



Supplement of

Explaining trends and changing seasonal cycles of surface ozone in North America and Europe over the 2000–2018 period: a global modelling study with NO_x and VOC tagging

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S1: Ozone production from ship NO_x: zero-order sanity check

To ascertain the potential overestimation of ozone produced from shipping NO_x in the model, we performed a zero order sanity check as suggested by one of the reviewers: they suggested that in the northern hemispheric midlatitudes, within the marine boundary layer (MBL), approximately 10 molecules of O₃ are produced from 1 molecule of emitted NO_x from ships during daytime in the photochemically active season of the year (based on the findings of Chen et al., 2005) and approximately 1.5 molecules of O₃ are lost as N₂O₅ per molecule of emitted NO_x at nighttime (based on Duncan et al., 2008). Let's assume a constant NO_x emission rate from ships for the entire 24h day. This would mean 10 molecules of O₃ produced from 1 molecule of NO_x in the daytime and 1.5 molecules of O₃ lost due to 1 molecule of NO_x at nighttime, or 8.5 net molecules of O₃ produced from 2 molecules of emitted NO_x in 24h. In other words, the net O₃ production is expected to be 4.25 molecules per molecule of emitted NO_x.

We tried performing this sanity check with the output data available to us. However, there were a number of obstacles to ascertaining the suggested 4.25 : 1 O₃-from-ship : ship-NO_x molar ratio as suggested by the reviewer. First, we only have monthly mean emissions from each source in the input and therefore cannot explicitly distinguish daytime and nighttime NO_x emitted from the ships. Second, (due to storage constraints) we do not output 3D ozone from different tags, including ships, at the hourly frequency; we output surface ozone from each tag at the hourly level but 3D ozone from all tags only at the monthly mean level. Therefore, we could only perform this MBL-wide analysis at the monthly mean scale. Using July 2018 as a representative month for the peak season, we calculated the total NO emitted from the shipping sector over northern hemisphere midlatitudes (30°N-60°N) to be 1.138e+10 moles. We then utilized the monthly mean 3D ozone concentration field from the ship NO_x tag (raw output being in mol/mol-of-dry-air) to calculate moles of O₃ attributed to ship NO_x over July 2018. We found the total global O₃ attributed to global ship NO_x to be 5.308e+11 moles, O₃ within the MBL attributed to global ship NO_x to be 8.703e+10 moles, and O₃ within the northern hemisphere midlatitude (NHML) band MBL attributed to global ship NO_x to be 8.019e+10 moles. The ratio of NHML MBL ozone produced from ship NO_x and the ship NO_x emissions over NHML turns out to be $8.019\text{e}+10 / 1.138\text{e}+10 = 7.04$ which is higher than the expected ratio of 4.25 as suggested by the reviewer.

However, we can immediately see the issue with this approach: here we have a large number of moles of NO in the denominator which were arrived at by multiplying the per second emission rate with the number of seconds in a month (a large number), while the numerator was governed by the monthly average O₃ concentration. If we perform the same calculation on a daily scale, the numerator won't change much (a daily O₃ concentration maybe quite similar to a monthly mean O₃ concentration) but the denominator (i.e. moles of NO emitted by ships in a day) would be substantially smaller, thereby making the ratio much larger. Therefore, a reliable sanity check could only be performed if we had tagged ozone

production rates rather than tagged ozone concentrations. Unfortunately, our current tagging system does not provide source-tagged ozone production rates so it is not feasible to estimate the molar ratio in a manner suggested by the reviewer.

However, the reviewer suggested that we can still derive some insights even from the tagged monthly steady-state ozone in the absence of tagged ozone production rates if we make use of ozone lifetime τ . Assuming the total global O₃ attributed to ship NO_x had a lifetime τ relative to total gross destruction of one month, it would be likely shorter in the summertime over northern mid-latitudes. In July in the marine boundary layer (where the ozone derived from ship emissions is primarily formed) that lifetime is estimated to be ~10 days (see discussion in Mims et al., 2022 and their Figures S4 and S5). However, some of the ship-derived ozone is transported to the cooler and drier free troposphere before destruction, so the effective overall lifetime for ship-derived ozone in summer at northern mid-latitudes might be approximately estimated as ½ month; thus, the ship NO_x-tagged ozone production rate in the NH MBL would be $8.019\text{e}+10/\tau$, or $8.019\text{e}+10/0.5$. Therefore, the *O₃-produced-from-ships:NO_x-emitted-from-ships* molar ratio would be $8.019\text{e}+10 * 2$ (ozone produced from ship NO_x in July) / $1.138\text{e}+10$ (NO_x emitted from ships in July) = 14.08, or $3.3*4.25$, which suggests an overestimation by a factor of 3.3.

S2: Technical description of fourier decomposition of ozone seasonal cycles:

We use the NCL function *fourier_info* (https://www.ncl.ucar.edu/Document/Functions/Built-in/fourier_info.shtml) to decompose the MDA8 O₃ seasonal cycles for individual years as well as multi-year averages into two harmonics. The Fourier transform is similar to the one described in Parrish et al. (2016) where they express ozone seasonal cycle time series as following: $y = y_0 + A_1 \sin(x + \phi_1) + A_2 \sin(2x + \phi_2)$.

Here, y represents the full seasonal cycle, y_0 is the annual mean, A_1 and A_2 (expressed in ppb) represent the amplitudes of the fundamental and second harmonics respectively, and ϕ_1 and ϕ_2 are phase offsets expressed in months. Here, x spans a year's time in months from 0 to 2π . While Parrish et al. (2016) report these five parameters (y_0 , A_1 , A_2 , ϕ_1 , and ϕ_2), we report y_0 , A_1 and A_2 but report the phases for the two harmonics (p_1 and p_2) in months spanning from 0 to 12. They refer to the exact timing of the peak in months for the two harmonics.

For intercomparison with previous studies which report the actual phase angles in months, the following conversion formula may be used:

$$\text{Phase angle for the fundamental harmonic: } \phi_1(\text{rad}) = \frac{\pi}{2} - \frac{2\pi}{T} p_1$$

$$\text{Phase angle for the second harmonic: } \phi_2(\text{rad}) = \frac{\pi}{2} - \frac{4\pi}{T} p_2$$

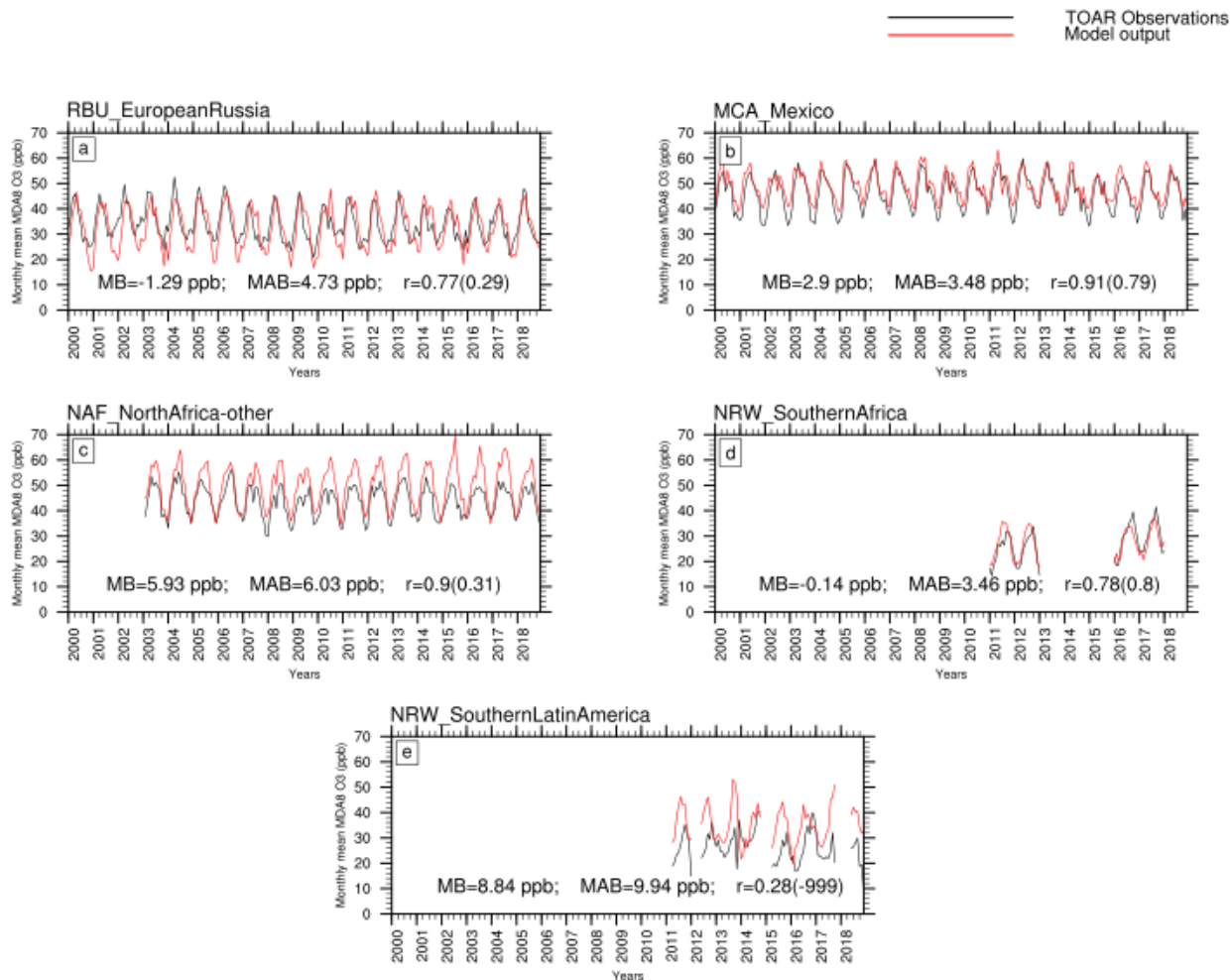


Figure S1: Time series of observed versus simulated monthly mean MDA8 O₃ for various receptor regions. Only rural stations data were utilized from the TOAR database and model output was fetched only for those gridcells where observations were available.

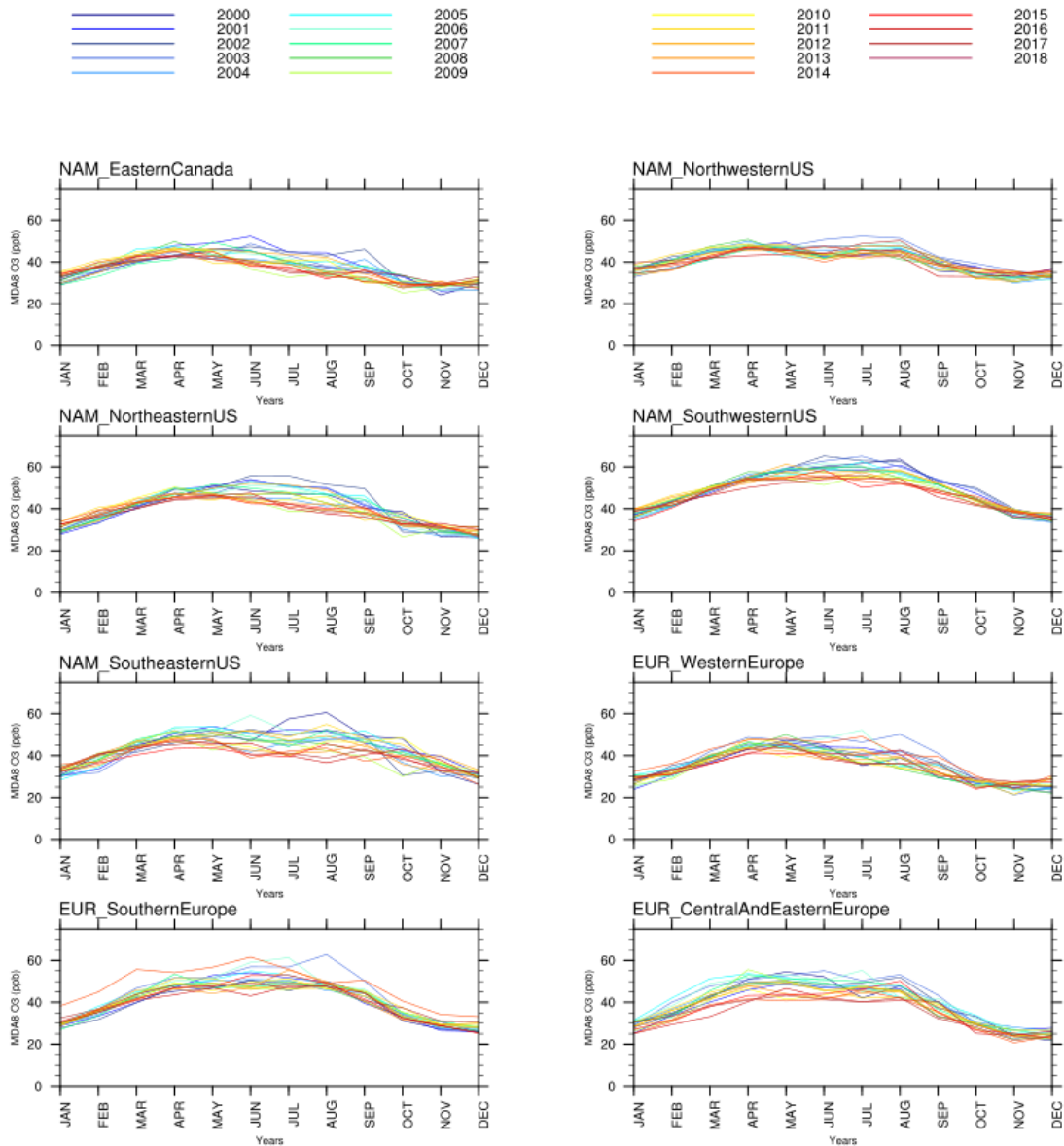


Figure S2: Envelope plots for regional averaged observed MDA8 O₃ seasonal cycles for 2000-2018 for different receptor regions in North America and Europe. Data was sampled from the gridded TOAR-II dataset.

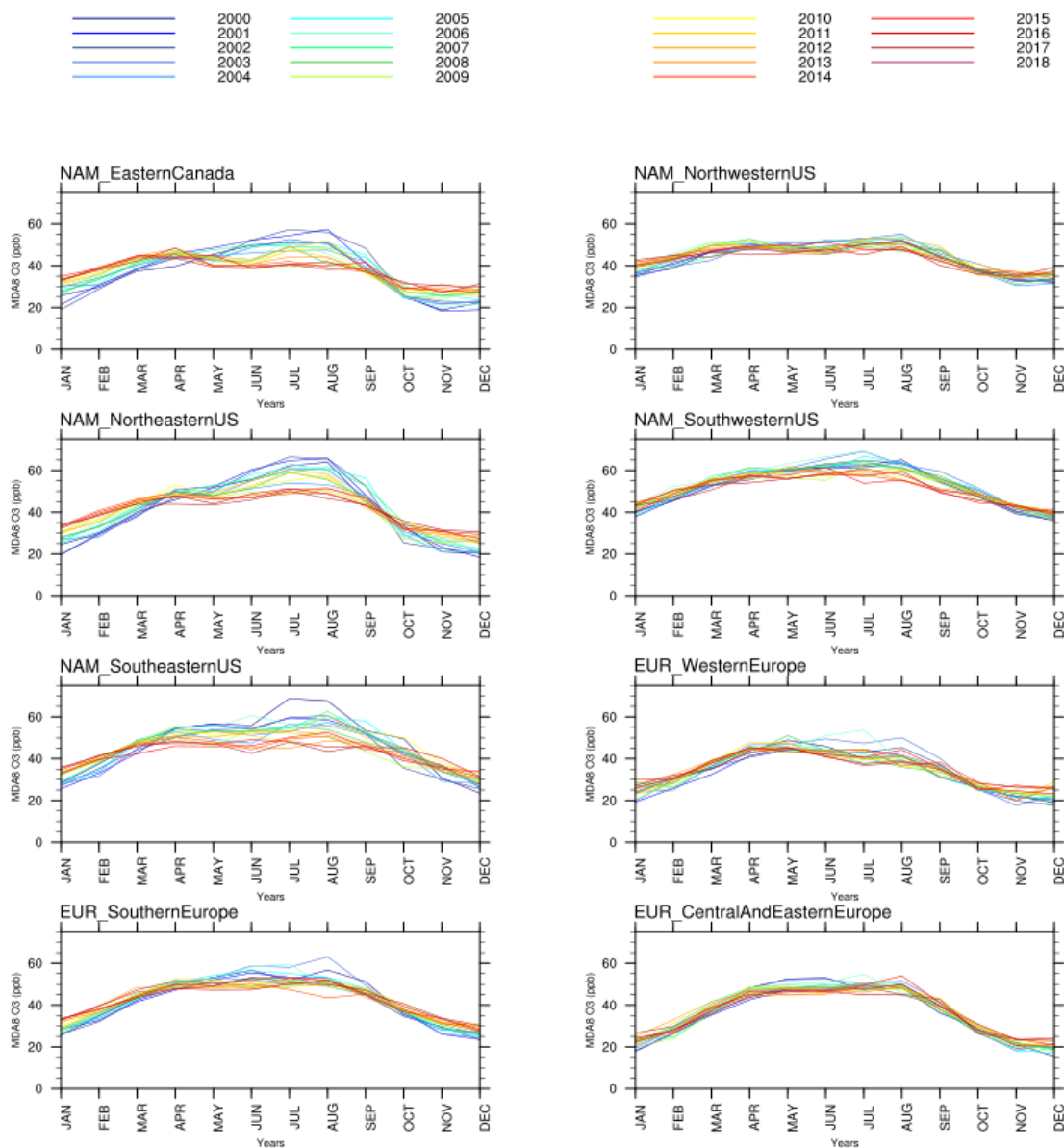


Figure S3: Envelope plots for regional averaged modelled MDA8 O₃ seasonal cycles for 2000-2018 for different receptor regions in North America and Europe. Model output was sampled only from TOAR-valid grid cells.

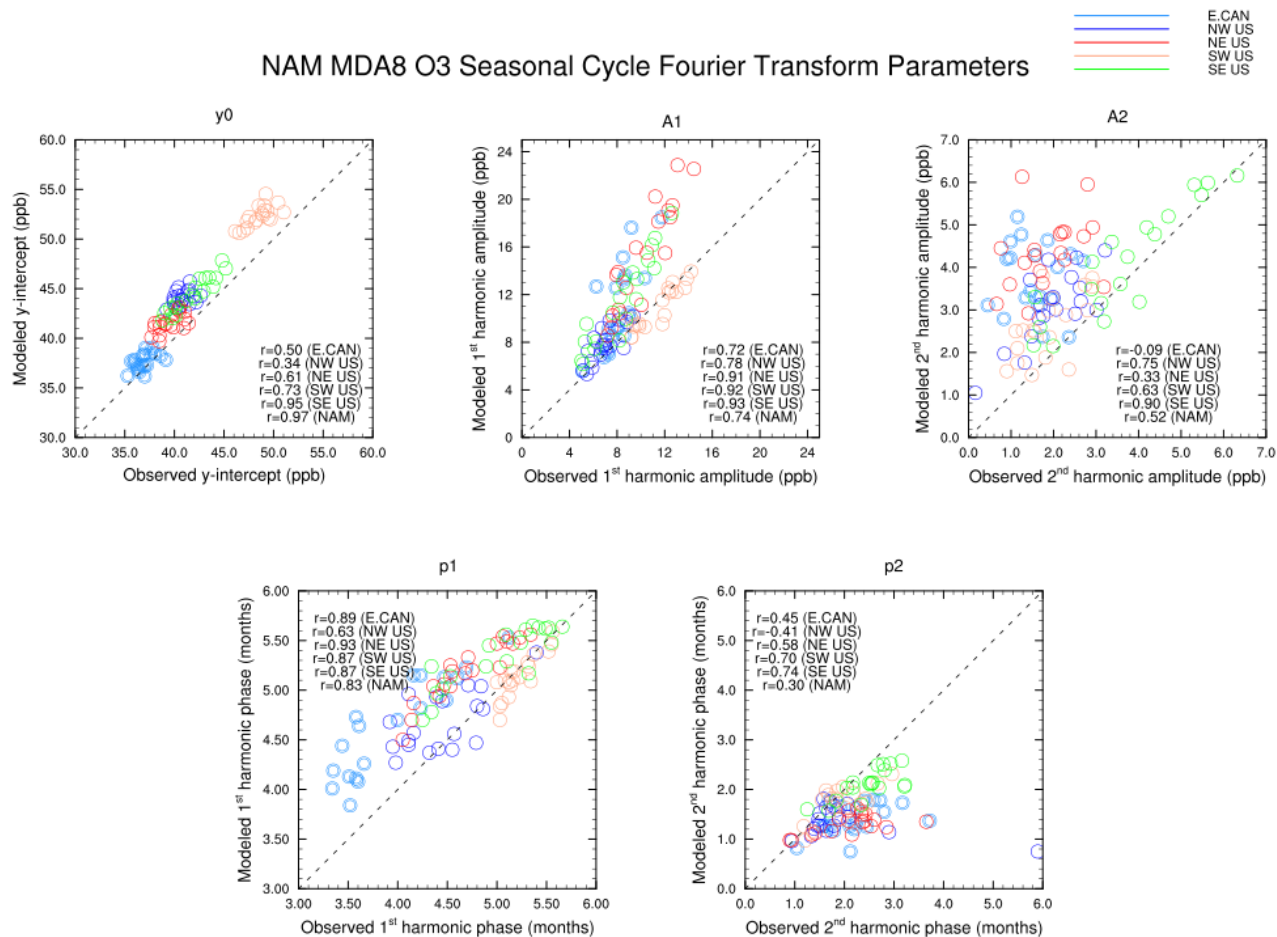


Figure S4: Scatterplots showing correlations between various Fourier transform parameters for observed and modelled MDA8 O3 seasonal cycles. Each plot contains 95 markers representing 19 data points per year for the five NAM receptor regions. Correlation coefficients are reported for modelled vs observed parameters in individual receptor regions as well as for all five regions combined (NAM).

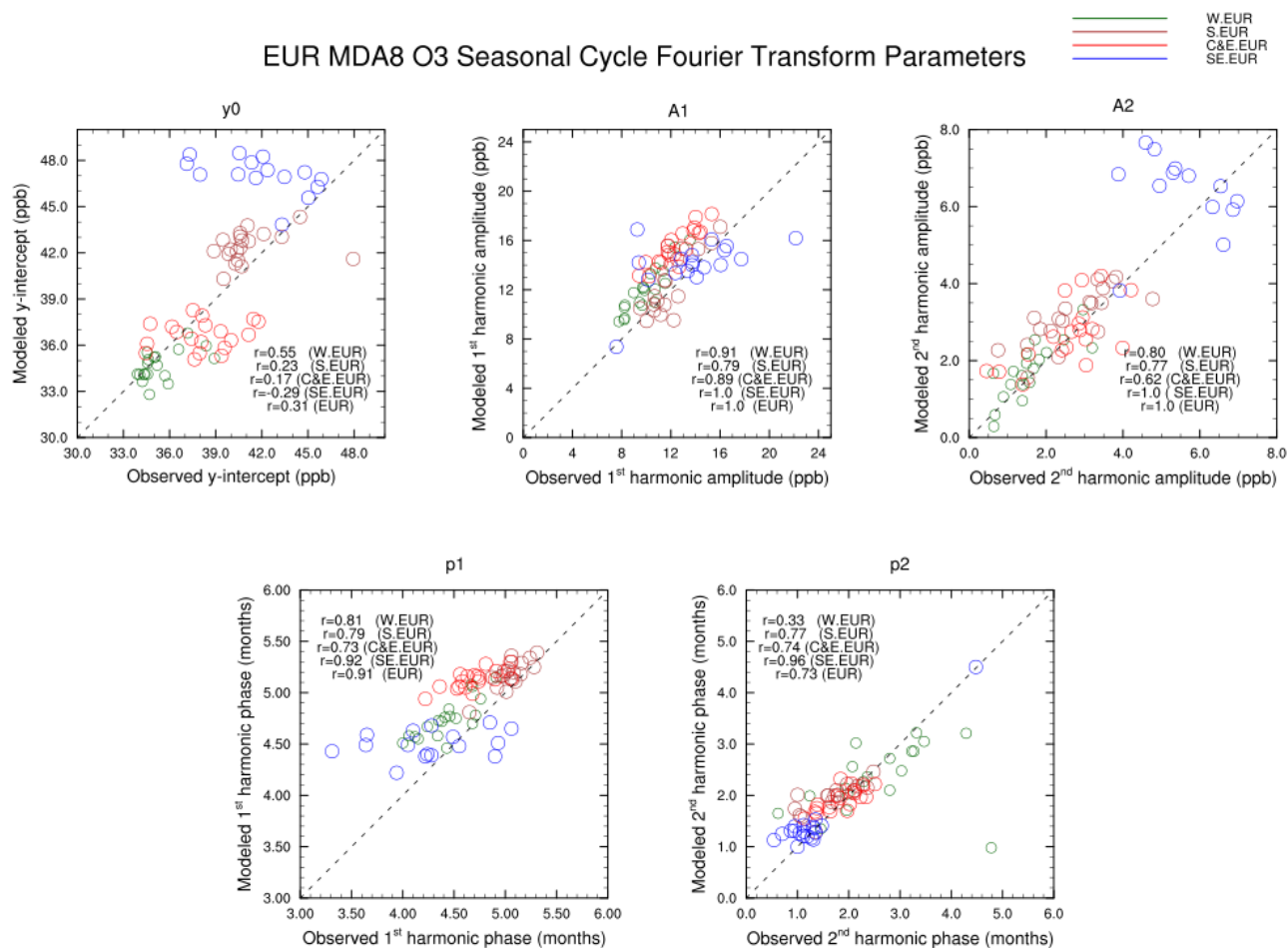


Figure S5: Scatterplots showing correlations between various Fourier transform parameters for observed and modelled MDA8 O3 seasonal cycles. Each plot contains 76 markers representing 19 data points per year for the four EUR receptor regions. Correlation coefficients are reported for modelled vs observed parameters in individual receptor regions as well as for all four regions combined (EUR).

O3 Vertical Profiles at Trinidad Head for July (2000-2018)

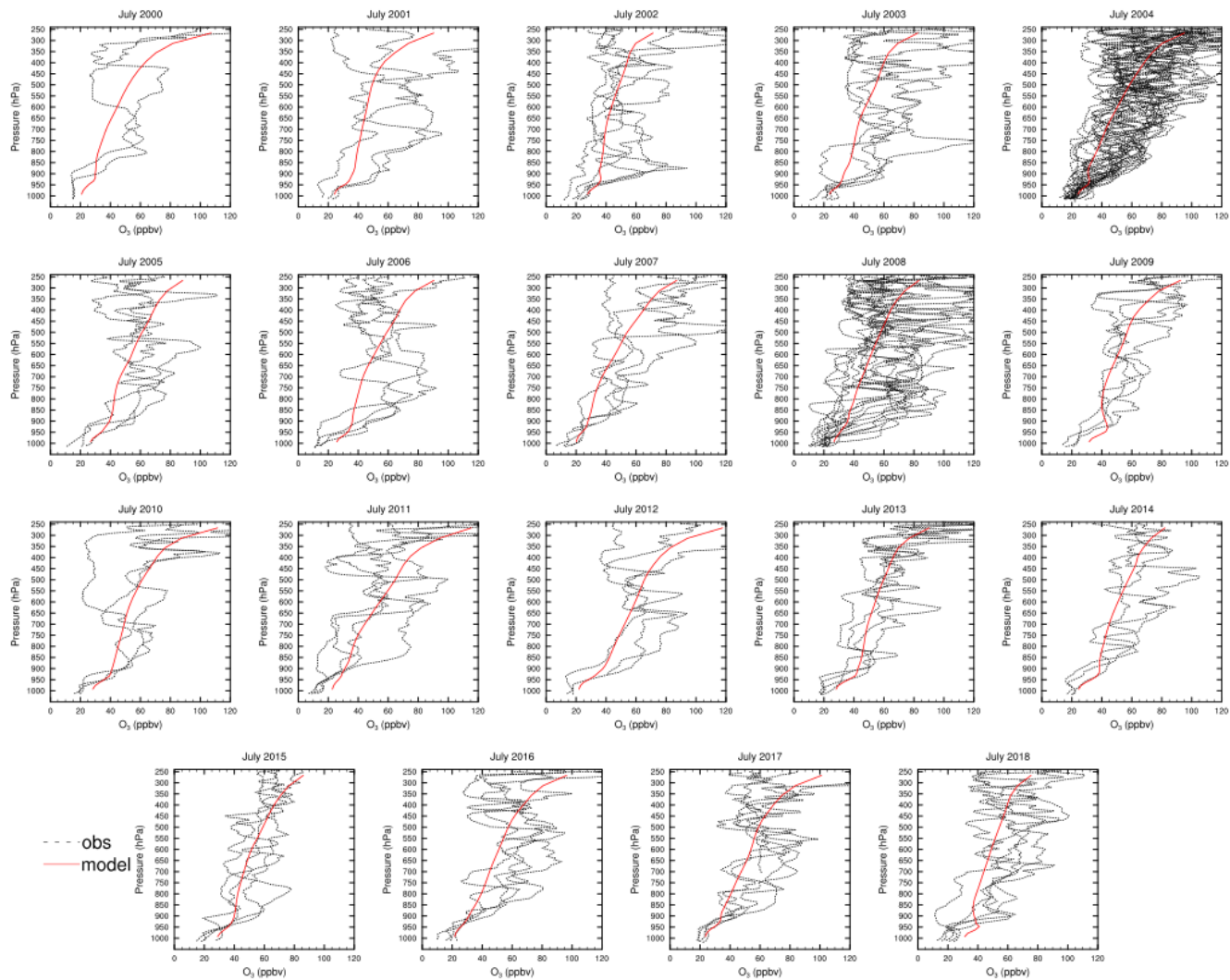


Figure S6: Vertical profiles of daily observed ozone (black) and model simulated monthly mean ozone at Trinidad Head for the month of July over 2000 to 2018.

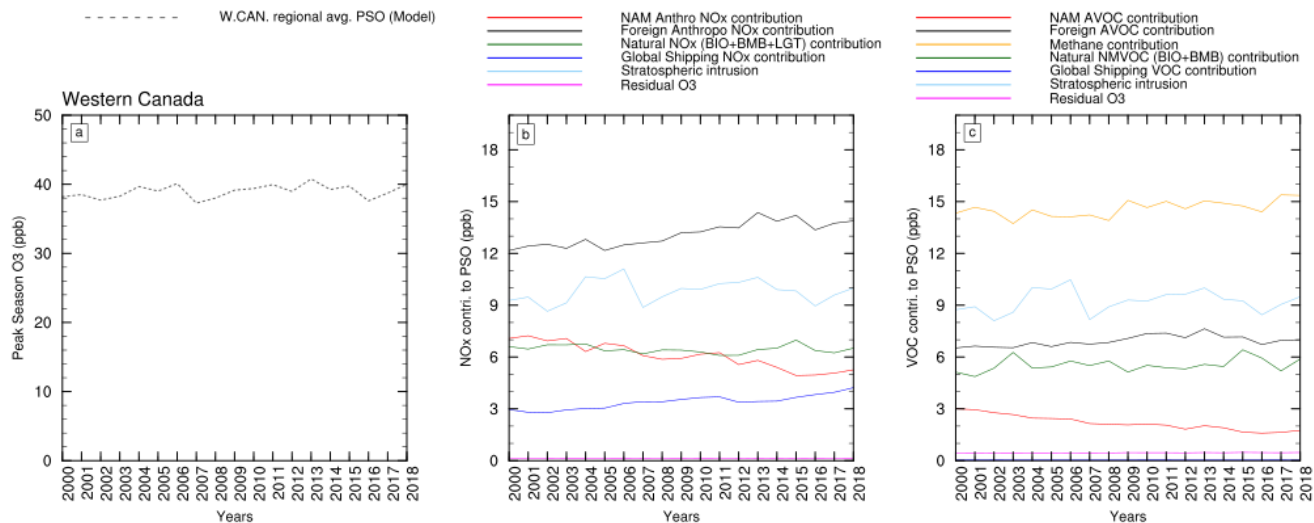


Figure S7: Time-series of model-derived PSO for Western Canada for 2000-2018 (a) and its source contributions in terms of NO_x sources (b) and VOC sources (c). Model output was sampled from the entire Western Canada HTAP Tier 2 region since TOAR observations were not available.

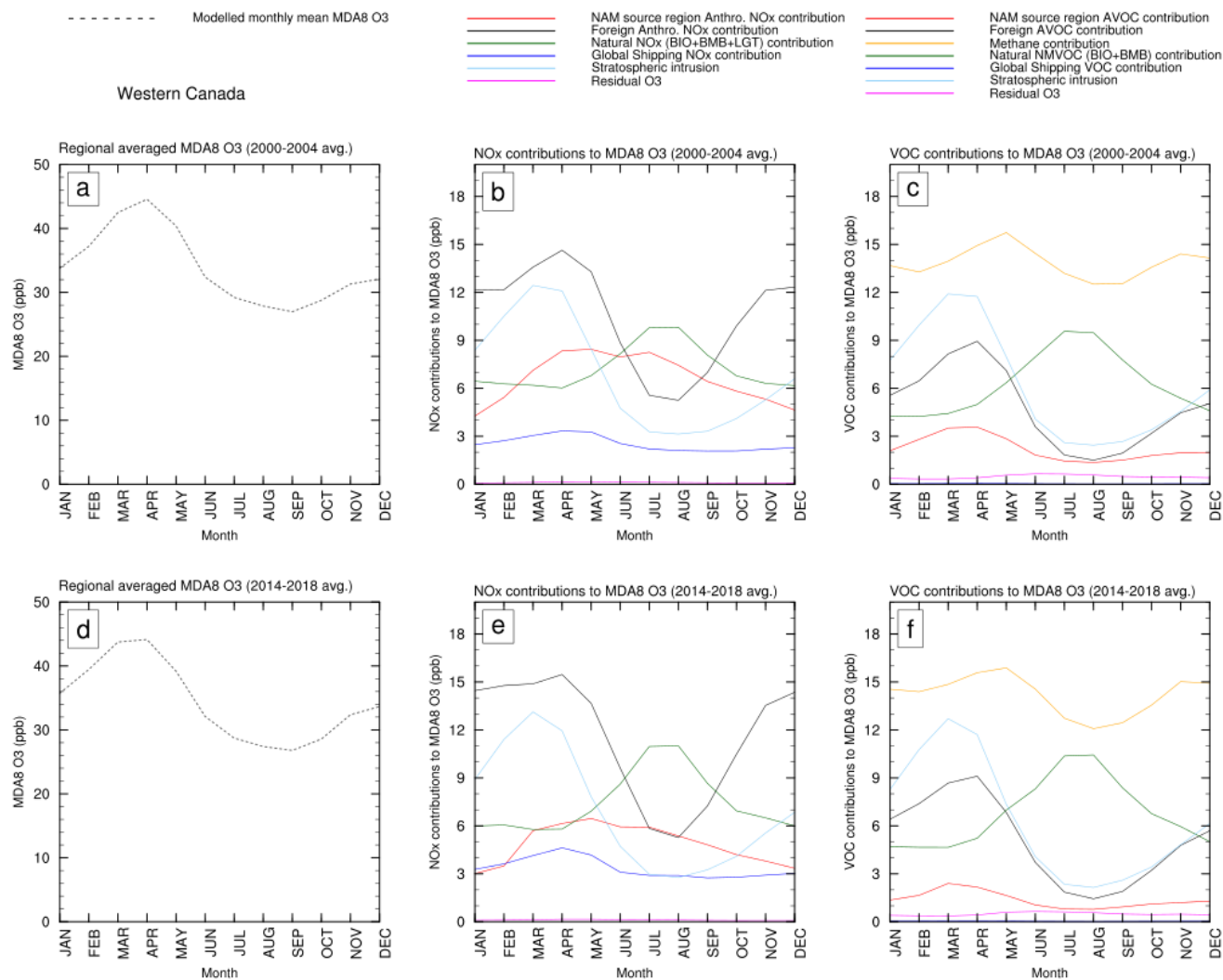


Figure S8: 5-year average MDA8 O₃ seasonal cycles for Western Canada for 2000-2004 (a) and 2014-2018 (d) along with their NO_x (b,e) and VOC contributions (c,f).

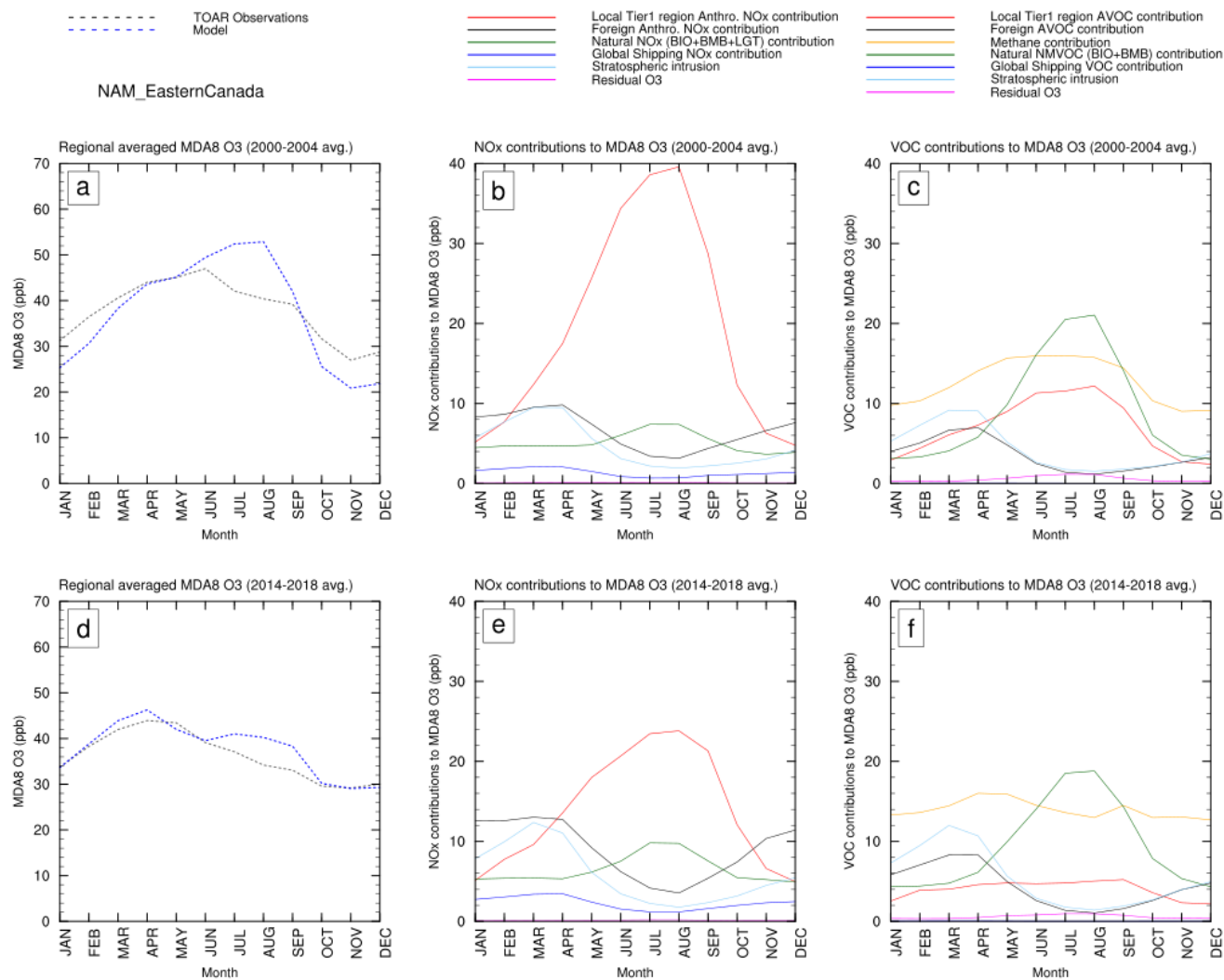


Figure S9: 5-year average MDA8 O₃ seasonal cycles for Eastern Canada for 2000-2004 (a) and 2014-2018 (d) along with their NO_x (b,e) and VOC contributions (c,f).

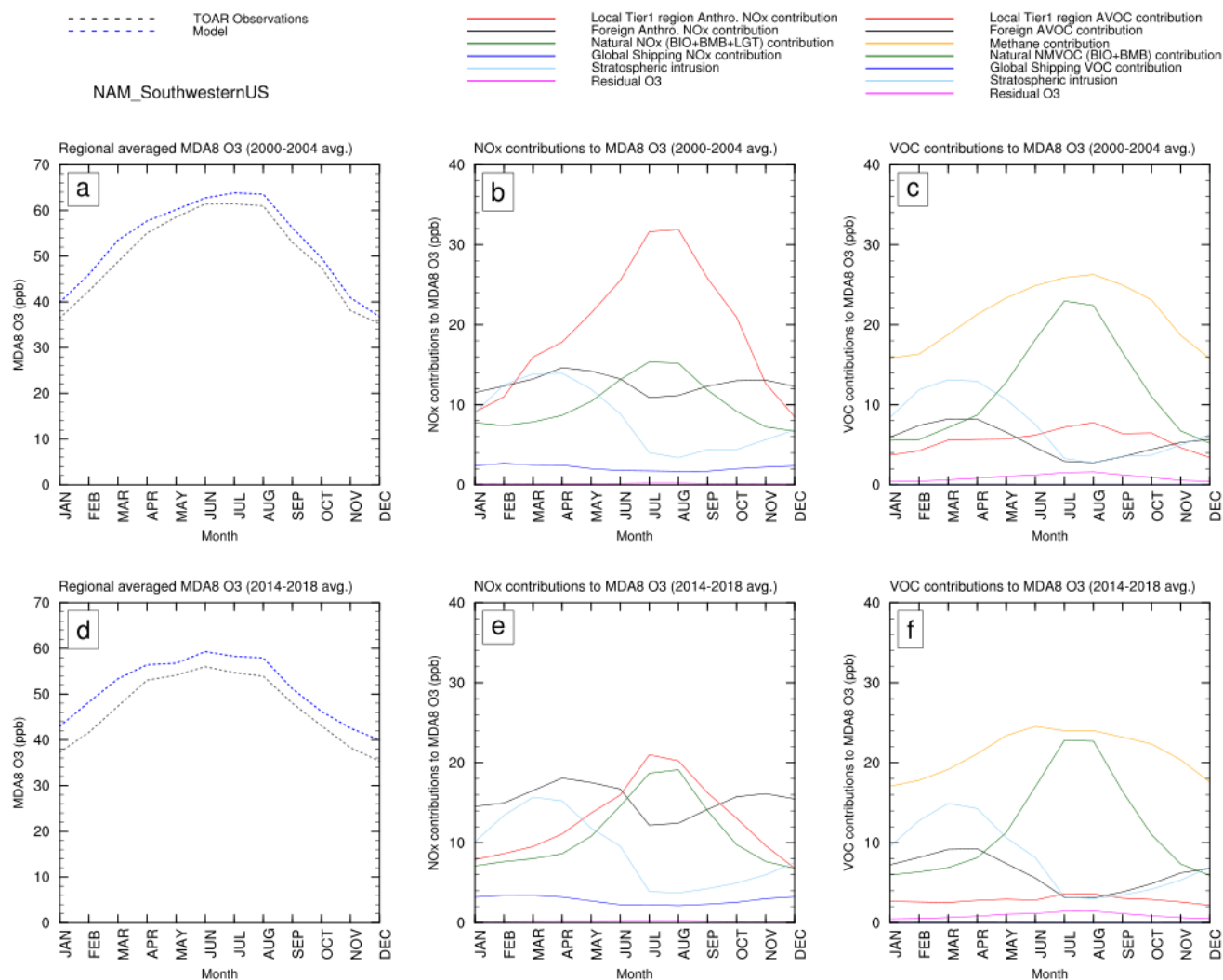


Figure S10: 5-year average MDA8 O₃ seasonal cycles for Southwestern US for 2000-2004 (a) and 2014-2018 (d) along with their NO_x (b,e) and VOC contributions (c,f).

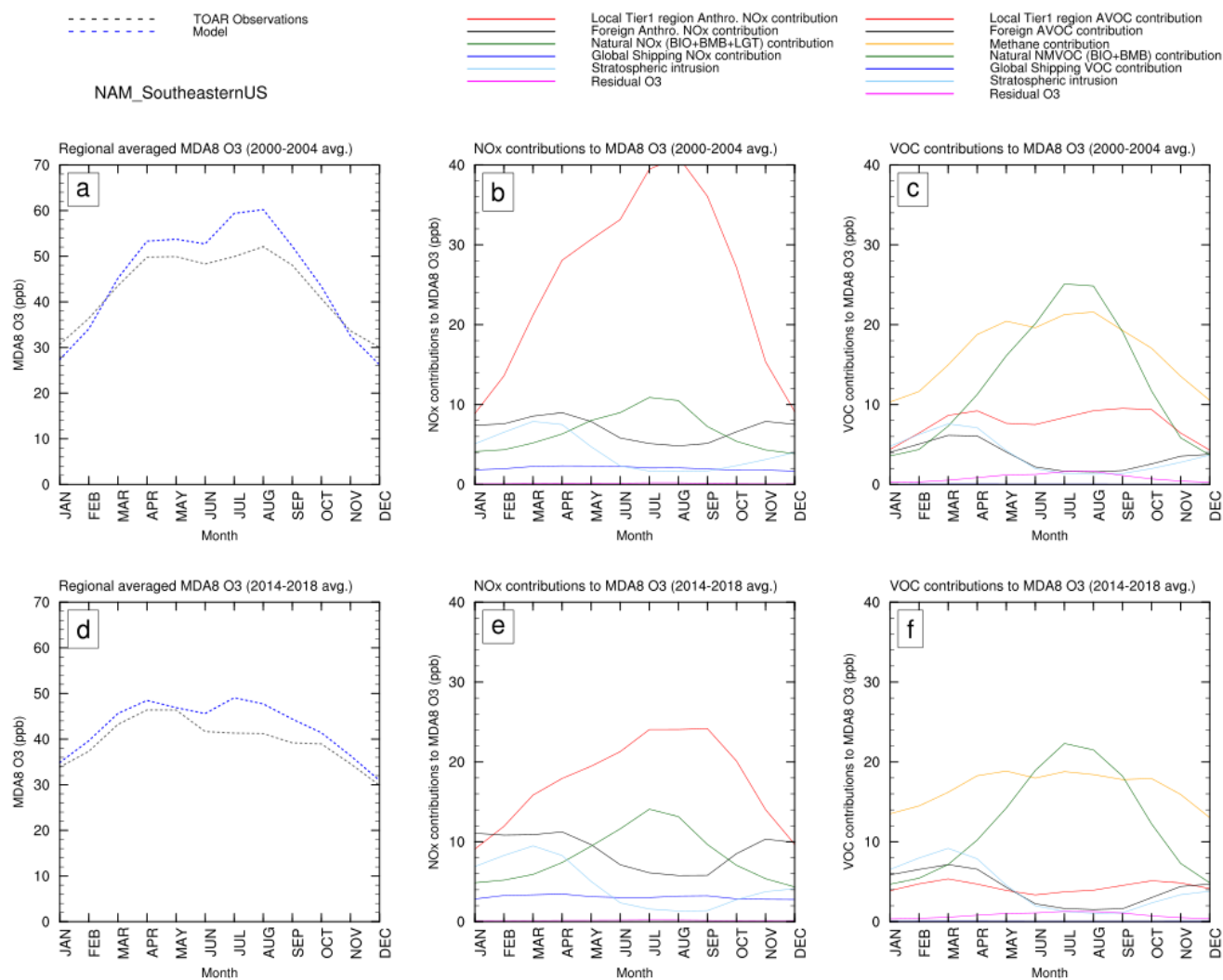


Figure S11: 5-year average MDA8 O₃ seasonal cycles for Southeastern US for 2000-2004 (a) and 2014-2018 (d) along with their NO_x (b,e) and VOC contributions (c,f).

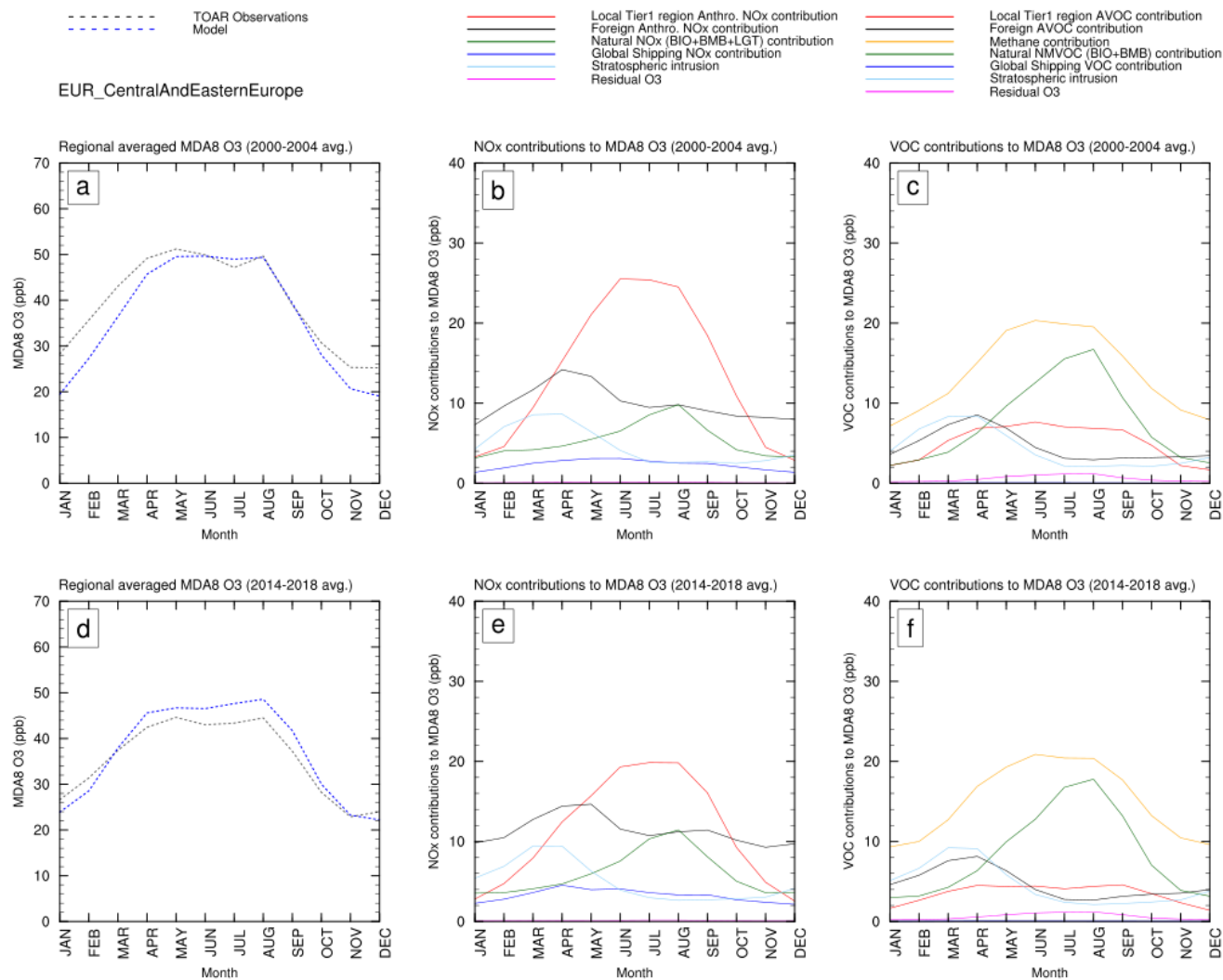


Figure S12: 5-year average MDA8 O₃ seasonal cycles for Central & Eastern Europe for 2000-2004 (a) and 2014-2018 (d) along with their NO_x (b,e) and VOC contributions (c,f).

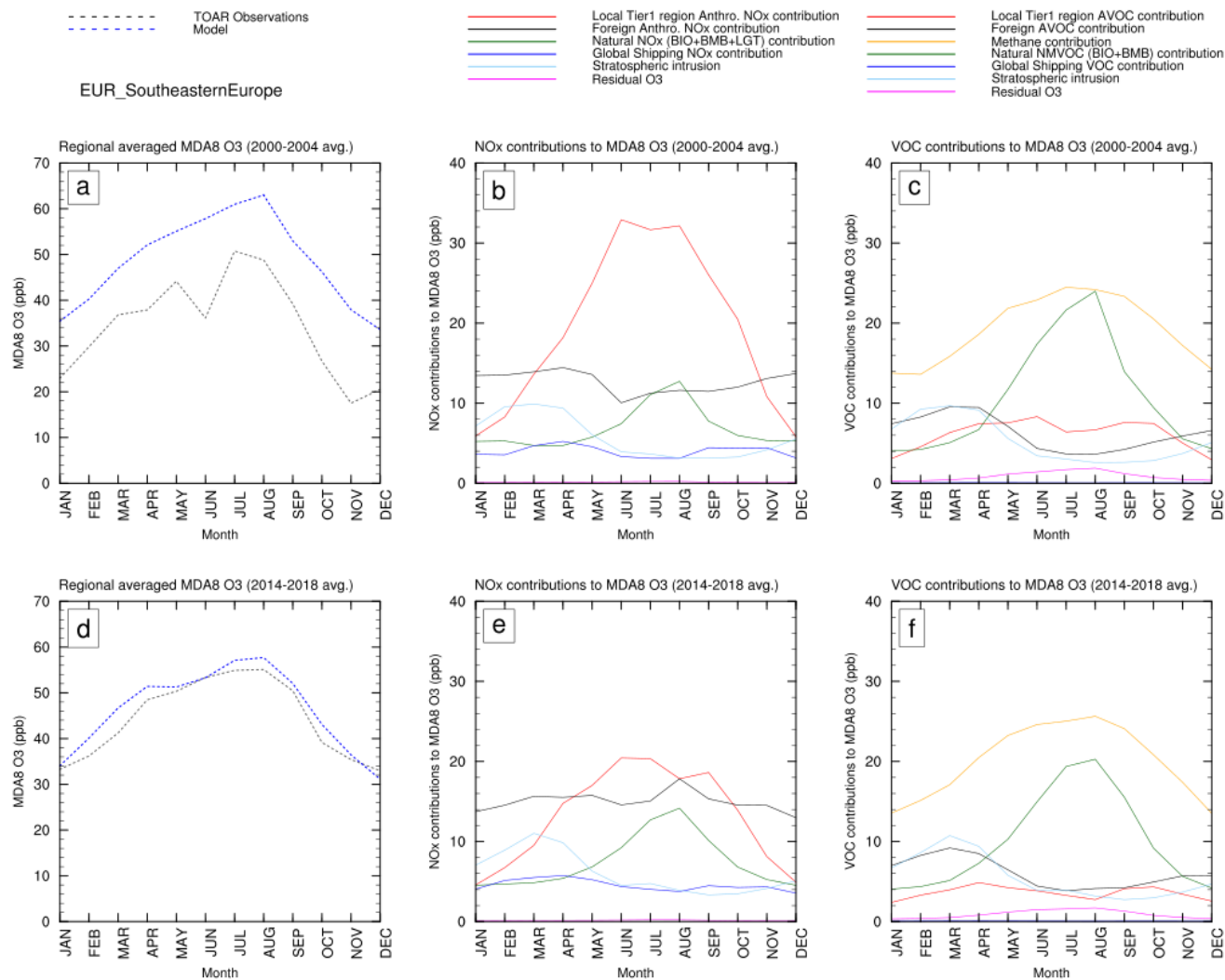


Figure S13: 5-year average MDA8 O₃ seasonal cycles for Southeastern Europe for 2000-2004 (a) and 2014-2018 (d) along with their NO_x (b,e) and VOC contributions (c,f).

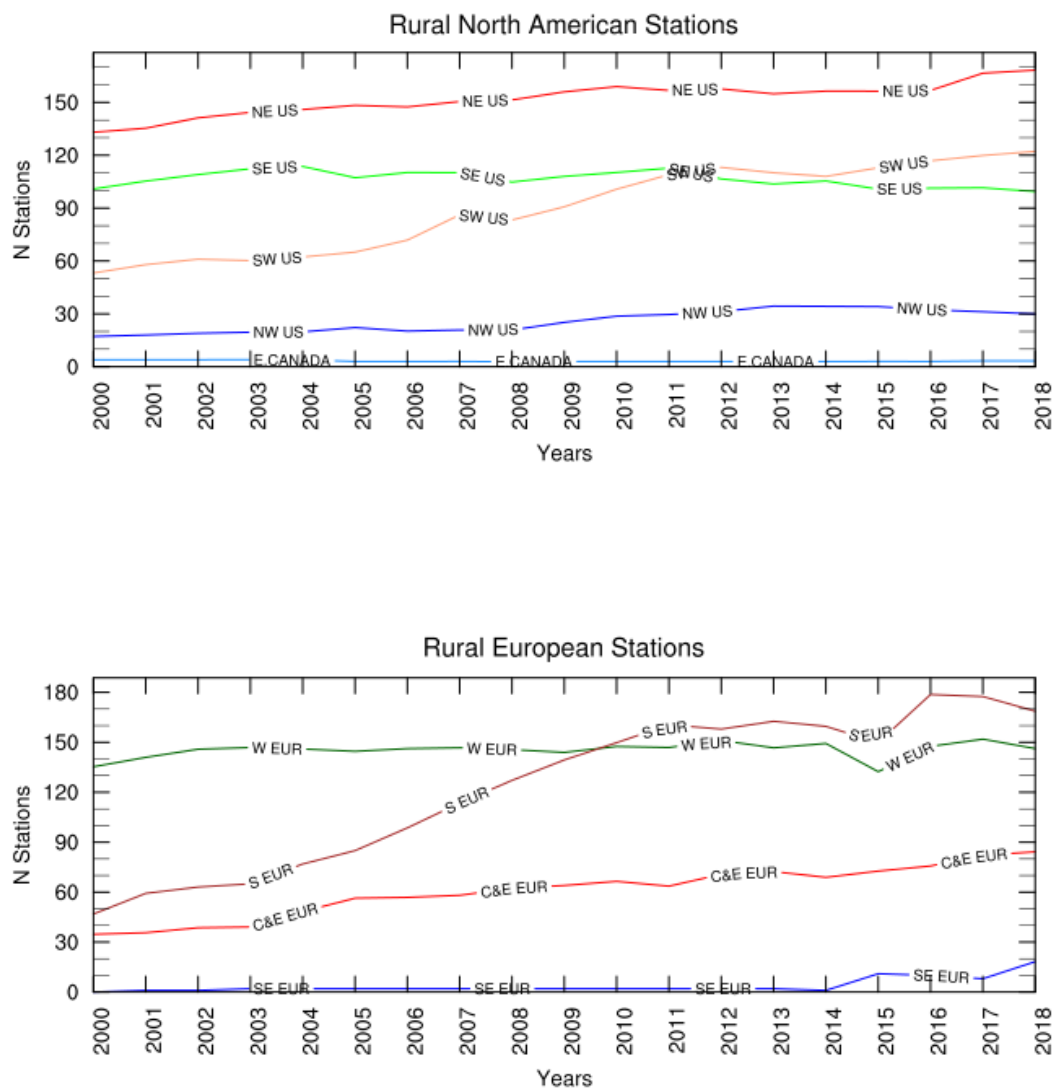


Figure S14: Average number of TOAR rural stations available per year within each receptor region for North America (top) and Europe (bottom) for the 2000-2018 period.

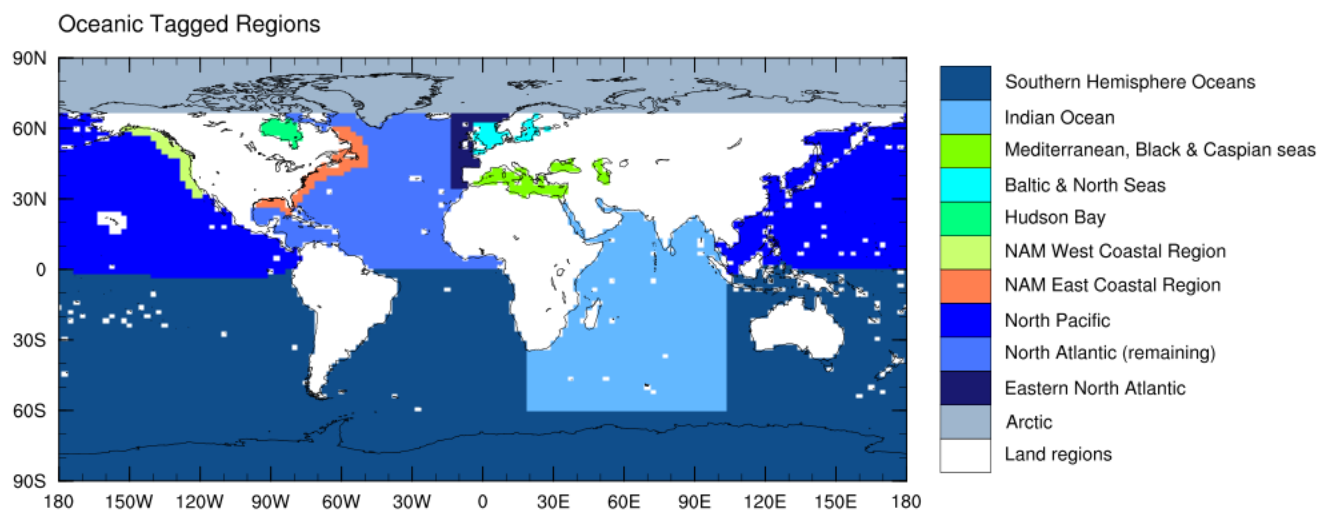


Figure S15: Map of oceanic tagged regions in the NO_x- and VOC-tagged simulations.

Local anthro. NOx contr. to PSO with exponential fit $y = A \exp(-1/\tau t)$

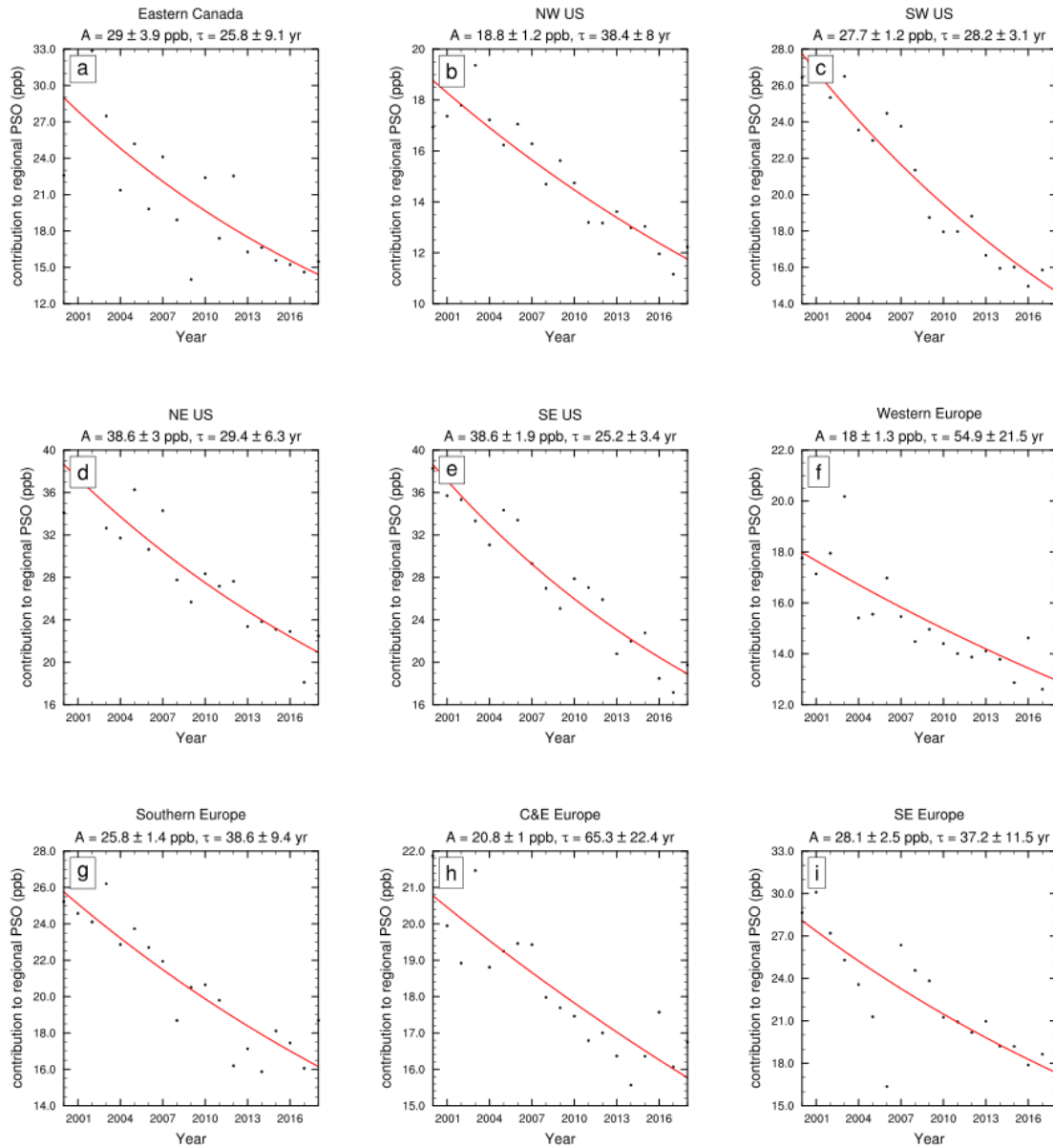


Figure S16: Exponential fits to the local anthropogenic NOx contribution to regional PSO values for all the nine receptor regions. The fit parameters A and τ are also included for each region along with their respective uncertainty values (half width of the 95% confidence intervals).

Table S1: Harmonic Analysis parameters derived from observed and modelled yearly MDA8 O3 seasonal cycle for Eastern Canada. A1 and p1 denote the amplitude and frequency of the first harmonic while A2 and p2 denote the amplitude and frequency of the second harmonic

Year	y0 (ppb)		A1 (ppb)		p1 (months)		A2 (ppb)		p2 (months)	
	obs	model	obs	model	obs	model	obs	model	obs	model
2000	37	36.16	8.49	15.13	4.23	5.15	0.9	4.2	2.12	0.75
2001	39.14	37.83	11.75	18.48	4.69	5.23	1.24	4.77	2.2	1.2
2002	38.62	38.24	9.2	17.62	5.12	5.53	1.86	4.64	1.79	1.17
2003	37.23	37.3	8.69	13.6	4.47	5.13	0.99	4.61	1.04	0.82
2004	36.95	37.16	6.25	12.68	4.23	4.82	2.4	4.31	1.7	1.25
2005	38.03	38.46	8.58	13.29	4.16	5.15	2.7	4.15	2.11	1.26
2006	36.45	36.62	10.32	13.39	4	4.7	1.15	5.19	2.45	1.25
2007	37.08	39.02	7.9	12.58	4.6	5.12	2.36	2.36	3.72	1.37
2008	36.29	36.94	8.98	10.44	3.58	4.73	1.74	2.37	2.8	1.55
2009	35.28	36.22	7.92	9.07	3.35	4.19	1.68	3.31	2.72	1.78
2010	37.56	38.43	8.07	9.26	3.61	4.64	1.46	3.45	1.6	1.27
2011	36.65	37.33	7.27	9.05	3.44	4.44	1.58	4.29	1.57	1.26
2012	37.8	39.05	9.11	10.15	4.49	4.9	0.98	4.22	2.22	1.32
2013	37.01	38.39	7.58	8.48	3.66	4.26	1.34	3.29	2.23	1.63
2014	35.97	37.47	7.3	7.01	3.34	4.01	1.64	3.1	1.92	1.66
2015	35.99	37.84	7.19	7.26	3.58	4.11	2.09	4.01	2.4	1.77
2016	35.64	37.69	6.89	6.75	3.51	4.13	0.45	3.11	3.17	1.73
2017	36.31	37.24	5.09	5.59	3.6	4.08	1.99	3.25	2.59	1.79
2018	36.82	38.26	8.59	8.55	3.52	3.84	0.83	2.79	1.69	1.77
2000-2004	37.78	37.33	7.85	15.22	5.19	5.51	1.09	3.00	3.04	1.02
2014-2018	36.13	37.69	4.07	5.13	4.42	5.03	2.19	2.22	3.43	2.34
2000-2018	36.93	37.66	5.86	9.89	4.82	5.36	1.89	2.07	3.35	1.62

Table S2: Same as Table S2 but for NW US

Year	y0 (ppb)		A1 (ppb)		p1 (months)		A2 (ppb)		p2 (months)	
	obs	model	obs	model	obs	model	obs	model	obs	model
2000	40.18	43.06	6.73	9.19	4.11	4.96	1.76	2.86	1.63	1.64
2001	41.51	43.44	6.05	8.36	4.39	4.93	1.99	3.3	2.06	1.71
2002	42.2	43.64	7.37	9.81	4.71	5.05	2.51	2.91	1.5	1.27
2003	42.65	44.29	9.37	10.19	5.4	5.38	0.84	1.97	1.58	1.81
2004	40.64	43.32	8.16	9.88	4.11	4.49	2.06	3.01	1.48	1.4
2005	40.18	44.75	7.02	8.2	4.45	4.89	3.21	4.4	1.5	1.52
2006	41.56	45.71	8.83	9.69	4.57	4.56	2.42	3.77	1.39	1.21
2007	39.92	43.81	6.99	7.79	4.84	5.04	1.32	1.76	1.79	1.27
2008	40.76	43.81	7.43	7.69	3.95	4.43	2.54	4.23	1.72	1.75
2009	40.86	44.34	6.82	7.75	4.11	4.45	1.65	2.81	1.89	1.44
2010	40.4	44.24	5.55	7.26	4.16	4.57	1.45	3.71	1.78	1.67
2011	41.47	44.86	5.85	6.42	3.92	4.68	3.01	3	1.85	1.59
2012	40.42	45.14	8.55	7.52	4.8	4.84	1.88	4.18	1.63	1.17
2013	39.93	44.11	6.7	7.52	4.32	4.37	1.92	3.26	1.33	1.06
2014	39.95	43.6	5.12	5.62	4.55	4.4	1.7	3.12	2.1	1.45
2015	40.76	43.9	7.04	7.5	4.79	4.47	0.16	1.05	2.9	1.14
2016	39.24	42.89	5.46	5.33	3.98	4.27	1.48	2.38	5.9	0.75
2017	41.98	44.23	5.91	5.88	4.86	4.81	2.62	3.52	0.94	0.96
2018	41.31	44.73	6.6	6.96	4.41	4.41	2.64	3.2	1.45	1.27
2000-2004	41.43	43.54	6.50	9.01	5.22	5.43	1.08	1.82	2.38	1.86
2014-2018	40.64	43.87	5.24	5.33	5.18	5.33	0.29	1.14	1.94	1.25
2000-2018	40.83	44.09	5.87	7.06	5.16	5.38	0.97	1.71	2.3	1.66

Table S3: Same as Table S2 but for NE US

Year	y0 (ppb)		A1 (ppb)		p1 (months)		A2 (ppb)		p2 (months)	
	obs	model	obs	model	obs	model	obs	model	obs	model
2000	39.88	41.11	11.21	20.23	5.0	5.47	2.26	4.83	2.15	1.09
2001	41.06	41.93	13.08	22.87	5.23	5.53	1.32	4.11	2.85	1.24
2002	41.44	41.53	14.45	22.55	5.34	5.56	2.8	5.95	0.9	0.98
2003	40.94	41.03	12.46	18.5	5.16	5.47	1.55	4.28	1.74	1.16
2004	38.47	39.71	9.59	15.94	4.68	5.17	2.92	4.94	1.89	1.4
2005	41.04	42.67	12.65	19.49	5.06	5.54	2.2	4.83	2.08	1.37
2006	39.62	41.31	12.3	19.06	4.75	5.20	1.26	6.13	1.34	1.09
2007	40.49	43.1	11.47	18.13	5.10	5.49	2.15	4.78	2.43	1.5
2008	39	41.45	10.5	15.51	4.71	5.33	1.74	3.63	2.54	1.26
2009	37.68	40.09	8.77	12.57	4.16	4.87	1.68	3.91	2.37	1.34
2010	40.39	42.92	7.94	13.65	4.53	5.25	3.18	3.54	2.35	1.55
2011	39.64	42.31	8.09	13.89	4.55	5.19	1.55	4.41	1.41	1.12
2012	40.52	42.76	12.04	15.49	5.03	5.23	0.76	4.45	0.93	0.98
2013	39.15	41.44	8.12	10.73	4.42	4.94	2.17	4.34	2.08	1.57
2014	38.55	41.17	8.24	10.43	4.14	4.7	2.26	4.18	2.26	1.62
2015	38.48	41.63	7.62	10.23	4.53	5.04	2.71	4.73	2.34	1.49
2016	38.03	41.52	7.55	9.24	4.36	5.04	1.41	2.92	3.65	1.35
2017	38.49	40.29	7.21	8.56	4.47	5.06	0.97	3.6	2.41	1.37
2018	37.98	41.12	10.04	11.14	4.05	4.50	0.66	3.14	2.6	1.39
2000-2004	40.35	41.06	11.85	20.01	5.40	5.59	1.31	3.94	2.37	1.18
2014-2018	38.29	41.13	6.70	9.26	5.01	5.44	2.17	2.31	3.35	1.72
2000-2018	39.51	41.52	9.3	14.89	5.24	5.53	1.58	3.11	2.94	1.38

Table S4: Same as Table S2 but for SW US

Year	y0 (ppb)		A1 (ppb)		p1 (months)		A2 (ppb)		p2 (months)	
	obs	model	obs	model	obs	model	obs	model	obs	model
2000	49.69	51.99	13.87	13.34	5.32	5.24	2.91	3.55	1.55	1.79
2001	49.44	52.11	12.3	12.53	5.52	5.39	1.88	2.98	2.18	1.93
2002	51.03	52.7	13.7	12.57	5.55	5.46	1.28	2.52	1.78	1.65
2003	50.46	53.67	14.21	13.94	5.56	5.59	1.15	2.1	2.34	1.71
2004	48.93	52.38	12.97	12.23	5.12	5.08	2.29	2.88	1.85	1.80
2005	48.49	53.34	12.57	12.31	5.37	5.36	1.74	3.8	1.85	1.97
2006	49.21	54.54	12.66	13.05	5.08	5.1	1.11	2.5	1.2	0.97
2007	49.11	52.9	11.8	11.53	5.31	5.28	1.15	1.75	2.46	1.73
2008	49.04	53.38	12.36	12.18	5.0	5.08	1.98	3.27	1.75	1.82
2009	47.31	51.8	9.58	9.46	5.14	5.19	2.74	3.59	2.01	1.63
2010	48.13	51.71	9.22	9.98	5.14	5.05	2.91	3.75	1.97	2.05
2011	48.82	52.57	9.85	9.55	5.16	5.1	2.8	2.99	1.68	1.89
2012	49.37	52.82	11.81	9.53	5.23	5.13	1.9	2.36	2.42	1.81
2013	48.27	51.92	9.36	9.33	5.03	4.84	0.9	1.56	1.63	1.98
2014	47.35	51.10	9.18	8.41	5.05	4.87	1.81	1.88	2.67	2.12
2015	46.54	50.61	10.33	9.28	5.03	4.7	2.36	1.6	2.96	2.31
2016	46.13	50.78	9.21	8.43	5.12	4.93	1.52	2.52	1.18	1.26
2017	46.97	50.82	9.86	9.35	5.17	5.19	1.49	1.47	1.94	1.43
2018	47.53	52.22	11.98	10.27	5.34	5.09	1.56	2.48	1.36	1.16
2000-2004	49.90	52.56	13.35	12.83	5.51	5.54	1.59	2.35	2.05	1.97
2014-2018	46.90	51.10	9.92	8.75	5.39	5.38	1.20	1.03	2.70	2.16
2000-2018	48.51	52.27	11.25	10.66	5.44	5.47	1.4	1.9	2.33	2.07

Table S5: Same as Table S2 but for SE US

Year	y0 (ppb)		A1 (ppb)		p1 (months)		A2 (ppb)		p2 (months)	
	obs	model	obs	model	obs	model	obs	model	obs	model
2000	44.81	47.84	12.6	18.85	5.66	5.64	5.48	5.7	1.83	1.77
2001	43.89	45.2	10.92	16.15	5.49	5.62	2.89	3.49	3.16	2.58
2002	42.09	44.03	11.19	16.75	5.24	5.48	2.91	4.13	1.25	1.6
2003	41.85	44.33	9.31	13.85	5.52	5.63	4.19	4.94	2.78	2.51
2004	41.14	43.75	8.53	13.03	4.92	5.45	5.31	5.94	2.17	2.04
2005	43.51	46.13	10.62	14.88	5.36	5.65	5.63	5.99	2.81	2.39
2006	45.18	47.04	11.12	14.22	5.1	5.29	1.56	3.3	2.53	2.1
2007	43.14	46.07	9.67	13.31	5.09	5.56	4.7	5.2	2.55	2.13
2008	42.11	45.1	8.24	11.78	4.89	5.24	3.12	3.16	2.7	2.03
2009	40.06	43.12	7.65	10.49	4.39	4.97	1.68	2.6	1.68	1.57
2010	42.55	46.01	5.43	9.54	5.29	5.61	6.32	6.16	2.67	2.49
2011	44.19	46.07	9.6	11.62	5.55	5.48	3.37	4.6	2.05	2.03
2012	42.94	44.74	8.74	9.97	5.32	5.17	1.99	2.15	3.22	2.09
2013	40.14	42.31	6.12	7.45	4.45	5.01	4.38	4.78	2.17	2.14
2014	39.6	43.04	6.25	8.06	4.53	5.14	3.74	4.25	2.57	2.14
2015	38.99	42.54	5.29	8.05	5.42	5.63	3.19	2.73	2.34	1.69
2016	40.31	43.5	5.01	6.45	4.34	5.24	4.02	3.19	2.93	2.52
2017	39.81	42.04	5.13	6.17	4.34	4.78	3.57	3.61	2.5	2.13
2018	38.82	41.81	8.18	8.15	4.25	4.7	1.53	2.17	3.21	2.06
2000-2004	42.75	45.02	10.39	15.73	5.49	5.57	3.42	4.52	2.29	2.08
2014-2018	39.50	42.58	5.17	7.09	5.15	5.48	3.34	2.84	2.91	2.33
2000-2018	41.84	44.44	8.0	11.39	5.36	5.53	3.32	3.78	2.64	2.22

Table S6: Same as Table S2 but for Western Europe

Year	y0 (ppb)		A1 (ppb)		p1 (months)		A2 (ppb)		p2 (months)	
	obs	model	obs	model	obs	model	obs	model	obs	model
2000	34.57	34.12	10.36	13.3	4.35	4.73	1.37	1.61	3.03	2.48
2001	34.69	32.8	11.33	13.53	4.68	5.06	0.67	0.59	4.29	3.21
2002	35.91	33.49	10.75	13.76	4.67	5.08	2.96	3.32	1.96	1.71
2003	38.38	35.96	13.55	16.04	4.91	5.15	3.2	2.33	1.45	1.35
2004	35.7	34.02	9.87	11.96	4.46	4.77	2.46	2.54	1.98	2.03
2005	35.19	34.7	9.73	12.22	4.24	4.67	1.67	1.79	2.29	2.27
2006	36.59	35.73	12.32	15.45	4.76	4.94	0.64	0.29	4.78	0.98
2007	34.23	33.64	9.45	10.98	4.06	4.58	1.38	0.96	3.32	3.22
2008	34.4	34.11	11.53	12.52	4.12	4.57	1.49	2.19	3.47	3.05
2009	33.91	34.12	9.78	12.12	4.45	4.84	2.01	2.21	2.8	2.72
2010	34.33	34.12	8.97	11.76	4.41	4.76	0.63	1.67	2.07	2.56
2011	34.62	35.06	9.66	10.75	4.00	4.51	1.82	2.03	3.23	2.86
2012	35.08	35.25	8.23	10.57	4.43	4.46	1.15	1.72	2.8	2.1
2013	35	35.2	8.26	10.75	4.38	4.72	0.89	1.06	2.14	3.02
2014	38.91	35.14	10.68	10.99	4.52	4.75	1.57	1.43	1.24	1.99
2015	34.54	35.54	8.24	9.69	4.68	4.7	1.4	1.38	0.62	1.65
2016	34.05	34.09	8.19	9.56	4.34	4.58	1.49	1.93	2.36	2.36
2017	34.57	34.84	7.78	9.42	4.15	4.55	1.71	2.54	3.27	2.86
2018	37.17	36.79	10.72	12.05	4.71	4.78	1.08	1.38	1.93	2.14
2000-2004	35.84	34.07	10.08	13.16	5.18	5.32	1.63	1.48	3.02	2.68
2014-2018	35.85	35.28	7.95	9.46	5.09	5.18	1.23	1.87	3.47	3.09
2000-2018	35.36	34.67	8.61	11.13	5.05	5.2	1.81	1.88	3.44	3.16

Table S7: Same as Table S2 but for Southern Europe

Year	y0 (ppb)		A1 (ppb)		p1 (months)		A2 (ppb)		p2 (months)	
	obs	model	obs	model	obs	model	obs	model	obs	model
2000	39.47	42.84	11.74	15.55	5.06	5.36	3.13	3.52	1.6	2
2001	40.28	41.3	14.22	15.3	5.06	5.3	0.75	2.27	0.95	1.74
2002	39.51	40.31	11.97	14.05	5.28	5.25	1.51	2.41	2.27	2.22
2003	44.49	44.33	16.01	17.11	5.31	5.39	4.77	3.6	1.35	1.29
2004	40.44	41.53	12.51	14.48	4.98	5.17	2.43	3.03	2.07	2.06
2005	42.12	43.22	12.9	15.36	5.02	5.21	1.85	2.82	1.58	1.99
2006	43.3	43.04	15.3	15.78	5.1	5.11	1.52	1.56	1	2.01
2007	40.68	41.12	11.48	12.76	5.08	5.2	3.82	4.17	2.36	2.15
2008	39.84	41.92	11.57	12.73	4.87	5.15	2.12	2.77	1.78	2.01
2009	40.38	42.1	10.67	11.48	4.99	5.21	3.48	3.88	2.11	2.1
2010	40.6	42.33	10.89	11.07	5.07	5.13	2.5	3.35	1.76	2.1
2011	41.15	42.75	10.61	10.81	4.96	5.16	3.73	4.06	2.48	2.46
2012	40.71	42.81	10.63	10.32	5.01	5.01	3.34	4.11	1.78	1.86
2013	39.97	42.22	11.48	10.79	5.15	5.18	3.35	2.75	1.04	1.61
2014	47.94	41.6	12.23	9.53	4.65	4.81	2.33	3.09	1.97	2.22
2015	40.6	43.06	12.59	11.47	5.05	5.14	2.32	2.09	1.08	1.58
2016	38.88	42.11	10.03	9.47	5.16	5.29	3.44	3.5	1.67	1.87
2017	41.07	43.77	9.5	10.5	4.92	5.05	1.69	3.11	2.17	2.18
2018	40.59	43.28	11.17	9.97	5.24	5.34	3.18	3.49	1.72	1.99
2000-2004	40.83	42.05	13.02	15.18	5.43	5.48	1.62	2.35	2.05	2.09
2014-2018	41.81	42.76	10.64	9.93	5.41	5.47	1.67	2.59	2.18	2.28
2000-2018	41.15	42.39	11.62	12.36	5.39	5.45	1.79	2.65	2.19	2.26

Table S8: Same as Table S2 but for C&E Europe

Year	y0 (ppb)		A1 (ppb)		p1 (months)		A2 (ppb)		p2 (months)	
	obs	model	obs	model	obs	model	obs	model	obs	model
2000	39.32	36.9	14.01	17.9	4.61	5.05	2.53	2.34	2.51	2.22
2001	37.62	35.08	12.03	16.04	4.81	5.28	0.45	1.73	2.34	1.97
2002	39.38	35.31	13.84	16.79	4.91	5.21	3.04	1.88	1.62	1.77
2003	41.78	37.53	15.32	18.15	4.74	5.11	3.99	2.33	1.38	1.75
2004	39.58	35.83	11.76	15.58	4.75	5.14	2.66	2.75	1.78	1.99
2005	41.14	36.68	12.95	16.57	4.22	4.94	4.21	3.83	2.11	2.04
2006	41.45	37.7	13.91	17.04	4.55	5.06	2.41	2.27	2.02	1.83
2007	40	36.32	14.26	16.6	4.63	5.16	1.39	1.38	1.97	1.7
2008	38.06	36.21	13.24	15.29	4.53	5.04	1.54	2.16	1.83	1.95
2009	37.95	35.48	14.41	16.68	4.7	5.17	3.2	2.82	2.28	2.19
2010	37.42	36.42	9.96	14.24	4.73	5.16	2.85	2.96	1.34	1.68
2011	38.33	37.29	11.86	14.84	4.36	5.06	2.93	4.09	2.11	2.09
2012	38.12	37.92	12.28	14.89	4.68	4.99	2.49	3.82	1.64	1.69
2013	36.47	36.86	11.2	14.21	4.58	5.11	3.03	2.55	1.84	2.32
2014	34.45	35.49	11.05	14.3	4.9	5.13	2.88	2.79	1.39	1.82
2015	36.16	37.2	11.75	15.07	5.05	5.3	2.95	3.12	1.14	1.55
2016	34.54	36.09	10.24	13.1	5.06	5.14	0.78	1.71	2.23	1.97
2017	34.74	37.39	9.42	13.14	4.56	5.18	2.19	2.62	1.37	1.65
2018	37.52	38.27	12.66	13.86	5.03	5.23	3.43	4.2	2.05	2.23
2000-2004	39.53	36.12	12.44	16.61	5.25	5.37	1.64	1.80	2.63	2.43
2014-2018	35.47	36.88	10.50	13.71	5.36	5.43	1.35	2.31	2.05	2.15
2000-2018	38.1	36.62	11.33	15.18	5.24	5.39	1.76	2.17	2.62	2.34

Table S9: Same as Table S2 but for SE Europe

Year	y0 (ppb)		A1 (ppb)		p1 (months)		A2 (ppb)		p2 (months)	
	obs	model	obs	model	obs	model	obs	model	obs	model
2000	-	-	7.57	7.37	2.5	2.5	3.92	3.82	1	1
2001	25.22	50.87	16.34	15.2	4.85	4.71	13.62	6.9	0.7	1.25
2002	19.02	45.52	491.24	497.98	9.66	9.67	281.59	297.05	4.48	4.5
2003	42.37	47.37	22.15	16.19	4.28	4.68	3.88	6.84	0.54	1.13
2004	37.98	47.08	13.76	14.23	3.64	4.49	6.33	5.99	1.32	1.36
2005	37.31	48.38	15.31	16.08	3.31	4.43	5.36	6.99	1.47	1.41
2006	29.65	47.74	17.72	14.49	2.76	4.47	8.4	6.39	0.94	1.31
2007	41.34	47.87	9.27	16.89	5.06	4.65	9.7	6.1	0.87	1.31
2008	40.54	48.47	16.53	15.55	4.49	4.57	6.97	6.14	1.19	1.2
2009	40.46	47.09	13.71	14.81	4.9	4.38	6.61	5.01	1.11	1.21
2010	43.47	46.93	13.36	13.52	3.65	4.59	4.95	6.54	1.27	1.17
2011	45.03	45.57	12.37	13.36	4.1	4.63	6.54	6.53	1.35	1.27
2012	42.07	48.24	12.84	14.51	4.05	4.49	9.85	6.51	1.31	1.14
2013	37.12	47.78	10.15	12.81	3.94	4.22	8.29	5.45	1.3	1.39
2014	43.31	43.83	9.39	14.21	4.28	4.39	4.59	7.66	0.95	1.4
2015	44.79	47.23	16.05	14.01	4.93	4.51	4.82	7.49	1.04	1.26
2016	45.87	46.78	14.69	13.81	4.24	4.4	6.86	5.92	1.12	1.42
2017	45.63	46.28	14.1	13.02	4.55	4.48	5.71	6.8	1.13	1.29
2018	41.61	46.86	13.73	14	4.22	4.38	5.3	6.88	1.35	1.53
2000-2004	34.27	48.53	12.95	13.27	5.58	5.64	4.25	2.63	1.34	1.58
2014-2018	44.23	46.19	11.56	11.72	5.58	5.62	1.58	3.34	1.43	1.83
2000-2018	39.86	47.35	10.35	12.5	5.55	5.6	2.76	2.72	1.43	1.73

Table S10: A comparison of the e-folding time (τ) of the decline in local anthropogenic NO_x contribution to PSO in different receptor regions derived from this study for 2000-2018 with observationally-derived τ values for local anthropogenic enhancements over a similar period as available in published literature. The τ values for European regions were derived from the τ values for individual stations reported in Table 2 of Derwent & Parrish (2022).

Receptor Region	τ (this study) in years	τ (obs-derived) in years	References
Eastern Canada	25.8 ± 9.1	N/A	N/A
NW US	38.4 ± 8.0	21.8 ± 0.8	Parrish et al. (2025)
SW US	28.2 ± 3.1	21.8 ± 0.8	Parrish et al. (2022)
NE US	29.4 ± 6.3	21.9 ± 1.2	Parrish & Ennis (2019)
SE US	25.2 ± 3.4	21.8 ± 0.8	Parrish et al. (2025)
Western Europe	54.9 ± 21.5	~ 43.4	Derwent & Parrish (2022)
Southern Europe	38.6 ± 9.4	~ 37.0	Derwent & Parrish (2022)
C&E Europe	63.3 ± 22.4	~ 43.8	Derwent & Parrish (2022)
SE Europe	37.2 ± 11.5	N/A	N/A

Table S11: PSO and local anthropogenic NO_x contribution to PSO at model grid cells corresponding to Trinidad Head and Mace Head stations. Numbers in brackets indicate the corresponding fields sampled from the grid cell immediately west of Trinidad Head and Mace Head accordingly.

Year	Trinidad Head		Mace Head	
	PSO (ppb)	Local contribution (ppb)	PSO (ppb)	Local contribution (ppb)
2000	39.2 (39.2)	7.6 (6.0)	40.7 (41.5)	5.5 (5.8)
2001	38.8 (39.0)	7.6 (5.6)	38.9 (40.2)	5.5 (5.7)
2002	37.8 (37.9)	10.0 (5.9)	39.3 (40.1)	6.7 (7.1)
2003	39.2 (39.4)	7.5 (6.3)	39.6 (41.0)	5.5 (5.9)
2004	39.5 (39.3)	7.8 (5.6)	41.2 (42.3)	6.2 (6.3)
2005	38.1 (38.5)	7.2 (5.9)	41.6 (42.5)	4.8 (4.9)
2006	42.1 (41.8)	6.5 (4.9)	42.0 (43.6)	4.7 (4.9)
2007	37.1 (37.6)	5.4 (3.9)	40.7 (41.3)	4.7 (4.8)
2008	39.7 (40.2)	5.6 (4.6)	41.2 (41.8)	4.4 (4.4)
2009	39.7 (39.1)	7.8 (5.1)	41.2 (42.3)	4.6 (4.8)
2010	39.3 (40.1)	4.6 (3.4)	39.2 (40.7)	4.0 (4.1)
2011	39.3 (40.1)	4.5 (3.7)	41.6 (42.8)	4.4 (4.6)
2012	38.8 (39.7)	4.3 (3.3)	41.9 (43.1)	3.6 (3.6)
2013	39.1 (39.8)	5.0 (4.2)	40.4 (42.4)	3.7 (4.0)
2014	38.2 (37.7)	4.9 (3.7)	40.1 (40.8)	4.1 (4.3)
2015	39.6 (38.9)	6.6 (4.6)	41.9 (42.5)	3.9 (4.0)
2016	39.2 (38.7)	5.6 (3.7)	40.2 (41.1)	3.9 (4.0)
2017	38.7 (39.4)	4.0 (3.2)	40.3 (41.3)	3.8 (4.0)
2018	39.6 (39.6)	4.2 (3.0)	42.3 (43.2)	3.3 (3.6)

Table S12: Background contribution to PSO in SW US:

Year	Foreign NOx	Natural NOx	Ship NOx	Total Background
2000	12.4	12.2	1.9	26.5
2001	12.3	12.1	1.8	26.2
2002	12.7	13.1	1.8	27.7
2003	12.9	12.7	1.9	27.6
2004	13.4	11.9	2.0	27.3
2005	14.5	12.3	2.1	28.9
2006	13.8	12.7	2.2	28.7
2007	14.2	12.6	2.3	29.1
2008	15.1	13.3	2.3	30.7
2009	14.8	12.0	2.4	29.1
2010	15.3	12.5	2.6	30.3
2011	15.7	12.4	2.5	30.6
2012	15.3	13.5	2.2	31.1
2013	15.6	12.2	2.5	30.2
2014	15.7	12.1	2.6	30.4
2015	15.4	12.7	2.5	30.6
2016	15.5	13.1	2.7	31.3
2017	15.5	14.7	2.6	32.8
2018	15.3	16.3	2.6	34.2