Supplement for:

Oxygenated VOCs as significant but varied contributors to VOC emissions from vehicles

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Section 1. Calculation of the emission factors and the emission ratios

Mileage-based emission factors (mg·km^{-1}) are calculated using Equation (1)

$$EF_i = \frac{\sum C_i * DR_j * V_j}{1000 \sum L_j} \tag{1}$$

Where EF_i is the emission factor of VOC species i, mg·km^{-1}; C_i is the concentration of VOC species i, μg·m^{-3}; DR_j is the dilution ratio for the test vehicles j; V_j is the exhaust flow rate for the test vehicles j, m^3·s^{-1}; L_j is the distance traveled by the test vehicles j, km. The mileage is based on the number of short transient driving cycle. The distance of a complete short transient driving cycle is 1.013 km.

Fuel-based emission factors (mg·kg$_{fuel}^{-1}$) are calculated using a carbon mass balance approach: Equation (2)

$$EF_i = \frac{\sum C_i * C_F}{\left(\frac{\sum C_{CO2}}{MW_{CO2}} + \frac{\sum C_{CO}}{MW_{CO}}\right) * MW_C} \tag{2}$$

Where EF_i is the emission factor of VOC species i, mg·kg$_{fuel}^{-1}$; C_i, C_{CO2}, and C_{CO} are the concentration of VOC species i, CO_2, and CO, respectively, mg·m^{-3}; C_F is the carbon mass fraction of the fuel, the value was 0.86 used here. MW_{CO2}, MW_{CO} and MW_C are the molecular weights of pollutant CO_2, CO, and carbon, g·mol^{-1}.

Emission ratios (ppb·ppm^{-1}) are calculated using Equation (3)

$$ER_i = \frac{\sum C_i}{\sum C_{co}} \tag{3}$$

Where ER_i is the emission ratio of VOC species i, ppb·ppm^{-1}; C_i and C_{co} are the concentration of VOC species i (ppb) and CO (ppm), respectively.

To calculate the weighted mean of the emission factors and emission ratios, we used the proportion of different standards in various types of gasoline and diesel vehicles, which reported in the China Mobile Source Environmental Management Annual Report (MEEPRC, 2019). Reallocate the proportion based on vehicles which were tested in this study. The proportion of gasoline and diesel vehicles in this study as follows Table S6. And the value of them shown in the table.

Section 2.The limit of detection for the emission factors and the $C_{16}H_{22}O_4H$ (m/z=279) in the mass spectrum

The limit of detection are commonly defined as the concentrations where the ratio of signal-to-noise ratio (S/N) is 3 (Yuan et al., 2017). So the limit of detection for VOC species were calculated, then we got the limit of detection for emission factors. Averaged limit of detection for emission factors in various kind of vehicles are shown in Fig. S13a-c. Due to some of the limit of detection for emission factors were higher than the emission factor in mass spectra accrording to Fig. 3. We choose a gasoline vehicle with China V emission standard to caculate the ratio of the emission factor to the limit of detection for emission factor. As shown in Fig. S13d, although some VOC species were lower than a ratio of 1 (means the emission factors were lower than the limit of detection), VOC species higher than a ratio of 1 contributed more than 90% of the total emission in mass spetra.

Time series of the $C_{16}H_{22}O_4H$ (m/z=279), several aromatics and OVOC species measured by proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS) during the test are shown in Fig. S8. Apparently, the temporal variations of the $C_{16}H_{22}O_4H$ is different from other VOC species, it had been increasing gradually. While the signal of it in the period of the background correction is significantly higher than other VOC species, and the signal of the $C_{16}H_{22}O_4H$ during the test of the vehicles are not always higher than that of the background correction.

Section 3. Calculation of the carbon oxidation states ($\overline{OS_C}$)

The scatterplot of $\overline{OS_C}$ as the function of carbon number, provides a framework for describing the bulk chemical properties and the evolution of organics (Kroll et al., 2011). The approximate $\overline{OS_C}$ was calculated as Equation (4)

$$\overline{OS_C} = 2 \times \frac{O}{C} - \frac{H}{C} \quad (4)$$

For $C_xH_yN_{1,2}O_z$ compounds, the influence of N is dependent on functional groups so we made several assumptions to classify them. (1) N-containing functional groups are nitro (-NO_2) or nitrate (-NO_3) in our case; (2) N-containing aromatics feature nitro moieties and N-containing aliphatic hydrocarbons feature nitrate moieties; (3) N-containing aromatics have 6-9 carbon atoms and less hydrogen atoms than aliphatic hydrocarbons with the same carbon atoms. This was not an absolutely right classification but at least it provided a rough separation between nitro compounds and nitrate compounds for most $C_xH_yN_{1,2}O_z$ species. After the above step, $3 \times \frac{N}{C}$ and $5 \times \frac{N}{C}$ was minus from Equation (5) for nitro compounds and for nitrate compounds, respectively.

$$\overline{OS_C} = 2 \times \frac{O}{C} - \frac{H}{C} - (3\ or\ 5) \times \frac{N}{C} \quad (5)$$

Section 4.The fractions of OVOCs in total VOC emissions

Combined with the measurements of other VOCs (Table. S4) from canisters measured by gas chromatography-mass spectrometer/flame ionization detector (GC-MS/FID), the fractions of OVOCs in total VOC emissions can determined for different vehicles. Due to the emission factors of toluene from PTR-ToF-MS and the offline canister-GC-MS/FID were consistent, the VOCs/toluene ratio were used to evaluate the fractions of OVOCs in total VOC emissions, calculated using Equation (6)

$$Fraction_{OVOCs,i} = \frac{\frac{EF_{OVOCs,i}}{EF_{toluene,PTR}}}{\left(\sum\frac{EF_{OVOCs,i}}{EF_{toluene,PTR}} + \sum\frac{EF_{other\ VOC,i}}{EF_{toluene,GC}}\right)} * 100\% \quad (6)$$

Where $Fraction_{OVOCs,i}$ is the fraction of OVOC species i; $EF_{OVOCs,i}$, and $EF_{toluene,PTR}$ are the emission factors of OVOC species i and toluene measured by PTR-ToF-MS, and $EF_{other\ VOC,i}$ and $EF_{toluene,GC}$ are the emission factors of other VOC species i and toluene measured by offline canister-GC-MS/FID.

Supplement tables

Table S1. Detailed information of the test gasoline vehicles used in chassis dynamometer tests.

Number	Fuel type	Vehicle type	Emission standard	Model year	Odometer /km	Displacement /ml	After-treatment
1				2001	210188	2500	
2			China I	2002	171876	2300	
3				2003	344417	1800	
4				2005	224329	3000	
5			China II	2004	488319	3000	
6				2005	N/A[a]	1600	
7				2009	136766	2000	
8			China III	2010	112389	2300	
9				2010	194555	1591	
10	Gasoline	LDGV		N/A	109024	2384	TWC
11			China IV	2014	155155	2500	
12				2011	59622	1200	
13				2016	114690	1998	
14			China V	2017	75064	2457	
15				2019	15382	1495	
16				2019	2479	1998	
17			China VI	2019	3121	1998	
18				2019	838	1998	

[a]: N/A stands for "not available".

Table S2. Detailed information of the test diesel and LPG vehicles used in chassis dynamometer tests.

Number	Fuel type	Vehicle type	Emission standard	Model year	Odometer /km	Displacement /ml	After-treatment
19				2013	39465	3800	N/A[a]
20			China III	2013	173046	2800	N/A
21				2012	370000	2800	N/A
22				N/A	53072	2800	SCR[b]
23		LDDT	China IV	2016	157982	3800	N/A
24				2013	166200	2800	SCR
25				2018	12749	2800	SCR
26			China V	2018	55358	2800	SCR
27	Diesel			2018	36336	3000	SCR
28			China III	2013	128694	4752	N/A
29		MDDT	China IV	2016	178567	5900	N/A
30			China V	2016	62952	3767	N/A
31			China III	2013	450000	6618	N/A
32		HDDT	China IV	N/A	175679	4040	N/A
33			China V	N/A	53949	N/A	SCR + DPF[c]
34		BUS	China III	2012	800000	9726	N/A
35			China IV	2015	155308	8424	N/A
36			China IV	2013	383946	1800	N/A
37	LPG	Taxi	China V	2016	366037	1795	N/A
38				2017	282809	1600	N/A

[a]: N/A stands for "not available". [b]: Selective Catalytic Reduction system. [c]: Diesel Particulate Filter.

Table S3. Sensitivities of PTR-ToF-MS for various VOC species calibrated with standard gas and Liquid Calibration Unit (LCU).

VOC species	Ion formula	Sensitivity, cps·ppb^{-1}
Species calibrated with gas standard		
Formaldehyde	CH_2OH^+	1169.23
Methanol	CH_4OH^+	1048.04
Acetonitrile	$C_2H_3NH^+$	3507.61
Acetaldehyde	$C_2H_4OH^+$	3297.24
Ethanol	$C_2H_6OH^+$	118.69
Acrolein	$C_3H_4OH^+$	3932.01
Acetone	$C_3H_6OH^+$	4641.00
Furan	$C_4H_4OH^+$	2745.69
Isoprene	$C_5H_8H^+$	2246.04
MVK	$C_4H_6OH^+$	4349.71
MEK	$C_4H_8OH^+$	4732.40
Benzene	$C_6H_6H^+$	3115.08
2-Pentanone	$C_5H_{10}OH^+$	3846.20
Toluene	$C_7H_8H^+$	3888.95
Phenol	$C_6H_6OH^+$	4617.76
Furfural	$C_5H_4O_2H^+$	8402.87
Methyl Isobutyl Ketone	$C_6H_{12}OH^+$	3207.56
Styrene	$C_8H_8H^+$	4825.33
O-xylene	$C_8H_{10}H^+$	4431.81
m-Cresol	$C_7H_8OH^+$	5790.90
1,2,4-Teimethylbenzene	$C_9H_{12}H^+$	4665.09
Naphthalene	$C_{10}H_8H^+$	6011.85
a-Pinene	$C_{10}H_{16}H^+$	1985.46
Species calibrated with the Liquid Calibration Unit (LCU)		
Formic acid	$CH_2O_2H^+$	856.60
Acetic acid	$C_2H_4O_2H^+$	1711.00
Propionic acid	$C_3H_6O_2H^+$	2072.00
Butyric acid	$C_4H_8O_2H^+$	2358.00
Pyrrole	$C_4H_5NH^+$	3219.67
Formamide	CH_3NOH^+	3252.52
Acetamide	$C_2H_5NOH^+$	4522.49
Catechol	$C_6H_6O_2H^+$	1856.04
Guaiacol	$C_7H_8O_2H^+$	5461.15
2-Nitrophenol	$C_6H_5NO_3H^+$	4075.26
2-Nitro-p-Cresol	$C_7H_7NO_3H^+$	2129.25

Table S4. VOCs list analysis by offline Canister-GC-MS/FID.

Num	Species	Num	Species	Num	Species
Alkanes (29)		33	1-Butene	64	1,1-Dichloroethene
1	Ethane	34	Cis-2-Butene	65	Cis-1,2-dichloroethylene
2	Propane	35	Trans-2-butene	66	Trans-1,2-Dichloroethene
3	n-Butane	36	Isoprene	67	1,1-Dichloroethane
4	Isobutane	37	1-Pentene	68	1,2-Dichloroethane
5	Cyclopentane	38	Cis-2-pentene	69	Vinyl Bromide
6	n-Pentane	39	Trans-2-pentene	70	Cis-1,3-dichloropropene
7	Isopentane	40	1-Hexene	71	Trans-1,3-dichloropropene
8	Cyclohexane	41	Acetylene	72	Chlorobenzene
9	Methyl-cyclopentane	**Aromatics (16)**		73	1,2-Dichloropropane
10	2-Methylpentane	42	Benzene	74	Chloroform
11	3-Methylpentane	43	Toluene	75	Freon-12
12	2,2-Dimethyl-butane	44	Styrene	76	Benzyl Chloride
13	2,3-Dimethylbutane	45	Ethyl-benzene	77	Trichloroethylene
14	n-Hexane	46	o-Xylene	78	1,1,1-Trichloroethane
15	Methyl-cyclohexane	47	m/p-Xylene	79	1,1,2-Trichloroethane
16	n-Heptane	48	n-Propylbenzene	80	Freon-11
17	2-Methyl-hexane	49	Isopropylbenzene	81	1,2-Dichlorobenzene
18	3-Methyl-hexane	50	o-Ethyltoluene	82	1,3-Dichlorobenzene
19	2,3-Dimethyl-pentane	51	m-Ethyltoluene	83	1,4-Dichlorobenzene
20	2,4-Dimethylpentane	52	p-Ethyltoluene	84	Carbon Tetrachloride
21	2,2,4-Trimethyl-pentane	53	1,2,3-Trimethylbenzene	85	Bromodichloromethane
22	2,3,4-Trimethyl-pentane	54	1,2,4-Trimethylbenzene	86	Tetrachloroethylene
23	2-Methyl-heptane	55	1,3,5-Trimethyl-benzene	87	1,1,2,2-Tetrachloroethane
24	3-Methyl-heptane	56	m-Diethylbenzene	88	Freon-114
25	n-Octane	57	p-Diethylbenzene	89	1,2,4-Trichlorobenzene
26	n-Nonane	**Halohydrocarbon (37)**		90	Freon-113
27	n-Decane	58	Chloromethane	91	1,2-Dibromoethane
28	n-U0ecane	59	Vinyl-chloride	92	Dibromochloromethane
29	n-Dodecane	60	Chloroethane	93	Bromoform
Alkenes and Alkynes (12)		61	Allyl Chloride	94	Hexachloro-1,3-butadiene
30	Ethylene	62	Methylene-chloride	**Others (1)**	
31	Propene	63	Bromomethane	95	Carbon disulphide
32	1,3-Butadiene				

Table S5. The average emission factors of CO_2 in various kinds of vehicles.

Fuel type	EF	Arithmetic mean	Weighted mean
Gasoline	$g \cdot km^{-1}$	319.8±53.0	286.9±58.2
	$g \cdot kg_{fuel}^{-1}$	310.9±35.7	310.3±35.5
Diesel	$g \cdot km^{-1}$	444.8±80.0	412.0±81.9
	$g \cdot kg_{fuel}^{-1}$	313.2±9.26	312.8±16.6
LPG	$g \cdot km^{-1}$	335.4±45.3	
	$g \cdot kg_{fuel}^{-1}$	311.5±29.2	

Table S6. Vehicle distribution in terms of various vehicle types and emission standard used in calculation of weighted mean for emission factor (MEEPRC, 2019).

(a) Gasoline vehicles

Emission standard	China I	China II	China III	China IV	China V/VI
Proportion %	3	4.5	19.1	42.5	30.9

(b) Diesel vehicles

Vehicle type	LDDT			MDDT			HDDT			Bus	
Emission standard	III	IV	V	III	IV	V	III	IV	V	III	IV
Proportion %	23.1	17.5	7.4	2.8	2.2	0.9	15.7	11.9	5.0	6.5	7.0

Supplement figures

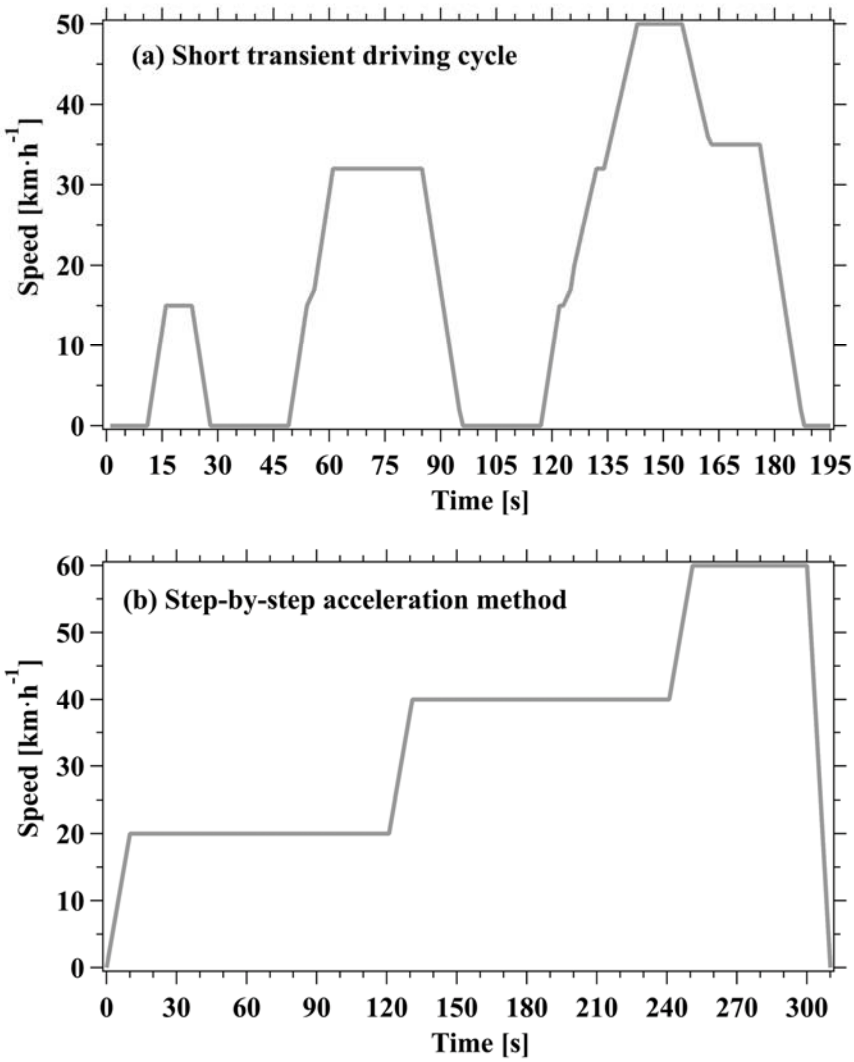

Figure S1. Speed change of the test vehicles in (a) the short transient driving cycle (GB 18285-2018) and (b) the step-by step acceleration method.

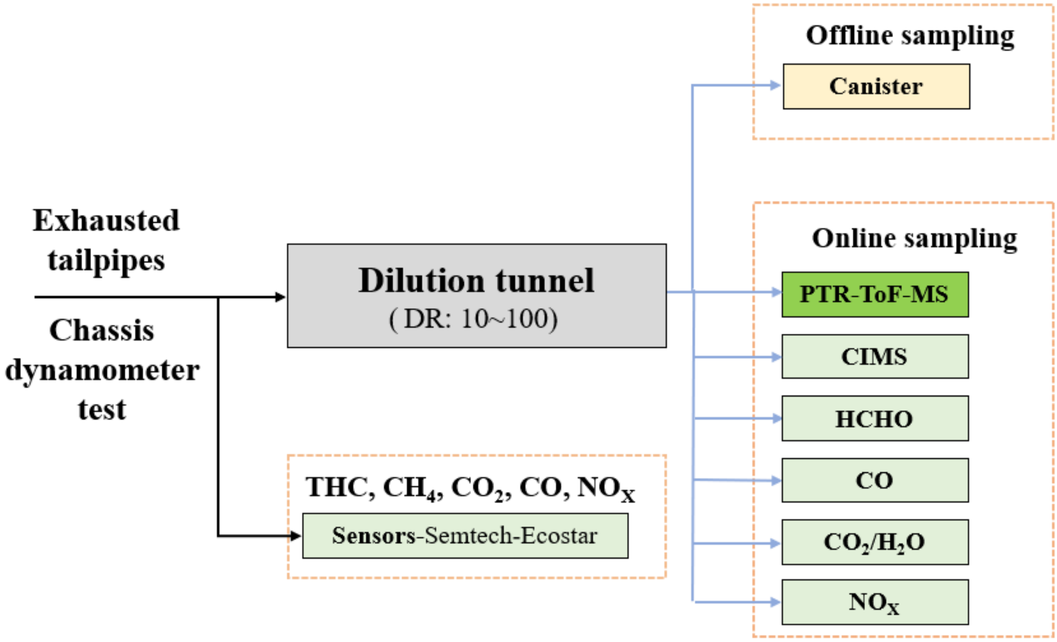

Figure S2. Diagram of the test setup used in the experiments including dilution system and instrumentation.

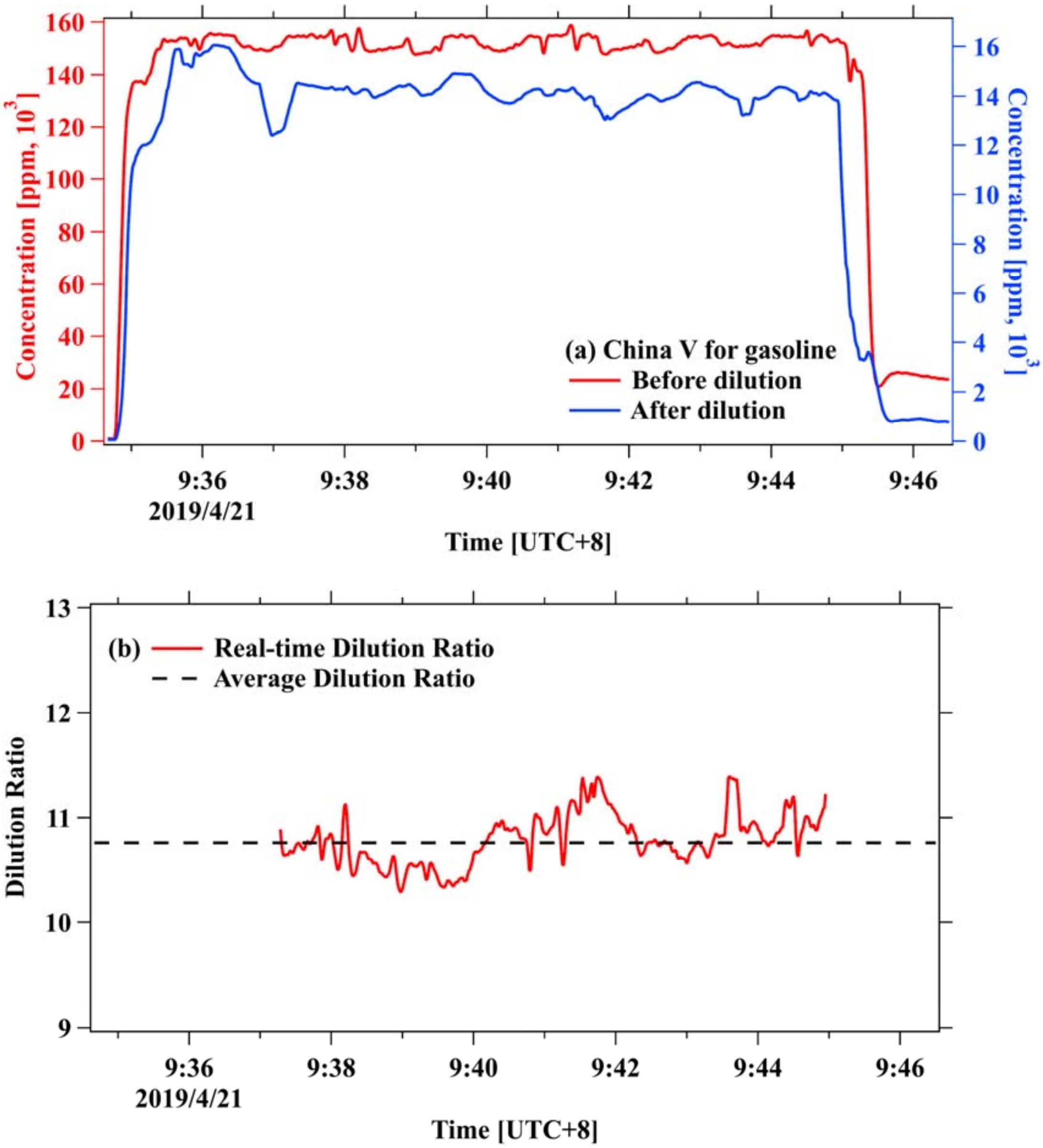

Figure S3. (a) Compared the concentration of CO_2 before and after dilution for a gasoline vehicle with the emission standard of China V. (b) Time series of real-time dilution ratio calculated by the concentration of CO_2, and the dashed line is average dilution ratio.

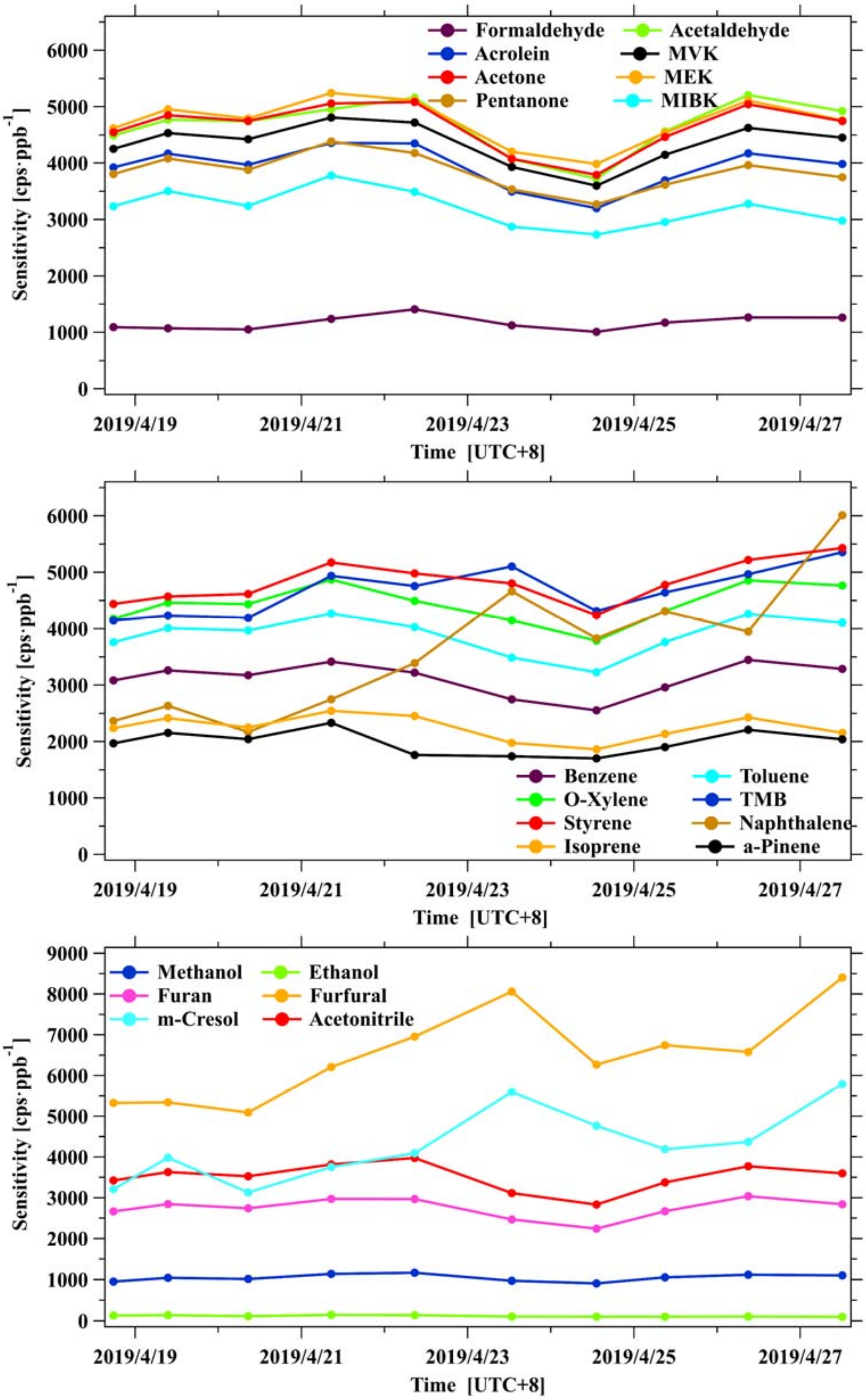

Figure S4. Calibration results of PTR-ToF-MS for different species during the campaign.

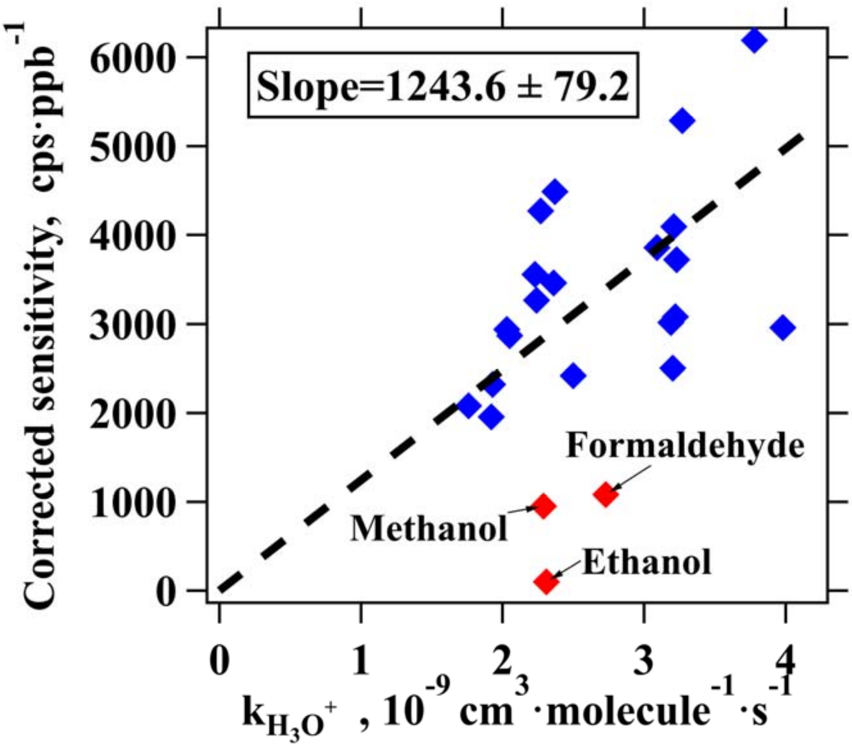

Figure S5. Corrected sensitivities as a function of kinetic rate constants for proton-transfer reactions of H_3O^+ with VOCs. The dashed line indicates the fitted line for blue points. The red points are not used, as these compounds (formaldehyde, methanol, ethanol) are known to have lower sensitivities.

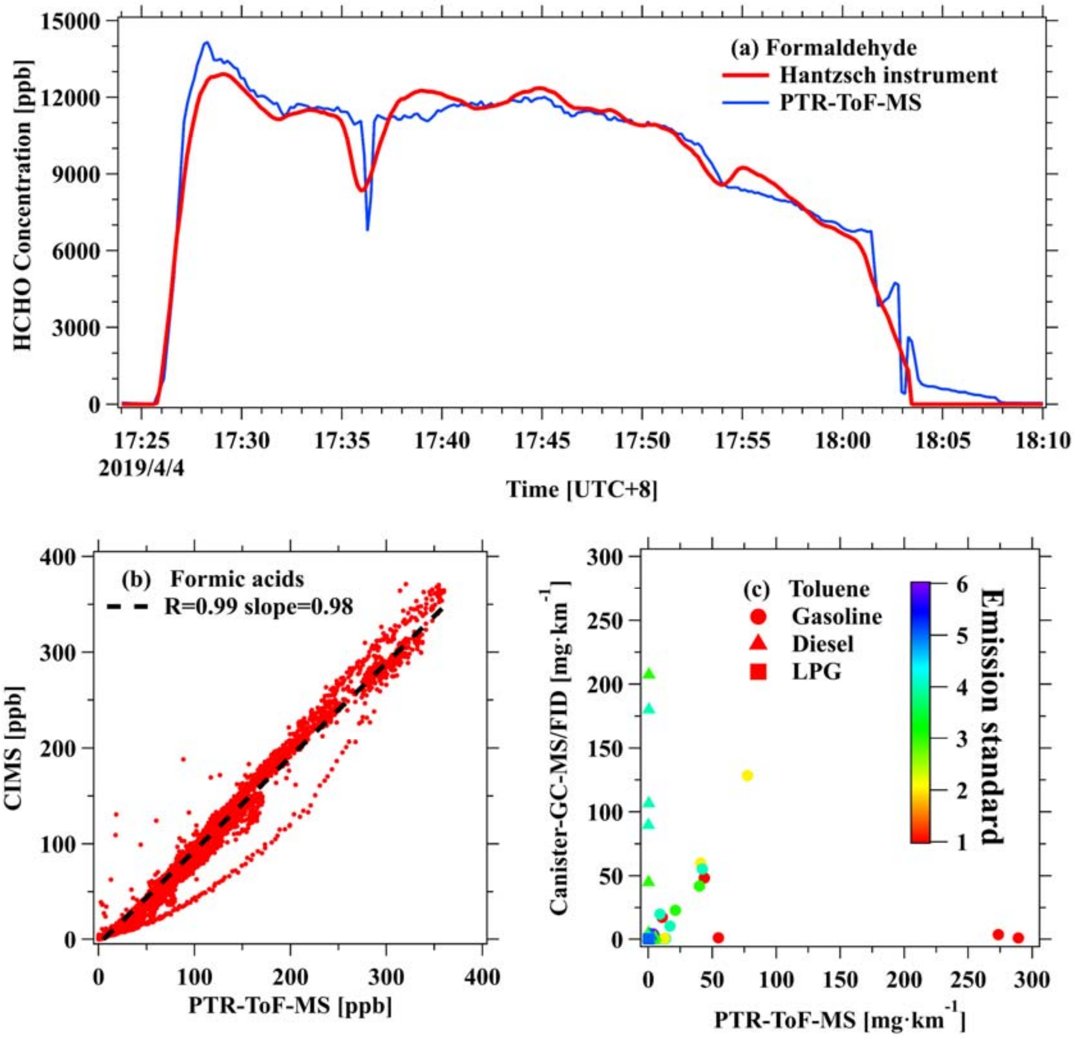

Figure S6. (a) Time series of formaldehyde measured by PTR-ToF-MS and the Hantzsch instrument. (b) Scatterplot of the concentration of formic acid between PTR-ToF-MS and the CIMS. (c) Scatterplot of the emission factor of toluene calculated by the data detected by PTR-ToF-MS and Canister-GC-MS/FID.

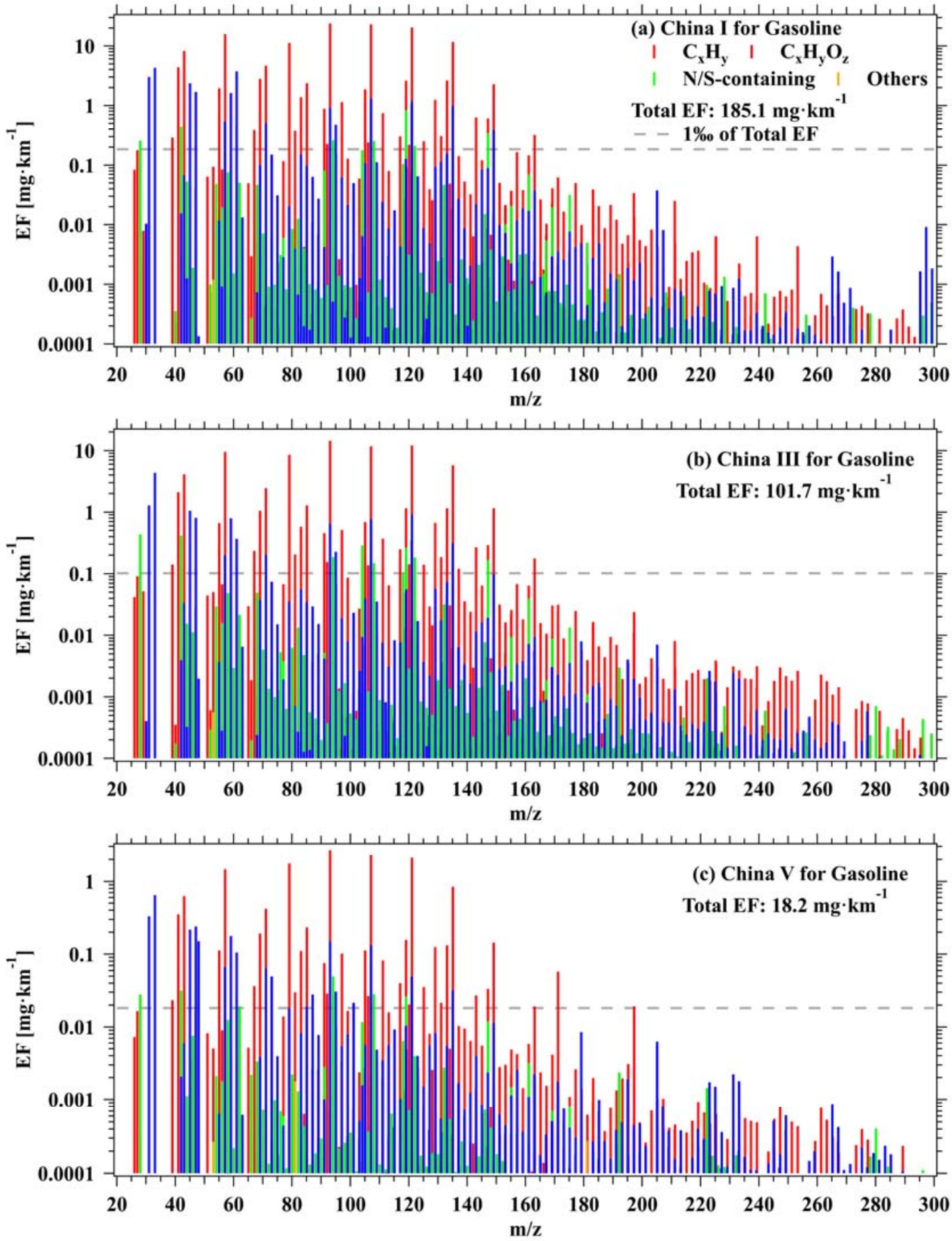

Figure S7. The determined average mileage-based emission factors of VOC species measured by PTR-ToF-MS from (a) China I, (b) China III, and (c) China V gasoline vehicles. The gray dashed lines represent 1‰ of total VOCs emission factors.

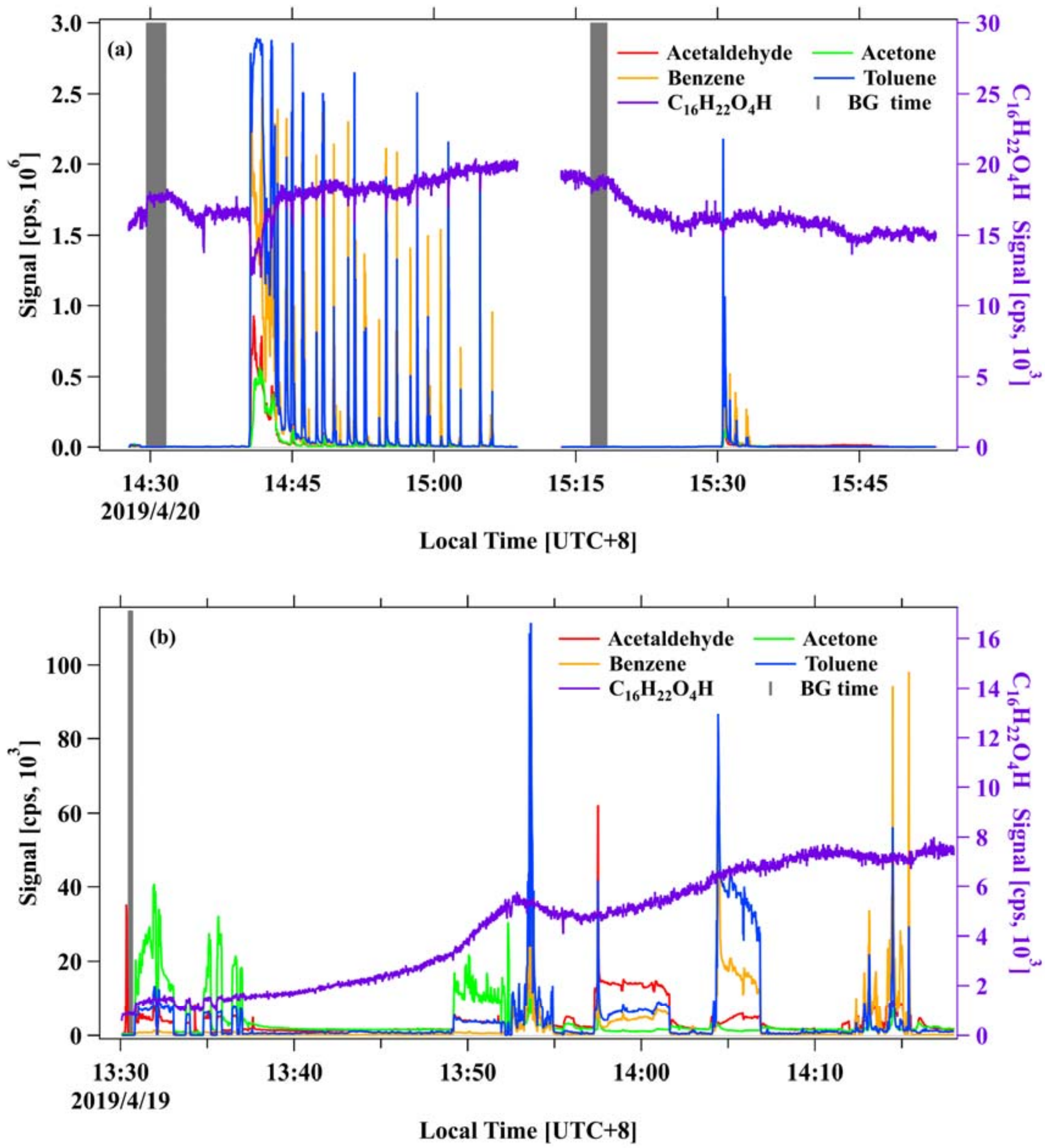

Figure S8. Real-time signals of acetaldehyde, acetone, benzene, toluene, and the $C_{16}H_{22}O_4H$ (m/z=279) of (a) a gasoline vehicle with China I emission standard from cold start and hot start. (b) Several gasoline vehicles with different emission standard measured by PTR-ToF-MS. The shaded areas represent the period of background.

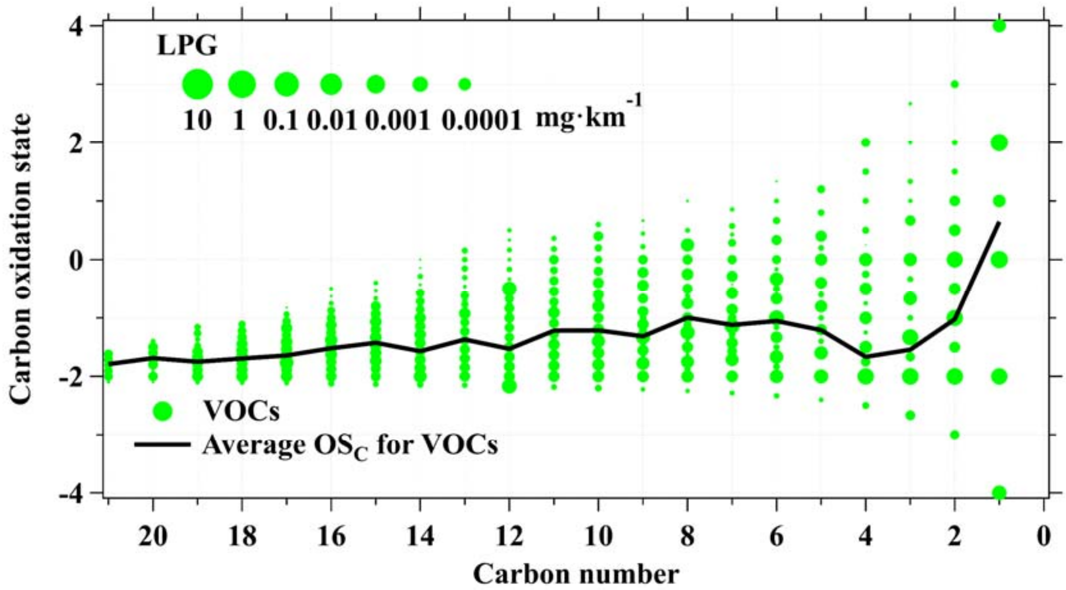

Figure S9. The two-dimensional space of $\overline{OS_C} - n_C$ with data points sized coded using emission factors of VOC species from LPG vehicles. The black line is the average $\overline{OS_C}$ of each carbon number for VOC species in LPG vehicles.

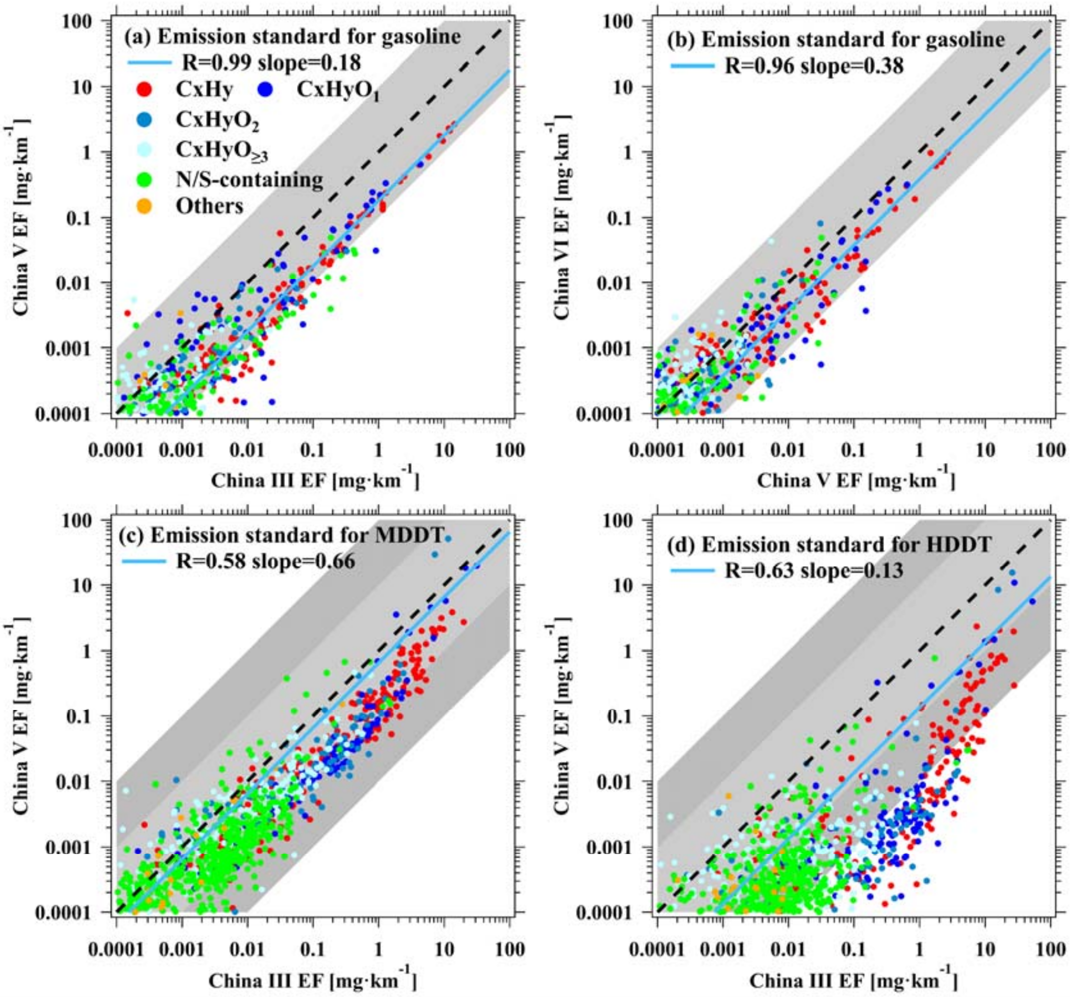

Figure S10. Scatterplots of VOCs emission factors between China III and China V emission standard (a) and between China V and China VI emission standard for gasoline vehicles(b). Scatterplots of VOCs emission factors between China III and China V emission standard for LDDT (c) and HDDT(d). Each data point indicates a VOC species measured by PTR-ToF-MS. The blue lines are the fitted results for all data points. The black dashed lines represent 1:1 ratio, and the shaded areas represent ratios of a factor of 10 and 100.

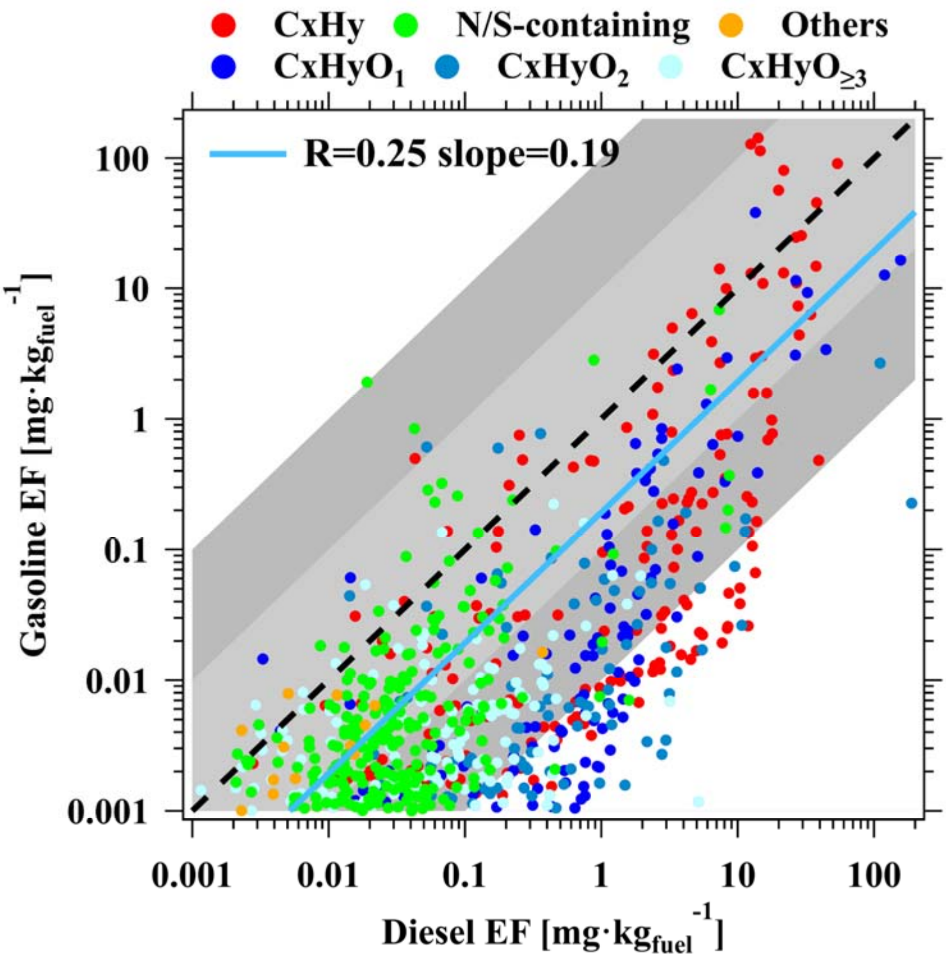

Figure S11. Scatterplot of the determined average fuel-based emission factors ($mg \cdot kg_{fuel}^{-1}$) of VOCs between gasoline and diesel vehicles. Each data point indicates a VOC species measured by PTR-ToF-MS. The blue line is the fitted result for all data points. The black line represents 1:1 ratio, and the shaded areas represent ratios of a factor of 10 and 100.

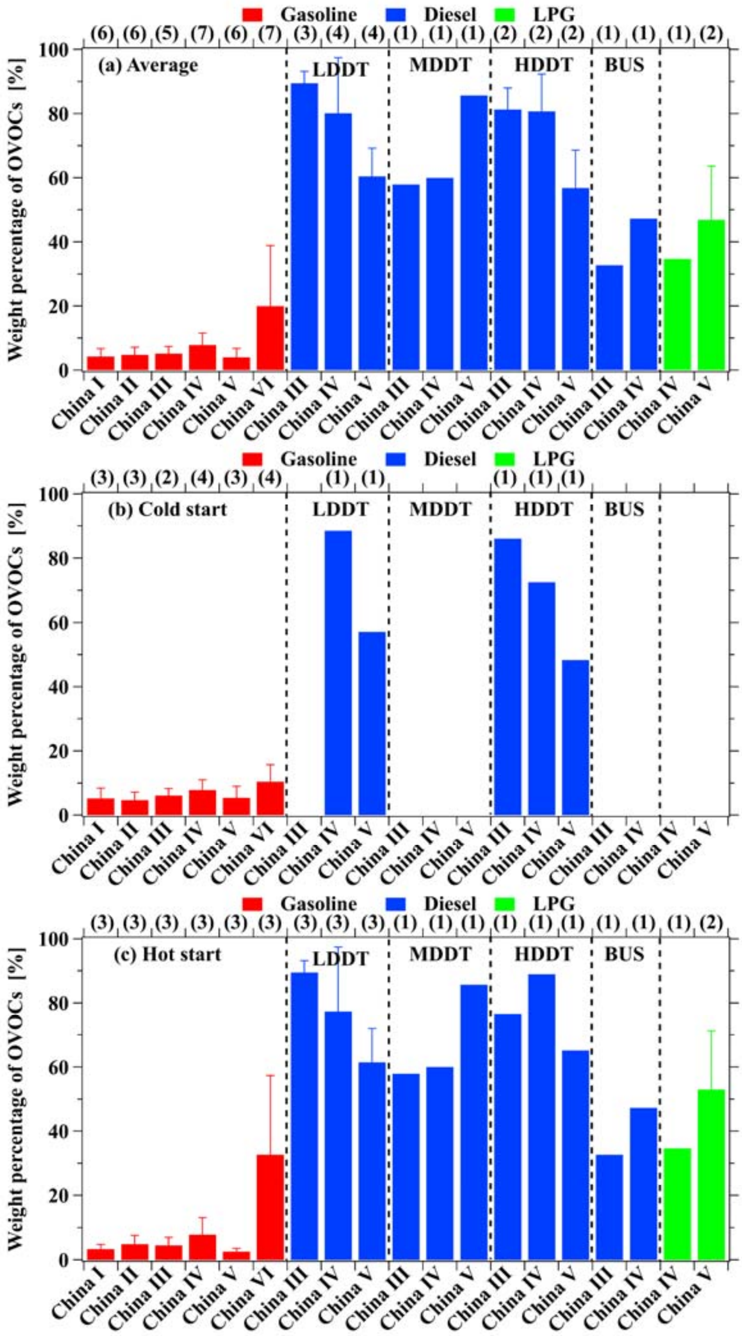

Figure S12. (a) Average OVOC fractions for vehicles with different emission standards, and some difference between (b) cold start and (c) hot start. Error bars represent the standard deviations of the fraction of OVOCs.

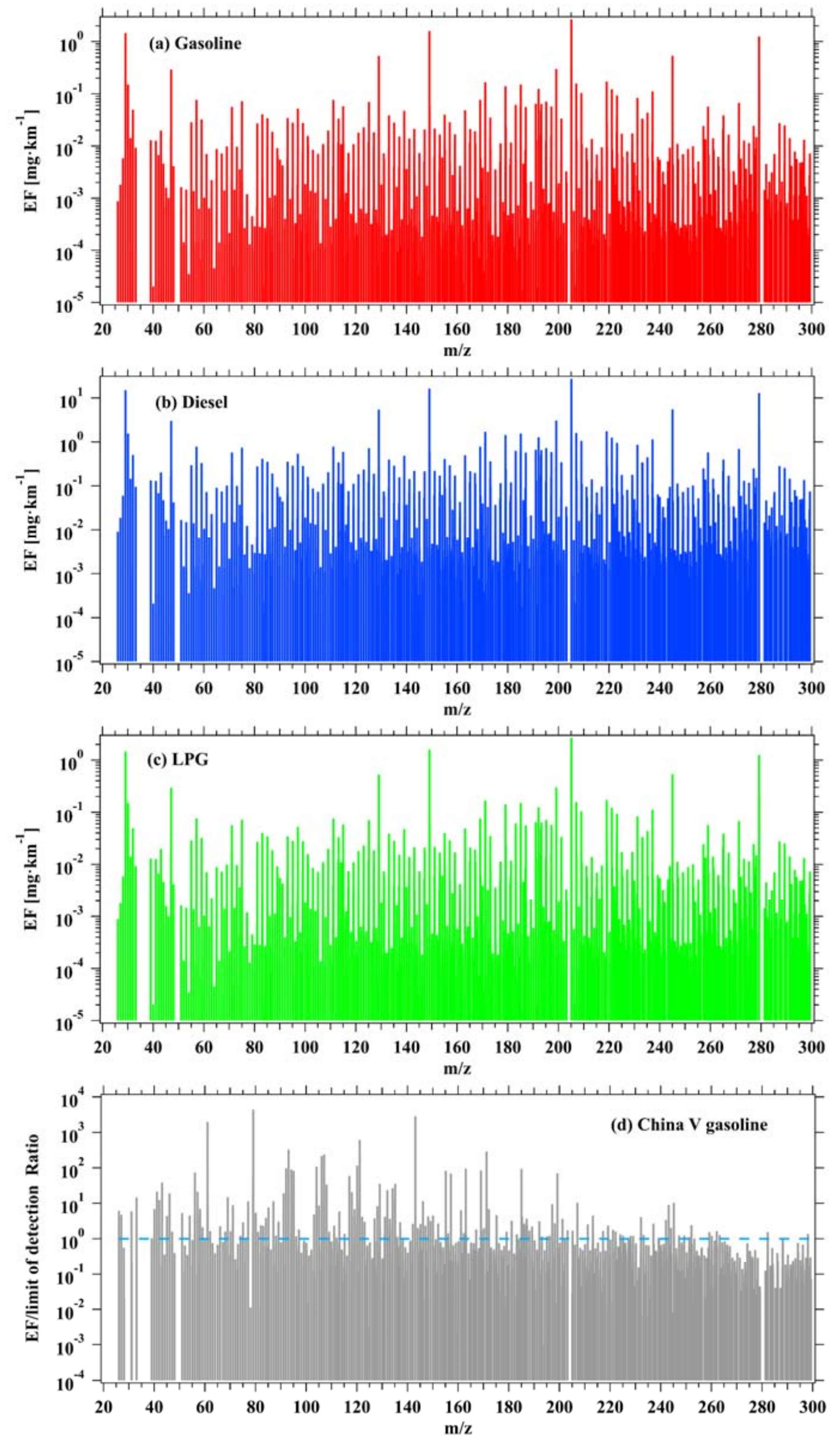

Figure S13. The limit of detection for emission factors in (a) gasoline (b) diesel, and (c) LPG vehicles. (d) The ratio of emission factors to the limit of detection in a China V gasoline vehicle, and the blue dashed lines represent a ratio of 1.

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