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Atmospheric Chemistry and Physics Discussions

Supplement of

Influence of oil and gas field operations on spatial and temporal distributions of atmospheric non-methane hydrocarbons and their effect on ozone formation in winter

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Supplemental Materials

Table S1 Measurement methodologies

Parameter[1]	Method & Instrument model	Averaging Time	Linearity	Precision	Accuracy	LDL[3]
O_3	UV Photometric (Thermo 55i)	5-min	± 1 % full scale	± 1.0 ppbv	< ± 5 %	0.4 ppbv
CO	NDIR (Thermo 48i TLE)	1 min	± 1 % full scale	± 10 ppbv	< ± 10 %	0.04 ppmv
NO-NO_2-NO_x	Chemiluminescence (Thermo 42i)	5-min	± 1 % full scale	± 0.4 ppbv	< ± 5 %	0.4 ppbv
CH_4 and NMHC	GC/FID (Thermo 55i)	1 min	± 1 % (10% to 90% range)	< 2 % or 50 ppbv	< ± 5 %	10 ppbv
Speciated NMHC[2]	GC/FID (Perkin Elmer OPA system)	Grab, 1-hr, 24-hour & 3-day	< ± 2 % calibration range	< 4 % or 0.01 ppbv	< ± 3 %	0.01 ppbv

[1]A Vaissla WXT520 was used for meteorological measurements of wind speed, wind direction, barometric pressure, relative humidity and temperature

[2]Sampling performed either on-line or through attachment of 6L Entech Inc. Silonite coated canisters that were filled from vacuum to ambient pressure using Entech Inc. CS1200E samplers

[3]LDL: Lower detection limit

Table S2 Speciated NMHC canister monitoring site descriptions and sampling frequency

No.	Site name	Co-ordinates	2010-11	2011-12	2012-13	Category
1	Dry Piney	42.4115, -110.1206	2			Background NW
2	Big Piney HS	42.5391, -110.1207	2			Background NW
3	WDEQ Juel Spring	42.3716, -109.5504	3			Background S
4	Speedway CD Trail Irish Canyon	42.6437, -109.4704	4			Background E
5	Calpet Road	42.3810, -110.2837	2			Background W
6	WDEQ Daniel	42.7913, -110.0543	2			Background W
7	WDEQ Pinedale	42.7913, -110.0543	2			Background N
8	Luman road	42.4656, -109.5776	4			Background S
9	Buckhorn	42.3522, -109.8543	4			Background S
10	WDEQ Boulder (BLDR)	42.7184, -109.7522	6	13	16	Boundary Pinedale Anticline
11	Olson Ranch	42.5993, -109.8696	3	12		Boundary Pinedale Anticline
12	Boulder Lake	42.7688, -109.6712	2			Background E
13	Warbonnet	42.5671, -109.7018	4			Pinedale Anticline
14	Mesa North	42.7530, -109.8577	4	13	17	Pinedale Anticline
15	Mesa South	42.7065, -109.8232	4	11		Pinedale Anticline
16	Yellowpoint Studhorse	42.4508, -109.6899	2			Background S (Jonah Field)
17	Mesa TOP	42.8357, -109.8838	2	13		Boundary Pinedale Anticline
18	Middle Fork	42.5430, -109.6614	2	13		Boundary Pinedale Anticline
19	Mesa Middle	42.7396, -109.8427	2			Pinedale Anticline
20	Paradise Road	42.6806, -109.7956	2	12		Pinedale Anticline
21	Boulder 351	42.6032, -109.7285	2	12		Pinedale Anticline
22	Boulder Crest	42.6593, -109.7845	2	12	14	Pinedale Anticline
23	Middle Crest	42.6274, -109.7540	2		3	Pinedale Anticline
24	UW Boulder South Road (BSR)	42.6840, -109.7083		12		Boundary Pinedale Anticline
25	Hennick Draw	42.8032, -109.9623			13	Background NW
26	Mesa South Loop	42.7283, -109.8604			4	Pinedale Anticline
27	Pinedale Complex	42.6887, -109.8082			2	Pinedale Anticline
28	Anticline Disposal Facility	42.6490, -109.7617		23	9	Pinedale Anticline

Table S3 Audit test results 2012

Species	**Reported (ppbv)**	**Audit Level (ppbv)**
ethane	33.5	36.5
ethene (ethylene)	18.6	18.0
propane	30.3	33.1
propene (propylene)	5.5	6.4
2-methylpropane (*i*-butane)	16.1	16.7
Butane (*n*-butane)	30.6	30.5
trans-but-2-ene (*t*-2-butene)	0.0	
1-butene (but-1-ene)	0.0	
cis-but-2-ene (*c*-2-butene)	9.7	9.8
cyclopentane	0.0	
2-methylbutane (*i*-pentane)	22.3	22.2
pentane (*i*-pentane)	26.7	26.8
1,3-butadiene	0.0	
prop-1-yne (propyne)	0.0	
trans-pent-2-ene (*t*-2-pentene)	0.0	
1-pentene	0.0	
cis-pent-2-ene (*c*-2-pentene)	10.5	10.7
2-methylpentane (*i*-hexane)	0.0	
3-methylpentane	0.0	
hexane (*n*-hexane)	11.9	11.6
benzene	11.7	11.7
cyclohexane	0.0	
Heptane (*n*-heptane)	22.7	19.9
toluene	21.1	20.7
octane	3.7	3.0
ethyl-benzene	7.2	6.8
m+*p*-Xylene	15.9	14.6
styrene	0.0	
o-Xylene	5.2	5.4

Table S4 Summary statistics of hourly measurements at Boulder South Road (BSR) 10/31/2010 to 3/18/2011

	Units	No.	Min.	25th %tile	50th %tile	Av.	75th %tile	95th %tile	Max.
Wind Speed	m/s	3222	0.1	1.6	2.3	3.2	4.2	8.5	13.6
Temperature	ºC	3222	-31.9	-8.3	-4.2	-5.3	-0.7	2.8	16.5
Relative Humidity	%	3222	29	69	79	77	86	92	96
O_3	ppbv	3303	0	30	38	38	44	59	119
CO	ppbv	3303	90	139	156	167	180	250	850
NO	ppbv	3303	0	0	0	1	1	4	19
NO_2	ppbv	3303	0	2	4	5	6	13	42
NO_x	ppbv	3303	0	2	4	6	8	16	50
Methane	ppmv	3209	1.80	1.93	2.06	2.22	2.29	3.27	6.71
NMHC	ppmC	3209	0.00	0.05	0.12	0.23	0.26	0.77	7.40
ethane	ppbv	2389	0.8	5.9	13.9	23.2	29.3	79.8	230.5
ethene	ppbv	2389	0.0	0.2	0.5	0.7	0.9	2.4	8.5
propane	ppbv	2389	0.2	2.5	5.7	8.9	11.5	28.6	82.6
propene	ppbv	2389	0.0	0.1	0.1	0.2	0.2	0.4	1.2
i-butane	ppbv	2389	0.0	0.5	1.3	2.1	2.8	7.0	21.3
n-butane	ppbv	2389	0.1	0.7	1.5	2.3	3.1	7.4	22.5
ethyne	ppbv	2392	0.0	0.3	0.5	1.0	1.1	3.5	15.5
t-2-butene	ppbv	2389	0.0	0.1	0.1	0.2	0.2	0.3	0.5
1-butene	ppbv	2389	0.0	0.0	0.0	0.0	0.0	0.0	0.1
c-2-butene	ppbv	2389	0.0	0.0	0.0	0.0	0.1	0.2	0.5
cyclopentane	ppbv	2389	0.0	0.0	0.1	0.1	0.1	0.4	2.0
i-pentane	ppbv	2389	0.0	0.3	0.8	1.3	1.6	4.1	14.1
n-pentane	ppbv	2389	0.0	0.2	0.6	0.9	1.2	3.1	13.6
1,3-butadiene	ppbv	2389	0.0	0.0	0.0	0.0	0.0	0.0	0.1
propyne	ppbv	2389	0.0	0.0	0.0	0.0	0.0	0.1	0.1
1-pentene	ppbv	2389	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-methylpentane	ppbv	2389	0.0	0.1	0.2	0.4	0.4	1.5	12.1
3-methylpentane	ppbv	2389	0.0	0.0	0.1	0.2	0.3	0.9	8.1
n-hexane	ppbv	2389	0.0	0.1	0.3	0.6	0.7	2.3	20.1
isoprene	ppbv	2389	0.0	0.0	0.0	0.0	0.0	0.0	0.0
benzene	ppbv	2389	0.0	0.3	0.6	1.0	1.2	3.3	16.0
cyclohexane	ppbv	2389	0.0	0.1	0.3	0.6	0.7	2.4	22.2
i-octane	ppbv	2389	0.0	0.1	0.1	0.2	0.2	0.5	4.5
n-heptane	ppbv	2389	0.0	0.1	0.3	0.6	0.6	2.2	19.7
toluene	ppbv	2389	0.0	1.0	1.7	2.8	3.0	7.6	274.4
n-octane	ppbv	2389	0.0	0.1	0.2	0.4	0.4	1.6	17.3
ethylbenzene	ppbv	2389	0.0	0.1	0.2	0.2	0.2	0.5	4.3
m+*p*-xylene	ppbv	2389	0.0	0.4	0.7	1.2	1.3	3.7	37.9
styrene	ppbv	2389	0.0	0.1	0.2	0.2	0.2	0.4	1.8
o-xylene	ppbv	2389	0.0	0.1	0.2	0.3	0.3	0.7	7.1
nonane	ppbv	2389	0.0	0.1	0.1	0.4	0.3	1.2	14.4
Factor 1	*	2311	-0.20	0.60	0.85	1.00	1.22	2.27	4.24
Factor 2	*	2311	-0.20	0.12	0.52	1.00	1.30	3.86	14.05
Factor 3	*	2311	-0.20	0.21	0.42	1.00	0.96	3.56	41.97

*Factor contribution of each hour relative to an average value of 1

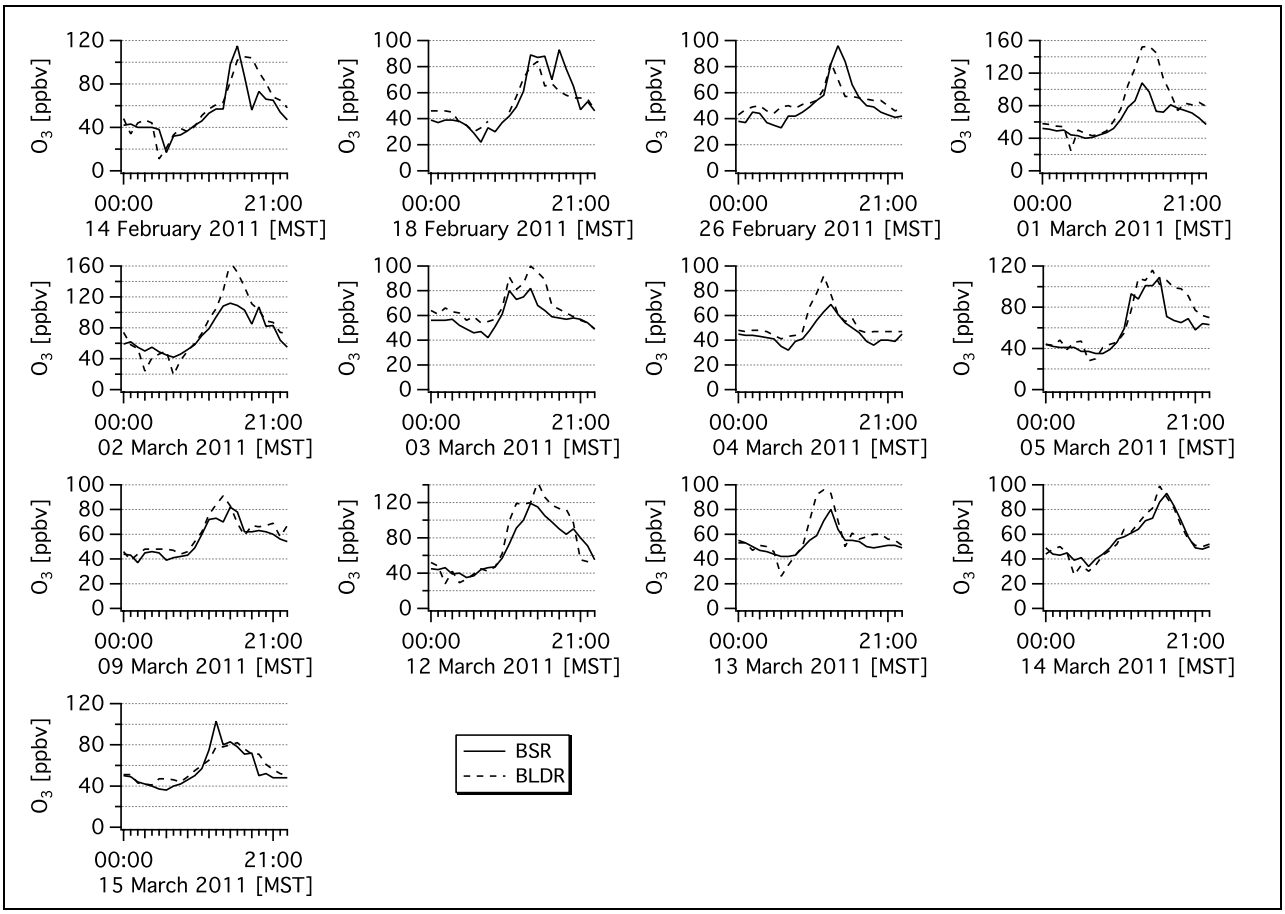

Figure S5 O_3 mixing ratios during 13 episodes at Boulder sites February to March 2011

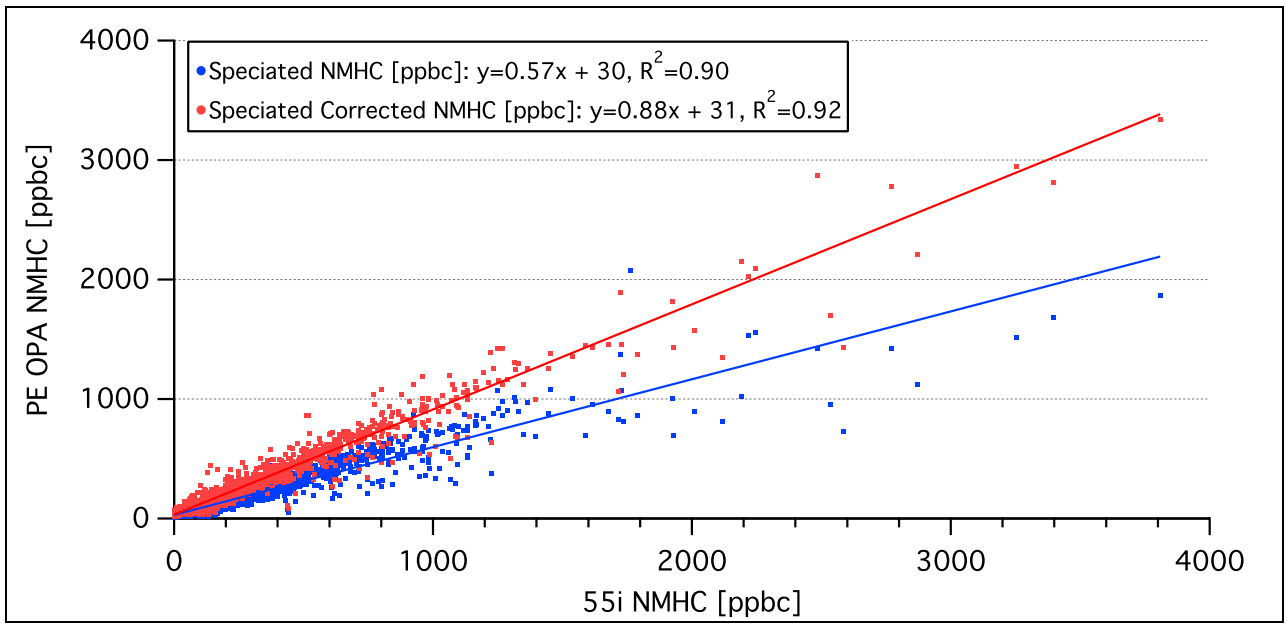

Figure S6 Sum of speciated NMHC as ppbC versus total NMHC as ppbC during the period October 2010 to March 2011 at 2012 Boulder South Road (BSR)

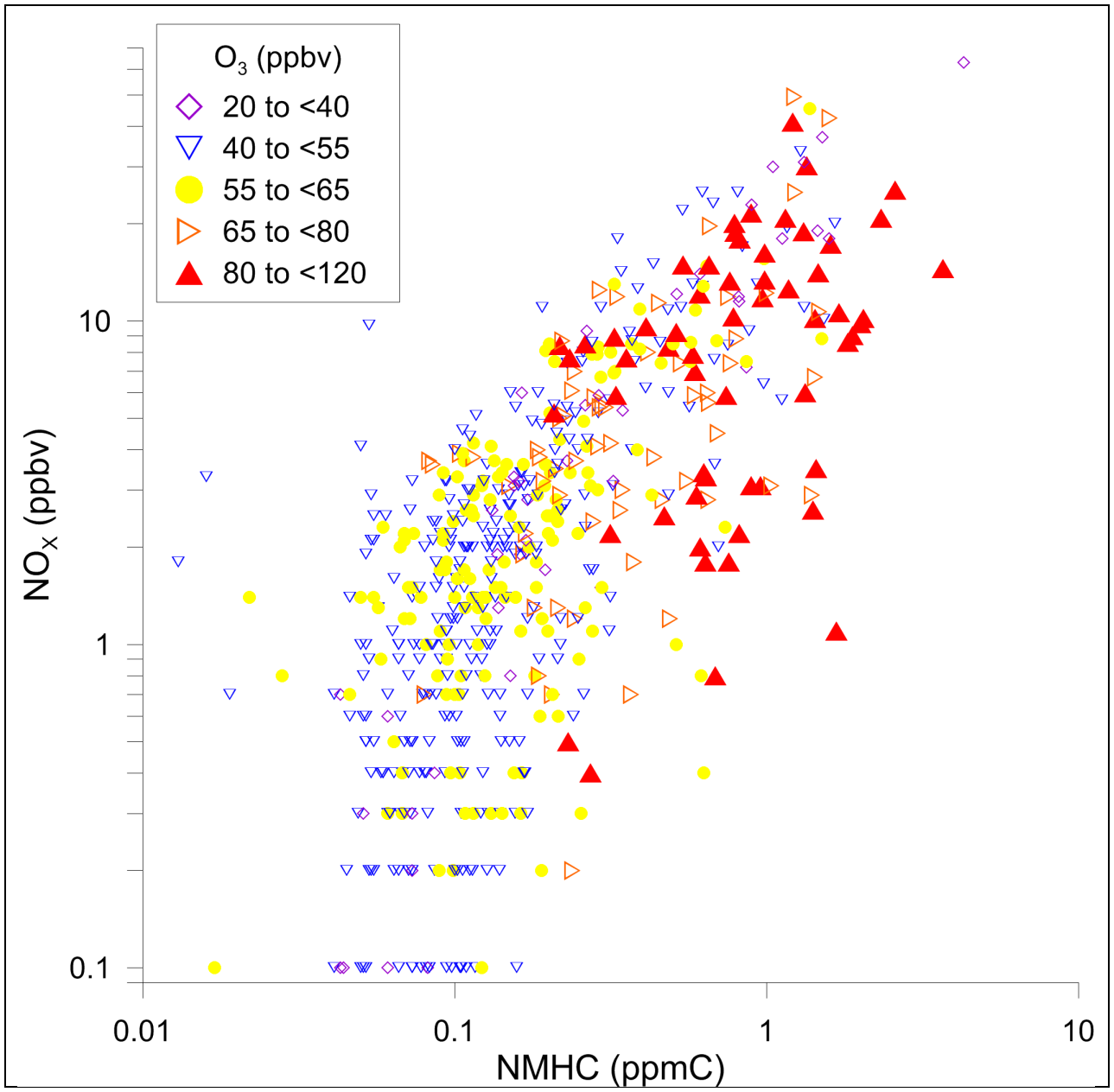

Figure S7 O_3, NMHC and NO_x during daytime for the period January to March 2011 at Wyoming DEQ Boulder site (BLDR)

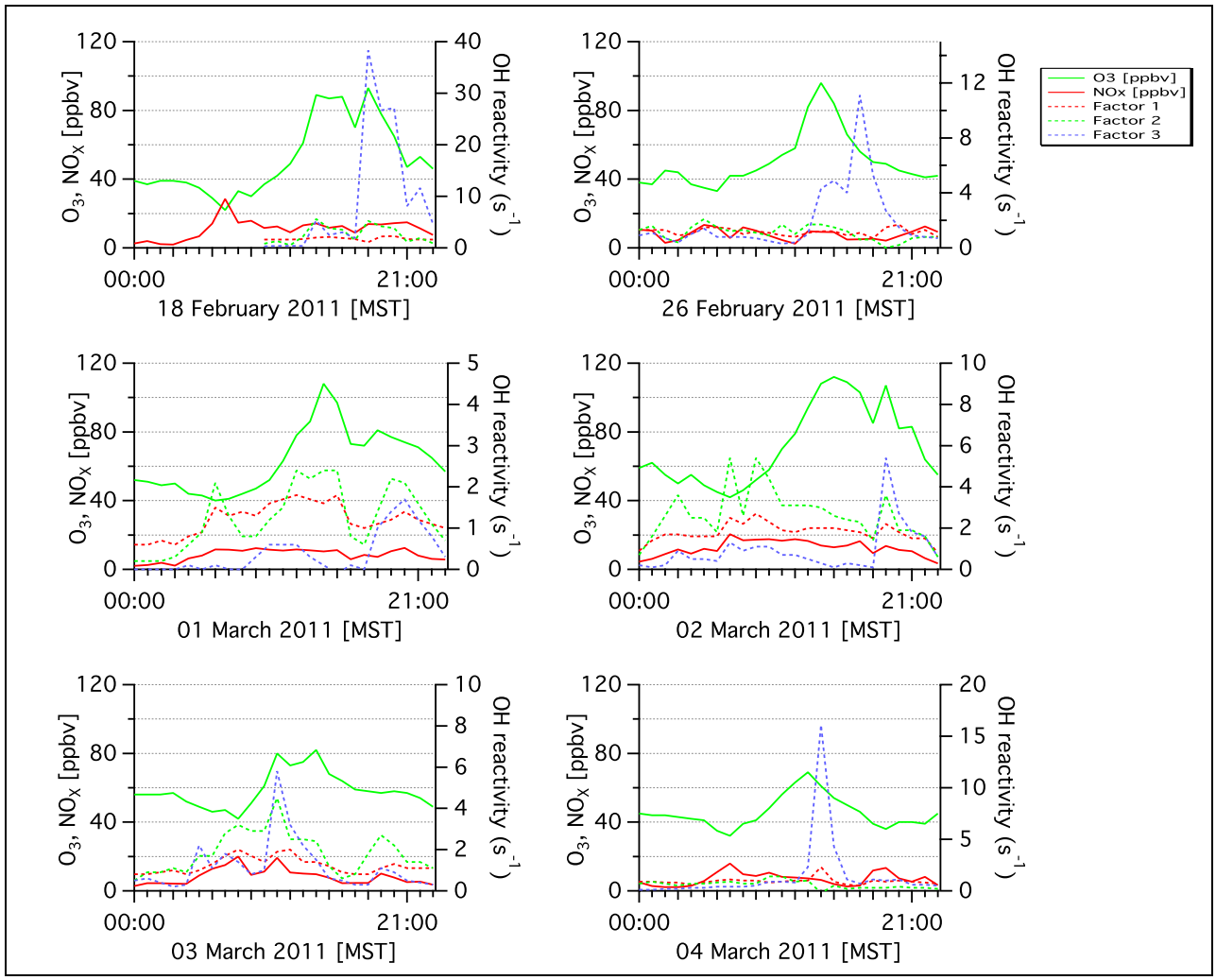

Figure S8 Relationship of PMF factor OH reactivity, NO_x and O_3 during selected episodes at Boulder South Road (BSR)

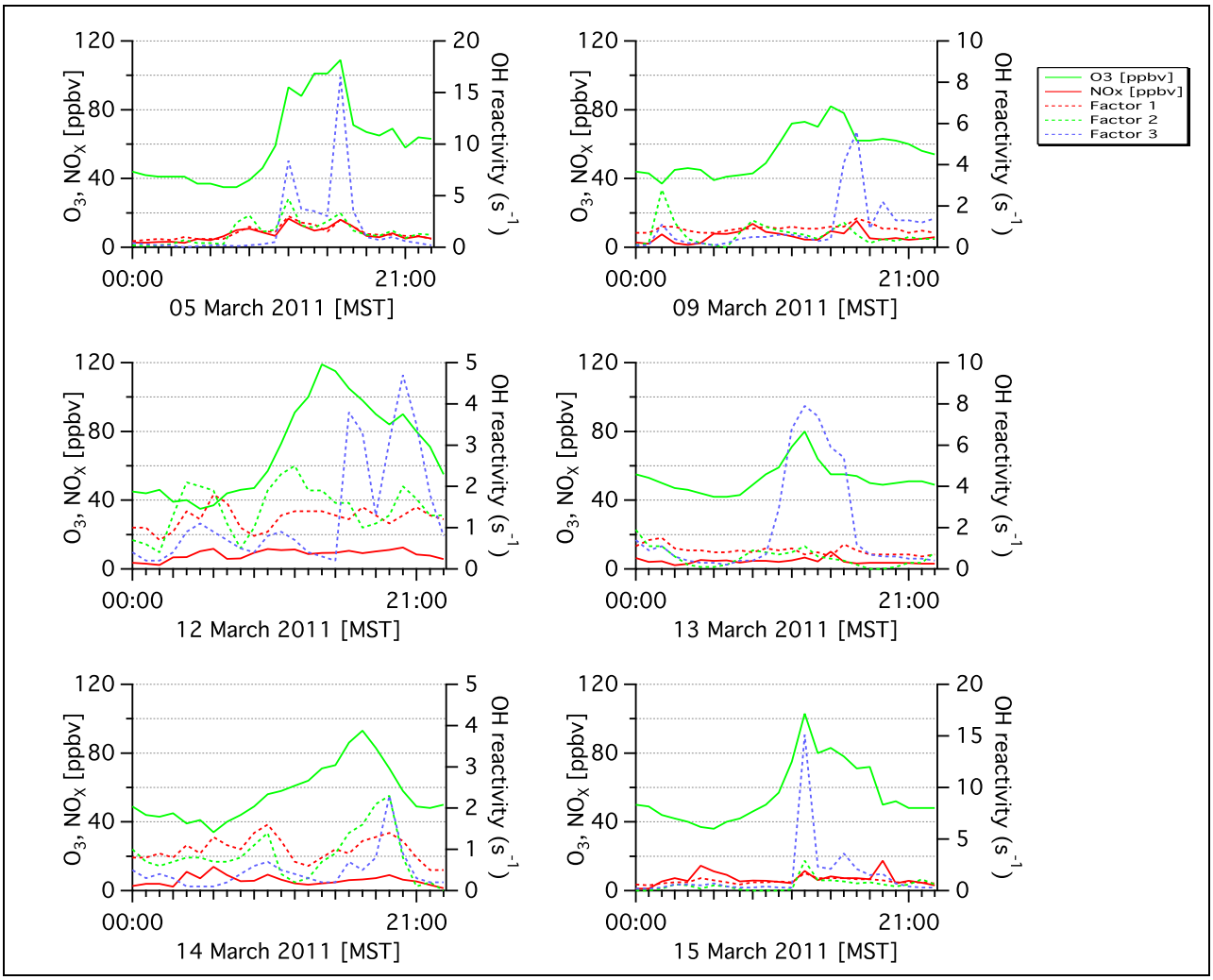

Figure S8 (continued) Relationship of PMF factor OH reactivity, NO_x and O_3 during selected episodes at Boulder South Road (BSR)

Table S9 Mixing ratios, OH reaction rate coefficients at 298.15K and 1013.25 hPa,, and OH reactivity for two selected hours at the Boulder South Road (BSR)

	2/20/2011 at 18:00 (ppbv)	2/18/2011 at 18:00 (ppbv)	Ref.	$10^{12}k_{OH}$*	2/20/2011 at 18:00 OH reactivity (s^{-1})	2/18/2011 at 18:00 OH reactivity (s^{-1})
O_3	35	93				
CO	169	297	5	0.2	0.83	1.46
CH_4	1930	3730	1	0.0064	0.30	0.59
ethane	1.97	99.97	1	0.25	0.01	0.62
ethene	0.19	2.39	1	8.52	0.04	0.50
propane	0.86	35.95	1	1.1	0.02	0.97
propene	0.11	0.27	1	26.3	0.07	0.17
i-butane	0.13	10.74	1	2.1	0.01	0.56
n-butane	0.29	11.32	1	2.4	0.02	0.67
ethyne	0.32	14.64	2	0.75	0.01	0.27
t-2-butene	0.12	0.14	1	64	0.19	0.22
1-butene	0.02	0.05	1	56.4	0.03	0.07
c-2-butene	0.00	0.27	1	64	0.00	0.43
cyclopentane	0.02	0.94	1	5	0.00	0.12
i-pentane	0.10	8.17	1	3.6	0.01	0.72
n-pentane	0.05	7.02	1	3.8	0.00	0.66
1,3-butadiene	0.01	0.02	1	66.6	0.02	0.03
propyne	0.01	0.04	3	6	0.00	0.01
1-pentene	0.02	0.04	1	31.4	0.02	0.03
2-methylpentane	0.01	5.14	1	5.2	0.00	0.66
3-methylpentane	0.00	3.68	1	5.2	0.00	0.47
n-hexane	0.02	9.64	1	5.2	0.00	1.23
isoprene	0.00	0.00	1	100	0.00	0.00
benzene	0.15	11.37	1	1.2	0.00	0.34
cyclohexane	0.03	11.93	1	7	0.01	2.06
i-octane	0.08	3.05	1	3.6**	0.01	0.27
n-heptane	0.06	15.86	1	6.8	0.01	2.65
toluene	0.92	46.26	1	3.7	0.08	4.18
n-octane	0.02	17.27	1	8.1	0.00	3.44
ethylbenzene	0.04	4.26	1	7	0.01	0.73
m+*p*-xylene	0.14	37.86	1	19**	0.07	17.71
styrene	0.07	1.53	4	58	0.10	2.18
o-xylene	0.05	7.06	1	13.6	0.02	2.36
nonane	0.03	13.36	1	9.2	0.01	3.04
				Total	1.89	49.42

*Adapted from Gilman et al. [2009], (1) Atkinson and Arey (2003); (2) Atkinson (1986); (3) Atkinson (1990); (4) Atkinson and Aschmann (1988); (5) DeMore et al. (1987). Units: $cm^3molecule^{-1}s^{-1}$.

**Calculated assuming equal contribution from isomers