Supplement

Speciated Volatile Organic Compounds and Hydroxyl Radical Reactivity Characteristics of Evaporation Emissions from China VI and China V In-use Light Duty Gasoline Vehicles

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Text S1. The GC-MS/FID analysis and calibration

The samples collected using the SUMMA canister were analyzed with a pressure dilution instrument (ENTECH 4700), preconcentrated using an atmospheric volatile organic compound preconcentrator (ZF-PKU-VOC1007) to collect VOCs, and then analyzed by GC-MS/FID (Agilent Technologies 8890+5977B). The mixed standard gases used for GC-MS/FID calibration curves. Set five concentration gradients were set during calibration, namely 0.5, 1, 2, 4, and 8 ppb, and the injection for each component was repeated, The R^2 of calibration curve was 0.98 or above. The VOCs species were shown in Table S3.

We have customized 7 branched alkenes, isobutene, 3-methyl-1-butene, 2-methyl-1-butene, 2-methyl-2-butene, 4-methyl-1-pentene, 2-methyl-1-pentene and 2-methyl-2-pentene. Characteristic ion fragments were considered in the measurement, peak retention times were identified and these fragments were added to the GC-MS/FID measurement method to obtain calibration data, thereby achieving quantitative determination of the sample concentration (Table S4). The R^2 of the calibration curve can reach 0.99.

Text S2. Measurement of the OH radical total reactivity

A schematic diagram of the structure of the k_{OH} measuring device for LP-LIF is shown in Fig. S2, and the instrument working principle is briefly described as follows. In a flow tube with a diameter of 40 mm, a 266 nm pulsed laser (Dawa-200) was used to photolyze O_3, which combines with H_2O to generate OH radicals. The energy of the laser is around 15 mJ, and the triggering frequency can be adjusted according to actual testing requirements, ranging from 1 - 3 Hz. The reactive gas in the sample reacts with OH radicals in the flow tube. The gas flow rate of the flow tube was 13 L/min. The sample in the flow tube enters a high vacuum environment (~3 mbar) through a nozzle with a diameter of 0.4 mm. Under irradiation with a 308nm laser, a fluorescence signal was generated, and the decay signal of OH radicals was obtained. The 308 nm laser was emitted by pulsed dye laser (Credo-Dye-N), which enter the fluorescence cavity through optical fibers and mirrors, with a power of about 40 mW. Before each test, the laser wavelength was scanned and adjusted to obtain OH radical fluorescence signals. The time resolution during the testing period was 2 min, and each sampling was repeated four times. To verify the reliability of LP-LIF, the OH reaction rate constant of methane was tested, and a deviation of 12% from the results reported in the literature was obtained (Atkinson, 2003).

Table S1. Parameters of Experimental Gasoline.

Name	Unit	Results
Density（20℃）	kg/m^3	745.4
Reid vapor pressure	kPa	56.5
Research octane number		95.3
Benzene	%（v/v）	0.4
Alkenes	%（v/v）	12.3
Aromatics	%（v/v）	30.7
Oxygen	%（m/m）	1.85
10% Evaporated	℃	53.2
50% Evaporated	℃	96.2
90% Evaporated	℃	162.9
End boiling point	℃	191.5

Table S2. VOCUS-Eiger quantification of species related parameters.

CAS	Name	Molecular formula	Sensitivity (cps/ppb)
107-02-8	Acrolein	C_3H_4O	412±36
96-22-0	3-Pentanone	$C_5H_{10}O$	593±63
100-52-7	Benzaldehyde	C_7H_6O	1273±89
110-00-9	Furan	C_4H_4O	536±43
431-03-8	2,3-Butanedione	$C_4H_6O_2$	295±25
98-01-1	2-Furaldehyde	$C_5H_4O_2$	1680±137

CAS: Chemical Abstracts Service.

Table S3. Offline sampling for quantitative species analysis.

CAS	Name	CAS	Name
74-84-0	Ethane	56-23-5	CarbonTetrachloride
74-85-1	Ethylene	71-43-2	Benzene
74-98-6	Propane	107-06-2	1,2-Dichloroethane
115-07-1	Propylene	540-84-1	2,2,4-Trimethylpentane
75-28-5	iso-Butane	142-82-5	n-Heptane
106-97-8	n-Butane	123-73-9	trans-2-Butenal
74-86-2	Acetylene	79-01-6	Trichloroethylene
624-64-6	trans-2-Butene	108-87-2	Methylcyclohexane
106-98-9	1-Butene	78-87-5	1,2-Dichloropropane
590-18-1	cis-2-Butene	80-62-6	Methylmethacrylate
287-92-3	Cyclopentane	110-62-3	Pentanal
78-78-4	iso-Pentane	123-91-1	1,4-Dioxane
109-66-0	n-Pentane	75-27-4	Bromodichloromethane
75-71-8	Freon-12	565-75-3	2,3,4-Trimethylpentane
76-14-2	Freon-114	592-27-8	2-Methylheptane
74-87-3	Chloromethane	589-81-1	3-Methylheptane

75-01-4	Vinylchloride	10061-02-6	trans-1,3-Dichloropropene
106-99-0	1,3-Butadiene	108-10-1	4-Methyl-2-pentanone
75-07-0	Acetaldehyde	108-88-3	Toluene
74-83-9	Bromomethane	111-65-9	n-Octane
75-00-3	Chloroethane	10061-01-5	cis-1,3-Dichloropropene
75-69-4	Freon-11	79-00-5	1,1,2-Trichloroethane
109-67-1	1-Pentene	127-18-4	Tetrachloroethylene
646-04-8	trans-2-Pentene	591-78-6	2-Hexanone
78-79-5	Isoprene	66-25-1	Hexanal
627-20-3	cis-2-Pentene	124-48-1	Dibromochloromethane
123-38-6	Propanal	106-93-4	1,2-Dibromoethane
75-35-4	1,1-Dichloroethene	108-90-7	Chlorobenzene
76-13-1	Freon-113	100-41-4	Ethylbenzene
75-83-2	2,2-Dimethylbutane	111-84-2	Nonane
67-64-1	Acetone	108-38-3/106-42-3	m/p-Xylene
67-63-0	2-Propanol	95-47-6	o-Xylene
75-15-0	Carbondisulfide	100-42-5	Styrene
75-09-2	MethyleneChloride	75-25-2	Bromoform
79-29-8	2,3-Dimethylbutane	98-82-8	Isopropylbenzene
107-83-5	2-Methylpentane	79-34-5	1,1,2,2-Trachloroethane
94-14-0	3-Methylpentane	103-65-1	n-Propylbenzene
156-60-5	Trans-1,2-Dichloroethene	620-14-4	m-Ethyltoluene
1634-04-4	MTBE	622-96-8	p-Ethyltoluene
592-41-6	1-Hexene	124-18-5	n-Decane
110-54-3	n-Hexane	108-67-8	1,3,5-Trimethylbenzene
78-85-3	Methacrolein	611-14-3	o-Ethyltoluene
75-34-3	1,1-Dichloroethane	95-63-6	1,2,4-Trimethylbenzene

108-05-4	Vinylacetate	541-73-1	1,3-Dichlorobenzene
108-08-7	2,4-Dimethylpentane	106-46-7	1,4-Dichlorobenzene
123-72-8	n-Butanal	526-73-8	1,2,3-Trimethylbenzene
96-37-7	Methylcyclopentane	100-44-7	BenzylChloride
156-59-2	cis-1,2-Dichloroethene	141-93-5	m-Diethylbenzene
78-93-3	MethylEthylKetone	105-05-5	p-Diethylbenzene
141-78-6	EthylAcetate	95-50-1	1,2-Dichlorobenzene
109-99-9	Tetrahydrofuran	1120-21-4	n-Undecane
67-66-3	Chloroform	620-23-5	m-Tolualdehyde
71-55-6	1,1,1-Trichloroethane	112-40-3	n-Dodecane
591-76-4	2-Methylhexane	120-82-1	1,2,4-Trichlorobenzene
110-82-7	Cyclohexane	87-68-3	Hexachloro-1,3-Butadiene
565-59-3	2,3-Dimethylpentane	91-20-3	Naphthalene
589-34-4	3-Methylhexane		

CAS: Chemical Abstracts Service

Table S4. Quantitative species related parameters of branched chain alkenes.

CAS	Name	Detector	Retention time (min)	Ionic fragments (m/z)
115-11-7	isobutene	FID	19.42	
563-45-1	3-Methyl-1-butene	MSD	7.28	55，70
563-46-2	2-methyl-1-butene	MSD	8.345	55，70，42
513-35-9	2-methyl-2-butene	MSD	9.083	55，70
691-37-2	4-methyl-1-pentene	MSD	10.31	56，69，43
763-29-1	2-methyl-1-pentene	MSD	11.53	69，56，41，55
625-27-4	2-methyl-2-pentene	MSD	12.198	84，69，41

CAS: Chemical Abstracts Service; FID: Flame Ionization Detector; MSD: Mass Spectrometry Detector.

Table S5. Summary of the OH reaction rate constants.

Name	Recommended formula/Value	Reference conditions*	k (298K)
Ethane	6.9*10^(-12)*exp(-1000/T)	200-300K	2.41E-13
Ethylene	9*10^(-12)*(T/300)^(-0.85)	100-500K	9.05E-12
Propane	7.6*10^(-12)*exp(-585/T)	200-300K	1.07E-12
Propylene	3*10^(-11)*(T/300)^(-1)	200-300K	3.02E-11
iso-Butane	5.4*10^(-12)*exp(-285/T)	210-300K	2.08E-12
n-Butane	9.8*10^(-12)*exp(-425/T)	180-300K	2.35E-12
Acetylene			7.5E-13
trans-2-Butene	1*10^(-11)*exp(553/T)	290-430K	6.4E-11
1-Butene	6.6*10^(-12)*exp(465/T)	290-430K	3.14E-11
isobutene	9.4*10^(-12)*exp(505/T)	290-430K	5.12E-11
cis-2-Butene	1.1*10^(-11)*exp(485/T)	290-430K	5.6E-11
Cyclopentane	2.67E-11*EXP(-4.23/8.314472E-3/T)	209-407K	4.84E-12
iso-Pentane	3.47*10^(-12)*(T/298)^1.3*exp(0.1/8.314472E-3/T)	213-407K	3.61E-12
n-Pentane	3*10^(-12)*(T/298)^1.7*exp(0.7/8.314472E-3/T)	224-1308K	3.98E-12
Freon-12	<1*10^(-10)*exp(-11910/T)	< 220-480K	4.39E-28
Freon-114			
Chloromethane	2.1*10^(-12)*exp(-1210/T)	220-300K	3.62E-14
Vinylchloride	6.3*10^(-11)*exp(-22.78/8.314472E-3/T)	293-560K	6.4E-15

1,3-Butadiene	1.39*10^(-11)*exp(3.9/8.314472E-3/T)	299-424K	6.71E-11
Acetaldehyde	4.7*10^(-12)*exp(345/T)	200-380K	1.5E-11
Bromomethane	1.7*10^(-12)*exp(-1215/T)	240-300K	2.88E-14
3-Methyl-1-butene	5.32*10^(-12)*exp(533/T)		3.18E-11
Chloroethane	7.78*10^(-18)*T^2*exp(-152/T)		4.15E-13
Freon-11	<1*10^(-10)*exp(-9695/T)	< 220-480K	7.43E-25
1-Pentene	5.86*10^(-12)*exp(500/T)		3.14E-11
2-methyl-1-butene	6.46E-11		6.46E-11
trans-2-Pentene	6.69E-11		6.69E-11
Isoprene	2.1*10^(-11)*exp(465/T)	240-630K	1E-10
cis-2-Pentene	6.54E-11		6.54E-11
2-methyl-2-butene	1.93E-11*exp(3.74/8.314472E-3/T)	298-425K	8.73E-11
Acrolein	6.55*10^(-12)*exp(2.77/8.314472E-3/T)	243-372K	2E-11
Propanal	4.9*10^(-12)*exp(405/T)	240-380K	1.91E-11
1,1-Dichloroethene	1.4*10^(-12)*exp(4.9/8.314472E-3/T)	260-640K	1.01E-11
Freon-113	3.01E-16		3.01E-16
2,2-Dimethylbutane	3.22*10^(-11)*exp(-781/T)		2.34E-12
Acetone	8.8*10^(-12)*exp(-1320/T)+1.7*10^(-14)*exp(423/T)	195-440K	1.75E-13
2-Propanol	2.71*10^(-12)*exp(1.58/8.314472E-3/T)	270-340K	5.13E-12
Carbondisulfide	8.8*10^(-16)*exp(19.12/8.314472E-3/T)	260-300K	1.96E-12

4-methyl-1-pentene	3.8E-11		3.8E-11
MethyleneChloride	1.8*10^(-12)*exp(-860/T)	210-400K	1E-13
2,3-Dimethylbutane	1.24*10^(-17)*T^2*exp(494/T)		5.78E-12
2-Methylpentane	1.96*10^(-11)*exp(-3.18/8.314472E-3/T)	283-398K	5.43E-12
3-Methylpentane	1.77*10^(-11)*exp(-2.74/8.314472E-3/T)	283-398K	5.86E-12
Trans-1,2-Dichloroethene	1.86*10^(-13)*(T/298)^1.73*exp(6.04/8.314472E-3/T)	293-720K	2.13E-12
MTBE	6.54*10^(-18)*T^2*exp(483/T)		2.94E-12
2-methyl-1-pentene	6.23E-11		6.23E-11
1-Hexene	3.70E-11		3.7E-11
n-Hexane	1.22*10^(-12)*(T/298)^2.2*exp(3.68/8.314472E-3/T)	292-1299k	5.39E-12
Methacrolein	8*10^(-12)*exp(380/T)	230-380K	2.86E-11
1,1-Dichloroethane	1.79*10^(-11)*exp(-10.85/8.314472E-3/T)	292-775k	2.24E-13
Vinylacetate	4.06*10^(-12)*exp(4.49/8.314472E-3/T)	287-313k	2.49E-11
2-methyl-2-pentene	8.75E-11		8.75E-11
2,4-Dimethylpentane	2.49*10^(-11)*exp(-3.68/8.314472E-3/T)	272-410k	5.64E-12
n-Butanal	6*10^(-12)*exp(410/T)	250-430K	2.38E-11
Methylcyclopentane	8.60E-12	296k	
cis-1,2-Dichloroethene	2.01*10^(-12)*exp(0.7/8.314472E-3/T)	240-400k	2.67E-12
MethylEthylKetone	1.3*10^(-12)*exp(-0.21/8.314472E-3/T)	240-300k	1.19E-12
EthylAcetate	4.8*10^(-13)*exp(3.3/8.314472E-3/T)	243-369k	1.82E-12

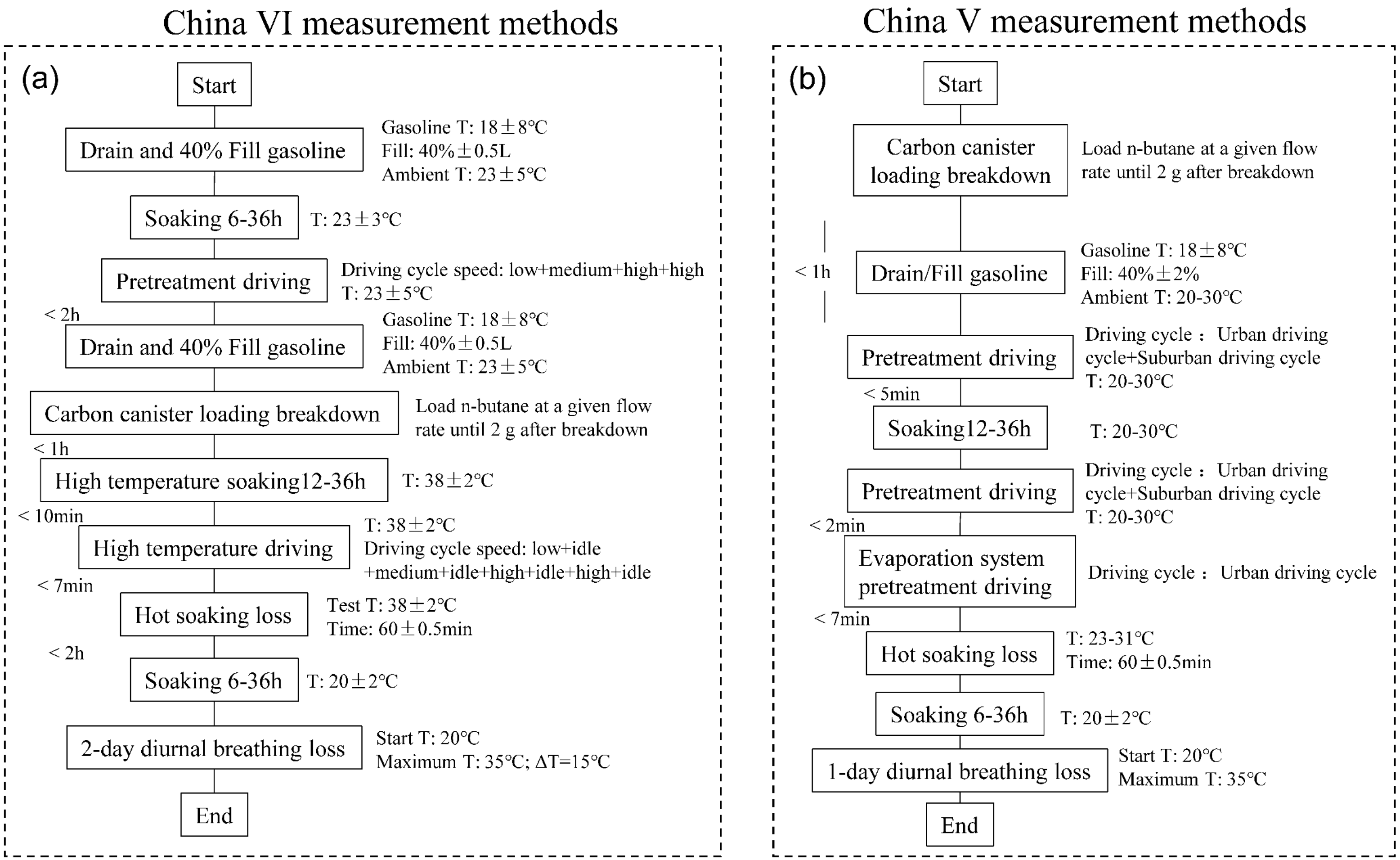
Tetrahydrofuran	5.7*10^(-12)*exp(2.9/8.314472E-3/T)	260-360k	1.84E-11
Chloroform	1.8*10^(-12)*exp(-850/T)	240-300k	1.04E-13
1,1,1-Trichloroethane	1.2*10^(-12)*exp(-1440/T)	240-300k	9.56E-15
2-Methylhexane	6.86E-12		6.86E-12
Cyclohexane	3.1*10^(-11)*exp(-3.92/8.314472E-3/T)	225-408k	6.37E-12
2,3-Dimethylpentane	1.95*10^(-11)*exp(-2.74/8.314472E-3/T)	287-403k	6.45E-12
3-Methylhexane	7.15E-12		7.15E-12
CarbonTetrachloride	< 1*10^(-10)*exp(-6220/T)	220-300k	8.61E-20
Benzene	2.3*10^(-12)*exp(-190/T)	230-350K	1.22E-12
1,2-Dichloroethane	1.79*10^(-11)*exp(-10.85/8.314472E-3/T)	292-775k	2.24E-13
2,2,4-Trimethylpentane	2.09*10^(-12)*(T/298)^2*exp(1.16/8.314472E-3/T)	290-1190k	3.34E-12
n-Heptane	6.03*10^(-12)*(T/298)^1.4*exp(0.27/8.314472E-3/T)	241-1287k	6.72E-12
trans-2-Butenal	5.77*10^(-12)*exp(4.43/8.314472E-3/T)	243-372k	3.45E-11
Trichloroethylene	5*10^(-13)*exp(3.7/8.314472E-3/T)	230-420k	2.23E-12
Methylcyclohexane	1.85*10^(-11)*exp(-1.62/8.314472E-3/T)	273-343K	9.62E-12
1,2-Dichloropropane	2.1*10^(-12)*exp(-3.77/8.314472E-3/T)	243-372k	4.59E-13
Methylmethacrylate	2.45*10^(-12)*exp(6.9/8.314472E-3/T)	253-374k	3.97E-11
Pentanal	9.9*10^(-12)*exp(2.54/8.314472E-3/T)	243-372k	2.76E-11
3-Pentanone	2.81*10^(-12)*exp(0.08/8.314472E-3/T)	240-440K	2.9E-12
1,4-Dioxane	4.5*10^(-12)*exp(2.76/8.314472E-3/T)	263-372k	1.37E-11

Bromodichloromethane	9.4*10^(-13)*exp(-4.27/8.314472E-3/T)	230-330k	1.68E-13
2,3,4-Trimethylpentane	9.85*10^(-13)*exp(-1.03/8.314472E-3/T)	244-373k	6.5E-13
2-Methylheptane	9.10E-12	296k	
3-Methylheptane	1.40E-11	323k	
trans-1,3-Dichloropropene	1.44E-11		1.44E-11
4-Methyl-2-pentanone	2*10^(-12)*exp(4.45/8.314472E-3/T)	240-340k	1.21E-11
Toluene	1.8*10^(-12)*exp(340/T)	210-350K	5.63E-12
n-Octane	4.52*10^(-11)*exp(-4.47/8.314472E-3/T)	284-393k	7.44E-12
cis-1,3-Dichloropropene	8.45E-12		8.45E-12
1,1,2-Trichloroethane	1.6*10^(-12)*exp(-3.9/8.314472E-3/T)	280-420k	3.32E-13
Tetrachloroethylene	3.5*10^(-12)*exp(-920/T)	290-420k	1.6E-13
2-Hexanone	1.89*10^(-13)*(T/298)^2*exp(8.6/8.314472E-3/T)	263-405k	6.08E-12
Hexanal	4.2*10^(-12)*exp(4.7/8.314472E-3/T)	263-353k	2.8E-11
Dibromochloromethane	9*10^(-13)*exp(-3.52/8.314472E-3/T)	230-330K	2.17E-13
1,2-Dibromoethane	1.46*10^(-11)*exp(-10.64/8.314472E-3/T)	292-366k	1.99E-13
Chlorobenzene	6.02E-13		6.02E-13
Ethylbenzene	7.51E-12		7.51E-12
Nonane	1.11*10^(-11)*(T/298)^1.19*exp(-0.33/8.314472E-3/T)	298-2000k	9.72E-12
m/p-Xylene	1.985E-11		1.99E-11
o-Xylene	1.66*10^(-11)*exp(0.96/8.314472E-3/T)	250-325k	2.45E-11

Styrene	1.02*10^(-11)*exp(4.42/8.314472E-3/T)	298-340k	6.07E-11
Bromoform	1*10^(-12)*exp(-388/T)	290-370k	2.72E-13
Isopropylbenzene	6.61E-12	296k	
1,1,2,2-Trachloroethane	4.51*10^(-12)*exp(-7.3/8.314472E-3/T)	292-418k	2.37E-13
n-Propylbenzene	5.71E-12	298k	5.71E-12
m-Ethyltoluene	1.88E-11	298k	1.88E-11
p-Ethyltoluene	1.46E-11	296k	
n-Decane	1.47*10^(-11)*(T/298)^1.09*exp(-0.7/8.314472E-3/T)	298-2000k	1.11E-11
1,3,5-Trimethylbenzene	4.26*10^(-12)*exp(6.4/8.314472E-3/T)	275-348k	5.64E-11
o-Ethyltoluene	1.32E-11		1.32E-11
1,2,4-Trimethylbenzene	2.73*10^(-12)*exp(6.07/8.314472E-3/T)	275-340k	3.16E-11
Benzaldehyde	1.30E-11		1.3E-11
1,3-Dichlorobenzene	7.21E-13		7.21E-13
1,4-Dichlorobenzene	3.20E-13		3.2E-13
1,2,3-Trimethylbenzene	3.61*10^(-12)*exp(5.15/8.314472E-3/T)	275-340k	2.89E-11
BenzylChloride	2.81E-12		2.81E-12
m-Diethylbenzene	2.20E-11	296k	
p-Diethylbenzene	1.60E-11	296k	
1,2-Dichlorobenzene	4.20E-13		4.2E-13
n-Undecane	1.82*10^(-11)*(T/298)^1.02*exp(-0.92/8.314472E-3/T)	298-2000k	1.26E-11

m-Tolualdehyde	2.07E-10	295k	
n-Dodecane	2.21*10^(-11)*(T/298)^0.96*exp(-1.16/8.314472E-3/T)	298-2000k	1.38E-11
1,2,4-Trichlorobenzene	2.31*10^(-12)*exp(-3.58/8.314472E-3/T)	273-368k	5.45E-13
Hexachloro-1,3-Butadiene			/
Naphthalene	2.17E-11		2.17E-11
Formaldehyde	1.4*10^(-12)*(T/298)^1.63*exp(-4.41/8.314472E-3/T)	200-1670k	2.36E-13
Furan	1.32*10^(-11)*exp(2.78/8.314472E-3/T)	250-420k	4.05E-11
2,3-Butanedione	1.12*10^(-12)*exp(-3.74/8.314472E-3/T)	240-440K	2.48E-13
2-Furaldehyde	3.50E-11	300k	3.5E-11
NO2/NO[#]	3.00E-11		3E-11

*: If it is not within the temperature range, refer to the formula or recommended value results as a reference; /: Not found; #: Considering the influence of ozone in the flow tube used in this study, the constant corresponding to nitrogen dioxide was selected for the calculation of nitric oxide.



102
103 **Figure S1. Evaporative emission measurement method; (a) China VI; (b) China V.**

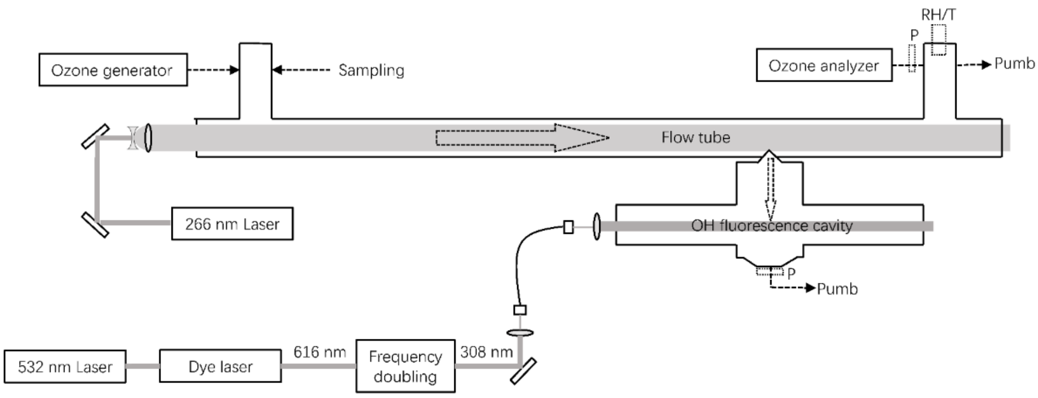


Figure S2. LP-LIF instrument structure. P: Pressure sensor, RH/T: Humidity and temperature sensor.

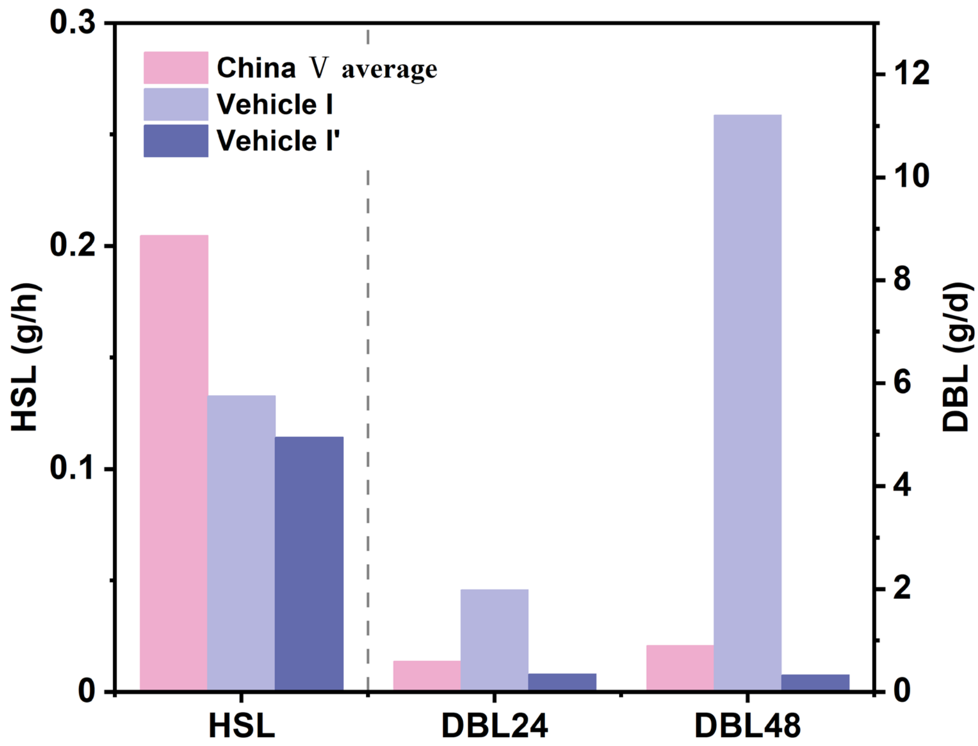


Figure S3. Comparison of the Impact of Abnormal Carbon Canister System on Evaporative Emissions in China V Vehicles; China V average refers to vehicles H, E, G, and F; Vehicle I`: replace the carbon canister test for vehicle I. Vehicle information can be found in Table 1.

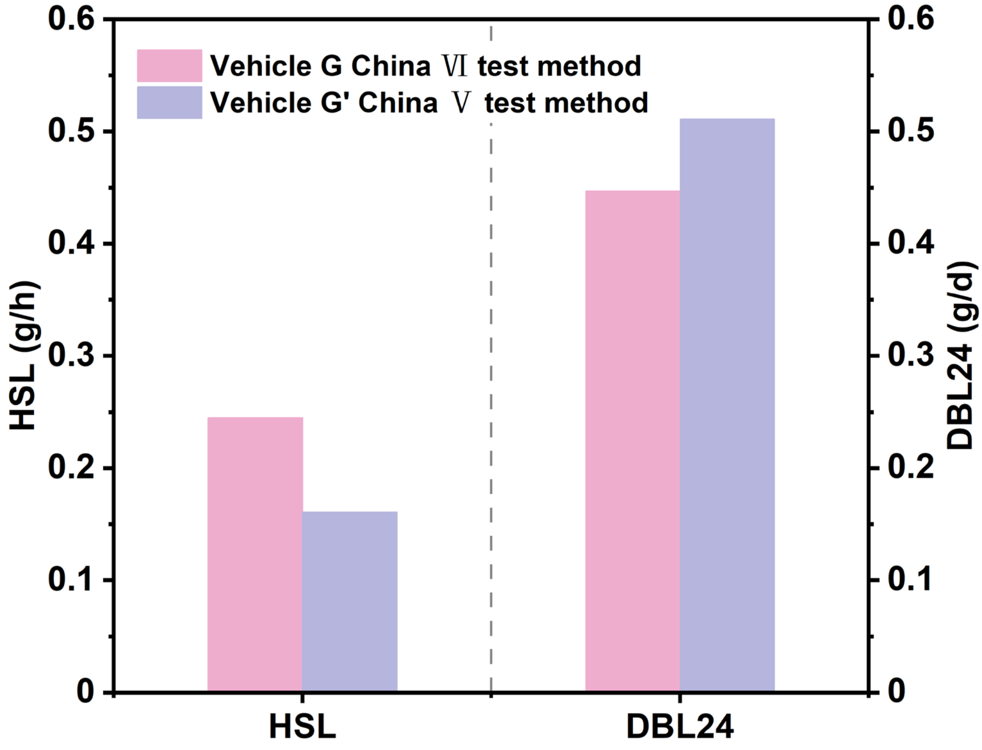


Figure S4. Comparison of evaporative emissions using different testing methods. Vehicle information can be found in Table 1.

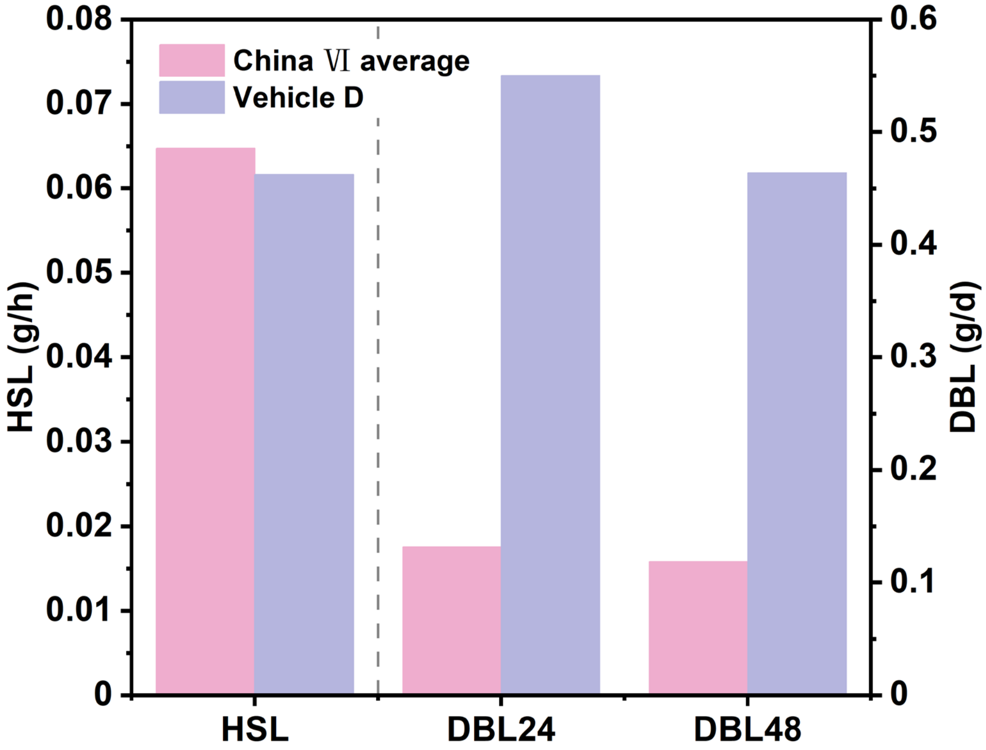


Figure S5. Comparison of Evaporative Emissions between China VI High Emission Vehicle D and Other Vehicles; China VI average refers to vehicles A, B, and C. Vehicle information can be found in Table 1.

References

Atkinson, R. Kinetics of the gas-phase reactions of OH radicals with alkanes and cycloalkanes, Atmos. Chem. Phys., 3, 2233-2307, https://doi.org/10.5194/acp-3-2233-2003, 2003.