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

Stephanie C. Pugliese, Jennifer G. Murphy, Jeffrey A. Geddes, Jonathan M. Wang

Response to Anonymous Referee #1

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

Major Comments

1. It would be more appropriate to analyze trends in terms of %/year changes. This is likely to better fit the data and better represent the underlying relationship, and would allow for easier comparison across sites and pollutants.

We agree that it would be more appropriate to analyze trends in terms of percent per year changes; this has been updated in Section 3.1 and throughout the rest of the manuscript.

2. Results are presented primarily in terms of summertime averages, which is appropriate. However, two other temporal metrics are of interest as well: (1) fourth-highest daily max 8-h ozone, to better align with the form of the Canadian regulatory standard, and (2) looking beyond summer, since some studies indicate health impacts of ozone extend to low concentrations and sensitivity relationships are likely to be very different in other seasons. In addition, it would be informative to comment on differences between conditions on high and low ozone days within the summer.

Thank you for the suggestion regarding the use of other temporal metrics.

(1) We do agree that there is value in using a metric that aligns with the Canadian regulatory standard. In Figure 4 we include the Design Value for each year and we think this is adequate to give the reader a sense of how the Canadian regulatory standard is being met (or exceeded). We feel that using summertime averages allows us to analyze correlations between ozone and meteorological parameters (for example: when air is from the W-NE, 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 4th highest daily max 8-hr ozone.

(2) It is true that the health impacts of ozone can extend to low concentrations (indeed this supports our focus on summer averages above) and therefore other seasons could be considered. However winter ozone levels in the GTA are generally much lower between October and April, and the balance of factors governing its abundance may be very different than during the summer months. For example, throughout the 13 year study period, Toronto North exceeded the 65 ppb 8-hr maximum once in the non-summer seasons in 2007 and 2008, with no exceedances for all other years. We chose to focus the scope of our analysis of chemical and meteorological factors on the most photochemically active time of the year.

To discern the differences between conditions of high and low ozone days within the summer, we considered a number of meteorological parameters (such as temperature, wind direction and incoming solar radiation) and found, for example, that days with wind from the W-SE and/or with higher levels of incoming solar radiation, ozone concentrations were higher (Figures 5 & 6).

3. Despite its usefulness in some other contexts, it's unclear that Ox is an appropriate metric for characterizing long-term trends in ozone, especially given the ozone regulatory context. Here, NO₂ declined far more steeply than O₃, so most of the Ox trend reflects reduction in NO₂.

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 NO₂. 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.

4. In Section 3.4, is there evidence to indicate where the transition lies between NO_{x} - and VOC-limited ozone formation regimes, in terms of the ratios of OH reactivity to NO_2 and to VOCs that are reported here?

A study done in 2009 by Geddes et al. analyzed long-term changes in nitrogen oxides and VOCs in Toronto and used a computational model to generate a contour plot of instantaneous ozone production as a function of VOC reactivity and NO₂ concentrations. This contour plot was produced under conditions of optimal ozone production. According to this plot, in order for Toronto to be NO_x -limited, NO_2 concentrations must be below ~2 ppb and VOC reactivity can range from ~1-6 s⁻¹. While for the suburban sites, such as Newmarket, some hours of the day reach these low levels of NO_2 , averaged over the midday and throughout the summer, NO_2 concentrations are higher than this and therefore production of ozone is consistently on the VOC-limited side of the contour plot at all eight sites. This is a result consistent with Figure 7 in the manuscript which outlines in the "late" period of the study, the GTA is in a VOC-limited regime. This information has been included in the manuscript (Section 3.4, lines 361-364).

5. The text and Figures 2c have helpful delineation between types of VOCs, but then it becomes unclear which VOCs are being included in Table 2, Figure 7 and some portions of the text. This should be clarified.

We thank the reviewer for pointing this out, we have clarified in the text that the original suite of \sim 40 NAPS compounds are included in Table 2 and Figure 7.

6. The authors adopt a thoughtful technique to use VOC ratios to gauge trends in OH, and find evidence for increasing OH. Was this expected? Has modelling been conducted to examine whether it predicted a rise in OH under large-scale NOx and VOC reductions as have occurred in Toronto?

Yes, an increase in OH concentration throughout the study was expected. Assuming that the production rate of OH has not changed significantly, which is reasonable if ozone has stayed nearly constant and $O^1D + H_2O$ is the main OH source, then a large decrease in the sinks of OH (VOC and NO₂) would likely lead to an increase in its concentration. To our knowledge, no modeling has been conducted to examine whether a predicted rise in OH under large-scale NO_x and VOC reductions has occurred in Toronto.

Minor Comments

p. 10211, line 3: Pointing to a \$9.6 billion impact in Ontario is somewhat misleading in a paper focused on ozone, since most of that impact presumable arose from particular matter.

We thank the reviewer for this suggestion. To ensure the reader is not misled and to highlight that ozone is responsible for only a *fraction* of the \$9.6 billion in economic losses, we specified that the 2014 Toronto Public Health Burden of Illness Update reports that ozone is responsible for 14 % and 29 % of the premature morality and hospitalizations, respectively, in the city (Section 1, lines 40-43).

p. 10222, line 1: change "was" to "were"

We have changed "was" to "were".

Response to Anonymous Referee #2

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 NO₂. 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 NO₂ 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 NO₂ 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 8hr 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: O₃ + hv \rightarrow O(¹D) + O₂ (λ < 320 nm) and HONO + hv \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).

Response to Anonymous Referee #3

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

For the analysis of meteorological data and the corresponding influences on Ox, two different sites were chosen: Toronto North to investigate wind influence and Downtown2 for solar radiation. It is not clear why these two sites were selected; in fact, it is not clear if the same conclusions hold if the analysis is conducted for other sites. This should be clarified.

We thank the reviewer for this suggestion. The two sites for the different meteorological analyses were arbitrarily chosen (all sites show generally the same trends and offer the same conclusions), however we recognize that this is confusing. Therefore, in the revised manuscript the Downtown2 site has been chosen as the example site for all meteorological analyses and it has been indicated in

the text that analyses with other stations give the same general conclusions (Section 3.3, lines 291-292 & lines 323-325).

I found confusing the analysis conducted on the influence of wind patterns on Ox. First of all, the analysis is carried out only for 2008-2012, why not use more years to have more data and do a more robust statistical analysis? Authors indicate that "...the summer of 2012 was affected by a larger number of days with air transport from the W-SE, the fewest days with air transport from the W-NE and the highest number of stagnant periods..." Comparatively, the summer of 2012 had less W-SE than 2010 and about the same as 2008. Similarly, all years have about the same days of stagnant conditions (2010 being the lowest). Using "fewest", "highest", "large" can be confusing: between use a more quantitative analysis. Lastly, in the conclusions, the authors indicate that "...air transport from upwind regions may have [played a role in the O_x increase]..." However, in the discussion of the results, authors indicate that "...Ox concentrations cannot be explained by wind transport...". There is an apparent contradiction here. (Minor comment: error bars in Fig 5 might help to give an idea of the variability of the data).

We thank the reviewer for the comment. We chose to carry out this analysis for 2008-2012 and not more years because 2008-2011 were four years with consistently low ozone and O_x concentrations (Figure 3) and 2012 was an anomaly to this. Therefore, we thought it would be interesting to compare the 4 consistently low ozone years to the high 2012 anomaly.

Very good point, using descriptors like "fewest", "highest" and "large" is a confusing way to compare 5 years of data. Therefore, to be consistent with Table 1, we have changed this section to "Throughout this period, the summer of 2012 was affected by a large percentage of days with air transport from the W-SE, a small percentage of days with air transport from the W-NE and a large percentage of days experiencing stagnant periods (consistent with the previous four years)." This removes the use of text descriptors (like "fewest" and "large") and should be less confusing for a reader.

In the discussion of the results, we indicated that differences in O_x concentrations on days characterized as "local" cannot be explained by wind transport (because from our net wind vector analysis, any days termed local did not travel more than 120 km from Toronto and therefore presumably only has minimal reliance on wind direction). Because we saw that 2012 daily O_x (and O_3) was higher when air was termed "local" than in previous years we could not attribute this to precursors coming from the W-SE and so we continued our analysis to include photochemical activity. However, because we saw that 2012 daily O_x/O_3 reached higher levels on days when air is from the W-SE, we have indicated in the Conclusions that air transport from *upwind regions* may have played a role in this.

Thank you for the suggestion, we have added error bars to Figure 5.

OVOC data at a very limited extent are presented (Fig 2) and not discussed at all. If no additional insight can be derived from it, I suggest removing it from the paper.

We agree that further discussion of the OVOCs in Figure 2 should be included if it the data are kept in the paper. It is now discussed in Section 3.1 that OVOC reactivity shows a small increase from 2000-2004 however with only 4 years of data no significant conclusions can be drawn (lines 242-243). This is an important consideration because later in the paper we discuss how exclusion of OVOCs from NAPS monitoring results in a large underestimation of total VOC reactivity (since OVOCs account for ~60 % of total VOC reactivity). Therefore the apparent increasing trend observed at Junction from 2000-2004 further justifies the need to monitor OVOCs in the GTA (since they are not stagnant like biogenic VOCs).

Specific Comments

P 10210 line 6: Define GTA in abstract.

GTA has been defined in the abstract (line 18).

P 10211 line 3: For the international readership, define if \$ are US Dlls or else.

We have specified that the \$9.6 billion in losses is in Canadian currency (CAD) (Section 1, line 40).

P 10211 line 19: "...fuel combustion and transportation...". Clarify because there is an overlap here (part of the transportation emissions come from fuel combustion).

This is a very good point, the dominant sources of NO_x have been changed to transportation and electricity generation (Section 1, line 56).

P 10211 lines 26-27: References are quite old (particularly Wolff and Lioy, 1978). I suggest updating these.

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 10214 line 20: Use GTA instead of Greater Toronto Area.

We have changed Greater Toronto Area to its abbreviation, GTA (Section 2.1, line 134).

P 10215 line 2: "...emissions made directly in the city...". I found confusing this statement, please clarify.

To clarify this better, we have indicated that "emissions made directly in the city" neglects those that are from energy generation outside Toronto required to meet the city's needs (Section 2.1, lines 138-139).

P 10215 line 6: "...frequent smog episodes...". I found ambiguous this statement. I suggest giving quantitative data (e.g. % of days above a given limit for a given species [03, OMx, etc.])

We thank the reviewer for this suggestion, we have added details that smog advisories in the City of Toronto range from 1 (in 2011) to 14 (in 2005) (Section 2.1, lines 142-144).

P 10215 lines 24-26: Provide a reference where additional details on how the carbonyls sampling and analysis was conducted, or else provide the details here.

A reference (Wang et al., 2005) was included following the discussion of the carbonyl sampling and analysis to provide further insight into this technique (Section 2.2, line 163).

P 10216 line 13: Is Seinfeld and Pandis (2006) the best reference for this?

While we agree with that Seinfeld and Pandis (2006) may not be the best reference, in Section 5.13.1 it is explained in detail the use of a VOC's reactivity with OH over its concentration to determine its role as an ozone precursor. Therefore, we feel that any reader who is unfamiliar with using this method can easily become accustomed following reading this chapter of Seinfeld and Pandis (2006).

P 10217 lines 17-18: For completeness, provide coordinates or incorporate a marker in Figure 1 on the location where the solar radiation device was deployed.

A marker was added to Figure 1 marking the location of the UTMMS radiometer and a reference was made in the manuscript (Section 2.3, line 213).

P 10218 line 7: I guess it should be "continues."

It has been changed to continues.

P 10218 line 14: For completeness, provide coordinates or incorporate a marker in Figure 1 on the location where the Lakeview Generating Station was located.

A marker was added to Figure 1 marking the location of the Lakeview Generating Station and a reference was made in the manuscript (Section 3.1, line 231).

Figure 4. Right vertical axis should read "30 Deg C", not "30 Dec C".

It has been changed to "30 Deg C."

Manuscript with all changes tracked:

The following is a draft of the manuscript with referee suggestions addressed and all changes tracked:

The impacts of precursor reduction and meteorology on ground-level ozone in the Greater Toronto Area

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Abstract

Tropospheric ozone (O_3) is a major component of photochemical smog and is a known human health hazard as well as a damaging factor for vegetation. Its precursor compounds, nitrogen oxides (NO_x) and volatile organic compounds (VOCs), have a variety of anthropogenic and biogenic sources and exhibit non-linear effects on ozone production. As an update to previous studies on ground-level ozone in the Greater Toronto Area (GTA), we present an analysis of NO_2 , VOC and O_3 data from federal and provincial governmental monitoring sites in the GTA from 2000-2012. We show that over the study period, summertime 24-hr VOC reactivity and NO₂ midday (11:00-15:00) concentrations at all sites decreased significantly; since 2000, all sites experienced a decrease in NO_2 of 28-62 % and in measured VOC reactivity of at least 53-71 %. Comparing 2002-2003 to 2011-2012, the summed reactivity of OH towards NO₂ and a suite of measured VOCs decreased from 8.6 to 4.6 s⁻¹. Ratios of reactive VOC pairs indicate that the effective OH concentration experienced by primary pollutants in the GTA has increased significantly over the study period. Despite the continuous decrease in precursor levels, ozone concentrations are not following the same pattern at all stations; it was found that the Canada-Wide Standard for ozone continues to be exceeded at all monitoring stations. Additionally, while the years 2008-2011 had consistently lower ozone levels than previous years, 2012 experienced one of the highest recorded summertime ozone concentrations and a large number of smog episodes. We demonstrate that these high ozone observations in 2012 may be a result of the number of days with high solar radiation, the number of stagnant periods and the transport of high ozone levels from upwind regions.

1. Introduction

At ground level, O_3 is toxic to both humans and vegetation as a result of its ability to oxidize biological tissues (Bell et al., 2005). It is well documented that human exposure to ozone leads to respiratory symptoms and increased risk for hospital admissions (Bell et al., 2004) and as a result of these and reduced agricultural yields, yearly economic losses attributed to ozone and fine particulate matter pollution are as high as \$9.6 billion <u>CAD</u> in the province of Ontario alone (MOE., 2005). In Toronto, ground-level ozone is responsible for 13 and 29 % of incidences of premature mortality and hospitalizations associated with air pollution (with PM_{2.5} and NO₂ responsible for the remainder) [Toronto Public Health., 2014]. In response to this, many governments and regulatory agencies have imposed air quality standards to protect the population against exposure to O_3 and other pollutants. In 2000, Canada adopted a Canada-Wide Standard (CWS) for ozone, which states that the 3 year average of the 4th highest daily maximum 8-hr average should not exceed 65 ppb. In 2007 the City of Toronto, Canada's largest urban area, made a commitment in its Climate Change Clean Air and Sustainable Energy Action Plan to reduce emissions of local smog-causing pollutants 20 % below 2004 levels by 2012 (City of Toronto., 2007). This regulation is happening in the context of regional scale initiatives to control emissions of ozone precursor compounds, such as the "Drive Clean" vehicle test program in Ontario (MOE., 2013) and the phasing out of coal-fired power generating stations (Bradley, 2013). However, as a secondary pollutant, O_3 has proven to be one of the most difficult pollutants to bring into compliance with air quality standards. Its precursor compounds, VOCs and NO_x ($NO_x = NO + NO_2$), are emitted by a variety of anthropogenic and biogenic sources, the former dominated by combustion, fuel evaporation and chemical manufacturing while the latter dominated by fossil fuel combustion and transportation and electricity generation (ICF., 2007). These primary pollutants interact in the presence of sunlight (forming a condition known as photochemical smog) producing ground-level ozone and other secondary pollutants; Thowever, the production rate of ozone depends on precursor concentrations in a non-linear fashion. Furthermore, pPrevious studies

of O₃ concentrations have indicated considerable variability from day to day and from year to year as a result of not only changes in precursor emissions but also meteorology (Agudelo-Castaneda et al., 2013; Figueiredo et al., 2013; Jacob et al., 1993; Pekey and Ozaslan, 2013; Psiloglou et al., 2013). Empirical <u>and model</u> studies have shown very strong positive correlations between O₃ production and temperature (Wolff and Lioy, 1978) and weaker correlations of ozone accumulation with wind speed and direction, pressure, cloud cover and humidity (Baertsch-Ritter et al., 2004; Camalier et al., 2007; Dawson et al., 2007; Jacob et al., 1993). All of these meteorological parameters affect the photochemistry occurring in the troposphere and therefore the rate of O₃ production.

In the troposphere in the summertime, ozone is produced rapidly via the photochemical oxidation of VOCs in the presence of NO_x . During the day, the interconversion of NO and NO_2 occurs with O_3 on the order of minutes (following R1a-2).

$$NO_2 + hv \rightarrow NO + O$$
 (R1a)

$$0 + O_2 + M \rightarrow O_3 + M \tag{R1b}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{R2}$$

This chemistry produces a null cycle with respect to NO_x and O_3 , there is no net production or consumption of either. However, in the presence of VOCs, net production of O_3 can occur following oxidation of a hydrocarbon (RH, where R is any organic group) by the hydroxyl radical, OH, producing an organic peroxy radical, RO_2 (R3). The organic peroxy radical can then further react with NO to form NO_2 and an organic alkoxy radical, RO (R4).

$$OH + RH + O_2 \rightarrow H_2O + RO_2$$
(R3)

$$RO_2 + NO \rightarrow RO + NO_2 \tag{R4}$$

The NO₂ formed in R4 can photolyze during the daytime to regenerate NO and an oxygen atom (R1a), which can then recombine with an oxygen molecule to form O_3 (R1b). There are several

possible fates for the RO radical, it may react with O_2 , thermally decompose or isomerize. Typically, carbonyl compounds and an HO_2 radical are produced (R5) and the net reaction (R1-R6) results in the formation of two ozone molecules (R7).

$$RO + O_2 \rightarrow R'CHO + HO_2$$
 (R5)

$$HO_2 + NO \rightarrow OH + NO_2$$
 (R6)

$$RH + 4O_2 \rightarrow R'CHO + 2O_3 + H_2O \tag{R7}$$

In this study, the total oxidant, O_x , is defined as the sum of NO_2 and O_3 ($[O_x] = [NO_2] + [O_3]$) and therefore O_x can only increase in the presence of VOCs when O_3 is formed via reactions (R3) and (R4) followed by (R1a+b), whereas it is conserved when O_3 is formed via (R2) followed by reactions (R1a+b). It is often advantageous to analyze O_x over O_3 because it The advantage of analyzing O_x over O_3 is that O_x -is a better measure of the photochemical production of ozone as it more closely represents the total oxidant; it is not affected by the titration of O_3 with NO.

This catalytic ozone production chain is terminated by the loss of HO_x radicals ($HO_x = OH + RO + HO_2 + RO_2$), which can occur by multiple pathways. In an environment with a low NO_x :VOC ratio, such as a rural location, peroxy radicals may undergo a self-reaction instead of reacting with NO to produce peroxides or other oxygenated compounds (R8).

$$RO_2 + R'O_2 \rightarrow ROOR' + O_2 \tag{R8}$$

Under this pathway, the addition of NO_x increases O_3 production by enhancing the rate of (R6) while addition of VOCs has a negligible effect as they can react with nearly every OH produced. Thus, O_3 production increases linearly with increasing NO_x and is less sensitive to VOC reactivity. However, in an environment with a high NO_x :VOC ratio, the dominant sink for HO_x is the oxidation of NO_2 by OH, forming nitric acid (R9).

$$NO_2 + OH + M \rightarrow HNO_3 + M$$
 (R9)

Under this pathway, the addition of NO_x decreases O_3 production because NO_2 can compete with VOCs for OH. Thus, O_3 production becomes inversely proportional to NO_x levels and more sensitive to VOC reactivity.

Alternatively, chain termination can also occur following the reaction between peroxy radicals and NO_x, forming peroxy acyl nitrates (PNs = RC(O)O₂NO₂, R10) or alkyl nitrates (ANs = RONO₂, R11) (Farmer et al., 2011). PNs serve as a temporary reservoir for NO_x and suppress Θ_x - Ω_3 formation in the near-field but transport and release NO_x in the far-field, extending the formation of ozone (Perring et al., 2010). Conversely, ANs are considered permanent sinks for NO_x, affecting only local Θ_x - Ω_3 production (Perring et al., 2010).

$$RC(0)O_2 + NO_2 \leftrightarrow RC(0)O_2NO_2$$
(R10)

$$RO_2 + NO + M \rightarrow RONO_2 + M$$
 (R11)

This analysis extends an earlier study by Geddes et al. (2009) that demonstrated how summertime VOC reactivity and ambient concentrations of NO₂ decreased from 2000 to 2007 by up to 40 % in the Greater Toronto Area (GTA), but no significant ozone reductions were observed. It was argued that decreased titration may have contributed to higher O₃ mixing ratios, and that air transport from the southwest may have contributed to early morning O_x levels (Geddes et al., 2009). In this work, we discuss how GTA <u>ozone Θ_x -levels</u> now appear to be responding to decreases in precursor compounds, as significant reductions are observed from 2000 to 2012. We also identify that in the short term, 2012 marked one of the highest years in GTA <u>ozone Θ_x -during the study period</u>. We discuss the strong link between <u>ozone Θ_x -levels</u> and local meteorology, particularly solar radiation as well as the degree of regional air transport, to help explain this occurrence. We also examine changes in OH reactivity and abundance over the study period.

2. Methods

The City of Toronto (43°40' N, 79°23'W) is located in Southern Ontario on the northwest shore of Lake Ontario, and is the largest urban area in Canada as well as one of its most densely populated regions (945.4 persons per square kilometre) (Statistics Canada., 2012). The Greater Toronto AreaGTA comprises four municipalities, Halton, Durham, Peel and York, which together have a population exceeding 6 million (Statistics Canada., 2012). During the summer, the GTA is affected by warm southerly and south-westerly air transport, as well as local land-lake breezes from Lake Ontario (Makar et al., 2010). The city's NO_x emissions are dominated by the transportation sector (63 %), with diesel trucks accounting for a disproportionately large percentage (36 %) (ICF., 2007). When considering only emissions made directly in the city (neglecting those from energy generated outside the City of Toronto required to meet the city's needs), transportation accounts for an even increasingly-larger amount (73 %) of total NO_x emissions, with diesel vehicles accounting for 45 % of this total (ICF., 2007). In Toronto, anthropogenic VOC emissions are almost exclusively from gasoline powered cars and light trucks (ICF., 2007). Despite efforts made by the city to reduce emissions of smog precursors, the GTA issues frequent smog advisories each year, historically ranging from 1 advisory in 2011 to 14 advisories in 2005 (MOE, 2014). The GTA experiences frequent smog episodes despite efforts made by the city to reduce emissions of smog precursors.

 NO_x , O_3 and VOC data used in this study were obtained from the National Air Pollution Surveillance (NAPS) network. For the NO_x and O_3 analyses, eight sites across the GTA were selected, four of which are considered urban (Downtown2, Toronto North, Toronto East, and Toronto West2) and four which are considered suburban (Oshawa, Brampton2, Newmarket and Oakville), see Fig. 1. Hourly data for both NO_x and O_3 are available from the year 2000 onwards and are publically accessible at <u>http://www.airqualityontario.com</u>. At all stations, NO_2 and O_3 measurements were made by automated continuous chemiluminescent and UV-absorption analyzers respectively, with sampling heights varying from 4-12 m above ground level. <u>All datasets were complete (less than ~24</u> individual hours per summer not having a measurement) and any missing data were treated as undefined values. During the same study period, VOC data were obtained from Environment Canada for four stations across the GTA (Downtown1 (sampling from 2002-present), Toronto West1 (sampling from 2000-2010), Junction (sampling from 2000-2005) and Brampton1 (sampling from 2001-2010)), also shown in Fig. 1. At all stations, 24-h samples were collected once every 6 days by evacuated electropolished stainless steel canister and sent to Environment Canada (Ottawa, Ontario) for analysis by gas chromatography/flame ionization detection (for C2 hydrocarbons) and gas chromatography/mass spectrometric detection (for C_3 - C_{12} hydrocarbons) as described in Wang et al. (2005). In 2000, 2001, 2004 and 2005, carbonyl compounds were automatically sampled at the Junction site using 2,4-dinitrophenylhydrazine coated silica Sep-Pak cartridges for 24 h, then separated and identified using HPLC and UV DAD detection at 365 nm (Wang et al., 2005). Additional VOC sampling was carried out in 2011 at the Downtown Toronto sampling site (Downtown 1) using an automatic sampler (model 910PC, XonTech Inc., VanNuys, CA) with eight consecutive 3-h samples collected every 24 hours over five days during late summer (Aug 27, Aug 31, Sep 2, Sep 9 and Sep <u>12</u>). Samples were analyzed for both non-polar and polar VOCs using GC techniques described in (Wang et al., 2005).

2.2 O₃, NO_x and VOC Analyses

Daily 8-hr maximum O_3 and O_x were calculated for each site throughout the thirteen year study period; this was done 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 and 4 hours following that time (creating a 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. The O_3 diurnal cycle was examined and it was determined that the most photochemically relevant hours for O_3 production were between 11:00 and 15:00 (LEST; solar noon is approximately 12:30 EST during the summer). Therefore, NO₂ hourly data were

averaged during this time period (hereafter referred to as the "NO₂ midday average"). Using this data, annual summer averages were calculated (where summer is defined as May to September inclusive) as it is the most photochemically relevant time of year.

VOC reactivity was calculated as the product of the VOC's number density and its rate constant against the hydroxyl radical (Atkinson, 1997; Seinfeld and Pandis, 2006). Summer annual averages for total VOC reactivity were calculated as the sum of all VOC reactivity ($\sum k_i$ [VOC_i]) in units of inverse seconds. The influences of biogenic, anthropogenic and oxygenated VOCs (OVOCs) were distinguished by identifying the sum of isoprene (and terpenes), cymene, pinene, limonene and camphene as biogenic VOCs, the sum of formaldehyde, acetaldehyde, acrolein, acetone, and propionaldehyde as OVOCs (applicable for only the Junction site) and the sum of the remaining 40 VOCs as anthropogenic. Although the NAPS network monitors for a larger suite of VOC compounds, we chose the 50 compounds that were consistently measured across all sites and years included in this analysis to remove incorrect interpretation of inter-annual and inter-spatial variability in the data (removed compounds generally contributed less than ~9% of total VOC reactivity for a summer period).

For all compounds, annual trends were calculated by a linear regression analysis and their significance measured by their p-values. P-values were calculated from a standard T-test where the null hypothesis being tested is that the slope of the regression line is equal to zero. Annual trends with p-values < 0.05 are considered significant.

2.3 Meteorological Analyses

Hourly meteorological data was continuously collected throughout the study period at Toronto's Pearson International Airport<u>, Fig. 1</u>, and this data was accessed from National Climate Data and Information Archive operated by Environment Canada. Maximum daily temperatures were calculated for each summer and the number of days where this maximum exceeded 30 °C was recorded. From this same archive, hourly wind speed and direction were obtained and net wind vectors were calculated for a 12 hour period prior to each afternoon (00:00 to 12:00) to assess air mass history. This technique was adopted from Geddes et al. (2009) where the magnitude of the x- and y- component of the hourly wind vector was summed and used to calculate the resultant vector by trigonometry. The result is a single vector that represents the strength and the net direction of air transport for each day. This approach was chosen because the location of the GTA on the northern shore of Lake Ontario leads to frequent local lake breeze flow patterns that are not generally well-represented in back trajectory analyses (Sills et al., 2011).

To assess the level of photochemical activity occurring on each day, the amount of incoming solar radiation was analyzed. Data were collected using both a Net Radiometer (CNR1, Campbell Scientific Corp.) and a Pyranometer (CMP 11, Kipp and Zonen B.V.) operated at the University of Toronto Mississauga Department of Geography's Meteorological Station (UTMMS), Fig. 1. From the hourly data, midday (11:00 to 15:00) solar radiation averages were calculated in W m⁻².

3. Results and Discussion

3.1 Long term precursors and O_3 levels (2000-2012)

Annual summer midday averages of daily NO₂ are shown in Fig. 2a and b, demonstrating that an overall decrease is present throughout the thirteen year study period (2000-2012). The urban sites have the steepest slopes, between -0.64 and -0.92 ppb·year-1 (p<0.01)-<u>w</u>while the suburban sites also have decreasing trends of -0.20 to -0.55 ppb·year-1 (p<0.05). Overall, <u>throughout the</u> thirteen year study period, urban sites experienced an average decrease of -6.4 % per year (with Toronto Downtown2 experiencing the largest decreases at -6.9 % per year) while the suburban sites experienced an average decrease of -5.8 % per year (with Brampton experiencing the largest decreases at -7.2 % per year), the summer averages in 2012 were at least 45 % lower than 2000 levels at the urban sites (the largest difference is in North Toronto with a decrease of 54 %) and at least 28 % lower at the suburban sites (the largest difference is in Brampton2 with a decrease of 62 %).-The most urban station (Downtown2) and that closest to a major highway (West2) continues to report the highest NO₂ levels of all the monitoring stations. Furthermore, the stations furthest removed from the urban center and major highways, Newmarket and Oakville, report the lowest NO₂ levels. From 2000 to 2010, the number of registered vehicles in Ontario has increased from approximately 8.6 to 10.6 million (Statistics Canada., 2011) and therefore the decrease in NO₂ levels is likely related to improvements in vehicle catalyst technology or the phasing out of older, lessefficient vehicles (MOE., 2013). Other factors may include the closure of the Lakeview Generating Station, Fig. 1,-_within the GTA in 2005 (NO₂ emissions in 2004 were 5000 tonnes), as a part of Ontario's phasing out of coal-fired power generating stations (Bradley, 2013), and the large reduction of emissions from the Nanticoke Generating Station, located less than 100 km southwest of the GTA (NO₂ emissions decreased from 38000 to 3000 tonnes between 2002 and 2012).

A similar decreasing trend is apparent for anthropogenic VOCs in the GTA. Annual summer averages of VOC reactivity are shown in Fig. 2c and a steadily decreasing trend for anthropogenic VOCs is apparent across all sites. Monitoring at Junction stopped in 2005 and at West1 and Brampton1 in 2011; therefore only Downtown1 data are available for 2011 and 2012. All sites have statistically significant declining slopes, between -0.16 and -0.23 s⁻¹·year⁻¹ (p<0.01) and <u>an average</u> overall decreases <u>of -9.3 % per year of at least 53 % from 2000 levels</u> (excluding Junction site), with the <u>Downtown1-Brampton</u> site experiencing the largest decrease of 62 %.-11.5 % per year. <u>OVOC</u> reactivity shows a small increasing trend at the Junction site, however, with monitoring stopped in 2005, no significant conclusions can be drawn. VOC reactivity from biogenic sources shows no apparent trend across the study period₂-It is clear that at all sites, VOC reactivity from anthropogenic emissions is approaching the reactivity from biogenic emissions, particularly at the West1 site.

Fig. 3 shows annual summer daily 8-h maximum O_3 and O_x for the GTA. Following the reductions of both its precursor compounds, O_3 and O_x levels have also generally decreased over the study period. Linear regression analyses show that the eight sites have negative slopes for $\Theta_{x}O_{3}$, ranging between -0.03 and -0.29 ppb·year-1 at the urban stations and -0.34 and -0.64 ppb·year-1 at the suburban stations, although decreases are not statistically significant (with the exception of <u>Newmarket</u>). Over the entire study period, decreases in O₃ of -0.4 % per year occurred in the urban stations and -1.1 % per year at the suburban stations. Analyses also show that the eight sites also have negative slopes for O_{x} , ranging between -0.91 and -1.1 ppb·year-1 at the urban stations and -0.57 and -1.0 ppb·year⁻¹ at the suburban stations, most of which are statistically significant (with the exception of Oshawa and Oakville which are both missing data at the beginning of the study period). At all sites slopes are negative for O_3 -but are not statistically significant (with the exception of Newmarket). Over the entire study period, decreases in O_x of $\frac{2.4-7.6-1.8}{9}$ % per year occurred in the urban stations and 3.5-13.9-1.6 % per year at the suburban stations. If 2012 data is removed from the figures, the slopes for O_x become significant (p < 0.01) at all sites, except for Oshawa which has only been monitoring since 2005 (p < 0.07). While these decreases are likely following the reduction of ozone precursor compounds, other studies have found that changes in background concentrations are responsible for decreases at some monitoring stations (such as Whiteface Mountain, New York (Oltmans et al., 2013)) and therefore this cannot be ruled out as a possible influence to the decreasing trends reported here (Oltmans et al., 2013).

3.2 O_{*}-O₃ levels from 2008-2012

While over the entire study period Θ_x - Ω_3 levels in GTA have decreased, from 2008 onwards the same trend is not observed. Figures 3<u>ae</u> and <u>bd</u> show that at all monitored sites, between 2008 and 2011 Θ_x - Ω_3 levels in the GTA were consistent<u>ly</u> lower than from 2000-2007. However, the

measured average summer daily maximum 8-h Θ_{x} Ω_{3} in 2012 was significantly higher than that of the previous four years (an increase of 35-4-7 ppb). The data presented above demonstrates that NO₂ levels have not significantly changed from 2011 to 2012 (the largest change was a decrease of 1.7 ppb at the Toronto North site). Additionally, results show that VOC reactivity decreased from 2011 to 2012. Therefore, the 2012 Θ_{x} - Ω_{3} increase cannot be explained as a result of a change in either of the precursor compounds. Alternatively, this variability in Θ_{x} - Ω_{3} may be explained by meteorological influences, which is explored in the following section.

3.3 Meteorological influences on Θ_{*} O_{3}

Previous studies have provided evidence of a correlation existing between ozone levels and meteorological conditions, such as wind direction and speed, temperature and relative humidity (Agudelo-Castaneda et al., 2013; Figueiredo et al., 2013; Pekey and Ozaslan, 2013; Psiloglou et al., 2013). Specifically, Jacob et al. (1993) discuss the significant dependence of O₃ concentrations on temperature, indicating that at higher temperatures, local O₃ production is maximized as a result of the suppression of radicals being stored as peroxyacetylnitrate (PAN). Higher temperatures may also result in enhanced local production of O₃ by increasing HO_x production, or increasing local biogenic or fugitive anthropogenic (such as the evaporation of oil and/or gas) -VOC emissions. Fig. 4 displays the number of days each year where the <u>Toronto Downtown2 station</u> 8-hr O_3 average exceeded 65 ppb, the number of days which experienced temperatures exceeding 30°C-, as well as the Design Value (the 4^{th} highest 8-hr O_3 measurement annually, averaged over three consecutive years (Environment Canada, 2013)) for that year at the Toronto Downtown2 station. A relationship between ozone exceedances and high temperatures is clear during the 2000-2009 period, but less clear from 2010-2012. Although 2012 had a large increase in the number of days exceeding the O_3 standard, it did not have significantly more days experiencing warmer temperatures compared to 2010 or 2011. This analysis was completed for the other 7 stations and the same conclusions are

<u>drawn.</u> Therefore, based on this data, the warm temperatures experienced in the summer of 2012 did not play the dominant role in the Θ_{x} Ω_{3} increase observed.

High temperatures in the GTA are often associated with warm southerly flow and therefore it is possible that the correlation between O₃ and temperature is driven by air transport from upwind regions. As described in the *Methods* section, net wind vectors for each summer day from midnight to noon were determined. Following Geddes et al. (2009), we defined days when the wind speed and direction resulted in a net movement of >120 km from the south and southwest (135°-270°) as days influenced by "west to south-east flow (W-SE)"; days when the net wind speed and direction resulted in a net movement of >120 km from the north $(270^{\circ}-45^{\circ})$ as days influenced by "west to northeast flow (W-NE)"; and days when the net wind movement was <120 km as "stagnant" or "local". From this designation, days that were affected by W-SE air transport represent days most likely influenced by polluted air masses from surrounding urban areas in Canada and the US, whereas days that were affected by W-NE air transport represent days most likely influenced by transport from remote regions. Table 1 shows the percentage of days affected by each wind designation from 2008-2012. Throughout this period, the summer of 2012 was affected by a large number percentage of days with air transport from the W-SE, the fewest daysa small relatively lower percentage of days with air transport from the W-NE and the highesta large percentage number of days experiencing of stagnant periods (consistent with the previous four years). This could have contributed to the high $\Theta_{x} O_{3}$ levels measured in the GTA in 2012; more because fewer days were being affected by polluted air transport from the south and air being trapped over the city (allowing precursor levels to accumulate and enhance local O₃ production) as well as the fewest days withhad "clean" air transport from the north. Furthermore, Table 1 shows the percentage of exceedances at Downtown2 affected by each wind designation and it is evident that transport from the W-SE and local/stagnant air contributes to ozone exceedances to a higher degree than transport from the W-NE.

Fig. 5 displays the hourly summer averages at Toronto North-Downtown2 for $\Theta_* \Omega_3$ from the three designated air directions as well as from all directions. Overall, air transport from W-SE or locally produced resulted in the highest daily maximum $\Theta_* \Omega_3$ levels. Between 2010 and 2012, the inter-annual variability in the maximum daily Ω_3 reached when air arrived from W-NE was- did not have as large-inter-annual variability aswas much less than when air is-arrived from the W-SE the maximum daily Ω_* reached when air arrived from W-NE was consistent, a result expected as this air traveled over remote regions and therefore Ω_3 production is likely NO_{*} limited and dominated by biogenic VOC reactivity. The maximum daily $\Omega_* \Omega_3$ reached in 2012 when air was arriving from W-SE was significantly higher than in 2010 or 2011; this occurrence helps to explain the increase in Θ_* Ω_3 observed in 2012. FinallyLastly, the maximum daily $\Theta_* \Omega_3$ reached as a result of during stagnant conditions was again higher in 2012 than in 2010 or 2011. This increase in *local* $\Omega_* \Omega_3$ concentrations cannot be explained by wind transport or a change in precursor concentrations, as explained in *Section 3.2*, and therefore other meteorological influences must be affecting the local maximum level of $\Theta_* \Omega_3$ reached. This analysis was performed for other stations as well as using Ω_* concentrations and the same general conclusions can be made.

Since the local Θ_{x} - Ω_{3} -levels experienced in 2012 cannot be explained by changes in air transport or precursor concentrations, it is likely a result of changes in the photochemistry occurring in the troposphere. The level of photochemical activity occurring during each summer day was analyzed by considering the amount of incoming solar radiation in the GTA. Data collected from a net radiometer at UTMMS werewas_-analyzed for the period 2008-2012. Fig. 6 a) displays a regression between Downtown2 maximum 8-hr O₃ levels (ppb) and midday incoming solar radiation (from 11:00-15:00, the time when O₃ production is maximized, in W m⁻²) in 2012. From the R² value, it is clear that the variance in O₃ levels can partly (~16 %) be explained by midday radiation levels (variances ranged from ~8-19 % from 2008-2012). Based on this figure, a midday average of ~600 W m⁻² is required for an ozone exceedance. Fig. 6 b) shows the annual cumulative distribution

function of the midday average summer solar radiation data plotted against the number of days in each summer. For the period 2008-2012, 2012 experienced the greatest number of days affected by a midday solar radiation average >600 W m⁻²; 2012 experienced 103 days of >600 W m⁻² levels of incoming solar radiation whereas 2011 and 2010 experienced 84, 2009 experienced 92 and 2008 experienced 85. When this analysis was performed with the pyranometer data from the UTMMS site, the same qualitative result was obtained. The amount of incoming solar radiation will strongly influence the production of HO_x radicals, and thus the ability for O₃ to be produced; local O₃ production is minimized on "cloudy" days with lower levels of incoming solar radiation and maximized on "clear" days with medium to higher levels of incoming solar radiation.

3.4 VOC- or NO_x limited Ozone Production

The ozone production regime is dictated by the fate of HO_x radicals, whether the RO₂ radical self-reacts (denoting a NO_x-sensitive regime) or the OH radical reacts with NO₂ to form HNO₃ (denoting a VOC-sensitive regime) (R8 and R9). Based on the data available, we used the relative reactivity of OH to NO₂ and the sum of <u>40</u> speciated <u>NAPS</u> VOCs at the Downtown site as an approach to approximate the ozone production regime during the study period. Figure 7 shows OH reactivity to each species in "early" (2002-2003) and "late" (2011-2012) periods of the data set. In the early period, NO₂ accounted for a larger portion of OH reactivity relative to VOCs, 4.93 and 3.64 s⁻¹, respectively. In the late period, although reactivity toward both compounds decreased, NO₂ reactivity to OH accounts for an increasingly larger portion of total reactivity, 2.88 vs. 1.68 s⁻¹ for VOC reactivity. When these calculations were performed using data from the suburban Brampton site, the same conclusions were drawn indicating that most areas in the GTA (urban or not) have a NO₂ was also found to accounting for a larger proportion of OH reactivity. There are limited long-term CO measurements in the GTA during this period, however data from the Toronto West2 station suggests that midday reactivity with CO decreased from 1.4 s⁻¹ to 0.77 s⁻¹ between 2003 and 2012. These results suggest that the preferred fate of OH radical in the late period is reaction with NO₂ (R9),

thereby suggesting that ozone production has become more NO_x-saturated and more sensitive to VOC reactivity over the last decade. <u>Similar to the study by Geddes et al. (2009)</u>, when we use simple analytical model to generate a contour plot of instantaneous ozone production as a function of VOC reactivity and NO₂ concentrations, plotting the data from GTA surface monitoring stations also suggests the region is in a VOC-limited regime.

This analysis of the GTA ozone production regime is limited because the ambient concentrations of NO_x and VOCs were made at sites near the ground whereas ozone formation takes place in a convective layer which can extend hundreds of meters above the surface (Sillman, 1999). Surface observations likely overestimate the average concentration of primary pollutants within the boundary layer, especially for shorter-lived compounds. Another limitation to the VOC analyses performed in this study is the exclusion of OVOCs from all monitoring stations except Junction. In 2011, we performed five separate days of 3-hr canister measurements during a two week period between August 27 and September 12. The OH reactivity to non-methane hydrocarbons was calculated as two fractions: VOCs (the same 40 VOCs as chosen from Environment Canada data, with the exception of propylene and isopentane) and OVOCs (23 compounds). Throughout the two-week period, the OVOCs accounted for ~ 60 % of the total OH reactivity to VOCs. It is possible, however, that this may be an overestimate of midday OH reactivity; for the two week sampling period, the average 24-hr VOC reactivity from the traditional NAPS compounds was 1.6 s⁻¹ and from the OVOC compounds was 2.4 s⁻¹. Focusing only on samples collected between 12:00 and 15:00, the reactivity from the traditional NAPS compounds was 1.3 s⁻¹ and from the OVOC compounds was 2.3 s⁻¹. Therefore, based on this limited set of more detailed measurements, we can infer that 24-hr average NAPS samples may over-estimate the midday reactivity from the traditional compounds by 19 % and the total VOC reactivity (VOC + OVOCs) by 10 %. These detailed measurements also suggest that ozone production may be more NO_x-sensitive than was determined using the traditional VOC

measurements. Overall, these results suggest that our current understanding of VOC reactivity in the GTA is <u>limitedincomplete</u>.

3.5 GTA OH radical concentration

Since the OH radical plays a key role in the production of ozone, it is important to understand how its abundance in the GTA has changed over the study period. By monitoring the ratio of two coemitted VOCs, we can estimate how the concentration of OH has changed, assuming the distribution of distances from the emission sources to the receptor (monitoring site) has not changed. Fig. 8 displays the ratio of two alkenes, 1-butene (k_{OH} = 3.0x10⁻¹¹ cm³ molec⁻¹ s⁻¹) and cis-2-butene (k_{OH} = 5.6×10^{-11} cm³ molec⁻¹ s⁻¹), as well as two aromatic VOCs, 1,2,3-trimethylbenzene (k_{0H} = 3.3×10^{-11} cm³ molec⁻¹ s⁻¹) and ethylbenzene ($k_{OH} = 7.1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$). All of these compounds have lifetimes in the atmosphere on the order of a few hours, assuming an OH concentration of 10⁶ molec cm⁻³, and therefore observations made in downtown Toronto should predominantly reflect oxidation rates in the GTA atmosphere. We assume that the emission ratios of these compound pairs have not changed substantially during the study period. Additionally, with O₃ levels changing minimally during the study period, we assume that the oxidation of these compounds from O_3 has not changed significantly during this time and will not significantly contribute to any change in the VOC ratios. As Fig. 8 displays, the ratio for each pair of compounds is smaller in the early period than in the late period, with medians changing from 3.5 to 4.5 for 1-butene:2-butene and 0.19 to 0.25 for 1,2,3trimethylbenzene:ethylbenzene. Since cis-2-butene and ethylbenzene have higher rates of reaction with OH with respect to their paired VOC, this increase in their ratio indicates that the OH concentration in the GTA has increased from the early to late period. Assuming that the rates of HO_x production have stayed relatively constant, higher levels of OH in 2011-2012 are consistent with the large reduction in total reactivity, described in Section 3.4. An increase in OH radical abundance has implications for ozone production, the relationship between precursor emissions and concentrations, and the oxidative capacity of the troposphere.

3.6 Assessing the Success of the Climate Change, Clean Air and Sustainable Energy Action Plan

In 2007, the City of Toronto made a commitment to reduce emissions of local smog-causing pollutants 20 % below 2004 levels by 2012. Table 2 shows the percent differences between 2004 and 2012 NO₂ and VOC concentrations at all sites monitored (using the original suite of 40 NAPS VOC compounds). Reductions in NO₂ concentrations ranged from 27.4 – 49.9 % (Toronto North and Brampton2, respectively), providing evidence of the success of the implemented mitigation strategies during the past decade, such as catalytic converters on vehicles and new combustion technology to reduce NO_x emissions from power plants (ICF., 2007). Additionally, reductions in VOC concentrations ranged from 31.7 – 52.8 % (Downtown1 and West1, respectively). Again, this result provides support for the success of the City of Toronto strategies aimed at reducing anthropogenic emissions of these compounds, such as the ChemTRAC initiative which includes a focus on reducing the VOC content in paints and wood coatings (Toronto Public Health., 2013). While these results suggest that the emission reduction target may have been achieved, there are limitations to our interpretation of the data. Monitoring network data suggests that the *concentrations* of NO₂ and VOCs have been reduced by more than 20 %, but the action plan commitments are actually for emissions. In Section 3.4 we showed that oxidation rates in the urban atmosphere appear to have accelerated, meaning that changes in emissions and concentrations will have a non-linear relationship, and that the data in Table 2 likely overestimate the changes in emissions. Nevertheless, the large reduction in concentrations is likely consistent with a decrease of more than 20 % in emissions, though exact quantification is difficult. Furthermore, as suggested in Section 3.3, the role of OVOCs as ozone precursors in the GTA is unclear due to lack of monitoring and therefore these conclusions about the success of the action plan are not necessarily comprehensive.

4. Conclusion

Significant reductions in the summertime mean daily concentrations of O_3 precursor compounds have been observed since 2000; NO₂ levels decreased by at least 45 % - 6.4 % per year in urban sites and 28 %-5.8 % per year in suburban sites and VOC reactivity decreased by at least 53 $\frac{9}{2}$ -9.3 % per year. These results provide evidence for the effectiveness of implemented vehicle emission clean-up technologies as well as other regulatory initiatives throughout the province and municipalities in the GTA. In response to these decreases, GTA O₃ levels have also decreased about -0.4 % per vear at urban sites and -1.1 % per vear at suburban sites during the 13 year study period. In response to these decreases, GTA O_x levels have also decreased about 2.4-13.9 % at all sites during the 13 year study period (with statistical significance at most sites). In 2012, however, some of the highest recorded Θ_{x} - Ω_{3} concentrations were observed following four years of consistently low levels. Since concentrations of both precursor compounds have continued decreasing since 2008, this increase must have been influenced by the meteorology experienced in 2012. We found that although the warm temperatures experienced in 2012 did not likely play a role in the $\Theta_{x} \Theta_{3}$ increase compared to 2010 and 2011, air transport from upwind regions may have. Compared to the preceding 5-4 years, the summer of 2012 was affected by a large number percentage of days with air transport from the W-SE (polluted air travelling over urban areas in Canada and the US), the fewesta small percentage of days with air transport from the W-NE (clean air travelling over remote regions) and the mosta large percentage of days affected by stagnant conditions (air trapped over the GTA allowing precursor compounds to accumulate and enhance local O_3 production). Additionally, since the production of O_3 depends on photochemistry in the troposphere, the levels of incoming solar radiation were analyzed during the study period. It was found that 2012 experienced the largest number of days with midday levels of incoming solar radiation exceeding 600 W m⁻², which likely contributed to the enhancement of local O_3 production.

The results of this study also demonstrate the success of the GTA in achieving the 20 % reduction in precursor emissions set by the Toronto Climate Change, Clean Air and Sustainable

Energy Action Plan in 2007. Between 2004 and 2012, NO₂ reductions ranged from 27.4 - 49.9 % and VOC concentration reductions ranged from 31.7-52.8 %. These results provide evidence of the benefits of municipal and provincial regulations aimed at controlling the emission of ozone precursors throughout the past decade. Nevertheless, the ozone design value at all GTA monitoring stations has exceeded the Canada-wide Standard every year between 2002 and 2012. Reductions in precursor emissions appear to have increased in the local abundance of OH, resulting in only moderate reductions in local ozone production rates. The importance of including OVOCs in O₃ production analyses has been demonstrated, as short-term measurements indicate that they account for a significant fraction of OH reactivity.

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Year	Days with transport from	Exceedances from	Days with transport from	Exceedances from	Days with transport from	Exceedances from	
	V	V-NE	V	V-SE	Local		
2008	29	0	18	17	52	83	
2009	33	20	14	40	53	40	
2010	29	0	26	33	45	66	
2011	38	33	9	17	53	50	
2012	25	6	20	29	54	65	

Table 1: Percent of days <u>and exceedances (at Downtown2)</u> each summer (2008-2012) that were affected by air transport from the W-NE, W-SE or local/stagnant air

Station	Downtown	North	East	West	Oshawa	Brampton	Newmarket	Oakville
NO ₂ (%)	31.2	27.4	29.1	42.1	34.6	49.9	26.8	30.3
VOC (%)	31.7	-	-	52.8	-	33.4	-	-

Table 2: The percent difference between 2004 and 2012 NO_2 and VOC concentrations (ppb) at all stations monitored (Junction was not included as monitoring stopped in 2005).



Figure 1: Monitoring stations in the Greater Toronto Area used for the collection of NO_x and O_3 data (blue and pink markers), VOC data (aqua markers) and meteorological data (yellow and green markers).



Figure 2: Annual summer midday NO₂ concentrations (ppb) in GTA urban (a) and suburban areas (b); slopes in ppb year⁻¹. Annual summer VOC reactivity (s⁻¹) (c); slopes in s⁻¹ year⁻¹.



Figure 3: Annual summer average maximum 8-hr O_3 (a and b) and O_x (c and d) concentrations (ppb) for Toronto urban and suburban areas; slopes in ppb year-1-.



Figure 4: The number of days exceeding 65 ppb O₃ Canada-wide Standard (green) and the number of days exceeding 30 °C (red) at the Toronto <u>North-Downtown2</u> station. The number above each marker is the Design Value for that year.



Figure 5: $\Theta_{*} O_{3}$ -hourly summer averages at <u>North Toronto Downtown2 Toronto station (error bars</u> represent standard deviation of the mean).



Figure 6: a) Regression of Downtown2 8-hr O_3 versus incoming solar radiation (W/m²) for 2012 (black lines are the thresholds of incoming solar radiation where 65 ppb of O_3 is exceeded); b) Cumulative distributions of the midday average solar radiation (W/m²) experienced on each summer day (2008-2012) (markers above the x-axis are provided to easily identify the difference in the number of days exceeding 600 W m⁻² for 2012 and the previous four years).²



Figure 7: OH reactivity (s⁻¹) to NO₂ and <u>NAPS</u>VOCs in the "early" period (2002-2003) and "late" period (2011-2012) at the Downtown sites.



Figure 8: Histograms of 1-butene:2-butene (a) and 1,2,3-trimethylbenzene:ethylbenzene (b) in the early (2002-2003) and late (2011-2012) periods.