Supplement for:

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

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Section 1. Supporting information for test vehicles in this study

Chemical composition of gasoline and diesel fuel in China

Fuel composition is one of the determining factor for VOCs emissions from vehicles (Gentner et al., 2017). The gasoline fuel used in China is mainly comprised of C_4-C_7 hydrocarbons. The chemical compositions of gasoline fuel are alkanes (55%-62%), alkenes (12%-17%), aromatics (27%-32%), and methyl tert-butyl ether (MTBE, 1%-4%) (Tang et al., 2015;Sun et al., 2021;Qi et al., 2021;Huang et al., 2022). Heavy hydrocarbons, namely C_8-C_{10} alkanes and aromatics, contributed most in diesel fuel. The chemical compositions of diesel are alkanes (70%-79%), alkenes (1%-7%), and aromatics (21%-25%) (Wang et al., 2015;Yue et al., 2015;Hou and Jiang, 2018;Liu and Zhang, 2015). Gasoline and diesel fuel are summer blends, and the gasoline fuel does not contain ethanol in this study.

China VI emission standard in China

The limits and measurement methods for emissions of light-duty vehicles (GB18352.6-2016; known as the China VI standard) have been recently introduced in China, which applies to light-duty vehicles using gasoline and diesel fuel. The China VI emission standard continued the EU standard system as the reference with various regulation details integrated from US emissions standards (Lyu et al., 2020). Vehicle emission limits are significantly lower for the China VI standard (Table S7, Table S8). For example, limits on gasoline vehicle exhaust emissions were tightened by 30 to 50% from China V to China VI, and a new particulate number (PN) limit was added in gasoline vehicles (Lyu et al., 2020).

Cold start in gasoline and diesel vehicles

Cold start, which occurs after several hours of nonoperation for vehicles (Drozd et al., 2016), is a major source of emissions for gasoline vehicles and have greater emissions due to two issues: (1) low engine temperatures lead to incomplete combustion that allow non/partially combusted fuel compounds to exit engine cylinders. (2) Effective operation of the catalytic converter requires a warm-up period to reach sufficient catalyst operating temperatures (Gentner et al., 2017;George et al., 2015). Due to diesel emissions have emphasized control of primary $PM_{2.5}$ and NO_X emissions, the after-treatment devices of diesel vehicles (e.g. DOC, DPF, SCR etc.) do not aim for VOCs control.

Section 2. Calculation of the emission factors and the emission ratios

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

$$EF_i = \frac{\sum C_i * DR_j * V_j}{1000 \sum L_j} \quad (1)$$

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

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

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

Where EF_i is the emission factor of VOC species i, $mg \cdot kg_{fuel}^{-1}$; C_i, C_{CO2}, and C_{CO} are the concentration of VOC species i, CO_2, and CO, respectively, $mg \cdot m^{-3}$; 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, $g \cdot mol^{-1}$.

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

$$ER_i = \frac{\sum C_i}{\sum C_{co}} \quad (3)$$

Where ER_i is the emission ratio of VOC species i, $ppb \cdot ppm^{-1}$; 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 S1. And the value of them shown in the table.

Section 3.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). Here, the limit of detection for VOC mixing ratios were calculated and applied to estimate the limit of detection for emission factors. Averaged limit of detection for emission factors in various vehicles are shown in Fig. S12a-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 calculate the ratio of the emission factor to the limit of detection for emission factor. As shown in Fig. S12d, 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.

It should be noted that the signals of $C_{16}H_{22}O_4H$ (m/z=279) were higher during the tests based on determined emission factors. However, we suspect that it may be emitted artifacts from the sampling or dilution system as it mainly showed higher signals in the latter period of each test when sampling materials absorb more heat from vehicle exhausts (Fig. S13), and thus it is not included in Fig. 5.

Section 4. 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)

$$\overline{OS_C} = 2 \times \frac{O}{C} - \frac{H}{C} \tag{4}$$

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.

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

Section 5. The feasibility of the C_{14} aromatics/toluene ratio used as diagnostic for diesel versus gasoline vehicles

It is necessary to consider the atmospheric lifetime of C_{14} aromatics and toluene for oxidation when used the C_{14} aromatics/toluene ratio as diagnostic for diesel versus gasoline vehicles. Here, we consider the change of C_{14} aromatics/toluene ratio with the OH reaction in the atmosphere (de Gouw et al., 2005):

$$\frac{[C_{14}\text{ aromatics}]}{[Toluene]} = ER \times exp[-(k_{C14} - k_{Toluene})[OH] \times t] \qquad (6)$$

Where $[C_{14}$ aromatics$]$ and $[Toluene]$ are the concentrations of C_{14} aromatics and toluene, respectively. ER is the emission ratio of C_{14} aromatics versus toluene (1.42 in diesel vehicles and 3.7E-4 in gasoline vehicles). $[OH]$ is the concentration of OH radicals (mole·cm^{-3}). k is the rate constant of the OH reaction with toluene (5.63×10^{-12} cm^3·mole^{-1}·s^{-1}) (Atkinson and Arey, 2003) and C_{14} aromatics, respectively. t is the photochemical age. Here, an averaged OH concentration in the PRD, China with 1.5×10^6 mole·cm^{-3} is used (Wang et al., 2020;Tan et al., 2019). The average rate constant for C_{14} aromatics has not been reported, so we assume a rate constant similar to representative C_{12} aromatics (1.33×10^{-10} $cm^3 \cdot mole^{-1} \cdot s^{-1}$) (Alarcon et al., 2015;Berndt and Böge, 2001), which may be a little lower than the real value of C_{14} aromatics rate constant.

Based on the Equation (6), the C_{14} aromatics/toluene ratio emitted from diesel vehicles will be higher than emission ratio of gasoline vehicles for photochemical reactions shorter than 12 h. Therefore, the C_{14} aromatics/toluene ratio could be applied to the ambient measurements in urban or downwind regions, especially for roadside measurements or tunnel study to distinguish the emission of diesel and gasoline vehicles. Therefore, we conclude that the C_{14} aromatics/toluene ratio should be applied for distinguishing emissions of gasoline and diesel vehicles in ambient measurements of urban or downwind regions, especially for roadside measurements or tunnel study to distinguish the emission of diesel and gasoline vehicles.

Section 6.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 as Equation (7)

$$Fraction_{OVOCs,i} = \frac{\frac{EF_{OVOCs,i}}{EF_{toluene,PTR}}}{\left(\sum\frac{EF_{OVOCs,i}}{EF_{toluene,PTR}}+\sum\frac{EF_{other\ VOC,i}}{EF_{toluene,GC}}\right)} * 100\% \qquad (7)$$

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. 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

Table S2. 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
1	Gasoline	LDGV	China I	2001	210188	2500
2				2002	171876	2300
3				2003	344417	1800
4			China II	2005	224329	3000
5				2004	488319	3000
6				2005	N/A[b]	1600
7			China III	2009	136766	2000
8				2010	112389	2300
9				2010	194555	1591
10			China IV	N/A	109024	2384
11				2014	155155	2500
12				2011	59622	1200
13			China V	2016	114690	1998
14				2017	75064	2457
15				2019	15382	1495
16			China VI[a]	2019	2479	1998
17				2019	3121	1998
18				2019	838	1998

[a]: China VI emission standard for the test gasoline vehicles is actually China VIa emission standard in this study. [b]: N/A stands for “not available”.

Table S3. 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
19				2013	39465	3800
20			China III	2013	173046	2800
21				2012	370000	2800
22				N/A	53072	2800
23		LDDT	China IV	2016	157982	3800
24				2013	166200	2800
25				2018	12749	2800
26			China V	2018	55358	2800
27	Diesel			2018	36336	3000
28			China III	2013	128694	4752
29		MDDT	China IV	2016	178567	5900
30			China V	2016	62952	3767
31			China III	2013	450000	6618
32		HDDT	China IV	N/A	175679	4040
33			China V	N/A	53949	N/A
34		Bus	China III	2012	800000	9726
35			China IV	2015	155308	8424
36			China IV	2013	383946	1800
37	LPG	Taxi	China V	2016	366037	1795
38				2017	282809	1600

Table S4. 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 S5. 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	i-Butane	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	i-Pentane	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	Ethylbenzene	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	i-Propylbenzene	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-Trimethylbenzene	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	**Halohydrocarbons (37)**		90	Freon-113
27	n-Decane	58	Chloromethane	91	1,2-Dibromoethane
28	n-Undecane	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 S6. 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 S7. Vehicle emission standards from China I - ChinaVI for light-duty vehicles (Gas: Gasoline vehicles, Die: Diesel vehicles).

Emission standard	Effective year	Vehicle category		Emission limits ($mg \cdot km^{-1}$) CO		THC		NMHC		NO_X		N_2O		PM		PN ($number \cdot km^{-1}$)	
				Gas	Die	Gas	Die	Gas	Die	Gas	Die	Gas	Die	Gas	Die	Gas	Die
China I	2001	Cat1	-	2720	2720	970	970	-	-	-	-	-	-	-	140	-	-
		Cat2	I	2720	2720	970	970	-	-	-	-	-	-	-	140	-	-
			II	5170	5170	1400	1400	-	-	-	-	-	-	-	190	-	-
			III	6900	6900	1700	1700	-	-	-	-	-	-	-	250	-	-
China II	2004	Cat1	-	2200	1000	500	700	-	-	-	-	-	-	-	80	-	-
		Cat2	I	2200	1000	500	700	-	-	-	-	-	-	-	80	-	-
			II	4000	1250	600	1000	-	-	-	-	-	-	-	120	-	-
			III	5000	1500	700	1200	-	-	-	-	-	-	-	170	-	-
China III	2009	Cat1	-	2300	640	200	-	-	-	150	500	-	-	-	50	-	-
		Cat2	I	2300	640	200	-	-	-	150	500	-	-	-	50	-	-
			II	4170	800	250	-	-	-	180	650	-	-	-	70	-	-
			III	5220	950	290	-	-	-	210	780	-	-	-	100	-	-
China IV	2013	Cat1	-	1000	500	100	-	-	-	80	250	-	-	-	25	-	-
		Cat2	I	1000	500	100	-	-	-	80	250	-	-	-	25	-	-
			II	1810	630	130	-	-	-	100	330	-	-	-	40	-	-
			III	2270	740	160	-	-	-	110	390	-	-	-	60	-	-
China V	2017	Cat1	-	1000	500	100	-	68	-	60	180	-	-	4.5	4.5	-	6×10^{11}
		Cat2	I	1000	500	100	-	68	-	60	180	-	-	4.5	4.5	-	6×10^{11}
			II	1810	630	130	-	90	-	75	265	-	-	4.5	4.5	-	6×10^{11}
			III	2270	740	160	-	108	-	82	280	-	-	4.5	4.5	-	6×10^{11}
China VI a	2021	Cat1	-	700		100		68		60		20		4.5		6×10^{11}	
		Cat2	I	700		100		68		60		20		4.5		6×10^{11}	
			II	880		130		90		75		25		4.5		6×10^{11}	
			III	1000		160		108		82		30		4.5		6×10^{11}	
China VI b	2023	Cat1	-	500		50		35		35		20		3		6×10^{11}	
		Cat2	I	500		50		35		60		20		3		6×10^{11}	
			II	630		65		45		45		25		3		6×10^{11}	
			III	720		80		55		50		30		3		6×10^{11}	

Cat1: Passenger cars with no more than six seats and test mass (TM, kg))≤2500; Cat2:Other light-duty vehicles, I: TM≤1305, II: 1305＜TM≤ 1760, III: TM＞1760;

Table S8. Vehicle emission standards from China I - ChinaV for heavy-duty diesel engines (HDDE).

Emission standard	**Effective year**	**CO ($g \cdot kW \cdot h^{-1}$)**	**THC ($g \cdot kW \cdot h^{-1}$)**	**NMHC ($g \cdot kW \cdot h^{-1}$)**	**NOx ($g \cdot kW \cdot h^{-1}$)**	**PM ($g \cdot kW \cdot h^{-1}$)**
China I	2001	4.5	1.1		8	0.36
China II	2004	4	1.1		7	0.15
China III	2008	5.45		0.78	5	0.16
China IV	2015	4		0.55	3.5	0.03
China V	2017	4		0.55	2	0.03

Supplement figures

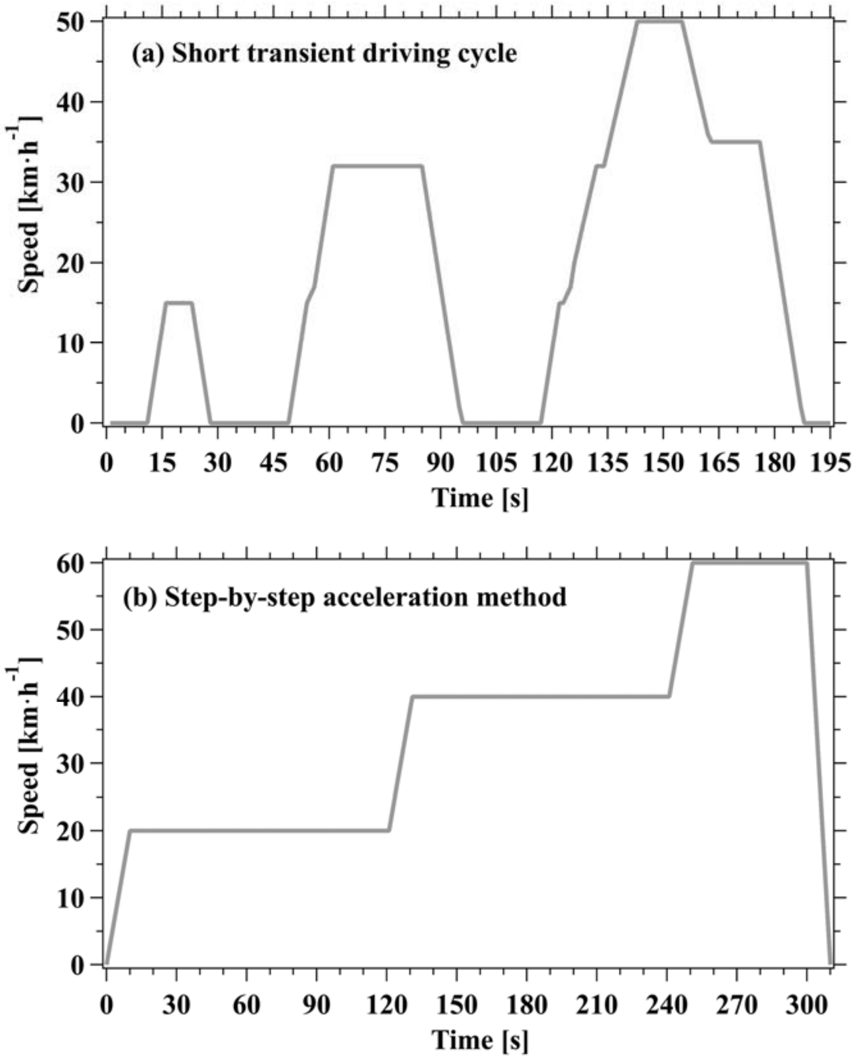

Figure S1. Speed change of the test vehicles in (a) the short transient driving cycle (GB 18285-2018) and (b) the step-by step acceleration method.

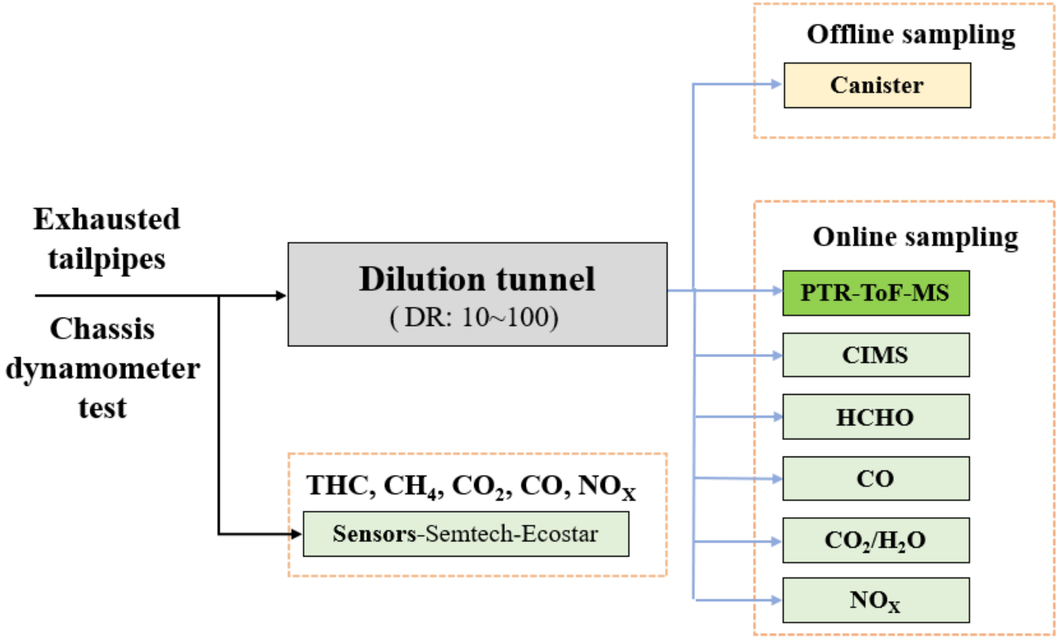

Figure S2. Diagram of the test setup used in the experiments including dilution system and instrumentation.

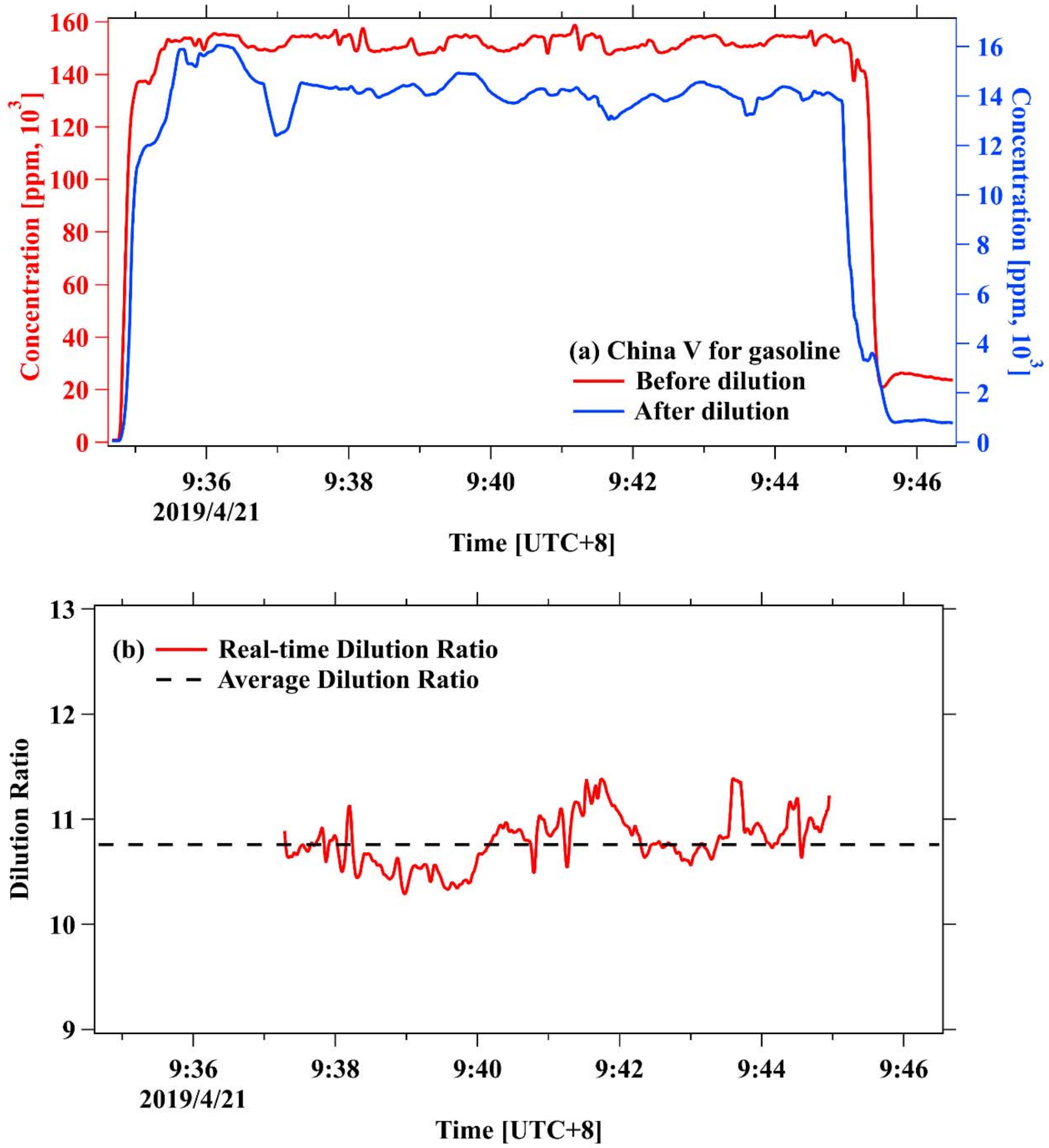

Figure S3. (a) Compared the concentration of CO_2 before and after dilution for a gasoline vehicle with the emission standard of China V. (b) Time series of real-time dilution ratio calculated by the concentration of CO_2, and the dashed line is average dilution ratio.

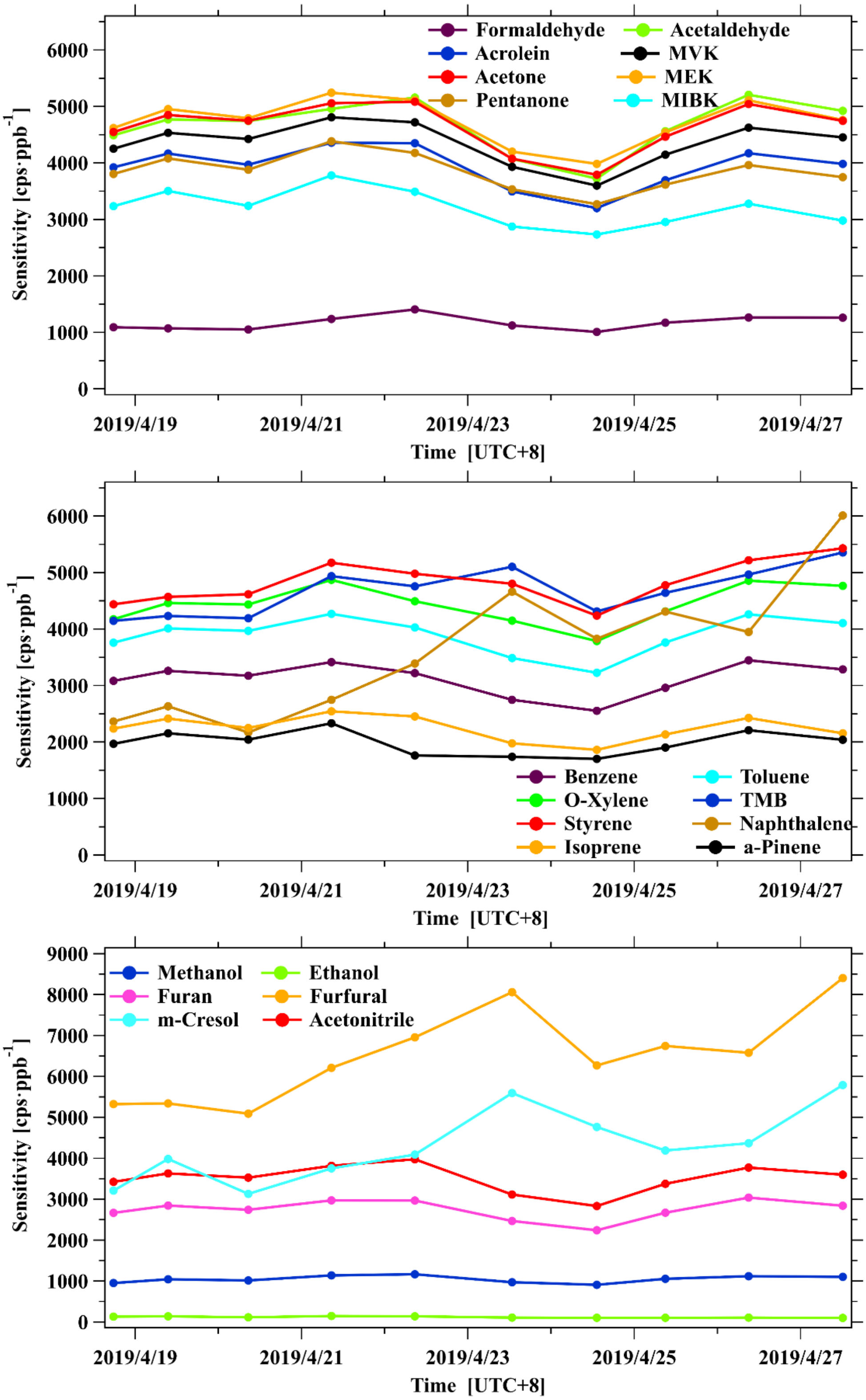

Figure S4. Calibration results of PTR-ToF-MS for different species during the campaign.

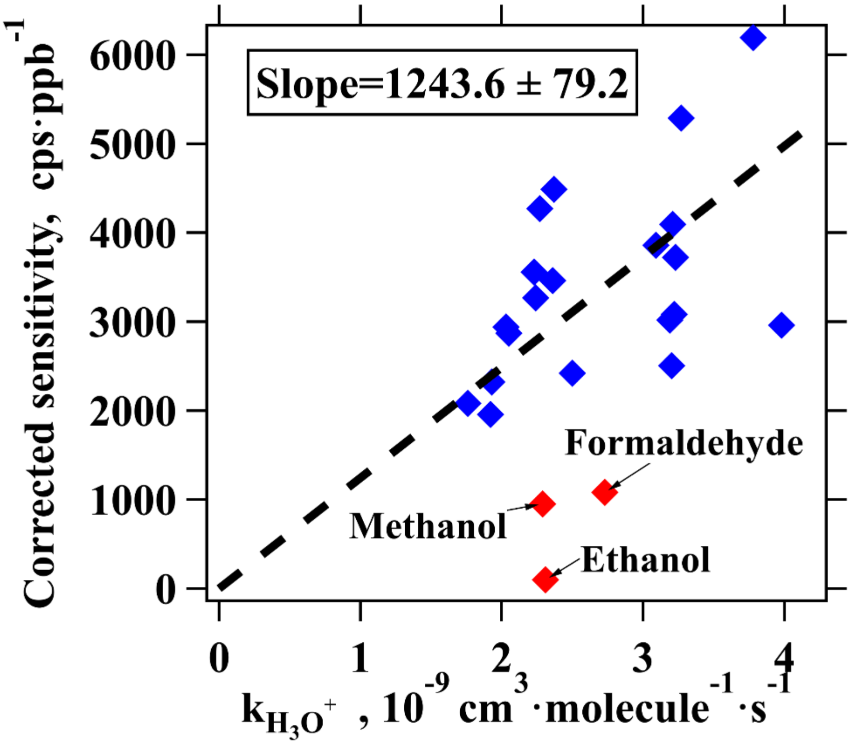

Figure S5. Corrected sensitivities as a function of kinetic rate constants for proton-transfer reactions of H_3O^+ with VOCs. The dashed line indicates the fitted line for blue points. The red points are not used, as these compounds (formaldehyde, methanol, ethanol) are known to have lower sensitivities.

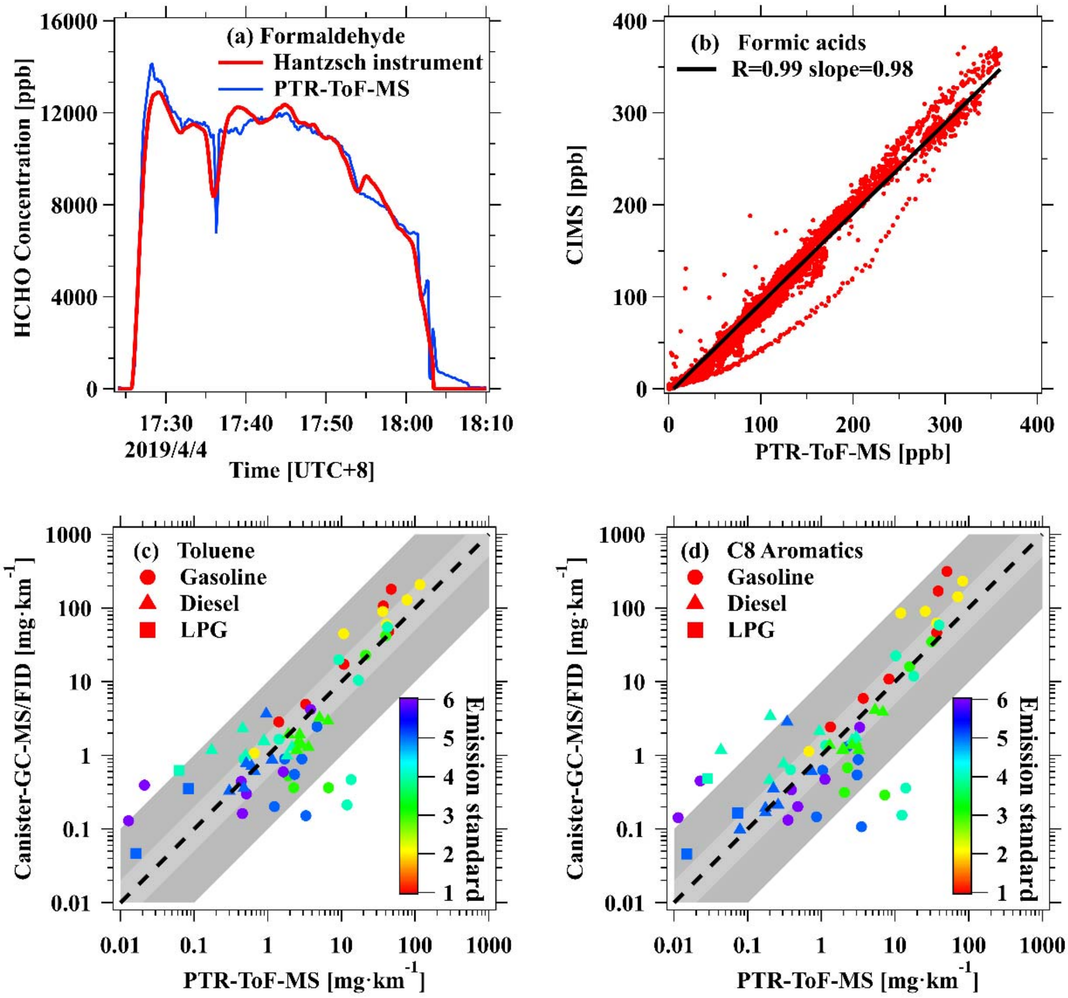

Figure S6. (a) Time series of formaldehyde measured by PTR-ToF-MS and the Hantzsch instrument. (b) Scatterplot of the concentration of formic acid between PTR-ToF-MS and the CIMS. Scatterplot of the emission factor of (c) toluene and (d) C_8 aromatics calculated by the data detected by PTR-ToF-MS and Canister-GC-MS/FID. The black dashed lines represent 1:1 ratio, and the shaded areas represent ratios of a factor of 2 and 10 in (c) and (d).

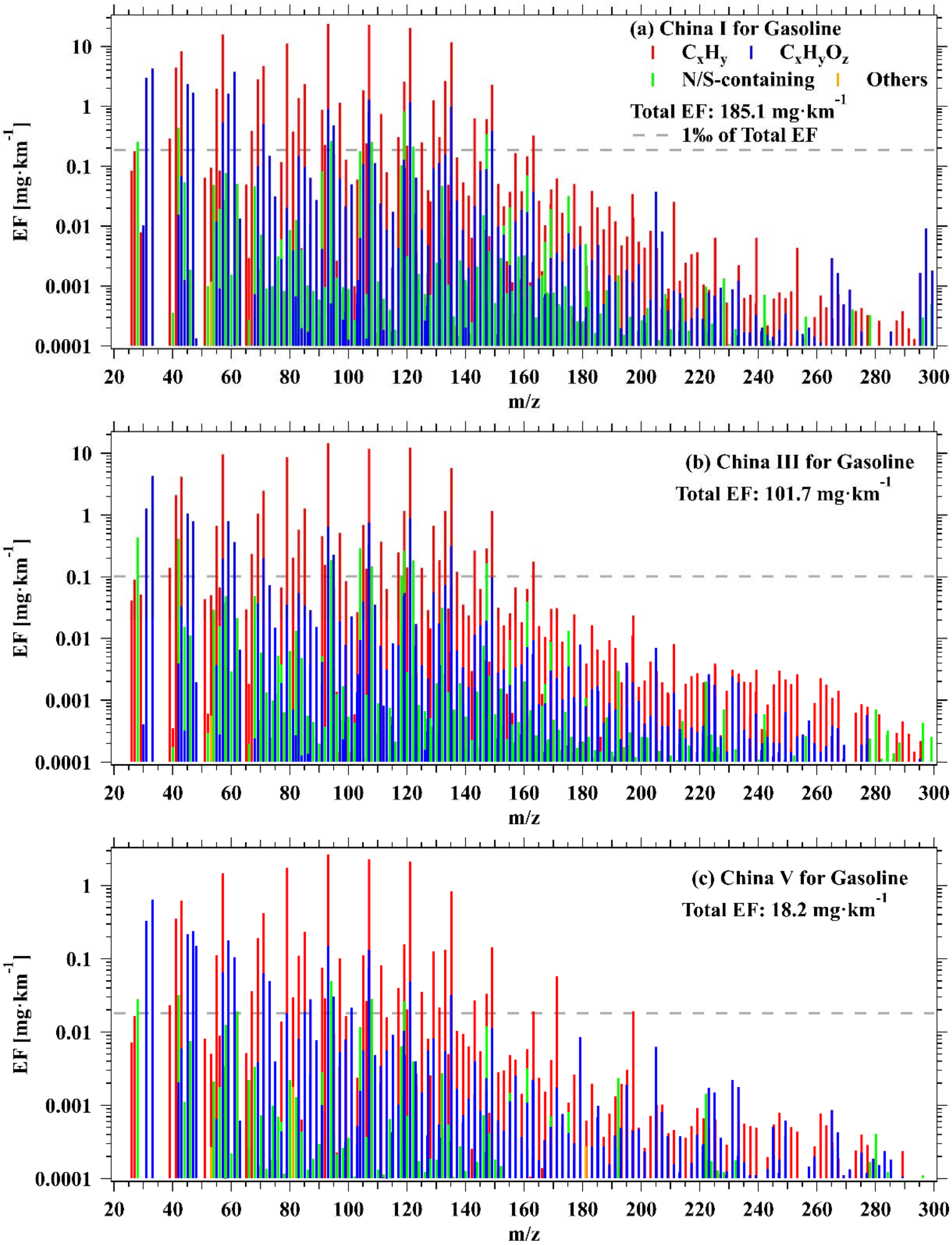

Figure S7. The determined average mileage-based emission factors of VOC species measured by PTR-ToF-MS from (a) China I, (b) China III, and (c) China V gasoline vehicles. The gray dashed lines represent 1‰ of total VOCs emission factors.

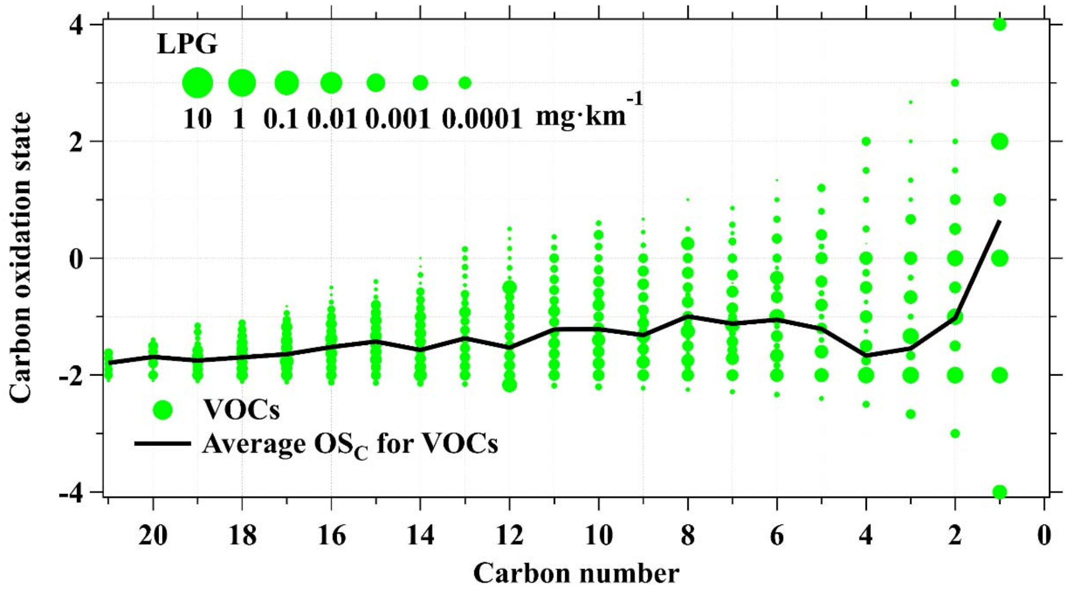

Figure S8. The two-dimensional space of $\overline{OS_C} - n_C$ with data points sized coded using emission factors of VOC species from LPG vehicles. The black line is the average $\overline{OS_C}$ of each carbon number for VOC species in LPG vehicles.

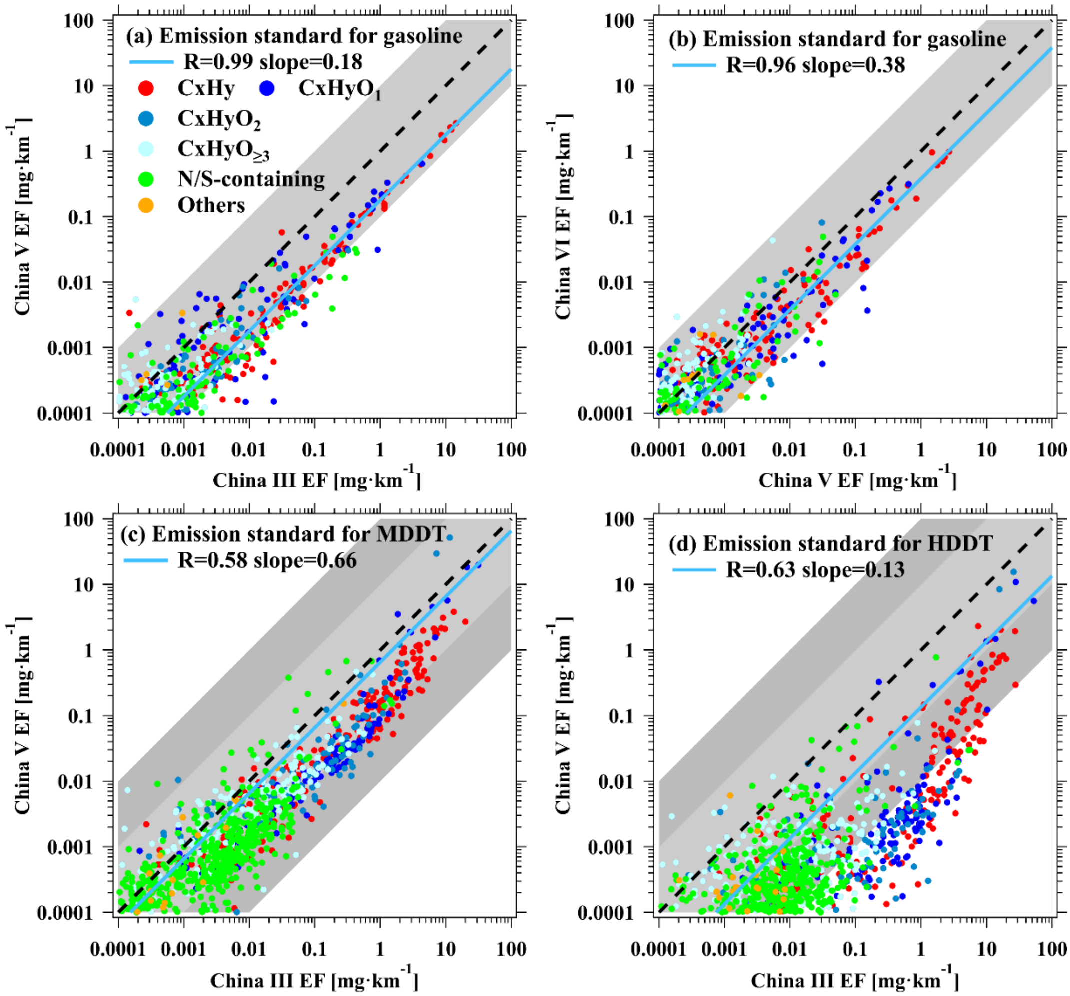

Figure S9. Scatterplots of VOCs emission factors between China III and China V emission standard (a) and between China V and China VI emission standard for gasoline vehicles(b). Scatterplots of VOCs emission factors between China III and China V emission standard for LDDT (c) and HDDT(d). Each data point 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.

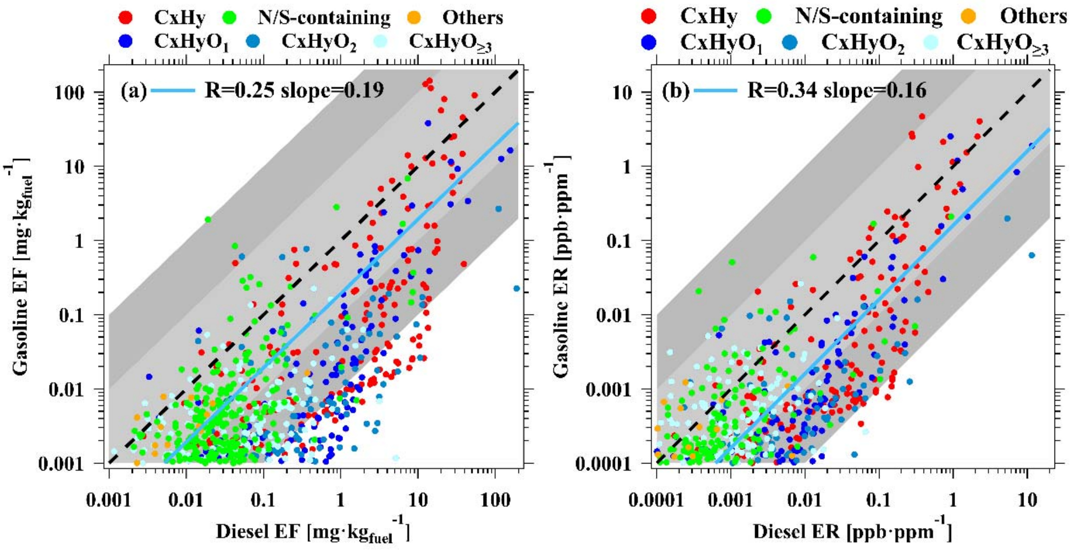

Figure S10. Scatterplot of (a) the determined average fuel-based emission factors ($mg \cdot kg_{fuel}^{-1}$) and (b) the emission ratios to CO ($ppb \cdot ppm^{-1}$) of VOCs between gasoline and diesel vehicles. Each data point indicates a VOC species measured by PTR-ToF-MS. The blue line is the fitted 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.

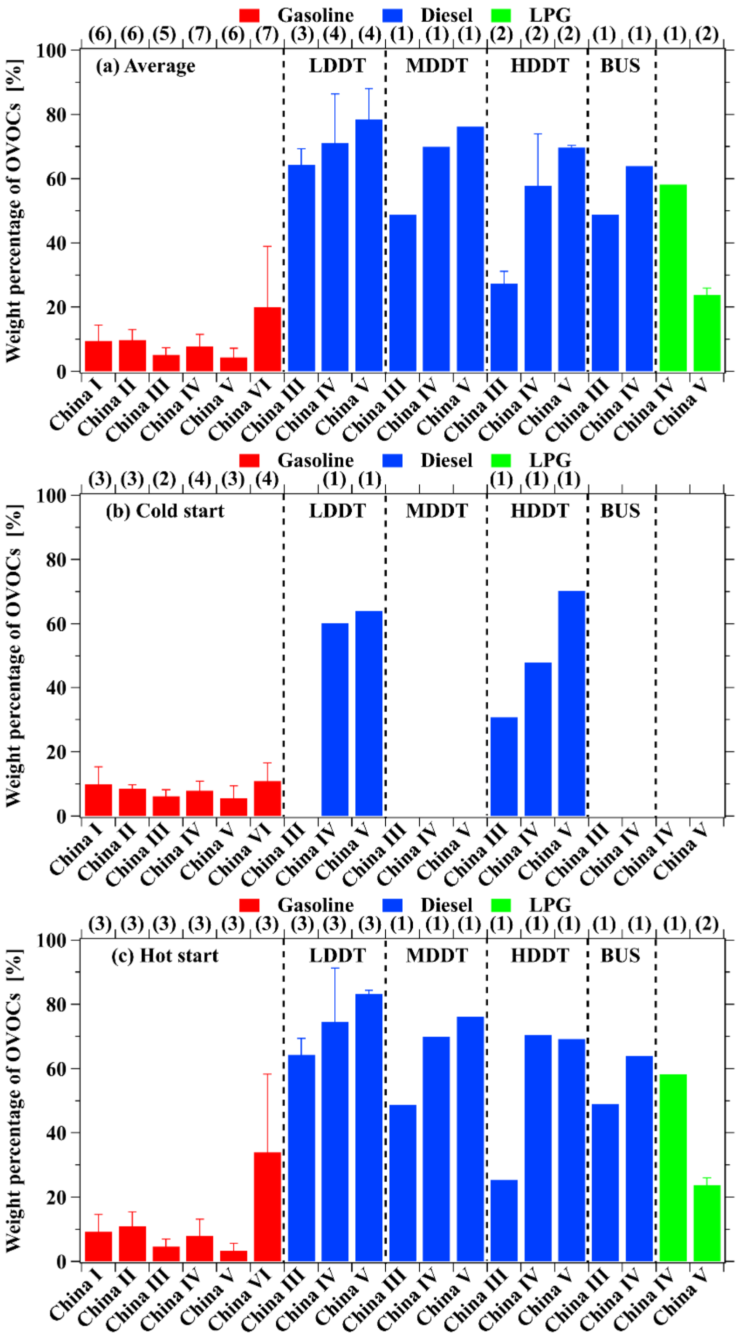

Figure S11. (a) Average OVOC fractions for vehicles with different emission standards, and some difference between (b) cold start and (c) hot start. Error bars represent the standard deviations of the fraction of OVOCs.

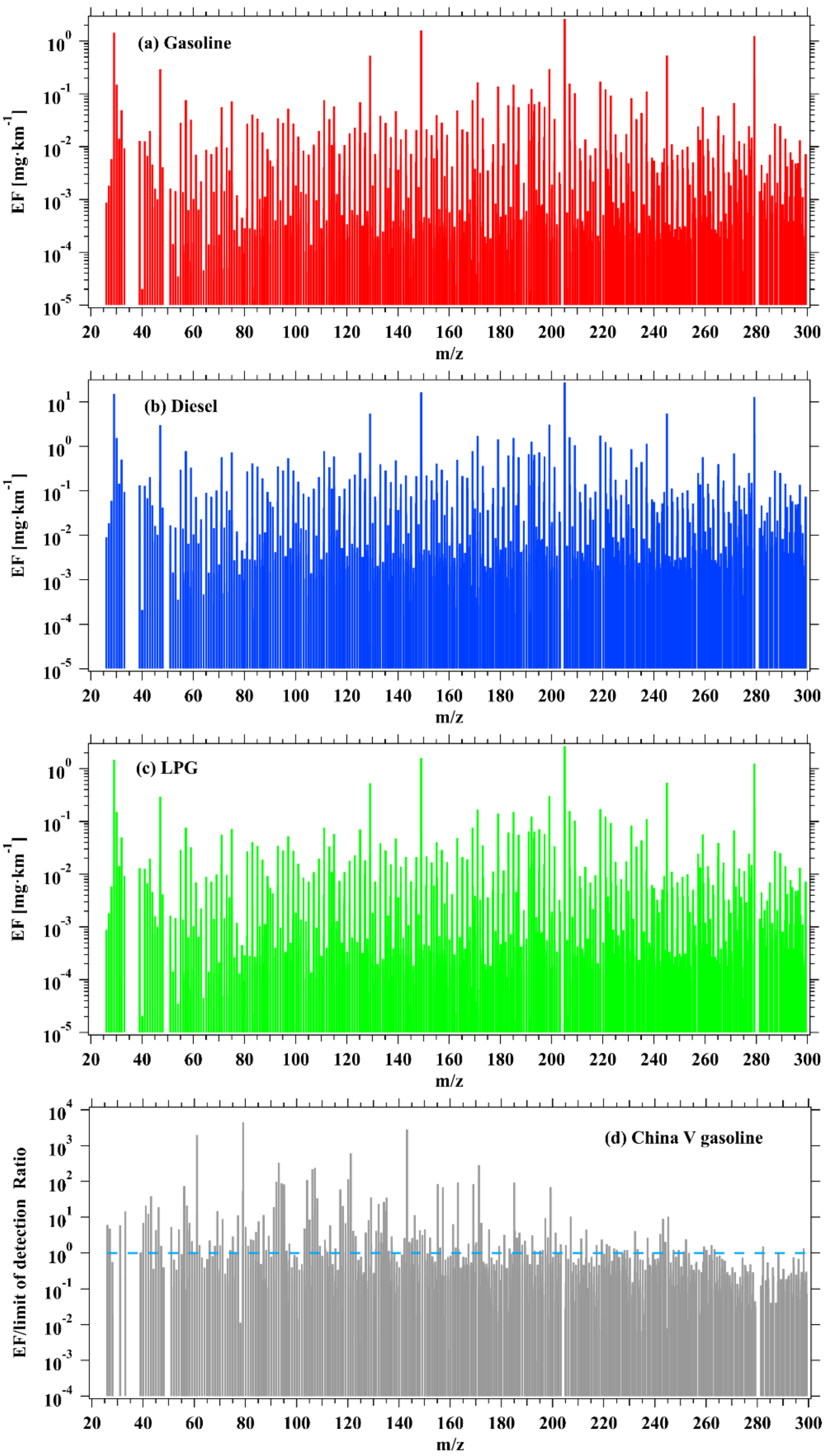

Figure S12. The limit of detection for emission factors in (a) gasoline (b) diesel, and (c) LPG vehicles. (d) The ratio of emission factors to the limit of detection in a China V gasoline vehicle, and the blue dashed lines represent a ratio of 1.

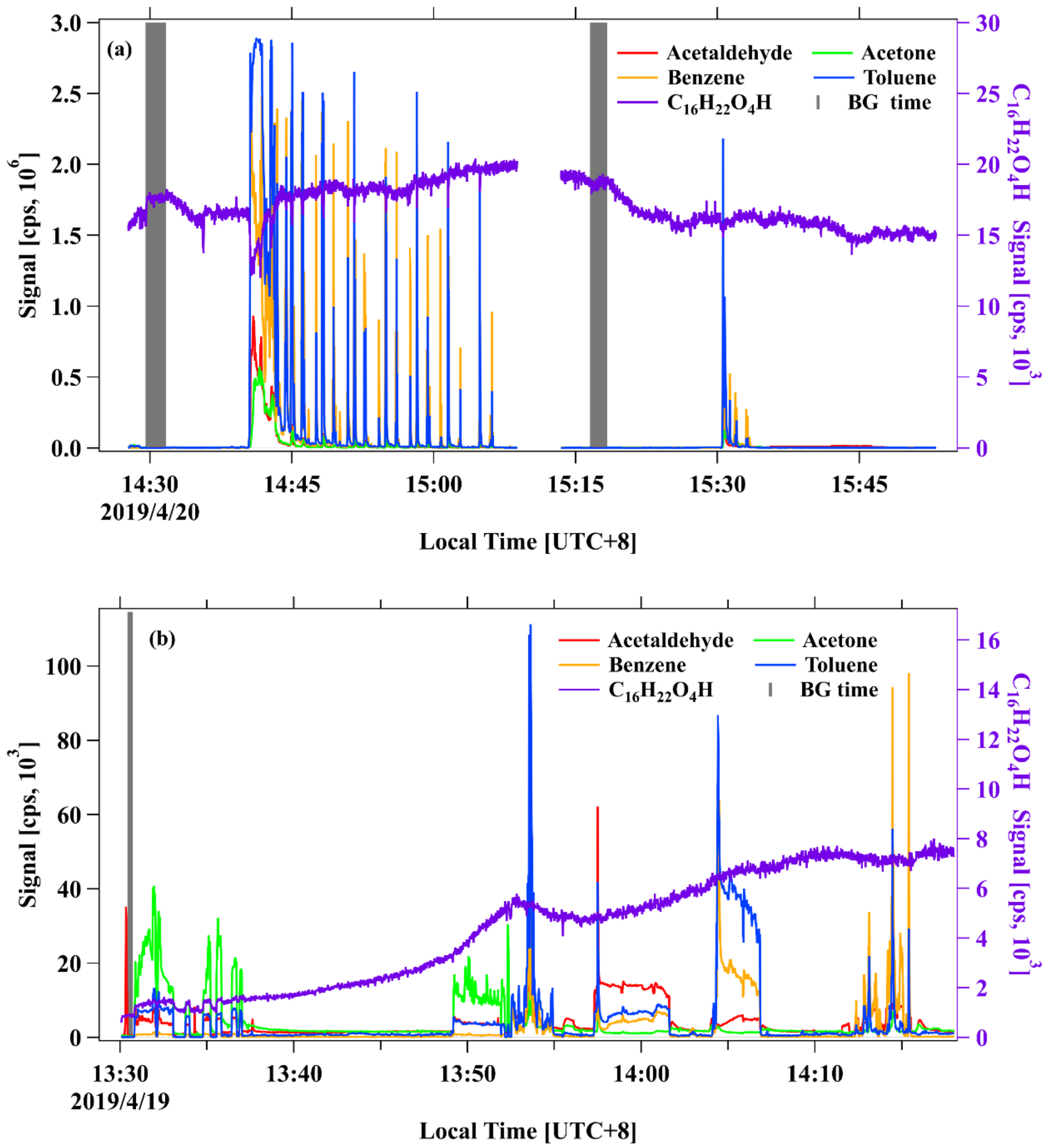

Figure S13. Real-time signals of acetaldehyde, acetone, benzene, toluene, and the $C_{16}H_{22}O_4H$ (m/z=279) of (a) a gasoline vehicle with China I emission standard from cold start and hot start. (b) Several gasoline vehicles with different emission standard measured by PTR-ToF-MS. The shaded areas represent the period of background.

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