Controls on the Production of Ground Level Ozone in Halifax, Nova Scotia

By Morgan Mitchell

A Thesis Submitted to Saint Mary's University, Halifax, Nova Scotia in Partial
Fulfillment of the Requirements for the Degree of B.Sc. Honours Environmental Science

September, 2018, Halifax, Nova Scotia

Supervisor: Dr. Aldona Wiacek

Readers: Andrew Teakles

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Abstract

Atmospheric ozone (O_3) is a secondary pollutant produced via complex chemical reactions involving precursors like nitrogen oxides (NO_x), Volatile Organic Compounds (VOC) and carbon monoxide (CO). The key to reducing ozone concentrations is to regulate the precursors. Using data from the National Air Pollutant Surveillance (NAPS) program, possible controls on ozone production are examined for Halifax and other regions across Nova Scotia, including meteorological and chemical variables.

Long-term trends of ozone and its precursors in Nova Scotia were analyzed to see the effect of emissions regulations across North America. Diurnal and monthly averages were also examined to show short-term patterns in Halifax. It was found that 1-hour average ozone levels are relatively steady in Halifax under decreasing NO_x emissions, due to a reduction of the strong NO_x titration effect on O_3; however, Total Ozone (TO), comprised of O_3 and NO_2, is decreasing, along with maximum 1-hr ozone. Additionally, it was found that there are no strong signatures of biogenic VOC influence on ozone levels in Halifax (as opposed to anthropogenic VOC), although more frequent measurements of VOC are needed to better study VOC-sensitivity. There is indication from the high NO_x levels that ozone production is on the whole VOC-sensitive in Halifax

Lastly, long-range transport was examined during an event of maximum elevated O_3 at the background air Aylesford NAPS station in 2016. The high O_3 levels were correlated with high values in Halifax and transport to both locations was consistent with pollutant import from the the northeast U.S. Flow to Halifax vs. Aylesford is in general more complicated because tThere is no obvious correlation between ozone in Halifax and at the Aylesford NAPS station, which requires further study.

All of the above findings are policy-relevant in the regulation of ozone precursors.

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1 Introduction

1.1 Atmospheric Ozone

Ozone is present in the two atmospheric layers that are closest to the earth's surface, the stratosphere and the troposphere. The troposphere extends from the surface of the Earth up to 8-18km depending on the location. The stratosphere is the second layer of the atmosphere which extends from 15-50 kilometers above earth’s surface and incorporates the ozone layer. The abundant stratospheric ozone protects life on earth from harmful ultra-violet rays from the sun. Here, concentrations of ozone are usually 100 times larger than concentrations in the troposphere (Jacob, 1999). The troposphere is the bottom most layer of the atmosphere that extends from the earth’s surface to anywhere from 8 to 18 kilometers, depending on latitude.

In the troposphere weather processes and air pollution, like ozone, can affect life on earth (Foresman and Strahler, 2012). The troposphere can be further divided into the surface layer or planetary boundary layer, which constitutes the bottom 10-25%, and the free troposphere (Monson, 2013). In the free troposphere ozone has a long atmospheric lifetime that can be up to several weeks, therefore this ozone can be transported across continents (Monks et al., 2015). In the troposphere, ozone is referred to as the air pollutant Ground Level Ozone (GLO) which is a secondary pollutant produced through complex chemical reactions involving NO_x (NO and NO_2), Volatile Organic Compounds (VOCs), hydrocarbons, and Carbon Monoxide (CO). Until the 1970s it was thought that stratospheric intrusions to the troposphere were the dominant source of ozone in this region (Monks, 2000). However, it is now known that ozone in the stratosphere has little impact on tropospheric ozone, except for small amounts of ozone that are carried to the troposphere through a mechanism called stratosphere-troposphere exchange (STE) (Tarasick & Slater, 2008). The STE is estimated to contribute anywhere from 400-1100 Tg of ozone per year to the 3400-5700 Tg per year of the global budget of tropospheric ozone (Jacob, 1999). Although the quantity of ozone imported to the troposphere through STE is small, there may be some significant interaction between stratospheric and tropospheric ozone during early spring at higher latitudes; the buildup of stratospheric ozone in late winter may lead to a spring peak in ozone in the troposphere (Tarasick & Slater, 2008; Whaley et al., 2015).

Ozone has the ability to oxidize human and plant tissues (Jacob, 1999, Ch.11). Ground level ozone can be harmful to vegetation at concentrations as low as 40 ppb, and building materials at 20 ppb (Gibson et al., 2009). Additionally, GLO is a main component of photochemical smog, along with particulate matter and NO_x, so it is a good indicator of the overall air quality of a region. Large urban centres in the United States like Los Angeles experience ambient ozone levels of about 180 ppb (National Research Council, 2008) which can be immediately deleterious to human health. Ozone is estimated to make up between 5-20% of all air pollution-related deaths (Monks et al., 2015). In addition to GLO being a direct hazard to the health of living things, it is also the third most important greenhouse gas (GHG) (Wang et al., 2017). As ozone is not directly emitted, the key to reducing its concentration is to reduce the precursor pollutants that lead to its production. Once produced, the atmospheric lifetime of ozone in the continental boundary layer is on average 2-5 days depending on the boundary layer depth and chemical loss rates. In the Eastern United States (US) the lifetime of ozone at surface levels is less than two days because of the abundance of reactive hydrocarbons (Fiore et al., 2002), and in polluted urban regions its lifetime can be a few hours (Monks et al., 2015). Due to this short atmospheric lifetime in the Eastern US and likely Eastern Canada, precursor reductions would reduce secondary O_3 quickly.

1.2 O_3 Production and Loss

1.2.1 Production

The production of ozone in polluted environments occurs when NO_x, reactive hydrocarbons, other VOCs and/or CO are present. There are many emission sources of these primary pollutants, both anthropogenic and biogenic. The largest source of tropospheric NO_x emissions is from the burning of fossil fuels and biomass, with other natural emissions coming from soil and lightning (Jacob, 1999).

Provincial sources of ozone precursor emissions are described in The Air We Breathe Report (Nova Scotia Environment, 2009). About 53% of NO_x emissions in Nova Scotia come from mobile sources, with 25% of that being from ships and another 35% is from electric power generation. Carbon monoxide is primarily emitted by mobile sources (81%) and residential wood combustion emits about 15% of Nova Scotia’s CO. Natural sources emit 84% of the province’s VOCS, called biogenic VOCs or BVOCs, with mobile and industrial sources making up only a small percentage of the emissions, known as anthropogenic VOCs or AVOCs (Nova Scotia Environment, 2009). In Halifax there is a large source of NO_x and VOCs emissions from harbor activity including container ships and recreational boats (Wiacek et al., 2018).

In the presence of its precursor emissions, ozone is produced through complex reaction pathways that differ slightly depending on the dominant precursors. The reaction pathways are presented below beginning with the production of HO_x ($H + OH + HO_2$) radicals (R1-R3), which initiate the reactions that produce ozone. Paradoxically, ozone photodissociates in R1, where O(*D) is an excited oxygen radical, R2 is a quenching reaction where the O atom quickly recombines with oxygen to form O_3 in most cases (M is any third body chemical participating in the reaction). Next, R3 leads HO_x production in the form of OH, the hydroxyl radical which is a strong oxidant that quickly reacts with H-containing species (Jacob, 1999, Ch.11). RH is used to represent any hydrocarbon alkyl group in the reaction sequence and $RO_{(2)}$ is any organic (per)oxy radical. R may be, in the simplest case, CH_3 so that the reaction chain described by R4-R8 is the partial methane (CH_4) oxidation mechanism. R' represents H in this case so that R'H may be CH_2O or formaldehyde (Jacob, 1999):

$O_3 + h\nu \rightarrow O_2 + O(*D)$ (R1)

$O(*D) + O_2 + M \rightarrow O_3 + M$ (R2)

$H_2O + O(*D) \rightarrow 2OH$ (R3)

$RH + OH + O_2 \rightarrow RO_2 + H_2O$ (R4)

$RO_2 + NO \rightarrow RO + NO_2$ (R5)

$RO + O_2 \rightarrow R'CHO + HO_2$ (R6)

$HO_2 + NO \rightarrow OH + NO_2$ (R7)

$2NO_2 + 2O_2 + h\nu \rightarrow 2NO + 2O_3$ (R8)

NET (R4-R8): $RH + 4O_2 \rightarrow R'CHO + 2O_3 + H_2O$

The NO_2 produced in R5 and R7 will rapidly photolyze to NO and O with the addition of sunlight. The net reaction leads to the production of two ozone molecules and formaldehyde.

In polluted environments or in the remote troposphere, carbon monoxide may replace hydrocarbons such as methane and produce ozone through the net reaction:

$CO + 2O_2 \rightarrow CO_2 + O_3$ (R9)

The production pathway of ozone is terminated by the loss of HO_x, 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 serves as the dominant sink for HO_x radicals:

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (R10)

However, if NO_x concentrations are high in the area then HO_x (as OH) will react with NO_2 and nitric acid serves as the dominant sink for HO_x radicals (Jacob, 1999):

$NO_2 + OH + M \rightarrow HNO_3 + M$ (R11)

These two reaction pathways lead to different ozone production regimes, as discussed next.

1.2.2 Production Regime

The two different pathways for the production of ozone present a problem for emission controls. It is therefore necessary to determine the dominant reaction pathway for ozone production to implement appropriate reduction policies. Ozone production in any given region may be classified as NO_x-sensitive or VOCs-sensitive depending on the dominant emission source and the HO_x-radical sink (Sillman, 1999). The ozone production regime is unique to each polluted environment and the regime can help describe the driving chemistry of ozone production in that location. The NO_x-sensitive regime describes ozone production in an area that is saturated by VOCs but limited by NO_x. In this case ozone production will increase almost linearly with the addition of NO_x (Equation 1), whereas, the addition of VOCs will not cause a change in ozone production.

In a VOC-sensitive regime ozone will only be produced with the addition of VOC emissions (Equation 2), and because the region is NO_x-saturated additional NO_x will titrate the ozone resulting in decreased production (Sillman, 1999).

$$p(O3) \propto NOx \qquad \text{(Equation 1)}$$

$$p(O3) \propto \frac{VOC}{NOx} \qquad \text{(Equation 2)}$$

The regime change is transitional and many regions fall within this production zone where reductions in either NO_x or VOCs could decrease ozone production. A fourth possible regime as described by Sillman (2002) is the NO_x-titration regime, where a reduction in NO_x would cause an increase in ozone but a reduction in VOCs would not cause an ozone reduction. This regime occurs near large NO_x emission sources when ozone is being titrated by NO (R13). The ozone production regimes are well illustrated in Figure 1. The bottom right part of Figure 1 illustrates a NO_x-sensitive regime, and the upper right part illustrates the VOCs-sensitive regime. A freshly emitted air mass is likely to be VOCs-limited when it first receives urban NO_x emissions, but as it moves downstream it becomes NO_x-limited due to the short photochemical lifetime of NO_x of about 2-4 hours (Sillman, 1999).

Some scientists argue that VOC-limited is an inaccurate term for describing the ozone production regime (Wenneberg, 2013), and radical-limited is more accurate due to the peroxy radicals that are produced from the oxidation of VOCs (Shroeder et al., 2017). For the remainder of this study a region where ozone production is dominated by NO_x will be called VOC-sensitive and a region dominated by VOCs will be deemed NO_x-sensitive. Although the terminology may be complex it is important to know the

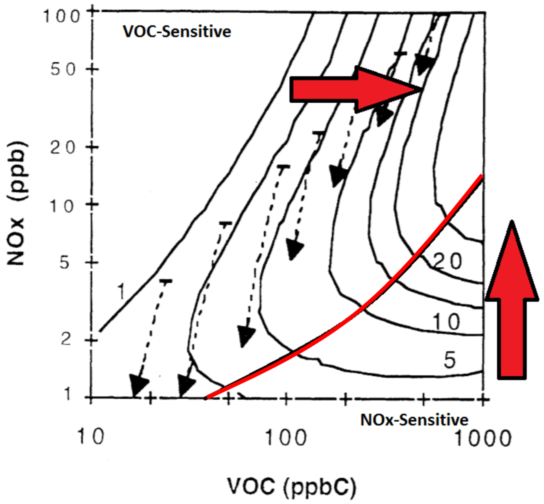


Figure 1. Isopleth plot showing the instantaneous rate of ozone formation (labels on thin solid lines ppb/hour) as a function of NO_x *and VOCs concentrations (ppb). The red arrows show the additional pollutant needed to increase ozone production. The red curve represents the "ridge" line of the isopleth plot and marks the transition between the* NO_x*-sensitive and VOCs-sensitive regimes, as labelled. The black-hatched arrows represent regime changes in transport (see text for details, reproduced from Sillman, 1999).*

production regime of a region so policy-makers can put the correct emission controls in place to reduce ozone, i.e., either by reducing emissions of NO_x or of VOCs, whichever would be most beneficial (Geddes et al., 2009).

1.2.3 Loss

Usually, R12-R13 is in a steady state reaction sequence called the "null cycle" as no net ozone is produced, however, if Reaction 13 dominates, this "null" cycle produces a net loss of ozone. This occurs mainly in one of two situations: in the vicinity of large NO_x sources and at nighttime (Sillman, 1999). Both loss pathways are primarily impermanent and represent a local loss. At nighttime loss can occur through surface deposition or by titration of NO. Due to the lack of sunlight at night, NO_x exists only as NO_2 and no ozone can be produced. In fact, NO_2 can react with O_3 to produce the nitrate radical (R14) and these reactions continue to deplete ozone until the next morning.

$NO_2 + O_2 + hv \rightarrow NO + O_3$ (R12)

$NO + O_3 \rightarrow NO_2 + O_2$ (R13)

$NO_2 + O_3 \rightarrow NO_3 + O$ (R14)

Ozone in urban centres at night is usually lower than surrounding areas due to the buildup of NO_x during the day (Sillman, 1999). Ozone is lost locally in the vicinity of a large NO_x source like a power plant, this regime is called NO_x-titration and no ozone production occurs, during day or night. About 90% of NO_x emissions are NO and the remaining 10% is NO_2 (Itano et al., 2007). The abundance of NO titrates ozone rapidly (R13) close to the source, however as the plume moves downstream and ages NO_2 will photolyze to NO and O and ozone can be produced (Sillman, 1999). As an air mass is transported from the Eastern United States to Nova Scotia we can expect it to be NO_x-sensitive, due to the short lifetime of NO_x,and have an impact on ozone in Halifax where there are large sources of NO_x.

1.3 Background Ozone

Background ozone refers to ozone that would be present in an area without anthropogenic sources of pollution. The most accurate measurement of background levels can be found in isolated, rural regions without nearby upstream pollution sources. Background levels can also represent the lowest level of ozone achievable with emission controls in urban or rural areas (Zhang et al., 2011).

There is evidence that background ozone levels are increasing in the Northern Hemisphere (Karlsson et al., 2017, Monks et al., 2015). Increasing background ozone may be attributed to rising temperatures and an increase in global carbon monoxide levels (Vingarzen, 2004), or increasing transported emissions (Zhang et al., 2011), as discussed below in Section 1.3.1. Particularly, Northern Europe is seeing an increase in background ozone levels but a decrease in peak ozone enhancements from precursor reduction (Karlsson et al., 2017). The 2016 Air Quality Ontario report notes that Ontario's average ozone levels seem to be decreasing in the summer due to precursor reductions but increasing in the winter because of increasing background levels (ON Ministry of Environment and Climate Change, 2016). However, enhanced background levels do not mean that urban ozone levels will necessarily increase everywhere. In fact, many studies show the opposite for urban ozone as it is more dependent on local emissions sources than background levels. A study by Cooper et al. (2012), shows that between 1990-2010 major metropolitan areas in the Eastern United States experienced significant decreases in ozone in summer due to reduced precursors. Similar trends have been found in Toronto, where the overall decreasing total ozone levels are likely due to precursor reduction (Pugliese et al., 2014 and Whaley et al., 2015). Osaka City, Japan has also experienced a gradual decrease in ozone levels (Itano et al., 2007).

It is important to distinguish between surface background ozone levels and ozone enhancements caused by primary pollutants during photochemical processes that occur in the warmer months. This will help to compare the ever-present ozone levels to enhancements caused by pollution.

1.3.1 The role of transport

Not all background ozone is produced locally; transported ozone and precursors can play a role in regional background ozone levels. As mentioned in Section 1.1, ozone has a lifetime of a few weeks in the free troposphere and therefore has influence on global ozone budgets (Monks et al., 2015). Intercontinental transport can cause increases to background ozone levels in areas that are decreasing their emissions locally. For example, rising Asian emissions may have significant impacts on rising background ozone levels in the Western United States (Cooper et al., 2012). It may be possible to reduce local ozone enhancements with precursor emissions controls, but to reduce background ozone is a global effort.

1.4 Natural Variation

There are a few natural ozone fluctuations that occur in Nova Scotia which are important to note when analyzing the data for enhancements above background conditions. Every location experiences similar natural fluctuations in ground level ozone but they have regionally unique characteristics. Firstly, there are diurnal ozone variations due to the photochemical nature of ozone production where a maximum typically occurs in the afternoon (Bloomer et al., 2010). Sunlight is needed to photolyze the ozone and NO_2 molecules and drive the ozone production process, so no production will occur at night in the absence of sunlight (see Section 1.2.3). In the summer in rural areas it is common to see an early afternoon peak in ozone levels because this is when photochemistry is most active (Tarasick & Slater, 2008). Yet, urban areas may see diurnal patterns that reflect anthropogenic activities, for example, morning or afternoon ozone minima. If NO_x emissions are large enough this may titrate ozone by the ozone loss reaction and cause a dip in ozone levels during times of high anthropogenic activity, especially if monitoring stations are heavily influenced by traffic.

Another natural ozone variation is the seasonal change in background ozone that is observed globally. According to Tarasick and Slater (2008) surface ozone levels commonly experience a minimum in the fall or winter and peak in late spring or summer. However, megacities with high pollution levels and local wind patterns can cause differences in the seasonal patterns at each location. Latitude may also affect the seasonal ozone patterns as Tarasick and Slater (2008) note that the usual spring maximum is replaced by a minimum at Arctic sites. A field study in the Annapolis Valley of Nova Scotia observed this spring maximum in early to late May, and authors attributed this maximum to a buildup of precursors like peroxyacetyl nitrate, carbon monoxide, isoprene and increased temperatures and solar radiation during late April to the end of May (Gibson et al., 2009).

1.5 Biogenic VOCs

Most NO_x is emitted anthropogenically from fossil fuel burning while natural or biogenic sources make up a very small portion of NO_x in the troposphere. In contrast, a significant amount of VOC emissions come from biogenic sources, like large forested areas, and are known as BVOCs (Biogenic Volatile Organic Compounds), which are represented by the RH in Reaction 4 (R4). The most abundant and reactive BVOCs in a region are most likely to be oxidized by OH and used in the production of ozone (Jacob, 1999, Ch.12). The largest BVOCs in terms of global concentrations are methane and isoprene with global emissions estimated at 500-550 TG C/year (Monson and Baldocchi, 2013). Biogenic methane is emitted from microbial sources and isoprene is emitted by terrestrial plants at comparable rates, but methane is not highly reactive like most other VOCs and has a chemical lifetime upwards of eight years (Jacobson, 2012). Isoprene is a monoterpene that constitutes about one third of all global biogenic and anthropogenic VOCs emissions (Guenther et al., 2006). Due to its large abundance and highly reactive chemical structure (Figure 2), with an atmospheric lifetime of less than an hour, isoprene is the most common hydrocarbon in the ozone production reaction sequence in the troposphere (Jacob, 1999, Ch.12). The exact cause of isoprene emissions by plants is still being investigated, but all agree that it is released when plants experience some kind of stress. Due to the dependence of isoprene on temperature, heat stress is the most well-known trigger for isoprene release but some studies show it could also be linked to water stress or light and nutrient competition (Kegge and Pierik, 2010).

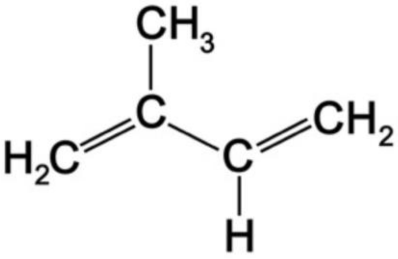


Figure 2. Chemical structure of Isoprene. High reactivity due to two double carbon bonds.

Isoprene emissions are a large player in the production of ozone; in fact, "isoprene emissions would be sufficient to make O3 production NO_x-limited everywhere in the United States except in large urban centers" (Jacob, 1999). Although this quote comes from studies done throughout the United States it is also true for many parts of Canada. More than 75% of Nova Scotia's land is covered in forests, with the majority of that being softwood forests but mixedwoods and hardwoods make up about a third of the total forest cover (Nova Scotia Department of Natural Resources, 2017). Large isoprene emissions come from hardwood deciduous forests which make up a large part of Eastern North American forests including Acadian forest which is dominant in Nova Scotia, for example, in Kejimkujik National Park. Isoprene emissions from Kejimkujik National Park are likely large during the summer and depending on transport direction this could lead to ozone production locally or elsewhere if NO_x are also present or if the isoprene is carried into an area with high NO_x emissions. A study by Biesenthal et al. (1998) quantified the isoprene emissions in a large forested area of Nova Scotia during the summer. It was found that the atmospheric chemistry in the area was dominated by biogenic hydrocarbons, however, due to low NO_x emissions at this site, ozone production was limited locally. There is a possibility of an elevated ozone episode if this isoprene-saturated air mass was transported to Halifax, where NO_x emissions would be injected.

Atlanta is a well-researched urban area with ozone production dominated by BVOCs due to the large amount of biogenic sources nearby (Sillman et al., 1995). Terpenes, primarily isoprene, can account for 40% of ozone above background levels in Atlanta (Jacobson, 2012). Here, isoprene is also emitted in smaller quantities by anthropogenic sources like vehicle emissions, therefore it is important to distinguish these from biogenic emissions. Von Schneidemesser et al. (2011) looked for a correlation between isoprene and anthropogenically sourced benzene, and found it present in the winter (when biogenic isoprene emissions are suppressed) but not in the summer. One can also analyze the relationship between isoperene and temperature, or the timing of the isoprene emissions, which will correlate with sunlight for biogenic sources and with vehicle patterns for anthropogenic sources.

The ozone production regime of Halifax is unknown, as are the effects from biogenic emissions like isoprene on local ozone. There is a possibility that isoprene has a key role in ozone production in Halifax due to the proximity of forested areas surrounding Halifax and the large fossil fuel emissions within Halifax giving a constant supply of NO_x. Isoprene emissions are highest during the day when there is sunlight and during the growing season of May to September. Since ozone production in the United States (outside of the cores of large cities) is primarily NO_x-limited in the summer months due to the large source of biogenic emissions (Jacob et al., 1995); it is reasonable to assume the same for Nova Scotia (outside of the the busiest core).

There is a phenomenon being studied recently in which an ozone peak is produced in the early morning due to reaction of NO_x with biogenic hydrocarbons accumulated overnight (Millet et al., 2016). This study was done in St. Louis, Illinois which exists downwind of a major deciduous forest. Isoprene that is emitted in the evening when OH concentrations are low may not be oxidized and can persist overnight. Due to the nighttime reaction of NO_3 with isoprene, various oxides of nitrogen are produced (like N_2O_5) and can be transported into an urban area at night and serve as an additional source for NO_x when sunlight hits the next morning (Millet, 2016):

$N_2O_5 + h\nu\ (\lambda < 400\ \text{nm}) \rightarrow NO_3 + NO_2$ (R15)

$\rightarrow NO_3 + NO + O^*(D)$ (R16) (Brown and Stutz, 2012)

Additionally, in an area with high NO, O_3 will be titrated and NO_3 production will be suppressed via Reaction 14. If NO_3 concentrations are too low to react with isoprene at night, most isoprene will be present the following morning to be oxidized by OH and produce ozone. Millet (2016) found that this process can change the diurnal cycle of ozone production by moving the usual afternoon ozone peak to the morning.

1.6 Meteorology

Determining the impacts that local weather conditions have on the ozone production in a given region can give a better understanding of local chemical production. Although local emissions and transported pollution can lead to ozone production, it is local weather conditions that determine the rate of production and buildup of ozone. Factors like temperature, wind speed and direction, sunlight and pressure systems can be just as important in creating ozone enhancements in an urban area as locally emitted and transported precursors. The impact of a certain meteorological factor on a region's ozone is variable, for example daily maximum surface temperature decreases in its impact on ozone production towards lower latitudes (Camalier et al., 2007). Therefore, this section will focus specifically on factors that may influence Halifax's ozone.

1.6.1 Temperature

Temperature by itself does not usually have a linear relationship with ozone levels, but other weather patterns that are associated with high surface temperatures can have large impacts on ozone production (Sillman, 1999). For example, "Lower temperature usually coincides with decreased sunlight, decreased water vapor and sharply lower biogenic emissions, all of which favor VOC-sensitive chemistry" (Sillman, 1999). Camalier et al. (2007) found that temperature has almost no effect on ozone below temperatures of 20ºC but above that threshold temperature and ozone have a positive relationship because of increased photochemistry. Photochemistry is needed to drive the ozone production reactions and high ultraviolet radiation is usually associated with cloudless skies and high temperatures. Higher temperatures are associated with faster reaction kinetics (Atkinson et al., 2004) and higher VOC reactivity (Geddes et al., 2009). Halifax experiences lower annual average temperatures than continental cities like Toronto and Windsor for example (Martin et al., 2012). This means there are less days with maximum temperatures above 20^{o}C which indicates less radiation on annual and daily timescales than what can be found in cities closer the Equator, and therefore less photochemistry. This could contribute to the generally good air quality seen across the province.

Another role temperature can have in the accumulation of ozone is through a temperature (or subsidence) inversion. Generally, the temperature of the boundary layer decreases with increasing altitude, so air masses originating from the surface will rise and displace the colder air above. In an inversion layer temperature increases with altitude so this layer is warmer higher up, inhibiting the rise of air masses and vertical mixing (Jacobson, 2012). Strong inversion layers can trap pollution at the surface and create dangerous levels of ozone and smog as is often seen in Los Angeles and Mexico City, which experience persistent inversion patterns due to their geography (Jacob, 1999). According to Jacob (1999), the highest ozone levels can be found in urban areas under stagnant conditions with subsidence inversions.

1.6.2 Synoptic Pressure Systems

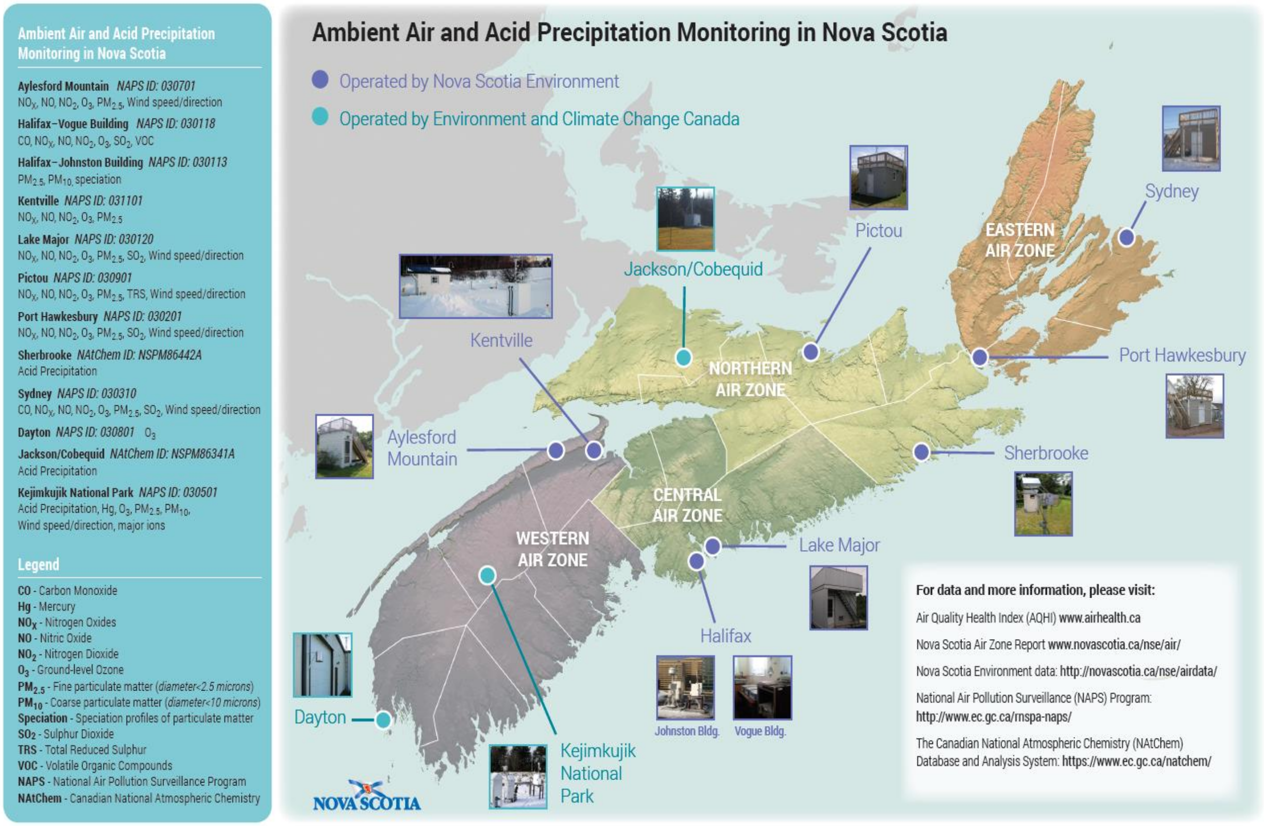
Synoptic, i.e., 1000-km scale, high and low pressure systems can also affect the buildup of pollutants in an area and corresponding ozone levels. Low pressure systems are associated with cloudy skies, which reduce the amount of solar radiation that can reach the surface to drive photochemical reactions. Low pressure systems can also produce strong surface winds which disperse pollutants and therefore help to reduce local ozone levels. In comparison, high pressure systems create stagnant conditions by trapping pollution with anticyclonic air masses converging towards the surface. These conditions are also associated with cloudless skies and primarily high temperatures which help drive the photochemical production of ozone (Jacobson, 2012).

1.6.3 Sea Breeze

Cities that are located along a coastline are subject to unique air pollution accumulation and dispersal due to the sea breeze effect. The sea breeze effect is a circulation pattern produced due to differential temperatures between the land and adjacent ocean. The land heats faster than water, due to lower heat capacity, so air masses above the land rise and create a pressure difference so that an air mass near the surface and above the sea is advected over the land during the afternoon. This phenomenon reverses at night causing the near-surface air mass above land to move back over the sea. This relates to air quality because it moves polluted air masses inland during the day and out to sea at night (Lalas et al., 1983). The sea breeze has more prominent effects in coastal urban centres that are situated in basins where pollutants normally become trapped and are unable to disperse, as is the case in Athens, Greece (Mavrakou et al., 2012) and Los Angeles (Sillman, 1999). Halifax is relatively flat, and not surrounded by a mountain chain, so pollutants can easily disperse as the sea breeze pushes urban ozone inland.

1.7 Monitoring and Standards

Ground Level Ozone in Nova Scotia is monitored by stations operated by both Environment and Climate Change Canada (ECCC) and Nova Scotia Environment (NSE) (Figure 3), with data collected and sent to ECCC and archived in the publicly available



March 2016

Figure 3. Nova Scotia's air quality monitoring network with stations operated by both Nova Scotia Environment and Environment and Climate Change Canada. Map from https://novascotia.ca/nse/air/docs/AirMonitoringNetworkMap.pdf.

National Air Pollution Survey (NAPS) database. Monitoring stations across Nova Scotia measure a wide range of pollutants over various ranges of years, and at different time intervals, including species relevant to this study, i.e., O_3 and Isoprene (see Appendix A).

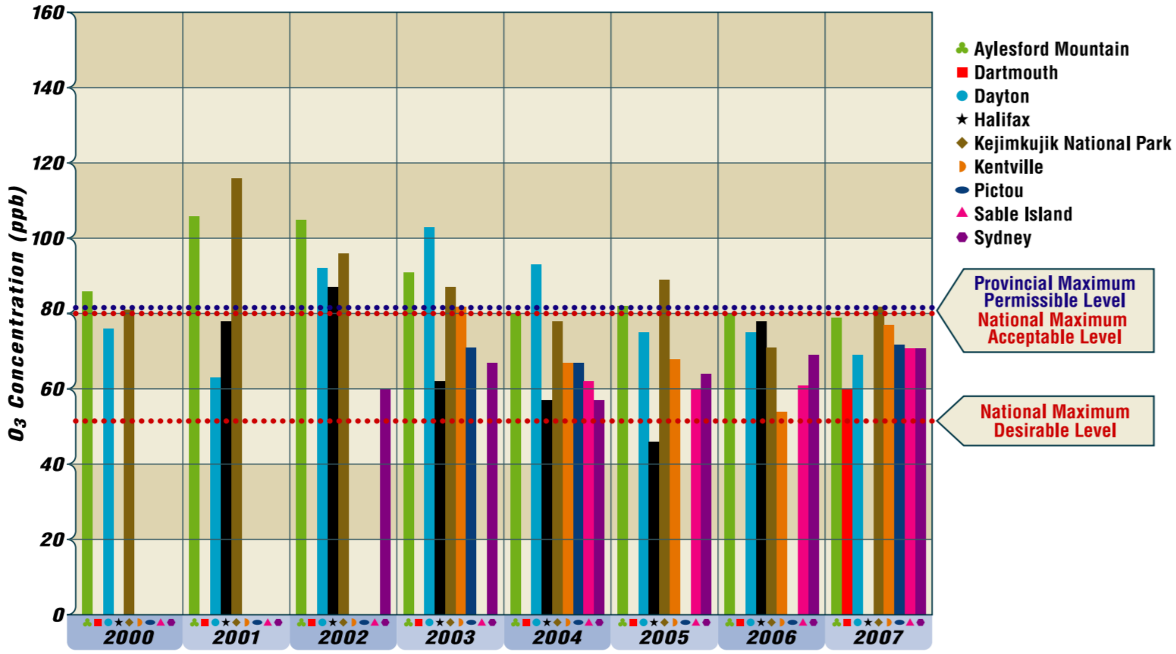
Air quality standards are set at both provincial and national levels but require similar levels of limits on pollutants (Appendix B). The National Ambient Air Quality Objectives (NAAQO, Appendix B) set the Maximum Acceptable Level of ozone at 80 ppb for one hour, while the Nova Scotia Air Quality Regulations set the Maximum Permissible level of ozone at 82 ppb. The Maximum Desirable Level is also set by the NAAQO and is 50 ppb for one hour ozone as a long term goal that policy makers can strive to reach. The

Canadian Ambient Air Quality Objectives (CAAQOs), which replaced the Canada Wide Standards (CWS) in 2015, are used to look at longer term air quality using the 3-year-average of the annual fourth highest daily maximum 8-hour averages to assess air quality for ozone; for Particulate Matter ($P.M._{2.5}$) a slightly different metric is used, i.e., the 3-year average of the annual 98th percentile of the daily 24-hour averages (NSE, 2015).

According to the 2015 Air Zone Report which uses CAAQSs, the Central Air Zone, including Halifax, falls into the "yellow" management level which means the 3-year average of annual 4th highest maximum 8-hour concentrations exceeded 50 ppb, but remained under the standard of 63ppb. This means that Halifax requires "actions for preventing air quality deterioration" (NSE, 2015, p.5), and one-hour ozone levels in Halifax commonly reach values above the NAAQO 50 ppb desirable level in the summer months (Nova Scotia Air Quality Unit, 2015). With transported pollution episodes ozone levels are likely to exceed the desirable levels and perhaps even the permissible levels. It is worth noting that the O_3 and $PM_{2.5}$ CAAQS will become slightly more stringent in 2020 at 62 ppb and 27 $\mu g/m^3$, along with the introduction of CAAQS for SO_2 and NO_2 (http://airquality-qualitedelair.ccme.ca/en/).

The 2009 Air We Breathe Report (NSE, 2009) provides an analysis of ozone trends for the annual average, one-hour maximums and some diurnal trends for all stations across Nova Scotia. This analysis shows that Nova Scotia's air quality is usually under standards but there is room for improvement, however, this analysis is only done up to 2007.

Figure 3-2 Annual maximum one-hour average O_3 concentration, 2000–2007



Notes: Insufficient data available from, Dartmouth (2006), Halifax (2000, 2007), Kentville (2002), Pictou (2000–2002, 2005–2006), Sable Island (2003), Sydney (2001).

Figure 4. Maximum one-hour ozone concentrations from all stations across Nova Scotia (2000-2007). From The Air We Breathe report NSE, 2009.

1.8 Scope of Work

The focus of this study will be on the production of Ground Level Ozone in the planetary boundary layer where it can have the most impact on life on Earth. The relationship between ozone and its precursors NO_x and VOCs is examined in several ways to determine the chemistry involved in Halifax ozone production. The role of isoprene is examined in detail as it has the highest ozone production potential (Section 1.5) and similar geographic conditions exist in Halifax that were described by Millet (2016) (Section 1.5). One specific hypothesis that will be tested is whether elevated O_3 levels in Halifax, when present, follow the morning peak associated with biogenic isoprene emissions. Other controls on ozone production such as meteorology and transport, are also examined and discussed. Finally, this thesis will look at trends in years beyond 2007, updating aspects of the NSE 2009 report.

2 Methods & Datasets

2.1 National Air Pollution Surveillance (NAPS) Network

The data used for this thesis was taken from the NAPS online database (http://maps-cartes.ec.gc.ca/rnspa-naps/data.aspx) unless otherwise indicated. NAPS compiles the data on criteria air pollutants (see Section 1.7) recorded at stations across Canada. The downtown Halifax station is located on the fourth floor of the Vogue Optical building at 1649 Barrington Street, Halifax (NAPS ID #30118), and is the main station used for analysis in this research. This downtown Halifax station has been relocated to the Johnston Building located at 1672 Granville Street, Halifax (NAPS ID #30113), although both stations recorded data for the year 2017, and both are influenced by city traffic. Other stations used for analysis include Lake Major located outside Dartmouth (urban background) at 341 Cherrybrook Road, Halifax (NAPS ID #30120), and Aylesford Mountain (rural background) located at 1009 Mountain Brow Road, Kings County (NAPS ID #30701), (See Appendix A for details). Data from the NAPS database is quality checked up to the end of 2016, however, unverified 2017 data is available through the Nova Scotia Environment Air Quality database (https://novascotia.ca/nse/airdata/) and used for some preliminary analysis.

Some ozone data was also used from the downtown Toronto station at Bay St./Wellesley St. W. (NAPS ID #60424) and a Mississauga station located next to a highway at 3359 Mississauga Road North (NAPS ID #60434). Data is available online currently for all years 1974 to 2016 and 2017 data should be available later this year after quality checks. Since stations often monitor different pollutants during different years, the Nova Scotian stations are described in detail in Appendix A. Finally, datasets used in this study were available for download in either Excel or HLY formats and were analyzed using scripts created by Dr. Li, modified by myself, in the computing program Matlab.

2.2 HYSPLIT

In order to analyze air mass transport trajectories to estimate where certain pollution and precursors originated from, this research made use of NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory model, or HYSPLIT. This free online atmospheric transport model allows one to estimate where an air mass originated and travelled over different time frames. HYPLIT can use different meteorological fields (i.e. winds) and can compute trajectories backwards or forwards in time. In this project, HYSPLIT was used with North American Mesoscale Forecast System (NAM) wind fields available every 6 hours (0h, 6h, 12h, 18h), with forecast values filling in the intermediate times (3h, 9h, 15h, 21h), to calculate where air masses in Halifax likely originated from using ensemble backwards trajectories launched at 500 m above ground level. The trajectories are internally computed in time steps shorter than 1 hour and then displayed at user-selected intervals of 6-hrs in this work. The geographic coordinates, date and time are specified and a plot is automatically produced showing the trajectories.

2.3 Distinguishing Production Regime

The ozone production regime for Halifax is not obvious due to its small area and population, despite it being the largest city in Atlantic Canada. The production regime for most major urban centres is VOCs-sensitive, while less urban areas with an abundance of biogenics and an absence of NO_x emissions have a NO_x-sensitive ozone production (Jacob, 1999). To distinguish the production regime for a region where it may not be obvious, like Halifax, there are several methods that have been used by scientists and policy-makers. For this study the relationship between ozone and NO_x and ozone and VOCs was the most used method.

2.3.1 Formaldehyde Ratios

Several studies have been conducted using Formaldehyde (HCHO) to nitrogen dioxide (NO_2) ratios in order to find the O_3 production regime of an area with satellite data. HCHO/NO_2 Data from the NASA Ozone Monitoring Instrument (OMI) satellite was used by Millet et al. (2008) and Duncan et al. (2010), while Martin et al., (2004) have used the Global Ozone Monitoring Experiment (GOME) space-based column abundance measurements to estimate surface levels by proxy because precursor pollutants are emitted in the surface boundary layer and the majority of pollution is presumed to stay within that layer. HCHO is used to estimate VOC reactivity because isoprene measurements are not available from satellites and HCHO is an oxidation product of VOCs, including isoprene; NO_2 on the other hand is a good proxy for NO_x available in the region for ozone production. This ratio gives insight to the abundance of each precursor and also the dominant sink for HO_x radicals in the ozone production sequence. The ratios corresponding to each regime are not widely agreed on among researchers. Martin et al. (2004) concluded that HCHO/NO_2 ratios >1 indicate a NO_x-sensitive regime while ratios <1 indicate VOC sensitivity. However, Duncan et al. (2010) argued that the transition ratio of one, proposed by Martin et al. (2004), is geographically and temporally variable so it not be applicable for all regions. Duncan et al. (2010) concluded that VOCs-sensitive conditions occur at a $HCHO/NO_2$ <1 while NO_x-sensitive conditions occur at $HCHO/NO_2$ > 2, while between 1 and 2 represents a transition regime where reductions in NO_x are no more useful to reduce ozone production than reductions in VOCs. A more recent study by Shroeder et al. (2017) provides new insights on this $HCHO/NO_2$ ratio using in situ measurements, which the authors argue are more accurate than satellite data because the sampling is done in the boundary layer. This study reported that in Colorado the transition regime was found between $HCHO/NO_2$ ratios of 1.1 and 3, while in Houston the transition ratio was found to be between 1.3 and 4.3, highlighting the uncertainty of using the $HCHO/NO_2$ ratio method to determine ozone production regimes. $HCHO/NO_2$ ratios were not derived for this project due to time constraints, and, more importantly because HCHO is not available from NAPS and, moreover, Sillman (2002) has argued that NO_2 and/or NO_x are insufficient to accurately predict the O_3 production regime suggesting instead that total reactive nitrogen NO_y should be used, which includes HNO_3 but which is *also* unavailable from NAPS .

2.3.2 Ozone-Precursor Ratios

The *efficiency* of local conditions for ozone production can be described using ratios of the primary pollutants $VOCs/NO_x$, where VOC is defined as any C2-C10 nonmethane hydrocarbon (Main & Roberts, 2000). These ratios can also distinguish the production regime by characterizing the dominant ozone precursor in the region of interest. The US Environmental Protection Agency (EPA) created documents to advise policy-makers about enhanced ozone monitoring techniques, in particular by using the $VOCs/NO_x$ ratio (Main & Roberts, 2000). If the $VOCs/NO_x$ <5 ozone formation is very slow and suppressed by high NO_x; ozone production efficiency will then increase with removal of

NO_x. When VOCs/NO_x is >15 ozone formation is limited by NO_x availability, and between the ratio of 5 and 15 ozone is in a transitional production regime and may be limited by both NO_x and VOCs (Main & Roberts, 2000). The VOCs/NO_x ratio is usually calculated in the morning hours between 6-9AM. A generalization can be made in cities with high NO_x emissions that VOCs control the initial buildup of ozone but the amount of NO_x released controls how much ozone is produced as that air mass moves downstream into suburban and rural areas with high ambient VOCs levels (Sillman, 1999).

A simple way to estimate the ozone production regime is to look at the relationship between an ozone precursor, like NO_x and ozone. According to Geddes et al. (2009), under VOCs-sensitive conditions ozone production is inversely proportional to NO_x levels as an increase in NO_x would suppress ozone production and eventually titrate ozone. Conversely, at NO_x-limited conditions ozone production will linearly increase with additional NO_x. However, in very polluted regions, close to NO_x emission sources, or in winter when ozone production is slow ozone formation is suppressed by NO_x titration (Sillman, 1999).

3 Results and Discussion

3.1 Effect of NAPS Station Placement

In the past year of monitoring (2017) the NAPS program has moved the downtown Halifax station from the Vogue building to the Johnston building, about 100m away and facing different streets. The difference in ozone levels at these two locations has been analyzed to note the effect from the change in monitoring conditions. The intake height of the O_3 sensor on the Vogue building was at 9m, while the new Johnston location has an intake height of 12m. Although both locations are downtown and exposed to high pollution sources, the Vogue location was on a busier street and interection, slightly closer to the sources on the ground, and would have been impacted more by mobile emissions i.e. NO_x, CO and VOCs. The higher NO_x titration effect on ozone largely explains the lower ozone concentration at the Vogue station (Figure 5), although a comparison to the y=x line reveals this is not a simple offset bias. At low ozone values (<30 ppb) the Johnston station records higher values than the Vogue but at high ozone (>30 ppb) this bias reverses and the Vogue station has higher values. It is not clear how this is connected to sensor bias (if any), distance to emission sources and complex urban corridor mixing, and this is beyond the scope of this study.

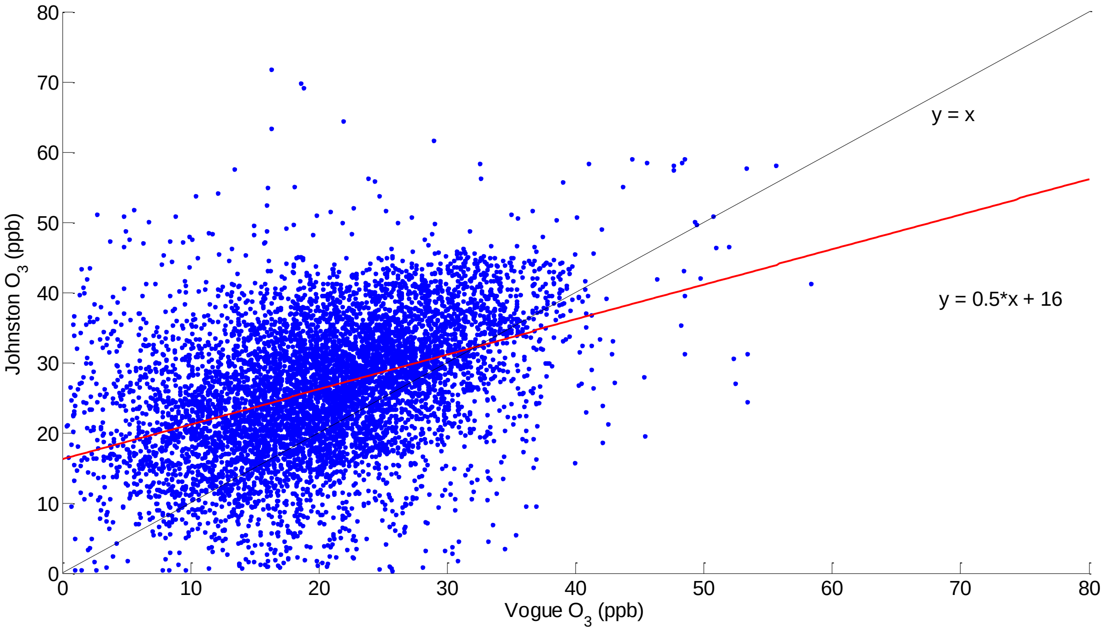


Figure 5. 1 hour ozone averages for 2017 at the Vogue Building vs. at the new station location at the Johnston building (3m higher and 100m apart). Red line is the line of best fit and the black line is the 1:1 line for comparison.

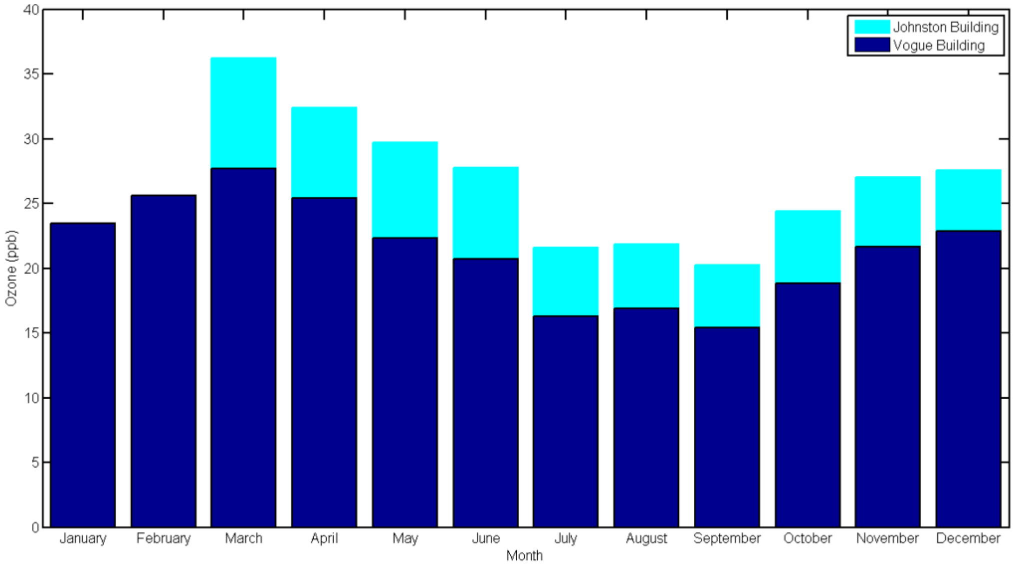


Figure 6. Monthly average ozone at two downtown Halifax stations during a period of overlapping measurements. Johnston came online in March 2017, while the Vogue building went offline in January 2018.

Based on the average difference in monthly mean values from March to December 2017 (Figure 6), the Johnston building records ozone that is 6.1 ppb higher compared to the Vogue building. These plots highlight the impact that NO_x emissions have on ozone concentration in Halifax and also show the importance of monitoring station placement for accurate ozone concentrations; Nova Scotia Environment is aware of this change (Personal Communication, Matt Seaboyer, 2018), and it is beneficial to have an overlapping period between monitoring stations if one is replacing another.

3.2 Urban vs Suburban Ozone Levels

By comparing the downtown Halifax station data to the more suburban Lake Major data we can distinguish patterns that are unique to downtown Halifax, as these stations are only 11 kilometres from one another. First of all, it is interesting that the difference in ozone at Halifax and Lake Major is variable throughout the years. As shown in Figure 7 Halifax recorded ozone higher than Lake Major more often before 2013 than afterwards. Furthermore, the mean difference between ozone at the Lake Major and Halifax stations from 2006-2013 is 3.7ppb, and from 2013-2016 is 8.4ppb. Overall ambient ozone levels at Halifax are on average 5.8 ppb lower than ambient ozone at Lake Major, which is reasonable as Halifax experiences titration from large sources of NO_x absent at Lake Major. Lake Major is seeing an increase in ozone (Figure 11, discussed below), which would contribute to the increased difference in ozone between Lake Major and Halifax. It is interesting to note that in July of 2013 Imperial Oil announced plans to close and phase out the Dartmouth Refinery by the end of that year (CBC News, 2013), which processed 89,000 barrels of oil a day, producing ashphalt, heating oil, bunker fuel, gasoline, propane and butane. This removd a source of VOCs, NO_x, CO and SO_2, although the timing (2013-2014) does not agree well with the dramatic NO_x reduction in 2011 presented next, which needs further study.

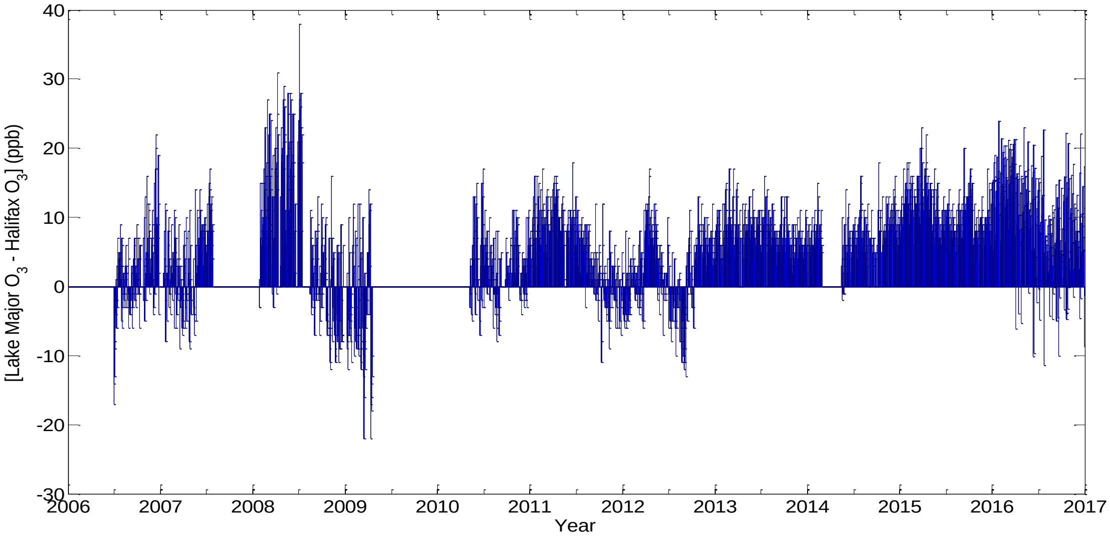


Figure 7. Difference between 24-hour ozone at Lake Major and Halifax for 2006-2017. Lake Major began monitoring in 2006.

Further comparing Halifax to Lake Major, it is shown that NO_x in Halifax is consistently much higher than Lake Major's NO_x (Figure 8), especially post 2011, which reinforces previous questions about just how much ozone in Halifax is impacted by the NO titration effect as the ozone difference is smaller than the NO_x difference. Where ozone between these two stations differs by about 6 ppb, NO_x is on average 17 ppb higher in Halifax. The extremely low NO_x levels in Lake Major from 2011-2016, as shown, likely represent continental background levels of NO_x as there are no nearby sources. The Lake Major station is in a forested area on the outskirts of Dartmouth, 2 km from the nearest main road. However, the slightly higher levels of ozone in Lake Major are likely due to downwind transport of pollution from Halifax, which, as the previous wind analysis has shown, leaves the transport mechanism unclear. High NO_x will titrate ozone close to the source but as the VOC-limited air mass moves downwind ozone will be produced in the presence of high VOCs present in the forested area of the Lake Major station, in addition to O_3 being restored as NO_2 reverts back to NO.

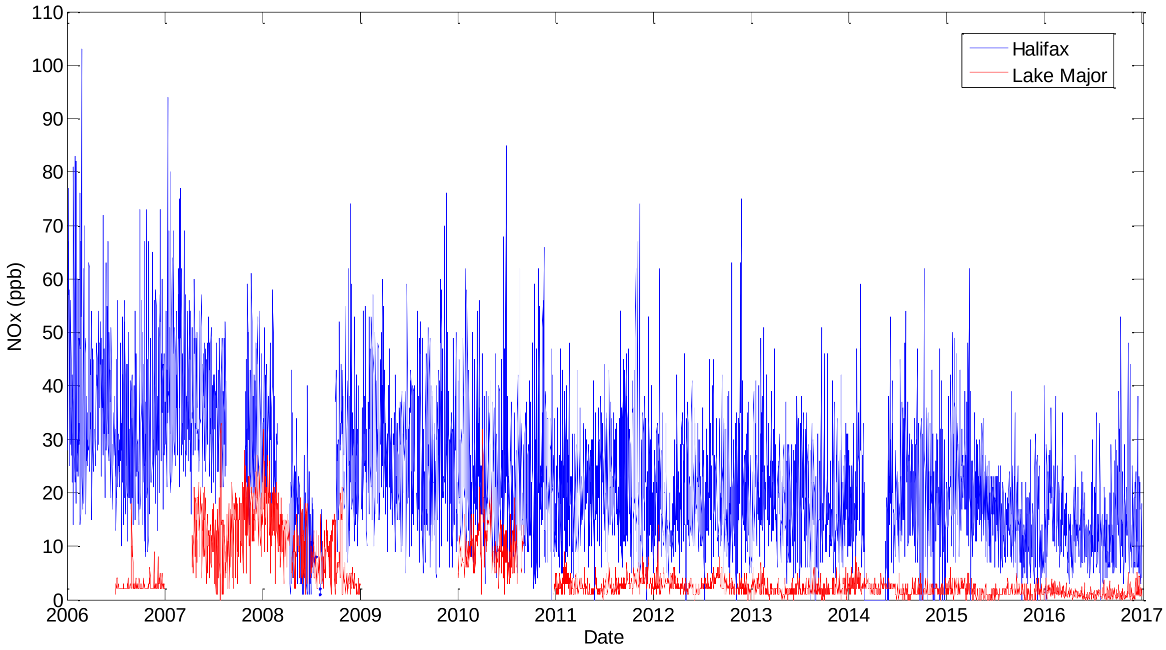


Figure 8. 24-hour average NO_x concentrations over 10 years from 2006-2016 in Halifax (blue) and Lake Major (red).

To further explore the effect of lower, titrated ozone at a downtown station vs. higher, un-titrated ozone at a suburban station I analyzed NAPS data in Toronto and Mississauga in 2016. This was also done to give context to Halifax and Lake Major pollution levels compared to Canada's largest city. Specifically, the expectation was that downtown Toronto would experience more ozone titration and Mississauga would see higher ozone levels like Lake Major. Mississauga, which is the more suburban of the two actually experiences slightly higher NO_x than Toronto (Figure 9), and both have very similar ozone levels (Figure 10) with an R^2 value of 0.79 (correlation plot not shown). The Mississauga station chosen is therefore not representative of a true suburban area such as the Lake Major station is to Halifax; in hind sight, this is not surprising since the Mississauga sensor is also close to a major highway. NO_x measurements from

Downtown Toronto exceeded 40 ppb five times in 2016 with a yearly average of 16 ppb (Figure 9) whereas, Downtown Halifax NO_x exceeded 40 ppb three times with an average of 14 ppb (Figure 8).

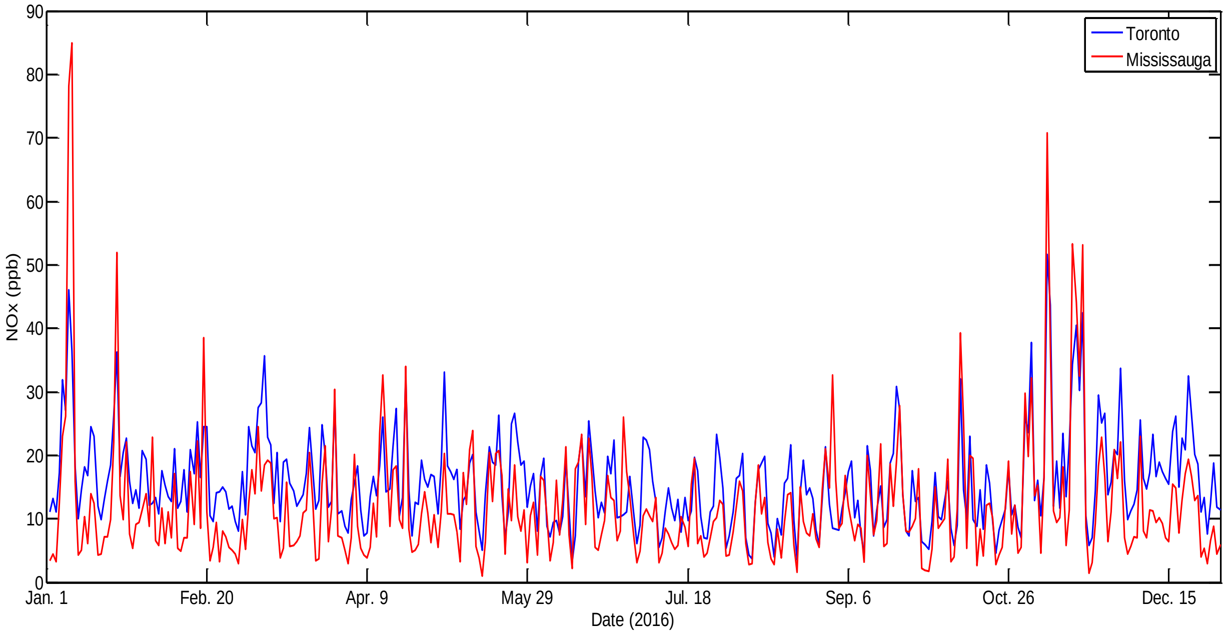


Figure 9. 24-hour average NO_x concentrations in Mississauga and Toronto for 2016.

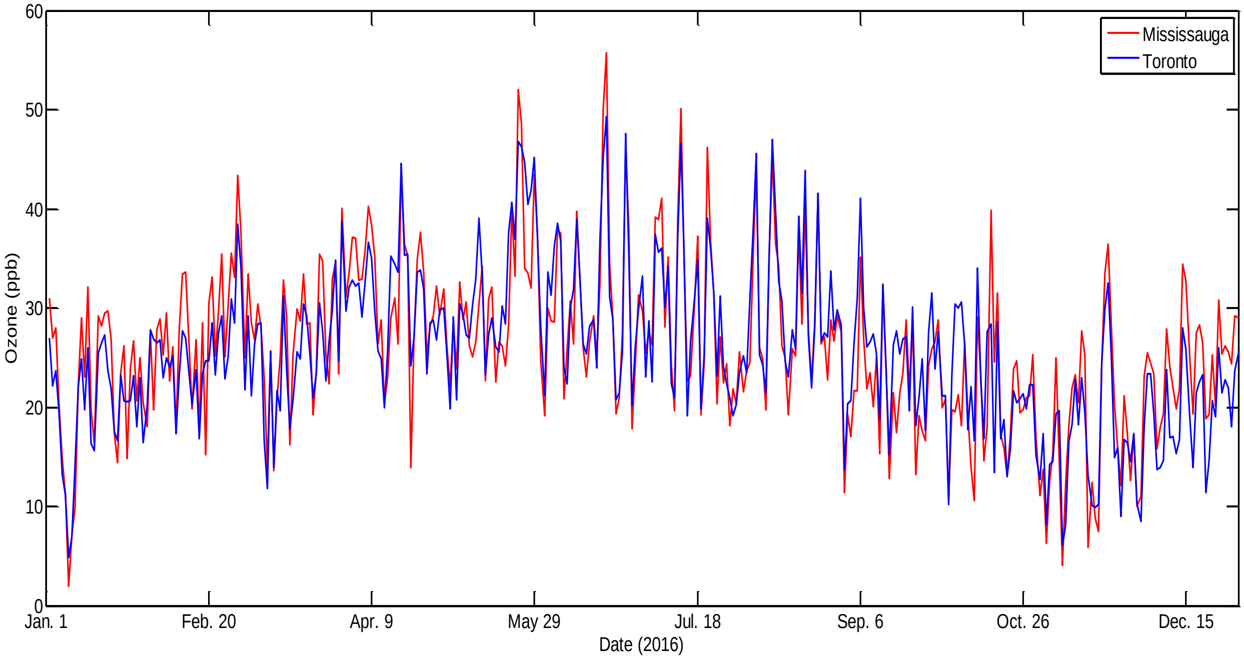


Figure 10. 24-hour ozone concentrations for Mississauga and Toronto in 2016.

Although NO_x levels are almost equal between both Toronto and Halifax, annual average ozone at Toronto is 26 ppb while the annual average in Halifax is 19 ppb. This means either there is less ozone production in Halifax or a more intense titration effect, or both. Overall, Halifax and Toronto stations experience similar levels of pollutants despite Halifax being much smaller in population than Toronto, which was not expected, although both places experience a sea-breeze effect so similar processes may be involved in afternoon O_3 production and dispersion. Notably, this analysis discussed annual averages of 24-hour averages, which do not allow large enhancements to be seen as in the daily maximum ozone, which would most likely distinguish the larger Toronto from Halifax.

3.3 Long-term Ozone Trends in Nova Scotia

As noted above, it is important to have a good understanding of background ozone levels so we can distinguish between these and local ozone production. We can estimate background ozone levels in Nova Scotia by analyzing data from areas that are not impacted by local pollution like Kejimkujik National Park and Aylesford Mountain then compare to Halifax and Lake Major which both experience higher levels of anthropogenic pollution (Figure 11).

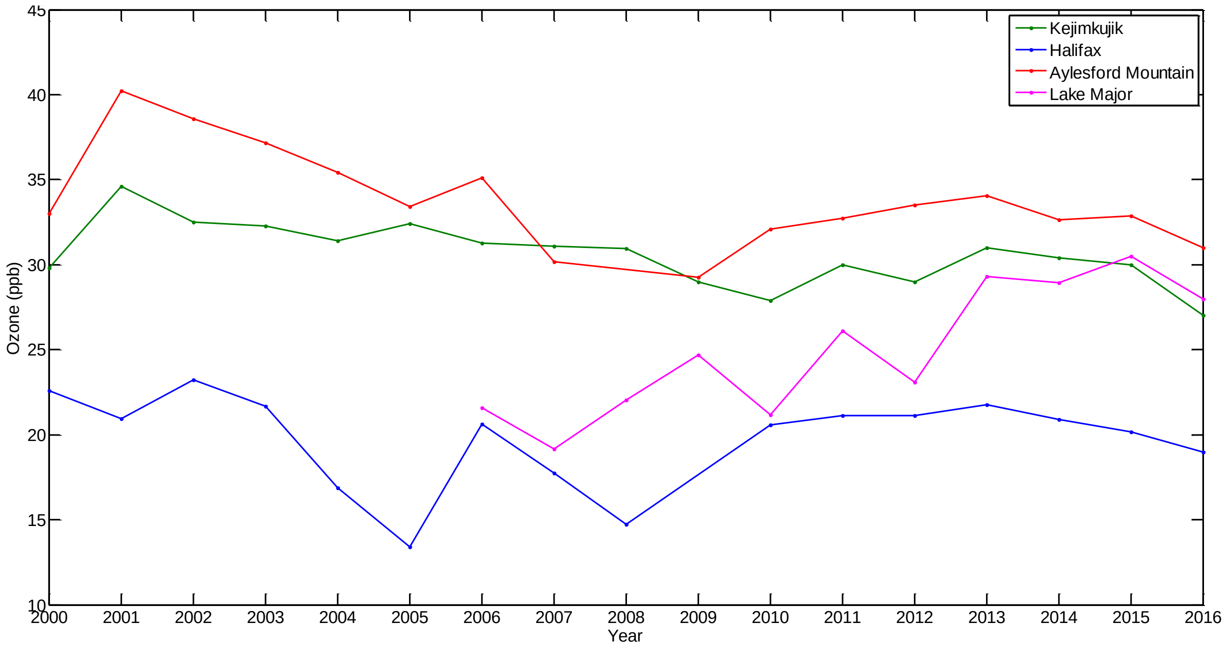


Figure 11. Annual average ozone levels in Aylesford Mountain, Lake Major (Dartmouth), Halifax and Kejimkujik National Park over 16 years. Ozone monitoring in Lake Major began in 2006.

Figure 11 shows that Halifax has always had lower ambient ozone levels on average than the rural sites of Kejimkujik and Aylesford Mountain. This may seem counterintuitive due to the higher pollution sources within the city but the high NO_x emissions in Halifax titrate ozone near the monitoring station and reduce levels to low concentrations. Aylesford Mountain has the highest ambient ozone levels out of all four locations and is in the Western air zone management area according to The Nova Scotia Air Zone Report (2015). It was suggested in Nova Scotia’s 2009 Air Quality Report that Aylesford’s high elevation of 259m is the cause for such high ozone levels, as it is well known that ozone concentration increases with elevation. A European study deploying the MOZAIC observation system found the ozone vertical gradient to be 30 ppb/km up to 1000m above sea level (Cousin et al., 2007). This would mean that the Aylesford station would have an additional 7.8 ppb of ozone just from its elevation. Additionally, the

Western air zone management area receives pollution transported from the Eastern United States due to proximity and typical air flow patterns. In fact, the 2015 Air Zone Report shows that emission controls that were implemented for NO_x pollution in Ohio were correlated with reduced Western Nova Scotia ozone from 1999 to 2005. Aylesford's ozone roughly decreases between 2000 and 2009, in agreement with Cooper et al. (2012), who document a decreasing trend for ozone in the Eastern United States up to 2010. Beyond that, NAPS data since the 2009 Air Zone Report (i.e., after 2007) show that Aylesford and the Western Nova Scotian air zone do not continue to decrease in ozone, whereas, between 2005-2013 NO_2 columns from the OMI-Aura instrument show a general decrease over the entire United States, especially over the Eastern USA due to power plant emissions reductions (Lamsal et al., 2015).

By using annual averages we get a better idea of typical ozone levels as short-term enhancements are "averaged out". It can be seen that our average ozone levels fluctuate greatly and can even differ by more than 10 ppb within the province (Figure 11). The annual average ozone over 16 years of data is 19.8 ± 2.8 ppb for Halifax, 33.8 ± 2.9 ppb for Aylesford, 30.6 ± 1.8 ppb for Kejimkujik and 25.0 ± 3.8 ppb between 2006-2016 at Lake Major. It is, therefore, likely that any ozone level significantly higher than about 20 ppb in Halifax is an enhancement from either local or transported sources. It is worth noting that there exists an annual average acceptable ozone level objective under the NAAQO (Appendix B) and it is only 15 ppb, which is routinely exceeded in Nova Scotia, and elsewhere in Canada.

3.4 Diurnal and Seasonal Ozone Patterns in Nova Scotia

Figure 12 shows the typical diurnal ozone pattern in Downtown Halifax. Ozone levels experience a minimum during the morning rush hour, about 7-9 AM, when NO_x experiences a peak. Ozone levels are not strongly affected during the afternoon rush hour between 4-5PM. The lowest daily average levels occur in the morning between 7-9 AM.

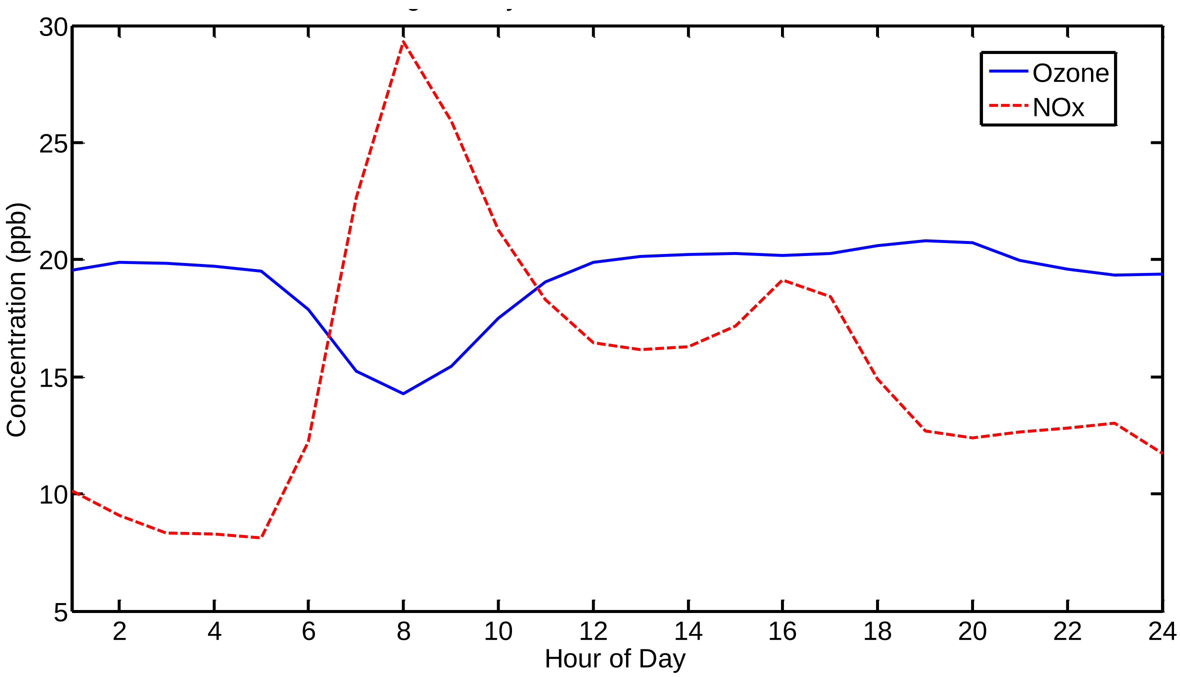


Figure 12. Diurnal pattern of 1-hour average ozone at Halifax in 2016.

The peaks and lows in O_3 are inverse of the diurnal NO_x pattern in the morning because of the NO_x titration effect. Most of the diurnal pattern can be explained by this relationship, but there is a difference in the magnitude of the effect NO_x has on ozone throughout the day which suggests there are other processes in effect. For example, the abrupt NO_x peak caused by the morning rush hour titrates the morning ozone very intensely, perhaps because the stable nocturnal layer is still present and convective mixing has not begun (Monson, 2013). In contrast, the smaller peak in NO_x between

3-6 PM is associated with near constant ozone concentrations. There does not seem to be enough NO_x in the afternoon to produce a titration effect on ozone, likely because enhanced boundary layer ventilation and/or the active sea breeze in the afternoon may be preventing NO_x buildup.

The plots showing diurnally averaged ozone and NO_x in Lake Major (Figure 13**Error! Reference source not found.**) and Aylesford (Figure 14**Error! Reference source not found.**) are qualitatively and quantitatively different than in Halifax (Figure 12). While ozone concentrations in Halifax are clearly inversely correlated with NO_x levels during morning rush hour, the concentration of ozone on Aylesford Mountain and at Lake Major seems mostly driven by the daily sun cycle as peak ozone occurs when photochemistry would be most active, pronounced on **Error! Reference source not found.** between the hours 12 and 19. Peak afternoon NO_x in Lake Major, almost ten times lower than in Halifax, occurs around 20 hours which may be due to transport from Halifax, although the downtown core is only 12 km away, which would dictate transport times of ~1 hr under even winds of 12 km/hr. The Lake Major station lies on the outskirts of Halifax so wind flowing from the direction shown in Figure 15 has the potential to carry pollution from Downtown Halifax and Dartmouth i.e. between 160 and 300 degrees. However, shows that air flowing from the urban areas does not correspond to a significant increase in average NO_x or O_3 concentrations at Lake Major. Sea breezes may be at play, but this was not tested in this work. The diurnal NO_x pattern at Aylesford Mountain (Figure 14**Error! Reference source not found.**) shows a slight increase in NO_x between 9 and 11 suggesting some influence from a nearby populated area which conflicts with Aylesford Mountain being labelled as a pure "background" site.

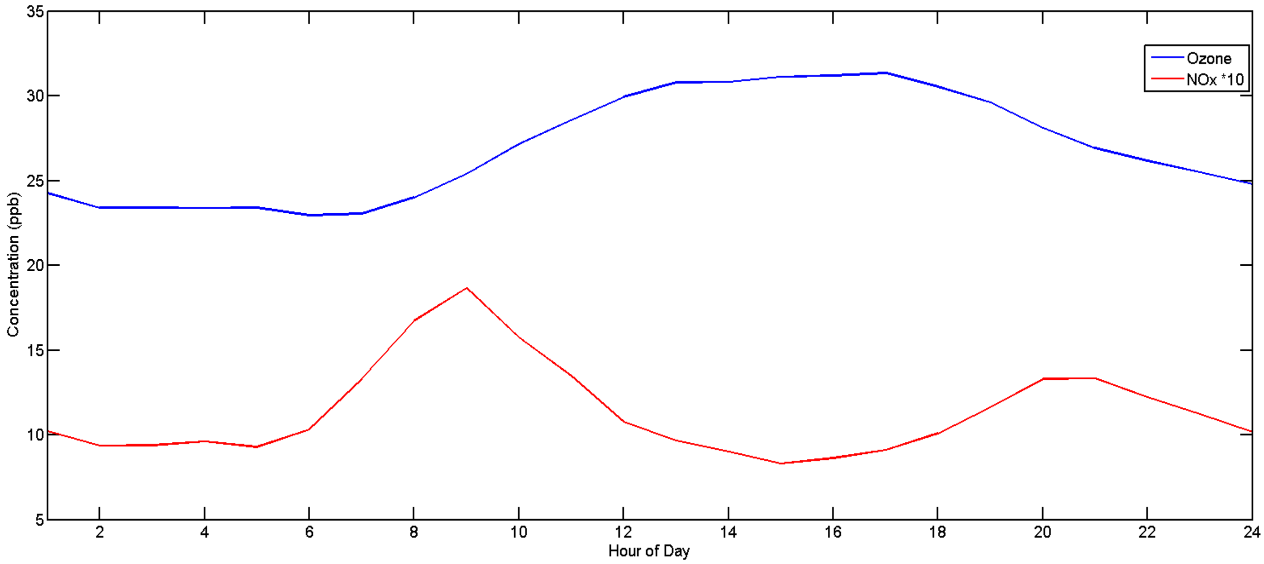


Figure 13. Diurnal pattern of 1-hour average ozone at Lake Major in 2016. Note that NO$_x$ is scaled by a factor of 10 for display purposes.

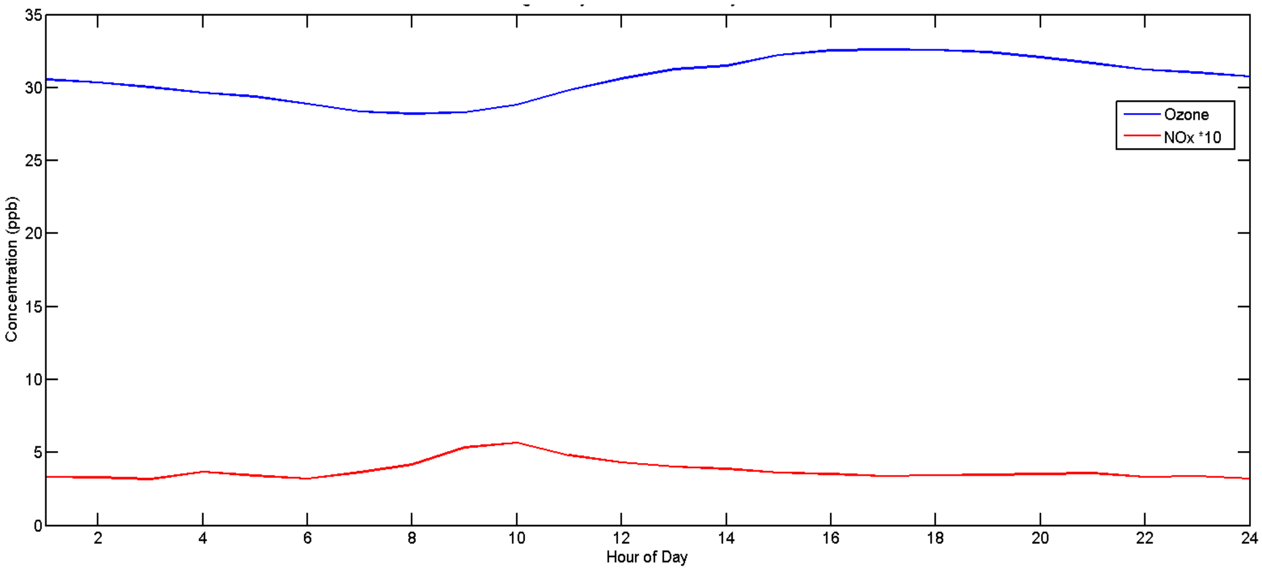


Figure 14. Diurnal pattern of 1-hour average ozone at Aylesford Mountain in 2016. Note that NO$_x$ is scaled by a factor of 10 for display purposes.

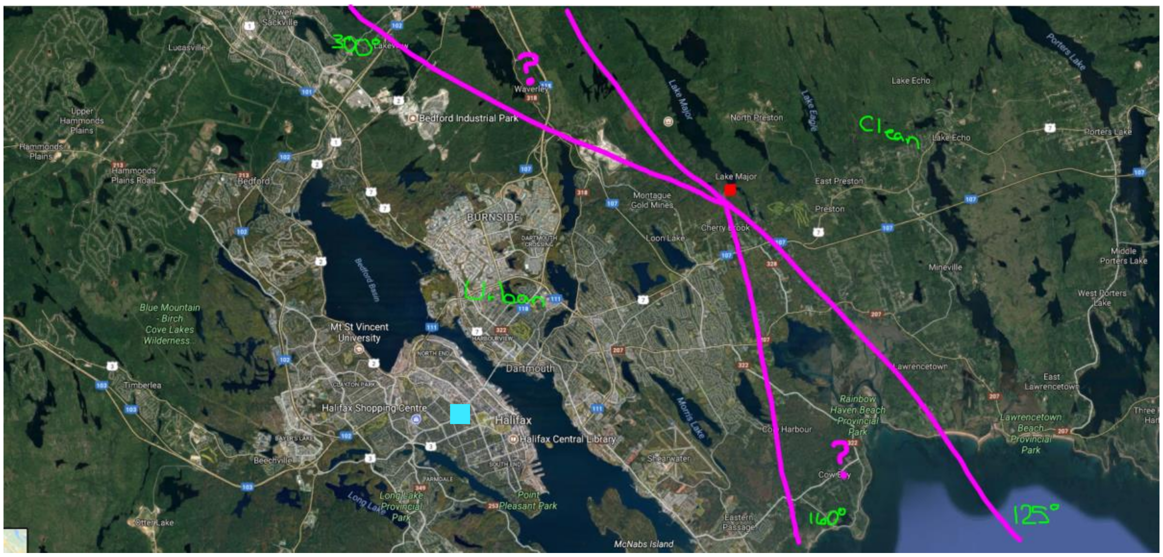


Figure 15. Map of Lake Major NAPS station (red square) with sources of clean and urban air marked by pink lines. The downtown core (blue square) is 12 km from the NAPS station. Note: peripheral areas with question marks are neither clean nor urban so they were left out of this analysis.

Table 1. Average concentration of O3 and NO_x at the Lake Major station in 2016 separated by direction of air flow.

Lake Major Pollutant Transport	From Polluted Region (160°-300°)	From Clean Region (335°-125°)
Average O_3 (ppb)	28.2 ± 9.5	27.1 ± 8.4
Average NO_x (ppb)	1.0 ± 1.8	0.4 ± 1

As shown in Figure 16 Halifax experiences the usual spring maximum which Tarasick and Slater (2008) explain by the stratospheric ozone maximum during the late winter, which can lead to ozone transport to the troposphere. This same seasonal maximum is seen in suburban (Figure 18) and remote (Figure 17) stations across Nova Scotia, showing that it is not caused by local production but by seasonal background ozone patterns. The 24-hour average ozone exceeds the 24-hour ozone NAAQO of 25 ppb (Appendix B) during the springtime maximum. The typical summer enhancements above the local background seen between May and October in Figure 16 and Figure 17 has been previously explained by the positive relationship between ozone and temperature. Most notably higher temperatures are associated with increased biogenic hydrocarbons emissions and enhanced stagnation conditions which accumulate ozone and its precursors (Rasmussen et al., 2012), however, we know that more than local production is involved, i.e., long-range transport, dicussed next.

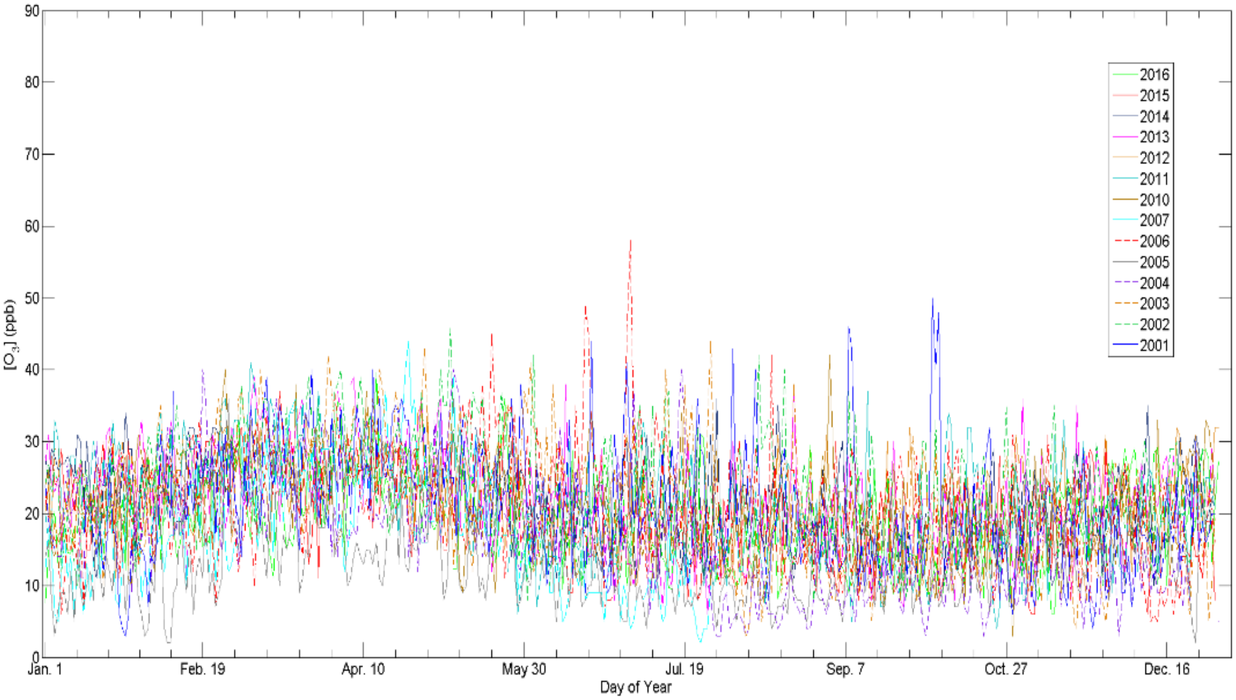


Figure 16. 24-hour average ozone from 2001-2016 in Downtown Halifax.

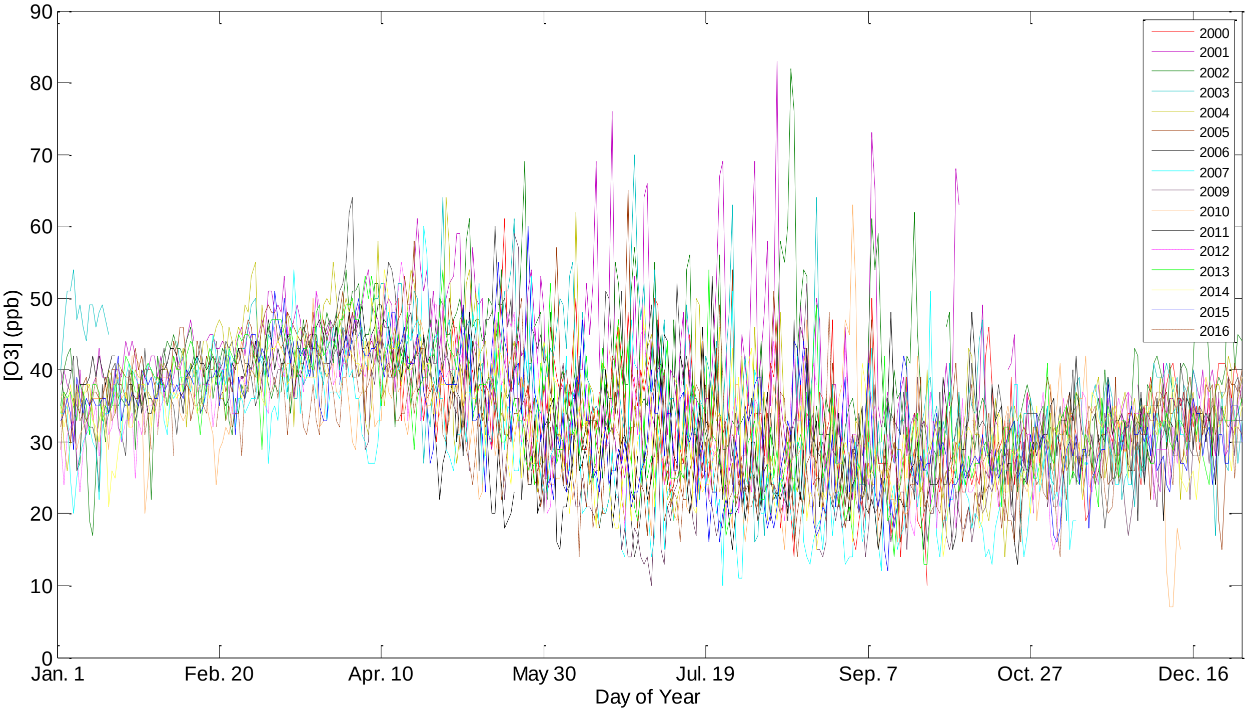


Figure 17. 24-hour average ozone from 2000-2015 at Aylesford Mountain.

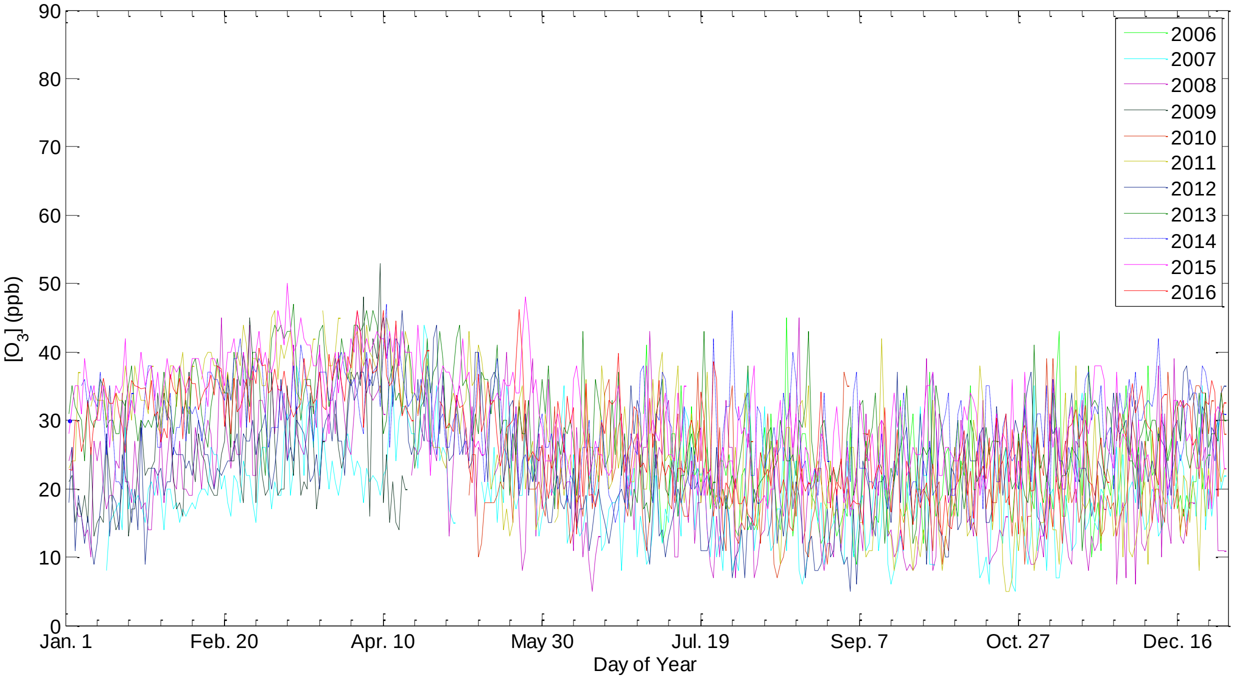


Figure 18. 24-hour average ozone from 2006-2016 at Lake Major. Monitoring for ozone began in 2006 for this station.

The average ozone at the Aylesford and Halifax stations is much more variable than at the Lake Major station in the summer months. Between May and October the Halifax station sees significant ozone enhancements, but as there are no obvious enhancements at the nearby Lake Major station (Figure 18) this points to local production within Halifax. Ozone enhancements are much more pronounced at the remote Aylesford Mountain station, rising to 80 ppb in some cases which is likely due to pollution transport episodes as there is little local pollution sources in that area. It is worth noting that the transported O_3 pollution signature at Aylesford is completely absent from Lake Major and not obviously correlated with Halifax O_3, although this was not formally tested, implying that long-range transported O_3 to Western Nova Scotia does not simply propagate to Halifax and Lake Major, only ~100 km further to the southeast. Site elevation may be important if the transported pollutants remain aloft, flowing over stable surface conditions; moreover, there are some storm tracks/weather patterns that could favor transport only to the western portion of NS (Personal Communication, Andrew Teakles, 2018).

3.5 BVOCs and Halifax Ozone

Biogenic isoprene emission is temperature and light dependent and it is therefore released primarily during the summer months in Nova Scotia. Figure 19 shows the relationship between temperature and isoprene in Kejimkujik National Park, where isoprene peaks with temperature and falls to zero in the winter months. Halifax's isoprene-temperature relationship was analyzed to compare a heavily forested area to an urban center (Figure 20). Isoprene in Halifax is almost negligible showing there are no significant sources within the city, but there is still a slight peak during the summer months. Due to the high reactivity of isoprene it is possible that it is consumed in

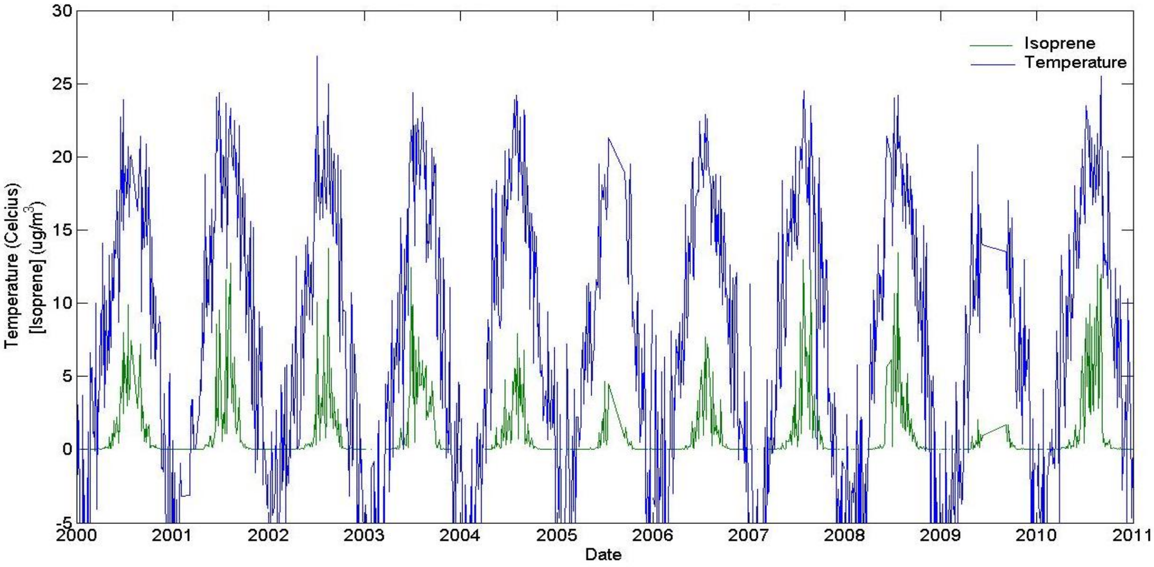


Figure 19. Annual daily average temperature and Isoprene concentrations at Kejimkujik National Park.

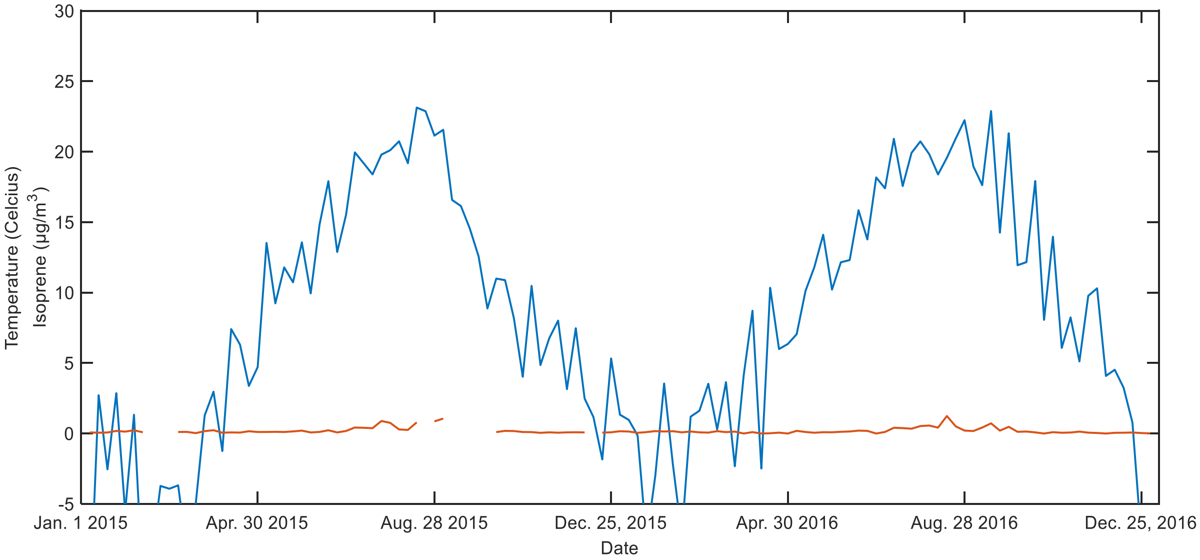


Figure 20. Daily average temperature (blue) and isoprene (red) in Halifax for 2015-2016.

reactions too quickly to be detected with the 24-hour canister sampling technique. The large biogenic source of VOCs during the summer puts the Eastern United States in a NO_x-sensitive production regime (Jacob et al., 1995). The same is likely for Nova Scotia due to its abundance of forested areas (see pp. 21 Section 1.5). It is common to observe a transition from NO_x-sensitive to hydrocarbon-sensitive ozone production in the fall when the isoprene-emitting species begin to lose their leaves and the growing season ends. This phenomenon was studied in the Eastern United States by Jacob et al. (1995) and has important policy applications as one area may experience more than one production regime throughout the year, requiring controls on both NO_x and VOCs emissions at different times of the year. Still, it is uncertain whether greater Halifax follows the general pollution production patterns of an urban or rural region and whether this varies seasonally.

To see if the phenomenon observed by Millet et al. (2016) is occurring in Halifax the highest 10% maximum 1-hr O_3 was compared to coincident 24-hour average canister isoprene measurements in Halifax between 2000 and 2015. Figure 21 shows that the relationship is weak (R=0.34) and that not much data remains after filtering. Given this negative result, morning and afternoon ozone were next compared using box-and-whisker plots (Figure 22 - Figure 24). These plots show outliers or maximum ozone levels for morning and afternoon trends. If abnormally high ozone levels appear during the morning hours previous studies have suggested that overnight biogenic precursors could be responsible. To further investigate this it is helpful to know if the air mass in Halifax experienced transport from a forested area. The NOAA HYSPLIT model was used to trace air masses backwards from Halifax at a given time to estimate the origin of the air mass. If the air mass originated in Western Nova Scotia, close to Kejimkujik Park, it is likely to have carried BVOCs like isoprene into Halifax. If the air mass originated in the uppermost Northeastern United States it is likely to have brought pollution like longerlived VOCs and O_3 into Halifax. Therefore, the HYPLIT model is used to examine the origin of the air mass and suggest the possible composition of that air mass.

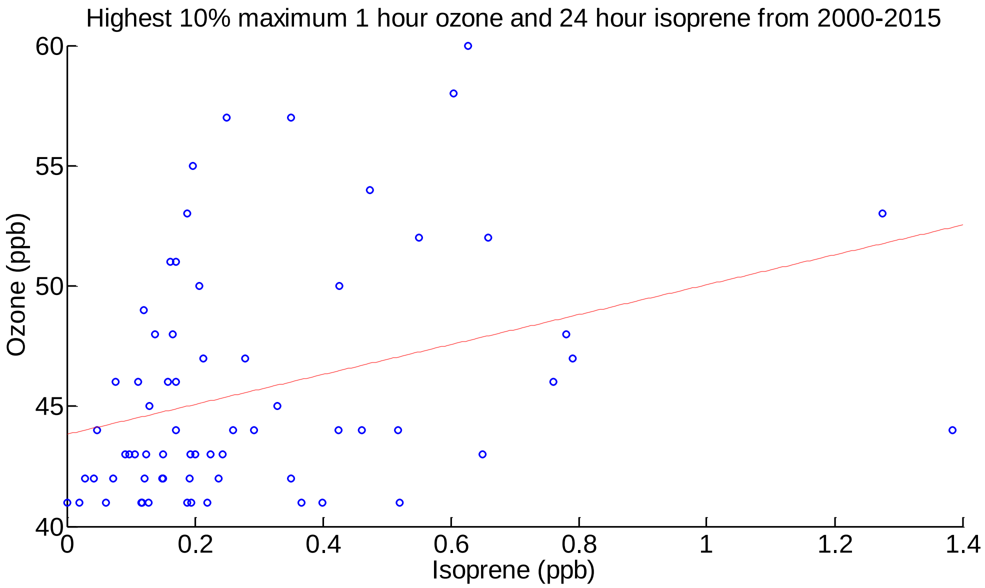


Figure 21. 90th percentile 1-hr maximum ozone from 2000-2015 with coincident 24-hr average canister measurements of isoprene in Halifax.

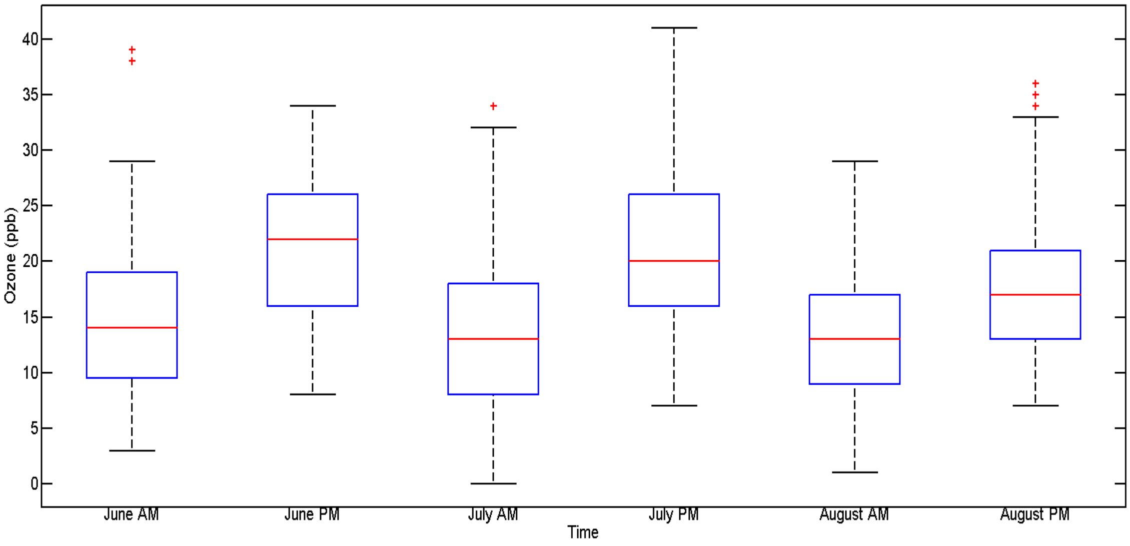


Figure 22. Boxplot of morning (6-10AM) and afternoon (2-6PM) hourly ozone averages in Halifax for 2016. The red line represents the median value in the data set and the box edges show the 25th (bottom) and 75th (top) percentiles of data. The whiskers extend to the minimum and maximum values. The red stars are outliers, defined by Matlab as more than three median absolute deviations from the median.

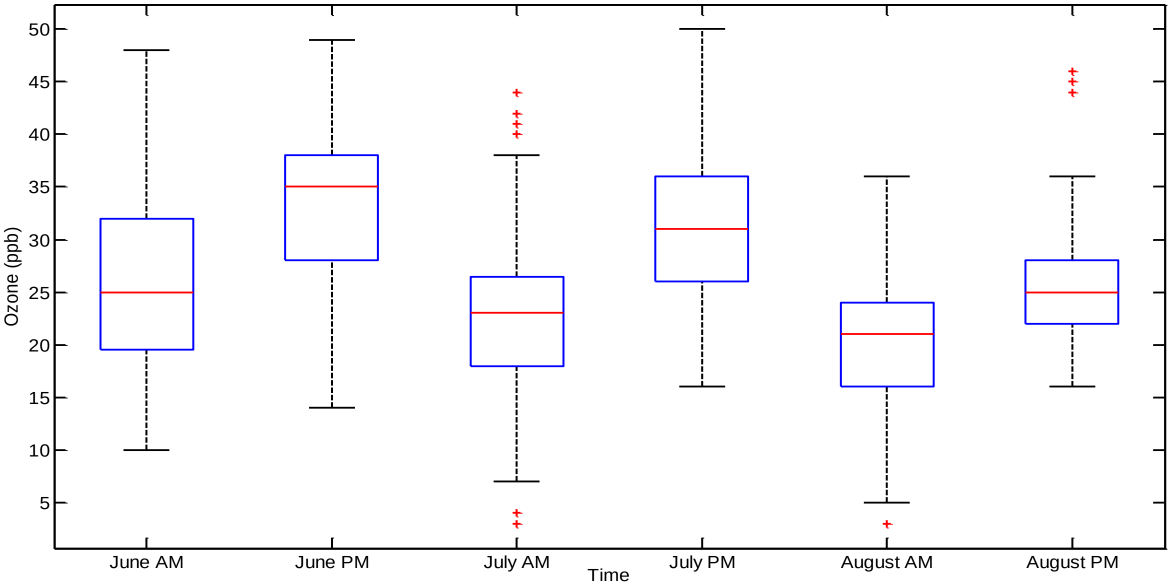


Figure 23. Boxplot of morning (6-10AM) and afternoon (2-6PM) hourly ozone averages in Lake Major for 2016. The red line represents the median value in the data set and the box edges show the 25th (bottom) and 75th (top) percentiles of data. The whiskers extend to the minimum and maximum values. The red stars are outliers, defined by Matlab as more than three median absolute deviations from the median.

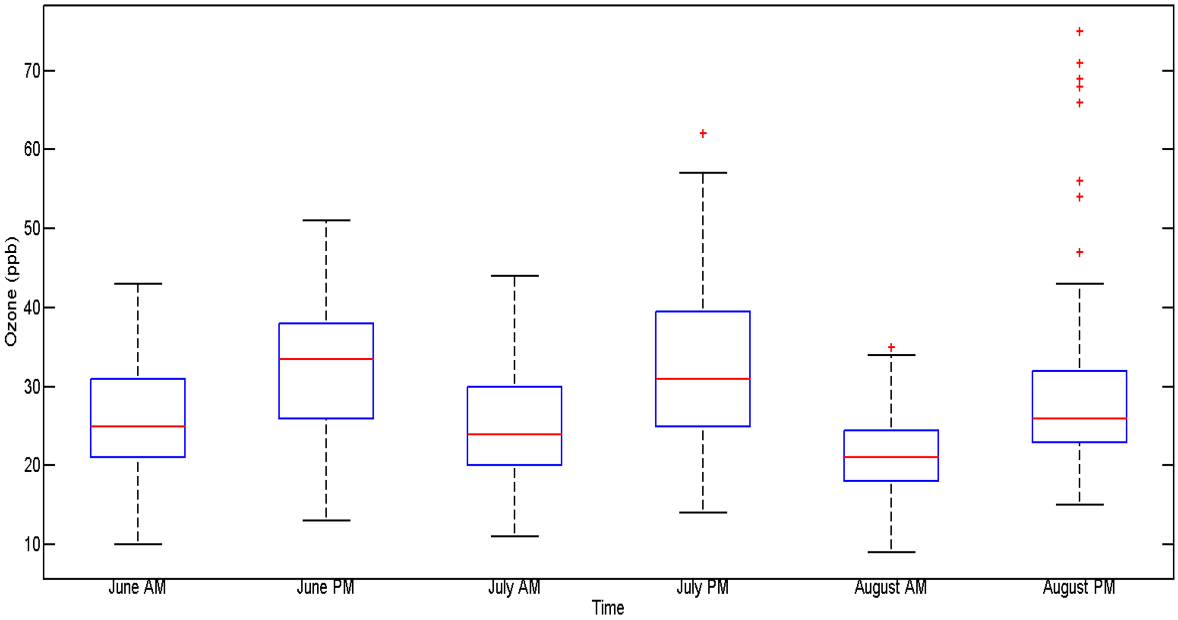


Figure 24. Boxplot of morning (6-10AM) and afternoon (2-6PM) hourly ozone averages in Aylesford Mountain for the summer of 2016. The red line represents the median value in the data set and the box edges show the 25th (bottom) and 75th (top) percentiles of data. The whiskers extend to the minimum and maximum values. The red stars are outliers, defined by Matlab as more than three median absolute deviations from the median.

Figure 22, Figure 23 and Figure 24 all show a large increase between morning and afternoon ozone, with the afternoon median greater than the morning 75th percentile in all cases. So there is no pervasive pattern of high morning ozone due to biogenic isoprene, or any other causes, neither in Lake Major nor in Halifax, nor in Aylesford. Three individual cases of high morning ozone in Halifax were analyzed further using HYSPLIT transport trajectories. The two ozone outliers in June AM on the Halifax figure were both observed on June 12, 2016 when concentrations reached 38 and 39ppb. Below-normal NO_x levels of about 6 ppb were recorded during this time, which is both needed for ozone formation and an indicator of transport of ozone (because transported air masses will be depleted in the short lifetime NO_x, as discussed previously). The normally NO_x-saturated Halifax air was possibly carried out of the city as a result of the strong winds, shown in Figure 25 by the large separation between squares showing 6-hour time periods. The strong winds likely carried ozone that was produced further upstream; although the 24-hour trajectories show ozone coming from over the ocean, the boundary layer lifetime for ozone of about 2-5 days could mean it was produced further upstream (Fiore et al., 2002). Due to the direction of the trajectories it is unlikely that biogenic precursors from within Nova Scotia were carried into downtown Halifax at this time resulting in the high ozone. Ozone during the morning of June 12 was also high in Lake Major and Aylesford Mountain reaching 48 and 43ppb, respectively. High ozone across all three stations is more consistent with a transport event rather than local production.

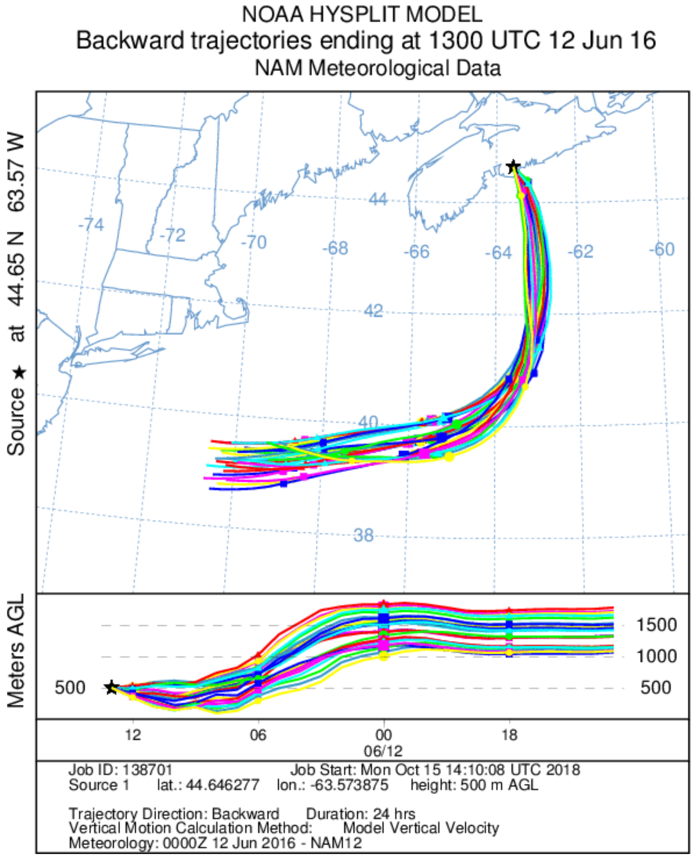
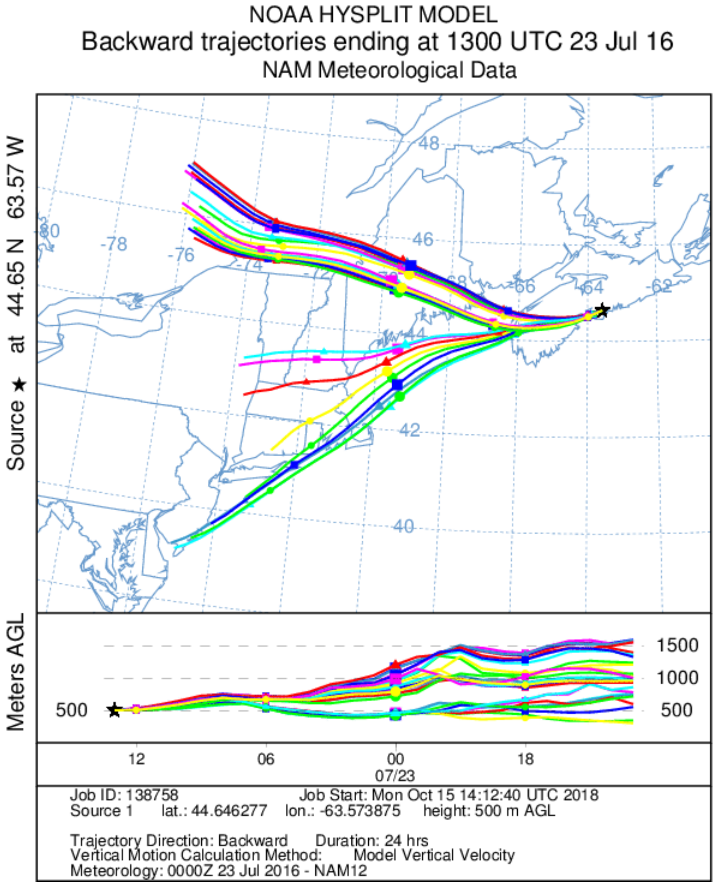


Figure 25. Backward trajectories from the Downtown Halifax station ending on June 12, 2016, 10AM ADT and showing air mass flow for previous 12 hours.

The Halifax outlier on the morning of July 23, reaching 34 ppb, was also investigated using the HYSPLIT model (Figure 26). NO_x during the morning was very low at an average of 5 ppb, which will not suppress ozone production. Some trajectories show air flow from the Eastern United States, including Boston and New York, while a second cluster passed over Montreal, and both clusters arrived in Halifax travelling over forested Nova Scotia during the night. It would seem that both transport and more local production of O_3 with biogenic precursors may have happened, which may have contributed to the high ozone on this morning. However, several outliers above the maximum from July AM at Lake Major occur on July 22 and July 23 (42 ppb and 44 ppb in Figure 23), and, more significantly, maximum July morning ozone values were recorded at the Aylesford Mountain station on July 22 and July 23 (42 ppb and 37 ppb). Aylesford Mountain is encountered before the trip over forested Nova Scotia, and already high O_3 values were observed, which, together with the spatial and temporal extent of this event suggests a pollution transport event as multiple provincial air zones were impacted over two days.

Spatially analyzing individual high ozone events across the province could allow one to distinguish between a widespread transport event and a more localized pollution event, for example, if the high ozone event was limited to Halifax. An extensive analysis of spatial correlations in ozone values across various NAPS stations in Nova Scotia is beyond the scope of the current study, as further discussed in the future work section. The relative role of biogenic hydrocarbons in localized high ozone events in urban areas like Halifax will be increasingly important as anthropogenic VOCs (AVOCs) and NO_x are decreased with emission controls (Main & Roberts, 2000, Biogenic Emissions), however, transport played a bigger role in elevated morning ozone concentrations in all three above examples.



Job ID: 138758 Job Start: Mon Oct 15 14:12:40 UTC 2018
Source 1 lat.: 44.646277 lon.: -63.573875 height: 500 m AGL

Trajectory Direction: Backward Duration: 24 hrs
Vertical Motion Calculation Method: Model Vertical Velocity
Meteorology: 0000Z 23 Jul 2016 - NAM12

Figure 26. Backward trajectories from the Downtown Halifax station ending on July 23, 2016, 10AM ADT and showing air mass flow for previous 12 hours. Most trajectories show air flow from the Eastern United States and Montreal via Western Nova Scotia, including Kejimkujik.

3.6 Ozone Production Regime

3.6.1 VOCs/NO_x Ratio

Using the NAPS database, 24-hour VOC averages, taken every six days with canister measurements can be downloaded, which include measurements of 167 VOCs. The 24-hour averages for the available VOCs were summed to give a total VOC load (µg/m^3) for each measured day in summer 2016. The corresponding 24-average NO_x, which is given in ppb, was converted to µg/m^3 using the equation:

$$NOx\left(\frac{\mu g}{m^3}\right) = ppb\ \times \frac{molecular\ weight}{molecular\ volume}$$

Where the molecular weight of NO_x is assumed to be the weight of NO_2 (46g/mol), and the molecular volume at standard temperature and pressure is 24.5 L (http://www.apis.ac.uk/unit-conversion).

These values were used to determine VOCs/NO_x ratios which are presented in Table 2 below. The ratio is well below five in all cases (average 1.4), indicating a VOCs-sensitive regime according to Main & Roberts (2000), as discussed in Section 2.3.2. Since isoprene is an abundant and highly reactive VOC component, the low ratio implies that isoprene does not play a strong role in Halifax O_3 chemistry, which is consistent with a lack of AM O_3 peaks (Figure 22). The summer months were chosen for analysis because that is when the largest amount of VOCs is present. What is notable is that the VOC/NO_x ratio is highest on or within one day of the two days suspected of long-range transport of O_3 pollution, which would involve air masses with depleted NO_x.

Table 2. 24-hr average VOCs and NO_x concentrations in Downtown Halifax (Summer 2016).

Date	VOCs (μg/m^3)	NO_x (μg/m^3)	Ratio
2016-05-06	27.13	42.086	0.64
2016-05-12	23.58	28.695	0.82
2016-05-18	35.76	47.825	0.75
2016-05-24	37.51	43.999	0.85
2016-05-30	27.20	40.173	0.68
2016-06-05	26.02	17.217	1.51
2016-06-11	32.79	13.391	**2.45**
2016-06-17	21.00	24.869	0.84
2016-06-29	51.99	59.303	0.88
2016-07-05	39.67	19.13	2.07
2016-07-11	20.67	26.782	0.77
2016-07-17	36.62	19.13	1.91
2016-07-23	45.10	15.304	**2.95**
2016-07-29	44.18	30.608	1.44
2016-08-04	34.81	15.304	2.27
2016-08-10	47.94	21.043	2.28
2016-08-16	35.75	26.782	1.34
2016-08-22	39.26	32.521	1.21
2016-08-28	28.04	15.304	1.83

Table 3. 24-hr average VOCs and NO_x in Downtown Halifax (Winter 2015/16).

Date	VOCs (μg/m^3)	NO_x (μg/m^3)	Ratio
2015/12/02	51.645	48.89	1.06
2015/12/08	35.955	39.49	0.91
2015/12/14	0.000	26.33	NaN
2015/12/20	32.144	11.28	2.85
2015/12/26	33.276	13.16	2.56
2016/01/01	33.905	16.92	2.00
2016/01/07	39.317	56.41	0.70
2016/01/13	26.826	28.21	0.95
2016/01/19	31.461	39.49	0.80
2016/01/25	56.581	69.60	0.81
2016/01/31	38.290	26.33	1.45
2016/02/06	36.62	22.57	1.62
2016/02/12	45.10	43.25	1.04
2016/02/18	44.18	48.89	0.90
2016/02/24	34.81	39.49	0.88

Winter VOCs/NO$_x$ ratios for December 2015-February 2016 were also calculated as a comparison to the summer months (Table 3). The winter ratio is also below 5 (average 1.3) in all cases, which again indicates a VOCs-sensitive regime according to Main & Roberts (2000), though this was more expected.

Due to the negligible amount of BVOCs during the winter and the abundance of BVOCs over AVOCs in the summer, it was assumed that VOCs during the winter months would be insignificant. However, a brief analysis of the summed amount of the 167 VOCs available from NAPS throughout the year shows that there is no obvious difference between VOCs in the summer and winter (Figure 27). However, VOCs vary greatly in their reactivity and the role they can play in ozone production so this analysis may be weakly correlated with ozone production. It is possible that BVOCs in the summer give way to AVOCs in the winter due to increased heating combustion. A comparison of VOCs/NO$_x$ ratios in Halifax to those at Kejimkujik Park could shed light on this, but during this analysis period NO$_x$ was never measured at Kejimkujik, and VOC were stopped in 2010. Finally, VOC/NO$_x$ ratios at a higher temporal resolution, i.e. with hourly VOC measurements, would also improve the correlation with ozone production.

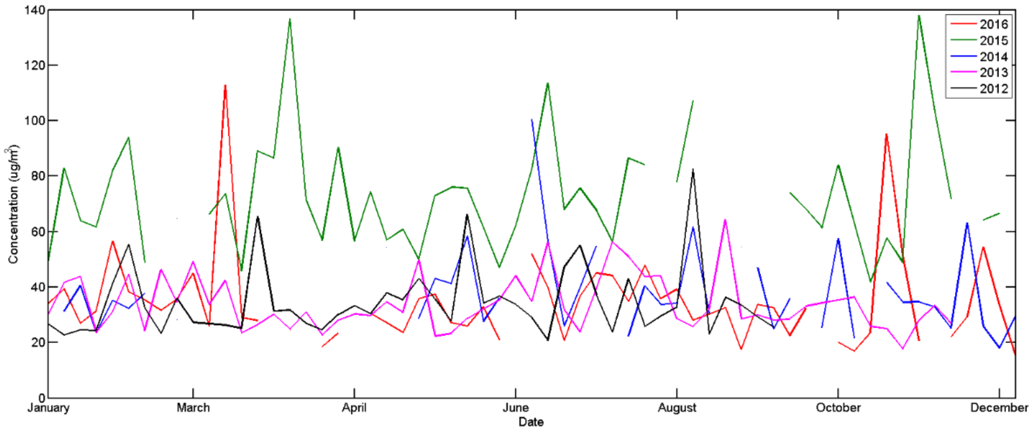


Figure 27. Summed 24 hour average VOCs for 5 years of data in Downtown Halifax.

3.6.2 Ozone-NO_x Relationship

According to Figure 28 there is an inverse relationship between NO_x and ozone in Halifax for 24-hour average O_3 in 2016, which, at first glance appears to indicate VOCs-sensitive conditions. Figure 29 shows time-resolved model simulation data for the different ozone production regimes in Los Angeles, based on a high ozone event from August 26-29, 1987 (before smog reduction policies were implemented) and using meteorological variables from the Urban Airshed Model (Sillman et al., 1997). When comparing the Halifax 2016 data to Sillman's plotted production regimes (Figure 28 and Figure 29) it appears at first glance that Halifax's NO_x-O_3 pattern is similar to the VOCs-sensitive regime data (green squares); however, the NO_x titration data also shows a weaker negative relationship between O_3 and NO_x (blue circles). A more careful examination shows that ozone in Los Angeles is clearly much higher than ozone in Halifax; in fact, Halifax ozone is well below the titration regime ozone levels in Sillman's simulation. While Los Angeles ozone will always be higher due to its high insolation and pollution trapping persistent weather patterns and topography, nevertheless, it appears that Halifax ozone data falls in the titration regime, as supported by results from Section 3.1. Interestingly, there is no significant relationship between ozone and NO_x at Lake Major (Figure 30) when the very low NO_x levels combined with abundant VOCs in a forested setting would imply a NO_x-sensitive regime.

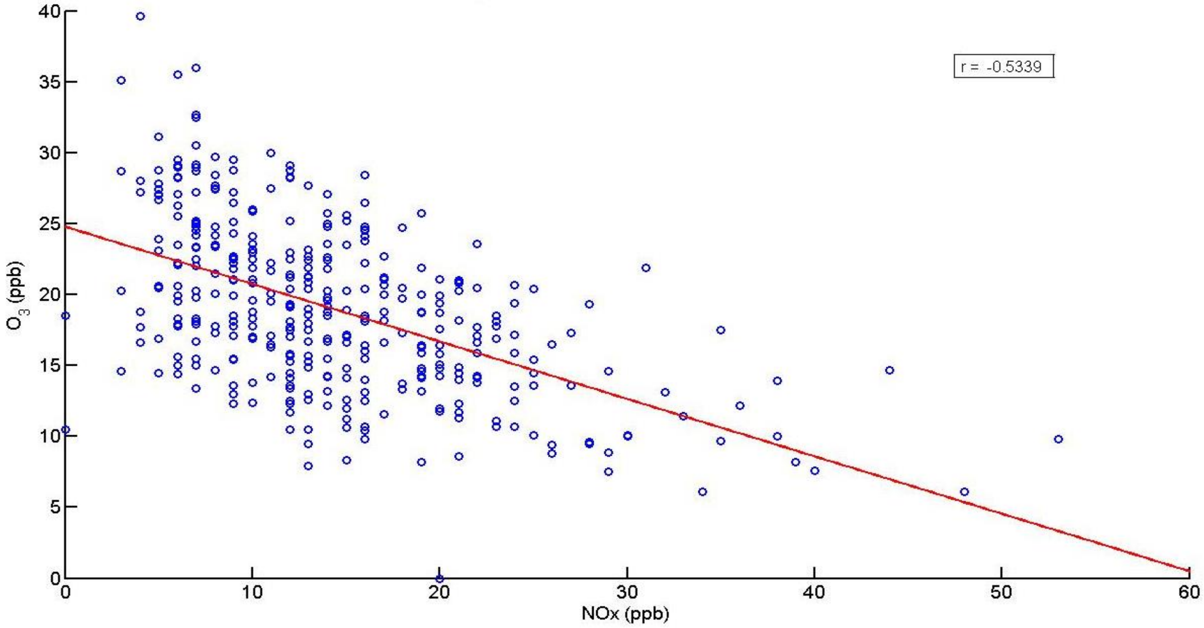


Figure 28. 24-hour average ozone and NO$_x$ relationship at Downtown Halifax for 2016. Line of best fit shown in red.

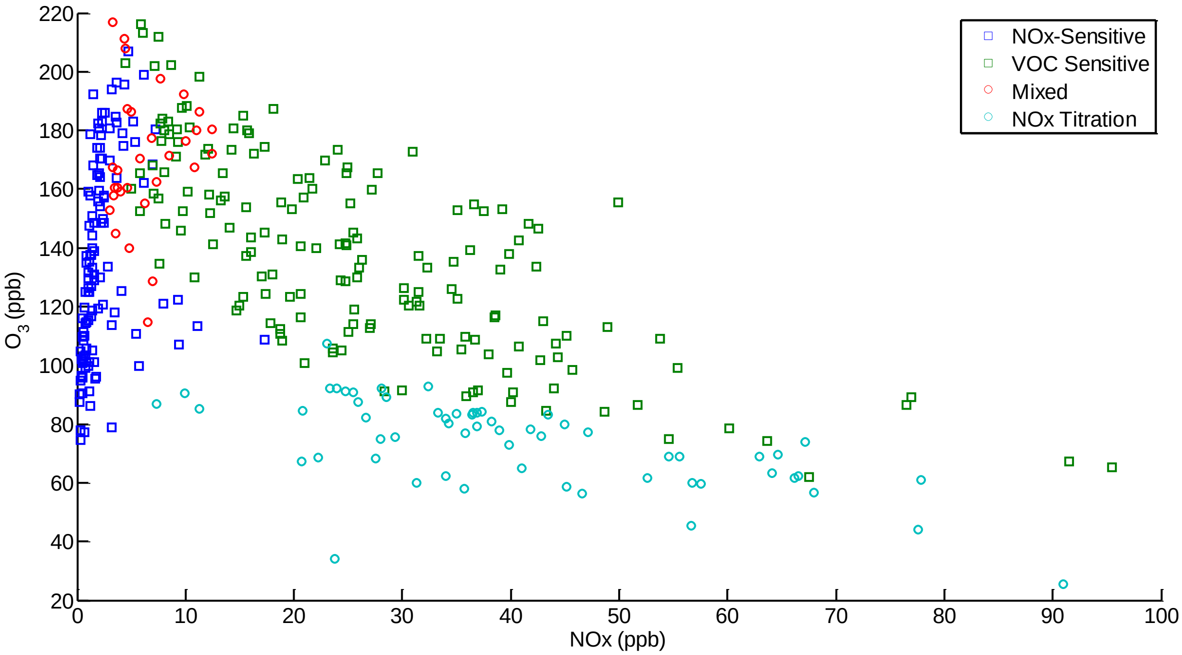


Figure 29. Ozone production regimes plotted from Sillman et al. (1997) model data for Los Angeles on Aug 26-29, 1997.

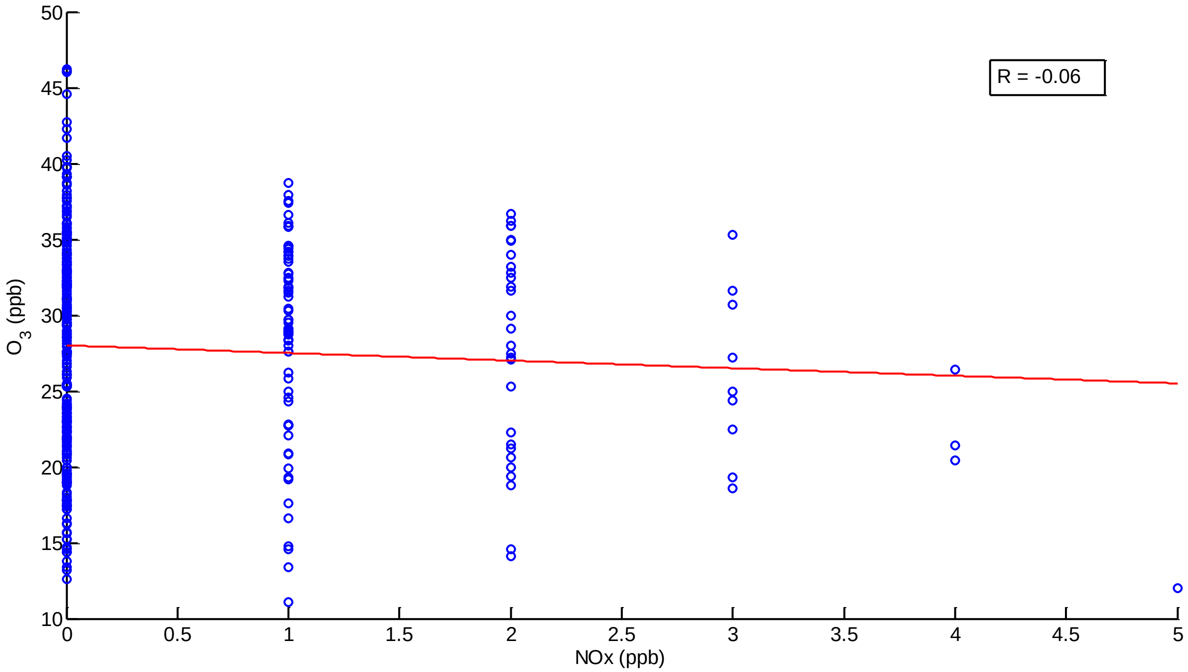


Figure 30. 24-hour average ozone and NO_x relationship at Lake Major for 2016. Line of best fit shown in red.

A correlation plot was made to show the relationship between morning and afternoon NO_x levels and the average 24-hour ozone level for every day in 2016 (Figure 31), which shows that morning and afternoon NO_x levels do not differ in their impact on overall ozone levels. Main and Roberts (2000) state that the morning data are usually used for VOCs/NO_x ratios, and since most NO_x in Halifax is emitted during the morning rush hour it was assumed the morning concentrations would have more influence on daily ozone than afternoon concentrations. This analysis shows that both NO_x measurement time periods have a similar relationship with 24-hour ozone, so for Halifax it does not matter which hours are used for analysis. It would be interesting to investigate if this conclusion also holds for daily maximum O_3 instead of the daily average. The relationship between morning NO_x and ozone and afternoon NO_x and ozone both indicate inverse relationships between ozone and NO_x due to the abundance of NO_x in Halifax.

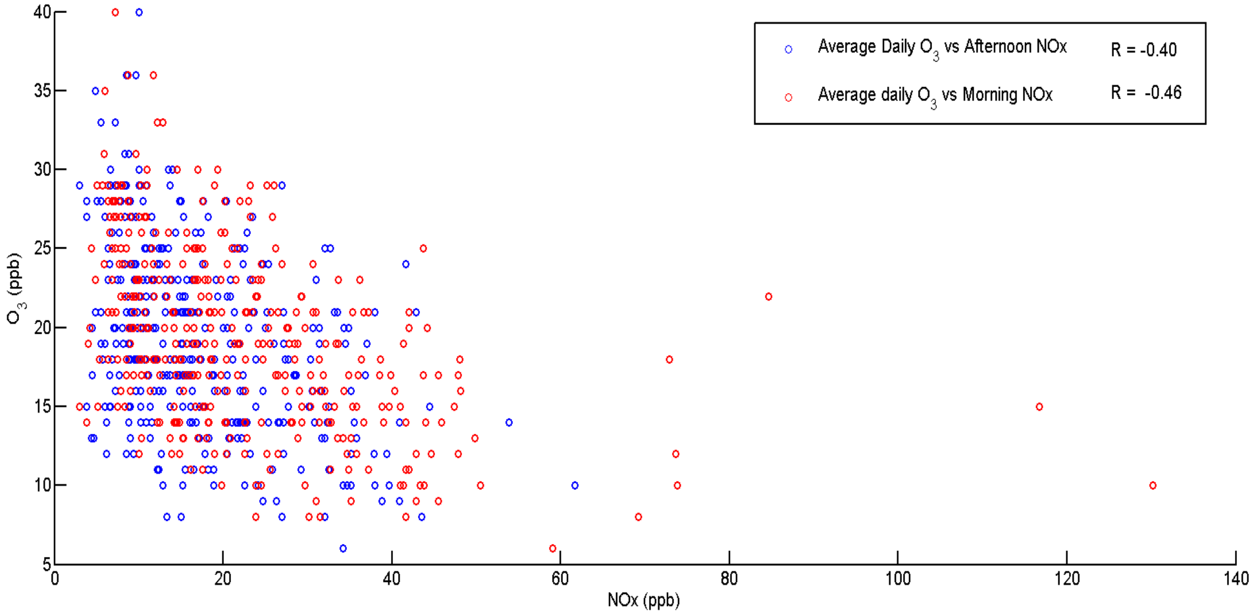


Figure 31. Relationship between morning (6-10AM) NO_x and 24-hour average ozone levels compared to afternoon (2-6PM) NO_x and 24-hour average ozone levels in Halifax for 2016.

3.7 Long-Term Ozone and Total Ozone Trends in Halifax

An analysis of hourly measurements of ozone shows shorter pollution episodes that are hidden in 24-hour average data. Figure 32 shows one hour ozone averages throughout the year from 2001-2016 in Halifax. Notably, there is only one circumstance when ozone levels surpass Nova Scotia Air Quality Regulations one hour maximum ozone level of 82 ppb, which was in 2002. Otherwise, ozone levels are lower than regulations but do infrequently exceed the NAAQO's 1-hour desirable level of 50 ppb. About 0.25% of recorded values have exceeded 50 ppb over the time period in Figure 32, with 82% of these values occuring before 2009; suggesting an improvement in our air quality. This suggestion is evident in Figure 33 where outliers and maxima have decreased over 15 years at approximately 0.63 ppb/yr, except for 2017 which exceeds 2016.

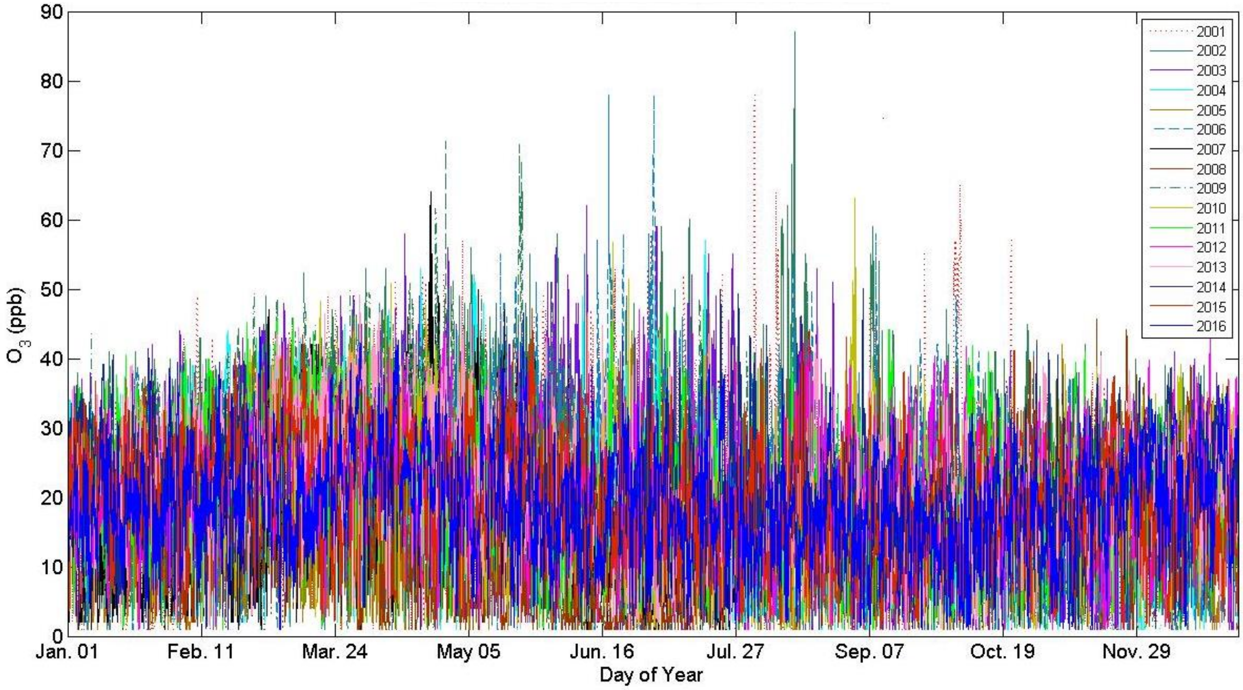


Figure 32. 1- hour average ozone measurements in Downtown Halifax from 2001-2016.

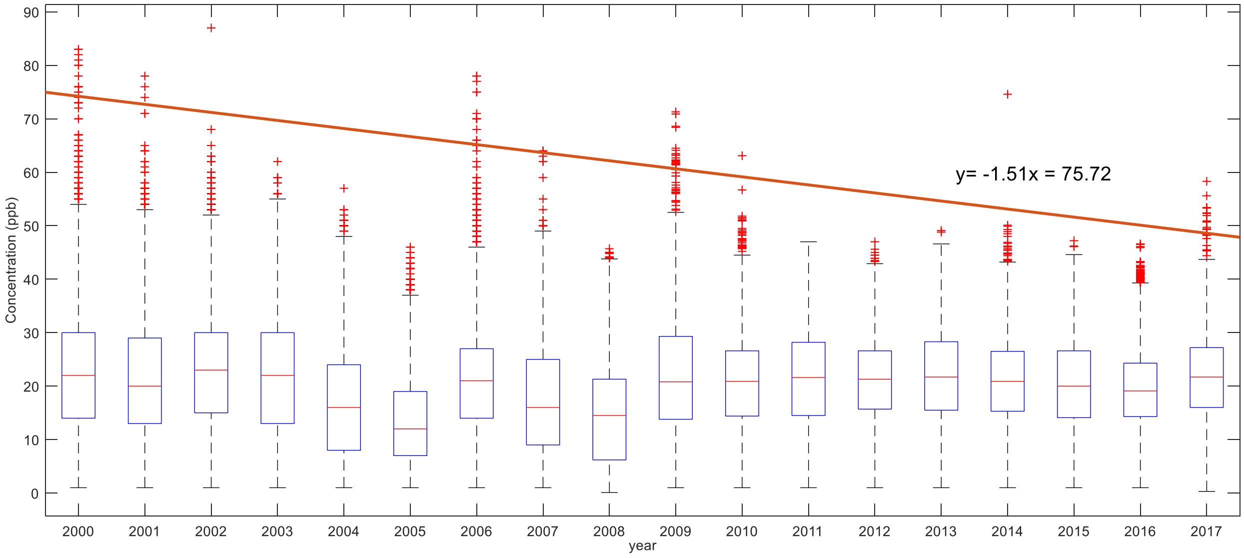


Figure 33. 1-hour average ozone for years 2000-2017 in Downtown Halifax. The red lines represent the median value in the data set and the box edges show the 25th (bottom) and 75th (top) percentiles of data. The whiskers extend to the minimum and maximum values in this dataset while the red stars are outliers, defined by Matlab as more than three median absolute deviations from the median. The orange trendline is fitted through the maximum values of each year. Note: 2017 data has not been entirely quality checked by NSE.

Since 2000, the annual maximum 1-hour average ozone has been slightly decreasing in Halifax at 1.5ppb/year (orange line Figure 33), although the precise trend value is unstable as it is based on outliers. This decrease is thought to be due to emissions regulations in areas we receive transported pollution from, like the Ohio Valley and Eastern United States (NSE Air Quality Unit, 2015). Cooper et al. (2012) have estimated that in the Eastern USA anthropogenic NO_x and VOC emissions decreased 49% between 1990-2010 and ozone has decreased by 17%. The median value of ozone in Halifax was decreasing between 2000-2008 but rose after that and has since been nearly constant at approximately 20 ppb. The Halifax 2017 ozone showed a small increase in outlier values, so it will be interesting to see whether this upward tick will continue in future years and whether it is due to increased transported O_3 pollution or local production (due to increased VOCs, not NO_x), or both. It is likely that the Halifax NO_x concentrations reductions are responsible for the lack of decreasing trends in ozone levels, along with the increasing global background ozone levels (Geddes et al., 2009).

Daily average ozone and NO_x concentrations at Halifax were plotted together over 17 years to examine long term trends (Figure 34). The NO_x decrease can be attributed to successful emissions reduction in Nova Scotia and abroad (NSE Air Quality Unit, 2015), however, Halifax's ozone appears steady at an average of 20 ppb for the same time period. As an ozone precursor is decreasing, ozone levels are also expected to decrease. The exception to this happens in the VOCs-sensitive regime, where ozone production increases as NO_x decreases. It may appear that this is what is happening in Halifax except NO_x is at levels so high that no ozone is being produced, but rather it is titrated away, albeit temporarily. The same scenario was observed in Windsor, Ontario where NO_x

concentrations were dropping but ozone was not (Zhang, 2017), which was attributed to observations of ozone that were also being temporarily titrated by nearby NO emissions. A study done in Osaka City, Japan showed that emission controls had successfully reduced NO_x levels within the city; unfortunately, ozone concentration continued to rise with the decreasing NO_x but Total Ozone remained steady, suggesting that a reduced NO titration effect was causing ozone levels to increase (Itano et al., 2007).

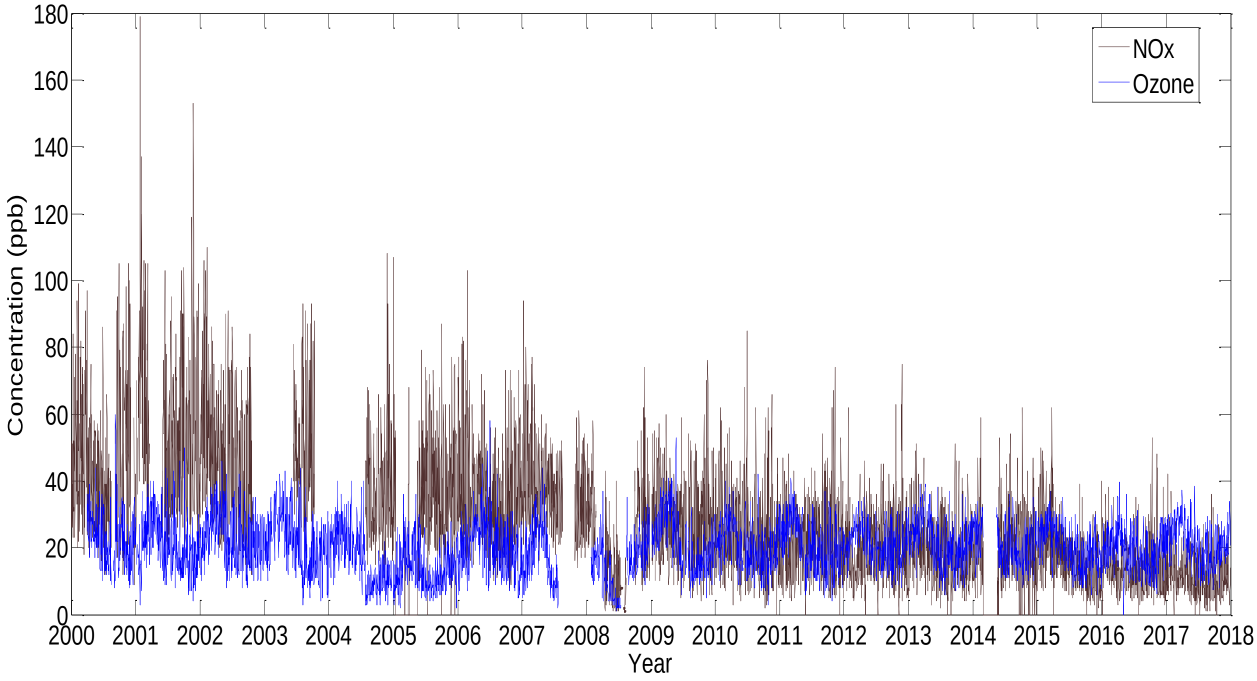


Figure 34. 24-hour ozone (light blue) and NOx (brown) trends over 16 years in Downtown Halifax.

As we know, there is a large NO-O_3 titration process in effect in Halifax due to large NO emissions within the city, and suppressed ozone levels. Long term trends are more accurately analyzed when this titration is accounted for, as the titration only represents a temporary loss in ozone close to emissions sources. To determine a representative ambient ozone in Halifax we need to look at Total Ozone (TO), which is a measure of ozone not impacted by the temporary NO titration. Total ozone is defined as the sum of ozone and NO_2, excluding primary emitted NO_2, which is usually estimated as 10% of freshly emitted NO_x (Carslaw & Beevers, 2005):

$TO = O_3 + NO_2 - 0.1 \cdot NO_x$ (Equation 3)

In this way it is shown that ambient Total Ozone levels in Halifax are in fact decreasing at a rate of about 0.5 ppb/year (Figure 35). With the assumption that Halifax is VOCs-sensitive, the decrease in Total Ozone would be due to VOC reductions rather than NO_x reductions, that is, if Halifax Total Ozone was entirely due to local production within the city. In reality, much of our Total Ozone is thought to be imported in long-range transport. Nevertheless, NO reductions are causing an immediate increase in O_3 near the Halifax NAPS station.

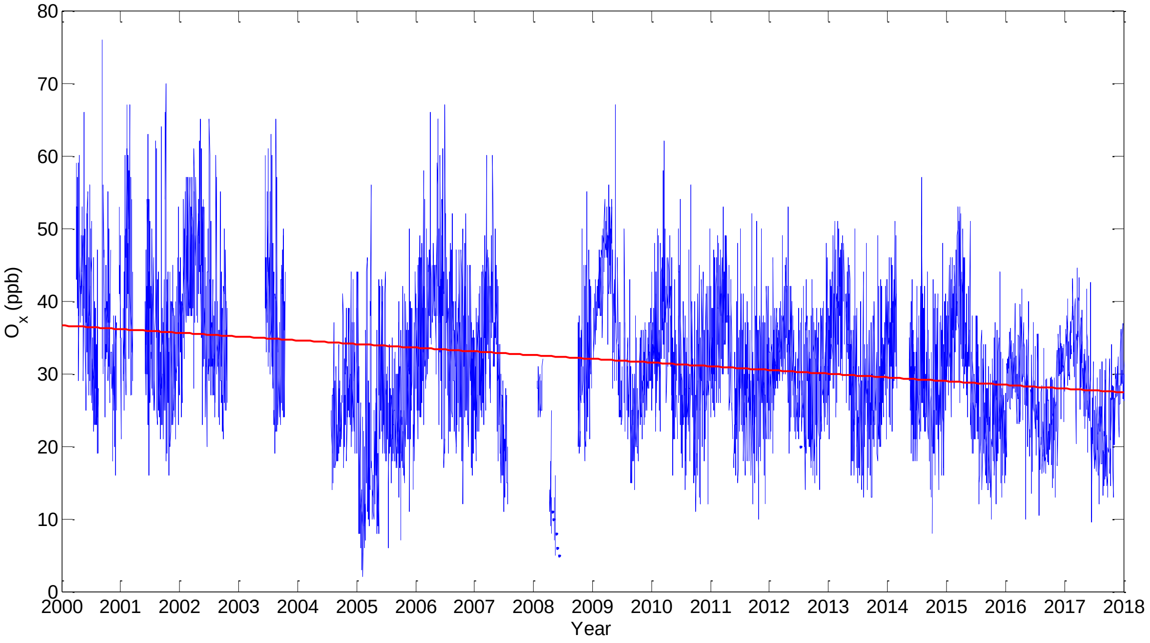


Figure 35. Total Ozone (O_3 and secondary NO_2) trends in Downtown Halifax from 2000-2017.

3.8 The Role of Long-Range Transport

Due to the long atmospheric lifetime of ozone in the upper troposphere, up to a few weeks (Zhang et al., 2011), the transportation of ozone from different countries and even continents can play a role in regional ozone budgets. It is estimated that transported ozone from Asia can contribute up to 9 pbb of ozone to the annual North American ozone budget (Tarasick & Slater, 2008). However, the largest sources of transboundary air pollution in Nova Scotia are from other North American regions. A study examining lead isotopes in Kejimkujik National Park showed the heavy metals that were deposited had originated in air masses carrying particulate matter. It was concluded that over 60% of the isotopes examined had originated in the United States (Desjardins et al., 2004).

Figure 36 shows the Halifax air shed map for July of 2014, where the yellow and red colours indicate more common source regions for Halifax air. These common source regions are highly polluted areas like the Great Lakes region, Montreal and Québec, and the north eastern USA. The large transboundary air pollution seen in Nova Scotia has caused the province to be referred to as the "tailpipe of Canada" (Government of Nova Scotia, 2017), although it is not clear how frequently transported pollution "touches down" at the surface in Nova Scotia. In the case of the previously analyzed morning O_3 maxima in Halifax June and July of 2016 (Figure 25 and Figure 26) transport trajectories touched down in Halifax after travelling at altitudes up to 1500 m.

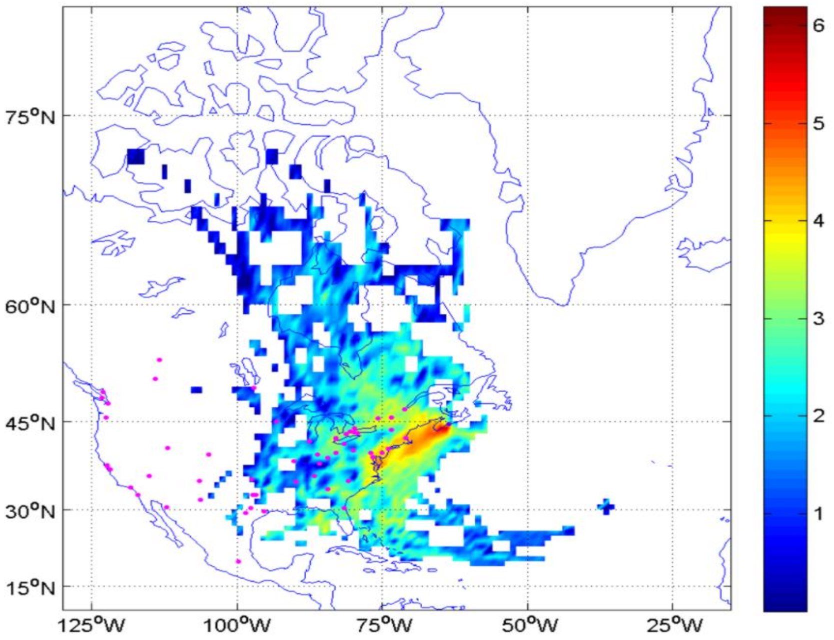


Figure 36. Frequency of air mass source region in Halifax July, 2014. Colour bar shows log of trajectory sum. Created by summing coordinates of 7-day backward trajectories from Halifax in 1º by 1º grid boxes. Four trajectories were ran per day in July. Created using HYPLIT by Keane Tobin, Master's Candidate at SMU.

The frequent ozone enhancements during the summer months at Aylesford (259 m elevation) shown in Figure 17, also point to transported pollution episodes as there are few local sources of NO_x emissions in this remote location. After examining all the Aylesford 1-hour ozone data in 2016 it was found that on August 25 ozone reached the highest 1-hour maximum of 75 ppb from 5-6 PM, which is 156% above its August PM mean. Halifax ozone peaked at 36 ppb at the same time which is 107% above its August PM mean, and Lake Major recorded 44 ppb of ozone which is 71% above its August PM mean during this time, but it peaked at 46 ppb an hour earlier. The multi-station ozone exceedances suggest a transport event that extended over Nova Scotia but more evidence is again provided using the NOAA Hysplit trajectory model to trace air flow backwards from Aylesford Mountain, and also from Halifax, where elevated values were also observed. It was found that trajectories were flowing into Nova Scotia on that day from the Eastern Atlantic Ocean but likely originated in the polluted Eastern United States further upstream (Figure 37 & Figure 38); both Halifax and Aylesford trajectories show the same pattern, which suggests the same transported pollution source to explain the elevated O_3 readings. Finally, the trajectories are traveling at low altitudes, consistent with elevated surface measurements.

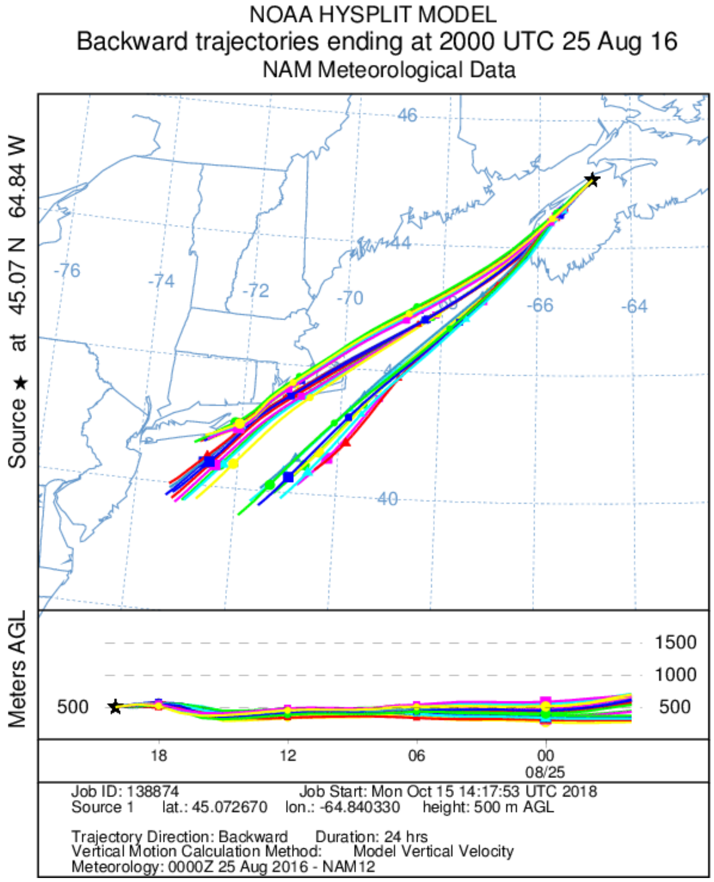


Figure 37. Backward trajectories starting at Aylesford Mountain station on August 25, 2016, 5PM ADT and showing air mass flow for previous 24 hours.

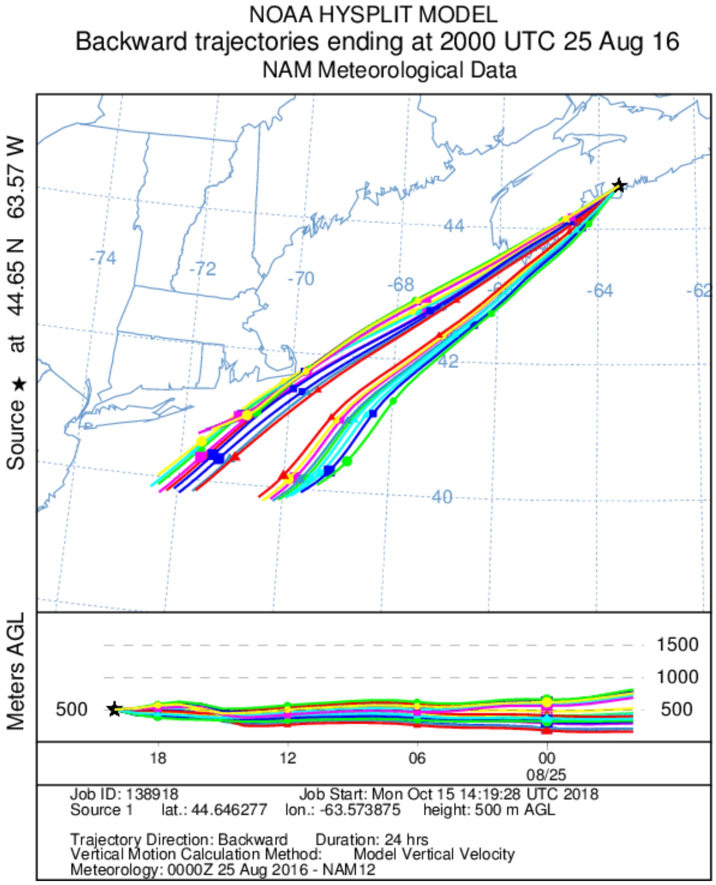


Figure 38. Backward trajectories starting at Halifax on August 25, 2016, 5PM ADT and showing air mass flow for previous 24 hours.

4 Conclusions

This work examined the controls on ground level ozone production in Halifax, initially focused on the role of isoprene in morning O_3 production. It was found instead that ozone in Halifax follows a typical afternoon peak pattern and that the two separate incidences of eleveated morning ozone are in fact cases of long-range transported pollution to Halifax. Attempts were also made to identify the local O_3 production regime in Halifax as either NO_x-sensitive or VOC-sensitive, but the available VOC data in Halifax was found to be in fact too sparse (24-hour canister samples every 6 days) to accomplish this reliably, even with a long (1990-2017) Halifax VOC data set. VOC/NO_x ratios were computed on the available 24-hour-average basis and they were found to be $<$ 5, coarsely indicating a VOC-sensitive production regime. There is also indication from the high NO_x levels that ozone production is on the whole VOC-sensitive in Halifax; while Halifax is much smaller in area and population, its daily average ozone and NO_x were found to be comparable to Toronto levels.

Long-term trends of ozone and its precursors in Nova Scotia were analyzed to see the effect of emissions regulations across North America. It was found that 1-hr ozone levels are relatively steady in Halifax under decreasing NO_x emissions, due to a reduction of the strong NO_x titration effect on O_3; however, Total Ozone (TO), comprised of O_3 and NO_2, was found to be decreasing, along with maximum 1-hr ozone. Ozone trends are variable at other NAPS stations across the province of Nova Scotia.

Lastly, long-range transport was examined during one maximum elevated O_3 event in 2016 at the background air Aylesford NAPS station. The high O_3 levels were correlated with high values in Halifax and transport to both locations was consistent with pollutant import from the the northeast U.S. Flow to Halifax from Aylesford is in general more complicated because there is no obvious correlation between ozone in Halifax and at the Aylesford NAPS station, which requires further study.

4.1 Policy Implications

There is some evidence that ozone production in and near Halifax is VOCs-sensitive given that there is an abundance of NO, which consistently suppresses ozone formation close to the source; VOC-sensitivity is also coarsely indicated by 24-hour VOC/NO_x ratios. This means that additional anthropogenic VOCs and BVOCs have a greater potential to increase ozone production within Halifax, outside the region of NO titration. It is important to distinguish the production regime of an area in order to determine the correct emission controls that will successfully suppress ozone formation. According to the above results, VOCs emissions reductions could reduce ozone more than NO_x reductions in the greater Halifax area. Furthermore, it is most likely that further NO_x emissions reductions would increase ozone concentrations within downtown Halifax due to the strong NO titration effect that has been found in this work. The scope of this VOCs-sensitivity and titration is uncertain, but it is unlikely that it extends throughout the HRM as very low NO_x is recorded at Lake Major.

4.2 Future Ozone

Our planet is undergoing climate change due to anthropogenic activities like fossil fuel burning and land use change. It is predicted that ground level ozone levels will change in the near future making the ability to correctly regulate its production crucial. For example, there is an increase in the amount of people moving to urban areas, which will likely increase fossil fuel burning and NO_x emissions. It can be expected that with more NO_x emissions ozone production in and around urban centres will become more VOCs-sensitive if this migration to urban areas continues (Fini et al., 2017). In the future it may be more effective to emphasize VOCs emission controls. Another influence changing ozone production is deforestation and the conversion of forests to farmland. Forests are home to some of the highest isoprene emitters in contrast to farmland where crops are usually very low emitters of isoprene. In the last century there was a 15% decrease in global isoprene levels that can be attributed just to the conversion of forests to cropland (Fini et al., 2017). However, if plantations continue to expand in the tropics this could increase the emission of BVOCs because plants like the oil palm and the rubber tree emit up to ten times more isoprene than natural forests (Penuelas and Staudt, 2010). Therefore, conversion of natural land to farmland or plantations could shift ozone production in either direction. According to the International Panel on Climate Change (IPCC) Fifth Assessment Report (2013) there is high confidence that global background ozone levels will decrease with climate change, but there's medium confidence urban ozone levels will increase. The exact ways that ozone production regimes will shift in the future is not yet certain, but these changes may be significant. So, it is important to be aware of a place's production and transport regime, especially in urban centres where pollution and population are the highest so that ozone production can be regulated effectively.

4.3 Future Work

A more detailed analysis is needed for VOCs species and their contribution to ozone production. Within the existing NAPS dataset, VOCs need to be analyzed by species and not in aggregate, to see how the composition of VOCs changes between summer and winter in Halifax and elsewhere, i.e., at Keji (1995-2010) and in Granton (2006-2015), and in general, why the concentration of isoprene in Halifax is so low during the summer given our forested surroundings. A better temporal resolution for VOCs will help this analysis, especially more frequent monitoring (see below) of isoprene and its oxidation products like formaldehyde. It would be beneficial to compare the VOCs/NO_x ratios in Halifax to those at Kejimkujik, a place with very high VOCs and little NO_x, but NO_x is not measured within the NAPS program at Kejimkujik. Further work on the most important BVOCs for ozone production (highest reactivity) would be valuable to continue the analysis of VOCs-sensitive ozone production in Halifax.

Completing the same analyses shown here for Halifax for other stations around Nova Scotia will give a deeper insight into how atmospheric processes differ between urban, suburban and remote areas. For example, comparing morning and afternoon NO_x and ozone in more remote places like Aylesford Mountain, and average hourly ozone concentrations over long term (15 years) for all stations across Nova Scotia. Extending the Total Ozone analysis to all stations will show which stations are impacted by NO_x titration and could improve our understanding of long-term ozone trends across Nova Scotia in stations that are significantly affected.

It is also important to consider the amount of ozone that is being transported from outside of Nova Scotia versus the ozone that is being produced within the vicinity of the station in question. Moving forward this will be investigated in the course of an MSc project by spatially analyzing across Nova Scotia the extent of individual high pollution events. If there are high ozone levels at all stations across the province, transport is likely the cause, as compared to a high ozone day that is observed only within Halifax. Quantitative results for the number of transported versus localized pollution events will help us to explain and account for ozone production in Nova Scotia, leading to better regulatory policies.

Within Halifax, it is important to understand the spatial extent of the VOC-sensitivity from the downtown NAPS measurement station, which can be addressed by additional O_3 and NO_x measurements of the "NO_x bubble" around the city at the same time, i.e., combining the measurement and personnel resources of Saint Mary's University, Nova Scotia Environent and Environment and Climate Change Canada. The current work revealed interesting differences between NAPS measurements made 10 km away from the downtown core at Lake Major, e.g., an 8 PM NO_x "peak" within a set of extremely low NO_x values recorded there, a lack of a NO_x-sensitive relationship with O_3, increasing O_3 values over time under strong NOx decreases post 2011, as well as a lack of strong correlation with Halifax and Aylesford under regional pollution events.

Within the coming year the Tropospheric Remote Sensing Laboratory at Saint Mary's University will become a new and active monitoring station. The Open-Path Fourier Transform Infrared (OP-FTIR) spectrometer will be located on top of the Student Centre Building in a shipping container and it will make continuous measurements of various trace gases in Halifax, including VOCs. This will lead to long term continuous datasets of isoprene and its oxidation products which is crucial for a deeper analysis of ozone production in Halifax.

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6 Appendices

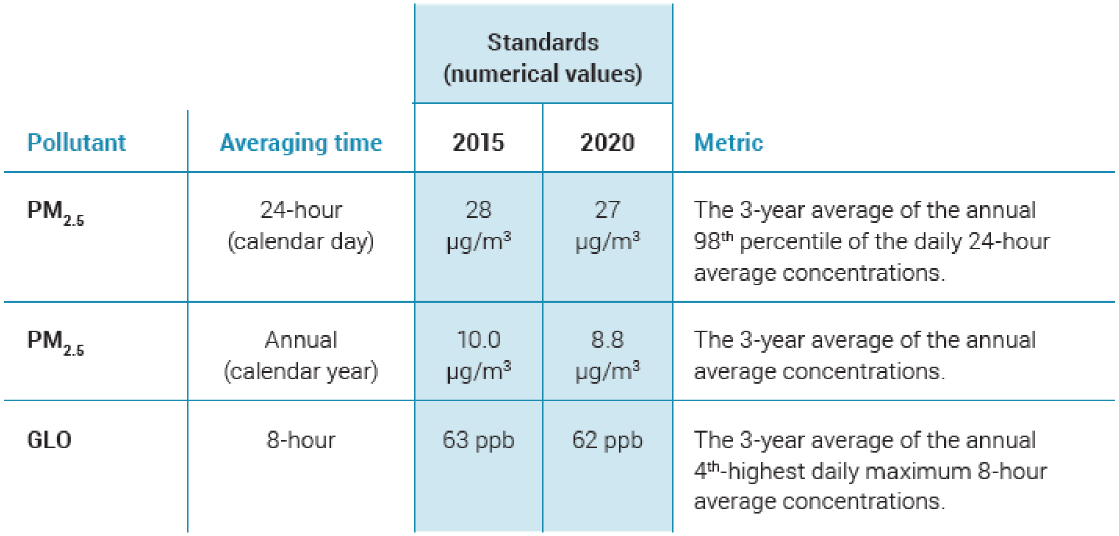
6.1 Appendix A : NAPS station descriptions

Station Name	**Address**	**Station ID Number**	**Pollutants**	**Instrument**	**Years**	**Measurement Interval**
Kejimkuijik Park	Kejimkujik national Park	30501	**O_3**		1985-2017	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
			NO_x		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)	1 hour average
			NO_x		2017 (start March)	1 hour average

			SO_2		2017 (March start)	1 hour average
			CO		2017 (start March)	1 hour average
			$PM_{2.5}$	BAM	2006-2017	1 hour average
			$PM_{2.5}$	TEOM	2006 - 2017	1 hour average
			PM_{10}	Speciation	2006 – 2017	24hr, Every 3rd day
			$PM_{2.5}$ PM_{10}	Dichot	2006 - 2017	24hr, Every 3rd day
Aylesford Mountain (Elevation = 235m)	Mountain Brow Rd., Kings County	30701	**O_3**		1991 – 2017 (Missing 2008)	1 hour average
			NO_x		2010- 2017	1 hour average
			$PM_{2.5}$	BAM	2007-2017	1 hour average
Granton	20 Pumphouse Rd., Granton	31201	**VOCs**		2006-2015	24hr average, every 6th day
Pictou	91 Beeches Rd., Pictou	30901	**O_3**		2001-2017	1 hour average
			NO_x		2011-2017	1 hour average
			PM2.5	BAM	2003-2017 (missing 2010 & 2014)	1 hour average
Lake Major (Dartmouth)	Cherrybrook Rd., Halifax	30120	**O_3**		2006- 2017	1 hour average
			NO_x		2006- 2017 (missing 2009)	1 hour average
			SO_2		2006- 2017	1 hour average
			PM2.5	BAM35, TEOM	2001-2017	

Dayton (Yarmouth)	Yarmouth Weather Office	30801	**O_3**		1994-2010	1 hour average
Kentville	32 Main St., Kentville	31101	**O_3**		2002-2011, 2017	1 hour average
			NO_x		2017	
			PM 2.5	BAM	2017	
Sydney	71 Welton St., Sydney	**30310** OR **30301 (before 2013)**	**O_3**		2001-2017 (missing 2007)	1 hour average
			NO_x		2006- 2017 (missing 2007)	1 hour average
			SO_2		1974-2017	1 hour average
			CO		2005- 2017 (missing 2007)	1 hour average
			PM 2.5	BAM35, TEOM	1998- 2017 (no 2000)	1 hour average
					2010 -2017	1 hour average
Port Hawkesbury	23 Embree St., Port Hawkesbury	30201	**O_3**		2010-2017	1 hour average
			NO_x		2010-2017	1 hour average
			SO_2		2003-2007 & 2010-2015	1 hour average
			PM2.5	BAM35	2010-2017	1 hour average
Sable Island	Sable Island	31001	**O_3**		2001-2013 (missing 2007)	1 hour average
			NO_x		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

6.2 Appendix B: CAAQS, NAAQO and NS regulation targets



		Standards (numerical values)		
Pollutant	**Averaging time**	**2015**	**2020**	**Metric**
$PM_{2.5}$	24-hour (calendar day)	28 µg/m^3	27 µg/m^3	The 3-year average of the annual 98th percentile of the daily 24-hour average concentrations.
$PM_{2.5}$	Annual (calendar year)	10.0 µg/m^3	8.8 µg/m^3	The 3-year average of the annual average concentrations.
GLO	8-hour	63 ppb	62 ppb	The 3-year average of the annual 4th-highest daily maximum 8-hour average concentrations.

CAAQS (Canadian Ambient Air Quality Standards). Nova Scotia Environment Air Quality Unit, 2015.

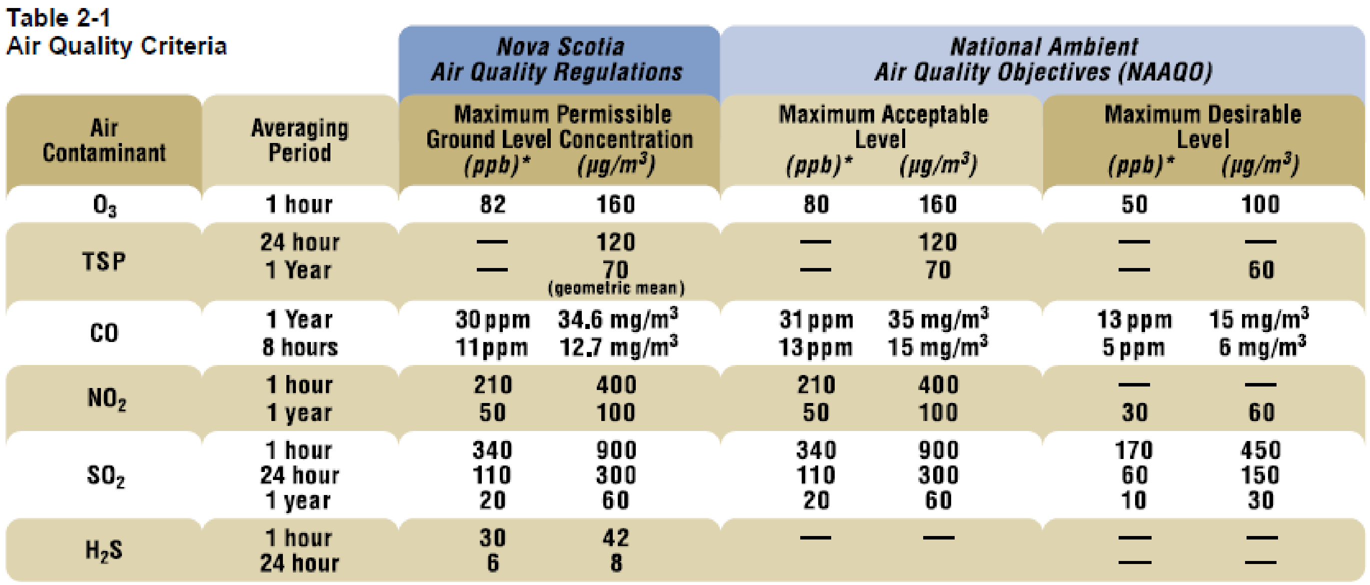
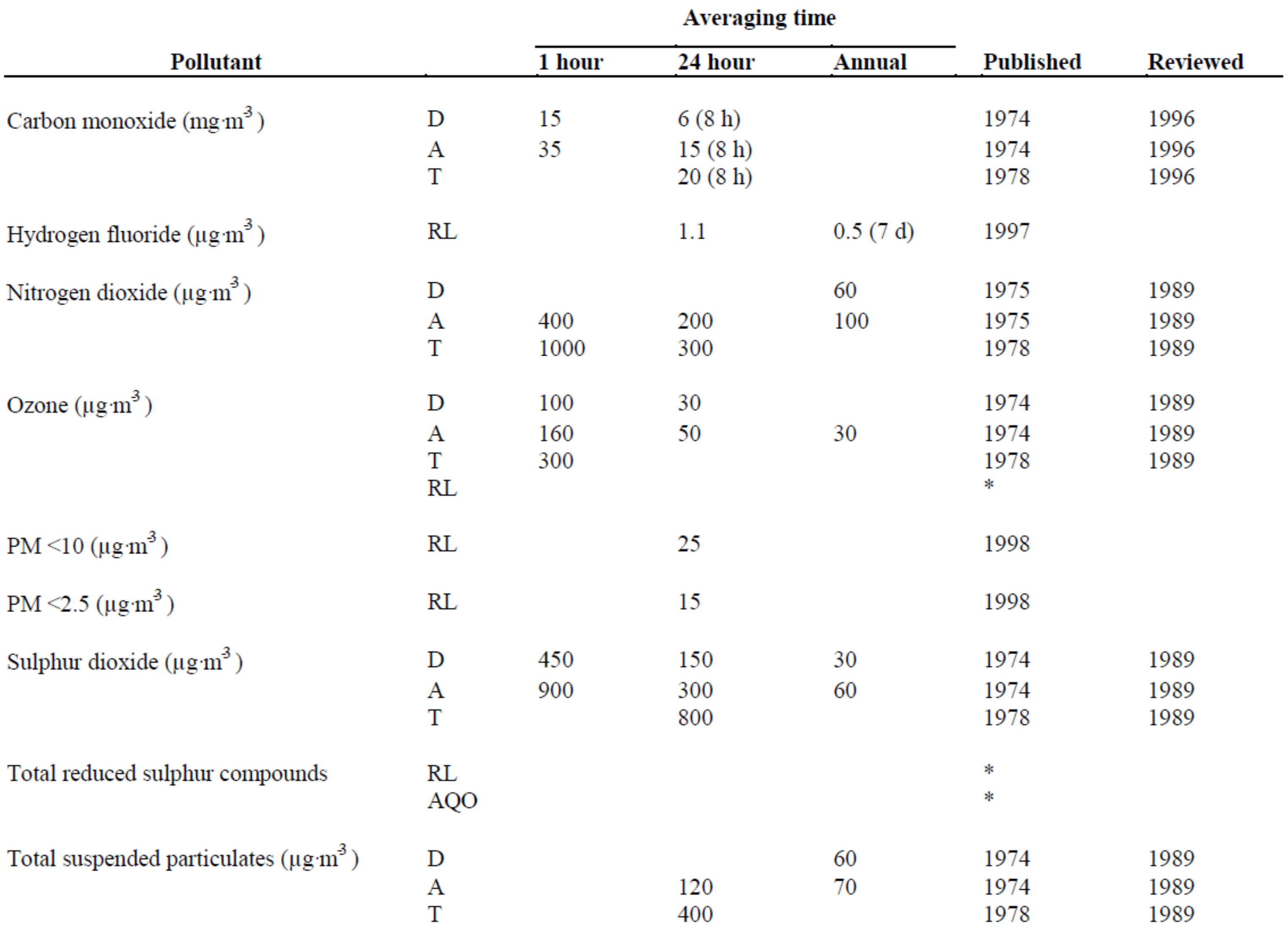


Table 2-1
Air Quality Criteria

Air Contaminant	Averaging Period	*Nova Scotia Air Quality Regulations*		*National Ambient Air Quality Objectives (NAAQO)*			
		Maximum Permissible Ground Level Concentration		Maximum Acceptable Level		Maximum Desirable Level	
		*(ppb)**	*($\mu g/m^3$)*	*(ppb)**	*($\mu g/m^3$)*	*(ppb)**	*($\mu g/m^3$)*
O_3	1 hour	82	160	80	160	50	100
TSP	24 hour 1 Year	— —	120 70 (geometric mean)	— —	120 70	— —	— 60
CO	1 Year 8 hours	30 ppm 11 ppm	34.6 mg/m^3 12.7 mg/m^3	31 ppm 13 ppm	35 mg/m^3 15 mg/m^3	13 ppm 5 ppm	15 mg/m^3 6 mg/m^3
NO_2	1 hour 1 year	210 50	400 100	210 50	400 100	— 30	— 60
SO_2	1 hour 24 hour 1 year	340 110 20	900 300 60	340 110 20	900 300 60	170 60 10	450 150 30
H_2S	1 hour 24 hour	30 6	42 8	—	—	— —	— —

NS Air Quality Regulations and NAAQOs for Canadian criteria air pollutants. (NSE, 2009).



		Averaging time				
Pollutant		**1 hour**	**24 hour**	**Annual**	**Published**	**Reviewed**
Carbon monoxide (mg·m^{3})	D	15	6 (8 h)		1974	1996
	A	35	15 (8 h)		1974	1996
	T		20 (8 h)		1978	1996
Hydrogen fluoride (µg·m^{3})	RL		1.1	0.5 (7 d)	1997	
Nitrogen dioxide (µg·m^{3})	D			60	1975	1989
	A	400	200	100	1975	1989
	T	1000	300		1978	1989
Ozone (µg·m^{3})	D	100	30		1974	1989
	A	160	50	30	1974	1989
	T	300			1978	1989
	RL				*	
PM <10 (µg·m^{3})	RL		25		1998	
PM <2.5 (µg·m^{3})	RL		15		1998	
Sulphur dioxide (µg·m^{3})	D	450	150	30	1974	1989
	A	900	300	60	1974	1989
	T		800		1978	1989
Total reduced sulphur compounds	RL				*	
	AQO				*	
Total suspended particulates (µg·m^{3})	D			60	1974	1989
	A		120	70	1974	1989
	T		400		1978	1989

NAAQO's taken from Canadian Council of Ministers for the Environment (CCME, 1999). D = Desirable, A = Acceptable, T = Tolerable, RL = Reference Level, AQO = Air Quality Objective, * = review in progress.

6.3 Appendix C : VOC monitored by NAPS

VOCs monitored at NAPS stations			
Ethylene	3-methyl-1-Butene	Chloromethane	Bromomethane
Acetylene	Isopentane	2-Methylpentane	2,3-Dimethylbutane
Ethane	Freon 11	cis-4-Methyl-2-Pentene	1,1,1-Trichloroethane
Propylene	1-Pentene	MTBE	Benzene
Propane	2-Methyl-1-butene	3-Methylpentane	Carbontetrachloride
Freon 22	Pentane	1-Hexene/2-Methyl-1-Pentene	Cyclohexane
Freon 12	Isoprene	Hexane	2-Methylhexane
Chloromethane	trans-2-Pentene	Chloroform	2,3-Dimethylpentane
Isobutane	1,1-Dichloroethylene	trans-2-Hexene	3-Methylhexane
Freon 114	cis-2-Pentene	trans-3-Methyl-2-pentene	1,2-Dichloropropane
Vinylchloride	Dichloromethane	cis-2-Hexene	1-Heptene
1-Butene/Isobutene	2-Methyl-2-butene	cis-3-Methyl-2-Pentene	Trichloroethene
1,3-Butadiene	2,2-Dimethylbutane	1,2-Dichloroethane	2,2,4-Trimethylpentane
Butane	1,1-Dichloroethane	Methylcyclopentane	Heptane
trans-2-Butene	Cyclopentane	2,4-Dimethylpentane	Methylcyclohexane
trans-2-Octene	b-Pinene	1,1,2-Trichloroethane	2,5-Dimethylhexane
Tetrachloroethylene	Decane	2,3,4-Trimethylpentane	

cis-1,2-Dimethylcyclohexane	Benzylchloride	Toluene
Chlorobenzene	1,3-Dichlorobenzene	2-Methylheptane
Ethylbenzene	1,4-Dichlorobenzene	4-Methylheptane
m and p-Xylene	1,2,3-Trimethylbenzene	3-Methylheptane
Bromoform	p-Cymene	Octane
Styrene	1,2-Dichlorobenzene	
1,1,2,2-Tetrachloroethane	d-Limonene	
o-Xylene	Indane	
Nonane	1,3-Diethylbenzene	
iso-Propylbenzene	1,4-Diethylbenzene	
a-Pinene	Undecane	
n-Propylbenzene	1,2,4-Trichlorobenzene	
3-Ethyltoluene	Naphthalene	
Camphene	Dodecane	
4-Ethyltoluene	Hexachlorobutadiene	
1,3,5-Trimethylbenzene	1,2,4-Trimethylbenzene	
2-Ethyltoluene	2,4-Dimethylhexane	