Long term changes in nitrogen oxides and volatile organic compounds in Toronto and the challenges facing local ozone control

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Abstract

Ground level ozone represents a significant air quality concern in Toronto, Canada, where the national 65 ppb 8-h standard is repeatedly exceeded during the summer. Here we present an analysis of nitrogen dioxide (NO2), ozone (O3), and volatile organic compound (VOC) data from federal and provincial governmental monitoring sites from 2000 to 2007. We show that summertime VOC reactivity and ambient concentrations of NO2 have decreased over this period of time by up to 40% across Toronto and the surrounding region. This has not resulted in significant summertime ozone reductions, and in some urban areas, it appears to be increasing. We discuss the competing effects of decreased ozone titration leading to an increase in O3, and decreased local ozone production, both caused by significant decreases in NOx concentrations. In addition, by using local meteorological data, we show that annual variability in summer ozone correlates strongly with maximum daily temperatures, and we explore the effect of atmospheric transport from the southwest which has a significant influence on early morning levels before local production begins. A mathematical model of instantaneous ozone production is presented which suggests that, given the observed decreases in NOx and VOC reactivity, we would not expect a significant change in local ozone production under photochemically relevant conditions. These results are discussed in the context of Toronto’s recent commitment to cutting local smog-causing pollutants by 20% by 2012.

1. Introduction

Tropospheric ozone is a major component of photochemical smog, and is a significant human health hazard (Mudway and Kelly, 2000; Sillman, 2003), but as a secondary pollutant its atmospheric levels are often difficult to control. Its precursor compounds, nitrogen oxides (NOx) and volatile organic compounds (VOC), have a wide variety of sources and can exhibit a non-linear effect on local ozone production, while its accumulation is strongly influenced by meteorological processes. For example, recent studies of long term monitoring data in Japan and Taiwan report steadily increasing ozone levels despite significant reductions in precursor concentrations and attribute this to increasing background levels in air transported from neighbouring regions (Chou et al., 2006; Itano et al., 2007). Therefore, it is vital to distinguish the impacts of local production, meteorology, and background levels to understand annual trends and variability in ozone.

Ground level ozone was recently estimated to cost the province of Ontario several billions of dollars in economic losses due to human health impacts and an additional two hundred million dollars in agricultural crop damages each year (MOE, 2005; OMA, 2005). As a result, there have been major provincial and municipal efforts including both regulatory initiatives and incentive programs to control emissions of ozone precursor compounds. In 2000, Canada adopted a new nation-wide 8-h average of 65 ppb (CCME, 2000), called the Canada-wide Standard (CWS) for ozone. In 2007, Toronto committed to reducing locally-generated smog-causing pollutants by 20% from 2004 levels by 2012 (TEO, 2007). It is therefore worthwhile to assess how past changes in precursor emissions have impacted ozone levels in this region.

In the troposphere during the day, interconversion of NO and NO2 occurs with O3 on the time scale of minutes by the following reactions:

\[
\begin{align*}
\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} & \quad \text{(R1a)} \\
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} & \quad \text{(R1b)} \\
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 & \quad \text{(R2)}
\end{align*}
\]

This rapid chemistry constitutes a null cycle in which there is no production or loss of either NO or O3. Net production of ozone is...
2.1. Study region and monitoring stations

These results lend important insight into local air quality and policy. The main sink of OH and NO$_3$ precursors is non-linear and depends on the relative proportions with the introduction of new particulate filters on heavy-duty diesel vehicles.

In Toronto have remained constant. We demonstrate the strong link in O$_3$ production given the observed decreases in precursor levels. Present, which suggests that Toronto has been in a VOC-limited production regime where we would not expect a significant decrease in O$_3$ production given the observed decreases in precursor levels. These results lend important insight into local air quality and policy, especially in the context of the city of Toronto’s recent commitment to reducing locally-generated smog-causing pollutants.

2. Methods

2.1. Study region and monitoring stations

Toronto, Canada (43°40’N, 79°23’W) is located in southern Ontario on the northwest shore of Lake Ontario. The Greater Toronto Area (GTA) has a population of 5.5 million within 7000 km$^2$, and lies along the “Windsor-Quebec” corridor, the most populated and industrialized region of Canada. During the summer, the GTA is often affected by warm southerly and southwesterly air flow from this corridor which may also have passed over American cities (e.g. Cleveland, Detroit, Pittsburgh). Local meteorology is also often influenced by regular land-lake breezes. According to a 2004 estimate, transportation accounted for roughly 63% of NO$_x$ emissions in Toronto, with diesel trucks contributing disproportionately (36%); the remainder of emissions are from natural gas and electricity (ICF, 2007). In Ontario, transportation is a large source of VOC emissions (33%), with industrial emissions and general solvent use contributing another 33% cumulatively; the last third of emissions are from other miscellaneous sources (EC, 2008).

NO$_x$, O$_3$, and VOC data are available from the federal and provincial cooperative National Air Pollution Surveillance (NAPS) network. Hourly NO$_2$ and O$_3$ data for eight sites in the Greater Toronto Area are publicly available from 2000 forward and updated annually at http://www.airqualityontario.ca. NO$_x$ and O$_3$ measurements are made by automated continuous chemiluminescent- and UV-absorption analyzers respectively which satisfy requirements of the US EPA as equivalent or reference methods. Sampling heights varied from 4 m to 12 m. Recent detailed intercomparisons assessing the performance of molybdenum converters on chemiluminescent analyzers show that sometimes over 50% of what is reported as NO$_2$ during photochemically active times of the day may actually be interferences from higher nitrogen oxides (Dunlea et al., 2007; Steinbacher et al., 2007). We estimate that, since most of the stations in this study are urban locations where NO$_2$ will be a high fraction of total nitrogen oxides, the error is likely significantly less than 50%, and that this bias has a minimal impact on the observed trends. VOC data throughout the same period was obtained from Environment Canada for four stations in the area (Downtown, West 1, Junction, and Brampton), which 24-h samples are collected once every 6 days by evacuated canister followed by analysis by gas chromatography with flame ionization detection (for C$_2$ hydrocarbons) or mass spectrometric detection (for C$_3$-C$_{12}$ hydrocarbons) as described by Wang et al. (2005). Loss of hydrocarbons to processes occurring on the internal canister surfaces was evaluated by analyzing canister samples within a few hours for terpenes, then again after storage for several weeks, and no decrease in terpene concentrations was observed. However, no comparisons to on-line GC measurements have been made to date. Carbonyl compounds were automatically sampled 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 (EPA, 1999). Hourly meteorological data at Toronto’s Pearson International Airport, Toronto’s major weather reporting station which has been in operation continuously during the period of interest, was obtained from 2000 to 2007 from the National Climate Data and Information Archive operated by Environment Canada.

The MOE and EC site locations in this study represent a variety of urban and suburban environments across the Greater Toronto Area. The location and name of each site is shown in Fig. 1. Some are in close proximity to major intersections or major highways, and some are located close to large recreational parks or in residential neighbourhoods (see Fig. 1).

2.2. Data

Daily 8-h maximum ozone and O$_3$ were calculated for each site. Diurnal cycles were examined to determine the most photochemically relevant hours during the day for ozone production. This was identified to be between 11:00 and 15:00, so hourly data for NO$_2$ was averaged during this 4-h-period for each day (hereafter referred to as “daily NO$_2$ midday average”). Annual summer
averages were calculated, where summer is defined as May to September, being the most photochemically relevant time of year. Annual averages also remove seasonal variability in the time series making it easier to identify trends. VOC reactivity was calculated as the product of VOC concentration and the rate constant against OH (found in Atkinson (1997) and Seinfeld and Pandis (2006)). Summer annual averages of the sum of all VOC reactivity ($\sum_j$[VOC$_j$]) were calculated. The contributions of biogenic and anthropogenic reactivity were distinguished by separating the sum of isoprene, cymene, pinenes, limonene, and camphene (considered “biogenic” (Seinfeld and Pandis, 2006)) from the rest of the measured VOC (considered “anthropogenic”, consisting of 40 different VOCs). Annual trends were calculated by linear regression, and their significance is measured by $p$-values calculated from a standard $t$-test where we are testing the null hypothesis that the slope of the regression line is equal to zero. Therefore the $p$-values reported represent the probability of observing a trend of that extreme in a T-distribution of the same degrees of freedom.

Maximum daily temperatures were calculated during each summer, and net wind vectors were calculated for a 12-h period prior to each afternoon (from midnight to 12:00 pm). This was done by summing the magnitude of each $x$- and $y$-component of the wind at every hour, then calculating the resultant vector by trigonometry. The result is a single value that estimates the strength of the wind and net direction of air transport for each day throughout the immediately preceding night and early morning.

3. Results and discussion

3.1. Precursor levels

Annual summer averages of daily midday NO$_2$ are shown in Fig. 2a and b. It is clear that an overall decrease is present throughout the whole study region. The most urban station (Downtown Toronto) and the station closest to a significant highway (West 2) report the highest NO$_2$ in the region, reflecting the important transportation source of NO$_x$ and indicating that these sites likely represent some of the highest NO$_x$ levels found throughout the region. Stations furthest from the main roads and urban centre (e.g. Newmarket and Oakville) report the lowest levels. Downtown Toronto, West 2, and Oshawa all have the steepest slopes, between $-1.2$ and $-1.4$ ppb year$^{-1}$ ($p < 0.01$), while all other sites have strong decreasing trends of $-0.4$ to $-1.0$ ppb year$^{-1}$ (with $p < 0.01$ except for Newmarket). Overall, the North, East and Downtown Toronto summer averages in 2007 were over 35% lower than 2000 levels (the highest difference is in East Toronto, at 40%). At the West 2 station, 2007 levels were already almost 35% lower than when it began reporting in 2003. Similar magnitudes of change are found at the surrounding sites ($\sim 30$–$38$%), and Oakville is the only station which reported a change less than 30% since the year it began reporting (13% since 2003).

We observe the steepest decrease in NO$_2$ at stations closest to major transportation arteries and intersections, even though the number of vehicles registered in Ontario increased by over 700,000 between 2000 and 2007 (Statistics Canada, 2000, 2007). This is evidence that the reductions are driven strongly by improvements in vehicle technology. Decreasing NO$_2$ in areas where its abundance is high will lead to increases in local OH concentrations (because of Reaction (R6)). This changes the lifetime of NO$_2$ so that it is oxidized more quickly near its source, meaning that a reduction in emissions can have a proportionally even larger reduction in ambient concentrations. Whatever combination of these factors, the fact that NO$_2$ levels across Toronto and surrounding areas have decreased between 13% and 40% reflects considerable achievements in NO$_x$ emission controls and improvements in technology over the past decade.

From the available data, the situation appears to be similar for volatile organic compounds across Toronto. The annual summer averages in anthropogenic VOC reactivity, shown in Fig. 3, show a steadily decreasing trend since 2000. VOC reactivity at the Brampton and Downtown sites in 2007 was already 40% lower than reactivity in 2001 and 2002 respectively. VOC reactivity attributed to biogenic compounds shows no apparent trend.

While the magnitude of biogenic reactivity seems to be quite spatially consistent (around 0.4–0.7 s$^{-1}$ at all locations), the magnitude of anthropogenic VOC reactivity does not (from between 2 and 3 s$^{-1}$ in Brampton and West 1 to around 3–5 s$^{-1}$ at the Downtown and Junction stations). Consequently, the relative importance of biogenic emissions is not evenly distributed. At the West 1 and Brampton site, for example, biogenic VOC reactivity in 2007 represented almost 25% of all recorded reactivity, whereas at the Downtown station the proportion is closer to 18%. At the
Junction station, the most recent data in 2005 showed the biogenic fraction to be about 13%. Emission controls are more easily implemented for anthropogenic VOC, thus controlling total reactivity is not an equal task across the Toronto region, and progress in reducing anthropogenic emissions will not result in a uniform decrease in overall VOC reactivity. Additionally, as anthropogenic VOC reactivity continues to decrease, the biogenic fraction will rise, making it increasingly difficult to control VOC reactivity during the photochemical season most relevant to ozone production. Moreover, photochemical conditions favouring ozone production such as increasing temperature and light can also favour higher biogenic emission rates (for example, see Kesselmeier and Staudt, 1999 and Harley et al., 1999). Indeed, the correlation between daily biogenic VOC reactivity and maximum temperature at each station ranges from 0.02 to 0.05 s⁻¹°C⁻¹ (R² = 0.10–0.42).

This analysis of VOC reactivity is limited, since the governmental data used here do not include oxygenated compounds at all stations. Formaldehyde, acetaldehyde, acrolein, acetone, and propionaldehyde were measured at the Junction station in 2000, 2001, 2004 and 2005, and the average sum of their reactivity during the summer is shown in Fig. 3. While the trend here seems to be increasing, this is difficult to say with the limited availability of data. However, we are able to estimate the contribution of oxygenated VOC to overall reactivity at the Junction station. This value is ~1 s⁻¹ and is therefore an important contribution that is not being accurately captured at other Toronto stations. In addition, our analysis using simple VOC reactivity only considers the initial OH reaction, and subsequent reactions (which may be especially important for longer chained VOC) are not always represented. However, these data show that efforts to reduce anthropogenic VOC emissions are in general producing significant results throughout Toronto, but also suggest several challenges facing pollutant reductions like the increasing fraction of, and the effect of temperature on, biogenic emissions.

3.2. Ozone and Ox

Fig. 4a and b show annual summer daily 8-h maximum O₃ for Toronto and surrounding sites respectively, and Fig. 5a and b show annual summer daily 8-h maximum Ox. Linear regression shows that the trends in ozone are not statistically different from zero, and at some of the more urban sites it may be increasing. The slopes in Ox are all decreasing, but with varying levels of significance (from p < 0.05 to p > 0.50). The most significant decrease is seen at the Brampton site, where the slope is -0.87 ppb year⁻¹, however this trend should be taken cautiously, since it is probably in part due to the fact that data from 2000 is not available (which for all other sites was around 2005 levels, and would weaken the significance). Nevertheless, there seems to be some evidence that ozone production may be decreasing slowly in the area. Annual summer daily 8-h maximum Ox averages show less variability between sites, which illustrates the importance of using Ox (NO₂ + O₃) to remove the titration effect.

The titration reaction (R2) explains many of the differences between the trends in O₃ and Ox and between urban and surrounding sites. For example, Newmarket, located around 40 km north of Toronto, has consistently higher maximum O₃ averages but lower maximum Ox averages than Downtown Toronto. Because there is significantly more NO at the Downtown station to react...
with O$_3$ via reaction (R2), the ozone is temporarily titrated there. Thus there appear to be competing effects responsible for the lack of a trend in ozone; mainly, the fact that decreasing NO$_x$ and VOC reactivity levels could be slowly driving down the production of O$_3$ (as seen by the weakly decreasing trend in O$_x$ levels), while at the same time having less NO to titrate ozone causes levels to increase in proximity to NO sources. Unravelling these competing chemical influences is complicated by the variability in ozone resulting from meteorological conditions, which is explored in the following section.

3.3. Meteorological considerations

Numerous studies report high correlations between ozone levels and temperature for sites all over the United States (Vukovich, 1994; Sillman and Samson, 1995; Vukovich and Sherwell, 2003; Abdul-Wahab et al., 2005), and several methods have been developed to derive “meteorologically adjusted” trends. These include probabilistic models, moving average filters, and cluster analysis (Cox and Chu, 1993; Yang and Miller, 2002; Wise and Comrie, 2005; Walsh et al., 2008). The eight-year time series available in the present study is probably too short to be explored accurately by most of these methods, but recognizing and understanding the effect of temperature on ozone production is obviously crucial in explaining year-to-year variability in O$_3$ and O$_x$ levels throughout the GTA. We illustrate this in Fig. 6, where the number of ozone exceedances in North Toronto is plotted along with the number of days where the maximum temperature reached above 30°C. This figure shows that a great deal of the annual variability in high ozone levels can be explained by variability in the number of summer days with high temperatures. In fact, summer O$_x$ levels at this station correlate with maximum daily temperatures with a slope of 1.7 ppb/°C ($R^2 = 0.33$). Mechanistically, increased temperatures could lead to enhanced local production of O$_3$ by enhancing HO$_x$ production, increasing local biogenic VOC emissions (or volatilization of VOC), suppressing the...
net formation of peroxyacetyl nitrate, or may simply correlate with high solar radiation (Jacob et al., 1993; Sillman, 2003). For example, a correlation between biogenic VOC reactivity and maximum daily temperature can be seen for at the Toronto sites, and might become stronger if hourly instead of 24-h average VOC concentrations were available.

Because high temperatures in Toronto are often associated with southerly flow, it is also possible that the correlation between ozone and high temperatures is driven by transport of ozone and precursor compounds from the polluted upwind region. Since we were interested in separating and comparing the effects of increased local production and increased transport on warm days, we used the net wind vectors for each day from midnight to noon of that day as described in the Methods section. Fig. 7 shows a polar graph where the radius represents the summer net wind vectors from 2000 to 2007 for each day, and the points are coloured by average Toronto daily maximum 8-h O$_3$ levels. In general, when air is being transported from the southwest, O$_3$ reaches higher levels than on days when air is being transported from the north and northwest.

Each summer, 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 southeast flow (W–SE)” ($n = 197$); days when the net wind speed and direction resulted >120 km net movement from the north (270°–45°) as days influenced by “west to northeast flow (W–NE)” ($n = 431$); and days when the net wind movement was less than 120 km as “stagnant” (or influenced most by local conditions, $n = 596$). The data in the W–SE group represent days most likely influenced by polluted air masses from surrounding urban areas in Canada and the US, while data in the W–NE group are generally influenced by transport from remote regions.

Hourly averages of O$_3$, O$_3$, and NO$_2$ for these separate conditions at the North Toronto site are shown in Fig. 8. North Toronto was selected since it is representative of a location influenced directly by GTA emissions (no matter what direction air might be transport ing), but not as biased toward high NO$_2$ as stations such as Downtown or West 2. We see that on days that were influenced by W–SE flow there are significantly higher morning O$_3$ levels than on...
days with stagnant conditions or influenced by W–NE flow. Stagnant days show a sustained O₃ increase of around 3 ppb h⁻¹ from 8 am to 3 pm, at which point levels start to decrease. Meanwhile, days with W–SE flow show similar production rates, but only until about noon at which point levels start to level out. These results suggest that stagnant conditions allow ozone to accumulate for a longer period through the day, probably because precursors are not swept out of the city. This includes occasions when the landlake breeze causes precursors to be swept out across the lake in the early morning, but swept back into the city later in the day, resulting in very little net transport of air. The diurnal profile of odd oxygen on days with strong W–SE flow more closely follows the instantaneous rate of ozone production, which likely peaks near noon because ozone and its precursors are being advected away from the city and not left to accumulate. The evidence suggests that under strong W–SE flow, airmasses over Toronto start out with more O₃, but that daytime increases are less significant. Interestingly, the maximum 8-h average in O₃ is quite similar for both stagnant and strong W–SE flow days but on stagnant days the impact of titration is more significant, which keeps the ozone lower.

Previous studies using back trajectory clusters during summer months from 1989 to 1995 and from 1994 to 2003 similarly found that the highest ozone levels are associated with trajectories from the south and southwest, passing over the Detroit-Windsor area (Brankov et al., 2003; Johnson et al., 2007). Along with the present evidence, these results are highly relevant to the Canada-wide Standard for Ozone which makes a provision for “transboundary-influenced communities” that fail to meet the standard even after their “best efforts” to reduce precursor emissions (CCME, 2000).

3.4. Computational model

While variability in meteorological conditions drives much of the interannual variability in ozone over Toronto, it is useful to assess the extent to which changes in precursor concentrations have impacted local ozone productions rates. In this section, we apply a model that was developed by Murphy et al. (2006) to calculate the instantaneous production rate of ozone as a function of NO₂ levels and VOC reactivity. By situating the surface observations of NO₂ and VOC from Toronto during the last 8 years on this plot, we can estimate how the local production regime may or may not be changing and suggest control measures that would most efficiently result in improved air quality.

We refer readers to the above paper for a full derivation, but by assuming conditions of rapid ozone production where chain propagation is more significant than chain termination and that the production of each RO₂ ultimately results in an HO₂ radical, we arrive at the following equation for instantaneous ozone production:

\[
P(O_3) = k_4[HO_2 + RO_2][NO] = 2k_3[VOC][OH]
\]

where [OH] is estimated by:

\[
[OH] = \frac{-(k_6[NO_2] + a_k_3[VOC]) + \sqrt{(k_6[NO_2] + a_k_3[VOC])^2 + 24P(\text{HO}_x)k_{\text{S.PNG File}}} \left(\frac{k_6[VOC]}{k_{\text{S.PNG File}}} \right)^2}{12k_{\text{S.PNG File}}}
\]

With an initial O₃ concentration of 40 ppb, relative humidity of 65%, and an average formaldehyde concentration of 4 ppb, the estimated midday summertime \(P(\text{HO}_x)\) for Toronto was calculated as 2.3 ppb h⁻¹. To solve the above equations, we estimate a to be 0.04 (Cleary et al., 2005), \([NO_2]/[NO] = 3, k_6 = 1.1 \times 10^{-11} \text{ s cm}^3 \text{ mole}^{-1}\) (Sander et al., 2003), \(k_{\text{S.PNG File}} = 8 \times 10^{-12} \text{ s cm}^3 \text{ mole}^{-1}\) (Tyndall et al., 2001), and \(k_5 = 5.0 \times 10^{-12} \text{ s cm}^3 \text{ mole}^{-1}\) (Tyndall et al., 2001; Sander et al., 2003). Finally, we are able to plot \(P(O_3)\) as a function of VOC reactivity \((-\Sigma k_i[VOC])\) and NO₂. The result is shown in Fig. 9.

This contour plot clearly shows two separate ozone production regimes; one in which decreasing NO₂ levels decreases ozone production \((\text{NO}_x\text{-limited})\), and one in which decreasing NO₂ levels increases ozone production \((\text{VOC-limited})\). Since the data show both precursors have been decreasing linearly, and at roughly consistent rates over most of the Greater Toronto Area we can estimate a vector of precursor changes from 2000 to 2007 on the contour plot to indicate how instantaneous local ozone production might be changing year-to-year. We use a wide arrow on the plot to indicate the general chemical space over which the GTA region atmosphere
has transitioned between 2000 and 2007. According to this simple model we do not expect instantaneous summertime ozone production to have changed very much in the last 8 years. The precursor changes produce a vector (red arrow) that does not cross contour lines in Fig. 9. It is interesting to note that if either the VOC reactivity or NO\textsubscript{2} concentrations had changed in isolation, there would have been more dramatic changes in ozone production. For example a 40% reduction in NO\textsubscript{2} with constant VOC reactivity at 4 s\textsuperscript{-1} leads to model predictions of a doubling in ozone production rates, while a 40% reduction in VOC reactivity with constant NO\textsubscript{2} reduces ozone production rates by approximately half.

While this model is quite simple and relies on several assumptions, we note that the ozone production rates that it predicts (~4 ppb h\textsuperscript{-1}) are consistent with the rates of O\textsubscript{3} increase (~3 ppb h\textsuperscript{-1}) observed in the GTA (Fig. 8). The model is useful as an aid to approximate the chemical regime of ozone production in Toronto based on the non-linear relationship with NO\textsubscript{x} and VOC levels, and provides a sound scientific explanation for why the past 8 years of precursor reductions have not resulted in statistically significant reductions in O\textsubscript{3} and O\textsubscript{3}. Because the model calculations were for a single value of P(HO\textsubscript{x}), the impact of possible changes to P(HO\textsubscript{x}), which may be driven by changes in O\textsubscript{3} or formaldehyde levels, are not represented by the model realization in Fig. 9. There is no strong evidence for changes in P(HO\textsubscript{x}) between 2000 and 2007, and this would have a greater impact on the magnitude of O\textsubscript{3} production rates than on their NO\textsubscript{x}–dependence. We can say with a great deal of certainty that present levels place Toronto in a VOC-limited production regime and thus VOC emission reductions will be most effective at decreasing local ozone production during photochemically relevant periods.

4. Conclusion

Significant reductions in NO\textsubscript{2} and VOC have been observed in the city of Toronto and surrounding areas. At most sites, summertime NO\textsubscript{2} concentrations and VOC reactivity have decreased by between 30 and 40% since 2000, likely in response to improving vehicle technology, regulatory initiatives and incentive programs by the province and municipality to control emissions. Throughout the same period summer ozone levels have shown no significant changes, with many sites showing average conditions in 2007 were similar to those in 2000. We interpret this as a response to competing effects; a nominal reduction in ozone production as demonstrated by slightly decreasing O\textsubscript{3} levels, counteracted by the reduced titration effect on a short time scale. We have also shown evidence that air transported from the west and south on some of those warm days is contributing to higher 8-h ozone maxima, mainly through higher early morning concentrations before local production begins. For example, we have shown that days influenced by strong W–SE transport reach similar 8-h maximum ozone concentrations as stagnant days on which ozone starts out lower but accumulation extends later into the day.

These results lend insight into ozone production in the Greater Toronto Area, but also point at several future challenges. For example, an increasing fraction of biogenic VOC activity means that it will become increasingly difficult to control total VOC reactivity, which our analysis indicates would be the most effective strategy for significant reductions in a VOC-limited ozone production regime. Moreover, biogenic VOC reactivity in Toronto has shown a correlation with maximum daily temperature, and we can therefore expect some efforts may be compounded by increasing temperatures in a warming climate. The loss of O\textsubscript{3} due to reactions with biogenic VOCs (thus counteracting increases in O\textsubscript{3} production from reactions with OH) was estimated to be at least an order of magnitude lower than O\textsubscript{3} production over the conditions presented here. In a VOC-limited production regime, the collection of VOC data with higher time resolution and good spatial coverage across the city and surrounding areas ought to be a priority. The VOC data used in this analysis is based on 24-h averages, and we are therefore lacking specific information about VOC reactivity during photochemically relevant times of the day. Moreover, we have noted the lack of oxygenated VOC data which comprises a significant fraction of the total VOC reactivity.
of VOC reactivity in the area. Also, there continue to be strong incentives to reduce NOx emissions, due to the role NOx plays in the production of fine particulate matter (PM$_{2.5}$).

These conclusions should have important implications on both the recent commitment to a 20% reduction in ozone precursor emissions in Toronto since 2004, and on the Canada-wide Standard for Ozone which provides leniency for transboundary-influenced communities that cannot meet the standard despite their best efforts to reduce emissions.

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References


