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Supplement of

Measurement report: Emissions of intermediate-volatility organic compounds from vehicles under real-world driving conditions in an urban tunnel

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Text S1

Quantification of IVOCs

Speciated IVOCs were identified based on their retention times and mass spectra, and were quantified by 18 authentic standards including C_{12}-C_{22} n-alkanes and 8 polycyclic aromatic hydrocarbons (PAHs). The pristane and phytane were quantified by the calibration curves of the n-alkanes (n-C_{17} and n-C_{18}) near them.

Total IVOCs mass were quantified by using the method developed by Zhao et al. (2014). Firstly, the total ion chromatogram (TIC) was divided into 11 chromatogram bins based on retention times of C_{12}-C_{22} n-alkanes. The start time and end time of chromatogram bin were determined by successive n-alkanes. The example was illustrated as following:

$$t_{n,\ Bin-start} = \frac{t_{n-1} + t_n}{2}$$

$$t_{n,\ Bin-end} = \frac{t_n + t_{n+1}}{2}$$

Where n refers to the carbon number of n-alkane which centered in the corresponding chromatogram bin. The $t_{n,\ Bin\text{-}start}$ and $t_{n,\ Bin\text{-}end}$ respectively represent the start time and end time of chromatogram bin. The t_{n-1}, t_n and t_{n+1} are the retention times of C_{n-1}, C_n and C_{n+1} n-alkanes, respectively.

Secondly, the IVOCs mass in each defined chromatogram bin ($M_{IVOCs,\ Bn}$) was calculated by following equation:

$$M_{IVOCs,\ Bn} = \frac{TA_{TIC,\ Bn}}{RF_{n-alkans,\ C_n}} = \frac{TA_{m/z\,57,\ Bn}}{RF_{n-alkanes,\ C_n}} \times \frac{1}{f_{m/z\,57,\ TIC,\ Bn}}$$

Where $TA_{TIC,Bn}$ is the abundance of TIC in the B_n chromatogram bin; $RF_{n\text{-}alkane,\ Cn}$ is the response factor of the C_n n-alkane; $TA_{m/z\,57,\ Bn}$ refers to the abundance of m/z 57 in the B_n chromatogram bin; $f_{m/z\,57,\ TIC,\ Bn}$ is the fraction of the m/z 57 in TIC of the B_n chromatogram bin. The total IVOCs mass was the sum of the IVOCs mass calculated in each defined chromatogram bin.

Thirdly, the residual IVOCs (subtracting the speciated IVOCs), which was named as unresolved complex mixtures IVOCs (UCM IVOCs) in previous studies (Zhao et al., 2014, 2015, 2016), were further divided into unspeciated branched alkanes (b-alkanes) and unspeciated cyclic compounds. Here, we assumed that the signal of m/z 57 all came from n-alkanes and b-alkanes. The unspeciated b-alkanes mass ($M_{b\text{-}alkane,\ Bn}$) was defined as the difference between calculated mass of m/z 57 and n-alkane that falling in the same chromatogram bin (Zhao et al., 2015, 2016). Obviously, this assumption would somewhat cause an overestimation of b-alkanes in that other compounds like cyclic alkanes also could contribute to the abundance of m/z 57 (Zhao et al., 2014).

$$M_{b-alkane,\ Bn} = \frac{BA_{b-alkane,Bn}}{RF_{n-alkane,Cn}} = \frac{BA_{m/z\,57,\ Bn}}{RF_{n-alkane,\ Cn}} \times \frac{1}{f_{m/z\,57,\ b-alkane}}$$

$$= \frac{(TA_{m/z\,57,\ Bn} - NA_{m/z\,57,\ Cn})}{RF_{n-alkane,\ Cn}} \times \frac{1}{f_{m/z\,57,\ b-alkane}}$$

Where $BA_{b\text{-alkane},\ Bn}$ is the abundance of b-alkanes in B_n chromatogram bin. The $BA_{m/z\ 57,\ Bn}$ represents the abundance of m/z 57 came from b-alkanes in the B_n chromatogram bin while $NA_{m/z\ 57,\ Cn}$ is the abundance of m/z 57 produced by the C_n n-alkane. $TA_{m/z57,\ Bn}$ is the total abundance of m/z 57 in B_n chromatogram bin. The $f_{m/z\ 57,\ b\text{-alkane}}$ is the average fraction of m/z 57 in the TIC of b-alkanes.

Lastly, the mass of unspeciated cyclic compounds were calculated as a consequence of subtracting both the masses of speciated IVOCs and unspeciated b-alkanes from the total determined IVOCs mass.

Text S2

Calculation of fuel-based emission factor

The fuel-based emission factor of IVOCs was calculated as following:

$$\text{fuel} - \text{based EF (mg kg}^{-1}) = \frac{\text{mileage} - \text{based EF (mg km}^{-1})}{\text{fuel density (kg L}^{-1}) \times \text{fuel efficiency (L km}^{-1})}$$

Here, the 7.87 L/100 km and 7.5 L/100 km were used as the average gasoline and diesel efficiency, respectively (http://icet.org.cn/admin/upload/2014101812382577.pdf). The fuel density was 0.74 g mL^{-1} for gasoline and 0.85 g mL^{-1} for diesel (Zhang et al., 2016).

Text S3

Linear regression analysis of diesel vehicles fraction and SOA_{IVOCs}-to-SOA_{VOCs} ratio

$$R = R_{DVs} \times \alpha + R_{GVs}(1 - \alpha)$$

where R represents the fleet average SOA_{IVOCs}-to-SOA_{VOCs} ratio calculated during the campaign. R_{DVs} and R_{GVs} are the SOA_{IVOCs}-to-SOA_{VOCs} ratios for DVs and GVs, respectively. α is the fraction of DVs in the total IVOCs-emitting vehicles traveling through the tunnel.

Text S4

Estimations of IVOCs emission

Firstly, we used the mileage-based EF_{IVOCs} and the average vehicle fleet composition observed in tunnel to calculate IVOCs emissions percentage of DVs and GVs (Table S4). Then, as showed in Table S4, the fuel-based EF_{IVOCs} and fuel consumptions in China in 2019 (http://www.mee.gov.cn/hjzl/sthjzk/ydyhjgl/) were used to estimate IVOCs emissions from diesel- and gasoline-fueled engines.

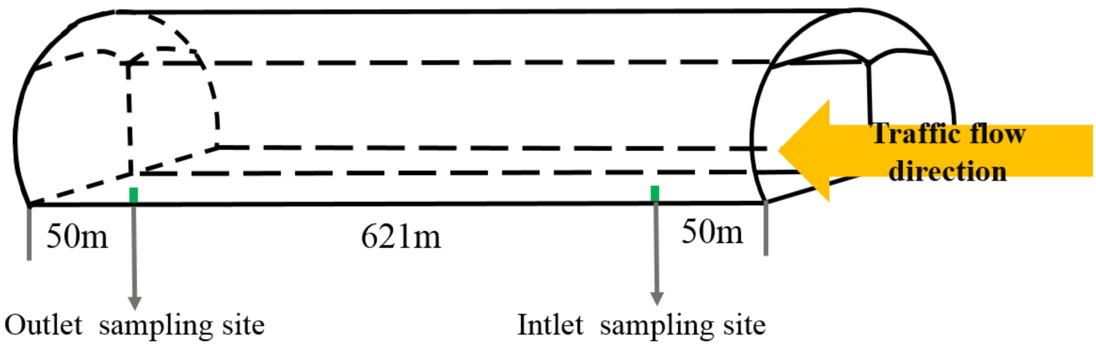


Figure S1. The schematic diagram of the sampling stations inside the Zhujiang tunnel.

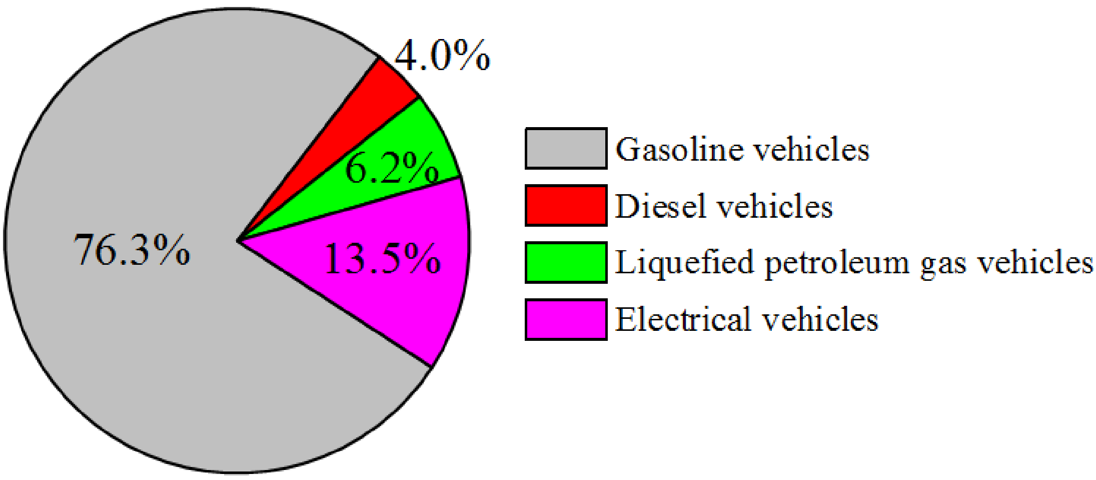
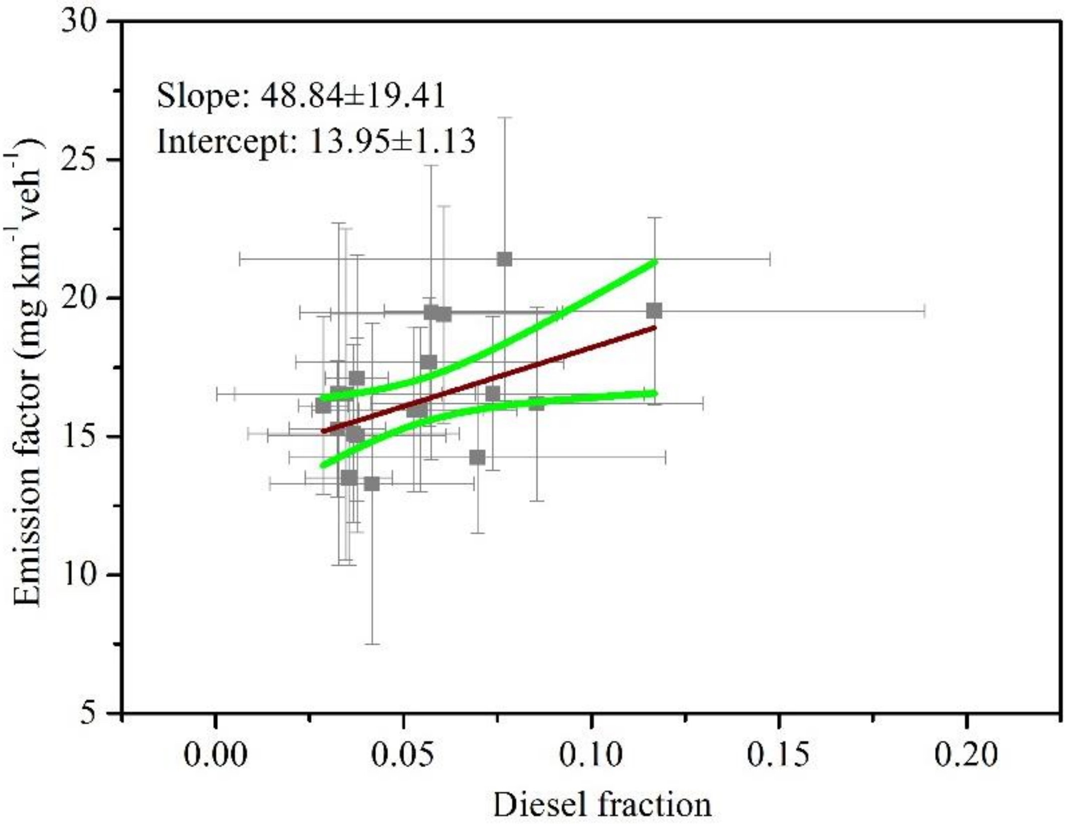


Figure S2. The vehicle fleet compositions during the campaign.



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89 Figure S3. Linear regression analysis of diesel fraction and fleet-average EF_{IVOCs} during the

90 campaign. The green lines represent 95% confidence intervals.

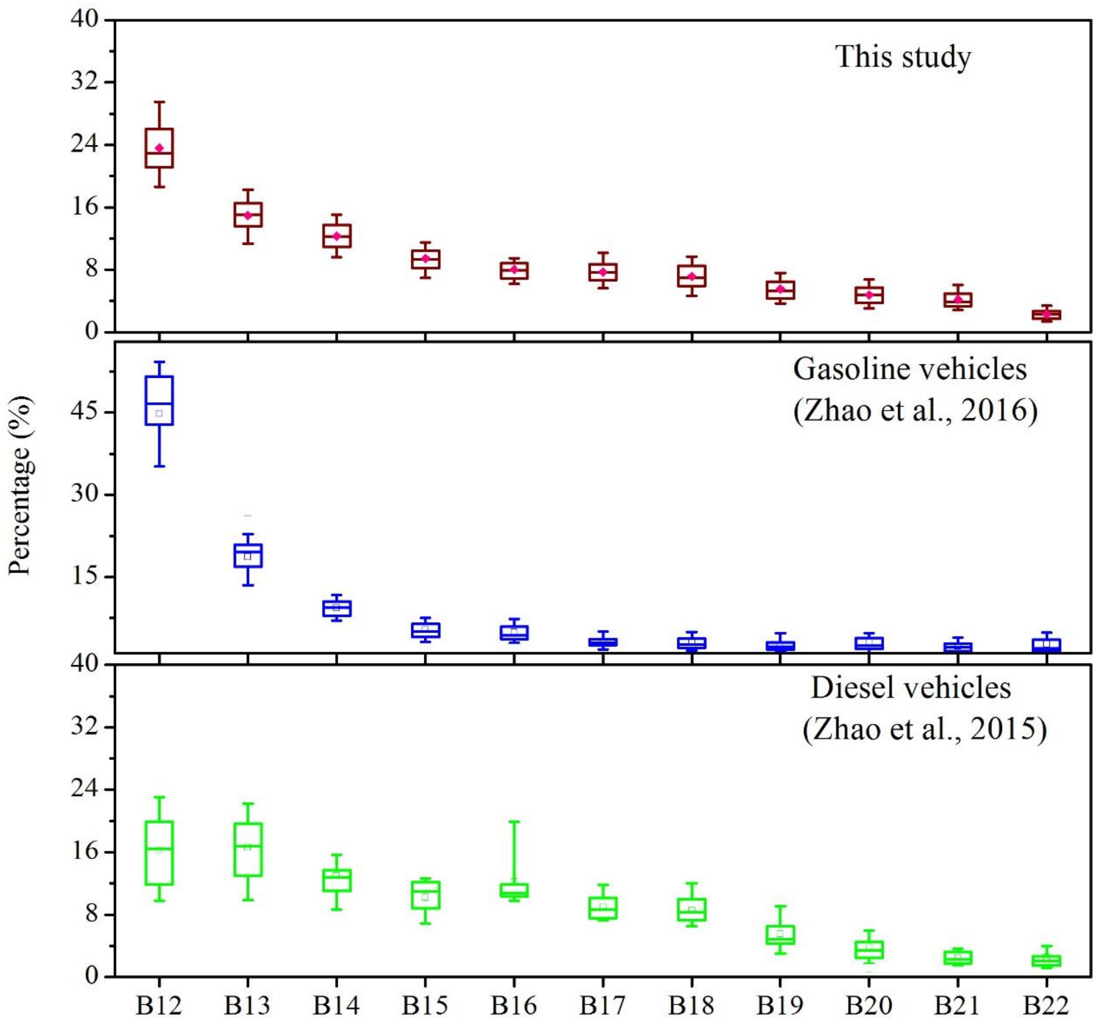

Figure S4. The comparison of distributions of total IVOCs in different volatility bins determined in this study and in previous studies. The boxes represent the 75th and 25th percentiles, the centerlines are the medians and squares are the averages. The whiskers represent 10th and 90th percentiles.

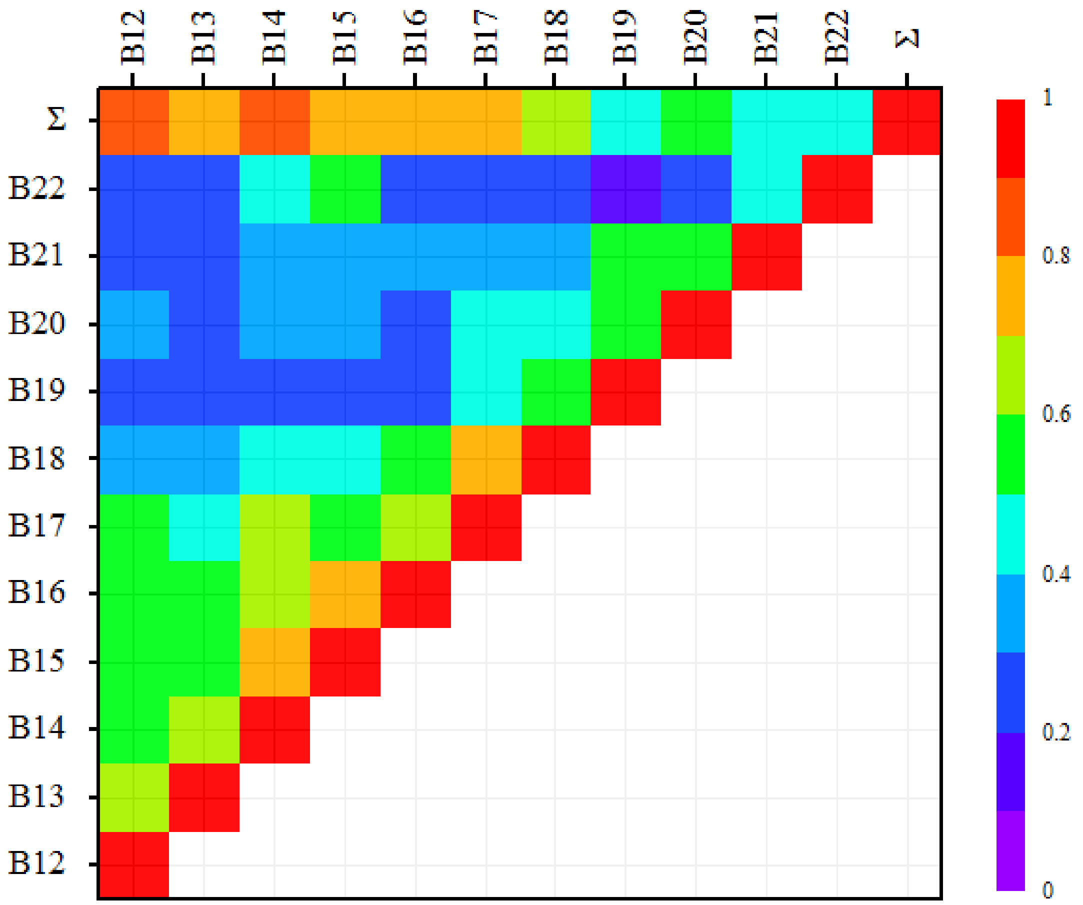

Figure S5. The Pearson correlations among IVOCs in each volatility bins (Σ represents sum of IVOCs from B12 to B22).

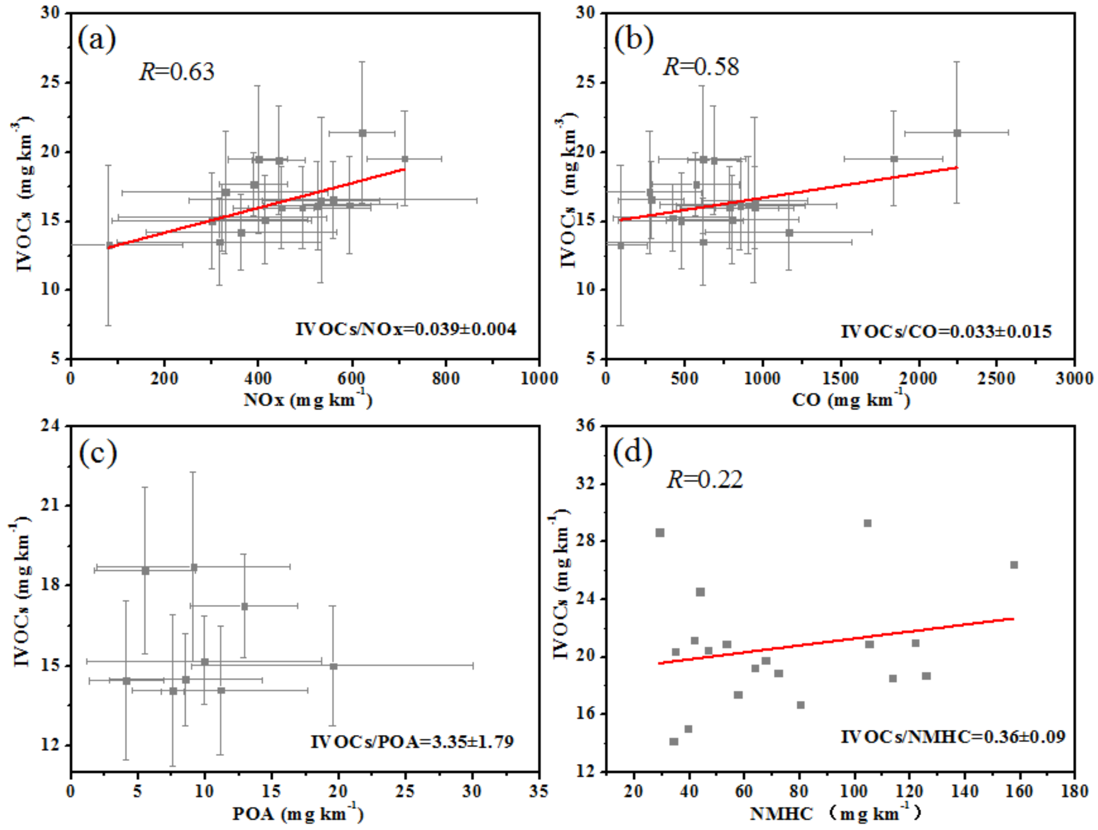

Figure S6. The relationships of IVOCs with other primary species that concurrently measured in the tunnel.

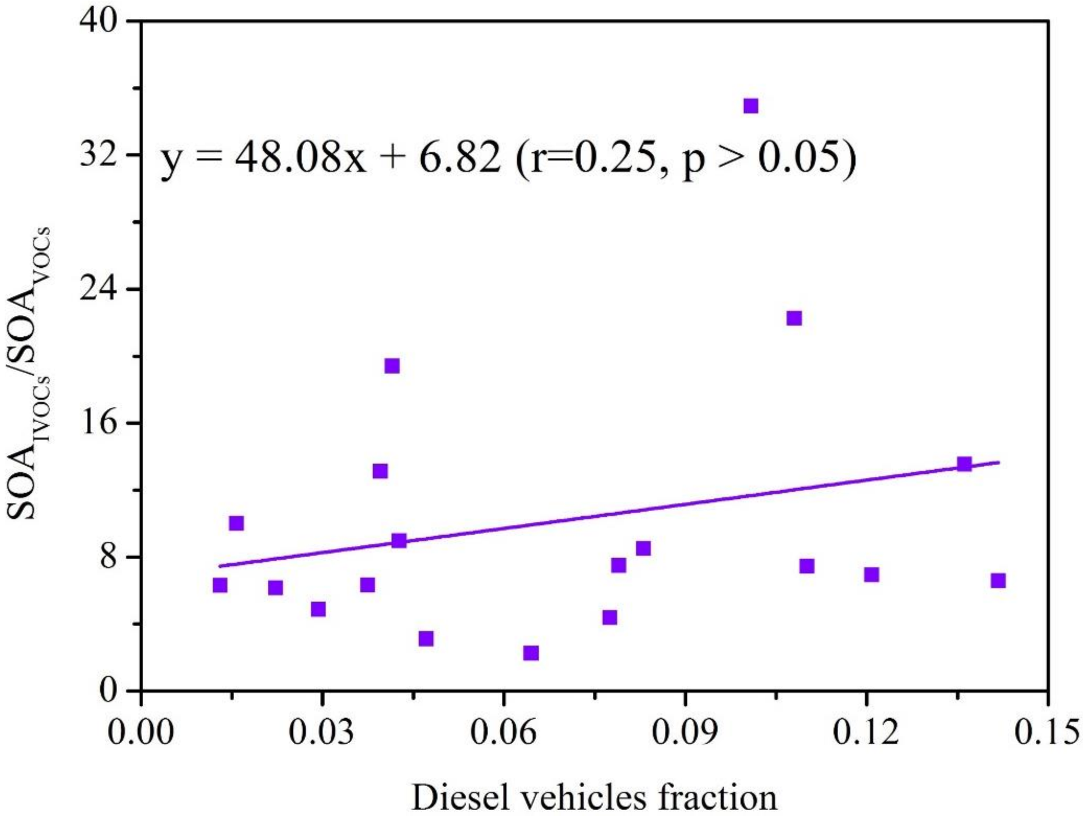

Figure S7. Linear regression analysis of diesel vehicles fraction and SOA_{IVOCs}-to-SOA_{VOCs} ratio.

Table S1. The emission factors of IVOCs species (mg km^{-1}).

Species	Mean ± 95% C.I.	Range
Dodecane	0.38±0.03	0.12−0.81
Tridecane	0.23±0.02	0.11−0.61
Tetradecane	0.22±0.02	0.10-0.53
Pentadecane	0.19±0.02	0.08-0.50
Hexadecane	0.16±0.01	0.06−0.38
Heptadecane	0.15±0.01	0.06−0.29
Pristane	0.10±0.01	0.03−0.24
Octadecane	0.13±0.01	0.05−0.25
Phytane	0.10±0.01	0.04−0.22
Nonadecane	0.10±0.01	0.03−0.24
Eicosane	0.10±0.01	0.01−0.21
Heneicosane	0.08±0.01	0.01−0.19
Docosane	0.04±0.00	0.00-0.11
Naphthalene	0.35±0.03	0.14−0.82
2-Methylnaphthalene	0.11±0.01	0.05−0.29
1-Methylnaphthalene	0.05±0.00	0.02−0.13
Acenaphthylene	0.06±0.01	0.00-0.17
Acenaphthene	0.01±0.00	0.00-0.05
Fluorene	0.00±0.00	0.00-0.01
Phenanthrene	0.01±0.00	0.00-0.05
Anthracene	0.02±0.00	0.00-0.11
Unspeciated b-alkanes B12	0.89±0.07	0.27−1.87
Unspeciated b-alkanes B13	0.58±0.04	0.19−1.03
Unspeciated b-alkanes B14	0.52±0.04	0.21−1.29
Unspeciated b-alkanes B15	0.43±0.03	0.17−1.11
Unspeciated b-alkanes B16	0.37±0.04	0.13−1.30
Unspeciated b-alkanes B17	0.34±0.03	0.15−0.81
Unspeciated b-alkanes B18	0.35±0.03	0.09−0.86
Unspeciated b-alkanes B19	0.25±0.03	0.04−0.64
Unspeciated b-alkanes B20	0.21±0.02	0.04−0.46
Unspeciated b-alkanes B21	0.19±0.02	0.04−0.61
Unspeciated b-alkanes B22	0.08±0.01	0.02−0.27
Unspeciated cyclic compounds B12	2.36±0.23	0.96−7.13
Unspeciated cyclic compounds B13	1.54±0.13	0.21−3.74
Unspeciated cyclic compounds B14	1.33±0.10	0.42−2.69
Unspeciated cyclic compounds B15	0.89±0.07	0.19−2.01
Unspeciated cyclic compounds B16	0.82±0.07	0.21−2.27
Unspeciated cyclic compounds B17	0.71±0.07	0.12−1.61
Unspeciated cyclic compounds B18	0.59±0.06	0.00−1.67
Unspeciated cyclic compounds B19	0.57±0.05	0.16−1.42
Unspeciated cyclic compounds B20	0.49±0.06	0.08−1.71
Unspeciated cyclic compounds B21	0.42±0.04	0.15−1.18
Unspeciated cyclic compounds B22	0.26±0.03	0.07−0.68
Σ Speciated IVOCs	2.59±0.14	1.43−4.37
Σ UCM IVOCs	14.19±0.79	7.41−25.60
Σ IVOCs	16.77±0.89	9.04−29.32

Table S2. The correlations and mass ratios of IVOCs with normal alkanes in the same volatility bin.

	B12/n-C12	B13/n-C13	B14/n-C14	B15/n-C15	B16/n-C16	B17/n-C17
Ratios	11.20±0.61	11.59±0.76	10.03±0.60	9.00±0.64	9.02±0.63	9.37±0.64
Correlations (R)	0.76**	0.51**	0.60**	0.56**	0.63**	0.53*
	B18/n-C18	B19/n-C19	B20/n-C20	B21/n-C21	B22/n-C22	
Ratios	9.90±0.73	10.15±0.83	9.71±1.62	10.73±1.97	15.74±5.38	
Correlations (R)	0.65**	0.54**	0.34	0.40*	0.42**	

The asterisks shown in table represent significance. **p < 0.01, *p < 0.05, no asterisks mean p > 0.05.

Table S3. SOA yields that used in this study.

	Species	SOA yields	Species	SOA yields
Speciated IVOCs	Dodecane	0.12	Heneicosane	0.55
	Tridecane	0.3	Docosane	0.55
	Tetradecane	0.4	Naphthalene	0.22
	Pentadecane	0.46	2-Methylnaphthalene	0.26
	Hexadecane	0.51	1-Methylnaphthalene	0.31
	Heptadecane	0.55	Acenaphthylene	0.31
	Pristane	0.46	Acenaphthene	0.31
	Octadecane	0.55	Fluorene	0.31
	Phytane	0.51	Phenanthrene	0.31
	Nonadecane	0.55	Anthracene	0.31
	Eicosane	0.55		
Unspeciate b-alkanes IVOCs	Bin12	0.05	Bin18	0.51
	Bin13	0.09	Bin19	0.55
	Bin14	0.12	Bin20	0.55
	Bin15	0.3	Bin21	0.55
	Bin16	0.4	Bin22	0.55
	Bin17	0.46		
Unspeciated cyclic compounds IVOCs	Bin12	0.12	Bin18	0.55
	Bin13	0.3	Bin19	0.55
	Bin14	0.4	Bin20	0.55
	Bin15	0.46	Bin21	0.55
	Bin16	0.51	Bin22	0.55
	Bin17	0.55		
VOCs	Benzene	0.21	n-Heptane	0.009[a]
	Toluene	0.11	n-Octane	0.041[a]
	Ethylbenzene	0.11	n-Nonane	0.08[a]
	m/p-Xylene	0.06	n-Decane	0.146[a]
	Styrene	0.11	2-Methylhexane	0.009[b]
	o-Xylene	0.06	3-Methylhexane	0.009[b]
	Isopropylbenzene	0.11	2,3-Dimethylpentane	0.009[b]
	n-Propylbenzene	0.11	2,4-Dimethylpentane	0.009[b]
	m-Ethyltoluene	0.11	2,2,4-Trimethylpentane	0.041[c]
	p-Ethyltoluene	0.11	2,3,4-Trimethylpentane	0.041[c]
	1,3,5-Trimethylbenzene	0.06	2-Methylheptane	0.041[c]
	o-Ethyltoluene	0.06	3-Methylheptane	0.041[c]
	1,2,4-Trimethylbenzene	0.06	Cyclohexane	0.04
	1,2,3-Trimethylbenzene	0.06	Methylcyclohexane	0.04[d]

SOA yields of IVOCs and single-ring aromatics were from Zhao et al. (2015); [a] SOA yields are from Lim and Ziemann. (2009); [b] SOA yields are assumed the same as n-Heptane; [c] SOA yields are assumed the same as n-October; [d] SOA yields are assumed the same as cyclohexane.

Table S4. Estimations of IVOCs emission from on-road DVs and GVs and from diesel- and gasoline-fueled engines.

	Diesel vehicles	Gasoline vehicles
Mileage-based EF (mg km^{-1})	62.79±18.37	13.95±1.13
Fleet composition	5%	95%
IVOCs emission percentages	19.1%	80.9%
	Diesel-fueled engines	Gasoline-fueled engines
Fuel-based EFs (mg kg^{-1})	984.9±288.2	239.5±19.5
Fuel consumptions (Tg)	150	120
IVOCs emissions (Gg)	147.7	28.74

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