SATELLITE AND IN SITU MEASUREMENT OF NO₂

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
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A novel method was developed for producing high-resolution (∼11km) maps of surface NO₂ concentrations by combining satellite retrieved NO₂ columns from OMI with in situ measurements made by permanent monitoring networks. Field data from the BAQS-met field campaign in the Windsor area during 2007 was used to validate this method and explore the uncertainties and biases in the inferred values. Good correlation with the network of passive monitors was found (R = 0.69). Interference of NOₓ in traditional NO₂ measurements was found to be small (0.9 ppb) when considered for 24-hr averages. The inference method was extended to qualitatively analyze long-term trends in Windsor. Comparison against a land-use regression model in Toronto showed similar overall trends, but the downtown core was underestimated considerably by the OMI-inferred map. While the presented inference method can simplify and increase the utility of OMI NO₂ data, limitations remain as to the spatial and temporal resolution achievable.
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Glossary

CL chemiluminescence; a type of NO\textsubscript{x} monitoring where NO is titrated with a known concentration of O\textsubscript{3} and the resulting light is measured

**Column Density** the number density of a chemical species multiplied by the path-length over which it is being measured

EC Environment Canada

**Footprint** The area on the Earth’s surface which a particular OMI pixel represents

GOME Global Ozone Monitoring Experiment; satellite-borne spectrometer

MoE Ontario Ministry of the Environment

MoO Molybdenum/oxygen; heated molybdenum surface frequently used to reduce NO\textsubscript{2} to NO in CL monitors

OMI Ozone Monitoring Instrument; satellite-borne spectrometer

Pixel Can either refer to the physical row of light-sensors (in the spectral dimension) or the area on the Earth’s surface measured by these sensors.

SCIAMACHY SCanning Imaging Absorption spectroMeter for Atmospheric Cartography; satellite-borne spectrometer
Chapter 1

Introduction

Nitrogen oxides (NO\textsubscript{x}), composed of nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}) are an important family of atmospheric pollutants (NO\textsubscript{x}=NO + NO\textsubscript{2}). NO\textsubscript{x} is created by many processes both natural and anthropogenic: combustion from vehicles, airplanes, industrial processes and biomass burning; soil bacteria and fertilizer application in agriculture; lightning. The main source of NO\textsubscript{x} in Ontario is transportation, with a smaller component originating from electricity generation and industrial processes (MOE, 2008). NO\textsubscript{x} is typically emitted as NO but in the presence of O\textsubscript{3} it is quickly oxidized to NO\textsubscript{2}. In daylight, NO\textsubscript{2} undergoes photolysis on a short time scale, generating NO and O\textsubscript{3}. NO\textsubscript{2}, NO and O\textsubscript{3} reach photochemical steady state soon after emission. Of the two constituents of NO\textsubscript{x}, NO\textsubscript{2} is considered to be the more harmful (Last et al., 1994): in the province of Ontario, the government guideline exposure limit for NO\textsubscript{2} is 100 ppb averaged over 24 hours and 200 ppb averaged over 1 hour. NO\textsubscript{2} has also been used as a marker for vehicle emissions, thereby strengthening the association with adverse human health effects (Brook et al., 2007; Jerrett et al., 2009; Clark et al., 2010; Lenters et al., 2010). Despite the association of NO\textsubscript{2} with adverse health outcomes, and its utility as a marker for traffic and/or combustion pollution, NO\textsubscript{2} monitoring networks only provide sparse coverage of its spatial patterns.
NO\(_2\) is commonly measured by chemiluminescence (CL) monitors which work by reducing NO\(_2\) to NO and measuring the light produced by titrating the NO with O\(_3\). There are a number of methods for reducing the NO\(_2\), the most common being a heated molybdenum surface, which becomes oxidized to MoO\(_2\) and MoO\(_3\) and must be periodically recharged. This monitor will be referred to as MoO. These monitors are known to suffer from interference due to other oxidized nitrogen species (NO\(_z\), NO\(_z\)\(=\)HNO\(_3\) + HONO + N\(_2\)O\(_5\) + RONO\(_2\) + ...), since the heated molybdenum surface exhibits low selectivity (WINER et al., 1974; Steinbacher et al., 2007). This interference can especially be a problem in rural areas with low NO\(_2\) concentrations and high NO\(_z\) due to aged air masses or high organic concentrations. Photolytically converted CL monitors do not suffer from this interference (Ryerson et al., 2000). These photolytic monitors operate on essentially the same principle as the MoO-CL monitors, however, the NO\(_2\) is reduced by applying intense light at \(\sim 420\) nm which is specific to NO\(_2\) and therefore is expected to produce almost no interference from other oxidized nitrogen species.

Due to the low relative per-monitor cost, NO\(_2\) has also been measured using networks of passive monitors. For example, the networks have been used to assess human exposure to traffic related air pollution at high spatial resolution (Jerrett et al., 2009). These passive monitors consist of a chemically treated filter pad placed in a protective housing and exposed to ambient air for a period of time, usually two or more days. At the end of the sampling period, the filter is removed and the treatment is dissolved off the filter and analyzed using ion chromatography. Although the filters themselves are inexpensive, the method is labour intensive. As well, since there are no pumps, the exposure, and therefore the collection efficiency, is influenced by local meteorology.

Beginning with the Global Ozone Monitoring Experiment (GOME) in 1995, satellite-based spectroscopic measurements of atmospheric NO\(_2\) have been taken by a series of instruments (Bovensmann et al., 1999; Burrows et al., 1999; Levelt et al., 2006), The Ozone Monitoring Instrument (OMI), launched in 2004 aboard the Aura satellite, has
provided near daily-global NO\textsubscript{2} column measurements at unprecedented spatial resolution. OMI estimates of surface concentrations could potentially contribute to air quality research by:

- allowing examination of the impact of urban areas
- improving estimates of chronic human and ecosystem exposure patterns
- identifying transboundary flows of NO\textsubscript{x}
- providing data to evaluate high-resolution air quality models

Many recent works have compared OMI NO\textsubscript{2} columns with measurements provided by in situ surface monitors (Kramer et al., 2008; Boersma et al., 2009), long-path surface measurements (Kramer et al., 2008) and in situ aircraft measurements (Bucsela et al., 2008). Recent validation studies indicate that biases in the satellite retrievals remain and must be addressed when interpreting the data (Hains et al., 2010; Herron-Thorpe et al., 2010; O’Byrne et al., 2010; Lamsal et al., 2010).

The objectives of this thesis were to develop an approach to use OMI tropospheric column data to estimate spatially-resolved surface NO\textsubscript{2} concentrations at a regional-to-local scale and then to explore the insights that can be gained by applying this methodology to evaluate spatial and temporal patterns of surface NO\textsubscript{2}. A major contribution of previous work in this area was the use of a CTM to estimate a surface-concentration-to-column-density ratio which was applied to satellite NO\textsubscript{2} columns for this purpose (Lamsal et al., 2008). The primary hypothesis of this thesis was that this ratio could be calculated using publicly available data from a network of permanent surface monitoring stations in place of the CTM, in regions with sufficient ground-based monitors. This approach would have the advantage of simplicity since it would not be dependent upon CTM runs, which are relatively costly and not available to all OMI data users. Another potential advantage to this method would be the empirical nature by which it is calculated, making it less
sensitive to the OMI data product used and eliminating the possibility of introducing additional biases from the model used in the inference process.

Several related facets of this hypothesis were also examined. The OMI results were compared with passive NO$_2$ measurements obtained at 18 sites across Southwestern Ontario in 2007. Since the passive sites were spaced as closely as 15 km and were not used to calculate the ratio (i.e., were independent), they were well suited for determining the accuracy of the estimated concentrations on a spatial scale not yet examined, across a variety of land-use types spanning from urban to rural locations. Further, collocated conventional and photolytic NO$_2$ monitors allowed for quantification of the NO$_x$ interference known to impact conventional measurements. Additionally, it was possible to examine the diurnal patterns in the interference and to assess the impact of these patterns on the comparison of the 14-day integrated passive NO$_2$ with the 14-day average OMI NO$_2$ based upon the midday overpasses. Finally, because of the additional rural chemiluminescence monitoring provided during the campaign, the value of these more spatially representative rural monitoring sites for improving the exploitation of the freely available OMI satellite observations was examined.

This thesis is composed of 5 chapters, including this introduction. Chapter 2 includes a thorough literature review of the current state of knowledge in the emissions, transport and chemistry of NO$_x$ and NO$_2$ in particular, the human health effects of NO$_2$, current monitoring practices and their limitations and the remote sensing of tropospheric NO$_2$ by satellite-borne instruments. Chapter 3 provides an overview of Digital Optical Absorption Spectroscopy and the uncertainties introduced by each step of the satellite retrieval process. Chapter 4 outlines the procedures used for data collection, the data used from the Ontario Ministry of the Environment and finishes with a detailed description of the proposed surface NO$_2$ concentration inference method. In situ results for Ontario as well as their implications for conventional NO$_2$ monitoring and comparison with satellite remote sensing are presented in section 5.1.1. The passive monitor results are then be
applied to the validation of the inferred OMI surface concentrations in section 5.1.2. In the final section of chapter 5, OMI data is used to infer maps for longer time periods and wider spatial domains to demonstrated potential uses of the methodology laid out in this thesis.
Chapter 2

Literature Review

This section provides an overview of the current body of work related to atmospheric NO$_2$ required to frame this research project as an extension of that body of work. Included in this section is a discussion of the deleterious effects of NO$_2$ on human health and the environment, indirectly as a precursor to atmospheric ozone O$_3$, and on human health, directly. The findings of previous studies in local, regional and global emission, transport and fate of NO$_2$ is presented. A summary of remote and in situ measurement techniques is provided. Additional background on remote sensing techniques with particular attention to sources of error is presented in chapter 3 as this complex topic requires particular attention for the work presented in this thesis.

2.1 NO$_2$ in the environment

2.1.1 The Nitrogen Cycle

Molecular nitrogen (N$_2$) is the most abundant gas in Earth’s atmosphere. It is extremely stable and has only a few pathways to other, more reactive nitrogen species. Nitrogen fixing bacteria in plant roots and in soil can convert N$_2$ to ammonia NH$_3$. Lightning can split N$_2$ and O$_2$ to form NO. In addition to these natural processes, human activities have
also contributed to the fixing of nitrogen. Nitrogen is split by the Haber-Bosch process to create ammonia for industrial nitrogen fertilizer production. High temperature fossil-fuel combustion can produce nitrogen oxides, principally NO. In the soil, nitrifying bacteria oxidize ammonium (NH$_4^+$) to nitrites (NO$_2^-$) and nitrates (NO$_3^-$), which are biologically available for plants. After the plants are eaten, or die and decompose, their nitrogen is returned to the soil as ammonium. The reactive nitrogen species are eventually returned to the atmosphere by denitrifying soil bacteria which convert nitrates to N$_2$ (Smil, c1997; Draper and Reed, 2009).

2.1.2 Reactive nitrogen in the atmosphere

The story of nitrogen from when it is fixed (i.e., converted from N$_2$ to reactive NH$_3$ or NO$_x$) until it is returned to the atmosphere as stable N$_2$ is far more interesting. After NO is created by lightning or combustion it reacts quickly to form NO$_2$, in the oxygen rich environment. Conversely, NO$_2$ is converted to NO by photolysis. Because of this fast null cycling, we define the nitrogen oxides family (NO$_x$=NO + NO$_2$) (Logan, 1983). NO$_x$ has several sources: it can be generated directly by lightning and by fossil fuel combustion. It is also created by combustion of nitrogen rich fuels during biomass combustion. Microbial action in the soil can create NO$_x$, as can the oxidation of NH$_3$. Stratospheric incursions and direction emission from volcanic eruptions has also been discussed as possible sources for NO$_x$ (Logan, 1983). Most of this stratospheric NO$_x$ is the result of N$_2$O, which, although emitted mainly from soil and ocean biological processes, has a long enough lifetime to reach the stratosphere and react with ozone to create NO$_x$ (Wuebbles, 2009; Intergovernmental Panel on Climate Change, 2007). This reaction is the main natural loss mechanism of stratospheric ozone.

NO$_x$ can react in many ways in the environment to form other oxidized nitrogen compounds (NO$_y$=NO$_x$ + HNO$_3$ + HONO + ΣAN + PAN + N$_2$O$_5$). Of these, hydrogen nitrate (HNO$_3$) provides an important pathway for NO$_x$ elimination, either in precipitation or
dry deposition, especially on surfaces of particulate matter (Holland et al., 1999). Once hydrogen nitrate has been deposited in the soil, it can be used by plants, or returned to the atmosphere as N\textsubscript{2} by nitrifying bacteria.

Hydrogen nitrite (HONO) is an important reactive species. During the day, HONO is quickly converted to NO by photolysis, creating OH, an important radical which greatly affects the oxidative capacity of the troposphere (Kleffmann, 2007). Formation mechanisms of hydrogen nitrite are not well understood, but hydrolysis of NO\textsubscript{2} on wet particle (or ground, or plant) surfaces is thought to be a main contributor to nighttime HONO concentrations (Kleffmann, 2007; Kotamarthi et al., 2001; Yu et al., 2009). Daytime formation appears to be driven by reduction of NO\textsubscript{2} on photosensitized hydrocarbon surfaces, which provide an order of magnitude higher HONO production during the day than hydrolysis of NO\textsubscript{2} and primary HONO emissions at night (George et al., 2005). Since the types of hydrocarbons proposed for this mechanism are ubiquitous, this would also explain rural formation of HONO, including high concentrations observed in the arctic. However, high NO\textsubscript{2} concentrations would also be required to explain these concentrations. Instead, it is possible that these extremely elevated rural concentrations are instrument artefacts (Liao et al., 2006), which demonstrates the difficulty in providing accurate measurements of this important species.

Although daytime conversion between NO and NO\textsubscript{2} neither creates nor destroys NO\textsubscript{x} or O\textsubscript{3}, any mechanism which circumvents this null cycle can have a strong effect on O\textsubscript{3} concentrations: a process which creates NO\textsubscript{2} or destroys NO without enacting a corresponding change in the other NO\textsubscript{x} species will result in the production of ozone; an opposing shift in the NO/NO\textsubscript{2} balance will destroy ozone. When volatile organic compounds react with OH to form peroxy radicals, these radicals can oxidize NO to NO\textsubscript{2} without the reduction of an O\textsubscript{3} molecule (to O\textsubscript{2}). This newly formed NO\textsubscript{2} is then rapidly photolyzed to produce O\textsubscript{3}.
Figure 2.1: Important daytime reactions including NO\textsubscript{x}. This does not include other mechanisms which are less important than those shown. Adapted from Clemitshaw (2004)

2.2 Variability in NO\textsubscript{2}

NO\textsubscript{x} emissions sources tend to be localised in space, for example, as in industrial processes and roadways. Emissions are also localised in time, for example, high traffic related emissions can be expected during rush hour. Therefore, considerable variability can be expected in NO\textsubscript{2} concentrations both in time and space. This section reviews the current reported findings on diurnal variability, day-to-day variability, seasonal variability and long-term (multi-year) trends. The section will also discuss the current understanding of spatial distribution patterns including roadway dispersion, regional variability including urban and rural comparison and a discussion of observed NO\textsubscript{2} values seen around the globe.
2.2.1 Measured spatial variability in ambient NO\textsubscript{2}

Between cities, in 2008, annual mean NO\textsubscript{2} concentrations varied from as little as a few ppb for small, remote cities such as Yellowknife, NWT up to 30 ppb for densely populated areas such as Mexico City, Hong Kong and Los Angeles, CA [MOE, 2008].

Few studies have reported measured surface NO\textsubscript{2} concentrations downwind of urban sources. However, the effects of urban NO\textsubscript{x} emissions on O\textsubscript{3} concentrations have been noted as far downwind from Toronto as 40 km (Lin et al., 1995).

Within cities, average concentrations have been found to vary considerably even on the scale of meters. In the street canyon in London, UK in the 1980s, using a series of passive sampling devices, it was found that concentrations were greatest at the centre of the roadway (∼200 ppb) but 15m away from the centre of the roadway, concentrations had dropped to background levels (∼100 ppb, as measured by more distant monitors) (Laxen and Noordally, 1987). In suburban and residential settings, concentrations close to background levels were observed right next to roadways, indicating less spatial variability in these areas (Hewitt, 1991).

2.2.2 Measured indoor NO\textsubscript{2} concentrations

Indoor concentrations have been found to vary within the house if the home has a gas stove, but in homes with electric stoves, concentrations are spatially invariant (Moschandreas and Zabransky Jr., 1982).

2.2.3 Roadway dispersion measurements

Passive monitors and a host of other instruments have been used to compare poorly-spaced non-representative measures of traffic-related air pollution (TRAP) with the overall diffusion pattern displayed around major roadways in Toronto (Beckerman et al., 2008). As expected, NO\textsubscript{2} was observed to be higher at the highway and lower as distance
from the roadway increased. Other passively measured pollutants were NO, NO\textsubscript{x}, O\textsubscript{3} and VOCs. Handheld monitors measured PM\textsubscript{2.5} and PM\textsubscript{10}. Mobile laboratory measurements included PM\textsubscript{2.5} mass, PM\textsubscript{0.01–2.5} number concentration, black carbon (BC), VOCs, NO, NO\textsubscript{2} and NO\textsubscript{x}. This work followed on a previous study using only the Ogawa passive NO\textsubscript{2} samplers in Montreal (Gilbert et al., 2003). The authors of that study showed a negative correlation between the log of NO\textsubscript{2} and distance from the highway, both upwind and downwind, although the “background” concentration reached on the downwind side was higher and the dropoff in NO\textsubscript{2} was less sharp. The obvious limitation in this study is defining “downwind” when comparing 7-day integrated averages; presumably the wind did not blow in the same direction at the same speed for the entire period. In spite of this limitation, in terms of assessing human exposure for subjects living near a highway, these integrated averages could provide value.

In Tokyo, Japan near-roadway dispersion of vehicle emissions of NO\textsubscript{x} was studied by placing 3 towers with NO, NO\textsubscript{2} and O\textsubscript{3} instruments measuring at 1m, 3m and 10m height placed at roadside, 20m and 100m from an intersection on a busy roadway (Minoura and Ito, 2010). Because of the high time-resolution of the measurements, it was possible to segregate the measurements and use only those taken when the instruments were downwind of the roadway. All concentrations were compared against time elapsed since traffic light change, to observe the elevated levels from closely-packed idling and accelerating vehicles followed by a drop as traffic reached steady state. It was found that short-term changes in NO\textsubscript{x} and O\textsubscript{3} were quite pronounced at the roadway while substantially diminished at 20m and indistinguishable from background concentrations at 100m downwind. It should be pointed out that in this case, background meant the average concentrations at the furthest downwind site, which was a reasonable assumption, as there was no relationship between concentrations at the 100 m station and time elapsed since the light change.
2.2.4 Modeling of surface-level NO$_x$ and NO$_2$ concentrations

Since measurement at all locations is not practical, a number of methods of interpolating concentrations in space and time have been created. The most common methods relevant to this thesis are, roughly in order of increasing complexity: inverse distance weighting (IDW), Kriging, Land Use Regression (LUR) and Chemical Transport Models (CTMs).

IDW is a simple 2D interpolation scheme where the concentration at an unmonitored point is a weighted average of concentrations measured at nearby monitoring stations, where the weights are inversely proportional to the distance of the point from the monitors. It has been found to produce poor results with typical permanent monitoring station densities and a highly-variable pollutant such as NO$_2$ ([Stedman et al. 1997](#)).

Kriging is similar to IDW, except in that the weights applied to the concentrations from nearby stations are computed based on the observed spatial covariance of the available measurements ([Wartenberg et al. 1991](#)).

A more complicated scheme takes advantage of the fact that most significant sources of NO$_x$ are vehicular and the wealth of geographical information systems (GIS) information available for most populated areas. Typically, a large number of densely spaced monitors are placed for a short period of time. A multivariable regression is then performed using land use variables (and sometimes other variable such as geographical or socioeconomic variables) to get a set of weights which most accurately reproduces the measured concentrations. If the $n$ measured concentrations are collected in a vector $y$ of length $n$, and the $m$ land-use (or geographical or socioeconomic) variables for each of the $n$ sampling locations are placed in an $m \times n$ matrix, $X$, a regression is performed to find row vector $b$ (length $m$) which minimizes the value

$$\sum_{i=1}^{n} (y_i - (b \cdot X_i))^2$$

where $y_i$ is the $i^{th}$ observation and $X_i$ is the $i^{th}$ column of $X$, that is, the column vector...
of land use variables for sampling location $i$.

Typical $R^2$ values (for predicted values vs. observed values) for NO$_2$ are in the 0.6–0.9 range. The most important (that is, most heavily weighted) variables often include proximity to a major roadway (as a categorical variable) and geographical location corresponding to prevailing meteorological conditions.

2.2.5 Global- and national-scale variability

In-depth study of NO$_x$ chemistry and transport is fairly recent. Even as recently as 1983, basic science questions such as the nighttime loss mechanism of NO$_x$ remained unanswered (Logan, 1983). N$_2$O$_5$ deposition was proposed: N$_2$O$_5$ + H$_2$O $\rightarrow$ 2HNO$_3$. Surface deposition was also shown to be a strong NO$_2$ loss mechanism near emissions sources (about one quarter to one half the reported average deposition velocity of HNO$_3$ rainout). A combination of measurements – airplane, rainfall, surface deposition, ambient air – and modeling was used to infer important information about global nitrogen cycles in the troposphere. Column shape, i.e., the vertical distribution of NO$_2$ upwards through the air column, was discussed with continental columns decreasing with altitude and ocean columns increasing with altitude. Logan et al. also noted that wet deposition in Canada provides a higher sink than the source from fossil fuels – approximately equal to the entire NO$_x$ emissions for Canada – which implies that some of our NO$_x$ is being imported, probably from the US (Logan, 1983).

Global distributions of NO$_x$ and HNO$_3$ were studied for January and July by comparing modeled values with measured results from various studies (Penner et al., 1991). At this stage, global modeling was still crude; due to computational limitations zonally and seasonally averaged winds were used. One powerful insight provided by this study was a comparison between contributions to the global distribution of NO$_x$ and HNO$_3$ from anthropogenic and natural sources, made possible by switching off anthropogenic emissions. It was concluded that lightning makes an insignificant contribution to sur-
face NO\textsubscript{x} even at 10TgNyr\textsuperscript{-1} (which the authors deem high, although lower than some suggested values from previous work). Annual average surface mixing ratios were found to range from 0.01 ppb over Southern ocean to 4ppb in dense urban/industrial areas. While this value may seem low, it is mainly due to the wide averaging area used for air parcels in the model, with an average size of 320km \times 320km. The Great Lakes / Eastern seaboard region and continental Europe were shown to have the highest concentrations overall. While the paper highlighted the importance of NO\textsubscript{x} as an ozone precursor, the results also showed the importance of global transport of NO\textsubscript{x} and HNO\textsubscript{3} (and thus the anthropogenic influence) on open-ocean fertilization, an important biogeochemical process.

In an effort to understand the O\textsubscript{3} budget of the tropical troposphere, Jacob et al. (1996) used airplane data from TRACE A to measure O\textsubscript{3}, CO, CH\textsubscript{4}, NO\textsubscript{x}, HNO\textsubscript{3}, H\textsubscript{2}O\textsubscript{2} and many organics including PAN and PPN. The authors concluded that O\textsubscript{3} production was limited by NO\textsubscript{x} concentrations. Of particular relevance to this study was the schematic for convective currents in the tropics including updrafts over land, especially in biomass burning regions, which results in O\textsubscript{3} production in the high troposphere due to NO\textsubscript{x}, which could be seen as analogous to the summer lake-breeze effect observed near the Great Lakes and injection of NO\textsubscript{x} into the troposphere by transportation and industry.

Later, attempts were made to find a unified inventory of NO\textsubscript{x} sources to be used as a standardised input set in other works, to compare different models (Lee et al., 1997). Values from different papers were combined to come up with a “best” estimate which put fossil fuel combustion as the highest source of NO\textsubscript{x} at 22TgNyr\textsuperscript{-1}. Contributions from biomass burning, soil microbial production and lightning were all determined to be of similar order of magnitude, 7.9, 7.0 and 5.0 TgNyr\textsuperscript{-1}, respectively. Very small components were found to be from stratospheric decomposition of N\textsubscript{2}O, ammonia oxidation and aircraft emissions, all < 1TgNyr\textsuperscript{-1}. Although, these sources seem small, it is important to note that they are upper-tropospheric sources and are not quite so small when
compared with the other main upper tropospheric NO\textsubscript{x} source, lightning. Uncertainties on the estimates were discussed, the most uncertain being lightning at least partly because of the difficulty presented in measuring lightning emitted NO\textsubscript{x}. High uncertainty in biomass burning inventories due to uncertainty in both the amount of burning and the composition of the fuel was also reported.

Since these early studies, a number of incremental improvements have been to the body of knowledge of global emissions inventories (e.g., Benkovitz et al. 1996; Olivier and Berdowski 2001; Streets et al. 2003). See also section 2.5.2.

2.2.6 Regional-scale variability

To demonstrate the usefulness of LUR models for predicting traffic related air pollution between permanent monitoring sites, Henderson et al. (2007) used 116 passive samplers to generate LUR maps of NO and NO\textsubscript{2} in Vancouver, BC. NO\textsubscript{2} was found to range from 4.8 ppb in suburban areas to 24.1 ppb in dense areas with many major roadways. The authors treated road length and vehicle density as mutually exclusive variables, although models based on each were similar in their predictive power, reporting $R^2 = 0.56$ and $R^2 = 0.60$, respectively.

In order to estimate population exposure in a long-term, large-scale study, Beelen et al. (2007) used a combination of GIS variables, kriging and IDW to generate ambient concentration maps for NO\textsubscript{2}, SO\textsubscript{2}, BS and PM\textsubscript{2.5} at the postal-code scale. To get an exposure metric, the ambient concentration was considered to be a superposition of 3 components: regional, urban and local signals. Permanent monitoring stations were used to estimate the regional signal using kriging and IDW (which gave similar results, so the IDW was used to calculate final values) and the urban component was estimated based on the local population distribution while the local component was done by LUR using traffic density as the most important variable. The most important contribution of this paper was the use of traffic data over a long time scale to show that traffic patterns
stayed relatively stable over the period from 1986 to 1996. Interestingly, the increase in traffic intensity over the 10 year period was much lower for municipal roads (\(\sim 6\%\)) than for provincial roads (\(\sim 17\%\)), for which the increase was significantly lower, in turn, than for national roads (\(\sim 33\%\)).

Another population exposure study around Toronto, Ontario used 94 passive NO\(_2\) monitors in the fall of 2002 spread across the city of Toronto to inform a spherically kriged surface and a very high spatial resolution land use regression (LUR) model to predict NO\(_2\) concentrations (Jerrett et al., 2007). The kriged model showed very high concentrations in the downtown core and also displayed an overall east-to-west increase, but failed to capture the influences of roadways on nearby concentrations. The LUR model showed a similar downtown elevation as well as the same east-to-west increase, but also was able to resolve increases in NO\(_2\) concentration within a few hundreds of metres of heavily trafficked roadways. This model was then improved by including a second set of passive monitor data taken in the spring of 2004 (Jerrett et al., 2009). To show that the spatial distribution of NO\(_2\) did not change greatly over time, some monitoring locations were duplicated between the two studies. The authors claim that the patterns remained stable and the surfaces for 2002 and 2004 showed a strong correlation (Pearson’s r=0.73).

### 2.2.7 Temporal variability

#### Seasonal trends

In mid- to high latitudes, surface NO\(_2\) and NO\(_x\) concentrations are higher in winter than in summer (Penner et al., 1991; MOE, 2008; Lamsal et al., 2010). This is mostly due to enhanced mixing and decreased lifetime of NO\(_x\) in the summer because of the increased oxidizing capacity of the troposphere.
Weekly trends

Due to traffic and industry sources, NO$_2$ is generally higher on weekdays than on weekends. In particular, in North America and Europe, Saturday usually displays a drop compared to Friday and Sunday even further, with a return to weekday concentrations on Monday ([Bigi and Harrison 2010]).

Diurnal trends

Reported hourly trends typically show an increase in the morning, due to the morning rush hour and photolysis of any overnight build-up of HONO ([Kleffmann 2007]), followed by a decrease at midday as traffic emissions decrease and the mixing height increases. The late-afternoon/evening rush hour increases concentrations again and concentrations decrease overnight. Recently, morning rushhour peak values in the range of 14–22 ppb have been reported in medium sized cities ([MOE 2008; Makra et al. 2010]), while London, UK was reported to have a morning peak concentration of approximately 32 ppb. Ratios between morning rush hour and midday concentrations ranged from approximately 1.1 to 3.5.

Atmospheric lifetime of NO$_x$

Related to the diurnal variability is the atmospheric lifetime of NO$_x$. Recent studies have established the atmospheric lifetime of NO$_x$ in the troposphere as ranging from 3 hours to 23 hours with the lower bounds corresponding to summer lifetimes and the upper bounds to winter ([Leue et al. 2001; Martin et al. 2003; Schaub et al. 2007; Lamsal et al. 2010]). Different methods have been used, each with its own sources of uncertainty. [Leue et al. (2001)] utilized GOME satellite measurements along the coastal edge of the continental U.S. and the average windspeed to infer the lifetime of NO$_x$ to be close to 26 hours. [Martin et al. (2003)] and [Lamsal et al. (2010)] used NO$_x$ lifetime values from a CTM (GEOS-Chem) to constrain top-down emissions inventories and gain
insight into seasonal patterns in NO\textsubscript{x} emissions and concentrations, respectively. Schaub et al. (2007) combined bottom-up emissions inventories with NO\textsubscript{2} columns measured by SCIAMACHY to infer NO\textsubscript{x} lifetime between 3 hours in the summer and 19 hours in the winter, under a no-horizontal transport assumption.

### 2.3 Human health effects

Most research into health effects of NO\textsubscript{2} exposure has fallen into one of four categories: indoor exposure (long-term, periodic moderate exposure); occupational exposure (acute or long-term moderate exposure); as an ozone precursor; or as a marker for spatial gradients in the complex cocktail of air pollutants produced by industry and, especially, vehicular traffic.

Examination of health effects of air pollution can be either epidemiological in nature or toxicological in nature. Epidemiological studies compare measured or reported health outcomes with estimates of environmental exposure to determine if increased exposure leads to an increased risk of a particular negative health outcome. Toxicological studies seek to discover specific health outcomes and pathways by exposing patients, animal surrogates or cells in vitro to pollutants and measuring the responses.

#### 2.3.1 Toxicology

To establish a causal relationship between a pollutant and a health outcome, it is important first to establish a mechanism by which the outcome can be effected and for that mechanism to be relevant at concentrations like those encountered in common situations.

The case for pulmonary damage resulting from very high concentrations of NO\textsubscript{2} has long been established as a condition called Silo Filler’s disease (Grayson, 1956). In farmers and industrial workers it was shown that exposures at 500 ppm NO\textsubscript{2} in air resulted in acute pulmonary edema and death within a few days of exposure while more mild edema,
bronchial fibrosis and chemopneumonia was experienced by humans exposed to lower concentrations in tens to hundreds of parts per million (Grayson, 1956). Interestingly, it was shown that therapeutic use of NO improved the condition of a patient suffering from Silo Filler’s disease (Leavey et al., 2004). However, these concentrations are 100 to 1000 times ambient concentrations that would be experienced by the urban populace.

A number of studies have been conducted on human responses to NO₂ concentrations more relevant to normal human exposure. A variety of impacts on human health have been hypothesized. A recent review of these exposure studies since the 1970s concluded that exposures at less than 1 ppm were unlikely to cause any lasting harm (Hesterberg et al., 2009). Of 37 papers reviewed that examined lung function response to NO₂ exposure from 100 ppb to 2 ppm, only 10 showed significant results and these were typically small (Hesterberg et al., 2009). No difference was observed between asthmatic and healthy patients. Of 30 studies of change in response to a non-specific bronchoconstrictor challenge after NO₂ exposure from 100 ppb to 3 ppm only thirteen showed significant results and again, these were minor (Hesterberg et al., 2009).

Although not part of a controlled study, an incident involving a malfunctioning of a propane-powered ice-resurfacing machine in an arena during a hockey tournament in Sweden exposed a group of children to high concentrations of NO₂. When conditions were simulated, concentrations up to 1250 ppb were observed (Rosenlund and Bluhm, 1999). A 5-year follow-up study found odds ratios of 2.4 to 3.1 for upper and lower respiratory symptoms, although the 95% confidence intervals included unity (Rosenlund et al., 2004).

In addition to direct toxicological effects from NO₂, it is important to note that there are two indirect pathways for NO₂ to affect human health. As a result of vehicular air pollution, NOₓ and volatile organic compound mixtures can create ozone which has been linked with immediate effects on lung function as well as long term developmental problems, cancer and mortality, although these long term effects are less well-established
in the literature (Katsouyanni, 2003; Knuckles et al., 2010; Zhang and Smith, 2003). It is also possible that NO$_2$ deposition on particle surfaces can increase acidity of particles, although examination of the relationship between particle nitrate (NO$_3^-$) concentrations and human health effects has been minimal and is thus far fairly inconclusive (Reiss et al., 2007).

When exposure to traffic related air pollutants was modeled for a group of healthy young adults only NO$_2$ and SO$_2$ were found to increase arterial wall stiffness (Lenters et al., 2010), providing another possible pathway for long term cardiovascular health effects.

### 2.3.2 Epidemiology

An important shortcoming of toxicological studies is the small sample sizes; it is often difficult, expensive or unethical to expose human subjects to very elevated levels of air pollution. Epidemiological studies take advantage of natural variations in exposure across populations to establish relationships between ambient pollution levels and human health outcomes.

#### Indoor exposure

A number of studies have indicated that indoor NO$_2$ exposure dominates outdoor exposure due to the amount of time most people spend at home or at work (Piechocki-Minguy et al., 2006). Indoor exposure is typically attributed to gas stoves and kerosene heaters (Berglund et al., 1993). Dockery et al. (1981) found indoor NO$_2$ concentrations to be significantly higher than outdoor in homes with gas cooking stoves, as compared to electric: $\sim$ 20 ppb average for inside homes with gas stoves compared with $\sim$ 8 ppb outdoors and in homes with electric stoves. (Spengler et al., 1983) found similar concentrations, although they found more variation in the gas stove homes than had previously been reported. Subsequently, many studies sought to determine a relationship between indoor
NO$_2$ concentrations due to gas stoves and health impacts which were reviewed by Basu et al. [Basu and Samet, 1999]. This systematic review of gas stove-related literature found very few significant relationships between indoor NO$_2$ concentrations or gas stove ownership and health outcomes for any healthy population, in spite of having reviewed 45 different studies.

**Environmental exposure**

[Bates and Sizto, 1987] found a weak, negative correlation between same-day averages of 1 hour maximum NO$_2$ concentrations and hospitalizations for asthma in Southern Ontario.

Recently, more detailed exposure analysis have allowed for neighborhood-scale differentiation of individual exposure. [Jerrett et al., 2009] found a statistically significant increase in non-accidental deaths, including a 40% increase in death from circulatory causes, across the inter-quartile range of NO$_2$ exposure of approximately 2 ppb (the study cohort had 25, 50 and 75% NO$_2$ exposures of 20.8, 22.9 and 24.8 ppb, respectively). Because data was collected after hospitalization, meaning all patients belonged to a susceptible group, it is difficult to generalize this conclusion. The authors also point out that there was an unusually high prevalence of existing chronic cardiopulmonary conditions in the sample group.

[Clark et al., 2010] conducted a population-based birth cohort study in Vancouver, BC to measure prenatal and early life effects of TRAP. A variety of pollutants were explored: NO, NO$_2$, O$_3$, CO, SO$_2$, PM$_{10}$, PM$_{2.5}$, black carbon (BC) and woodsmoke. Proximity to industrial sources and proximity to roadways was also tested, although it does not appear that the traffic conditions of the roadway were considered, nor the amount and type of pollution produced by the industrial sources. Exposure to most pollutants was measured in two ways: using an intensive sampling campaign to generate a LUR model and by inverse distance weighted (IDW) averaging of the 3 nearest permanent monitoring stations.
stations. The LUR model has the advantage of high spatial resolution but since it was based on two intensive sampling campaigns lacks temporal resolution, while the IDW, used daily average measurements, but the sparsity of the monitoring stations would have smoothed out even fairly large scale spatial differences in the pollutant distribution. An increase in asthma risk due to prenatal and first-year exposure to NO$_2$ was shown, with an asthma risk ratio of 1.12 for a $\sim$5ppb increase in first-year exposure with $\sim$5ppb being approximately twice the inter-quartile range for cohort NO$_2$ exposure.

In addition to the birth cohort study, adult risk of hospitalization and death due to coronary disease was conducted with the same exposure assessment maps (Gan et al., 2010). After taking into account BC and PM$_{2.5}$ exposures in a multiple regression model, NO$_2$ was not found to significantly impact hospitalization for coronary disease while risk for mortality was 3% for an inter-quartile range increase in NO$_2$ exposure and the confidence interval included unity. After adjusting for PM$_{2.5}$ and NO$_2$, BC was shown to have 3% and 6% increased risks for hospitalization and mortality, respectively, while neither confidence interval included unity. It should be noted here that the LUR map for BC was generated using far fewer real observations (39 mobile samples, as compared to hundreds of passive samples for the NO$_2$ regression) and both the BC and NO$_2$ maps reproduced the observed data with lower fidelity than seen in other studies (i.e., $R^2 = 0.56$ for both NO$_2$ and BC versus $R^2 = 0.7$ for Jerrett et al. (2009)).

### 2.3.3 Summary of Human Health Effects

Although the mechanisms for NO$_2$ affecting human health are not well understood, ambient exposure to NO$_2$ appears to be linked, either on its own or as a marker of the complex cocktail of air pollutants produced by vehicular traffic, to coronary health problems, morbidity and mortality. The ability to estimate long-term ambient exposure to NO$_2$ at high spatial resolution will remain an important tool in the epidemiological toolkit as research into this relationship continues to develop.
2.4 In Situ Measurement of NO$_2$

Although there are many methods for in situ measurement of NO$_2$, only the two most common are pertinent to this thesis: chemiluminescence monitor and passive sampler.

2.4.1 Chemiluminescence monitors

Chemiluminescence monitors work by titrating NO with a known concentration of O$_3$, which reaction creates light at a very specific wavelength. By measuring this light with a photomultiplier tube, the concentration of NO can be calculated \cite{PARRISH1990, FEHSENFIELD1990, DUNLEA2007}. In order to utilize this reaction to measure NO$_2$, it must first be reduced to NO. This is accomplished by passing the air over a heated metal surface, most commonly heated molybdenum. The Mo is oxidized to MoO$_2$ or MoO$_3$. Unfortunately, this surface exhibits low selectivity and can reduce other oxidized nitrogen species which may be present. This bias has been shown to be as high as 130% in summer months in relatively unpolluted areas \cite{STEINBACHER2007}.

It is also possible to convert the NO$_2$ to NO photolytically, using a very specific wavelength ($\sim 400nm$) light source \cite{RYERSON2000}. However, narrow-band light sources are difficult to build and these types of converters tend to be expensive, so heated Mo (MoO) converters are more common in permanent monitoring setups. Typical detection limits for CL monitors equipped with photolytic converters are given to be around 0.5 ppb \cite{THORNTON2003}.

Advantages to chemiluminescence monitoring are high-time resolution, often as high as 1 second resolution although typically reported to 1 minute - 1 hour resolution \cite{RYERSON2000, THORNTON2003, ORODEZ2006}. Disadvantages include fairly large size, power and data-logging requirements, regular maintenance and calibration as well as the cost of the instrument itself.
2.4.2 Passive diffusion-tube samplers

Another common method for measurement of NO₂ is passive sampling (Laxen and Nordal, 1987; Jerrett et al., 2007; Clark et al., 2010). These passive monitors consist of a chemically treated filter pad placed in a protective housing and exposed to ambient air for a period of time, usually two or more days. At the end of the sampling period, the filter is removed and the treatment is dissolved off the filter and analyzed using ion chromatography. Another advantage to this method is that, due to the sampler’s small size, it can be affixed to an individual to monitor their actual exposure as they go about their daily routine (Mukala et al., 1999).

Although the filters themselves are inexpensive, the method is labour intensive. As well, since there are no pumps, the exposure, and therefore the collection efficiency, is influenced by local meteorology. Additionally, the measurements must be corrected for relative humidity. Interference from other oxidized nitrogen species has been reported to be negligible (Bush et al., 2001). Overall uncertainties for 2-week passive samplers when measured against chemiluminescence monitors in the field range between ±10% and ±35% (Bush et al., 2001; Buzica et al., 2005; Cape, 2009).

2.5 Satellite Remote Sensing of NO₂

This section will provide an overview of the verification and uses of satellite NO₂ data products. A brief description of the technical details of the retrieval process is provided and is intended to ensure the reader is familiar enough with the methods to follow the literature discussion. The retrieval process is a complicated one involving many variables and warrants a chapter of its own. A comprehensive treatment of the methodology of satellite remote sensing by spectroscopy and the uncertainties present in each step of the process is provided in chapter 3.

Satellite remote sensing of NO₂ is generally based on the DOAS technique (Platt, ...
This method is based on the Beer-Lambert law which relates incoming radiation \((I_0(\lambda))\) to outgoing radiation \((I(\lambda))\) by a function of path length \((L)\) of the light and the concentration \((c)\) and absorption cross section \((\sigma(\lambda))\) of the species in question:

\[
I(\lambda) = I_0(\lambda) \cdot e^{-L\sigma(\lambda)c}
\] (2.1)

In the simplest case, this relationship can be used to calculate the concentration of a trace gas by setting up a light source of known spectral intensity and a sensor at some distance, \(L\). This case is limited to near-surface measurements and requires a long, unobstructed path sometimes with a reflector at the end. Often, to obtain ground-based remote measurements upwards through the air column, the sensor is pointed straight up and the sun is taken to be the source. Since knowing the solar spectrum exactly would require removal of the atmosphere, the incoming spectrum is instead estimated by fitting a slowly-varying-with-wavelength polynomial to the measured spectrum. This method means that it is not necessary to know the incoming spectrum exactly, and that absorption or scattering processes which vary slowly with wavelength are removed from the analysis, but only gases with sharp absorption features can be measured using this technique – \(\text{NO}_2\) is just such a species [Platt 1994].

In the case of satellite remote sensing, there are two possible viewing modes: limb and nadir. Limb mode looks through the atmosphere approximately parallel to the Earth’s surface, while nadir viewing points down through the atmosphere, measuring the radiation reflected from the Earth’s surface [Rodgers 2000].

The first satellite-borne spectroscope capable of measuring \(\text{NO}_2\) was the Global Ozone Monitoring Experiment (GOME). Launched in 1995, the instrument achieves global coverage ever 3 days with a nadir pixel size of 320km \(\times\) 40km on the Earth’s surface [Leue et al. 2001]. Following this was the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) with 6-day global coverage and 30km \(\times\) 60km
pixel size in nadir viewing mode \cite{Richter2004, Bovensmann1999}. The Ozone Monitoring Instrument (OMI) was launched in 2004 and has the best spatial and temporal resolution to date; with nearly global coverage every day and a nadir pixel footprint of 13km $\times$ 24km \cite{Boersma2007}. All three satellites describe sun-synchronous orbits, meaning they orbit from the north pole to the south pole passing over a given spot on the Earth’s surface at the same \textit{local} time each day. The satellite orbits approximately 14 times per 24-hour rotation of the Earth at 800 km altitude.

Several important factors affect the retrieval process. The angle of the sun and the satellite with respect to the ground, or the viewing geometry, affect the path length. Not all NO$_x$ in the atmosphere is constrained to the boundary later, or even the troposphere. Mean stratospheric vertical columns have been reported to be an order of magnitude larger than tropospheric columns, compared to global averages which are mainly ocean-surface area with very low NO$_2$ concentrations \cite{Leue2001}, so the contribution of stratospheric NO$_2$ must be considered. It is also important to note that the absorption cross section of NO$_2$ is temperature dependent, causing NO$_2$ molecules at different altitudes to absorb differently, however, assuming a temperature independent profile has only small effects on the final retrieval \cite{Vandaele1998, Burrows1998, Boersma2002, 2004}.

Additional complications not normally found in ground-based instruments can be presented by the inaccessibility of instruments aboard an orbiting platform, the hostility of the environment and the difficulty of testing instruments in advance. GOME was thought to suffer from a permanent systematic bias in slant column retrievals due to a spectral diffuser plate problem \cite{Wenig2004, Boersma2004}. OMI has had a number of pixels out of service due to interference from a suspected stray strip of insulation.
2.5.1 Review of satellite verification and applications

Satellite retrievals of NO$_2$ have found use in many scientific applications; a Web of Science search for the terms (OMI OR GOME OR SCIAMACHY) AND NO$_2$ returns 350 papers.

Chief contributions among these applications have been:

- proof of concept of tropospheric observation of tropospheric NO$_2$ from space ([Leue et al., 2001](#) [Martin et al., 2003](#))

- calculation of atmospheric lifetime of NO$_x$ (∼24hr, [Leue et al., 2001](#))

- observation of small scale emissions patterns in a global context ([Richter et al., 2004](#))

- calculation of surface NO$_2$ concentrations ([Lamsal et al., 2008](#))

- tracking diurnal variations in tropospheric NO$_2$ concentrations by taking advantage in the difference in local overpass times of SCIAMACHY and OMI ([Boersma et al., 2008](#) [2009](#))

- observation of weekly variation ([Russell et al., 2010](#))

- model verification (e.g., [Martin et al., 2002](#) [Kim et al., 2009](#) [Huijnen et al., 2010](#))

- top-down emissions inventory calculation to supplement bottom-up inventories ([Martin et al., 2003](#) [Boersma et al., 2008](#) [Kim et al., 2009](#) [Russell et al., 2010](#))

2.5.2 Satellite Emissions Constraints

One area of research that has gotten much coverage over the past decade is estimating and improving emissions inventories. Because monitoring actual emissions tends to be expensive and difficult, most inventories are calculated in a “bottom-up” fashion, meaning that they are based on applying some emissions factor to an easier to measure quantity
such as electrical usage or fuel input. Satellite measurements of tropospheric NO$_2$ provide an obvious additional tool for improving these estimates for NO$_x$ emissions. Such an approach, inferring emissions from observed atmospheric concentrations is usually referred to as a “top-down” process.

One process is the mass-balance approach: if horizontal transport is considered negligible, which can be true if a large enough air parcel is considered, the emission rate in a particular grid cell are a simple function of the observed NO$_x$ in that cell and the atmospheric lifetime of NO$_x$. Using GEOS-Chem and GOME measurements, Martin et al. (2003) found that inventories consistently underestimated NO$_x$ emissions over the continental U.S., but none by more than the estimated uncertainty in the bottom-up inventory. Using a similar approach but with OMI observations, U.S. bottom-up inventories were found to be consistent with top-down except for on-road NO$_x$ emissions, which were found to be 30% too low in the bottom-up inventory, while power-plant emissions, especially over the Ohio River valley were found to be 25% too high (Boersma et al., 2008). In the same study, top-down NO$_x$ emissions over Mexico City suggested that bottom-up inventories were underestimating emissions by 50% (Boersma et al., 2008). A decreasing trend in U.S. emissions during the beginning of the 2000s has also been shown (Kim et al., 2009). By exploiting the high spatial and temporal resolution of OMI, Russell et al. (2010) developed a 5km × 5km daily emissions inventory over California and found that bottom-up inventories underestimated the decrease in weekend emissions by as much as 75%.
Chapter 3

Theoretical Principles

At the abstract level, the retrieval of atmospheric concentrations by satellite remote sensing is a straightforward process. To understand the results of these retrievals properly, however, a certain level of detail is required. This chapter will develop the theoretical principles from the literature which are required to adequately characterise the uncertainties in the measurements provided in the form of satellite data products. This idea will be further explored in extending the retrieval methods to estimate surface concentrations.

There are two separately available OMI tropospheric NO$_2$ data products: the standard product (SP) and the Dutch OMI product (DOMINO). Most of the differences between the products are subtle. It has been shown that there exist different biases and uncertainties in each product (Lamsal et al., 2010; Celarier et al., 2008a). However, the empirical nature of the algorithm presented in this thesis should correct for these biases. Since the product used in this work was the DOMINO product, this chapter will only discuss the details of that data retrieval, while making only minor note of any departures from the SP.
3.1 Calculation of Vertical Columns

The core of the satellite retrieval process is Differential Optical Absorption Spectroscopy (DOAS), which relies on the Beer-Lambert law (Eq. 2.1). Solving the equation for the concentration of NO$_2$, or any optically thin trace gas, for that matter, requires knowledge of the light entering the atmosphere ($I_0$), the amount of light reflected by the Earth’s surface (the albedo), the geometry of the satellite viewing angle and a rough idea of the distribution of NO$_2$ in the atmosphere, since the concentration of NO$_2$ is not constant.

To measure the light exiting the top of the atmosphere, the backscatter, a satellite borne spectrometer is employed. A lens collects sunlight which is backscattered off the Earth’s surface (Fig. 3.1). The light is focused through a diffraction grating and the subsequent spectrally-spread line of light is cast onto an array of sensors. Typically the array is 2-dimensional. The cross-track dimension, that is, the dimension which runs perpendicular to the direction of travel, is the spatial dimension. The along-track dimension is the spectral dimension. This setup creates a row of spectra which are then divided, spatially, in the along-track direction by periodically resetting the sensors – taking limited-time snapshots. As an example, OMI takes 2 second snapshots which corresponds to a row height of roughly 13 km on the ground.

This measurement process produces a slant column density, which differs from a vertical column in that a vertical column assumes the measurement path is perpendicular to Earth’s surface whereas the slant column density is the column density along the path through the atmosphere which the light actually travelled. It is more useful, however, to compare values which do not depend on the viewing geometry of the satellite (which changes every overpass) or the exact position of the sun in the sky (which changes with the precise time of day of the overpass as well as seasonally). Therefore, the slant columns must be converted to vertical columns. This is done with an air mass factor (AMF) which accounts for the 2-way trip through the atmosphere and the viewing geometry. Additionally, for the tropospheric component, the stratospheric contribution to
the column density must be removed. All these factors are encompassed by equation (1) from Boersma et al. (2007):

$$V_{tr} = \frac{S - S_{st}}{M_{tr} (x_{a, tr}, b)}$$

(3.1)

where $S$ represents the total slant column density obtained by the DOAS procedure, $S_{st}$ the stratospheric contribution to the slant column and $M_{tr}$ the AMF, which is a function of the tropospheric a priori shape profile ($x_{a, tr}$) of NO$_2$ and the set of forward model parameters ($b$), which accounts for clouds, surface albedo and viewing geometry (Boersma et al., 2007). The forward model parameters control how the AMF responds to changes in the a priori shape profile. As an example, the forward model parameters may characterise polluted areas as having stronger radiative transfer above the boundary layer due to aerosol reflectance and absorbance near the surface, making the AMF less sensitive to NO$_2$ predicted to be near the ground. Explicit accounting for aerosol can alter the AMF by up to 20% in polluted areas (Martin et al., 2003).
It has been shown that the AMF can be separated into components due to radiative transfer (roughly, the sensitivity to the satellite-borne instrument to the altitude of the trace gas species) and shape profile (that is, the height-distribution of the species) (Palmer et al., 2001). Generally, the radiative transfer component is tabulated and the shape profile is extracted from a CTM; in the case of the DOMINO product the DAK method is used to calculate radiative transfer and the data-assimilated TM-4 and TM-5 models are used to obtain the shape profiles for the retrieved pixels (Boersma et al., 2007).

The basic idea is that as any given photon travels through and interacts with the atmosphere, at any point it can be transmitted, absorbed or scattered. The relative frequency of these events is strongly influenced by the photon’s wavelength. In an ideal space-based DOAS setup, the wavelengths measured would be chosen such that transmission was the most common choice, absorption happened only when the photon encounters the species of interest and scattering happened only when the photon reaches the surface of the earth.

In a more realistic scenario, many other possibilities must be considered: photons will be absorbed by other atmospheric species and the earth; photons which would have reached the sensor are scattered out of the observable light path; photons which would not have reached the sensor are scattered into the light path. These possibilities are treated by the AMF. The initial DOAS fitting provides a measure of how many molecules of the species of interest were encountered over the course of the lightpath. The AMF provides additional information from models and independent measurements as to where those molecules were most likely to have been encountered.

Uncertainties in retrieved column values over polluted areas come largely from this AMF (Boersma et al., 2004). This is one of the reasons that the radiative-transfer / shape-profile separation is so important; this separation allows the error contribution of the shape profile to be removed when comparing two different but similarly retrieved column density measurements (Rodgers and Connor, 2003; Eskes and Boersma, 2003).
Overall uncertainty in tropospheric columns has been reported to be as high as \( \geq 100\% \) over very clean areas (Boersma et al., 2004), however this can be thought of as being below the detection limit of the instrument as the areas in question had tropospheric column values \(< 0.3 \times 10^{15}\text{molec cm}^{-2}\). For more polluted areas, total column uncertainties are reported to be 35%–125% with an average error \(< 50\% \) for areas with tropospheric column densities \( > 1.0 \times 10^{15}\text{molec cm}^{-2}\) (Boersma et al., 2004).

In general, DOMINO tropospheric column densities have been found to agree well (typically \( 0.6 \leq R \leq 0.9 \)) with other satellite products (Boersma et al., 2009), surface-observation-assimilated model columns (Lamsal et al., 2008; Zhou et al., 2009; Huijnen et al., 2010), ground based DOAS measurements (Lamsal et al., 2008), and columns derived from in situ measurements taken from aircraft (Lamsal et al., 2008; Hains et al., 2010).

### 3.2 Estimation of Surface Concentrations

In an effort to make utilization of OMI tropospheric column data more relevant to some fields of research, e.g., epidemiological exposure assessment, Lamsal et al. (2008) calculated surface NO\(_2\) concentrations for the continental U.S. by combining OMI tropospheric NO\(_2\) column measurements and output from the GEOS-Chem CTM.

To generate the surface NO\(_2\) concentrations, the OMI SP was used. One important difference between the SP the DOMINO product is the *a priori* profile generating procedure. In the SP, annual mean columns are taken from GEOS-Chem whereas in the DOMINO product, columns for overpass time are taken from the TM4 model which is assimilated and forecasted every 6 hours. Lamsal et al. (2008) found large seasonal discrepancies with the SP, which uses an annual average profile. However, it has been shown that the TM4 model has a less accurate representation of vertical mixing in the planetary boundary layer which can lead to errors in the DOMINO retrieval (Huijnen
This difference led to the creation of a 3rd product which replaced the time-of-overpass \textit{a priori} columns from TM4 in the DOMINO product with time-of-overpass columns from GEOS-Chem, in order to remove the seasonal error introduced by the annual mean GEOS-Chem while taking advantages of GEOS-Chem’s more representative boundary layer mixing \cite{Lamsal2010}.

After obtaining NO$_2$ columns using one of the above 3 procedures (i.e., the SP, the DOMINO product and the combined DOMINO/GEOS Chem product), these columns were multiplied by the ratio of surface NO$_2$ concentration to column density as reported by GEOS-Chem \cite{Lamsal2008}:

\begin{equation}
S_O = \frac{S_G}{\Omega_G} \times \Omega_O
\end{equation}

where $S_G$ is the local GEOS-Chem predicted surface NO$_2$ concentration, $\Omega_G$ the local GEOS-Chem predicted NO$_2$ tropospheric column density and $\Omega_O$ the OMI retrieved NO$_2$ column density.

The underlying assumption is that the retrieved OMI column is an accurate measurement of the amount of NO$_2$ in the local troposphere while GEOS-Chem has accurately captured the transport and chemistry of emitted NO$_x$ and that any discrepancies between the GEOS-Chem column and the OMI column are the results of incorrectly modeled emissions. This is a fairly reasonable assumption since the chemical mechanisms are fairly well understood and characterised, and transport comes from historical data, while emissions are difficult to measure or model and can change substantially from one day to the next.

Because the grid cells in GEOS-Chem average over a fairly wide area on the Earth’s surface, the GEOS-Chem column will be lower than what is actually observed by OMI over polluted areas while over clean regions adjacent to sources of NO$_x$ OMI will measure
lower columns than the GEOS-Chem average, which is pulled upwards by the nearby polluted area. Therefore, in order to improve upon the spatial resolution provided by GEOS-Chem, a further refinement was made to equation 3.2 (Lamsal et al., 2008):

\[ S_O = \frac{\nu S_G}{\nu S_G - (\nu - 1) \Omega_G^F} \times \Omega_O \]

where \( \nu \) is the ratio of the local OMI column density to the average OMI measured column density for the entire GEOS-Chem grid cell and \( \Omega_G^F \) is the GEOS-Chem free-tropospheric column density, that is the tropospheric column density reported by GEOS-Chem minus the contribution to the column contained within the planetary boundary layer. In uniform GEOS-Chem grid cells, i.e. cells without local ground-level sources of NO\(_x\), \( \nu \) becomes 1 and equation 3.3 collapses back down to 3.2.

Using this procedure, OMI-derived surface NO\(_2\) concentrations were compared with data from in situ monitoring stations equipped with CL monitors the continental United States and Canada. Moderate temporal correlations (between 0.49 and 0.86) were found (Lamsal et al., 2008). Strong seasonal biases were found in the OMI derived data (as high as -27% for rural sites in the summer/autumn) which the authors attribute mainly to the use of annual average GEOS-Chem NO\(_2\) profiles (Lamsal et al., 2008). It should be noted, however, that these annual profiles are used only in the SP; the DOMINO product uses overpass time TM4 profiles.

It is important to note that the comparison was with overpass-time-only CL measurements. OMI measurements are specific to NO\(_2\) while CL monitors are subject to interference from other oxidized nitrogen species. This interference is worst at OMI overpass time and so comparison with only overpass-time measurements would exacerbate the problem.

The goal of this thesis was to develop a process for inferring surface NO\(_2\) concentrations from OMI column densities for use in epidemiological exposure studies and other
types of research requiring high-resolution NO\textsubscript{2} data without requiring output from a computationally expensive CTM. In order to do this, a way of generating the surface to column ratio ($\frac{{\text{S}}_{\text{G}}}{\text{H}_{\text{G}}}$) from observation data was required. For this purpose, the surface concentration data was taken from permanent and temporary CL monitoring stations and the column data from OMI.
Chapter 4

Methodology

Much of the analysis in this thesis revolves around NO$_2$ concentration data collected as part of the 2007 BAQS-met field campaign carried out by a group of researchers representing Environment Canada, the Ontario Ministry of the Environment, the University of Toronto and York University. The first section of this chapter will describe the campaign area and reasons for its selection, the field instrumentation and the procedures for collecting data therefrom, as well as any deviations from that procedure, the data quality assurance procedures, where appropriate. The subsequent section will discuss the details of implementation of the procedures from section 3.2 in particular, the specific in situ monitoring sites used and the specific data product, overpasses and pixels used for the satellite NO$_2$ column data.

4.1 2007 Border Air Quality and Meteorology Study

The BAQS-met campaign was conducted in Southwestern Ontario, around the Windsor-Detroit area, from June 1 to September 10, 2007. The main goal of BAQS-met was to study the effects of transboundary air pollution and the Great Lakes meteorology on local air quality. The area was chosen due to its unique geography (i.e. frequent influence of lake breezes), proximity to the U.S.-Canada border and local industry. Among
a comprehensive suite of measurements, which have been described in other papers in a special issue of the journal Atmospheric Chemistry and Physics (e.g., Levy et al., 2010), the campaign included a network of 18 passive NO\textsubscript{2} sampling sites along with three photolytic NO\textsubscript{2} monitors operated by Environment Canada. The Ontario Ministry of the Environment (MoE) also operated 3 temporary MoO NO\textsubscript{2} monitors for the intensive campaign period (June 20 to July 11) in addition to the 3 permanent monitoring stations run by the MoE in the area. This diverse and relatively dense array of surface NO\textsubscript{2} measurements provided a unique opportunity to develop and evaluate OMI-derived surface NO\textsubscript{2} concentration estimates.

4.1.1 Region characterisation

The BAQS-met campaign was carried out in the area surrounding Windsor, Ontario (Fig. 4.1). In order to accurately characterize the airshed of the entire region, the area encompassed approximately 10,000 km\textsuperscript{2}. A number of important factors affected the choice of location. Briefly, these are geography/meteorology, land use and proximity to an international border. Each of these factors will be discussed in detail below.

Windsor, Ontario, is located at the Southwestern tip of the province of Ontario. It is bordered by the Detroit River on the west side and Lake St. Clair to the North, as well as Lake Erie several km to the South. This type of waterfront geography can have effects on NO\textsubscript{2} concentrations due to lake breezes (Arain et al., 2009). Particularly interesting meteorology arises in the campaign area as it borders two separate Great Lakes, Lake Erie to the South and Lake Huron to the North.

Across the Detroit river lies Detroit, MI. Both cities are known for their auto industry. The Windsor metropolitan area has a population of 323,000 and an area of 1023 km\textsuperscript{2}, while the City of Windsor has a population of 216,500 and occupies an area of 147 km\textsuperscript{2} (Statistics Canada, 2006). Southeast Michigan, including Detroit-Warren-Flint, is the eleventh most populous combined statistical area in the U.S. with a population of
Chapter 4. Methodology

Figure 4.1: Location of BAQS-met study region, highlighted in green.

5,300,000 and an area of 15,000 km$^2$ (U.S. Census Bureau).

4.1.2 High-time resolution measurement by chemiluminescence

The Ontario Ministry of the Environment (MoE) operates a permanent monitoring network which includes 2 stations within Windsor and one in Chatham (Fig. 4.2). Due to their proximity to the campaign area, MoE permanent monitoring sites in Sarnia, at the Southern end of L. Huron, and London, approximately 150 km Northeast of Windsor were also included. As well, during the intensive campaign period (June 20 - July 10, 2007) 3 additional chemiluminescence (CL) monitors were set up at Harrow and Ridgetown, on the North shore of Lake Erie approximately 40 km and 100 km from Windsor, respectively, and on Pelee Island, a 42 km$^2$ island approximately 50 km Southeast of Harrow in L. Erie (Fig. 4.2). The monitors operated by MoE were Thermo TE42C instruments which provide NO, NO$_2$ and NO$_x$. Measurements were averaged to 1 hour.
Figure 4.2: NO$_2$ monitoring sites for the 2007 BAQS-Met campaign. Passive monitoring locations are denoted by black-and-white circles. High-time resolution chemiluminescence monitor locations are marked by yellow bubbles with text labels. Chatham, Windsor West and Windsor Downtown were Ontario Ministry of the Environment (MoE) permanent monitoring stations. Harrow, Pelee and Ridgetown also had monitors operated by MoE from June 20 to July 10. Harrow had a photolytically converted chemiluminescence monitor operated by Environment Canada from June 1 to Sept 10 and Bear Creek had both molybdenum and photolytically converted monitors operated by Environment Canada for the same period. Two additional MoE permanent monitoring station not shown by this map were also used (Sarnia and London).
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To evaluate the potential interference from non-NO$_2$ oxidized nitrogen species (Steinbacher et al., 2007; Ordonez et al., 2006; Lamsal et al., 2008), 3 CL monitors (TE42C and TE42CTL) were deployed by Environment Canada for the duration of the campaign (June 1, 2007 to Sept 11, 2007). These CL monitors were each equipped with a photolytic converter (Droplet Measurement Technologies, blue light converter) and an external molybdenum converter. By selecting ambient air, photolytically converted air, or molybdenum converted air, true NO$_2$ could be reported by subtracting NO from the measured post-conversion NO and applying the conversion efficiency of NO$_2$ to NO. One minute concentrations for NO, NO$_2$ and NO$_y$ (NO$_y$ = NO$_x$ + NO$_z$) were provided by running a 1-minute cycle with the three above channels and 2 internal zeros.

It is important to highlight that the method for measuring NO$_y$ is exactly the same as the method commonly used for measuring NO$_2$ with the exception that in traditional atmospheric NO$_2$ monitoring, the converter is internal to the monitor (Fig. 4.3). The NO$_z$ interference in MoO NO$_2$ measurements is therefore a product of the conversion efficiency of the constituent species of NO$_z$ as well as their respective line loss parameters; (HNO$_3$ is particularly noted for line losses (Steinbacher et al., 2007)). In the NO-NO$_2$-NO$_y$ setup used for measuring the interference, the MoO converter is positioned before the sampling line and NO$_y$ measurement is dependent only on the conversion efficiencies of the species.

4.1.3 Measurement by passive monitor

A network of passive NO$_2$ monitors was deployed at 18 locations (Figure 4.2). These sites were part of the Mesonet study (Levy et al., 2010) and were chosen to closely match the Environment Canada Global Environmental Multiscale model (Makar et al., 2010) meteorological forecast 15 km model grid in the region (every grid point where possible, alternate grid points in other locations). In some cases the need to access the monitors on a regular basis caused small deviations from the model grid. Weatherproof housings were anchored to the Mesonet towers at the sampling sites. These housings were designed
Figure 4.3: Chemiluminescence NO\textsubscript{x} monitor schematics. A) Traditional monitoring setup. Ambient air is drawn through a sampling line. Inside the monitor, a selector chooses either unprocessed air or air which has been run through a heated molybdenum converter which reduces NO\textsubscript{2} as well as the remaining fraction of HNO\textsubscript{3}, PAN and other oxidized nitrogen species to NO. The chemiluminescence cell measures light produced when NO is titrated with O\textsubscript{3}. To obtain NO\textsubscript{2} measurements, measurement of NO in unconverted air is subtracted from NO in converted air. B) True NO\textsubscript{2} setup used at rural sites during BAQS-met campaign. To measure NO\textsubscript{2} (+ NO), photolytic conversion, which is specific to NO\textsubscript{2}, was used. Heated molybdenum conversion was applied immediately at the sampling inlet to mitigate line losses of HNO\textsubscript{3}, etc., to obtain NO\textsubscript{2} measurements.
to allow ambient air contact with the monitors while providing protection from rain.

Further, since the filters needed to be collected for analysis and replaced with fresh
samplers manually, site locations were selected with the criterion that all sites could be
reached in a single day. The intention was to provide consistent sampling period start
and end dates across all sampling periods. However, this was not always possible and
some sites saw collection and replacement up to two days before others, although most
sites were collected and replaced on the same day in most cases. In total, there were
115 passive samples collected: the first 6 periods had 17 simultaneous sampling sites and
the final period had 13 sampling sites. On average, 70% of the filters were collected on
a single day, thus maximizing temporal overlap for the two-week period. For sampling
periods 1 and 3 through 7, all filters were collected within a 2 day period; for sampling
period 2, all filters were collected within a 2 day period, except one filter which was
collected 2 days later than the first.

Paired filters were deployed at each sampling location to ensure data quality and
consistency of results. Collocated filters were checked for consistency and if values differed
by more than 10% the two measured concentrations were subjected to additional quality
assurance checks to improve the IC results and, if acceptable (within 20%), averaged. In
the case of a known source of error, one filter was rejected and the site value was reported
from only the good filter. Multiple unexposed filters, carried to and from the sampling
locations during the campaign, were used for background/blank correction.

4.2 Ozone Monitoring Instrument retrieved NO$_2$ columns

All OMI data used for this thesis was DOMINO product level 3 v1.0.2/1.0.3 data which
can be retrieved at [http://temis.nl/airpollution/no2.html](http://temis.nl/airpollution/no2.html) [Boersma et al. 2007].
All pixels with a cloud radiance fraction $> 0.3$ were rejected. Because of the viewing
geometry of the satellite, pixels near the swath edge cover a much wider area on the
Earth’s surface than pixels nearer nadir. Pixels with a width over 50 km on the ground were rejected, i.e., all pixels within 6 pixels from either end of the swath were not used. Finally, all pixels which have been indicated as anomalies due to possible obstruction of the sensor were removed (see http://temis.nl/docs/omi_warning.html).

Each overpass path is slightly different. This makes it possible to extract additional spatial information beyond the $13 \times 24\text{km}^2$ resolution of the raw data by combining multiple overpasses (Leue et al., 2001). Because of warping due to the wide-angle lens used in OMI, pixels nearer the edge of the swath are wider than those close to nadir. It is assumed that smaller pixels are more representative of the local column. Therefore, when combining pixels, an inverse-pixel-area weighted average is used. In detail:

- the area is split into a regular grid

- for each overpass:
  
  - each grid cell that is covered by a pixel is given the value $(\hat{x}_{i,j,t}$ in equation 4.1) of the pixel $(x_k)$ and a weight $(w_{i,j,t})$ of the area of a grid cell divided by the area of the OMI pixel
  
  - each grid cell that is covered by more than one pixel is given the average of each contributing pixel’s value, weighted by the portion of the grid cell covered by a pixel divided by that pixels total area and a weight that is of the sum of those weights
  
  - in both cases, larger pixels will have smaller weights and therefore contribute less to the final average, which reflects their increased uncertainty

- each grid cell then represents a time series of OMI values and weights

- the average for a grid cell over a number of overpasses is given by the sum of the weights times the values divided by the sum of the weights
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Mathematically, the average at grid cell \(i, j\), \(\bar{x}_{i,j}\), is calculated by

\[
\bar{x}_{i,j} = \frac{\sum_t w_{i,j,t} \cdot \hat{x}_{i,j,t}}{\sum_t w_{i,j,t}}
\]

where

\[
w_{i,j,t} = \sum_k \frac{\text{Area (cell}_{i,j} \cap \text{pixel}_k)}{\text{Area (pixel}_k)} \quad \text{and} \quad (4.2)
\]

\[
\hat{x}_{i,j,t} = \frac{\sum_k \text{Area (cell}_{i,j} \cap \text{pixel}_k) \cdot x_k}{\sum_k \text{Area (cell}_{i,j} \cap \text{pixel}_k)} \quad (4.3)
\]

By using this algorithm, a regular grid of values can be produced at higher spatial resolution than the original raw OMI data. It should be noted, however, that this is at the expense of temporal resolution; a single overpass cannot be spatially improved using OMI data alone.

4.2.1 Procedure for inferring surface concentration using OMI columns

To infer the surface concentration data for the BAQS-met campaign period, 5 permanent MoE monitoring sites and 2 temporary EC monitoring sites (Bear Creek and Harrow) in the region were used for in situ concentration data (see section 4.1.2). For each overpass (of which up to two per day are available depending on the overpass path) a surface-to-column ratio was calculated for each monitoring site. This ratio was calculated by taking the 24-hour average from midnight EST to midnight EST and dividing by the OMI measured column density for the specific pixel from the overpass which contained the monitoring location. Missing in situ data was most often caused by maintenance while missing OMI data was caused by pixel exclusion due to the reasons mentioned above. To mitigate the effect of the inherent uncertainty in a single OMI column density measurement on the inferred data, the average surface-to-column ratio was then calculated by averaging all the sites for which both in situ and OMI data were available for a given overpass. Only overpasses with at least 3 valid surface-to-column ratios were used.
Additionally, to account for the free tropospheric contribution to OMI columns, it was assumed that in a 2.5° x 3° area around Windsor this free tropospheric concentration remained constant. The value separating the lowest 10% of column densities (i.e., the cleanest 10% of pixels) from the rest of the columns within the area around Windsor for that particular overpass was taken to be the free-tropospheric component. The bottom decile value was used rather than simply the lowest measured column because errors in the OMI column are expected to be highest in these clean areas.

With analogy to equations 3.2 and 3.3, the inference process for generating the OMI-inferred surface concentration ($S_O$) from OMI column densities ($\Omega_O$) follows along:

$$S_O = \left( \frac{1}{n} \sum_{i} S_i \frac{\Omega_i}{\Omega_i - \Omega_F} \right) \cdot (\Omega_O - \Omega_F) \quad (4.4)$$

where $n$ is the number of MOE stations reporting, $S_i$ is the 24-hr average concentration measured at permanent monitoring stations $i$, $\Omega_i$ the OMI column density for the pixel which overlaps monitoring station $i$ and $\Omega_F$ the bottom decile column density for the overpass, i.e., the free-tropospheric column density.
Chapter 5

Results and Discussion

In order to validate the methods described in chapter 3 and section 4.2, data from the BAQS-met campaign (described in section 4.1) were used. It is, therefore, important to properly characterize the airshed. Equally important is a comparison of the different measurements techniques utilized during the campaign. The first section of this chapter is dedicated to the discussion of those topics. The succeeding section describes the satellite data used and characterizes the airshed from a total-column perspective. Section 5.1.2 discusses the validation of the inferred data using the in situ data from the campaign. The remainder of the chapter discusses the application of the inferred data to other time periods and areas.
5.1 BAQS-met campaign results and validation of experimental method

5.1.1 Characterising surface NO$_2$

High-time-resolution measurements

NO$_2$ concentrations varied significantly both in time and between sampling locations. In order to demonstrate this, Fig. 5.1 shows a typical week of measurements at 1 urban and 2 rural sites from the campaign period. The differences between locations can be clearly seen with urban concentrations often an order of magnitude higher than rural. Diurnal variation can also be observed with early morning concentrations generally showing higher values than daytime and nighttime values.

Diurnal trends were observed at urban, suburban and rural locations. The trends were similar at all 3 types of location and consistent with previously reported trends, with a morning peak around 8AM local standard time and a low period between 1PM and 6PM local time, however absolute values were different between different environments (Fig. 5.1).

Figure 5.1: NO$_2$ measured at 1 urban (Windsor) and 2 rural (Harrow, Bear Creek) locations during 1 week of the BAQS-met 2007 campaign. This week was selected as generally representative of patterns observed over the whole campaign. NO$_2$ concentrations can be seen to exhibit significant diurnal and day-to-day variation.
Chapter 5. Results and Discussion

Figure 5.2: Diurnal trend in NO$_2$ concentrations at urban (Windsor), suburban (Chatham) and rural (Bear Creek) locations. Data included begins June 1, 2007 and ends September 10, 2007. Dotted lines indicate 95% confidence intervals.

Absolute values observed in Windsor (urban) matched values reported for similarly sized cities while concentrations in Chatham (suburban) and Bear Creek (rural) were markedly lower. The ratios between 8AM peak values and midnight and midday low values were similar between locations and were consistent with values from the literature (Fig. 5.3).

The pattern of the diurnal trend is likely the result of a number of factors. Firstly, as temperatures rise and photon flux increase at sunrise, reservoir species such as HONO, HNO$_3$, PAN and N$_2$O$_5$ whose concentrations have been building overnight are rapidly converted to NO$_x$. Additionally, local vehicular sources of NO$_x$ rise rapidly as the morning rush hour gets under way. The decline after this period is mostly a result of daytime loss mechanism due to the daytime increase in the oxidation capacity of the boundary layer, as well as the increasing boundary layer height, which lowers concentrations by increasing mixing and stretching the same amount of NO$_x$ through a much taller column of air.

The concentrations of NO$_2$ showed moderate to weak correlations between the sites over the duration of the campaign for both hourly and daily average measurements (Table
In most situations, correlations based on daily measurements were similar to those based on hourly measurements.

In general, correlations decreased as distance between sites increases. An exception to this was Ridgetown, which showed a relatively high correlation with the urban sites. This was surprising because Ridgetown is over 100 km from the urban and industrial centres of Windsor. However, the Ridgetown measurement site was 5 km from highway 401, a major provincial highway in the region which terminates in Windsor, at a large roadway which leads directly to the Ambassador Bridge border crossing. This relatively strong correlation despite the spatial separation implied that 401 traffic was an important source at both sites, possibly due to commercial vehicle traffic.

Values frequently below the instruments’ limits of detection were observed at the rural sites, especially Pelee Island, and a maximum 1-hour measurement of 66 ppb was observed at both MoE monitoring stations in Windsor (at 9AM EDT on July 31, 2007).

**Passive monitor results**

A summary of the results of the passive monitoring campaign is provided in this subsection. For full details, all data is provided in Appendix B.

Campaign average NO$_2$ measurements recorded at the passive monitoring sites ranged
Table 5.1: Minimum, median and maximum observed 1-day and 1-week average NO$_2$ concentrations measured by chemiluminescence monitor during the BAQS-met campaign. All monitors not marked with an * were heated molybdenum converted chemiluminescence monitors while those marked with an * were photolytically converted chemiluminescence monitors.

<table>
<thead>
<tr>
<th>Site</th>
<th>Daily</th>
<th>Weekly</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min (ppb)</td>
<td>Median (ppb)</td>
</tr>
<tr>
<td>Pelee</td>
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<td>2.8</td>
</tr>
<tr>
<td>Harrow (MoE)</td>
<td>3.1</td>
<td>5.3</td>
</tr>
<tr>
<td>Ridgetown</td>
<td>2.5</td>
<td>5.8</td>
</tr>
<tr>
<td>Windsor West</td>
<td>5.5</td>
<td>13.2</td>
</tr>
<tr>
<td>Windsor Downtown</td>
<td>4.4</td>
<td>13.1</td>
</tr>
<tr>
<td>Chatham</td>
<td>2.2</td>
<td>7.0</td>
</tr>
<tr>
<td>Harrow (EC)*</td>
<td>2.6</td>
<td>4.5</td>
</tr>
<tr>
<td>Bear Creek*</td>
<td>1.1</td>
<td>2.9</td>
</tr>
</tbody>
</table>

from a minimum site average of 3.3 ppb (rural) to a maximum of 18.8 ppb (urban). The passive monitors also revealed that over the long-term the magnitude of the spatial variability was greater than the magnitude of the differences between time periods at a given location. This is exemplified in Figure 5.4 comparing the concentrations measured at each location for sampling period 6 (August 7 to August 21) to the campaign average concentration at each sampling site. In fact, the minimum correlation coefficient between a single sampling period and the campaign average was observed during period 6 (R= 0.97); all other sampling periods correlated with campaign averages with R> 0.98, with a slope near 1. The maximum ratio between minimum and maximum two-week average NO$_2$ concentrations at any given site was 1.8, while the ratio between the highest site median value and the lowest site median value was 6.4. This result is consistent with the findings presented in section 5.1.1 that long term spatial patterns remain relatively stable compared with the differences in concentration across the region. This also highlights the potential for midday satellite observations averaged over multiple days to capture the spatial pattern.
Table 5.2: Correlation (Pearson R) between NO$_2$ measurement sites during the BAQS-met campaign (June 1 to Sept 10, 2007). The first row for each location represents the correlation between hourly measurements while the second represents correlation between daily average measurements. All monitors not marked with a * were heated molybdenum converted chemiluminescence monitors while those marked with a * were photolytically converted chemiluminescence monitors.

<table>
<thead>
<tr>
<th>Site</th>
<th>Harrow (MoE)</th>
<th>Ridgetown</th>
<th>Windsor West</th>
<th>Windsor Downtown</th>
<th>Chatham</th>
<th>Harrow (EC)*</th>
<th>Bear Creek*</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.51</td>
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<td>0.41</td>
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<tr>
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<tr>
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<td>0.63</td>
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<td>0.41</td>
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<tr>
<td>Windsor Downtown</td>
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<td>0.63</td>
<td>0.42</td>
<td>0.46</td>
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<td></td>
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<td></td>
<td>0.50</td>
<td>0.32</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>Chatham</td>
<td>0.30</td>
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<td>0.47</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>0.34</td>
</tr>
</tbody>
</table>
A passive monitor was located at Harrow for the first 3 two-week sampling periods (June 1, 2007 to July 10, 2007) as well a photolytically converted CL monitor for the entire campaign and a MoO-CL monitor for the intensive campaign (June 20 to July 10). Bear Creek (BEA) had a passive monitor for the remaining 4 periods (July 11, 2007 to Sept 4, 2007) along with both photolytically and MoO converted CL monitors. As well, the permanent MoE site (molybdenum converted NO₂), Windsor West, had a passive monitor. The passive monitors were in reasonably good agreement with the collocated CL monitors (Figure 5.5a). The average absolute difference between the passive and the MoO CL and the photolytic CL were 11% and 15%, respectively. The overall slope of the relationship was 1.04.

Passive monitors provide time integrated averages while OMI only measures once daily, between 1200 and 1400 local time at this latitude. It was therefore important to understand how the average NO₂ values just around OMI overpass times (1200 to 1400 local time each day) relate to concentrations averaged over the two-week timescale of the
Figure 5.5: Comparison between passive measurements and (A) daily and (B) midday averages from collocated chemiluminescence monitors. Only 3 of the monitoring sites contained both passive and CL monitors concurrently. X-error bars represent 95% confidence intervals on averages from hourly data. Y-error bars represent 95% confidence intervals on averages from approximately 2-week sampling period data.

passive monitor measurements. Although the slope was, as expected, substantially higher since the midday NO$_2$ values were lower than daily averages, the correlation remained strong (Figure 5.5b). Similar results were obtained when daily average CL data were compared to midday averages from the same monitors. This indicated that, with a suitable correction factor, OMI overpass averages could be adjusted so as to be representative of long-term integrated averages.

NO$_2$ interference

Much of the NO$_2$ monitoring data available are taken by MoO converted CL monitors. As indicated above, these converters are not specific to NO$_2$, suffering from interference from other oxidized nitrogen species (NO$_x$). Previous studies have reported MoO-converted CL NO$_2$ measurements to be as much as 2.3 times higher than simultaneous photolytically-converted CL measurements during summer months in a rural setting [Steinbacher et al., 2007]. Quantifying this interference is important for the interpretation of satellite remote sensing data, which are specific to NO$_2$ and provide averages over a large area on the
Figure 5.6: A) Comparison of collocated high-time resolution NO$_2$ measurements made by heated molybdenum converted (vertical axis) and photolytically converted (horizontal axis) chemiluminescence monitor. The solid line is the best-fit linear regression. B) Comparison of difference between molybdenum converted and photocatalytic NO$_2$ measurements with NO$_z$ measurements.

Earth’s surface. Often satellite measurements are compared to rural monitors to ensure that the in situ data are representative of a wide local area and not affected by local sources (Lamsal et al., 2010). It is these rural monitors where the relative importance of the interference is expected to be the largest (Boersma et al., 2009).

In this study photolytic and heated molybdenum converted chemiluminescence monitors were collocated to evaluate the effects of NO$_z$ interference on the molybdenum converted measurements. All data were averaged to 1 hour resolution, which corresponds with the resolution of the publicly available data for the permanent CL monitoring sites. At the Bear Creek (BC) site, the molybdenum-converted CL monitor hourly concentration was found to be 45% (±3%) higher, on average, than the photolytically-converted CL. The MoO measurements correlated strongly with the photolytic (R = 0.96, n = 1472), with a slope of 1.05 and an offset 0.65 ppb. This offset was responsible for the apparently large relative difference as the average NO$_2$ concentration for the site was only 2.9 ppb. When the difference between the two monitors was compared with NO$_z$
measurements taken by the photolytic monitor (Figure 5.6), there was only a weak correlation ($R = 0.26$, $n = 1464$) with a slope of 0.11 and an offset similar to that found when comparing the two sets of NO$_2$ measurements. Since the only difference between NO$_x$ as measured by the photolytic monitor and NO$_2$ measured by the molybdenum converted monitor was the point of conversion, the most likely explanation for the low slope and high offset is inlet deposition of NO$_x$ species. That is, about 90% of the NO$_x$ is deposited on the way to the MoO CL monitor, but some of this is later released, resulting in NO$_x$ interference even in the absence of detectable ambient NO$_x$. In the 3 locations where NO$_x$ measurements were available, mean NO$_x$ between noon and 1400 EDT were found to be low (2.62 ppb and 3.22 ppb for rural locations and 2.62 ppb for urban), indicating that NO$_x$ concentrations (and therefore NO$_x$ interference) remain low across the entire campaign region.

The interference by NO$_x$ did show a diurnal trend (Figure 5.7). The median ratio of the MoO-CL to photolytic-CL monitor data was around to 1.15 for hours between midnight and 8AM, with a rise towards the afternoon and a maximum of 1.97 for 1PM local standard time, then back down to 1.0 from 6PM to midnight. Because of the rural location chosen for this comparison, the high midday ratio was partly due to the low NO$_2$ concentrations observed around midday – while the ratio of the MoO-CL to the photolytic-CL measurements was almost 2, the median difference between the monitors was only 0.9 ppb for the same time (1PM local). This is largely due to the relatively low NO$_2$ concentrations at the monitoring location. When only hours when the average photolytic NO$_2$ concentration was greater than or equal to 1 ppb were considered, this 1PM median ratio is reduced to 1.53. Thus, the interference by NO$_x$ could cause significant uncertainties (up to 97%) if the OMI data were compared only to midday MoO CL in situ concentration data for rural areas. However, the goal of this thesis was to compare long-term average NO$_2$ concentrations with OMI measurements over a range of environments including rural areas with low concentrations and urban and industrial areas with
Figure 5.7: Diurnal trend in ratio of \((\text{NO}_2)_m\) to NO\textsubscript{2} measured from June 1 to Sept 10, 2007 at Bear Creek, Ontario, a rural site located approximately 60 km northeast of downtown Detroit, MI. \((\text{NO}_2)_m\) denotes NO\textsubscript{2} measured by heated molybdenum catalyst chemiluminescence monitor, which can suffer from interference due to reducing non-NO\textsubscript{2} oxidized nitrogen species. True NO\textsubscript{2} was measured by a collocated photolytic converted chemiluminescence monitor, which reduces NO\textsubscript{2} selectively. Solid line represents median ratio for that hour. Dotted lines represent 5\textsuperscript{th} and 95\textsuperscript{th} percentiles. Hours are Eastern Standard Time. OMI overpasses occur between 1200 and 1400 EST, which display some of the highest average ratios.
higher NO$_2$ concentrations. Since all of the permanent monitoring locations (with MoO converted CL monitors) were in urban settings with higher average NO$_2$ levels, this 0.9 ppb median difference at midday was deemed to be acceptable. Thus it was concluded that NO$_2$ data from the MoO-CL and photolytic-CL monitors could be combined and used for comparison with the OMI or passive monitor data.

5.1.2 Inference of surface NO$_2$

Comparison with in situ passive measurements

Twenty-four hour surface NO$_2$ concentrations were estimated from OMI column data using the CL monitor data in conjunction with equation 4.4. The accuracy of the resulting ground-level spatial maps derived from this approach was evaluated by comparison with the passive monitoring data from the 17 sites. All regridding was performed on a 0.1° × 0.1° grid, which was chosen because of its common use in the literature and after analysing which regrid spacing provided the best correlation with the in situ data from the campaign (See Appendix C).

Without using equation 4.4, inverse-area-weighted averages of OMI tropospheric NO$_2$ vertical column measurements showed moderate correlation (R= 0.52, N= 115) with passive monitor concentrations. This was considered the baseline correlation, against which the inference method could be evaluated. Further analysis of OMI column data with in situ passive monitors was done with passive monitors from Beijing during the summer of 2008 (see Appendix F).

Qualitatively, OMI-inferred concentrations showed a similar geographical pattern to the passive monitoring network (Fig. 5.8). The highest concentrations were observed in the Detroit and Windsor urban areas with moderate values observed along the U.S.-Canada border between L. St. Clair and L. Huron. The geographical pattern observed in the OMI-inferred NO$_2$ concentrations also follows the distribution of emissions sources
Figure 5.8: Map of the campaign area with passive monitoring site campaign averages and emissions sources. False colour indicates OMI-inferred NO$_2$. The passive sites are marked by coloured circles with the colour of the circle representing the campaign average NO$_2$ concentration (same scale as false colour map. US EPA emissions sources with 2005 emissions greater than 100tons NO$_x$ / yr are marked on the US side, while Environment Canada NPRI emissions greater than 100 tonnes NO$_2$ / year are marked.
Figure 5.9: Passive measurements taken during the BAQS-met campaign over 7 sampling periods at 17 simultaneous locations versus OMI inferred NO$_2$ concentrations at those same locations for the same periods.

with many of the NO$_2$ point sources, as reported by the Environment Canada National Pollutant Release Inventory and the United States Environmental Protection Agency. Figure 5.8 shows that many sources are clustered around the Detroit-Windsor urban area and along the border between L. St. Clair and L. Huron.

The procedure for calculating surface NO$_2$ from OMI columns was performed in two ways: once using the campaign-only NO$_2$ data in addition to the permanent MoE monitoring sites (7 sites total), and once using only the permanent MoE monitoring sites (5 sites). Correlation between OMI measurements and passive measurements improved from 0.52 using raw OMI NO$_2$ columns to 0.69, with a slope of 1.18, using the OMI inferred surface concentrations (Fig. 5.9). Interestingly, when only the MoE permanent monitoring stations were used, a correlation of 0.66 was obtained, but the slope increased from 1.18 to 1.32. The higher slope obtained when using only the five permanent MoE sites is attributed to their locations near NO$_x$ sources in urban sites. These in-situ NO$_2$ measurement are expected to be less representative of the overall pixel area whose average
column is measured by OMI.

### 5.1.3 Uncertainties in inference process

In calculating the surface-to-column ratios, there are several important sources of uncertainty to consider. Firstly, the error embodied by the spatial extent of the OMI pixel, that is, how representative the point measurement taken by the in situ monitor is of the spatial average measurement taken by OMI, or vice versa. Secondly, the error in the OMI retrieval which comes from the uncertainties in the DOAS fitting, the AMF, cloud interference and albedo (see Chapter 3). Additionally there is the error in the assumption that the NO$_2$ concentration at OMI overpass time bears the same relationship to the 24-hour average at every location. And finally, the measurement error in the CL monitor data which is largely a function of NO$_x$ interference for most monitors of interest. These sources of uncertainty must be separated into systematic biases and random errors so that they may be appropriately characterised.

**Spatial representativeness**

The systematic biases can be detected by comparing the long-term averages of the surface-to-column ratios at the different locations across the region. These were found to vary somewhat across the 7 CL monitor sites with the lowest average ratio being $0.36 \text{ ppb}/1 \times 10^{15}\text{molec}\cdot\text{cm}^{-2}$ (i.e., $8.6 \times 10^{-6}\text{cm}^{-1}$) at the Environment Canada Bear Creek site and the maximum average ratio being $1.66 \text{ ppb}/1 \times 10^{15}\text{molec}\cdot\text{cm}^{-2}$ ($4.0 \times 10^{-5}\text{cm}^{-1}$) at the MoE Chatham site. It is worth noting that the inverse of these surface-to-column ratios represents a characteristic height ($H$) that varied from 250 to 1160m. This metric provides a measure of the vertical extent of the NO$_2$, assuming that the ground based measurement was representative of the OMI pixel.

In the case of the MoE Chatham site, the most likely local emission source is on-road vehicles. The urban area of Chatham itself is small ($\sim 5\text{km} \text{ in diameter or } 20\text{km}^2$) and
surrounded by rural areas. Thus, the surface NO$_2$ concentration within Chatham tends to be higher than that in the surrounding rural region. As a result, measurement at this MoE site is less representative of the area over which the OMI measurements are averaged, which is a minimum of 300km$^2$. Since most of the area included in the OMI pixel footprint is the surrounding rural area, as opposed to the urban area of Chatham, the high in situ concentration in Chatham and the low overall column density would result in a high surface-to-column ratio, as observed.

In the region upwind of the Bear Creek site there are a number of stack emissions sources (Figure 5.8). Thus, NO$_2$ in this rural region has a higher potential to be above the boundary layer, compared to the vehicle emissions in Chatham. The low surface-to-column ratio determined for this site reflects this situation. The hypothesis of lofted NO$_2$ in this rural area is also borne out by the inferred NO$_2$ at the location of the passive monitor 18 km to the north of the Bear Creek monitoring site. At this location, OMI inferred concentrations were 5.4 ppb higher, on average, than the concentrations measured by this passive monitor.

These two extreme situations highlight some of the limitations of this approach. It is also easy to see how these insights might be applied to more temporally transient effects such as a localised, lofted plume. If such an airmass was high enough not to affect surface measurements and large enough to enhance the NO$_2$ columns observed by OMI on a particular overpass, the surface-to-column ratio would be biased high over the entire region of interest, due to the use of an average ratio for the region. The use of overpasses from multiple days mitigates such biases, but correcting for them completely would be difficult.

Using a high-resolution CTM to provide an estimate of the free-tropospheric column and applying equation 4 of Lamsal et al. (2008) could potentially lead to improvements in the surface NO$_2$ estimates, especially in rural areas, provided the region was well characterised.
Figure 5.10: Comparison of 24-hr average to midday average NO2 concentrations at 5 MoE permanent monitoring stations (equipped with MoO CL monitors) and 1 EC monitoring station (equipped with a photolytic CL monitor) for June 1, 2007 to Sept 10, 2007. Error bars represent 95% confidence intervals. Bear Creek site had a very large 95% CI because of missing data and was not included.

Another possible approach would be to empirically determine a spatially varying surface-to-column ratio, by determining site-specific correction factors. However, for this approach to work, a higher density in situ monitoring network would be required to capture the variability and to account for the uncertainty in each individual surface-to-column measurement.

The simplest step towards improving the inference of ground-based NO$_2$ from OMI data would be to increase the proportion of NO$_2$ monitoring locations at rural sites and these results highlight the importance in characterising a region for remote sensing data interpretation using these spatially-representative sites.

**Overpass-to-24-hour ratios**

Implicit in the assumption that the surface-to-column ratio remains constant over all available in situ monitoring locations is the assumption that the 24-hour-to-midday ratio also remains constant over all available in situ monitoring sites. A comparison of the long term average of this ratio at each of the monitoring sites shows that this assumption could
Chapter 5. Results and Discussion

Figure 5.11: Comparison of daily-average in-situ-measured NO$_2$ on overpass (clear) vs. non-overpass (cloudy) days at permanent MoE locations for year 2007. Error bars indicate 95% confidence intervals. Approximately 1/3 of the year had cloud-free OMI measurements at at least 3 sites (n = 122) and the remaining 2/3 had clouded OMI measurements at 2 or more sites (n = 243).

lead to as much as 20% uncertainty in the surface to column ratio at a given location (Fig. 5.10).

Retrieval uncertainty

Because of the number of steps required to turn observed top-of-atmosphere solar-backscatter radiation into tropospheric column densities, the final, individual OMI reported tropospheric column densities carry with them a certain uncertainty. The BAQS-met area and the area surrounding Toronto can be considered to be polluted enough that average errors on individual retrievals can be considered to be less than 50%. By combining multiple overpasses, these uncertainties are decreased in the average – if all 14 overpasses are available for a 2-week period, the overall uncertainty in the average tropospheric column density becomes 13%.

Loss of data due to occlusion by clouds

One important consideration in satellite remote sensing is occlusion by clouds. In particular, a systematic bias would be introduced if surface NO$_2$ concentrations or distributions
were significantly different on days with heavy cloud cover than on clear days when OMI measurements were available over the majority of the region. In a comparison of daily average NO$_2$ concentrations measured at the 5 regional MoE permanent monitoring stations, no significant differences were found between days with OMI overpass data (clear days) versus days without (cloudy days) (Fig. 5.11, 5.12). This implies that cloud cover and surface occlusion do not significantly affect the distribution of NO$_2$ concentrations observed by OMI.

5.1.4 Comparison with surface measurements over a longer time period

In order to verify the validity of the surface NO$_2$ procedure developed from the BAQS-Met period for use over longer time spans, two-week average OMI-derived surface-level NO$_2$ concentrations were calculated using only 4 of the 5 available permanent MoE monitoring sites, retaining the last site for evaluation. For this purpose, two week averages were calculated for both in situ CL measured NO$_2$ concentration at the hold-back site and OMI-inferred NO$_2$ concentration for the nearest 0.1° grid cell. This procedure was done...
for every 2-week period from January 2005 to December 2009, randomly changing which site was held back each time. Surface inferred OMI concentrations showed a stronger correlation ($R = 0.68$, Fig. 5.13) with in-situ CL-measured 2-week averages than OMI column values ($R = 0.61$, Fig. A.4). This provides confidence that the inference method is applicable to other periods (i.e., not just the summer 2007 BAQS-met campaign period), continuing to add skill to the estimates of surface NO$_2$. This improvement (i.e. increase in correlation) is largely due to a few specific periods which appear to benefit the most from the inference method. These periods all occurred between the months of November and March, and were observed across all 5 years. These months tend to have more pixels excluded due to clouds and snow. Column averages calculated from fewer overpasses would suffer more from day-to-day variations in the surface-to-column ratio, whereas our method removes this influence from each overpass. Furthermore, OMI NO$_2$ retrievals are expected to be biased over snow (O’Byrne et al., 2010); our approach empirically corrects for that bias.
5.1.5 Comparison with more distant surface measurements

In order to examine the validity of the OMI inferred concentrations over distance, OMI columns were inferred for a wide area using only the 5 Windsor area MoE monitoring stations to calculate the surface-to-column ratio. The same criteria as above were used to determine when to not use an overpass (to retain an overpass, at least 3 of the 5 available surface stations required both in-situ and OMI measurements).

These inferred values (inferred using only the Windsor-area monitoring sites) were then compared with Toronto area MoE stations. 1-month average inferred concentrations were compared with 1-month average in-situ CL-measured concentrations from 5 Toronto area MoE monitoring stations, making the total possible number of comparisons 300. However, particularly in winter months, a number of inferred concentrations were deemed to be invalid due to insufficient data, i.e., too few OMI overpasses were kept during the inference process because of clouds over over the monitoring station in one or the other region.

This point should be emphasised in this situation – when using inferred data in the vicinity of the stations used to calculate the inferred values, overpasses are likely to include cloud-free data over much of the region. However, when using inferred data far away from the stations used to infer surface concentrations, clouds may obscure the area of interest on days when the area used for the surface-to-column ratio was cloud free. In addition to this, valid cloud-free data for the area of interest may be rejected as part of an overpass which was thrown out due to lack of coincident in situ and cloud-free satellite measurements. This lack of cloud-free measurements resulted in many winter months having inferred concentration averages made up from only 1 or 2 measurements. The criterion for including a month in the comparison was based on the inverse-pixel-area weighting.

Comparing 1-month averages over 5 years (after removing values with fewer than approximately 3 overpasses included in their calculations), a moderate correlation was
found ($R = 0.41$, $N = 173$) and using a least normal squares regression, a large slope and large negative offset were found (Fig. 5.14). If the requirement for inclusion was increased to approximately 5 overpasses, the offset was nearly halved, and the slope decreased from 1.61 to 1.38. This value can be compared to the slope of 1.15 (Fig. 5.13) for inference within the region.

There are a number of factors which would bear on the accuracy of the inferred concentrations when using a surface-to-column ratio calculated using distant measurements. The most obvious is the possible geographical differences in the surface to column ratio caused by different meteorology or local chemistry. There is also the somewhat more subtle difference in cloud cover: since an entire overpass must be rejected if there are fewer than three surface stations with which to compute the surface-to-column ratio, overpasses which contain perfectly valid data for the Toronto area are not included while, conversely, overpasses which contain no data over Toronto (if it is cloudy in Toronto and clear in Windsor) are kept. Of the 563 overpasses used in the calculation of the monthly Toronto
Figure 5.15: Two-week average OMI column density (left) and inferred surface NO\textsubscript{2} (right) vs. in situ measurements for 2005-2009 in Toronto. The same leave-one-out method was used where surface values were inferred using 6 of the 7 available Toronto area monitoring stations and the remaining station was used for comparison.

concentrations, only 453 overpasses had data for Toronto.

This implies that, over the 5 year period, approximately 20\% of clear days in Windsor had cloud cover over Toronto. Since there is no reason to believe that this relationship would not be symmetrical, approximately 20\% of Toronto data is therefore missing. Especially in winter months when overpasses are sparse, this can be an important loss. This loss of data can explain the lower correspondence between the inferred values and in situ concentration data. It can be concluded from this that it is therefore important to calculate individual ratios for each area of interest, possibly interpolating over space to provide the best local estimates possible.

When Toronto values were used to infer Toronto values, the same leave-one-out verification process showed an improvement from R=0.4 for OMI column densities vs. in situ monitors to R=0.49 for inferred values, which is also better than the R=0.41 observed for Toronto values inferred using Windsor surface monitoring data (Fig. 5.15).

Another possible source of bias is the ratio of midday concentrations to 24-hour aver-
Figure 5.16: Midday vs 24-hour NO\textsubscript{2} averages in Southwestern Ontario and Toronto averaged over 5 years, by station. Each point represents a 5-year average at an individual in situ monitoring station. Y-axis represents the average of all available measurements from January, 2004 to December, 2010, inclusive. X-axis represents only measurements taken between noon and 1400 hours local standard time for the same 5-year period. Error bars represent 95% confidence intervals in averages.

- ages – if, for example, the rush-hour in Toronto resulted in higher midday concentrations while the lifetime was short enough to reduce nighttime concentrations enough to result in similar 24-hour average concentrations to Southwestern Ontario. However, when comparing 24-hour to midday concentrations at all 5 Southwestern Ontario stations to all 5 Toronto area stations, no discrepancy was observed (Fig. 5.16).
5.2 Application of Inferred Surface NO$_2$ maps

5.2.1 Temporal trends in surface-to-column ratios

Temporal patterns in the OMI data and inferred ground-based concentrations were explored to illustrate the application of this methodology. The patterns examined included the variation in inferred concentrations across the region over four years, and the seasonality in the surface-to-column ratio. Over a span of 4 years, using only the 5 permanent MoE monitoring stations, the seasonal average surface-to-column ratio was found to vary from a minimum of 0.81 ppb/1 x 10$^{15}$ molec-cm$^{-2}$ (H=525m) in the autumn and a maximum of 2.0 ppb/1 x 10$^{15}$ molec-cm$^{-2}$ (H=210m) in the winter (Table 5.3). No significant relationship with characteristic height was found for any meteorological variable. However, Lake Erie’s water temperature normally follows a very similar seasonal trend, with winter and spring (December through May) having lower lake temperatures than summer and autumn (June through November) [NOAA 2010]. Therefore, it may be that higher lake temperatures in the summer and autumn may be driving the vertical mixing of NO$_2$ in the region, as seen in the seasonal pattern in characteristic height.

<table>
<thead>
<tr>
<th>Season</th>
<th>Mean Surface-to-Column Ratio (±95% CI) [ppb / 1 x 10$^{15}$ molec-cm$^{-2}$]</th>
<th>Mean Characteristic Height (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter</td>
<td>2.0(±0.41)</td>
<td>210</td>
</tr>
<tr>
<td>Spring</td>
<td>1.7(±0.13)</td>
<td>245</td>
</tr>
<tr>
<td>Summer</td>
<td>0.94(±0.07)</td>
<td>450</td>
</tr>
<tr>
<td>Autumn</td>
<td>0.81(±0.07)</td>
<td>525</td>
</tr>
</tbody>
</table>

Table 5.3: Mean surface-to-column ratio (±95% confidence interval) and characteristic height, by season.
5.2.2 Changes in NO\textsubscript{2} over 4 years

As an illustrative example, Figure 5.17 provides regional snapshots of OMI-inferred surface NO\textsubscript{2} concentrations for 4 years. From 2006 to 2009, OMI-inferred NO\textsubscript{2} in the region displayed a slow decline in and around the industrial areas on both sides of the border overall, with a sudden drop in the summer of 2009. This decrease in regional NO\textsubscript{2} concentrations may have coincided with a drop in manufacturing in the area during the economic slowdown after the fall of 2008. Concentrations over the West end of L. Erie remained fairly stable relative to concentrations onshore nearby, suggesting that meteorologically driven dispersion of NO\textsubscript{2} remained constant over 3 of the 4 years in question.

![Figure 5.17: OMI inferred NO\textsubscript{2} concentrations for summers of A) 2006, B) 2007, C) 2008 and D) 2009.](image)

Figure 5.17: OMI inferred NO\textsubscript{2} concentrations for summers of A) 2006, B) 2007, C) 2008 and D) 2009.
5.2.3 NO$_2$ outflow and meteorology

Figure 5.18 shows average OMI inferred surface NO$_2$ concentrations for the entire 2007 year separated by wind direction. It is important to acknowledge the implicit assumption that exclusion of some days due to clouds does not introduce any bias in the maps. The long term comparison using the leave-one-out approach indicates that this is true, in general. It is possible, however, that, when separating overpasses by wind direction, we are exposing systematic errors which are masked by combining all overpasses. That is, if cloudy days from the southeast direction are cleaner than clear days and if cloudy days from the southwest direction are more polluted than clear days, combining the days from both of these directions causes the errors to cancel each other out. Also, it should be pointed out that the same single surface-to-column ratio calculated for the BAQS-met study area was applied across the entire range of the maps. The error introduced by this assumption may grow as the distance from the original points of calculation grows and therefore what appear to be large differences between wind directions around the Toronto area (Northeast corner of the maps) could in fact be errors introduced by this assumption.

Figure 5.18d includes OMI measurements when the wind was blowing from due East to due South directions. This quadrant was particularly important to the study of the region because it illustrated the impact of easterly airflows nearly perpendicularly across the Canada-U.S. border at Windsor-Detroit, thus highlighting any NO$_x$ emissions sources on the Canadian side. The sharpness of the boundary can be observed on the NW shore of Lake St Clair (marked in fuchsia in figure 5.18d): over the lake the column measures approximately half those immediately adjacent the lake on the NW shore.

In order to more clearly see the effects of wind direction on surface level NO$_2$ concentrations, figure 5.19 shows the difference between the average concentration grouped by wind direction and the annual average concentration for the region (all wind directions). Overall, NO$_2$ concentrations were higher when the wind blew from the SE and SW.
Looking at the campaign area, the area between L. Erie and L. St. Clair (circled in red in figure 5.19(d)), a different pattern emerges: the area remains relatively unaffected by wind direction except for markedly elevated NO$_2$ concentrations across the entire region, as well as the west end of L. Erie, when the wind blows from the NW. Good agreement between the satellite-derived, wind-direction-dependent concentrations and in-situ, wind-direction-dependent concentrations was also found ($R = 0.89$, comparing in situ midday NO$_2$ at 5 stations to inferred satellite values for those same locations, separated by 4 wind directions, $n = 20$).

It should also be possible to discern areas of intense emissions from the difference maps. Indeed, the core of Detroit / Windsor, near the Ambassador Bridge over the Detroit River, is consistently found to be a boundary between below average for all wind directions (Figure 5.19). Another area of interest is the area to the north of L. St. Clair, just south of Sarnia where a large power generation station is situated in Ontario, as well as several emissions sources on the U.S. side. Outflow can be seen from Cleveland, on the south side of L. Erie, especially over the lake when wind flows from the SW.

**Lifetime of NO$_2$**

Another potential application of spatial information about NO$_2$ concentrations when combined with meteorological data is calculation of the atmospheric lifetime of NO$_x$. This is made possible because the lifetime of NO$_x$ is generally regarded to be between 1 hour and 24 hours and because emissions sources tend to be geographically localized (either in urban or industrial areas). Previously, the average lifetime along the eastern coast of North America was calculated to be 26 hours using GOME NO$_2$ columns and average windspeed and direction (Leue et al., 2001). More recently, OMI measurements, which are higher-resolution than GOME measurements, were grouped based on the wind direction at the time of overpass to show an average lifetime between 5 and 8 hours in China (Beirle et al., 2010). Both of these improvements (i.e., increased spatial resolution
Figure 5.18: OMI inferred NO$_2$ concentrations for 2007 grouped by surface wind direction as measured at Windsor. A) represents only OMI measurements taken when wind was blowing from the NW direction. B, C, D) Same as A but NE, SW and SE directions, respectively. NW coast of L. St. Clair indicated by black arrow in figure D; inferred concentrations over the lake are approximately half those onshore when the lake is upwind of the onshore emissions sources (i.e. when the wind blows from the SE). Number of overpasses used to generate each average was 21 (21% of available overpasses) for A, 70 for B, 98 for C and 48 for D. The total number of overpasses used is less than the total number of days in the year because of rejection of overpasses for which > 2 surface stations were occluded by clouds.
Figure 5.19: Difference between OMI inferred NO$_2$ grouped by wind direction and annual average OMI inferred NO$_2$. Purple (positive), indicates higher than average NO$_2$ concentrations when the wind blows from that direction while blue indicates lower than average concentrations. Uncoloured regions are less than 1 ppb Difference. Labeled points in figure A represent surface monitoring stations (1: WW and WD; 2: CH; 3: SA; 4: LO) A) represents only OMI measurements taken when wind was blowing from the NW direction. B, C, D) Same as A but NE, SW and SE directions, respectively. See text for in-depth description regarding marked areas in figures C and D.
Figure 5.20: The path of the transect taken to determine decay distance from Detroit, which was assumed to be a point source. Decay fitting is showed in figure 5.21.

Based on the wind-separated OMI-inferred concentrations from figure 5.18, an artificial transect along the 45° line was taken directly through the grid cell containing downtown Detroit (Fig. 5.20). This grid cell was assumed to be a point-source of NO$_x$ emissions for the purposes of this calculation. A truncated exponential decay curve was then fitted to the NO$_2$ concentration data from the transect (Fig. 5.21). The explained variance of the decay model was 89%. The decay constant was approximately 171 km (95% CI ±24 km) and the vector-average windspeed for the hours of 6 AM to 2 PM (E.S.T.) on days which had overpasses included in the calculation of the concentrations was 10.7 km/h (±1.4 km/h) which provided a mean atmospheric lifetime of NO$_x$ of approximately 16 hours (±3 h). When decay to a background level of approximately 3 ppb was considered (instead of decay to 0 ppb), the falloff of the best-fit curve was much
Figure 5.21: Utilizing downtown Detroit as a point emissions source, a truncated exponential decay curve was fitted to the concentrations along a 45° (NE-heading) transect (Fig. 5.20). The best fit parameters provided a decay constant of approximately 171 km, which, when divided by the vector-average wind speed, provided a mean lifetime of approximately 16 hours.

shaper the resultant mean atmospheric lifetime was 11 hours (±2h, see Fig. A.2).

This value is somewhat larger than values of 5 to 8 hr reported in Beirle et al. (2010) and somewhat shorter than values reported in other studies. Elimination rates of NO\textsubscript{x} by species such as OH may well be higher in China than in Southwestern Ontario. Another possible reason for the difference with Beirle et al. (2010) is the fitting methodology. Beirle et al. (2010) fit a Gaussian function convolved with a truncated exponential to account for the source spreading observed by satellite measurements. This would have added great uncertainty to the fitting process in the case of the Detroit-Southwestern Ontario region as many sources upwind of the assumed point-source would have confounded the Gaussian fitting process, so only the truncated exponential portion was fitted. On the downwind side, Sarnia’s influence may have contributed to a positive bias in the estimate. If the transect points which are believed to be affected by Sarnia’s outflow are removed, the fit decreases to 7 hr, which agrees well with Beirle et al. (2010).

The values included in the wind speed average included from 8 hours prior to overpass
time, although changing this length of time by as many as 4 hour did not change the average windspeed more than 10%. While this value is a year-long average day-time lifetime, over 75% of the days considered for this wind direction fell between May and October, making the calculation slightly biased to the summer and autumn; particularly in the summer months the lifetime of NO\textsubscript{x} in the troposphere would be expected to be shortest.

It is important to note that a temporal influence on these downwind concentrations would be expected but quantifying the magnitude and even the direction of this influence is difficult. The concentrations observed 10 hours downwind from the source were emitted at a different part of the diurnal emissions profile than the concentrations observed much closer to the emissions source. Since the original OMI measurements provide a snapshot between noon and 1400 local time, one would expect the elevated concentrations as a result of the morning rush hour to present an increase in concentrations 3 to 5 hr downwind. Ostensibly, the inferred concentrations used in these lifetime calculations are 24-hr averages, however the regional average nature of the inference process means it is impossible to account for a downwind “bump” when inferring concentrations. It is most likely that this diurnal emissions and processing bias would therefore flatten the fitted decay curve and bias the estimates slightly high.

Additionally, no horizontal dispersion was considered which would be more appropriate for a line-source than the point-source which Detroit was assumed to be. This assumption would have biased the results low since decay along a linear path downwind was considered.

### 5.2.4 Spatial variability in Toronto

One potential application of satellite inferred surface NO\textsubscript{2} concentration maps is assessment of public exposure to traffic pollution (see section 2.3). Recently, Jerrett et al. (2009) utilized a land-use-regression (LUR) model to assess public exposure to traffic-
related air pollution in Toronto, Ontario. The model was informed by approximately 200 passive samplers placed across the city during a 2-week period in the fall of 2002 and another during the spring of 2004.

The model predicted a fairly strong gradient from West to East across the city from consistently > 20 ppb at the West end to 10–15 ppb on the East side. Additionally major roadways were characterised by concentrations of > 30 ppb. The downtown core, especially near the waterfront, also showed high concentrations (> 30 ppb) (Fig. 5.22).

Since OMI data is only available starting in late 2004, to generate a map of inferred surface concentration data which mostly closely matched the circumstances of the LUR map used in Jerrett et al. (2009), OMI data from Dec 1, 2004 to Nov 30, 2006 were utilized. Surface concentrations were inferred using 7 local MoE monitors (4 city of Toronto monitors plus Brampton, Oshawa and Newmarket). Maps of Toronto NO$_2$ column densities as well as time series plots of in situ concentrations and OMI column
densities over 5 years are provided in Appendix A. Additional analysis of characteristic height at 4 Toronto MOE permanent monitoring stations is provided in Appendix E.

In order to provide a map which was comparable to the resolution of the LUR map, 0.005° (~ 560km) grid-cell spacing was used. This is clearly much lower than the resolution used for the LUR map, but provides adequate resolution to examine some of the patterns shown.

Overall, values were similar and the West-to-East gradient is born out by the inferred map, which shows concentrations near 25 ppb in the West and concentrations below 15 ppb in the East (Fig. 5.23). Roads and smaller gradients were not visible in the OMI data as they were in the much finer-resolution LUR map. One particular discrepancy was in the downtown area which showed overall concentrations > 25 ppb in the LUR map (Fig. 5.22) while showing values below to 20 ppb in the OMI inferred map.

The source of this discrepancy is not entirely clear, although the MoE Toronto Downtown monitor showed an average value of 19.9 ppb over the period used in the OMI inferred map. It is, therefore, possible that concentrations downtown decreased, in comparison to the 2002-2004 period used to calculate the LUR map.

A more plausible explanation is that the area characterised by elevated concentrations is simply too small to extract from the OMI measurements. This is because the smallest possible OMI pixel spans an area 13km by 24 km and the downtown area highlighted by the LUR map is perhaps 5km by 2.5 km, or 4% of the area of the smallest OMI pixel. Since the values predicted by the LUR are not drastically dissimilar from the concentrations in the neighboring areas, it is possible that their contributions to the OMI columns are too small to be extracted by the regridding process.

In addition to this, the downtown area contains a large number of tall buildings. It is possible that the urban canyon created by these buildings is increasing concentrations very near the ground whereas much of the light observed by OMI is reflected by the tops of the very buildings which are creating the urban canyon effect.
Figure 5.23: OMI inferred NO\textsubscript{2} concentrations in Toronto, Ontario for years 2005-6. This map is truncated, including at the waterfront, to provide a better visual comparison with figure 5.22. A complete version is provided in appendix A.

Yet another possible factor is the area’s proximity to the waterfront, although this was not shown to be a factor in the Windsor area which is along a waterfront.

Additionally, it has been suggested that cloud occlusion may present a significant bias in Toronto, as in situ monitors showed a difference in concentrations between cloud occluded days and days on which OMI made observations (Celarier et al., 2008b).
Chapter 6

Conclusions and Recommendations

In this thesis, a novel method was developed for producing high-resolution (∼ 11km) maps of surface NO$_2$ concentrations by combining satellite retrieved NO$_2$ columns from OMI with in situ measurements made by permanent monitoring networks such as the one maintained by the Ontario Ministry of the Environment (MoE). While current methods for estimating surface NO$_2$ concentrations from satellite remote sensing data utilize CTM output, this method empirically converts columns to surface concentrations using publicly available in situ monitoring network data.

To validate this method and explore the uncertainties and biases in the inferred values, field data obtained from the BAQS-met field campaign in the Windsor area during 2007 was used. When 2-week average surface NO$_2$ concentrations were inferred for the campaign area using the 5 local MoE monitors plus the 2 temporary EC rural, photolytic CL monitoring stations, a good correlation between inferred values and a network of passive monitors was found (R = 0.69).

While this method is not accurate enough to use in exposure assessments at the postal code level, broad patterns are evident in both space and time. This means that the data produced by this method can be used to check the temporal scaling of high-resolution LUR maps, for example, or explore patterns between monitoring site locations.
An important limitation of this work which needs to be explored further is the loss of real information about how the vertical distribution of NO$_2$ in the troposphere (i.e., the characteristic height) varies across space. This loss of information comes from the averaging process which is currently required to eliminate the large uncertainty associated with any single pixel. Information from emissions inventories and high resolution CTMs could be used to separate this real variation in characteristic height from the uncertainties in the satellite retrieval process to improve the inference process.

Traditional NO$_2$ monitors are known to suffer from interference from other oxidized nitrogen species (NO$_x$). The campaign data showed that, even in rural areas, although NO$_x$ interference is a problem, sampling line “stickiness” appears to smooth the signal for this out so that the interference remains fairly constant. Additionally, while the relative value of this interference can be over 100% in clean areas at midday in the summer, the absolute value averages 0.9 ppb. When compared to 24-hour average values, this 0.9 ppb bias is much smaller.

### 6.1 Implications for air quality monitoring

#### 6.1.1 Human health impacts

Overall, the correlation was good at a scale which could be used for some types of epidemiological studies. However, when compared with a LUR map over the city of Toronto, reasonable agreement was found for most locations. However, while the downtown core shows up as a hot spot with many areas near roadways with concentrations > 25 ppb, this area is somewhat lower than the northwest of the city on the OMI-inferred map. The reasons for this discrepancy are not entirely clear, however, it is likely that some of this bias comes from the urban street canyon effect, where the tops of buildings reflect most of the sunlight before it has passed through the bulk of the boundary-layer air pollution in the street canyon, below the building tops.
6.1.2 Monitoring site placement

OMI inferred values for the BAQS-met campaign agreed well with the network of passive monitors when the rural sites were included but this agreement decreased when only the MoE sites were considered. This is due in part to the normal placement of monitoring stations to be near strong sources such as roadways, which makes the values reported by those stations less spatially representative on the scale of the OMI retrievals. Therefore, this thesis recommends additional rural monitoring capacity if the Ministry wants to take advantage of remote sensing data in the future.

6.2 Algorithm improvement and future work

While it was not within the scope of this work, it would be useful to perform a side-by-side comparison of results obtained using the inference method presented in this thesis and results obtained using the GEOS-Chem method on which the present method was based.

As well, further exploration of the NO_x lifetime values provided by this method is warranted. For example, seasonal trends could be analysed using measurements of other species or additional meteorological data to determine root causes for those trends.

A number of improvements could be made to the process developed in this thesis. For example, the spatial resolution of the inferred data could be increased by exploring the spatial relationship of the surface-to-column ratio, or by incorporating data from a high-resolution CTM.

Improvements to the DOMINO product have led to a version 2 product, which at the time of this thesis is available only up until mid 2008. As well, if the DOMINO/GEOS-Chem hybrid product became publicly available, it could be utilized in this process [Lamsal et al., 2010].

Although the resolution is not as good, more data could be provided by adding other
satellites’ products, such as SCIAMACHY and GOME-2. Because these satellites have different overpass times, they can provide additional information in spite of their lower resolution (Boersma et al., 2009).
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Appendix A

Extra figures
Figure A.1: OMI inferred NO$_2$ concentrations in Toronto, Ontario for years 2005-6. (As figure 5.23 but without truncation)
Figure A.2: Lifetime calculation supplement to section 5.2.3. Decay to background NO$_2$ concentration of 3 ppb and resultant e-folding distance. Atmospheric lifetime of NO$_x$ was calculated to be 11 hours ($\pm 2$ h) based on this best-fit curve (compared to 16 hr for best-fit decay curve to 0 ppb background.)
Figure A.3: Histogram plot of cloud radiance fraction of all OMI pixels from an area bounded by latitudes 40°–44° and longitudes −85°–−80° from all overpasses from June 1, 2007 to September 10, 2007, inclusive.
Figure A.4: Two-week average OMI column densities vs. in situ measurements for 2005-2009 for Windsor area. The start dates of 2-week periods which lay far from the linear regression line are highlighted.
Appendix A. Extra figures

Figure A.5: Year 2005 average OMI NO₂ column density for Toronto

Figure A.6: Year 2006 average OMI NO₂ column density for Toronto
Figure A.7: Year 2008 average OMI NO₂ column density for Toronto

Figure A.8: Year 2008 average OMI NO₂ column density for Toronto
Figure A.9: Year 2009 average OMI NO$_2$ column density for Toronto

Figure A.10: Long term timeseries of in situ concentration measurements and OMI column densities at MOE Toronto Downtown site.
Figure A.11: Long term timeseries of in situ concentration measurements and OMI column densities at MOE Toronto East site.

Figure A.12: Long term timeseries of in situ concentration measurements and OMI column densities at MOE Toronto North site.
Figure A.13: Long term timeseries of in situ concentration measurements and OMI column densities at MOE Toronto West site.
Appendix B

Surface sampling data from BAQS-met campaign

Table B.1: Campaign NO$_2$ data for Largie (LAR, 42°42.001N, 81°33.895W, Glencoe)

<table>
<thead>
<tr>
<th>Start</th>
<th>End</th>
<th>Passive NO$_2^1$</th>
<th>OMI NO$_2^2$</th>
<th>Temp (°C)</th>
<th>H (%)</th>
</tr>
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<tbody>
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<td>06/13/11 15:50</td>
<td>5.14</td>
<td>4.04</td>
<td>20.17</td>
<td>59.45</td>
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<tr>
<td>06/13/11 15:56</td>
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<td>6.63</td>
<td>1.61</td>
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<td>54.54</td>
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</table>

$^1$ units: ppb

$^2$ units: ×10$^{15}$ molec cm$^{-2}$
Appendix B. Surface sampling data from BAQS-met campaign

Table B.2: Campaign NO\textsubscript{2} data for Palmyra (PAL, 42°26.525N, 81°44.37W, Ridgetown)

<table>
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<tr>
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<th>OMI NO\textsubscript{2}\textsuperscript{2}</th>
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<th>H (%)</th>
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</thead>
<tbody>
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<td>3.44</td>
<td>3.26</td>
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<td>80.21</td>
</tr>
</tbody>
</table>

\textsuperscript{1} \textbf{units: ppb}
\textsuperscript{2} \textbf{units: }×10^{15} \text{ molec cm}^{-2}

Table B.3: Campaign NO\textsubscript{2} data for Alvinston (ALV, 42°50.636N 81°51.936W, Strathroy)

<table>
<thead>
<tr>
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<th>OMI NO\textsubscript{2}\textsuperscript{2}</th>
<th>Temp (° C)</th>
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<td>07/11/11 15:44</td>
<td>07/26/11 10:02</td>
<td>2.86</td>
<td>1.93</td>
<td>20.49</td>
<td>69.04</td>
</tr>
<tr>
<td>07/26/11 10:05</td>
<td>08/09/11 9:09</td>
<td>3.16</td>
<td>2.84</td>
<td>21.95</td>
<td>63.02</td>
</tr>
<tr>
<td>08/09/11 9:42</td>
<td>08/23/11 9:51</td>
<td>4.66</td>
<td>4.36</td>
<td>19.79</td>
<td>80.8</td>
</tr>
</tbody>
</table>

\textsuperscript{1} \textbf{units: ppb}
\textsuperscript{2} \textbf{units: }×10^{15} \text{ molec cm}^{-2}

Table B.4: Campaign NO\textsubscript{2} data for Croton (CRO, 42°36.571N, 82°04.812W, Thamesville)

<table>
<thead>
<tr>
<th>Start</th>
<th>End</th>
<th>Passive NO\textsubscript{2}\textsuperscript{1}</th>
<th>OMI NO\textsubscript{2}\textsuperscript{2}</th>
<th>Temp (° C)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/01/11 14:26</td>
<td>06/13/11 12:51</td>
<td>5.48</td>
<td>5.29</td>
<td>20.17</td>
<td>59.45</td>
</tr>
<tr>
<td>06/13/11 12:54</td>
<td>06/27/11 16:31</td>
<td>4.87</td>
<td>4.97</td>
<td>23.8</td>
<td>54.54</td>
</tr>
<tr>
<td>06/27/11 16:34</td>
<td>07/11/11 21:20</td>
<td>4.19</td>
<td>2.69</td>
<td>21.41</td>
<td>64.68</td>
</tr>
<tr>
<td>07/11/11 21:22</td>
<td>07/25/11 11:56</td>
<td>4.07</td>
<td>3.26</td>
<td>20.5</td>
<td>68.72</td>
</tr>
<tr>
<td>07/25/11 11:58</td>
<td>08/09/11 11:53</td>
<td>4.21</td>
<td>2.82</td>
<td>21.83</td>
<td>63.11</td>
</tr>
<tr>
<td>08/22/11 12:20</td>
<td>09/05/11 13:29</td>
<td>4.15</td>
<td>4.17</td>
<td>19.96</td>
<td>86.97</td>
</tr>
</tbody>
</table>

\textsuperscript{1} \textbf{units: ppb}
\textsuperscript{2} \textbf{units: }×10^{15} \text{ molec cm}^{-2}
Table B.5: Campaign NO\textsubscript{2} data for Sombra (SOM, 42°41.78N, 82°25.781W, Wallaceburg)

<table>
<thead>
<tr>
<th>Start</th>
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<th>Passive NO\textsubscript{2} \textsuperscript{1}</th>
<th>OMI NO\textsubscript{2} \textsuperscript{2}</th>
<th>Temp (° C)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/01/11 17:26</td>
<td>06/13/11 15:03</td>
<td>6.42</td>
<td>9.14</td>
<td>20.17</td>
<td>59.45</td>
</tr>
<tr>
<td>06/13/11 15:04</td>
<td>06/28/11 14:40</td>
<td>5.31</td>
<td>6.06</td>
<td>23.87</td>
<td>55.75</td>
</tr>
<tr>
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<td>07/26/11 10:02</td>
<td>5.77</td>
<td>5.00</td>
<td>20.71</td>
<td>66.67</td>
</tr>
<tr>
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<td>08/09/11 9:36</td>
<td>6.03</td>
<td>8.18</td>
<td>22.72</td>
<td>73.71</td>
</tr>
<tr>
<td>08/09/11 9:36</td>
<td>08/23/11 9:27</td>
<td>5.67</td>
<td>6.74</td>
<td>20.09</td>
<td>79.17</td>
</tr>
<tr>
<td>08/23/11 9:25</td>
<td>09/06/11 9:15</td>
<td>5.81</td>
<td>6.70</td>
<td>20.39</td>
<td>80.9</td>
</tr>
</tbody>
</table>

\textsuperscript{1} units: ppb
\textsuperscript{2} units: $\times 10^{15}$ molec cm\textsuperscripts{-2}

Table B.6: Campaign NO\textsubscript{2} data for Paincourt (PAI, 42°23.417N, 82°15.516W, Chatham)

<table>
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<tr>
<th>Start</th>
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<th>OMI NO\textsubscript{2} \textsuperscript{2}</th>
<th>Temp (° C)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/02/11 9:18</td>
<td>06/14/11 15:04</td>
<td>4.95</td>
<td>5.08</td>
<td>20.48</td>
<td>58.52</td>
</tr>
<tr>
<td>06/14/11 15:09</td>
<td>06/28/11 13:11</td>
<td>5.38</td>
<td>4.64</td>
<td>23.9</td>
<td>56.21</td>
</tr>
<tr>
<td>07/11/11 17:01</td>
<td>07/25/11 16:06</td>
<td>4.63</td>
<td>3.12</td>
<td>21.33</td>
<td>66.53</td>
</tr>
<tr>
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<td>08/09/11 10:31</td>
<td>5.41</td>
<td>4.09</td>
<td>22.6</td>
<td>75.89</td>
</tr>
<tr>
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<td>08/22/11 13:02</td>
<td>3.77</td>
<td>4.15</td>
<td>20.86</td>
<td>79.24</td>
</tr>
</tbody>
</table>

\textsuperscript{1} units: ppb
\textsuperscript{2} units: $\times 10^{15}$ molec cm\textsuperscripts{-2}

Table B.7: Campaign NO\textsubscript{2} data for Merlin (MER, 42°14.14N 82°13.55W, Tilbury)

<table>
<thead>
<tr>
<th>Start</th>
<th>End</th>
<th>Passive NO\textsubscript{2} \textsuperscript{1}</th>
<th>OMI NO\textsubscript{2} \textsuperscript{2}</th>
<th>Temp (° C)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>06/13/11 17:11</td>
<td>3.88</td>
<td>3.61</td>
<td>19.67</td>
<td>65.67</td>
</tr>
<tr>
<td>06/13/11 17:13</td>
<td>06/28/11 12:06</td>
<td>3.82</td>
<td>3.69</td>
<td>21.88</td>
<td>63.25</td>
</tr>
<tr>
<td>06/28/11 12:08</td>
<td>07/11/11 12:45</td>
<td>4.63</td>
<td>2.39</td>
<td>21.51</td>
<td>66.18</td>
</tr>
<tr>
<td>07/11/11 12:47</td>
<td>07/25/11 13:57</td>
<td>5.14</td>
<td>2.62</td>
<td>19.87</td>
<td>70.32</td>
</tr>
<tr>
<td>07/25/11 13:58</td>
<td>08/08/11 18:48</td>
<td>4.24</td>
<td>3.29</td>
<td>22.87</td>
<td>76.78</td>
</tr>
<tr>
<td>08/08/11 18:48</td>
<td>08/23/11 11:42</td>
<td>3.35</td>
<td>3.19</td>
<td>20.45</td>
<td>79.71</td>
</tr>
<tr>
<td>08/23/11 11:44</td>
<td>09/06/11 14:30</td>
<td>3.60</td>
<td>3.80</td>
<td>29.47</td>
<td>82.0</td>
</tr>
</tbody>
</table>

\textsuperscript{1} units: ppb
\textsuperscript{2} units: $\times 10^{15}$ molec cm\textsuperscripts{-2}
### Table B.8: Campaign NO₂ data for Woodslee (WOO, 42°12.714N, 82°44.903W, Essex)

<table>
<thead>
<tr>
<th>Start</th>
<th>End</th>
<th>Passive NO₂¹</th>
<th>OMI NO₂²</th>
<th>Temp (° C)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/02/11 10:17</td>
<td>06/14/11 14:52</td>
<td>7.56</td>
<td>5.64</td>
<td>21.55</td>
<td>62.09</td>
</tr>
<tr>
<td>06/14/11 14:52</td>
<td>06/27/11 9:32</td>
<td>7.12</td>
<td>4.90</td>
<td>21.98</td>
<td>58.29</td>
</tr>
<tr>
<td>06/27/11 9:34</td>
<td>07/11/11 16:00</td>
<td>5.49</td>
<td>5.26</td>
<td>21.82</td>
<td>67.68</td>
</tr>
<tr>
<td>07/11/11 16:02</td>
<td>07/25/11 16:01</td>
<td>6.63</td>
<td>3.91</td>
<td>20.91</td>
<td>68.27</td>
</tr>
<tr>
<td>07/25/11 16:03</td>
<td>08/08/11 14:08</td>
<td>8.33</td>
<td>6.93</td>
<td>22.62</td>
<td>74.17</td>
</tr>
<tr>
<td>08/08/11 14:08</td>
<td>08/22/11 15:32</td>
<td>5.57</td>
<td>6.27</td>
<td>21.18</td>
<td>80.86</td>
</tr>
<tr>
<td>08/22/11 15:34</td>
<td>09/07/11 10:21</td>
<td>5.33</td>
<td>6.00</td>
<td>20.41</td>
<td>68.8</td>
</tr>
</tbody>
</table>

¹ **units:** ppb  
² **units:** ×10¹⁵ molec cm⁻²

### Table B.9: Campaign NO₂ data for Paquette Corners (PAQ, 42°11.717N, 82°57.922W, Windsor)

<table>
<thead>
<tr>
<th>Start</th>
<th>End</th>
<th>Passive NO₂¹</th>
<th>OMI NO₂²</th>
<th>Temp (° C)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/02/11 10:47</td>
<td>06/14/11 12:18</td>
<td>6.61</td>
<td>5.80</td>
<td>20.31</td>
<td>67.51</td>
</tr>
<tr>
<td>06/14/11 12:18</td>
<td>06/27/11 8:58</td>
<td>8.42</td>
<td>6.53</td>
<td>22.27</td>
<td>61.87</td>
</tr>
<tr>
<td>07/11/11 16:35</td>
<td>07/25/11 16:46</td>
<td>8.65</td>
<td>4.28</td>
<td>20.26</td>
<td>66.05</td>
</tr>
<tr>
<td>07/25/11 16:48</td>
<td>08/08/11 14:49</td>
<td>7.87</td>
<td>7.49</td>
<td>22.93</td>
<td>75.58</td>
</tr>
<tr>
<td>08/08/11 14:49</td>
<td>08/22/11 16:04</td>
<td>6.35</td>
<td>8.52</td>
<td>20.95</td>
<td>77.3</td>
</tr>
<tr>
<td>08/22/11 16:06</td>
<td>09/07/11 11:33</td>
<td>5.97</td>
<td>7.23</td>
<td>21.04</td>
<td>86.48</td>
</tr>
</tbody>
</table>

¹ **units:** ppb  
² **units:** ×10¹⁵ molec cm⁻²

### Table B.10: Campaign NO₂ data for Cottam (COT, 42°07.048N 82°46.214W, Essex)

<table>
<thead>
<tr>
<th>Start</th>
<th>End</th>
<th>Passive NO₂¹</th>
<th>OMI NO₂²</th>
<th>Temp (° C)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/02/11 11:29</td>
<td>06/14/11 12:30</td>
<td>7.25</td>
<td>4.28</td>
<td>19.93</td>
<td>61.51</td>
</tr>
<tr>
<td>06/14/11 12:35</td>
<td>06/28/11 11:02</td>
<td>6.59</td>
<td>4.78</td>
<td>22.03</td>
<td>61.12</td>
</tr>
<tr>
<td>07/25/11 9:55</td>
<td>08/08/11 10:16</td>
<td>6.05</td>
<td>5.68</td>
<td>22.99</td>
<td>72.17</td>
</tr>
<tr>
<td>08/08/11 10:20</td>
<td>08/22/11 10:22</td>
<td>5.46</td>
<td>6.07</td>
<td>21.54</td>
<td>78.77</td>
</tr>
</tbody>
</table>

¹ **units:** ppb  
² **units:** ×10¹⁵ molec cm⁻²
Table B.11: Campaign NO\textsubscript{2} data for Leamington (LEA, 42°04.12N, 82°36.826W, Leamington)

<table>
<thead>
<tr>
<th>Start</th>
<th>End</th>
<th>Passive NO\textsubscript{2}\textsuperscript{1}</th>
<th>OMI NO\textsubscript{2}\textsuperscript{2}</th>
<th>Temp (°C)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/02/11 11:41</td>
<td>06/14/11 11:09</td>
<td>10.81</td>
<td>4.19</td>
<td>19.93</td>
<td>61.51</td>
</tr>
<tr>
<td>06/14/11 11:11</td>
<td>06/27/11 11:42</td>
<td>10.23</td>
<td>3.76</td>
<td>21.74</td>
<td>60.43</td>
</tr>
<tr>
<td>06/27/11 11:46</td>
<td>07/12/11 10:17</td>
<td>7.20</td>
<td>3.52</td>
<td>22.19</td>
<td>67.38</td>
</tr>
<tr>
<td>07/12/11 10:19</td>
<td>07/25/11 15:16</td>
<td>8.49</td>
<td>3.98</td>
<td>20.87</td>
<td>65.47</td>
</tr>
<tr>
<td>07/25/11 15:18</td>
<td>08/08/11 16:47</td>
<td>8.70</td>
<td>4.14</td>
<td>22.99</td>
<td>72.17</td>
</tr>
<tr>
<td>08/08/11 16:47</td>
<td>08/22/11 17:27</td>
<td>6.27</td>
<td>5.90</td>
<td>21.54</td>
<td>78.77</td>
</tr>
<tr>
<td>08/22/11 17:29</td>
<td>09/07/11 14:38</td>
<td>8.56</td>
<td>4.57</td>
<td>21.45</td>
<td>82.09</td>
</tr>
</tbody>
</table>

\textsuperscript{1} units: ppb
\textsuperscript{2} units: $\times 10^{15}$ molec cm\textsuperscript{-2}

Table B.12: Campaign NO\textsubscript{2} data for Wheatley (WHE, 42°07.978N, 82°23.731W, Leamington)

<table>
<thead>
<tr>
<th>Start</th>
<th>End</th>
<th>Passive NO\textsubscript{2}\textsuperscript{1}</th>
<th>OMI NO\textsubscript{2}\textsuperscript{2}</th>
<th>Temp (°C)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/02/11 13:51</td>
<td>06/13/11 20:13</td>
<td>3.56</td>
<td>3.45</td>
<td>19.67</td>
<td>65.67</td>
</tr>
<tr>
<td>06/13/11 20:13</td>
<td>06/27/11 13:00</td>
<td>4.10</td>
<td>3.44</td>
<td>23.8</td>
<td>54.54</td>
</tr>
<tr>
<td>06/27/11 13:01</td>
<td>07/11/11 14:19</td>
<td>4.27</td>
<td>2.39</td>
<td>21.67</td>
<td>68.49</td>
</tr>
<tr>
<td>07/11/11 14:21</td>
<td>07/25/11 14:39</td>
<td>4.29</td>
<td>3.05</td>
<td>20.72</td>
<td>70.39</td>
</tr>
<tr>
<td>07/25/11 14:41</td>
<td>08/08/11 17:38</td>
<td>3.35</td>
<td>4.62</td>
<td>22.37</td>
<td>76.37</td>
</tr>
<tr>
<td>08/08/11 17:38</td>
<td>08/22/11 18:03</td>
<td>3.36</td>
<td>5.86</td>
<td>21.22</td>
<td>80.45</td>
</tr>
<tr>
<td>08/22/11 18:05</td>
<td>09/07/11 16:21</td>
<td>3.09</td>
<td>3.99</td>
<td>21.15</td>
<td>79.87</td>
</tr>
</tbody>
</table>

\textsuperscript{1} units: ppb
\textsuperscript{2} units: $\times 10^{15}$ molec cm\textsuperscript{-2}

Table B.13: Campaign NO\textsubscript{2} data for Lighthouse Cove (LTC, 42°17.499N, 82°31.343W, Tilbury)

<table>
<thead>
<tr>
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<th>End</th>
<th>Passive NO\textsubscript{2}\textsuperscript{1}</th>
<th>OMI NO\textsubscript{2}\textsuperscript{2}</th>
<th>Temp (°C)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>06/14/11 8:16</td>
<td>6.61</td>
<td>5.37</td>
<td>20.48</td>
<td>58.52</td>
</tr>
<tr>
<td>06/14/11 8:16</td>
<td>06/27/11 10:08</td>
<td>7.19</td>
<td>4.65</td>
<td>23.82</td>
<td>54.94</td>
</tr>
<tr>
<td>06/27/11 10:10</td>
<td>07/11/11 18:00</td>
<td>6.21</td>
<td>4.29</td>
<td>21.95</td>
<td>65.79</td>
</tr>
<tr>
<td>07/11/11 18:03</td>
<td>07/25/11 18:16</td>
<td>6.31</td>
<td>2.99</td>
<td>21.33</td>
<td>66.53</td>
</tr>
<tr>
<td>07/25/11 18:18</td>
<td>08/08/11 12:52</td>
<td>8.35</td>
<td>4.65</td>
<td>22.48</td>
<td>74.97</td>
</tr>
<tr>
<td>08/08/11 12:52</td>
<td>08/22/11 14:30</td>
<td>4.55</td>
<td>6.35</td>
<td>21.1</td>
<td>79.72</td>
</tr>
<tr>
<td>08/22/11 14:32</td>
<td>09/06/11 11:45</td>
<td>7.22</td>
<td>4.84</td>
<td>20.85</td>
<td>76.78</td>
</tr>
</tbody>
</table>

\textsuperscript{1} units: ppb
\textsuperscript{2} units: $\times 10^{15}$ molec cm\textsuperscript{-2}
### Table B.14: Campaign NO\textsubscript{2} data for Staples (STA, 42\textdegree11.369N, 82\textdegree35.406W, Tilbury)

<table>
<thead>
<tr>
<th>Start</th>
<th>End</th>
<th>Passive NO\textsubscript{2}\textsuperscript{1}</th>
<th>OMI NO\textsubscript{2}\textsuperscript{2}</th>
<th>Temp (\degree C)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/02/11 9:12</td>
<td>06/14/11 9:31</td>
<td>6.50</td>
<td>11.67</td>
<td>21.55</td>
<td>62.09</td>
</tr>
<tr>
<td>06/14/11 9:33</td>
<td>06/27/11 10:47</td>
<td>5.64</td>
<td>5.82</td>
<td>21.98</td>
<td>58.29</td>
</tr>
<tr>
<td>06/27/11 10:49</td>
<td>07/12/11 9:43</td>
<td>5.60</td>
<td>5.62</td>
<td>22.12</td>
<td>67.73</td>
</tr>
<tr>
<td>07/12/11 9:45</td>
<td>07/25/11 17:39</td>
<td>4.02</td>
<td>5.28</td>
<td>20.41</td>
<td>68.8</td>
</tr>
<tr>
<td>07/25/11 17:41</td>
<td>08/08/11 13:26</td>
<td>6.24</td>
<td>4.47</td>
<td>22.62</td>
<td>74.17</td>
</tr>
<tr>
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<td>08/22/11 16:57</td>
<td>4.65</td>
<td>5.02</td>
<td>21.18</td>
<td>80.86</td>
</tr>
<tr>
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<td>09/07/11 9:25</td>
<td>6.53</td>
<td>7.49</td>
<td>23.3</td>
<td>90.1</td>
</tr>
</tbody>
</table>

\textsuperscript{1} \textit{units:} ppb  
\textsuperscript{2} \textit{units:} \times10^{15} \text{molec cm}^{-2}

### Table B.15: Campaign NO\textsubscript{2} data for University of Windsor (UOW, 42\textdegree18.263N, 83\textdegree03.964W, Windsor)

<table>
<thead>
<tr>
<th>Start</th>
<th>End</th>
<th>Passive NO\textsubscript{2}\textsuperscript{1}</th>
<th>OMI NO\textsubscript{2}\textsuperscript{2}</th>
<th>Temp (\degree C)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/02/11 14:46</td>
<td>06/14/11 10:07</td>
<td>19.34</td>
<td>10.13</td>
<td>21.55</td>
<td>62.09</td>
</tr>
<tr>
<td>06/14/11 10:14</td>
<td>06/28/11 8:52</td>
<td>18.03</td>
<td>6.92</td>
<td>23.9</td>
<td>56.21</td>
</tr>
<tr>
<td>06/28/11 8:59</td>
<td>07/11/11 10:54</td>
<td>18.13</td>
<td>6.39</td>
<td>23.36</td>
<td>59.38</td>
</tr>
<tr>
<td>07/11/11 10:56</td>
<td>07/25/11 14:17</td>
<td>20.23</td>
<td>5.32</td>
<td>22.27</td>
<td>59.09</td>
</tr>
<tr>
<td>07/25/11 14:19</td>
<td>08/08/11 14:00</td>
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<td>10.50</td>
<td>24.42</td>
<td>71.12</td>
</tr>
<tr>
<td>08/08/11 14:02</td>
<td>08/22/11 9:23</td>
<td>15.28</td>
<td>10.31</td>
<td>22.06</td>
<td>69.03</td>
</tr>
<tr>
<td>08/22/11 9:27</td>
<td>09/05/11 13:00</td>
<td>20.22</td>
<td>9.82</td>
<td>22.34</td>
<td>74.26</td>
</tr>
</tbody>
</table>

\textsuperscript{1} \textit{units:} ppb  
\textsuperscript{2} \textit{units:} \times10^{15} \text{molec cm}^{-2}

### Table B.16: Campaign data for Ministry of Environment (MOE, 42\textdegree17.573N, 83\textdegree04.385W, Windsor)

<table>
<thead>
<tr>
<th>Start</th>
<th>End</th>
<th>Passive NO\textsubscript{2}\textsuperscript{1}</th>
<th>OMI NO\textsubscript{2}\textsuperscript{2}</th>
<th>Temp (\degree C)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/02/11 14:47</td>
<td>06/16/11 13:22</td>
<td>14.49</td>
<td>9.39</td>
<td>21.82</td>
<td>60.95</td>
</tr>
<tr>
<td>06/16/11 15:38</td>
<td>06/28/11 8:20</td>
<td>12.79</td>
<td>7.02</td>
<td>23.71</td>
<td>57.38</td>
</tr>
<tr>
<td>06/28/11 8:20</td>
<td>07/11/11 12:53</td>
<td>14.88</td>
<td>5.96</td>
<td>23.36</td>
<td>59.38</td>
</tr>
<tr>
<td>07/11/11 12:55</td>
<td>07/25/11 10:49</td>
<td>14.71</td>
<td>5.31</td>
<td>22.27</td>
<td>59.09</td>
</tr>
<tr>
<td>08/08/11 14:20</td>
<td>08/22/11 9:41</td>
<td>13.24</td>
<td>10.31</td>
<td>22.06</td>
<td>69.03</td>
</tr>
<tr>
<td>08/22/11 9:44</td>
<td>09/05/11 13:46</td>
<td>14.36</td>
<td>9.74</td>
<td>22.34</td>
<td>74.26</td>
</tr>
</tbody>
</table>

\textsuperscript{1} \textit{units:} ppb  
\textsuperscript{2} \textit{units:} \times10^{15} \text{molec cm}^{-2}
Table B.17: Campaign NO$_2$ data for Harrow (HAR, 42°02.041N, 82°53.926W, Harrow)

<table>
<thead>
<tr>
<th>Start</th>
<th>End</th>
<th>Passive NO$_2$</th>
<th>OMI NO$_2$</th>
<th>Temp (°C)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/02/11 12:09</td>
<td>06/14/11 11:38</td>
<td>5.24</td>
<td>3.88</td>
<td>21.55</td>
<td>62.09</td>
</tr>
<tr>
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<td>06/28/11 10:37</td>
<td>4.99</td>
<td>4.61</td>
<td>23.9</td>
<td>56.21</td>
</tr>
</tbody>
</table>

1 units: ppb
2 units: ×10$^{15}$ molec cm$^{-2}$

Table B.18: Campaign NO$_2$ data for Bear Creek (BEA, 42°32.130N, 82°23.381W, Wallaceburg)

<table>
<thead>
<tr>
<th>Start</th>
<th>End</th>
<th>Passive NO$_2$</th>
<th>OMI NO$_2$</th>
<th>Temp (°C)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.88</td>
<td>19.8</td>
<td>69.94</td>
</tr>
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<td>4.22</td>
<td>6.81</td>
<td>21.59</td>
<td>75.45</td>
</tr>
<tr>
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<td>08/22/11 12:30</td>
<td>3.68</td>
<td>5.33</td>
<td>20.44</td>
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<td>09/05/11 15:32</td>
<td>3.86</td>
<td>5.10</td>
<td>20.39</td>
<td>80.9</td>
</tr>
</tbody>
</table>

1 units: ppb
2 units: ×10$^{15}$ molec cm$^{-2}$
Appendix C

Effect of regrid spacing on correlation with surface monitors

In order to determine that the grid-spacing used to average multiple satellite overpasses together was appropriate, different resolutions from 0.01° to 1° were used and the resulting regridded columns were compared in situ passive monitor results from the BAQS-met campaign (Fig. C.1). Most averaging resolutions provided similar correlation coefficients (Pearson’s R) so the common value from the literature, 0.1° was used.
Figure C.1: Spatial correlation of OMI data with passive monitors vs. Regrid spacing. For this comparison, full-campaign average in situ passive sampling concentrations at each location were compared to full-campaign average OMI column density.
Appendix D

Surface/column comparisons at MoE stations
Figure D.1: Long term surface monthly-average NO$_2$ and OMI NO$_2$ columns measurements at several Southern Ontario MoE monitoring stations. To obtain columns, bottom decile (representing free-tropospheric contribution) from each overpass was subtracted.
Appendix D. Surface/column comparisons at MoE stations

Figure D.1 (continued)
Figure D.1 (continued)
Appendix E

Toronto Characteristic Height Graphs
Appendix E. Toronto Characteristic Height Graphs

Figure E.1: Ontario Ministry of the Environment Toronto permanent monitoring location long-term characteristic height timeseries.

Figure E.2: Ontario Ministry of the Environment Toronto permanent monitoring location long-term characteristic height seasonal averages from December, 2004 to November 2008. Boxes represent mean ± standard deviation while whiskers represent min and max values.
Appendix F

Beijing Olympic Passive Campaign Data

During weeks and months leading up to the Beijing Olympics, the Chinese government imposed driving restrictions in order to improve air quality in Beijing during the Olympic Games. A number of in situ passive monitors were placed for periods between 4 and 10 days (Fig. F.1). This data was used in the development of the inference process presented by this thesis. The most interesting observation provided by this extra data was that the relationship between column and surface concentration appears to remain stable between the two cities (Fig. F.2). A linear regression revealed a slope of 0.24 ppb/1 × 10^{15}molec·cm^{-2} which corresponds with a characteristic height of 1800 m.

It should be noted that this is somewhat different than the characteristic heights found in section 5.2.1 because the best fit line allows for an offset. If the offset in figure F.2 is forced to zero, the slope becomes 0.43 ppb/1 × 10^{15}molec·cm^{-2} which corresponds to a characteristic height of 850 m which is closer to the values reported for the Windsor region. When only the BAQS-met passives are considered and no offset is allowed, the slope increases even further to 0.66 ppb/1 × 10^{15}molec·cm^{-2} which provides a characteristic height of 600 m.
Figure F.1: Beijing Satellite and Passive NO₂. Map colours correspond to OMI average column densities, in $10^{15}$ molec cm$^{-2}$. Dots represent passive monitor campaign averages, in ppb.
Figure F.2: BAQS-met and Beijing passive NO2 vs OMI NO2. Full-campaign averages for each sampling site for the BAQS-met campaign (2007) and the Beijing Olympics campaign (2008). It is important to note the two Beijing outliers. These points represent monitors which were placed very near to major Beijing highways, one of them at a junction between two major highways. With these monitors, for the total set of passive data from BAQS-met and Beijing, correlation $R$ was 0.78. Excluding the outliers, $R = 0.85$. 

$R = 0.78$
$y = 0.24 x + 3.74$