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Supplementary material

Evaluation of aromatic oxidation reactions in seven chemical mechanisms with an outdoor chamber

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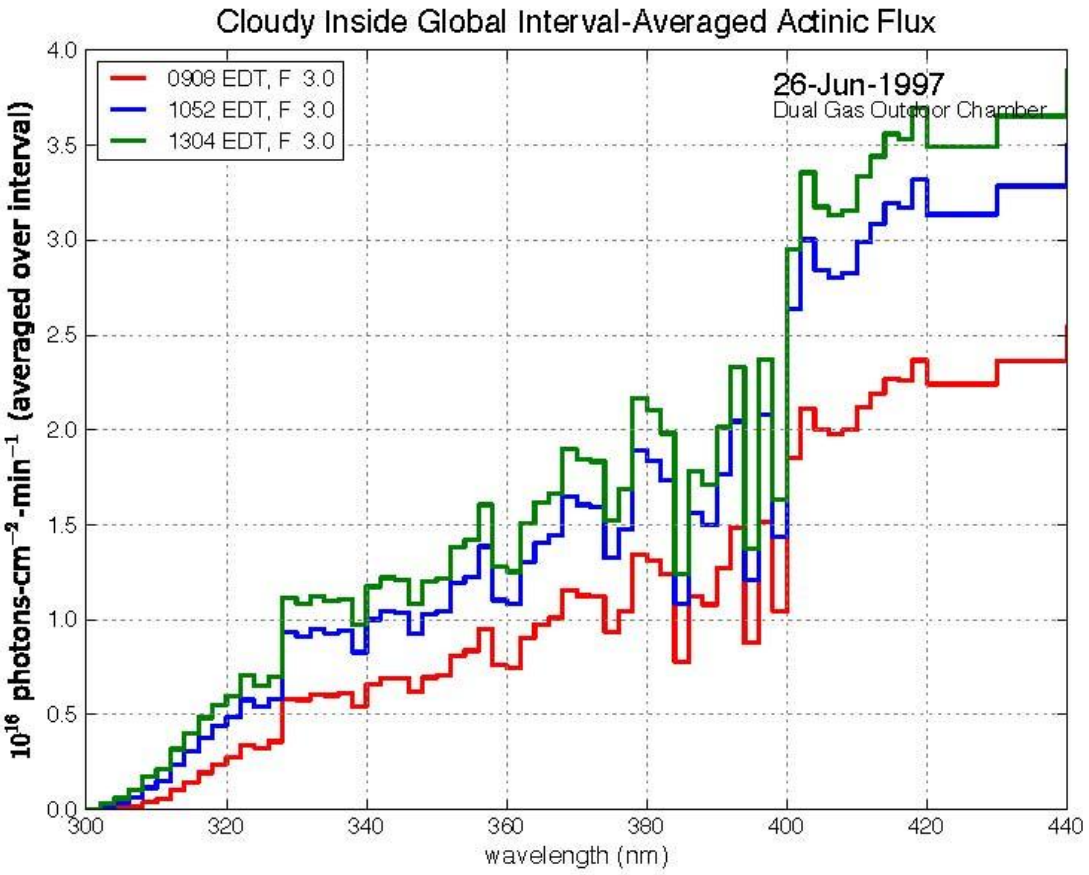

Fig. S1. Model predicted actinic flux inside the UNC chamber for 26 June 1997.

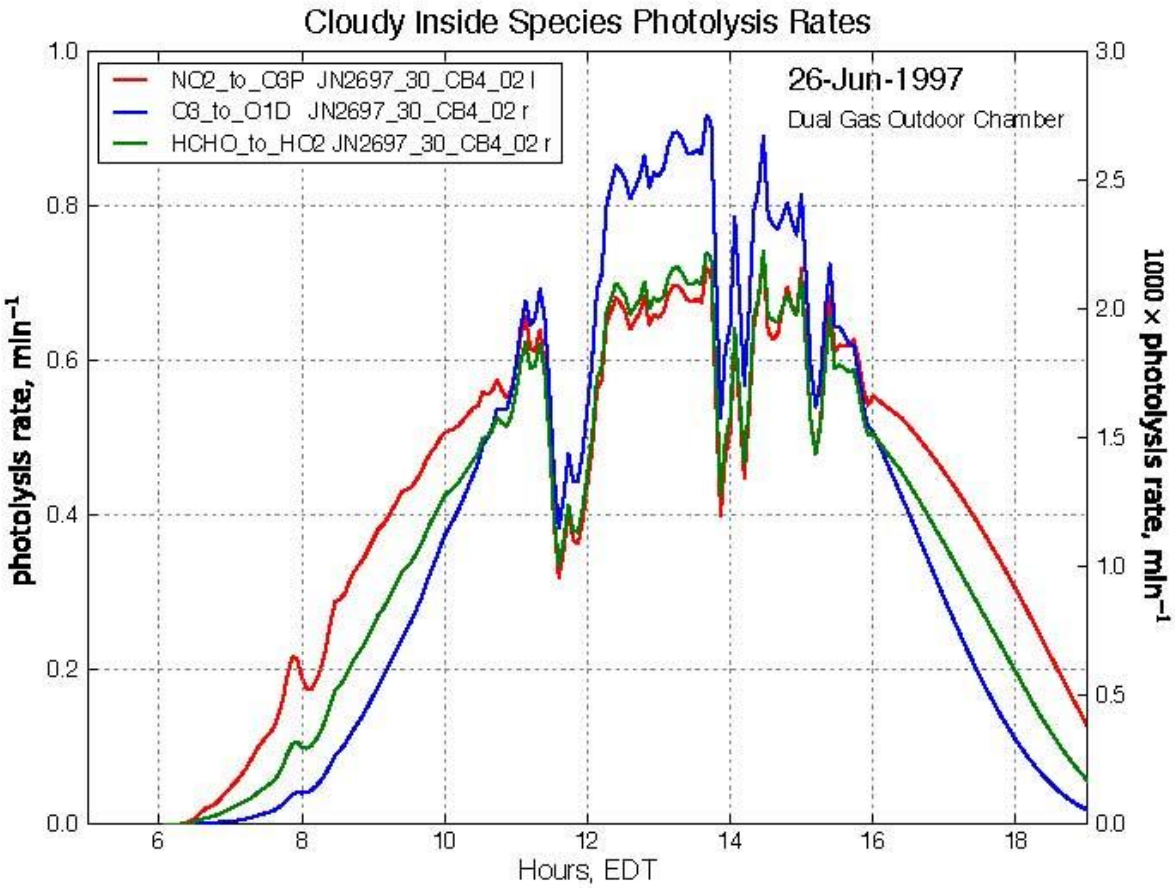

Fig. S2. Model predicted photolysis rates inside the UNC chamber for 26 June 1997.

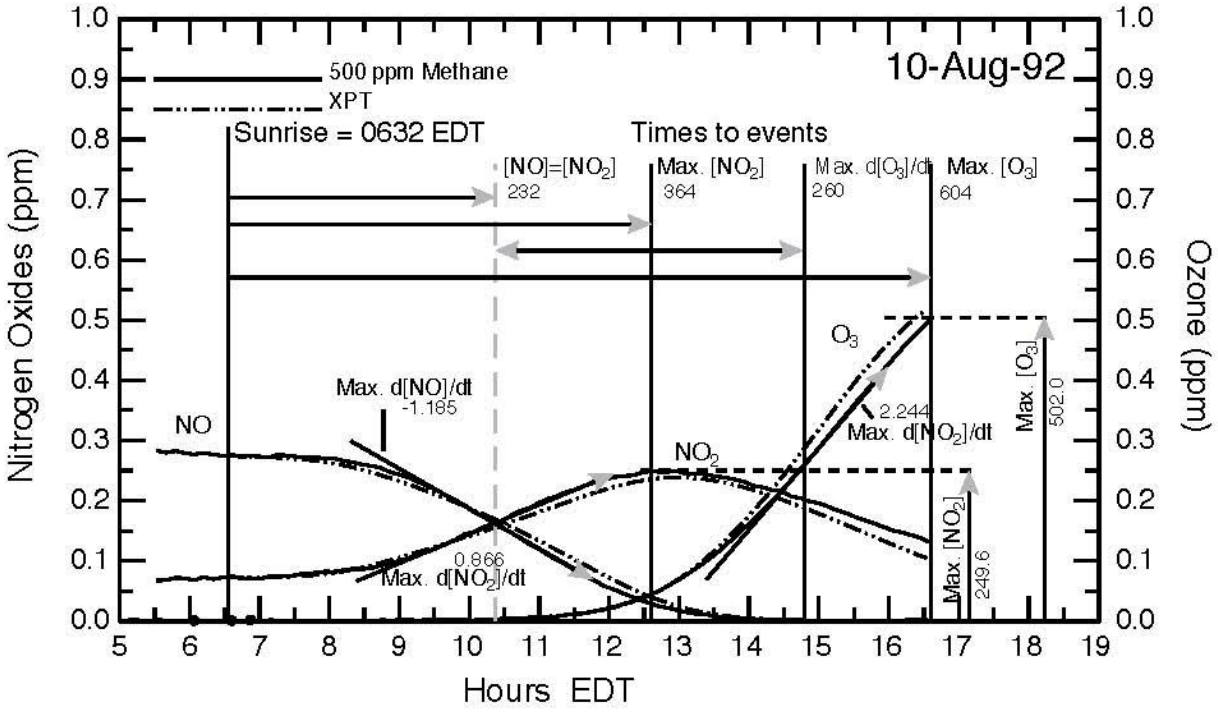

Fig. S3. Definition of all metrics used to evaluate mechanism performance and appear in the bar plots.

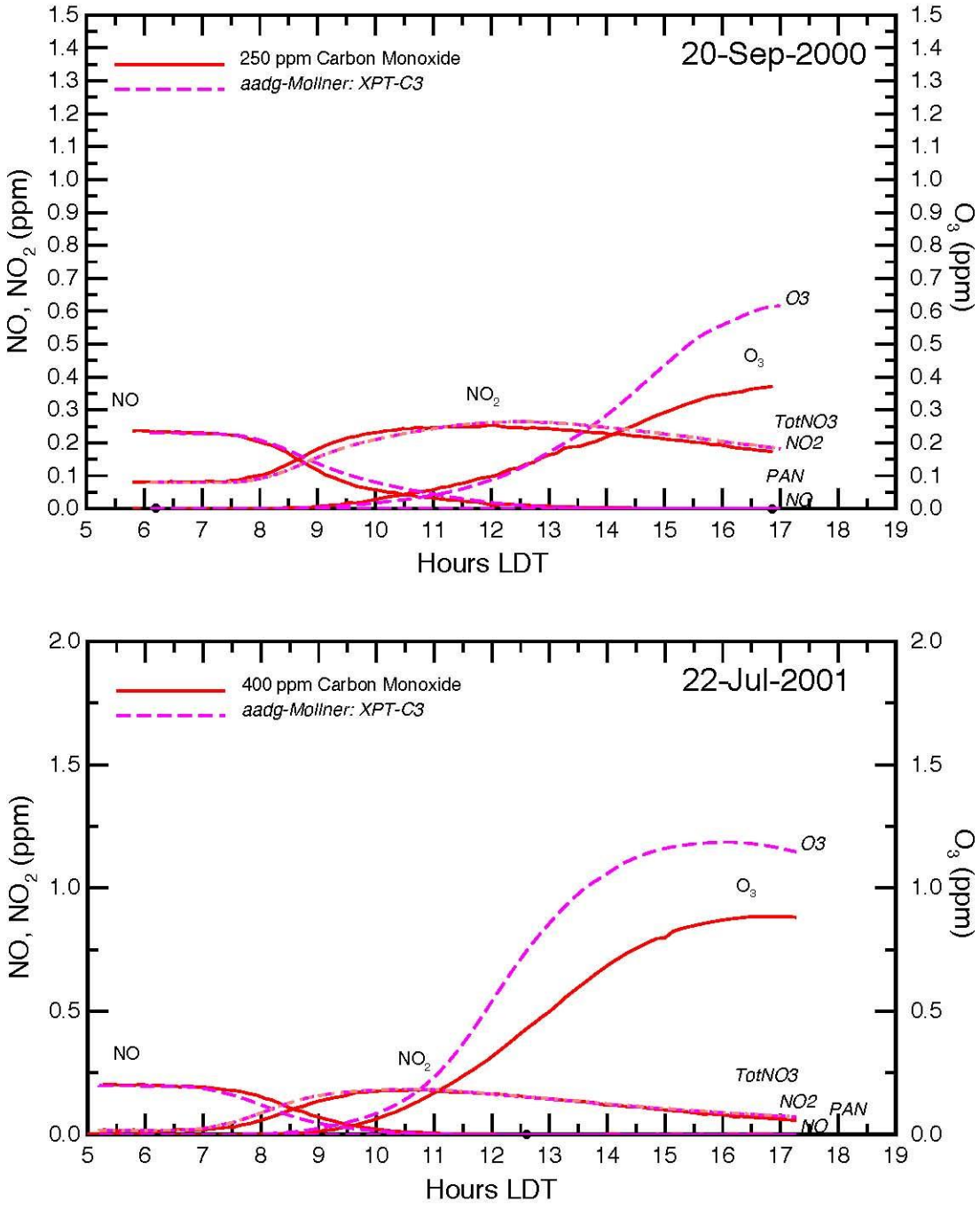

Fig. S4. Observed and modelled O_3, NO and NO_2 for chamber characterisation experiments of carbon monoxide.

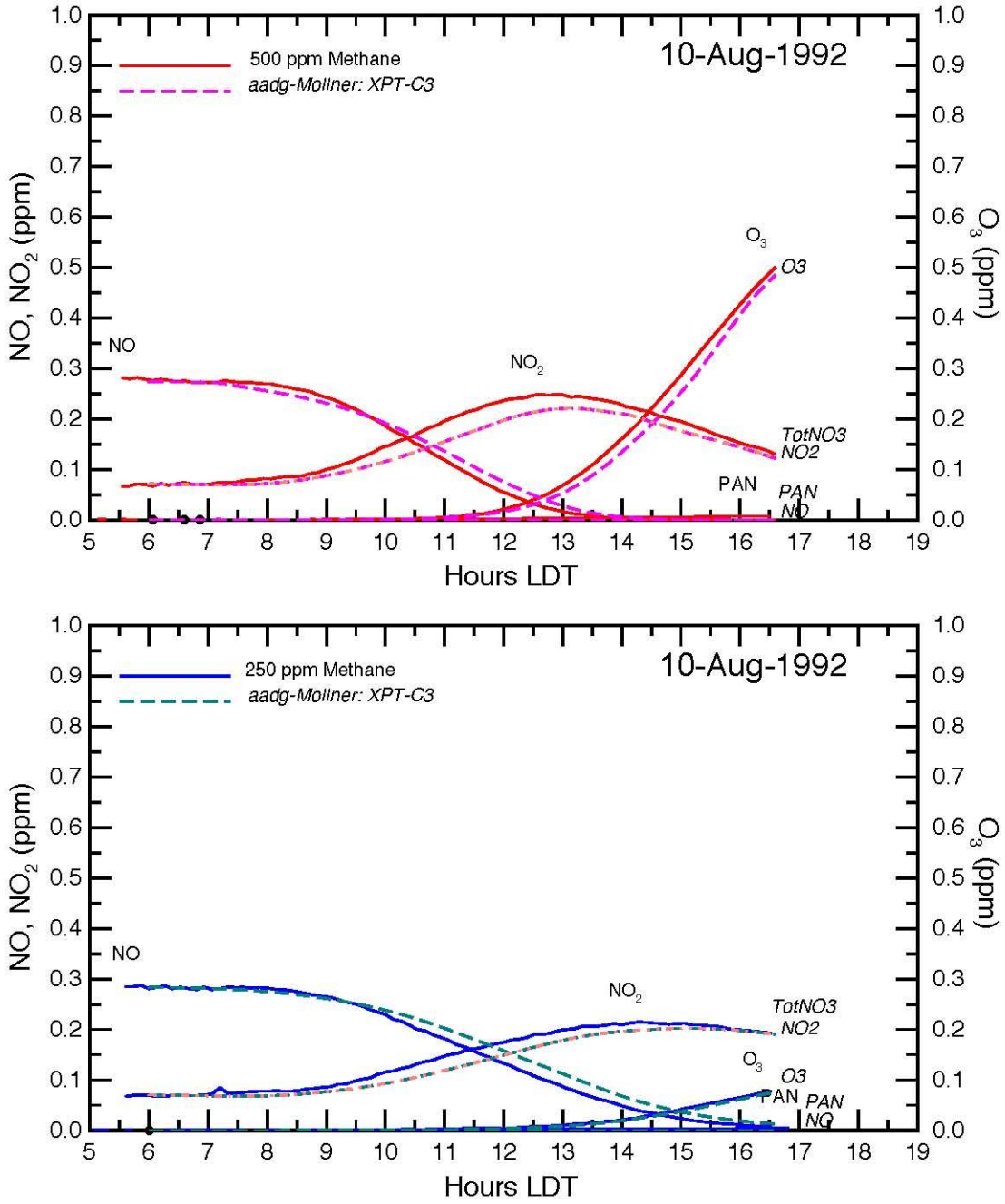

Fig. S5. Observed and modelled O_3, NO and NO_2 for chamber characterisation experiments of methane on 10 August 1992.

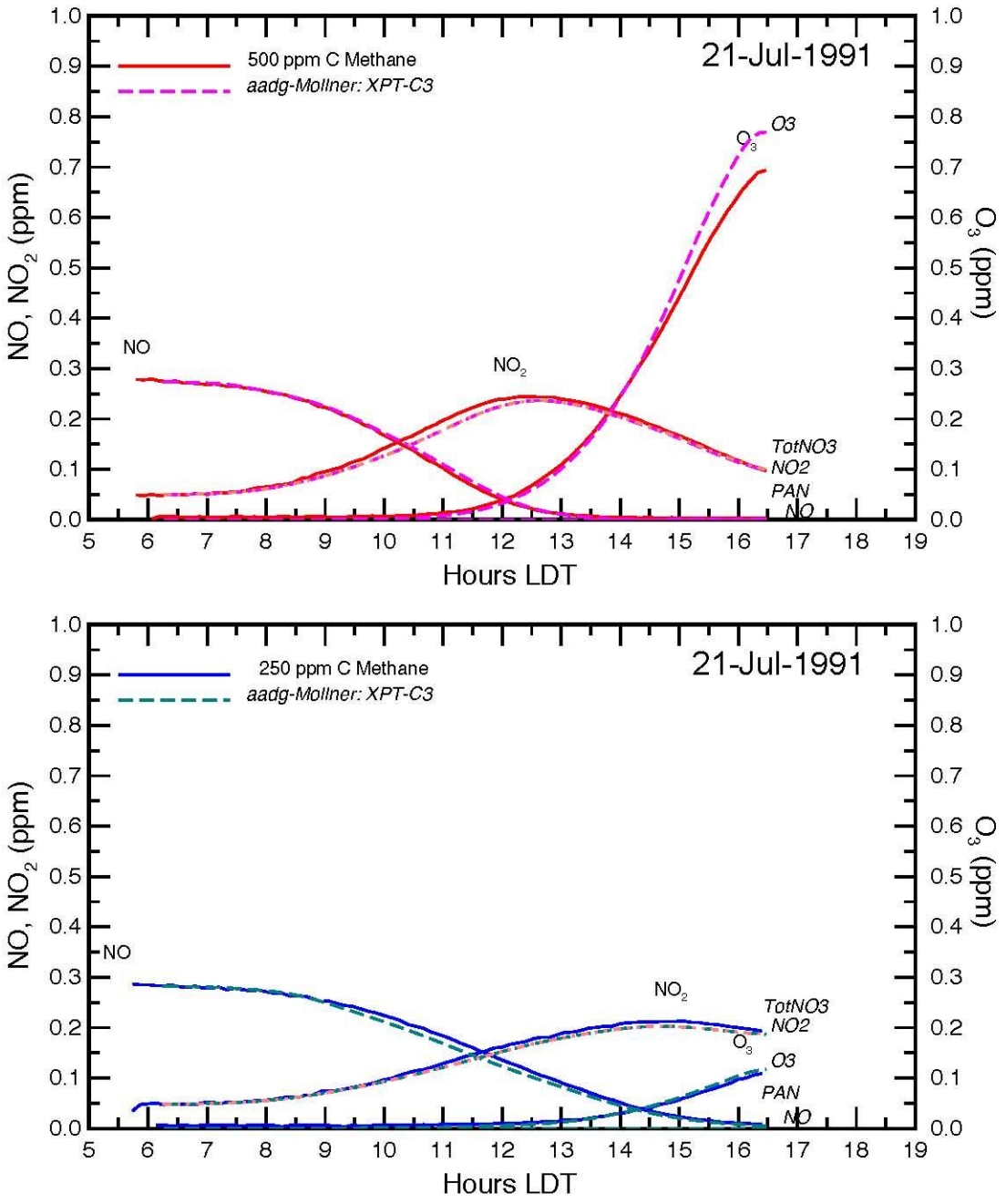

Fig. S6. Observed and modelled O_3, NO and NO_2 for chamber characterisation experiments of methane on 21 July 1991.

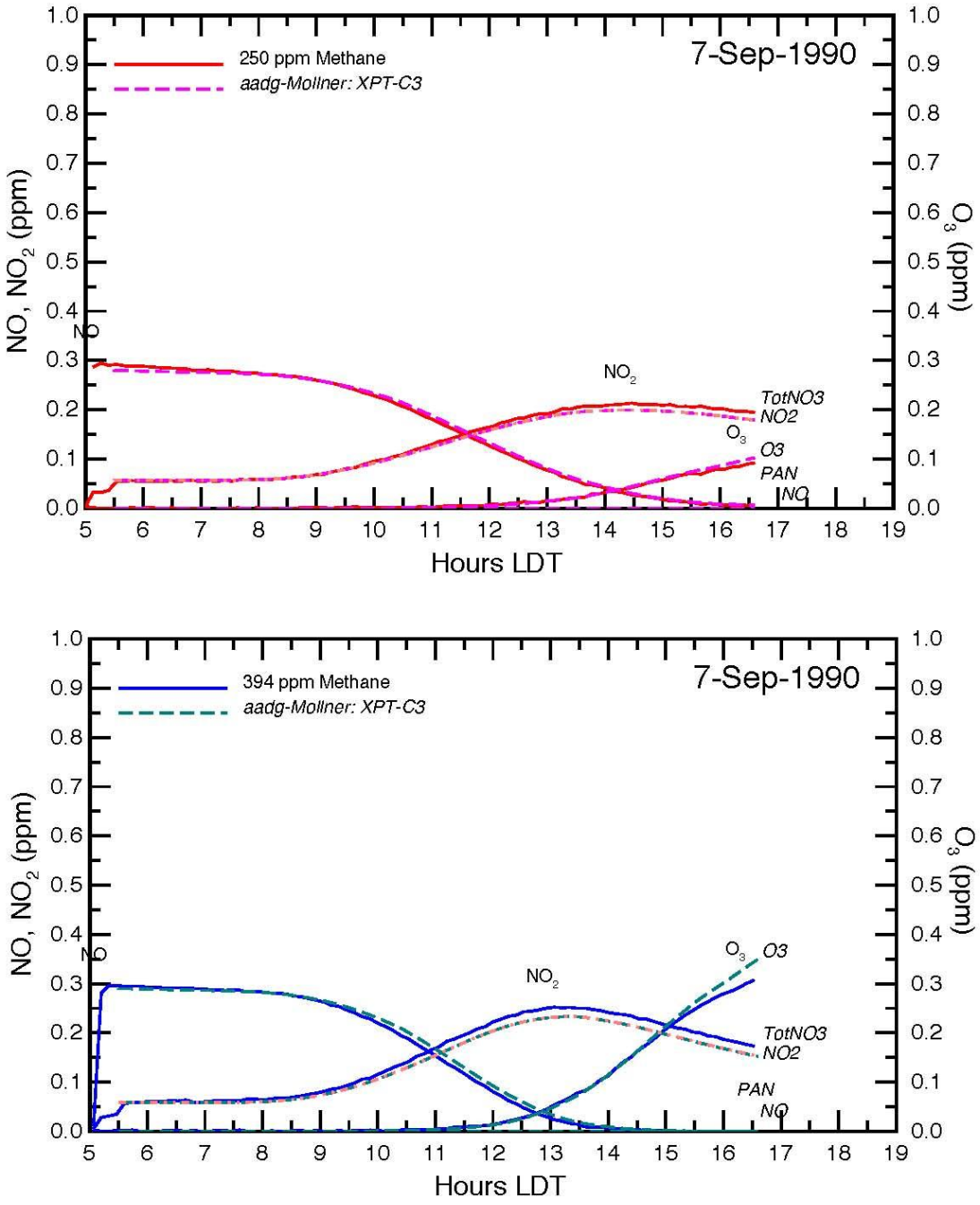

Fig. S7. Observed and modelled O_3, NO and NO_2 for chamber characterisation experiments of methane on 7 September 1990.

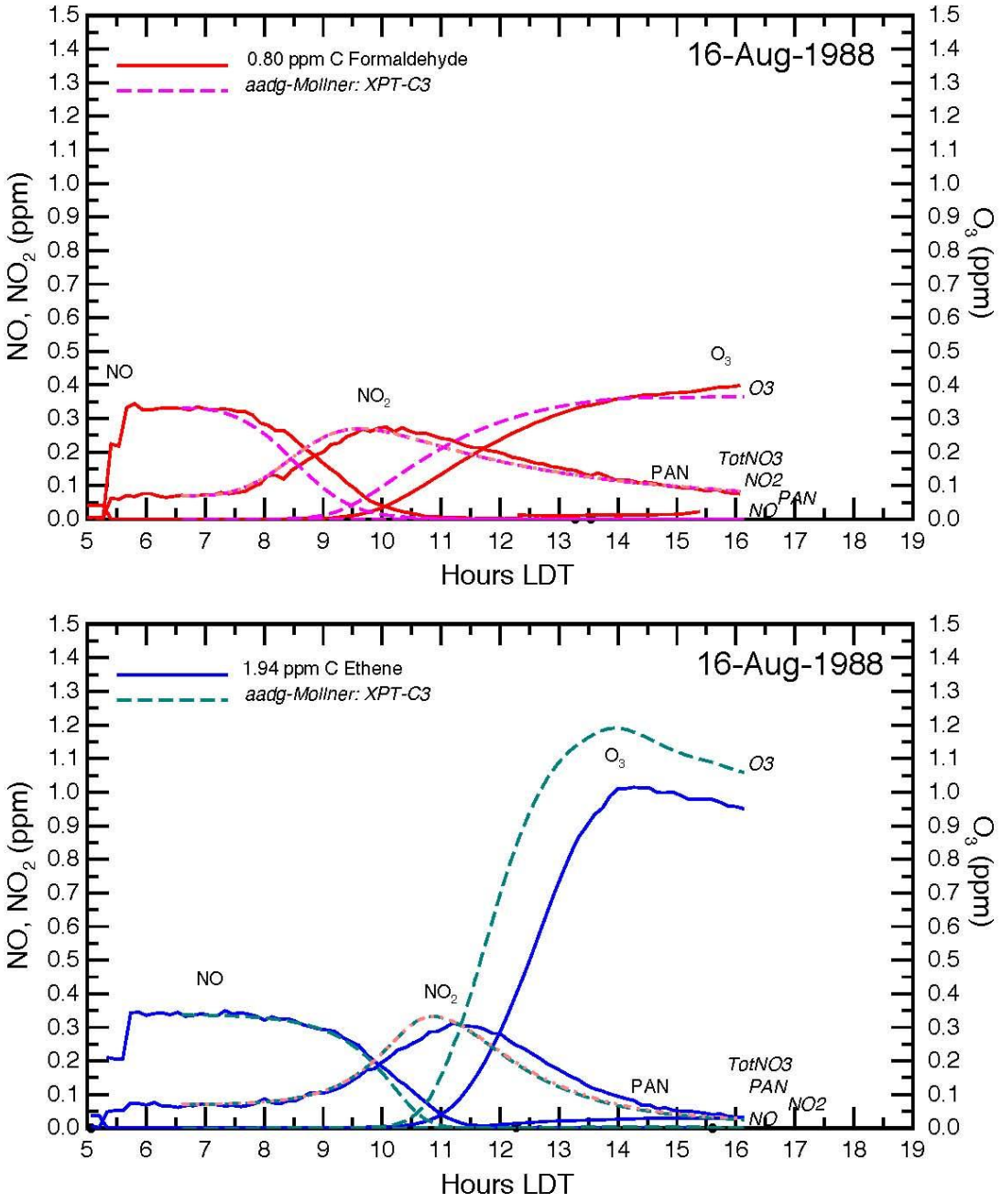

Fig. S8. Observed and modelled O_3, NO and NO_2 for chamber characterisation experiments of formaldehyde (top) and ethene (bottom) methane on 16 August 1998.

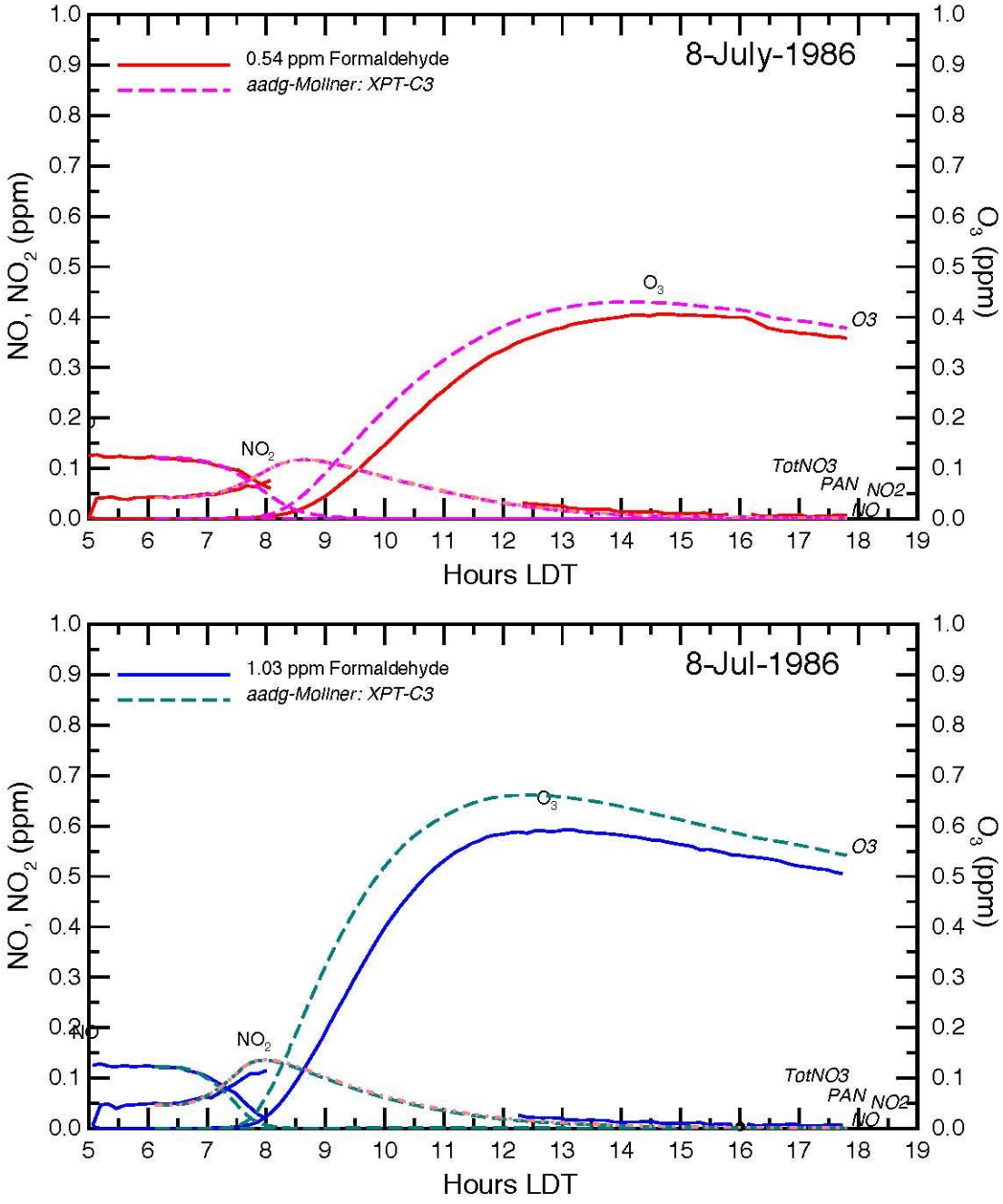

Fig. S9. Observed and modelled O_3, NO and NO_2 for chamber characterisation experiments of formaldehyde on 8 July 1986.

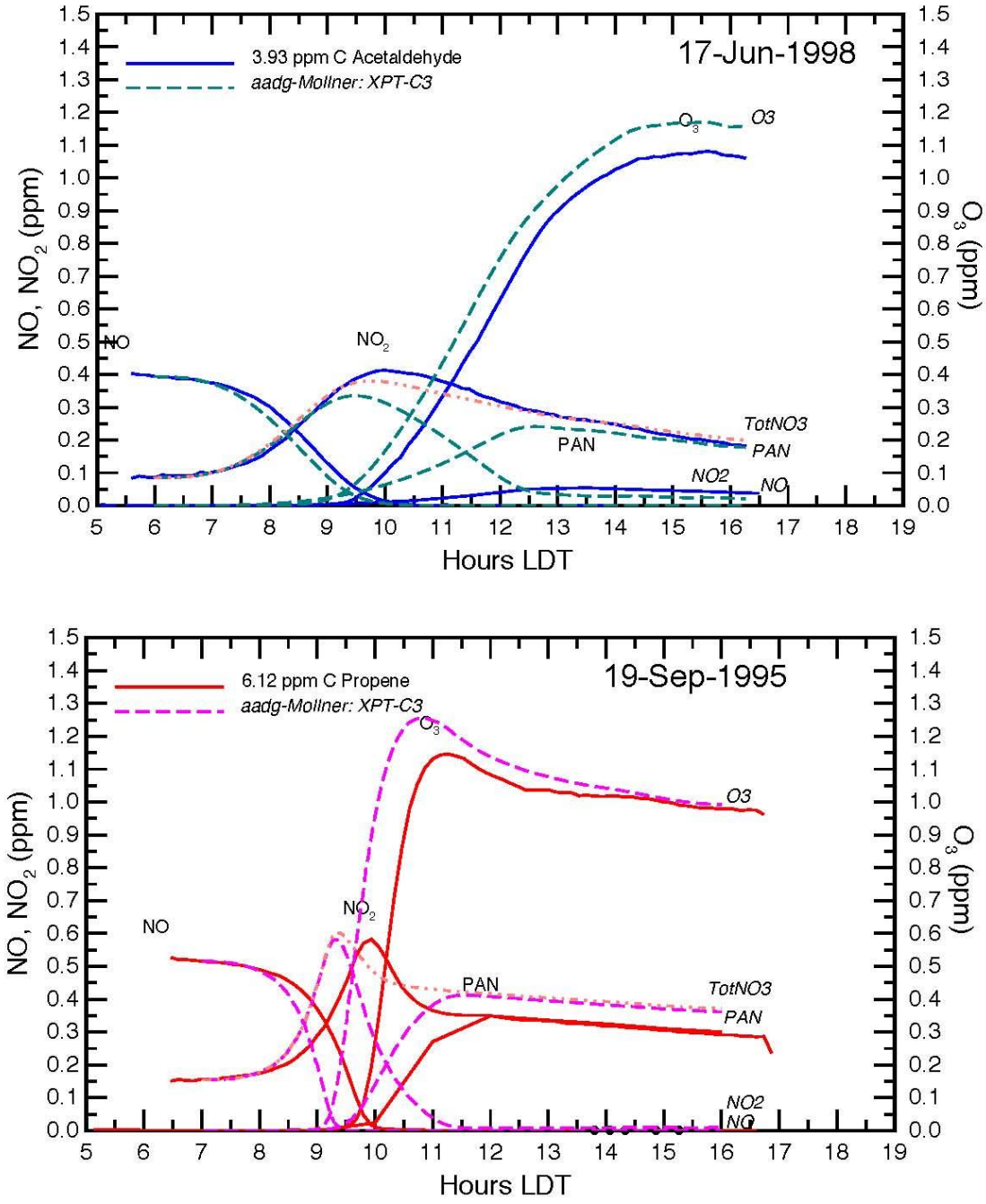

Fig. S10. Observed and modelled O_3, NO and NO_2 for chamber characterisation experiments of acetaldehyde (top) and propene (bottom) on 17 June 1998.

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Table S1. Carbon fractions of various alkanes, alkenes, carbonyls, and aromatics across different hydrocarbon mixtures injected in experiments conducted at the University of North Carolina outdoor chamber

For SynE85, carbon fractions are without ethyl alcohol

Species or mixture	Carbon fraction								
	UNCMIX80	Carter Mix	SynCNG	SynLPG	SynUrban	SynE85BART	SynE85IAG	SynM85	SynE85E
Alkanes									
Methane			0.9536	0.1354					
Ethane			0.0316	0.0625	0.0497	0.0648	0.0102	0.0050	0.0962
Propane			0.0042	0.7754	0.0595				
iso-Butane					0.0425		0.0044	0.0064	
n-Butane					0.0948	0.0147	0.1456	0.0968	0.0248
iso-Pentane	0.1555				0.1115	0.0989	0.0344	0.1349	0.0689
n-Pentane	0.2547				0.0401	0.0706	0.0181	0.0529	0.0273
2,2-Dimethylbutane							0.0109		
2,3-Dimethylbutane					0.0051		0.0137	0.0163	
2-Methylpentane	0.0908				0.0186	0.1726	0.0492	0.0802	0.0287
3-Methylpentane					0.0136		0.0232		
n-Hexane		0.5000			0.0119	0.1172	0.0219	0.0154	0.0119
2,2,3-Trimethylbutane	0.0860					0.0701			
2-Methylhexane							0.0273	0.0094	
2,3-Dimethylpentane					0.0144		0.0178	0.0072	
3-Methylhexane					0.0296				
n-Heptane					0.0136		0.0123		
2,2,4-Trimethylpentane	0.1084				0.0110	0.0272	0.0383	0.0189	0.0640
2,5-Dimethylhexane					0.0093		0.0068		
2,3,4-Trimethylpentane					0.0085		0.0123		
n-Octane					0.0102				
n-Nonane					0.0136				
4-Methylnonane					0.0195				
n-Decane					0.0169				
n-Dodecane								0.0043	
Methylcyclopentane					0.0093		0.0109	0.0141	
Cyclohexane					0.0084				
Methylcyclohexane					0.0051				

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Species or mixture	Carbon fraction								
	UNCMIX80	Carter Mix	SynCNG	SynLPG	SynUrban	SynE85BART	SynE85IAG	SynM85	SynE85E
Alkenes									
Ethene	0.1286	0.3500	0.0073	0.0057	0.0345	0.2231	0.0159	0.0072	0.2023
Propene	0.0517			0.0211	0.0108	0.0281	0.0063	0.0025	0.0326
iso-Butene					0.0058		0.0024		0.0194
1-Butene	0.0286						0.0019		
1-Pentene					0.0103			0.0023	
2-Methyl-1-butene	0.0383				0.0055		0.0014	0.0056	
2-Methyl-1-pentene					0.0068				
2,3,3-Trimethyl-1-butene					0.0136				
1-Octene					0.0068				
1-Nonene					0.0059				
trans-2-Butene					0.0150				
cis-2-Butene	0.0307						0.0018		0.0286
trans-2-Pentene							0.0017	0.0057	
cis-2-Pentene					0.0174		0.0013	0.0043	
2-Methyl-2-butene	0.0268						0.0038	0.0097	
2-Methyl-2-pentene					0.0026				
Cyclopentene							0.0041		
Cyclohexene					0.0009			0.0045	
1,3-Butadiene					0.0028		0.0009		
2-Methyl-1,3-butadiene					0.0026		0.0014		

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Species or mixture	Carbon fraction					
	UNCMIX80 Carter Mix	SynCNG	SynLPG	SynUrban	SynE85BART	SynE85IAG	SynM85	SynE85E
Aromatics/carbonyls								
Acetaldehyde					0.0882	0.1774		
Propionaldehyde					0.0147			
Crotanaldehyde					0.0147			
p-Tolualdehyde					0.0441			
Acetone					0.0882	0.1559		
Benzene			0.0186	0.0555	0.0563	0.0339	0.0606
Toluene			0.0584	0.0335	0.0779	0.0535	0.2563
Ethylbenzene			0.0093		0.0217	0.0120		
m/*p*-Xylene	0.1500		0.0313	0.0178	0.0444	0.0267	0.0434
o-Xylene			0.0136		0.0141	0.0097		
Styrene					0.0022			
n-Propylbenzene			0.0093			0.0044		
1-Methyl-3-ethylbenzene			0.0085	0.0063	0.0152	0.0111	0.0353
m-Ethyltoluene			0.0085	0.0063	0.0152	0.0111	0.0353
p-Ethyltoluene			0.0127					
a-Methylstyrene			0.0026					
1,3,5-Trimethylbenzene					0.0043			
1,2,4-Trimethylbenzene			0.0474		0.0108	0.0101		
sec-Butylbenzene			0.0059					
1,3-Diethyl-benzene			0.0153		0.0022			
1,2,3,5-Tetramethylbenzene			0.0051					
Naphthalene					0.0011	0.0015		

Table S2. List of experiments that were performed at University of North Carolina chamber and modelled for this study

VOC, volatile organic compound; 1,3,5-TMB, 1,3,5-trimethylbenzene. See Table S1 for composition of VOC mixtures

Experiment ID	Chamber side	VOC species or mixture	NO (ppm)	NO_2 (ppm)	VOC (ppm C)	VOC : NO_x (ppm C : ppm)
AU0183	Red	Toluene	0.344	0.051	4.586	11.61012658
	Blue	*o*-Xylene	0.323	0.05	2.622	7.029490617
AU0395	Red	*p*-Xylene	0.5323	0.0984	8.03	12.73188521
	Blue	1,3,5-TMB	0.5368	0.0841	9	14.49508778

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Experiment ID	Chamber side	VOC species or mixture	NO (ppm)	NO_2 (ppm)	VOC (ppm C)	VOC : NO_x (ppm C : ppm)
AU1788	Red	Toluene	0.2894	0.0718	4.93	13.64894795
	Blue	*m*-Xylene	0.2951	0.0651	1.71	4.747362576
AU2297	Red	Toluene	0.542	0.091	10.105	15.96366509
	Blue	Toluene + *p*-Xylene + 1,3,5-TMB	0.552	0.078	8.1417	12.92333333
AU3095	Red	*m*-Xylene	0.503	0.119	8	12.86173633
	Blue	Toluene	0.524	0.094	7	11.32686084
ST1393	Red	*m*-Xylene	0.277	0.044	0.789	2.457943925
	Blue	Toluene	0.282	0.04	1.909	5.928571429
ST1481	Red	*m*-Xylene + UNCMIX80	0.2	0.054	2.188	8.614173228
	Blue	Toluene + UNCMIX80	0.198	0.054	2.174	8.626984127
ST2496	Red	2-methyl-1,4-butene	0.559	0.078	10.341	16.23390895
	Blue	Toluene	0.565	0.073	13.377	20.96708464
AU0394	Red	SynE85B in SynUrban	0.2786	0.0546	2	6.00240096
	Blue	SynE85IAG in SynUrban	0.2843	0.0478	2	6.022282445
AU0696	Red	SynUrban	0.314	0.04	1.5	4.237288136
	Blue	SynUrban with Isoprene	0.308	0.04	1.5	4.310344828
AU2191	Red	SynUrban + SynM85	0.2859	0.0657	2.91	8.276450512
	Blue	SynUrban/SynE85IAG	0.2953	0.066	3.17	8.773872128
AU2594	Red	SynE85E in SynUrban	0.2681	0.0608	1.5	4.560656735
	Blue	SynE85IAG in SynUrban	0.2674	0.0593	1.5	4.591368228
AU2601	Red	SynUrban	0.29	0.029	1.474	4.620689655
	Blue	SynUrban	0.291	0.028	1.474	4.620689655
AU2694	Red	SynCNG in SynUrban	0.2619	0.0589	3	9.351620948
	Blue	SynE85IAG in SynUrban	0.2635	0.0578	3	9.337068161
AU3091	Red	SynUrban/SynE85IAG	0.2656	0.0688	1.54	4.605263158
	Blue	SynUrban/SynM85	0.2675	0.0635	1.55	4.682779456
JL1392	Red	CARTER Mix	0.276	0.07	2	5.780346821
	Blue	SynUrban	0.279	0.072	2	5.698005698
JL2491	Red	SynE85IAG	0.266	0.059	3.033	9.332307692
	Blue	SynM85	0.267	0.062	2.937	8.927051672
JN1997	Red	SynUrban	0.296	0.056	1.96	5.568181818
	Blue	SynUrban	0.303	0.05	1.96	5.552407932
ST0491	Red	SynE85IAG	0.2664	0.0627	2.09	6.350653297
	Blue	SynM85	0.2669	0.0614	2.03	6.18336887
ST0591	Red	SynM85	0.2617	0.0747	2.12	6.302021403

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Experiment ID	Chamber side	VOC species or mixture	NO (ppm)	NO_2 (ppm)	VOC (ppm C)	VOC : NO_x (ppm C : ppm)
	Blue	SynUrban	0.2645	0.0707	2.2	6.563245823
ST1091	Red	SynUrban	0.2594	0.0614	2.1	6.546134663
	Blue	SynE85IAG	0.2673	0.0574	1.97	6.067138897
ST1099	Red	SynUrban	0.267	0.069	1.474	4.386904762
	Blue	SynUrban	0.264	0.075	1.474	4.348082596
ST1194	Red	SynE85E	0.2868	0.0596	2	5.773672055
	Blue	SynURB	0.2879	0.0569	2	5.800464037
ST1291	Red	SynE85IAG	0.254	0.066	2.17	6.78125
	Blue	SynUrban	0.259	0.0679	2.2	6.729886816
ST1294	Red	SynUrban	0.2666	0.0563	2	6.193868071
	Blue	SynUrban	0.2662	0.0534	2	6.257822278
ST1400	Red	Butyraldehyde	0.2431	0.075	6	18.86199308
	Blue	SynUrban	0.241	0.073	6	19.10828025
ST1494	Red	SynUrban + SynE85E	0.2865	0.0604	2	5.765350245
	Blue	SynUrban	0.2864	0.0576	2	5.813953488
ST1591	Red	SynUrban + SynM85	0.2662	0.0553	2.14	6.6562986
	Blue	SynUrban + SynE85IAG	0.2703	0.0558	2.12	6.50107329
ST1594	Red	SynUrban + SynE85E (minus EtOH)	0.2794	0.0639	2	5.825808331
	Blue	SynUrban	0.2799	0.0637	2	5.820721769
ST1791	Red	SynUrban/SynE85IAG	0.2682	0.066	2.14	6.403351287
	Blue	SynUrban/SynM85	0.2676	0.0698	2.16	6.401896858
ST2699	Red	SynUrban	0.242	0.087	1.414	4.29787234
	Blue	SynUrban	0.2445	0.087	1.474	4.446455505
ST2794	Red	SynUrban + SynLPG	0.2718	0.0536	2	6.1462815
	Blue	SynUrban + SynE85IAG	0.2721	0.0532	2	6.148170919
ST2894	Red	SynUrban + SynE85 + EtOH	0.26	0.0657	2	6.140620203
	Blue	SynUrban + SynE85IAG	0.2641	0.0636	2	6.103143119
JN1898	Red	4-oxo-2-pentenal	0.57	0.089	7.5	11.38088012
	Blue	2-butenedial	0.569	0.092	4	6.051437216
JL0298	Red	4-oxo-2-pentenal	0.567	0.0946	4.05	6.121523579
	Blue	3-hexene-2,5-dione	0.564	0.0678	5.7	9.021842355

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Table S3. List of injected species not present in MCMv3.1 and closest surrogate species used to model MCMv3.1 in this study

Name	Full name	Carbon number	Surrogate species	Surrogate species MCMv3.1 name	Carbon number (surrogate species)
CCCC(C):C	2-Methyl-1-pentene	6	2-Methyl-1-Butene	ME2BUT1ENE	5
CC(C2)C(C):C	2,3,3-Trimethyl-1-butene	7	1-Hexene	HEX1ENE	6
CCCCCCC:C	1-Octene	8	1-Hexene	HEX1ENE	6
CCCCCCCC:C	1-Nonene	9	1-Hexene	HEX1ENE	6
CCC:C(C)C	2-Methyl-2-pentene	6	2-Methyl-2-butene	ME2BUT2ENE	5
Cy:5	Cyclopentene	5	3-Pentene	TPENT2ENE	5
Cy:6	Cyclohexene	6	1-Hexene	HEX1ENE	6
C:C:C	Propadiene(Allene)	3	1,3-Butadiene	C4H6	4
C:C(C)C(C):C	2,3-Dimethyl-1,3-butadiene	6	2-Methyl-1,3-butadiene	C5H8	5
CC(C)C(C)2C	2,2,3-Trimethylbutane	7	2,2-Dimethylbutane	M22C4	6
CC(C)CC(C)C	2,4-Dimethylpentane	7	2-Methylpentane	M2PE	6
CCC(C)C(C)C	2,3-Dimethylpentane	7	2-Methylpentane	M2PE	6
CC(C)CC(C)2C	2,2,4-Trimethylpentane	8	2-Methylpentane	M2PE	6
CC(C)CCC(C)C	2,5-Dimethylhexane	8	3-Methylhexane	M3HEX	7
CCC(C)CC(C)C	2,4-Dimethylhexane	8	3-Methylhexane	M3HEX	7
CC(C)C(C)C(C)C	2,3,4-Trimethylpentane	8	2-Methylpentane	M2PE	7
CCCCCC(C)CCC	4-Methylnonane	10	*n*-Decane	NC10H22	10
C-Cy5	Methylcyclopentane	6	Cyclohexane	CHEX	6
C-Cy6	Methylcyclohexane	7	Cyclohexane	CHEX	6
C:C(C)-Bz	*a*-Methylstyrene	9	Styrene	STYRENE	8
CC(Bz)CC	*sec*-Butylbenzene	10	*n*-Propylbenzene	PBENZ	9
CC-1(CC-3)Bz	1,3-Diethylbenzene	10	1-Ethyl-2-methylbenzene	OETHTOL	9
C-1(C-2)(C-3)Bz5-C	1,2,3,5-Tetramethylbenzene	10	1,3,5-Trimethylbenzene	TM135B	9
NAPTH	Naphthalene	10	1,3,5-Trimethylbenzene	TM135B	9
CC#C	Methylacetylene	3	Acetylene	C2H2	2
MYRCENE	Myrcene	10	α-Pinene	APINENE	10
D-3-CARENE	*d*-3-Carene	10	α-Pinene	APINENE	10
LIMONENE	Limonene	10	α-Pinene	APINENE	10
CC(C2)CHO	2,2-Dimethylpropionaldehyde	5	*n*-Valeraldehyde	C4H9CHO	5
CC:CCHO	Crotanaldehyde	4	Methacrolein	MACR	4
C1:CC(=O)C:C(C)C1(=O)	Methylbenzoquinone	7	CC(=O)C=CC(=O)C	C4DBDIKET	6