Controls on surface ozone concentrations and local production in the North American pollution outflow region of Nova Scotia

By

Morgan Mitchell

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Approved: Dr. Aldona Wiacek
Supervisor
Approved: Prof. Mary Sheppard
Committee Member
Approved: Dr. Erin Cameron
Committee Member
Approved: Dr. Patrick Hayes
External Examiner
Date : April 30, 2021

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Abstract:

High concentrations of tropospheric ozone are a concern due to its detrimental effects on human and plant health. As the world population expands and ozone precursor emissions become more challenging to limit, understanding the drivers of ozone production is necessary to minimize ozone concentrations. This research analyzed the relationship between ozone concentrations and precursor emissions in Nova Scotia to explain long-term decreasing ozone concentrations (99^{th} percentile and median total ozone) alongside very recent rising ozone concentrations at stations across the province. This project calculated long-term trends of ozone, its precursors and transported pollution frequency, and examined variables leading to elevated ozone concentrations in Halifax where production was found to be limited by volatile organics. A novel method for diagnosing pollution transport days was developed and applied to estimate the frequency of transboundary air pollution in the province as 45-63% of elevated ozone days in Halifax, increasing over the study period.

April 30, 2021

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Contents

Introduction

Surface ozone (O_3) is an air pollutant that is notoriously difficult to regulate due to its non-linear production that is dependent on emissions of precursor gases (NO_x, VOCs) and meteorological conditions. The amount of ozone and its precursors that are produced and emitted from local processes compared to the amounts that are transported into Halifax from places outside Nova Scotia has not been quantified. While previous episodic studies of elevated ozone events in the province assist in understanding transboundary pollution influence, long-term analysis of ozone and precursor trends is needed to assess the success of air pollution regulations. This thesis consists of two separate chapters of work contributing to the greater understanding of surface ozone in Nova Scotia. Part 1 contains an in-depth introduction to the topic of surface ozone in the province of Nova Scotia. It also contains intermediate methods and additional results behind the development of the algorithm used to diagnose pollution transport days in the province and a complementary analysis of the impact various meteorological variables have on ozone production in Halifax. By analyzing case study days of elevated ozone and examining the production regime of Halifax, Part 1 contributes to a greater understanding of locally produced ozone in the province. Part 2 contains the refinement of my MSc work that has been submitted to *Atmospheric Environment*, apart from elements of the manuscript's introduction, which are included in the thesis as Section 1.1 for greater clarity. The manuscript includes the analysis of ozone and precursor gas concentration and emissions trends over 19 years, as well as an estimate of transboundary pollution influence in the province using an algorithm I developed based on spatially correlated elevated ozone levels across the province. Finally, future work, pertaining to all results, is discussed at the end of the thesis document.

Part 1

Algorithm development and local production

Contents

1.1 Introduction

Ground Level Ozone (GLO, or surface ozone) is a secondary pollutant produced from a complex chain of photochemical reactions involving its gas precursors: oxides of nitrogen ($NO_x = NO + NO_2$), volatile organic compounds (VOCs) and carbon monoxide (CO). The production of ozone begins paradoxically by the destruction of an ozone molecule via sunlight, which yields an oxygen molecule and an oxygen radical. This radical goes on to react with water vapour and produces two hydroxyl radicals (OH). The hydroxyl radical is the most important oxidant found in the atmosphere, and it can oxidize organic gases, in this case any available VOC, which, via further oxidation, will lead to the production of HO_x (HO, HO_2) radicals that go on to react with NO_x. The reaction between HO_2 and

NO will yield NO_2 and OH, where NO_2 goes on to produce ozone by the following reaction involving sunlight (hv) (Jacob, 1999; Sillman, 1999):

$NO_2 + O_2 + hv \rightarrow NO + O_3$

An illustration of tropospheric ozone production is shown in Figure 1, together with the main termination mechanisms for the photochemistry via hydrogen peroxide (H_2O_2) and nitric acid (HNO_3), which are readily deposited to the surface in wet processes.

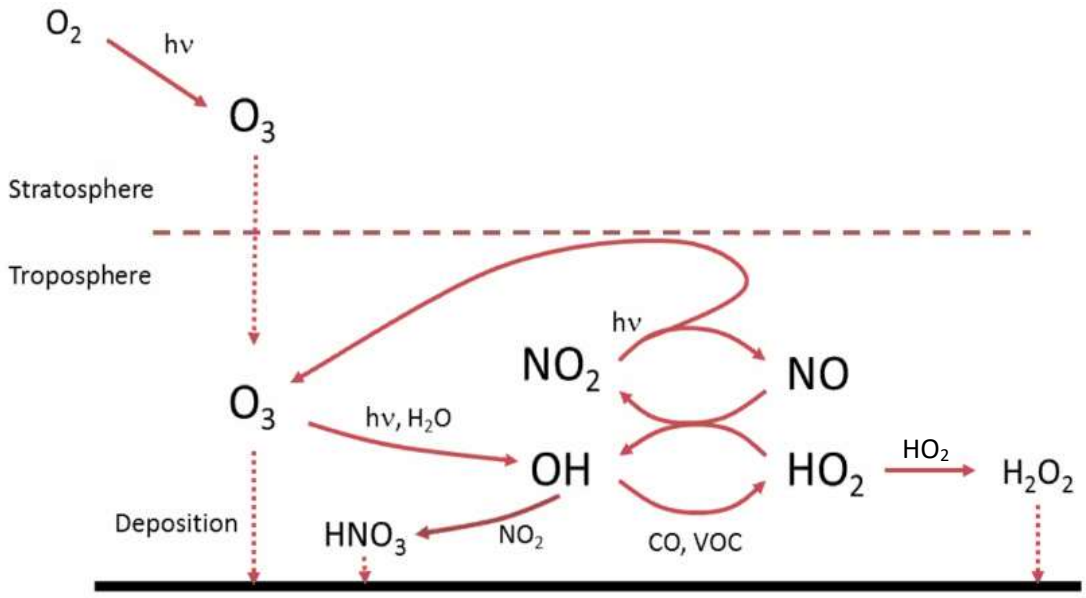

Figure 1. Mechanism of ozone production chemistry in the troposphere, adapted from Jacob (1999), courtesy of Dr. Hayes.

Surface ozone is deleterious to human health and is estimated to be responsible for between 5-20% of all air pollution-related deaths (Monks, 2015). The Canadian Medical Association estimated there to be 2682 premature deaths in Canada from acute exposure to surface ozone and particulate matter in 2008, in addition to many more deaths caused by chronic exposure (Canadian Medical Association, 2008). Additionally, high ground level ozone concentrations cost Canadian farmers millions of dollars a year in crop yield

losses and higher fertilization costs (Environment and Climate Change Canada, 2010). Furthermore, an ozone threshold below which no health impacts are observed has not been defined, making it prudent to keep ozone levels as low as possible (Bell et al., 2006).

To limit surface ozone production, its precursor gas emissions must be reduced, but the non-linear production of ozone makes regulation difficult. The production of ozone falls into two regimes that reflect the dominant precursor gas needed to increase production. In a *NO_x-sensitive* production regime, the area of production is saturated by VOCs and ozone will increase with additional NO_x, while additional VOCs will not increase ozone production. When the production regime is *VOC-sensitive,* the area is saturated by NO_x and ozone will increase only with additional VOCs (Sillman, 2002). In areas with the highest levels of NO_x emissions, e.g., near a power plant or in the downtown core of an urban centre, a temporary ozone titration effect readily occurs involving the rapid oxidation of NO to NO_2. As this ozone-depleted air mass moves away from the NO_x source, ozone production resumes and high concentrations of GLO are observed in these downstream plumes (Sillman, 2002).

Nova Scotia Air Quality Regulations list the maximum permissible ground level concentrations (1-hour) of ozone and NO_2 as 82 ppb and 210 ppb, respectively, and 50 ppb for annual average NO_2 (Nova Scotia Environment Act, https://novascotia.ca/just/regulations/regs/envairqt.htm). The one-hour ozone regulation was exceeded three times from 2000-2018 and the NO_2 regulation was never exceeded. Nationally, air pollution in Canada is monitored and managed using the Canadian Ambient Air Quality Standards (CAAQS), which were implemented in 2015 to replace the older Canada Wide Standards (CWS). The CAAQS outline the national standards for

several criteria air pollutants and are followed by all provinces, with the exception of Quebec. The CAAQS surface ozone metric consists of the 3-year average of the annual fourth highest daily 8-hour concentration, and it is currently compared against the standard of 62 ppb (Bell et al., 2006; WHO European Centre for Environment and Health, 2013). As of 2020, the CAAQS have added a 1-hour NO_2 metric defined as the 3-year average of the annual 98^{th} percentile of the NO_2 daily maximum 1-hour average concentration, with the standard set at 60 ppb; an annual NO_2 metric was also defined as the single year annual average of all 1-hour concentrations, with the standard set at 17 ppb. The CAAQS have also defined (in a similar fashion to NO_2) a new 1-hour SO_2 and an annual SO_2 metric, with the standards set at 70 ppb and 5 ppb, respectively. All standards will become more stringent in 2025 at 60 ppb (O_3), 42 ppb (1-hour NO_2), 12 ppb (annual NO_2), 65 ppb (1-hour SO_2) and 4 ppb (annual SO_2). In order to appropriately manage air pollution across the province, Nova Scotia is divided into four air zones: Western, Central, Eastern and Northern, where the Central air zone contains over half of the provincial population and the largest urban center, Halifax. CAAQS were achieved for all Nova Scotia air zones in 2017 (NS Department of Environment, 2019). However, CAAQS values increased in all but the Eastern air zone from 2016 to 2017. The increasing CAAQS values represent deteriorating air quality in these regions, which threatens the priority of continuous improvement (NS Department of Environment, 2019), and motivates our work, also in light of more stringent standards in 2025.

Surface ozone-related publications in the eastern coastal province of Nova Scotia, Canada, are limited to the following episodic studies and long-term trajectory analyses. The episodic studies are focused on high ozone events and their controlling factors, while

the trajectory analyses span 5 to 10 years of atmospheric flow and trace gas concentration analysis. During several elevated 8-hour ozone episodes in August 2001, when the CWS for ozone was exceeded at sites across Nova Scotia, Farrell (2006) found, using a chemical transport model, that an average of 45% of pollution was transported into Nova Scotia from the United States. Similarly, from July 1 to August 15, 2004 a field study examining air quality at Chebogue Point, Nova Scotia; found ozone elevated by 56% on average during continental outflow events from the USA (Millet et al., 2006). However, Li et al., (2005) conducted a four-year GEOS-CHEM simulation which showed the majority (70%) of transboundary pollution is exported overhead of the boundary layer and does not affect the surface air quality of Nova Scotia. This is in agreement with much earlier work during the 1993 North Atlantic Regional Experiment (NARE), when an aircraft was flown over Chebogue Point, Nova Scotia between August 12 and September 8 to measure trace gases, including ozone, in the horizontal and vertical. This study also found that during a pollution outflow event where a continental plume travelled over Nova Scotia, the highest concentrations of ozone were found at the top of a surface inversion layer (300 m) rather than at the surface (Kleinman et al., 1996). Angevine et al. (1996a) confirmed that due to the stability in the surface inversion layer that is almost always present at this unique coastal site, vertical mixing is inhibited and transported pollution is not often advected to the surface. However, at the inland and rural Nova Scotia site at Kejimkujik Park, which is not subject to a persistent inversion layer like coastal Chebogue Point, Sirois & Bottenheim (1995) nevertheless linked the highest measured surface concentrations of GLO and PAN (peroxyacetyl nitrate) to urban centers lying to the southwest of Nova Scotia (with the exception of GLO in winter, due to titration processes in transport). Finally, Chan & Vet (2010) designed a methodology

to distinguish baseline ozone levels using backward trajectories launched during highest and lowest percentile ozone at 14 different stations across North America, including Kejimkujik Park in Nova Scotia. They also found that over their study period (1997-2006) the most polluted air mass trajectories observed at Kejimkujik Park originated over the Northeastern USA. A major motivation of our work is that the long-term significance of transported pollutants to the air quality of Nova Scotia's largest population center (Halifax) has not been systematically quantified, even as these episodic and long-term trajectory studies suggest a key role.

Global ground-level ozone is well documented in the Tropospheric Ozone Assessment Report (TOAR), which details regional trends using observations at over 9000 monitoring stations across the world (https://igacproject.org/activities/TOAR). This report includes information on long-term trends in eastern North America, also including observations from the monitoring site in Kejimkujik Park, Nova Scotia. Notably, there has been a uniform decrease in average summer surface ozone across Eastern North America between 2000-2014 as a result of precursor emissions reductions in this region, whereas Asia has shown increased ozone levels over the same period (Chang et al., 2017). Decreased precursor emissions in Eastern North America are somewhat confounded by increasing background ozone concentrations, which has been attributed to rising Asian concentrations by, e.g., Cooper et al. (2012); Zhang et al. (2011). However, Parrish et al., (2020) investigated trends in baseline ozone using stations only on the west coast of North America and Europe and found that while ozone in the Northern Hemisphere increased from the 1980s to the early 2000s, a maximum has been reached in 2005, and

since then baseline ozone, as captured in their study, has been decreasing in agreement with precursor emission trends.

Effective surface ozone regulation involves understanding both ozone trends and trends in ozone production regimes, with the latter naturally studied at the city scale, in the context of ozone precursor trends. Jiang et al. (2018) documented a 76% slowdown in top-down derived NO_x emissions reductions in 2011-2015 in the United States, as compared to larger bottom-up derived reductions modelled by the US Environment Protection Agency (EPA). The reductions were most pronounced in the northeast US, directly upstream of Nova Scotia, and likely influenced a slowdown in reductions of surface ozone concentrations over the same period. Jin et al. (2020) studied the ozone production regime response to NO_x and VOCs in seven major US cities from 1996-2016 using satellite and ground-based observations. Their study found the largest NO_2 reductions in four of the seven cities occurred from 2005-2012, followed by a levelling out of NO_x emissions reductions in all seven cities (four in the northeast US, upstream of Nova Scotia) between 2013-2016. Despite the slowdown, the study presents evidence for a spatial expansion of NO_x-limited O_3 production regimes using satellite-derived ratios of VOC to NO_x ($HCHO/NO_2$); consistent with this finding, surface observations of O_3 show a reversal of the weekend effect and a movement of peak O_3 concentrations (found in transition production regimes) towards city centers. Consistent with the above precursor emissions trends in the USA, a Toronto study detailing precursor reduction effects on ozone between 2000 and 2012 also found steady, decreasing NO_2 trends at 6.4% / year and decreasing VOC reactivity of 9.3% / year (Pugliese et al., 2014), even as ozone standards continued to be exceeded at all monitoring stations. However, using this earlier

data these authors conclude that the understanding of ozone production regimes in Toronto is incomplete, lacking continuous measurements of oxygenated VOCs. Finally, Xu et al. (2019) found a 58% decrease in NO_x, a 61% decrease in non-methane hydrocarbons, and a 73% decrease in Ozone Formation Potential (OFP) in Windsor, ON from 1996-2015, even as annual mean O_3 concentrations increased by 33% and smog season peak ozone concentrations decreased. Correcting for titration, these authors report slightly decreasing total ozone annual means and conclude that emissions reductions are successful at controlling peak ozone concentrations.

1.2 Development of a transported pollution classification algorithm

Air quality researchers in Nova Scotia have known for a long time that the province often receives transboundary pollution from various source regions like Southern Ontario, Québec, the Ohio River Valley and northeastern United States. There is a gap in our knowledge of the frequency of transboundary pollution influence in Halifax and if this influence has changed over time. Although Halifax has not recently exceeded provincial or national ozone standards, the Halifax CAAQS metric has increased by 3 ppb from 2017 to 2018 (43-46 ppb) representing rising ozone levels and deteriorating air quality in the city core (NSE, 2020). Due to the relatively long lifetime of ozone in the upper troposphere, it is a challenge to separate local production based on Halifax precursors from transported ozone from regional production in highly urbanized regions upstream. To assess the frequency of transboundary pollution in the province we used the spatial correlation of elevated ozone concentrations occurring simultaneously across the province. Since this had not been done previously, the algorithm went through several iterations of methodology to classify transport days before we arrived at the method described in Chapter 2. Below are the intermediate results with earlier algorithm versions.

1.2.1 Initial analysis

On the top four highest ozone concentration days in Halifax in each year the percent change of the daily maximum ozone concentration from the monthly mean at all stations across Nova Scotia were examined. On these top four Halifax concentration days, most of the stations across the province also had high positive anomalies that correlated with the high ozone in Halifax, which was an indication of transport. We then estimated the frequency of transport days across all elevated ozone days in Halifax during the study period by developing an algorithm to find ozone anomalies, with respect to a monthly mean, at all stations in NS (9 excluding Halifax) and diagnosing a transport day based on the spatial correlation of high ozone across the province. The method consisted of the following steps:

1. In the first iteration of the algorithm, elevated ozone days in Halifax were defined as the top 1% daily maximum ozone concentrations over 20 years, but we found that this led to an uneven distribution of days in each year. This uneven distribution of elevated ozone days, caused by temporal decreasing ozone trends over the last 20 years, affected the distribution of identified transport days and biased later analyses about temporal change. We therefore redefined elevated ozone as the monthly top quartile (75th percentile & above in each month) daily maximum ozone concentrations to remove the annual bias towards the spring ozone maximum. From the 19 years of data we were left with 1444 days of elevated ozone in Halifax. These elevated ozone days were next analyzed for transport signatures.
2. The criteria with which transport days were diagnosed were defined based on a percent change from the monthly mean ozone concentration at each station, and

whether ‘enough’ of the stations showed this percent change. The sensitivity analysis for diagnosed transport days at different selection of threshold criteria is shown in Figure 2. The initial criteria used to define a transport day were if 80% of stations showed daily maximum ozone that was at least 70% above the monthly mean of the daily means. The reasoning behind the first (80%) criterion was that if a transported air mass reached stations in the Central air zone it must also pass through stations in the Western air zone, and it is then less likely to have reached the two stations in the Eastern zone. The transported air mass could have been diluted or dispersed before reaching those stations, which are approximately 200-300 km from Halifax, therefore making the criterion of 100% of stations showing a positive anomaly unrealistic. The second criterion, requiring these stations to have at least 70% positive anomalies, came from a sensitivity analysis where the criterion gave a central estimate, with only a difference of 7 transport days between the 70% and 80% anomalies. Results from this algorithm iteration are discussed below.

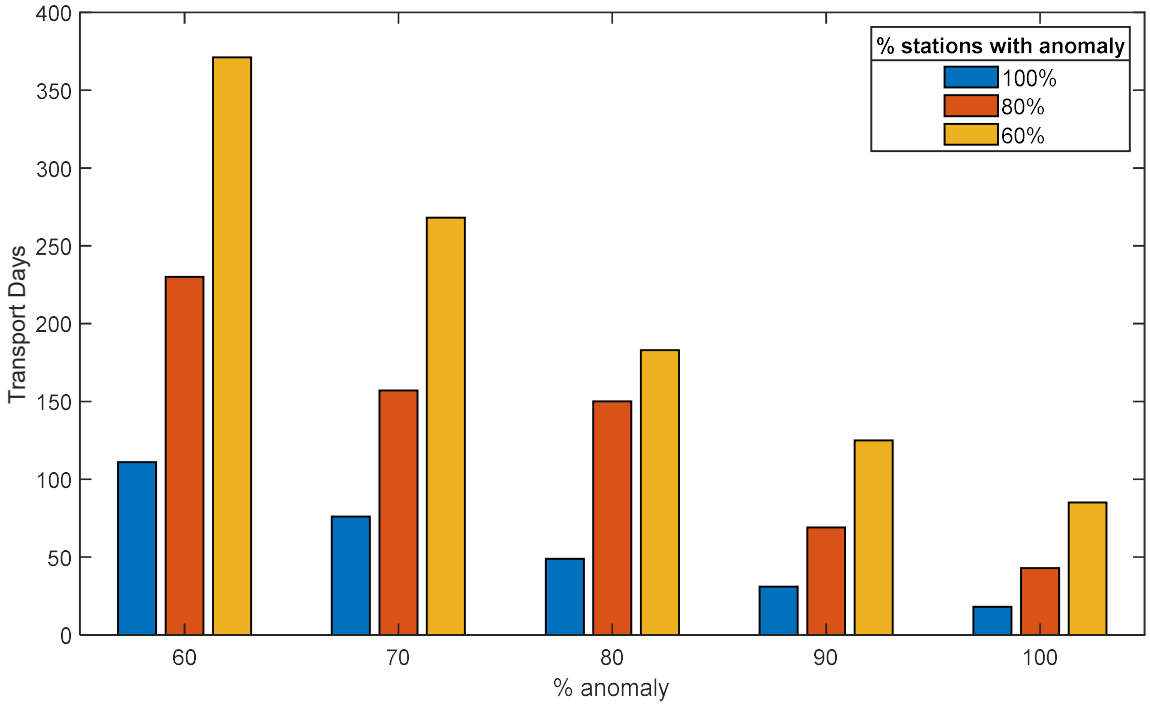

Figure 2. Sensitivity of positive transport day classification to selection criteria. Colours show the minimum percentage of nine stations other than Halifax that must achieve a given % anomaly in daily maximum ozone concentration. The % anomaly (x axis) corresponds to the percentage elevation of daily maxima at each station with respect to the monthly mean of the daily means at that station. Classification results are based on the subset of monthly top quartile daily maximum ozone days in Halifax.

With monthly top quartile daily maximum ozone there is more consistency in the number of elevated ozone days in each year (Figure 3) than with the top 1% approach.

When some years have fewer days, this is due to missing monthly data (notably, 2000, 2007 and 2014). By using this data set with the criteria of 80% of stations showing positive anomalies of more than 70% from the monthly means, 157 elevated ozone in Halifax days from 2000-2018 were diagnosed as transport-related. The frequency of transport days is decreasing at -0.65 %/year ($p < 0.01$) throughout the study period but the annual percentage is highly variable.

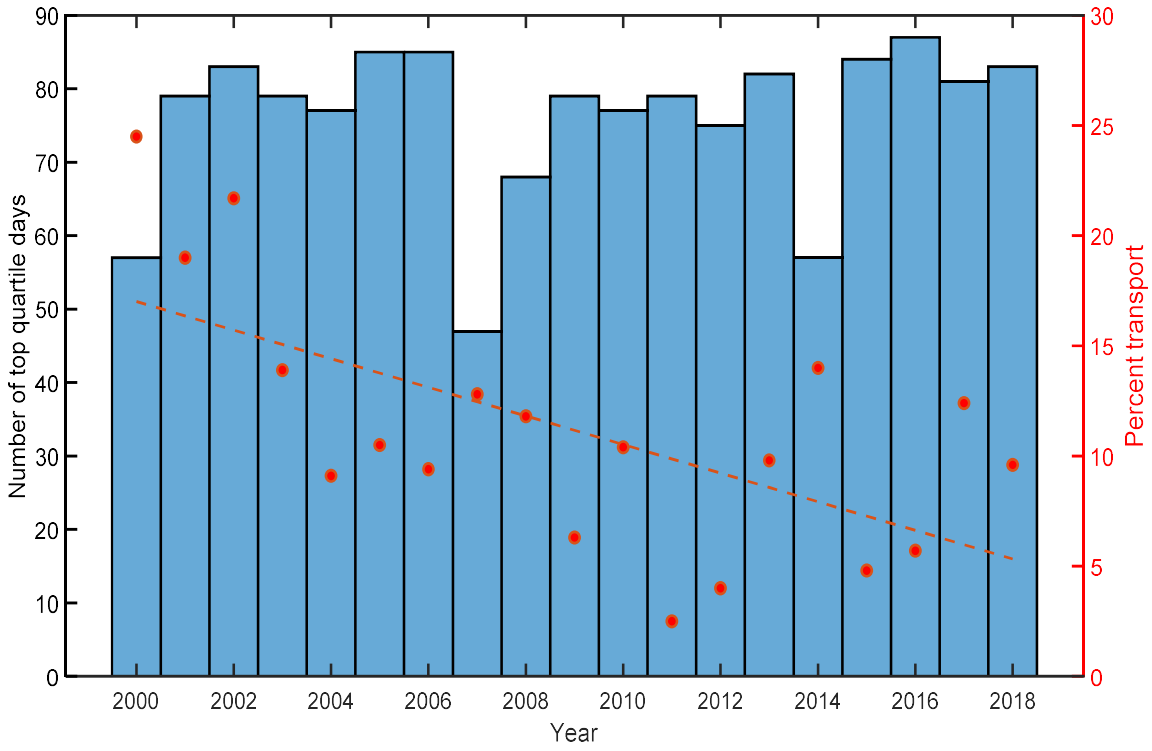

Figure 3. Top monthly quartile elevated ozone days in Halifax summed over each year (blue), n=1444. The percent due to transport and the associated linear regression is shown in red.

The source of pollution on the 157 transport-related days is of interest to understand the precise regions contributing to Nova Scotia's elevated ozone. Further knowledge on this subject informs bi-lateral agreements to decrease emissions in upstream source areas, like the Canada-United States Air Quality Agreement (Environment and Climate Change Canada, 2017). The National Oceanic and Atmospheric Administration's Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) was used to calculate backward trajectories (see Stein et al., 2015 for details on HYSPLIT) to identify potential source regions for ozone transported into Halifax (and Nova Scotia in general) on days identified as transport-related. Ensembles of 72-hour backward trajectories using WRF (Weather Research and Forecasting model, 12 km resolution) meteorological data were

run for each transport-related day, initiated on the hour of maximum ozone in Halifax. The coordinates of these trajectories were used to calculate the frequency of trajectories that pass through each grid box (Figure 4). The largest proportion (25-100%) of air masses on transport days pass through the northeast USA region, which encompasses many densely populated and urban/industrial regions with a large concentration of emissions sources of ozone precursors. A considerable fraction (10-25%) of air masses pass through the US urban centres of Philadelphia, Pittsburgh and Cleveland and the Canadian megacities of Toronto and Montreal. This study validates and further characterizes pollution source regions in the episodic studies of long-range pollution transport to Nova Scotia, which described elevated ozone periods following pollution outflow from the eastern USA (Farrell, 2006; Johnson et al., 2007; Millet et al., 2006).

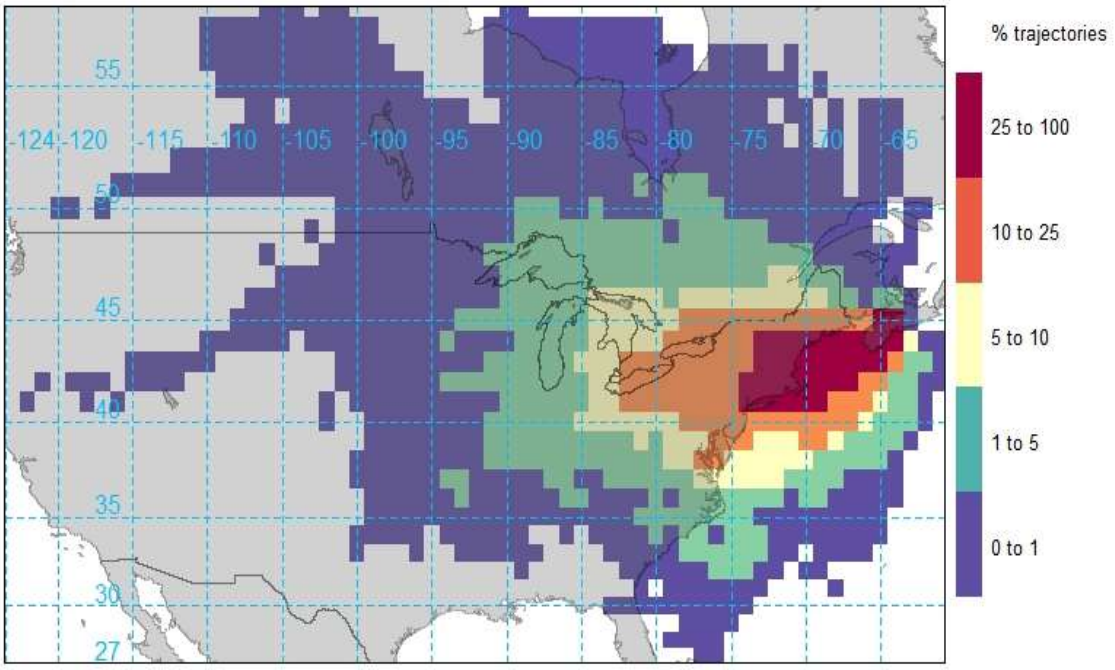

Figure 4. Frequency of 72-hour back trajectories initiated on the 157 transport-related days identified by the 70/80% criteria in the initial transport algorithm.

1.2.2 Algorithm refinement

Clearly, the number and percentage of diagnosed transport-related days are sensitive to the thresholds set for the classification algorithm (Figure 2); therefore, to give a transport-related day fraction we defined an upper and lower estimate. For the upper estimate we required 60% of stations to show a positive anomaly of 60%. This diagnosed 371 elevated Halifax ozone days (26%) between 2000-2018 as transport-related and is in better agreement with literature that finds 30% of pollution outflow to the north Atlantic from the eastern US passes through the boundary layer and is detectable by surface stations, while the rest travels higher overhead (Li et al., 2005). The lower estimate used the threshold of 100% of stations showing a positive anomaly of 100%. The upper estimate diagnosed 18 elevated Halifax ozone days (1%) as transport-related.

At this point, the research moved to identifying controls on local ozone production in Halifax on the assumption that the transport algorithm diagnosing 1-26% of elevated Halifax ozone days as transport-related was reasonably accurate. However, the case study of top 10 non transport-related elevated ozone days in Halifax (outlined in Section 1.3.1) showed that the current version of the algorithm was clearly missing transport days. We therefore moved to refine the algorithm further with the following methods.

The sensitivity analysis summarized in Figure 2 was extended to fully understand the impact of the thresholds on the number of stations with a given anomaly and the percent anomaly on classified transport-related days. The percent of transport-related elevated ozone days in Halifax was calculated for 0-100% of stations with a daily maximum ozone concentration that had *any* positive change from the monthly mean of the daily maxima at each station (Table 1). At this step, we fully understood the predictive importance of

remote stations upwind of Halifax that are likely to receive transported pollution on the same day as Halifax, as opposed to stations to the northeast and east of Halifax, which may not receive transported air masses before they are dispersed (see Chapter 2, Section 2.4.3 for more detail). Based on Figure 5 we see that requiring an anomaly to just be positive with respect to a monthly mean is too lenient because nearly all (98.5%) elevated days in Halifax have a positive anomaly at 10% or more of all stations and about half (45.8%) of elevated days in Halifax occur when 100% of all other stations also exhibit a positive anomaly. This is understandable, since there will always be some degree of natural variability around the monthly mean, irrespective of the potential influence of transported ozone or local emissions. In fact, when repeated with key indicator stations only (Aylesford, Dayton and Kejimkujik), this analysis shows nearly three quarters (72.3%) of elevated days in Halifax correspond to positive anomalies at 100% of (all 3) key indicator stations. This further reinforces that indicator stations are a good proxy for transport-related elevated ozone in the province.

We decided to apply the same threshold used for defining elevated ozone in Halifax and consider top quartile anomalies at each station as indicating unusually elevated ozone, instead of using a fixed percent anomaly threshold. The fact that we require multiple stations to show top quartile ozone minimizes the likelihood of natural noise causing a transport day to be detected. The final version of the algorithm used top quartile daily maximum ozone anomalies, with respect to the monthly mean of the daily maxima at each station from 2000-2018 to signal elevated ozone at a station. Results and detailed methods for this most recent iteration are found in Chapter 2; briefly, it gave an estimate of 45-63% transport-related elevated ozone days in Halifax over the study period.

Although this is a considerably higher estimate than given by percent anomalies, the case study analysis in Section 1.3.1 clearly showed that 1-26% was a large underestimate. As a sign of consistency between the two approaches we have that the 157 transport-related days discussed above are all diagnosed as transport-related in the ALL50 and IND50 criteria in Chapter 2, based on top quartile anomalies instead of the arbitrary percentage above mean thresholds. Further, 92% and 76% of the 157 transport-related days are diagnosed by the IND100 and ALL100 criteria, respectively. The upstream source regions shown in Figure 4 are not incorrect, but rather based on a subset of transport-related days that were diagnosed using more stringent criteria based on 70% of stations with 80% anomalies above the monthly mean. A significant difference between the top quartile versus the percent anomaly approaches is that the percent of transport-related elevated ozone days in Halifax is increasing as a function of time in the former and decreasing in the latter (Section 2.4.3). More careful investigation of the reason for a decrease over time would be prudent, but if taken as the truth, the implication would be that Halifax is becoming more self-pollution with regard to ozone production. Is this likely in the context of regionally decreasing precursor emissions, as well as decreasing precursor emissions in Halifax itself? The next section will show that it is not.

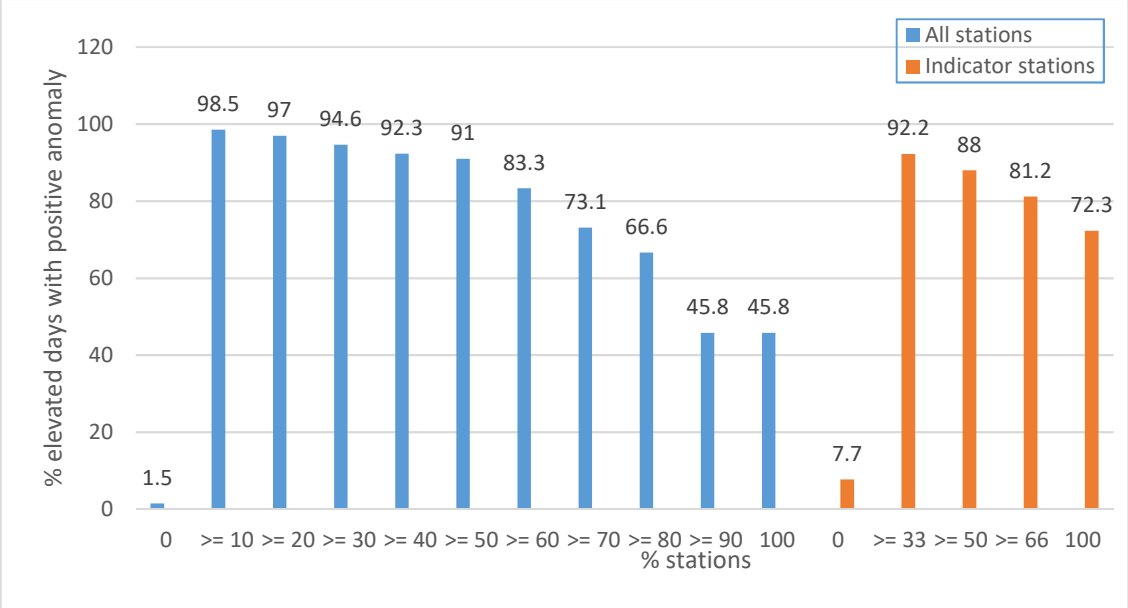

Figure 5. Sensitivity analysis of the % of elevated Halifax ozone days (n=1444) that show *any* positive anomalies from the monthly mean at different thresholds of stations. Blue bars refer to analysis for all stations and orange bars for the three key indicator stations.

1.3 Local production of ozone in Halifax

1.3.1 Top 10 non-transported pollution days

The goal of this analysis was to look for clear meteorological signals of local ozone production, but it also served as a test for the reliability of the transport-related pollution classification algorithm. Using the upper estimate with the 60% criteria as discussed in Section 1.2.2, the top 10 non-transport-related days by daily maximum ozone concentration were analyzed as case studies. Temperature, solar irradiance, pressure and wind speed data are from the Shearwater weather station and ECCC's historical weather database: https://climate.weather.gc.ca/historical_data/search_historic_data_e.html.

For each day, the following meteorological and chemical variables were analyzed:

- daily maximum temperature and solar irradiance, since both variables drive the photochemical reactions needed to produce ozone by initiating HO_x radical production;

- pressure, since high pressure systems tend to bring clear skies and warm weather, which are also conditions that facilitate high ozone production;
- wind speed, since low wind speeds are needed for ozone precursor pollutants to build up;
- NO_x, since high NO_x levels supress ozone production near the emission source, while production is most efficient at low NO_x;
- VOC, since high VOCs can cause high ozone production in a VOC-limited area like Halifax.

The ozone concentrations at other stations were examined to see if ozone anomalies were just outside the bounds for the diagnosis of a transport event and HYSPLIT back trajectories were run for each day using the same methods as in Figure 4. With the help of meteorologists Al Wilson and Lucy Chisholm from Environment and Climate Change Canada (ECCC), tephigrams, constructed every 12 hours with data from Yarmouth were analyzed for the presence of temperature inversions, which could cause a build-up of pollutants at the surface via limited vertical mixing. Although Yarmouth is located 225 km southwest of Halifax, it is the nearest location with vertical profile data and is typically used as a proxy for Halifax (http://weather.uwyo.edu/upperair/sounding.html). The following is a detailed example of the analysis done for one of the top 10 non-transport days. A summary of all ten days is shown in Table 1.

On May 3, 2018 at 4 AM O_3 peaked at 58 ppb, 28 ppb above the monthly mean. Ozone anomalies at other stations on this day were close to meeting transport criteria, i.e., all stations 6-50% above monthly means. The back trajectory in Figure 6 shows air masses mainly from continental USA (regions of emissions sources). The tephigram in Figure 7

shows a strong temperature inversion near the surface (temperature increasing with height in bottom layer of atmosphere). Data from Table 1 show that local conditions are mostly cloudy, pressure is low and temperature is average for the time of year. These conditions are not conducive to local pollution build-up, however, very low NO_x concentrations would allow for efficient production in the normally titrated downtown core if VOCs were present. The surface inversion could trap pollutants near the surface and limit vertical mixing but pollution could have been advected to the province before the inversion formed and trapped at the surface. The positive anomalies at other stations and the HYSPLIT transport trajectory from urban USA and Canadian regions points to transport rather than local production as the cause of this elevated ozone event.

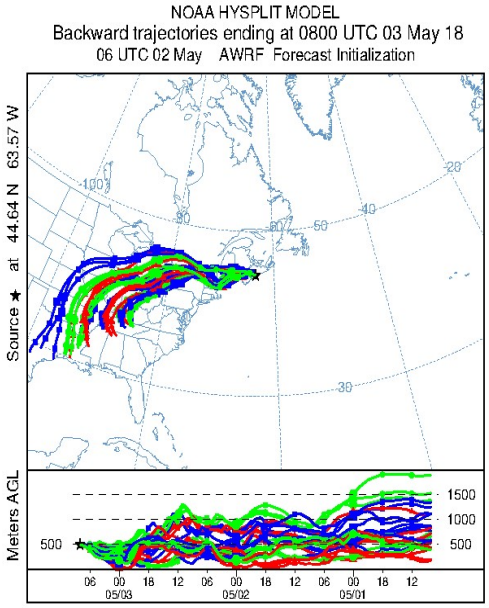

Figure 6. HYSPLIT backward trajectory ensemble ending in Halifax at 08:00 UTC (04:00 AM AST).

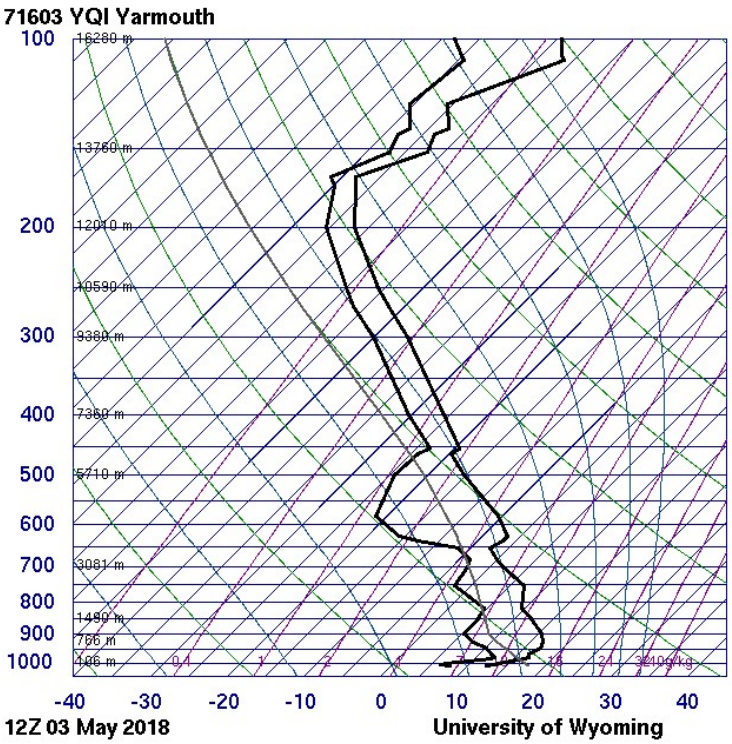

Figure 7. Radiosonde data taken at 12 UTC (8AM local time) on May 3, 2018 at Yarmouth, NS and recorded by http://weather.uwyo.edu/upperair/sounding.html. X-axis shows temperature in degrees Celsius and y-axis shows height and corresponding pressure (hPa).

Table 1. Meteorological and chemical characteristics of elevated ozone days. Table shows the daily maximum value, the anomaly from the monthly mean (in brackets), and the anomaly expressed as number of standard deviations from the monthly mean (to give an indication of whether or not this anomaly is "extreme"). NO_x at time of ozone peak is shown instead of daily maximum since NO_x concentration varies throughout the day and the daily max is therefore not as relevant. Missing data is noted as '--'.

Date	O_3 (ppb)	Temp °C	Solar (kW/m^2)	Pressure (hPa)	Wind (km/hr)	Conditions	[NO_x] at peak O_3 (ppb)	[VOC] $\mu g/m^3$	Trajectory	Presence of inversion?
Sep. 12 2014, 10 AM	75	19.6 (0.5) + 0.14 sd	770 (170) +1.0 sd	100.8 (-0.7) -1 sd	24	Mainly clear	18	No data within 1 day	continental (remote)	no
Sep. 18, 2000 11 AM	67	21.3 (2.5) +0.69 sd	706 (129) +0.59 sd	101.3 (-0.1) -0.1 sd	19	Mostly cloudy	68	--	continental	yes
Apr. 25, 2009 4 PM	62	--	921 (205) +0.95 sd	--	--	--	--	--	continental	yes
May 3, 2018 4 AM	58	14.9 (0.06) 0.01 sd	--	101 (-0.3) -0.59 sd	No data at peak; 0 at 5 AM	Mostly cloudy	4	--	continental	yes
Sep. 10, 2006 1 AM	58	--	228 (-356) -1.9 sd	--	--	--	15	Sum = 53.1, below average summer	continental	yes
Apr. 16, 2003 2 AM	58	12.6 (6.3) +1.3 sd	588 (-84) -0.39 sd	100.9 (-0.8) -0.94 sd	15	--	--	Apr. 15 sum = 65.3, 16% above m. mean	mostly continental	yes
Jul. 5, 2000 3 AM	57	23.1 (2.3) +0.85 sd	691 (-40) -0.17 sd	100.2 (-0.9) -1.4 sd	24	Rain and fog	1	--	mostly ocean	yes
Jun. 15, 2006 4 AM	57	14.6 (-3.8) -1.0 sd	203 (-422) -1.5 sd	100.5 (-0.5) -0.75 sd	11	Rain and fog	14	--	mostly continental	yes
May 19, 2000 1 AM	57	15 (2.4) +0.72 sd	888 (226) +0.90 sd	101.8 (0.6) +0.86 sd	41	Rain showers	3	--	ocean	yes
Jun. 2, 2003 3 AM	56	17.4 (-1.4) -0.33 sd	753 (34) +0.13 sd	99.9 (-1.1) -2.4 sd	19	Rain and fog	--	--	mixed	yes

Of the top 10 Halifax ozone days not diagnosed as transport-related in the algorithm discussed in Section 1.2.2, all 10 of them showed some indication of ozone transport. Local production could not be ruled out completely for a few of these days that showed some conditions conducive to ozone production but in these cases there is also indication of transport that may be mixing with local precursors. For example, on May 19, 2000, the daily maximum temperature, solar irradiance and pressure are all above the monthly mean; however it was rainy that day which typically is not suitable conditions for ozone production. The trajectory for this elevated ozone day shows the majority of trajectories coming from the ocean, which signals clean air, but further back the trajectories may have continental origins. Tephigrams and HYSPLIT ensemble runs for all the days in Table 1 are shown in the Appendix (Section 1.7).

To assess differences in transport trajectory origin compared to the 157 transport days (Figure 4) the HYSPLIT analysis was repeated for the top 10 non-transport-related days (Figure 8). More trajectories on the non-transport days originate across the ocean, which points to cleaner air arriving in Halifax and implies some role for local production in generating the elevated ozone values on those days. Air originating near Hudson Bay, a remote region of Canada and northern Québec, shows some regions of 5-10% trajectory frequencies, whereas this area shows only 0-1% frequency during transport days. The trajectories from the Hudson Bay area are clean air but could contain high ozone concentrations from a stratospheric intrusion characteristic of high northern latitudes in the spring, as four of these days occurred in April and May (Vingarzan, 2004). Nevertheless, Figure 4 and Figure 8 show a similar southwestern direction for the

majority of the trajectories, which is from the northeastern US, implying that these air masses could be bringing polluted air into the province.

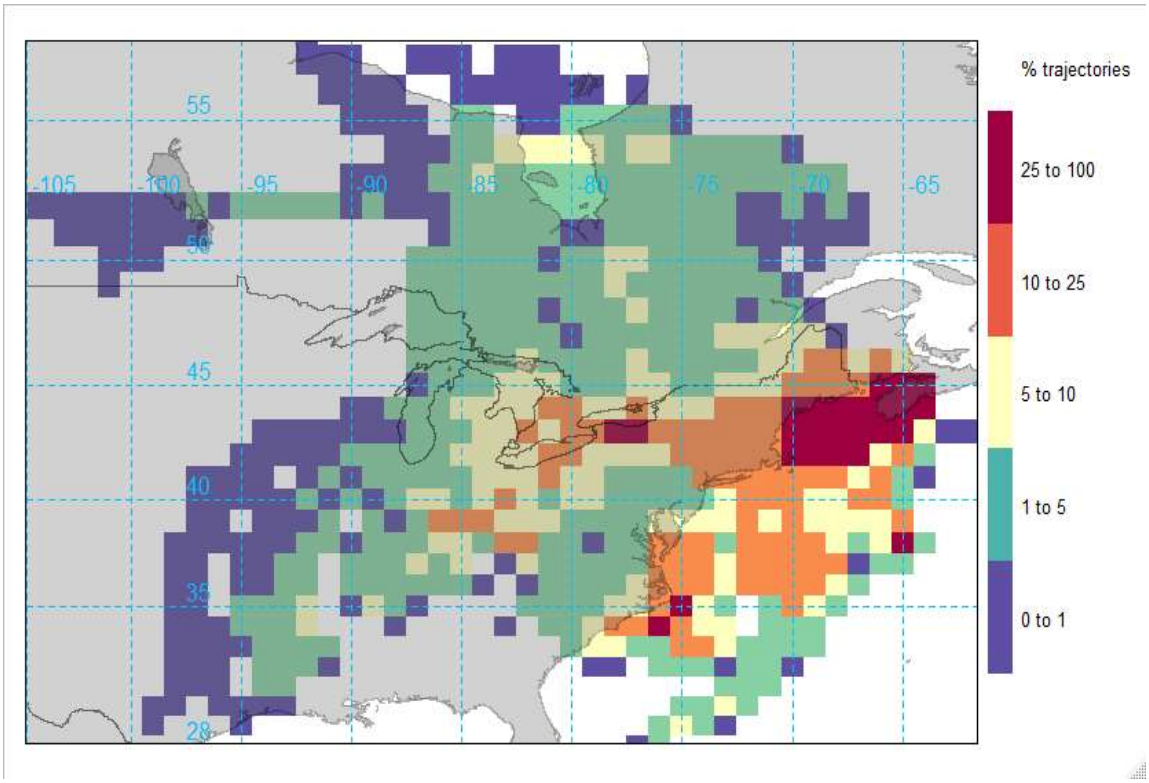

Figure 8. Frequency of 72-hour back trajectories initiated on the 10 non-transport-related days with the highest ozone concentrations in Halifax. Selection algorithm was set to a threshold of 60% of stations exhibiting positive anomalies > 60% above the monthly mean for transport classification. C.f. Figure 4.

Analyzing the top 10 Halifax ozone non-transport days as case studies provided evidence that the transport algorithm needed to be further refined and that the estimate of 1-26% transport was suspiciously low. Results from the refined algorithm are shown in Chapter 2, Section 2.4.3.

1.3.2 Meteorological conditions

Due to ozone's nature as a secondary chemical produced via photochemical reactions, there are known meteorological conditions that enhance ozone production. Some of these variables were mentioned in the case study of non-transport-related days but this section

provides a deeper analysis of their relationship with Halifax ozone. Higher temperatures increase local ozone production by increasing the availability of water vapour, which is needed to produce HO_x radicals and initiate ozone production chemistry (Jacob, 1999). High temperatures also shorten the lifetime of PAN which is a sink of both NO_x and HO_x radicals needed for reactions leading to ozone production (Sillman, 1999). Additionally, biogenic VOC emissions increase at high temperatures and lead to ozone production, especially in VOC-limited areas (Pugliese et al., 2014). Unlike Halifax, some continental cities like Toronto and Windsor have conditions more conducive to ozone production and thus have a summertime seasonal ozone peak driven by increasing temperatures and solar radiation (Pugliese et al., 2014; Xu et al., 2019). Halifax's seasonal peak occurs in the spring and is driven by natural processes (Chapter 2, Figure 15). Camalier et al., (2007) found the relationship with ozone and temperature to be minimal under 20°C but significant above that. In this study temperature was a statistically significant variable in predicting ozone in 36 of 39 urban areas in the USA. The relationship between temperature and ozone in Halifax was analyzed using daily maximum ozone and daily maximum temperature measurements from the nearby Shearwater weather station. Figure 9 shows an insignificant relationship (R^2=0.04, $p < 0.01$) between daily maximum temperature above 20°C and daily maximum ozone. Urban areas with higher average temperatures and a summer seasonal ozone peak driven by temperature would see a more significant relationship. Figure 9 does not provide strong evidence of local ozone production based on the expected relationship with temperature, however, as shown by Camalier et al. (2007), ozone production in regions upstream of Halifax is very strongly temperature dependent, which Figure 9 is unable to distinguish.

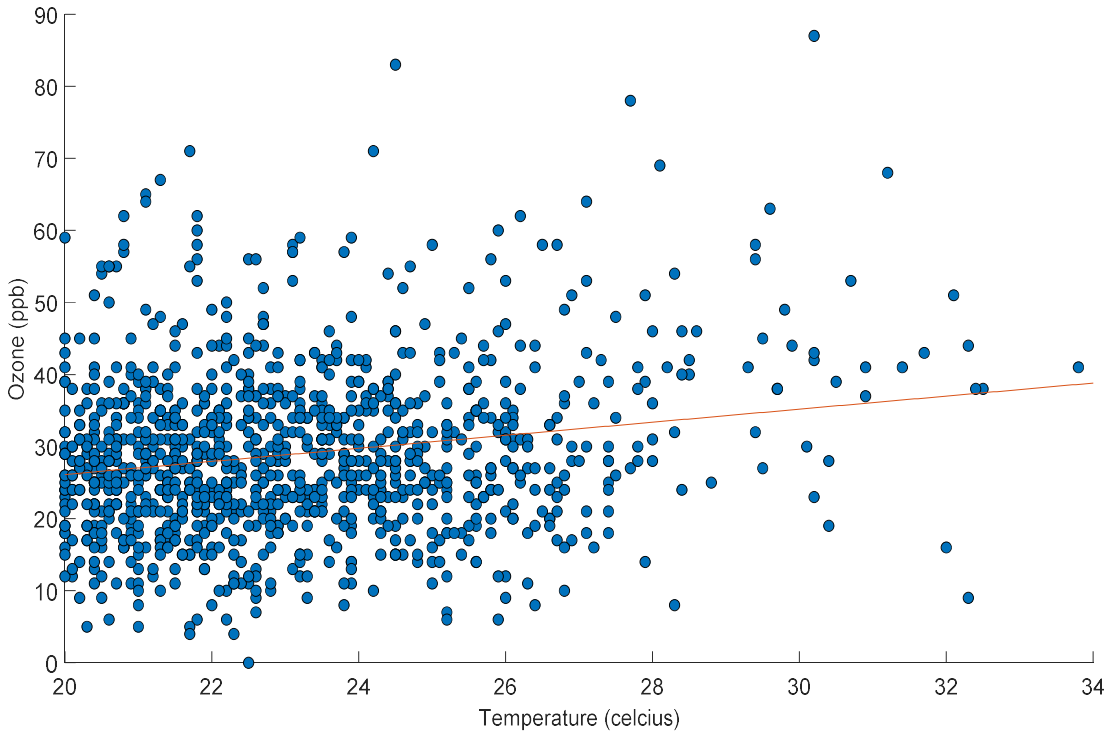

Figure 9. Daily maximum Halifax temperature above 20°C and daily maximum Halifax ozone from 2000-2018.

In addition to high temperature, high pressure and solar irradiance are also conducive to ozone production. The distribution of pressure, solar irradiance and temperature on the top 100 non-transport days of daily maximum ozone concentration was compared to non-transport days with the bottom 100 daily maximum ozone concentrations. Transport days were diagnosed with the most refined algorithm iteration, at the most lenient criteria (IND50) in Chapter 2, and they were removed (912 days removed from 6935 total). Figure 10 shows daily mean solar irradiance on the top and bottom 100 daily maximum ozone days in Halifax; daily mean was chosen over maximum as a long period of high solar radiation is more likely to produce high ozone than a single high hourly maximum (e.g. due to a temporary break in cloud cover on an otherwise overcast day). There is overlap in the distributions between the top and bottom 100 days but using an

independent sample t-test it was found that the daily mean solar irradiance is significantly higher on the top 100 days of ozone concentration. Daily maximum temperature in the top and bottom 100 ozone concentration days is shown in Figure 11. A significantly higher daily maximum temperature is seen on the top 100 days even though no significant relationship was found in Figure 9. The daily mean temperature was also used in this analysis but produced less significant results. The same analysis was done with mean and maximum pressure and no significant differences were found.

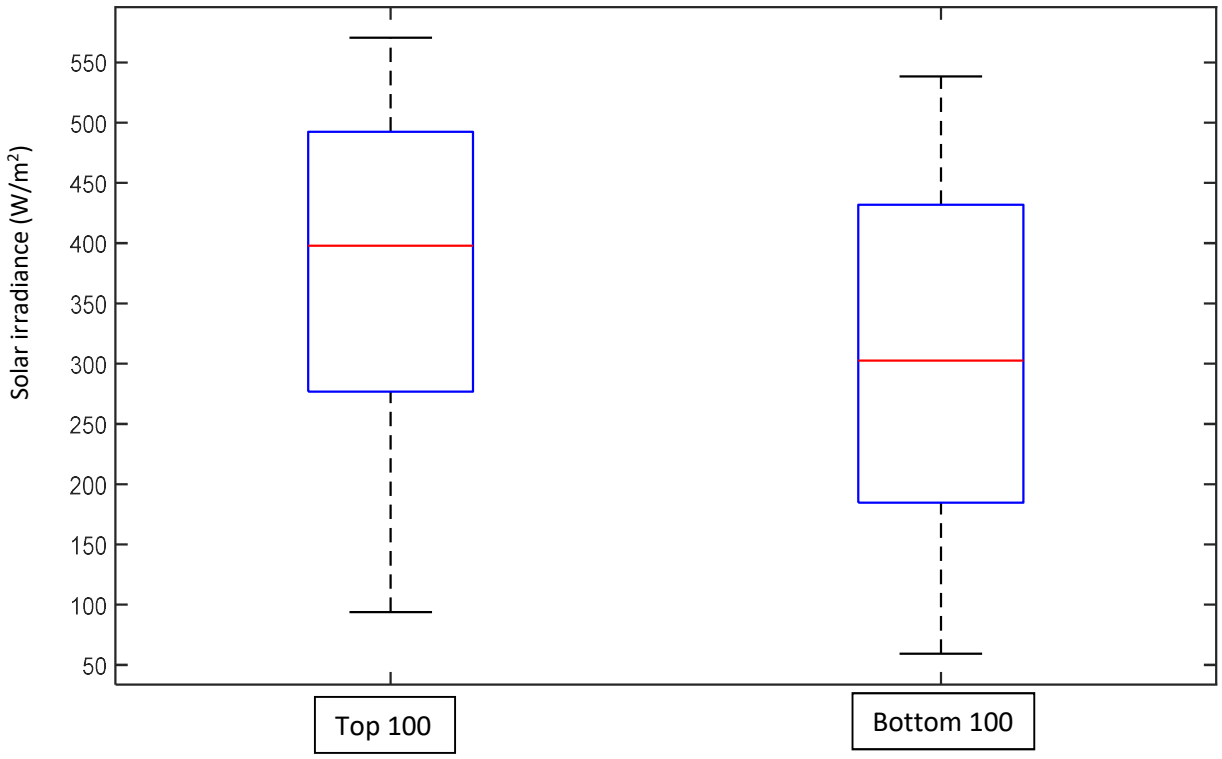

Figure 10. Daily mean solar irradiance on the top and bottom 100 daily maximum ozone days in Halifax with transport days diagnosed under IND_{50} criteria removed. The independent t-test results shows the means are significantly ($p < 0.01$) different from one another. Horizontal lines represent medians, upper and lower box edges represent 75th and 25th percentiles ("q3" and "q1", respectively), upper and lower whiskers represent maximum and minimum data limits (defined as +/-2.7σ (approx. 99.3 percentile)), and grey crosses are outliers (defined as $> q3 + w \times (q3 - q1)$ or $< q1 - w \times (q3 - q1)$, where w is the maximum whisker length).

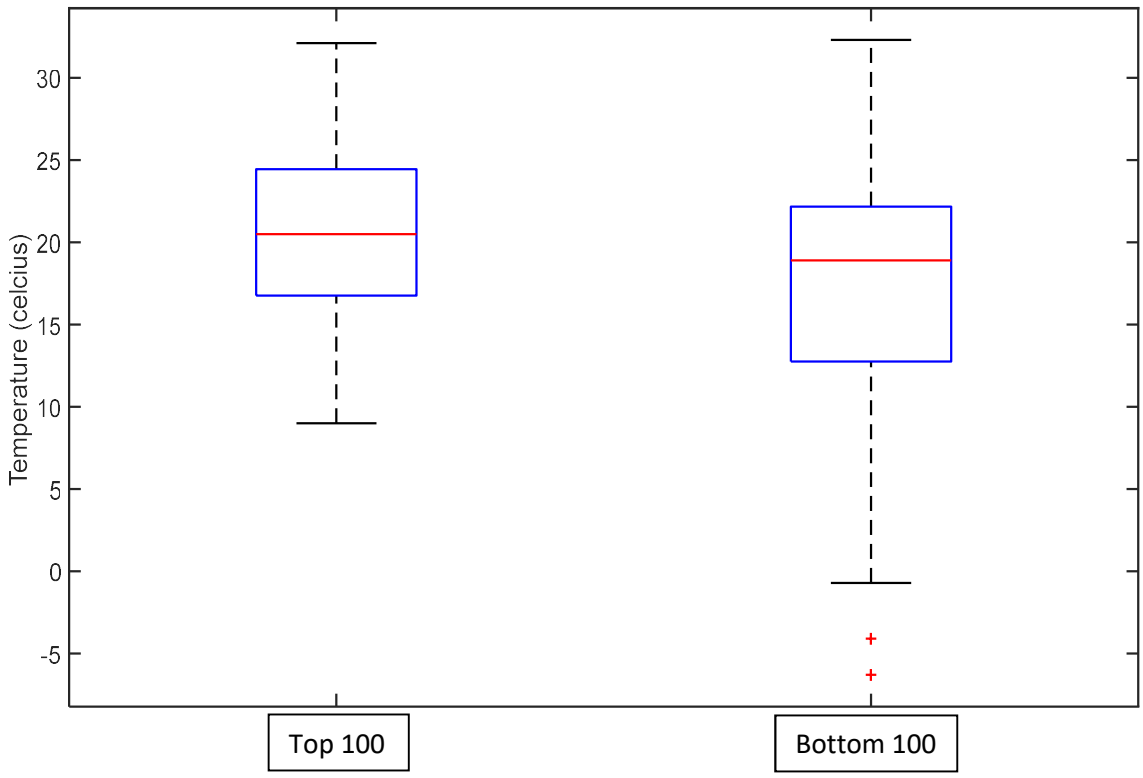

Figure 11. Daily maximum temperature on the top and bottom 100 daily maximum ozone days in Halifax with transport days diagnosed under IND_{50} criteria removed. Boxplot properties are described in Figure 15. The independent t-test results shows the means are significantly ($p < 0.01$) different from one another.

In conclusion, there is no obvious relationship between temperature and high ozone levels in all the data, as expected from the literature, however there are significant differences seen in the top 100 ozone concentrations compared to the bottom 100. On a day with high ozone that has *not* been identified as transport-related, based on the most refined version of the algorithm, we find the daily maximum temperature and the daily mean solar irradiance to be higher in the top 100 ozone concentration than in the bottom 100 ozone concentrations. This provides some evidence of local ozone production on these days, however more work is needed to distinguish local production in Halifax from transported ozone pollution from upstream source regions, which are also temperature dependent.

1.3.3 Ozone production regime

The production regime for ozone tells us which of the two precursors should be reduced to limit ozone production in any given area. When ozone production is NO_x-limited it will increase linearly with added NO_x, so regulations should focus on limiting NO_x emissions. In a VOC-sensitive regime ozone will only be produced with the addition of VOCs, so the emissions should then be the focus of regulations. A transitional production regime is also possible where production rates are similar for both precursors and reductions of either can reduce ozone production (Sillman, 1999). Urban centres tend to have VOC-sensitive production regimes due to the high NO_x emissions from vehicle traffic but the regime for Halifax has not been previously quantified. The production regime of an area is diagnosed by the dominant ozone loss mechanism, which can occur in one of two ways, depending on the dominant pollutant acting as a sink for HO_x (Sillman, 1999). If the concentration of NO_x is low in the area HO_2 will self-react and hydrogen peroxide is the dominant sink of HO_x radicals:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

In this case, ozone production is NO_x-sensitive. However, if NO_x concentrations are high in the area then HO_x (as OH) will react with NO_2 and nitric acid is the dominant sink of HO_x radicals (Jacob, 1999):

$$NO_2 + OH + M \rightarrow HNO_3 + M$$

In this case, production is sensitive to VOCs.

These secondary species, i.e., reactive nitrogen and peroxides, are produced alongside ozone and are widely used to understand the conditions in which ozone was produced (e.g., Sillman, 1999). NO_y is a family of secondary species that includes HNO_3, which is

the dominant sink of HO_x in a VOC-sensitive production regime. Sillman (2002) used results from chemical transport modelling in several US urban centres to define chemical species indicator ratios involving ambient ozone and NO_y, as follows: if the ratio of O_3 to NO_y is less than 5, the production regime is VOC-sensitive; if the ratio of O_3 to NO_y is greater than 11, the production regime is NOx-sensitive; a ratio between 6 and 8 indicates a transition regime.

Although measurements of secondary species are not available routinely from NAPS, NO_y data were collected for the restricted period of May-October 2016 (Wilson, 2017). The production regime was inferred over this period using hourly ozone concentrations from downtown Halifax (NAPS station) and the hourly NO_y data obtained ~2 km away. Ratios of O_3 to NO_y were analyzed diurnally, and the median ratio (Figure 12) was found to be within the range of 2.6 to 4.4 at all times of the day, signifying a VOC-sensitive ozone production regime (< 5) in 64.9% of the data, in this situation reducing VOC concentrations will be more effective in limiting ozone production than reducing NO_x concentrations. There are some hourly indicator ratios above 11 (13.4% of the data) which signify a NO_x-limited regime and only 7.5% of the hourly ratios fall within the transition regime ($6 < O_3/NO_y < 8$), but 35.1% of the ratios fall between 5 and 11. The increase in VOC emissions in the last three years may outweigh the benefits of decreasing NO_x emissions, as the production regime is VOC-limited in 2016 in 64.9% of the days. This does not mean that less effort should be made to control NO_x as many regions are likely to become more sensitive to it in the future with continuing emissions reductions, as has occurred in Europe (Beekmann & Vautard, 2010). Moreover, NO_x leads to other air pollution consequences other than ozone production, like particle formation and acid

deposition. In the largely VOC-limited downtown Halifax, we expect ozone production to increase with increasing VOC concentrations in recent years (Chapter 2, Figure S2).

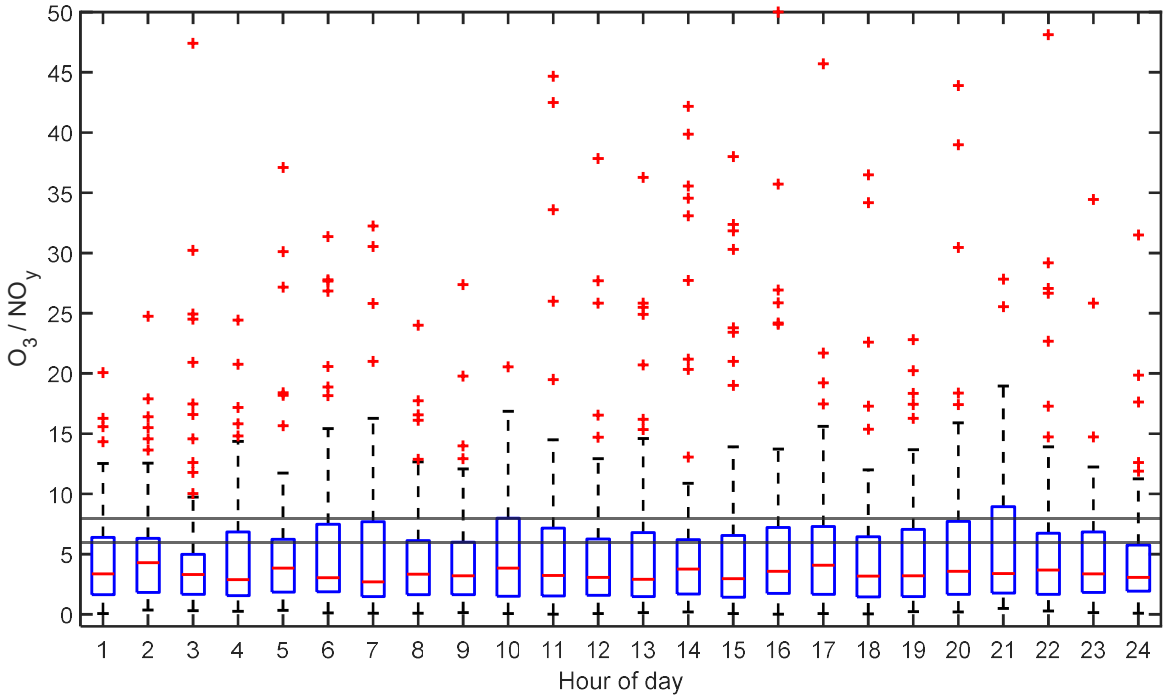

Figure 12. Hourly O_3/NO_y ratios (May-October 2016) plotted diurnally. Black horizontal lines show the transition regime limits ($6< O_3/NO_y <8$). NO_x-limited ozone production occurs at $O_3/NO_y > 11$ while VOC-limited occurs at $O_3/NO_y < 5$. Boxplot properties are as described in Figure 15.

1.4 Suburban titration of ozone near Halifax

To further analyze the observed decreasing annual NO_x concentration and the decreasing titration effect in downtown Halifax (Figure 18), ozone, NO_x and total ozone (O_x) were also plotted in 5-year intervals at suburban Lake Major (Figure 13). The location of this station has little to no local NO_x sources but is in a forested area with likely high levels of biogenic VOCs; measurements of VOCs are not available there. Briefly, total ozone is the sum of ozone and the amount of ozone titrated, therefore, the titrated ozone is the difference between ozone and total ozone (for details on the calculation of total ozone see Chapter 2, methods).

$[O_x] = [O_3]$ + titrated ozone

Figure 13 compared to Figure 18 shows that on average, NO_x concentrations are about ten times lower at Lake Major than in downtown Halifax and the morning rush hour peak is offset about one hour, consistent with downstream transport from the urban centre. In the 2006-2011 period there is between 5-7 ppb of titrated ozone throughout the day but as NO_x decreased in the 2012-2017 period there was only about 1 ppb of ozone being titrated throughout the day. Over the two 5-year periods, ozone increased an average of 6 ppb and total ozone increased an average of 1.5 ppb. This is different from Halifax where total ozone decreased with decreasing NO_x concentrations as expected. I believe this is due to the specific ozone production chemistry taking place at the clean suburban station.

According to Sillman, (1999) at low NO_x concentrations such as at Lake Major the rate of ozone production is very efficient and increases with increasing NO_x, which in this case is transported to Lake Major from Halifax. At high NO_x concentrations, such as those present in downtown Halifax, the rate of ozone production slows with increasing NO_x until eventually ozone production is entirely suppressed due to titration by NO_x. As NO_x decreased at Lake Major to an average of 1-3 ppb, it appears that ozone production became more efficient in the NO_x-limited production regime. These factors are likely responsible for the increase in total ozone and ozone.

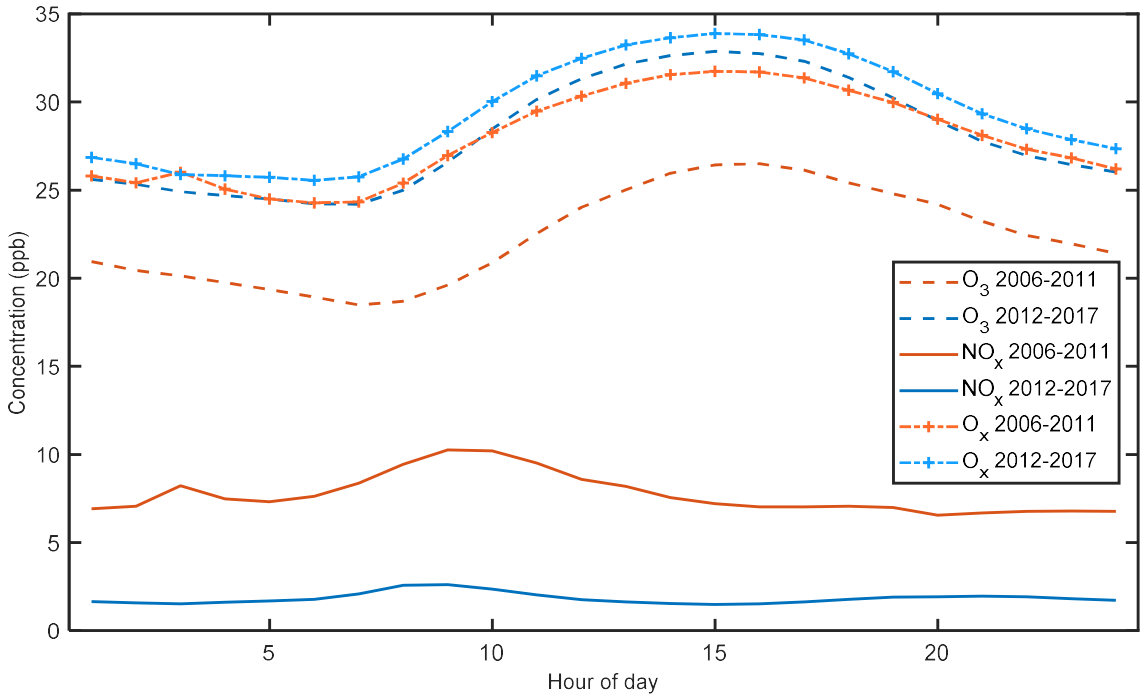

Figure 13. Diurnal O_3, NO_x and total ozone (O_x) in five-year intervals at Lake Major station, which began operating in 2006. C.f. Figure 18.

This part of the research provides information on the extent of the NO_x titration urban "bubble" that is evident in downtown Halifax. We know that decreasing NO_x levels in the downtown core have the ability to increase ozone production in surrounding areas via change in the production efficiency. This information can be used to apply appropriate ozone reduction strategies in areas of different ozone chemistry.

1.5 Conclusions

Chapter 1 of this thesis has shown the development of the initial steps of quantifying transported pollution frequency to the province of Nova Scotia. By scrutinizing the logic behind each step of the methodology as well as scrutinizing the elevated ozone days that did not meet the early (percentage-based) transport criteria we were able to produce an algorithm that we believe accurately diagnoses transport days in the province as detailed in Chapter 2. An analysis of back trajectories for the 157 transport days diagnosed by the

early algorithm iteration confirmed the suspected source regions for pollution from the literature as the northeastern USA, the Ohio River Valley and southern Ontario and Quebec.

Moreover, in Chapter 1 a detailed analysis of elevated ozone days that could be produced from Halifax's own pollutants was presented, with the unexpected result that the top 10 daily maximum ozone days that were not classified as transport-related (based on the criteria in Section 1.2.2) all showed some indication of transport. This result showed that the initial algorithm was underestimating transport-related days and needed further refinement. Next, meteorological variables that are known to produce high levels of ozone were found to have a weaker relationship with ozone in Halifax than expected in more polluted and hotter continental Canadian cities like Toronto and Windsor (Figure 9). When transport days are removed significant differences in solar irradiance and temperature are observed on the top 100 daily maximum ozone days compared to the bottom 100 such days (Figure 10 and Figure 11). It is likely that transported pollution is one of the most important variables in creating elevated ozone days in Halifax and the ability of the city's own pollution to be the only cause of a given elevated ozone day is still uncertain.

The production regime of ozone in downtown Halifax in summer 2016 was determined to be mostly VOC-limited, implying that the rising VOC emissions shown in Chapter 2 could be responsible for increasing ozone levels in recent years (Figure 16). Lastly, evidence was presented for emissions of NO_x in downtown Halifax influencing a suburban station 12 km away. Analysis of titrated and total ozone at the suburban Lake Major station showed that titrated ozone decreased along with decreasing Halifax NO_x

over the twelve-year period of analysis, while both ozone and total ozone concentrations increased. It is possible that increased ozone production efficiency at low NO_x is the cause of increasing total ozone at Lake Major while total ozone at Halifax is decreasing. Unfortunately, data is not currently available for other suburban locations outside the city centre to examine the spatial distribution of the production regime, with the related implications for most effective ozone pollution control measures.

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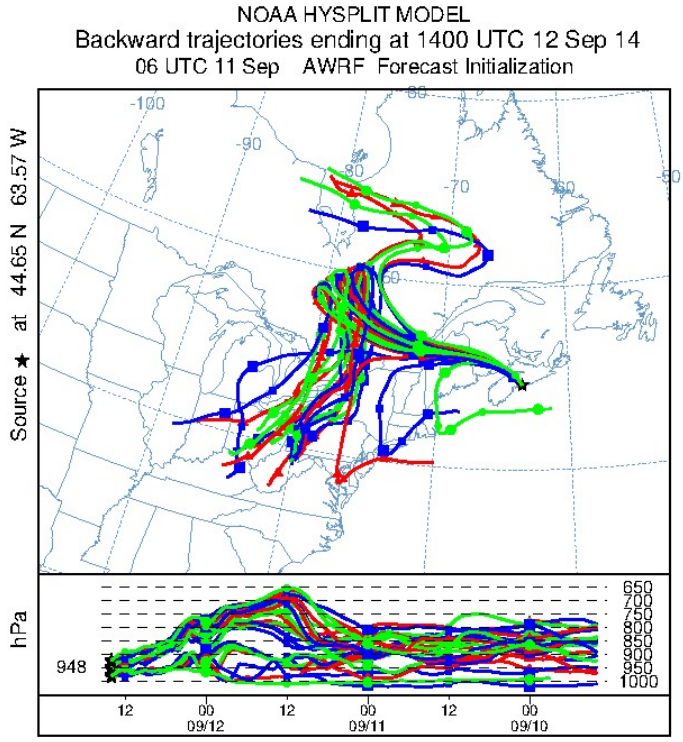
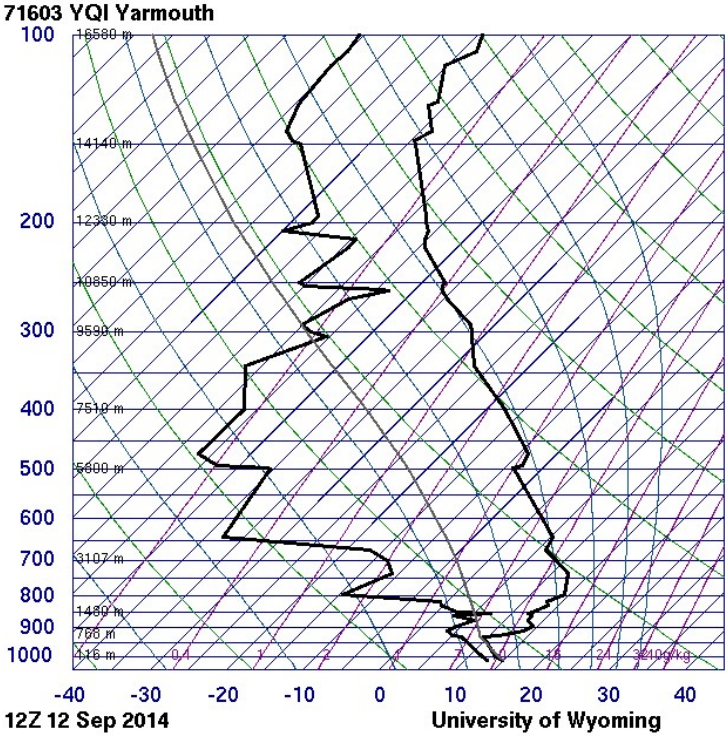
1.7 Appendix

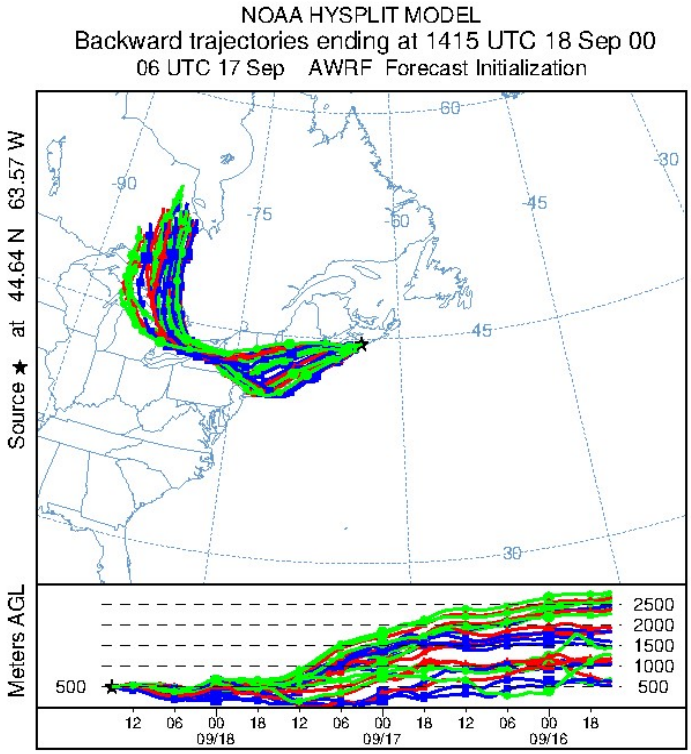
HYSPLIT ensemble trajectories and tephigrams for the top 10 non-transport days in Section 1.3.1.

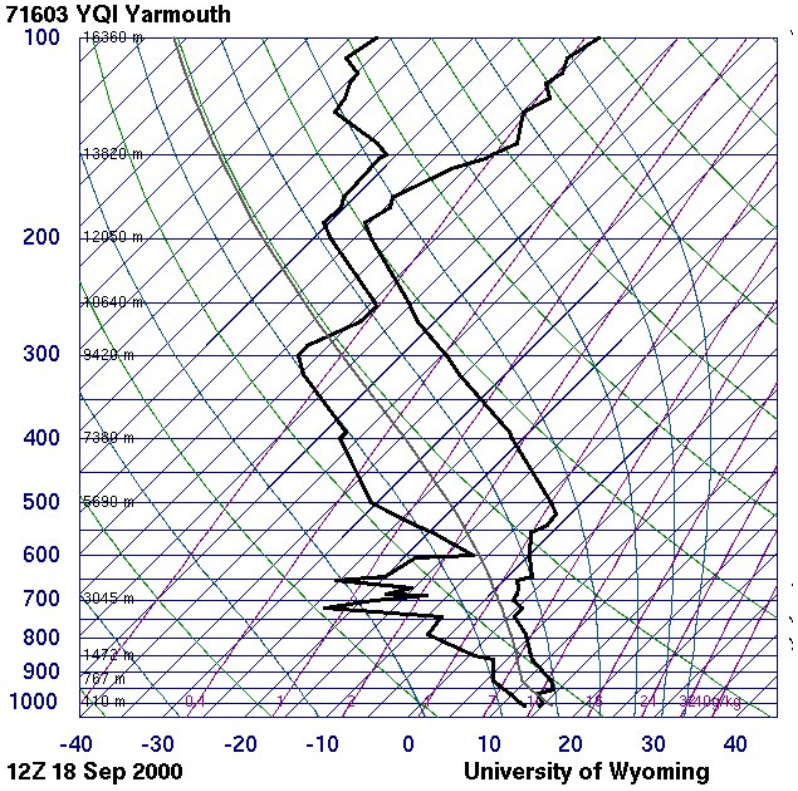
1. September 12, 2014 10AM – 75 ppb ozone



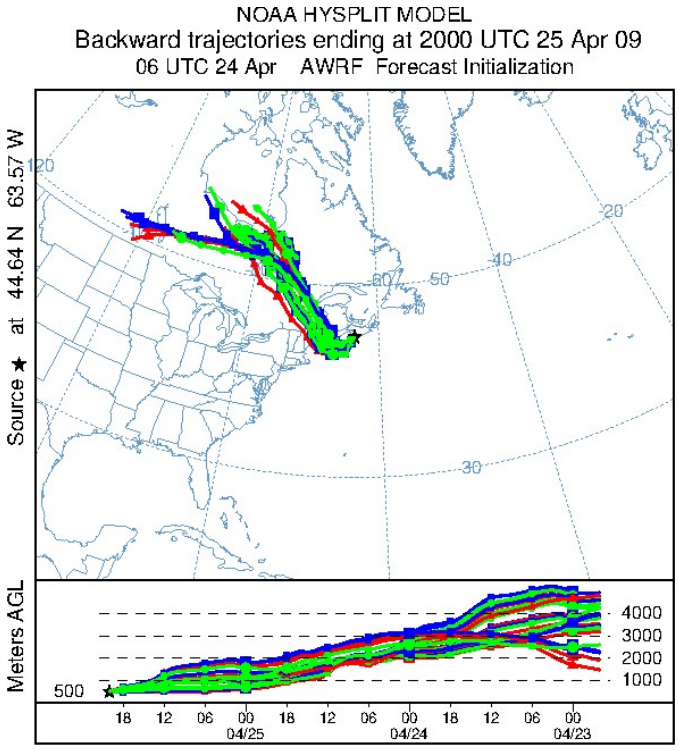


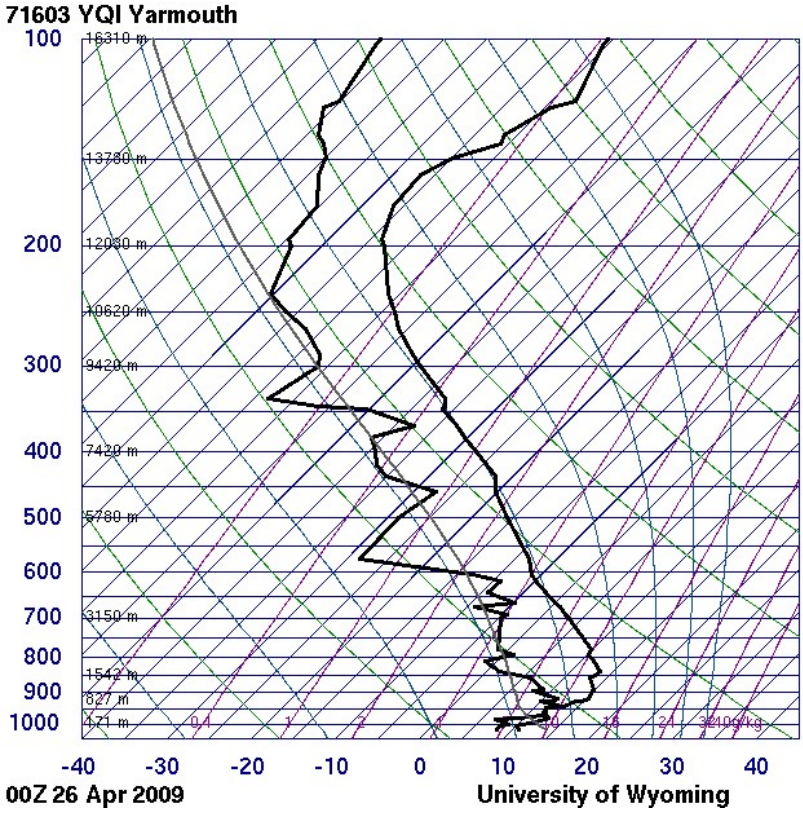
2. September 18, 2000 11AM – 67 ppb ozone



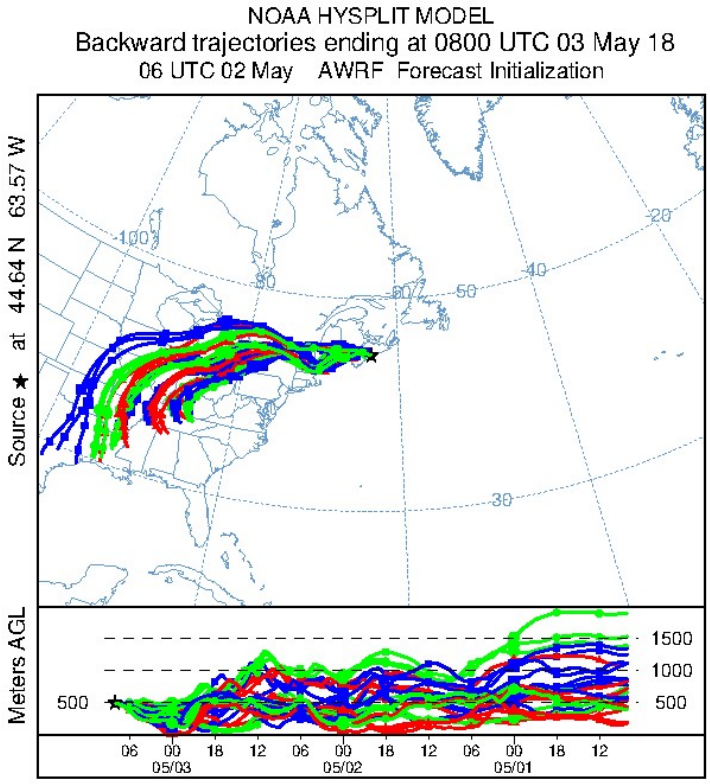


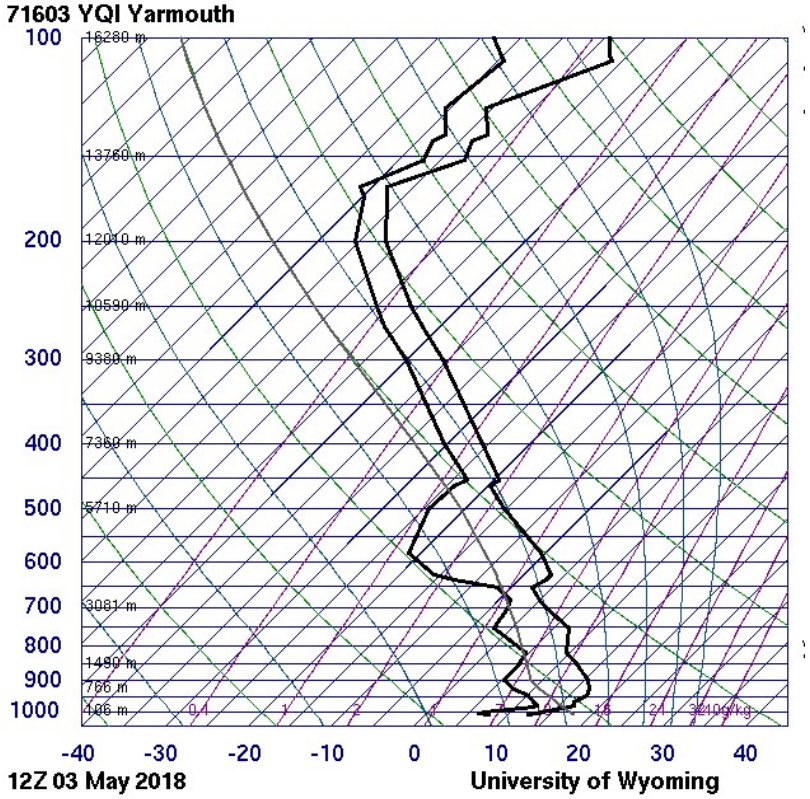
3. April 25, 2009 4PM – 62 ppb ozone



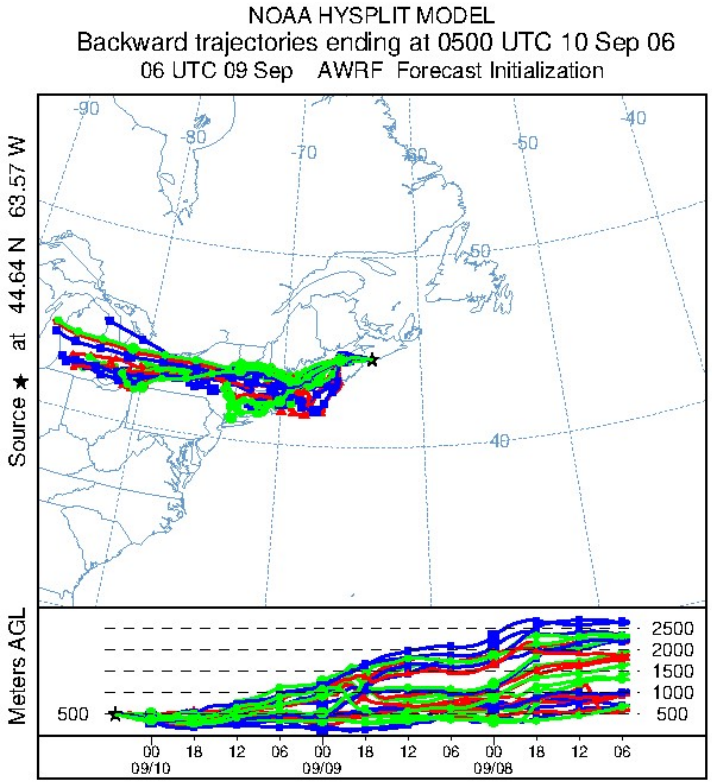


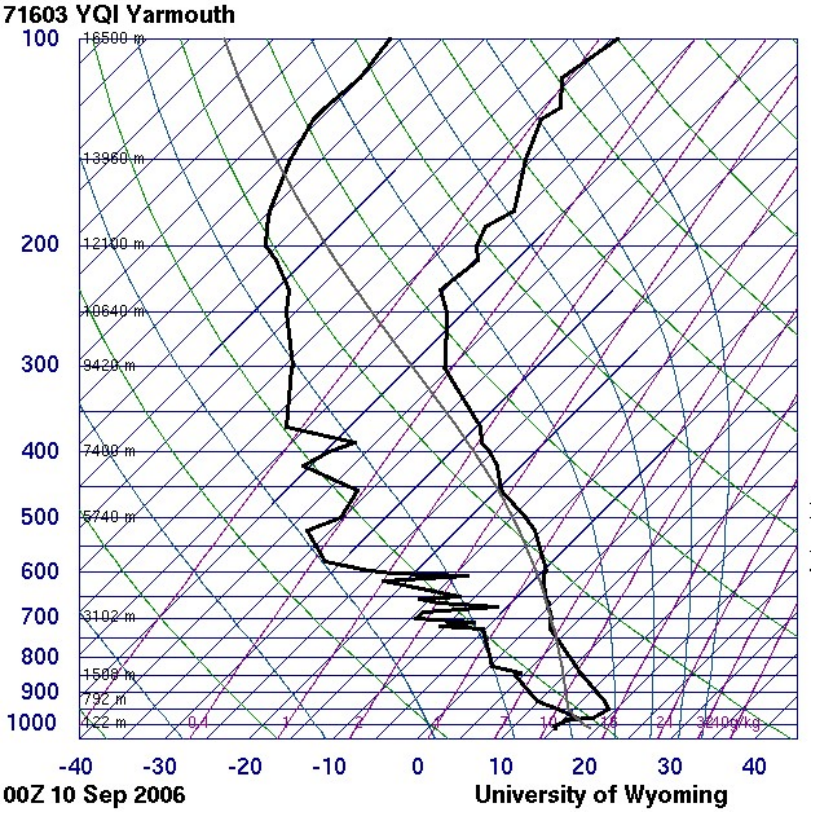
4. May 3, 2018 4AM – 58 ppb



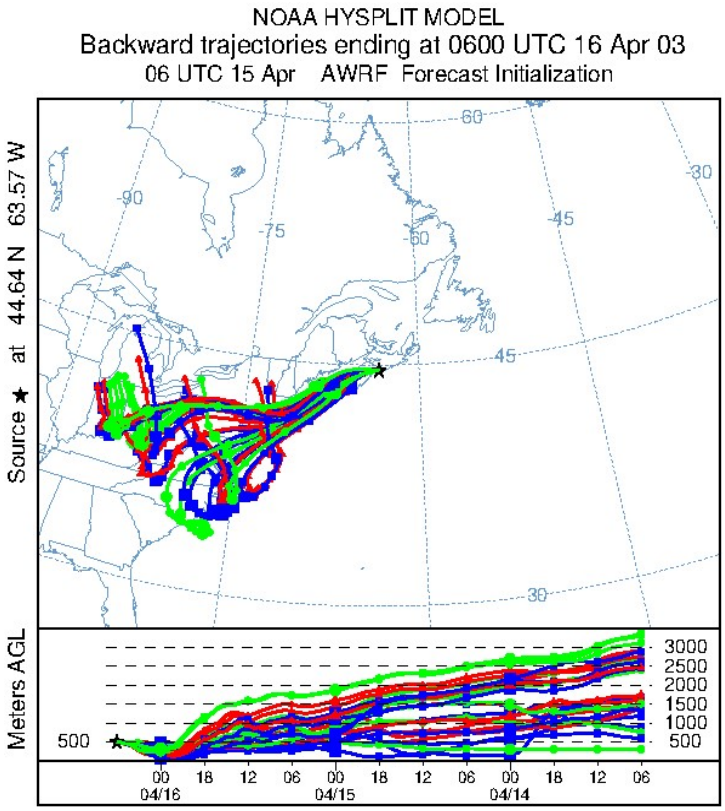


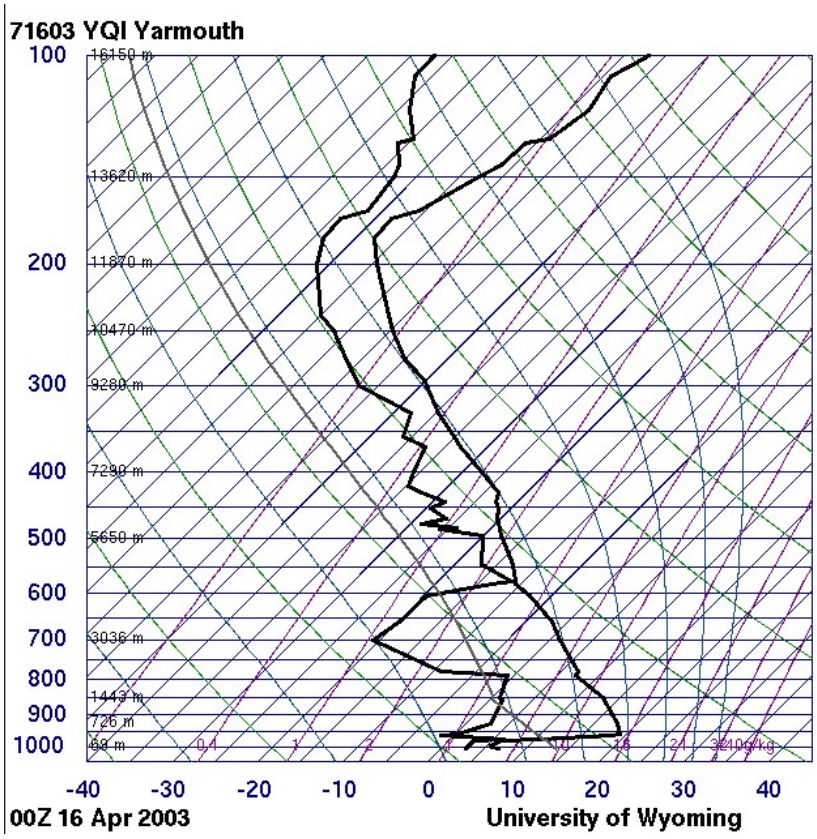
5. September 10, 2006 1AM – 58 ppb



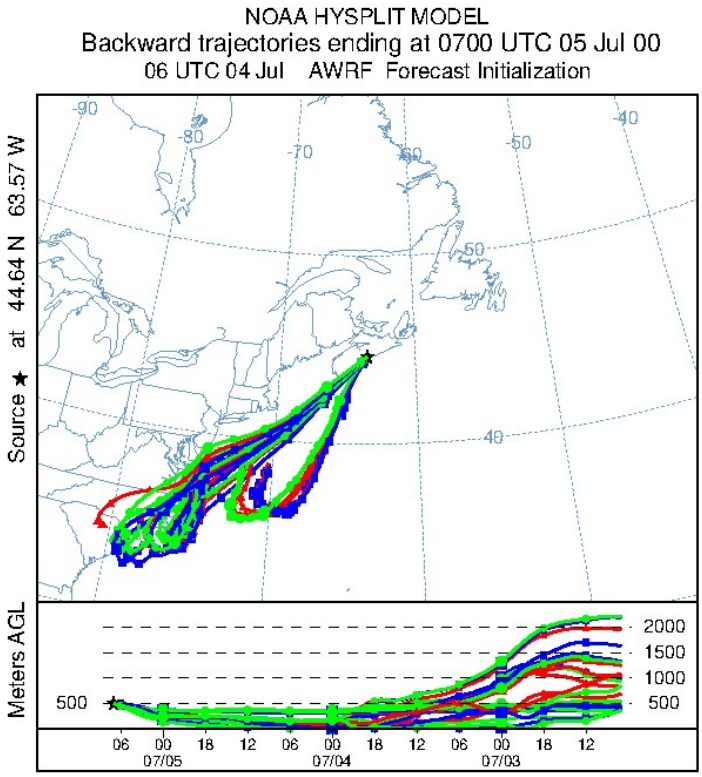


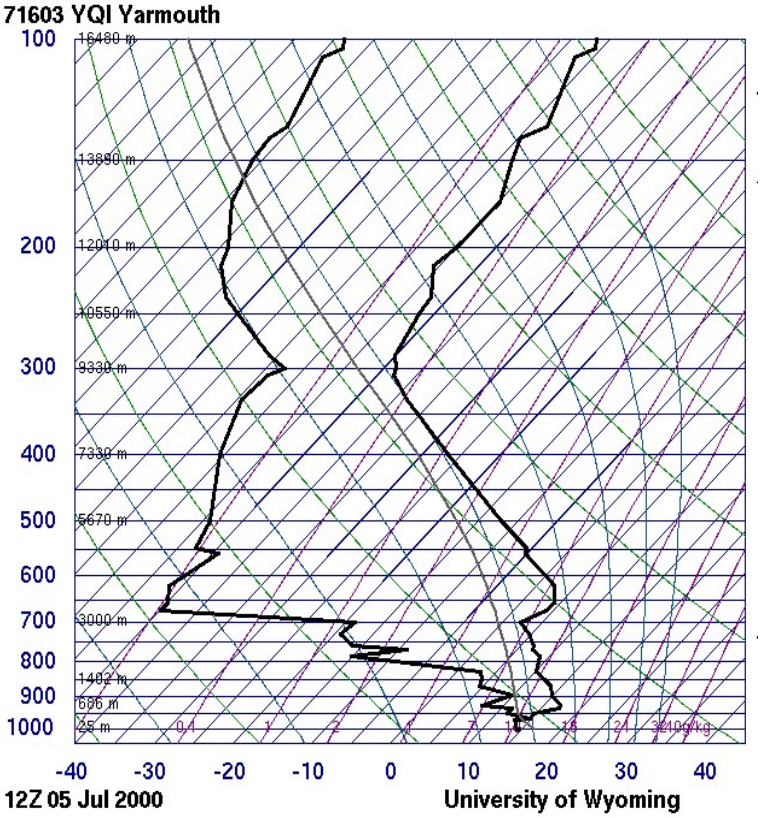
6. April 16. 2003 2AM – 58 ppb



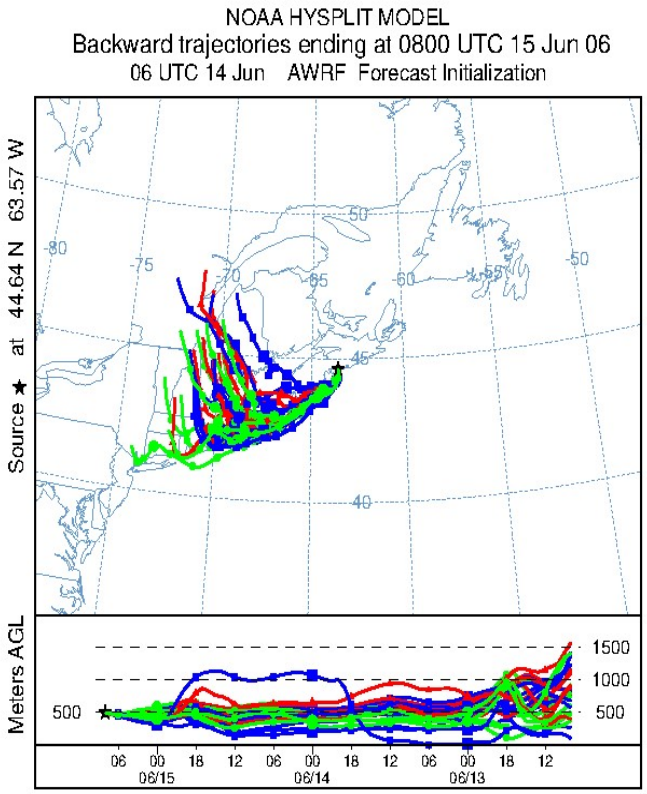


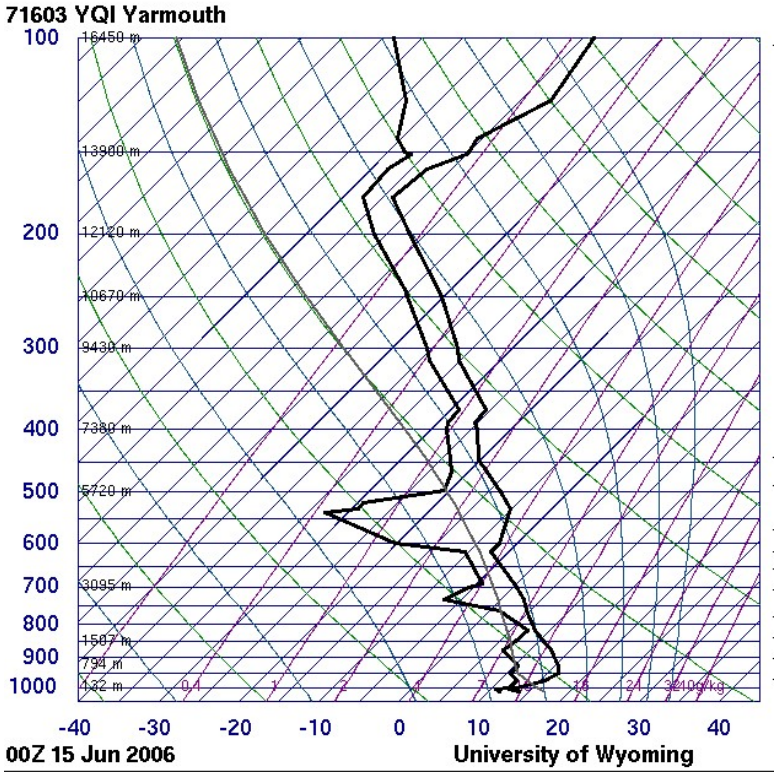
7. July 5, 2000 3AM – 57 ppb



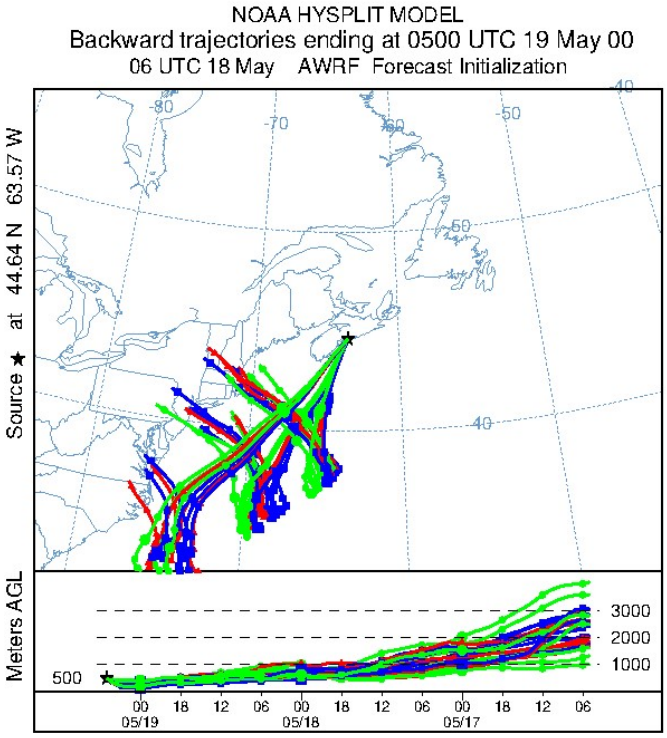


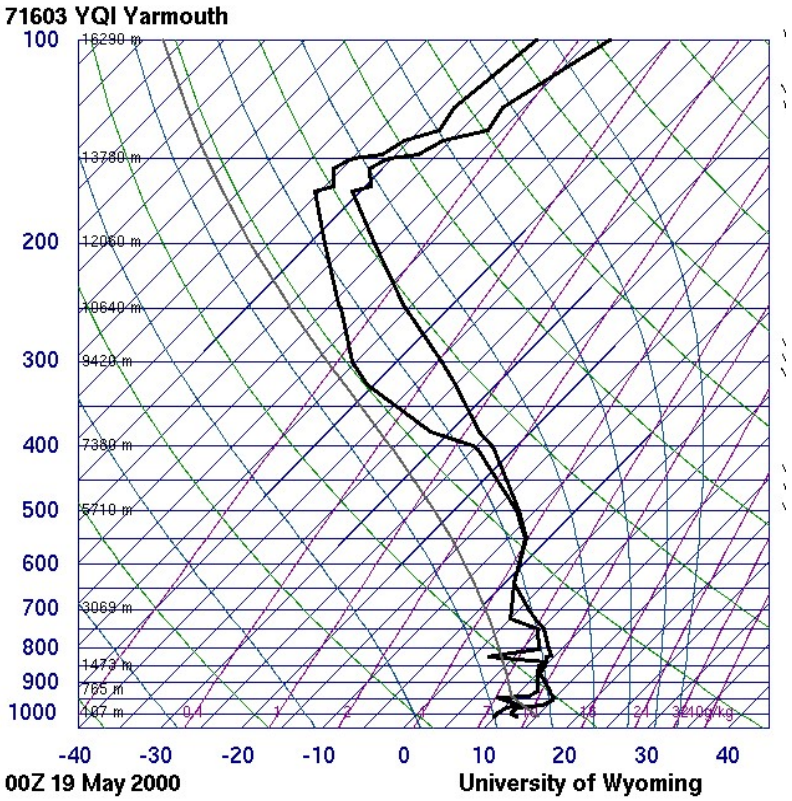
8. June 15, 2006 4AM – 57 ppb



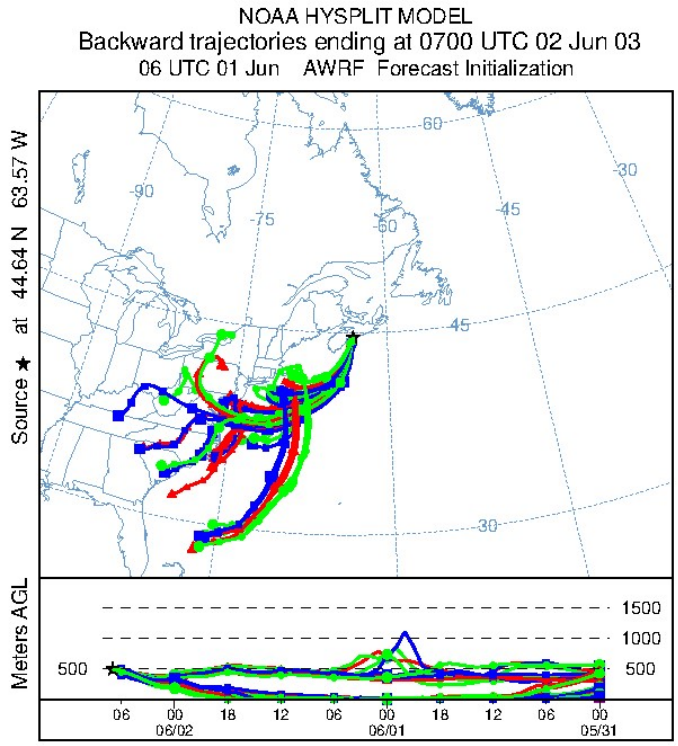


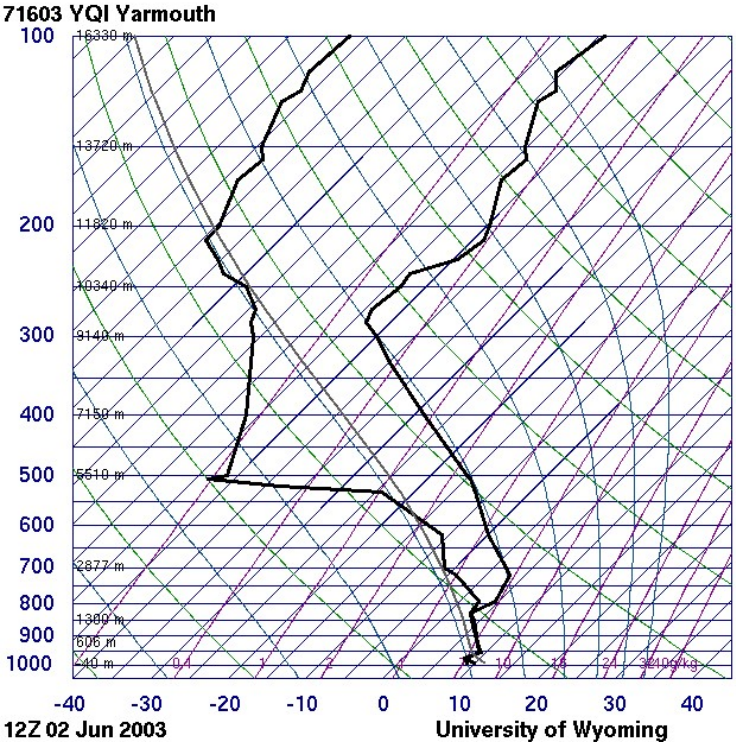
9. May 19, 2000 1AM – 57 ppb





10. June 2, 2003 3AM – 56 ppb





Part 2

Surface ozone in the North American pollution outflow region of Nova Scotia: Long-term analysis of surface concentrations, precursor emissions and long-range transport influence

Keywords: ozone, transboundary, transport, Nova Scotia, precursor emissions, trends

Authors: Morgan Mitchell[1], Aldona Wiacek[1,2], Ian Ashpole[1]

[1] Saint Mary's University, Environmental Science, [2] Saint Mary's University, Astronomy and Physics

2.1 Abstract

Nova Scotia is in the air pollution outflow region of North America and experiences elevated surface air pollution episodes regularly. We present the first analysis of long-term (2000-2018) hourly ozone (O_3) and ozone precursor gas trends at three Nova Scotia provincial monitoring locations ('urban' Halifax, 'suburban' Halifax at Lake Major and 'regional background' at Aylesford Mountain), together with an examination of provincial ozone precursor emission trends. The precursors considered are nitrogen oxides (NO_x) and volatile organic compounds (VOC). Over the common data period for the three stations (2006-2017) the annual 99th percentile hourly ozone concentrations decreased significantly in Halifax (-0.77 ppb/year; $p = 0.02$) and at Aylesford (-0.65 ppb/year; $p = 0.03$), in agreement with regional trends. No statistically significant changes were found in high ozone at suburban Lake Major (-0.02 ppb/year; $p = 0.94$), but the annual 25th percentile, median, and 75th percentile hourly ozone concentrations increased significantly ($p < 0.01$) only at this location (1.09 ppb/year, 1.23 ppb/year, 1.03 ppb/year, respectively). This is consistent with the strong NO_x-O_3 titration effect in downtown Halifax decreasing over time. After correcting for the titration effect over the

full study period, the annual median Halifax total ozone is found to be decreasing (-0.45 ppb/year; $p = 0.02$).

Over the full study period, ambient concentrations of precursors decreased significantly ($p < 0.01$) in Halifax by -2.34 ppb/year for NO_x and -3.41 $\mu g/m^3$/year for VOCs, as did the ozone formation potential (OFP) of VOCs (-9.66 $\mu g/m^3$/year; $p < 0.01$). The underlying emissions of precursors also decreased significantly ($p < 0.01$) in and near Halifax (provincial NO_x: -3982 ppb/year; provincial VOCs: -1680 tonnes/year), also in agreement with regional trends. However, a linear regression during 2012-2018 showed a decelerating reduction of provincial NO_x emissions. Provincial total VOC emissions also decreased approximately ten times slower during 2012-2018, albeit this was not statistically significant. Finally, we present an algorithm to identify events of long-range transported pollution in Halifax, based on spatial correlations in ozone across surface monitoring stations in Nova Scotia. Between 2000 and 2018, transported upstream pollution was found to be connected to between 45% and 63% of 1444 days when surface ozone was elevated in Halifax. The frequency with which transported pollution events occur increased by 15% across this time period.

Contents

2.2 Introduction

The complex combination of global, regional and city-scale factors described in Section 1.1 makes ozone control notoriously difficult to implement and verify, and motivates our study of the particular mixture of conditions in the Atlantic urban center of Halifax, in the North American pollution outflow region of Nova Scotia. The most recent analysis of ozone monitoring station trends in Nova Scotia considered stations in isolation from one another between 2000 and 2007 (Nova Scotia Environment, 2009), without considering

underlying ozone precursor concentration and emission trends, or the influence of transport. Our work is thus the first long-term (2000-2018) analysis of trends in Nova Scotia surface ozone, ozone precursor concentrations, precursor emissions, and transport influences. This paper is structured as follows: in Section 2.3 we describe the data sources and station locations, as well as calculations of total ozone, ozone formation potential and the development of our transported pollution detection algorithm. In Section 2.4 the results are discussed, focusing on variations in ozone time series, precursor concentration and emission trends, as well as transported pollution case studies and long-term frequency of transported pollution occurrence. Finally, we present conclusions in Section 2.5.

2.3 Methods

2.3.1 Concentration and emission data sources

The National Air Pollutant Surveillance (NAPS) network measures continuous criteria air pollutant concentrations at stations across Canada. Free access to this data is provided online through the NAPS website (http://data.ec.gc.ca/data/air/monitor/national-air-pollution-surveillance-naps-program). Nova Scotia has ten trace gas monitoring stations across the province (*Figure 14*). Pollutants used in this study include ozone and NO_x, which are available in one-hour average concentrations, and 160 VOC species, which are available as 24-hour average concentrations every sixth day. Although data for some stations is available from 1995-2018, data coverage before 2000 is inconsistent and contains large gaps so our analysis begins in 2000. Pollutants with less than 70% of possible measured values for the year were excluded from the analysis.

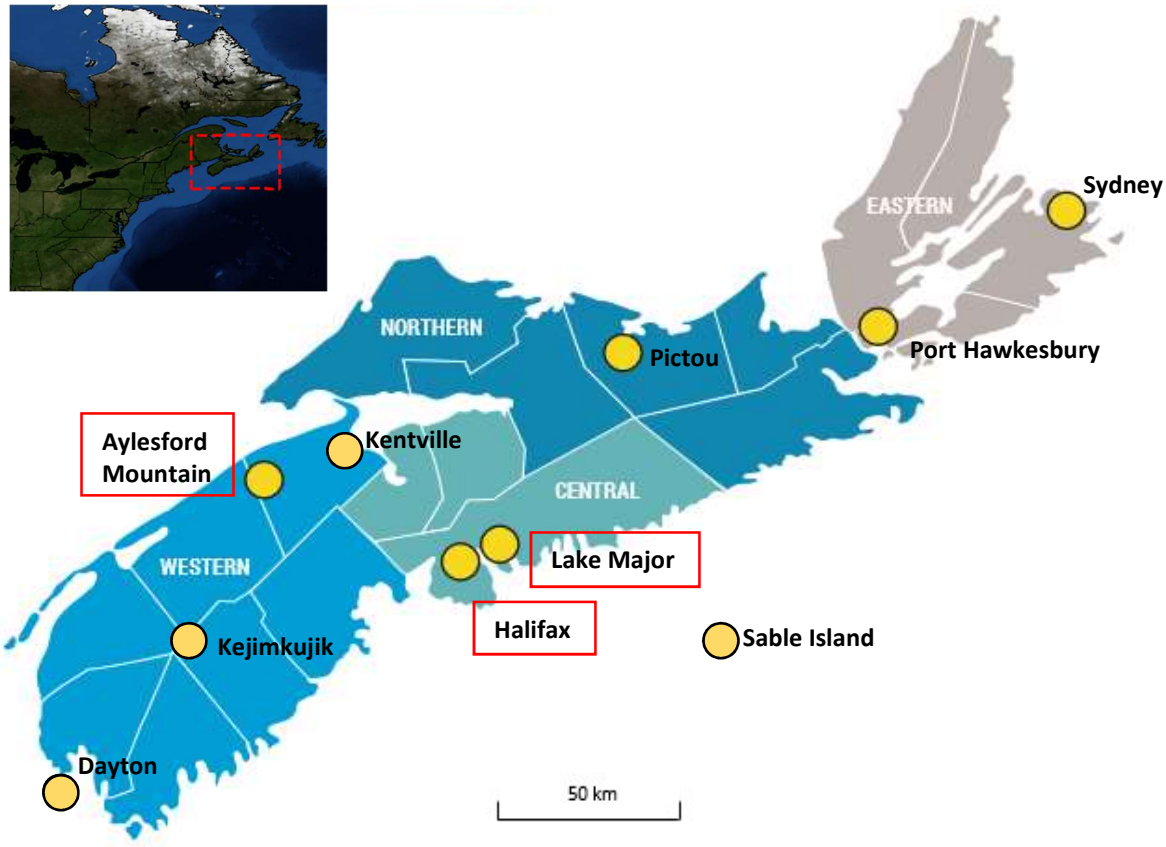


Figure 14. NAPS station locations across Nova Scotia with the three main stations analyzed in this work enclosed by red boxes. Nova Scotia is broken up into four Air Zones used for air quality management (see Introduction). Map modified from NSE (2019).

Three stations across Nova Scotia were chosen for the time series analysis (Section 3.1) in this study based on their distinct locations (urban, suburban and remote) and greater availability of data (Figure 14, Table 2). Other stations available in the NAPS network as well as the monitoring period for pollutants at each station are listed in Table S1 in Supplementary Information. The Halifax NAPS station ('urban') is located in its downtown core facing a heavily trafficked street (NAPS ID #30118). This downtown station was relocated to the rooftop on the other side of the building in 2018 (NAPS ID #30113) and has now replaced station #30118. Lake Major is a NAPS station located 12 km downwind of downtown Halifax (NAPS ID #30120) and is representative of a

suburban area with no nearby point sources of pollutants; nevertheless, it is still classified as a large urban area as it is commonly affected by upwind pollution of the urban Halifax core. We chose to analyze Lake Major because it is located far enough from the city centre so as to not directly monitor urban pollution; and at 2 km from the nearest highway, it is a good indicator of how far urban Halifax pollution will extend downstream. The third station is Aylesford Mountain (NAPS ID #30701), classified as a regional background site at 235 m elevation, 105 km upwind of Halifax in the western air zone, which receives the largest amount of long-range transported pollution in all of Nova Scotia (NS Department of Environment, 2019). Ozone and its two precursors, NO_x and VOCs, are measured at the Halifax station, but Aylesford Mountain and Lake Major only measure ozone and NO_x (Table 2).

Table 2. Station summary including location, elevation, classification by NAPS and data period.

Station	Coordinates	Elevation (m)	Classification	Data
Halifax	44.64° N 63.57° W	18	Large Urban, population 50,000-99,999	O_3, NO_x, VOC (2000-2018)
Lake Major	44.72° N 63.48° W	68	Large Urban, population 500-9,999	O_3, NO_x (2006-2018)
Aylesford Mountain	45.07° N 64.84° W	235	Background station	O_3, NO_x (2000 - 2018)

To assess the contribution of Nova Scotia's own emissions to ozone formation as well as to long-term ozone and precursor trends, NAPS precursor concentration data is compared to precursor data from an online emissions inventory. The Air Pollutant Emission Inventory (APEI) accounts for all sources of emissions including stationary, marine and land transportation at the provincial level by including reported industry emissions and

emissions estimates for unreported point, line and area sources; biogenic emissions of VOCs are not included. Although NO_x emissions have a short atmospheric lifetime, as do many VOCs, about 45% of Nova Scotia's population lies within the Halifax Regional Municipality, which is also home to Nova Scotia's main shipping port; as such, we assume that a large portion of the provincial-level transportation sector (the largest source of NO_x emissions and a significant source of VOC emissions, see Figure S1 and S2) is attributable to Halifax.

2.3.2 Total ozone and ozone formation potential

Due to the temporary low bias in surface ozone concentrations introduced by NO titration near NO_x emission sources, it is useful to model urban ozone concentrations using total ozone (O_x), which is defined as ozone together with any NO_2 produced in the NO oxidation reaction, but not counting primary emissions of NO_2, which are modelled as 10% of fresh NO_x emissions at the source (Carslaw & Beevers, 2004; Itano et al., 2007). Following Xu et al. (2019) we also refer to ozone lost to titration as $[DO_3]$:

$$[O_x] = [O_3] + [NO_2] - 0.1 \times [NO_x]$$

$$= [O_3] + [DO_3]$$

To assess the contribution of VOCs to ozone production during the study period, the ozone formation potential (OFP) is calculated in each year as the sum of the annual average individual VOC concentration ($[VOC_i]$) weighted by the maximum incremental reactivity constant of each individual VOC species (MIR_i), as calculated by Carter (1994) and applied previously by Yan et al. (2017):

$$\text{OFP} = \sum_i [VOC]_i \times MIR_i$$

The OFP gives the grams of ozone produced for each gram of VOC added. The reactivity of biogenic VOCs (BVOC) is assessed separately and includes isoprene, cymene, pinene, limonene and camphene, following the methodology used by Pugliese et al. (2014) in examining precursor reductions on ozone concentration in Toronto.

2.3.3 Statistical analysis

Quantification of long-term changes in data is given by linear regression analysis with square of Pearson correlation coefficient calculated for all regressions. Use of the parametric Pearson coefficient assumes the data follows a normal distribution, which is unlikely for air quality data. However, due to the widespread use of the method in the literature for air quality research, we also adopt it in our analysis as the most understood method. The Pearson coefficient and other statistics were calculated using Matlab 'fitlm' function. P values less than 0.1 are considered significant.

2.3.4 Method for diagnosing transported pollution days

To expand our understanding of how transported pollution affects surface ozone levels in Nova Scotia, we developed a method to diagnose transported pollution days throughout the study period (2000-2018). The method (outlined below) is based on the assumption that, if multiple NAPS stations across the province show high positive anomalies of ozone concentration on the same day, then regional pollution transport must be occurring, since many of these stations are in rural locations with few local sources of NO_x precursor emissions. The method consists of three steps:

1) Select days when ozone concentrations are elevated in Halifax ("elevated ozone days"). We classified these as days when the daily maximum ozone concentration measured in Halifax exceeded the top quartile (75^{th} percentile) of the daily maximum concentrations for that month. Using monthly instead of annual statistics avoids

seasonal bias in data selection due to the seasonal cycle of ozone in Halifax, which exhibits a pronounced springtime maximum as outlined in section 3.1.1. This selection resulted in 1444 elevated ozone days to be further analyzed for possible regional transport signatures by the algorithm.

2) For each of these 1444 days, determine whether ozone concentrations are "elevated" at other stations across Nova Scotia. For each station, we base this on comparing the daily maximum ozone concentration (hourly resolution) to the respective monthly mean of the daily maxima. Ozone concentrations are considered to be elevated if a station exhibits a positive anomaly within the top quartile (75^{th} percentile) of anomalies at each station.
3) Determine whether "enough" stations other than Halifax (maximum of 9) experience elevated ozone to indicate a widespread elevated-ozone day that is likely caused by pollution from another source, i.e. transported upstream pollution. This is based on a given percentage threshold of stations (xx), calculated among either all Nova Scotia stations (ALL_{xx}) or only 'indicator' Nova Scotia stations (IND_{xx}).

The threshold selection in step 3 influences the number of elevated ozone days that get classified as being related to transported upstream pollution. We define two sets of thresholds to represent a lower and upper estimate on the classification. For the lower estimate we require 100% of stations (with data available) to pass the criteria outlined in (2) and refer to this as ALL_{100}. For the upper estimate, these thresholds are set to 50% of stations (with data available) exhibiting a daily maximum ozone concentration anomaly that is in the top quartile of anomalies from the monthly mean of the daily maxima at each station (ALL_{50}). Since transboundary pollution is predominantly transported into

Nova Scotia from northeastern USA (NSE, 2019), the likelihood of this pollution being received by stations to the northeast of Halifax is decreased due to air mass dispersion. Moreover, at least two of these northeastern Nova Scotia stations (Pictou and Sydney) have substantial local NO_X and VOC pollution sources, which may cause their ozone anomaly time series not to be strongly correlated with Halifax. To account for this, we repeat the analysis using three NAPS stations that are located upwind of Halifax in the Western air zone, which is the first air zone to receive transboundary pollution from northeastern USA (NSE, 2019). These stations (Dayton, Kejimkujik, and Aylesford Mountain) are also in rural locations, distant from local pollution sources, which we therefore consider to be key "indicator" stations for transported pollution. We apply the same lower and upper estimate criteria as outlined above to these stations, which we refer to as IND_{100} and IND_{50}, respectively.

2.4 Results and Discussion

2.4.1 Analysis of ozone time series

2.4.1.1 Monthly variations

Monthly variations of hourly surface ozone from 2006-2018, when data were available at all three representative stations, are shown in Figure 15. All stations show a peak in median ozone in March and April (26 ppb, 36 ppb and 41 ppb at urban Halifax, suburban Lake Major and remote background Aylesford, respectively), which corresponds to the spring peak characteristic of the Northern Hemisphere. This spring maximum is understood to be caused by stratosphere-troposphere exchange as well as increasing photochemistry acting on a build-up of NO_x (as PAN) and hydrocarbons from the winter season (Monks et al., 2015; Vingarzan, 2004). The seasonality in Nova Scotia is different from other Canadian cities like Toronto and Windsor, which show an ozone peak (in

mean values) in the summer season, presumably due to higher ozone precursor emissions and higher continental surface temperatures there, both of which promote ozone production (Whaley et al., 2015; Xu et al., 2019). The seasonal cycles for Halifax, Aylesford and Lake Major follow the same pattern found by Chan and Vet (2010, Figure 6, albeit based on earlier data from 1997-2006) for "coastal eastern Canada" in their study, with a spring peak in average concentrations and high summertime maxima (not medians or average concentrations) shown by the gray outliers in Figure 15. Ozone at Aylesford is the highest in part because of its elevation of 250m above sea level. According to a European MOZAIC study (Chevalier et al., 2007) the vertical ozone gradient is 30 ppb/ km, meaning that Aylesford Mountain ozone can be 7.5 ppb higher due to its elevation alone. Halifax has the lowest ozone due to large NO_x emissions causing temporary suppression of ozone through titration. Lake Major shows average ozone concentrations because it is neither an urban nor an elevated remote station. Median concentrations at all stations reach a low in September (16 ppb, 20 ppb and 26 ppb at Halifax, Lake Major and Aylesford, respectively), again showing that hemispheric processes are the driving factors of seasonality in Nova Scotia, unlike at more densely populated and continental urban centres.

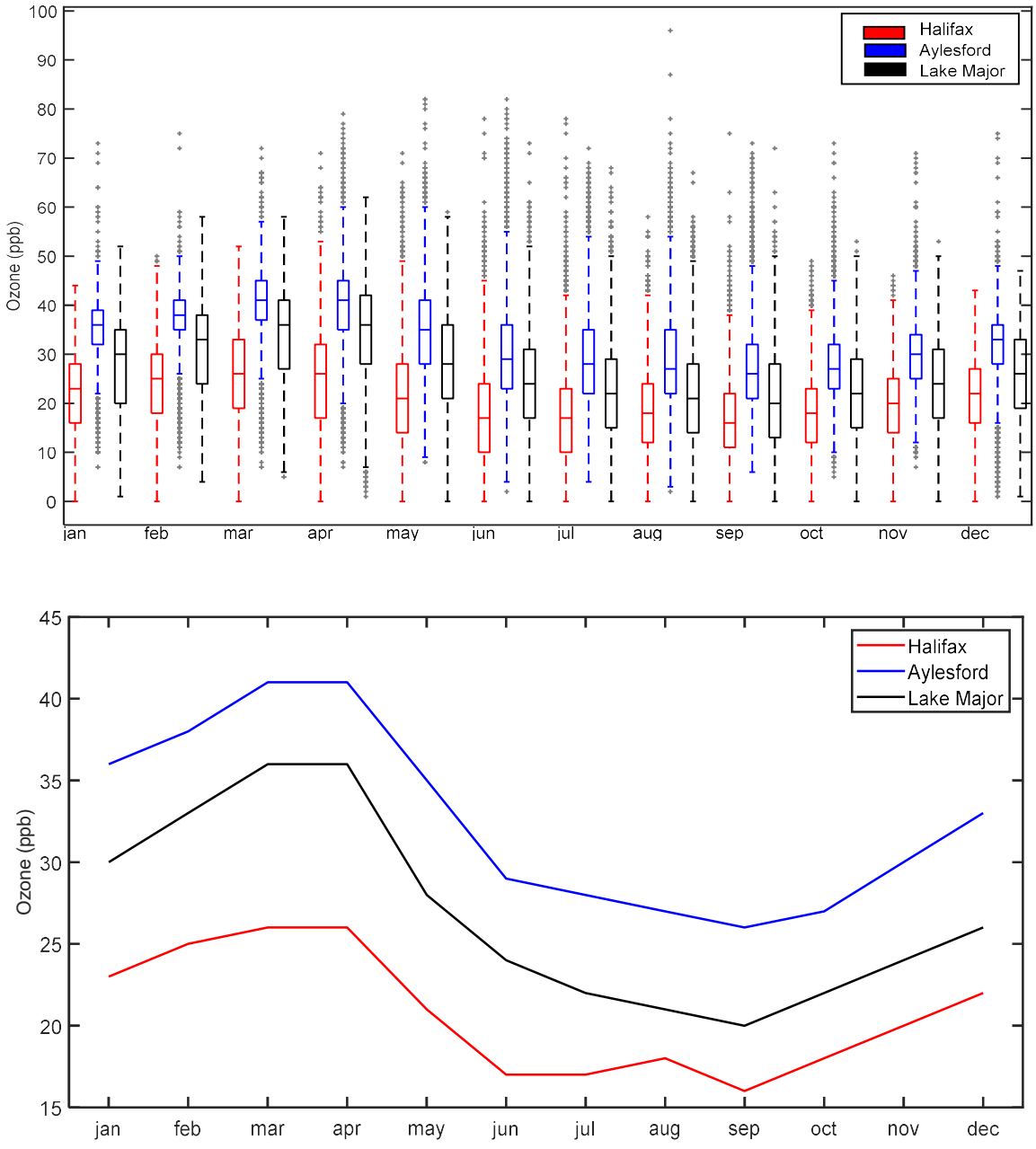


Figure 15. (top) Monthly variation of hourly ozone at Halifax (urban core), Lake Major (suburban), and Aylesford (remote background) when data was available at all three stations (2006-2018). (bottom) Corresponding monthly median ozone concentrations shown separately for clarity. Boxplot properties are described in Figure 15.

2.4.1.2 Long term trends

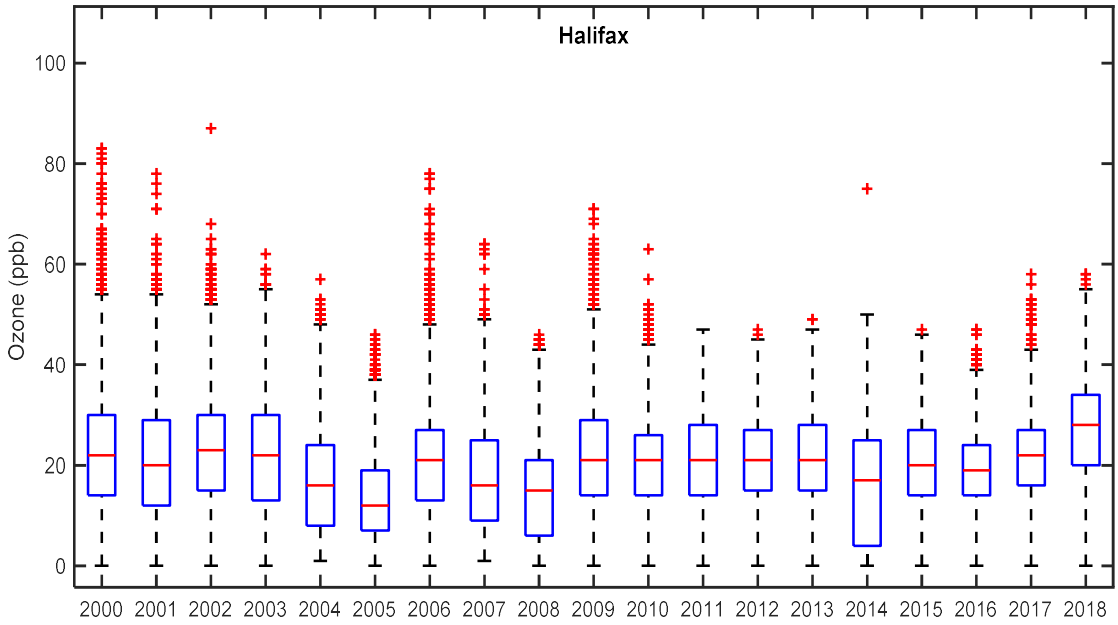
The long-term annual variations of hourly surface ozone are shown in Figure 16 between 2000 and 2018, using all available data during this time period. Aylesford Mountain has the highest average median (30 ppb) ozone concentrations across all years, in part due to the elevation of this remote background station without any local NO_x emissions. Suburban Lake Major shows the second highest average median ozone levels (25 ppb), while the urban Halifax station shows the lowest (20 ppb). According to Chan and Vet (2010) the annual average 'baseline' mixing ratio is 27 ppb for coastal Eastern Canada, which is in best agreement with the annual average of Lake Major, i.e., the station that is neither elevated nor in close proximity to NO_x sources.

Table 3 shows the slopes and statistics (R^2, p-value and standard error) for temporal trends during the common data period (2006-2017) in the annual maximum ozone values (i.e., the top whiskers in Figure 16 boxplot, below the outliers, which represents 99th percentiles), as well as the annual 75th percentile, median and 25th percentile ozone values. To avoid possible confounding effects of the Halifax station relocation (see methods section 2.3.1), 2018 data was excluded from this analysis. The 99th percentile ozone is decreasing at all stations (2006-2017) with mixed significance: -0.77 ppb/year at Halifax (p=0.02), -0.02 ppb/year at Lake Major (p=0.94) and -0.65 ppb/year at Aylesford (p=0.03). This is likely due to successful precursor emissions reductions over the last decade locally (especially for the Halifax trend) and upstream (especially for the Aylesford trend) in Canadian as well as transboundary source areas in northeastern USA (Chang et al., 2017). While the top whisker ozone changes at Lake Major are close to zero and clearly not significant, annual 75th percentiles, medians and 25th percentiles at this location are strongly increasing (as compared to Halifax and Aylesford) and with

significance ($p < 0.01$). We attribute this to a reduced ozone titration effect in upwind Halifax due to decreasing NO_x emissions there (discussed below), which affects ozone concentrations measured at downwind sites. While not significant, the weakly increasing Halifax annual 25th percentile and median ozone is also likely driven by the decreasing titration effect in downtown Halifax. Similar upward trends in ozone caused by decreasing NO_x emissions have been reported elsewhere in Canada (e.g., Ainslie et al., 2018), the rural United States (Cooper et al., 2012) and eastern China (Wang et al., 2019). The combination of decreasing maximum ozone values alongside rising regional background levels are seen in many areas in the Northern Hemisphere like the Contiguous USA (e.g., Simon et al., 2015), as well as Northern Europe (e.g., Karlsson 2017).

The much smaller increases in annual median and 25th percentile ozone at Aylesford (a regional background station) are not significant and thus are not being interpreted here as representative of rising global background ozone levels in the Northern Hemisphere (Monks et al., 2015; Tarasick et al., 2019). In fact, we analyzed trends in the longer time period (2000-2018, see Table S2 in Supplementary Information) and found significant ($p < 0.06$) *decreasing* annual median and 25th percentile ozone levels, which confirms that the Aylesford background station is more representative of a regional, rather than a global background (the latter also referred to as a 'baseline'). This is consistent with the recent work of Parrish et al. (2019) in two ways: first, Aylesford is unable to sample global baseline ozone levels since it is not on the western margin of North America (in fact, the opposite is true and Aylesford samples North American pollution outflow); second, as shown by the nonlinear trend analysis in their work, baseline ozone levels have in fact

stopped increasing in the mid-2000's and have begun decreasing, thus even a baseline monitoring station should show decreasing trends from 2006 onwards. Finally, in the longer time period (2000-2018), the decreasing trend in maximum ozone doubles and is statistically significant in Aylesford at a higher level (-0.65 ppb/year, p=0.03 → -1.21 ppb/year, $p < 0.01$), clearly pointing to the strong regional influence on this station.



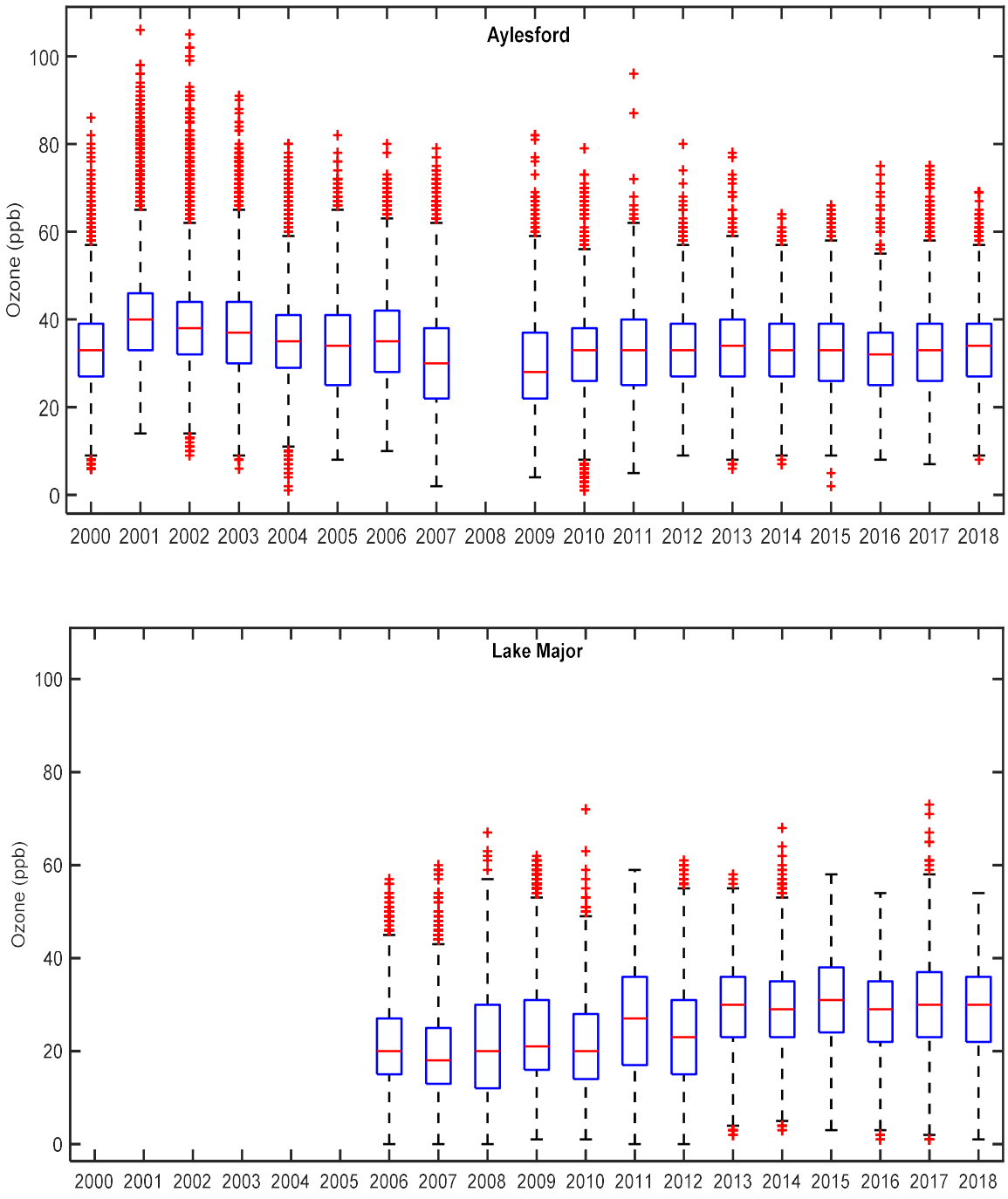


Figure 16. Annual variation of hourly ozone concentrations from 2000-2018 at Halifax (urban core), Lake Major (suburban background) and Aylesford (remote background). Boxplot properties are described in Figure 15. Note the Lake Major station came online only in 2006 and the Aylesford Mountain station was offline in 2008.

Table 3. Slope and statistics (square of the Pearson coefficient (R^2), p-value and standard error (STE)) for metrics derived from boxplots of hourly ozone values in Figure 16 for 2006-2017, when data overlapped at all stations. Slopes corresponding to $p < 0.1$ are shown in bold red.

Metric		Halifax (urban)	Lake Major (suburban)	Aylesford (regional background)
Upper whisker value (99.3 percentile)	Slope (ppb/year)	**-0.77**	- 0.02	**-0.65**
	R^2	0.46	0.01	0.42
	p-value	0.02	0.94	0.03
	STE	0.27	0.31	0.26
75th percentile	Slope (ppb/year)	0.06	**1.03**	-0.10
	R^2	0.01	0.74	0.06
	p-value	0.74	< 0.01	0.45
	STE	0.19	0.19	0.13
Median	Slope (ppb/year)	0.19	**1.23**	0.11
	R^2	0.08	0.81	0.04
	p-value	0.36	< 0.01	0.55
	STE	0.47	0.19	0.17
25th percentile	Slope (ppb/year)	0.31	**1.09**	0.15
	R^2	0.08	0.76	0.07
	p-value	0.36	< 0.01	0.42
	STE	0.32	0.19	0.18

2.4.1.3 *Diurnal variation and trends of O_3 and O_x*

Diurnal variations of NO_x and ozone are plotted for Halifax (urban core), Lake Major (suburban), and Aylesford (remote background) in 2017 to examine the relationship between ozone and NO_x in the most recent year before the Halifax station was relocated and NO_x measurements ceased at Aylesford Mountain (Figure 17). The downtown Halifax station is subject to high NO_x emissions due to heavy vehicle traffic during the morning rush hour (07:00 – 10:00) and there exists a corresponding strong inverse relationship between NO_x and O_3, driven by NO titration of O_3 during this time.

Although the urban center of Halifax also experiences a pronounced afternoon rush hour, the build-up of NO_x is limited by vigorous boundary layer mixing and, at times, the sea breeze effect, which facilitates the dispersion of pollutants throughout the course of the day and limits ozone titration in the afternoon.

Since the titration effect only occurs close to the source of emissions, there is no signature of rush hour titration of ozone at Lake Major, which is ~12 km outside the urban core; moreover, NO_x concentrations at Lake Major are ten times lower than in Halifax. Lake Major NO_x begins to rise approximately one hour later (08:00) than Halifax and peaks from 08:00 - 09:00, consistent with transport from the urban core rather than local sources; the 12 km distance of Lake Major from the urban core dictates transport times of around one hour at low wind speeds (< 12km/hr). The afternoon increase in ozone at Lake Major means that the suburban station maintains a pattern of photochemistry that peaks in the afternoon (Bloomer et al., 2010), i.e., with a peak in ozone from 12:00 – 16:00. This timing of maximum ozone driven by photochemistry is shared with the smaller amplitude and broader peak of ozone at the background Aylesford station, which, as a remote station, has even lower NO_x than suburban Lake Major. During times of suppressed mixing overnight (20 h – 08 h), ozone at Lake Major is consistently lower by ~6 ppb than at Aylesford, which may be due to a combination of differing rates of ozone loss by surface deposition and the elevated station location at Aylesford (discussed above).

To assess the effect of decreasing NO_x emissions on ozone in downtown Halifax both total ozone (O_x) and NO_x concentrations are plotted in 6-year intervals in Figure 18. Strode et al. (2018) found that the diurnal cycle of rural ozone concentration is compressing in magnitude between daily maximum and minimum values due to NO_x reductions in northeastern USA; likewise, the diurnal cycle of O_x compressed in Halifax from 6.4 ppb in 2000-2005 to 4.7 ppb in 2012-2017. While morning rush hour NO_x concentrations in 2000-2005 reached ~85 ppb, this decreased to less than half (~35 ppb; a 59% decrease) between 2012-2017 but resulted in only a 0.2 ppb decrease (<1%) in the corresponding morning rush hour (08:00) total ozone. The decrease in late afternoon (17:00) NO_x between 2000-2005 and 2012-2017 was 44 ppb, resulting in a 2.4 ppb decrease in the corresponding afternoon rush hour total ozone. The relative change at 17:00 between the 2000-2005 and 2012-2017 was a 61% decrease in NO_x and a 7% decrease in total ozone. The disproportionate change in hourly average ozone is consistent with a VOC-sensitive production regime that is characteristic for downtown areas in urban centers, and requires larger reductions in VOCs to reduce ozone (Sillman, 1999). While we may continue to try to decrease NO_x emissions, Figure 18 shows that this may not meaningfully decrease ozone concentrations in downtown Halifax, without further reductions in VOCs.

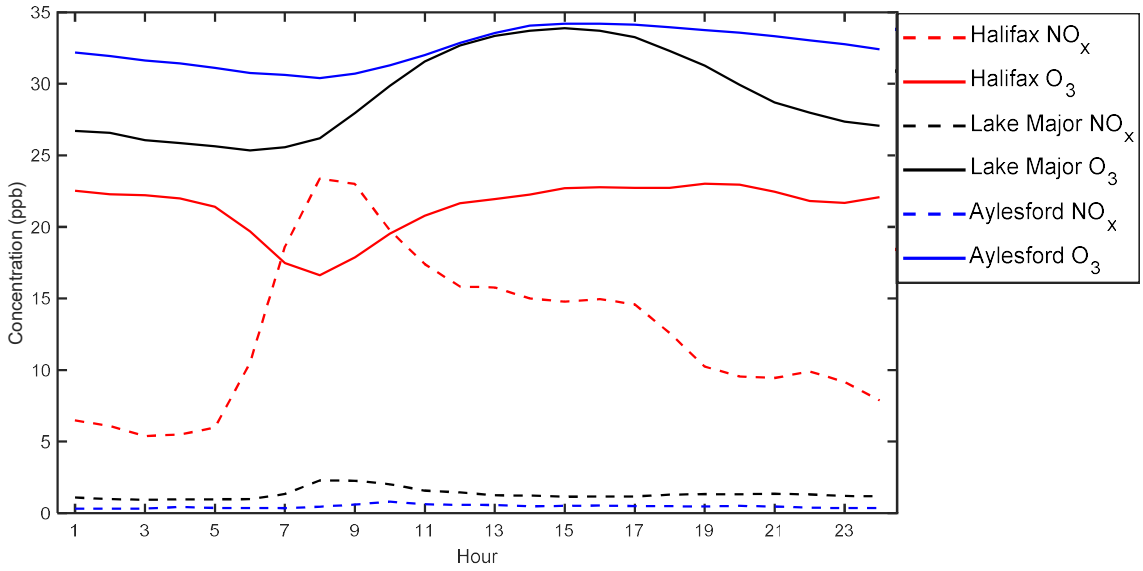


Figure 17. Diurnal variation of hourly NO_x and O_3 at Halifax (urban core), Lake Major (suburban), and Aylesford (remote background) in 2017.

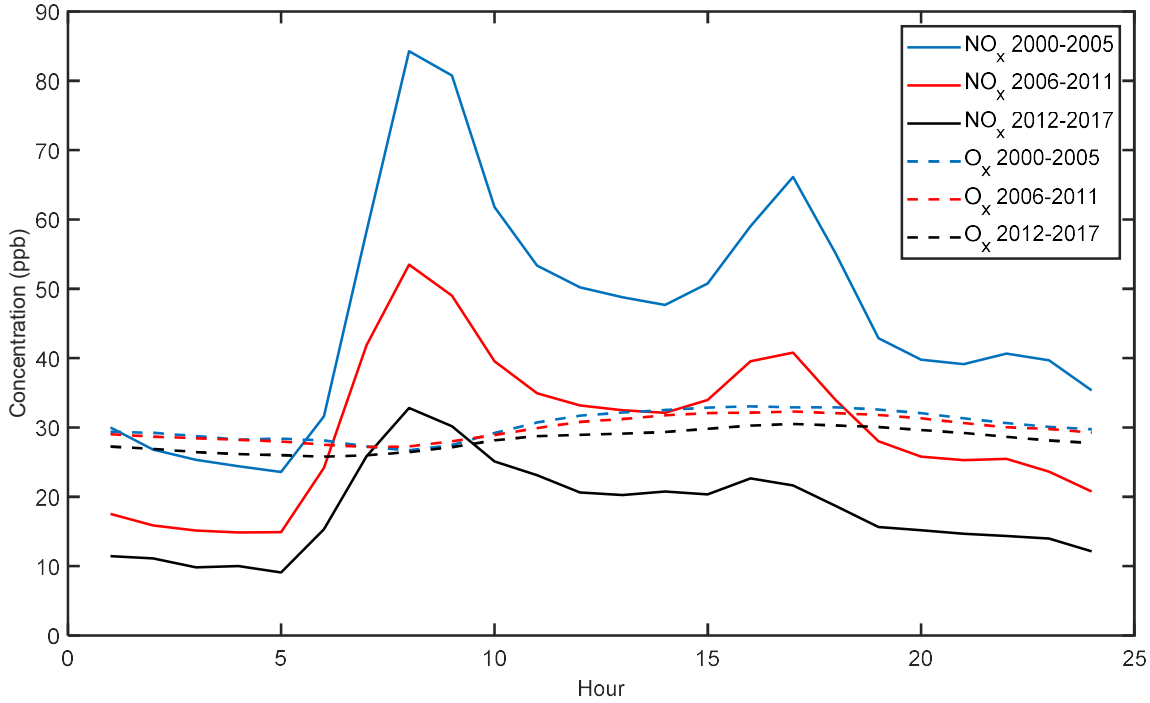


Figure 18. Diurnal variation of hourly NO_x and O_x at Halifax (urban core), binned into 6 year intervals.

Next, we take the observed titration effect into account for the long-term ozone trend analysis in Halifax (Figure 19). During 2000-2017 the annual median ozone concentration in Halifax showed effectively no change (0.02 ppb/year; p=0.88), while the annual median DO_3 (loss of ozone due to titration) decreased by -0.42 ppb/year ($p < 0.01$), which in part explains the lack of detectable change in median ozone concentrations over the same period. However, median total ozone (O_x), i.e., ozone accounting for the local and temporary titration effect near the observation station, decreased by -0.44 ppb/year (p=0.02), resulting in a total decrease of 7.9 ppb over this period, which is consistent with steady precursor reductions reported and measured in Halifax and regionally. This shows the importance of examining total ozone in an analysis of the effects of precursor reductions on ozone in the downtown core. Similarly, Canada's most populous province of Ontario has reported select annual average VOC concentrations decreasing by 28-53% at seven urban stations over the 10-year period from 2007-2016, together with a 30% decrease in annual average NO_2 concentration based on 31 sites, but a 1% *increase* in surface ozone during this period, based on 39 sites (10 classified as "roadside"). This lack of a proportional ozone decrease is thought to be, in part, due to the decreased titration effect (Ontario Ministry of the Environment and Climate Change, 2016).

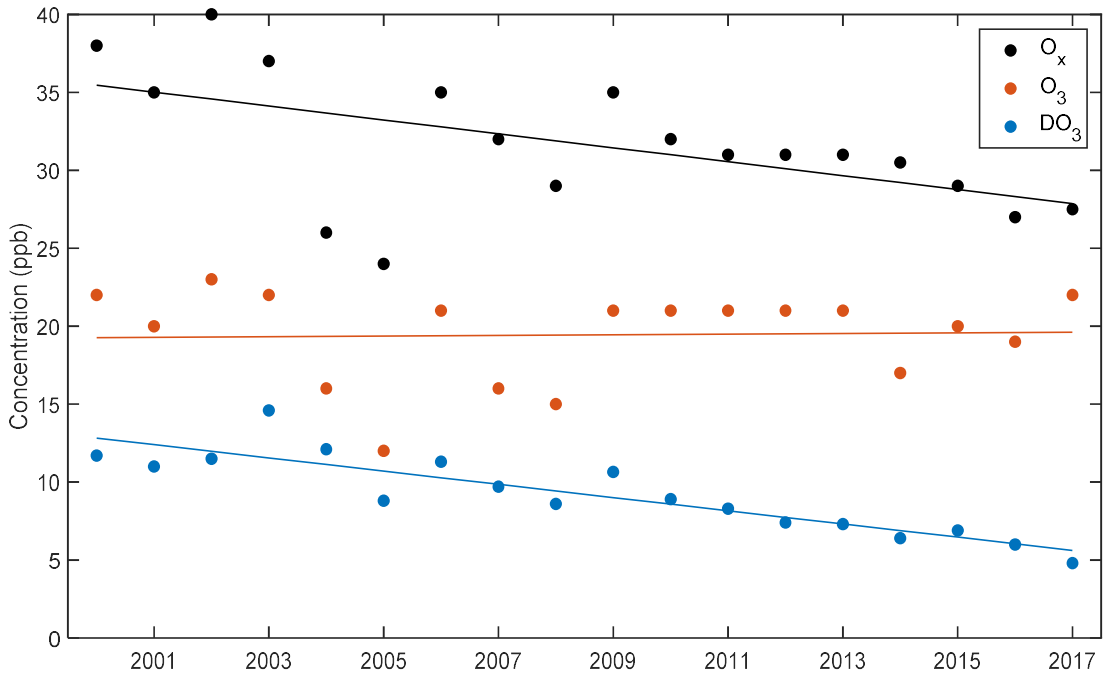


Figure 19. Long-term annual medians of hourly measured ozone (O_3), calculated ozone lost to titration by NO (DO_3) and corresponding total ozone (O_x) at Halifax (2000-2017).

Table 4. Statistics for trends corresponding to Figure 19.

pollutant	**slope**	**p-value**	**STE**	**R^2**
DO_3	-0.42	< 0.01	0.06	0.79
O_3	0.02	0.88	0.14	0.01
O_x	-0.44	0.02	0.17	0.30

2.4.2 Precursor concentration and emissions trends

Since VOCs and NO_x are both precursors to ozone production, we examine the relationship between their concentrations and the underlying emissions reductions and, in the case of VOCs, the relationship with ozone formation potential, which accounts for the variable reactivity of different VOCs. Emissions of NO_x and VOCs have been decreasing since 1990 in North America as a result of the Canada-United States Air Quality Agreement (Environment and Climate Change Canada, 2017). In Canada, NO_x emissions from the transportation sector (the largest NO_x source sector) have decreased rapidly

since 2000 (CCME, 2017). Annual average NO_x concentrations (NAPS) are plotted along with annual average provincial-level NO_x emissions (Figure 20). Linear regressions of annual mean NO_x values included for both emissions and concentrations (Table 5) show that NO_x concentrations are decreasing significantly (-2.34 ppb/year, $p < 0.01$), in tandem provincial-level transportation emissions (-2180.6 tonnes/year, $p < 0.01$).

Linear regressions are also included for the most recent 7 years, 2012-2018, chosen to follow reports of a slowdown of NO_x emissions reductions in recent years (discussed above). Although the period is short, statistically significant differences from the long-term trends are apparent (Table 5), with emissions of NO_x decreasing at a slower rate (-1731 tonnes/year, $p < 0.01$), possibly responsible for the slightly decreasing rate of NO_x concentrations reductions (-2.12 ppb/year, $p < 0.01$). The reasons behind the apparent decreasing effectiveness of NO_x emissions reductions in reducing NO_x concentration burdens may be related to NO_x pollution transported from upstream sources in temporary reservoirs (i.e., PAN) from regions where NO_x emissions are rising (Chang et al., 2017; Jiang et al., 2018), and/or the increasing importance of organic NO_x reservoirs (Romer Present et al., 2020), as well as the actual slowing of reductions in provincial emissions. Longer time series of concentration observations and reported emissions are necessary, as well as consideration of meteorologically driven variations (Kroll et al., 2020).

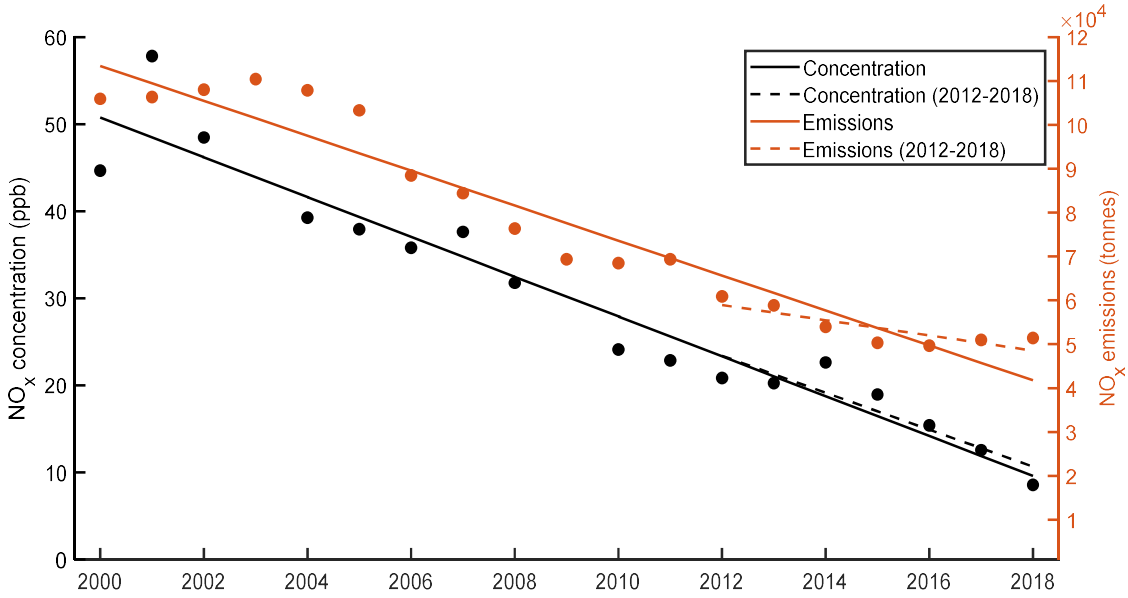


Figure 20. Annual average measured NO_x concentrations in Halifax (NAPS); annual estimated NO_x emissions in Nova Scotia (APEI, province-wide). Linear trends are plotted for regression analyses performed on the full time periods of data availability and the restricted period of 2012-2018 (see text for details and Table 5 for linear regression results).

Table 5. Statistics for NO_x concentration, [NO_x], and emission trends corresponding to Figure 20.

	Slope (unit/year)	p-value	STE	R^2
[NO_x] (2000-2018; ppb)	-2.34	< 0.01	0.24	0.85
[NOx] (2012-2018; ppb)	-2.12	<0.01	0.45	0.82
NO_x emissions (2000-2018; tonnes)	-3982.30	< 0.01	260.19	0.93
NO_x emissions (2012-2018; tonnes)	-1730.90	0.02	498.41	0.71

Next, annual average VOC concentrations measured in Halifax (NAPS) are plotted together with annual average reported VOC emissions for Nova Scotia (APEI), and calculated OFP (Figure 21). Trends from linear regressions of yearly mean values for the full study period, and for the restricted period of 2012-2018 are also included (regression details are given in Table 5). VOC concentrations are decreasing across the full study period (-3.41 µg/m^3/year, $p < 0.01$), in tandem with decreasing VOC emissions (-1680

tonnes/year, $p < 0.01$). The reactivity of the VOC mixture, as indicated by the OFP, is also decreasing (-9.66 $\mu g/m^3$/year, $p < 0.01$). As is the case with NO_x emissions and concentrations, there is an indication of different trends for the latter portion of the time series. This is especially notable for VOC emissions, which appear to have levelled off during this period, as indicated by a trend that is approximately 10 times weaker than for the full study period and shows no statistically significant difference from zero. According to emissions inventory data, emissions from the three largest sectors (transportation, residential / commercial / institutional, and electric power generation) appear to be rising or levelling off in the last four years (see Supplementary Materials Figure S1). Consistent with the above, the average annual VOC concentration decrease between 2012 and 2018 has slowed by nearly a factor of two (-1.91 $\mu g/m^3$/year, $p=0.04$) and the corresponding OFP decrease slowed by more than a factor of two (-3.78 $\mu g/m^3$/year, $p=0.05$).

By mass, biogenic VOCs make up the majority of all Nova Scotia VOC emissions (Nova Scotia Environment, 2009), however, based on their OFP they account for a small amount of total VOC reactivity. OFP from biogenic VOCs has been relatively constant over the study period; in 2018 it was responsible for 3.5 $\mu g/m^3$ of the total 50.4 $\mu g/m^3$, or 7% of the total OFP for the year (Figure 21). If – or when – anthropogenic VOC emissions begin to decrease again, biogenic VOCs will become more important in local ozone production. Since biogenic emissions are highly temperature-dependent, they are projected to increase in a warmer climate. Finally, since they cannot be regulated, biogenic emissions are of relevance to Halifax due to its setting in the forested province of Nova Scotia.

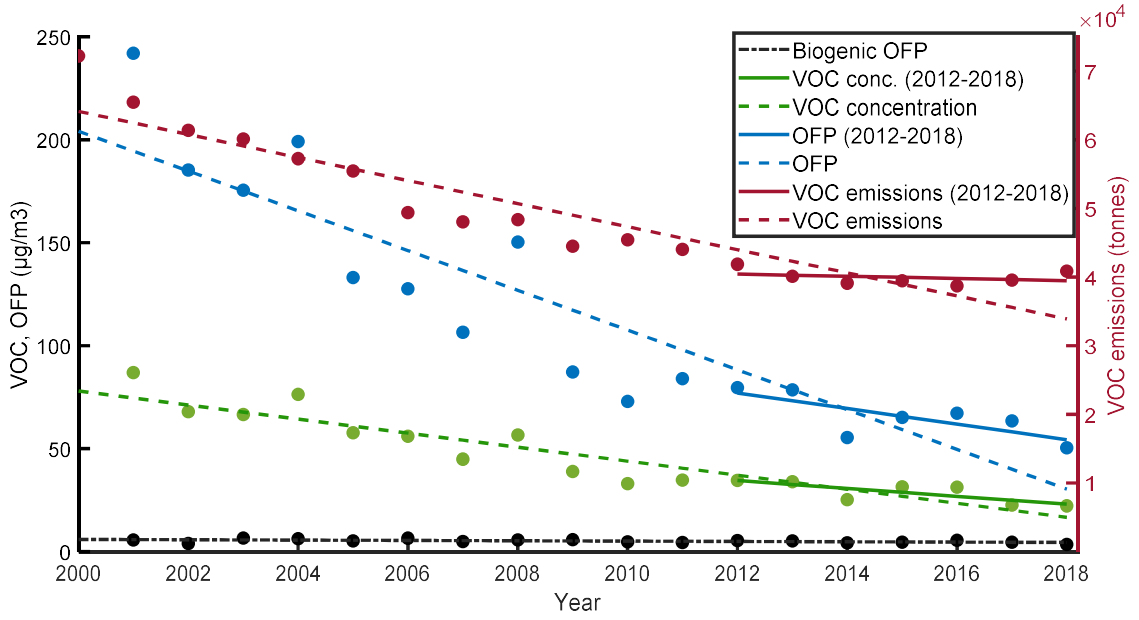


Figure 21. Annual average measured VOC concentrations in Halifax (NAPS) and annual reported VOC emissions (APEI, province-wide). The OFP is calculated for all NAPS VOC species and also separately for biogenic species only. Linear trends are also plotted for regression analyses performed on the whole time period of data availability, and for the restricted period of 2012-2018 (see text for details and Table 6 for further information on linear regression results).

Table 6. Statistics for VOC concentration, [VOC], and emission trends, as well as OFP for all NAPS VOCs and biogenic NAPS VOCs in isolation, corresponding to Figure 21.

(unit)	Slope (unit/year)	p-value	STE	R^2
[VOC] 2001-2018 (µg/m^3)	-3.41	< 0.01	0.32	0.87
[VOC] 2012-2018 (µg/m^3)	-1.91	0.04	0.68	0.62
VOC Emissions 2000-2018 (tonnes)	-1680.00	< 0.01	153.10	0.88
VOC Emissions 2012-2018 (tonnes)	-158.30	0.49	214.10	0.01
OFP 2001-2018 (µg/m^3)	-9.66	< 0.01	1.11	0.83
OFP 2012-2018 (µg/m^3)	-3.78	0.05	1.48	0.57
Biogenic OFP 2001-2018 (µg/m^3)	-0.08	0.03	0.04	0.26

2.4.3 Transport influence

Episodic studies provide evidence that transported air from the United States underlies elevated surface ozone in coastal, southern Nova Scotia (Farrell 2006, Gong et al., 2000 and Kleinman et al., 1996). The Western air zone of Nova Scotia, monitored primarily via the Aylesford Mountain station, shows statistically significant decreasing ozone concentrations in all percentile categories (Table S2, 2000-2018), which suggests that this regional background site continues to be influenced by net decreasing transboundary pollution sources, albeit with interannual variations (NS Department of Environment, 2019).

Given that many Nova Scotia air quality monitoring station locations have few local sources of precursor emissions, we reason that regional pollution transport days are in progress when most NAPS stations across the province show high positive anomalies of ozone concentration on the same day. A representative example of such an event is shown in Figure 22, where all active monitoring stations show a daily maximum ozone concentration that is between 17% and 84% (58% in Halifax) above the monthly mean of the daily maxima on June 11, 2015. Positive anomalies are the largest at Aylesford and Kejimkujik, two of the three stations we chose as key indicator stations for transport. Smaller anomalies are seen at stations in the Eastern air zone where the air mass has likely been diluted before reaching these stations, or where surface ozone may be on average higher due to local precursor emissions.

A backward trajectory ensemble calculation was performed using the HYSPLIT model (Stein et al., 2015), ending in Halifax at 20:00 AST (00:00 UTC, June 12), the time when ozone hourly concentrations reached their maximum in Halifax. The air mass arriving in

Halifax at this time is traced back broadly to the northeastern USA, which encompasses several densely populated and industrial regions that are well known ozone precursor and ozone pollution sources. The transport trajectory ensemble was initiated at 500 m above ground level and remained confined mostly to < 1000 m altitude in the 24 hours of transport. The ensemble trajectory is constructed from starting points offset by one grid point in X, Y and Z to produce 27 trajectory members shown in different colours in Figure 22. Meteorological fields from the North American Mesoscale (NAM) Forecast System, with a horizontal resolution of 12 km, were used in the calculation.

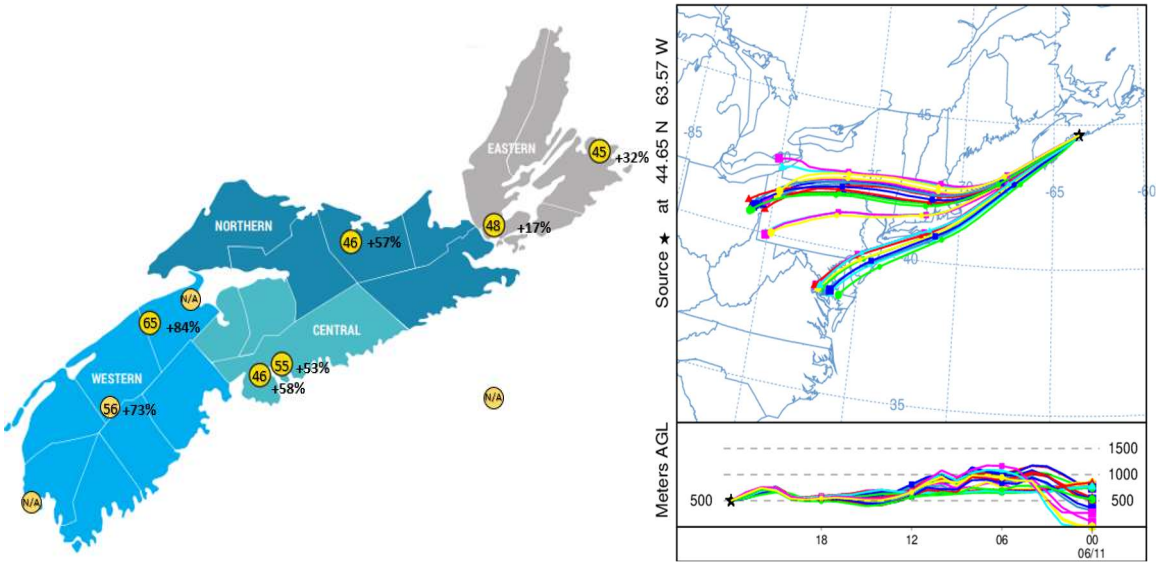


Figure 22. (Left) Province-wide elevated ozone pollution event indicative of regional pollution transport (June 11, 2015). One-hour maximum ozone concentrations (ppb) are noted within the yellow NAPS station circles, with percent differences from the monthly mean of the daily maxima adjacent to each station (58% in Halifax). (Right) HYSPLIT backward trajectory ensemble ending in Halifax at 00:00 UTC (20:00 AST).

In contrast to what is most likely a regional pollution transport event above, Figure 23 shows an example of a high ozone episode in Halifax on September 12, 2014 (daily maximum 160% above monthly mean of daily maxima) that does not correlate with elevated ozone at any other station, including the upwind key indicator stations. This high

ozone anomaly confined to Halifax is therefore likely a result of local production. The HYSPLIT ensemble trajectory calculation shows air masses arriving primarily from northern Ontario via southern Quebec, Maine and New Brunswick. The continental air masses had contact (< 1000 m altitude) with densely forested areas, but also Québec City (population 800,000) and, within the last six hours of transport, St. John (population 126,000), which is home to Canada's largest oil refinery at 320,000 barrels / day. As such, these air masses may have been VOC-rich, leading to increased ozone production in Halifax's VOC-limited regime.

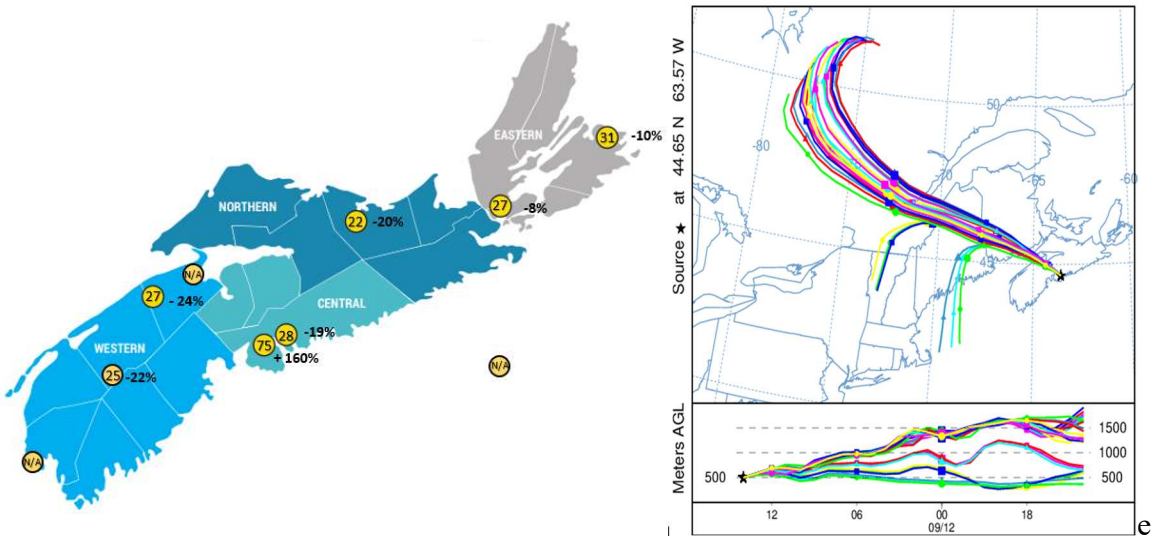


Figure 23. (Left) Elevated ozone pollution day confined to Halifax (+160%) and indicative of local ozone production (September 12, 2014). One-hour maximum ozone concentrations (ppb) are noted within the yellow NAPS station circles, with percent differences from monthly mean of the daily maxima adjacent to each station. (Right) HYSPLIT backward trajectory ensemble ending in Halifax at 14:00 UTC (10:00 AM AST).

Building on these two case studies, we quantify the proportion of "elevated ozone days" in Halifax – which we define as days where the daily maximum ozone concentration exceeds the 75th percentile of the daily maximum concentrations for a given month – that show evidence of being related to transported upstream pollution, as opposed to local

production. Our method is outlined in detail in Section 2.3.4; briefly, it is based on the assumption that, if multiple NAPS stations across the province show high positive anomalies of ozone concentration on the same day, then regional pollution transport must be occurring since many of these stations are in rural locations with few local sources of precursor NO_x emissions. Using this method, we link between 273 (19 %) and 912 (63 %) of 1444 elevated ozone days in Halifax to transported upstream pollution (Table 7), based on the lower and upper estimate threshold criteria outlined in Section 2.3. The lower estimate (19% from ALL_{100}) is certainly an underestimate of the real number of transport days since it depends on *all* stations in the province showing top quartile daily maximum ozone anomalies. This is likely a rare occurrence owing to, e.g. differing air mass trajectories and pollutant deposition or dispersal between the most southwestern and most northeastern stations in the province (a distance of at least 500 km; see *Figure 14*). The upper estimate (63% from IND_{50}) uses observations at only a subset of three rural stations upwind of Halifax, where the most likely cause of elevated ozone is due to transported pollution. Nevertheless, this result is very similar to ALL_{50} (62% transport-related), which subsumes the three indicator stations. Finally, if 100% of the three indicator stations (with data) are required to correlate with Halifax on elevated ozone, this results in 45% of transport-related pollution in Halifax. This suggests that the true value of transport-related days is likely between 45% and 63%.

We next examine whether there is any temporal change in the proportion of elevated Halifax ozone days that are classified as being transport-related across the study period. Figure 24 shows the percent of elevated ozone days in Halifax that are identified as transport days in each year from 2000 to 2018. Both the lower and upper estimates

(100% vs. 50% of stations) of each selection criterion (all stations vs. only indicator stations) are shown. Statistically insignificant trends of opposite magnitude, also associated with large standard errors, are evident for transport-related pollution event fractions (Table 7) when correlations between all stations are required (ALL_{100} and ALL_{50}). Based on the more reliable indicator stations, significant trends ($p < 0.01$) of a very similar magnitude (0.87%/year for IND_{100} and 0.84%/year for IND_{50}) are observed for the 2000-2018 period, representing ~15% increase over the study period. The increase of transported pollution days over the study period implies that Nova Scotia is becoming more impacted by transboundary emissions given that our local emissions have also decreased; the increasing impact of transboundary emissions is likely associated with decelerating emissions reductions in the main upstream source region in recent years (Jiang et al., 2018). Moreover, there are fluctuations in the proportion of transport days every 2-4 years, likely related to some variability in circulation patterns as well as variability in summertime temperatures at upstream pollution source regions (this is currently under investigation, but beyond the scope of this paper).

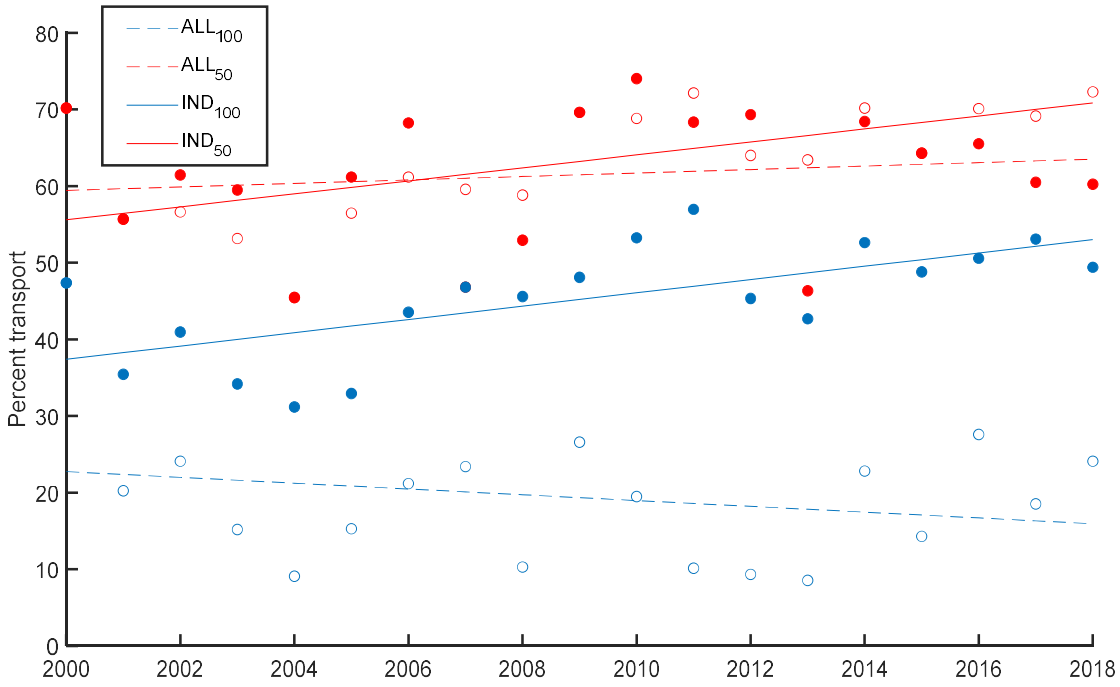


Figure 24. Percentage of elevated ozone days in Halifax (1444 days between 2000 and 2018) that are classified as transported pollution days according to spatial correlation criteria among all Nova Scotia stations (ALL, open circles and dashed lines) and only the indicator stations (IND, closed circles and solid lines). See text for details and Table 7 for linear regression details.

Table 7. Percent of 1444 high ozone events in Halifax identified as transport-related (see text for details) and statistics for the linear regressions shown in Figure 24.

Selection Criteria	**% transport - related (2000-2018)**	**Slope** (% / year)	**p-value**	**STE**	**R^2**
ALL_{100}	19	-0.38	0.34	0.39	0.05
ALL_{50}	62	0.22	0.55	0.37	0.02
IND_{100}	45	0.87	<0.01	0.24	0.43
IND_{50}	63	0.84	<0.01	0.25	0.40

Finally, we examine the monthly distribution of elevated ozone days in Halifax that are classified as transport-related (Figure 12). For clarity, monthly distributions are only plotted for IND_{50} and IND_{100} selection criteria, however, the pattern also holds for ALL_{100} and ALL_{50} selection criteria. Most such days occur in May to October, consistent with

this being the peak ozone production season in upstream source regions. Over the study period (2000-2018) the frequencies shown in Figure 25 represent ~5 transport-related ozone pollution days per month. With 2-3 times less transport days between January and March, when photochemistry is less active, the number of transport-related ozone pollution days is ~1-2 per month. While photochemical ozone production is considered a summertime, urban phenomenon, high ozone production has been noted in the unique circumstances (high precursor emissions, strong temperature inversion, snow cover) near natural gas production fields in Wyoming (Schnell et al., 2009); however, correlated winter time top quartile ozone values at Halifax and the upstream rural indicator stations may also be associated with stratospheric air intrusions. Finally, we note that the peak in transport-related ozone pollution days occurs when ozone concentrations are at their seasonal minima in Nova Scotia (Figure 15).

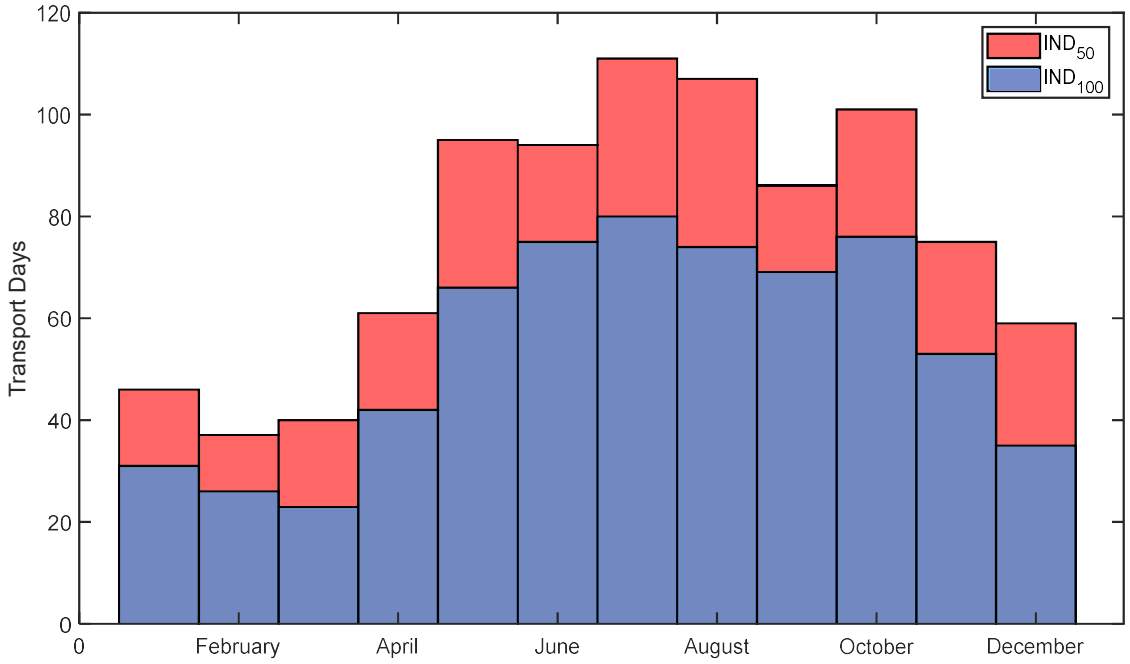


Figure 25. Monthly distribution of transport-related Halifax ozone pollution days (2000-2018), based on correlations with ozone pollution at either 50% (IND_{50}) or 100% (IND_{100}) of rural and upstream indicator stations.

As described in Section 1, the majority of transported North American pollution was found to travel eastward *overhead* of the boundary layer (e.g., 70% reported by Li et al., 2005, in their modeling study), where it is not detectable by surface NAPS stations. The converse of this is that 30% of North American pollution outflow travels eastward *within* the boundary layer, with a strong potential of detection by surface monitoring stations, i.e., in Halifax. However, whereas this past work investigated questions of continental pollution export (e.g., Li et al., 2002, 2005), our analysis specifically quantifies the frequency with which NA pollution outflow affects surface ozone concentrations in the urban centre of Halifax, Nova Scotia, just as it leaves the continent. Our results show that within the subset of top quartile ozone concentrations in Halifax, between 45% and 63% are related to transported pollution events, putting our work in better agreement with Millet et al. (2006), who concluded that "the effects of North American pollution on the

chemistry of the western North Atlantic boundary layer are pervasive and not restricted to particular events." Moreover, past work showing vertical stratification in overhead flow (and the resultant isolation of pollutants from the surface layer) used surface observations only at Nova Scotia's coastal Chebogue Point, which is essentially a marine station primed to receive southwesterly flow across the Gulf of Maine, and subject to unique and complex flow patterns, as discussed by, e.g., Angevine et al., 1996a; Gong et al., 2000; Kleinman et al., 1996. In contrast to this, our work uses observations from all surface NAPS stations in Nova Scotia, which are located to the northeast of Chebogue Point (nearly overlapped with Dayton in Figure 14). These other Nova Scotia stations sample air masses that had a greater chance of experiencing at least some vertical mixing over a land mass (Angevine, et al., 1996b), 230 km to the northeast of the unique setting of Chebogue point. Our spatial correlation analysis using this expanded surface data set provides a better quantitative estimate of the frequency of North American pollution outflow influence at the surface in Halifax.

2.5 Summary and Conclusions

In this paper, we have presented the first long-term (2000-2018) analysis of trends in Nova Scotia surface ozone, ozone precursor concentrations and emissions, as well as transport influences on surface ozone. Long-term trends and shorter-term variations in ozone were examined at three Nova Scotia stations characteristic of urban (Halifax), suburban (Lake Major) and remote (Aylesford Mountain) areas. Monthly patterns showed a clear springtime ozone maximum at the three stations. Unlike in larger urban centers in warmer continental climates, the monthly median ozone in Nova Scotia is low throughout the summer, reaching a minimum in September.

Hourly ozone concentrations were analyzed by year at each station over the entire study period and we observed opposing trends in different metrics. While 99th percentile ozone levels are decreasing in Halifax and at Aylesford Mountain, the 25th percentile, median, and 75th percentile ozone show a statistically significant increase at suburban Lake Major for 2000-2018. At the remote background Aylesford station, without significant local emissions sources, the decrease in 99th percentile annual ozone (-1.21 ppb/year) for 2000-2018 is likely caused by successful regional and transboundary emissions reductions. The same 99th percentile decrease in Halifax (-0.70 ppb/year) is likely the result of both regional and local emissions reductions. The rise in 25th, 50th, and 75th percentile ozone at suburban Lake Major (0.99, 1.14 and 0.93 ppb/year, respectively) is consistent with the strong NO_x-O_3 titration effect in downtown Halifax (upstream of Lake Major) decreasing over time. This was confirmed with a long-term analysis of the annual average ozone lost to titration (DO_3), which was found to be decreasing significantly (-0.42 ppb/year) from 2000-2017.

The strong NO-titration effect on ozone in urban Halifax is obvious during the morning rush hour, but less pronounced during the afternoon, when stronger vertical mixing allows for the dispersion of pollutants. To account for this effect, total ozone (O_x) was used to show the changes in the diurnal cycle in six-year averages. While average morning (08:00 h) and afternoon (17:00 h) rush hour NO_x decreased by ~60% between 2000-2005 and 2012-2017, total ozone at the same times of day decreased only by 0.2 ppb and 2.4 ppb (<1% and 7% decreases). The disproportionate change in hourly average ozone compared to NO_x precursor reductions is consistent with a VOC-sensitive production regime that is characteristic for downtown areas in urban centers, and requires larger

reductions in VOCs to further reduce ozone. Despite the marginal effect of decreasing NO_x emissions on total ozone in Halifax, we expect ozone concentrations to rebound during transport to Lake Major, thereby partially accounting for increasing annual ozone at 25th percentile, median and 75th percentile levels.

Another cause of rising 25th percentile, median and 75th percentile ozone at Lake Major over 2000-2018 may be the slowdown of provincial and regional emissions reductions. Linear regressions for Halifax ozone precursors over the most recent six years (2012-2018) showed that NO_x emissions have been decreasing at a slower rate (-1731 tonnes/ year) compared to the 2000-2018 (-3982 tonnes/year). Despite the short atmospheric lifetime of NO_x, we assume, based on population, that about half of the transportation sector corresponds to the Halifax area. As such, the slowdown of these NO_x emissions will contribute to changes in Halifax ozone concentrations. VOC emissions were also found to have decreased at -1680 tonnes/year on average for 2000-2018, but this decrease became more than 10 times slower for the shorter period (the latter not statistically significant). Rising provincial VOC emissions in several sectors, including transportation, are likely the cause of the slowdown in reductions. The ozone formation potential (OFP) of all VOCs was also found to be decreasing by - 9.3 $\mu g/m^3$ /year for the full time period and slowed to a decrease of approximately one third of this during the shorter time period. Although biogenic VOCs are cited to be important in ozone production due to their abundance and high reactivity, biogenic VOCs in Halifax were found to account for a small portion of total OFP, e.g., 7% in 2018, unchanging over time. This means that reducing anthropogenic VOC emissions is the more effective way to reduce locally produced ozone in Halifax.

There is an understanding that Nova Scotia is regularly impacted by transboundary pollution episodes from source regions, although the frequency of transport episodes had not been previously quantified. Based on the correlation of top quartile daily maximum ozone days in Halifax with upstream and rural 'indicator' stations, 45-63% of these days in Halifax (2000-2018) were found to be associated with upstream transported pollution. Furthermore, the frequency with which transported pollution events occur increased by 15% across this time period. Since our work focused on the clear 'signal' contained in the province-wide spatial correlation of top quartile ozone events at Halifax, a "pervasive" influence of North American pollution is indeed justified.

2.6 References

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2.7 Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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2.9 Supplementary Information

2.9.1 Data availability

Table S1. Summary of data availability for NAPS Nova Scotia stations.

Station Name	Address	Station ID Number	Pollutants	Instrument	Years	Measurement Interval
Kejimkuijik Park	Kejimkujik national Park	30501	**O_3**		1985-2018	1 hour average
			VOCs		1995-2010	24hr average, every 6th day
			$PM_{2.5}$, PM_{10}	Dichot	1998-2004 & 2008-2009	24hr, Every 3rd day
Halifax Vogue Building	1649 Barrington St., Halifax	30118	**O_3**		1990 – 2017 (missing 1997, 1999)	1 hour average
			NOx		1990 – 2017 (missing 2003, 2009)	1 hour average
			SO_2		1990-2017 (missing 1997, 1999, 2008 & 2009)	1 hour average
			CO		2000- 2017 (missing 2009)	1 hour average
			PM 2.5	BAM	2008-2013 (missing 2009-2012)	1 hour average
			VOCs		1990-2017	24hr average, every 6th day

Halifax Johnston Building	1672 Granville St., Halifax	30113	**O_3**		2017 (start March)-2018	1 hour average
			NOx		2017 (start March)-2018	1 hour average
			SO_2		2017 (March start)-2018	1 hour average
			CO		2017 (start March)-2018	1 hour average
			VOCs		2017-2018	24hr, every 6th day
			$PM_{2.5}$	BAM	2006-2018	1 hour average
			$PM_{2.5}$	TEOM	2006 - 2018	1 hour average
			PM_{10}	Speciation	2006 – 2018	24hr, Every 3rd day
			$PM_{2.5}$ PM_{10}	Dichot	2006 - 2018	24hr, Every 3rd day
Aylesford Mountain (Elevation = 235m)	Mountain Brow Rd., Kings County	30701	**O_3**		1991 – 2018 (Missing 2008)	1 hour average
			NOx		2010- 2017	1 hour average
			$PM_{2.5}$	BAM	2007-2018	1 hour average
Granton	20 Pumphouse Rd., Granton	31201	**VOCs**		2006-2016	24hr average, every 6th day
Pictou	91 Beeches Rd., Pictou	30901	**O_3**		2001-2018	1 hour average
			NOx		2011-2018	1 hour average
			PM2.5	BAM	2003-2018 (missing 2010 & 2014)	1 hour average
Lake Major (Dartmouth)	Cherrybrook Rd., Halifax	30120	**O_3**		2006- 2018	1 hour average
			NOx		2006- 2018	1 hour average

					(missing 2009)	
			SO_2		2006- 2018	1 hour average
			PM2.5	BAM35, TEOM	2001-2018	
Dayton (Yarmouth)	Yarmouth Weather Office	30801	**O_3**		1994-2010	1 hour average
Kentville	32 Main St., Kentville	31101	**O_3**		2002-2011, 2017-2018	1 hour average
			NOx		2017-2018	
			PM 2.5	BAM	2017-2018	
Sydney	71 Welton St., Sydney	**30310** OR **30301 (before 2013)**	**O_3**		2001-2018 (missing 2007)	1 hour average
			NOx		2006- 2018 (missing 2007)	1 hour average
			SO_2		1974-2018	1 hour average
			CO		2005- 2018(missing 2007)	1 hour average
			PM 2.5	BAM35, TEOM	1998- 2018 (no 2000)	1 hour average
					2010 -2018	1 hour average
Port Hawkesbury	23 Embree St., Port Hawkesbury	30201	**O_3**		2010-2018	1 hour average
			NOx		2010-2018	1 hour average
			SO_2		2003-2007 & 2010-2015, 2018	1 hour average

			PM2.5	BAM35	2010-2018	1 hour average
Sable Island	Sable Island	31001	**O_3**		2001-2017 (missing 2007)	1 hour average
			NOx		2006- 2017 (missing 2007)	1 hour average
			SO_2		2008-2014	1 hour average
			$PM_{2.5}$	BAM	2003-2014 (missing 2009, 2010)	1 hour average

2.9.2 Long-term trends during entire period of data availability

Table S2. Slope and statistics (R_2, p-value and standard error (STE)) for metrics derived from boxplots of hourly ozone values in Figure 16 for the entire data period at each station (2000-2018 at Halifax and Aylesford and 2006-2018 at Lake Major). Metric slopes where $p < 0.1$ are shown in bold red.

		Halifax (2000-2018)	Lake Major (2006-2018)	Aylesford (2000-2018)
Upper whisker value (99.3 percentile)	Slope (ppb/year)	**-0.70**	- 0.07	**-1.21**
	R^2	0.43	0.007	0.64
	P value	<0.01	0.79	<0.01
	STE	0.20	0.27	0.21
75th percentile	Slope	0.02	**0.93**	**-0.27**
	R^2	0.001	0.72	0.41
	P value	0.89	<0.01	<0.01
	STE	0.15	0.17	0.08
Median	Slope	0.15	**1.14**	**-0.22**
	R^2	0.06	0.81	0.22
	P value	0.31	<0.01	0.05
	STE	0.15	0.17	0.10
25th percentile	Slope	0.21	**0.99**	**-0.23**
	R^2	0.09	0.74	0.21
	P value	0.21	<0.01	0.06
	STE	0.16	0.18	0.11

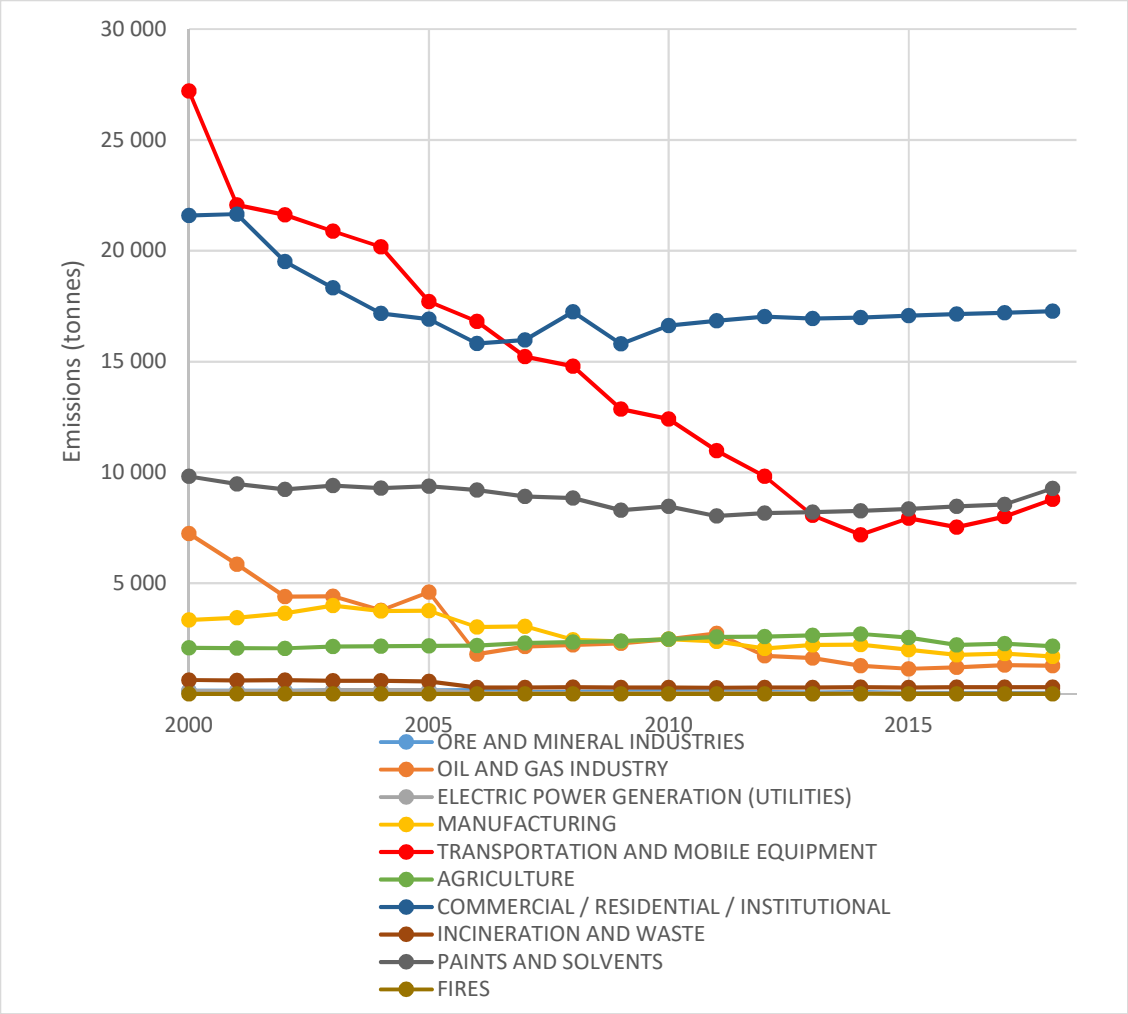

Figure S1. Annual average VOC emissions in Nova Scotia by sector from the APEI database.

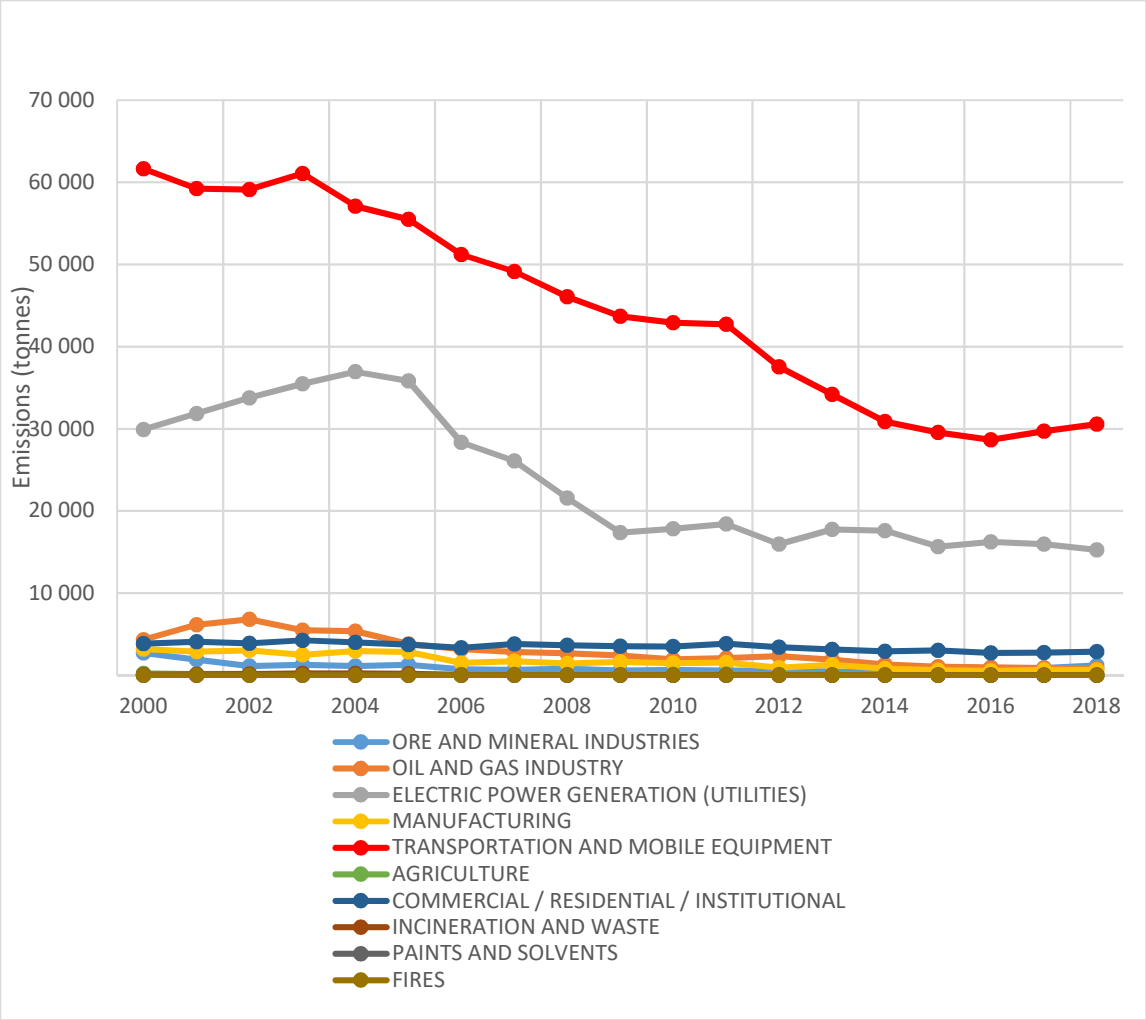

Figure S2. Annual average NO_x emissions in Nova Scotia by sector from the APEI database.

Future Work

As I worked through the case study analysis in section 1.3.1 and attempted to produce a local ozone production day algorithm at earlier stages of the research (not shown), I was daunted by classifying elevated ozone days as either transport-related or local when it is so complicated to distinguish between the two. Some of the 10 case study days from Section 1.3.1 had signatures of both transport and local production, therefore, days not diagnosed as transport should not be assumed to be locally produced because they could be caused by a mix of transported and local pollutants, even under the refined classification. Additionally, transport may still be involved in the case of net ozone loss in a polluted air mass in the winter, where remote stations would show very low concentrations of ozone but this NO_x-sensitive air mass could cause ozone production as it encounters high NO_x emissions in Halifax (Sillman, 1999). Future work on transport algorithm development may focus on further verifying the accuracy of the refined algorithm to diagnose transport days. One way to do this would be by starting the transport algorithm using elevated ozone days at Aylesford Mountain, a station well known for receiving transboundary pollution, and comparing the resulting transport dates to those from the Halifax elevated days algorithm. If the resulting transport dates are similar to those from Halifax, we know the algorithm is robust and accurately depicts transport frequency irrespective of the station used as the starting point. If the resulting dates are very different the algorithm may still be missing many transport days. It would be instructive to again analyze the top-10 non-transport-related elevated ozone days, but this time selected by the refined transport algorithm. Once the accuracy of the algorithm is further established, the transported pollution source maps completed for the algorithm iteration in Section 1.2.1 could be recreated for the most recent version of the algorithm, providing a more accurate picture of source regions. This would involve automating

HYSPLIT to run for the IND_{50} or IND_{100} transport days and creating a composite plot of the trajectories.

Refinement of the local production analysis could be done by examining the 1.5% or 7.7% of days with no "other" stations having *any* positive anomaly on an elevated Halifax ozone day (Figure 5), which are not necessarily highest in terms of ozone concentration. If any of these days occur in winter, they can indicate ozone titration during transport in winter (detected at the "other" stations) with local production in Halifax from transported pollution mixing with precursors emitted in Halifax. If they occur in the summer, they may be local production elevated days or local production mixed with upstream production from a few days before. More refinement is needed on local conditions that could cause ozone production locally, as in Figure 9. It is well known that the temperature dependence was stronger when precursors were higher so separating the temperature data into the 2000-2010 period and the 2011-2018 period may show a more significant relationship for temperature and ozone in the earlier part of the time series. Repeating this for just transport days could show a stronger dependence on temperature because Halifax air masses experience transport from continental regions with higher temperatures; a more complex consideration of temperature in source regions is necessary, e.g., one or two days before airmass arrival in Halifax. Furthermore, an explicit consideration of seasonality in local production analysis will help to elucidate trends and relationships more clearly, e.g., stronger decreasing maximum and median ozone values in June-July-August, or a stronger relationship between daily maximum ozone and temperature, or stronger diurnal signals of (afternoon) ozone production.

Repeating analyses done for Halifax, Lake Major and Aylesford at other stations in Nova Scotia will increase our understanding of ozone production in areas with different geographic

characteristics. Ozone production chemistry is complex and emissions decreases may not produce the desired outcome everywhere, as shown with decreasing NO_x and increasing total ozone at Lake Major (Figure 13). There are a few stations in moderately populated areas like Kentville, Pictou and Sydney and the impact of provincial NO_x reductions on ozone production and titration at these stations could help us understand changes in annual CAAQS values. Additional analysis from this research like hourly annual station trends (Chapter 2, Figure 16) or diurnal station trends (Chapter 2, Figure 18) could be completed for the remaining six Nova Scotia stations with a focus on trends in the more recent part of the time series. This will certainly be of interest to provincial forecasters and policy makers working to continuously improve Nova Scotia's air quality.

Next, it is important to keep all analysis up to date as new data becomes available from emissions inventories and from the NAPS database. Annual trends are highly variable in many of the figures and an uptick in one year could change the direction or significance of long-term slope trends. As I write this in 2021, analysis has been done with NAPS data up to 2018 and 2019 became available in December 2020. The uncertain effects of the 2017 Halifax station relocation, climate change and Covid-19 on ozone production should be taken into account for future trend analysis.

Satellite measurements like the Tropospheric Monitoring Instrument (TROPOMI, horizontal resolution of 3.5 km x 7 km) can be used to visualize the approximate spatial distribution of pollutants in the Halifax Regional Municipality (HRM) related to ozone production. Since there are only two air quality measurement stations in the HRM, and only one that provides limited measurements of VOCs, satellite measurements of NO_2 and HCHO (formaldehyde) from TROPOMI can be used to calculate the ozone production regime. Long term changes of the

$HCHO/NO_2$ ratio should be examined to see the effect of decreasing NO_x emissions on the production regime over time as done by Jin et al. (2020). Additionally, TROPOMI offers tropospheric column measurements of ozone and can be used to address the question of transboundary pollution by looking at these measurements in upstream source regions. High ozone production in source regions (identified by HYSPLIT) prior to elevated Halifax ozone days provides evidence that precursor pollutants were high in these areas and were likely transported into Halifax as ozone or precursor, or their reservoirs.

Finally, Chemistry-Transport Model (CTM) simulations, such as from GEOS-Chem, can additionally be run to provide a quantitative analysis of contributions to Halifax O_3 and precursors from upstream pollution source regions. While species-tagged simulations, where the provenance of emitted precursors or produced ozone is individually tracked, are computationally expensive, these types of analyses are increasingly being conducted to inform policy regarding transboundary pollution transport. For example, simulations can be conducted where precursors are tagged separately for several regions in the USA, Ontario, Quebec, as well as Nova Scotia and/or Atlantic Canada, identifying their individual contributions to O_3 and other pollution in Halifax. While this analysis would be short-term on account of the computational cost, it could span the four seasons, providing information on ozone production and transport that is highly complementary to the above satellite analysis and the statistical analysis conducted in this work.