Supporting information for:

Distinct Emissions and Volatility Distribution of Intermediate Volatility Organic Compounds from on-road Chinese Gasoline Vehicle: Implication of High Secondary Organic Aerosol Formation Potential

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S1 Description of the experimental procedures

The measurements were performed on a Chinese in-use gasoline vehicle recruited from a rental car agency in Beijing in August-September, 2018. All the tests were conducted using the vehicle chassis dynamometer at the State Key Laboratory of Automotive Safety and Energy at Tsinghua University. Test cycled included a specially designed CLTC cycle based on Chinese real-world road condition and a widely used world-wide unified cycle called World-wide harmonized Light duty Test Cycle (WLTC). WLTC was designed to harmonize driving cycle from "real world" driving data in different regions around world i.e. Europe, India, Japan, Korea and USA, combined with suitable weighting factors²⁰. There are four speed classes in WLTC cycle: low, medium, high and extra-high speed phases, which can cover different road types (urban, rural,

motorway) and driving conditions (peak, off-peak, weekend). To better investigate the real emissions of IVOCs in China, a specially designed cycle called CLTC was applied in this study. It was developed to represent real driving condition in megacities (like Beijing) of China. In total, it has three velocity stages, namely low, medium and high-speed phases. The total duration time for the two cycles was 1800 seconds. Previous studies found that cold- versus hot-strart can also have an influence on the IVOC emission. Therefore, hot-start and cold-start system were both used in the tested CLTC and WLTC to evaluate the IVOC emission effects. Apart for this, specially designed acceleration rate cycles were also applied in this study to assess the reasons for the differences occurred during CLTC and WLTC cycle.

S2 Quantification and qualification of specified IVOCs

IVOCs collected by the adsorption tube filled with Tenax TA were thermally desorbed using Gerstel thermal desorption module (TDS3) followed by pre-concentration using a Gerstel cooled injection system (CIS4). The CIS4 was then heated to 300 °C by programming heating and transported the organic precursors to the GC/MS for analysis. Prior to analysis, a known amount of deuterated standards including d8-naphthalene and C12, C16, C20, C24, C30, C32, C36 deuterated n-alkanes were injected into the adsorption tube to track IVOC recovery during analysis. Concentrations of individual IVOCs were quantified using calibration curves developed by injecting a series of known amount of standard solutions into preconditioned clean tubes. The calibration standards include C8-C40 n-alkane and some aromatics, the results were listed in Table. S1.

S3. Quantification of unspeciated IVOCs

Unspeciated IVOCs, which we call as IVOC UCMs, could not be fully characterized by GC-MS. To quantify the total IVOC concentration, we used the total ion current (TIC) signal from the chromatography following the approach of Zhao et al. (ref). The TIC was divided into 11 bins based on the n-alkanes retention time (equivalent as the volatility). The IVOC UCM were classified as unspeciated b-alkanes and unspeciated cyclic compounds following Zhao et al. (ref). The IVOCs were then categorized into each bins corresponding to the n-alkane (Cn) where n represents the carbon number of n-alkane, called Bn.

The time range of the Bn bins could be calculated using the following method,

$$t_{n,binstart} = t_n - \frac{t_n - t_{n-1}}{2} \tag{1}$$

$$t_{n,binend} = t_n + \frac{t_{n+1} - t_n}{2} \tag{2}$$

In the above equations, t_n is the retention time of the n-alkane, while t_{n-1} and t_{n+1} stand for the retention time of the C_{n-1} and C_{n+1} n-alkanes.

The IVOC mass in each bin was calculated using the mass/signal response of the C_n n-alkane in the same bin, which could be described as follows:

$$M_{IVOCS,Bn} = \frac{TA_{TIC,Bn}}{RF_{n-alkane,Cn}} = \frac{TA_{m/Z57,Bn}}{RF_{n-alkane,Cn}} \times \frac{1}{f_{m/Z57,TIC_Bn}}$$
(3)

 $TA_{TIC,Bn}$ means the TIC abundance in the Bn bin, $RF_{n-alkane,Cn}$ is the response factor for n-alkane (Cn); $TA_{mz/57,Bn}$ respresents the m/z57 abundance in Bn bin, while $f_{m/z,57,TIC,Bn}$ denotes the fraction of m/z 57 to TIC in the Bn bin. The IVOC UCM_{Bn} was determined as the total IVOC minus the speciated IVOC in each Bn bin.

The mass of b-alkanes in each Bn bin was calculated as:

$$M_{b-alkane,Bn} = \frac{BA_{b-alkane,Bn}}{RF_{n-alkane,Cn}} = \frac{BA_{m/z57,Bn}}{RF_{n-alkane,Cn}} \times \frac{1}{f_{m_{/z57,b-alkane_Bn}}} = \frac{TA_{m/z57,Bn} - NA_{m/z57,Bn}}{RF_{n-alkane,Cn}} \times \frac{1}{f_{m_{/z57,b-alkane_Bn}}}$$

$$(4)$$

In this equation, $BA_{b-alkane,Bn}$ denotes the abudance of b-alkane of b-alkane in the Bn bin, BA $_{m/z57,Bn}$ represents the m/57 abundance derived from b-alkane in Bn bin, while TA $_{m/z57,Bn}$ is the total m/z57 signal in Bn bin. NA $_{m/z57,Bn}$ is the m/z 57 abundance produced by n-alkanes; $f_{m/z57,b-alkane,Bn}$ means the m/z57 fraction of the TIC for b-alkanes.

Based on the calculation above, we determine the mass of the unspeciated cyclic compounds.

S4. Comparison between China V and LEV-2 vehicles

IVOCs and VOCs are both subgroups of THC, so higher contribution of IVOC to THC reduces the VOC-to-THC ratio. Using the same set of 65 VOCs measured by both the US and Chinese tests, the median VOC-to-THC ratios for China V and US vehicle were 0.36 and 0.46, respectively (Figure S7). Comparison of VOCs emissions by chemical compositions can be found in Figure S8. For most of the speciated VOC/THC ratio, China V was lower than that of the LEV-2, except for benzene and C7-C11 n-alkanes where China V has higher values. This might suggest a shift of emissions to low volatility range happen to China V vehicles.

Supplemental Figures



Figure S1. Speed profiles of WLTC, CLTC and UC protocols



Figure S2. Specific designed cycles at different acceleration rates.



Figure S3. Histogram distribution of acceleration rate for WLTC and CLTC



Figure S4. Comparison of IVOC fraction under different operating conditions.



Figure S5. IVOC volatility distributions under different operations. The boxes represent the 75^{th} and 25^{th} percentiles, with the centerline being the median. The whiskers are the highest and lowest values.



Figure S6. Scatter plots of IVOC EFs and (a) THC EFs and (b) POA EFs from the tested gasoline vehicle under different operating conditions. The gray triangles represent data obtained using gasoline as the fuel. The light red triangles stand for data taken when the gasoline vehicle was fueled with E10.



Figure S7. Comparison of selected VOC/THC between China V and US vehicles in different model years. Selected VOC means restrained 65 VOC species which both measured in China V and US vehicles.



Figure S8. Comparison of VOC/THC between China V and LEV-2, grouped by VOC composition.



Figure S9 Median enrichment mass fraction (exhaust vs fuel) grouped by volatility bins, indicating the composition change after combustion process.



Figure S10. Comparison of the contribution to SOA formation by different chemical compositions, including single-ring VOCs and IVOCs



Figure S11. Comparison of the contribution to SOA formation by different chemical compositions, including single-ring VOCs and IVOCs: (a) low NO_x condition; (b) at an OA loading of 10 μ g·m⁻³ under high NO_x condition; (c) at an OA loading of 20 μ g·m⁻³ under high NO_x condition; (d) at an OA loading of 80 μ g·m⁻³ under high NO_x condition.

Name	Retention time	\mathbf{R}^2
Naphthalene-d8	16.843	
Naphthalene	16.93	0.99949
Acenaphthene-d10	24.85	
Acenaphthene	24.993	0.999436
Acenaphthylene	24.145	0.999289
2-Methylnaphthalene	20.129	0.989588
1-Methylnaphthalene	20.545	0.980587
1,4-Dimethylnaphthalene	23.902	0.999524
Phenanthrene-d10	31.673	
Phenanthrene	31.779	0.998865
Anthracene	32.011	0.995482
Fluorene	27.406	0.932439
Fluoranthene	37.279	0.978092
Pyrene	38.245	0.977327
Chrysene-d12	43.966	
Benz(a)anthracene	43.933	0.998571
Chrysene	44.074	0.998533
Perylene-d12	50.046	
Benzo(b)fluoranthene	48.58	0.998833
Benzo(k)fluoranthene	48.691	0.997682
Benzo(a)pyrene	49.806	0.996461
Dibenz(a,h)anthracene	54.503	0.990335
Indeno(1,2,3-cd)pyrene	53.881	0.989301
Benzo(g,h,i)perylene	54.703	0.995117
n-Dodecane-D26	16.979	
n-nonane	8.845	0.989794
n-Decane	11.549	0.998578
n-Undecane	14.495	0.999511
n-Dodecane	17.498	0.99785
n-Tridecane	20.328	0.994602
n-Hexadecane-D34	27.324	
n-Tetradecane	23.017	0.999821
n-Pentadecane	25.523	0.999981
n-Hexadecane	27.892	0.999897
n-Heptadecane	30.153	0.998814
Pristane	30.236	0.978048
n-Eicosane-D42	35.646	
n-Octadecane	32.284	0.996472
Phytane	32.407	0.991827
n-Nonadecane	34.319	0.986211
n-Eicosane	36.266	0.997022
n-Tetracosane-D50	42.596	
n-Heneicosane	38.126	0.999801
n-Docosane	39.906	0.999822

Table S1. The calibration compounds used in this study

n-Tricosane	41.61	0.999767
n-Tetracosane	43.247	0.99957
n-Pentacosane	44.822	0.999071
n-Hexacosane	46.341	0.998805
n-Triacontane-D62	51.215	
n-Heptacosane	47.808	0.999798
n-Octacosane	49.221	0.99968
n-Nonacosane	50.585	0.999368
n-Dotriacontane-D66	53.718	
n-Triacontane	51.907	0.999498
n-Hentriacontane	53.185	0.999478
n-Dotriacontane	54.421	0.998975
n-Tritriacontane	55.626	0.998547
n-Tetratriacontane	56.792	0.997054
n-Hexatriacontane-D74	58.302	
n-Pentatriacontane	57.933	0.999103
n-Hexatriacontane	59.032	0.997554
n-Heptatriacontane	60.145	0.993378
n-Octatriacontane	61.381	0.990468
n-Tetracontane	64.493	0.97258

 Table S2. Key characteristics of driving cycles

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Index	WLTC	CLTC	UC	
Average velocity	46.5	29.0	39.6	
(km/h)				
Average	0.477	0.415	0.673	
acceleration (m/s ²)				
Average	-0.514	-0.464	-0.754	
deceleration (m/s ²)				
Percentage of idling	12.2%	22.4%	16.3%	
time				

Name	OH	reaction	SOA yield	SOA yield	SOA yield	SOA yield
	rate		Low NO _x	High NO _x	High NO _x	High NO _x
				$10 \ \mu g \cdot m^{-3}$	$20 \ \mu g \cdot m^{\text{-}3}$	80 μg·m ⁻³
Dodecane	1.32H	E-11	0.35	0.09	0.12	0.24
Tridecane	1.51H	E-11	0.44	0.22	0.30	0.52
Tetradecane	1.58H	E-11	0.54	0.30	0.40	0.62
Pentadecane	1.82H	E-11	0.63	0.35	0.46	0.67
Hexadecane	1.96I	E-11	0.78	0.40	0.51	0.70
Heptadecane	2.10H	E-11	0.88	0.44	0.55	0.73
Octadecane	2.24H	E-11	0.88	0.44	0.55	0.73
Nonadecane	2.38H	E-11	0.88	0.44	0.55	0.73
Eicosane	2.52H	E-11	0.88	0.44	0.55	0.73
Heneicosane	2.67H	E-11	0.88	0.44	0.55	0.73
Docosane	2.81H	E-11	0.88	0.44	0.55	0.73
Naphthalene	2.30H	E-11	0.73	0.21	0.27	0.45
2-methylnaphthalene	4.86H	E-11	0.58	0.31	0.40	0.50
1-methylnaphthalene	4.09E	E-11	0.68	0.26	0.34	0.45
Acenaphthylene	1.24H	E-10	0.31	0.31	0.31	0.31
Acenaphthene	8.00H	E-11	0.31	0.31	0.31	0.31
Fluorene	1.60H	E-11	0.31	0.31	0.31	0.31
Phenanthrene	3.20H	E-11	0.31	0.31	0.31	0.31
Anthracene	1.78H	E-10	0.31	0.31	0.31	0.31
Fluoranthene	3.30H	E-11	0.31	0.31	0.31	0.31
Pyrene	5.60H	E-11	0.31	0.31	0.31	0.31

Table S3. OH reaction rate constants (cm³ molec⁻¹ s⁻¹) and SOA yields for speciated IVOCsincluded in the SOA model under different NOx conditions

Name	ОН	rate	SOA	SOA	SOA yield	SOA yield
	constant		yield	yield	High NO _x	High NO _x
			Low	High NO _x	$20 \ \mu g {\cdot} m^{\text{-}3}$	$80 \ \mu g \cdot m^{-3}$
			NO _x	$10 \ \mu g \cdot m^{-3}$		
Benzene	1.22E-12		0.37	0.14	0.21	0.44
Toluene	5.63E-12		0.30	0.08	0.11	0.15
o-xylene	1.36E-11		0.36	0.05	0.06	0.09
m/p-xylene	1.87E-11		0.36	0.05	0.06	0.09
Ethylbenzene	7.00E-12		0.30	0.08	0.11	0.15
Styrene	5.80E-11		0.30	0.08	0.11	0.15
isopropylbenzene	6.3E-12		0.30	0.08	0.11	0.15
n-propylbenzene	5.80E-12		0.30	0.08	0.11	0.15
p-ethyl-toluene	1.18E-12		0.30	0.08	0.11	0.15
o-ethyl-toluene	1.19E-11		0.30	0.08	0.11	0.15
m-ethyl-toluene	1.86E-11		0.30	0.08	0.11	0.15
1,3,5-trimethyl-benzene	5.67E-11		0.36	0.05	0.06	0.09
1,2,4-trimethyl-benzene	3.25E-11		0.36	0.05	0.06	0.09
1,2,3-trimethyl-benzene	3.27E-11		0.36	0.05	0.06	0.09

Table S4. OH reaction rate constants (cm³ molec⁻¹ s⁻¹) and SOA yields for single-ring aromatics compounds included in SOA model under different NO_x condition.

Table S5. Surrogate compounds (n-alkanes) used for OH reaction rate constants ($cm^3 molec^{-1} s^{-1}$) and SOA yields for unspeciated cyclic compounds

		Surrogate compounds for SOA yields			
Bins	OH rate constant	Unspeciated cyclic	Unspeciated cyclic		
		compounds	compounds		
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		