Interactive comment on "The impacts of precursor reduction and meteorology on ground-level ozone in the Greater Toronto Area" by S.C. Pugliese et al.

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We thank the review for their consideration of our manuscript. Our response to their comments are below (original comment in small indented text).

General Comments

> The title refers to the impacts of precursor reductions on ground-level ozone but much of the analysis deals with O_x. While looking at the odd-oxygen budget might be the proper reference for a chemistry point of view, the health based standards referred to in the text are all based on ozone levels. Additionally, the O_x trends are likely being driven by the NO_2 trends, thus masking the important ozone trends. Either the title of the article should be changed to reflect the central role of O_x in the present analysis or the analysis should emphasize ozone and its trends to a greater extent.

We think the reviewer raises an interesting point and agree that O_x may not be an appropriate metric given it reflects the large reductions in NO_2. We have changed our emphasis to focus on the trends of ozone, not O_x during the 13 year study period. This includes a new revised discussion on the percentage decreases of ozone during the study (in Section 3.1) as well as focusing the net wind vector analysis on ozone concentrations.

> Would the analysis be different if instead of looking at trends in the mean summertime daily maximum concentrations, trends in annual maximum (or 99th, 95th, etc. percentiles) daily maximum values were used? Such an analysis would be more in line with the Canada Wide Standard.

We designed our analysis to consider trends in both average and extreme ozone concentrations. To specifically address the Canada Wide Standard, we included the Design Values in Figure 4 to give the reader insight into whether this target is being met. We feel that using summertime averages allows us to more fully analyze correlations between ozone and meteorological parameters (for example: when air is from the W-NE, we saw that ozone concentrations are typically lower than when air is transported from the W-SE) and these correlations would not be visible if we solely looked at the 99th or 95th percentiles.

> Is there any sense that an air mass around the GTA region switches from VOC- to NOx-sensitive as one moves from the heavily urbanized downtown core? Such a switch, while potentially occurring on days most conducive to ozone formation, might alter the interpretation of trends.

This is an interesting point that we considered but struggle to address with the available data. The only site that provides VOC data that is not in a heavily urbanized core is Brampton (a suburb to the southwest, and thus generally upwind, of Toronto). When we calculated the relative reactivity of OH to NO_2 and the sum of 40 speciated VOCs during an "early" (2002-2003) and "late" (2009-2010) period at Brampton, it is consistent with the Downtown station in that during the "early" period has an OH reactivity of each class was almost equivalent, while in the "late" period a transition occurs where NO_2 represents a larger fraction. Therefore, to the best of our ability to characterize it, ozone production regime remains VOC-limited. This detail has been included in the manuscript (Section 3.4, lines 355-356).

> Oltmans et al . (2013) show that background ozone concentrations as measured at Whiteface Mountain show a small decreasing trend between 2000-2010. Could changing eastern North American background concentrations be influencing the reported trends, especially since trends reported here are based on annual summertime mean concentrations?

We think the review has brought up a very good point that we did not initially address. It is certainly possible that changing North American background concentrations could be influencing the reported trends in this study. Unfortunately, we do not have access to any other stations in Southern Ontario that we could use as a "background" reference (all other provincial monitoring stations are in an urban center or near a large body of water that complicates interpretation) and therefore since we cannot rule out this potential, we have included in the manuscript that there is a possibility of changing background concentrations influencing our reported trends (Section 3.1, lines 260-264)

Specific Comments

> P 10211 Line 18: Aren't NO_x emissions from transportation also a result of fossil fuel combustion?

We have clarified that NO_x emissions are dominated by transportation and electricity generation (Section 1, line 56).

> P 10211 Line 26-27: The Wolff and Lioy (1978) and Jacob et al. (1993) references are very dated and a lot of research has been more recently done on empirical relationships between ozone and meteorological variables.

We have included in this section references to recent studies done by Camalier et al. in 2007, Dawson et al. in 2007 and Baertsch-Ritter et al. in 2004, all of which us various models to define the relationship between ozone concentrations and various meteorological parameters (such as temperature, specific humidity, wind speed, etc.). (Section 1, line 65).

> P 10215 Line 3: "…increasingly larger amount…". Is the increase over time or increase with respect to the larger inventory?

We understand the confusion with using "…increasingly larger amount…" to describe the increase in proportion of NO_x inventory to transportation. This has been changed to "When considering only emissions made directly in the city, transportation accounts for an *even* larger amount (73 %)…" (Section 2.1, lines 137-141).

> P 10215 Line 8: Has smog been defined? Is this meant to be photochemical smog? Many definitions of smog include PM2.5, and I wonder if the authors mean to introduce PM2.5 trends into the discussion.

The reference to smog in this study was meant to be a suggestion of photochemical smog, we have included a definition of it in the Section 1, lines 56-57.

> P 10215 Line 15: How complete were the datasets? How were missing data treated?

Datasets were very complete (less than ~24 individual hours in each summer were missing O_3 or NO_2 measurements). Any missing data was treated as an undefined value (NaN). This has been included in the manuscript (Section 2.1, lines 152-154).

> P 10216 Line 1: List the 5 sampling dates.

We have added the 5 sampling dates (Aug 27, Aug 31, Sep 2, Sep 9 and Sep 12) (Section 2.1, lines 166-167).

> P10216 Line 5: How were 8hr averages calculated – were the 24 such averages in a day? Was the date of the starting hour used to assign the 8-hr average to a specific day? How was missing data treated in calculating the averages?

8-hr averages were calculated by considering each hour in a particular day (0:00-23:00) and averaging the ozone (or O_x) concentration during a time period that includes 3 hours prior to that time and 4 hours following that time (total 24 points of 8 hour concentrations). The largest value was reported as the maximum 8-hr average for the given day, assigned using the fourth hour. Any missing data were treated as undefined values and left as such while calculating the averages. This information has been included in the manuscript (Section 2.2, lines 170-175).

> P 10261 Line 15: The authors should be aware that only isoprene was measured in NAPS canister prior to 2003, with isoprene and terpenes being analyzed post-2003 (Daniel Wang, personal communications). Thus biogenic concentrations can potentially show increasing trends over time.

We thank the reviewer for this information. In our analysis we began reporting biogenic VOC reactivity in 2003 and therefore the issue of changing the isoprene collection does not affect the interpretation of our results. We have included in the manuscript that terpenes were collected as well as isoprene (Section 2.2, line 185).

> P 10217 Line 1: The description of meteorological datasets should be moved to section 2.1 (study region and data collection).

We thank the reviewer for their suggestion to move the description of meteorological datasets to Section 2.1, however, we feel that leaving it in its own section allows the reader to more easily refer to it while they are reading the results/discussions of these particular analyses.

> P 10217 Line 20: Why is 11:00 to 15:00 defined a midday – is the average summer time of solar noon in Toronto at 13:00? Are the times Local Standard or Local Daylight Savings time?

11:00-15:00 was defined as midday as these were the most photochemically relevant hours for O_3 production (following examination of the O_3 diurnal cycle) and the time period is fairly consistent with the timing of solar noon in Toronto during the summer (~12:30 EST). Times are in Eastern Standard Time. This information was included in the manuscript (Section 2.2, lines 175-177).

> P 10220 Line 10: Fugitive anthropogenic VOC emissions should also increase with higher temperatures.

We agree that fugitive anthropogenic VOC emissions (such as oil/gas evaporation) would increase with temperatures and we have included this in the manuscript (Section 3.3, line 284).

> P 10220 Line 11: How were the number of exceedance days calculated? If multiple stations exceed the 65 ppb (8-hr averaged) ozone concentration, was this day counted multiple times (once for each of the exceeding stations) or just once? How would the change in number of stations reporting ozone influence this exceedance total?

Exceedances were calculated by counting the number of days each summer where the maximum 8-hr O_3 average exceeded 65 ppb. Exceedances were calculated and reported for each individual station (for example: Toronto North had 20 exceedances in 2012 while the Toronto Downtown2 station had 17 exceedances in that same year) and are never reported as a total sum of exceedances for the GTA. Therefore, if multiple stations exceed the 65 ppb maximum, this day was not counted multiple times. For this reason, changing the number of stations will not influence reporting the ozone exceedance total. This was clarified in the manuscript (Section 3.3, lines 284-285) by indicating exceedances in Figure 4 represent those at the Toronto Downtown2 station and not the GTA as a whole region.

> P 10221 Line 6: Is the proportion of days in 2012 with W-NE, W-SE or stagnant days statistically significantly different from the other years?

It is not straightforward to calculate the statistical significance of the relative frequency of transport categories. We have amended the text to emphasize that the more important insight from the categorization is that the diurnal profiles on stagnant and southerly flow day reach the highest maxima in 2012.

> P 10221 Line 13: Why was the Toronto North Station singled out for this analysis? Are the conclusions the same if other stations are used?

Analysis of data from all stations produced the same conclusions, so only one station was included as an example (now mentioned in Section 3.3, lines 291-292). To keep the analyses consistent, we have changed the example station displayed in Figures 4 and 5 to the Downtown2 station to remain uniform with the wind vector and radiation analyses.

> P 10221 Line 15: Figure 5 only tells us that W-SE direction is associated with the highest average summertime levels, not the highest or exceedance levels.

We agree with the reviewer that Figure 5 only demonstrates that W-SE and Local wind designations are associated with the highest average summertime levels. To demonstrate that these two wind designations correlate with ozone exceedances, we have included in Table 1 the percentage of exceedances at the Downtown2 station that arise from each wind designation for 2008-2012. During these five years, it is evident that majority of the exceedances at the Downtown2 station occur on days when air transport is from the W-SE or local/stagnant. This has been updated in the manuscript (Section 3.3, lines 310-313).

> P 10221 Line 15+: Figure 5 also shows that in 2010, W-NE air masses were associated with lower average Ox temporal profiles, but the text says all years had consistent profiles.

We think the reviewer raises a good point, the three years in fact did not have consistent temporal profiles when the air mass was from the W-NE. A better description is that the variability between the three years when the air mass is from the W-NE is not as great as the variability for the W-SE or Local designations. This has been included in the manuscript (Section 3.3, lines 316-318).

> P 10222 Line 3+: Why were only the midday hours considered in the radiometer data? Would total cumulative radiation be more relevant? Aren't ozone and HONO photolysis important morning sources of radical initiation?

The HO_x production reactions have a λ dependence: $O_3 + h\nu \rightarrow O(^1D) + O_2$ ($\lambda < 320$ nm) and $HONO + h\nu \rightarrow OH + NO$ (300 nm < λ < 405 nm). Since the relationship between the photolysis rates and the radiometer data is not constant with time of day, we chose to select for midday data to ensure we were examining variability of radiation when HO_x, and thus ozone, production is maximized.

> P 10222 Line 10+: Could figure 6b be redone so that the number of summer days with a certain radiation threshold is reached can be read directly from the x-axis?

We thank the reviewer for the suggestion, we have added markers for each year just above the x-axis so a reader can easily see that 2012 had more days with radiation exceeding 600 W/m^2. A description of this has been provided in the caption for Figure 6.

> P 10223 Line 17: I thought the NAPS data are analyzed for 176 VOC compounds, not 40?

Yes, it is correct that the NAPS data are analyzed for a much larger suite of VOC compounds. We ended up analyzing for 40 compounds for 2 reasons: (1) not all 160 VOC compounds that are

measured at our 4 chosen sites have reported rate constants with OH and therefore could not be included in our VOC reactivity analyses; (2) because we are calculating summer summations of VOC reactivity, we needed to ensure that we chose a consistent suite of VOC compounds that were present at all 4 sites as well as continuously reporting data over the entire summer for all summers considered (if a compound had data reported one summer but not the subsequent summer, the VOC reactivity would have been interpreted as a decrease but this is not an actual trend and just missing of VOC data for that year). Therefore, once both of these conditions were considered, we were left with a suite of 40 VOC compounds. It is possible that exclusion of some of these VOCs lead to our analysis underestimating total VOC reactivity. For example at the West1 station in 2010, the contribution of removed VOCs was ~9 % to the total VOC reactivity but because these compounds were not consistently measured across sites and years, they had to be excluded. The majority of excluded compounds individually contribute minimally to total VOC reactivity, <1 %. This was clarified in the manuscript (Section 2.2, lines 188-192).

> P 10224 Section 3.5: Do each of the VOC pairs have similar ozonolysis rates? If they don't, then changes in daily ozone concentrations would potentially confound this analysis. This problem would be most severe for the butene pair.

This is an interesting point that we considered as well. The VOC pairs do not have similar ozonolysis rates however we know how the concentration of O_3 has changed from the "early" to the "late" period and it is not significant (a few percent) and therefore we have assumed that any change to the ratio of the two VOC pairs is not significantly affected by a change in their ozonolysis. This was clarified in the manuscript (Section 3.5, lines 397-399).

> P 10226 Line 1+: Should state that the results are for summertime mean daily concentrations of ozone precursors.

This sentence has been changed in the manuscript to refer to summertime mean daily concentrations of ozone precursors (Section 4, line 431).

> P 10226 Line 22: It should state mid-day levels incoming solar radiation…

This sentence has been changes in the manuscript to state midday levels of incoming solar radiation (Section 4, line 449).