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Ozone response to emission reductions in the southeastern United States

Charles L. Blanchard and George M. Hidy

Correspondence to: Charles L. Blanchard (cbenvair@pacbell.net)

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This supplement presents tables and figures that document measurement methods and site locations. It also shows figures that are complementary to those of the main article, including comparisons of measurements for consistency, time series of data using different metrics, and complementary analyses based on measurements of other chemical species.

Supplement References

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Pollack, I., T. Ryerson, M. Trainer, J. Neuman, J. Roberts, and D. Parrish: Trends in ozone its precursors and related secondary oxidation products in Los Angeles, California: a synthesis of measurements from 1960-2010, J. Geophys. Res. Atmos., 118, 5891-5911, 2013.

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Xing, J., J. Pleim, R. Mathur, G. Pouliot, C. Hogrefe, C.-M. Gan, and C. Wei: Historical gaseous and primary aerosol emissions in the United States from 1990-2010, Atmos. Chem. Phys., 13, 7531-7549, doi 10.5194/acp-13-7531-2013, 2013.

Table S1. Basic measurements at SEARCH sites from 1999-2014 (Hidy et al., 2014). Sites having instrument differences are noted under "Comments." Operations began at CTR, OAK, and YRK in 1992. PNS, OAK, and GFP were decommissioned at the end of 2009, 2010, and 2012, respectively; other sites decommissioned during 2016.

a. Continuous meteorology at SEARCH sites (5- and 60-minute reporting intervals).

Parameter	Method	Instrument	Sampling Height (magl)	Comments
Temperature		Vaisala HMT3303	2	2m added in 2011
	platinum RTD	Paroscientific Met 4B	9	
Relative humidity		Vaisala HMT3303	2	2m added in 2011
	thin film capacitance	Paroscientific Met 4B	9	
Barometric pressure	quartz crystal resonator	Paroscientific Met 4B	9	
Surface wetness	conductivity	Decagon LSW-1	2	Added in 2011
Wind Speed/Direction	sonic anemometer	RMYoung 8100	10	
Solar Radiation (PAR)	pyranometer	Licor-200X	2	
Precipitation	gravimetry	ETI NOAH-IV	2	
Aerosol/cloud layers/mixing depth	laser ceilometer	JenOptik CHM 15k	50-15,000	GFP and OLF 2012-13 CTR and BHM 2013-14

b. Continuous trace gases at SEARCH sites (5- and 60-minute reporting intervals).

Parameter	Method[a]	Instrument	Sampling Hgt. (m agl)	Comments
O_3	UV absorption	Thermo-Scientific 49S/i	10	1992 or ≥1999[b]
CO	NDIR	Thermo-Scientific 48ctl/i	10	1992 or ≥1999[b]
SO_2	Pulsed UV fluorescence	Thermo-Scientific 43ctl/i	10	1992 or ≥1999[b]
NO, NO_y	Mo reduction/CL	Thermo-Scientific 42ctl/i	10	1992 or ≥1999[b]
NO_2	Photolysis/CL	Thermo-Scientific 42ctl/i	10	1997 or 2001[c]
HNO_3	Denuder difference/Mo reduction/CL	Thermo-Scientific 42ctl/i	10	1996 or ≥1999[d]
PANS/Alkylnitrates	Thermal decomposition/Blue LED photolysis/CL	Thermo-Scientific 42i	5	CTR only, starting 6/13
NH_3	Denuder difference/Pt oxidation/Mo reduction/CL	Thermo-Scientific 42i	5	Added in 2007

a. CL=NO-O_3 chemiluminescence
b. CTR, OAK, and YRK O_3, CO, SO_2, NO, and NO_y sampling started in 1992; other sites started 1999 – 2001
c. NO_2 started in 1997 at CTR and YRK; 2001 at other sites. Photolysis method changed from 300 W xenon lamp through 2001 to 200 W mercury lamp between 2002 and 2007 to blue LED beginning in 2008 (Hansen et al., 2006)
d. HNO_3 sampling started 1996 at CTR, OAK, and YRK; 1999 – 2002 at other sites. Difference between NO_y and denuded NO_y

Table S2. Regional comparisons of anthropogenic emissions and ambient ozone trends.

Location	Period	NO_x Emission Decrease	VOC Emission Decrease	Ozone Decrease[a]	Reference
Los Angeles	1960 – 2010	2.6% yr^{-1}	7.3% yr^{-1}	2.8% yr^{-1} (66%)	Pollack et al. (2013)[b]
Los Angeles	1975 – 2015	3.2% yr^{-1} (74%)	4.9% yr^{-1} (84%)	2.7% yr^{-1} (58%)	Hidy and Blanchard (2015)[c]
Los Angeles	1990 – 2015	3.2% yr^{-1} (74%)	5.9% yr^{-1} (84%)	2.6% yr^{-1} (41%)	Hidy and Blanchard (2015)[d]
Atlanta	1990 – 2014	5.9% yr^{-1} (63%)	2.5% yr^{-1} (32%)	1.7% yr^{-1}	Hidy et al. (2014); Hidy and Blanchard (2015)[e]
SEARCH JST	1999 – 2014	5.9% yr^{-1} (63%)[f]	2.5% yr^{-1} (32%)[f]	1.9% yr^{-1} (3.6% yr^{-1})[h]	Figure 3[g]
SEARCH YRK	1992 – 2014	5.9% yr^{-1} (63%)[f]	2.5% yr^{-1} (32%)[f]	1.8% yr^{-1} (4.1% yr^{-1})[h]	Figure 3[g]
SEARCH CTR	1992 - 2014	5.9% yr^{-1} (63%)[f]	2.5% yr^{-1} (32%)[f]	1.6% yr^{-1} (3.9% yr^{-1})[h]	Figure 3[g]

a. Trend in annual maximum daily peak 8-hr O_3 (Pollack et al., 2013 and this study) or 4th-highest daily peak 8-hr O_3 (Hidy et al., 2014; Hidy and Blanchard, 2015)

b. Ozone trend is for 1973 – 2010

c. Emission and ozone trends are from Figure S3 of Hidy and Blanchard (2015), compiled from data reported by the California Air Resources Board for the South Coast Air Basin

d. Emission trend is from Figure S3 of Hidy and Blanchard (2015) limited to 1990 – 2015 data. Ozone trend is for 1990 – 2014, from Table 2 of Hidy and Blanchard (2015). Percentage reductions are determined from the differences between starting and ending years except the 66% ozone decrease for Pollack et al. (2013) is based on their factor of 2.9 regression fit decrease

e. Emission decreases are for the southeastern U.S. (AL, GA, MS, NW FL) for 1996 – 2014 (Hidy et al., 2014; Figure 9, updated to 2014). Ozone trend is for 1990 – 2014 from Table 2 of Hidy and Blanchard (2015). For Birmingham, the ozone trends is -1.2% yr^{-1} (Hidy and Blanchard, 2015)

f. Emission decreases for the southeastern U.S. (AL, GA, MS, NW FL) for 1996 – 2014 (Hidy et al., 2014; Figure 9, updated to 2014).

g. Ozone trends are for the annual maximum daily peak 8-hr O_3 (derived from Figure 3 of the present study). Maximum ozone mixing ratios increased between 1992 and 1999; YRK and CTR trends are -2.6% y^{-1} and -3.1% y^{-1} and, respectively, between 1999 and 2014.

h. Rate of decrease of O_3 adjusted by subtraction of assumed 50 ppbv regional background.

Table S3. Trends in standard deviations and ranges of monthly maxima of daily peak 8-hour O_3 and monthly means of 2 p.m. O_3 mixing ratios. Statistically significant ($p < 0.01$) trends are shown in bold.

Site	Period[a]	N Yrs[a]	Trend in Standard Deviation of Monthly Maxima ($ppbv\ y^{-1}$)[b]	Trend in Range of Monthly Maxima ($ppbv\ y^{-1}$)[c]	Period[d]	N Yrs[d]	Trend in Range of Monthly Means ($ppbv\ y^{-1}$)[e]
BHM	2005-2014	10	**-1.35 ± 0.31**	**-3.66 ± 0.95**	2003-2014	12	-0.97 ± 0.44
CTR	1993-2014	19	**-0.58 ± 0.08**	**-1.89 ± 0.30**	1993-2014	20	**-0.93 ± 0.28**
GFP	2000-2012	10	**-0.48 ± 0.11**	**-1.14 ± 0.31**	2000-2011	9	-0.70 ± 0.53
JST	1999-2014	15	**-0.69 ± 0.14**	**-1.89 ± 0.54**	1999-2014	16	**-1.80 ± 0.35**
OAK	1993-2010	17	-0.18 ± 0.09	-0.49 ± 0.35	1993-2010	17	-0.43 ± 0.29
OLF	2000-2014	14	**-0.47 ± 0.13**	**-1.54 ± 0.51**	2000-2014	15	**-0.94 ± 0.29**
PNS	2000-2009	9	-0.67 ± 0.25	-2.40 ± 1.01	2000-2009	9	-1.15 ± 0.64
YRK	1993-2014	20	**-0.67 ± 0.11**	**-1.83 ± 0.38**	1993-2014	21	**-1.24 ± 0.22**

a. Period of record and number of years with monthly maxima of daily peak 8-hour O_3 satisfying completeness criteria. Daily peak 8-hour O_3 satisfy the criterion of 18 or more sampling hours per day. Monthly maxima were treated as missing if fewer than 24 days were available with daily peak 8-hour O_3. Standard deviations and ranges of monthly maxima were computed for each year having at least 9 months of non-missing monthly maxima.

b. Slope of linear regression of the standard deviation of monthly maxima of daily peak 8-hour O_3 versus year with one standard error of the slope. Statistically significant ($p < 0.01$) except at PNS and OAK; significant ($p < 0.05$) at PNS, not significant ($p > 0.05$) at OAK.

c. Slope of linear regression of the yearly range of monthly maxima of daily peak 8-hour O_3 versus year with one standard error of the slope. Statistically significant ($p < 0.01$) except at PNS and OAK; significant ($p < 0.05$) at PNS, not significant ($p > 0.05$) at OAK.

d. Period of record and number of years with monthly means of 2 p.m. O_3 satisfying completeness criteria. Monthly means were treated as missing if fewer than 24 days were available with 2 p.m. O_3. Ranges of monthly 2 p.m. means were computed for each year having at least 9 months with non-missing values.

e. Slope of linear regression of the yearly range of monthly mean 2 p.m. O_3 versus year with one standard error of the slope. Statistically significant ($p < 0.01$) at CTR, JST, OLF, and YRK; not significant ($p > 0.05$) at BHM, GFP, OAK, and PNS.

Table S4. Statistical summary of regressions of 2 pm O_3 vs 2 pm NO_z, by site and year.

Site	Year	Count	Mean 2 pm NO_z	Slope 2 pm O_3 vs NO_z	p-Value	Intercept	p-Value	r^2
BHM	2004	29	0.96 ± 0.28	5.9 ± 1.5	0.0006	35.4 ± 2.7	<.0001	0.36
BHM	2006	43	3.46 ± 0.27	9.1 ± 0.9	<.0001	31.0 ± 3.7	<.0001	0.69
BHM	2007	55	2.62 ± 0.22	9.1 ± 1.1	<.0001	35.9 ± 3.3	<.0001	0.58
BHM	2008	59	2.90 ± 0.17	8.5 ± 1.2	<.0001	34.4 ± 3.9	<.0001	0.48
BHM	2009	56	2.30 ± 0.13	9.7 ± 1.4	<.0001	22.2 ± 3.5	<.0001	0.49
BHM	2010	56	2.11 ± 0.12	11.6 ± 1.1	<.0001	21.2 ± 2.6	<.0001	0.67
BHM	2011	56	0.98 ± 0.18	5.0 ± 1.9	0.0116	44.8 ± 3.0	<.0001	0.11
BHM	2012	58	2.19 ± 0.13	11.7 ± 1.6	<.0001	27.9 ± 3.9	<.0001	0.48
BHM	2013	54	1.58 ± 0.11	13.1 ± 1.2	<.0001	20.8 ± 2.1	<.0001	0.70
CTR	1997	48	2.11 ± 0.18	9.1 ± 1.1	<.0001	31.6 ± 2.6	<.0001	0.62
CTR	1998	52	1.87 ± 0.14	11.0 ± 1.8	<.0001	30.5 ± 3.9	<.0001	0.43
CTR	2002	49	1.71 ± 0.17	9.2 ± 1.2	<.0001	38.9 ± 2.5	<.0001	0.55
CTR	2003	55	1.39 ± 0.11	20.2 ± 1.3	<.0001	17.6 ± 2.1	<.0001	0.82
CTR	2004	42	0.99 ± 0.11	22.0 ± 1.7	<.0001	20.9 ± 2.1	<.0001	0.80
CTR	2005	47	1.21 ± 0.12	17.2 ± 1.6	<.0001	24.7 ± 2.5	<.0001	0.80
CTR	2006	58	1.34 ± 0.08	19.8 ± 1.8	<.0001	32.9 ± 2.7	<.0001	0.69
CTR	2007	56	1.36 ± 0.08	20.6 ± 2.3	<.0001	26.7 ± 3.5	<.0001	0.59
CTR	2008	61	1.41 ± 0.07	25.0 ± 1.7	<.0001	14.0 ± 2.6	<.0001	0.78
CTR	2009	60	1.07 ± 0.04	21.5 ± 2.8	<.0001	21.4 ± 3.1	<.0001	0.52
CTR	2010	55	1.21 ± 0.07	12.3 ± 2.1	<.0001	26.0 ± 2.7	<.0001	0.40
CTR	2011	59	1.25 ± 0.08	24.3 ± 1.7	<.0001	15.3 ± 2.3	<.0001	0.79
CTR	2012	59	1.02 ± 0.07	25.1 ± 2.0	<.0001	17.8 ± 2.2	<.0001	0.74
CTR	2013	59	0.79 ± 0.04	25.7 ± 2.8	<.0001	16.5 ± 2.4	<.0001	0.61
CTR	2014	59	0.84 ± 0.04	24.6 ± 3.6	<.0001	17.4 ± 3.2	<.0001	0.46
GFP	2006	58	1.23 ± 0.14	8.6 ± 2.3	0.0004	39.2 ± 3.7	<.0001	0.22
GFP	2007	59	1.33 ± 0.13	7.8 ± 2.1	0.0004	38.9 ± 3.5	<.0001	0.24
GFP	2008	49	1.16 ± 0.09	15.2 ± 3.2	<.0001	24.2 ± 2.4	<.0001	0.71
GFP	2009	53	1.30 ± 0.08	21.6 ± 1.9	<.0001	25.8 ± 2.7	<.0001	0.72
GFP	2010	52	1.18 ± 0.09	15.9 ± 1.7	<.0001	23.3 ± 2.4	<.0001	0.63
GFP	2011	60	1.12 ± 0.07	24.3 ± 2.0	<.0001	19.2 ± 2.5	<.0001	0.72
JST	2001	60	8.77 ± 0.57	1.6 ± 0.7	0.0242	47.7 ± 6.6	<.0001	0.09
JST	2002	59	5.82 ± 0.36	4.9 ± 0.8	<.0001	40.2 ± 4.8	<.0001	0.44
JST	2003	61	4.79 ± 0.38	6.6 ± 0.6	<.0001	28.0 ± 3.3	<.0001	0.70
JST	2004	41	2.75 ± 0.38	4.8 ± 0.9	<.0001	45.0 ± 3.2	<.0001	0.45
JST	2005	39	4.13 ± 0.49	4.5 ± 1.0	<.0001	33.6 ± 5.0	<.0001	0.36
JST	2006	58	4.72 ± 0.38	7.0 ± 0.6	<.0001	38.9 ± 3.1	<.0001	0.74
JST	2007	58	4.29 ± 0.25	8.0 ± 0.7	<.0001	28.0 ± 3.3	<.0001	0.70
JST	2008	59	3.58 ± 0.24	9.3 ± 0.6	<.0001	27.9 ± 2.6	<.0001	0.79
JST	2009	57	2.54 ± 0.19	10.3 ± 0.8	<.0001	30.6 ± 2.4	<.0001	0.75
JST	2010	59	2.88 ± 0.14	12.0 ± 1.0	<.0001	19.2 ± 3.0	<.0001	0.73
JST	2011	57	2.38 ± 0.22	9.4 ± 0.9	<.0001	38.1 ± 2.7	<.0001	0.65
JST	2012	58	2.96 ± 0.15	14.7 ± 1.3	<.0001	15.9 ± 4.0	0.0002	0.70
JST	2013	57	2.18 ± 0.14	14.8 ± 0.9	<.0001	11.4 ± 2.1	<.0001	0.84
JST	2014	61	2.30 ± 0.11	13.5 ± 1.1	<.0001	17.4 ± 2.7	<.0001	0.72
OAK	2003	50	0.63 ± 0.05	29.0 ± 4.2	<.0001	22.5 ± 3.0	<.0001	0.44
OAK	2004	51	0.80 ± 0.06	25.4 ± 2.6	<.0001	18.0 ± 2.4	<.0001	0.69
OAK	2005	54	1.22 ± 0.08	19.7 ± 2.0	<.0001	18.8 ± 2.7	<.0001	0.66

Site	Year	Count	Mean 2 pm NO_z	Slope 2 pm O_3 vs NO_z	p-Value	Intercept	p-Value	r^2
OAK	2006	54	1.38 ± 0.10	11.8 ± 1.8	<.0001	29.8 ± 2.8	<.0001	0.45
OAK	2007	53	0.85 ± 0.07	27.4 ± 3.0	<.0001	20.5 ± 2.9	<.0001	0.63
OAK	2008	56	0.59 ± 0.04	35.2 ± 4.8	<.0001	22.2 ± 3.1	<.0001	0.49
OAK	2009	54	0.87 ± 0.05	22.9 ± 3.8	<.0001	27.3 ± 3.6	<.0001	0.41
OAK	2010	61	0.61 ± 0.04	18.4 ± 2.5	<.0001	22.2 ± 1.7	<.0001	0.49
OLF	2002	40	1.86 ± 0.12	12.7 ± 2.9	<.0001	26.6 ± 5.5	<.0001	0.35
OLF	2003	53	0.83 ± 0.10	17.1 ± 1.7	<.0001	25.9 ± 1.9	<.0001	0.67
OLF	2004	53	1.34 ± 0.14	5.7 ± 1.9	0.0036	36.3 ± 3.1	<.0001	0.16
OLF	2005	42	1.25 ± 0.12	13.4 ± 2.2	<.0001	27.9 ± 3.2	<.0001	0.48
OLF	2006	59	1.22 ± 0.10	20.6 ± 1.8	<.0001	26.6 ± 2.5	<.0001	0.72
OLF	2007	55	1.06 ± 0.09	23.3 ± 1.5	<.0001	21.8 ± 1.9	<.0001	0.82
OLF	2008	58	0.91 ± 0.11	17.7 ± 1.2	<.0001	26.7 ± 1.5	<.0001	0.78
OLF	2009	60	1.25 ± 0.06	24.3 ± 2.4	<.0001	19.7 ± 1.8	<.0001	0.68
OLF	2010	57	0.87 ± 0.07	14.0 ± 2.8	<.0001	26.7 ± 2.7	<.0001	0.33
OLF	2011	57	1.13 ± 0.10	12.9 ± 2.1	<.0001	27.8 ± 2.9	<.0001	0.40
OLF	2012	56	1.12 ± 0.08	15.6 ± 2.4	<.0001	24.5 ± 3.0	<.0001	0.44
OLF	2013	58	0.81 ± 0.05	19.6 ± 2.2	<.0001	18.5 ± 2.0	<.0001	0.59
OLF	2014	51	1.15 ± 0.05	13.2 ± 3.5	0.0004	25.1 ± 4.2	<.0001	0.23
PNS	2003	52	0.71 ± 0.09	16.5 ± 2.1	<.0001	24.5 ± 2.0	<.0001	0.56
PNS	2004	52	0.88 ± 0.23	5.8 ± 1.1	<.0001	38.0 ± 2.3	<.0001	0.46
PNS	2005	39	1.14 ± 0.16	10.9 ± 2.2	<.0001	29.0 ± 3.4	<.0001	0.41
PNS	2006	58	0.89 ± 0.14	13.9 ± 1.5	<.0001	39.7 ± 2.1	<.0001	0.59
PNS	2007	49	1.09 ± 0.09	23.6 ± 2.4	<.0001	20.3 ± 3.0	<.0001	0.67
PNS	2008	55	0.70 ± 0.07	27.0 ± 2.1	<.0001	21.3 ± 1.8	<.0001	0.76
PNS	2009	60	1.21 ± 0.10	13.5 ± 1.5	<.0001	32.7 ± 2.2	<.0001	0.58
YRK	1997	57	4.54 ± 0.26	4.8 ± 0.8	<.0001	37.5 ± 4.0	<.0001	0.39
YRK	1998	57	4.78 ± 0.36	5.9 ± 0.5	<.0001	35.9 ± 2.6	<.0001	0.74
YRK	2002	45	4.54 ± 0.48	5.6 ± 0.8	<.0001	42.0 ± 4.3	<.0001	0.57
YRK	2003	32	2.24 ± 0.37	7.6 ± 0.6	<.0001	36.0 ± 1.9	<.0001	0.83
YRK	2004	56	2.03 ± 0.13	11.5 ± 1.2	<.0001	27.4 ± 2.8	<.0001	0.62
YRK	2005	57	2.14 ± 0.19	7.5 ± 1.3	<.0001	36.5 ± 3.6	<.0001	0.48
YRK	2006	45	2.47 ± 0.19	9.2 ± 1.0	<.0001	38.4 ± 2.7	<.0001	0.67
YRK	2007	52	1.93 ± 0.15	5.9 ± 1.4	<.0001	38.2 ± 3.1	<.0001	0.29
YRK	2008	59	1.80 ± 0.10	11.9 ± 1.3	<.0001	31.8 ± 2.6	<.0001	0.59
YRK	2009	56	0.97 ± 0.07	18.5 ± 1.5	<.0001	31.1 ± 1.7	<.0001	0.73
YRK	2010	60	1.34 ± 0.08	19.9 ± 1.5	<.0001	21.8 ± 2.2	<.0001	0.76
YRK	2011	59	1.67 ± 0.10	19.5 ± 1.1	<.0001	19.2 ± 2.0	<.0001	0.86
YRK	2012	49	1.96 ± 0.11	15.4 ± 1.5	<.0001	23.4 ± 3.2	<.0001	0.68
YRK	2013	53	1.07 ± 0.08	18.8 ± 1.4	<.0001	19.5 ± 1.7	<.0001	0.81
YRK	2014	57	1.10 ± 0.06	15.0 ± 2.2	<.0001	24.7 ± 2.6	<.0001	0.45

Table S5. Comparison of regression results.

Site	Year	Count	Slope 2 pm O_3 vs 2 pm NO_z	P-Value	r^2	Slope pm - am O_3 vs pm - am NO_z	P-Value	r^2	Slope late - mid am O_3 vs late - mid am NO_z	P-Value	r^2
BHM	2004	29	5.9 ± 1.5	0.0006	0.36	1.8 ± 1.1	0.136	0.09	-0.1 ± 0.7	0.9022	0.00
BHM	2006	43	9.1 ± 0.9	<.0001	0.69	4.3 ± 0.9	<.0001	0.36	1.1 ± 1.5	0.4841	0.01
BHM	2007	55	9.1 ± 1.1	<.0001	0.58	5.9 ± 0.8	<.0001	0.52	1.8 ± 0.6	0.0029	0.15
BHM	2008	59	8.5 ± 1.2	<.0001	0.48	4.8 ± 0.9	<.0001	0.35	2.1 ± 0.7	0.0071	0.14
BHM	2009	56	9.7 ± 1.4	<.0001	0.49	4.1 ± 1.0	0.0001	0.27	1.8 ± 0.8	0.0211	0.11
BHM	2010	56	11.6 ± 1.1	<.0001	0.67	8.6 ± 1.2	<.0001	0.51	6.1 ± 0.9	<.0001	0.51
BHM	2011	56	5.0 ± 1.9	0.0116	0.11	3.5 ± 0.8	<.0001	0.29	0.9 ± 0.5	0.0843	0.06
BHM	2012	58	11.7 ± 1.6	<.0001	0.48	8.1 ± 1.0	<.0001	0.57	4.8 ± 0.6	<.0001	0.51
BHM	2013	54	13.1 ± 1.2	<.0001	0.70	3.4 ± 0.8	<.0001	0.28	1.2 ± 0.5	0.0173	0.10
CTR	1997	48	9.1 ± 1.1	<.0001	0.62	5.1 ± 0.6	<.0001	0.62	5.3 ± 1.0	<.0001	0.38
CTR	1998	52	11.0 ± 1.8	<.0001	0.43	3.2 ± 1.0	0.0028	0.18	3.4 ± 0.8	<.0001	0.28
CTR	2002	49	9.2 ± 1.2	<.0001	0.55	6.8 ± 1.2	<.0001	0.44	3.4 ± 1.3	0.0134	0.12
CTR	2003	55	20.2 ± 1.3	<.0001	0.82	7.5 ± 2.1	0.0006	0.21	4.8 ± 1.8	0.0099	0.12
CTR	2004	42	22.0 ± 1.7	<.0001	0.80	12.0 ± 2.4	<.0001	0.43	6.8 ± 2.2	0.003	0.18
CTR	2005	47	17.2 ± 1.6	<.0001	0.80	7.4 ± 2.1	0.0016	0.30	5.3 ± 1.0	<.0001	0.47
CTR	2006	58	19.8 ± 1.8	<.0001	0.69	14.1 ± 1.6	<.0001	0.59	9.5 ± 2.1	<.0001	0.27
CTR	2007	56	20.6 ± 2.3	<.0001	0.59	5.9 ± 2.2	0.0086	0.12	8.2 ± 2.3	0.0007	0.20
CTR	2008	61	25.0 ± 1.7	<.0001	0.78	13.8 ± 1.5	<.0001	0.58	11.6 ± 1.7	<.0001	0.45
CTR	2009	60	21.5 ± 2.8	<.0001	0.52	13.3 ± 2.2	<.0001	0.39	9.2 ± 2.4	0.0003	0.21
CTR	2010	55	12.3 ± 2.1	<.0001	0.40	6.1 ± 1.9	0.0018	0.18	12.6 ± 1.8	<.0001	0.51
CTR	2011	59	24.3 ± 1.7	<.0001	0.79	7.4 ± 2.1	0.0009	0.20	8.9 ± 1.9	<.0001	0.29
CTR	2012	59	25.1 ± 2.0	<.0001	0.74	13.8 ± 2.0	<.0001	0.47	11.0 ± 1.3	<.0001	0.58
CTR	2013	59	25.7 ± 2.8	<.0001	0.61	16.4 ± 3.8	<.0001	0.26	8.1 ± 2.3	0.0009	0.19
CTR	2014	59	24.6 ± 3.6	<.0001	0.46	3.5 ± 3.2	0.2913	0.02	6.6 ± 3.0	0.031	0.08
GFP	2006	58	8.6 ± 2.3	0.0004	0.22	0.3 ± 2.1	0.8867	0.00	2.2 ± 1.1	0.0449	0.08
GFP	2007	59	7.8 ± 2.1	0.0004	0.24	2.2 ± 1.5	0.1543	0.05	1.5 ± 1.3	0.2702	0.03
GFP	2008	49	15.2 ± 3.2	<.0001	0.71	4.5 ± 2.1	0.039	0.11	3.5 ± 1.3	0.0102	0.16
GFP	2009	53	21.6 ± 1.9	<.0001	0.72	5.3 ± 1.6	0.0013	0.19	2.2 ± 1.5	0.1381	0.04
GFP	2010	52	15.9 ± 1.7	<.0001	0.63	10.0 ± 2.1	<.0001	0.32	8.0 ± 1.7	<.0001	0.32
GFP	2011	60	24.3 ± 2.0	<.0001	0.72	6.5 ± 2.3	0.0066	0.13	7.1 ± 1.6	<.0001	0.29
JST	2001	60	1.6 ± 0.7	0.0242	0.09	-0.1 ± 0.4	0.7821	0.00	-0.5 ± 0.3	0.1088	0.04
JST	2002	59	4.9 ± 0.8	<.0001	0.44	2.8 ± 0.7	<.0001	0.30	0.6 ± 0.7	0.4069	0.02
JST	2003	61	6.6 ± 0.6	<.0001	0.70	2.3 ± 0.6	0.0005	0.21	-0.3 ± 0.3	0.3907	0.01
JST	2004	41	4.8 ± 0.9	<.0001	0.45	3.4 ± 0.7	<.0001	0.37	0.7 ± 1.0	0.5033	0.01
JST	2005	39	4.5 ± 1.0	<.0001	0.36	2.8 ± 0.9	0.0042	0.24	0.1 ± 0.5	0.8334	0.00
JST	2006	58	7.0 ± 0.6	<.0001	0.74	6.8 ± 0.7	<.0001	0.65	2.5 ± 0.8	0.0023	0.15
JST	2007	58	8.0 ± 0.7	<.0001	0.70	5.8 ± 0.8	<.0001	0.52	4.4 ± 0.9	<.0001	0.31
JST	2008	59	9.3 ± 0.6	<.0001	0.79	6.7 ± 0.7	<.0001	0.65	3.2 ± 1.0	0.0013	0.17
JST	2009	57	10.3 ± 0.8	<.0001	0.75	7.7 ± 0.8	<.0001	0.68	4.5 ± 1.1	0.0002	0.25
JST	2010	59	12.0 ± 1.0	<.0001	0.73	9.8 ± 0.8	<.0001	0.75	7.3 ± 0.8	<.0001	0.62
JST	2011	57	9.4 ± 0.9	<.0001	0.65	6.2 ± 1.1	<.0001	0.39	3.6 ± 0.9	0.0001	0.25
JST	2012	58	14.7 ± 1.3	<.0001	0.70	6.2 ± 1.4	<.0001	0.26	5.0 ± 1.1	<.0001	0.26
JST	2013	57	14.8 ± 0.9	<.0001	0.84	10.1 ± 1.2	<.0001	0.59	8.7 ± 1.2	<.0001	0.49
JST	2014	61	13.5 ± 1.1	<.0001	0.72	10.1 ± 1.4	<.0001	0.47	6.0 ± 1.3	<.0001	0.28

Site	Year	Count	Slope 2 pm O_3 vs 2 pm NO_z	P-Value	r^2	Slope pm - am O_3 vs pm - am NO_z	P-Value	r^2	Slope late - mid am O_3 vs late - mid am NO_z	P-Value	r^2
OAK	2003	50	29.0 ± 4.2	<.0001	0.44	10.7 ± 2.6	0.0002	0.30	3.9 ± 1.3	0.0048	0.17
OAK	2004	51	25.4 ± 2.6	<.0001	0.69	10.2 ± 2.2	<.0001	0.37	13.0 ± 2.2	<.0001	0.47
OAK	2005	54	19.7 ± 2.0	<.0001	0.66	9.1 ± 1.7	<.0001	0.41	9.5 ± 1.5	<.0001	0.45
OAK	2006	54	11.8 ± 1.8	<.0001	0.45	8.4 ± 1.7	<.0001	0.32	4.4 ± 1.0	0.0001	0.25
OAK	2007	53	27.4 ± 3.0	<.0001	0.63	11.8 ± 2.2	<.0001	0.39	10.2 ± 2.0	<.0001	0.36
OAK	2008	56	35.2 ± 4.8	<.0001	0.49	15.3 ± 3.8	0.0002	0.24	15.6 ± 2.0	<.0001	0.56
OAK	2009	54	22.9 ± 3.8	<.0001	0.41	7.2 ± 2.2	0.0023	0.18	6.1 ± 1.6	0.0004	0.23
OAK	2010	61	18.4 ± 2.5	<.0001	0.49	10.3 ± 2.2	<.0001	0.28	2.0 ± 1.6	0.2277	0.03
OLF	2002	40	12.7 ± 2.9	<.0001	0.35	4.9 ± 1.6	0.0037	0.23	2.7 ± 0.8	0.0011	0.27
OLF	2003	53	17.1 ± 1.7	<.0001	0.67	7.8 ± 1.4	<.0001	0.42	5.3 ± 0.8	<.0001	0.49
OLF	2004	53	5.7 ± 1.9	0.0036	0.16	1.0 ± 0.7	0.1615	0.04	-1.7 ± 0.7	0.0123	0.12
OLF	2005	42	13.4 ± 2.2	<.0001	0.48	1.9 ± 0.9	0.0484	0.10	1.5 ± 0.7	0.036	0.10
OLF	2006	59	20.6 ± 1.8	<.0001	0.72	4.3 ± 1.2	0.0006	0.22	2.3 ± 0.8	0.0079	0.14
OLF	2007	55	23.3 ± 1.5	<.0001	0.82	9.7 ± 1.1	<.0001	0.62	7.3 ± 1.0	<.0001	0.49
OLF	2008	58	17.7 ± 1.2	<.0001	0.78	6.9 ± 1.3	<.0001	0.35	7.3 ± 0.9	<.0001	0.56
OLF	2009	60	24.3 ± 2.4	<.0001	0.68	7.9 ± 1.0	<.0001	0.52	7.5 ± 1.2	<.0001	0.41
OLF	2010	57	14.0 ± 2.8	<.0001	0.33	8.6 ± 1.7	<.0001	0.36	12.7 ± 2.1	<.0001	0.44
OLF	2011	57	12.9 ± 2.1	<.0001	0.40	4.6 ± 1.4	0.0023	0.16	4.8 ± 1.5	0.0028	0.15
OLF	2012	56	15.6 ± 2.4	<.0001	0.44	4.7 ± 1.8	0.0123	0.13	4.0 ± 1.5	0.0119	0.14
OLF	2013	58	19.6 ± 2.2	<.0001	0.59	11.1 ± 1.8	<.0001	0.44	8.2 ± 1.3	<.0001	0.43
OLF	2014	51	13.2 ± 3.5	0.0004	0.23	6.5 ± 1.9	0.0015	0.20	8.5 ± 1.7	<.0001	0.37
PNS	2003	52	16.5 ± 2.1	<.0001	0.56	1.4 ± 0.6	0.0302	0.10	-0.1 ± 0.4	0.7567	0.00
PNS	2004	52	5.8 ± 1.1	<.0001	0.46	1.8 ± 0.8	0.0255	0.14	0.1 ± 1.0	0.9448	0.00
PNS	2005	39	10.9 ± 2.2	<.0001	0.41	2.8 ± 1.4	0.0521	0.13	2.1 ± 1.4	0.1252	0.07
PNS	2006	58	13.9 ± 1.5	<.0001	0.59	1.6 ± 1.0	0.1273	0.04	1.9 ± 0.9	0.0269	0.10
PNS	2007	49	23.6 ± 2.4	<.0001	0.67	5.4 ± 1.1	<.0001	0.33	5.4 ± 0.6	<.0001	0.67
PNS	2008	55	27.0 ± 2.1	<.0001	0.76	7.8 ± 1.5	<.0001	0.36	3.7 ± 1.4	0.0107	0.12
PNS	2009	60	13.5 ± 1.5	<.0001	0.58	6.5 ± 1.4	<.0001	0.29	5.5 ± 0.9	<.0001	0.42
YRK	1997	57	4.8 ± 0.8	<.0001	0.39	5.0 ± 0.6	<.0001	0.60	3.4 ± 0.7	<.0001	0.33
YRK	1998	57	5.9 ± 0.5	<.0001	0.74	5.9 ± 0.6	<.0001	0.67	4.3 ± 0.5	<.0001	0.59
YRK	2002	45	5.6 ± 0.8	<.0001	0.57	6.5 ± 0.8	<.0001	0.65	3.5 ± 1.2	0.0047	0.21
YRK	2003	32	7.6 ± 0.6	<.0001	0.83	6.0 ± 1.1	<.0001	0.59	7.3 ± 2.1	0.0027	0.37
YRK	2004	56	11.5 ± 1.2	<.0001	0.62	5.2 ± 1.4	0.0007	0.22	4.7 ± 1.4	0.001	0.20
YRK	2005	57	7.5 ± 1.3	<.0001	0.48	6.4 ± 1.0	<.0001	0.52	7.1 ± 1.7	0.0001	0.33
YRK	2006	45	9.2 ± 1.0	<.0001	0.67	8.9 ± 1.2	<.0001	0.58	5.3 ± 0.9	<.0001	0.50
YRK	2007	52	5.9 ± 1.4	<.0001	0.29	6.1 ± 0.9	<.0001	0.50	3.6 ± 0.9	0.0003	0.23
YRK	2008	59	11.9 ± 1.3	<.0001	0.59	7.7 ± 1.3	<.0001	0.38	4.5 ± 1.0	<.0001	0.25
YRK	2009	56	18.5 ± 1.5	<.0001	0.73	11.1 ± 1.4	<.0001	0.56	5.7 ± 1.4	<.0001	0.24
YRK	2010	60	19.9 ± 1.5	<.0001	0.76	12.6 ± 1.3	<.0001	0.61	8.3 ± 1.6	<.0001	0.33
YRK	2011	59	19.5 ± 1.1	<.0001	0.86	9.5 ± 1.7	<.0001	0.37	7.0 ± 1.4	<.0001	0.33
YRK	2012	49	15.4 ± 1.5	<.0001	0.68	10.5 ± 1.2	<.0001	0.64	5.2 ± 1.9	0.0085	0.14
YRK	2013	53	18.8 ± 1.4	<.0001	0.81	9.7 ± 2.4	0.0003	0.28	10.4 ± 2.1	<.0001	0.37
YRK	2014	57	15.0 ± 2.2	<.0001	0.45	9.6 ± 1.8	<.0001	0.35	9.3 ± 1.7	<.0001	0.39

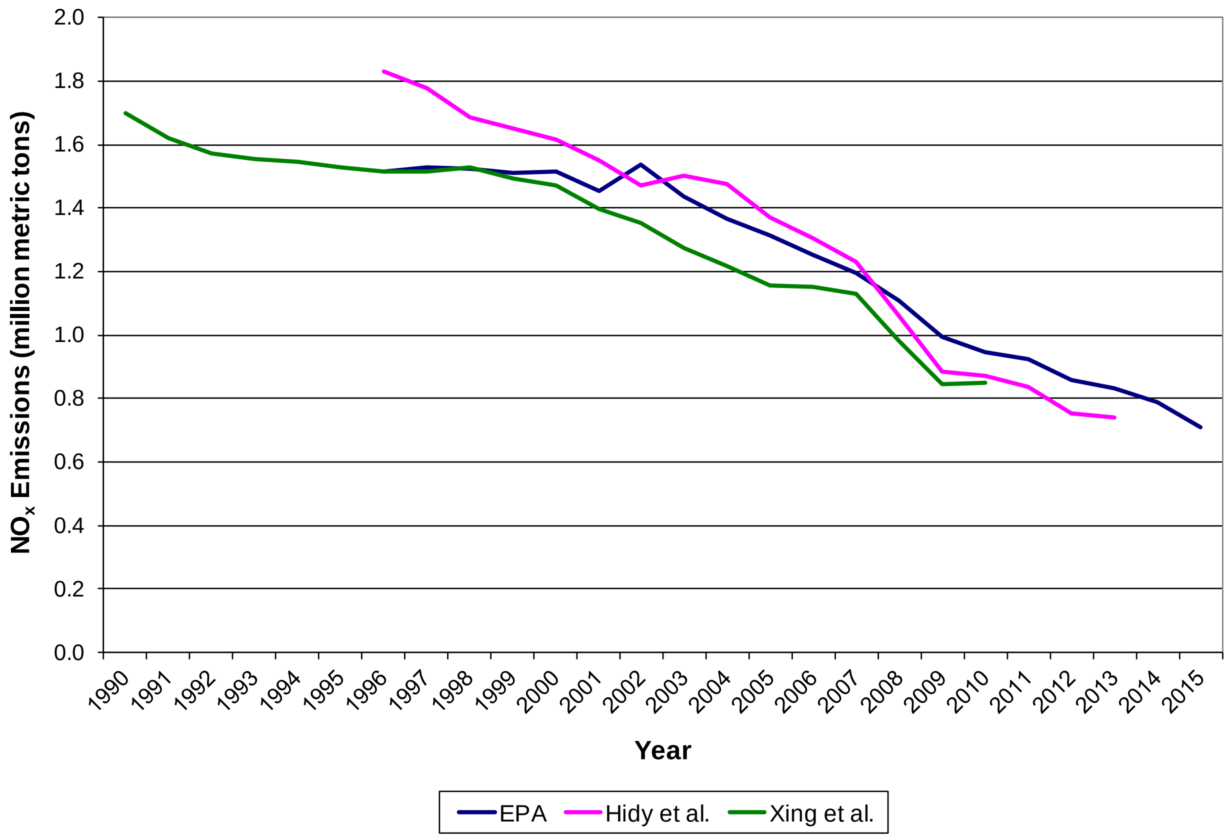

Figure S1. Total (all source sectors) annual anthropogenic NO_x emissions in Georgia, Alabama, and Mississippi obtained from U.S. EPA (2016a; 2016b), Xing et al. (2013), and Hidy et al. (2014). Continuous emission monitoring system (CEMS) data are stack measurements of SO_2, NO_x, and CO_2 made daily at facility and unit level at EGUs and other large emission sources. These measurements are actual emissions and have been incorporated into EPA's National Emission Inventory (NEI) since 1999. Other types of emission estimates are obtained through application of emission models. EPA estimated on-road mobile-source emissions using the EPA MOBILE6 model through the first version of the 2008 NEI. Beginning with version 2 of the 2008 NEI, EPA estimated on-road mobile-source emissions using the MOVES model. EPA recently backcast emissions to 2002 using MOVES to provide improved consistency in its emission trend inventory (U.S. EPA, 2016b). Therefore, the EPA trends inventory is not identical with the 2002 and 2005 NEIs. MOBILE6 and MOVES generate different emission estimates. Hidy et al. (2014) utilized the MOVES model to generate emission factors per unit energy and scaled them by on-road fuel sales. EPA also published a state-level historical emission inventory using consistent methods for all years, disaggregated by major source types, for the years 1990 to 2010, utilizing emission factors from the 2005 and 2008 NEIs (Xing et al., 2013).

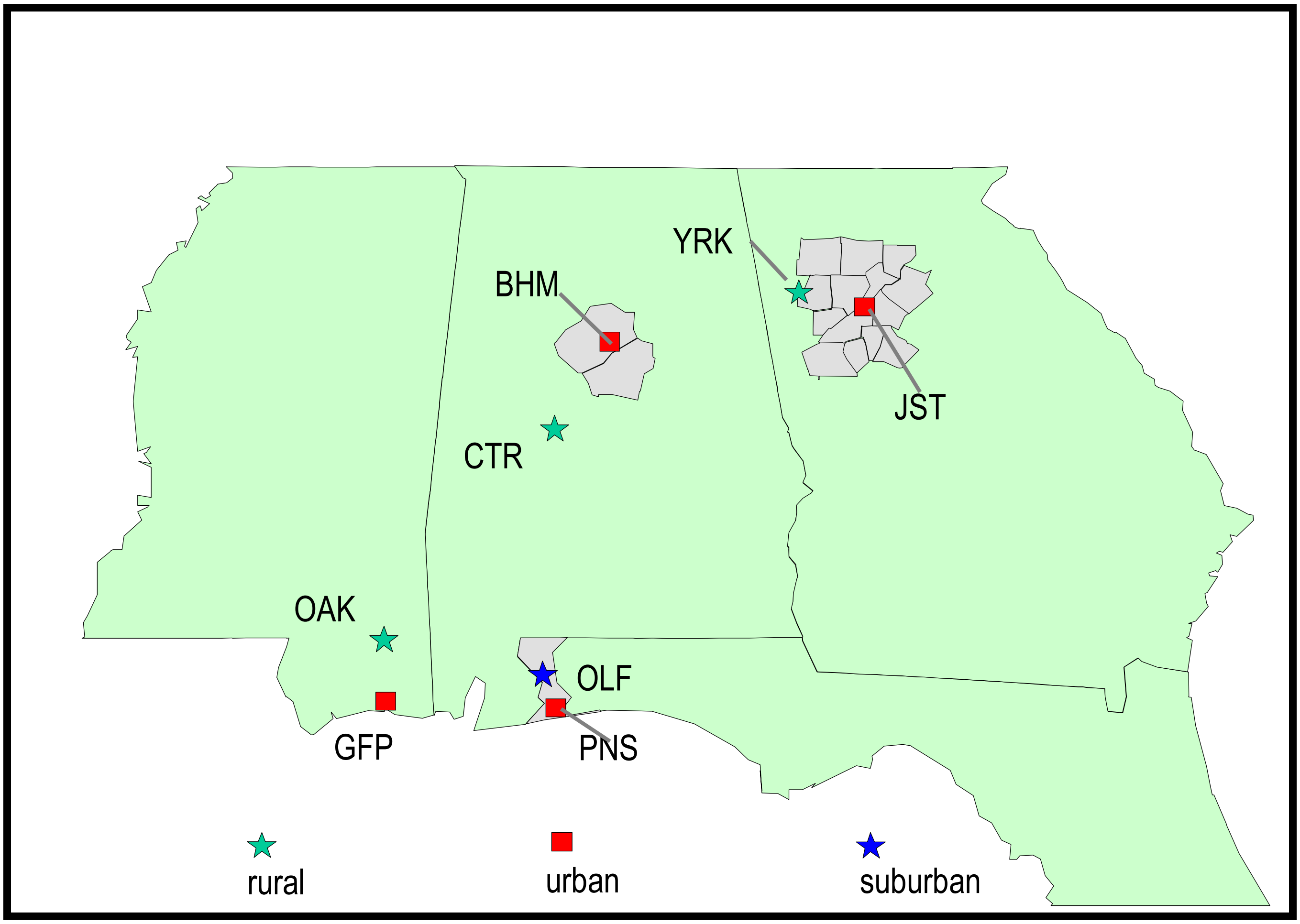

Figure S2. SEARCH site location map. PNS, OAK, and GFP were retired at the end of 2009, 2010, and 2012, respectively. Other sites were decommissioned during 2015. The grey shading denotes counties corresponding to the urban metropolitan areas of Birmingham, AL, Atlanta, GA, and Pensacola, FL.

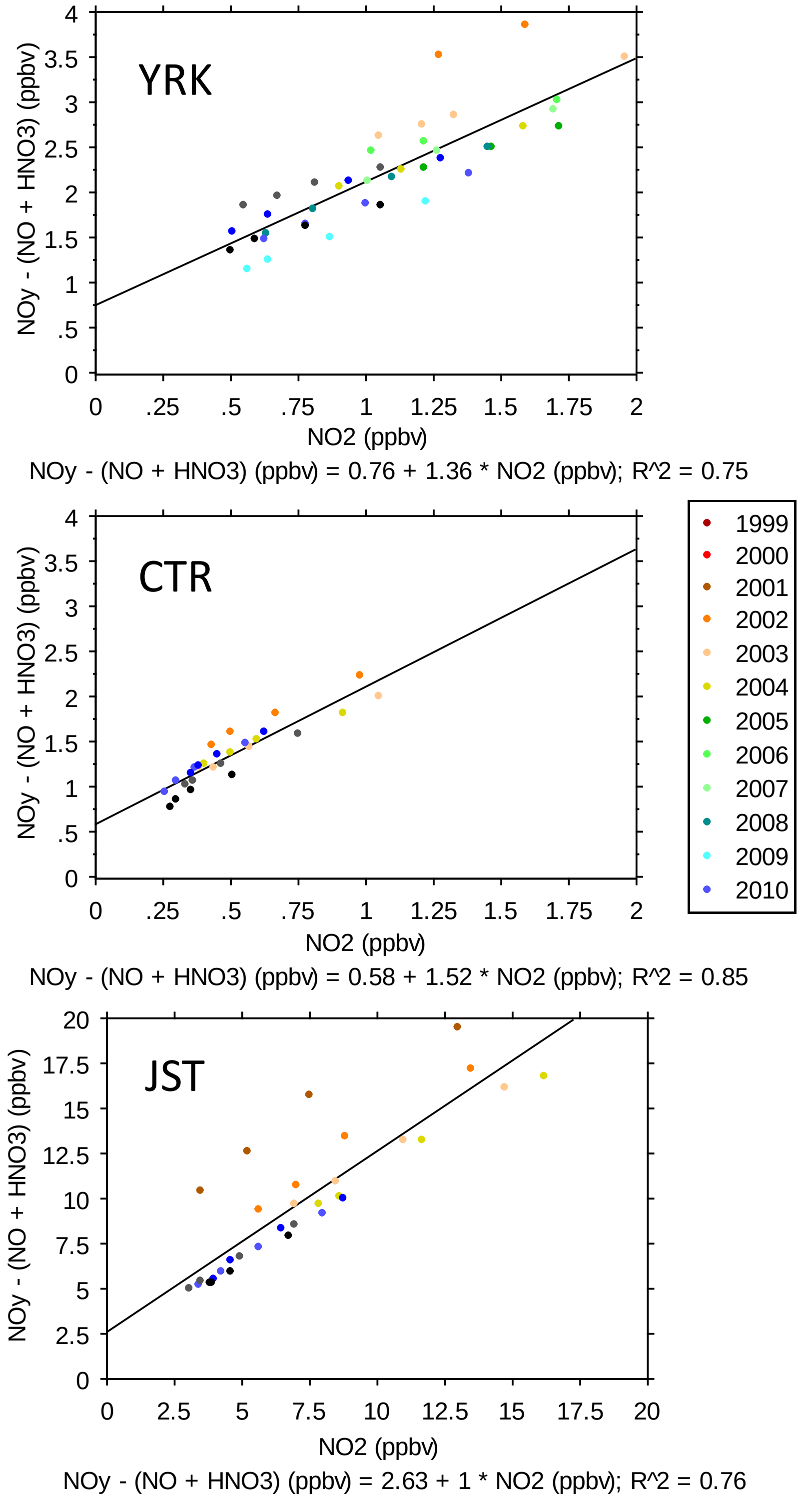

Figure S3. Mean NO_y minus the sum of NO plus HNO_3 vs NO_2. Means are computed by year and hour for starting hours of 9 a.m. through 12 noon, yielding four hourly averages per year. The data are from June through August. The quantity NO_y minus the sum of NO plus HNO_3 approximates the sum of NO_2 plus PAN plus other alkyl nitrates. Although different types of NO_2 measurement instruments were deployed, the comparison to NO_y minus the sum of NO plus HNO_3 is consistent over time, but with larger deviations occurring in 2001 and 2002.

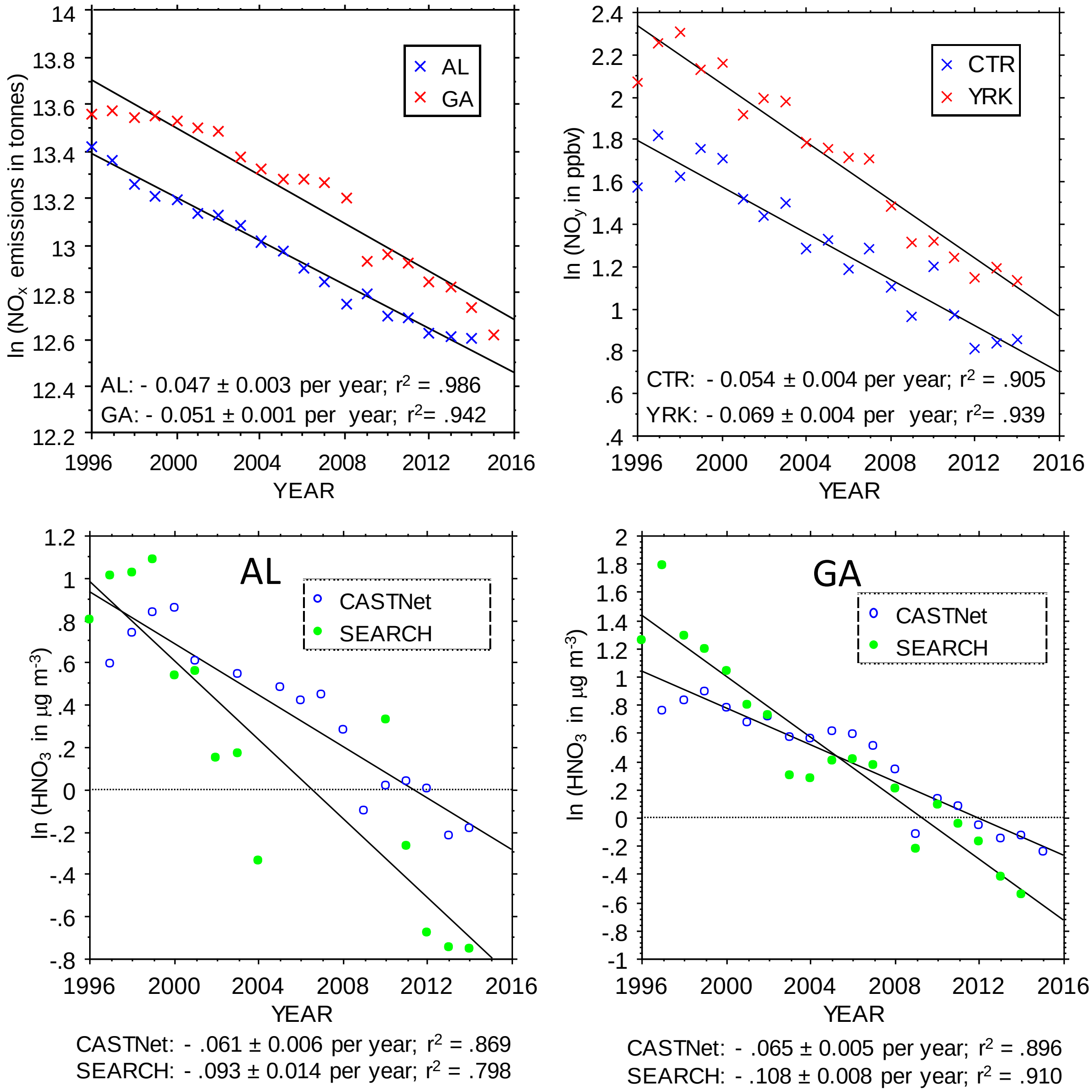

Figure S4. Semi-log trends: (a) NO_x emissions, (b) mean annual NO_y at CTR (AL) and YRK (GA) SEARCH sites, (c) mean annual HNO_3 concentrations at AL SEARCH and CASTNet sites, and (d) mean annual HNO_3 concentrations at GA SEARCH and CASTNet sites. SEARCH HNO_3 measurements are hourly denuder-difference mixing ratios (Table S1b) converted to units of concentration. CastNet HNO_3 concentrations are weekly filter-pack measurements.

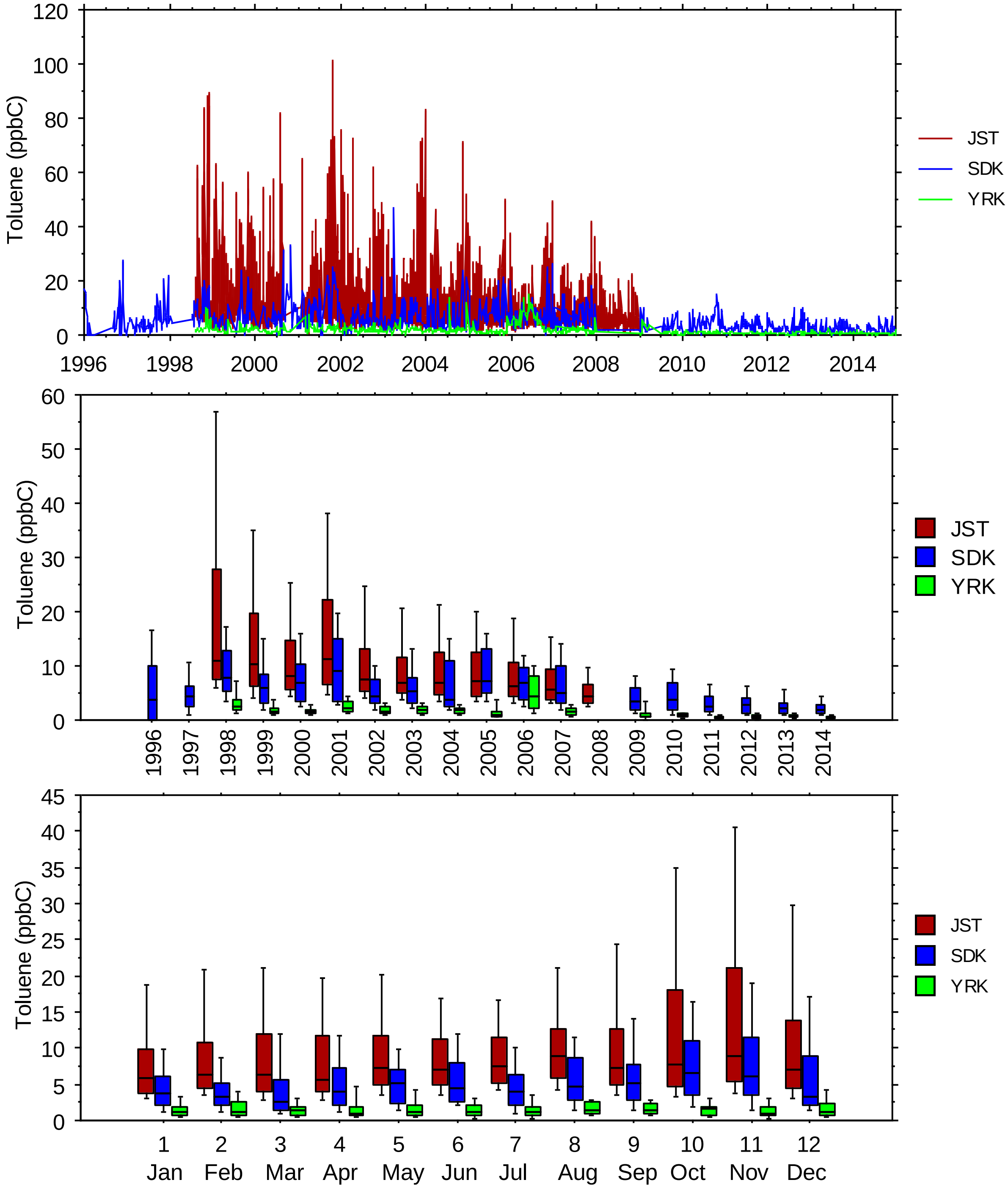

Figure S5. (a) Time series of daily-average toluene mixing ratios, (b) statistical distributions of daily-average toluene mixing ratios vs. year, and (c) statistical distributions of daily-average toluene mixing ratios vs. month. Samples were obtained every day at JST and once every six days at YRK and SDK (Blanchard et al., 2010). Statistical distributions indicate the 10th, 25th, 50th, 75th, and 90th percentiles.

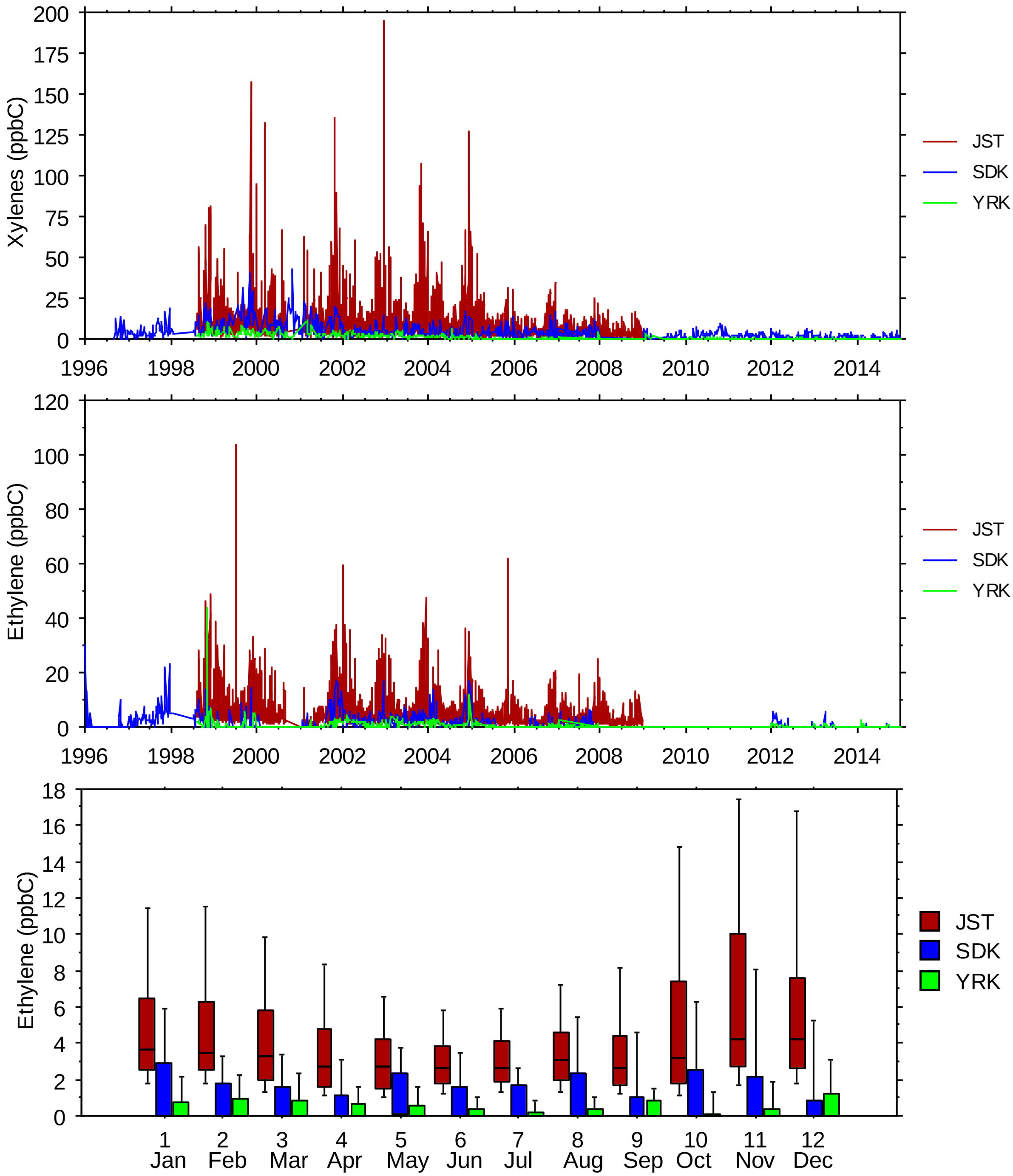

Figure S6 (a) Time series of daily-average mixing ratios of xylenes, (b) daily-average ethylene mixing ratios vs. year, and (c) statistical distributions of daily-average ethylene mixing ratios vs. month. Samples were obtained every day at JST and once every six days at YRK and SDK (Blanchard et al., 2010). Statistical distributions indicate the 10^{th}, 25^{th}, 50^{th}, 75^{th}, and 90^{th} percentiles.

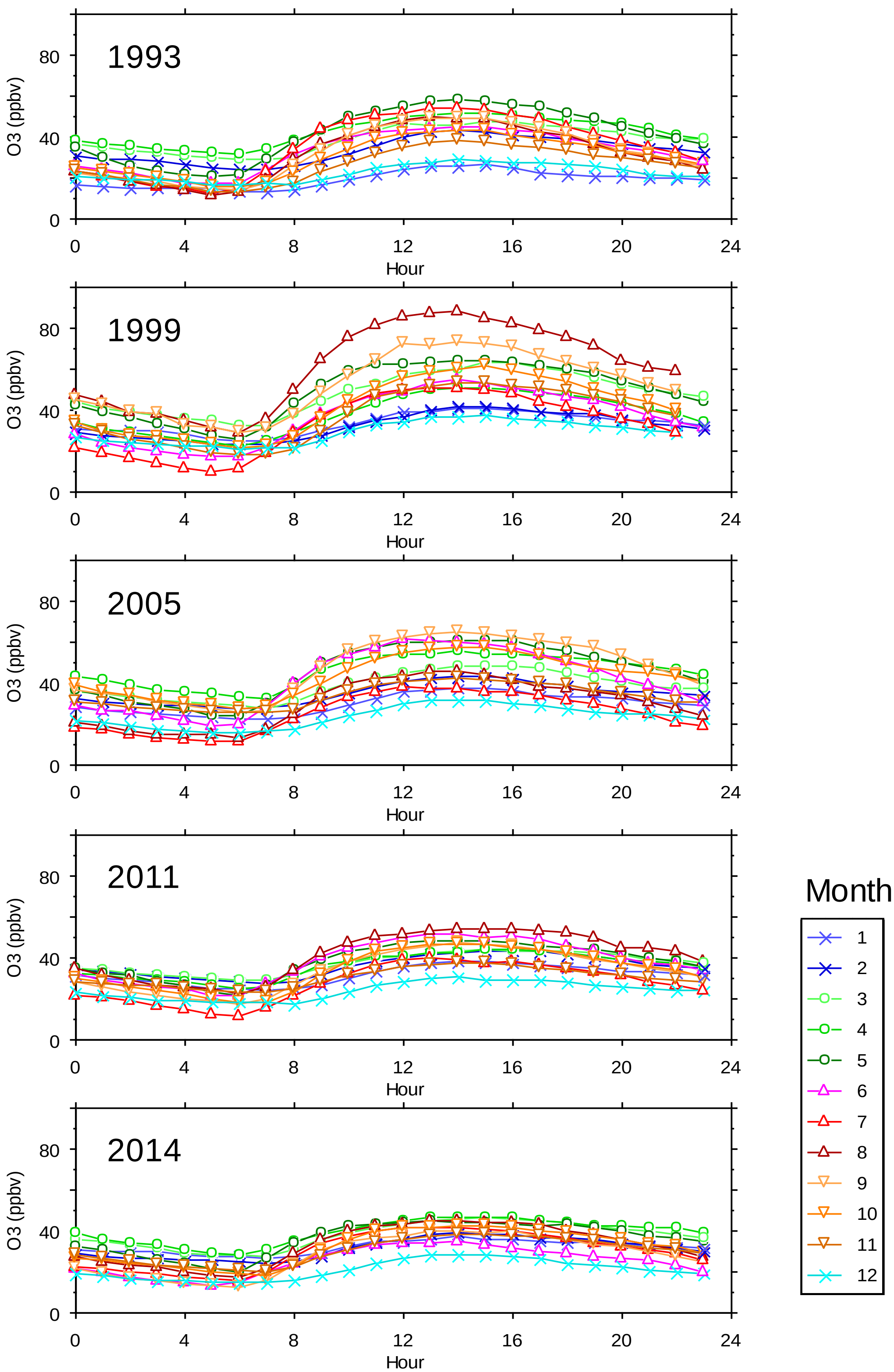

Figure S7. Average O_3 mixing ratios at CTR vs. hour, by year and month. Each data point is the mean of all hourly measurements made during each month.

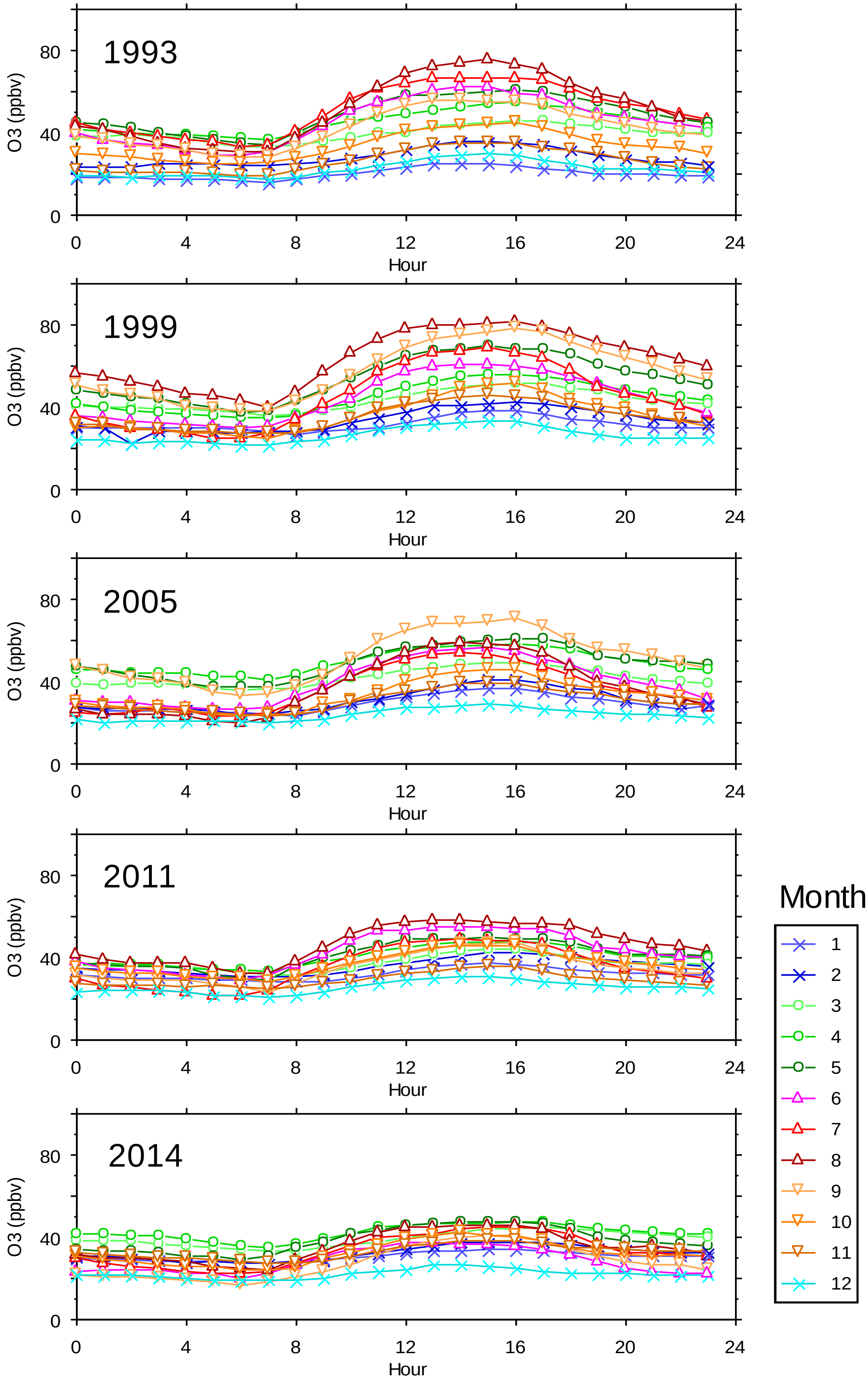

Figure S8. Average O_3 mixing ratios at YRK vs. hour, by year and month. Each data point is the mean of all hourly measurements made during each month.

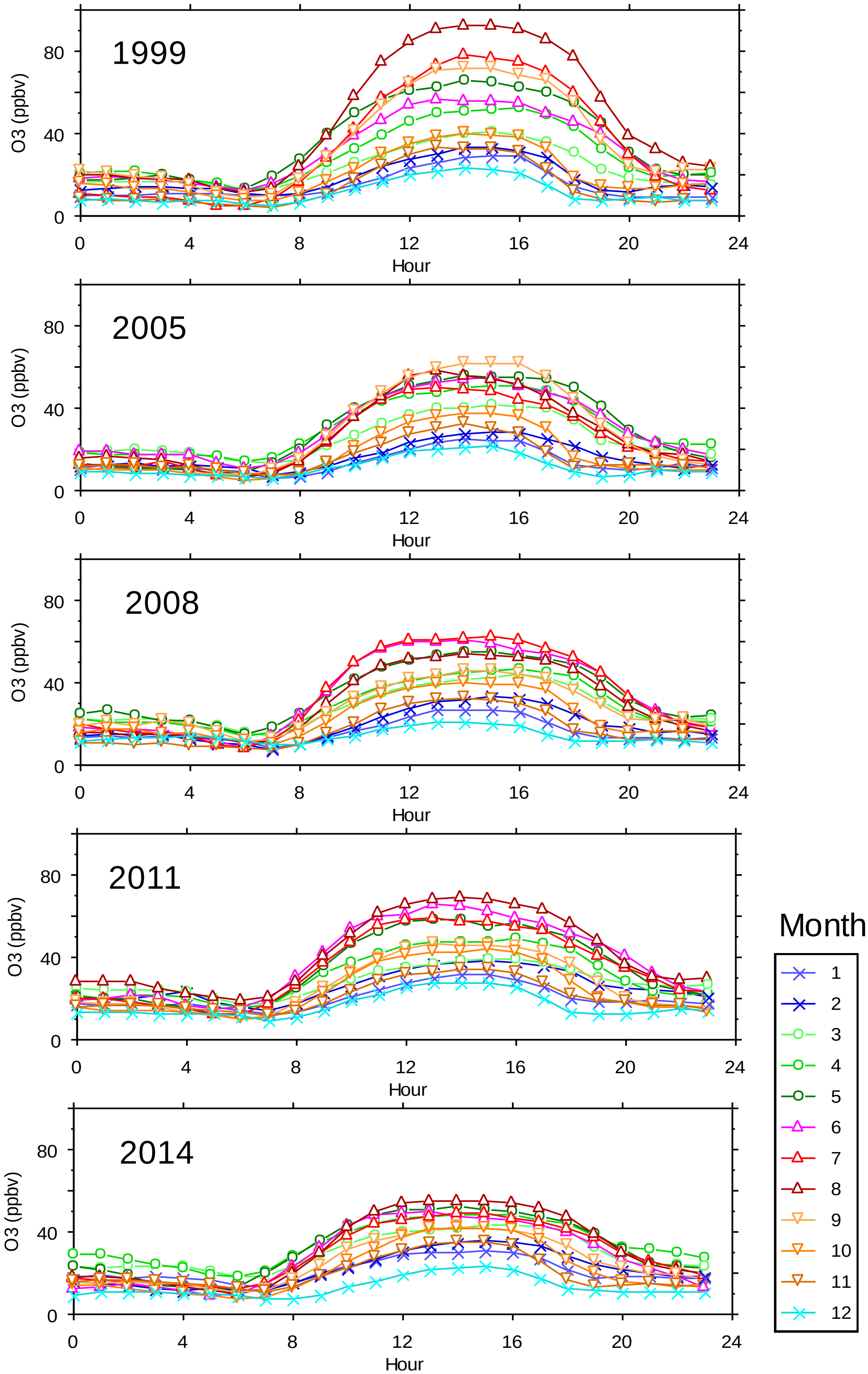

Figure S9. Average O_3 mixing ratios at JST vs. hour, by year and month. Each data point is the mean of all hourly measurements made during each month.

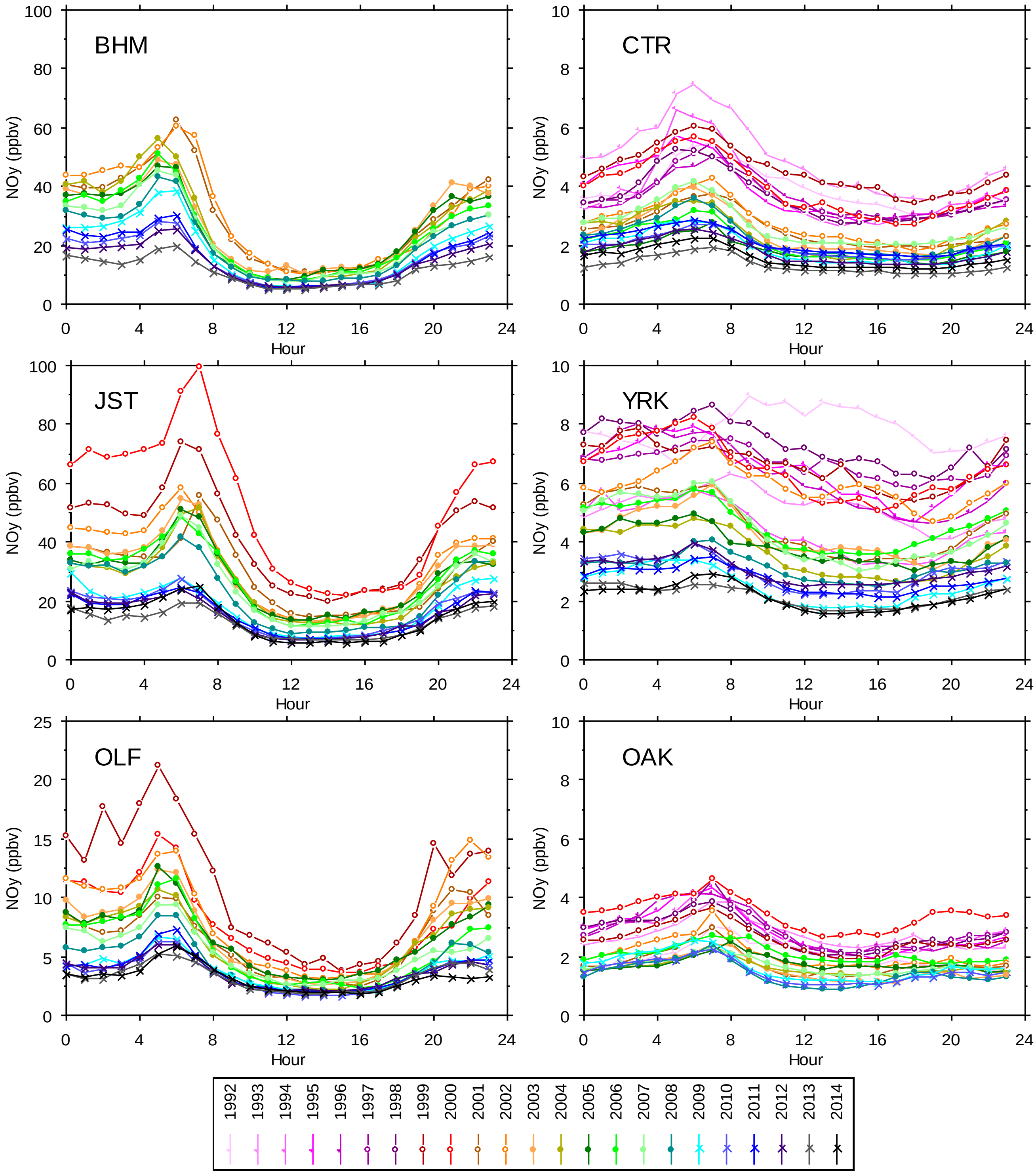

Figure S10. Average NO_y mixing ratios vs. hour, by year. Each data point is the mean of hourly measurements during June through August. PNS and GFP (not shown) exhibit similar diurnal profiles and trends (sampling at those sites ended after 2009 and 2012, respectively). Standard errors of the means are 0.04 – 9 ppbv, approximately proportional (~8%) to NO_y mixing ratios.

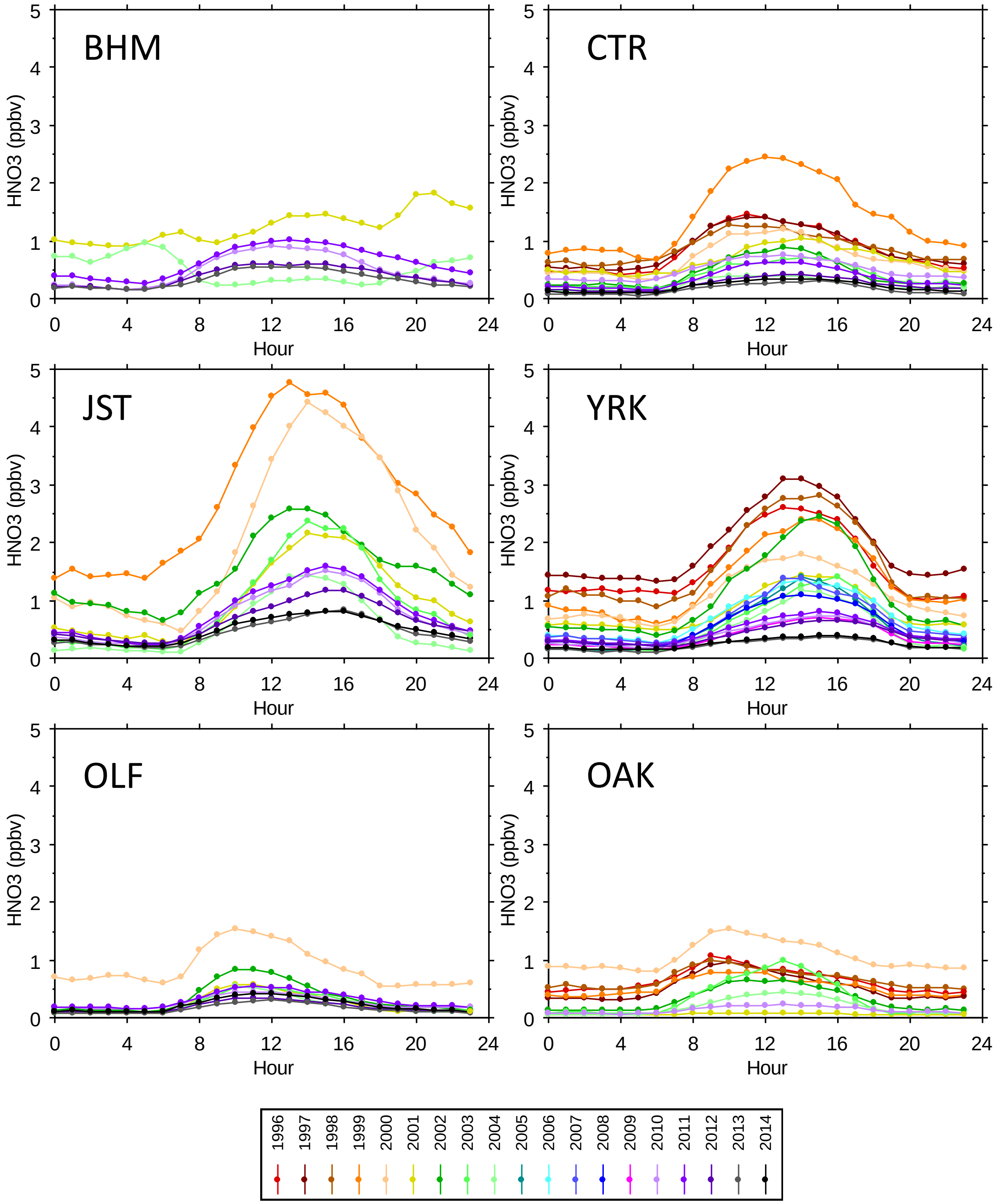

Figure S11. Average HNO_3 mixing ratios vs. hour, by year. Each data point is the mean of hourly measurements during June through August. PNS and OAK (not shown) exhibit similar diurnal profiles and trends (sampling at those sites ended after 2009 and 2010, respectively). Standard errors of the means are 0.01 – 1.4 ppbv, approximately proportional (8%) to HNO_3 mixing ratios.

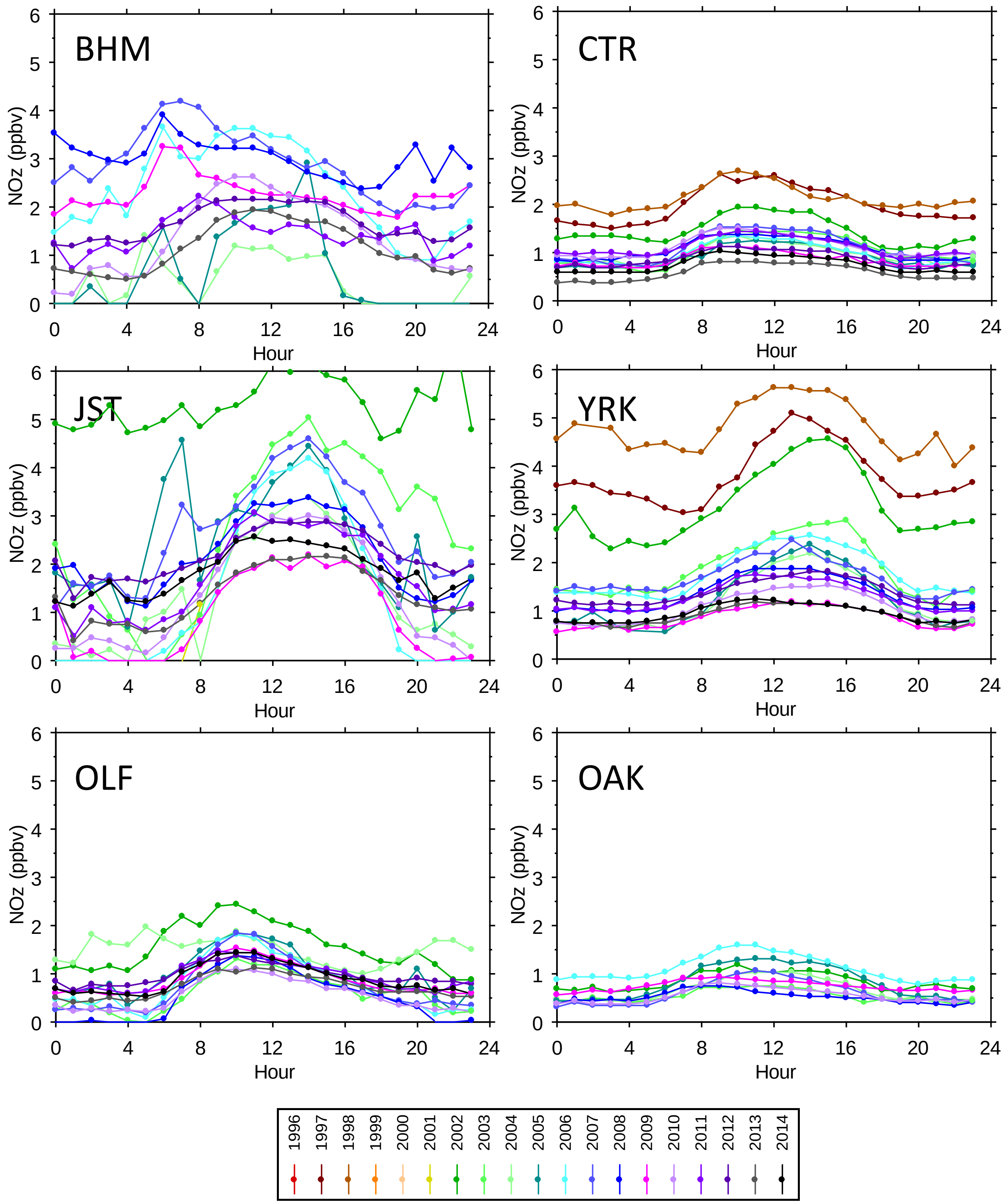

Figure S12. Average NO_z mixing ratios vs. hour, by year. Each data point is the mean of hourly measurements during June through August. PNS and GFP (not shown) exhibit similar diurnal profiles and trends (sampling at those sites ended after 2009 and 2012, respectively). Standard errors of the means are 0.05 – 1.5 ppbv (average 0.3 ppbv); measurement uncertainties for the averages are 0.03 – 0.8 ppbv (average 0.2 ppbv).

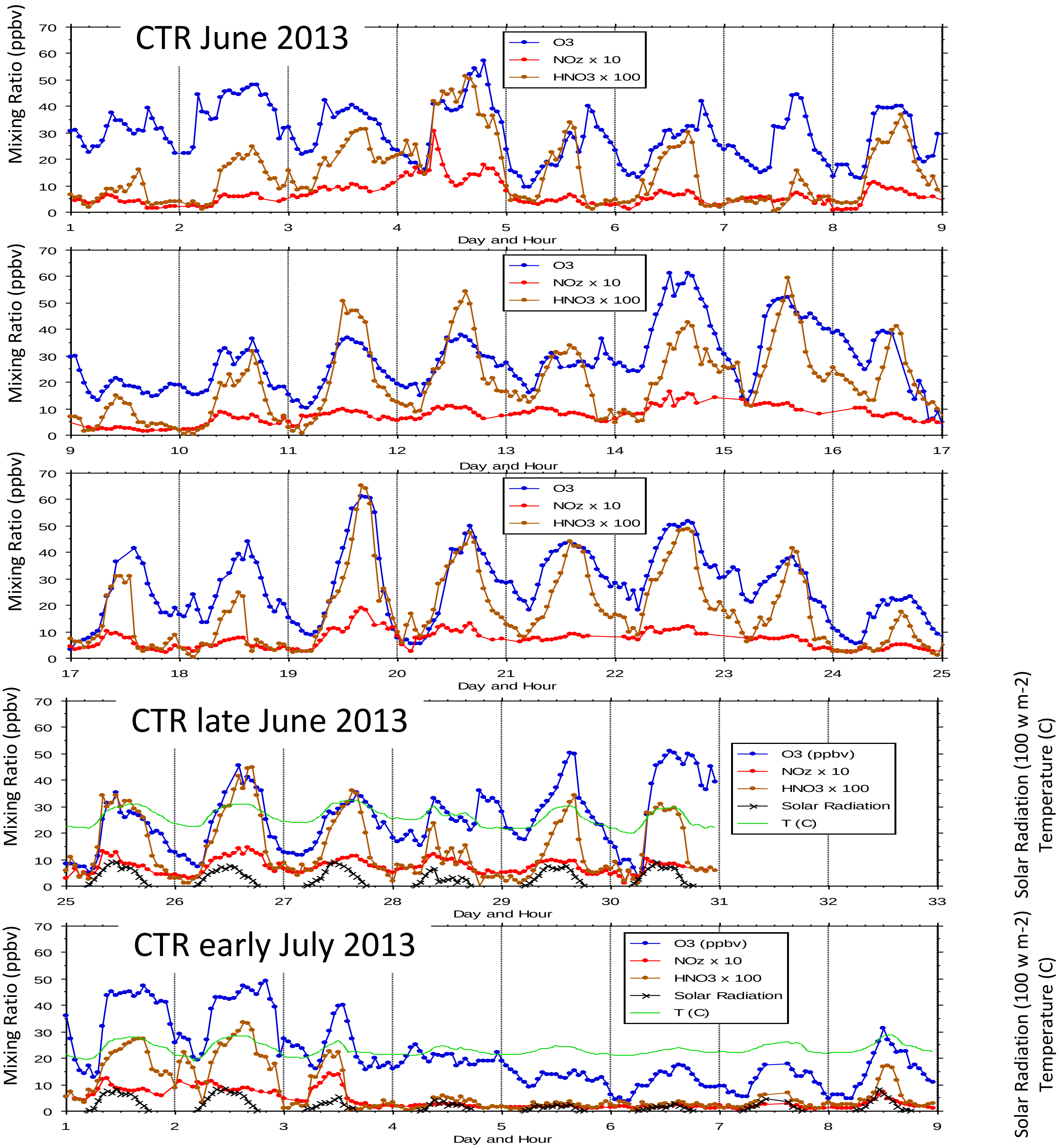

Figure S13. Hourly O_3, NO_z, HNO_3, temperature, and solar radiation at CTR, June 1 through July 8, 2013. Meteorological y-axis is scaled to the range of values of the mixing ratio y-axis.

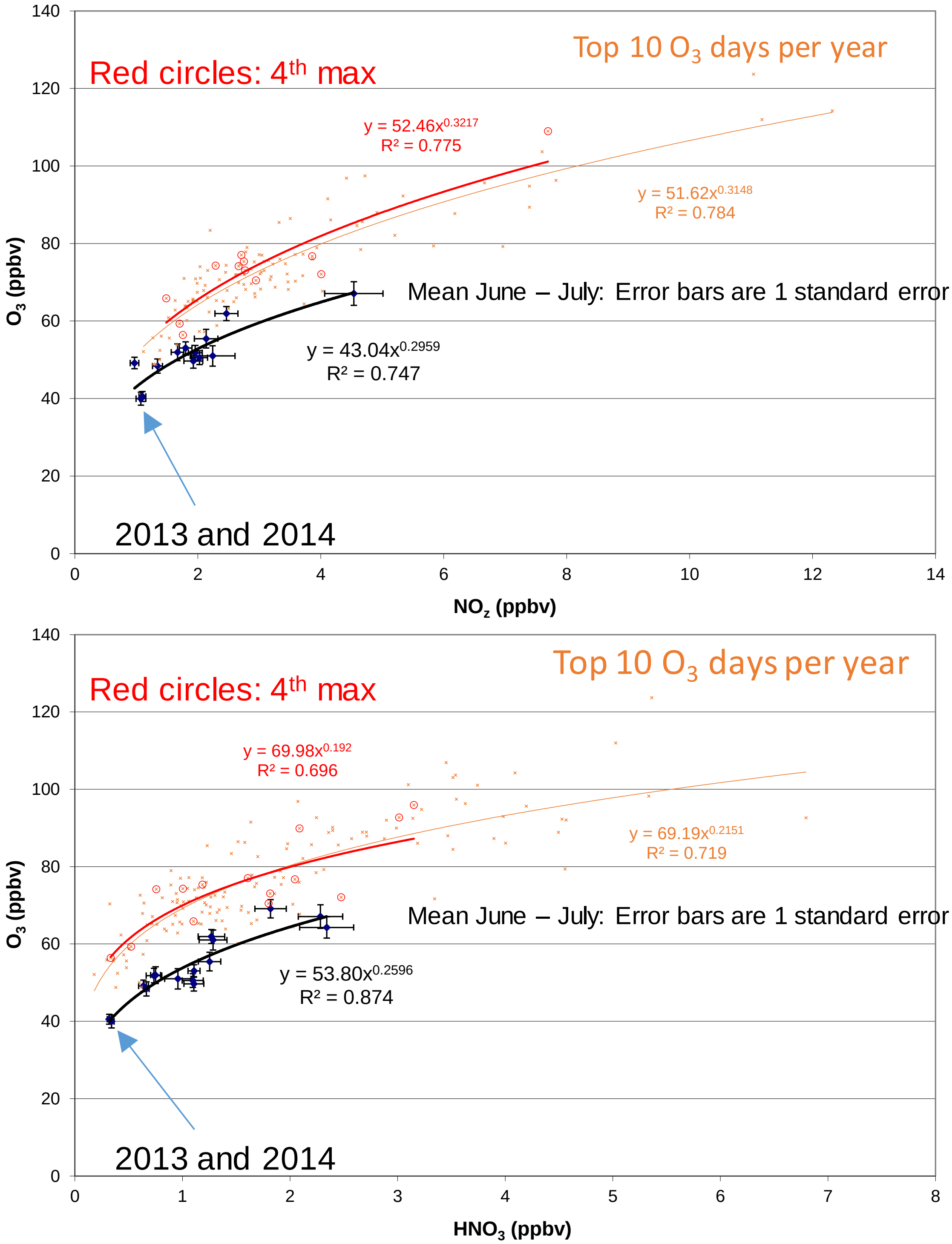

Figure S14. YRK 2 p.m. O_3 vs 2 p.m. NO_z (top) and 2 p.m. HNO_3 (bottom). The data are the top 10 O_3 days during June and July of each year (small symbols, with power-law curve fit), the 4th-highest O_3 day during June and July of each year (red circles, with power-law curve fit), and the mean of all days during June and July of each year (symbols with one standard error of the mean, and with power-law curve fit). Extrapolation of the power law fits to infer zero O_3 at zero HNO_3 extends the curves beyond the ranges of the observed data and such extrapolation is neither shown nor implied.

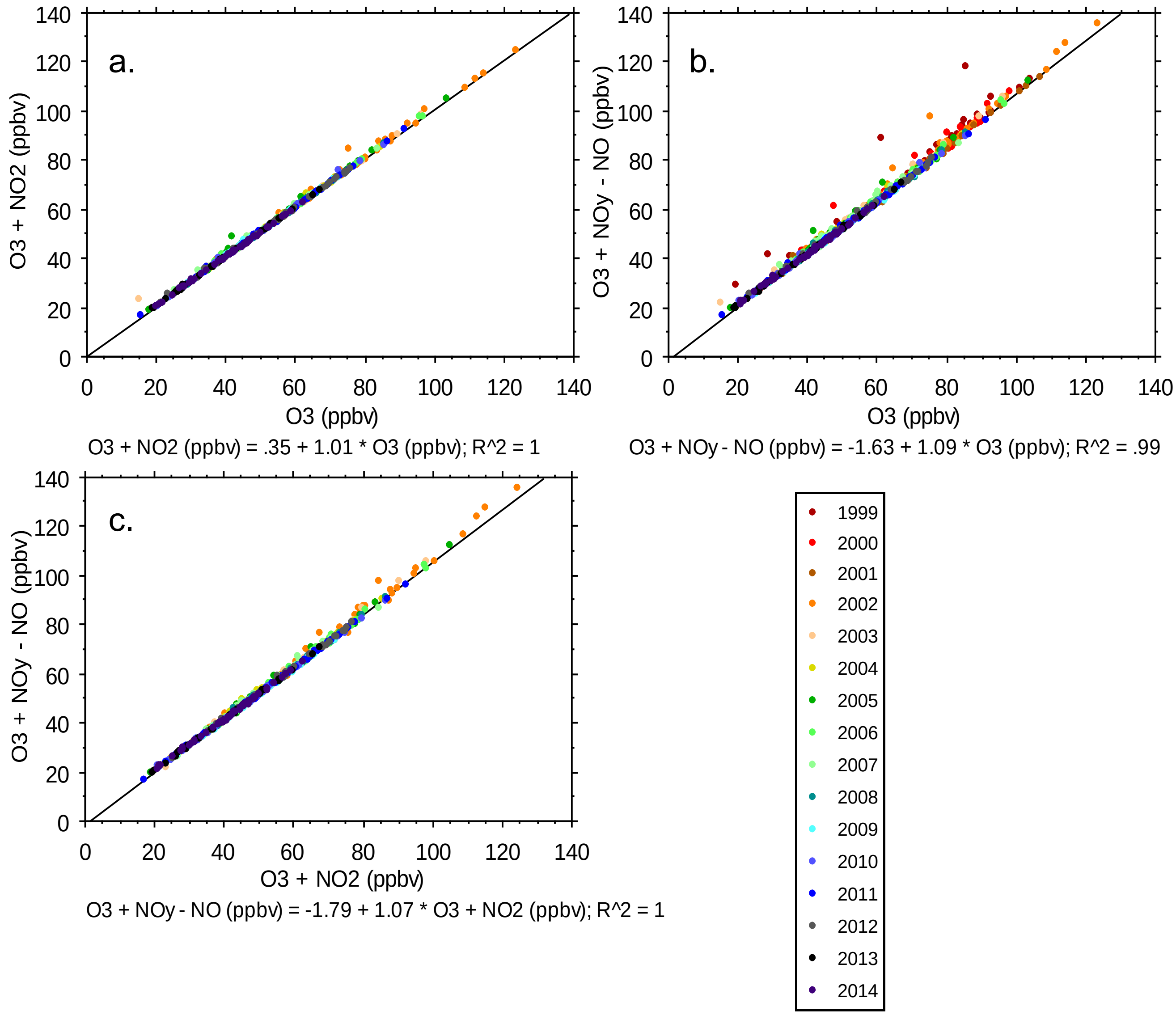

Figure S15. YRK 2 p.m. (a) $O_3 + NO_2$ vs O_3, (b) $O_3 + NO_y - NO$ vs O_3, and (c) $O_3 + NO_y - NO$ vs. $O_3 + NO_2$. Measurements are 2 – 3 p.m. hourly data from June and July of each year.

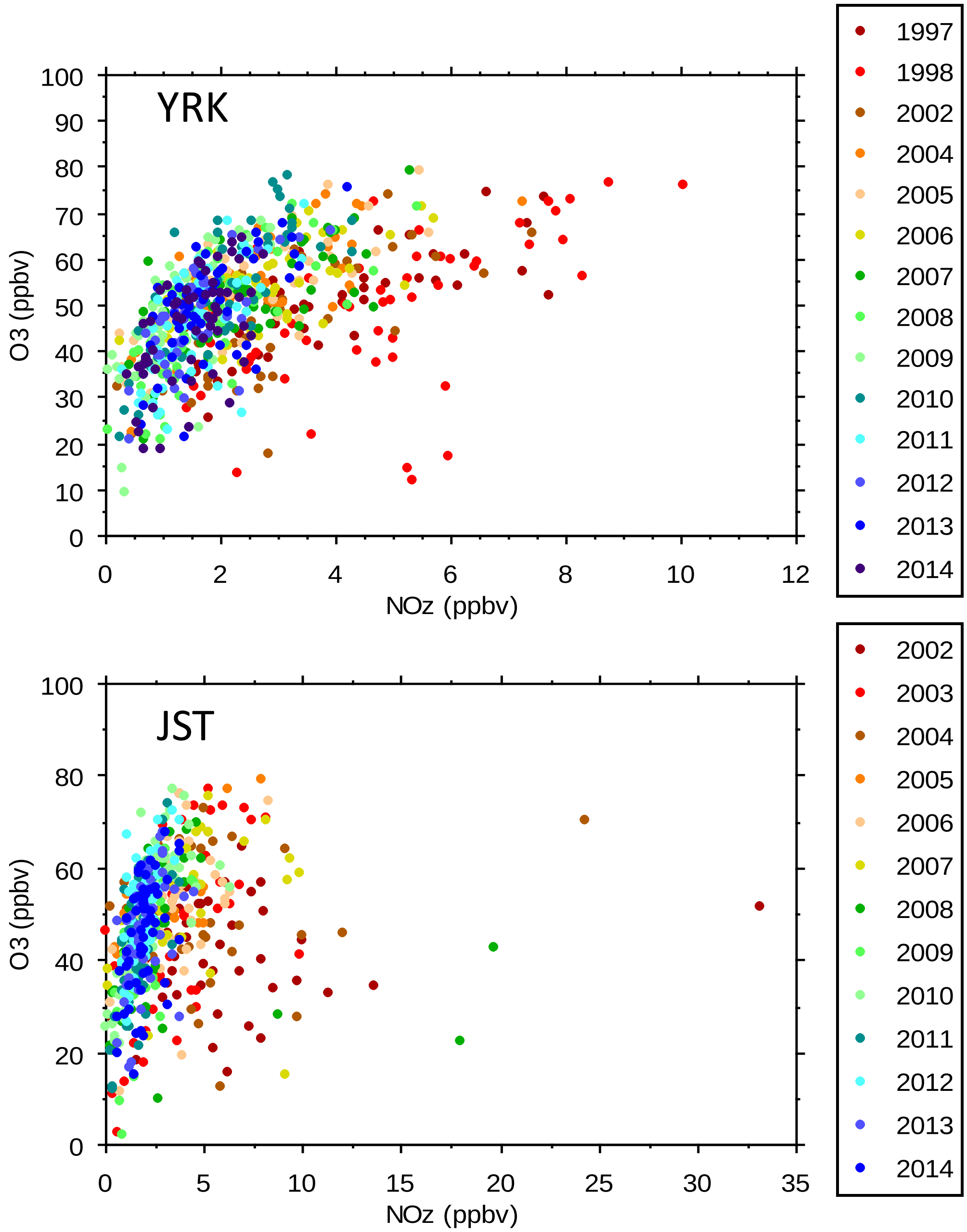

Figure S16. O_3 vs. NO_z during April and May at JST and YRK. Each point is the 2 – 3 p.m. hourly average on one day. YRK year-specific linear regressions are statistically significant ($p < 0.0001$) for all years. Example slopes are 4.85 ± 0.64 (1 SE) in 1997, 5.89 ± 0.79 in 2005, 8.95 ± 1.46 in 2013, and 10.3 ± 2.0 in 2014. JST year-specific linear regressions are statistically significant ($p < 0.001$) for 2003 (slope = 4.67 ± 1.01, 1 SE), 2005 (slope = 3.92 ± 0.88), 2006 (slope = 3.81 ± 0.94), and 2009 – 2014 (slopes = 9.53 ± 1.65 in 2009, 8.19 ± 0.95 in 2010, 9.79 ± 1.64 in 2012, and 8.25 ± 1.97 in 2014).

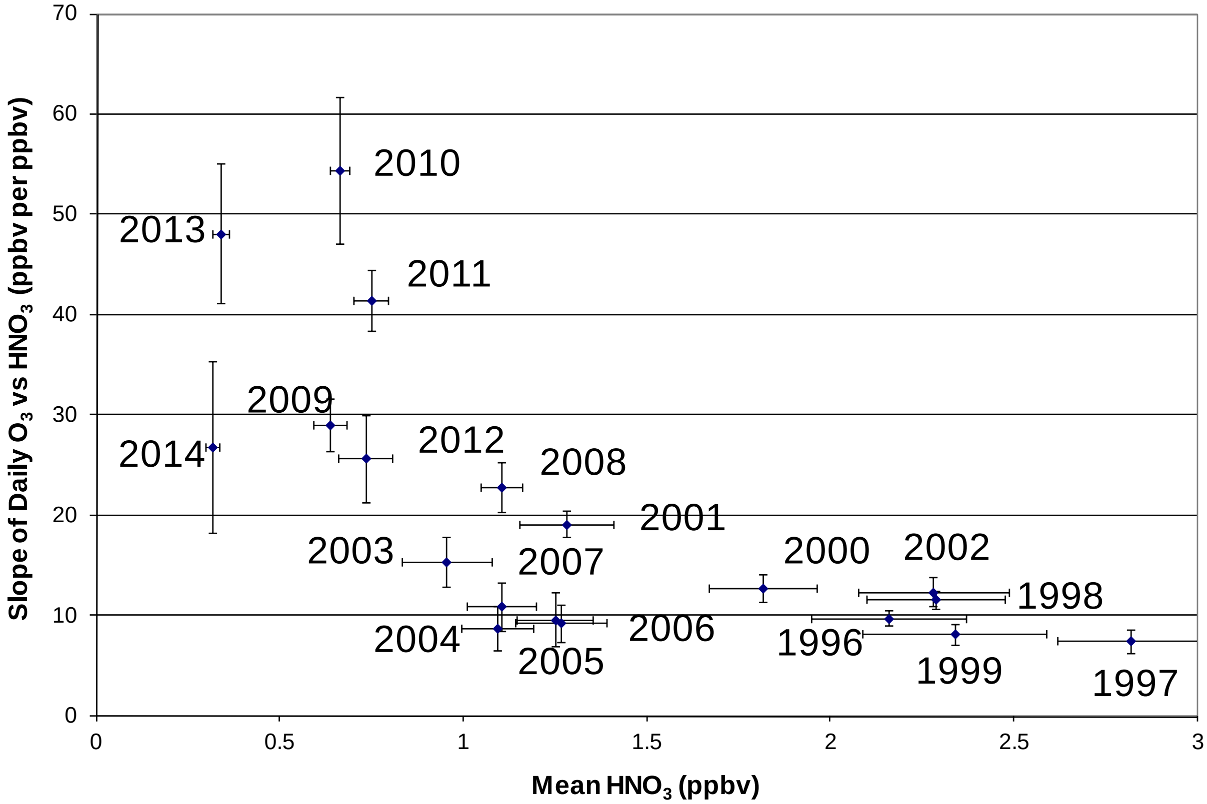

Figure S17. Summer slope of daily (2 p.m.) O_3 and HNO_3 vs. mean (2 p.m.) HNO_3 at YRK. Vertical and horizontal error bars are one standard error of the regression slopes and one standard error of the HNO_3 means, respectively.

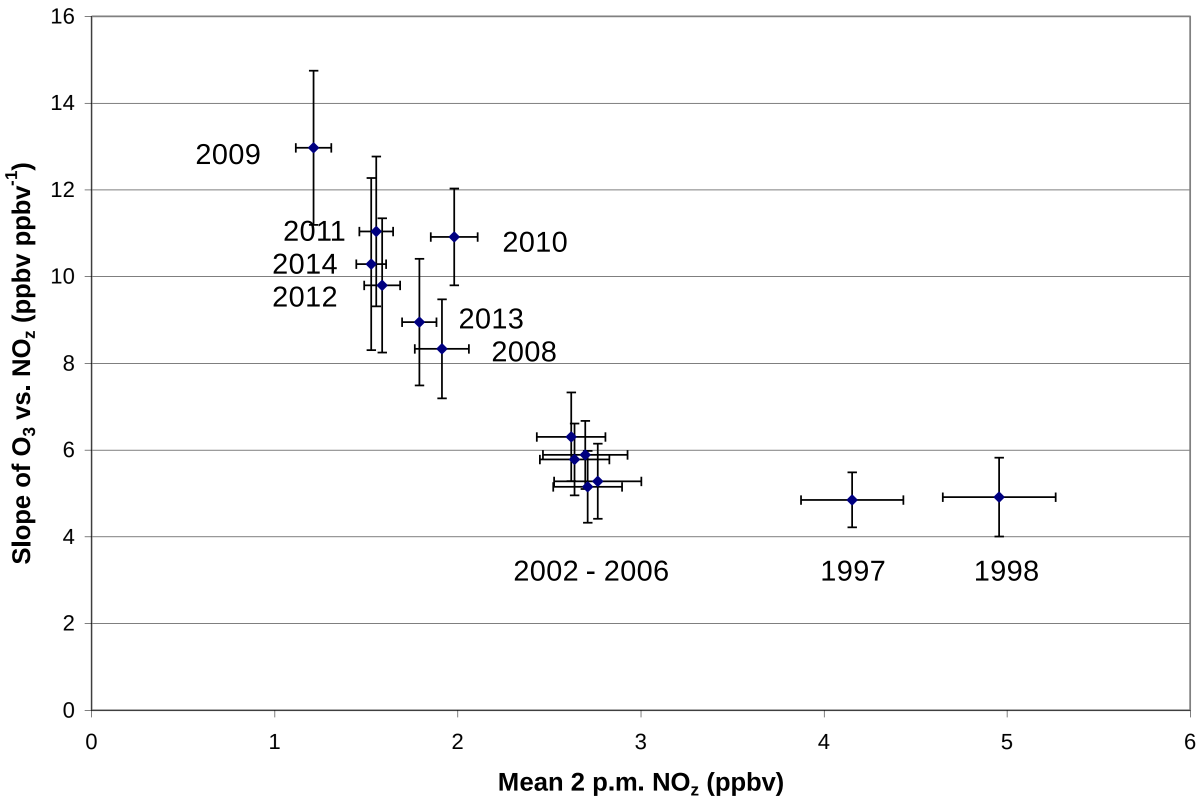

Figure S18. Spring slope of daily (2 p.m.) O_3 regressed against NO_z vs. mean (2 p.m.) NO_z at YRK. Vertical and horizontal error bars are one standard error of the regression slopes and one standard error of the NO_z means, respectively.

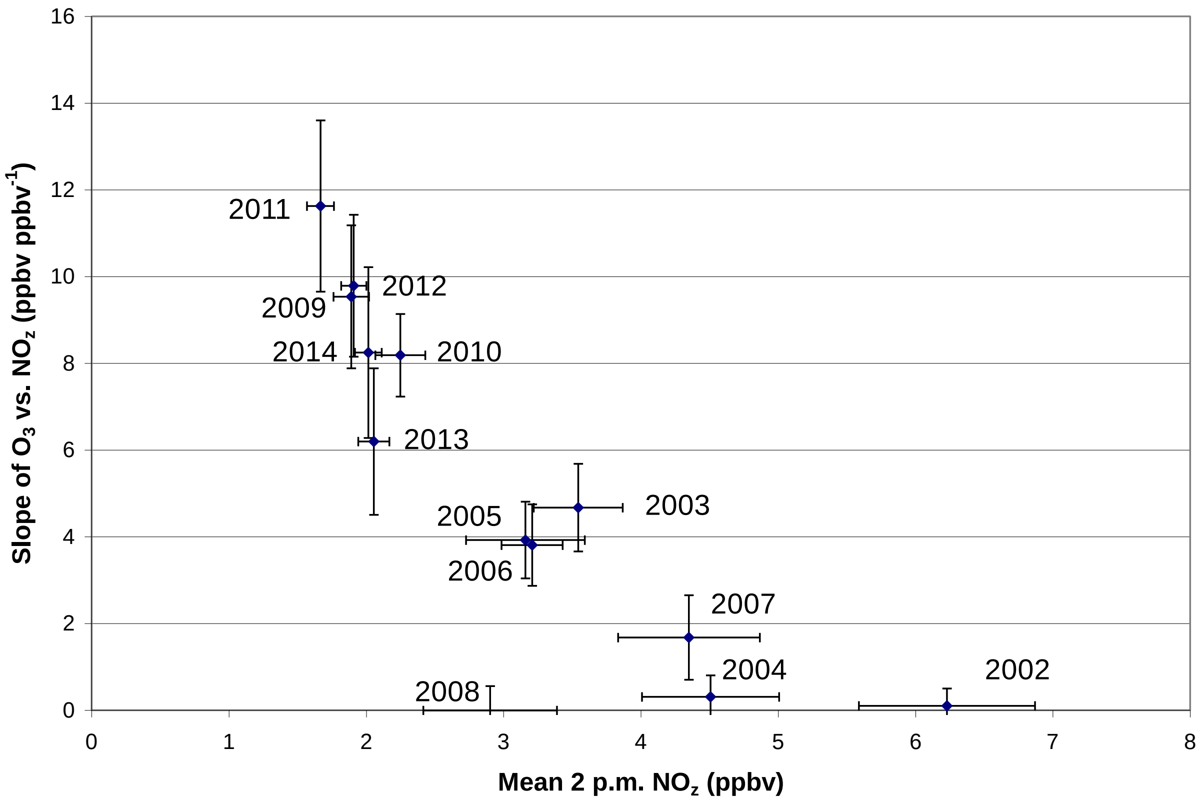

Figure S19. Spring slope of daily (2 p.m.) O_3 regressed against NO_z vs. mean (2 p.m.) NO_z at JST. Vertical and horizontal error bars are one standard error of the regression slopes and one standard error of the NO_z means, respectively.