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Strong wintertime ozone events in the Upper Green River basin, Wyoming

B. Rappenglück et al.

Correspondence to: B. Rappenglück (brappenglueck@uh.edu)

S1: Overview of air quality instrumentation used in this study (1-min data available, unless noted otherwise). At all sites standard meteorological systems.

Boulder site 42.7186°N, -109.7531°W; 2,160 m asl	**Method**	**Model**	**Accuracy**	**Precision**	**Detection Limit**
O_3	UV Photometric	T-API 400E		0.5%	0.6 ppbv
NO[*,+)]	Chemiluminescence	Air Quality Design, Inc 2-channel NO detector	± 5.4% +3 pptv		3pptv
NO_2[*,+)]	Chemiluminescence	Air Quality Design, Inc 2-channel NO detector with photolytic converter (BLC)	± 13.6% + 6 pptv		6 pptv
NO_y[*,+)]	Chemiluminescence	Air Quality Design, Inc 2-channel NO detector with molybdenum catalytic converter	± 14.8% + 4 pptv		4pptv
HNO_3[#]	Redox Denuder Difference, chemiluminescence detector	Custom-built instrument by Air Quality design. Includes use of a T-API model 200EU chemiluminescence NO detector	± 26.9% + 50 pptv		0.1 ppbv
HONO[**)]	Long Path Absorption Photometry	QUMA-LOPAP	± 10%	5%	1-2 pptv
HCHO[***)]	Fluorometric Hantzsch Reaction	AL 4021	± 2%	10%	60 pptv
$NMHC/CH_4$[1)]	Flame Ionization Detection	Baseline-Mocon Series 9000 $NMHC/CH_4$ analyzer	± 5%	± 5%	0.1 ppmv
Speciated particulates[2)]	IMPROVE_A/TORTOT Elements: X-ray Fluorescence Major ions: Ion Chromatography	URG-3000N Carbon Sampler Met One SASS Speciation Air Sampler System	Total OC: 2-6 % Total EC: 2-6% < 10%	< 10 % < 10%	0.45 $\mu g/cm^2$ 0.06 $\mu g/cm^2$
Mixing Layer height[3)]	Doppler Sodar	ASC Model 4000 miniSodar			15 m
Radiosondes[3)]	GPS-based Upper Air Sounding System	InterMet iMet-3050 403 MHz GPS	± 0.5 m/s (horiz.) ± 5° (horiz.) ± 0.2°C ± 2%		
Ozone sondes[3)]	Titration of ozone in KI	EN-SCI Corp. KZ-ECC O_3 sondes	± 10%		2-3 ppbv
Boulder South Road 42.6840°N, -109.7083°W; 2139 m asl					
NO_x[1)]	UV Photometric	Thermo Scientific 42i	< ± 5 %	< 5 %	0.4 ppbv
CO[1)]	NDIR	Thermo Scientific 48i TLE	< ± 5 %	< 10 %	0.04 ppmv
Speciated NMHCs [1)]	GC/FID	Perkin Elmer Ozone Precursor Analyzer	< ± 3 %	< 5 %	0.01 ppbv

Tethered Balloon site 42.6822°N, -109.8089°W; 2,143 m asl					
Temperature[3)]		HOBO U23 Pro V.2	± 0.21°C (0° to 50°C) ± 0.28°C (at - 20°C) ± 0.5°C (at - 30°C)		
Relative Humidity[3)]		HOBO U23 Pro V.2	± 2.5 % (10%-90% RH) ± 4.5 % (at 100% RH)		
O_3[3,4)]	UV Photometric	T-API 400E		0.5%	0.6 ppbv
$NO/NO_2/NO_x$[3,4)]	Chemiluminescence	T-API 200E		0.5 % > 50 ppb	0.4 ppbv
$NMHC/CH_4$[3,4)]	Flame Ionization Detection	Baseline-Mocon Series 9000 $NMHC/CH_4$ analyzer	± 5%	± 5%	0.1 ppmv

1) hourly data, 2) available as integrated 24 h measurements, 3) available on IOP days

4) surface-based instrumentation collecting data through a system of solenoid valves in the balloon inlet package which allowed the measurements to cycle between tethersonde height levels (4 m, 33 m, 67 m, and 100 m) and provided a measurement at each level every 12 minutes.

*) Ridley and Grahek (1990); Reidmiller et al. (2010), **) Heland et al., 2001; Kleffmann et al., 2002, Ródenas et al., 2011, ***) Rappenglück et al., 2010

[+] The Air Quality Design, Inc chemiluminescence instrument is a two-channel, high performance NO detector that uses a remote-mounted inlet system which houses the catalytic and photolytic converters. The instrument was operated with one channel time-sharing between the NO and NO_x ($NO+NO_2$) measurements, and one channel continuously measuring the NO_y signal. The instrument was calibrated using a custom-built gas-phase titration calibration system that provided sensitivity measurements for both NO and NO_2 channels. In addition, the NO_y channel was priodically challenged with a permeation-tube based HNO_3 calibration source that was in place for calibration of the HNO_3 instrument to ensure that the NO_y converter was providing quantitative conversion of HNO_3. Standard addition calibration was used in all cases to ensure that the measured sensitivities were representative of the ambient sample matrix. The NO_{xy} remote inlet was mounted on the roof of the instrument enclosure at a height of about 3 m from the surface.

[#] The HNO_3 measurement system was comprised of a commercial chemiluminescence NO detector with a remote mounted inlet system. The inlet system included a two-channel molybdenum catalytic NO_y converter, one of which also included a calcium carbonate coated denuder. The difference in signal between the two-channels represented the ambient [HNO_3]. The instrument was calibrated using the same NO, NO_2, HNO_3 calibration source utilized for the NO_{xy} instrument. The HNO_3 instrument inlet was co-located with the NO_{xy} inlet at 3 m above the surface.

S2. Results for selected time periods for the Boulder site. Data in [ppbv], except for CH_4 and NMHC [ppmv]. Hourly data presented.

IOP days

	0500-0900 MST				1100-1700 MST				2100-0500 MST			
	Q_1^*	**$Q_2^\#$**	**Q_3^+**	**Max.**	**Q_1^***	**$Q_2^\#$**	**Q_3^+**	**Max.**	**Q_1^***	**$Q_2^\#$**	**Q_3^+**	**Max.**
O_3	42.7	46.6	48.7	50.9	63.2	73.0	119.6	165.8	46.3	51.0	58.7	87.7
NO	0.019	0.310	1.408	23.535	0.315	0.575	2.093	18.681	BDL	0.002	0.012	0.550
NO_2	1.416	5.362	10.862	25.815	0.791	1.863	3.229	29.012	1.899	3.353	9.748	29.648
NO_x	1.523	7.107	13.457	49.350	1.213	2.710	5.757	42.367	1.904	3.355	9.757	29.666
NO_y	3.045	9.587	15.977	55.398	5.902	11.287	19.498	66.443	4.914	7.848	13.170	30.493
HNO_3	0.283	0.893	2.549	10.906	1.225	2.484	5.951	15.795	0.481	1.295	2.477	6.525
HONO	0.130	0.317	0.442	1.360	0.201	0.510	0.972	1.397	0.093	0.164	0.363	0.908
HCHO	0.100	0.401	0.603	2.180	0.295	0.855	1.252	1.995	0.137	0.313	0.577	1.182
CH_4	2.00	2.65	3.40	9.30	2.00	2.80	3.90	6.1.	2.00	2.30	2.80	6.10
NMHC	0.10	0.45	0.73	1.20	0.20	0.60	1.20	2.20	0.20	0.30	0.50	2.00

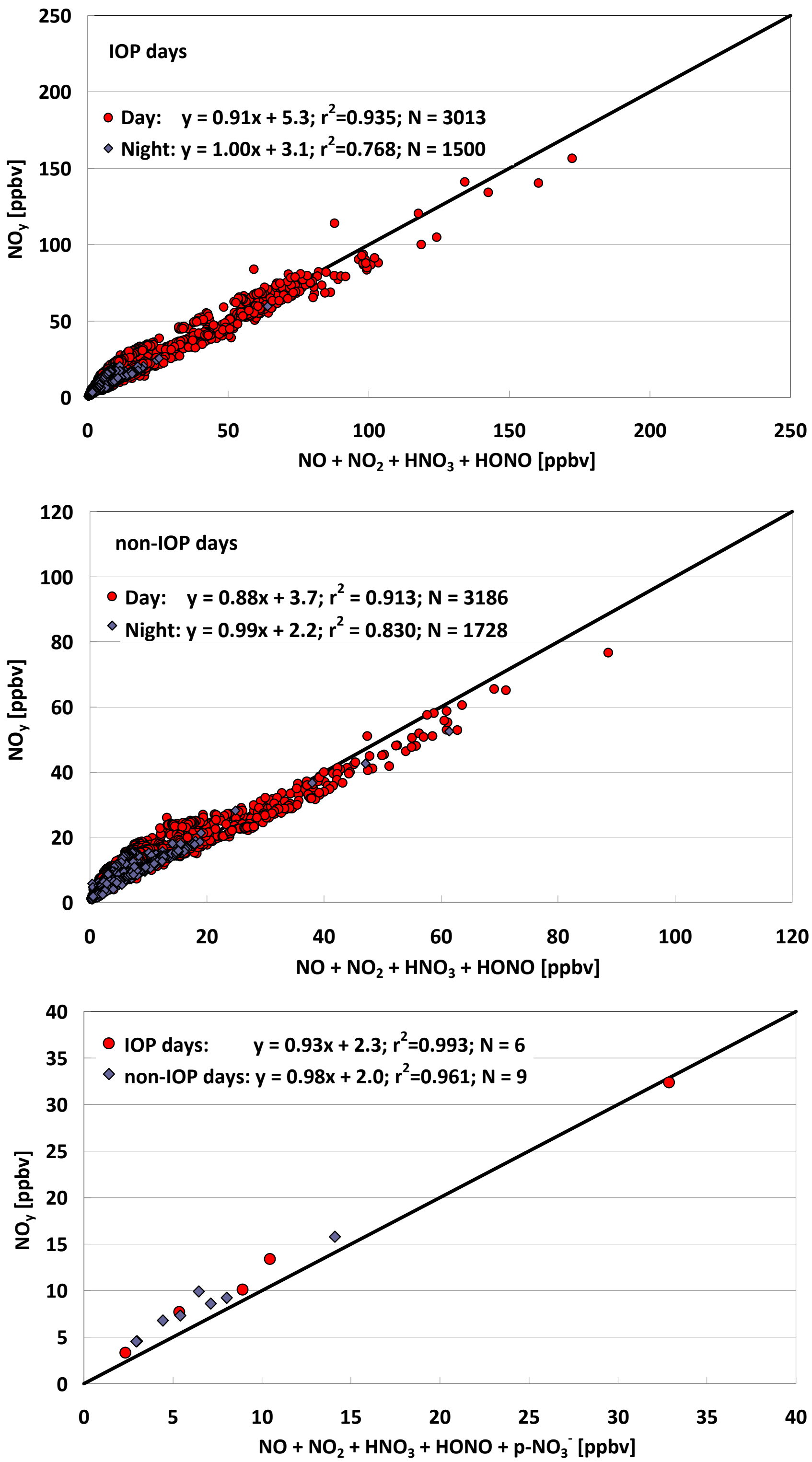
*) Q_1: first quartile (25th percentile)
#) Q_2: second quartile (median)
+) Q_3: third quartile (75th percentile)
BDL: below detection limit

S2. continued.

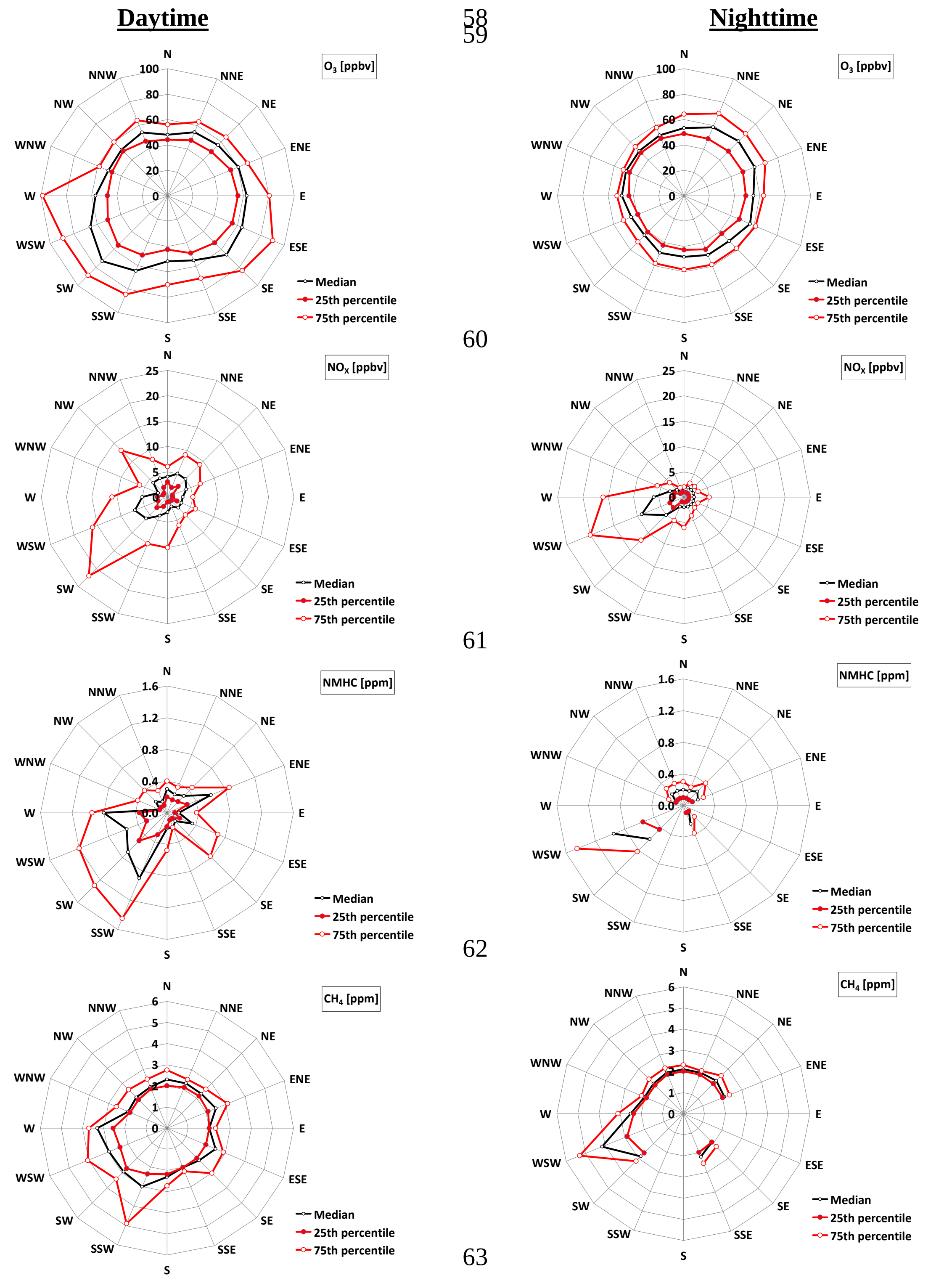
non-IOP days

	0500-0900 MST				**1100-1700 MST**				**2100-0500 MST**			
	$\mathbf{Q_1}^{*}$	$\mathbf{Q_2}^{\#}$	$\mathbf{Q_3}^{+}$	**Max.**	$\mathbf{Q_1}^{*}$	$\mathbf{Q_2}^{\#}$	$\mathbf{Q_3}^{+}$	**Max.**	$\mathbf{Q_1}^{*}$	$\mathbf{Q_2}^{\#}$	$\mathbf{Q_3}^{+}$	**Max.**
$\mathbf{O_3}$	40.1	45.4	49.1	59.5	53.3	65.0	81.9	116.4	47.6	50.0	53.6	77.4
NO	0.038	0.399	1.778	6.591	0.181	0.672	1.376	20.737	BDL	0.002	0.007	0.053
$\mathbf{NO_2}$	2.199	3.399	5.804	22.054	0.573	0.970	2.366	17.994	0.953	1.516	2.420	9.674
$\mathbf{NO_x}$	2.255	4.455	6.243	25.725	0.817	1.617	3.685	38.730	0.962	1.516	2.446	9.677
$\mathbf{NO_y}$	4.300	7.961	10.569	26.068	4.460	7.226	13.191	43.660	3.401	4.381	6.621	12.383
$\mathbf{HNO_3}$	0.509	1.044	1.300	4.383	0.682	1.295	3.050	8.556	0.180	0.544	0.869	2.398
HONO	0.062	0.150	0.255	0.590	0.065	0.135	0.250	1.030	0.045	0.083	0.128	0.628
HCHO	0.126	0.209	0.360	0.926	0.219	0.316	0.593	1.346	0.110	0.191	0.286	1.105
$\mathbf{CH_4}$	2.00	2.25	2.65	4.30	2.00	2.25	2.80	6.10	2.00	2.10	2.30	4.30
NMHC	0.10	0.20	5.25	1.40	0.10	0.25	0.60	1.60	0.10	0.20	0.30	1.00

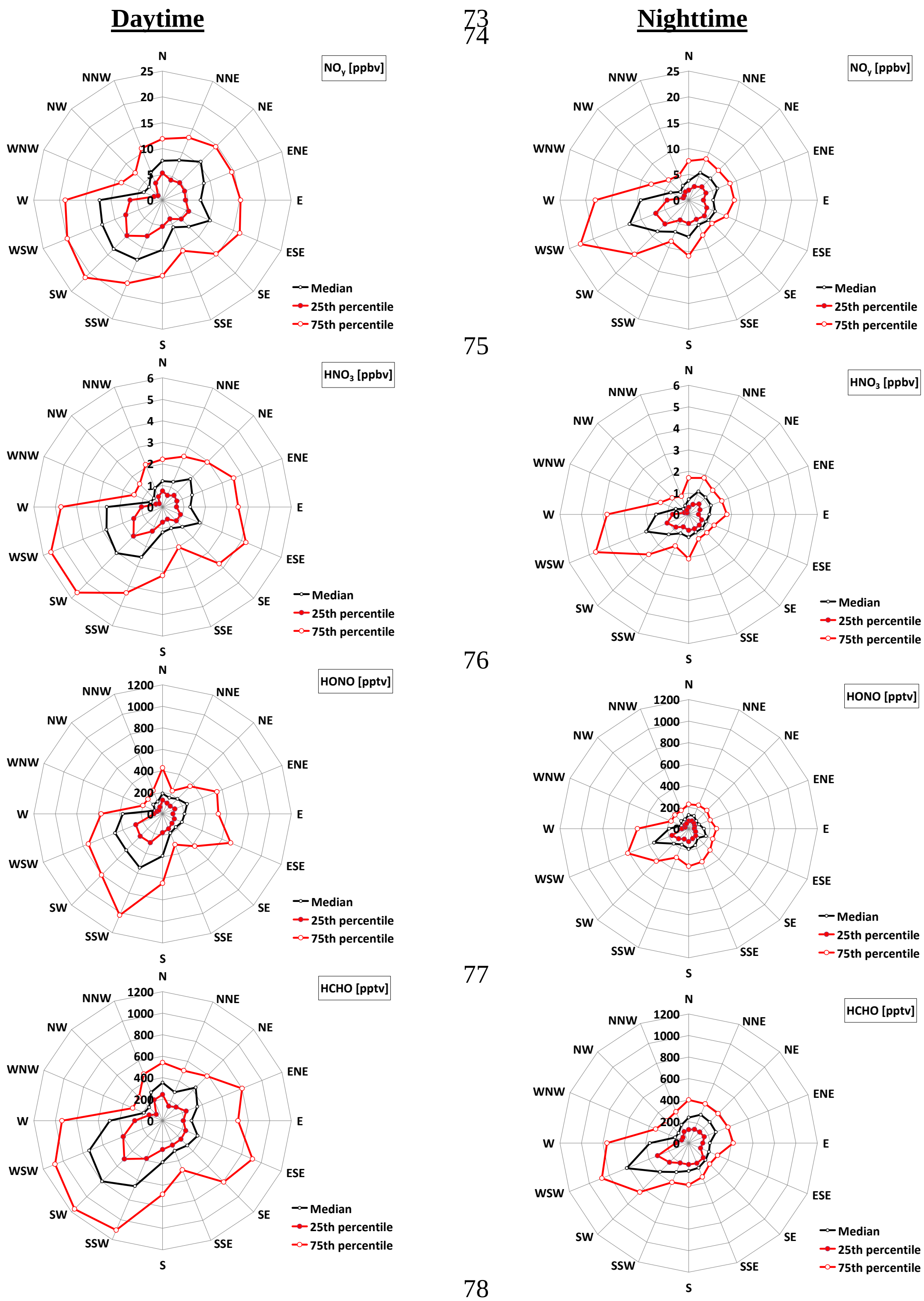
$^{*)}$ Q_1: first quartile (25th percentile)
$^{\#)}$ Q_2: second quartile (median)
$^{+)}$ Q_3: third quartile (75th percentile)
BDL: below detection limit



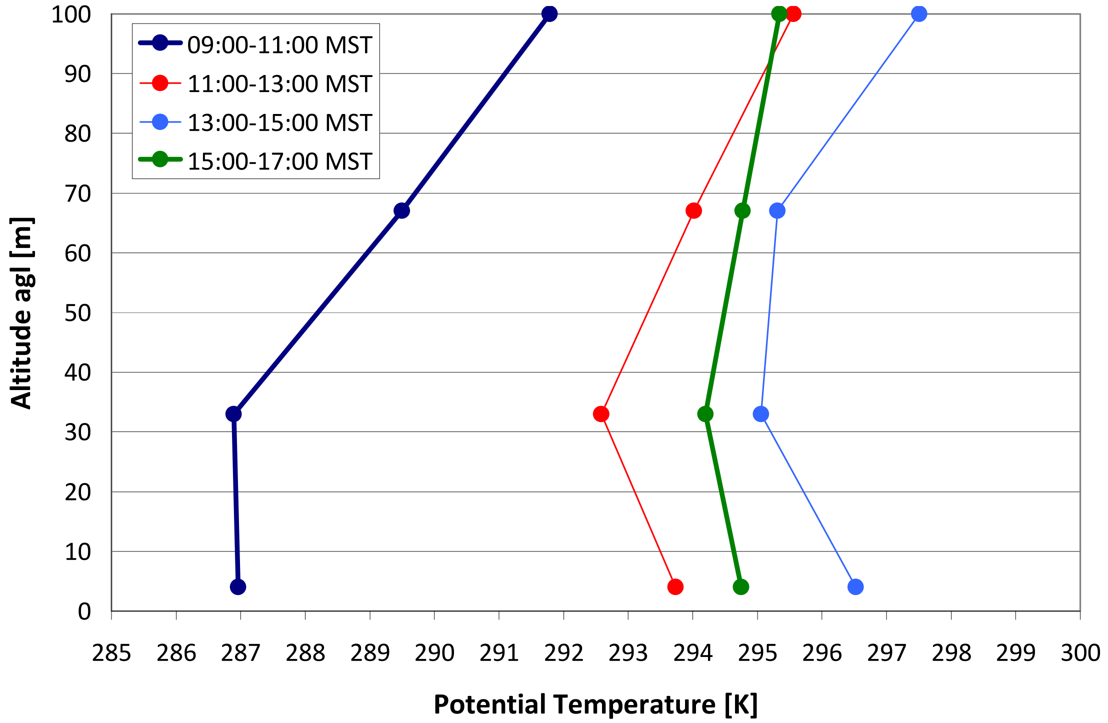
S3. NO_y mixing ratios versus sum of mixing ratios of individual NO_y compounds NO, NO_2, HNO_3, HONO, and particulate NO_3. N denotes number of data points.



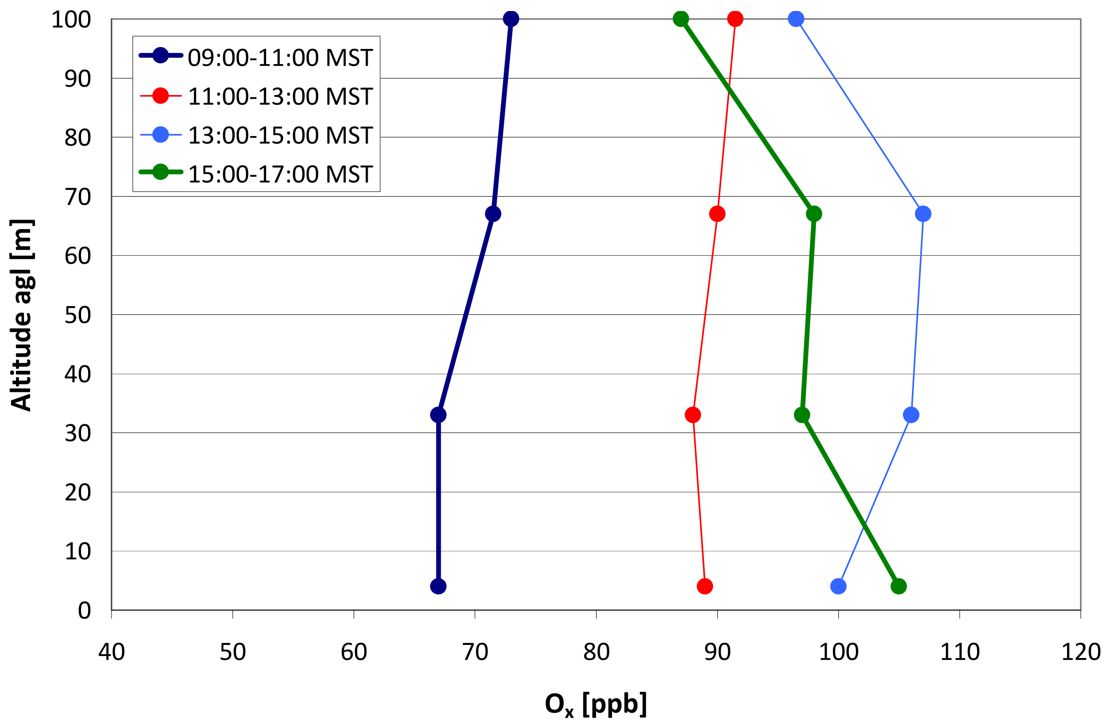
S4a. Wind directional dependence of selected trace gases for day- and night-time conditions (night-time defined as time periods with solar radiation less than 1 W/m^2). Units shown in brackets refer to the radial direction of the corresponding trace gas plot.



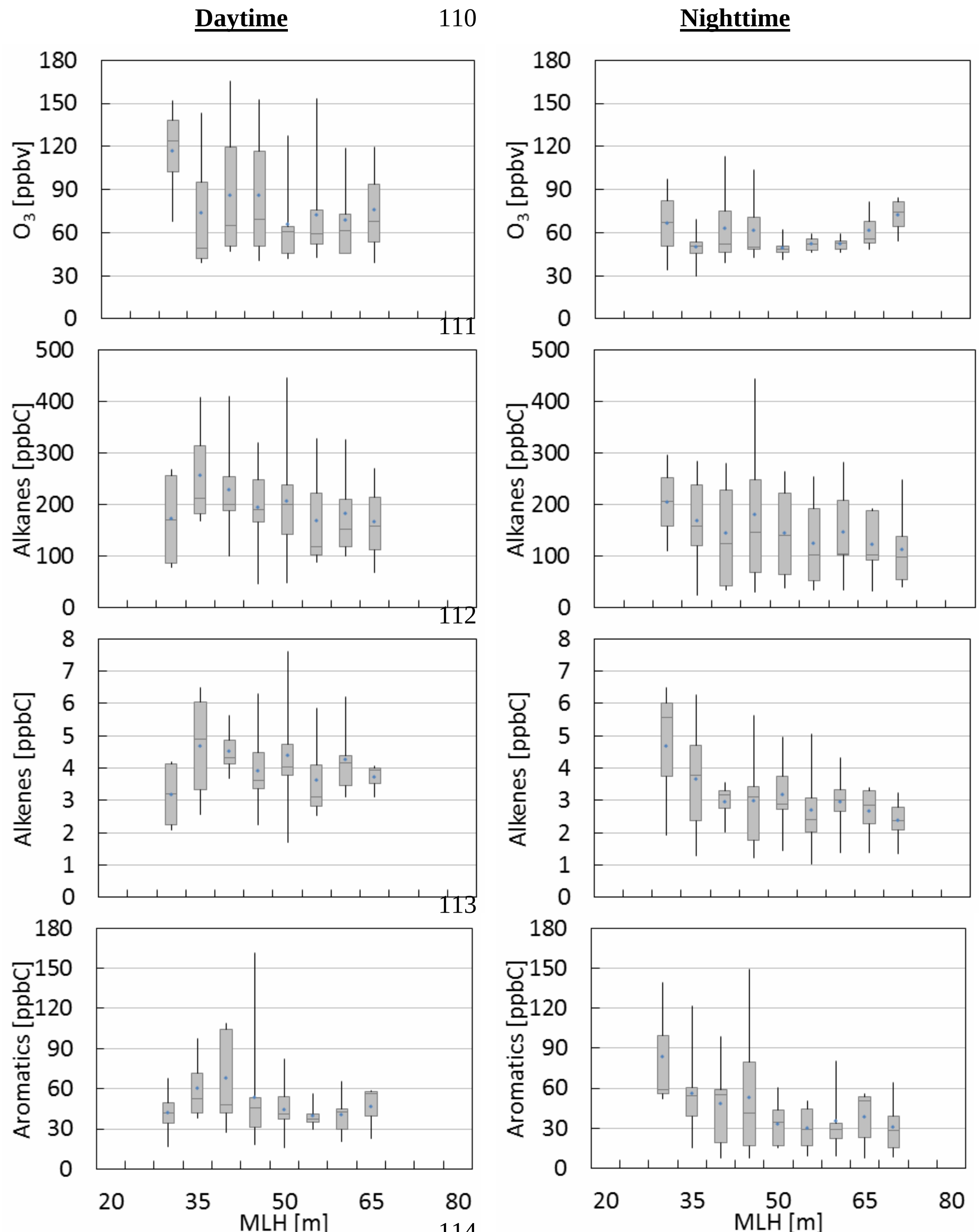
S4b. Wind directional dependence of selected trace gases for day- and night-time conditions (night-time defined as time periods with solar radiation less than 1 W/m^2). Units shown in brackets refer to the radial direction of the corresponding trace gas plot.



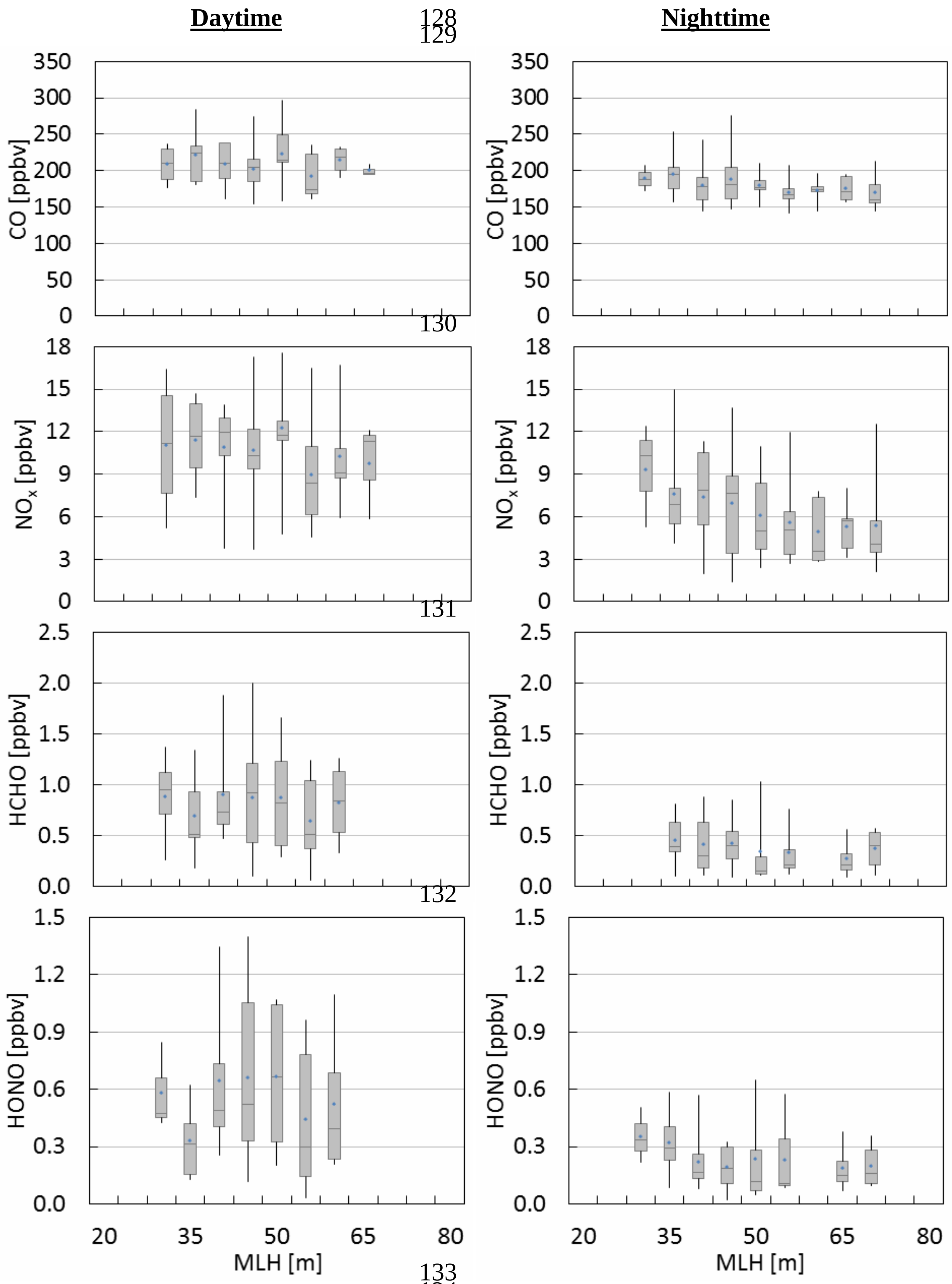
S5. Potential temperature profiles on IOP days based on tethersonde measurements segregated into selected time frames.



S6. Profiles of potential ozone O_x (O_x=O_3+NO_2) on IOP days based on tethersonde measurements segregated into selected time frames.



S7. Selected trace gas mixing ratios versus mixing layer heights (MLH) for day- and night-time conditions on IOP days (night-time defined as time periods with solar radiation less than 1 W/m^2). Speciated NMHC, CO, and NO_x data from the Boulder South Road site.



S7. continued.

S8. Results of correlation analysis of HCHO and HONO versus selected other trace gases at the Boulder site for nighttime conditions and wind direction 180°-270°. All data 10-min values, apart from correlations which include NMHC or CH_4, which are hourly values.

	a*)	b**)	r^2
HCHO vs CH_4	0.223 (±0.040)	-148.4 (±158.7)	0.71
HCHO vs NMHC	0.493 (±0.098)	258.3 (±102.6)	0.66
HCHO vs NO_x	15.44 (±1.45)	324.7 (±31.2)	0.60
HONO vs CH_4	0.188 (±0.036)	-225.9 (±138.5	0.70
HONO vs NMHC	0.441 (±0.070)	91.2 (±69.2)	0.77
HONO vs NO_2	16.82 (±0.95)	148.5 (±19.1)	0.80
HONO vs NO_x	15.20 (±0.88)	161.5 (±19.1)	0.79
HONO vs HNO_3	100.92 (±5.95)	88.1 (±22.6)	0.80

***) a: slope in [pptv/ppbv]**
****) b: intercept in [pptv]**

S9. Values of indicator ratios for NO_x-sensitive, transitional, and VOC-sensitive conditions according to Sillman (2002) and Sillman and He (2002). Photochemical indicators for the moderatley polluted case (80 ppbv < O_3 < 200 ppbv), unless otherwise stated.

Indicator	Median VOC sensitive	Transition (O_3 < 80 ppbv)	Transition	Median NO_x sensitive
O_3/NO_y	5	11-15	6-8	11
O_3/NO_z	6	15-20	8-10	14
O_3/HNO_3	9	n.a. **)	12-15	20
EOR*)	EOR < 0.6	n.a. **)	0.6 < EOR < 0.9	EOR > 0.9

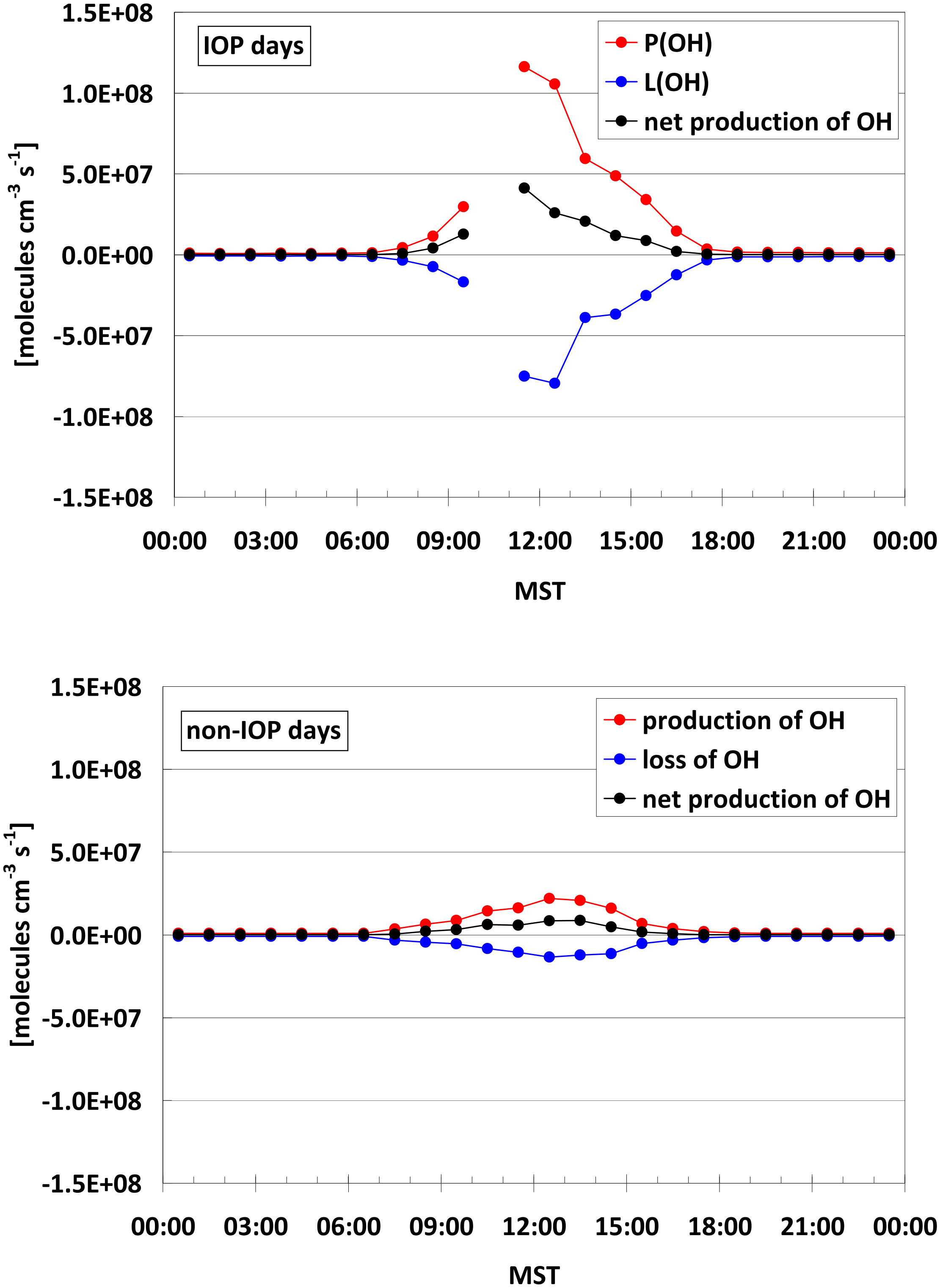
*) Extent of Reaction

**) no information given by Sillman and He (2002), but presumably higher than for the moderately polluted case.

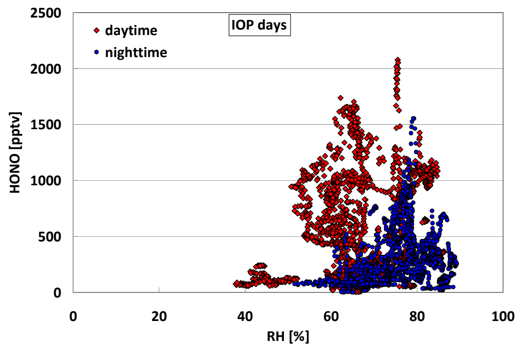
S10. Average minimum values of photochemical indicators at the Boulder site and time periods and wind directions associated with these minimum values.

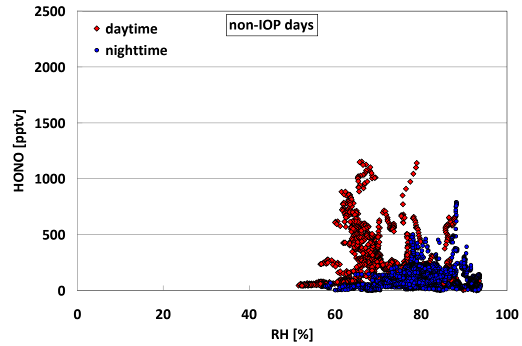
Indicator	Average minimum median values and time of occurrence	Average minimum median values and wind direction of occurrence
O_3/NO_y	3.1 (09:00 MST)	3.2 (SSW)
O_3/NO_z	10.1 (14:00 MST)	9.2 (SSW)
O_3/HNO_3	14.1 (09:00 MST)	11.0 (W)
EOR*)	0.53 (08:00 MST)	0.55 (WSW)

*) Extent of Reaction

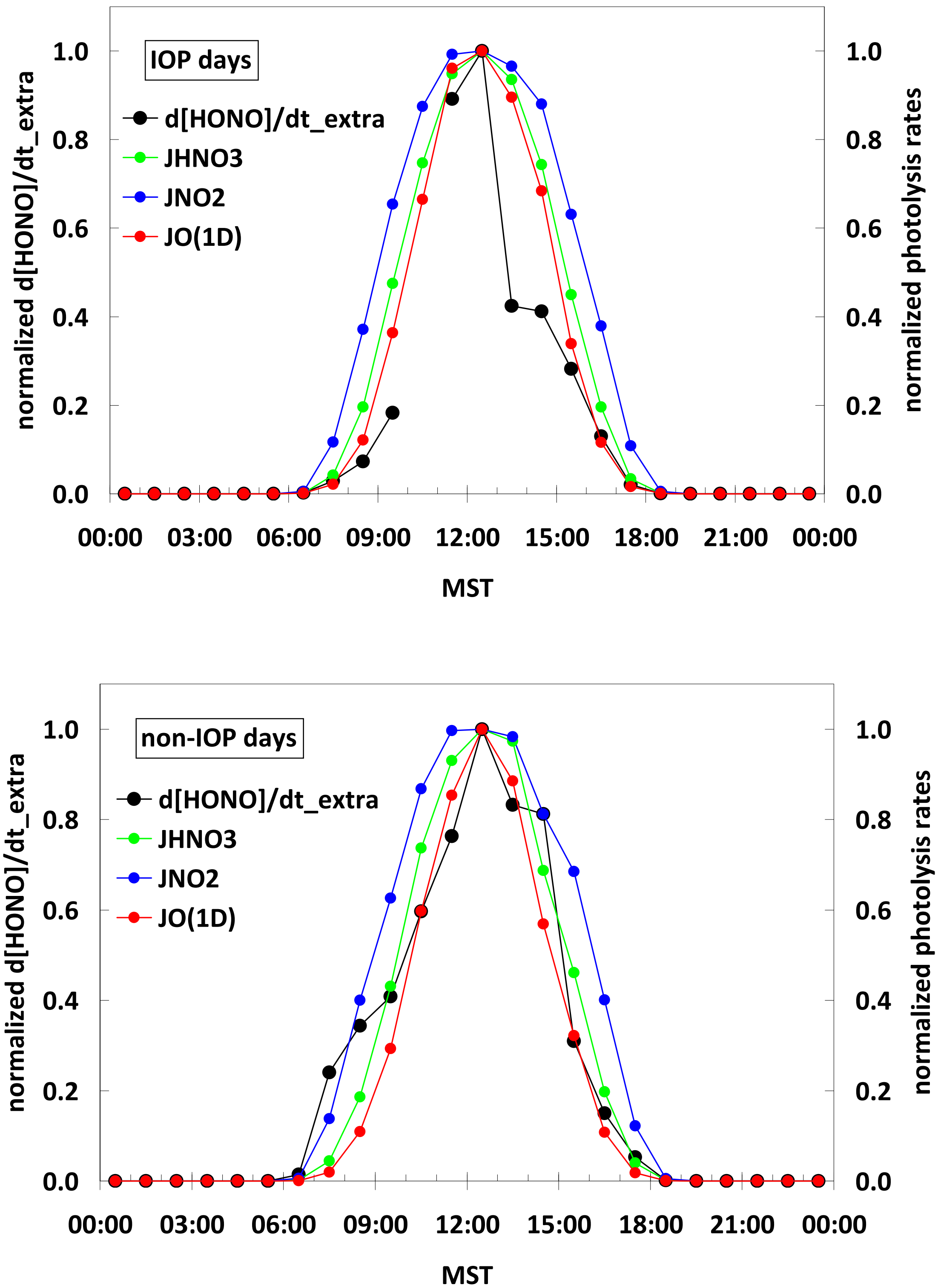


S11. Calculated production and loss rates of OH production, as well as net production rate of OH on IOP and non-IOP days.

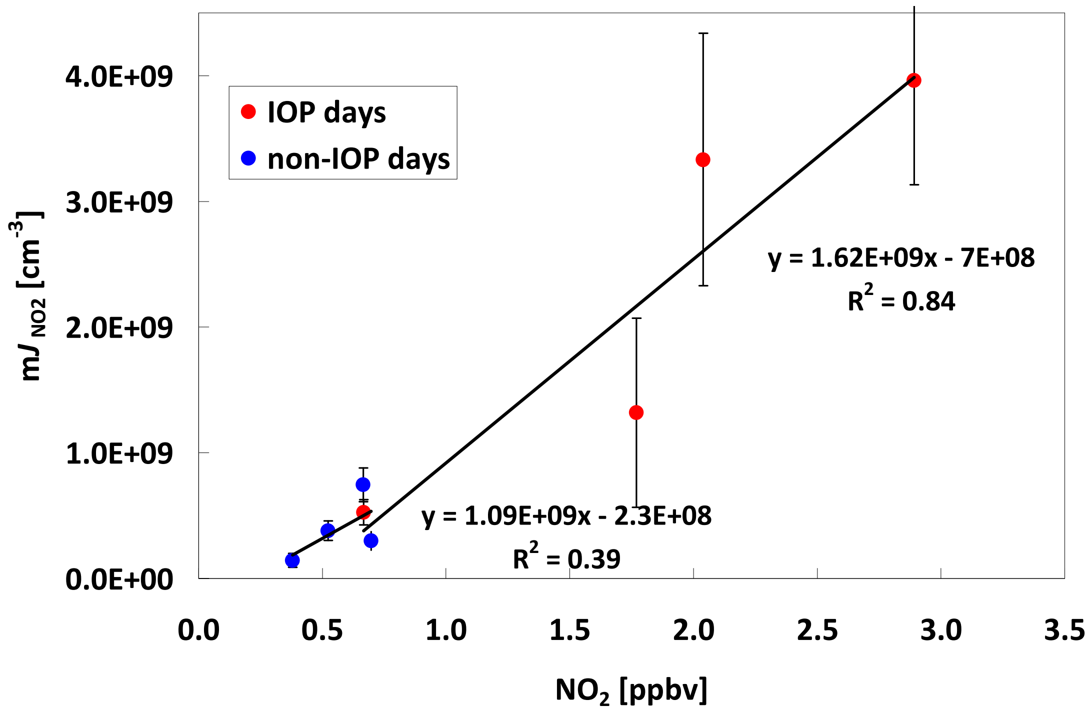


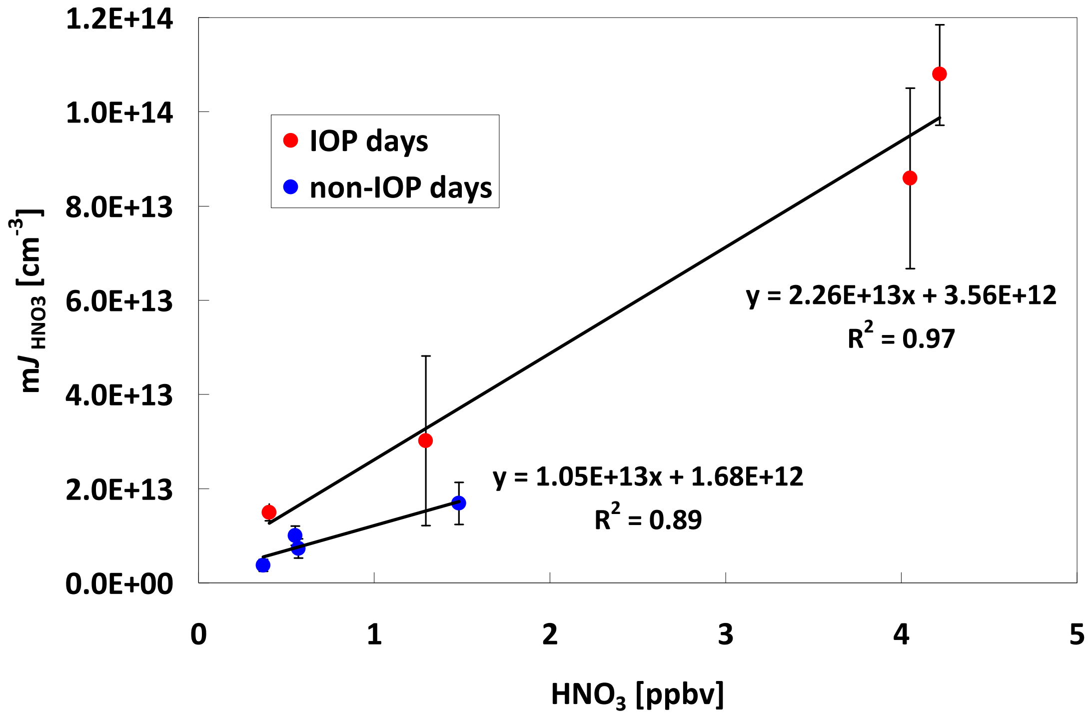


S12. HONO mixing ratios versus relative humidity for day- and night-time conditions on IOP and non-IOP days (night-time defined as time periods with solar radiation less than 1 W/m^2).



S13. Median diurnal variation of HONO extra source and J_{HNO3}, J_{NO2}, and $J_{O(1D)}$, normalized to their corresponding daily maximum median value on IOP and non-IOP days.





S14. Correlations of mJ_{NO2} and mJ_{HNO3} versus daily median NO_2 and HNO_3 mixing ratios on IOP and non-IOP days. Days with daily median NO mixing ratios than 500 pptv were excluded.