

Supplementary Material

ARA TON Schematic

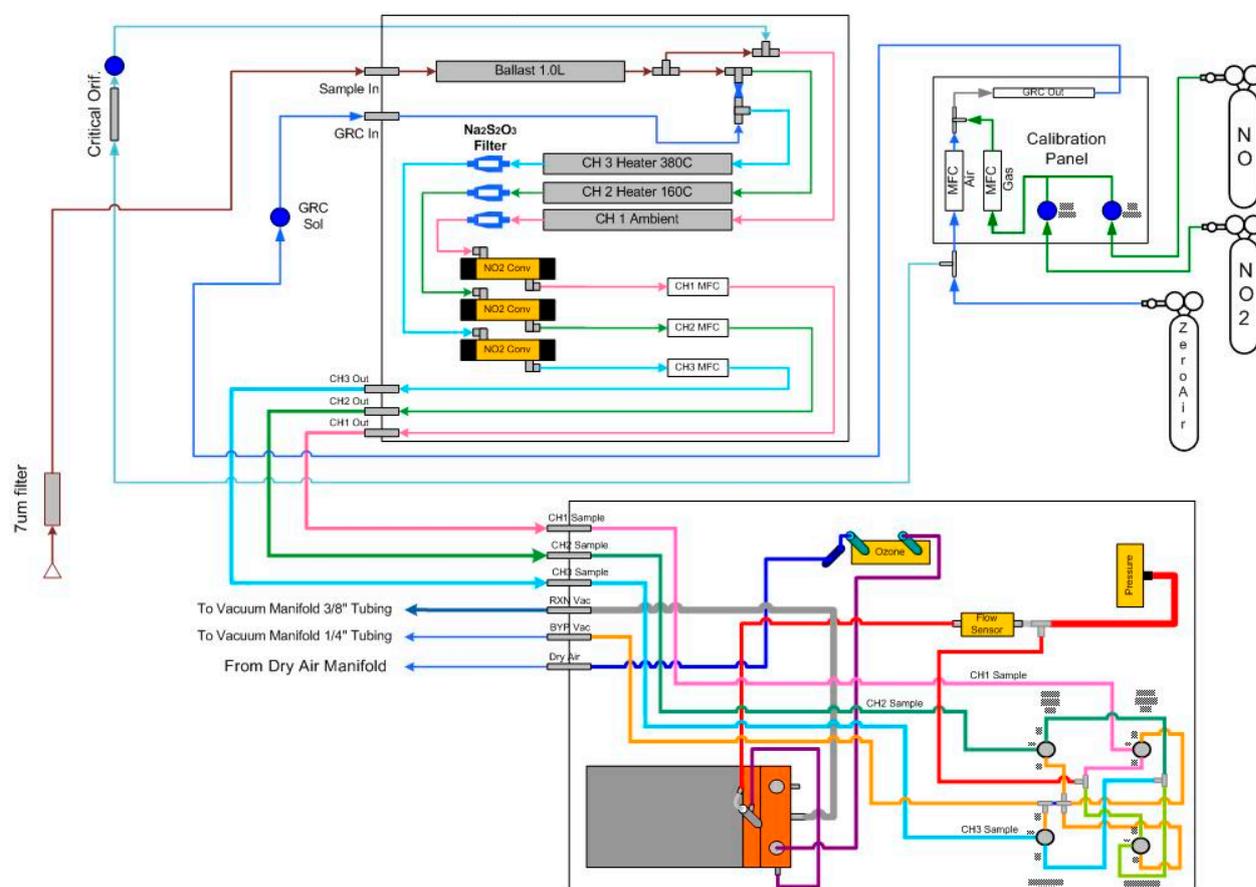


Figure S1. Schematic of the Thermo 42i-TL NO_x analyzer implemented by ARA that used a continuous three-channel thermal-photolytic difference technique to make PANs and ANs measurements at QC. Figure courtesy of Gingrey and Haker [19].

Additional PSP and QC OPE Statistics

Table S1. Model-predicted and observed p -values and standard errors for the OPEs (SE_{OPE}) and y -intercepts (SE_{Y-INT}) at PSP and QC during summer 2016. See text for details regarding approaches 1 and 2 at QC.

Site	Month	Data Type	P -Value	SE_{OPE}	SE_{Y-INT} (ppb)
PSP	June	v4.6	< 0.0001	0.66	1.01
		v5.0.2	< 0.0001	0.74	1.24
		OBS	< 0.0001	1.08	1.38
	July	v4.6	< 0.0001	0.52	0.83
		v5.0.2	< 0.0001	0.66	1.04
		OBS	< 0.0001	2.25	2.02
	August	v4.6	< 0.0001	0.35	0.57
		v5.0.2	< 0.0001	0.44	0.77
		OBS	< 0.0001	1.44	1.23
	September	v4.6	< 0.0001	0.50	0.95
		v5.0.2	< 0.0001	0.45	0.82
		OBS	< 0.0001	1.19	1.69
QC	August – Approach 1	v4.6	< 0.0001	0.42	1.88
		v5.0.2	< 0.0001	0.35	1.55
		OBS	< 0.0001	1.48	1.24
	August – Approach 2	v4.6	< 0.0001	0.42	1.88
		v5.0.2	< 0.0001	0.35	1.55
		OBS	< 0.0001	0.47	1.56
	September – Approach 1	v4.6	< 0.0001	0.42	1.25
		v5.0.2	< 0.0001	0.38	1.16
		OBS	< 0.0001	1.78	1.48
	September – Approach 2	v4.6	< 0.0001	0.42	1.25
		v5.0.2	< 0.0001	0.38	1.16
		OBS	< 0.0001	0.52	1.88

Additional PSP OPE versus [NO_x] Statistics

Table S2. Observed p -values and standard errors (SEs) for the OPE versus [NO_x] analysis at PSP during photo-chemically productive hours (11 a.m. – 4 p.m. EST) in summer 2016. See Table 1 in the text for additional information regarding the NO_x bins.

Bin Number	P -Value	SE
1	< 0.0001	2.22
2	< 0.0001	2.62
3	< 0.0001	1.57
4	< 0.0001	1.22
5	< 0.0001	1.29

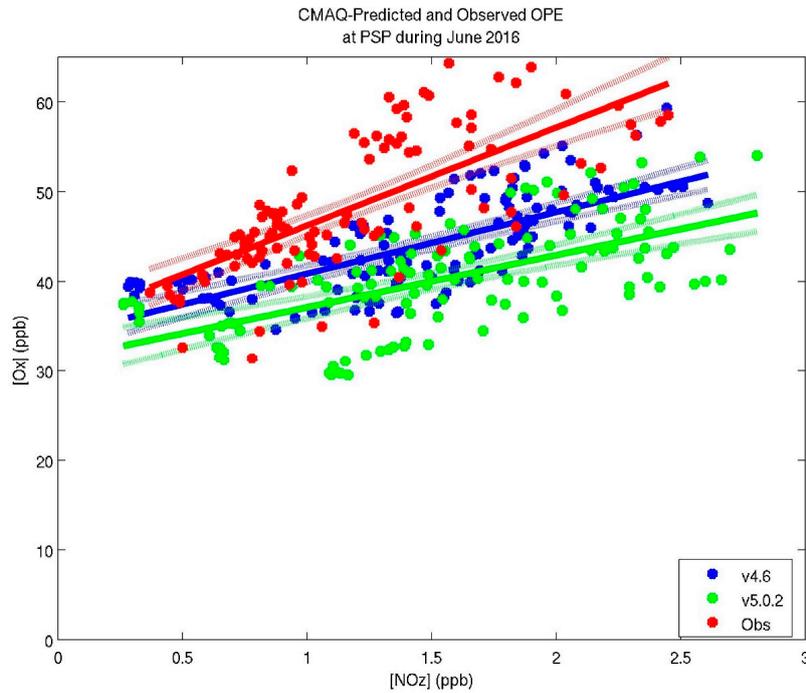


Figure S2. CMAQ v4.6-predicted (blue dots), CMAQ v5.0.2-predicted (green dots), and observed (red dots) OPE at PSP during June 2016. The blue, green, and red solid and dashed lines represent straight-line fits and 95 percent confidence intervals, respectively, of CMAQ v4.6-predicted, CMAQ v5.0.2-predicted, and observed OPE using robust regression with bisquare weights.

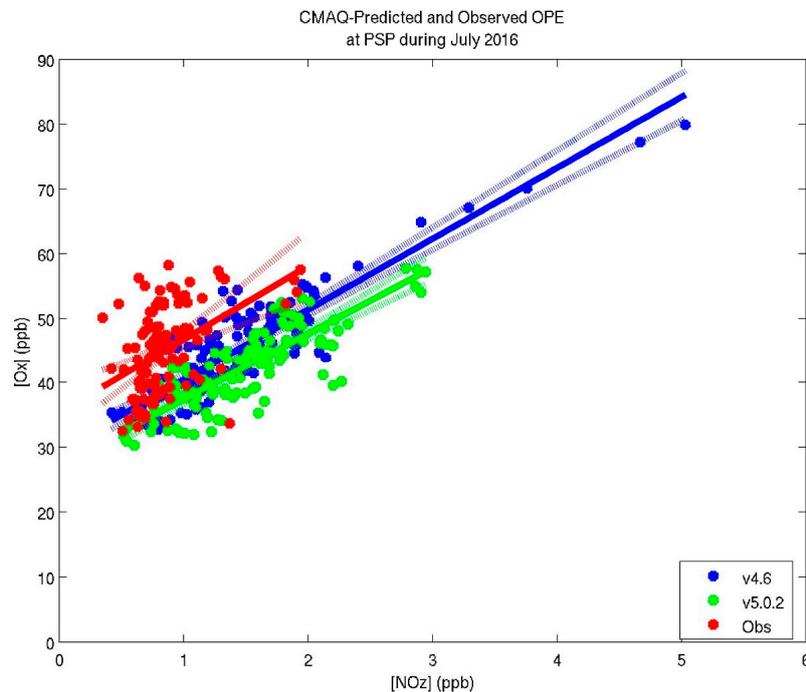


Figure S3. CMAQ v4.6-predicted (blue dots), CMAQ v5.0.2-predicted (green dots), and observed (red dots) OPE at PSP during July 2016. The blue, green, and red solid and dashed lines represent straight-line fits and 95 percent confidence intervals, respectively, of CMAQ v4.6-predicted, CMAQ v5.0.2-predicted, and observed OPE using robust regression with bisquare weights.

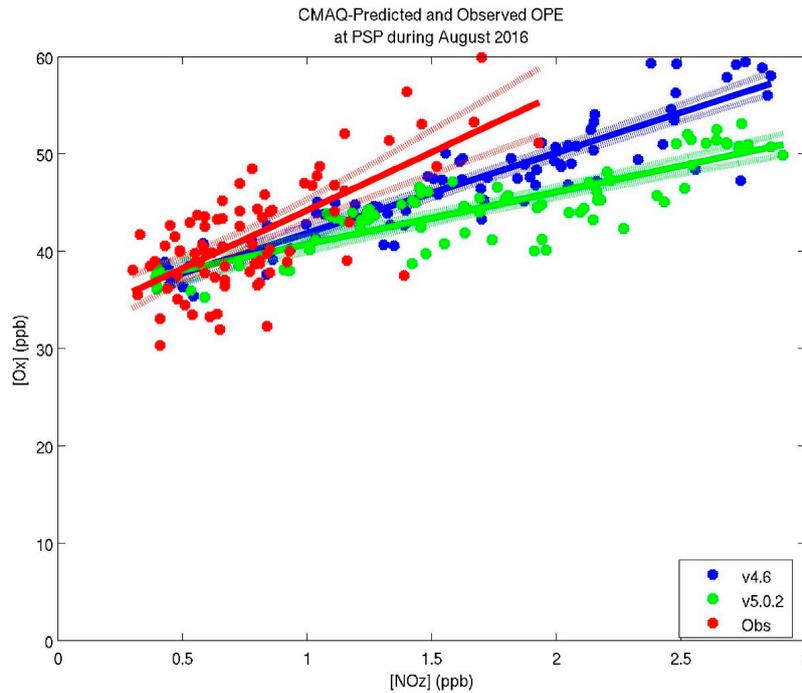


Figure S4. CMAQ v4.6-predicted (blue dots), CMAQ v5.0.2-predicted (green dots), and observed (red dots) OPE at PSP during August 2016. The blue, green, and red solid and dashed lines represent straight-line fits and 95 percent confidence intervals, respectively, of CMAQ v4.6-predicted, CMAQ v5.0.2-predicted, and observed OPE using robust regression with bisquare weights.

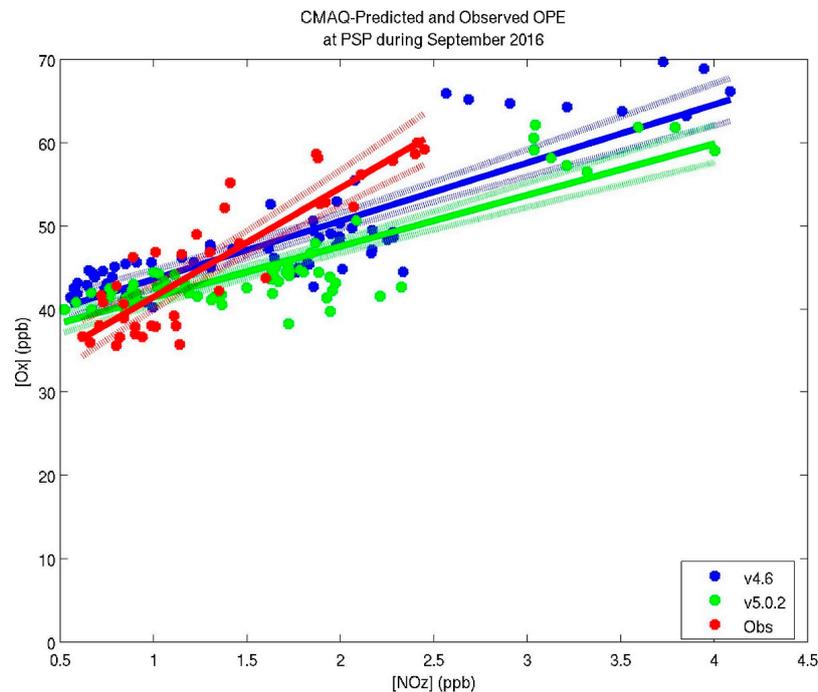


Figure S5. CMAQ v4.6-predicted (blue dots), CMAQ v5.0.2-predicted (green dots), and observed (red dots) OPE at PSP during September 2016. The blue, green, and red solid and dashed lines represent straight-line fits and 95 percent confidence intervals, respectively, of CMAQ v4.6-predicted, CMAQ v5.0.2-predicted, and observed OPE using robust regression with bisquare weights.

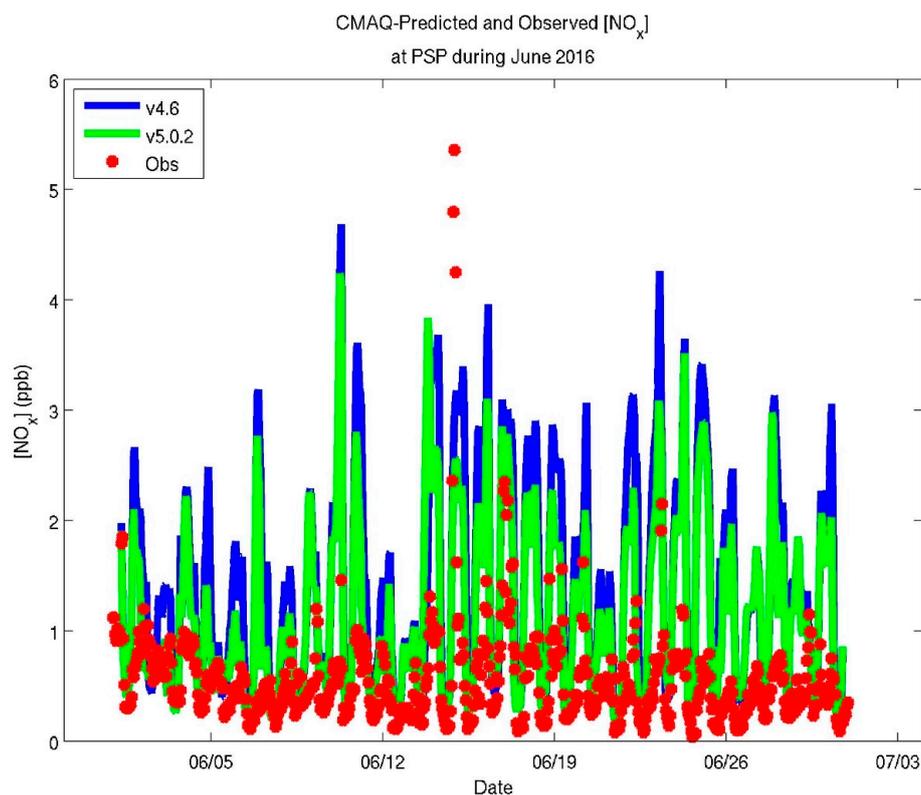


Figure S6. CMAQ v4.6-predicted (blue line), CMAQ v5.0.2-predicted (green line), and observed (red dots) [NO_x] concentrations at PSP during June 2016.

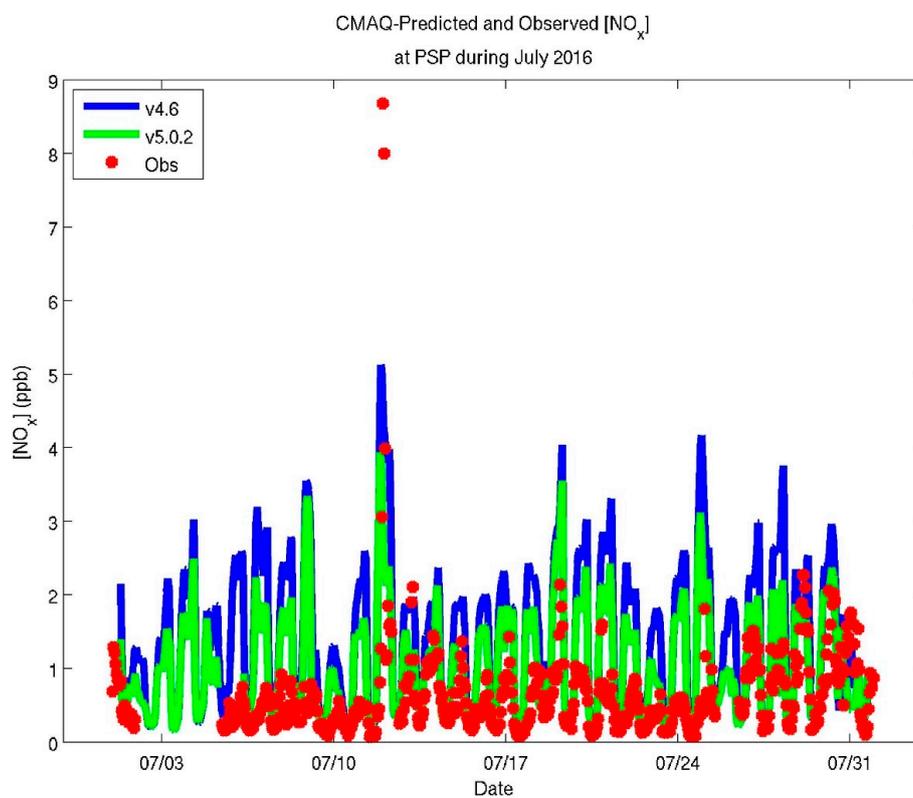


Figure S7. CMAQ v4.6-predicted (blue line), CMAQ v5.0.2-predicted (green line), and observed (red dots) [NO_x] concentrations at PSP during July 2016.

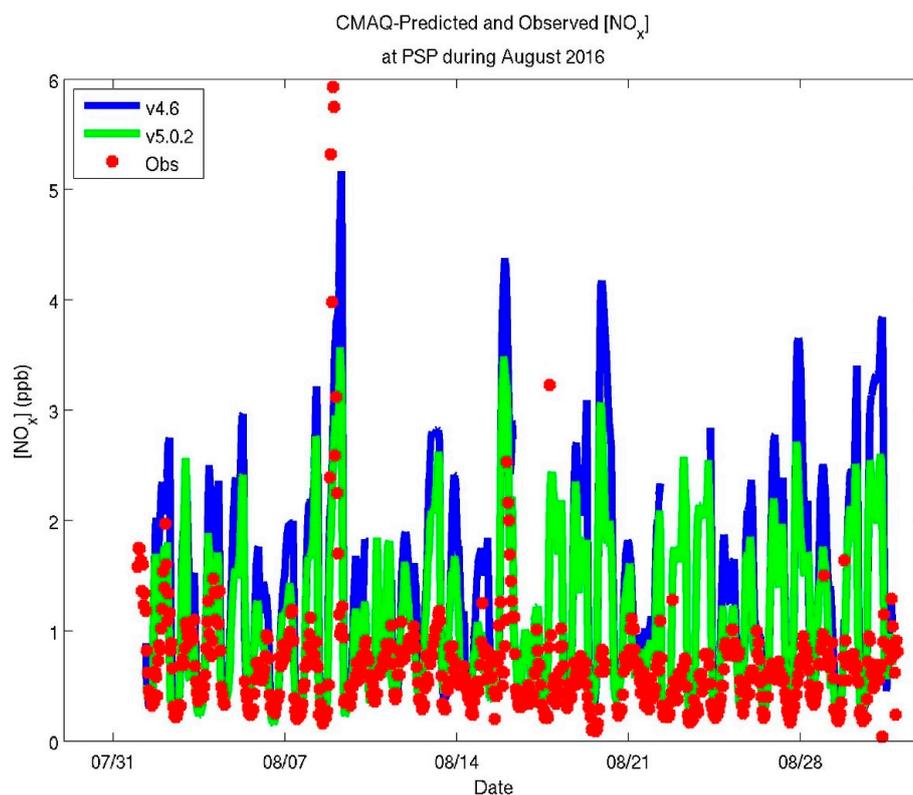


Figure S8. CMAQ v4.6-predicted (blue line), CMAQ v5.0.2-predicted (green line), and observed (red dots) [NO_x] concentrations at PSP during August 2016.

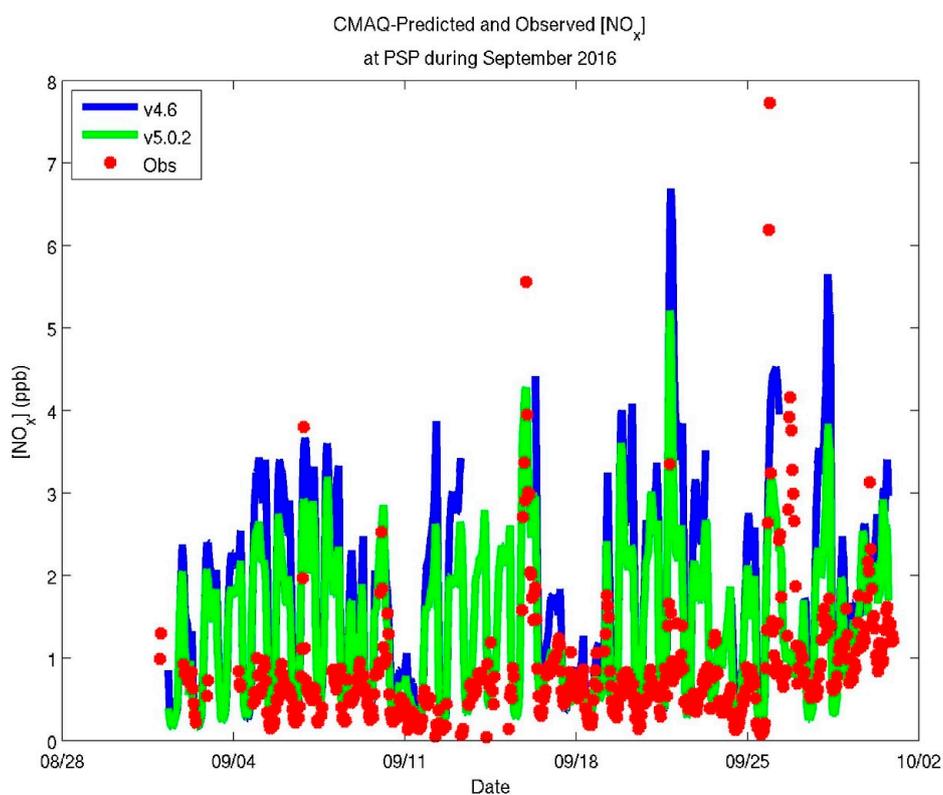


Figure S9. CMAQ v4.6-predicted (blue line), CMAQ v5.0.2-predicted (green line), and observed (red dots) [NO_x] concentrations at PSP during September 2016.

Observed OPE Comparison at PSP and QC: Two Different Approaches

Table S3. A comparison of the observed monthly OPEs at PSP and QC computed by 1) aggregating one month of data (superscript 1), and 2) averaging daily OPEs over a given month (superscript 2). See text for details regarding how both types of observed monthly OPEs were determined.

Site	Month	Observed Monthly OPEs ¹	Observed Monthly OPEs ²
PSP	June	10.89	9.09
	July	11.38	2.05
	August	11.94	9.30
	September	13.08	13.62
QC	August	7.70	5.80
	September	6.16	8.68

¹ Observed monthly OPEs found by aggregating one month of data

² Observed monthly OPEs found by averaging the daily OPEs

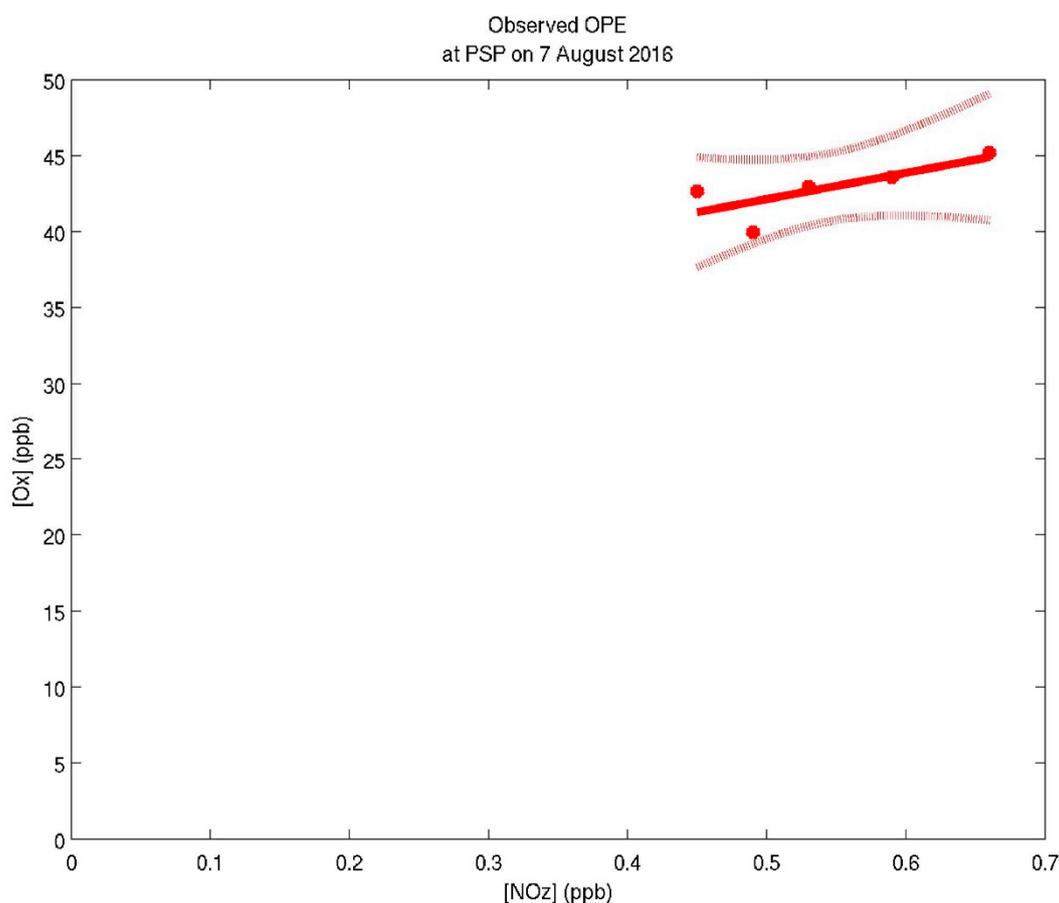


Figure S10. Observed daily OPE at PSP on 7 August 2016. The red solid and dashed lines represent straight-line fits and 95 percent confidence intervals, respectively, of observed OPE using robust regression with bisquare weights. Key statistics: OPE = 17.27, $R^2 = 0.53$.

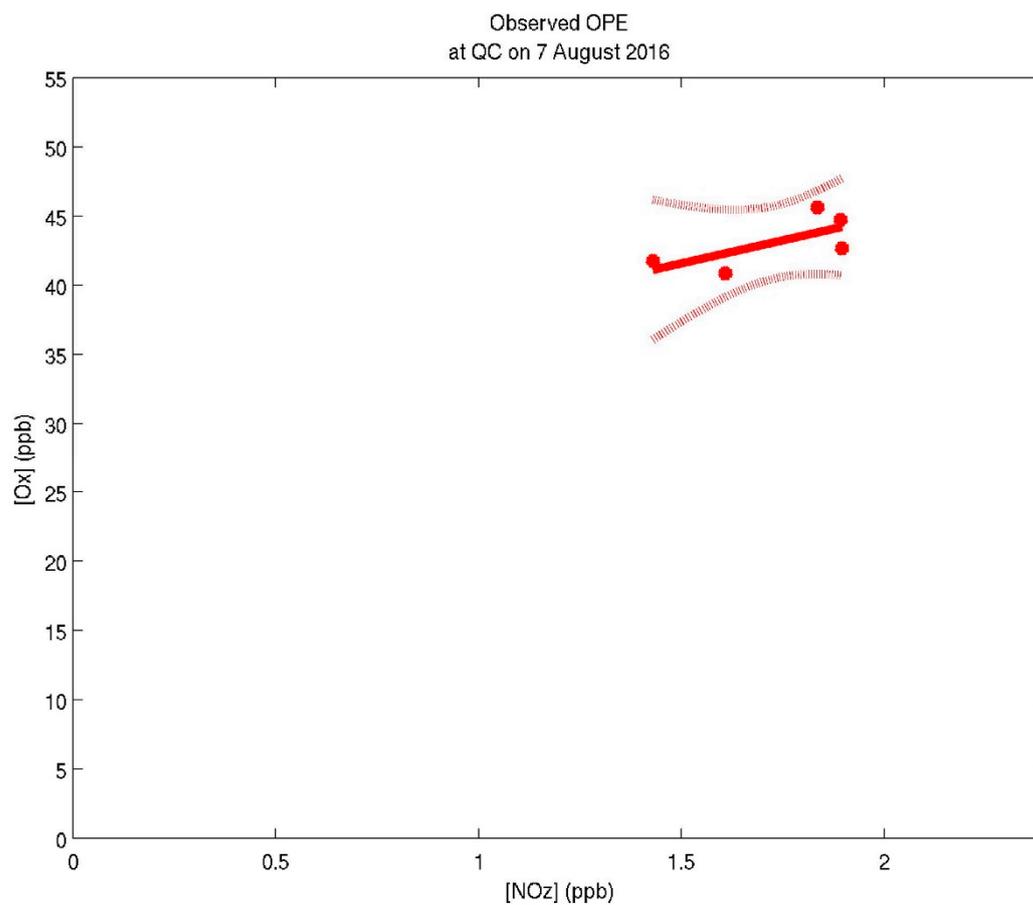


Figure S11. Observed daily OPE at QC on 7 August 2016. The red solid and dashed lines represent straight-line fits and 95 percent confidence intervals, respectively, of observed OPE using robust regression with bisquare weights. Key statistics: OPE = 6.67, $R^2 = 0.43$.