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 S1(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 S1(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), Fig. S1(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). This total organic emission is then partitioned at T = 298K and OA = 10 µg/m^3 to provides both gas- and particle-phase profiles. The SAPRC version in Table S3(b) is designed to be applied to NMOG emissions, and the VBS version in Table S3(c) is designed to model the POA emissions. In most emission inventories, where NMOG and POA are provided separately, we recommend applying the profiles Table S3(b) to speciate NMOG emissions and the profiles in Table S3(c) to POA.

Supporting Tables

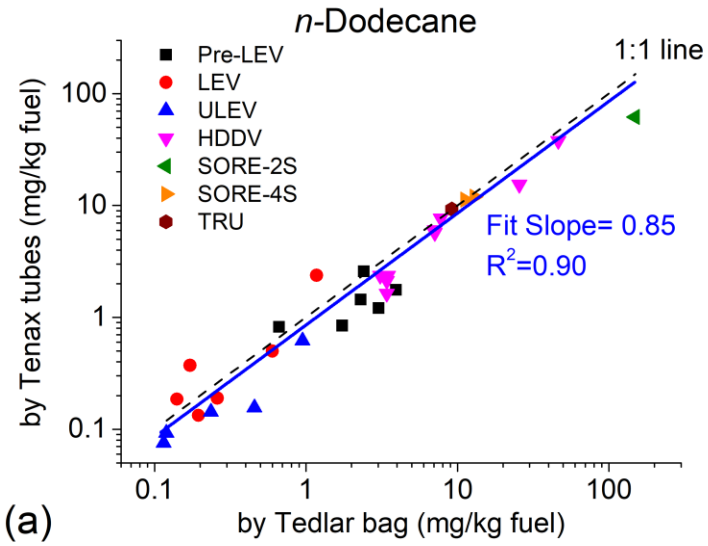
Table. S1 Summary of all tested engines, fuels and test cycles with complete characterization data

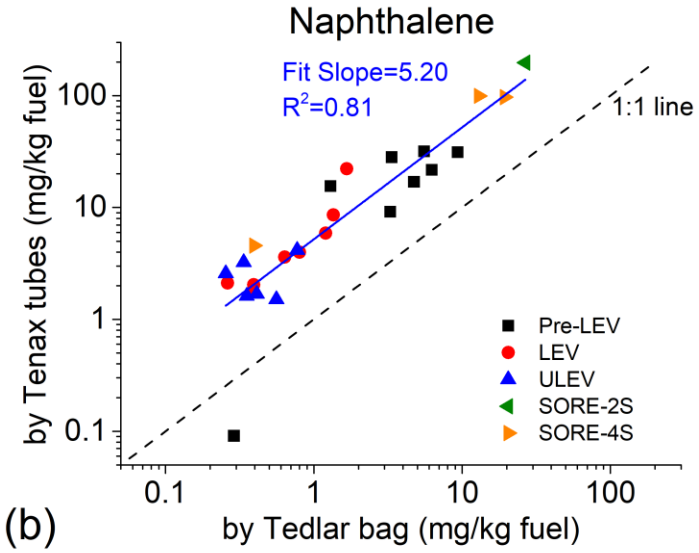
Source type	Category	Class / Model	Number of engines	Number of tests	Model year	Fuel	Test cycle / Thrust
Gasoline	LDGVs (on-road)	Pre-LEV	10	10	1987-1999	Commercial summertime California gasoline	Cold-start unified cycle (UC)
		LEV	9	10	1991-2009		
		ULEV	10	12	2003-2012		
	SOREs (off-road)	SORE-2S	2	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 Comparison of different estimates of IVOC fraction in NMOG emissions for mobile sources based on measurement data

	Estimated from	Source Categories		
		Gasoline	Gas-turbine	Diesel
Robinson et al.	(1.5*) POA	1.2%	6.1%	8.0%
Murphy et al.	(9.656*) POA	7.5%	39.5%	51.7%
Pye et al.	(66*) Naphthalene	19.9%	22.3%	6.9%
Gentner et al.	Unburnt fuel	1%	N/A	62%
Jathar et al.	Inverting chamber experiment results	25%	N/A	20%
This work	Direct measurement	4.6%	27.9%	54.3%

Supporting Figures





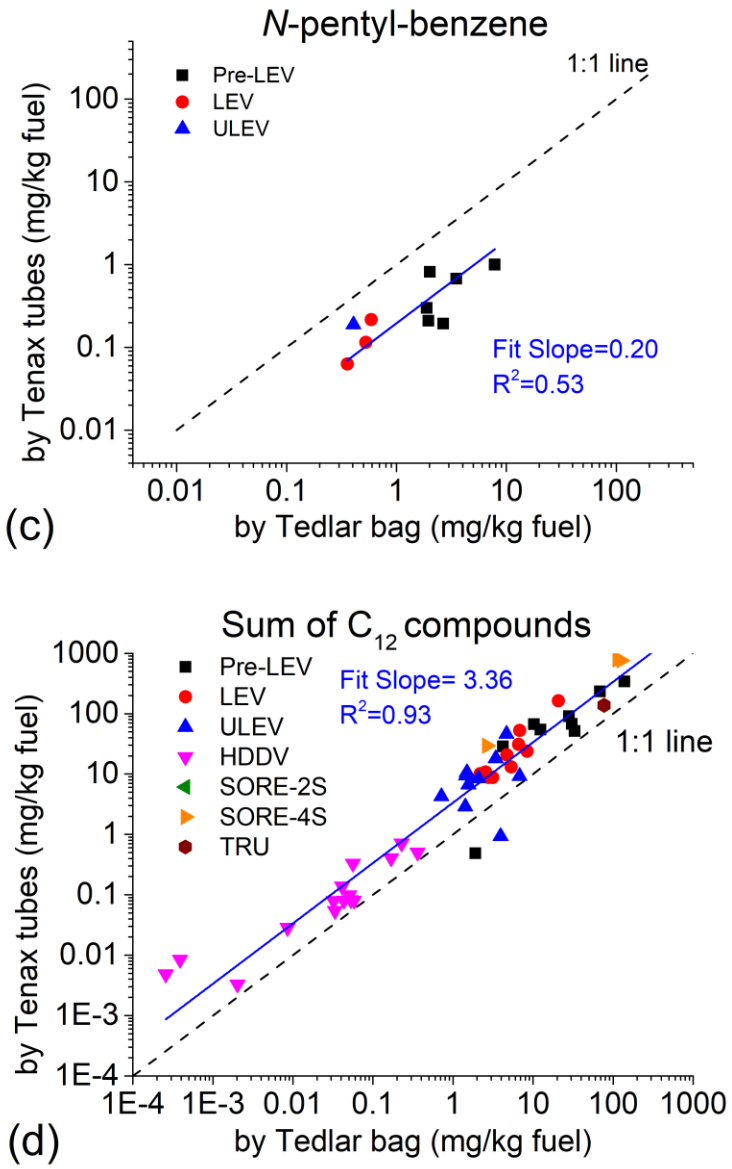


Fig. S1 Comparison of (a) *n*-dodecane (b) naphthalene (c) n-pentyl-benzene (d) sum of all C_{12} compounds results measured using GC/MS analysis of Tedlar bag versus Tenax adsorbent samples (everything elutes in the C_{12} carbon number bin), demonstrating the consistency of two technique in *n*-dodecane measurement

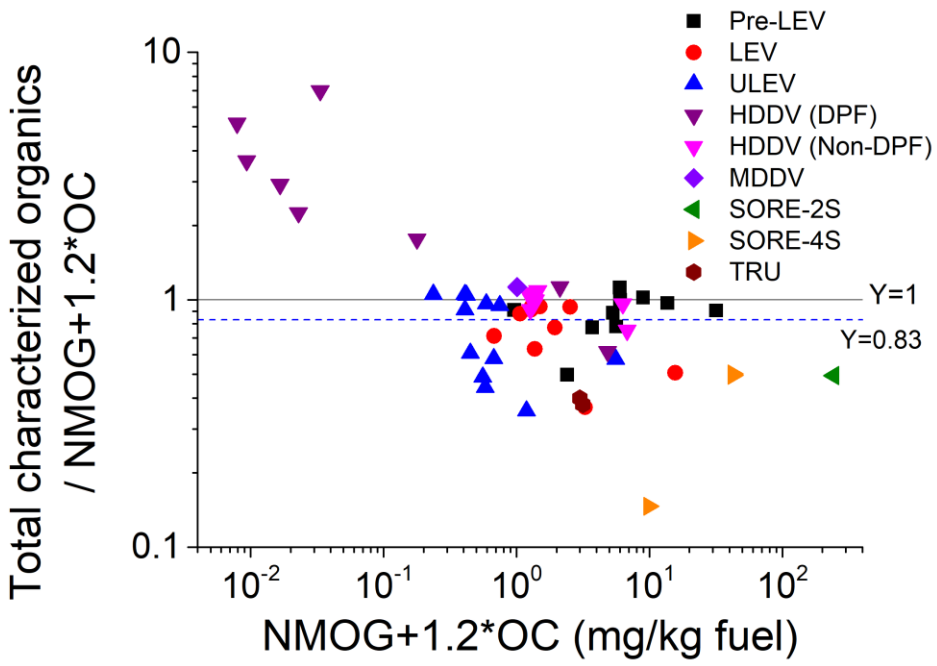


Fig. S2 Ratio of total characterized organics integrated from all techniques to total organics by bulk measurement (NMOG+1.2*OC), indicating mass closure for on-road non-DPF diesel source and partial mass closure (0.83) for on-road gasoline sources

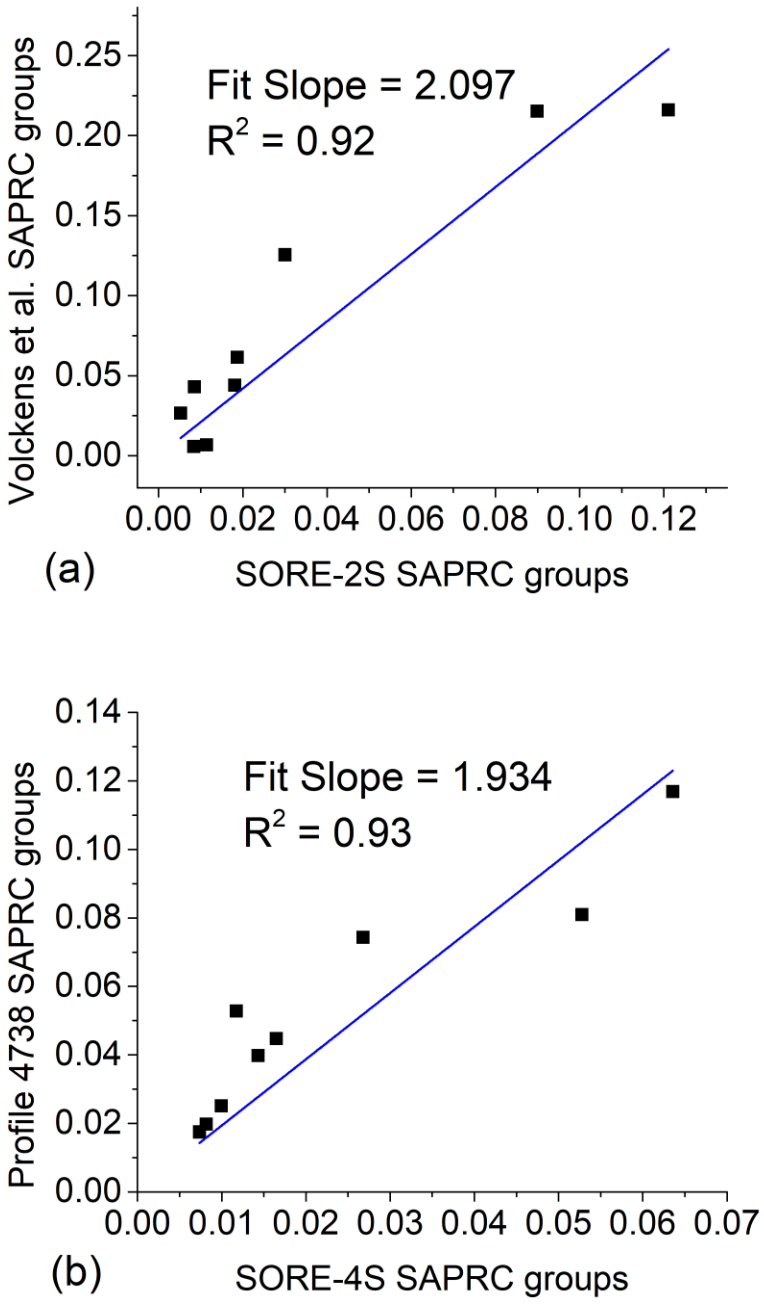


Fig. S3 Correlation of all SOA-forming SAPRC groups (ALK4, ALK5, ARO1, ARO2, BENZ, TOLU, PXYL, MXYL, OXYL, B124) fraction in NMOG emission between measurement and literature value for (a) SORE-2S (b) SORE-4S, indicating the need to factorize VOC mass in off-road measurement results by 2

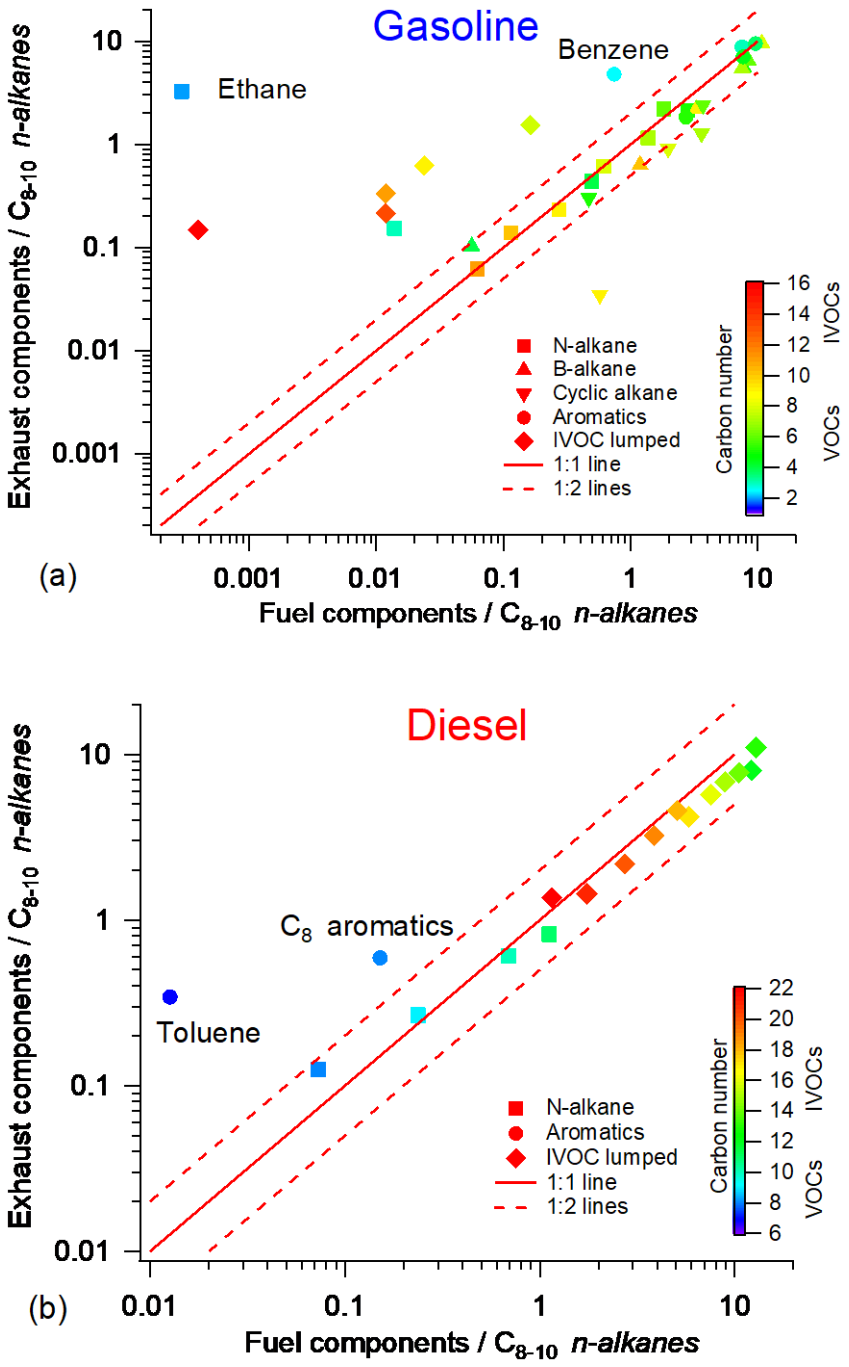
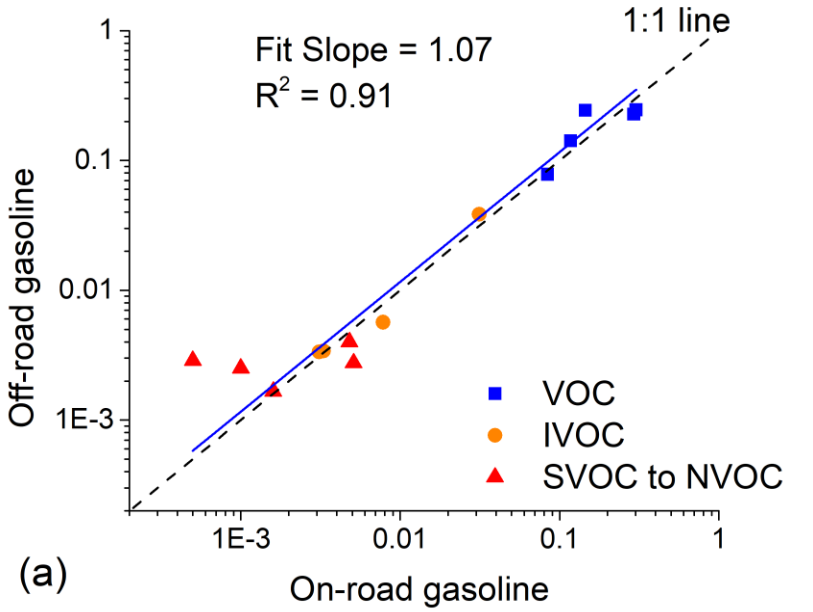
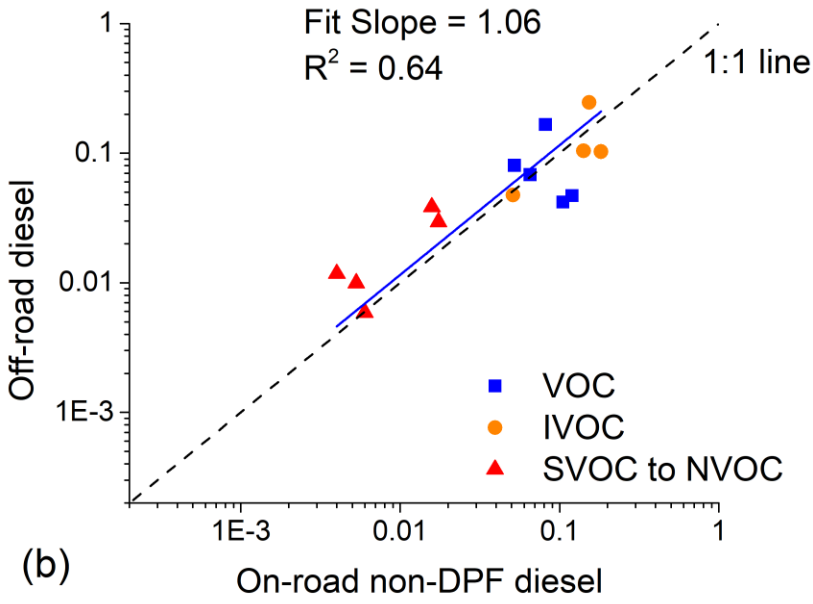


Fig. S4 Scatter plot of exhaust components versus fuel (VOCs and IVOCs) normalized by $C_{8\text{-}10}$ *n*-alkanes for (a) Gasoline (b) Diesel sources, demonstrating the overall consistency of chemical composition between exhaust and fuel


Fit Slope = 1.07
R^2 = 0.91
1:1 line
VOC
IVOC
SVOC to NVOC
Off-road gasoline
On-road gasoline
1
0.1
0.01
1E-3
1E-3
0.01
0.1
1
(a)


Fit Slope = 1.06
R^2 = 0.64
1:1 line
VOC
IVOC
SVOC to NVOC
Off-road diesel
On-road non-DPF diesel
1
0.1
0.01
1E-3
1E-3
0.01
0.1
1
(b)

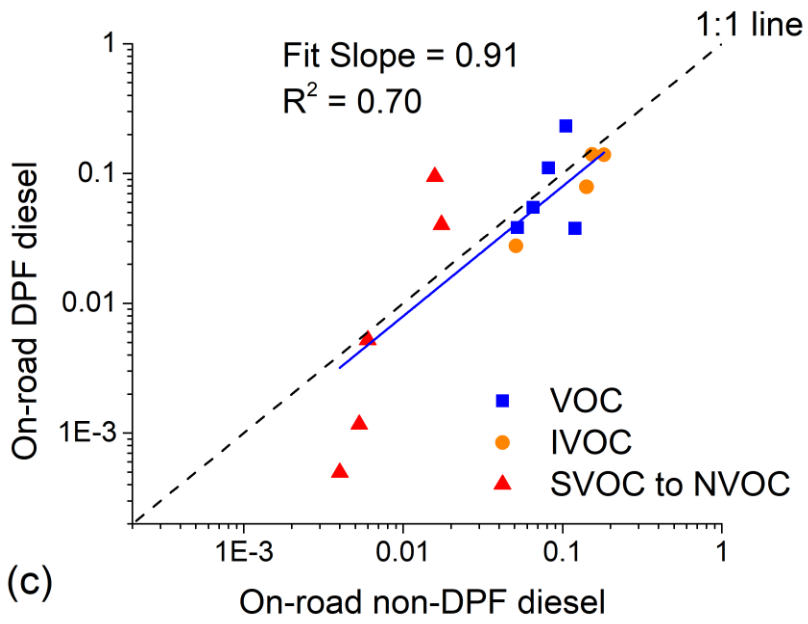
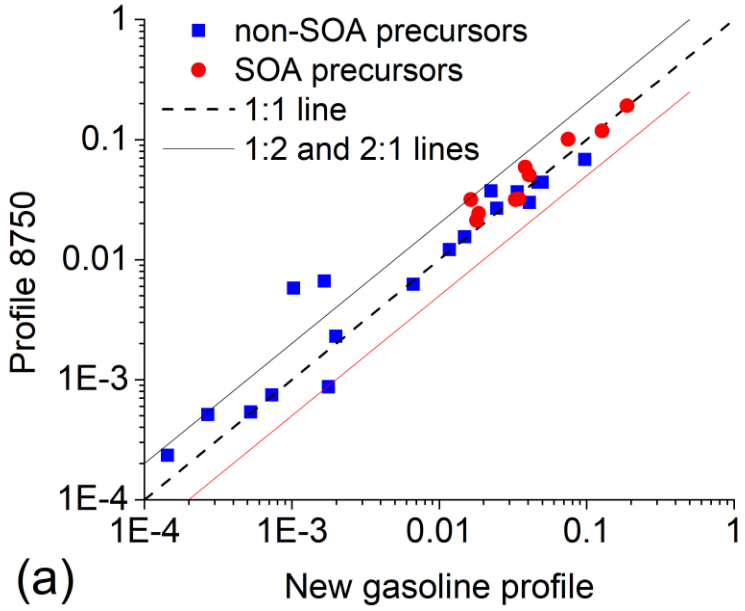
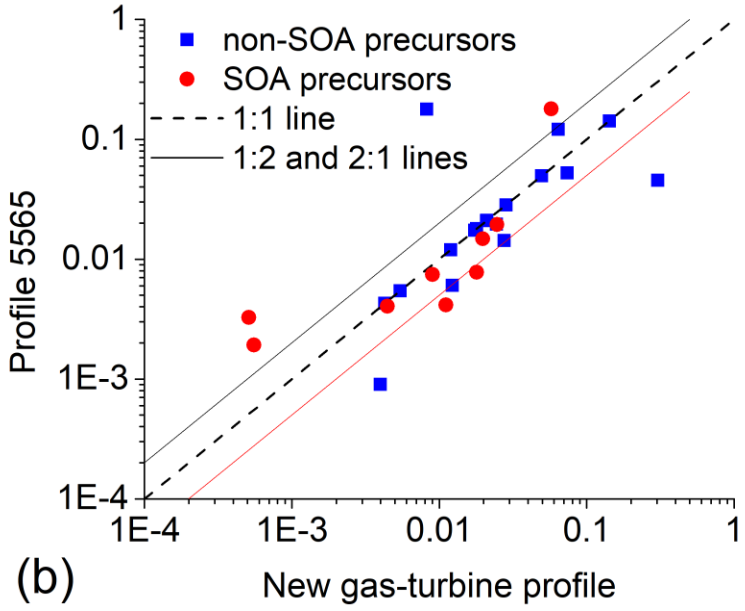


Fig. S5 Scatter plot of volatility distribution between (a) on-road and off-road gasoline (b) on-road and off-road non-DPF diesel (c) on-road DPF and non-DPF diesel sources, demonstrating the consistency of volatility distributions for sources within same category


non-SOA precursors
SOA precursors
1:1 line
1:2 and 2:1 lines
Profile 8750
New gasoline profile
1
0.1
0.01
1E-3
1E-4
1E-4
1E-3
0.01
0.1
1

(a)


non-SOA precursors
SOA precursors
1:1 line
1:2 and 2:1 lines
Profile 5565
New gas-turbine profile
1
0.1
0.01
1E-3
1E-4
1E-4
1E-3
0.01
0.1
1

(b)

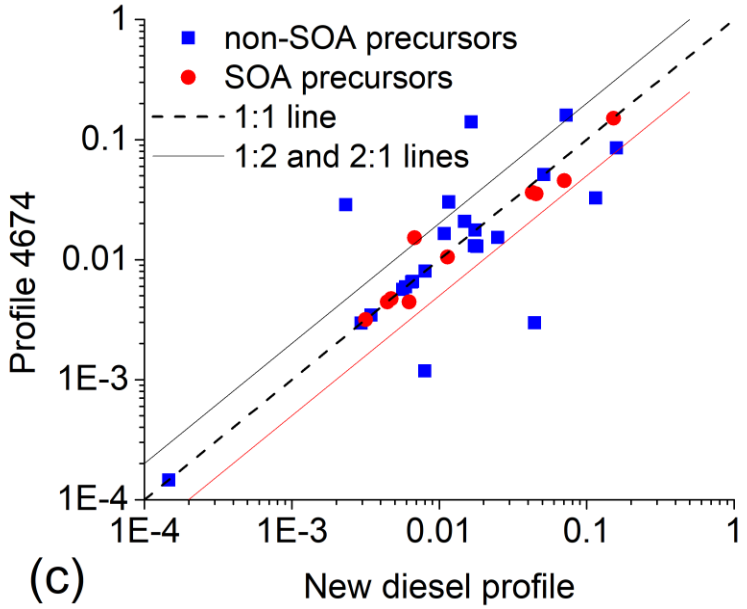


Fig. S6 Scatter plot of all SAPRC groups in the new profiles and in SPECIATE database for (a) on-road gasoline (b) gas-turbine (c) on-road diesel sources, demonstrating consistency between traditional and new profiles in VOC speciation

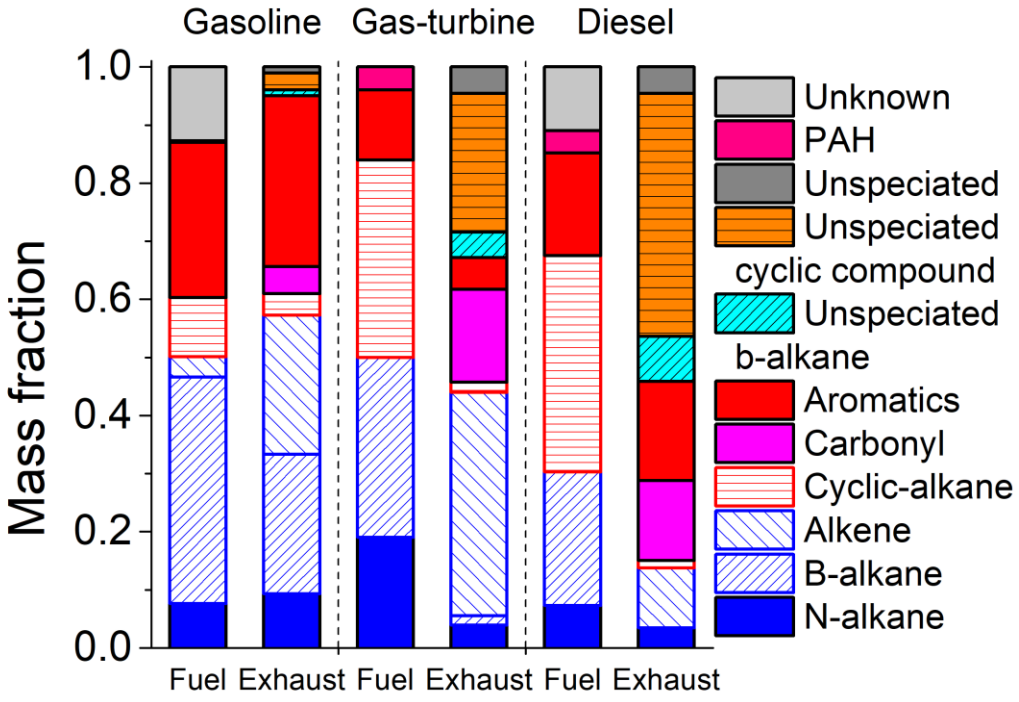


Fig. S7 Comparison of overall chemical composition between fuel and exhaust for gasoline, gas-turbine and diesel sources, indicating the compositional changes after combustion

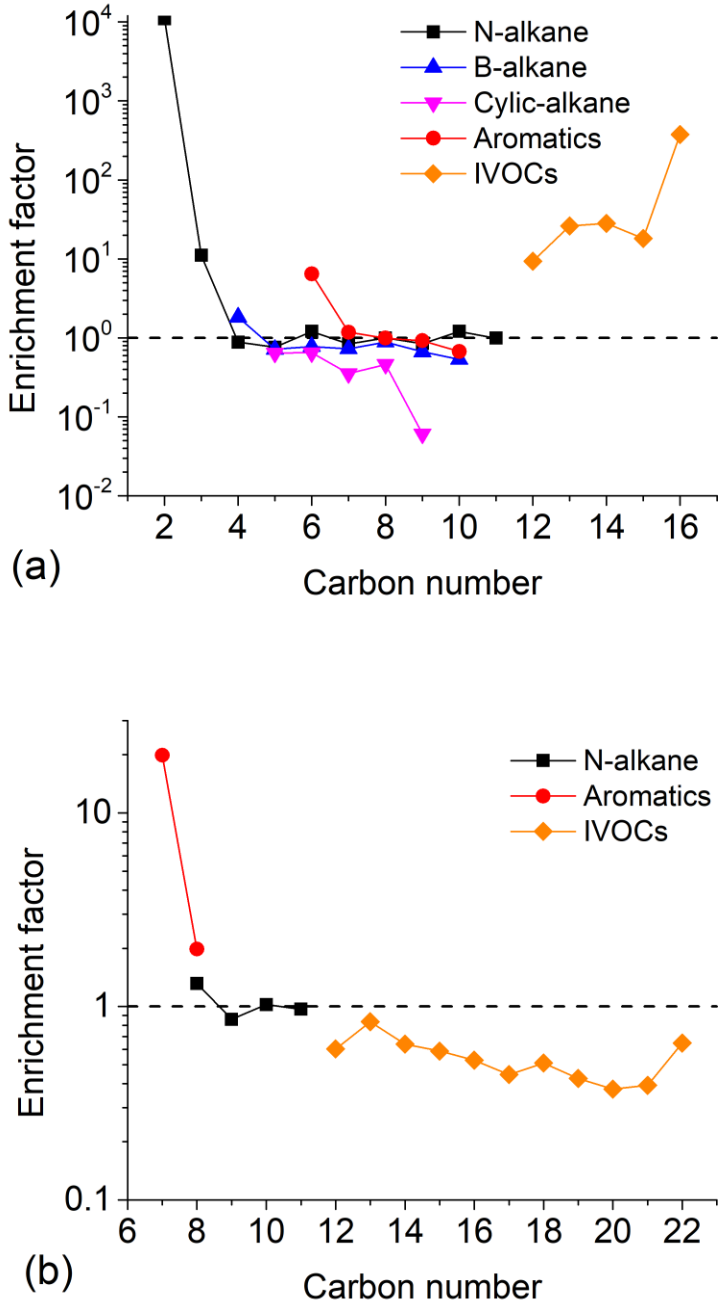


Fig. S8 Enrichment factors of exhaust and fuel components (VOCs and IVOCs) normalized by $C_{8\text{-}10}$ *n*-alkanes (a) Gasoline (b) Diesel, demonstrating the enrichment for certain compounds (VOCs and/or IVOCs) in difference sources