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

Stephanie C. Pugliese[a], Jennifer G. Murphy[a,*], Jeffrey A. Geddes[b], Jonathan M. Wang[c]

[a] University of Toronto, Department of Chemistry, 80 St. George St, Toronto, ON, Canada M5S 3H6

[b] now at Dalhousie University, Department of Physics and Atmospheric Science, P.O. Box 15000, Halifax, NS, Canada B3H 4R2

[c] now at University of Toronto, Department of Chemical Engineering and Applied Science, 200 College St. Toronto, ON, Canada M5S 3E5

*Correspondence author. Email address: jmurphy@chem.utoronto.ca (J.G. Murphy)

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 NO_2 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 NO_2 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 CAD in the province of Ontario alone (MOE., 2005). In Toronto, ground-level ozone is responsible for 13 and 29 % of the incidences of premature mortality and hospitalizations associated with air pollution (with $PM_{2.5}$ and NO_2 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 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; however, the production rate of ozone depends on precursor concentrations in a non-linear fashion. Previous studies of O_3 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 and model studies have shown very strong positive correlations between O_3 production and temperature 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 O_3 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)

$O + O_2 + M \rightarrow O_3 + M$ (R1b)

$NO + O_3 \rightarrow NO_2 + O_2$ (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)

$RO_2 + NO \rightarrow RO + NO_2$ (R4)

The NO_2 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)

$RH + 4O_2 \rightarrow R'CHO + 2O_3 + H_2O$ (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 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).

$RO_2 + R'O_2 \rightarrow ROOR' + O_2$ (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 = $RC(O)O_2NO_2$, R10) or alkyl nitrates (ANs = $RONO_2$, R11) (Farmer et al., 2011). PNs serve as a temporary reservoir for NO_x and suppress O_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 O_3 production (Perring et al., 2010).

$RC(O)O_2 + NO_2 \leftrightarrow RC(O)O_2NO_2$ (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 NO_2 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 O_3 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 ozone levels now appear to be responding to decreases in precursor compounds, as reductions are observed from 2000 to 2012. We also identify that in the short term, 2012 marked one of the highest years in GTA ozone during the study period. We discuss the strong link between ozone levels 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

2.1 Study Region and Data Collection

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 GTA 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 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).

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 http://www.airqualityontario.com. 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. All datasets were complete (less than ~24 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 C_2 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 12). Samples were analyzed for both non-polar and polar VOCs using GC techniques described in (Wang et al., 2005).

2.2 O_3, 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 (EST; solar noon is approximately 12:30 EST during the summer). Therefore, NO_2 hourly data were averaged during this time period (hereafter referred to as the "NO_2 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 to be 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, Fig. 1, 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 NO_2 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} ($p<0.01$) while the suburban sites also have decreasing trends of -0.20 to -0.55 ppb·year^{-1} ($p<0.05$). Overall, throughout the 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 most urban station (Downtown2) and that closest to a major highway (West2) continues to report the highest NO_2 levels of all the monitoring stations. Furthermore, the stations furthest removed from the urban center and major highways, Newmarket and Oakville, report the lowest NO_2 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 NO_2 levels is likely related to improvements in vehicle catalyst technology or the phasing out of older, less-efficient vehicles (MOE., 2013). Other factors may include the closure of the Lakeview Generating Station, Fig. 1, within the GTA in 2005 (NO_2 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 (NO_2 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 an average overall decrease of -9.3 % per year (excluding Junction site), with the Brampton site experiencing the largest decrease of -11.5 % per year. OVOC 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 period. 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 O_3, ranging between -0.03 and -0.29 $ppb{\cdot}year^{-1}$ at the urban stations and -0.34 and -0.64 $ppb{\cdot}year^{-1}$ at the suburban stations, although decreases are not statistically significant (with the exception of Newmarket). Over the entire study period, decreases in O_3 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 $ppb{\cdot}year^{-1}$ at the urban stations and -0.57 and -1.0 $ppb{\cdot}year^{-1}$ 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). Over the entire study period, decreases in O_x of -1.8 % per year occurred in the urban stations and -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.

3.2 O_3 levels from 2008-2012

While over the entire study period O_3 levels in GTA have decreased, from 2008 onwards the same trend is not observed. Figures 3a and b show that at all monitored sites, between 2008 and 2011 O_3 levels in the GTA were consistently lower than from 2000-2007. However, the measured average summer daily maximum 8-h O_3 in 2012 was significantly higher than that of the previous four years (an increase of 5-7 ppb). The data presented above demonstrates that NO_2 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 O_3 increase cannot be explained as a result of a change in either of the precursor compounds. Alternatively, this variability in O_3 may be explained by meteorological influences, which is explored in the following section.

3.3 Meteorological influences on 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 O_3 concentrations on temperature, indicating that at higher temperatures, local O_3 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 O_3 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 Toronto Downtown2 station 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 4th highest 8-hr O_3 measurement annually, averaged over three consecutive years (Environment Canada, 2013)) for that year. 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 drawn. Therefore, based on this data, the warm temperatures experienced in the summer of 2012 did not play the dominant role in the O_3 increase observed.

High temperatures in the GTA are often associated with warm southerly flow and therefore it is possible that the correlation between O_3 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°-45°) 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 relatively lower 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 could have contributed to the high O_3 levels measured in the GTA in 2012 because fewer days had "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 Downtown2 for O_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 O_3 levels. Between 2010 and 2012, the inter-annual variability in the maximum daily O_3 reached when air arrived from W-NE was much less than when air arrived from the W-SE. The maximum daily O_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 O_3 observed in 2012. Finally, the maximum daily O_3 reached during stagnant conditions was again higher in 2012 than in 2010 or 2011. This increase in *local* O_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 O_3 reached. This analysis was performed for other stations as well as using O_x concentrations and the same general conclusions can be made.

Since the local O_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 were analyzed for the period 2008-2012. Fig. 6 a) displays a regression between Downtown2 maximum 8-hr O_3 levels (ppb) and midday incoming solar radiation (from 11:00-15:00, the time when O_3 production is maximized, in W m^{-2}) in 2012. From the R^2 value, it is clear that the variance in O_3 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 O_3 to be produced; local O_3 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 RO_2 radical self-reacts (denoting a NO_x-sensitive regime) or the OH radical reacts with NO_2 to form HNO_3 (denoting a VOC-sensitive regime) (R8 and R9). Based on the data available, we used the relative reactivity of OH to NO_2 and the sum of 40 speciated NAPS 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, NO_2 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, NO_2 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, NO_2 was also found to account 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 NO_2 (R9), thereby suggesting that ozone production has become more NO_x-saturated and more sensitive to VOC reactivity over the last decade. Similar to the study by Geddes et al. (2009), when we use a simple analytical model to generate a contour plot of instantaneous ozone production as a function of VOC reactivity and NO_2 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 incomplete.

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 co-emitted 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} cm^3 $molec^{-1}$ s^{-1}) and cis-2-butene (k_{OH} = 5.6x10^{-11} cm^3 $molec^{-1}$ s^{-1}), as well as two aromatic VOCs, 1,2,3-trimethylbenzene (k_{OH} = 3.3x10^{-11} cm^3 $molec^{-1}$ s^{-1}) and ethylbenzene (k_{OH} = 7.1x10^{-11} cm^3 $molec^{-1}$ s^{-1}). All of these compounds have lifetimes in the atmosphere on the order of a few hours, assuming an OH concentration of 10^6 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 O_3 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. 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 1,2,3-trimethylbenzene: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 NO_2 and VOC concentrations at all sites monitored (using the original suite of 40 NAPS VOC compounds). Reductions in NO_2 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 NO_2 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; NO_2 levels decreased by -6.4 % per year in urban sites and -5.8 % per year in suburban sites and VOC reactivity decreased by at least -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 O_3 levels have also decreased about -0.4 % per year at urban sites and -1.1 % per year at suburban sites during the 13 year study period. In 2012, however, some of the highest recorded O_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 O_3 increase compared to 2010 and 2011, air transport from upwind regions may have. Compared to the preceding 4 years, the summer of 2012 was affected by a large percentage of days with air transport from the W-SE (polluted air travelling over urban areas in Canada and the US), a small percentage of days with air transport from the W-NE (clean air travelling over remote regions) and a 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, NO_2 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 O_3

production analyses has been demonstrated, as short-term measurements indicate that they account for a significant fraction of OH reactivity.

Acknowledgements

The authors are grateful to Environment Canada's NAPS (National Air Pollutant Surveillance) for the VOC data used in this study. Additionally, the authors are thankful to the Environmental Monitoring and Reporting Branch at the Ontario Ministry of the Environment for providing hourly O_3 and NO_x data as well as to the UTMMS for providing hourly incoming solar radiation data.

References

Agudelo-Castaneda, D., Teixeira, E., Rolim, S., Pereira, F., and Wiegand, F. (2013). Measurement of Particle Number and Related Pollutant Concentrations in an Urban Area in South Brazil. *Atmospheric Environment, 70*, 254-262.

Atkinson, R. (1997). Gas-Phase Tropospheric Chemistry of Volatile Organic Compounds. 1. Alkanes and Alkenes. *Journal of Physical and Chemical Reference Data, 26*, 215-290.

Bell, M. L., Dominici, F., and Samet, J. M. (2005). A Meta-Analysis of Time-Series Studies of Ozone and Mortality with Comparison to the National Morbidity, Mortality and Air-Pollution Study. *Epidimiology, 16*, 436-445.

Bell, M. L., Samet, J. M. and Dominici, F. (2004). Ozone and mortality: A meta-analysis of time-series studies and comparison to a multi-city study (the national morbidity, mortality, and air pollution study). Retrieved 11/18, 2013, from http://biostats.bepress.com/jhubiostat/paper57

Bradley, H. J. J. (2013). Bill 138, ending coal for cleaner air act, 2013. Retrieved 03/05, 2014, from http://www.ontla.on.ca/web/bills/bills_detail.do?locale=en&Intranet&BillID=2901

Camalier, L., Cox, W., and Dolwick, P. (2007). The Effects of Meteorology on Ozone in Urban Areas and their use in Assessing Ozone Trends. *Atmospheric Environment, 41*, 7127-7137.

City of Toronto. (2007). Climate change, clean air and sustainable energy action plan: Moving from framework to action. Retrieved 12/14, 2013, from http://www.toronto.ca/legdocs/mmis/2007/pe/bgrd/backgroundfile-4982.pdf

Environment Canada. (2013). Canada wide standards (CWS). Retrieved 12/19, 2013, from http://www.ec.gc.ca/rnspa-naps/default.asp?lang=En&n=07BC2AC0-1

Farmer, D., Perring, A., Wooldridge, P., Blake, A., Meinardi, S., Huey, L., Tanner, D., Vargas, O., and Cohen, R. (2011). Impact of Organic Nitrates on Urban Ozone Production. *Atmospheric Chemistry and Physics, 11*, 4085-4094.

Figueiredo, M., Monteiro, A., Lopes, M., Ferreira, J., and Borrego, C. (2013). Air Quality Assessment of Estarreja, an Urban Industrialized Area, in a Coastal Region of Portugal. *Environmental Monitoring and Assessment, 185*, 5847-5860.

Geddes, J., Murphy, J., and Wang, D. (2009). Long Term Changes in Nitrogen Oxides and Volatile Organic Compounds in Toronto and the Challenges Facing Local Ozone Control. *Atmospheric Environment, 43*, 3407-3415.

ICF. (2007). Greenhouse gases and air pollutants in the city of Toronto: Towards a harmonized strategy for reducing emissions. Retrieved 08/13, 2013, from http://www1.toronto.ca/city_of_toronto/environment_and_energy/key_priorities/files/pdf/ghg-aq-inventory-june2007.pdf

Jacob, D., Logan, J., Gardner, G., Yevich, R., Spivakovsky, C., and Wofky, S. (1993). Factors Regulating Ozone over the United States and its Export to the Global Atmosphere. *Journal of Geophysical Research, 14*, 817.

Makar, P., Zhang, J., Gong, W., Stroud, C., Sills, D., Hayden, K., Brook, J., Levy, I., Mihele, C., Moran, M., Tarasick, D., and He, H. (2010). Mass Tracking for Chemical Analysis: The Causes of Ozone Formation in Southern Ontario during BAQS-Met 2007. *Atmospheric Chemistry and Physics, 10*, 11151-11173.

MOE. (2014). Smog advisory statistics. Retrieved 06/11, 2014, from http://www.airqualityontario.com/press/smog_advisories.php

MOE. (2005). Transboundary air pollution in Ontario. Ontario Ministry of the Environment. Retrieved 09/06, 2013, from http://www.ene.gov.on.ca/stdprodconsume/groups/lr/@ene/@resources/documents/resource/std01_079137.pdf

MOE. (2013). Drive clean. Retrieved 03/05, 2014, from http://www.ene.gov.on.ca/environment/en/category/drive_clean/index.htm

Oltmans, S. J., Lefohn, A. S., Shadwick, D., Harris, J. M., Scheel, H. E., Galbally, I., Tarasick, D. W., Johnson, B. J., Brunke, E. -., Claude, H., Zeng, G., Nichol, S., Schmidlin, F., Davies, J., Cuevas, E., Redondas, A., Naoe, H., Nakano, T., and Kawasato, T. (2013). Recent Tropospheric Ozone Changes - A Pattern Dominated by Slow or no Growth. *Atmospheric Environment, 67*, 331-351.

Pekey, B., and Ozaslan, U. (2013). Spatial Distribution of SO2, NO2 and O3 Concentrations in an Industrial City of Turkey using a Passive Sampling Method. *Clean-Soil, Air, Water, 41*(5), 423-428.

Perring, A., Bertram, T., Farmer, D., Wooldridge, P., Dibb, J., Blake, N., Blake, D., Singh, H., Fuelberg, H., Diskin, G., Sachse, G., and Cohen, R. (2010). The Production and Persistence of $RONO_2$ in the Mexico City Plume. *Atmospheric Chemistry and Physics, 10*, 7215-7229.

Psiloglou, B., Larissi, I., Petrakis, M., Paliatsos, A., Antoniou, A., and Viras, L. (2013). Case Studies on Summertime Measurements of O_3, NO_2, and SO_2 with a DOAS System in an Urban Semi-Industrial Region in Athens, Greece. *Environmental Monitoring and Assessment, 185*, 7763-7774.

Seinfeld, J., & Pandis, S. (2006). *Atmospheric chemistry and physics: From air pollution to climate change*. New Jersey: John Wiley & Sons Inc.

Sillman, S. (1999). The Relation between Ozone, NOx and Hydrocarbons in Urban and Polluted Rural Environments. *Atmospheric Environment, 33*, 1821-1845.

Sills, D., Brook, J., Levy, I., Makar, P., Zhang, J., and Taylor, P. (2011). Lake Breezes in the Southern Great Lakes Region and their Influence during BAQS-Met 2007. *Atmospheric Chemistry and Physics, 11*, 7955-7973.

Statistics Canada. (2011). *Table405-0004 - road motor vehicles, registrations, annual (number),* CANSIM (database). Retrieved 08/14, 2013, from http://www.statcan.gc.ca/tables-tableaux/sum-som/l01/cst01/trade14a-eng.htm

Statistics Canada. (2012). *Focus on geography series, 2011 census.* Statistics Canada catalogue no. 98-310-XWE2011004. Retrieved 08/13, 2013, from https://www12.statcan.gc.ca/census-recensement/2011/as-sa/fogs-spg/Facts-cma-eng.cfm?LANG=Eng&GK=CMA&GC=535

Toronto Public Health. (2013). Tracking and reducing chemicals in Toronto: ChemTRAC annual report - 2011 reporting year. Retrieved 12/19, 2013, from http://www.toronto.ca/legdocs/mmis/2013/hl/bgrd/backgroundfile-59180.pdf

Toronto Public Health. (2014). *Path to healthier air: Toronto air pollution burden of illness update.*

Wang, D., Fuentes, J., Travers, D., Dann, T., and Connolly, T. (2005). Non-Methane Hydrocarbons and Carbonyls in the Lower Fraser Valley during PACIFIC 2001. *Atmospheric Environment, 39*, 5261.

Year	Days with transport from	Exceedances from	Days with transport from	Exceedances from	Days with transport from	Exceedances from
	W-NE		**W-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 and exceedances (at Downtown2) 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).

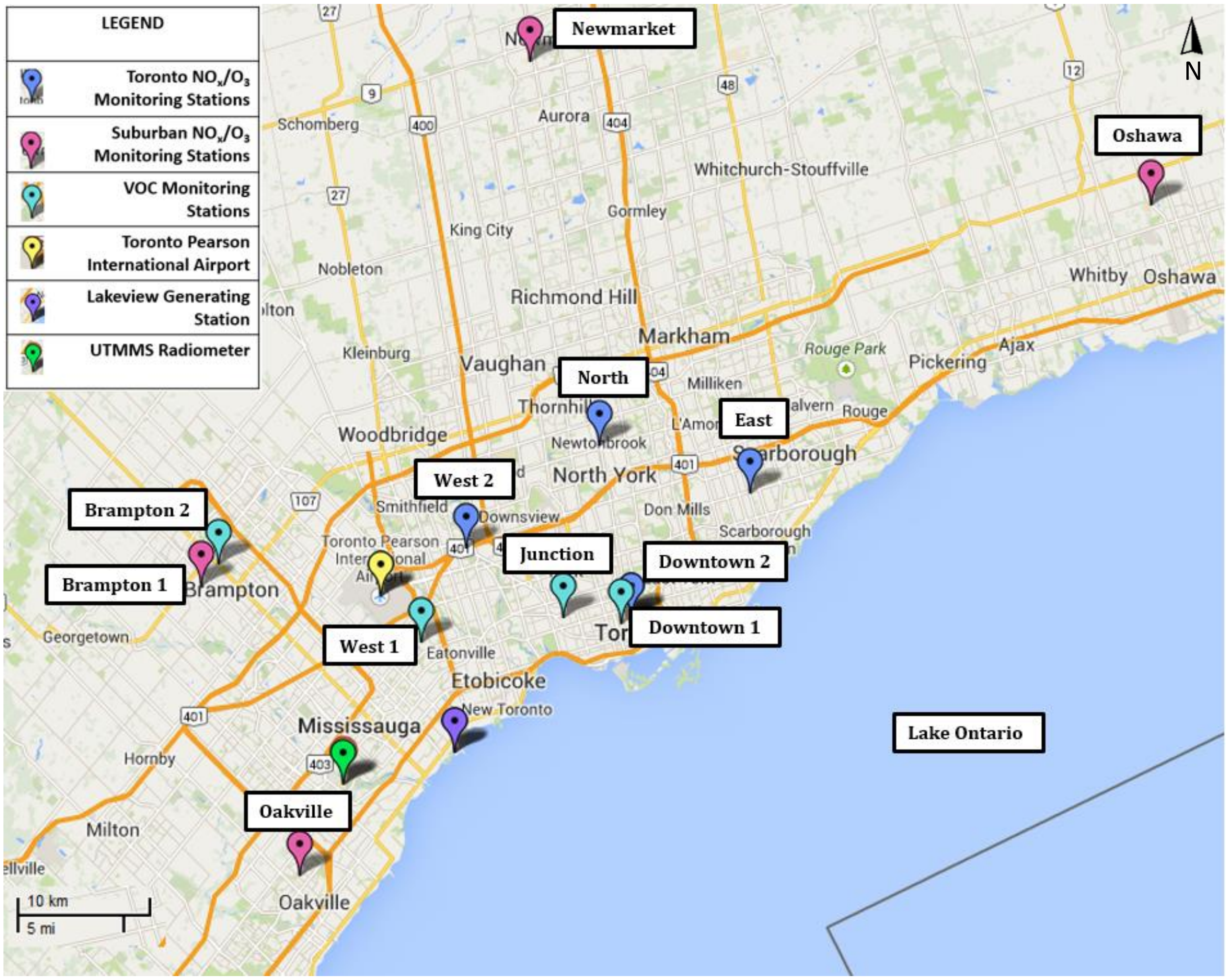

Figure 1: Monitoring stations in the Greater Toronto Area used for the collection of NO$_x$ and O$_3$ data (blue and pink markers), VOC data (aqua markers) and meteorological data (yellow and green markers).

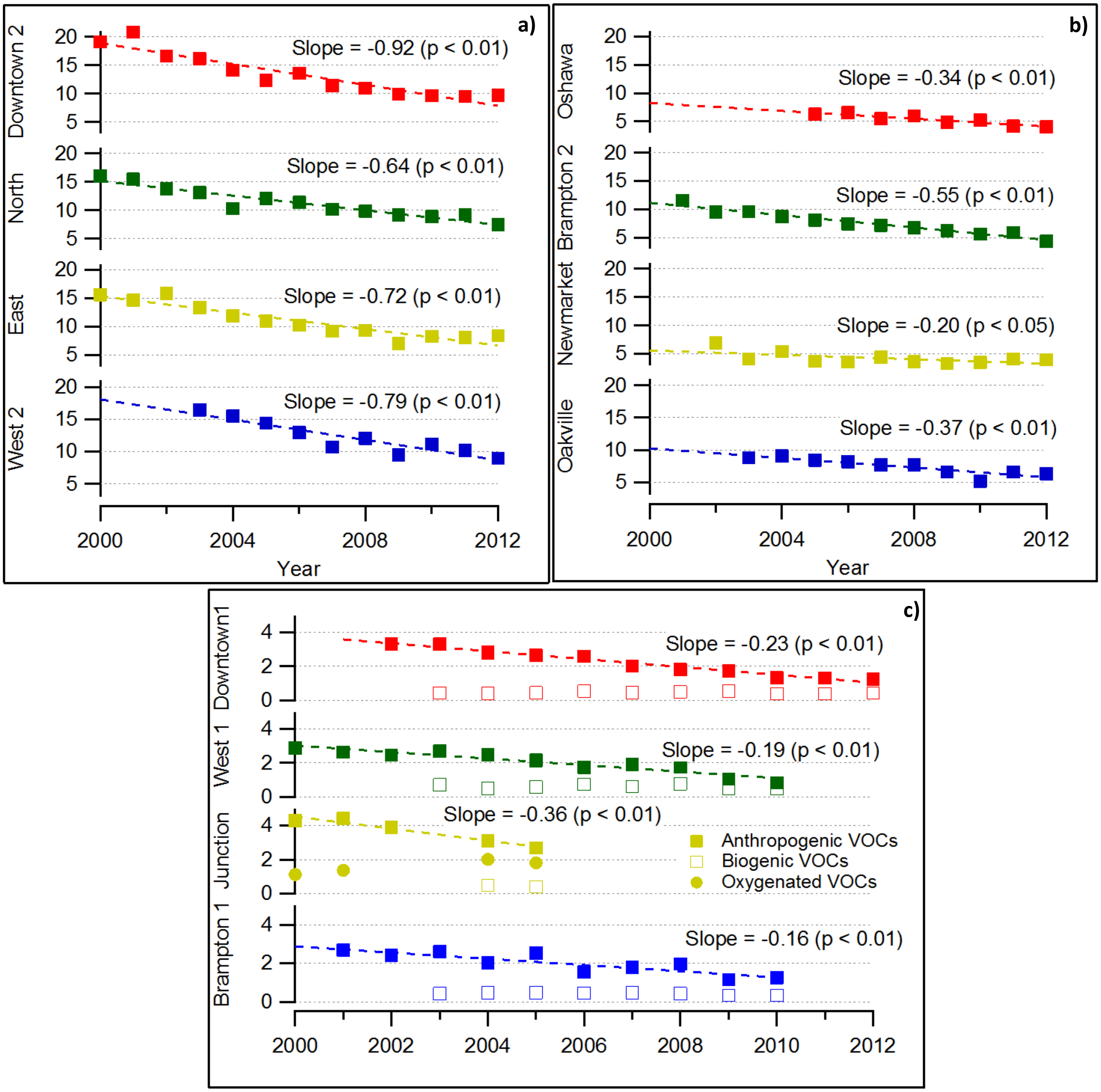

Figure 2: Annual summer midday NO_2 concentrations (ppb) in GTA urban (a) and suburban areas (b); slopes in ppb year^{-1}. Annual summer VOC reactivity (s^{-1}) (c); slopes in s^{-1} year^{-1}.

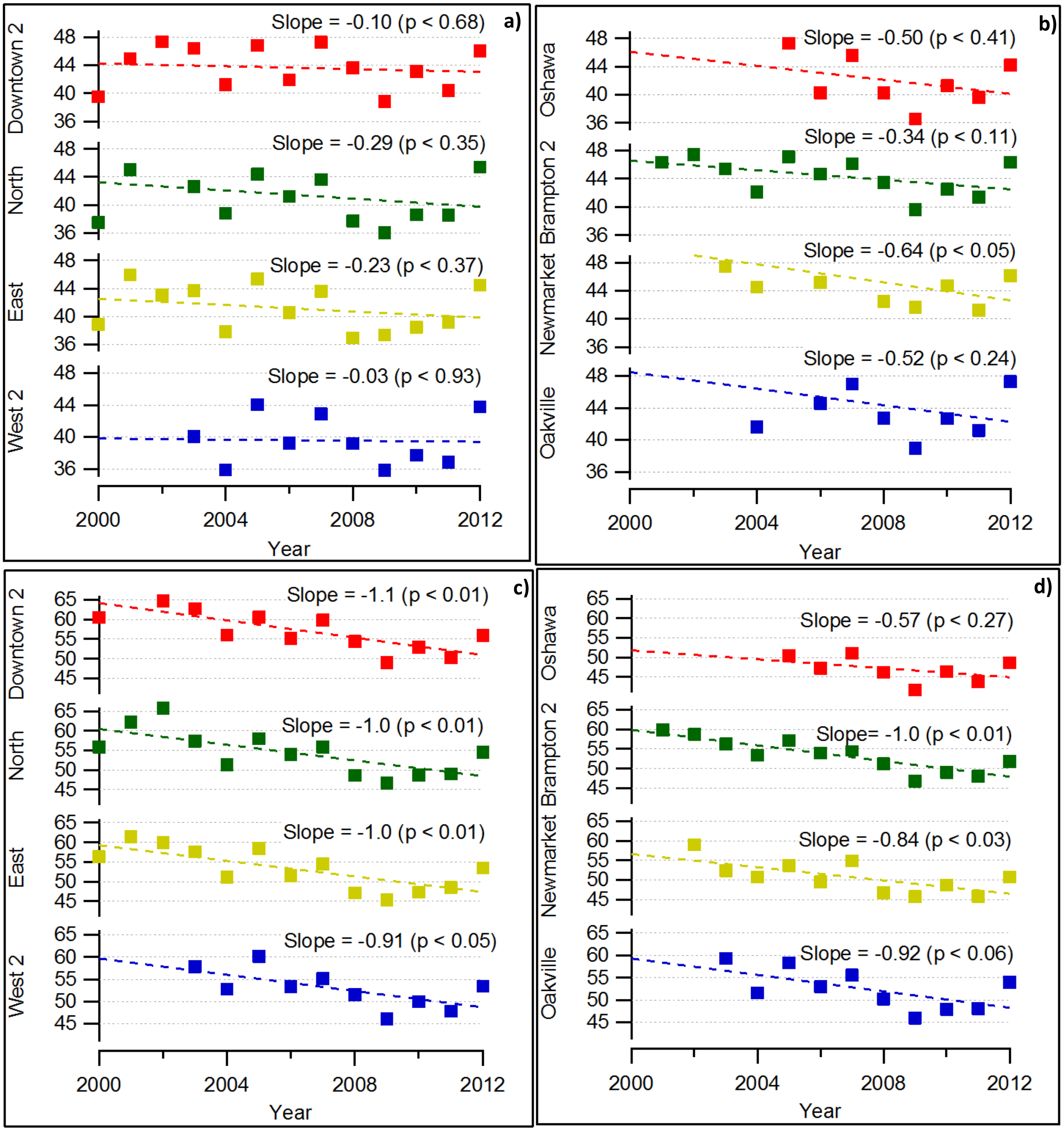

Figure 3: Annual summer average maximum 8-hr O_3 (a and b) and O_x (c and d) concentrations (ppb) for Toronto urban and suburban areas; slopes in ppb year^{-1}.

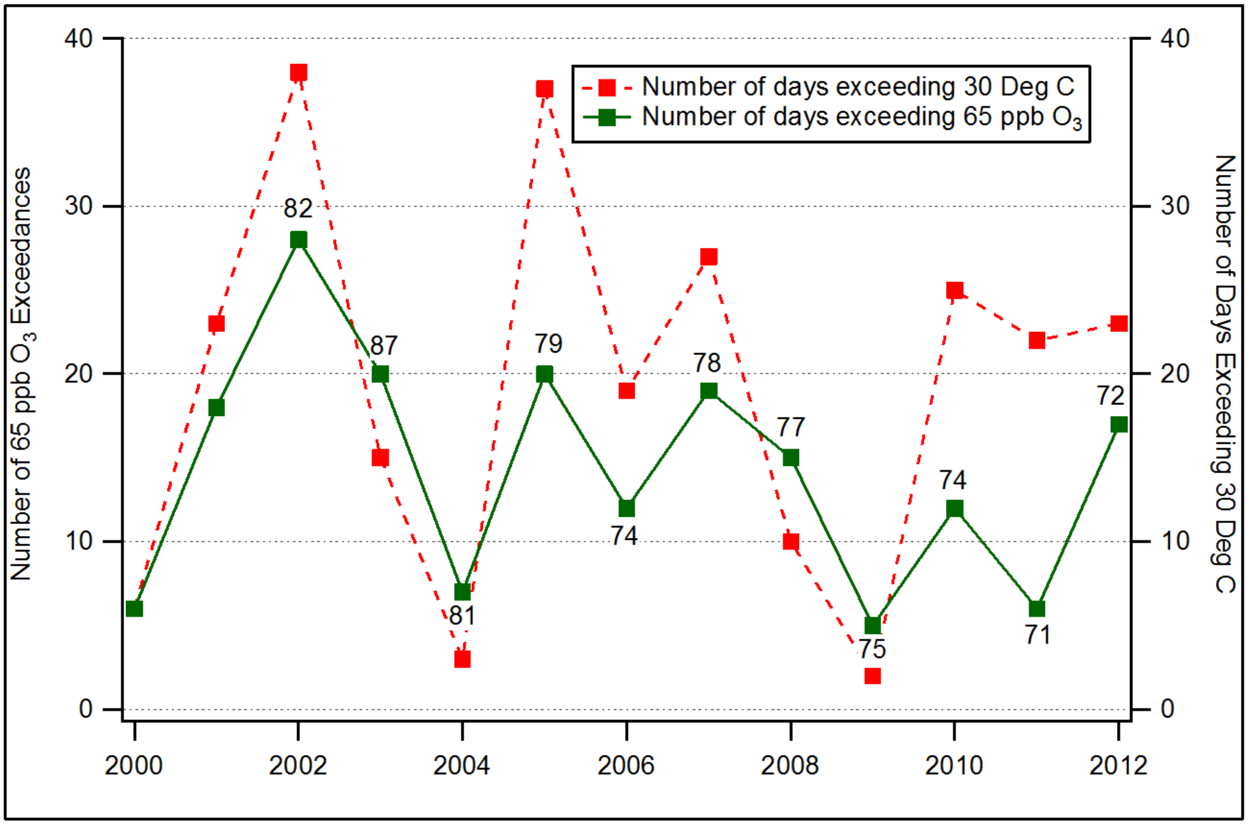

Figure 4: The number of days exceeding 65 ppb O_3 Canada-wide Standard (green) and the number of days exceeding 30 °C (red) at the Toronto Downtown2 station. The number above each marker is the Design Value for that year.

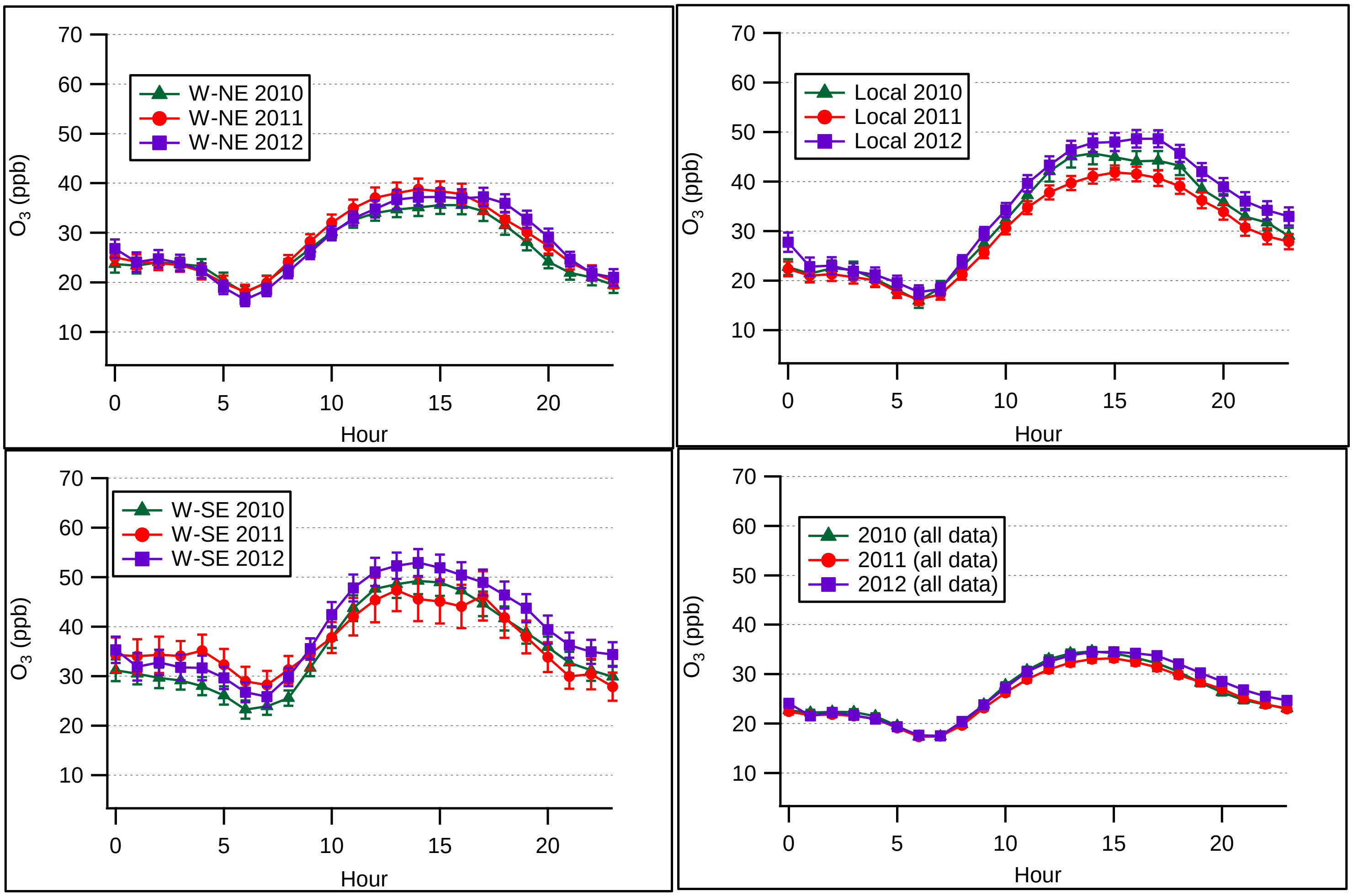

Figure 5: O_3 hourly summer averages at Downtown2 Toronto station (error bars represent standard deviation of the mean).

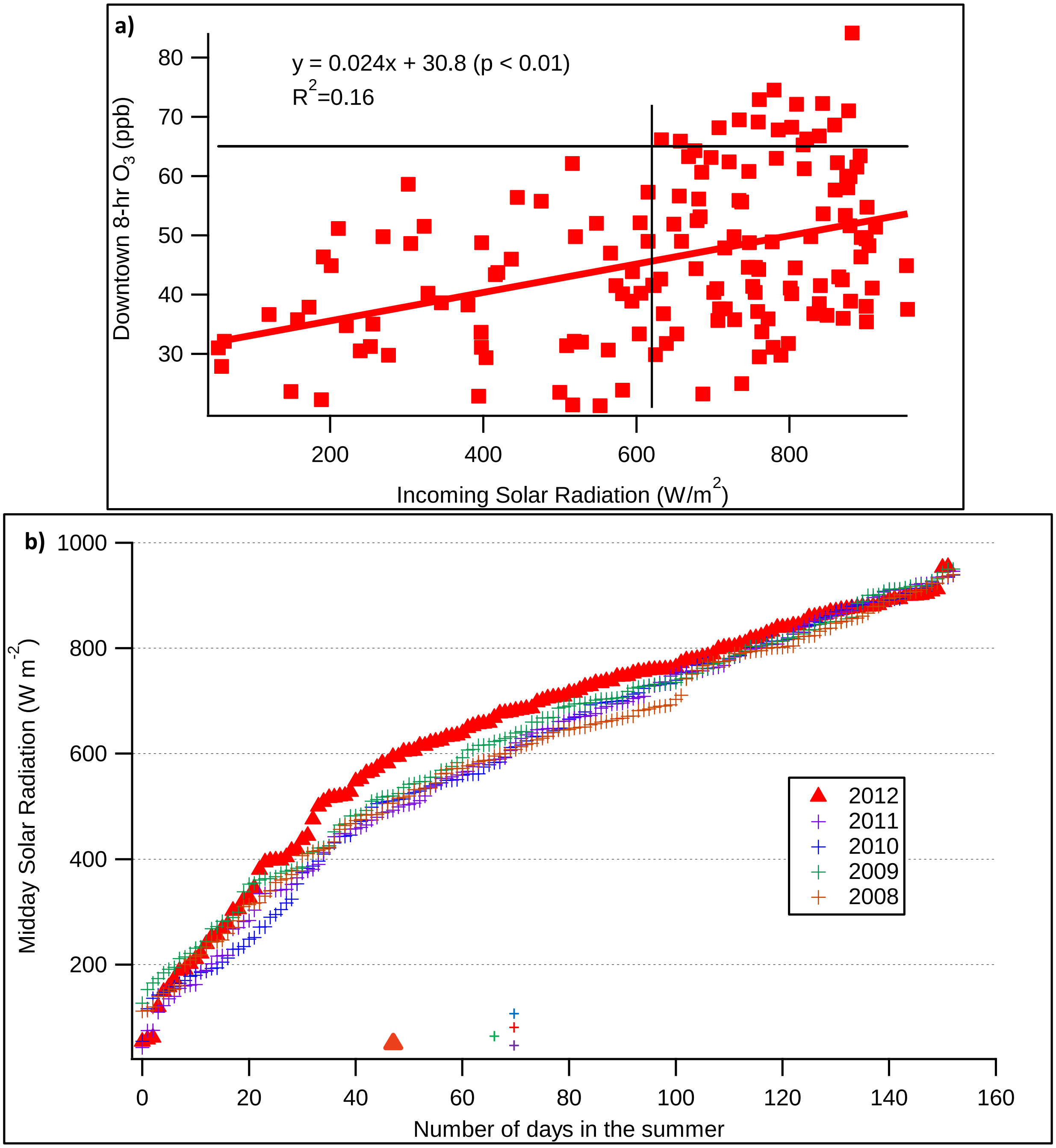

Figure 6: a) Regression of Downtown2 8-hr O_3 versus incoming solar radiation (W/m^2) for 2012 (black lines are the thresholds of incoming solar radiation where 65 ppb of O_3 is exceeded); b) Cumulative distributions of the midday average solar radiation (W/m^2) experienced on each summer day (2008-2012) (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).

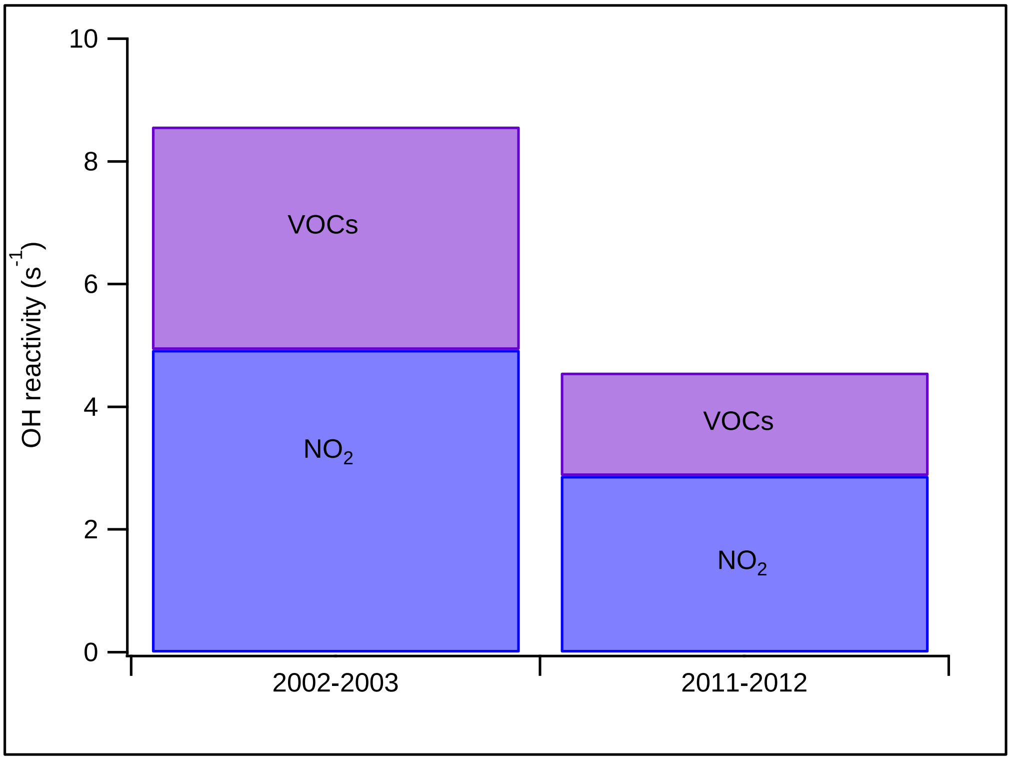

Figure 7: OH reactivity (s^{-1}) to NO_2 and NAPS VOCs in the "early" period (2002-2003) and "late" period (2011-2012) at the Downtown sites.

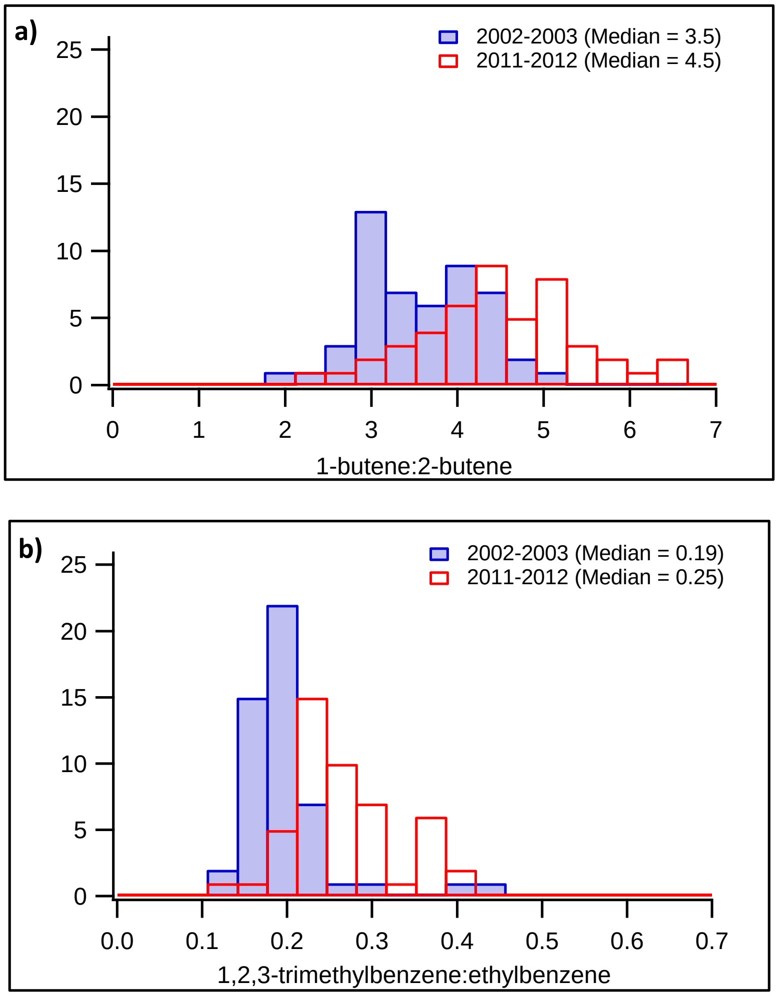

Figure 8: Histograms of 1-butene:2-butene (a) and 1,2,3-trimethylbenzene:ethylbenzene (b) in the early (2002-2003) and late (2011-2012) periods.