Supplement for:

Measurement report: Vertical and temporal variability of near-surface ozone production rate and sensitivity in an urban area in Pearl River Delta (PRD) region, China

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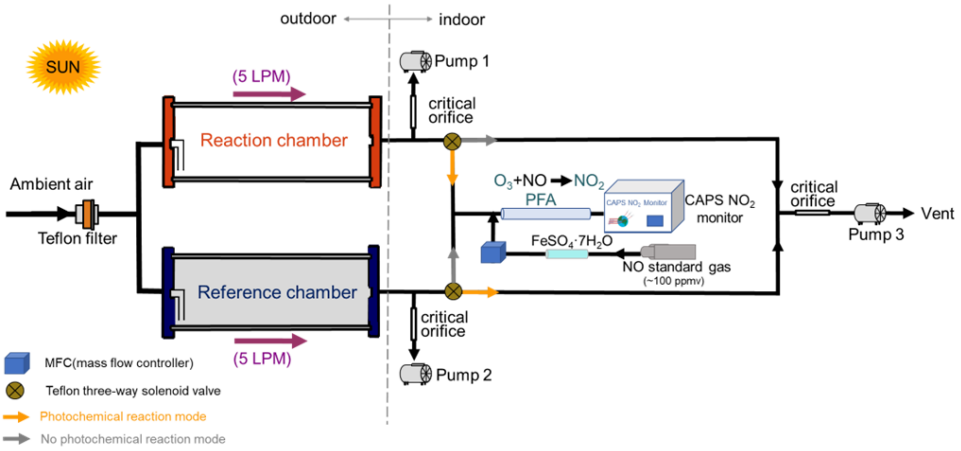

Figure S1： **Schematic of the NPOPR detection system.**

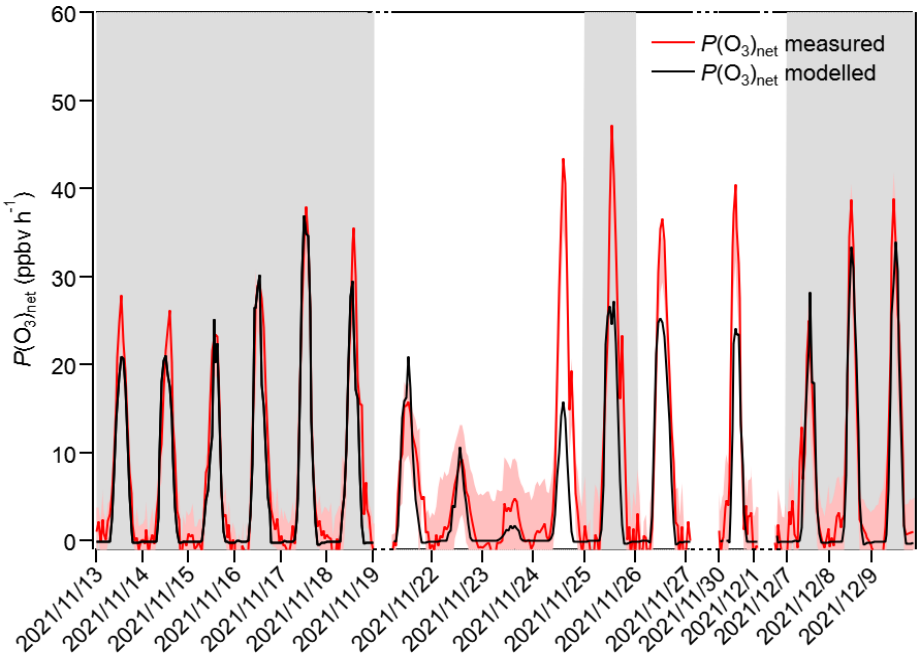

Figure S2：Measured and modelled $P(O_3)_{net}$ during the observation period from 13 November-9 December 2021

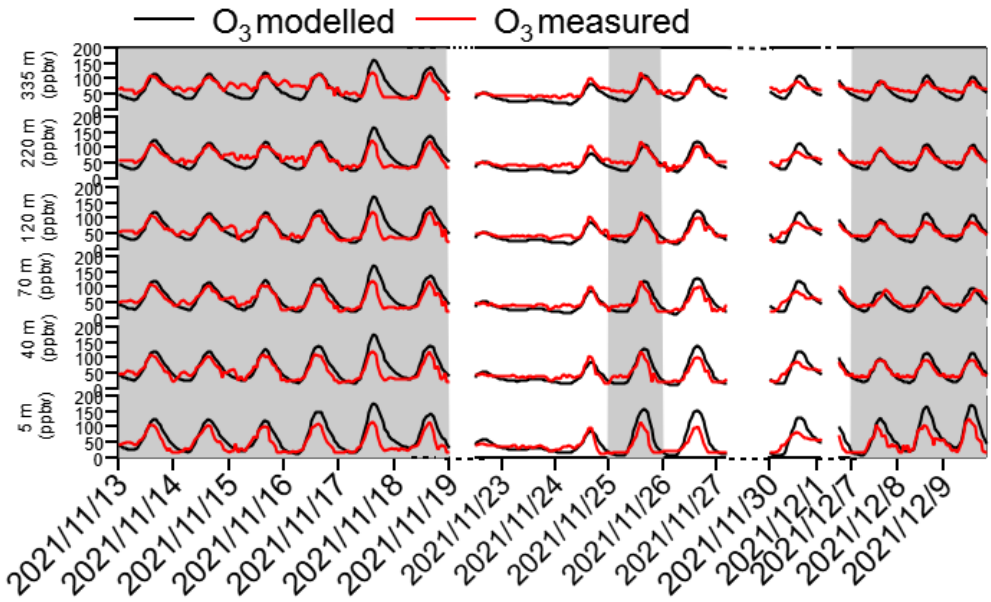

Figure S3：Measured and modelled O_3 concentrations at different heights during the observation period from 13 November-9 December 2021. The gray columns show the typical ozone episodes that occurred.

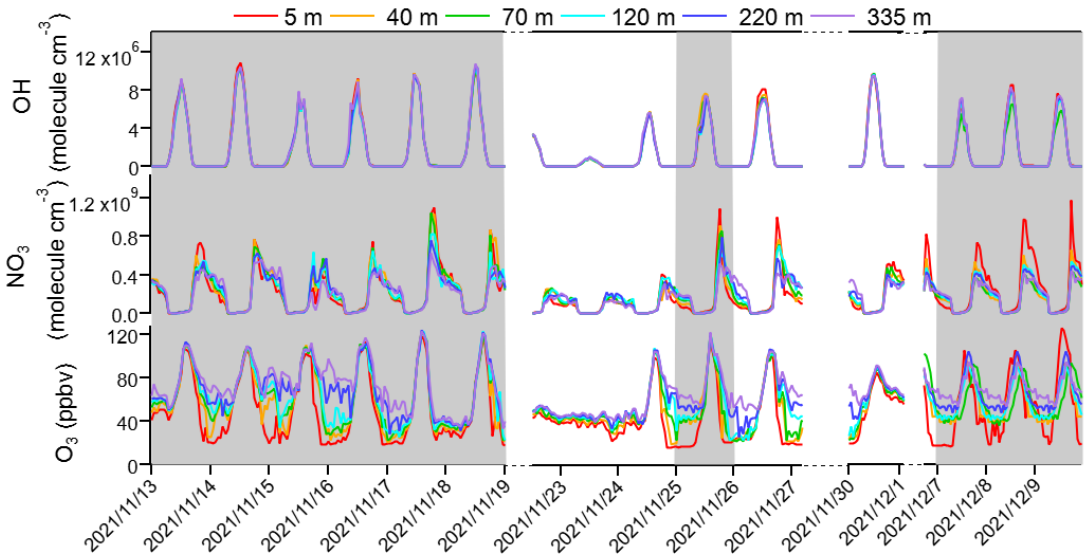

Figure S4：Time series of model-simulated OH and NO_3 concentrations in molecule cm^{-3}, and measured O_3 concentrations in ppbv at six different heights during 13 November-9 December 2021, at SZMGT, the gray columns show the typical ozone pollution episodes that occurred.

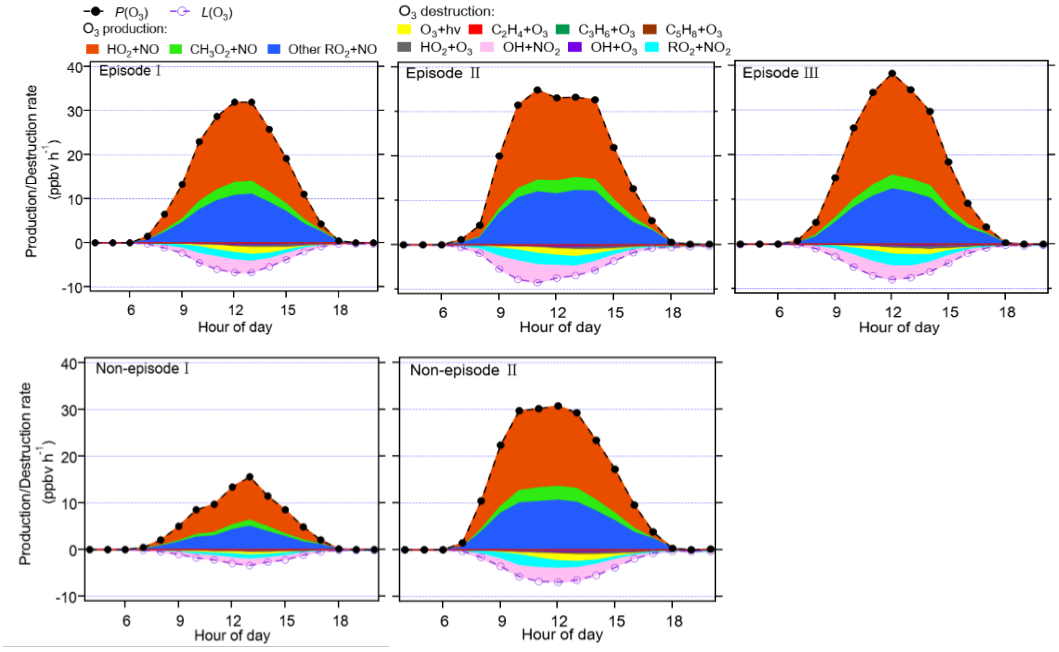

Figure S5. Average diurnal cycles of the model-simulated O_3 production and destruction rates at 5 m ground level during different episodes/non-episodes over the observation period.

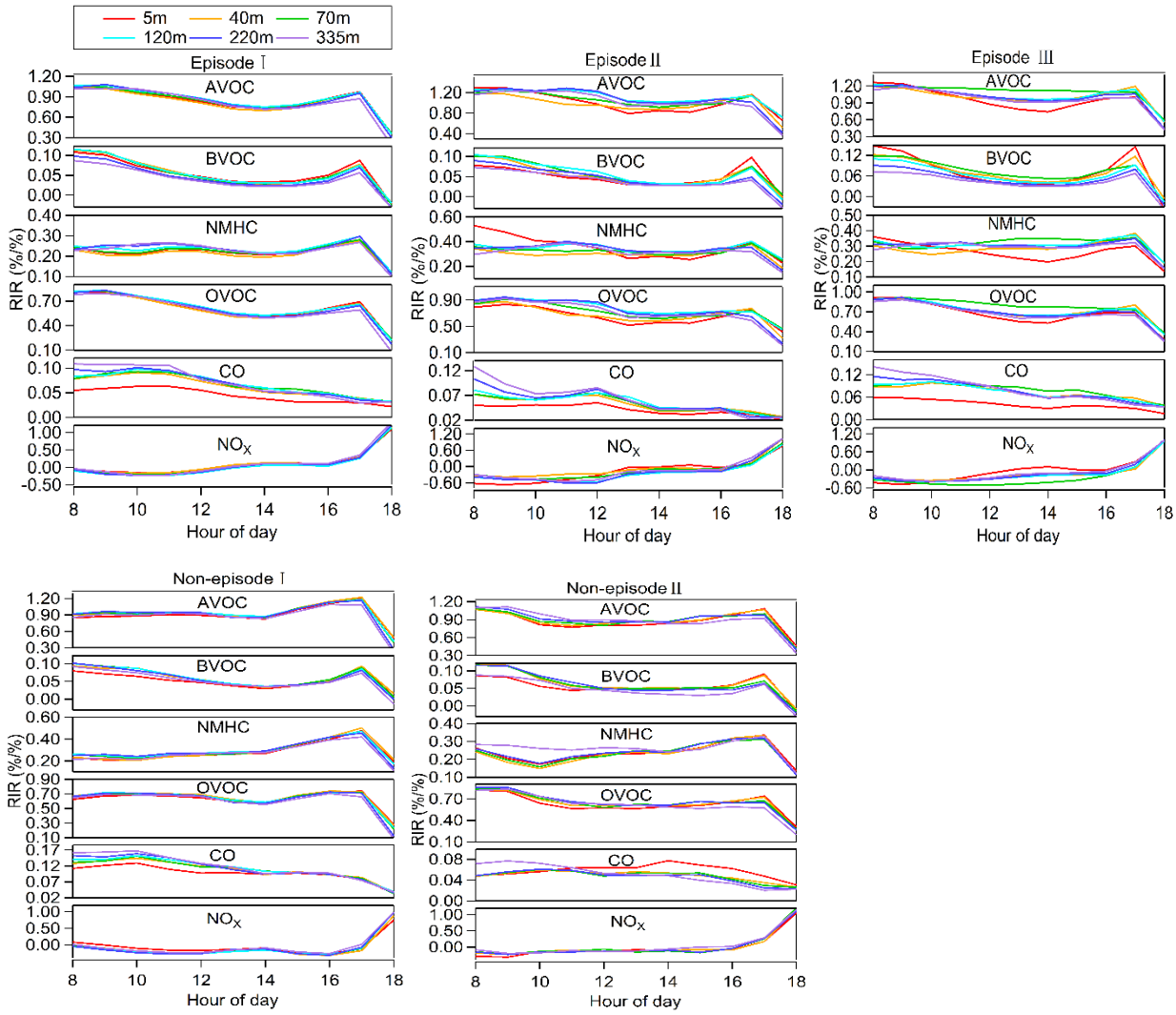

Figure S6: RIRs for O_3-precursor groups at different heights during local daytime (6:00-18:00).

Table S1. Modelled O_3 production and destruction reactions and their reaction rates used in MCM in this study

Reactions	Rate coefficient / unit	Number
O_3 production pathways ($P(O_3)$)		
$RO_2 + NO \rightarrow RO + NO_2$	$2.7\times10^{-12}\times\exp(360/T)$ / molecules $^{-1}$ cm^3 s^{-1}	(R1)
$HO_2 + NO \rightarrow OH + NO_2$	$3.45\times10^{-12}\times\exp(270/T)$ / molecules $^{-1}$ cm^3 s^{-1}	(R2)
O_3 destruction pathways ($D(O_3)$)		
$O_3 + hv \rightarrow O^1D + O_2$	Measured JO^1D / s^{-1}	(R3)
$O_3 + C_2H_4 \rightarrow HCHO + CH_2OOA$	$9.1\times10^{-15}\times\exp(-2580/T)$ / molecules $^{-1}$ cm^3 s^{-1}	(R4)
$O_3 + C_3H_6 \rightarrow CH_2OOB + CH_3CHO$	$2.75\times10^{-15}\times\exp(-1880/T)$ / molecules $^{-1}$ cm^3 s^{-1}	(R5)
$O_3 + C_3H_6 \rightarrow CH_3CHOOA + HCHO$	$2.75\times10^{-15}\times\exp(-1880/T)$ / molecules $^{-1}$ cm^3 s^{-1}	(R6)

$O_3 + C_5H_8 \rightarrow CH_2OOE + MACR$	$3.09\times10^{-15}\times\exp(-1995/T)$ / molecules $^{-1}$ cm^3 s^{-1}	(R7)
$O_3 + C_5H_8 \rightarrow CH_2OOE + MVK$	$2.06\times10^{-15}\times\exp(-1995/T)$ / molecules $^{-1}$ cm^3 s^{-1}	(R8)
$O_3 + C_5H_8 \rightarrow HCHO + MACROOA$	$3.09\times10^{-15}\times\exp(-1995/T)$ / molecules $^{-1}$ cm^3 s^{-1}	(R9)
$O_3 + C_5H_8 \rightarrow HCHO + MVKOOA$	$2.06\times10^{-15}\times\exp(-1995/T)$ / molecules $^{-1}$ cm^3 s^{-1}	(R10)
$O_3 + HO_2 \rightarrow OH$	$2.03\times10^{-16}\times (T/300)^{4.57}\times\exp(693/T)$ / molecules $^{-1}$ cm^3 s^{-1}	(R11)
$RO_2 + NO_2 \rightarrow$ peroxy nitrates	$(3.28\times10^{-28}\times7.24\times10^{18}\times P/T\times(T/300)^{-6.87}\times1.125\times10^{-11}\times(T/300)^{-1.105})\times10^{\wedge}(\log10(0.30)/(1+(\log10(2.916\times10^{-17}\times7.24\times10^{18}\times P/T\times(T/300)^{-5.765})/(0.75-1.27\times\log10(0.30)))^2))/(3.28\times10^{-28}\times7.24\times10^{18}\times P/T\times(T/300)^{-6.87}+1.125\times10^{-11}\times(T/300)^{-1.105})$ / molecules $^{-1}$ cm^3 s^{-1}	(R12)
$NO_2 + OH \rightarrow HNO_3$	$(3.2\times10^{-30}\times7.24\times10^{18}\times P/T\times(T/300)^{-4.5})\times3\times10^{-11}\times10^{\wedge}(\log10(0.41)/(1+(\log10((3.2\times10^{-30}\times7.24\times10^{18}\times P/T\times(T/300)^{-4.5})/(3\times10^{-11}))/(0.75-1.27\times(\log10(0.41))))^2))/(3.2\times10^{-30}\times7.24\times10^{18}\times P/T\times(T/300)^{-4.5}+3\times10^{-11})$ / molecules $^{-1}$ cm^3 s^{-1}	(R13)
$O_3 + OH \rightarrow HO_2$	$1.70\times10^{-12}\times\exp(-940/T)$ / molecules $^{-1}$ cm^3 s^{-1}	(R14)

Table S2. Measured VOCs concentrations during the observation periods at SZMGT (units: pptv).

Chemicals	Classification	Mean±SD (pptv)				
		Episode I	Episode II	Episode III	Non-episode I	Non-episode II
Aromatics		6738±5151	15147±8995	7107±5771	4748±3343	10530±10027
toluene	NMHC/ AVOCs	3336±2496	7864±4298	3682±2648	2364±1697	5281±4919
m/*p*-xylene	NMHC/ AVOCs	1444±1188	3097±2069	1390±1354	968±768	2223±2279
ethylbenzene	NMHC/ AVOCs	613±504	1315±878	590±575	411±297	944±968
o-xylene	NMHC/ AVOCs	593±489	1273±850	571±556	398±288	914±937
benzene	NMHC/ AVOCs	445±227	819±349	527±316	382±182	654±399
styrene	NMHC/ AVOCs	137±119	379±332	159±188	106±93	246±276
1,2,4-trimethylbenzene	NMHC/ AVOCs	36±27	84±46	39±28	25±18	57±53
m-ethyltoluene	NMHC/ AVOCs	35±26	82±45	38±28	25±18	55±51
p-ethyltoluene	NMHC/ AVOCs	19±14	45±25	21±15	14±10	30±28
n-propylbenzene	NMHC/ AVOCs	19±14	44±24	21±15	13±10	30±28
o-ethyltoluene	NMHC/ AVOCs	18±14	43±24	20±15	13±9	29±27
isopropylbenzene	NMHC/ AVOCs	12±9	28±15	13±10	9±6	19±18
1,2,3-trimethylbenzene	NMHC/ AVOCs	11±8	26±14	12±9	8±6	17±16
*p*_diethylbenzene	NMHC/ AVOCs	8±6	20±11	9±7	6±4	13±12

1,3,5-trimethylbenzene	NMHC/ AVOCs	7±5	13±9	7±5	5±3	11±10
*m*_diethylbenzene	NMHC/ AVOCs	4±3	10±6	5±3	3±2	7±6
OVOCs		39720±20318	66267±28451	48377±29973	26783±15486	47046±33037
methanol	OVOC	8418±3917	15131±5681	10324±6640	6136±3448	10682±7116
formaldehyde	OVOC	9449±4089	11853±3042	10562±4843	5303±3053	9165±4511
ethanol	OVOC	7710±3756	14390±7288	10535±6910	6005±3201	10312±8417
acetone	OVOC	4365±2953	7549±4676	5701±3897	2699±1586	4275±2829
hydroxyacetone	OVOC	4047±2445	7007±2751	4543±3121	2766±1884	5448±4699
acetaldehyde	OVOC	2532±1355	4367±1729	3007±1880	1697±956	3126±2244
methyl ethyl ketone	OVOC	2310±1432	4723±2757	2715±2226	1653±984	3171±2722
acrolein	OVOC	512±191	731±263	605±227	301±208	487±295
methyl vinyl ketone	OVOC	179±70	207±80	185±98	89±73	170±78
methacrylaldehyde	OVOC	124±49	144±55	128±68	62±51	118±54
m-cresol	OVOC	50±40	97±50	46±41	43±25	55±37
phenol	OVOC	24±20	66±79	26±22	28±18	36±35
Acetylene		1836±1259	3967±2168	1857±1336	1192±855	2664±2481
Acetylene	NMHC/ AVOCs	1836±1259	3967±2168	1857±1336	1192±855	2664±2481
Alkanes		28108±21030	66256±36213	31017±22307	19916±14296	44495±41443
n-butane	NMHC/ AVOCs	7972±5965	18793±10271	8797±6327	5649±4055	12620±11755
propane	NMHC/ AVOCs	6417±4801	15127±8268	7081±5093	4547±3264	10159±9462
isobutane	NMHC/ AVOCs	4513±3376	10637±5814	4980±3581	3198±2295	7144±6654
ethane	NMHC/ AVOCs	3134±2345	7388±4038	3458±2487	2221±1594	4961±4621
isopentane	NMHC/ AVOCs	1550±1160	3654±1997	1710±1230	1098±788	2454±2285
n-pentane	NMHC/ AVOCs	1422±1064	3353±1832	1569±1128	1008±723	2251±2097
n-hexane	NMHC/ AVOCs	574±429	1352±739	633±455	406±291	908±846
2-methylpentane	NMHC/ AVOCs	428±321	1010±552	473±340	304±218	678±632
3-methylpentane	NMHC/ AVOCs	383±286	902±493	422±304	271±195	606±564
3-methylhexane	NMHC/ AVOCs	228±171	538±294	252±181	162±116	361±336
2-methylhexane	NMHC/ AVOCs	177±132	417±228	195±140	125±90	280±261
cyclohexane	NMHC/ AVOCs	176±	414±227	194±140	125±89	278±259
n-heptane	NMHC/ AVOCs	161±121	380±208	178±120	114±82	255±238
methylcyclopentane	NMHC/ AVOCs	113±85	267±146	125±90	80±58	180±167
2,3-dimethylbutane	NMHC/ AVOCs	110±83	260±142	122±88	78±56	175±163
n-octane	NMHC/ AVOCs	99±74	233±127	109±78	70±50	156±146
methylcyclohexane	NMHC/ AVOCs	92±69	217±119	102±73	65±47	146±136
2,3-dimethylpentane	NMHC/ AVOCs	86±64	203±111	95±68	78±56	136±127

2,2-dimethylbutane	NMHC/ AVOCs	64±48	151±83	71±51	46±33	102±95
cyclopentane	NMHC/ AVOCs	63±47	149±82	70±50	45±32	100±93
n-dodecane	NMHC/ AVOCs	62±46	145±80	68±49	44±31	98±91
2,4-dimethylpentane	NMHC/ AVOCs	49±37	116±64	54±39	35±25	78±73
n-decane	NMHC/ AVOCs	44±33	104±57	49±35	31±22	70±65
n-nonane	NMHC/ AVOCs	42±32	100±55	47±34	30±22	67±62
n-undecane	NMHC/ AVOCs	37±28	88±48	41±30	26±19	59±55
3-methylheptane	NMHC/ AVOCs	37±27	84±46	32±23	25±18	57±53
2-methylheptane	NMHC/ AVOCs	29±21	68±37	39±28	20±15	45±42
2,2,4-trimethylpentane	NMHC/ AVOCs	26±19	61±34	29±21	18±13	41±38
2,3,4-trimethylpentane	NMHC/ AVOCs	19±14	44±24	21±15	13±10	30±28
Alkenes	NMHC/ AVOCs	2202±1561	5043±2664	2492±1716	1530±1119	3422±3120
ethylene	NMHC/ AVOCs	1494±1326	3187±1742	1492±1073	958±688	2141±1994
propylene	NMHC/ AVOCs	412±365	878±480	411±296	264±190	590±549
1-butene	NMHC/ AVOCs	163±145	348±190	163±117	105±75	234±218
1-pentene	NMHC/ AVOCs	29±26	62±34	29±21	19±13	42±39
1-hexene	NMHC/ AVOCs	15±13	31±47	15±11	9±7	21±20
trans-2-butene	NMHC/ AVOCs	11±10	24±13	11±8	7±5	16±15
cis-2-butene	NMHC/ AVOCs	11±10	24±14	11±8	7±5	16±15
trans-2-pentene	NMHC/ AVOCs	5±4	10±6	5±3	3±2	4±4
cis-2-pentene	NMHC/ AVOCs	3±3	6±3	3±2	2±1	7±6
isoprene	NMHC/ BVOC	277±185	471±165	351±176	156±132	351±260