

The impacts of
precursor reduction
and meteorology

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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 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 h 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

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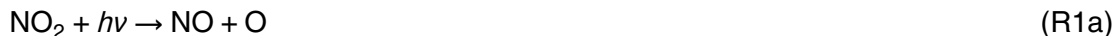
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ozone leads to respiratory symptoms and increased risk for hospital admissions (Bell et al., 2004) and as a result of these and reduced agricultural yields, yearly economic losses attributed to ozone and fine particulate matter pollution are as high as \$9.6 billion in the province of Ontario alone (MOE, 2005). In response to this, many governments and regulatory agencies have imposed air quality standards to protect the population against exposure to O₃ 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 h 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, O₃ 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 + NO₂), 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 (ICF, 2007). The production rate of ozone depends on precursor concentrations in a non-linear fashion. Furthermore, previous 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 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 (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 Reactions R1a–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 (Reaction R3). The organic peroxy radical can then further react with NO to form NO_2 and an organic alkoxy radical, RO (Reaction R4).



The NO_2 formed in Reaction (R4) can photolyze during the daytime to regenerate NO and an oxygen atom (Reaction R1a), which can then recombine with an oxygen molecule to form O_3 (Reaction 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 (Reaction R5) and the net Reactions (R1)–(R6) results in the formation of two ozone molecules (Reaction R7).



In this study, the total oxidant, O_x , is defined as the sum of NO_2 and O_3 ($[\text{O}_x] = [\text{NO}_2] + [\text{O}_3]$) and therefore O_x can only increase in the presence of VOCs when O_3 is

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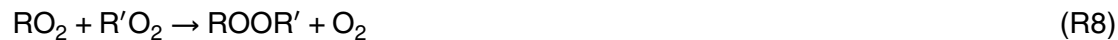
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formed via Reactions (R3) and (R4) followed by Reactions (R1a) and (R1b), whereas it is conserved when O_3 is formed via Reaction (R2) followed by Reactions (R1a) and (R1b). The advantage of analyzing O_x over O_3 is that O_x is a better measure of 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 (Reaction R8).



Under this pathway, the addition of NO_x increases O_3 production by enhancing the rate of Reaction (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 (Reaction 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 = $RC(O)O_2NO_2$, Reaction R10) or alkyl nitrates (ANs = $RONO_2$, Reaction R11) (Farmer et al., 2011). PNs serve as a temporary reservoir for NO_x and suppress O_x 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_x production (Perring et al., 2010).



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 O_x levels 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 O_x during the study period. We discuss the strong link between O_x 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 north-west 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 Area 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

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sector (63%), with diesel trucks accounting for a disproportionately large percentage (36%) (ICF, 2007). When considering only emissions made directly in the city, transportation accounts for an 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). 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 <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 a.g.l. 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. 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 h over five days during late summer. 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 h maximum O₃ and O_x were calculated for each site throughout the thirteen year study period. The O₃ diurnal cycle was examined and it was determined that the most photochemically relevant hours for O₃ production were between 11:00 and 15:00. 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 ($\sum k_i[\text{VOC}_i]$) in units of inverse seconds. The influences of biogenic, anthropogenic and oxygenated VOCs (OVOCs) were distinguished by identifying the sum of isoprene, 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.

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.

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2.3 Meteorological analyses

Hourly meteorological data was continuously collected throughout the study period at Toronto's Pearson International Airport 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 h 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). 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 O₃ 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 pe-

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riod (2000–2012). The urban sites have the steepest slopes, between -0.64 and -0.92 ppbyear $^{-1}$ ($p < 0.01$) while the suburban sites also have decreasing trends of -0.20 to -0.55 ppbyear $^{-1}$ ($p < 0.05$). Overall, 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) continue 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, less-efficient vehicles (MOE, 2013). Other factors may include the closure of the Lakeview Generating Station 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 38 000 to 3000 t 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 overall decreases of at least 53 % from 2000 levels (excluding Junction site), with the Downtown1 site experiencing the largest decrease of 62 %. 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.

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Figure 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_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 2.4–7.6% occurred in the urban stations and 3.5–13.9% 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 ($p < 0.07$).

3.2 O_x levels from 2008–2012

While over the entire study period O_x levels in GTA have decreased, from 2008 onwards the same trend is not observed. Figure 3c and d shows that at all monitored sites, between 2008 and 2011 O_x levels in the GTA were consistent lower than from 2000–2007. However, the measured average summer daily maximum 8 h O_x in 2012 was significantly higher than that of the previous four years (an increase of 3–4 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_x increase cannot be explained as a result of a change in either of the precursor compounds. Alternatively, this variability in O_x may be explained by meteorological influences, which is explored in the following section.

3.3 Meteorological influences on O_x

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 peroxyacetyl nitrate (PAN). Higher temperatures may also result in enhanced local production of O₃ by increasing HO_x production, or increasing local biogenic VOC emissions. Figure 4 displays the number of days each year where the 8 h O₃ average exceeded 65 ppb, the number of days which experienced temperatures exceeding 30 °C, as well as the Design Value (the 4th highest 8 h O₃ 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 O₃ standard, it did not have significantly more days experiencing warmer temperatures compared to 2010 or 2011. Therefore, based on this data, the warm temperatures experienced in the summer of 2012 did not play the dominant role in the O_x 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 Sect. 2, 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 north-east flow (W–NE)”; and days when the net wind movement was < 120 km as “stagnant”

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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 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. This could have contributed to the high O_x levels measured in the GTA in 2012; more 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 O_3 production) as well as the fewest days with “clean” air transport from the north.

Figure 5 displays the hourly summer averages at Toronto North for O_x 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_x levels. Between 2010 and 2012, the maximum daily O_x reached when air arrived from W–NE was consistent, a result expected as this air traveled over remote regions and therefore O_3 production is likely NO_x limited and dominated by biogenic VOC reactivity. The maximum daily O_x 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_x observed in 2012. Lastly, the maximum daily O_x reached as a result of stagnant conditions was again higher in 2012 than in 2010 or 2011. This increase in local O_x concentrations cannot be explained by wind transport or a change in precursor concentrations, as explained in Sect. 3.2, and therefore other meteorological influences must be affecting the local maximum level of O_x reached.

Since the local O_x 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

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in the GTA. Data collected from a net radiometer at UTMMS was analyzed for the period 2008–2012. Figure 6a displays a regression between Downtown2 maximum 8 h O₃ levels (ppb) and midday incoming solar radiation (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. Figure 6b 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) (Reactions R8 and R9). Based on the data available, we used the relative reactivity of OH to NO₂ and the sum of specified 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,

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NO_2 reactivity to OH accounts for an increasingly larger portion of total reactivity, 2.88 vs. 1.68 s^{-1} for VOC 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.

5 These results suggest that the preferred fate of OH radical in the late period is reaction with NO_2 (Reaction R9), thereby suggesting that ozone production has become more NO_x -saturated and more sensitive to VOC reactivity over the last decade.

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
10 five separate days of 3 h canister measurements during a two week period between 27 August and 12 September. The OH reactivity to non-methane hydrocarbons was calculated as two fractions: VOCs (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 $\sim 60\%$ 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 h 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
20 infer that 24 h 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 limited.

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. Figure 8 displays the ratio of two alkenes, 1-butene ($k_{\text{OH}} = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) and *cis*-2-butene ($k_{\text{OH}} = 5.6 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$), as well as two aromatic VOCs, 1,2,3-trimethylbenzene ($k_{\text{OH}} = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) and ethylbenzene ($k_{\text{OH}} = 7.1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$). All of these compounds have lifetimes in the atmosphere on the order of a few hours, assuming an OH concentration of $10^6 \text{ molec cm}^{-3}$, 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. 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 Sect. 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.

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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. 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 Sect. 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 Sect. 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.

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Significant reductions in the concentrations of O₃ precursor compounds have been observed since 2000; NO₂ levels decreased by at least 45 % in urban sites and 28 % in suburban sites and VOC reactivity decreased by at least 53 %. 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_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 O_x 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_x increase compared to 2010 and 2011, air transport from upwind regions may have. Compared to the preceding 5 years, the summer of 2012 was affected by a large number of days with air transport from the W–SE (polluted air travelling over urban areas in Canada and the US), the fewest days with air transport from the W–NE (clean air travelling over remote regions) and the most days affected by stagnant conditions (air trapped over the GTA allowing precursor compounds to accumulate and enhance local O₃ production). Additionally, since the production of O₃ 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 levels of incoming solar radiation exceeding 600 W m⁻², which likely contributed to the enhancement of local O₃ 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 %.

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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 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.

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 O₃ and NO_x data as well as to the UTMMS for providing hourly incoming solar radiation data.

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Table 1. Percent of days each summer (2008–2012) that were affected by air transport from the W–NE, W–SE or local/stagnant air.

Year	W–NE	W–SE	Local
2008	29	18	52
2009	33	14	53
2010	29	26	45
2011	38	9	53
2012	25	20	54

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Table 2. The percent difference between 2004 and 2012 NO₂ and VOC concentrations (ppb) at all stations monitored (Junction was not included as monitoring stopped in 2005).

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	–	–

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Fig. 1. Monitoring stations in the Greater Toronto Area used for the collection of NO_x and O₃ data (blue and pink markers), VOC data (aqua markers) and meteorological data (yellow marker).

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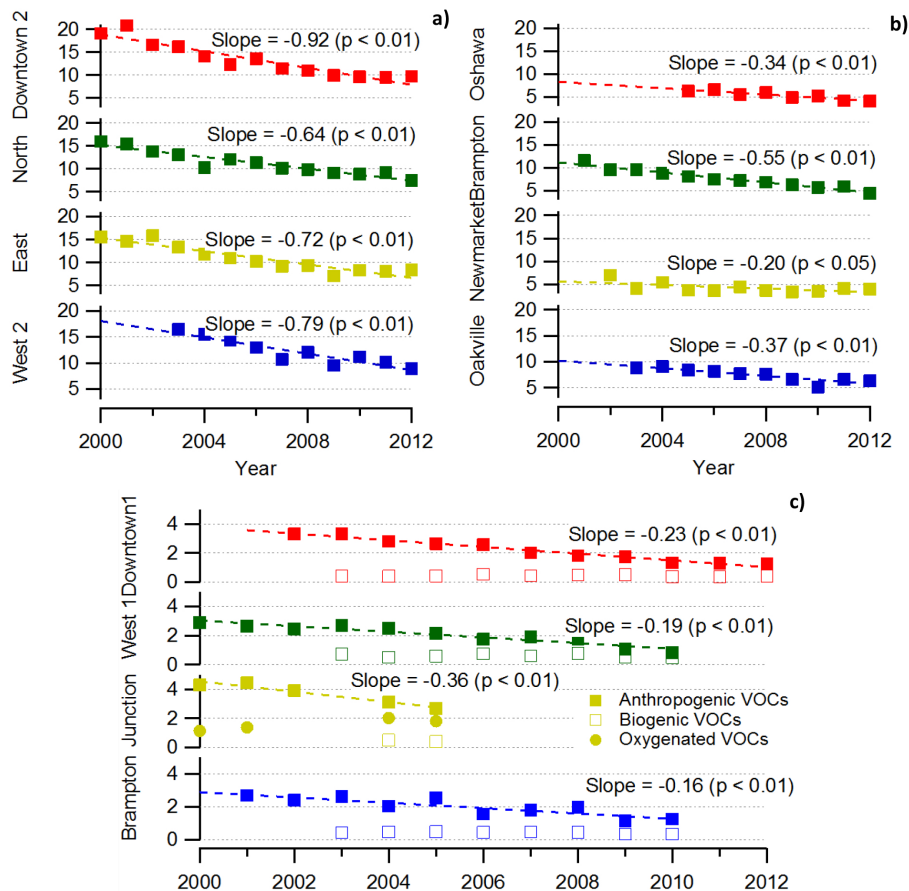


Fig. 2. Annual summer midday NO_2 concentrations (ppb) in GTA urban (a) and suburban areas (b); slopes in ppb year^{-1} . Annual summer VOC reactivity (s^{-1}) (c); slopes in $\text{s}^{-1} \text{ year}^{-1}$.

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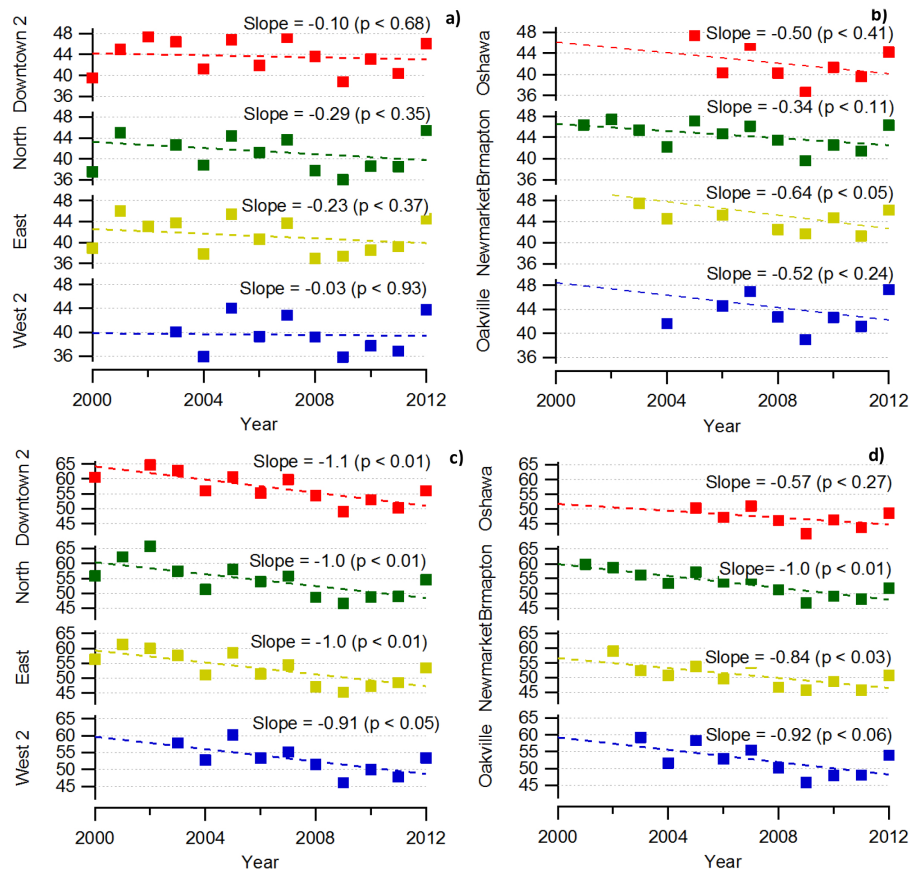


Fig. 3. Annual summer average maximum 8 h O_3 (a and b) and O_x (c and d) concentrations (ppb) for Toronto urban and suburban areas; slopes in $ppb\text{year}^{-1}$.

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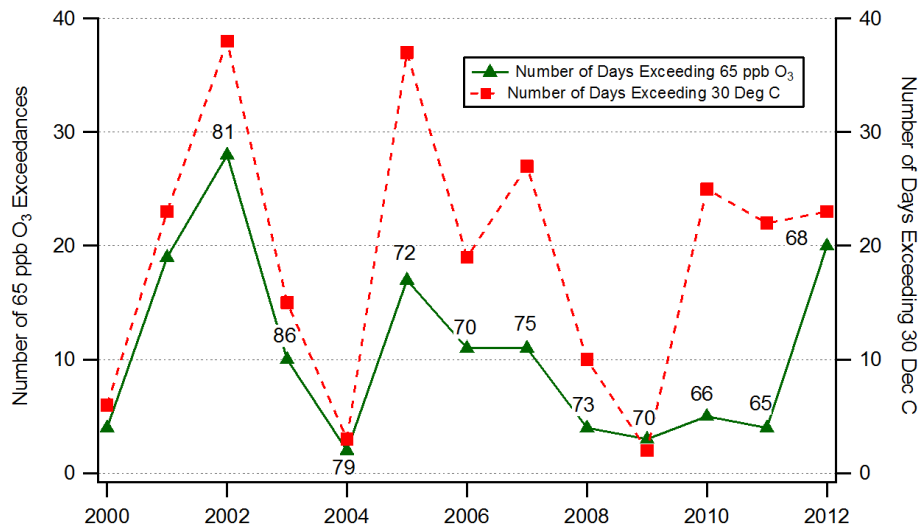


Fig. 4. The number of days exceeding 65 ppb O₃ Canada-wide Standard (green) and the number of days exceeding 30 °C (red) at the Toronto North station. The number above each marker is the Design Value for that year.

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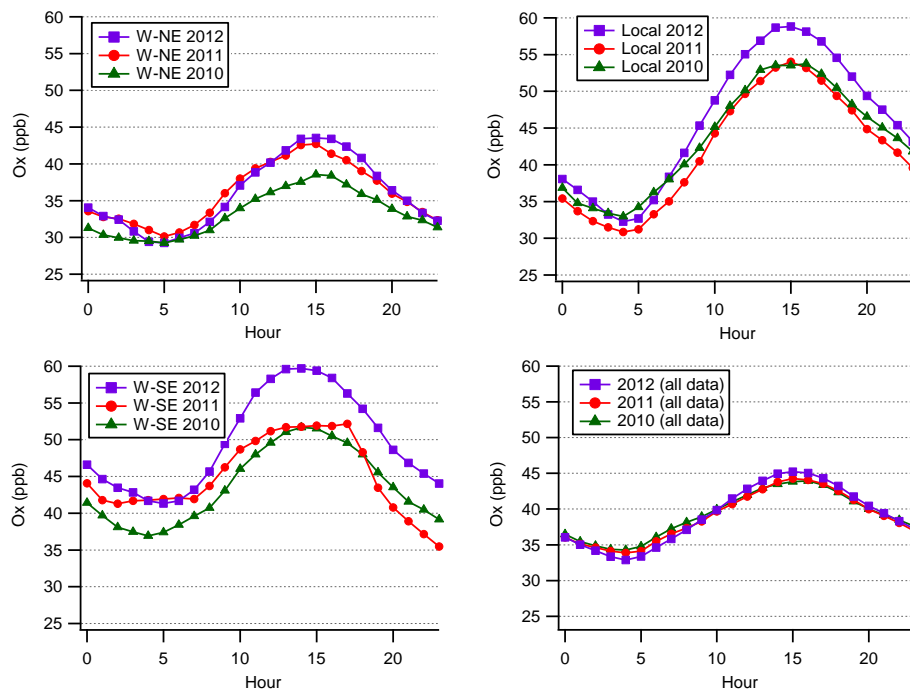


Fig. 5. O₃ hourly summer averages at North Toronto.

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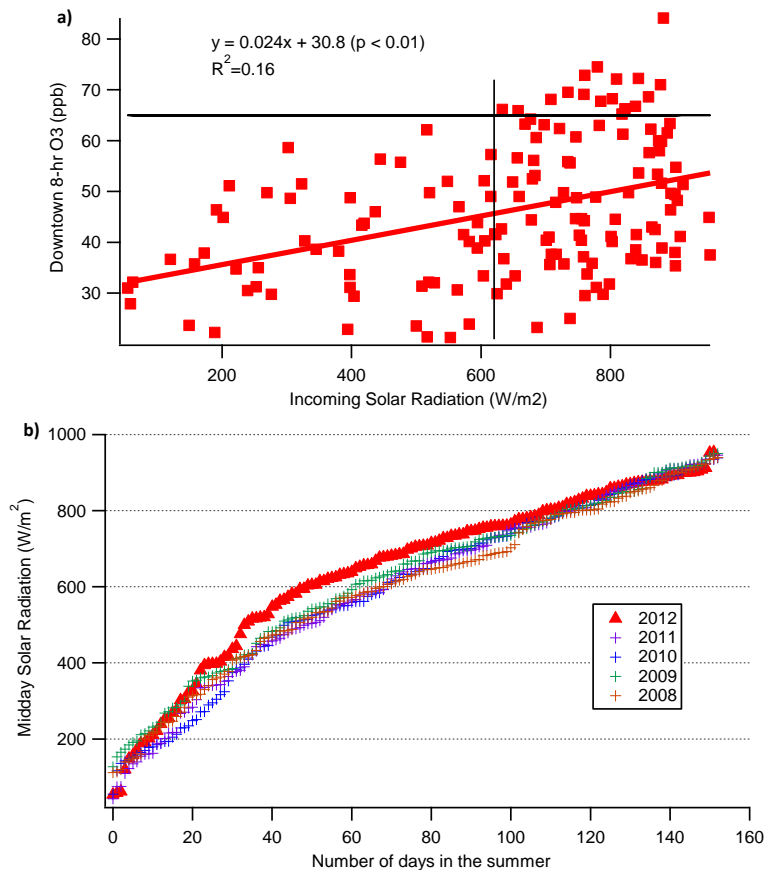


Fig. 6. (a) Regression of Downtown 8 h O₃ vs. incoming solar radiation (Wm⁻²) for 2012 (black lines are the thresholds of incoming solar radiation where 65 ppb of O₃ is exceeded); (b) cumulative distributions of the midday average solar radiation (Wm⁻²) experienced on each summer day (2008–2012).

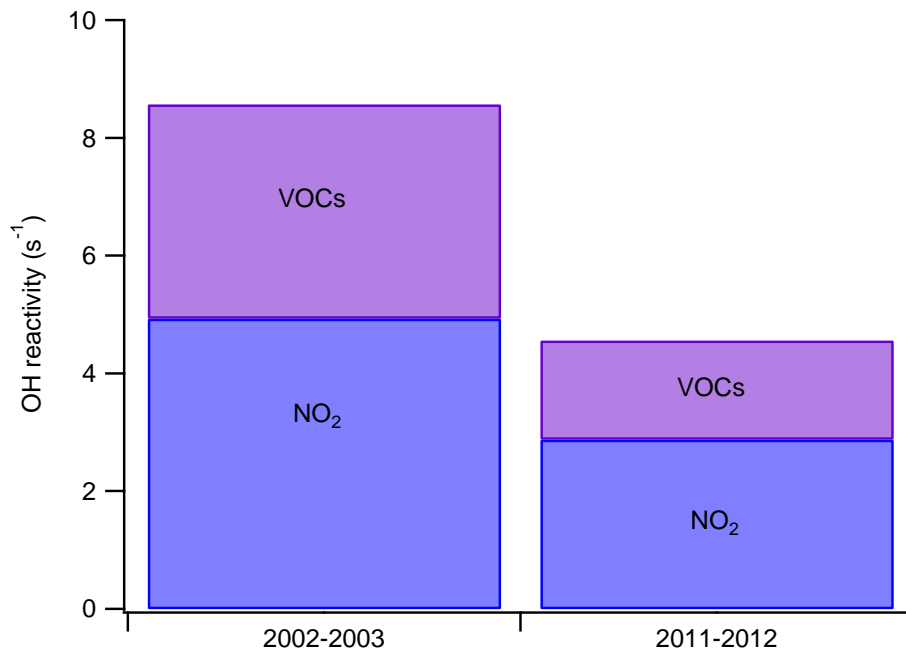


Fig. 7. OH reactivity (s^{-1}) to NO_2 and VOCs in the “early” period (2002–2003) and “late” period (2011–2012) at the Downtown sites.

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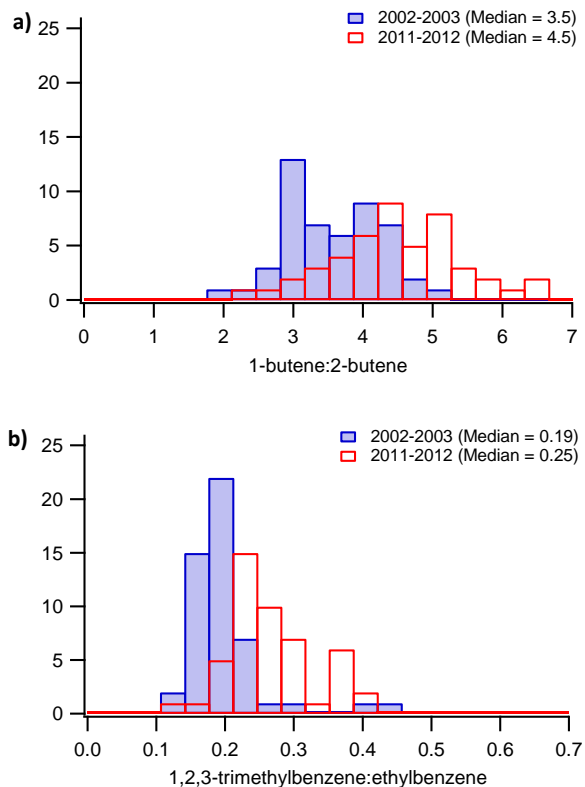


Fig. 8. Histograms of 1-butene : 2-butene **(a)** and 1,2,3-trimethylbenzene : ethylbenzene **(b)** in the early (2002–2003) and late (2011–2012) periods.