Real-world emission characteristics of VOCs from typical cargo ships and their potential contributions to SOA and O₃ under low-sulfur fuel policies

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Table S1 Characteristics of the fuels used in the test ships

	Unit	Detection limit	CCS1 /HFO	CCS1 /diesel	CCS2 /diesel	OGV1 /HFO	OGV1 /diesel	OGV2 /HFO	OGV2 /diesel	OGV3 /HFO	OGV3 /diesel	ICS /diesel
Gross calorific value	MJ kg^{-1}					44.21	45.76	42.62	45.72	43.08	45.64	
Net calorific value	MJ kg^{-1}					41.45	42.75	40.28	42.71	40.61	42.66	
Kinematic viscosity	(50°C), mm^2/s					44.04						
Kinematic viscosity	(40°C), mm^2/s											
Kinematic viscosity	(20°C), mm^2/s		6.3	105			5.216	152.3	4.724	161.1	5.363	
Moisture	%m		N.D.	0.35		0.03	N.D.	0.09	N.D.	0.12	N.D.	
Ash	%m		0.008	0.035								
Sulfur (S)	%m	0.01	0.39	N.D.	N.D.	0.50	0.03	0.43	0.02	0.43	0.05	N.D.
Carbon (C)	%m	0.30	86.95	85.5	85.82	86.62	80.80	82.4	79.6	69.9	66.5	85.5
Hydrogen (H)	%m	0.30	10.58	12.83	13.2	11.33	8.15	9.68	12.3	11.3	10.61	
Nitrogen (N)	%m	0.30	0.59	N.D.	N.D.	N.D.	N.D.	0.39	N.D.	2.36	N.D.	
Oxygen (O)	%m	0.30	N.D.	N.D.	2.26	0.36	N.D.	1.53	0.59	1.34	0.73	
Vanadium (V)	mg kg^{-1}	0.05	5.41	N.D.	N.D.			N.D.	0.20	4.00	N.D.	
Nickel (Ni)	mg kg^{-1}	0.01	18.91	N.D.	N.D.			16.0	0.10	15.0	N.D.	
Sodium (Na)	mg kg^{-1}	0.10	3.08	0.339	0.467			6.00	0.10	8.00	0.10	
Lead (Pb)	mg kg^{-1}	0.10	3.39	2.746	3.831			N.D.	0.30	N.D.	N.D.	
Zinc (Zn)	mg kg^{-1}	0.01	30.43	0.168	0.168			2.00	0.40	8.00	0.20	
Aluminum + Silicon (Al + Si)	mg kg^{-1}	0.10	10.31	1.09	0.956			8.00	0.80	12.0	0.90	

N.D., not detected.

Table S2 Engine type, operating mode, and fuel type of each ship for each measurement

Ship ID	Engine type	Operating mode	Ship ID	Engine type	Operating mode
CCS1	Main engine	Maneuvering_diesel	OGV3	Main engine	75%_diesel
		Cruise_HFO			25%_HFO
	Auxiliary engine	Diesel			50%_HFO
CCS2	Main engine	Idling_diesel			75%_HFO
		Maneuvering_diesel			95%_HFO
		Cruise_diesel		Auxiliary engine	50%_diesel
OGV1	Main engine	20%_diesel[a]			50%_HFO
		75%_diesel			75%_HFO
		75%_diesel (NCR)	ICS1	Main engine	Maneuvering_diesel
		25%_HFO			Cruise_diesel
		50%_HFO	ICS2	Main engine	Idling_diesel
		75%_HFO			Maneuvering_diesel
		85%_HFO			Cruise_diesel
		100%_HFO	ICS3	Main engine	Maneuvering_diesel
	Auxiliary engine	50%_diesel			Cruise_diesel
		50%_HFO	ICS4	Main engine	Maneuvering_diesel
OGV2	Main engine	50%_HFO			Cruise_diesel
		70%_HFO			
		90%_HFO			
	Auxiliary engine	60%_diesel			
		75%_diesel			
		50%_HFO			
		75%_HFO			
	Boiler	75%_HFO			

[a], means percentage of engine load under what type of fuel

Table S3 The detected VOC species, detection limits and MIR used in this study

No.	Description	Detection limit (mg/m³)	MIR	No.	Description	Detection limit (mg/m³)	MIR	No.	Description	Detection limit (mg/m³)	MIR
1	ethanol	0.0004	1.53	37	2,3-dimethyl butane	0.0008	0.97	73	ethyl chloride	0.0006	0.29
2	acrolein	0.0005	7.45	38	2-methyl pentane	0.0008	1.50	74	trichlorofluoromethane	0.0012	-
3	acetone	0.0005	0.36	39	3-methyl pentane	0.0008	1.80	75	1,1-dichloroethene	0.0009	1.79
4	isopropyl alcohol	0.0005	0.61	40	n-hexane	0.0008	1.24	76	dichloromethane	0.0008	0.041
5	methyl tertiary buty1 ether	0.0008	0.73	41	methyl cyclopentane	0.0008	2.19	77	chloroform	0.0011	0.022
6	vinyl acetate	0.0008	3.20	42	2,4-dimethyl pentane	0.0009	1.55	78	bromoform	0.0022	0.022
7	methyl ethyl ketone	0.0007	1.48	43	cyclohexane	0.0008	1.25	79	dichlorotetrafluoroethane	0.0015	-
8	ethyl acetate	0.0008	0.63	44	2-methyl hexane	0.0009	1.19	80	1,1,2-trichloro1,2,2 trifluoroethane	0.0017	
9	methyl methacrylate	0.0009	15.61	45	2,3-dimethyl pentane	0.0009	1.34	81	trans-1,2-dichloroethene	0.0009	1.70
10	methyl isobutyl ketone	0.0009	3.14	46	3-methyl hexane	0.0009	1.61	82	1,1-dichloroethane	0.0009	0.069
11	methyl n-butyl ketone	0.0009	3.14	47	2,2,4-trimethyl pentane	0.0010	1.26	83	cis-1,2-dichloroethene	0.0009	1.70
12	benzene	0.0007	0.72	48	n-heptane	0.0009	1.07	84	1,2-dichloroethane	0.0009	0.21
13	toluene	0.0008	4.00	49	methyl cyclohexane	0.0009	1.70	85	1,1,1-trichloroethane	0.0012	0.0049
14	ethyl benzene	0.0009	3.04	50	2,3,4-trimethyl pentane	0.0010	1.03	86	carbon tetrachloride	0.0014	-
15	m/p-xylene	0.0009	7.795	51	2-methyl heptane	0.0010	1.07	87	1,2-dichloropropane	0.0010	0.29
16	styrene	0.0009	1.73	52	3-methyl heptane	0.0010	1.24	88	monobromodichloromethane	0.0014	0.022
17	o-xylene	0.0009	7.64	53	n-octane	0.0010	0.90	89	trichloroethylene	0.0012	0.64
18	isopropyl benzene	0.0011	2.52	54	n-nonane	0.0011	0.78	90	cis-1,3-dichloropropene	0.0010	3.70
19	n-propyl benzene	0.0011	2.03	55	n-Decane	0.0013	0.68	91	trans-1,3-dichloropropene	0.0010	5.03
20	m-ethyl toluene	0.0011	7.39	56	n-undecane	0.0014	0.61	92	1,1,2-trichloroethane	0.0012	0.086
21	p-ethyl toluene	0.0011	4.44	57	n-dodecane	0.0015	0.55	93	1,2-dibromoethane	0.0017	0.102
22	1,2,3-trimethyl benzene	0.0011	11.97	58	ethylene	0.0003	9.00	94	perchloroethylene	0.0015	0.031
23	1,3,5-trimethyl benzene	0.0011	11.76	59	propene	0.0004	11.66	95	1,1,2,2-tetrachloroethane	0.0015	0.086
24	o-ethyl toluene	0.0011	5.59	60	butene	0.0005	9.73	96	hexachlorobutadiene	0.0023	-
25	1,2,4-trimethyl benzene	0.0011	8.87	61	pentene	0.0006	7.21	97	monochlorobenzene	0.0010	0.32
26	m-diethyl benzene	0.0012	7.10	62	1,3-butadiene	0.0005	12.61	98	benzyl chloride	0.0011	4.00
27	p-diethyl benzene	0.0012	4.43	63	trans-2-butene	0.0005	15.16	99	1,3-dichlorobenzene	0.0013	0.18
28	naphthalene	0.0011	3.34	64	cis-2-butene	0.0005	14.24	100	p-dichlorobenzene	0.0013	0.178
29	ethane	0.0003	0.28	65	isoprene	0.0006	10.61	101	o-dichlorobenzene	0.0013	0.178
30	propane	0.0004	0.49	66	trans-2-pentene	0.0006	10.56	102	1,2,4-trichlorobenzene	0.0016	0.178
31	isobutane	0.0005	1.23	67	cis-2-pentene	0.0006	10.38	103	dibromochloromethane	0.0018	0.022
32	n-butane	0.0005	1.15	68	hexene	0.0008	5.49	104	tetrahydrofuran	0.0006	4.31
33	isopentane	0.0006	1.23	69	dichlorodifluoromethane	0.0011	-	105	carbon disulfide	0.0007	0.25

34	n-pentane	0.0006	1.31	70	methyl chloride	0.0004	0.04	106	1,4-dioxane	0.0008	2.62
35	2,2-dimethyl butane	0.0008	1.17	71	vinyl chloride	0.0006	2.83				
36	cyclopentane	0.0006	2.39	72	methyl bromide	0.0008	0.0187				

Table S4 The SOA yields of VOC species used in this study

No.	Description	Yeild		Data sources
		High-NO$_x$	Low-NO$_x$	
1	Benzene	0.281	0.369	(Ng et al., 2007)
2	Toluene	0.107	0.303	(Ng et al., 2007)
3	Ethyl Benzene	0.064	0.363	(Ng et al., 2007)
4	m/p-xylene	0.064	0.363	(Ng et al., 2007)
5	Styrene	0.064	0.363	(Ng et al., 2007)
6	o-Xylene	0.064	0.363	(Ng et al., 2007)
7	Isopropyl Benzene	0.064	0.363	(Ng et al., 2007)
8	n-Propyl Benzene	0.064	0.363	(Ng et al., 2007)
9	m-Ethyl Toluene	0.064	0.363	(Ng et al., 2007)
10	p-Ethyl Toluene	0.064	0.363	(Ng et al., 2007)
11	Naphthalene	0.064	0.363	(Chan et al., 2009)
12	Cyclopentane	0.04	0.04	(Lim and Ziemann, 2009)
13	Methyl Cyclopentane	0.04	0.04	(Lim and Ziemann, 2009)
14	Cyclohexane	0.04	0.04	(Lim and Ziemann, 2009)
15	n-Heptane	0.009	0.009	(Lim and Ziemann, 2009)
16	Methyl Cyclohexane	0.04	0.04	(Lim and Ziemann, 2009)
17	2-Methyl Heptane	0.009	0.009	(Lim and Ziemann, 2009)
18	3-Methyl Heptane	0.009	0.009	(Lim and Ziemann, 2009)
19	n-Octane	0.041	0.041	(Lim and Ziemann, 2009)
20	n-Nonane	0.081	0.081	(Lim and Ziemann, 2009)
21	n-Decane	0.146	0.146	(Lim and Ziemann, 2009)
22	n-Undecane	0.27	0.27	(Lim and Ziemann, 2009)
23	n-Dodecane	0.348	0.348	(Lim and Ziemann, 2009)
24	Ethylene	0.0169	0.0169	(Derwent et al., 2010)
25	Propene	0.0208	0.0208	(Derwent et al., 2010)
26	Butene	0.0156	0.0156	(Derwent et al., 2010)
27	1,3-Butadiene	0.0234	0.0234	(Derwent et al., 2010)
28	Trans-2-Butene	0.052	0.052	(Derwent et al., 2010)
29	Cis-2-Butene	0.0468	0.0468	(Derwent et al., 2010)
30	Isoprene	0.02	0.02	(Grosjean, 1992)
31	Trans-2-Pentene	0.0403	0.0403	(Derwent et al., 2010)
32	Cis-2-Pentene	0.0403	0.0403	(Derwent et al., 2010)

Table S5 Emission factors of gaseous pollutants for the test ships

Ship ID	Engine type	Operating mode	CO_2 (g kg^{-1} fuel)	CO (g kg^{-1} fuel)	NO_2 (g kg^{-1} fuel)	NO (g kg^{-1} fuel)	NO_x (g kg^{-1} fuel)	VOCs (g kg^{-1} fuel)
CCS1	Main engine	Maneuvering_diesel	3124	18.6	2.46	32.8	35.3	1.87
		Cruise_HFO	3145	5.49	2.66	35	37.6	2.22
	Auxiliary engine	Diesel	3148	3.51	1.89	27.9	29.8	0.6
CCS2	Main engine	Idling_diesel	3129	15.7	5.15	31.2	36.4	3.01
		Maneuvering_diesel	3077	48.8	1.17	18	19.1	1.00
		Cruise_diesel	3145	5.38	1.18	19.7	20.9	0.10
OGV1	Main engine	20%_diesel	3128	2.49	22.9	59.8	82.7	2.10
		75%_diesel	3132	1.49	9.57	64.1	73.7	0.45
		75%_diesel (NCR)	3129	2.44	6.23	35.8	42.1	0.46
		25%_HFO	3173	2.59	22.2	66.9	89.1	0.75
		50%_HFO	3178	2.44	12.8	61	73.8	0.81
		75%_HFO	3170	2.46	8.18	51.7	59.9	0.59
		85%_HFO	3173	2.46	8.47	54	62.4	1.65
		100%_HFO	3173	3.8	6.31	56.7	63	0.95
	Auxiliary engine	50%_diesel	3108	13.8	1.38	27.1	28.4	0.94
		50%_HFO	3174	3.33	1.45	20.8	22.3	0.31
OGV2	Main engine	50%_HFO	3181	2.93	18.58	74.23	92.81	0.23
		70%_HFO	3182	2.35	12.2	64.7	76.8	0.14
		90%_HFO	3182	1.91	12	62.2	74.2	0.10
	Auxiliary engine	60%_diesel	3126	2.63	1.89	31.16	33.04	0.09
		75%_diesel	3132	1.32	1.98	25.82	27.8	0.12
		50%_HFO	3183	1.86	3.62	29.79	33.41	0.37
		75%_HFO	3183	2	3.28	33.83	37.11	0.23

	Boiler	HFO	3186	0.62	0.15	6.11	6.26	0.17
OGV3	Main engine	75%_diesel	3131	1.64	7.47	49.8	57.3	0.22
		25%_HFO	3183	1.9	18.8	62.2	81	0.14
		50%_HFO	3182	2.49	8.09	60.2	68.3	0.46
		75%_HFO	3183	1.78	7.11	56.5	63.6	0.34
		95%_HFO	3181	2.7	2.37	40.5	42.9	0.37
	Auxiliary engine	50%_diesel	3130	2.78	1.02	24.4	25.4	0.13
		50%_HFO	3184	2.51	0.57	25.8	26.3	0.23
		75%_HFO	3185	1.91	0.4	26.6	27	0.15
ICS1	Main engine	Maneuvering_diesel	3108	16.9	8.36	55.9	64.2	0.49
		Cruise_diesel	3068	42.5	7.64	46.2	53.8	0.43
ICS2	Main engine	Idling_diesel	2622	327	15.8	36.1	51.9	1.08
		Maneuvering_diesel	3117	11.5	14.5	68.2	82.7	0.11
		Cruise_diesel	3116	12.2	12.6	72.4	85	0.17
ICS3	Main engine	Maneuvering_diesel	2852	180	13.2	44.7	57.9	2.53
		Cruise_diesel	2924	134	11.2	57.5	68.8	2.87
ICS4	Main engine	Maneuvering_diesel	2998	87.2	-	-	-	-
		Cruise_diesel	3103	20.3	8.06	12.3	20.4	0.35
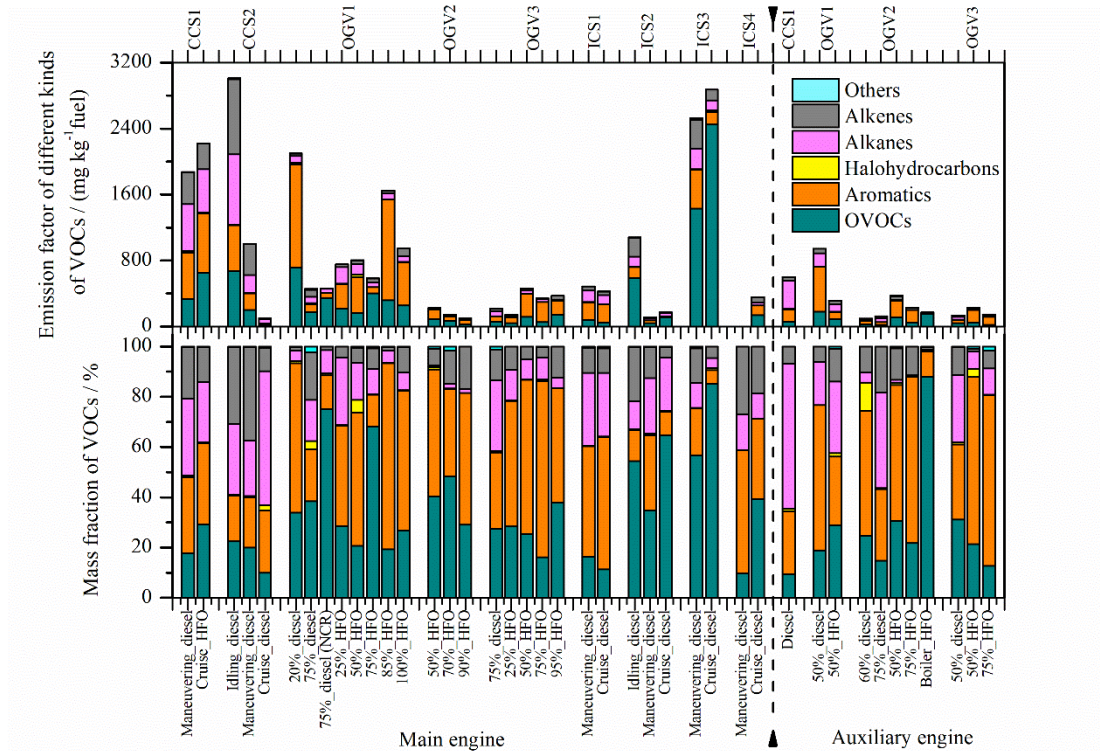
Figure S1 EFs of VOC components and their mass fractions
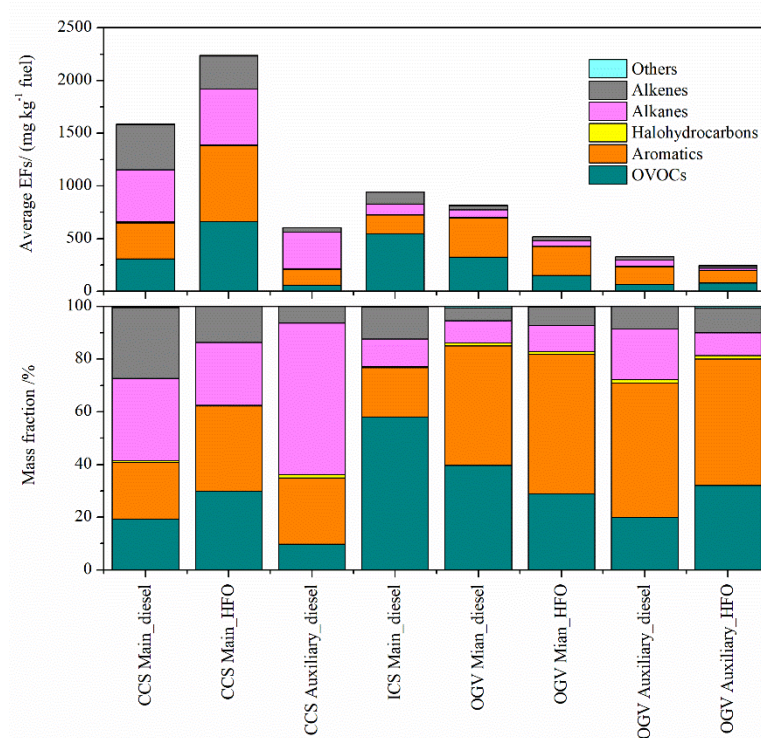
Figure S2 Average EFs of different kinds of VOCs and their mass fractions

Table S6 Mass concentrations of partial n-alkanes and PAHs in fuels (mg kg^{-1} fuel)

Species	Diesel	HFO		Diesel	HFO
n-dodecane	2.39±1.21	0.16±0.09	naphthalene	0.11±0.04	2.16±1.69
n-tridecane	2.05±0.80	0.31±0.08	alkylated nap	0.21±0.09	0.94±0.72
n-tetradecane	2.00±0.76	0.41±0.03	acenaphthylene	0.23±0.12	0.65±0.65
n-pentadecane	2.75±1.36	0.63±0.21	acenaphthene	0.11±0.04	0.18±0.12
n-hexadecane	3.34±1.97	0.83±0.39	fluorene	0.06±0.01	0.43±0.33
n-heptadecane	3.12±1.99	0.88±0.49	phenanthrene	0.07±0.01	0.43±0.26
n-octadecane	2.41±1.49	0.82±0.45	anthracene	0.05±0.00	0.15±0.07
n-nonadecane	1.99±1.19	0.83±0.47	fluoranthene	0.02±0.00	0.17±0.11
n-eicosane	1.57±0.85	0.78±0.45	pyrene	0.05±0.01	0.48±0.29
n-heneicosane	1.19±0.54	0.79±0.48	PAHs	89.4±29.8	146.1±75.6
n-docosane	0.88±0.34	0.77±0.46	UCM	19.6±11.9	17.57±9.95
n-alkanes	307.0±87.1	259.4±68.1			
b-alkanes	26.9±13.8	8.01±3.79			
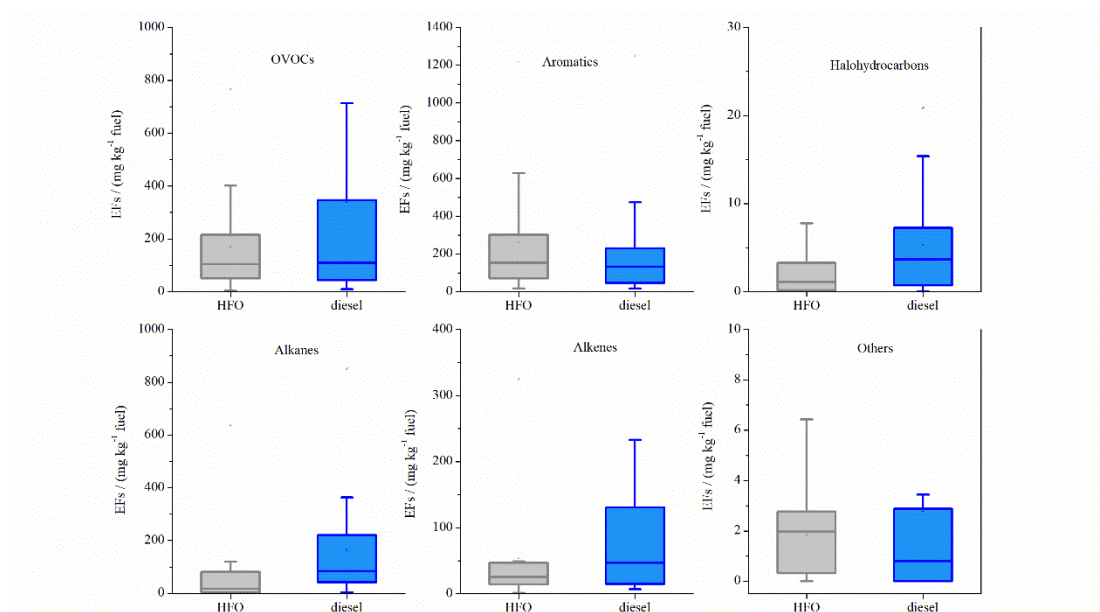
Figure S3 Box-whisker plots of VOC components between HFO and diesel
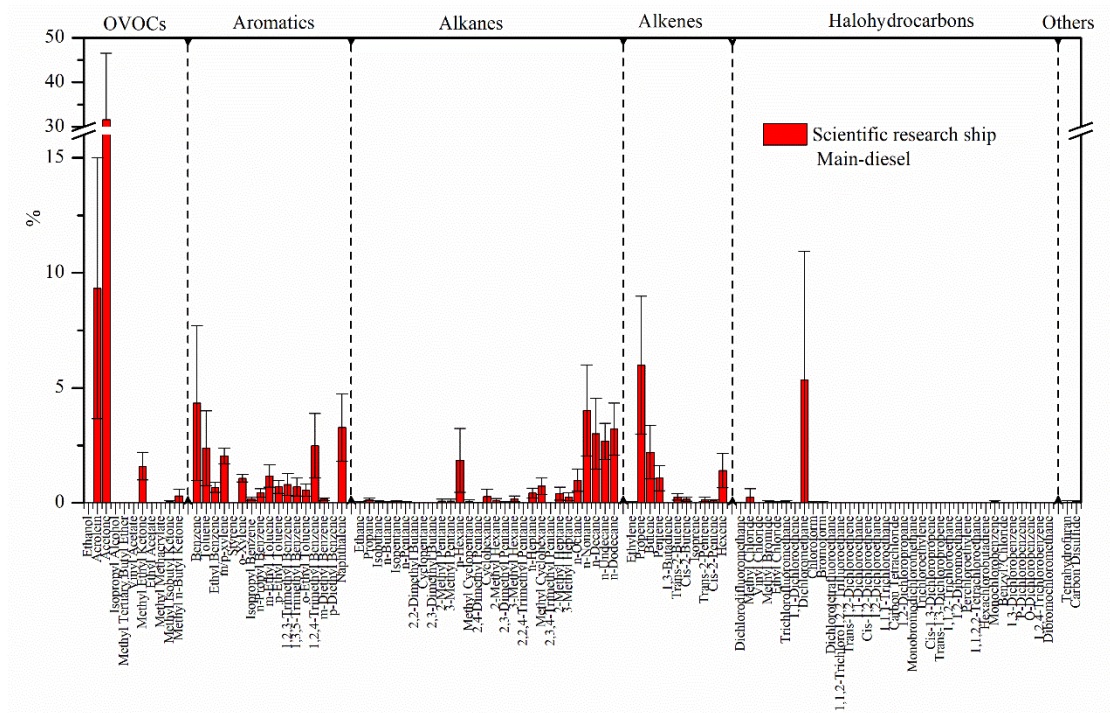
Figure S4 Profile of VOCs from a test scientific research ship

Table S7 Emission factors of the top 25 VOC species (mg kg⁻¹ fuel)

Species	CCS Main-diesel Mean±SD	Species	CCS Main-HFO Mean±SD	Species	CCS Auxiliary-diesel Mean±SD	Species	ICS Main-diesel Mean±SD
Acrolein	164±175	Acetone	510±134	n-Dodecane	50.7±9.43	Acetone	469±806
Propene	154±132	Benzene	194±38.5	n-Undecane	43.9±6.43	Propene	69.3±68.1
Acetone	108±96.8	Toluene	179±40.2	n-Decane	41.8±5.21	Acrolein	62.7±86.89
Butene	108±96.3	Propene	122±7.79	n-Nonane	41.5±5.66	Benzene	62.2±53.2
Benzene	90.2±67.3	m/p-xylene	101±16.5	n-Heptane	36.1±3.40	n-Decane	24.6±20.3
n-Dodecane	86.0±110	Acrolein	93.9±2.92	*n-Butane*	30.5±41.0	Naphthalene	24.5±30.8
n-Undecane	79.6±89.0	n-Heptane	91.2±27.6	Acetone	30.0±11.1	n-Undecane	22.3±16.7
n-Decane	60.6±57.8	Butene	72.0±4.56	Methyl Cyclohexane	27.6±2.83	Butene	20.1±21.1
Toluene	52.2±50.0	n-Nonane	55.5±4.54	Naphthalene	25.1±10.3	n-Dodecane	18.3±12.2
Hexene	47.2±43.4	Hexene	47.9±8.43	Acrolein	19.1±1.19	1,2,4-Trimethyl Benzene	17.4±18.9
Pentene	45.0±40.4	Methyl Cyclohexane	43.9±15.7	m/p-xylene	18.0±2.32	Toluene	16.2±14.4
Cis-2-Pentene	44.7±40.4	n-Decane	42.5±5.82	1,3,5-Trimethyl Benzene	17.4±2.20	Methyl Ethyl Ketone	15.7±18.2
Isobutane	43.1±50.4	Naphthalene	42.5±1.24	Toluene	16.5±1.60	n-Nonane	13.8±12.8
2-Methyl Hexane	36.9±NA.	o-Xylene	37.1±6.37	1,2,4-Trimethyl Benzene	16.26±2.20	m/p-xylene	10.4±10.0
n-Heptane	36±57.5	Ethyl Benzene	35.9±5.44	Butene	14.03±5.87	Pentene	10.1±10.4
n-Nonane	35.4±31.1	Isopentane	33.3±13.5	Propene	13.8±1.29	m-Ethyl Toluene	9.69±9.71
m/p-xylene	33.2±31.9	Methyl Ethyl Ketone	33.0±8.04	2-Methyl Hexane	13.0±1.19	Hexene	8.84±9.23
Naphthalene	26.2±20.4	n-Pentane	30.8±11.9	Benzene	12.8±1.07	o-Xylene	6.15±5.09
1,3,5-Trimethyl Benzene	26.1±22.1	1,3,5-Trimethyl Benzene	30.6±5.43	3-Methyl Heptane	10.8±1.04	Propane	5.30±7.95
Methyl Cyclohexane	24.5±34.4	Pentene	29.7±1.90	n-Pentane	10.1±10.3	p-Ethyl Toluene	5.22±5.17
Methyl Ethyl Ketone	23.8±25.2	Isobutane	27.6±1.95	Isopentane	9.85±7.74	1,2,3-Trimethyl Benzene	5.02±5.30
p-Diethyl Benzene	21.9±25.2	n-Undecane	27.4±8.55	Isobutane	9.44±3.83	Ethyl Benzene	4.93±4.45
Isopentane	20.4±15.9	n-Hexane	26.9±9.96	p-Diethyl Benzene	8.48±0.96	n-Octane	4.57±3.57
1,2,4-Trimethyl Benzene	18.8±15.6	2-Methyl Hexane	26.5±9.03	o-Xylene	7.98±1.05	1,3,5-Trimethyl Benzene	4.34±4.39
m-Ethyl Toluene	14.9±12.4	1,2,4-Trimethyl Benzene	24.7±4.49	m-Ethyl Toluene	7.74±1.07	o-Ethyl Toluene	4.18±4.09
Species	OGV Main-diesel Mean±SD	Species	OGV Main-HFO Mean±SD	Species	OGV Auxiliary-diesel Mean±SD	Species	OGV Auliliary-HFO Mean±SD

Naphthalene	317±593	Naphthalene	198±281	Naphthalene	117±193	Naphthalene	68.9±49.6
Acetone	292±267	Acetone	111±104	Acetone	48.2±51.9	Acetone	61.5±49.4
1,3-Butadiene	28.7±35.9	Acrolein	19.7±17.7	n-Dodecane	19.4±16.0	Acrolein	16.8±16.7
Acrolein	24.7±21.2	Propene	14.3±13.4	Acrolein	14.5±19.7	m/p-xylene	12.0±11.2
n-Dodecane	16.6±13.5	Toluene	14.0±26.5	Propene	13.3±14.0	Propene	10.9±10.2
n-Undecane	13.1±11.0	m/p-xylene	11.5±8.15	m/p-xylene	12.7±13.1	o-Xylene	7.51±7.34
n-Decane	13.0±5.80	1,3-Butadiene	9.57±14.4	n-Undecane	12.3±12.2	Benzene	7.31±4.14
Propene	12.2±7.05	n-Nonane	9.04±14.8	n-Decane	10.3±14.9	Ethylene	5.86±8.36
Benzene	11.8±7.13	n-Decane	8.84±11.7	n-Nonane	8.25±13.5	1,2,4-Trimethyl Benzene	5.33±4.61
m/p-xylene	10.5±6.35	Benzene	8.12±5.14	o-Xylene	7.68±8.07	Ethyl Benzene	5.25±5.13
n-Nonane	10.0±4.87	o-Xylene	6.86±4.63	1,2,4-Trimethyl Benzene	7.64±10.9	Toluene	4.88±4.09
1,2,4-Trimethyl Benzene	7.32±2.16	n-Dodecane	6.64±5.91	Ethylene	6.46±5.42	n-Dodecane	4.43±4.87
Methyl Chloride	7.16±5.22	1,2,4-Trimethyl Benzene	6.61±6.03	Benzene	4.88±4.19	1,4-Dioxane	4.18±4.21
o-Xylene	6.20±3.95	n-Undecane	6.21±5.59	Ethyl Benzene	4.36±3.4	n-Nonane	3.74±8.67
Toluene	5.18±2.70	n-Octane	4.52±6.95	Toluene	3.77±3.91	n-Decane	3.37±7.09
Methyl Ethyl Ketone	4.89±4.56	Ethyl Benzene	4.40±1.89	m-Ethyl Toluene	3.32±6.09	n-Undecane	3.17±3.96
n-Octane	4.20±3.12	Butene	3.62±2.17	n-Octane	2.91±5.38	Butene	2.79±2.92
Tetrahydrofuran	4.02±4.66	Methyl Cyclohexane	3.39±4.85	Pentene	2.56±4.53	n-Octane	2.38±4.76
m-Ethyl Toluene	3.60±1.26	m-Ethyl Toluene	3.38±3.42	Hexene	2.38±4.23	m-Ethyl Toluene	2.27±1.95
Methyl Cyclohexane	3.51±2.34	Ethylene	3.20±3.49	Methyl Isobutyl Ketone	2.22±3.85	Tetrahydrofuran	1.78±1.24
Cyclohexane	3.39±5.88	Methyl Ethyl Ketone	3.20±2.73	Methyl Cyclohexane	2.13±3.89	Bromoform	1.76±3.52
Methyl Isobutyl Ketone	3.38±4.77	Methyl Chloride	3.20±7.89	o-Ethyl Toluene	2.13±3.92	1,2,3-Trimethyl Benzene	1.75±1.98
Ethyl Benzene	3.23±1.92	Hexene	2.86±4.83	1,4-Dioxane	2.01±1.16	Pentene	1.54±2.47
1,2,3-Trimethyl Benzene	2.45±NA.	Pentene	2.82±3.77	1,2,4-Trichlorobenzene	1.92±3.10	Methyl Cyclohexane	1.54±3.08
Dichloromethane	2.06±2.59	Methyl Isobutyl Ketone	2.79±3.68	Butene	1.73±1.50	o-Ethyl Toluene	1.41±1.33
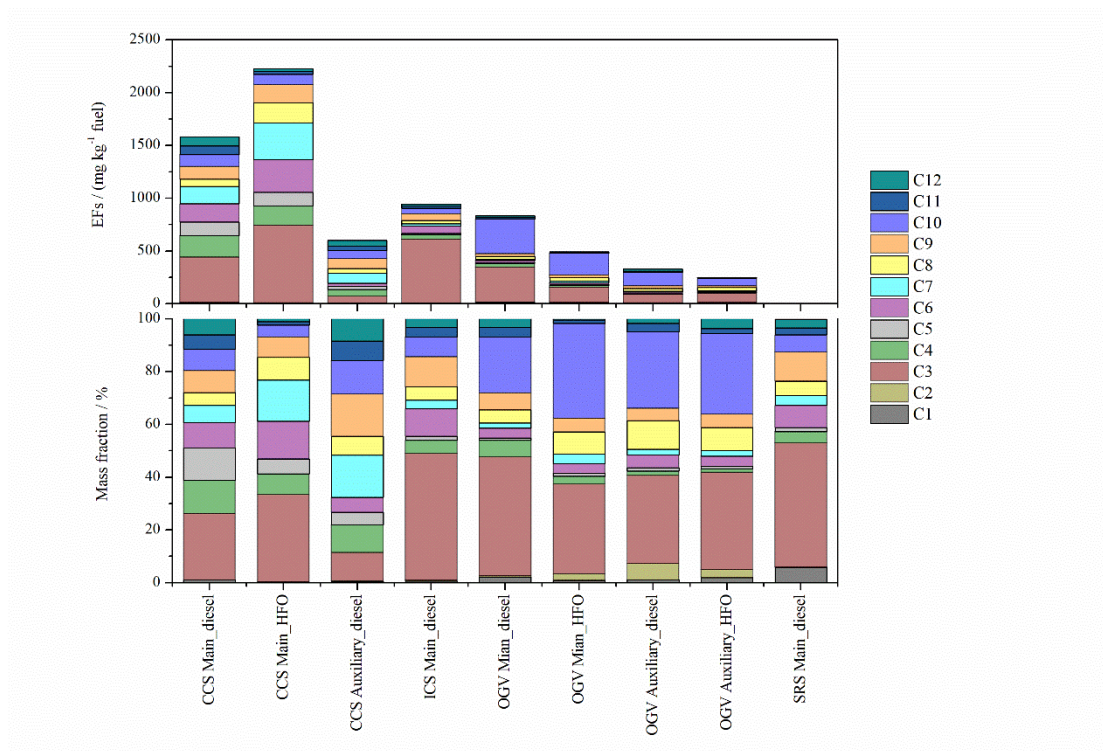
Figure S5 EFs and mass fractions of VOCs grouping based on carbon number

Table S8 Diagnostic ratios of VOCs from ship emissions

Vessel type/fuel	Toluene /Benzene	Ethylbenzene/m,p-Xylene	Isobutane/n-Butane	Isopentane/n-Pentane
CCS Main_diesel	0.72±0.41	0.38±0.05	1.70±0.00	0.93±0.07
CCS Main_HFO	0.90±0.02	0.35±0.00	2.09±1.06	1.08±0.02
CCS Auxiliary_diesel	1.28±0.02	0.32±0.00	2.26±2.91	1.24±0.50
ICS Main_diesel	0.29±0.09	0.49±0.07	0.67±0.18	1.09±0.22
OGV Mian_diesel	0.48±0.19	0.31±0.02	0.40±0.00	-
OGV Mian_HFO	0.83±0.41	0.46±0.17	0.33±0.03	0.67±0.20
OGV Auxiliary_diesel	0.73±0.22	0.44±0.24	0.60±0.00	0.44±0.63
OGV Auxiliary_HFO	0.57±0.27	0.48±0.16	0.34±0.00	0.87±0.00

Table S9 The R_{O_3}, R_{SOA}, OFP and SOAFP in this study and previous studies

Vessel type/fuel	Sulfur content (% m/m)	R_{O_3} (g O₃ g⁻¹ VOCs)	OFP (g O₃ kg⁻¹ fuel)	$R_{SOA, High NOx}$ (mg SOA g⁻¹ VOCs)	$R_{SOA, Low NOx}$ (mg SOA g⁻¹ VOCs)	SOAFP, High NOx (mg SOA kg⁻¹ fuel)	SOAFP, Low NOx (mg SOA kg⁻¹ fuel)	Sources
CCS Main_diesel	N.D.	4.60	7.44	81.8	141	121	201	This study
CCS Main_HFO	0.39	3.54	7.81	63.2	137	140	303	This study
CCS Auxiliary_diesel	N.D.	3.00	1.80	99.2	174	59.6	104	This study
ICS Main_diesel	N.D.	3.43	2.66	77.1	144	49.7	91.8	This study
OGV Mian_diesel	0.02-0.05	2.95	2.14	96.2	219	101	262	This study
OGV Mian_HFO	0.43-0.50	3.72	1.56	114	312	80.0	196	This study
OGV Auxiliary_diesel	0.02-0.05	3.67	1.15	134	294	47.7	116	This study
OGV Auxiliary_HFO	0.43-0.50	3.55	0.91	113	303	26.5	71.5	This study
Vessels at berth/ before IFSP[a]	1.60-2.90	3.19	0.35	288	313	37	40	(Wu et al., 2020)
Vessels at berth/ after IFSP[a]	0.01-1.14	5.41	10.37	73	105	96	137	(Wu et al., 2020)
River vessels/diesel	0.02-0.06	5.55	22.98	37	69	165	322	(Wu et al., 2020)
OGV	0.38, 1.12	4.22	0.09-2.56	80	228	1.05-41.0	3.40-126	(Huang et al., 2018)
Vessels at berth/diesel	0.02-0.3	2.63	-	17	-	-	-	(Xiao et al., 2018)
Inland cargo ship/diesel	-	~4.6-5.6[b]	0.33-0.83	-	~16-47[b]	-	2.8-8.9	(Wu et al., 2019)
Container ship/diesel	0.12	~4.5[b]	~0.8[b]		~17[b]		~4.5[b]	(Wu et al., 2019)
Container ship/HFO	2.07	~6.0[b]	~2.6[b]		~28[b]		~8.7[b]	(Wu et al., 2019)

[a], IFSP, implementation of the fuel switch policy;
[b], the values were estimated according to the bar chart.

Table S10 The top 20 contributing VOC species to OFP (%)

Species	CCS Main-diesel Mean±SD	Species	CCS Main-HFO Mean±SD	Species	CCS Auxiliary-diesel Mean±SD	Species	ICS Main-diesel Mean±SD
Propene	21.3±6.52	Propene	18.3±1.24	1,3,5-Trimethyl Benzene	11.3±0.19	Propene	27.7±11.8
Acrolein	13.4±6.15	m/p-xylene	10.1±0.32	Propene	8.94±0.15	Acrolein	15.1±15.0
Butene	13.0±3.85	Toluene	9.11±0.86	1,2,4-Trimethyl Benzene	8.00±0.20	1,2,4-Trimethyl Benzene	7.34±7.75
1,3,5-Trimethyl Benzene	6.08±4.32	Acrolein	9.03±0.91	Acrolein	7.94±0.38	Butene	6.69±3.08
Cis-2-Pentene	5.57±1.69	Butene	9.02±0.62	m/p-xylene	7.79±0.14	Acetone	5.67±7.82
m/p-xylene	4.64±3.11	1,3,5-Trimethyl Benzene	4.6±0.21	Butene	7.46±2.35	m/p-xylene	3.87±3.57
Pentene	3.88±1.19	o-Xylene	3.62±0.15	Naphthalene	4.57±1.4	m-Ethyl Toluene	3.31±3.29
Toluene	3.19±1.99	Hexene	3.36±0.15	Toluene	3.66±0.05	Naphthalene	3.12±1.83
Hexene	3.13±0.85	Cis-2-Pentene	2.81±1.9	o-Xylene	3.39±0.07	1,2,3-Trimethyl Benzene	2.98±3.01
1,2,4-Trimethyl Benzene	3.08±1.85	1,2,4-Trimethyl Benzene	2.8±0.14	m-Ethyl Toluene	3.17±0.09	Toluene	2.93±2.11
o-Xylene	2.11±1.37	Pentene	2.76±0.19	Methyl Cyclohexane	2.61±0.02	Pentene	2.39±1.05
m-Ethyl Toluene	2.08±1.31	Acetone	2.33±0.31	n-Heptane	2.15±0.03	1,3,5-Trimethyl Benzene	2.39±2.33
Naphthalene	1.98±1.65	m-Ethyl Toluene	2.27±0.11	*n-Butane*	2.11±2.85	o-Xylene	2.24±1.75
p-Diethyl Benzene	1.57±0.94	Naphthalene	1.84±0.29	p-Diethyl Benzene	2.09±0.01	Benzene	1.87±1.06
Trans-2-Butene	1.48±1.04	Benzene	1.78±0.12	Cis-2-Pentene	2.06±0.02	Hexene	1.58±0.73
n-Pentane	1.29±2.37	Trans-2-Butene	1.7±0.22	n-Nonane	1.79±0.05	p-Ethyl Toluene	1.06±1.04
Isopentane	1.21±1.87	Ethyl Benzene	1.4±0.03	n-Decane	1.58±0.02	o-Ethyl Toluene	1.06±0.95
Isobutane	1.13±1.05	n-Heptane	1.24±0.22	n-Dodecane	1.54±0.12	Methyl Ethyl Ketone	0.96±0.62
Benzene	0.85±0.39	Trans-2-Pentene	1.06±0.18	n-Undecane	1.49±0.05	Ethylene	0.92±2.75
n-Dodecane	0.8±0.59	Methyl Cyclohexane	0.94±0.22	Pentene	1.43±0.01	n-Decane	0.87±0.67
Species	OGV Main-diesel Mean±SD	Species	OGV Main-HFO Mean±SD	Species	OGV Auxiliary-diesel Mean±SD	Species	OGV Auliliary-HFO Mean±SD
Naphthalene	24.6±33.8	Naphthalene	32.3±20.01	Naphthalene	23.1±13.4	Naphthalene	31.3±28.9
1,3-Butadiene	14.5±21.8	Propene	11.9±6.73	Propene	16.1±7.38	Propene	11.4±8.14
Acrolein	9.86±1.61	Acrolein	10.0±6.57	m/p-xylene	11.2±5.86	Acrolein	11.3±7.62
Propene	9.74±7.13	m/p-xylene	8.68±8.75	Ethylene	10.6±11.4	m/p-xylene	9.52±5.70
Acetone	7.64±9.25	o-Xylene	5.38±5.94	Acrolein	8.25±5.92	Acetone	6.76±12.8

m/p-xylene	6.64±5.64	1,2,4-Trimethyl Benzene	4.16±2.07	o-Xylene	6.58±3.72	o-Xylene	5.88±3.92
1,2,4-Trimethyl Benzene	5.43±3.28	Toluene	4.09±7.97	1,2,4-Trimethyl Benzene	5.22±1.03	1,2,4-Trimethyl Benzene	4.63±2.2
o-Xylene	3.73±2.97	1,3-Butadiene	3.67±9.52	Butene	2.83±3.28	Ethylene	3.36±4.35
m-Ethyl Toluene	2.11±1.19	Ethylene	3.26±4.68	Acetone	1.93±1.15	Butene	2.60±2.05
Butene	1.90±3.80	Butene	2.81±2.82	Ethyl Benzene	1.75±0.81	Toluene	1.99±0.74
Toluene	1.82±1.52	Acetone	2.77±2.47	Toluene	1.59±0.55	Ethyl Benzene	1.62±0.90
1,2,3-Trimethyl Benzene	1.01±2.02	m-Ethyl Toluene	1.50±1.12	n-Dodecane	1.47±1.60	m-Ethyl Toluene	1.47±0.95
Benzene	0.96±1.20	Ethyl Benzene	1.46±1.30	m-Ethyl Toluene	1.06±1.32	1,2,3-Trimethyl Benzene	1.45±1.58
Pentene	0.95±1.21	Pentene	1.14±0.90	Pentene	0.90±1.05	Pentene	0.93±1.34
1,3,5-Trimethyl Benzene	0.81±1.62	1,3,5-Trimethyl Benzene	0.73±0.82	1,3,5-Trimethyl Benzene	0.86±1.01	1,3,5-Trimethyl Benzene	0.88±0.88
Ethyl Benzene	0.81±0.67	1,2,3-Trimethyl Benzene	0.68±0.97	n-Undecane	0.84±0.81	Benzene	0.68±0.29
n-Dodecane	0.71±1.02	Hexene	0.65±0.88	Trans-2-Butene	0.70±0.89	o-Ethyl Toluene	0.66±0.50
n-Nonane	0.67±0.63	Benzene	0.48±0.24	Hexene	0.64±0.74	Hexene	0.59±0.98
n-Undecane	0.66±1.00	o-Ethyl Toluene	0.46±0.55	1,2,3-Trimethyl Benzene	0.57±1.14	Trans-2-Butene	0.47±0.77
Hexene	0.65±1.31	Methyl Isobutyl Ketone	0.40±1.01	o-Ethyl Toluene	0.52±0.64	n-Dodecane	0.35±0.42

Table S11 The top 20 contributing VOC species to SOAFP (%)

Species	CCS Main-diesel Mean±SD	Species	CCS Main-HFO Mean±SD	Species	CCS Auxiliary-diesel Mean±SD	Species	ICS Main-diesel Mean±SD
Benzene	15.7±8.53	Benzene	24.0±0.71	Naphthalene	17.3±4.01	Benzene	24.6±11.8
n-Dodecane	15.4±7.82	Toluene	18.1±1.02	n-Dodecane	17.0±0.02	Naphthalene	17.7±10.9
Naphthalene	11.9±4.78	m/p-xylene	12.4±0.08	n-Undecane	11.5±0.47	n-Dodecane	8.74±4.65
n-Undecane	10.9±4.11	Naphthalene	10.6±2.10	m/p-xylene	6.34±0.37	n-Undecane	8.50±7.23
Toluene	7.60±4.07	co-Xylene	4.52±0.01	1,3,5-Trimethyl Benzene	6.11±0.37	1,2,4-Trimethyl Benzene	6.47±5.26
m/p-xylene	6.29±2.91	Ethyl Benzene	4.38±0.08	n-Decane	5.92±0.37	Toluene	5.67±3.17
1,3,5-Trimethyl Benzene	5.46±1.4	1,3,5-Trimethyl Benzene	3.73±0.03	1,2,4-Trimethyl Benzene	5.72±0.30	m/p-xylene	4.51±3.87
n-Decane	4.47±1.04	1,2,4-Trimethyl Benzene	3.01±0.04	Toluene	4.85±0.44	n-Decane	4.42±2.56
p-Diethyl Benzene	4.04±1.54	m-Ethyl Toluene	2.93±0.03	Benzene	4.60±0.48	m-Ethyl Toluene	3.53±2.67
1,2,4-Trimethyl Benzene	3.71±0.61	n-Dodecane	2.88±0.05	n-Nonane	3.25±0.17	o-Xylene	2.57±1.89
m-Ethyl Toluene	3.01±0.53	n-Undecane	2.45±0.36	p-Diethyl Benzene	2.99±0.22	Ethyl Benzene	2.08±1.66
o-Xylene	2.90±0.9	n-Decane	2.09±0.07	o-Xylene	2.81±0.16	1,2,3-Trimethyl Benzene	1.97±1.51
Ethyl Benzene	2.33±0.92	p-Ethyl Toluene	1.72±0.03	m-Ethyl Toluene	2.72±0.14	p-Ethyl Toluene	1.89±1.41
o-Ethyl Toluene	1.45±0.22	n-Nonane	1.52±0.13	Ethyl Benzene	2.02±0.14	1,3,5-Trimethyl Benzene	1.61±1.17
n-Nonane	1.37±0.51	p-Diethyl Benzene	1.46±0.05	o-Ethyl Toluene	1.57±0.08	o-Ethyl Toluene	1.52±0.99
n-Propyl Benzene	1.14±0.12	o-Ethyl Toluene	1.27±0.02	p-Ethyl Toluene	1.34±0.07	n-Propyl Benzene	1.34±0.73
p-Ethyl Toluene	1.02±0.69	n-Propyl Benzene	1.00±0.01	n-Propyl Benzene	1.08±0.04	n-Nonane	1.18±0.54
m-Diethyl Benzene	0.45±0.35	Methyl Cyclohexane	0.58±0.11	Methyl Cyclohexane	1.07±0.09	m-Diethyl Benzene	0.83±0.55
Isopropyl Benzene	0.29±0.22	Isopropyl Benzene	0.49±0.01	Isopropyl Benzene	0.58±0.00	Isopropyl Benzene	0.48±0.32
Methyl Cyclohexane	0.29±0.47	n-Heptane	0.27±0.04	m-Diethyl Benzene	0.58±0.01	n-Octane	0.21±0.12
Species	OGV Main-diesel Mean±SD	Species	OGV Main-HFO Mean±SD	Species	OGV Auxiliary-diesel Mean±SD	Species	OGV Auliliary-HFO Mean±SD
Naphthalene	48.0±33.8	Naphthalene	72.1±16.3	Naphthalene	57.7±21.5	Naphthalene	64.4±21.9
Benzene	10.4±12.7	m/p-xylene	6.16±6.30	n-Dodecane	13.2±16.0	m/p-xylene	7.72±5.63
m/p-xylene	7.30±7.03	o-Xylene	3.87±4.22	m/p-xylene	6.57±3.54	Benzene	5.31±3.96
n-Dodecane	6.99±8.82	Benzene	3.53±2.57	n-Undecane	4.95±5.06	o-Xylene	4.87±3.70

n-Undecane	4.61±5.97	Toluene	3.48±4.70	o-Xylene	3.95±2.30	1,2,4-Trimethyl Benzene	3.31±2.45
1,2,4-Trimethyl Benzene	4.50±2.91	Ethyl Benzene	2.62±2.55	Benzene	2.88±1.62	Ethyl Benzene	3.17±2.20
o-Xylene	4.23±4.06	1,2,4-Trimethyl Benzene	2.35±1.52	Ethyl Benzene	2.71±1.38	Toluene	2.52±1.64
Toluene	3.15±2.88	n-Dodecane	1.45±1.82	1,2,4-Trimethyl Benzene	2.61±0.28	n-Dodecane	2.23±2.73
Ethyl Benzene	2.27±2.15	n-Undecane	1.07±1.10	Toluene	1.59±0.85	n-Undecane	1.35±2.05
m-Ethyl Toluene	2.19±1.61	m-Ethyl Toluene	0.92±0.81	n-Decane	1.36±1.09	m-Ethyl Toluene	1.18±1.33
n-Decane	2.00±2.20	n-Decane	0.77±1.18	m-Ethyl Toluene	0.55±0.64	n-Decane	0.93±2.08
n-Nonane	1.56±1.54	n-Nonane	0.44±0.84	n-Nonane	0.45±0.30	o-Ethyl Toluene	0.75±0.90
o-Ethyl Toluene	0.79±1.09	o-Ethyl Toluene	0.30±0.42	o-Ethyl Toluene	0.36±0.41	1,2,3-Trimethyl Benzene	0.60±0.81
1,2,3-Trimethyl Benzene	0.42±0.83	p-Ethyl Toluene	0.23±0.31	1,3,5-Trimethyl Benzene	0.31±0.38	n-Nonane	0.59±1.40
n-Octane	0.41±0.47	1,3,5-Trimethyl Benzene	0.22±0.29	p-Ethyl Toluene	0.25±0.30	1,3,5-Trimethyl Benzene	0.47±0.71
1,3,5-Trimethyl Benzene	0.34±0.68	1,2,3-Trimethyl Benzene	0.21±0.33	1,2,3-Trimethyl Benzene	0.23±0.47	p-Ethyl Toluene	0.31±0.34
Methyl Cyclohexane	0.28±0.30	n-Propyl Benzene	0.14±0.23	n-Propyl Benzene	0.20±0.23	n-Octane	0.13±0.32
p-Ethyl Toluene	0.24±0.48	n-Octane	0.10±0.20	n-Octane	0.05±0.06	Methyl Cyclohexane	0.08±0.20
n-Propyl Benzene	0.13±0.25	Methyl Cyclohexane	0.06±0.14	Methyl Cyclohexane	0.04±0.05	n-Propyl Benzene	0.05±0.08
m-Diethyl Benzene	0.11±0.22	Isopropyl Benzene	0.01±0.02	Cyclohexane	0.01±0.02	n-Heptane	0.01±0.02

REFERENCES

Chan, A. W. H., Kautzman, K. E., Chhabra, P. S., Surratt, J. D., Chan, M. N., Crounse, J. D., Kuerten, A., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from photooxidation of naphthalene and alkylnaphthalenes: implications for oxidation of intermediate volatility organic compounds (IVOCs), Atmos. Chem. Phys., 9, 3049-3060, 2009.

Derwent, R. G., Jenkin, M. E., Utembe, S. R., Shallcross, D. E., Murrells, T. P., and Passant, N. R.: Secondary organic aerosol formation from a large number of reactive man-made organic compounds, Sci. Total Environ., 408, 3374-3381, 10.1016/j.scitotenv.2010.04.013, 2010.

Grosjean, D.: In situ organic aerosol formation during a smog episode: Estimated production and chemical functionality, Atmos. Environ. Part A. General Topics, 26, 953-963, https://doi.org/10.1016/0960-1686(92)90027-I, 1992.

Huang, C., Hu, Q., Li, Y., Tian, J., Ma, Y., Zhao, Y., Feng, J., An, J., Qiao, L., Wang, H., Jing, S. a., Huang, D., Lou, S., Zhou, M., Zhu, S., Tao, S., and Li, L.: Intermediate Volatility Organic Compound Emissions from a Large Cargo Vessel Operated under Real-World Conditions, Environ. Sci. Technol., 52, 12934-12942, 10.1021/acs.est.8b04418, 2018.

Lim, Y. B., and Ziemann, P. J.: Effects of Molecular Structure on Aerosol Yields from OH Radical-Initiated Reactions of Linear, Branched, and Cyclic Alkanes in the Presence of NO_x, Environ. Sci. Technol., 43, 2328-2334, 10.1021/es803389s, 2009.

Ng, N. L., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Kroll, J. H., Kwan, A. J., McCabe, D. C., Wennberg, P. O., Sorooshian, A., Murphy, S. M., Dalleska, N. F., Flagan, R. C., and Seinfeld, J. H.: Effect of NO_x level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes, Atmos. Chem. Phys., 7, 5159-5174, 2007.

Wu, D., Ding, X., Li, Q., Sun, J. F., Huang, C., Yao, L., Wang, X. M., Ye, X. N., Chen, Y. J., He, H., and Chen, J. M.: Pollutants emitted from typical Chinese vessels: Potential contributions to ozone and secondary organic aerosols, Journal of Cleaner Production, 238, 9, 10.1016/j.jclepro.2019.117862, 2019.

Wu, Z., Zhang, Y., He, J., Chen, H., Huang, X., Wang, Y., Yu, X., Yang, W., Zhang, R., Zhu, M., Li, S., Fang, H., Zhang, Z., and Wang, X.: Dramatic increase in reactive volatile organic compound (VOC) emissions from ships at berth after implementing the fuel switch policy in the Pearl River Delta Emission Control Area, Atmos. Chem. Phys., 20, 1887-1900, 10.5194/acp-20-1887-2020, 2020.

Xiao, Q., Li, M., Liu, H., Fu, M., Deng, F., Lv, Z., Man, H., Jin, X., Liu, S., and He, K.: Characteristics of marine shipping emissions at berth: profiles for particulate matter and volatile organic compounds, Atmos. Chem. Phys., 18, 9527-9545, 10.5194/acp-18-9527-2018, 2018.