Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-851
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2018

Atmospheric Chemistry and Physics Discussions

Long-term measurements of ground-level ozone in Windsor, Canada - Part I. temporal variations and trends

Xiaohong Xu[1]*, Tianchu Zhang[1], Yushan Su[2]

[1]Department of Civil and Environmental Engineering, University of Windsor, Windsor, Ontario, Canada

[2] Ontario Ministry of the Environment, Conservation and Parks, Toronto, Ontario, Canada

*Corresponding author: email: xxu@uwindsor.ca

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-851
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2018

Atmospheric Chemistry and Physics Discussions

Abstract

This study investigates temporal variations and long-term (1996-2015) trends of ground-level O_3 (ozone) and its precursors, NOx (nitrogen oxides) and volatile organic compounds in Windsor, Ontario, Canada. During the 20-year study period, NOx, non-methane hydrocarbon concentrations and ozone formation potential decreased significantly by 58%, 61%, and 73%, respectively, while O_3 concentrations increased by 33% (20.3 ppb in 1996 vs. 27 ppb in 2015). Our analysis revealed that the increased annual O_3 concentrations in Windsor were due to 1) decreased O_3 titration (by 50% between 1996 and 2015) owing to declining nitric oxide concentrations, which is suggested by a slightly decreasing trend of annual mean total O_3 concentrations after the titration effect is removed, 2) reduced local photochemical production of O_3, because of dwindling precursor emissions, and 3) increased background O_3 level that has more impact on the low-to-median concentrations. The net effect of those factors is decreasing peak O_3 levels during the smog season from May to September, but an overall increasing trend of annual means. These results indicate that the emission control measures are effective in reducing peak ozone concentrations. However, challenges in lowering annual O_3 levels call for long-term collaborative efforts in the region and around the globe.

1. Introduction

Ozone (O_3) at the ground-level is a main component of smog. Exposure to high O_3 concentrations causes wheezing and shortness of breath, resulting in absence from schools and hospital admissions (USEPA, 2018). People with respiratory diseases, children, and elders are at higher risks from O_3 exposure. Recent studies suggest that long-term exposure to high O_3 levels is associated with permanent lung damage and deaths from respiratory causes (USEPA, 2018). High O_3 concentrations also result in reduced crop yields by inhibiting breathing ability of plants, slowing down the photosynthesis rates, and making plants more susceptible to diseases (IDNR, 2018).

As a secondary air pollutant, ground-level O_3 is formed by photochemical reactions between nitrogen oxides (NOx) and volatile organic compounds (VOCs) in the presence of sunlight. Non-methane hydrocarbons (NMHCs) are more reactive than methane and other VOCs in forming

ozone (NAS, 1999); therefore, NMHCs are used to represent O_3 precursors (e.g. Jun et al., 2007; Akimoto et al., 2015). Because the reactivity of each NMHC is different, Carter (1994) and other researchers used O_3 formation potential (OFP) to quantify contributions of individual NMHCs or a group of NMHCs (Jia et al., 2016). Similarly, a study in Hong Kong investigated associations between O_3 and its precursors, i.e. NO_X and 21 NMHCs during 2005-2014 (Wang et al., 2017). O_3 concentrations in Hong Kong increased (0.56 ppb/year, $p<0.01$) while NOx decreased (-0.71 ppb/year, $p<0.01$). The study further showed that there were no significant changes in NMHCs (-0.03 ppb/year, $p>0.1$) during the 10-year study period. Nevertheless, the calculated daytime average contribution to O_3 concentrations by aromatics decreased (-0.23 ppb/year, $p<0.05$), while that by alkenes increased (0.14 ppb/year, $p<0.05$) and that by alkanes and biogenic VOCs did not change significantly (-0.04 ppb/year, 0.24ppb/year, respectively, $p>0.05$) (Wang et al., 2017).

In Ontario, Canada, emissions of NOx and VOCs decreased by 52% (from 651 to 311 kilo tonnes) and 54% (from 789 to 363 kilo tonnes) respectively during 1996-2015 (ECCC, 2018a). However, Ontario-wide O_3 composite mean increased by 22% from 22.4 ppb in 1996 (MOE, 2006) to 27.4 ppb in 2015 (MOECC, 2017). Previous studies showed that changes in O_3 concentrations were attributed to background O_3 and changes in photochemical O_3 production caused by the decrease in NO_X and VOC concentrations (e.g. Shin et al., 2012). Because NO (nitric oxide) reacts with O_3 to form NO_2 (nitrogen dioxide) and O_2 (also known as NO titration), decreased NO concentrations may lead to increases in O_3 concentrations due to weakened titration effect (Sicard et al, 2011, Akimoto et al., 2015). To remove the impact of the NO titration on ambient O_3 concentrations, "total ozone" (TO) was previously employed in trend analysis. For example, Akimoto et al. (2015) used TO in their ambient ozone study in four areas in Japan where O_3 concentrations were high (i.e., Tokyo, Nagoya, Osaka, and Fukuoka). During the 20-year study period, NO concentrations decreased from 16 ppb in 1990 to 6 ppb in 2010. The increasing rates of annual TO (0-0.22 ppb/year) were much smaller than those of O_3 (0.22-0.37 ppb/year) in the four areas during 1990-2010. The authors concluded that the decrease in the NO titration effect was one of the causes for the increased O_3 concentrations in Japan.

Recently, continuous O_3 observations (2-years or longer) from more than 9,600 stationary platforms around the world were assembled to assess a suite of metrics relevant to its impact on human health, vegetation, and climate under the International Global Atmospheric Chemistry (IGAC)'s Tropospheric Ozone Assessment Report (TOAR) project (Schultz et al., 2017; IGAC,

2018). Using 2010–2014 means from over 3300 vegetation sites, the highest ozone levels were found in mid-latitudes of the northern hemisphere, including southern USA, the Mediterranean basin, northern India, north, north-west and east China, the Republic of Korea and Japan (Mills et al., 2018). In a study of over 2,000 monitoring sites worldwide, negative (i.e. decreasing) trends in peak O_3 concentrations (i.e. 4th highest daily maximum 8-hour average) were observed at most North American sites and at some European sites, with very few sites exhibited positive trends (Fleming et al., 2018). Similar studies reported that O_3 levels (monthly mean of the daytime average and monthly mean of the daily maximum 8-hour average) continued to decrease significantly over eastern North America and Europe, while Asia experienced increasing O_3 concentrations through the end of 2014 (Chang et al., 2017; Gaudel et al., 2018). In Eastern North America, summertime daytime averages and daily maximum 8-hour concentrations declined at a slower rate at urban sites than at rural sites during 2000-2014 (Chang et al., 2017). Those studies showed that, over North America and Europe, decreasing peak O_3 levels is attributable to reduction in precursor emissions and a relatively slower decreasing rate at urban locations suggests weakened O_3 titration. In Asia, growing precursor emissions led to increasing ozone concentrations.

The objectives of this study were 1) to evaluate temporal variations and trends of ground-level O_3 and its precursors (NOx, and VOC) in Windsor, an urban location in Southern Ontario, Canada, during the 20-year study period of 1996-2015, and 2) to identify the driving force of long-term trends of O_3 concentrations in Windsor during the past 20 years, as well as seasonal and diurnal variations. Findings of this study will shed light on the effectiveness of emission control policies and possible approaches to reducing O_3 concentrations in the near future.

2. Methodology

2.1 Selection of station in Windsor

There are two air quality monitoring stations in Windsor: Windsor Downtown and Windsor West which are 3.5 km apart (Figure 1). Both stations monitor O_3 and a number of common air pollutions (e.g. NO, NO_2, NOx, SO_2, and $PM_{2.5}$) (MECP, 2018). The Windsor Downtown station was selected in this study due to 1) fewer invalid or missing O_3 values (1824 vs. 2660 during 1996-2015), and 2) a longer record of NO, NO_2, and NO_X data available (1996-2015) compared to the Windsor West station (2001-2015). Twenty-four-hour VOC samples were collected once every six days at the Windsor West station (ECCC, 2016).

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-851
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2018

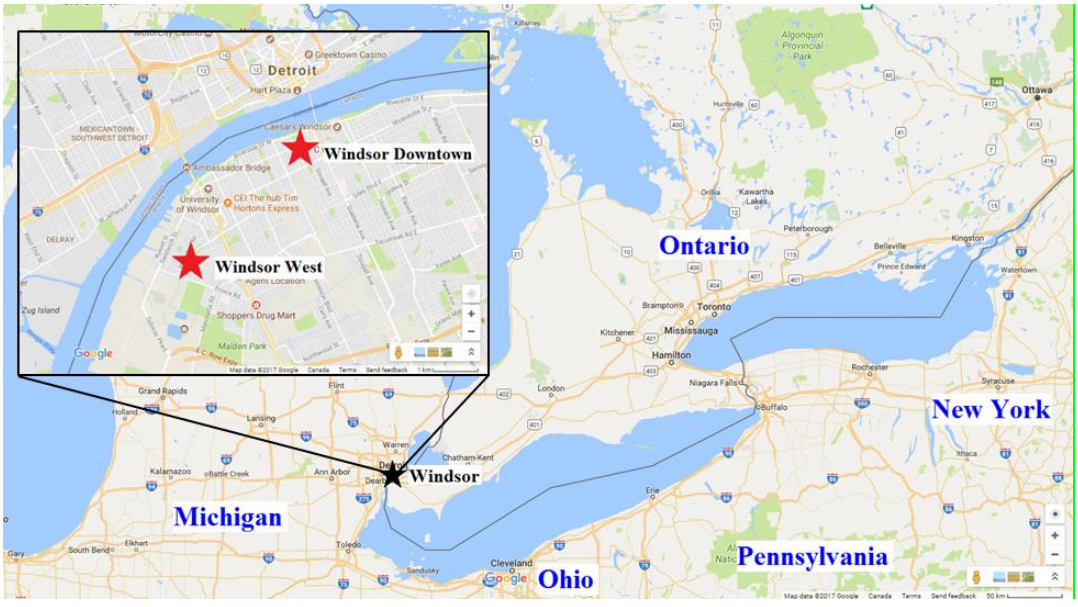


Figure 1. Air quality monitoring stations in Windsor, Ontario, Canada

2.2 Data sources

Hourly O_3, NO, NO_2, and NO_X concentrations in Windsor (1996-2015) were obtained from the Ontario Ministry of the Environment, Conservation and Parks (MECP). Twenty-four-hour VOC data at Windsor West station during 1996-2015 were downloaded from National Air Pollution Surveillance (NAPS) website (ECCC, 2018b).

2.3 Data processing

2.3.1 O_3, NO, NO_2, NO_X, and VOC concentrations and ratios

Numbers of data flags "-999" (i.e., invalid data), blank cells, and "0" data points in hourly O_3, NO, NO_2, and NO_X concentrations were counted by year. Then data flags "-999" were replaced with blank cells to maintain consecutive date/time for individual pollutants. If the total percentage of data flags and blank cells is greater than 40% (3504 hour/year) in a year, data in that year is considered invalid and excluded from further analysis. This is the case for hourly NO, NO_2, and NO_X concentrations in 2003. Results of data screening can be found in Zhang (2016) and in the Supplemental Materials (Table S1).

There are 176 VOC compounds reported in the NAPS dataset, of which 118 were used in this study. Missing samples were identified by comparing the sampling schedule with the dates of available samples in each year. Blank and "0" cells were counted for individual compounds in each year. A compound is excluded from analysis if the total number of blank and "0" cells is greater than 70% during the study period of 1996-2015. Blank and "0" cells were also counted for each sample. Samples with less than 60% compounds registered valid readings were removed. To reduce the undue influence of a few unusual events with extremely high concentrations, outliers were identified and removed.

Sixteen NMHCs were excluded from analysis, because less than 30% of samples had valid readings. Thus, 102 compounds were retained for further analysis. Out of 877 samples, 14 were excluded. The rest 863 samples each had at least 60% compounds with valid readings (range 64%-100%, mean=88%, median=91%) and they were used to calculate total NMHCs and OFPs. Daily NOx/total NMHCs ratios (refereed as NOx/VOC ratios) were calculated for the dates when VOC data are available. Hourly NO_2/NO_X ratios were calculated as well.

2.3.2 Total O_3 concentrations

Following Akimoto et al. (2015), TO in Windsor were calculated with equation (1),

$$[TO] = [O_3]+[NO_2]–0.1*[NO_X]$$
$$= [O_3]+[DO_3] \quad (1)$$

where DO_3 ($[NO_2]–0.1*[NO_X]$) represents loss of O_3 due to in situ NO titration; $[O_3]$, $[NO_2]$, and $[NO_X]$ are hourly concentrations; and the constant 0.1 is the fraction of NO_2 in primary NO_X emissions (Itano et al., 2007). In this study, the NO_2 fraction was determined from the slopes of regression of $[O_X]$ (= $[O_3]$ + $[NO_2]$) vs. [NOx] in Windsor in each year during the morning NO and NO_2 peak hours (from 5:00 to 8:00) as described in Kurtenbach et al. (2012). The 20-year average fraction was 0.1, consistent with that in the previous O_3 study in Japan (Itano et al., 2007).

2.3.3 NMHC concentrations and ozone formation potential

OFPs for individual VOC compounds were calculated using equation (2) as described in Yan et al. (2017),

$$OFP_i = Conc_i * MIR_i \quad (2)$$

where $Conc_i$ ($\mu g/m^3$) is the ambient concentration of the i th NMHC, and MIR_i is the corresponding maximum incremental reactivity coefficient in the unit of grams ozone formed per gram VOC added in the system (Carter, 1999). OFPs for individual samples in each year were calculated.

2.4 Temporal variation and trend

The analysis of variance (ANOVA) was used to determine whether there were statistical differences in O_3 and TO concentrations between weekdays and weekends. Linear regression was employed to examine long-term (1996-2015) trends of 1) annual means and means in the smog (May-September) and non-smog season (October-April) for O_3 and TO, 2) annual mean for NO, NO_2, NO_X, OFP, DO_3, NMHC concentrations and the ratio of NO/NO_X, 3) various annual percentile levels (5^{th}, 25^{th}, 50^{th}, 75^{th}, and 95^{th}) of hourly O_3 and TO.

Hourly O_3, TO, and DO_3 concentrations do not follow a normal distribution. Thus, the Mann-Kendall test, a non-parametric trend detection method (Gilbert, 1987) was used to detect long-term trends in each month of a year and at each hour in a day. Sens method (Sen, 1968) was used to estimate the slope of seasonal and diurnal trends when the trend is significant at the 95% level. Long-term trends of O_3 and TO in Windsor were compared to quantify the impact of the NO titration on O_3 concentrations.

All analysis outlined in sections 2.3-2.4 were carried out in Minitab release 16 (Minitab Inc., State College, Pennsylvania, USA) and MATLAB release 2017a (The MathWorks, Inc., Natick, Massachusetts, USA).

3. Results and discussion

3.1 General statistics

As shown in Table 1, the 20-year mean O_3 concentration was 24 ppb in Windsor. Higher O_3 levels were observed in the smog season than the non-smog season, reflecting photochemical production under sunny and warm conditions. TO concentrations were higher than O_3 concentrations in all seasons and at all concentration percentile levels because TO includes the fraction of O_3 lost through the NO titration. TO concentrations showed lower variability (i.e.,

lower coefficient of variation) than O_3 concentrations, which is expected because O_3 reacts with NO while TO is not affected by the NO titration (Akimoto et al., 2015).

Table 1. General statistics of O_3 and TO concentrations in Windsor during 1996-2015. (SD and CV stand for standard deviation and coefficient of variation, respectively)

Pollutant	Season	Mean (ppb)	SD (ppb)	CV (%)	Min (ppb)	25th (ppb)	Median (ppb)	75th (ppb)	Max (ppb)	Sample size
O_3	All months	24	17	71	0	11	22	34	128	171624
	Smog	32	19	59	0	18	30	44	128	72387
	Non- Smog	18	13	71	0	7	17	27	85	99237
TO	All months	39	14	36	0	30	37	46	138	161459
	Smog	45	17	37	0	33	43	54	138	68270
	Non- Smog	35	11	29	0	28	34	41	118	93189

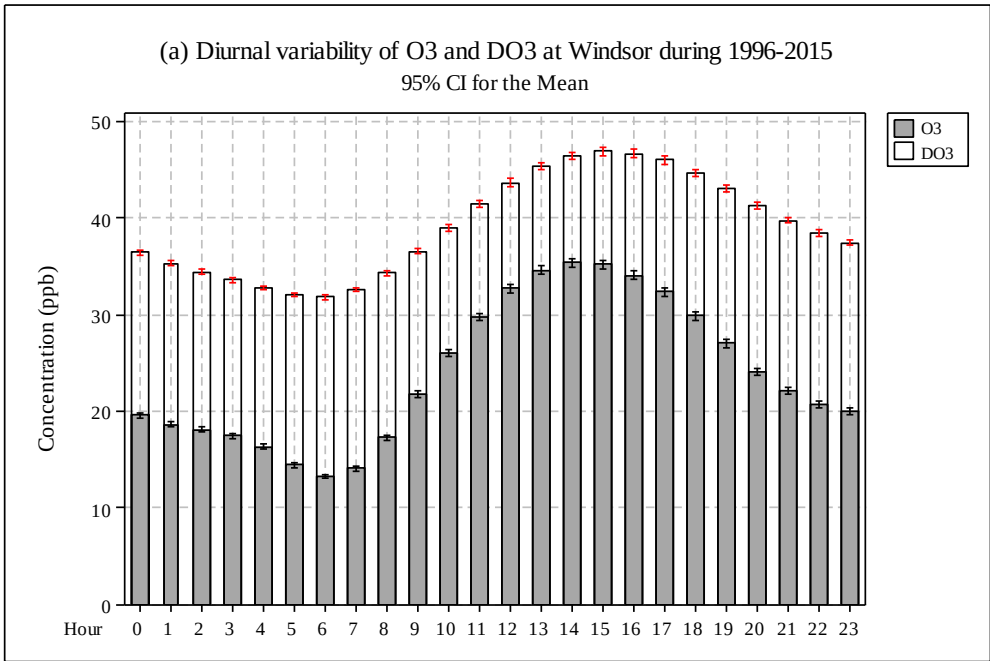
3.2 Diurnal, seasonal and weekday-weekend variation

3.2.1 Diurnal variation

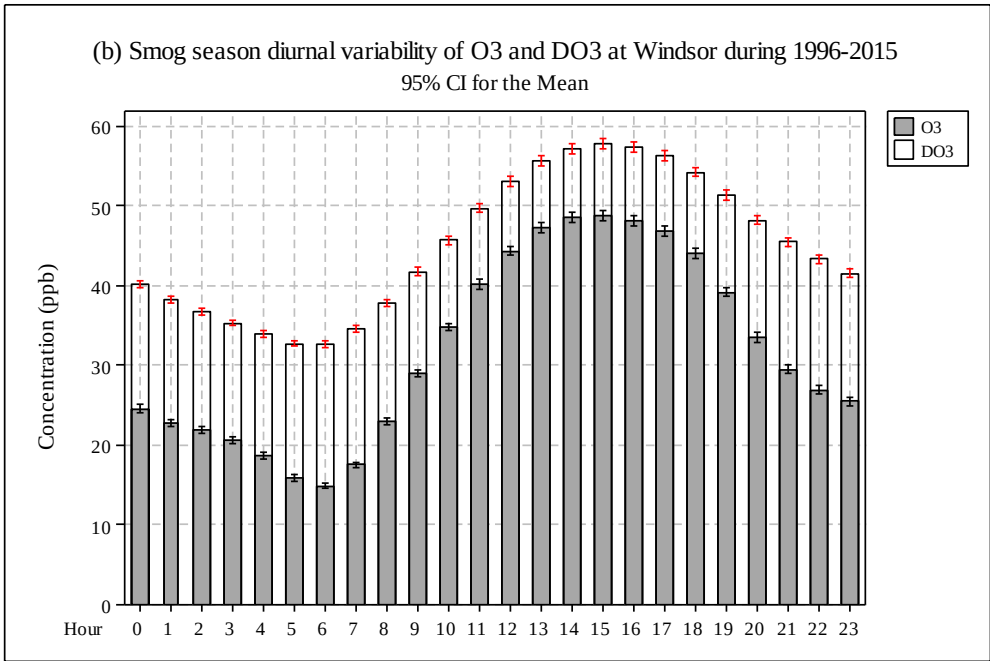
Diurnal variation of O_3 concentrations in Windsor during 1996-2015 is shown in Figure 2a and Table S2. There was a gradual increase in O_3 concentrations from the hour 6:00 to 14:00 local time, and a gradual decrease from the hour 15:00 to 6:00 next day. A similar trend was observed for TO. The diurnal variations for O_3 and TO indicate O_3 photochemical production was enhanced by increased solar radiation and temperature (So and Wang, 2003). DO_3 followed an opposite trend than O_3, i.e. lower at noon to afternoon (11.2 ppb from the hour 11:00-15:00) than that at other hours of the day (16.2 ppb), suggesting that relative loss due to the titration effect was reduced when O_3 concentrations were high.

O_3 concentrations were higher during the smog season than in the non-smog season especially around noon due to photochemical production (Fig 2b and Fig 2c). DO_3 levels were lower throughout the day in the smog season, suggesting relative loss due to the titration effect was reduced when O_3 concentrations were high. Furthermore, TO (O_3+DO_3) diurnal variation was rather smooth in the non-smog season due to weak photochemical production of O_3.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-851
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2018



195



196

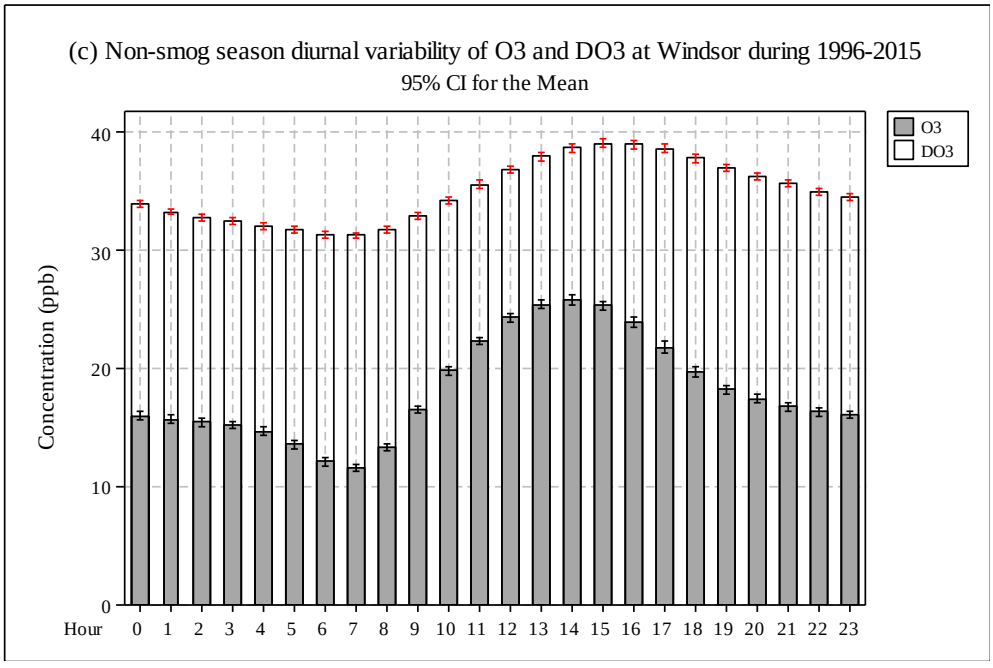


Figure 2. Diurnal O_3 and DO_3 concentrations during 1996-2015 in Windsor for (a) all months, (b) smog season and (c) non-smog season.

3.2.2 Seasonal variation

Monthly O_3 concentrations increased from January to May, reaching peak values in June and July, then decreased from July till the minima in December (Fig 3 and Table S3). This seasonal pattern is similar to that of solar radiation and ambient temperature, which control the photochemical production rate of O_3. A similar seasonal variation was observed for TO, but DO_3 followed an opposite trend than O_3, i.e. higher in non-smog season (16.6 ppb) and lower during smog season (13.1 ppb). Similar to the diurnal variation, relative loss due to the titration effect appears reduced when weather conditions favored O_3 formation. The seasonal O_3 pattern observed in Windsor is consistent with the study by Gaudel et al. (2018) reporting that in North America the maximum O_3 daytime averages occurred in spring/summer and the minimum values were found in autumn/winter during 2010-2014.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-851
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2018

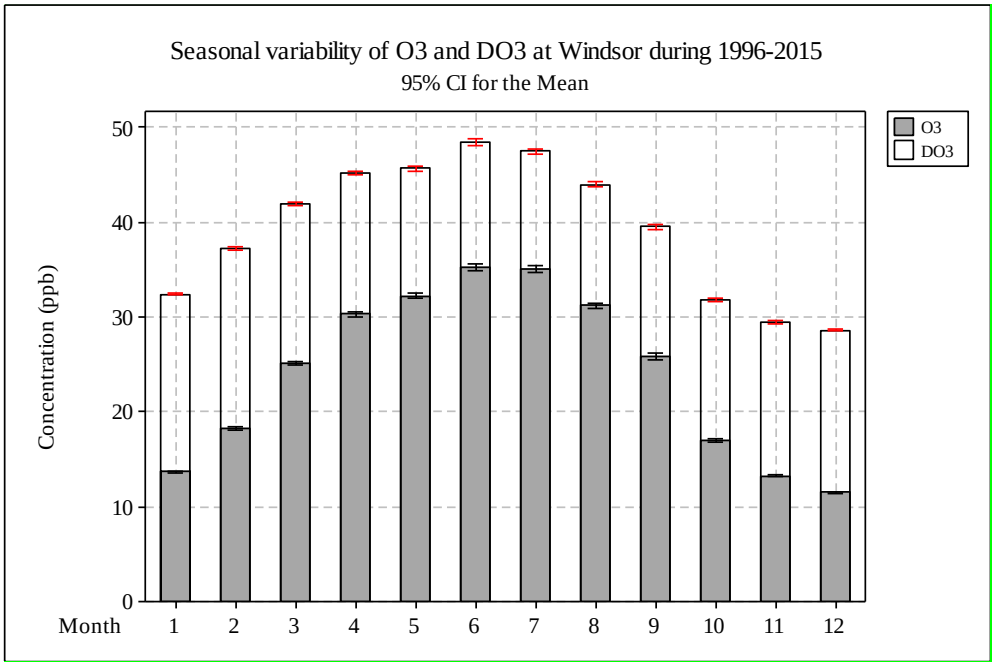


Figure 3. Monthly mean O_3 and DO_3 concentrations during 1996-2015 in Windsor.

3.2.3 Weekday-weekend variation

ANOVA indicates that O_3 concentrations on weekends (25.9 ppb) were statistically higher ($p<0.05$) than on weekdays (23.3 ppb). NO concentrations were lower on weekends (6.5 ppb) than on weekdays (9.6 ppb) due to less vehicular and industrial activities. Therefore, high O_3 concentrations on weekends were likely attributed to decreased NO emissions and weakened titration effect as reported by other researchers (Koo et al., 2012). This is supported by much comparable TO concentrations between weekdays and weekends (39.2 ppb vs. 39.5 ppb, $p<0.05$) which remove the titration effect. Differences in O_3 levels between weekday and weekend were also reported in other studies, e.g. in Nepal (Pudasainee et al., 2006) and Ontario, Canada (Huryn and Gough, 2014).

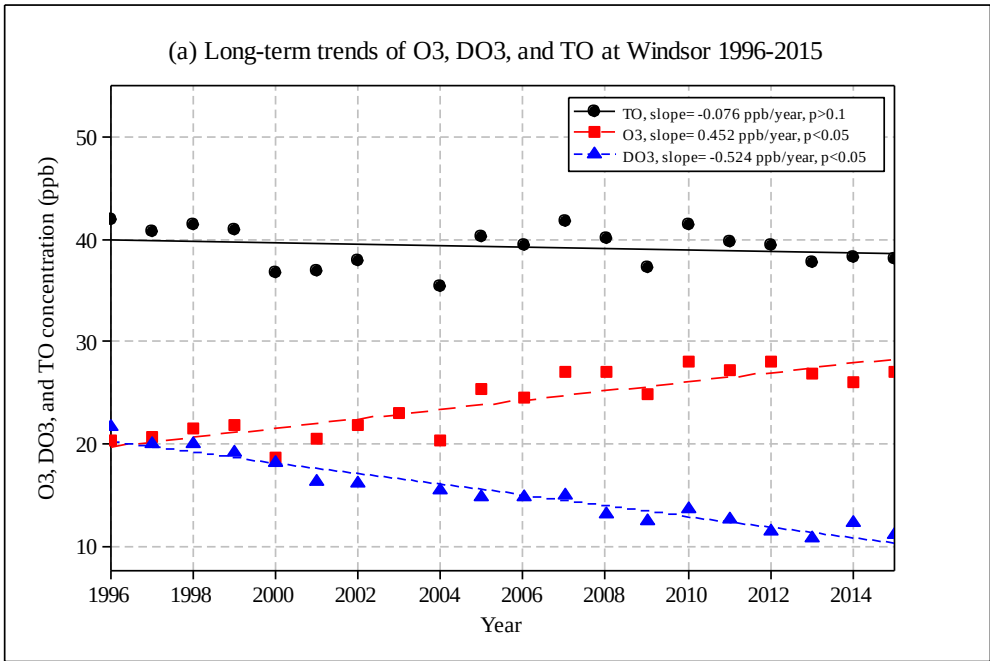
Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-851
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2018

3.3 Long-term trend

3.3.1 Trends of annual NOx, NMHC, ozone formation potential, O_3 and TO

During 1996-2015, annual mean O_3 concentrations increased significantly (0.452 ppb/year, Figure 4a) while annual mean DO_3 concentrations decreased at a greater rate (-0.524 ppb/year). Consequently, TO concentrations decreased slightly (-0.076 ppb/year, but not significant). In other words, O_3 decreased slightly when the NO titration effect is removed, suggesting that the decreased NO titration effect is one of the reasons for the increased O_3 concentrations in Windsor.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-851
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2018



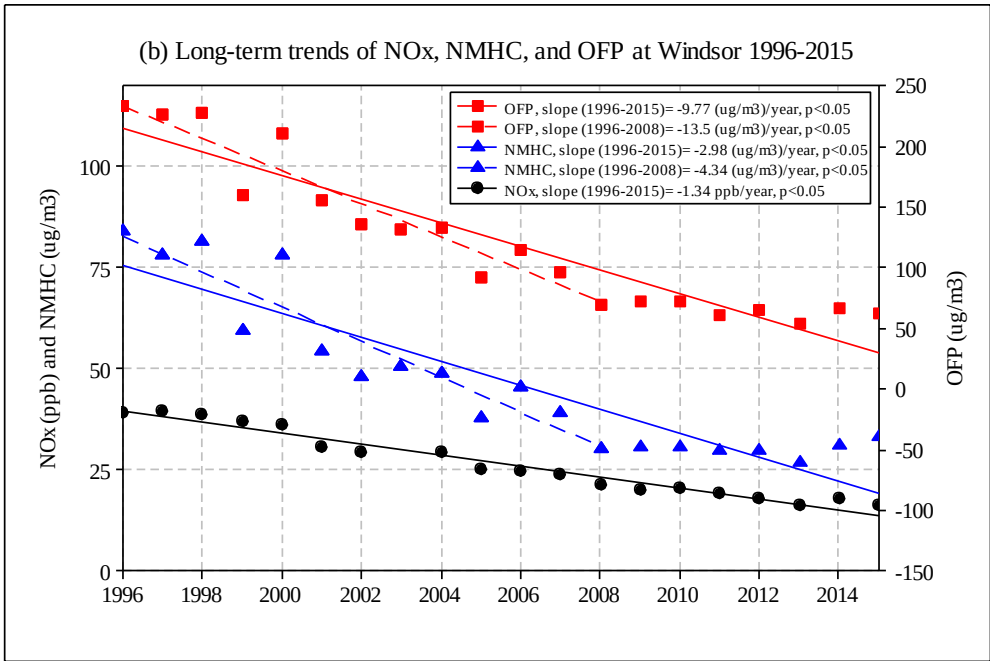


Figure 4. Annual mean concentrations for (a) O_3, DO_3, and TO, and (b) NOx, NMHC, and ozone formation potential (OFP) in Windsor during 1996-2015.

Significantly decreasing trends were observed in Windsor for annual mean NOx (-1.34 ppb/year), NMHC (-2.98 μg/m^3/year), and OFP (-9.77 μg/m^3/year) during the 20-year study period (Figure 4b). The percent decreases were 58%, 61%, 73% for NO_X, NMHC, and OFP, respectively, indicating effective emission control. It should be noted that during 1996-2008, some pollutants were changing at greater rates compared with the 20-years trend, including O_3 (0.55 ppb/year), NMHC (-4.34 μg/m^3/year) and OFP (-13.5 μg/m^3/year). After 2008, concentrations of O_3, NMHC, and OFP leveled off, while NOx and DO_3 concentrations continued to decrease.

The decreased NO titration effect was further investigated by examining the ratio of NO/NO_X (Figure S1). Significantly decreased NO (-0.73 ppb/year) and NO_2 (-0.66 ppb/year) were observed during the study period. Furthermore, the NO/NO_X ratio decreased from 0.34 in 1996 to 0.16 in 2015 with an average rate of -0.012/year, supporting the decrease in the NO titration effect in Windsor. Our results are consistent with studies in other counties. For example, NO_2/NOx ratio increased from 0.08 in 2005 to 0.15 in 2010 in Japan (Itano et al., 2014), implying a decreased NO/NO_X ratio. The NMHC/NOx ratios did not change much during the 20 years study period (min= 0.96, max= 1.3, mean and median = 1.1). The low VOC to NOx ratios (<5) suggest that the study area is VOC limited, thus reduced NOx emissions may lead to increased O_3 concentrations (Sillman, 1999; USEPA, 2000).

3.3.2 Ozone and TO trends at various percentile levels

Figure S2 depicts long-term O_3 and TO trends at 5th, 25th, 50th, 75th and 95th percentiles in Windsor during 1996-2015. The slopes of linear regression in three scenarios (i.e., all months, the smog season, and the non-smog season) are summarized in Figure 5 and Table S4. Peak O_3 concentrations (i.e., 95th percentile) decreased during the smog season and all-month, suggesting reduced precursor emissions and photochemical production. O_3 at all other percentile levels in all three cases had increased, with higher rates at 25th and 50th percentiles. The 25th percentile of O_3 concentrations were commonly considered as a background value (Lin et al., 2000; Aleksic et al., 2011; Parrington et al., 2013). Peak TO concentrations (95th percentile) deceased, especially during the smog season, due to effective emission control of O_3 precursors. TO concentrations increased at all other percentile levels during the non-smog season when O_3 photochemical production was limited, suggesting rising background O_3 concentrations.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-851
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2018

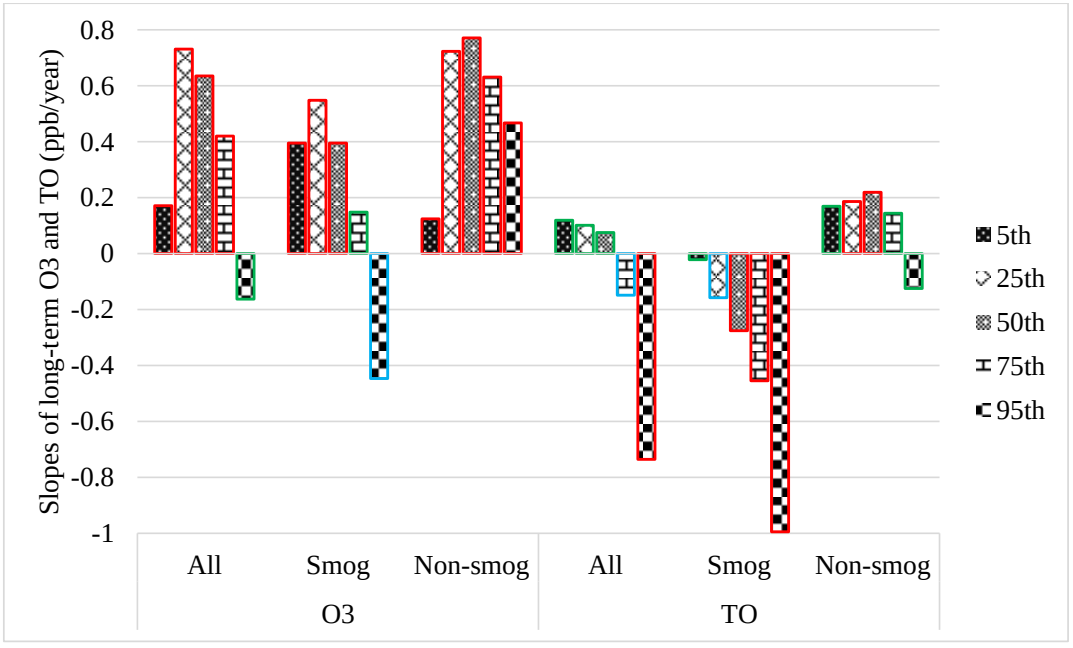


Figure 5. Slopes of long-term O_3 and TO trends at various percentile levels in all months, smog season, and non-smog season in Windsor during 1996-2015. (red border: significant at $p<0.05$, blue border: significant at $p<0.1$, green border: not significant, i.e. $p>0.1$)

In the smog season, O_3 concentrations increased at the 5^{th}-75^{th} percentile levels while TO concentrations decreased with a greater rate at higher percentile levels, supporting that the decrease in NO titration is one of the causes of increasing O_3 in Windsor. In terms of peak O_3 concentrations (95th percentile), the decreasing rate of TO (-1.0 ppb/year) is more than twice that of O_3 (-0.45 ppb/year). In other words, when the effect of NO titration is removed, peak O_3 concentrations decreased more intensely due to reduced emissions of O_3 precursors. During the non-smog season, the increasing rates of TO at 5-75^{th} percentiles were much slower than those of O_3. The results suggest that the decreased NO titration effect could be one of the causes for slower decrease of peak O_3 in the smog season and increase of O_3 at low-to-high percentiles during both the smog and non-smog seasons.

The decreasing trend of the 95^{th} percentile O_3 levels in Windsor is consistent with the decreasing concentrations at upper end of the distribution across the United States (Simon et al.,

2014), which evaluated maximum daily 8-h average O_3 at over 1,000 sites during 1998−2013 when NOx and VOC emissions were decreasing. The declining peak O_3 is also evident in the study of the 4th highest daily maximum 8-hour concentrations during 2000-2014 by Fleming et al. (2018), which indicated that up to 70% of North America stations experienced significant negative trends ($p<0.05$). The results of the seasonal O_3 trends in Windsor are consistent with previous studies. For instance, Simon et al. (2014) reported that the declining trends were more pronounced in summer than winter, and that increasing O_3 trends at all percentiles were found in both smog and non-smog seasons except for decreasing peak values at urban sites of the East North Central region (close to Windsor) (Simon et al., 2014). Moreover, Gaudel et al. (2018) reported the increasing O_3 levels across North America in winter time (December, January, and February).

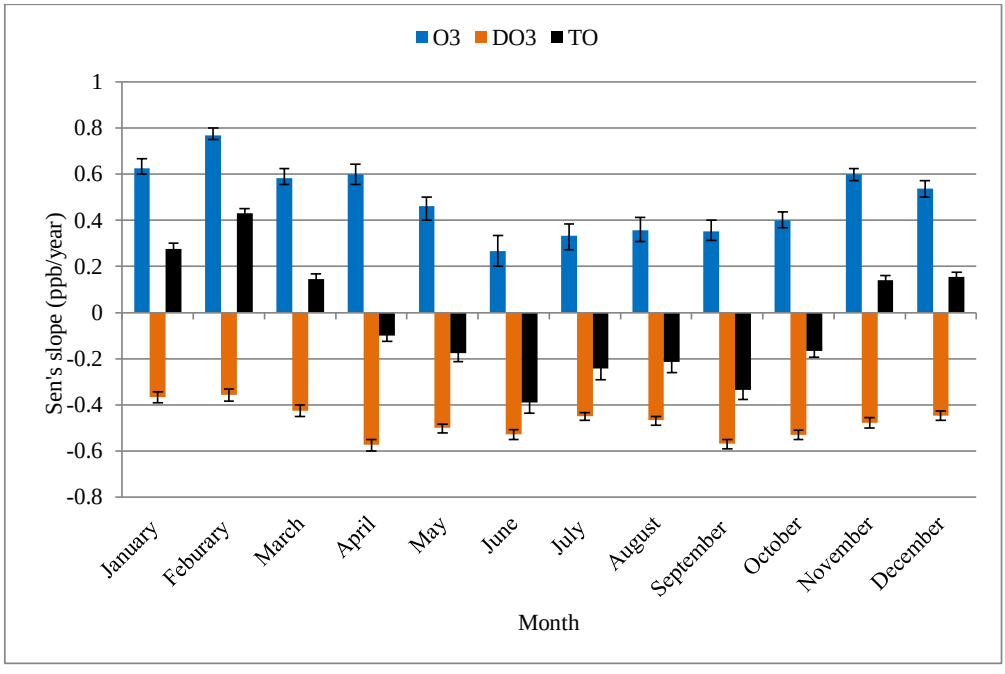
3.3.3 Monthly and diurnal rates of change for ozone and TO

This section further investigates which hour(s) of a day and which month(s) of a year experienced greater or less changes in O_3 concentrations during the 20-year study period, and to what degree those changes could be explained by the change in the NO titration effect. The estimated month-of-year slopes by Mann-Kendall and Sens test during 1996-2015 are shown in Figure 6. The rates of change during the smog and non-smog seasons are summarized in Figure S3.

The increased O_3 levels in non-smog season (mean= 0.58 ppb/year, Fig S3) suggest reduced titration effect and rising background O_3 levels since local photochemical production of O_3 is limited. Analysis of ambient data conducted by USEPA demonstrated that mid-tropospheric O_3 concentrations in the U.S. and globally have increased over the past two decades by 0.4 ppb/year (USEPA, 2015). Along the Pacific Coast, the rate of increasing background O_3 was estimated to be 0.5–0.8 ppb/year during 1985-2002. This trend of ground-level O_3 is consistent with the rate of increase (0.51 ppb/year, 1994 to 2002) derived using aircraft measurements (Jaffe et al., 2003). Another reason of increased O_3 is the decreased titration effect. A study in the South-Eastern France demonstrated that the decrease in the NO titration effect could be one of the reasons for increased O_3 concentrations in cold months (Sicard et al, 2011). The slower increasing rate of O_3 in smog season (0.32 ppb/year, Fig S3) is a result of increased background O_3 levels, decreased titration effect as well as reduced local photochemical O_3 production and

315 regional transport (MOECC, 2017). A similar trend of a greater rate of increasing composite
316 mean at 19 sites across Ontario in summer (49%) than in winter (14%) during 1991-2010 was
317 largely attributable to the reductions in local NO_X emissions and the rising global background
318 ozone levels (MOE, 2012).

319 O_3 concentrations increased while DO_3 concentrations decreased in all months during 1996-
320 2015 (Fig 6). During non-smog season, the increasing rate of O_3 (0.58 ppb/year, Fig S3) was
321 higher than the decreasing rate of DO_3 (-0.46 ppb/year). In other words, there was an additional
322 increase in O_3 beyond the decreased titration effect. After the NO titration effect is removed, TO
323 concentrations increased in non-smog season (0.13 ppb/year, Fig 6), suggesting rising
324 background O_3 levels. In smog season, the increasing rate of O_3 (0.32 ppb/year) was lower than
325 the decreasing rate of DO_3 (-0.50 ppb/year). TO concentrations had decreased in the smog
326 season (-0.27 ppb/year, Fig 6), attributable to the decreased regional O_3 production.



327

328 **Figure 6.** Monthly rates of change during 1996-2015 for O_3, DO_3, and TO.

329

330 On an hourly basis, greater increasing rates in O_3 concentrations were observed at evening
331 and night hours (18:00-3:00) in comparison with early morning and daytime (4:00-17:00) as

shown in Figure 7. The two minima in the morning at 6:00 and 13:00 coincided with the lowest and highest O_3 concentrations in a day, which were caused by different rates of change in smog and non-smog seasons (see below). Overall, O_3 increased while DO_3 decreased at all hours in a day during 1996-2015. The diurnal pattern of increasing rates for O_3 almost mirrored that of decreasing rates for DO_3. In other words, the increase in O_3 concentrations could be explained largely by the decreased NO titration effect. At most hours, the increasing rates of O_3 were higher than the decreasing rates of DO_3 especially in morning hours (6:00-12:00). Overall, TO concentrations increased slightly during daytime while decreased a little in evening.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-851
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2018

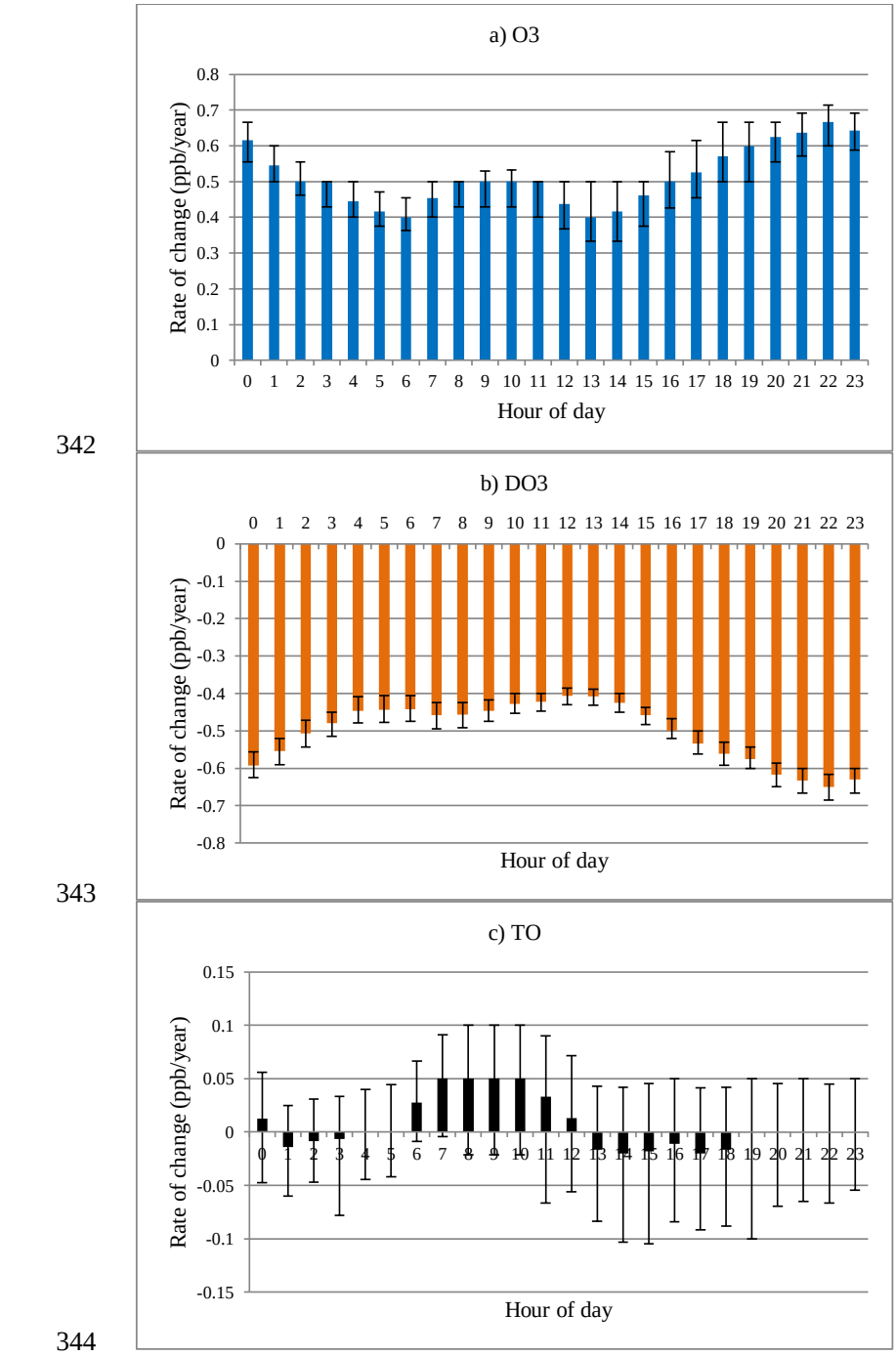


Figure 7. Rate of change by hour-of-day for all months during 1996-2015 for a) O_3, b) DO_3, and c) TO.

O_3 and DO_3 concentrations showed different diurnal patterns during the smog season (Figure 8). O_3 concentrations increased while DO_3 concentrations decreased at all hours as in the case of all months. During daytime (9:00-19:00), there was a sharp decline in the rates of change for O_3 till peak O_3 hours (14:00-16:00) followed by a speedy recovery. The peak hour O_3 concentrations have not changed much during the last 20 years, and daytime ozone levels have increased with a much slower rate (9:00-19:00, mean= 0.15 ppb/year) compared with nighttime (20:00-8:00, mean= 0.46 ppb/year). The daytime DO_3 decreasing trend is similar, however, with a less variability. The increasing rate of O_3 is lower than the decreasing rate of DO_3, and TO concentrations decreased at all hours, especially during the afternoon and early evening (14:00-19:00). It suggested decreased photochemical O_3 formation during the smog season due to emission reduction.

During the non-smog season (Figure 9), the rates of change in O_3 and DO_3 were similar as in the case of all months, i.e. the increase in O_3 concentrations could be explained largely by the decreased titration effect. Also similar to that of all months, the rates of change were lower in early morning (5:00-7:00). The greater rates of change were observed in late afternoon and evening (16:00-20:00), instead of at night with all months. The increasing rates of O_3 were higher than the decreasing rates of DO_3 at all hours. The hour-of-day TO trend is overall increasing with less diurnal variation, indicate rising background O_3 levels.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-851
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2018

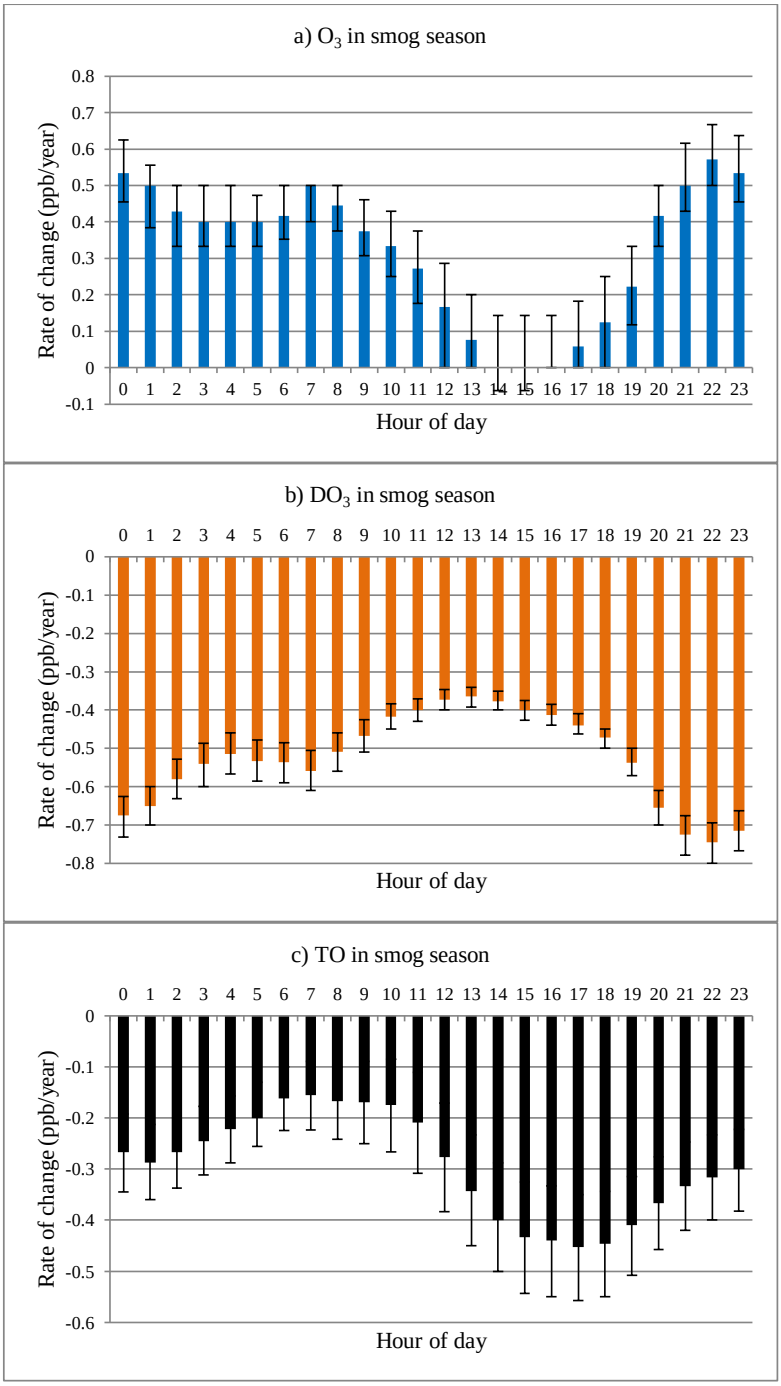


Figure 8. Rate of change by hour-of-day in smog season during 1996-2015 for a) O_3, b) DO_3, and c) TO.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-851
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2018

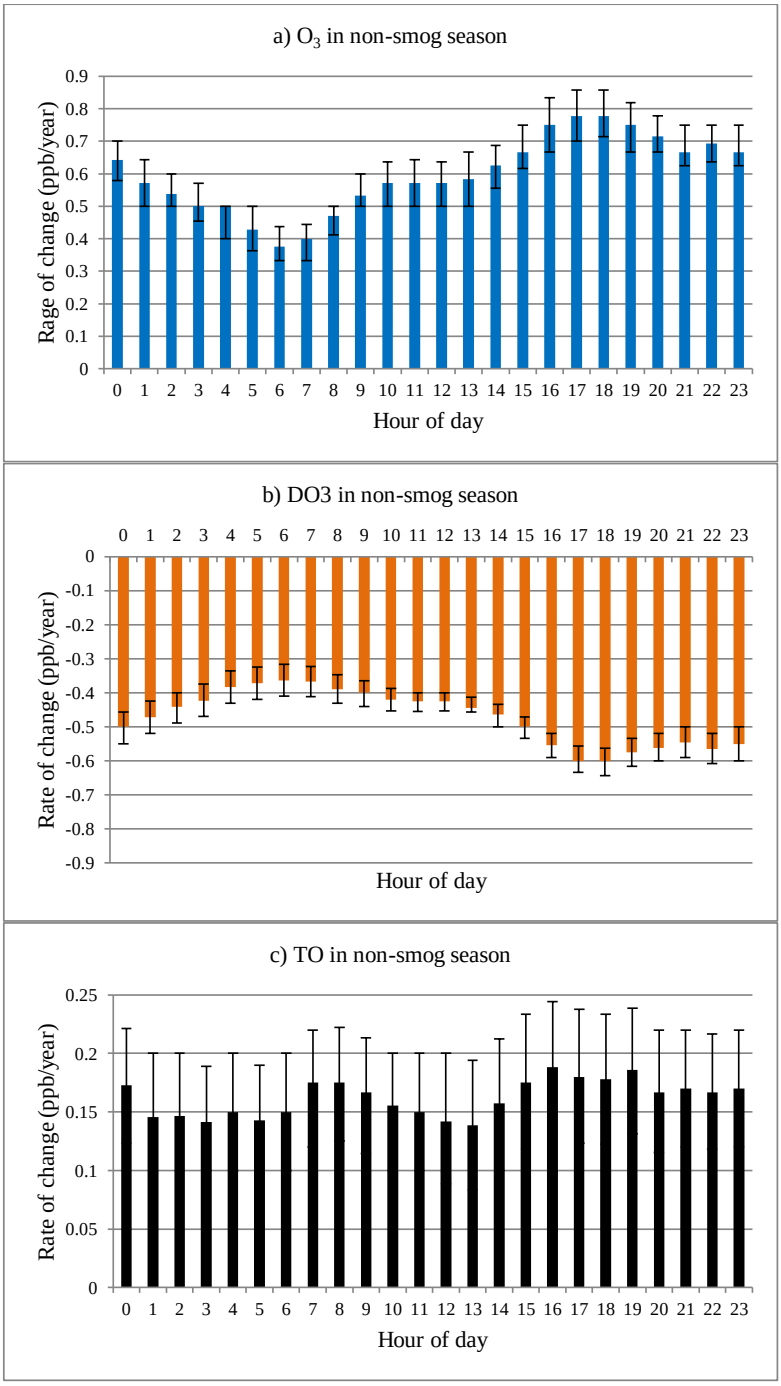


Figure 9. Rate of change by hour-of-day in non-smog season during 1996-2015 for a) O_3, b) DO_3, and c) TO.

4. Conclusions

This study investigates temporal variations and long-term trends (1996-2015) of ground-level O_3 and its precursors, NOx and VOCs, in Windsor, Ontario, Canada. The driving force of the observed variations was assessed by studying precursor emissions, photochemical production, NO titration, and background O_3 levels. One of the innovative approaches is the use of TO and trend analysis for different percentiles levels in different seasons and by hour-of-day.

O_3 concentrations increased by 33% during 1996-2015 (20.3 ppb in 1996 vs. 27 ppb in 2015) in Windsor, while concentrations of NOx (-58%) and NMHCs (-61%) and OFPs (-73%) decreased significantly during the same time period, owing to effective emission control. Increased O_3 concentrations were observed in all months in a year and all hours in a day, and at all percentile levels with a few exceptions.

Our analysis revealed that the increased annual O_3 concentrations in Windsor were caused by the following reasons. First, there were decreased O_3 titration and local photochemical production of O_3, both of which were induced by reduced precursor emissions. The O_3 loss due to the titration decreased by 50% in the 20 years study period, and the declined O_3 titration was observed in all months in a year and all hours in a day. Therefore, the observed increase in O_3 concentrations can be largely explained by the decrease in the titration. By removing the titration effect, TO concentrations increased in the non-smog season and decreased in the smog season, resulting in a slightly decreasing trend of annual means during 1996-2015 (-0.076 ppb/year). The declining photochemical production of O_3 is evident by decreased peak O_3 levels (95^{th} percentile) in the smog season as opposed to increased O_3 concentrations at all other percentile levels and all percentiles in the non-smog season. Second, background O_3 level was rising. This is supported by increasing O_3 concentrations in all months in a year and all hours in a day and at all O_3 percentile levels, with the exception of peak O_3 hours and the 95^{th} percentile O_3 levels in the smog season. Furthermore, the increasing rates of O_3 were higher than the decreasing rate of DO_3 at all hours in a day and all percentile levels during the non-smog season when O_3 photochemical production is limited.

It is apparent that control measures implemented in Ontario and the surrounding regions were effective in curbing NOx and VOC emissions during the study period of 1996-2015. The

reduced O_3 precursors led to decreasing peak O_3 values in the smog season over the past 20 years. However, those emission reductions also result in weakened O_3 titration effect in all months in a year and at all hours in a day. Meanwhile, the background O_3 concentrations appeared increasing in the study region, with more impact on the low-to-median levels (i.e. 25th and 50th percentiles) during non-smog season and at night. The net effect of those factors is decreasing peak O_3 levels but an overall increasing annual means in Windsor. The increases in O_3 concentrations in non-smog season (0.58 ppb/year), at night (20:00-8:00, 0.46 ppb/year), and at low-to-median percentiles pose less risk on human health because those O_3 levels are relatively low. The decreasing peak O_3 levels during the smog season is rather beneficial considering the detrimental effects of human exposure to high O_3 concentrations.

Our long-term (1996-2015) trends analysis show that annual O_3, NMHC, and OFP levels leveled off after 2008, while NOx concentrations and the O_3 titration effect appear to continuously decreasing. Considering that O_3 formation in Windsor remains to be VOC-limited, the weakened O_3 titration by NO_2 may lead to slightly increasing O_3 annual means. Moreover, the regional background levels are not expected to decline. Therefore, it is anticipated that O_3 concentrations in Windsor may level off or increase slightly in the next few years under similar weather conditions. Due to the complex nature of O_3 formation/consumption and regional transport, it is clear that long-term regional and international efforts are essential to lower O_3 concentrations and improve air quality. Results of this study provide insight into the causes of changing O_3 levels in Windsor and how to mitigate O_3 pollution and its adverse effects on human health and the environment. Future studies are warranted to quantify the background O_3 level in Windsor area and its long-term trend, and to explore regional transport of O_3 to Windsor.

Author contribution

Mr. Tianchu Zhang conducted data analysis and drafted the manuscript. Dr. Xu and Dr. Su designed the study and completed the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgements

The authors would like to thank all who contributed to collection of air quality data at MECP and ECCC and Yun Zhou at University of Windsor for processing some VOC data. This project was funded by MECP and the Natural Sciences and Engineering Research Council of Canada.

References

Akimoto, H., Mori, Y., Sasaki, K., Nakanishi, H., Ohizumi, T. and Itano, Y.: Analysis of monitoring data of ground-level ozone in Japan for long-term trend during 1990-2010: Causes of temporal and spatial variation, Atmos. Environ., 102, 302-310, 2015.

Aleksic, N., Sedefian, L. and Ku, M.: Empirical estimates of summer background ozone levels in New York State, New York State Department of Environmental Conservation, Albany, NY, 2011.

Carter, W. P. L.: Development of ozone reactivity scales for volatile organic compounds, J. Air Waste Manag. Assoc., 44(7), 881–899, 1994.

Carter, W. P. L.: Documentation of the SAPRC-99 chemical mechanism for VOC reactivity assessment, University of California, Riverside, CA. http://www.engr.ucr.edu/~carter/pubs/s99doc.pdf (last access: 4 June 2018), 1999.

Chang, K. L., Petropavlovskikh, I., Cooper, O. R., Schultz, M. G. and Wang, T.: Regional trend analysis of surface ozone observations from monitoring networks in eastern North America, Europe and East Asia, Elem. Sci. Anth., 5(50), 2017.Environment and Climate Change Canada (ECCC): Data sources and methods for the air quality indicators. https://www.ec.gc.ca/indicateurs-indicators/default.asp?lang=En&n=BA9D8D27-1&offset=4&toc=hide (last access: 4 June 2018), 2016.

Environment and Climate Change Canada (ECCC): Air pollutant emission inventory – online data search. http://ec.gc.ca/inrp-npri/donnees-data/ap/index.cfm?lang=En (last access: 4 June 2018), 2018a.

Environment and Climate Change Canada (ECCC): NAPS data products. http://maps-cartes.ec.gc.ca/rnspa-naps/data.aspx (last access: 4 June 2018), 2018b.

Fleming, Z. L., Doherty, R. M., von Schneidemesser, E., Malley, C. S., Cooper, O. R., Pinto, J. P., Colette, A., Xu, X., Simpson, D., Schultz, M. G., Lefohn, A. S., Hamad, S., Moolla, R.,

Solberg, S. and Feng, Z.: Tropospheric ozone assessment report: Present-day ozone distribution and trends relevant to human health, Elem. Sci. Anth., 6(12), 2018.

Gaudel, A. and 58 co-authors: Tropospheric ozone assessment report: Present-day distribution and trends of tropospheric ozone relevant to climate and global atmospheric chemistry model evaluation, Elem. Sci. Anth., 6(39), 2018

Gilbert, R. O.: Statistical methods for environmental pollution monitoring, Van Nostrand Reinhold Company Inc, New York, NY, 1987.

Huryn, S. and Gough, W.: Impact of urbanization on the ozone weekday/weekend effect in Southern Ontario, Canada, Urban Clim., 8, 11-20, 2014.

International Global Atmospheric Chemistry (IGAC), Tropospheric Ozone Assessment Report. http://www.igacproject.org/activities/TOAR (last access: 16 October 2018), 2018.

Iowa Department of Natural Resources (IDNR): Effects of ground-level ozone. http://www.iowadnr.gov/Environmental-Protection/Air-Quality/Air-Pollutants/Effects-Ozone (last access: 4 June 2018), 2018.

Itano, Y., Bandow, H., Takenaka, N., Saitoh, Y., Asayama, A. and Fukuyama, J.: Impact of NOx reduction on long-term ozone trends in an urban atmosphere, Sci. Total Environ., 379(1), 46-55, 2007.

Itano, Y., Yamagami, M. and Ohara, T.: Estimation of primary NO2/NOX emission ratio from road vehicles using ambient monitoring data, Studies Atmos. Sci., 1, 1-7, 2014.

Jaffe, D., Price, H., Parrish, D., Goldstein, A. and Harris, J.: Increasing background ozone during spring on the west coast of North America, Geophys. Res. Lett., 30(12), 1-4, 2003.

Jia, C., Mao, X., Huang, T., Liang, X., Wang, Y., Shen, Y., Jiang, W., Wang, H., Bai, Z., Ma, M. and Yu, Z.: Non-methane hydrocarbons (NMHCs) and their contribution to ozone formation potential in a petrochemical industrialized city, Northwest China, Atmos. Res., 169, 225-236, 2016.

Jun, T., Xia, Z. G., Wang, H. and Li, W.: Temporal variations in surface ozone and its precursors and meteorological effects at an urban site in China, Atmos. Res., 85(3-4), 310-337, 2007.

Koo, B., Jung, J., Pollack, A. K., Lindhjem, C., Jimenez, M. and Yarwood, G.: Impact of meteorology and anthropogenic emissions on the local and regional ozone weekend effect in Midwestern US, Atmos. Environ., 57, 13-21, 2012.

Kurtenbach, R., Kleffmann, J., Niedojadlo, A. and Wiesen, P.: Primary NO2 emissions and their impact on air quality in traffic environments in Germany, Environ. Sci. Europe., 24(21), 1-8, 2012.

Lin, C. Y. C., Jacob, D. J., Munger, J. M. and Fiore, A. M.: Increasing background ozone in surface air over the United States, Geophys. Res. Lett., 27(21), 3465-3468, 2000.

Mills, G., Pleijel, H., Malley, C. S., Sinha, B., Cooper, O. R., Schultz, M. G., Neufeld, H. S., Simpson, D., Sharps, K., Feng, Z., Gerosa, G., Harmens, H., Kobayashi, K., Saxena, P., Paoletti, E., Sinha, V. and Xu, X.: Tropospheric ozone assessment report: Present-day tropospheric ozone distribution and trends relevant to vegetation, Elem. Sci. Anth., 6(47), 2018.

Ministry of the Environment (MOE): Air Quality in Ontario 2006 Report, Queen's Printer for Ontario, PIBS 6041e, 2006.

Ministry of the Environment (MOE): Air Quality in Ontario Report for 2010, Queen's Printer for Ontario, PIBS 8640e, 2012.

Ministry of the Environment and Climate Change (MOECC): Air Quality in Ontario 2015 Report, Queen's Printer for Ontario, ISSN 1710-8136, 2017.

Ministry of the Environment, Conservation and Parks (MECP): Search: air pollutant data, http://airqualityontario.com/history/index.php (last access: 4 June 2018), 2018.

National Academy of Sciences (NAS): Ozone-forming potential of reformulated gasoline. The National Academies Press, Washington, DC. https://www.nap.edu/read/9461/chapter/5 (last access: 4 June 2018), 1999.

Parrington, M., Palmer, P. I., Lewis, A. C., Lee, J. D., Rickard, A. R., Di Carlo, P., Taylor, J. W., Hopkins, J. R., Punjabi, S., Oram, D. E., Forster, G., Aruffo, E., Moller, S. J., Bauguitte, S. J., Allan, J. D., Coe, H. and Leigh, R. J.: Ozone photochemistry in boreal biomass burning plumes, Atmos. Chem. Phys., 13, 7321-7341, 2013.

Pudasainee, D., Sapkota, B., Shrestha, M. L., Kaga, A., Kondo, A. and Inoue, Y.: Ground level ozone concentrations and its association with NOx and meteorological parameters in Kathmandu Valley, Nepal, Atmos. Environ., 40(40), 8081-8087, 2006.

Schultz, M. G. and 96 co-authors: Tropospheric ozone assessment report: Database and metrics data of global surface ozone observations, Elem. Sci. Anth., 5(58), 2017.

Sen, P. K.: Estimates of the regression coefficient based on Kendalls Tau, J. Am. Stat. Assoc., 63(324), 1379-1389, 1968.

527 Shin, H. J., Cho, K. M., Han, J. S., Kim, J. S. and Kim, Y. P.: The effects of precursor emission
528 and background concentration changes on the surface ozone concentration over Korea, Aerosol
529 Air Qual. Res., 12(1), 93-103, 2012.

530 Sicard, P., Dalstein-Richier, L. and Vas, N.: Annual and seasonal trends of ambient ozone
531 concentration and its impact on forest vegetation in Mercantour National Park (South-eastern
532 France) over the 2000-2008 period, Environ. Pollut., 159(2), 351-362, 2011.

533 Sillman, S.: The relation between ozone, NOx and hydrocarbons in urban and polluted rural
534 environments, Atmos. Environ., 33(12), 1821-1845, 1999.

535 Simon, H., Reff, A., Wells, B. Xing, J. and Frank, N.: Ozone trends across the United States
536 over a period of decreasing NOx and VOC Emissions, Environ. Sci. Technol., 49, 186-195,
537 2015.

538 So, K. L. and Wang, T.: On the local and regional influence on ground-level ozone
539 concentrations in Hong Kong, Environ. Pollut., 123(2), 307-317, 2003.

540 United States Environmental Protection Agency (USEPA): The relationships between NOx,
541 NOy, and ozone. https://www3.epa.gov/ttnamti1/files/ambient/pams/97workbook10.pdf (last
542 access: 16 August 2018), 2000.

543 United States Environmental Protection Agency (USEPA): Implementation of the 2015 primary
544 ozone NAAQS: Issues associated with background ozone.
545 https://www.epa.gov/sites/production/files/2016-03/documents/whitepaper-bgo3-final.pdf (last
546 access: 4 June 2018), 2015.

547 United States Environmental Protection Agency (USEPA): Health effects of ozone pollution.
548 https://www.epa.gov/ozone-pollution/health-effects-ozone-pollution (last access: 4 June 2018),
549 2018.

550 Wang, Y., Wang, H., Guo, H., Lyu, X., Cheng, H., Ling, Z., Louie, P. K. K., Simpson, I. J.,
551 Meinardi, S. and Blake, D. R.: Long term O3-precursor relationships in Hong Kong: Field
552 observation and model simulation. Atmos. Chem. Phys., 17, 10919-10935, 2017.

553 Yan, Y., Peng, L., Li, R., Li, Y., Li, L. and Bai, H.: Concentration, ozone formation potential and
554 source analysis of volatile organic compounds (VOCs) in a thermal power station centralized
555 area: A study in Shuozhou, China, Environ. Pollut., 223, 295-304, 2017.

556 Zhang, T.: Long-term trend of ground-level ozone through statistical and regional transport
557 analysis, Master thesis, University of Windsor, Windsor, Ontario, Canada.
558 http://scholar.uwindsor.ca/etd/5880/ (last access: 4 June 2018), 2016.