atmosphere

Supplementary Materials:

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Table S1. Canister sampling dates and analysis performed at the four MCAQD sites.

Date Sampled	Buckeye	Mesa	North Phoenix	Pinnacle Peak
5/04/21	Carb, SNMOC	Carb, , SNMOC	Carb, SNMOC	Carb, SNMOC
5/10/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
5/16/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
5/22/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
5/28/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
6/03/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
6/09/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
6/15/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
6/21/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
6/27/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
7/03/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
7/09/21	Carb, SNMOC	Carb, SNMOC	Carb	Carb, SNMOC
7/15/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
7/18/21	SNMOC	X	SNMOC	X
7/21/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
7/27/2021	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
8/02/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
8/08/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
8/14/21	SNMOC	Carb, SNMOC	Carb, SNMOC	SNMOC
8/20/21	Carb, SNMOC	Carb, SNMOC	Carb	Carb, SNMOC
8/26/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
9/01/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
9/07/21	Carb	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
9/13/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
9/19/21	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC
9/25/21	Carb	Carb, SNMOC	Carb, SNMOC	Carb, SNMOC

Table S2. Dates and times of TROPOMI retrievals.

Date	Buckeye Time	Pinnacle Peak Time	Phoenix JLG Time
05/04/21	11:52-14:30	11:52-14:30	N/A
05/10/21	11:21-14:19	11:21-14:19	N/A
05/16/21	13:10-14:07	13:10-14:07	N/A
05/22/21	12:56-13:55	12:56-13:55	N/A

06/03/21	12:31-13:30	12:31-13:30	12:31-13:30
06/06/21	N/A	N/A	13:16-14:14
06/09/21	12:38-15:00	12:38-15:00	12:38-15:00
06/12/21	N/A	N/A	13:03-14:02
06/15/21	12:06-14:45	12:06-14:45	12:06-14:46
06/18/21	N/A	N/A	12:51-13:49
06/24/21	N/A	N/A	12:38-13:36
06/27/21	13:22-14:21	13:22-14:21	13:22-14:21
06/30/21	N/A	N/A	12:25-15:05
07/03/21	13:09-14:46	13:09-14:46	13:09-14:46
07/12/21	N/A	N/A	12:00-15:39
07/21/21	12:31-13:29	12:31-13:29	N/A
07/27/21	12:18-14:56	12:18-14:56	12:18-14:58
07/30/21	N/A	N/A	13:02-14:00
08/02/21	12:05-14:43	12:05-14:43	12:05-14:44
08/05/21	N/A	N/A	14:49-14:25
08/08/21	13:33-14:25	13:33-14:25	13:33-14:25
08/11/21	N/A	N/A	12:36-13:34
08/14/21	N/A	N/A	13:20-14:18
08/20/21	13:07-14:05	13:07-14:05	13:07-14:05
08/23/21	N/A	N/A	12:09-14:49
08/26/21	12:53-13:46	12:53-13:46	12:53-13:46
08/28/21	N/A	N/A	12:15-14:55
08/29/21	N/A	N/A	11:56-14:36
09/01/21	12:40-13:38	12:40-13:38	N/A
09/07/21	12:27-13:25	12:27-13:25	N/A
09/13/21	12:13-14:56	12:13-14:56	N/A
09/19/21	12:00-14:40	12:00-14:40	N/A
09/25/21	13:28-14:21	13:28-14:21	N/A

Photolysis Rate Calculation

Equation (S1) states the preliminary formula used in the NO_2 photolysis rate calculation, where k_p is the photolysis rate, φ_{av} is the primary quantum yield, σ_{av} is the absorption cross-section (cm^2 $molecule^{-1}$), and F_{av} is the actinic flux (photons cm^{-2} s^{-1}) [65]. Primary quantum yield values for NO_2 were obtained from [64] for the wavelength range of 290-430 nm. Averaged absorption cross sections for NO_2 were calculated using Equation S2, the values provided in Finlayson-Pitts and Pitts, and the hourly temperature values (T) taken from the 13 sites using MCAQD and AZDEQ sensors. Our modified photolysis calculation is outlined below where F_{tot} is the total downward actinic flux, E_{dir} is the direct solar radiation as taken from the Maricopa County Flood Control District (MCFCD) meteorological stations, θ_z is the solar zenith angle for each site, E_{dif} is the diffuse solar radiation, and r_d is the ratio of diffuse actinic flux to diffuse solar radiation, estimated using Equation S6 [66]. Our analysis uses D as the ratio of direct irradiance to global irradiance estimated using [65]. It should be noted that this method assumes clear-sky conditions, an altitude of 1.6 km, and aerosol optical depths close to zero.

$$k_p = \sum_{\lambda=290nm}^{\lambda} \phi_{av}(\lambda)\sigma_{av}(\lambda)F_{av}(\lambda) \quad \text{(S1)}$$

$$\sigma(T) = \sigma(0℃) + aT \quad \text{(S2)}$$

$$N_p = \frac{I}{E_p} = \frac{I \times \lambda \times 10^{-9}}{hc \times 10{,}000} \quad \text{(S3)}$$

$$F_{av} \approx \frac{N_p}{\cos(\theta_z)} \quad \text{(S4)}$$

$$F_{tot} = \frac{E_{dir}}{\cos(\theta_z)} + \frac{E_{dif}}{r_d} \quad \text{(S5)}$$

$$r_d = \frac{E_{diff}}{F_{diff}} \cong 0.5 - \left(\frac{\lambda - 300}{1000}\right) \quad \text{(S6)}$$

$$F_{tot} = E\{\frac{1-D}{\cos(\theta_z)} + \frac{D}{r_d}\} \quad \text{(S7)}$$

- K_p: Photolysis rate (s^{-1})
- $\phi_{av}(\lambda)$: Primary quantum yield
- $\sigma_{av}(\lambda)$: Absorption cross-section (cm^2 $molecule^{-1}$)
- $F_{av}(\lambda)$: Actinic flux (photons cm^{-2} s^{-1})
- λ: Wavelength (nm)
- a: Temperature coefficient
- T: Temperature (°C)
- N_p: Photon flux (photons/m^2)
- I: Irradiance (W/m^2)
- E_p: Photon energy (J)
- hc: Plank's constant multiplied by the speed of light (J m)
- θ_z: Solar zenith angle (degrees)
- F_{tot}: Total downward actinic flux (photons cm^{-2} s^{-1})
- E_{dir}: Direct solar radiation (W/m^2)
- E_{dif}: Diffuse solar radiation (W/m^2)
- r_d: Ratio of diffuse actinic flux to diffuse solar radiation
- F_{diff}: Diffuse actinic flux (photons cm^{-2} s^{-1})
- E: Irradiance (W/m^2)
- D: Diffuse fraction, ratio of diffuse/global irradiance

Figure S1 demonstrates the results of this calculation for West Phoenix where the photolysis rate resembles a bell curve peaking midday which is what we would expect to see based on other published work, [66], and magnitudes are similar to a previous study conducted in Phoenix [67,68]. To add some more context to NO_2 photolysis rate, the inverse of the photolysis rate is the lifetime of the species due photolysis. At noon for example, a photolysis rate of 14 $\times 10^{-3}$ s^{-1} leads to a lifetime of 71s for a NO_2 molecule. To minimize errors in the final analysis we used the solar radiation values from the Maricopa County Flood Control District (MCFCD) meteorological station at City of Glendale for all 13 sites used in this study. The photolysis rates were then multiplied by the site measured NO_2 to compare to the measured ozone.

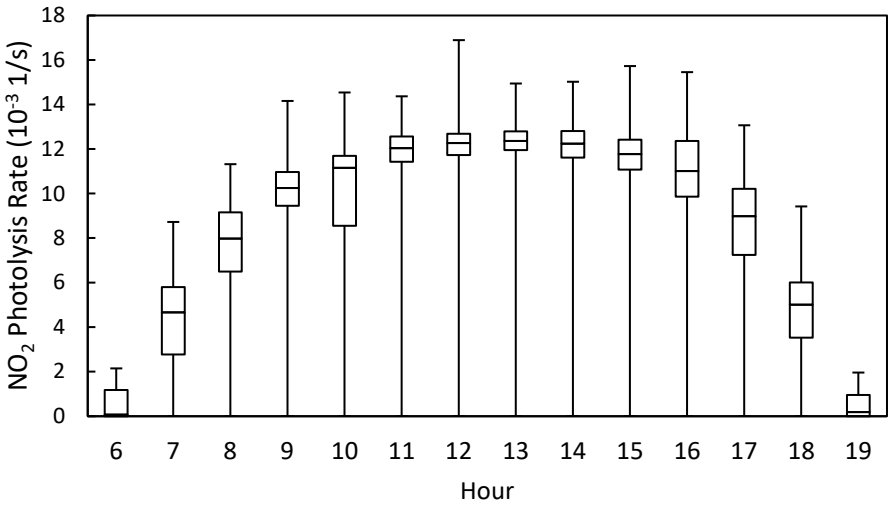


Figure S1. Box and whisker plot for the calculated NO_2 photolysis rates at West Phoenix during the study period. The lines within the boxes represent the medians, the interquartile range is the range of the boxes with the top representing the 75th and the bottom the 25th percentile. The whiskers represent the maximum and minimum values in the data.

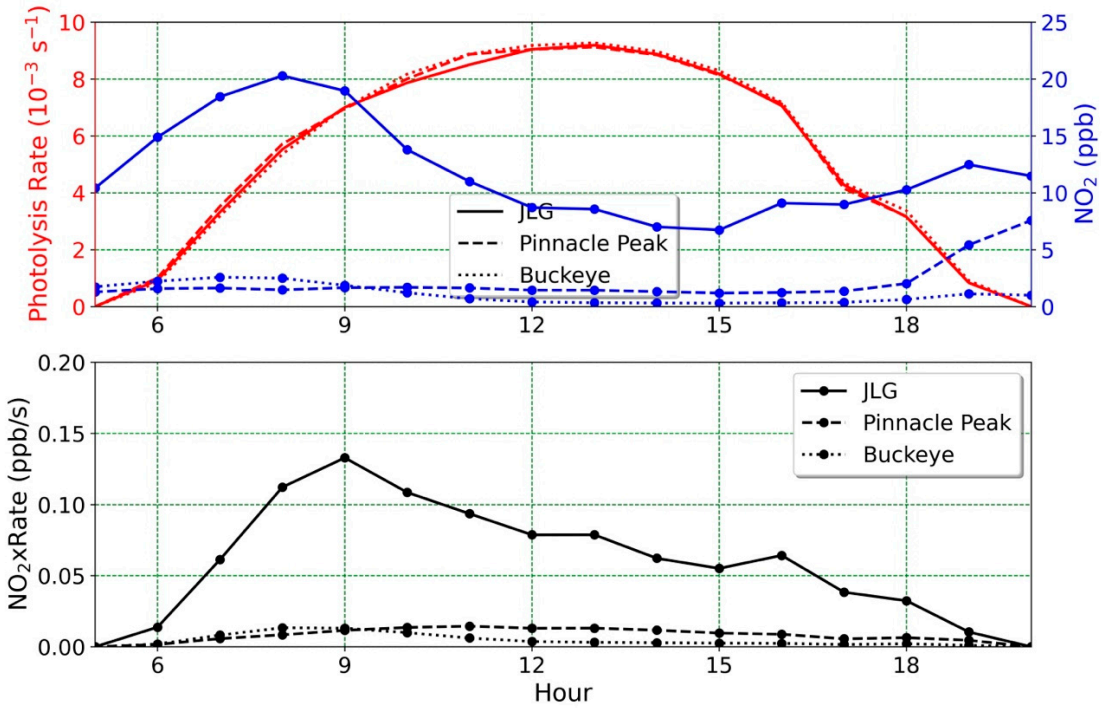
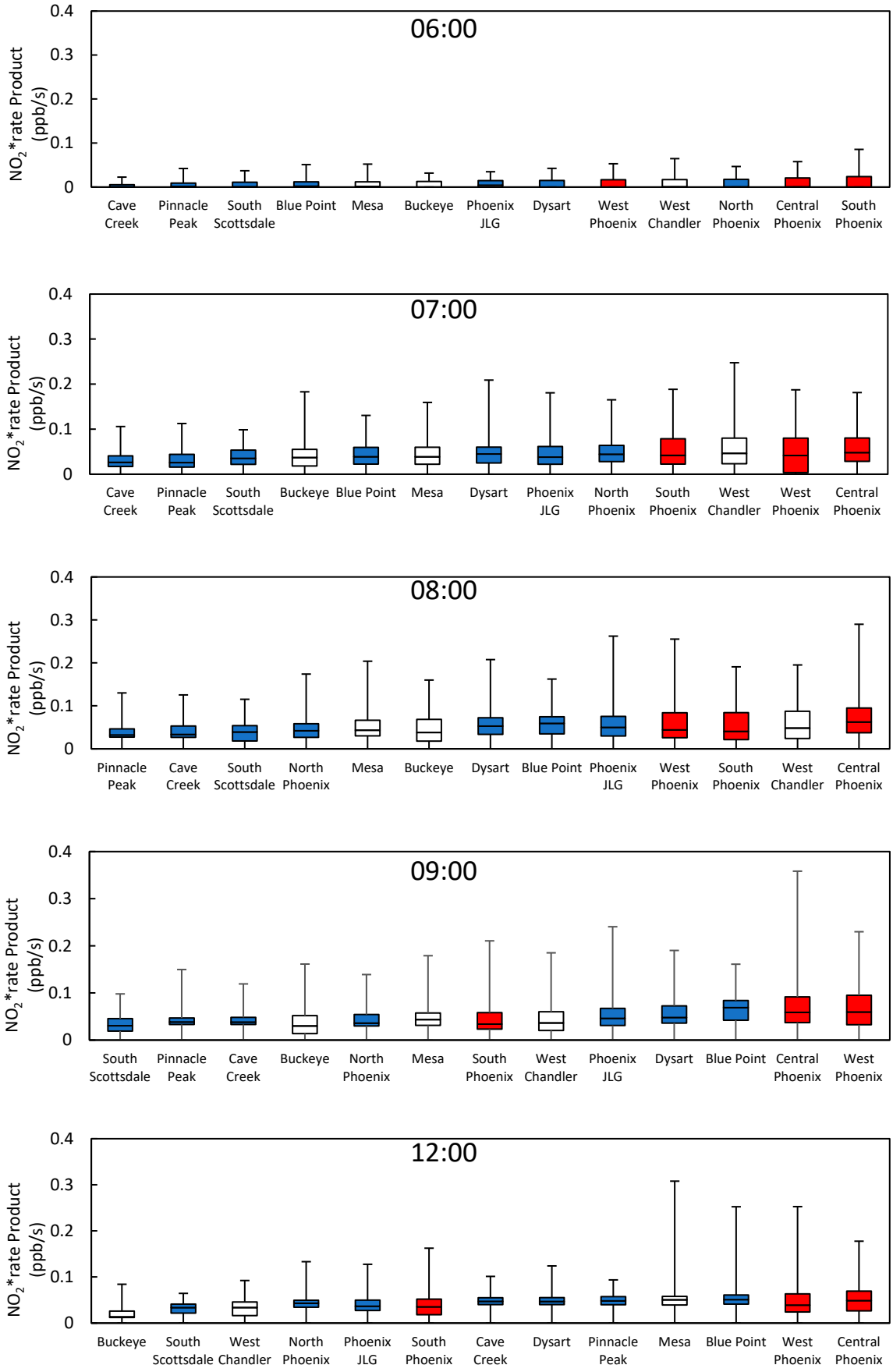


Figure S2. WRF-Chem simulated monthly mean diurnal variation of NO_2 photolysis rate and NO_2 concentration (top), and NO_2 × Rate (bottom) at three selected sites: JLG supersite, Pinnacle Peak, and Buckeye during June 2021.


06:00
NO_2*rate Product (ppb/s)
0.4
0.3
0.2
0.1
0
Cave Creek
Pinnacle Peak
South Scottsdale
Blue Point
Mesa
Buckeye
Phoenix JLG
Dysart
West Phoenix
West Chandler
North Phoenix
Central Phoenix
South Phoenix
07:00
NO_2*rate Product (ppb/s)
Cave Creek
Pinnacle Peak
South Scottsdale
Buckeye
Blue Point
Mesa
Dysart
Phoenix JLG
North Phoenix
South Phoenix
West Chandler
West Phoenix
Central Phoenix
08:00
NO_2*rate Product (ppb/s)
Pinnacle Peak
Cave Creek
South Scottsdale
North Phoenix
Mesa
Buckeye
Dysart
Blue Point
Phoenix JLG
West Phoenix
South Phoenix
West Chandler
Central Phoenix
09:00
NO_2*rate Product (ppb/s)
South Scottsdale
Pinnacle Peak
Cave Creek
Buckeye
North Phoenix
Mesa
South Phoenix
West Chandler
Phoenix JLG
Dysart
Blue Point
Central Phoenix
West Phoenix
12:00
NO_2*rate Product (ppb/s)
Buckeye
South Scottsdale
West Chandler
North Phoenix
Phoenix JLG
South Phoenix
Cave Creek
Dysart
Pinnacle Peak
Mesa
Blue Point
West Phoenix
Central Phoenix

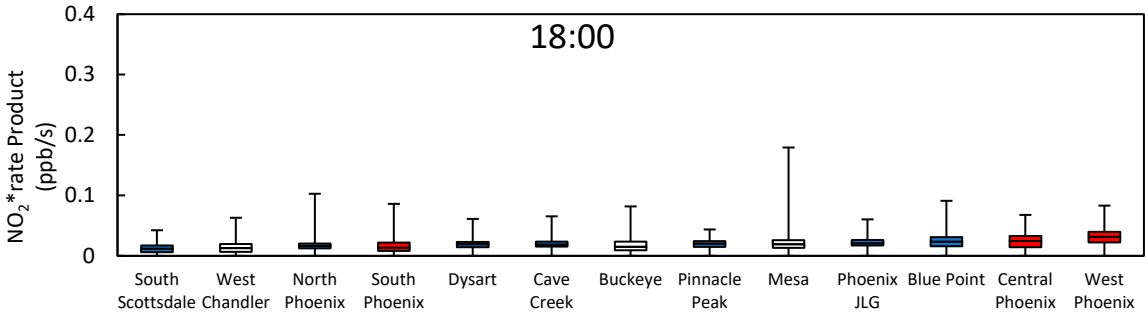


Figure S3. Box and whisker plots for the NO_2 × rate for the 13 sites at various hours. Red boxes correspond to sites dominated by NO_2, blue for sites dominated by ozone, and white for sites that have equivalent NO_2 and ozone as defined by log NO_2/O_3. The sites are ordered in terms of increasing 75th percentiles. The lines within the boxes represent the medians, the interquartile range is the range of the boxes with the top representing the 75th and the bottom the 25th percentile. The whiskers represent the maximum and minimum values in the data. The sites are sorted by the 75th percentile.

Table S3. Average Hourly NO_2 for each site.

Hr	WC	BP	B	CP	WP	SP	SS	PP	NP	D	M	CC	JLG
0	14.6	13.6	8.9	15.2	14.4	12.4	14.1	12.1	12.4	9.5	13.1	8.4	10.1
1	14.9	12.6	8.5	15.3	14.8	12.8	14.0	10.8	11.6	9.2	12.7	8.2	9.1
2	14.4	12.2	9.0	15.3	15.8	13.1	13.6	11.1	11.6	9.6	13.1	8.1	7.9
3	14.1	12.5	8.6	16.4	15.8	13.7	13.3	10.8	11.8	9.5	12.5	8.1	7.9
4	14.2	12.4	9.0	18.7	17.7	15.5	13.7	10.5	12.8	10.4	12.7	8.0	8.8
5	15.8	12.9	10.4	21.1	20.9	17.9	15.3	11.0	15.5	11.5	13.4	8.0	11.1
6	16.8	12.1	11.9	18.0	19.4	17.9	16.4	12.6	15.4	11.4	13.0	7.8	11.8
7	12.3	7.8	9.1	11.9	12.2	9.7	10.7	6.1	10.7	10.9	9.7	6.0	10.3
8	7.8	5.9	7.1	8.8	9.9	8.0	7.4	5.2	7.1	8.3	7.4	5.9	8.4
9	5.8	5.6	5.9	6.7	7.2	6.4	5.9	4.7	6.5	7.5	5.5	4.7	6.4
10	4.7	5.4	5.0	5.8	5.4	5.5	5.9	4.6	6.4	6.8	4.6	4.3	5.4
11	4.7	5.1	5.0	5.7	4.9	5.4	6.0	4.6	6.4	6.3	4.4	4.4	4.6
12	4.8	5.0	4.3	5.3	5.4	5.8	5.8	4.6	7.1	5.8	4.5	4.0	3.9
13	4.4	5.2	4.3	4.9	5.4	5.9	5.6	4.5	7.1	6.1	4.3	3.9	3.5
14	4.5	4.9	4.3	4.6	5.2	5.9	5.7	4.8	7.7	6.1	4.3	3.9	3.3
15	4.5	4.8	4.3	4.6	5.2	5.9	5.1	4.3	7.4	6.1	4.5	4.0	3.4
16	4.2	4.8	4.2	4.3	5.4	5.7	5.1	4.5	7.5	6.1	4.5	4.0	3.3
17	3.9	4.8	4.5	4.5	5.9	5.3	5.1	4.7	7.1	6.2	4.5	4.1	3.7
18	3.9	5.3	5.6	4.7	5.7	4.7	5.6	4.2	7.3	5.9	4.2	4.4	4.5
19	4.3	5.7	7.4	5.9	7.1	5.4	6.7	4.6	7.4	6.6	3.9	5.2	7.5
20	12.0	12.3	10.0	12.5	15.2	12.7	12.2	12.5	11.8	9.9	10.1	9.4	11.9
21	12.8	11.9	9.6	14.4	17.4	13.4	14.2	14.3	14.5	10.5	11.8	8.9	13.9
22	13.7	12.3	9.8	16.0	17.2	12.8	14.9	13.8	14.9	9.8	13.1	8.7	13.2
23	13.3	13.0	8.9	15.5	15.7	12.4	15.5	12.3	14.0	9.5	13.5	8.0	11.7

Table S4. Average Hourly FEM O_3 for each site.

Hr	WC	BP	B	CP	WP	SP	SS	PP	NP	D	M	CC	JLG
0	32.0	28.6	25.8	29.7	29.7	28.1	31.3	41.4	35.2	36.7	33.8	42.1	33.2
1	29.8	27.9	24.4	28.8	29.4	26.2	30.1	40.6	34.5	36.0	33.2	40.6	32.2
2	29.0	26.4	22.8	28.3	28.1	24.7	29.0	40.0	33.7	33.9	31.5	39.3	29.9
3	28.2	25.2	20.5	26.0	26.3	22.7	27.9	39.5	32.6	32.3	30.3	38.4	29.9
4	26.1	24.1	18.4	21.6	22.5	19.4	26.2	39.4	29.7	29.1	28.4	37.4	27.4

5	22.8	22.3	15.5	16.5	17.1	15.3	23.2	37.8	24.9	25.5	24.9	35.5	24.2
6	22.4	24.4	16.0	19.7	18.9	15.8	23.0	36.9	25.5	25.2	24.9	36.2	24.0
7	27.9	30.5	23.1	27.5	26.6	24.3	29.8	41.7	32.8	31.6	31.6	39.4	30.3
8	35.3	36.8	33.3	34.2	33.7	32.3	37.9	45.5	40.7	39.2	39.2	43.7	38.0
9	42.9	42.6	40.3	41.3	41.3	39.4	44.8	48.7	47.6	45.5	46.5	47.3	46.0
10	49.3	46.3	46.5	47.8	47.6	46.5	51.2	52.4	53.7	51.7	52.6	51.9	53.2
11	54.0	49.7	50.6	53.9	53.4	51.6	56.4	56.4	58.6	56.8	57.5	55.7	59.2
12	56.9	52.9	52.8	58.1	57.4	54.4	60.8	60.2	62.5	60.0	61.7	58.7	64.1
13	58.8	55.7	53.6	61.3	59.3	56.1	63.7	63.3	65.5	61.1	64.2	61.2	66.9
14	58.9	57.9	53.6	62.1	59.6	56.5	64.8	65.3	66.9	61.1	64.9	63.0	67.4
15	59.1	58.9	53.2	61.7	58.7	56.5	65.1	66.2	67.0	60.5	65.1	63.2	66.7
16	59.1	58.8	52.7	60.7	56.6	56.1	64.0	66.8	65.0	59.3	64.6	62.3	64.3
17	58.3	58.4	51.0	58.1	54.5	54.3	62.2	65.8	61.9	57.9	63.2	60.5	60.8
18	57.1	57.2	46.8	54.3	51.8	51.4	58.0	62.6	58.3	56.2	60.0	58.2	57.0
19	52.5	49.4	40.3	49.6	45.6	45.9	51.6	56.0	52.7	51.5	55.1	53.2	50.0
20	45.9	40.8	35.5	42.5	36.4	36.1	44.1	47.5	44.4	45.4	47.7	47.4	41.1
21	40.7	36.3	30.9	36.2	30.7	32.1	38.0	44.2	37.1	41.9	41.9	45.5	35.4
22	36.4	33.4	28.2	32.3	29.2	30.2	34.2	42.2	34.2	40.4	37.5	44.8	33.3
23	34.7	30.4	27.0	31.6	29.4	29.4	32.3	41.9	34.5	38.2	35.2	43.8	33.4

Wildfire Impact on Ozone Formation

The following days have been identified by Maricopa County as possibly impacted by regional transport of wildfire smoke. Comparison of the ozone formation between smoke days and non-smoke days allows comparison of the photochemical impact of regional transport of wildfire smoke.

- 06/15, 06/16, 06/18, 06/24, 06/26, 06/28, 06/29, 07/01, 07/02, 07/04, 07/08, 07/09, 07/13, 07/14, 07/17, 07/19, 07/20, 07/21, 07/22, 07/27, 07/28, 07/30, 07/31, 08/01, 08/02, 08/03, 08/04, 08/05, 08/06, 08/17, 08/24, 08/25, 08/26, 08/27, 08/28, 08/29, 09/03, 09/04, 09/05

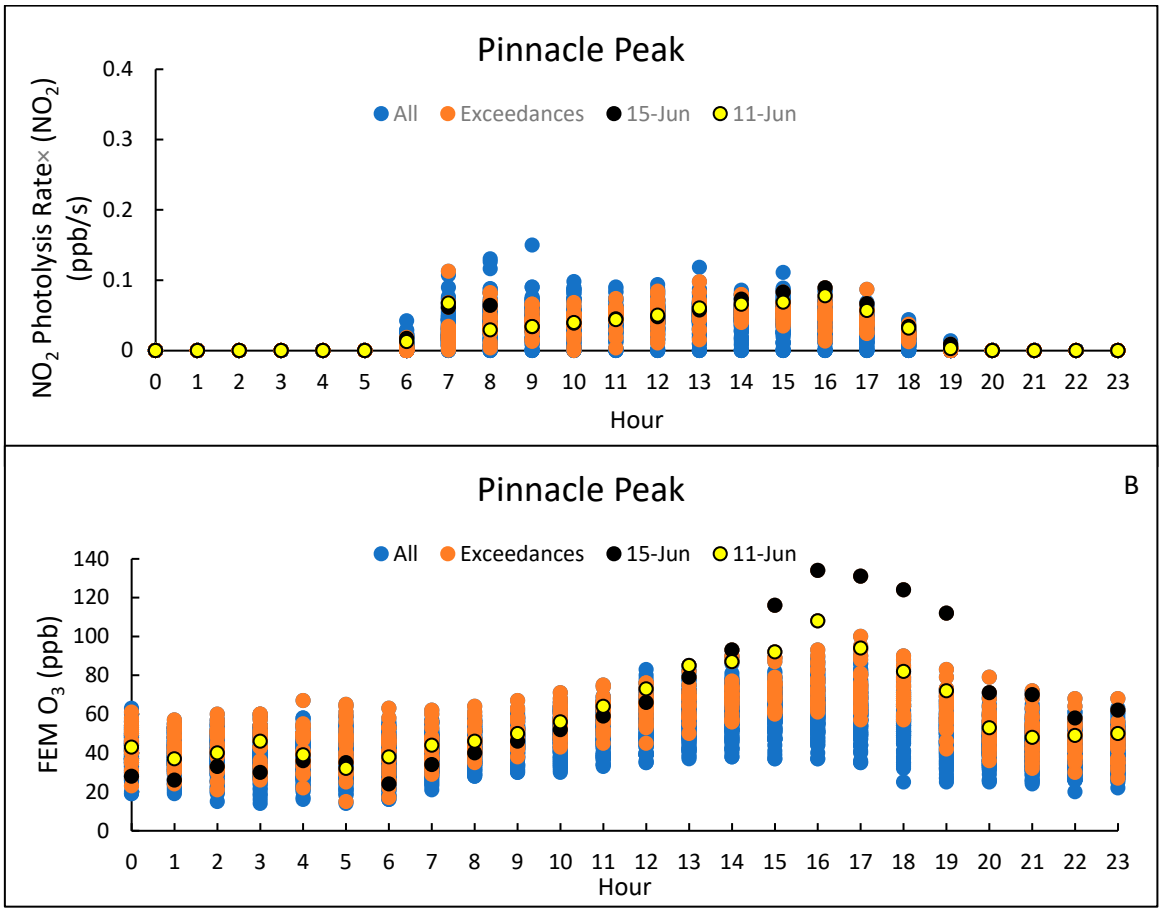


Figure S4. NO_2 × Rate (**A**) and O_3 (**B**) values versus hour for Pinnacle Peak for all days, ozone exceedance days, 06/11, and 06/15.

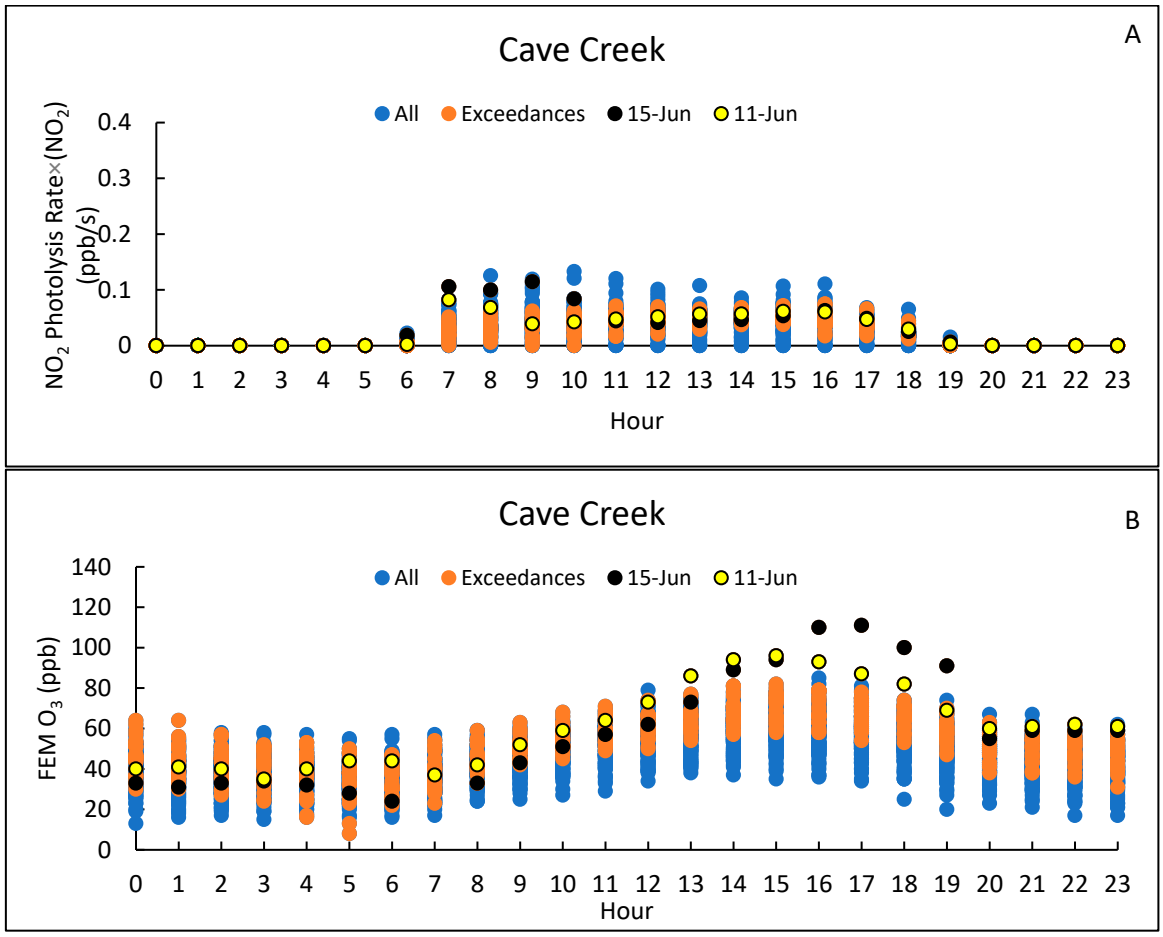


Figure S5. NO_2 × Rate (**A**) and O_3 (**B**) values versus hour for Cave Creek for all days, ozone exceedance days, 06/11, and 06/15.

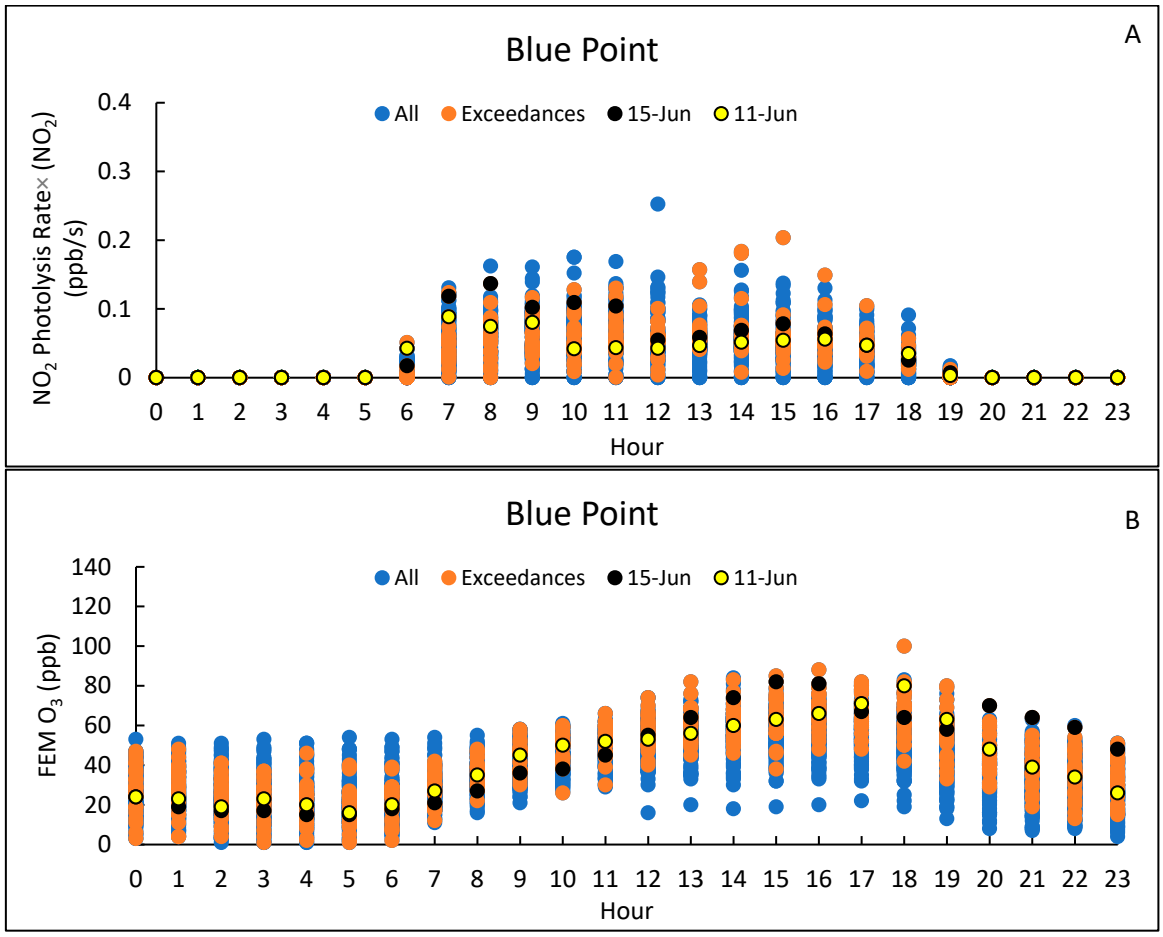


Figure S6. NO_2× Rate (**A**) and O_3 (**B**) values versus hour for Blue Point for all days, ozone exceedance days, 06/11, and 06/15.

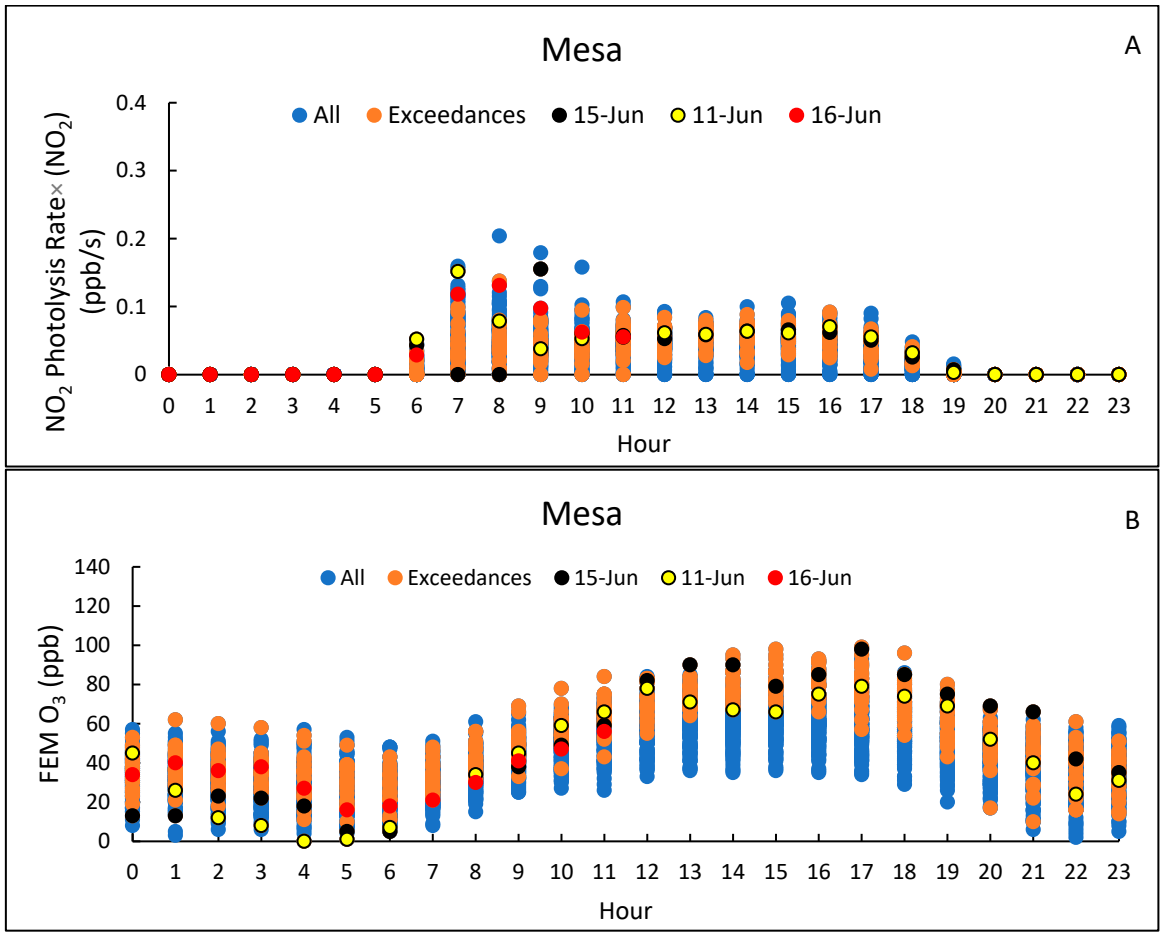


Figure S7. NO_2 × Rate (**A**) and O_3 (**B**) values versus hour for Mesa for all days, ozone exceedance days, 06/11, and 06/15. 06/15 07:00 and 08:00 FEM O_3 values were thrown out by MCAQD. Data in red is from 06/16 which was missing FEM O_3 values so the NO_2 data also needs to be nullified.

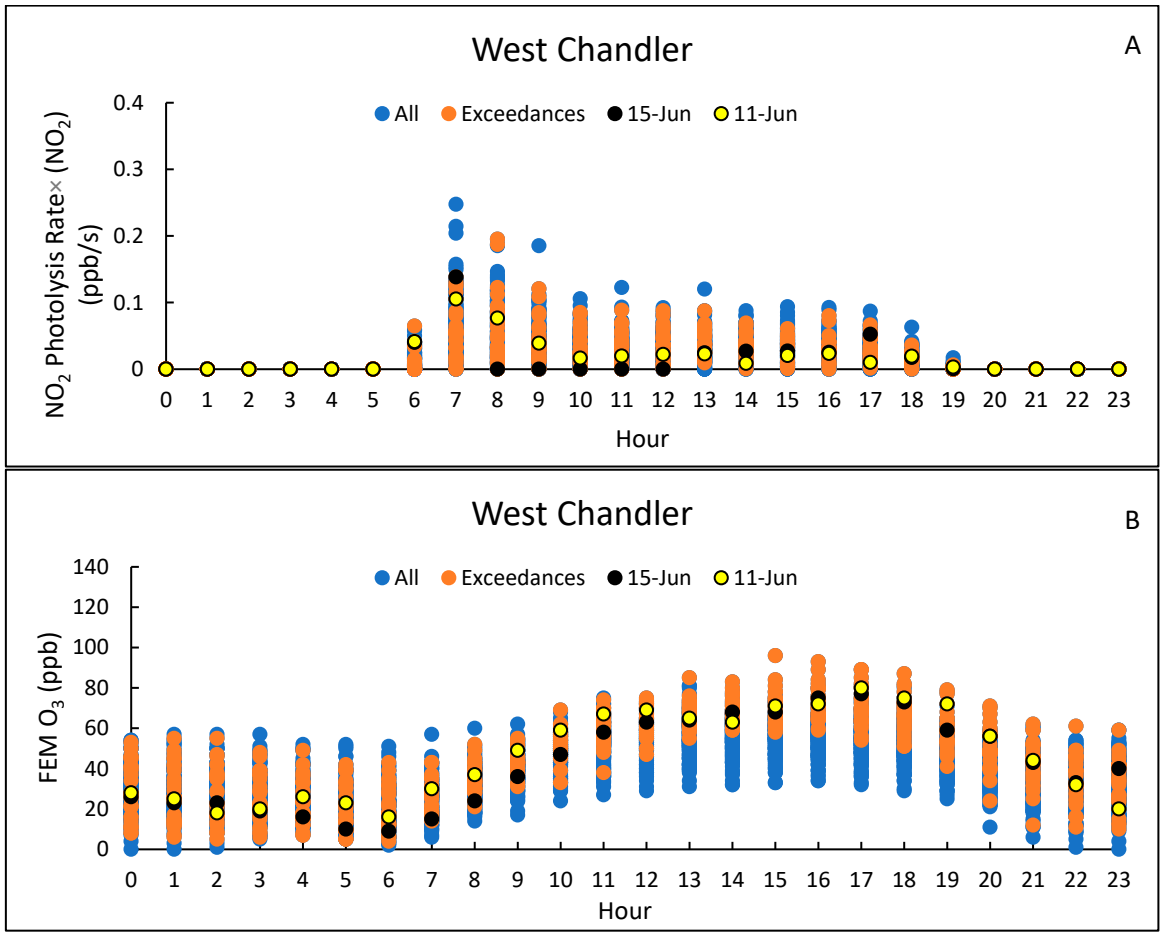


Figure S8. NO_2 × Rate (**A**) and O_3 (**B**) values versus hour for West Chandler for all days, ozone exceedance days, 06/11, and 06/15. 06/15 08:00 and 12:00 NO_2 values are N/A due to sensor rotations.

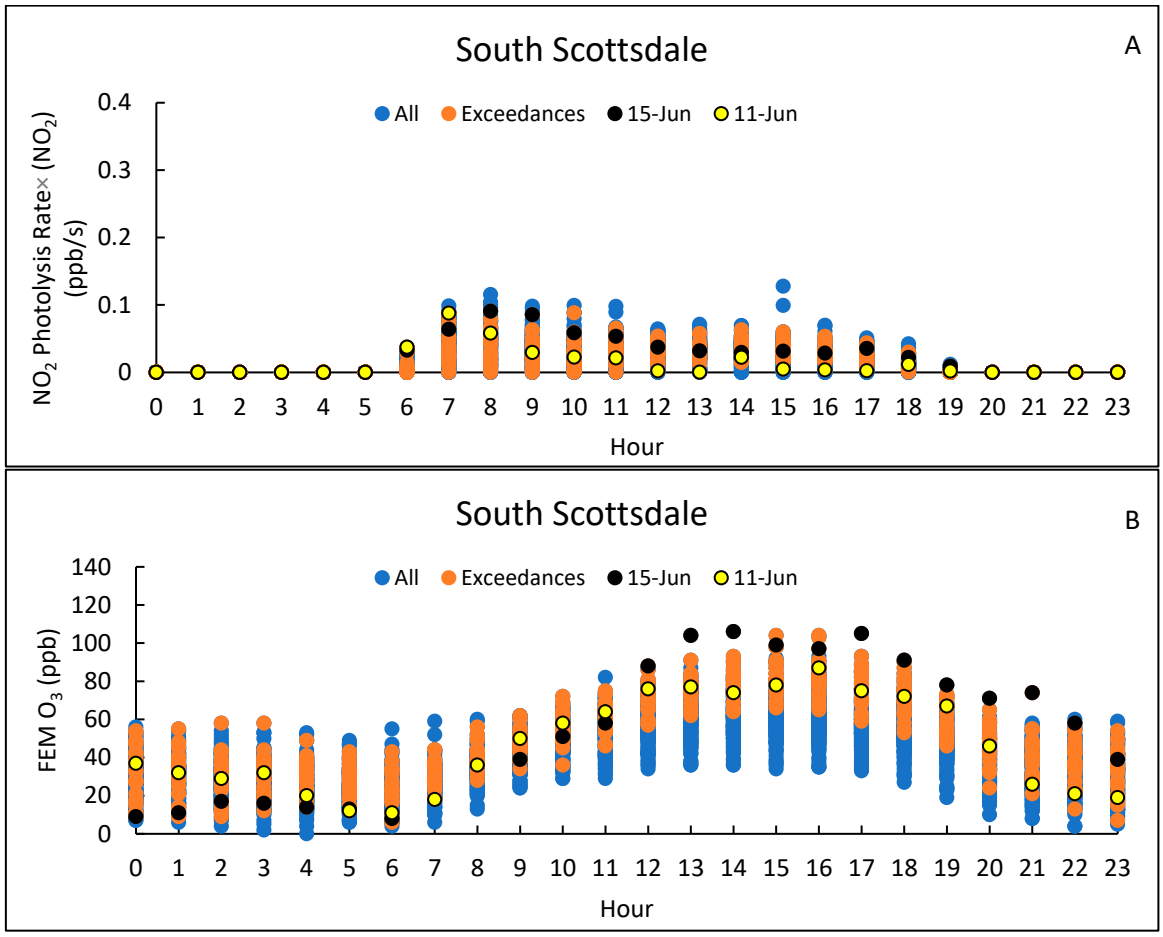


Figure S9. NO_2 × Rate (**A**) and O_3 (**B**) values versus hour for South Scottsdale for all days, ozone exceedance days, 06/11, and 06/15.

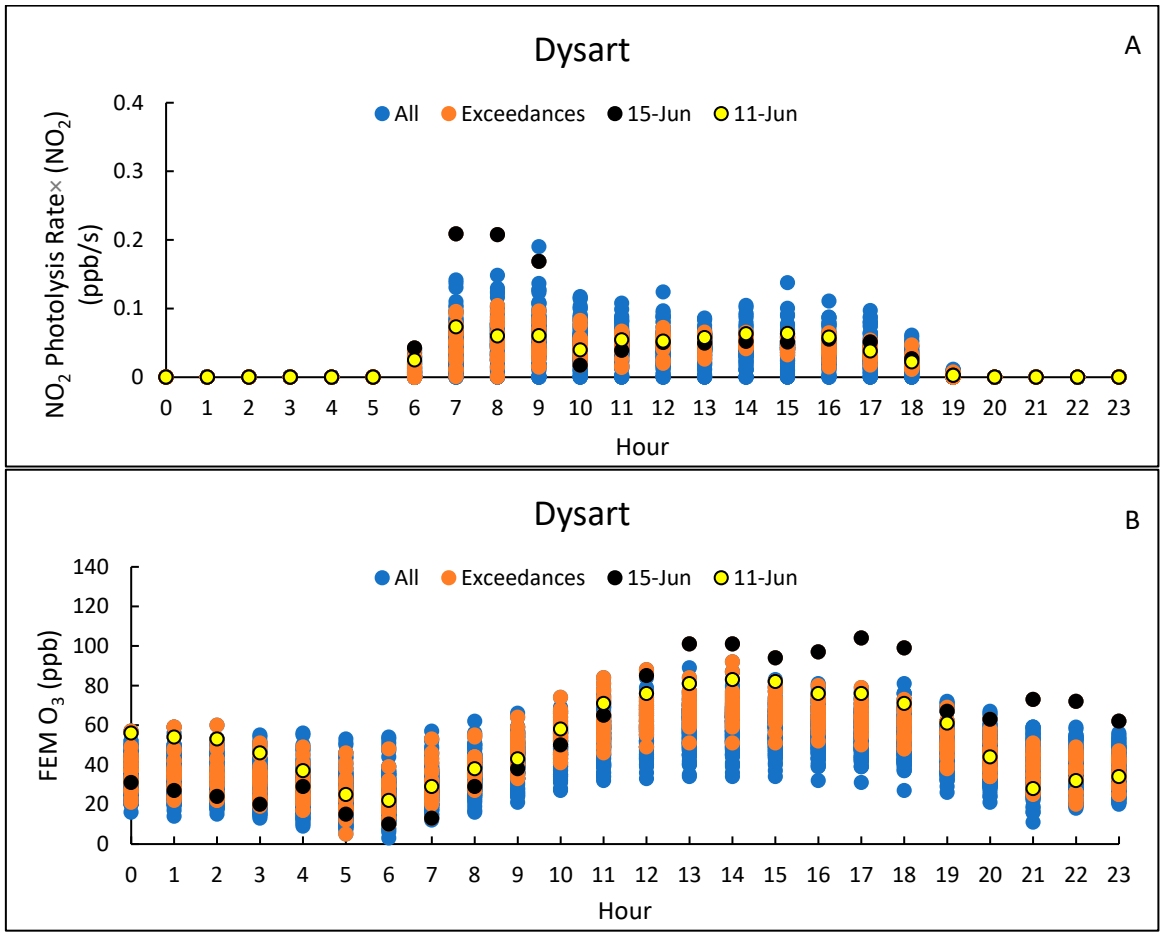


Figure S10. NO_2 × Rate (**A**) and O_3 (**B**) values versus hour for Dysart for all days, ozone exceedance days, 06/11, and 06/15.

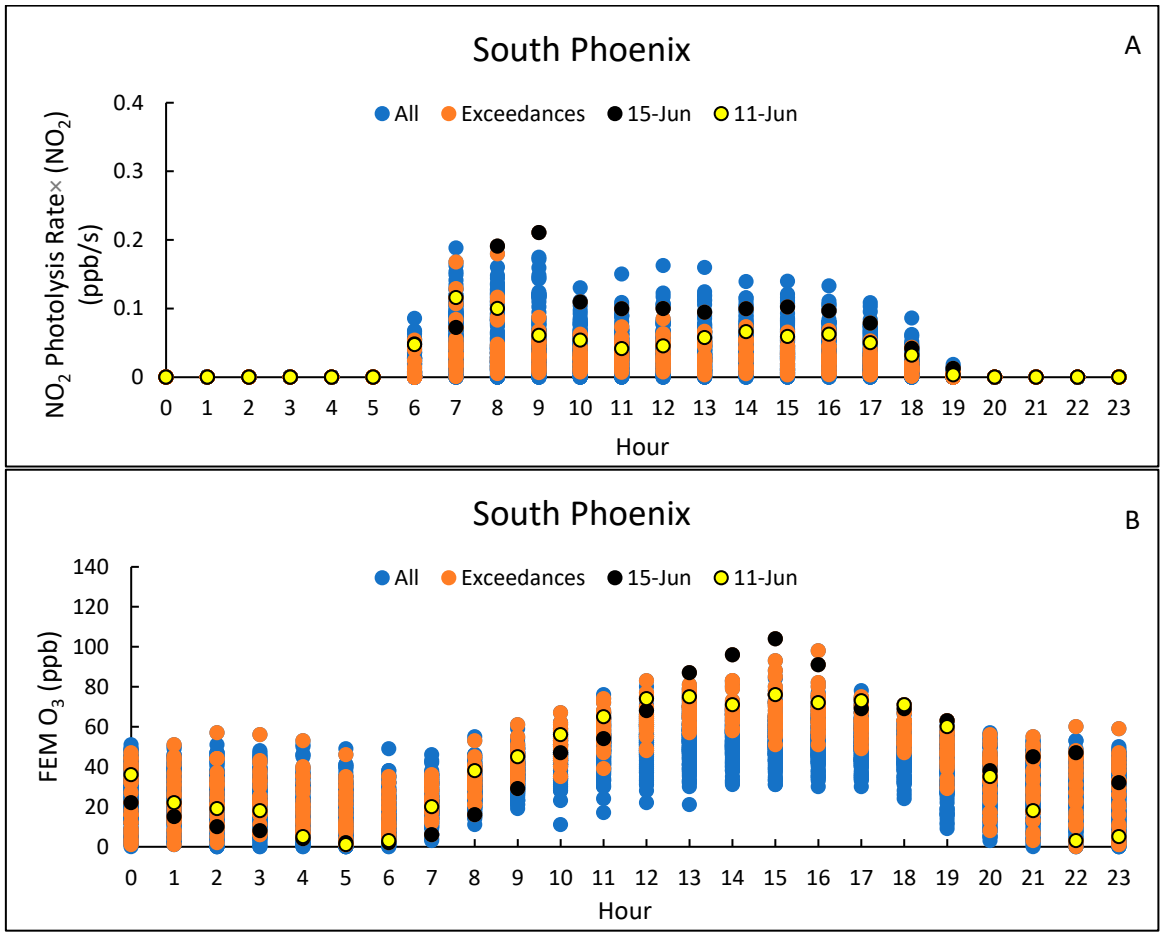


Figure S11. NO_2 × Rate (**A**) and O_3 (**B**) values versus hour for South Phoenix for all days, ozone exceedance days, 06/11, and 06/15.

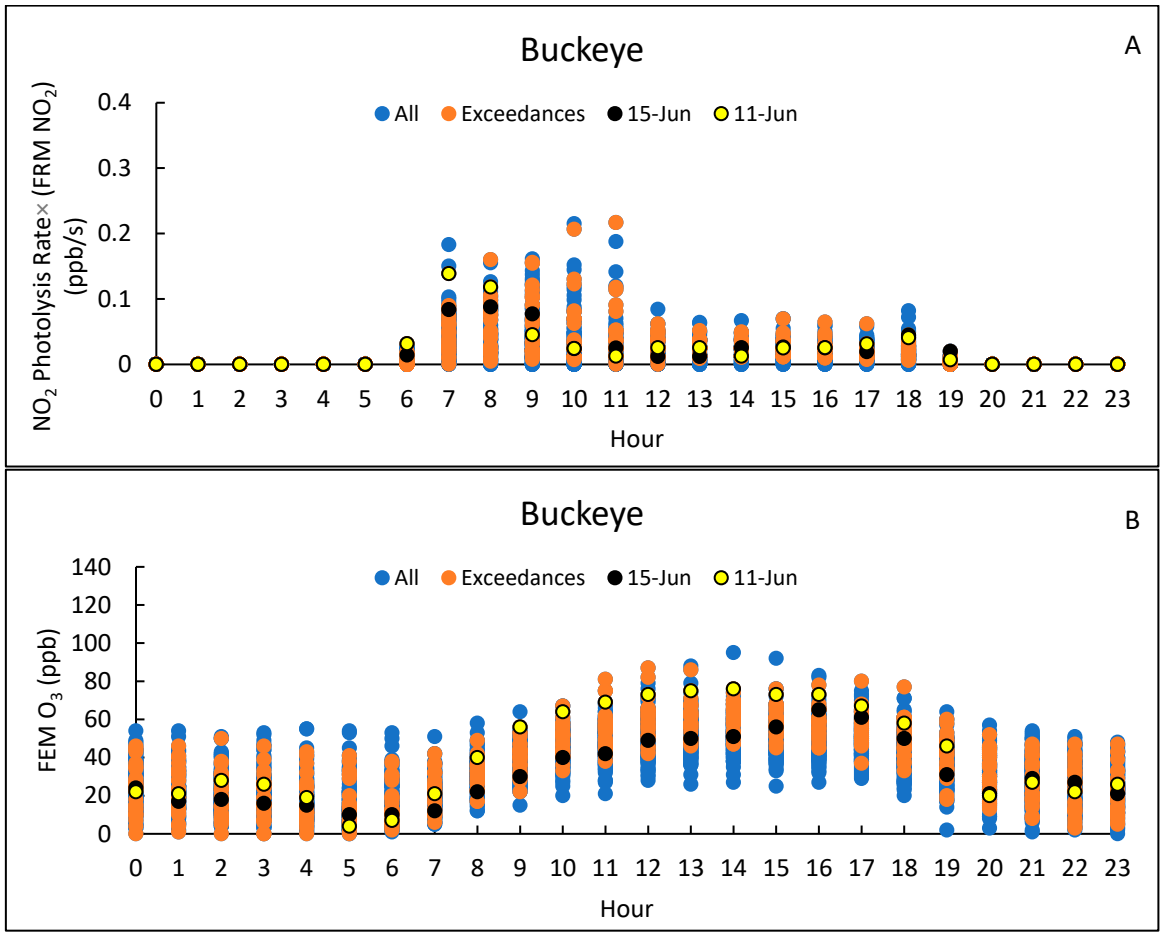
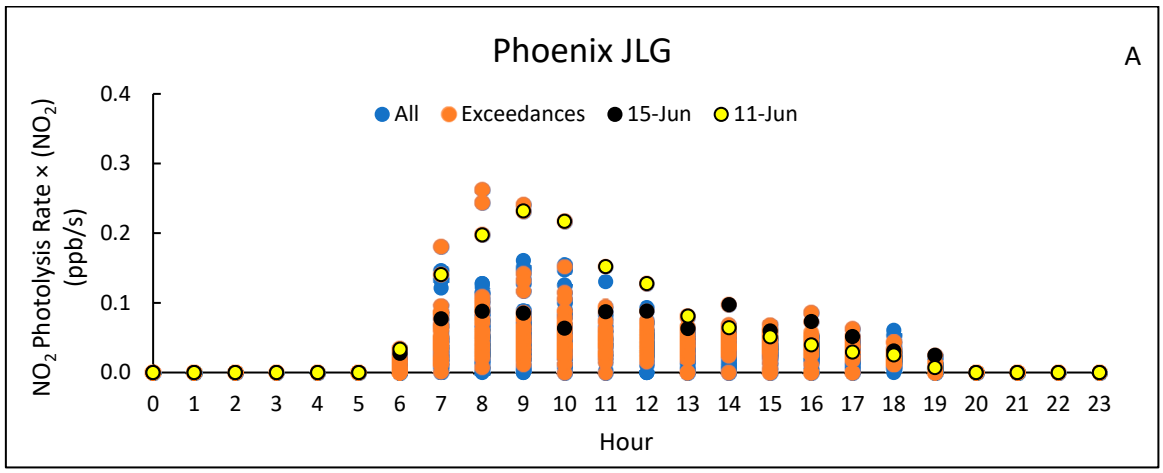


Figure S12. NO_2 × Rate (**A**) and O_3 (**B**) values versus hour for Buckeye for all days, ozone exceedance days, 06/11, and 06/15.



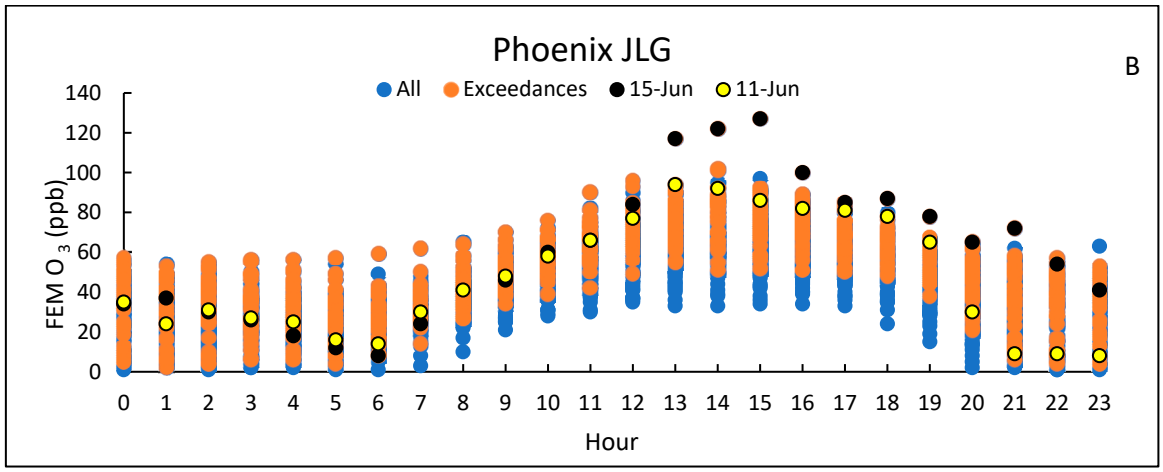
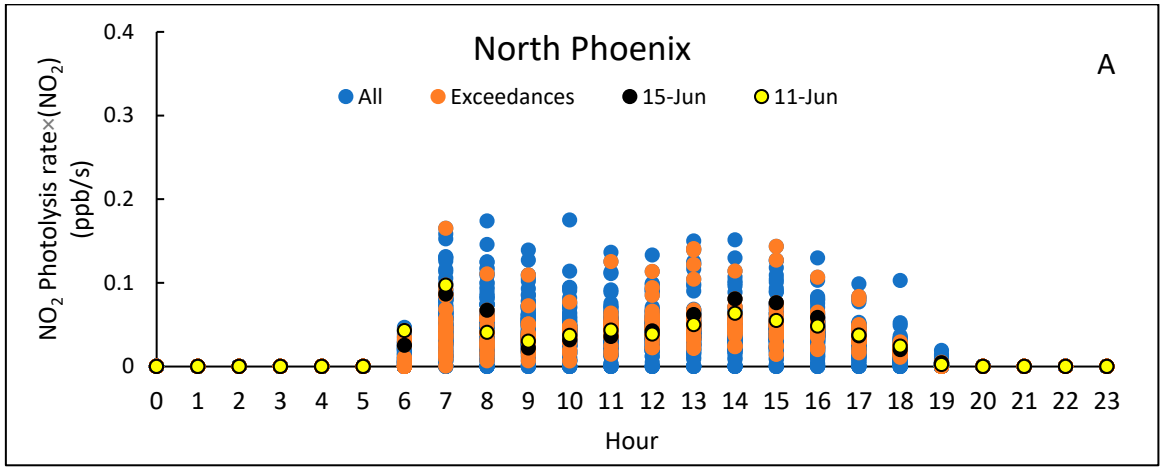


Figure S13. NO_2 × Rate (**A**) and O_3 (**B**) values versus hour for Phoenix JLG for all days, ozone exceedance days, 06/11, and 06/15.



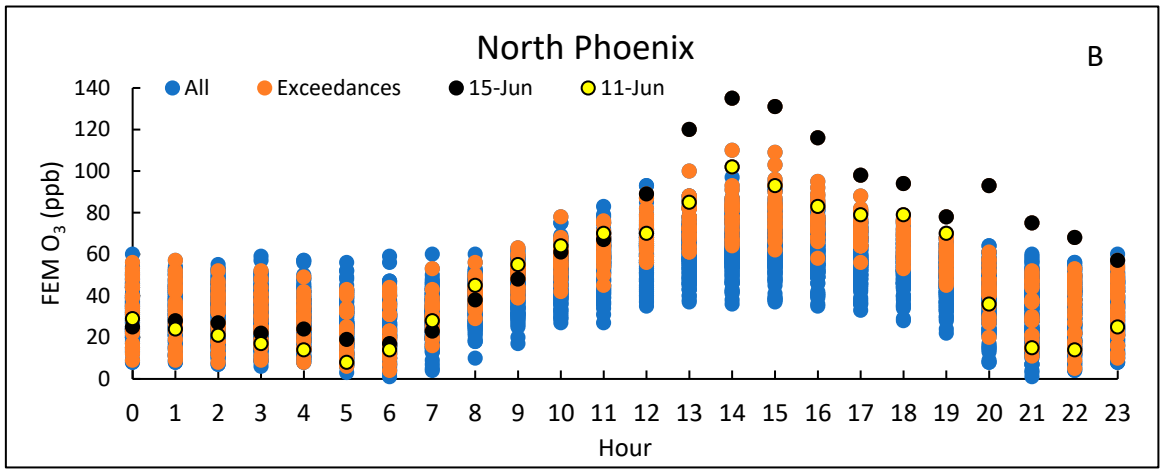


Figure S14. NO_2 × Rate (**A**) and O_3 (**B**) values versus hour for North Phoenix for all days, ozone exceedance days, 06/11, and 06/15.

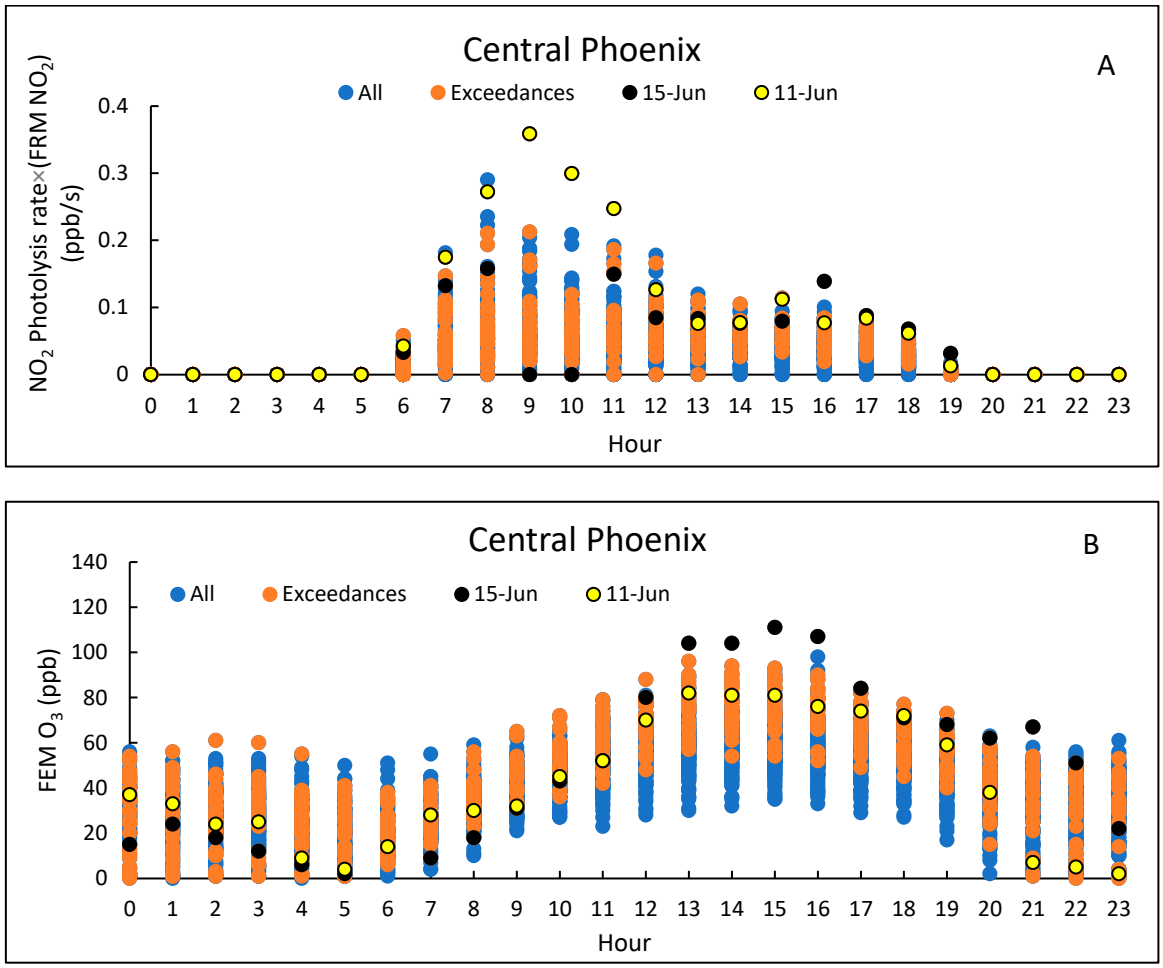
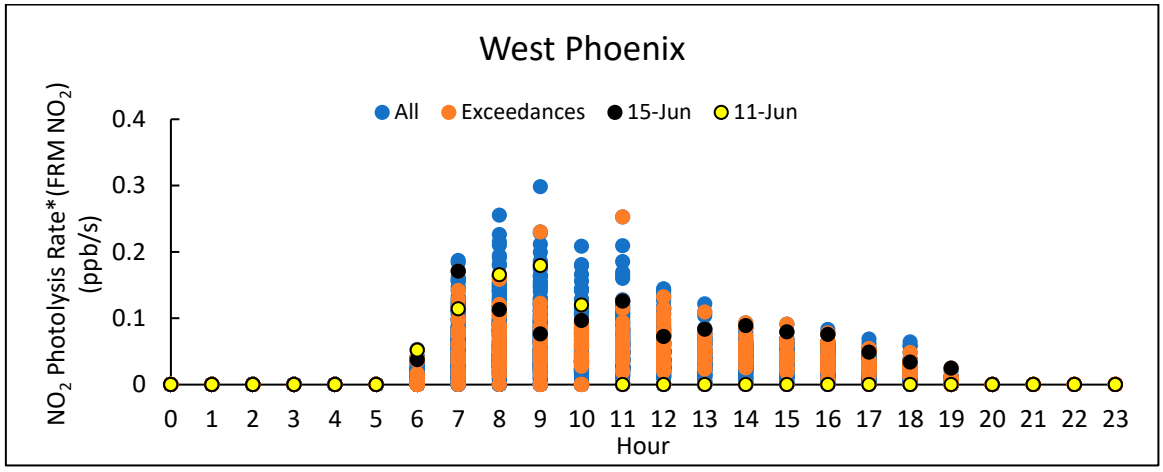


Figure S15. NO_2 × Rate (**A**) and O_3 (**B**) values versus hour for Central Phoenix for all days, ozone exceedance days, 06/11, and 06/15.



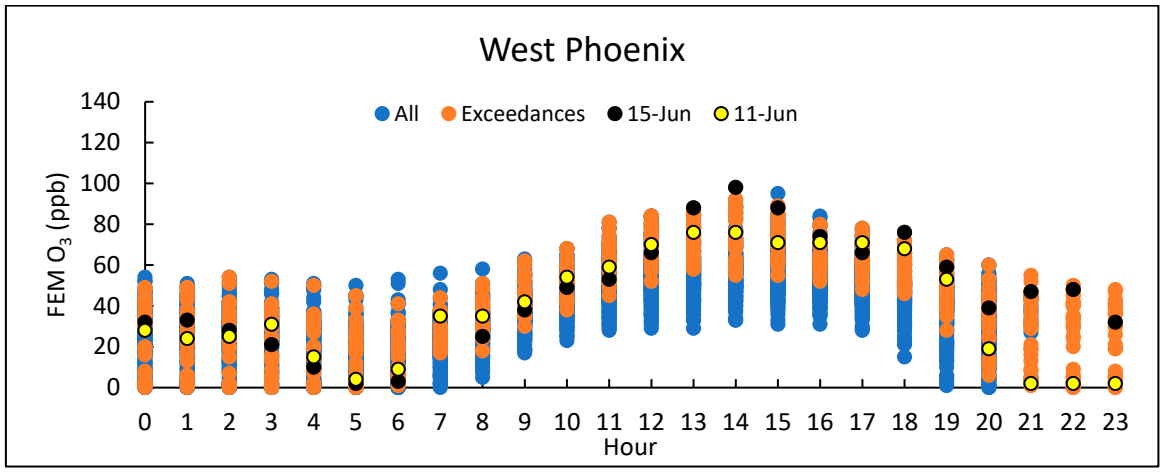


Figure S16. NO_2 × Rate (**A**) and O_3 (**B**) values versus hour for West Phoenix for all days, ozone exceedance days, 06/11, and 06/15.

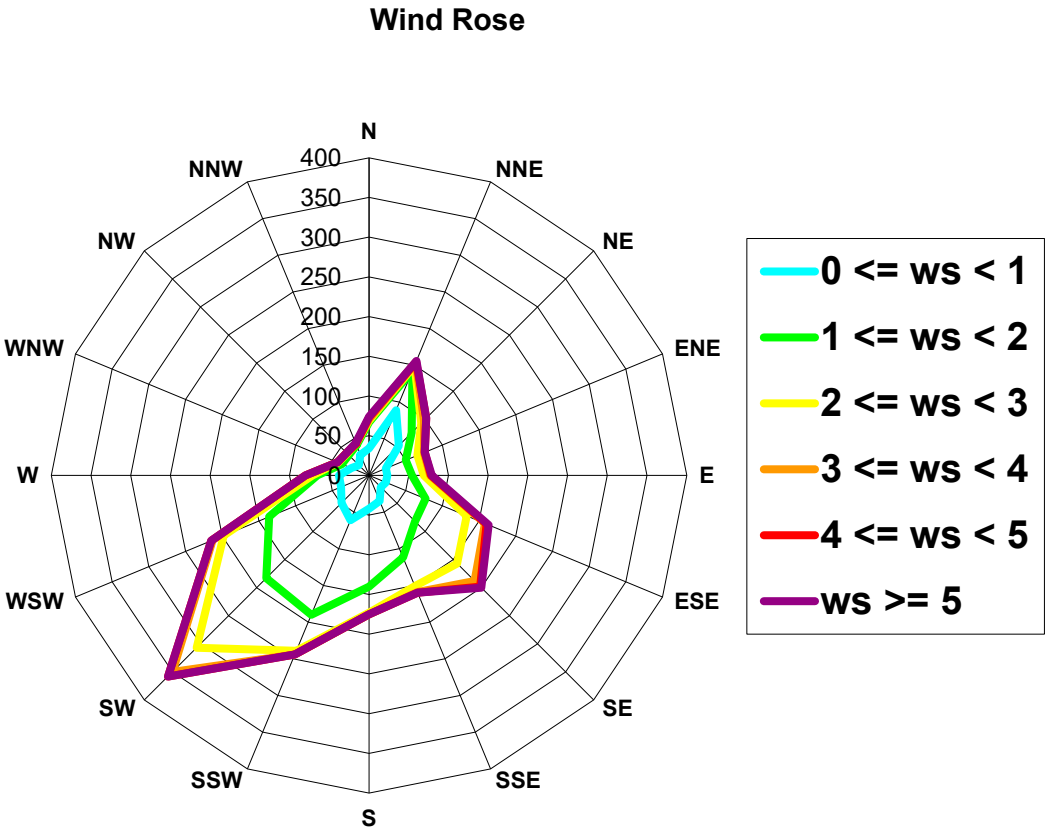


Figure S17. Wind Rose for the North Phoenix site, wind speed in knots.

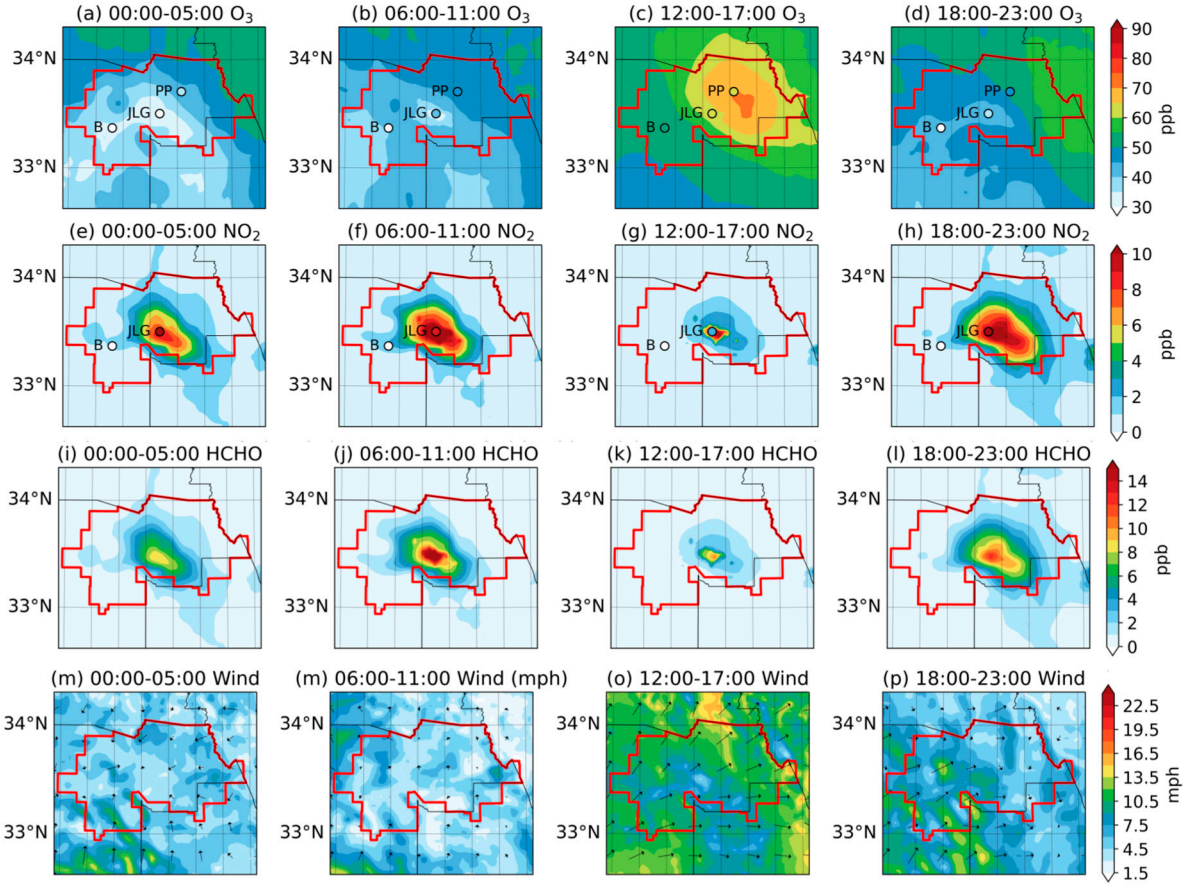


Figure S18. WRF-Chem simulated monthly mean of hourly O_3, NO_2, HCHO, and wind speed/direction averaged over 6 hours' time period during the day: 00:00-05:00, 06:00-11:00, 12:00-17:00, 18:00-23:00 in June 2021. AQS observations over sites including JLG Supersite (JLG), Buckeye (B), and Pinnacle Peak (PP). EPA's Ozone non-attainment area over Phoenix-Mesa is bounded by red lines.

Table S5. Correlation coefficients between morning NO_2 × Rate (row) and afternoon O_3 (column) for the whole deployment period for all site combinations with the peak hour listed to site abbreviation. Significant correlation coefficients ($p < 0.05$) are in bold and insignificant in italics (n = 154).

Total	CP O_3 14	WP 14	SP 15	NP 14	B 13	BP 15	WC 16	SS 16	PP 17	CC 16	D 14	M 15	JLG 14
CP NO_2×Rate 8	*.14*	*.10*	**.21**	**.31**	**.26**	**.30**	**.18**	*.14*	**.36**	**.41**	**.27**	*.13*	**.18**
WP 9	*.07*	*.10*	*.14*	**.23**	**.27**	**.25**	*.16*	*.10*	**.30**	**.40**	**.23**	*.13*	*.14*
SP 8	*.02*	*-.05*	*.08*	**.17**	*.09*	**.24**	*.05*	*-.03*	**.21**	**.17**	*.07*	*.01*	*.08*
NP 7	*.12*	*.05*	**.16**	**.22**	**.20**	**.18**	*.12*	*.07*	**.27**	**.22**	**.16**	*.06*	**.19**
B 9	**.27**	**.27**	**.28**	**.33**	**.44**	**.17**	**.26**	**.29**	**.33**	**.33**	**.36**	**.26**	**.20**
BP 9	*.14*	*.11*	*.06*	*.14*	*-.06*	*.12*	*.04*	*.11*	*.09*	*.08*	*.06*	*.07*	*.04*
WC 7	*.04*	*-.03*	*.10*	**.19**	**.18**	*.13*	*.11*	*-.01*	**.24**	**.23**	*.14*	*.06*	*.16*
SS 8	*.02*	*-.03*	*.10*	**.16**	*.16*	*.16*	*.06*	*-.01*	**.21**	**.22**	*.13*	*.04*	*.12*

PP 9	*.14*	**.16**	*.03*	**.18**	*-.05*	*.14*	*.00*	**.18**	**.19**	.10	*.01*	*.09*	*.12*
CC 9	*.05*	*.01*	*-.01*	*.13*	*-.12*	*.03*	*-.08*	*.03*	*.13*	*.07*	*.02*	*-.08*	*-.01*
D 9	*.01*	*.01*	*.02*	**.16**	*-.10*	**.23**	*-.06*	*.00*	*.15*	*.10*	*.03*	*.02*	*.01*
M 8	*-.01*	*-.07*	*-.04*	*.05*	*.05*	**.18**	*-.01*	*-.02*	**.24**	*.04*	*-.01*	*-.01*	*.01*
JLG 9	*.10*	*.11*	**.17**	**.27**	**.21**	**.31**	**.16**	*.15*	**.28**	**.33**	**.19**	*.15*	*.16*

Table S6. Correlation coefficients between morning NO_2 × Rate (row) and afternoon O_3 (column) for smoke days for all site combinations with the peak hour listed to site abbreviation. Significant correlation coefficients are in bold and insignificant in italics (n= 39).

Smoke	**CP O_3 14**	**WP 14**	**SP 15**	**NP 14**	**B 13**	**BP 15**	**WC 16**	**SS 16**	**PP 17**	**CC 16**	**D 14**	**M 15**	**JLG 14**
CP NO_2×Rate 8	*-.01*	*-.16*	*.11*	*.23*	*-.12*	*.11*	*-.02*	*-.01*	**.36**	**.32**	*.05*	*-.06*	*.07*
WP 9	*-.14*	*-.18*	*-.09*	*.07*	*.21*	*.26*	*-.08*	*-.18*	*.31*	**.33**	*.08*	*-.04*	*-.11*
SP 8	*.25*	*.11*	*.20*	**.42**	*-.13*	*.24*	*-.05*	*.16*	**.49**	**.39**	*.19*	*.02*	*.33*
NP 7	*.17*	*.11*	*.19*	*.25*	*-.11*	*-.08*	*-.04*	*.19*	*.25*	*.16*	*.19*	*-.12*	**.34**
B 9	*.06*	*.10*	*.15*	*.16*	**.37**	*-.01*	*.08*	*.11*	*.24*	*.15*	*.21*	*-.09*	*.20*
BP 9	*.11*	*.18*	*.15*	*.22*	*-.12*	*.25*	*-.06*	*.17*	*.25*	*.19*	*.08*	*-.15*	*.31*
WC 7	*.30*	*.12*	*.15*	**.45**	*-.17*	*.06*	*-.02*	*.23*	**.43**	**.47**	**.38**	*.10*	*.32*
SS 8	*.23*	*.15*	*.25*	**.36**	*-.13*	*.02*	*-.09*	*.23*	**.40**	**.37**	*.28*	*.00*	*.32*
PP 9	*.12*	*.18*	*-.06*	*.29*	*-.16*	*.05*	*-.12*	*.27*	*.30*	*.07*	*-.15*	*-.11*	**.38**
CC 9	**.32**	*.30*	*.28*	**.57**	*-.10*	*.21*	*-.05*	**.38**	**.57**	**.45**	**.33**	*-.15*	**.57**
D 9	**.40**	**.35**	**.38**	**.62**	*-.16*	**.35**	*.06*	**.39**	**.67**	**.58**	**.35**	*.09*	**.55**
M 8	*-.13*	*-.18*	*-.31*	*-.13*	*-.17*	*-.06*	*-.30*	*-.07*	*-.16*	*-.25*	*-.16*	*-.02*	*-.11*
JLG 9	*-.16*	*-.21*	*.01*	*.13*	*.10*	*.00*	*-.07*	*-.10*	**.32**	*.27*	*-.06*	*-.09*	*-.03*

Table S7. Correlation coefficients between morning NO_2 × Rate (row) and afternoon O_3 (column) for non-smoke days for all site combinations with the peak hour listed to site abbreviation. Significant correlation coefficients are in bold and insignificant in italics (n= 115).

Non-Smoke	**CP O_3 14**	**WP 14**	**SP 15**	**NP 14**	**B 13**	**BP 15**	**WC 16**	**SS 16**	**PP 17**	**CC 16**	**D 14**	**M 15**	**JLG 14**
CP NO_2×Rate 8	**.31**	**.30**	**.37**	**.47**	**.46**	**.41**	**.34**	**.29**	**.46**	**.52**	**.43**	**.29**	**.33**
WP 9	**.27**	**.32**	**.34**	**.43**	**.36**	**.36**	**.34**	**.29**	**.43**	**.53**	**.37**	**.30**	**.32**
SP 8	**.21**	*.08*	**.26**	**.30**	**.30**	**.36**	**.30**	*.12*	**.30**	**.25**	**.18**	**.25**	*.17*

NP 7	**.38**	**.25**	**.40**	**.48**	**.41**	**.32**	**.37**	**.28**	**.49**	**.48**	**.33**	**.32**	**.34**
B 9	**.34**	**.33**	**.31**	**.41**	**.44**	**.25**	**.30**	**.35**	**.35**	**.38**	**.41**	**.36**	*.18*
BP 9	**.19**	*.11*	*.04*	*.13*	*-.06*	*.09*	*.06*	*.11*	*.04*	*.05*	*.05*	*.13*	*-.04*
WC 7	**.30**	**.19**	**.38**	**.42**	**.43**	**.27**	**.41**	**.21**	**.44**	**.38**	**.29**	**.34**	**.35**
SS 8	**.24**	*.13*	**.30**	**.35**	**.39**	**.40**	**.34**	*.17*	**.37**	**.35**	**.26**	**.31**	**.26**
PP 9	*.14*	*.15*	*.02*	*.12*	*-.03*	*.16*	*-.01*	*.15*	*.12*	*.09*	*.05*	*.15*	*.00*
CC 9	*-.02*	*-.11*	*-.15*	*-.03*	*-.15*	*.01*	*-.12*	*-.08*	*-.03*	*-.04*	*-.11*	*-.07*	**-.24**
D 9	*.11*	*.07*	*.06*	**.20**	*.01*	**.33**	*.06*	*.08*	*.11*	*.08*	*.04*	**.23**	*-.04*
M 8	**.20**	*.10*	**.19**	**.28**	*.18*	**.32**	**.21**	*.15*	**.24**	*.18*	*.15*	**.19**	*.16*
JLG 9	**.23**	**.26**	**.29**	**.41**	**.28**	**.40**	**.29**	**.29**	**.34**	**.40**	**.31**	**.26**	**.23**

Table S8. Correlation coefficients between morning NO_2 × Rate (row) and afternoon O_3 (column) for non-smoke days with ozone exceedances for all site combinations with the peak hour listed to site abbreviation. Significant correlation coefficients are in bold and insignificant in italics (n= 12).

O_3 w/o smoke	**CP O_3 14**	**WP 14**	**SP 15**	**NP 14**	**B 13**	**BP 15**	**WC 16**	**SS 16**	**PP 17**	**CC 16**	**D 14**	**M 15**	**JLG 14**
CP NO_2×Rate 8	*.51*	**.66**	**.65**	**.85**	*.56*	*.16*	*.38*	**.64**	**.79**	**.86**	**.71**	*.08*	**.69**
WP 9	*.15*	*.48*	*.42*	*.49*	*.33*	*.40*	*.42*	*.43*	*.54*	*.56*	**.58**	*.37*	*.45*
SP 8	*.09*	*.24*	*.25*	*.16*	*.36*	*.15*	*.26*	*-.10*	*.19*	*.26*	*.27*	*.26*	*.33*
NP 7	*.41*	*.34*	*.29*	*.36*	*.22*	*.18*	*.03*	*.07*	*.56*	*.56*	*.12*	*.16*	*.55*
B 9	*.20*	*.19*	*.17*	*.02*	*.27*	*.19*	*.37*	*.00*	*.12*	*.07*	*.31*	*.49*	*.20*
BP 9	*-.14*	*-.42*	*-.46*	*-.25*	*-.37*	**-.84**	*-.50*	*-.16*	*-.35*	*-.45*	*-.41*	**-.66**	*-.48*
WC 7	*.10*	*.27*	*.03*	*.18*	*.08*	*-.20*	*.05*	*-.24*	*.18*	*.12*	*.07*	*.08*	*.34*
SS 8	*.39*	*.23*	*.23*	*.31*	*.08*	*.28*	*.04*	*.12*	*.46*	**.58**	*.33*	*.30*	*.41*
PP 9	**-.64**	*-.56*	*-.43*	*-.53*	*-.36*	*.15*	*-.27*	*-.24*	*-.43*	*-.42*	*-.36*	*-.13*	**-.58**
CC 9	*-.12*	*-.38*	*-.30*	*-.34*	*-.43*	*-.30*	*-.31*	*-.15*	*-.24*	*-.11*	*-.14*	*-.27*	*-.41*
D 9	*-.42*	*-.05*	*.04*	*-.05*	*.00*	*.41*	*.13*	*.03*	*.03*	*.13*	*.15*	*.12*	*-.07*
M 8	*.04*	*.00*	*-.03*	*.11*	*-.04*	*-.13*	*-.31*	*-.20*	*.20*	*.25*	*-.22*	*-.34*	*.18*
JLG 9	*.00*	*.25*	*.27*	*.43*	*.16*	*.26*	*.22*	*.40*	*.20*	*.28*	*.37*	*.28*	*.24*

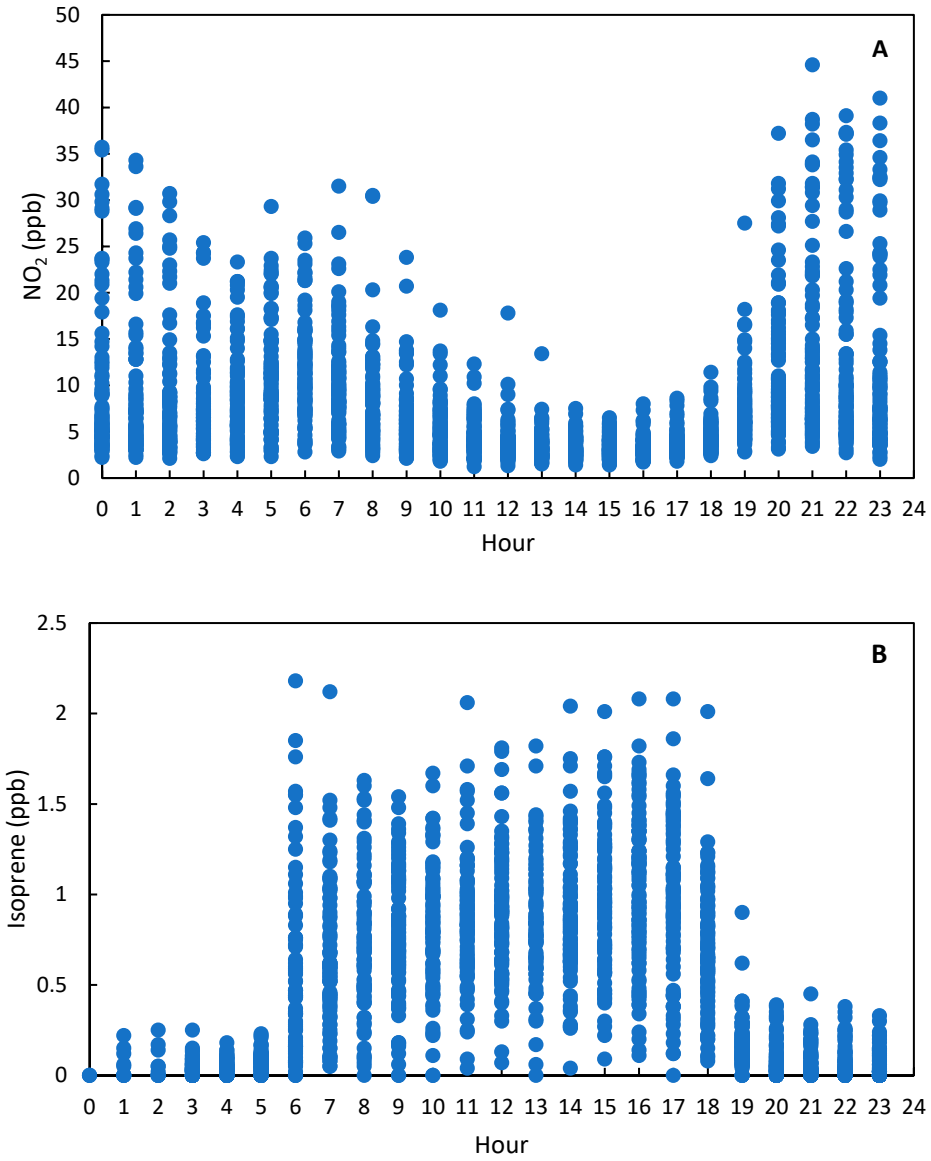


Figure S19. NO_2 (A) and isoprene (B) concentrations by hour at Phoenix JLG.

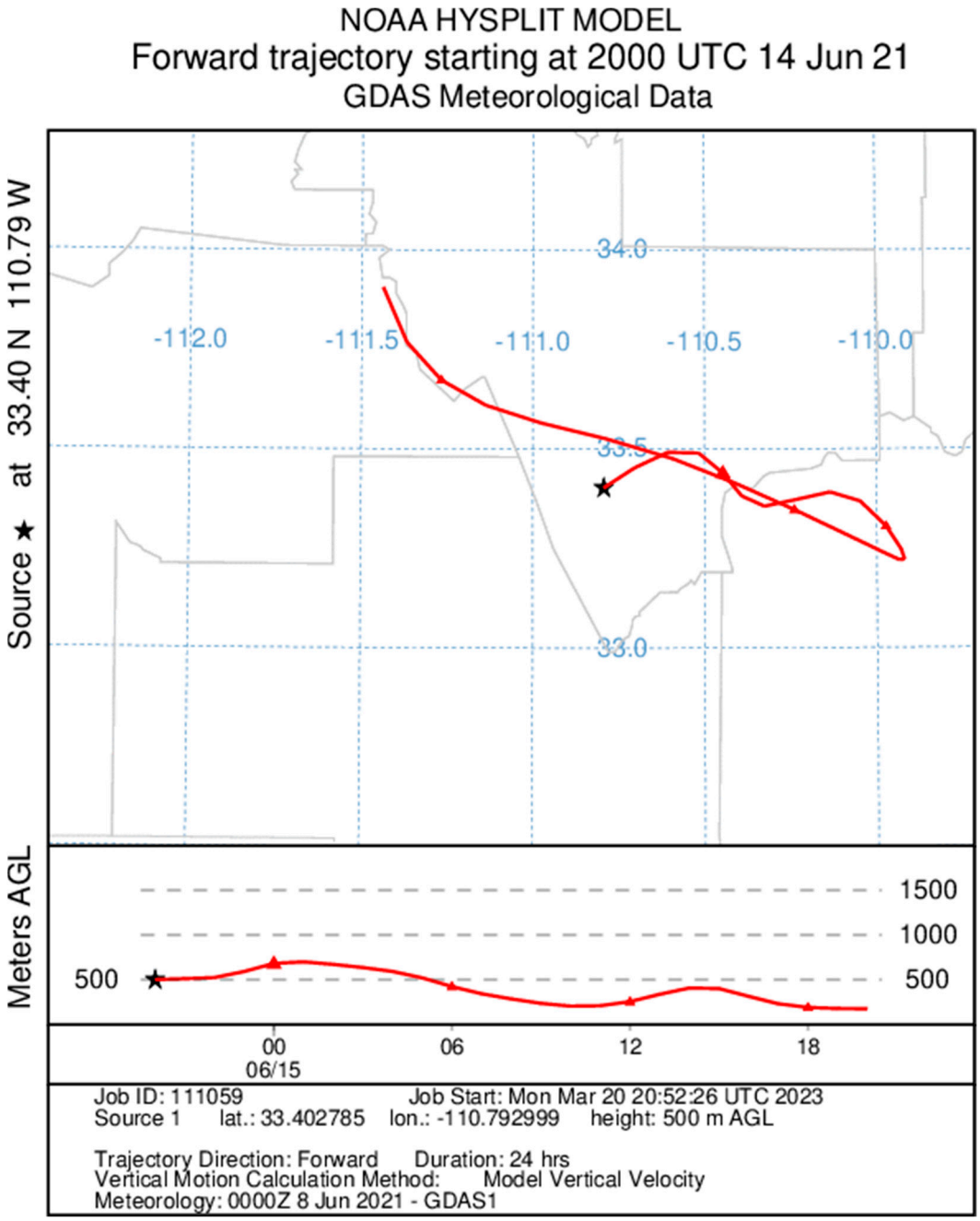


Figure S20. HYSPLIT air mass trajectory model from June 15th, 2021.

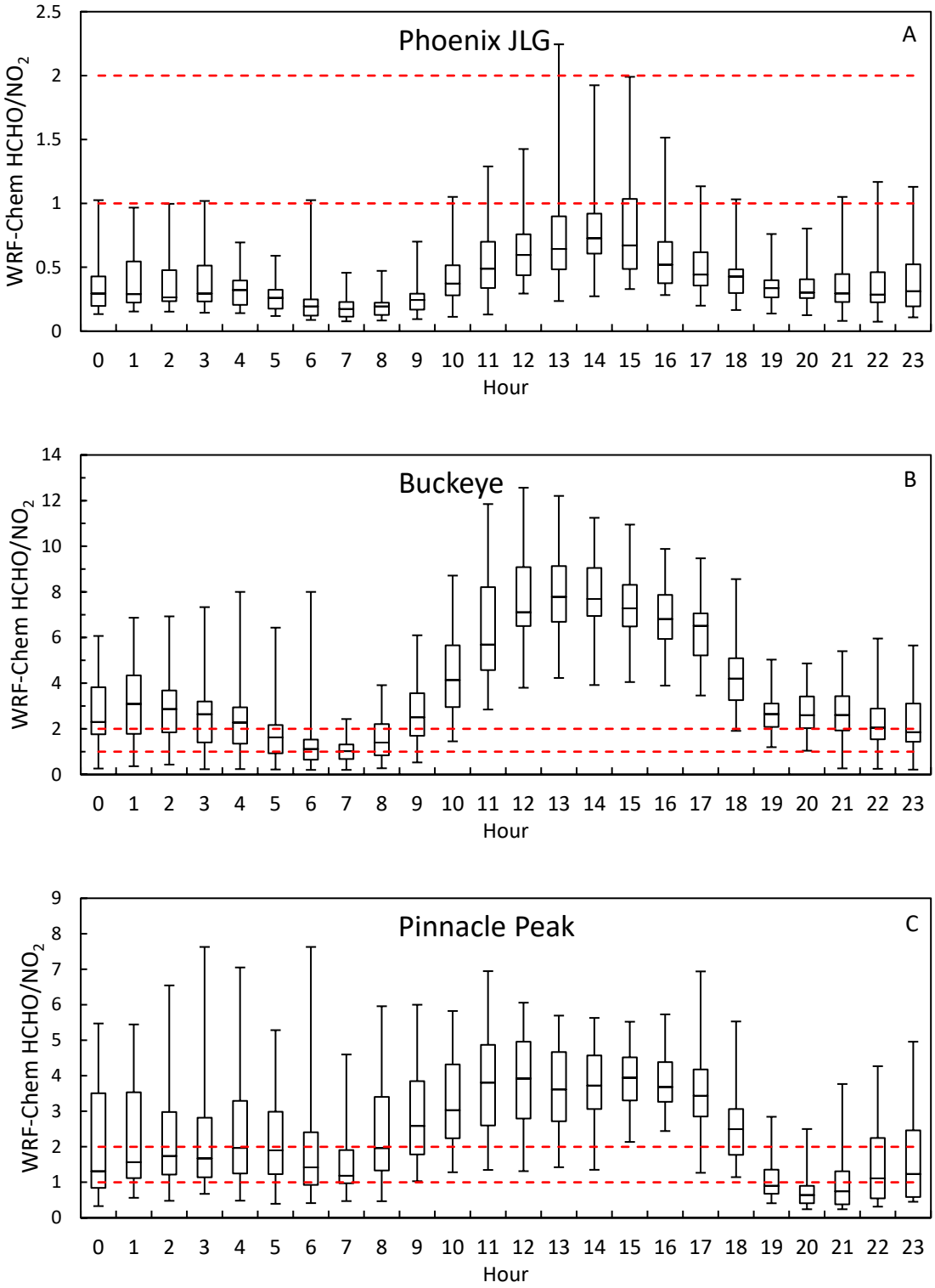


Figure S21. Box and whisker plots for WRF-Chem HCHO/NO_2 diurnal cycles for the Phoenix JLG (A), Buckeye (B), and Pinnacle Peak (C) sites. The lines within the boxes represent the medians, the interquartile range is the range of the boxes with the top representing the 75th and the bottom the 25th percentile. The whiskers represent the maximum and minimum values in the data. The horizontal dashed lines represent the regime transitions.

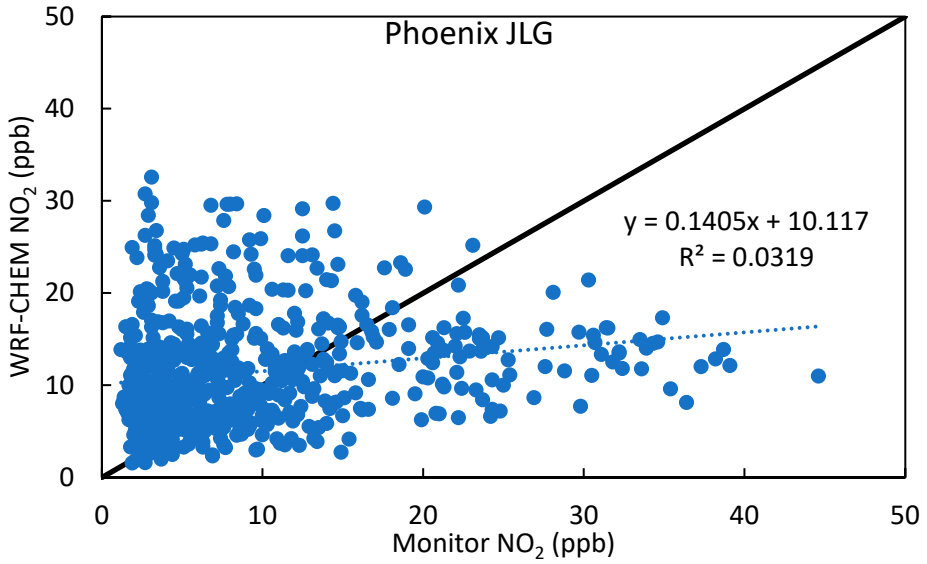


Figure S22. Sampled NO_2 from the Phoenix JLG site versus WRF-CHEM modeled NO_2 averaged to match the samples' time periods. Black line represents a 1:1 relationship.

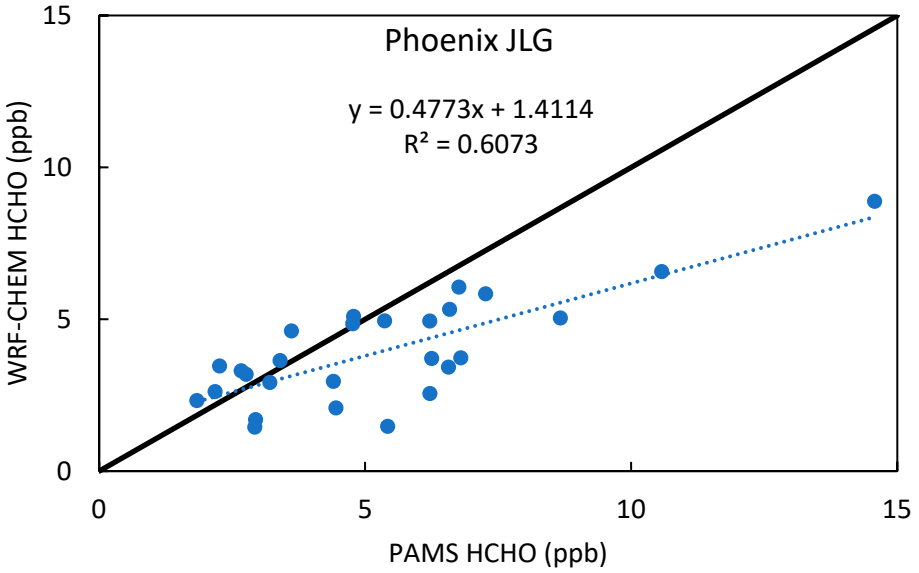


Figure S23. Sampled HCHO from the Phoenix JLG site versus WRF-CHEM modeled HCHO averaged to match the samples' time periods. Black line represents a 1:1 relationship.