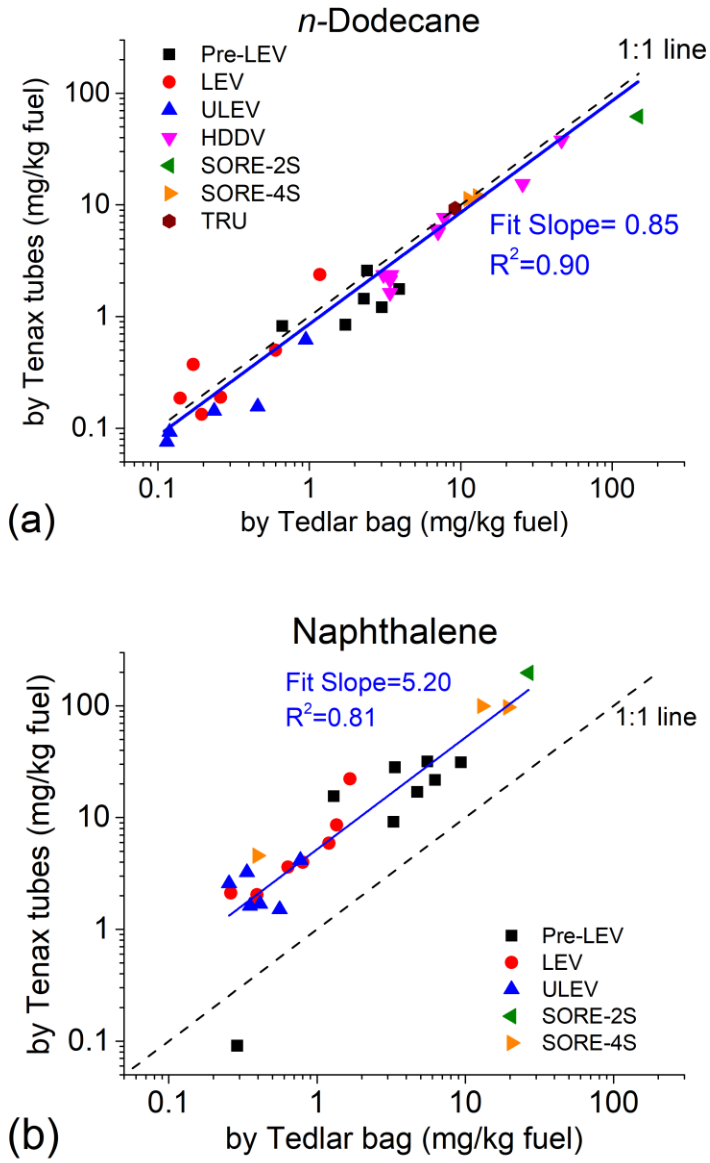
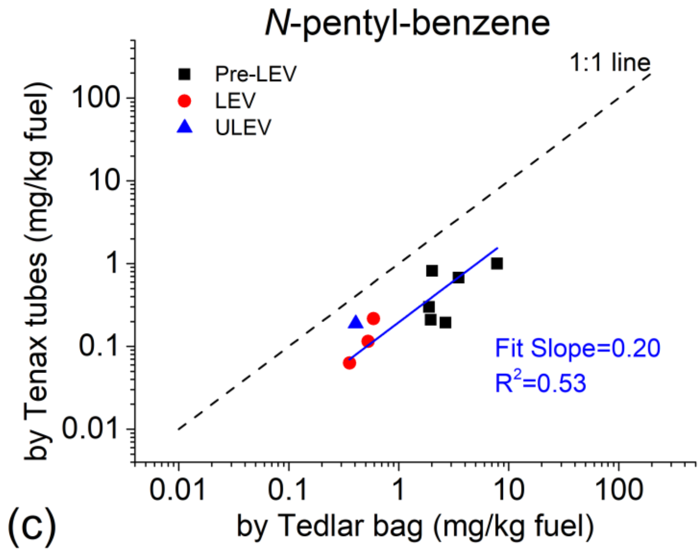


Figure S1 Schematic diagram of mapping speciated and unspeciated compounds data to volatility basis set (VBS), C_n* denotes the C* value for n-alkanes as surrogate.



n-Dodecane
Pre-LEV
LEV
ULEV
HDDV
SORE-2S
SORE-4S
TRU
1:1 line
Fit Slope= 0.85
R2=0.90
by Tenax tubes (mg/kg fuel)
by Tedlar bag (mg/kg fuel)
(a)
Naphthalene
Fit Slope=5.20
R2=0.81
1:1 line
Pre-LEV
LEV
ULEV
SORE-2S
SORE-4S
by Tenax tubes (mg/kg fuel)
by Tedlar bag (mg/kg fuel)
(b)



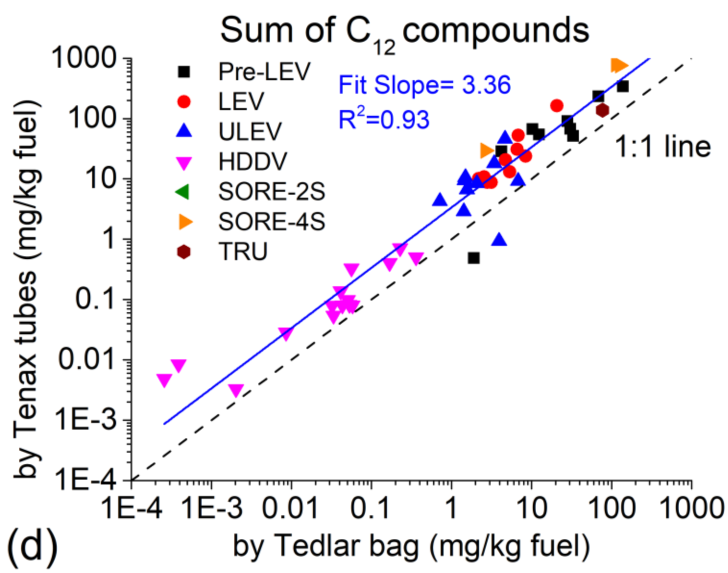


Figure S2 Comparison of (a) *n*-dodecane (b) naphthalene (c) n-pentyl-benzene (d) sum of all C_{12} compounds results measured using GC/MS analysis of Tedlar bag versus Tenax adsorbent samples (everything elutes in the C_{12} carbon number bin), demonstrating the consistency of two technique in *n*-dodecane measurement

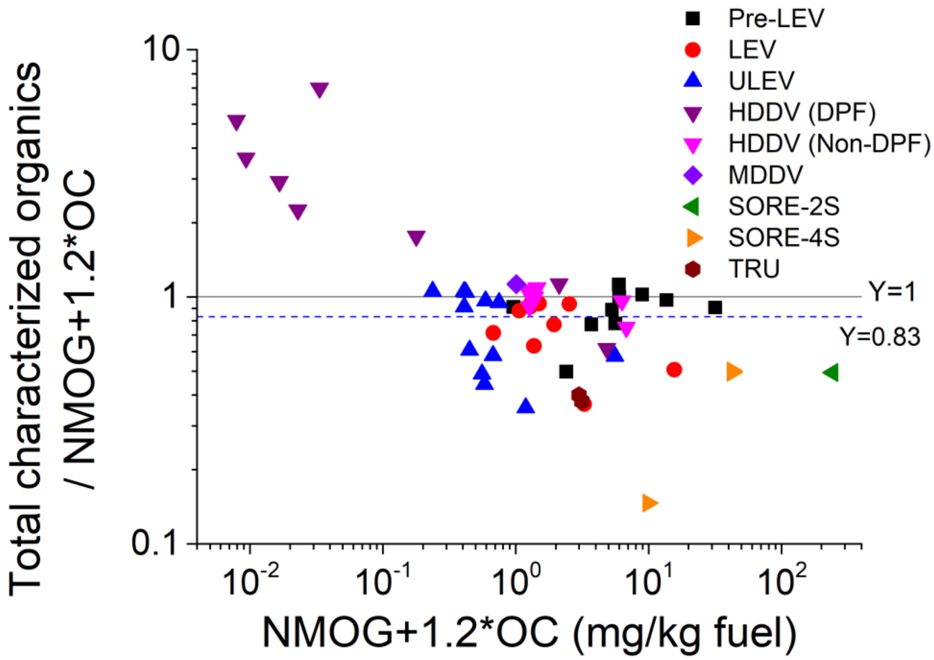
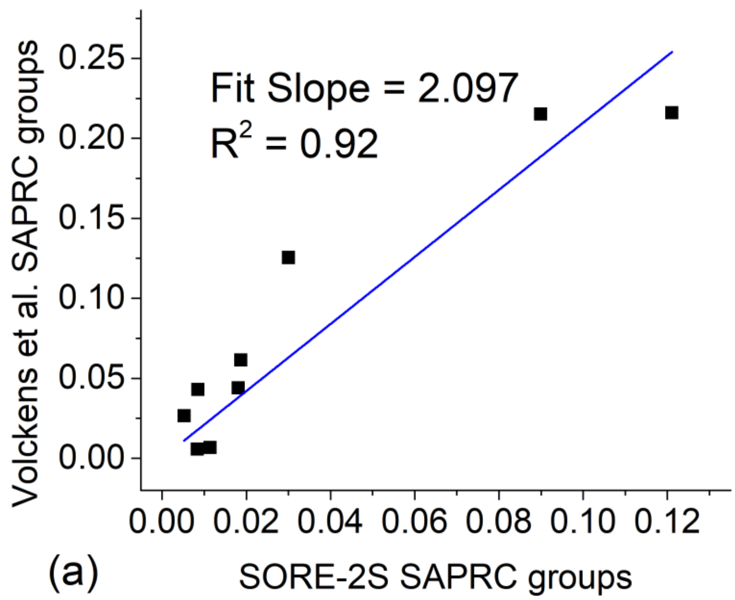


Figure S3 Ratio of total characterized organics integrated from all techniques to total organics by bulk measurement (NMOG+1.2*OC), indicating mass closure for on-road non-DPF diesel source and partial mass closure (0.83) for on-road gasoline sources



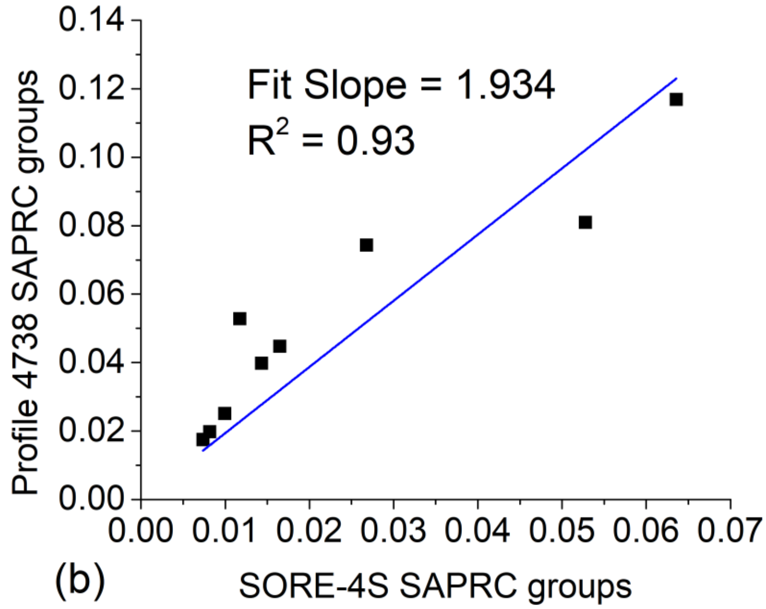


Figure S4 Scatter plot of SOA-forming SAPRC groups (ALK4, ALK5, ARO1, ARO2, BENZ, TOLU, PXYL, MXYL, OXYL, B124) mass fraction in NMOG emission versus literature value for (a) SORE-2S (b) SORE-4S, indicating the need to factorize VOC mass in off-road measurement results by 2

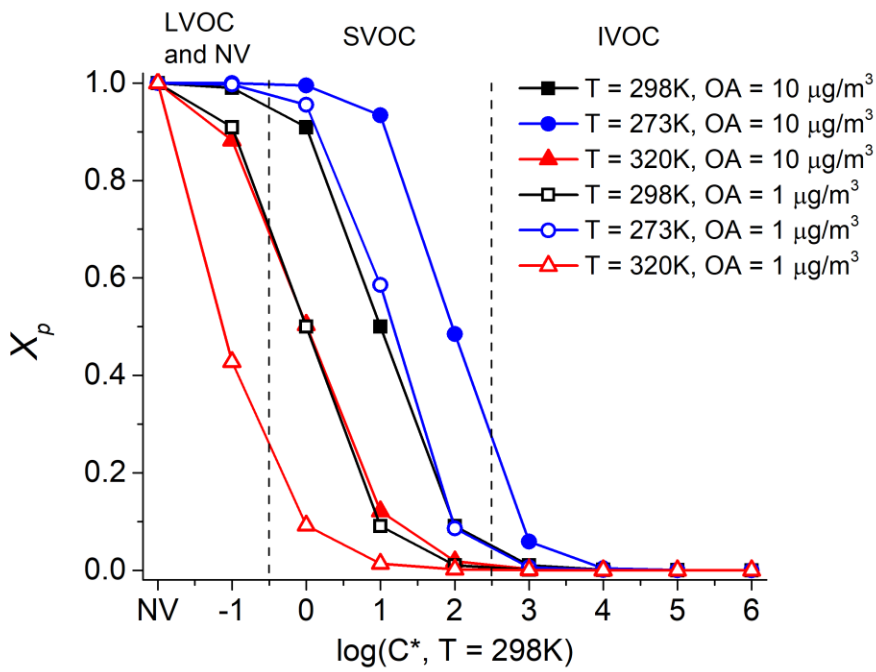
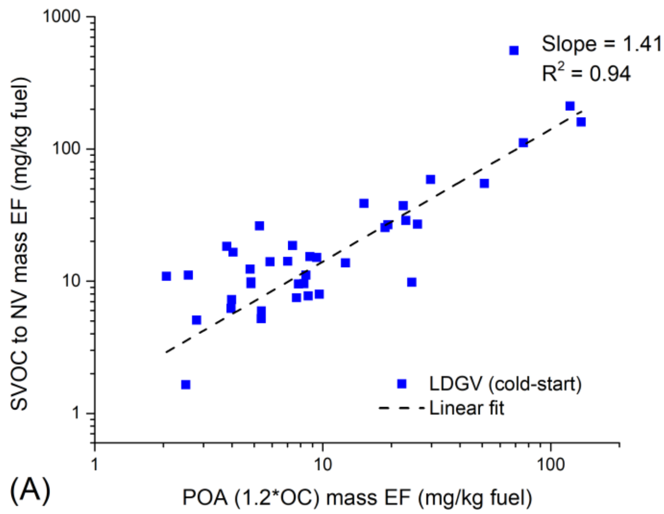
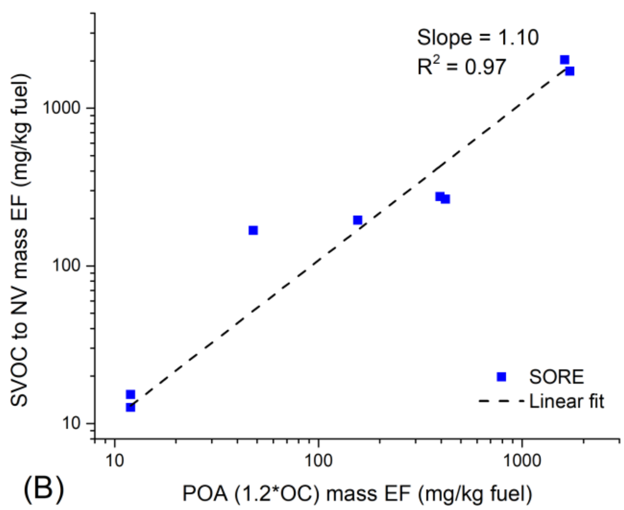


Figure S5 Effect of temperature and OA loading on gas/particle partitioning at equilibrium



Slope = 1.41
R^2 = 0.94
LDGV (cold-start)
Linear fit
SVOC to NV mass EF (mg/kg fuel)
POA (1.2*OC) mass EF (mg/kg fuel)
1000
100
10
1
1
10
100

(A)



Slope = 1.10
R^2 = 0.97
SORE
Linear fit
SVOC to NV mass EF (mg/kg fuel)
POA (1.2*OC) mass EF (mg/kg fuel)
1000
100
10
10
100
1000

(B)

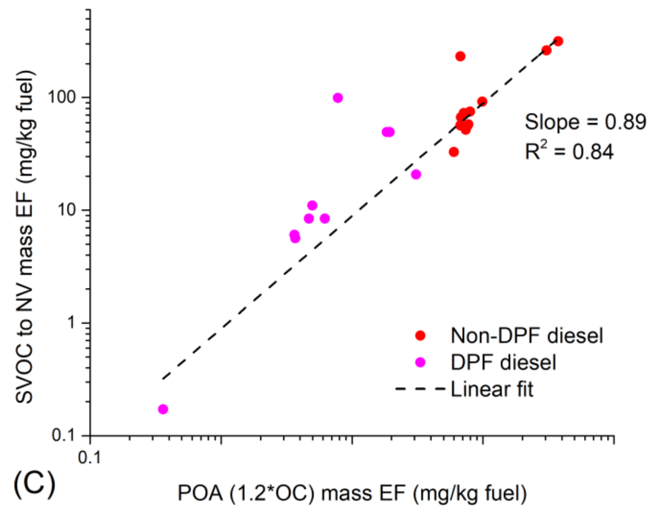


Figure S6 Scatter plot of sum of SVOC to NV mass versus filter-based POA measurements (A: On-road gasoline, cold-start B: off-road gasoline, C: non-DPF and DPF diesel)

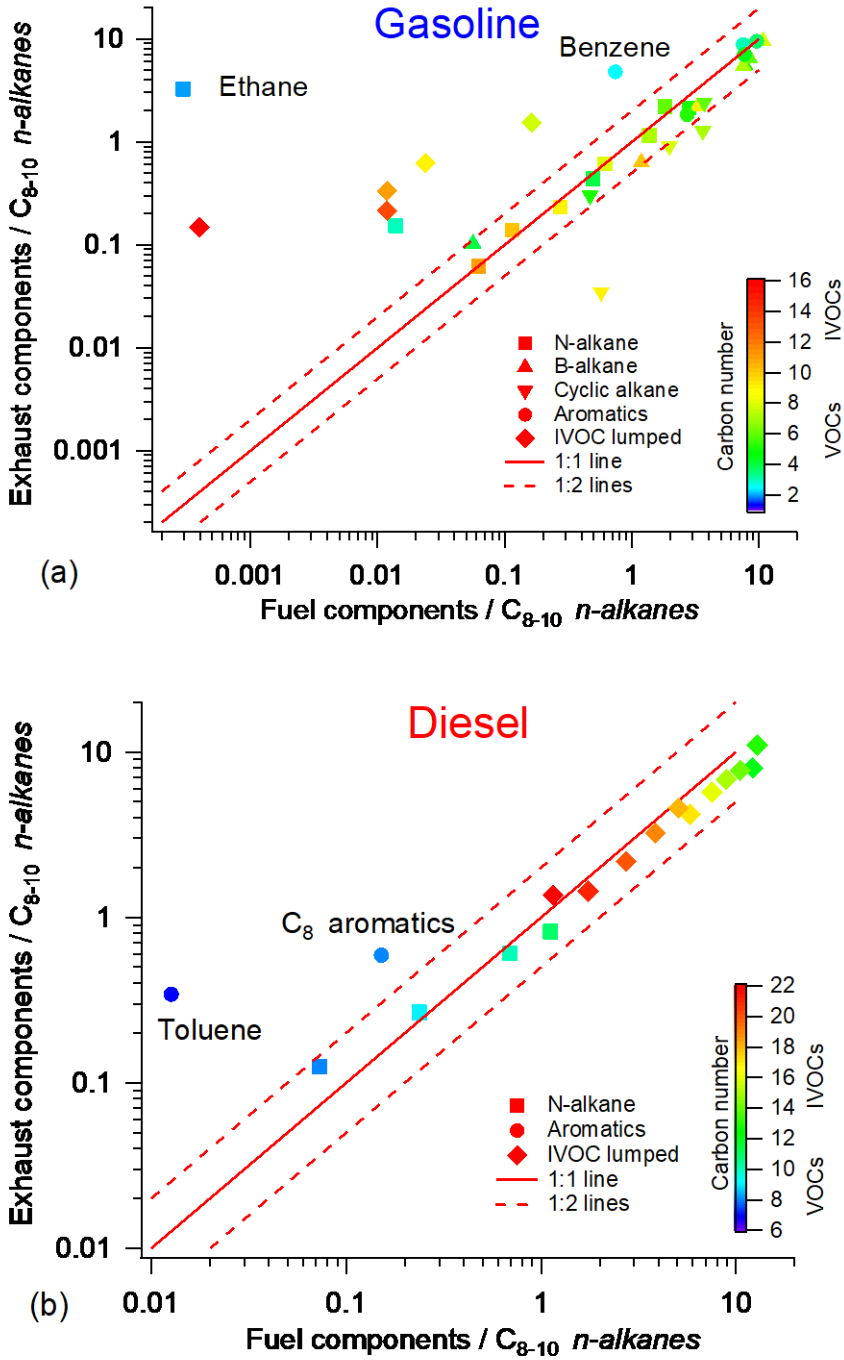


Figure S7 Scatter plot of exhaust components versus fuel (VOCs and IVOCs) normalized by $C_{8\text{-}10}$ *n*-alkanes for (a) Gasoline (b) Diesel sources, demonstrating the overall consistency of chemical composition between exhaust and fuel

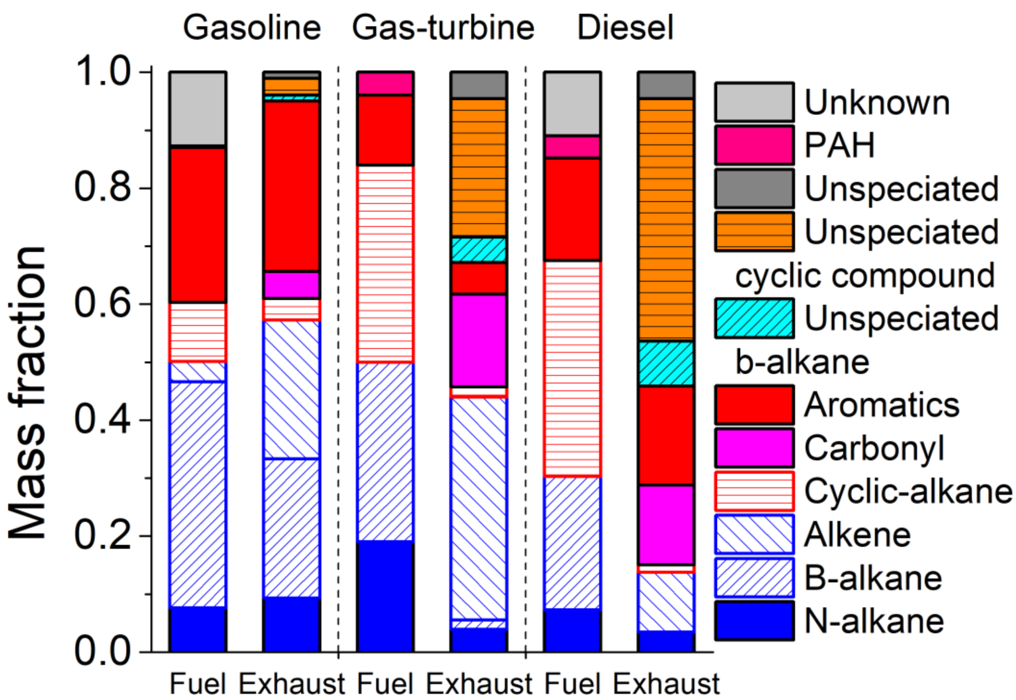


Figure S8 Comparison of median chemical composition between fuel and exhaust for gasoline, gas-turbine and diesel sources, indicating the compositional changes after combustion

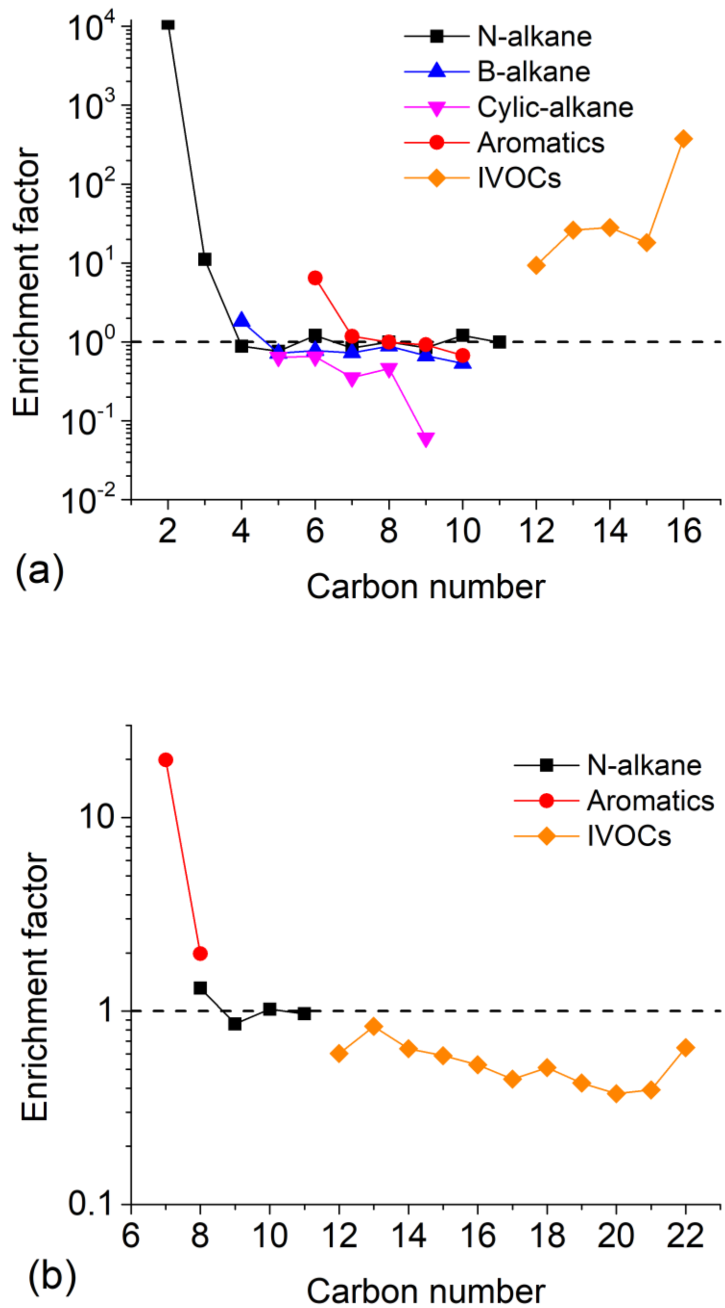


Figure S9 Enrichment factors of exhaust and fuel components (VOCs and IVOCs) normalized by $C_{8\text{-}10}$ *n*-alkanes (a) Gasoline (cold-start) (b) non-DPF diesel, demonstrating the enrichment for certain compounds (VOCs and/or IVOCs) in difference sources

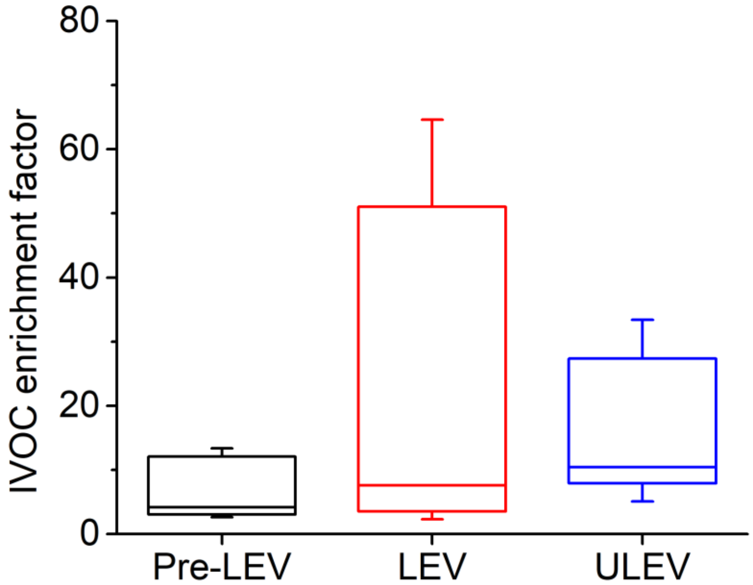


Figure S10 IVOC enrichment factors of Pre-LEV, LEV and ULEV vehicles exhaust

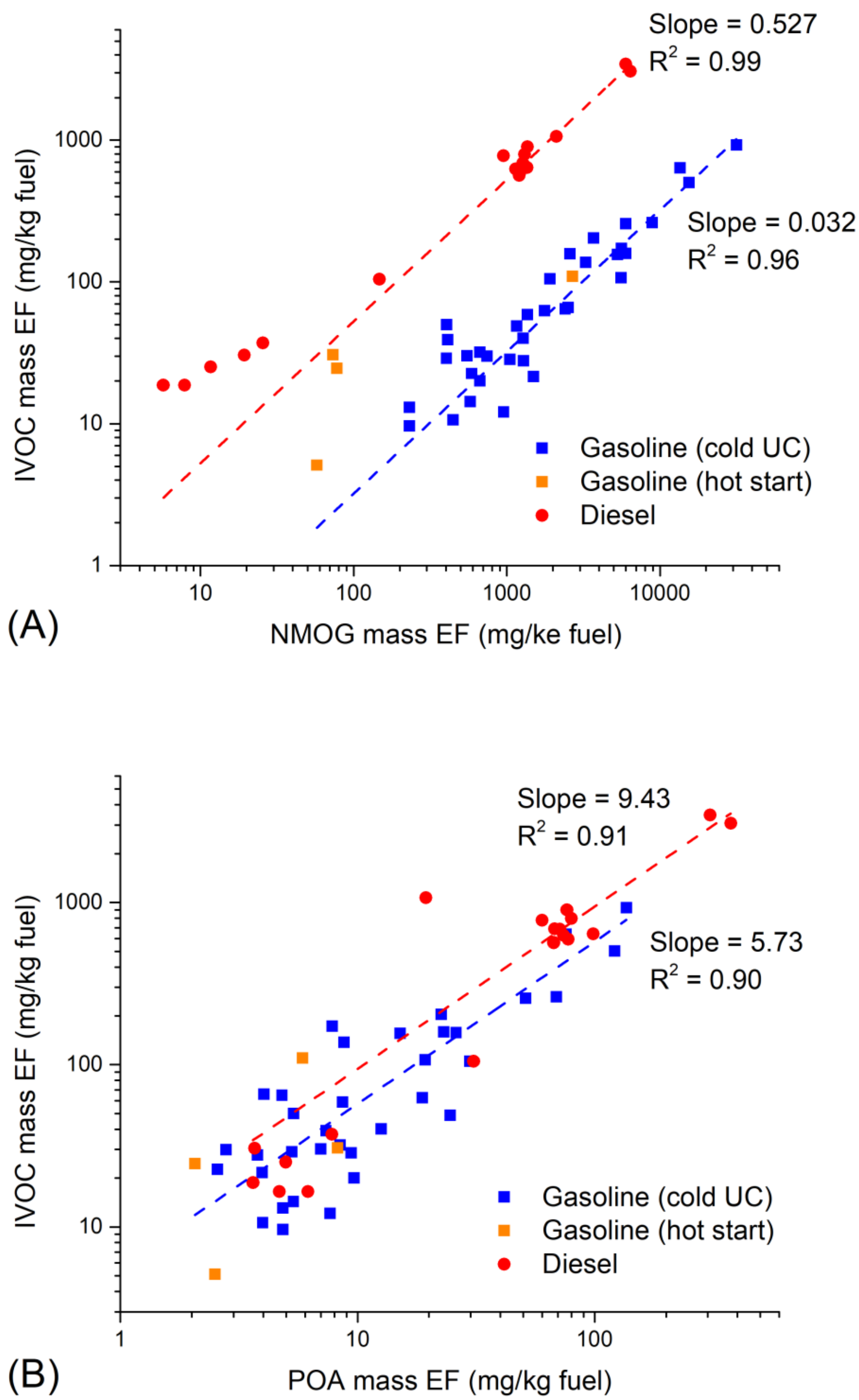


Figure S11 Comparison of the ratios and coefficients of determination, R^2 between (a) IVOC and NMOG and (b) IVOC and POA for tested gasoline and diesel sources

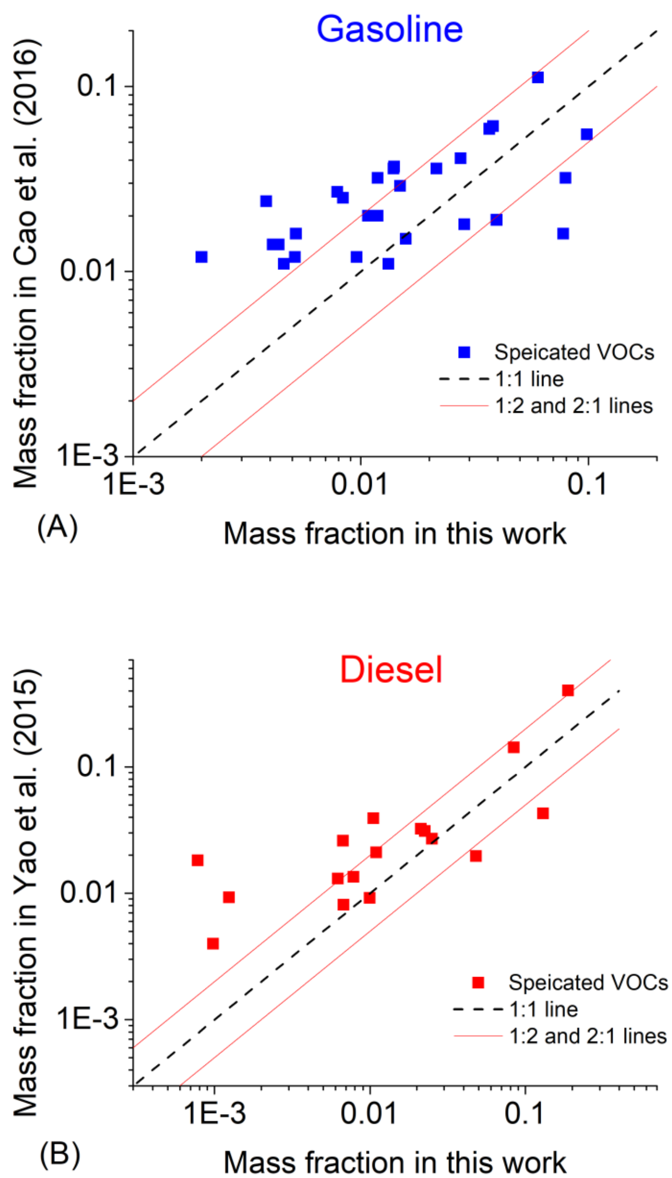


Figure S12 Scatter plots of mass fractions of speciated VOCs in new VOC emission profiles versus: on-road gasoline (left) and on-road diesel (right) vehicle VOC emissions in China