Supplementary Information for

Tropospheric Ozone (O_3) Pollution in Johannesburg, South Africa: Exceedances, Diurnal Cycles, Seasonality, O_x Chemistry and O_3 Production Rates

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Table S1: Number of exceedances in O_3, defined as the number of times 8h-running hourly averages of O_3 concentrations exceeded 61 ppbv in one year, between 2004-2011.

year	Air quality monitoring stations for O_3 (number of exceedances)		
	Buccleuch	**Delta Park**	**Newtown**
2004	0	110	8
2005	121	478	19
2006	0	181	29
2007	22	201	6
2008	1	138	24
2009	0	81	9
2010	0	47	75
2011	0	20	N/A

Table S2: Yearly averages of NO2 between 2004-2011. NO2 exceedances are defined as a yearly average above 21 ppbv.

year	Air quality monitoring stations for NO_2		
	Buccleuch	**Delta Park**	**Newtown**
2004	33.1	15	28.5
2005	23.8	20	49.7
2006	42.3	18	38.7
2007	35.0	16	28.0
2008	17.3	13	29.7
2009	31.1	14	26.8
2010	32.9	-	8.9
2011	38.3	16	0.8

Table S3: Diurnal mixing ratio values for O_3, NO, NO_2, NO_x and CO for Buccleuch over the 2004-2011 study period as depicted in Figure 7A. M stands for mean, SD stands for standard deviation and Mdn stands for median. Values are rounded to the nearest integer for O_3, NO, NO_2, NO_x and to the nearest decimal for CO.

Time of day	**O_3 (ppbv)**			**NO (ppbv)**			**NO_2 (ppbv)**			**NO_x (ppbv)**			**CO (ppmv)**		
	M	SD	Mdn	M	SD	Mdn	M	SD	Mdn	M	SD	Mdn	M	SD	Mdn
00:30	9	11	4	99	108	49	28	17	28	127	119	78	1.9	1.5	1.5
01:30	9	12	5	79	91	34	25	15	24	104	101	60	1.7	1.3	1.4
02:30	10	12	5	62	74	25	23	14	22	84	81	52	1.5	1.1	1.3
03:30	9	12	5	50	58	24	21	13	21	72	65	48	1.4	1.0	1.1
04:30	8	10	4	54	53	34	21	12	21	76	59	59	1.3	0.9	1.2
05:30	6	9	3	108	85	91	25	12	25	134	92	120	1.7	0.8	1.7
06:30	4	5	3	204	152	169	30	16	29	233	159	201	2.9	1.5	2.7
07:30	6	6	4	226	176	176	33	17	31	258	181	209	3.4	2.0	2.9
08:30	9	9	6	172	142	127	36	19	34	208	149	165	2.7	1.7	2.2
09:30	13	10	11	122	88	100	35	18	33	157	97	136	2.0	1.1	1.7
10:30	18	13	16	95	62	82	32	17	31	127	68	116	1.7	0.9	1.5
11:30	23	14	21	80	48	73	32	15	30	113	53	107	1.5	0.8	1.3
12:30	26	16	24	74	40	69	32	15	31	108	51	104	1.5	0.8	1.3
13:30	27	17	26	73	41	68	33	15	31	108	54	104	1.5	0.9	1.3

14:30	27	17	25	73	38	68	34	16	33	108	45	106	1.5	0.8	1.3
15:30	26	17	23	77	40	72	36	17	35	115	49	111	1.6	0.8	1.5
16:30	22	15	20	89	47	84	40	19	37	130	57	126	1.9	0.9	1.8
17:30	16	13	13	118	68	109	46	21	43	165	81	155	2.4	1.1	2.3
18:30	10	11	6	150	99	128	49	22	48	201	110	184	2.7	1.4	2.5
19:30	7	9	4	182	137	143	47	21	47	231	147	197	2.8	1.5	2.6
20:30	6	8	3	190	155	145	43	20	42	235	164	194	2.8	1.7	2.5
21:30	7	11	3	176	154	129	39	19	38	217	165	174	2.7	1.8	2.4
22:30	8	10	4	155	145	108	36	19	34	192	154	148	2.6	1.8	2.2
23:30	8	11	4	128	130	77	32	18	31	161	139	113	2.3	1.7	2.0

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Table S4: Diurnal mixing ratio values for O_3, NO, NO_2, and NO_x for Delta Park over the 2004-2011 study period as depicted in Figure 7B. M stands for mean, SD stands for standard deviation and Mdn stands for median. Values are rounded to the nearest integer for O_3, NO, NO_2, NO_x and to the nearest decimal for CO.

Time of day	**O_3 (ppbv)**			**NO (ppbv)**			**NO_2 (ppbv)**			**NO_x (ppbv)**		
	M	SD	Mdn	M	SD	Mdn	M	SD	Mdn	M	SD	Mdn
00:30	14	13	12	5	10	1	19	12	17	24	19	19
01:30	15	12	13	4	8	1	16	11	14	20	16	16
02:30	16	12	14	3	6	1	13	10	12	17	13	13
03:30	16	11	15	2	5	1	12	9	10	14	12	11
04:30	16	11	15	2	5	1	10	8	8	13	11	10
05:30	15	11	14	2	5	1	10	7	9	13	10	10
06:30	12	10	10	6	9	2	14	8	12	20	15	16
07:30	11	10	9	25	41	8	17	11	16	45	48	29
08:30	16	12	14	28	43	9	19	13	17	50	54	30
09:30	25	15	23	14	25	6	17	13	13	33	38	21
10:30	33	17	31	7	16	3	13	11	10	21	25	15
11:30	39	18	38	4	7	2	9	8	7	15	14	11
12:30	44	18	42	4	15	1	8	7	6	12	11	9
13:30	46	19	45	3	8	1	7	6	5	11	12	8
14:30	48	22	46	4	17	1	7	6	5	11	14	8
15:30	47	20	45	3	7	1	7	6	5	11	9	8
16:30	43	20	42	3	6	1	9	8	7	12	11	10
17:30	34	20	33	4	9	1	17	12	13	21	18	16
18:30	21	17	18	12	22	2	28	18	26	40	34	29
19:30	12	13	8	19	29	4	33	19	31	52	40	41
20:30	10	12	5	20	28	6	33	18	32	52	39	44
21:30	10	12	5	16	22	4	30	17	29	45	33	39
22:30	11	13	6	12	17	3	26	16	26	38	28	33
23:30	12	12	8	8	14	2	23	14	22	31	24	27

Table S5: Diurnal mixing ratio values for O_3, NO, NO_2, NO_x and CO for Newtown over the 2004-2011 study period as depicted in Figure 7A. M stands for mean, SD stands for standard deviation and Mdn stands for median. Values are rounded to the nearest integer for O_3, NO, NO_2, NO_x and to the nearest decimal for CO.

Time of day	O_3 (ppbv)			NO (ppbv)			NO_2 (ppbv)			NO_x (ppbv)			CO (ppmv)		
	M	SD	Mdn	M	SD	Mdn	M	SD	Mdn	M	SD	Mdn	M	SD	Mdn
00:30	18	14	16	29	61	5	24	21	19	47	67	24	0.8	1.1	0.5
01:30	18	14	17	24	50	3	21	19	16	39	58	19	0.7	0.9	0.4
02:30	19	14	18	21	45	3	19	18	14	34	53	16	0.6	0.9	0.4
03:30	20	14	19	19	40	3	17	17	13	30	47	14	0.6	0.8	0.3
04:30	19	14	18	18	36	3	17	17	13	31	45	15	0.6	0.8	0.3
05:30	16	13	14	35	65	8	21	18	17	54	74	27	0.7	0.9	0.5
06:30	11	11	8	92	155	32	30	22	26	117	157	62	1.3	1.5	0.8
07:30	10	9	7	116	177	54	35	26	30	143	175	86	1.8	1.9	1.2
08:30	13	10	11	75	94	49	35	25	31	107	105	81	1.6	1.6	1.1
09:30	19	12	17	43	43	32	31	22	27	74	60	62	1.1	1.0	0.9
10:30	25	14	24	33	36	24	28	19	25	61	47	52	0.9	0.9	0.7
11:30	30	16	29	27	25	20	26	17	24	53	36	47	0.8	0.7	0.7
12:30	32	17	33	25	29	19	26	17	24	51	38	45	0.8	0.8	0.6
13:30	34	17	34	24	28	18	27	17	24	51	37	45	0.8	0.7	0.6
14:30	33	18	32	26	30	19	28	18	26	54	40	48	0.8	0.8	0.6
15:30	31	18	29	29	27	22	31	20	29	60	43	53	0.8	0.8	0.7
16:30	26	17	24	36	34	26	36	23	33	72	50	62	1.0	0.9	0.8
17:30	19	15	16	49	51	33	42	27	39	91	67	75	1.3	1.1	1.0
18:30	13	12	9	59	67	37	48	30	44	106	82	86	1.4	1.1	1.2
19:30	10	10	7	54	68	31	48	32	44	101	84	78	1.4	1.1	1.2
20:30	12	11	8	44	69	18	43	30	39	86	83	61	1.2	1.1	0.9
21:30	13	12	10	41	71	12	38	28	34	76	82	49	1.1	1.2	0.8
22:30	15	12	12	39	76	8	33	25	28	68	86	38	1.0	1.2	0.7
23:30	16	13	14	34	67	6	29	23	24	58	76	31	0.9	1.1	0.6

Table S6: The data completeness of the pollutants presented in Figure 7 was analysed for each hour of the day. The percentages given represent the average data coverage across all 24 hours of a day with standard deviation. This analysis shows that all hours of the data contain approximately the same amount of data within the standard deviation given. Therefore, the diurnal analysis is valid.

Pollutant	Average percentage of available data <u>for each hour</u> in annual diurnal profile (after quality control)		
	Buccleuch	**Delta Park**	**Newtown**
O_3	58.8 ± 1.1 %	77.3 ± 1.9 %	65.2 ± 0.5 %

NO_x	54.3 ± 0.9 %	56.2 ± 0.5 %	64.1 ± 0.4 %
NO	54.2 ± 0.9 %	57.0 ± 0.4 %	58.6 ± 5.2 %
NO_2	53.3 ± 1.3 %	55.9 ± 0.4 %	63.2 ± 0.4 %
CO	66.4 ± 1.1 %	NA	40.5 ± 0.7 %

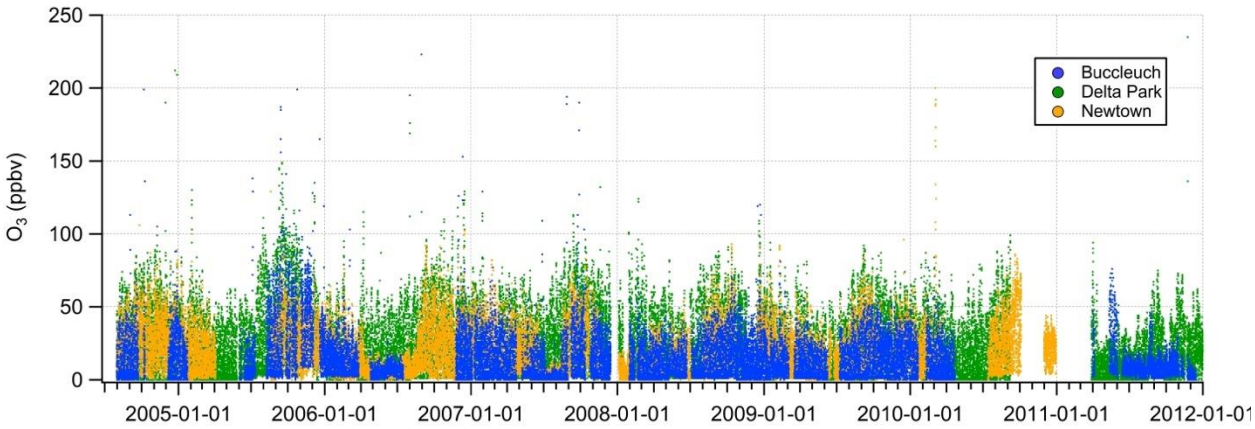

Figure S1: O_3 mixing ratio time series for the three sites considered in this study, Bucchleuch (in blue), Delta Park (in green) and Newtown (in orange).

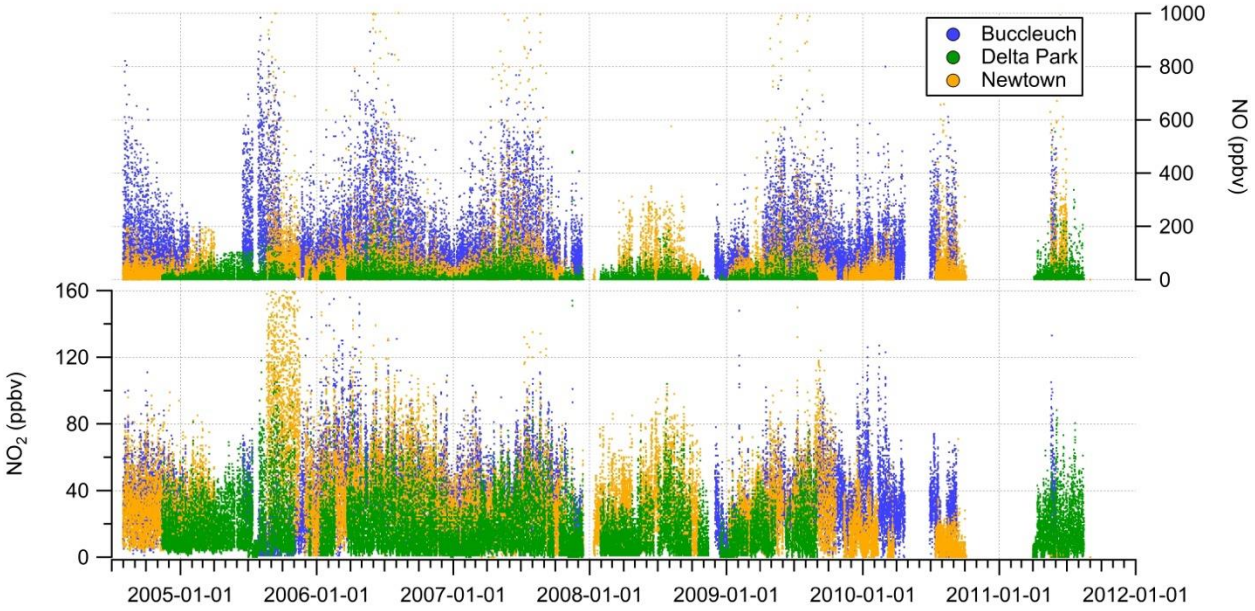

Figure S2: NO_2 (left axis) and NO (right axis) mixing ratio time series for the three sites considered in this study, Bucchleuch (in blue), Delta Park (in green) and Newtown (in orange).

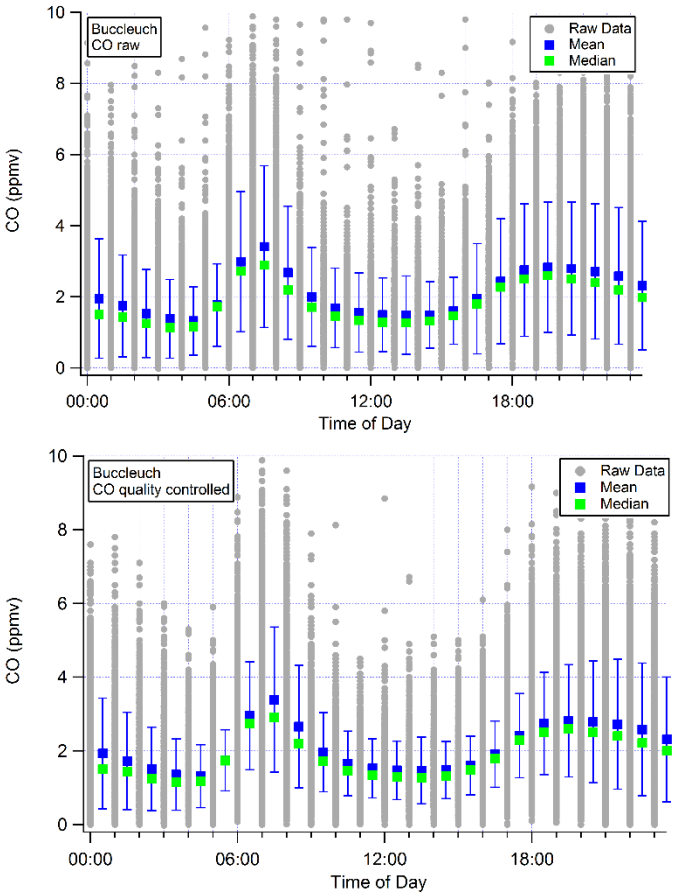

Figure S3: Quality control efforts on the time series of CO at Buccleuch. These graphs represent annual diurnal profiles of available CO mixing ratios over the 2004-2011 period. Top graph was created with the raw CO data, in other words, the data obtained directly from SAAQIS and the bottom graph was created with quality control discussed in the methods section of the main text. Little difference between the obtain diurnal is observed.

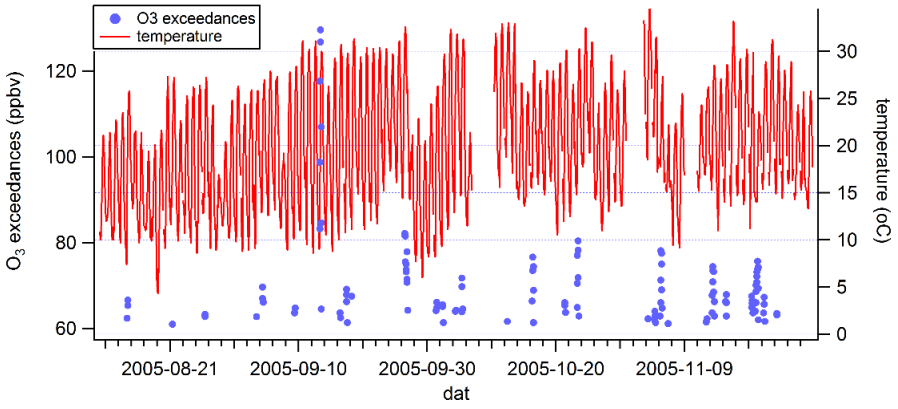

Figure S4: O_3 exceedances at Buccleuch are uncommon. Yet even during the spring of 2005, which saw many O_3 exceedances according to NAAQS, there was no correlation found between high O_3 and high temperature.

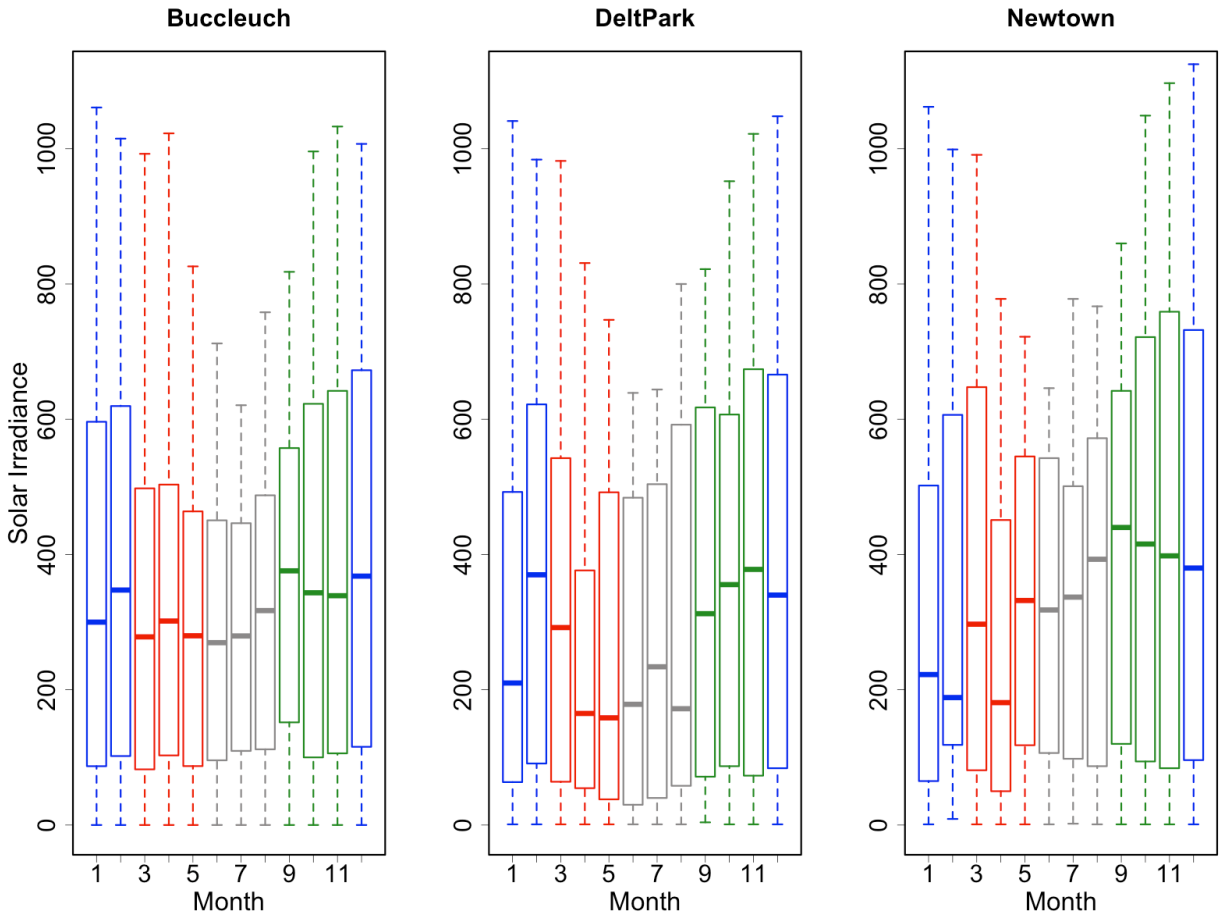

Figure S5: Solar irradiance (W/m²) binned per month and color coded per season. Buccleuch has irradiance data from 2004-2011 whereas the Delta Park and Newtown sites have only sporadic data from May 2009 to December 2011. The data displayed was analysed without nighttime, in other words zero values for solar irradiance were removed prior to the analysis. The graph is colour coded by season where blue is summer (DJF), red is autumn (MAM), grey is winter (JJA) and green is spring (SON). The line is the median and the box limits show the 25th and 75th percentile and the lower and upper whiskers the 1st and 99th percentile. Data out of this range are not shown in this graph. Corresponding monthly and seasonal O_3 data is shown in Figure 10.

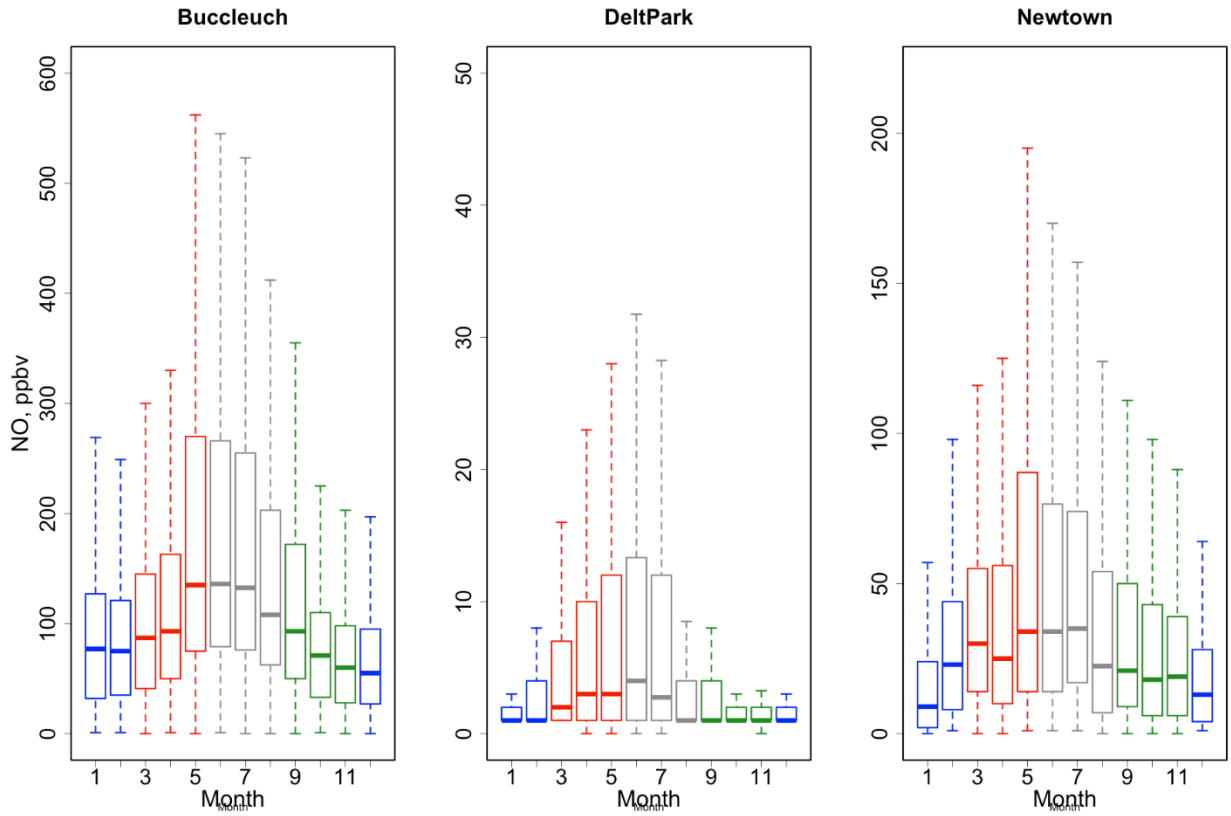

Figure S6: Box and whisker plots of monthly NO mixing ratios, colour coded by season where blue is summer (DJF), red is autumn (MAM), grey is winter (JJA) and green is spring (SON). The line is the median and the box limits show the 25th and 75th percentile and the lower and upper whiskers the 1st and 99th percentile.

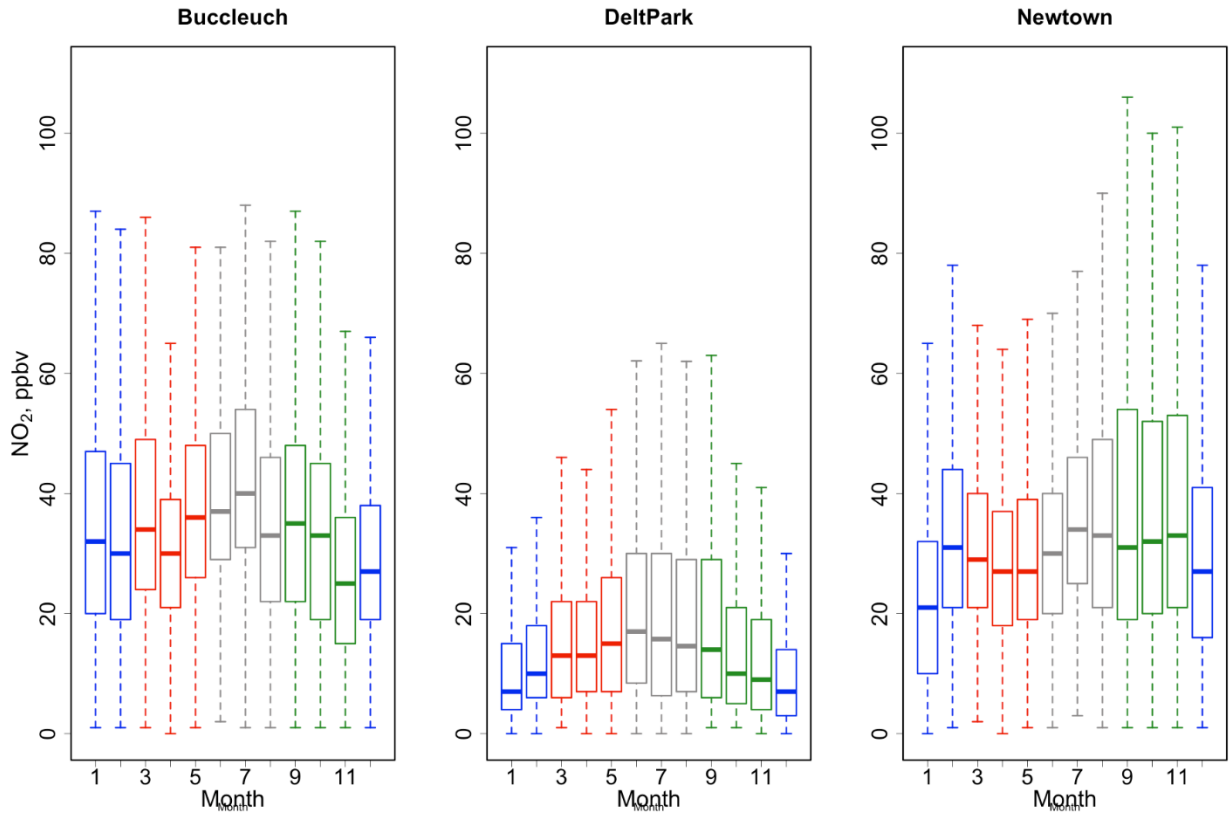

Figure S7: Box and whisker plots of monthly NO_2 mixing ratios, colour coded by season where blue is summer (DJF), red is autumn (MAM), grey is winter (JJA) and green is spring (SON). The line is the median and the box limits show the 25th and 75th percentile and the lower and upper whiskers the 1st and 99th percentile.

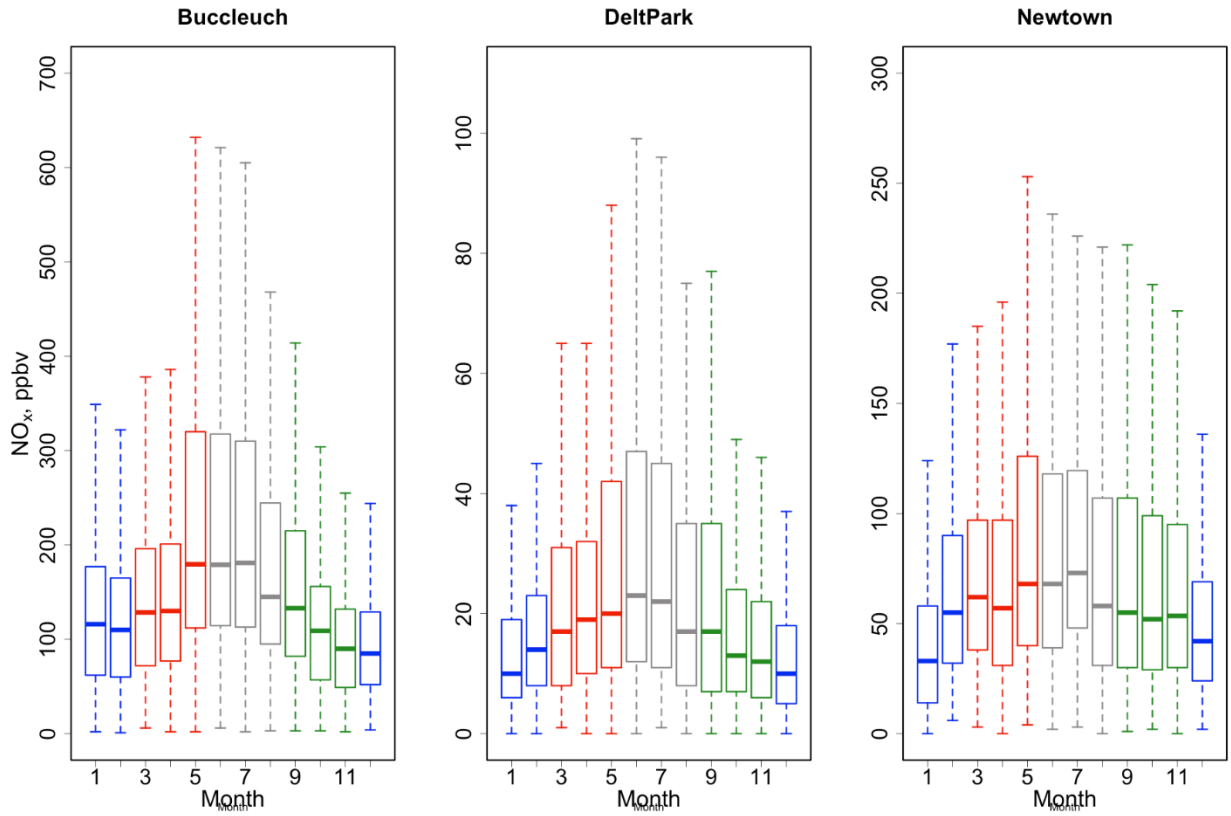

Figure S8: Box and whisker plots of monthly NOx mixing ratios, colour coded by season where blue is summer (DJF), red is autumn (MAM), grey is winter (JJA) and green is spring (SON). The line is the median and the box limits show the 25th and 75th percentile and the lower and upper whiskers the 1st and 99th percentile.

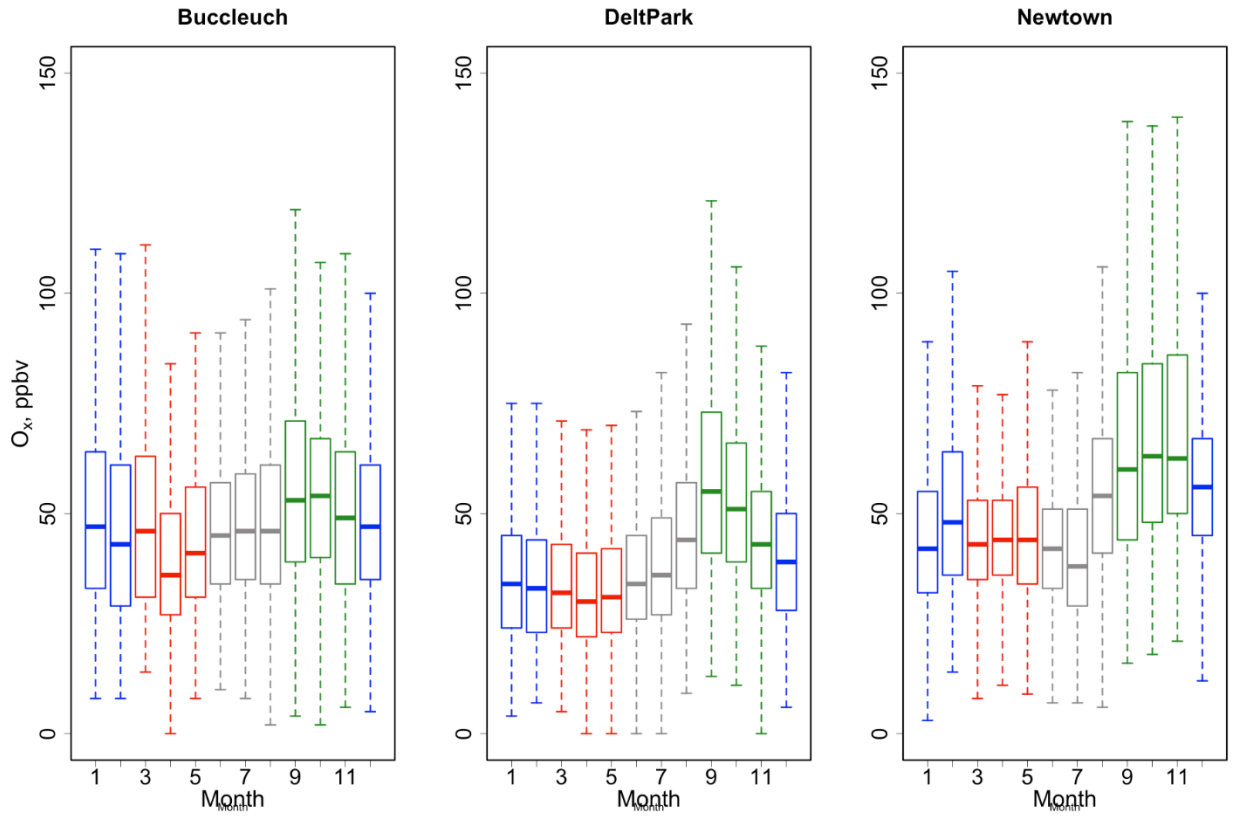

Figure S9: Box and whisker plots of monthly Ox mixing ratios, colour coded by season where blue is summer (DJF), red is autumn (MAM), grey is winter (JJA) and green is spring (SON). The line is the median and the box limits show the 25th and 75th percentile and the lower and upper whiskers the 1st and 99th percentile.

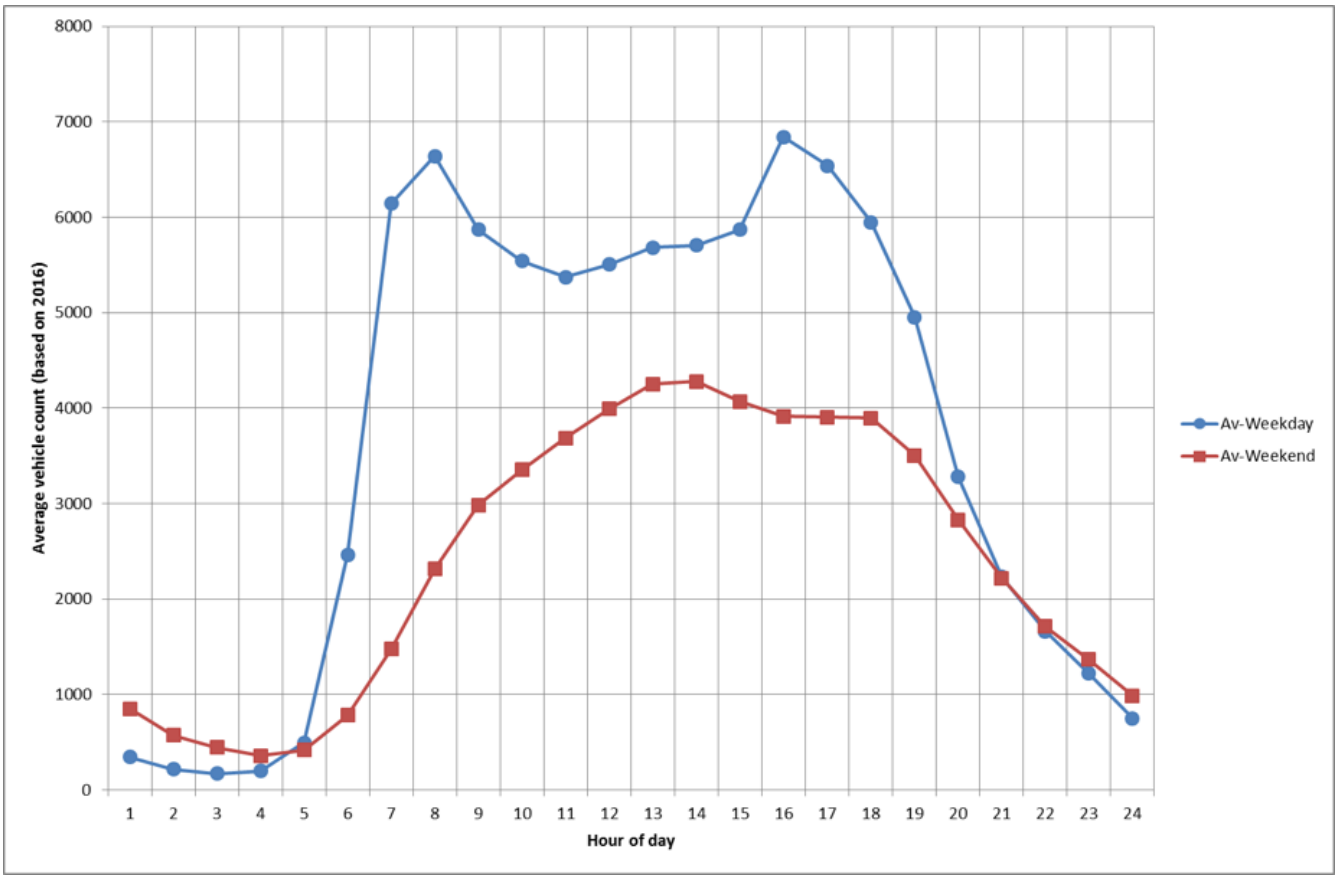

Figure S10: Diurnal variation of hourly vehicle traffic counts in hundreds of vehicles based on 2016 data at the Buccleuch interchange.

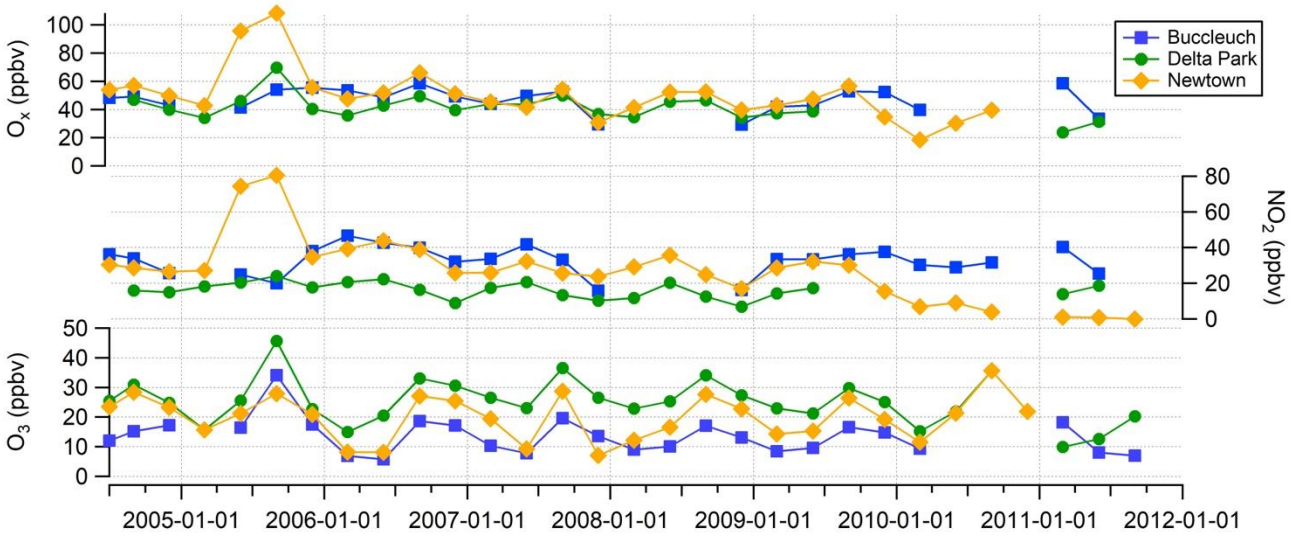

Figure S11: Seasonal averages for O_3, NO_2 and O_x over the study period. 2005 stands out as a year with unusually high concentrations of O_3 at all sites and high concentrations of NO_2 at Newtown. This anomaly prevents reliable trend analyses of these pollutants over the time period between 2004 and 2011.

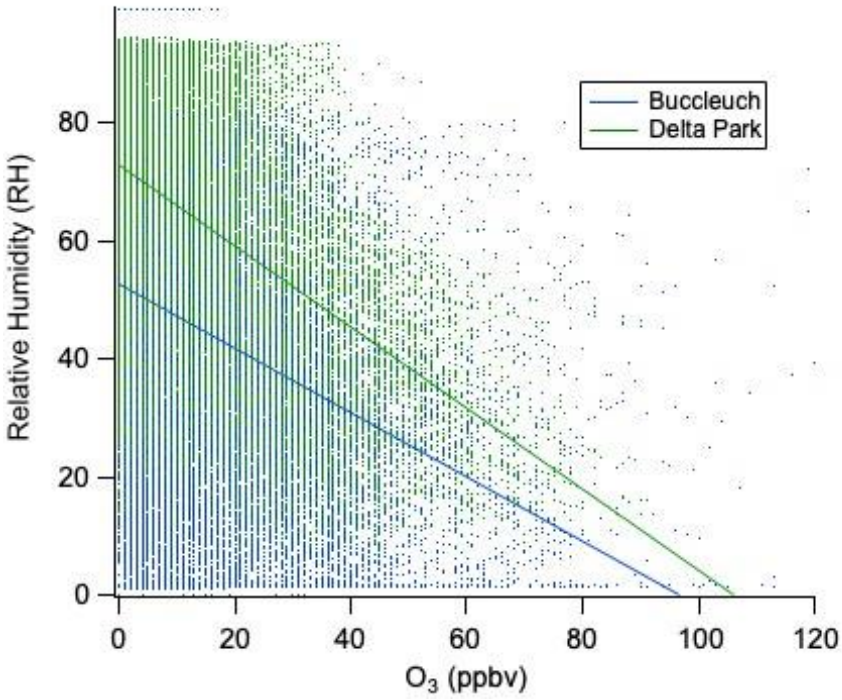

Figure S12: Linear regression between RH and O_3 at Buccleuch and Delta Park. Newtown did not have RH data available for this comparison. This RH data was not used in our P(HO_x) analysis since we did not have access to dewpoint temperature to calculate H_2O concentrations necessary for our mechanistic study.

Estimating P(HO_x) calculations

We employ a previously described simplified box-model that can estimate hourly concentrations of OH radicals and subsequently O_3 production following Equation 1 shown below (Geddes et al., 2009; Murphy et al., 2006). A similar model was also applied to South African air pollution in Laban et al., 2018. Equation 1 describes the production of HO_x as a function of O_3 and H_2O concentrations.

$$P(HO_x) = \frac{2J_{O_3}k_1[O_3][H_2O]}{k_2(0.99)(2.46 \times 10^{19})}$$

Equation 1: Estimated the production of HO_x species using ambient measurements of O_3 and water concentrations (in molecules cm^{-3}). In this case, O_3 concentrations are from Newtown whereas H_2O concentrations are calculated from the dew point temperature reported at O. R. Tambo Johannesburg airport. $J_{O3} = 6 \times 10^{-5}$ s^{-1}, $k_1 = 2.9 \times 10^{-11}$ cm^3 $molec^{-1}$ s^{-1}, $k_2 = 2.2 \times 10^{-10}$ cm^3 $molec^{-1}$ s^{-1}.

References:

Geddes, J. A., Murphy, J. G., and Wang, D. K.: Long term changes in nitrogen oxides and volatile organic compounds in Toronto and the challenges facing local ozone control, Atmos.Environ., 43, 3407–3415, https://doi.org/10.1016/j.atmosenv.2009.03.053, 2009.

Laban, T. L., Zyl, P. G. van, Beukes, J. P., Vakkari, V., Jaars, K., Borduas-Dedekind, N., Josipovic, M., Thompson, A. M., Kulmala, M., and Laakso, L.: Seasonal influences on surface ozone variability in continental South Africa and implications for air quality, Atmos. Chem. Phys., 18, 15491–15514, https://doi.org/10.5194/acp-18-15491-2018, 2018.

Murphy, J. G., Day, D. A., Cleary, P. A., Wooldridge, P. J., Millet, D. B., Goldstein, A. H., and Cohen, R. C.: The weekend effect within and downwind of Sacramento: Part 2. Observational evidence for chemical and dynamical contributions, Atmos.Chem.Phys.Discuss., 2006, 11971–12019, https://doi.org/10.5194/acpd-6-11971-2006, 2006.