MEASUREMENT OF NITROGEN DIOXIDE AND SULFUR DIOXIDE BY SATELLITE AND PASSIVE MONITORS IN NORTHEASTERN BRITISH COLUMBIA, CANADA

By

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Abstract

The Peace River district of Northeastern British Columbia (B.C.) Canada is a region of natural gas production that has undergone rapid development since 2005. Both satellite data products and Willems badge passive sampler measurements of nitrogen dioxide (NO$_2$) and sulfur dioxide (SO$_2$) were used to assess the air quality implications from gas development activities. Both satellite data products between 2005 and 2013 and Willems badge passive samplers during six two-week exposure periods between August and November, 2013 have been considered in this study. All satellite data products and passive monitoring of these two pollutants in Northeastern B.C. found higher values in Taylor, Fort St. John, and Dawson Creek. This spatial distribution of higher values has resulted from the large gas development activities in these areas. The temporal analysis of satellite NO$_2$ data revealed higher values near Dawson Creek after 2007 with annual increment of 1.7%. It was also found that Taylor is half as polluted as one of the Canada’s largest non-urban SO$_2$ emission source areas (Canadian oil sands area in Alberta).
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1. Study Rationale and Research Questions

1.1. Background

In 2012, the total production of natural gas in British Columbia (B.C.) was $40,482 \times 10^6$ m$^3$ (oil was $1,222 \times 10^6$ m$^3$) with total estimated reserves (proven plus probable recoverable) of $1,138 \times 10^9$ m$^3$ (oil was $19,108 \times 10^6$ m$^3$) which is a 146% increase over the natural gas reserves estimated in 2006 (OGC, 2012). The exploitation of these vast reserves of natural gas is a significant economic driver and revenue generator in the province, and as such, the B.C. provincial government is planning on expanding this industry by promoting development of liquefied natural gas (LNG) for export (MEM, 2012). This trend of increasing reserve estimates is largely due to the successful development of unconventional gas extraction including the application of horizontal drilling and hydraulic fracturing technology, which commenced extensively in 2007/2008. Most of this development has been in the Montney formation and the Horn River Basin of Northeastern B.C. (Fig. 2.1 and 2.2) and currently accounts for 60% of B.C.'s total natural gas production (OGC, 2012). It is also expected that natural gas from unconventional sources will continue to increase while conventional pools will be depleted in the next few years (OGC, 2012). The Montney formation is an unconventional Lower Triassic aged formation that includes dry, liquid rich gas and oil in over-pressured siltstones that stretches over 200 km from the B.C. – Alberta border near Dawson Creek to the B.C. foothills of the Rocky Mountains. Recently, the US EPA estimated that uncontrolled venting from guarding against over-pressuring wells during well completions involving hydraulic fracturing can vent approximately 230 times more natural gas to the atmosphere than wells without hydraulic fracturing (conventional well drilling) resulting in significant air pollution (US EPA, 2011). People who lived within half a
miles of the unconventional wells had a greater risk of developing non-cancer health effects from short-term exposure to the high emissions of hydrocarbons than those living further away (McKenzie et al., 2012).

1.2. Rationale of the Study

Concerns have arisen recently in Northeastern B.C. about increasing air pollution as a result of accelerating natural gas production (Fraser Basin Council, 2013; Krzyzanowski, 2012; MoE, 2014) without the simultaneous implementation of available technological advances to control emissions (Krzyzanowski, 2009). According to the 2010 emissions data reported to Canada’s National Pollutant Release Inventory (NPRI, http://www.ec.gc.ca/pdb/websol/querysite/query_e.cfm), sulfur dioxide (SO\textsubscript{2}) and nitrogen dioxide (NO\textsubscript{2}) are the dominant species among all gaseous air pollutants in Northeastern B.C. and are emitted from various stages of oil and gas activities, mostly during the production phase such as processing (e.g., flares, engines, and compressors), distribution (e.g., leaks of pipelines and flanges), and from storage tanks (e.g., vaporization) (Krzyzanowski, 2012). Once these two gaseous species enter the atmosphere they undergo chemical and/or physical reactions which will subsequently contribute to the acidic deposition in terrestrial ecosystem through both dry- and wet-deposition (Cox, 2003). These chemical compounds may impact on human health through a number of environmental pathways including air, water, and soil or through multiple pathways (Krzyzanowski, 2012). Although these two species have a deleterious impact on the environment, only four permanent SO\textsubscript{2} monitors have been installed in the previous 15 years and there has been no monitoring of NO\textsubscript{2} (MoE, 2014), which is considered insufficient by the Fraser Basin Council (2013) in the context of recent unconventional gas development in the Montney formation. The location of these four SO\textsubscript{2}
monitors include: Pine River Hasler and Pine River Gas Plant near Chetwynd, Taylor Townsite and Taylor South Hill near Taylor. Furthermore, communities in Northeastern B.C. are dissatisfied by what they consider as insufficient information, from both the government and the oil and gas sector, and the communities are also concerned with the perception of a lack of transparency with respect to specific oil and gas activities (Fraser Basin Council, 2013). Therefore, rigorous investigation and regulations are required for baseline assessments of air quality and adequate communication with the public should be conducted prior to oil and gas resource development activities.

Recently it has been suggested from the satellite observations of NO$_2$ and SO$_2$ over the Canadian oil sands in Alberta (McLinden et al., 2012 and 2014) and space-based ambient ground-level concentrations of NO$_2$ (inferred from VCDs and model-simulated vertical profiles) in North America (Lamsal et al., 2008) that satellite observations would be an alternative and complementary to surface based measurements in Northeastern B.C. where in-situ monitoring stations are limited or sparsely distributed. Therefore, the overall purpose of this study is to assess air quality between 2005 and 2013 using satellite remote sensing observations of NO$_2$ and SO$_2$ over portions of Northeastern B.C. that are undergoing a rapid expansion in natural gas production. A fieldwork campaign with NO$_2$ and SO$_2$ passive samplers was also carried out in order to indirectly validate the remotely-sensed air quality data. It is important to note that direct comparisons between VCDs and in-situ measurements are difficult (McLinden et al. 2012) due to pixel-based (horizontally averaged) VCDs which are vertically integrated column values assigned in the pixel center as the VCD of one pixel (the smallest area of one pixel among all current satellite data products is 312 km$^2$) while in-situ measurements are point observations at ground level. To date, there has been no
systematic study of the satellite and passive monitoring measurement of NO₂ and SO₂ in Northeastern B.C.

1.3. Objectives and Research Questions

The primary objective of this research is to use satellite-based tropospheric observations to analyze the air quality in Northeastern B.C. with particular focus on NO₂ and SO₂. The spatial and temporal distribution of satellite observations over Northeastern B.C. will also provide information on changes in air quality associated with oil and gas development activities. The three months field study in 2013, using passive monitors and available in-situ monitoring station information, will allow for an indirect validation of the satellite observations. In addition, this study will provide the necessary scope to do a comparative analysis of Northeastern B.C. with other known polluted areas such as Canadian oil sands in Alberta. Specific questions addressed in this thesis include:

1) What are the levels of these pollutants in this region?

2) Are the trends in satellite air quality observations between 2005 and 2013 related to the increased trends in oil and gas development activities in this region?

3) How do these pollutants vary spatially and temporally?

4) Are satellite observations of NO₂ and SO₂ from different data products consistent?

This analysis uses several NO₂ satellite data products (VCDs) including the OMI (Ozone Monitoring Instrument), SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY) and the GOME-2 (Global Ozone Monitoring Experiment-2). The OMI data products produced from different algorithms (e.g., NASA standard product,
DOMINO [Dutch OMI NO$_2$] data products, and EC [Environment Canada] data products) have been tested. Only the NASA OMI data products have been used for SO$_2$ analysis between 2005 and 2013. In addition to VCDs, air quality of Northeastern B.C. was analyzed using space-based ambient concentration of NO$_2$ in conjunction with a model-simulated (GEM-MACH: The Global Environmental Multi Scale Modeling- Air Quality and Chemistry) surface concentrations. Besides the pixel measurements, point observations were also analyzed using Willems badge passive measurements of NO$_2$ and SO$_2$ (August – November, 2013) along with SO$_2$ data from several in-situ monitoring stations.

1.4. Layout of the Thesis

This thesis involves two main components: 1) satellite observations of NO$_2$ and SO$_2$ over Northeastern B.C., Canada (Chapter three); and 2) passive monitoring of NO$_2$ and SO$_2$ over Northeastern B.C., Canada (Chapter four). The satellite and model investigation using data between 2005 and 2013 aims to address all the research questions of this current study, while the short term passive monitoring analysis also investigates this area separately with particular focus on research question 1 and partially the question 3 (spatial distribution of NO$_2$ and SO$_2$). Each of the two main components has been written in manuscript format with the intention of submitting each chapter to a suitable journal for publication. Each manuscript contains an abstract, introduction, and conclusion along with presenting data and methods involved in each component and providing results with discussions for each section separately. A reference list for each component is also provided at the end of each manuscript.

Chapter two provides a background literature review regarding the satellite observations and passive monitoring for the air quality study. A brief overview of oil and gas activities in
Northeastern B.C., with a particular focus on the unconventional Montney formation, is also provided. In addition, a detailed discussion of all the methods associated with the analysis of satellite data and passive monitoring have also been included in chapter two. Chapter five provides a summary of all of results and a conclusion that can partially answer all of the research questions. Some recommendations for future work are also included at the end of this chapter. The author of the present thesis is the principal investigator and the first author of the two main chapters (three and four) as well as all other parts of this thesis.
1.5. References

Cox, R.M., 2003. The use of passive sampling to monitor forest exposure to O₃, NO₂ and SO₂: a review and some case studies. Environmental Pollution 126, 301-311.


2. Literature Review and Methodology

2.1. Introduction

This chapter consists of two main sections: 1) a literature review; and 2) an overview of the methodology. The literature review section introduces the topic of natural gas development in Northeastern B.C. with a particular focus on gas reserves in the Montney formation. The air quality aspects of these extensive gas development activities are briefly discussed followed by a short theoretical background of satellite remote sensing of tropospheric trace gases and passive monitoring of ambient air quality. The methods section describes how the NO\textsubscript{2} and SO\textsubscript{2} data were collected and processed prior to analysis for the study area.

2.2. Literature review

2.2.1. Natural gas development in Northeastern B.C.

The BC Oil and Gas Commission (OGC), established in 1998, is the B.C. provincial single-window regulatory agency with responsibilities for fair regulation of oil and gas development activities (e.g., geophysical exploration, well drilling, pipelines, and gas processing) in B.C. The services the OGC provide include reviewing applications for industry activity and equitable participation in production, confirming industry complies with provincial legislation and all regulatory requirements, coordinating with partner agencies, consulting with First Nations, public safety, and protecting the environment (OGC, 2012a). Although this is the single-window regulatory agency, it has become relatively less independent since 2002 as the provincial government appointed the Deputy Minister of Energy and Mines to the position of chair and director of the commission. This gives the Deputy Minister the power of casting a vote in case of a tie and this casting vote is cause for concern because environmental approvals will be decided by the chair of the commission whose Ministry’s
(Ministry of Energy and Mines) first objective is to increase investment in energy and mineral resource development in B.C. (WCEL, 2003). Prior to 2002, environmental approvals were issued by the Ministry of Environment and then by a neutral commission (OGC). The development of natural gas activities was fairly consistent from 1992 to 2003 followed by a significant expansion in development of natural gas activities (OGC, 2012a). During the first couple of years of the expansion period the production was dominated by conventional wells (located in the B.C. part of large Western Canadian Sedimentary Basin which extends from southwestern Manitoba, southern Saskatchewan, Alberta, Northeastern B.C. and the southwest corner of the Northwest Territories) with only 20% of B.C.'s total production coming from the unconventional (horizontal drilling and multi-stage hydraulic fracturing) Jean Marie and Deep Basin (DB) Cadomin drilling (Fig. 2.1b) (OGC, 2012a). Contributions from conventional sources declined at 8% per year with minimal drilling occurring in 2012. In contrast, the development of the unconventional Montney and Horn River regional plays has been increasing dramatically since its commencement in 2007/2008 (OGC, 2012a).

The Montney formation is an unconventional Lower Triassic aged formation that includes dry, liquid rich gas in over-pressured siltstones (alternatively known as tight gas) that stretches northwest 200 km from the B.C. – Alberta border near Dawson Creek to the B.C. foothills of the Rocky Mountains (Fig. 2.2b). The unconventional mid-Devonian aged Horn River Basin is a shale play with dry gas over-pressured shale (alternatively known as shale gas) of the Muskwa, Otter Park and Evie Formations near Fort Nelson in Northeastern B.C. (Fig. 2.1a). The areal extent of the Montney formation in B.C. is approximately 29,850 km² (Fig. 2.2b) (OGC, 2012a) while the total area, including Alberta, is 130,000 km² (Fig. 2.2a)
(NEB, 2013). Although the total area in B.C. is small, the Montney formation’s most marketable unconventional gas resources are located in this province. This is due to the natural gas having a lower content of natural gas liquid (NGL) and oil (natural gas with lower content of NGL is generally known as dry gas) which makes it economically viable in the largely siltstone dominant geologic formation with poor porosity and ultralow permeability. This is in contrast to the more porous sandstone deposited to the east (Fig. 2.2a and b) (NEB, 2013). Low porosity and ultralow permeability within a formation (this combined feature alternatively known as tight formation) also reduces the effectiveness of the conventional well log (OGC, 2012b). In contrast, the unconventional horizontal drilling with multistage hydraulic fracturing directs pressurized fluids, typically containing any combination of water, proponent, and other chemicals, to penetrate tight rock formations in order to release the oil and gas which requires high rate of pumping and extended flow back to withdraw fracture fluids and solids.

The Montney formation in B.C. is subdivided into two main regional fields: the Heritage Field (south) and the Northern Montney Field (north) (Fig. 2.2b). The Heritage Field covers a large area (561,120 ha) with favorable conditions of reservoir parameters (e.g., porosity, permeability and pressure) for gas withdrawal, while the withdrawal of gas in the Northern Field is complicated due to the presence of a disturbed belt in the Northern Rockies (OGC, 2012a). Consequently, much of the new gas development activities are occurring in the south field which is approximately bounded from 55°N to 57°N and the Alberta border to 122°W encompassing the towns of Fort St. John, Taylor, Dawson Creek and Chetwynd (MoE, 2014). Unconventional gas production accounts for 60% of B.C.’s total production in 2012 (1.41 trillion cubic feet [tcf]) and the Montney formation contributed 40% of the
unconventional gas produced from its 1,270 wells which represent 33% of the province's total remaining recoverable raw gas reserves at the end of 2012 (40.2 tcf) (OGC, 2012a). Total production of natural gas in 2012 is approximately 45% higher than the production in 2005 (OGC, 2012). The total estimated prospective raw natural gas resource in the Montney formation is 1,965 tcf and the estimated marketable reserve is 271 tcf in B.C. while the prospective raw and estimated marketable Montney reserve in Alberta is 2,309 and 178 tcf, respectively. This total estimated marketable 271 tcf in B.C. is equivalent to 87 years of Canada's 2012 consumption (total Canadian natural gas demand in 2012 was 3.1 tcf) (NEB, 2013). The exploitation of these vast reserves of natural gas is a significant economic driver and revenue generator in B.C., and the province is planning to expand this industry by promoting development of liquefied natural gas (LNG) for export. It is estimated that 3 tcf per year will be produced for meeting three LNG facility development goals by 2020 (MEM, 2012).

2.2.1.1. Air quality aspects of gas development activities

Raw natural gas in the B.C. Montney formation is comprised of dry and wet (rich) gas, therefore, it is necessary to process the raw gas for the removal of impurities other than methane (such as: paraffinic hydrocarbons, nitrogen, carbon dioxide, hydrogen sulfide-H2S, helium) prior to supplying the pipeline as a marketable gas with specific grade for use in domestic, commercial or industrial purposes (OGC, 2012a). Two major gas processing plants (the Dawson processing plant in 16 km west of Dawson Creek and the McMahon gas plant in Taylor) are located in the Heritage Field (Fig. 2.2b) to process the raw natural gas generated in this field. The CO2 and H2S from the raw gas processed in the Dawson processing plant is blended and transported for further processing through a pipeline to the McMahon gas plant.
Previous research has shown that SO$_2$ and NO$_2$ are the dominant species among all gaseous air pollutants in Northeastern B.C. and these pollutants are emitted from the various stages of oil and gas production including the processing (e.g., flares, engines, and compressors), distribution (e.g., leaks of pipelines and flanges), and storage (e.g., vaporization from storage tanks) (Krzyszanowski, 2012). Besides this, unconventional natural gas development consists of two main phases: well development and production, and individual well development involves three stages: pad preparation, well drilling and well completion (US EPA, 2010). Recently, the US EPA estimated that well completions involving hydraulic fracturing in uncontrolled manner can vent natural gas to the atmosphere resulting in air pollution. This is done to guard against the over-pressuring of the well which results in approximately 230 times more natural gas being vented compared to wells without hydraulic fracturing (conventional well drilling) (US EPA, 2011). However, oil and gas industries are not required to report to the emissions during the well development phase (e.g., in pilot phase or in exploration or drilling phase) to the National Pollution Release Inventory (NPRI) (http://ec.gc.ca/inrp-npri/default.asp?lang=En&n=02C767B3-C9FD-4DD7-8072, accessed on: 19 September 2014).
Fig. 2.1. The study area. (a) Unconventional gas play trends in Northeastern B.C. (modified after OGC, (2012a)). White squares refer to towns. (b) Overall gas production in B.C. from both conventional and unconventional wells (modified after OGC, (2012a)), (c) Conventional oil and gas wells in 2012 in Northeastern B.C. (source: NPRI database, available at http://www.ec.gc.ca/npri-npri/default.asp?lang=en&n=1D892B9F-1, accessed on: 20 September 2014), however, an unconventional wells distribution map is not currently available in the NPRI database, and (d) Passive sampling sites in the study area. Red squares refer to the major towns across the study area. The passive monitoring network with major towns is also presented in Fig. 2.3.
Fig. 2.2. The location of the Montney formation in B.C. and Alberta. (a) Montney formation with major rock types in B.C. and Alberta (adapted from NEB, (2013)), (b) Montney regional fields in B.C. with dry, rich (wet) and oil distribution (adapted from OGC, 2012a).

2.2.2. Satellite remote sensing of trace gases in the troposphere

Lower tropospheric pollutant observations from satellite began with the GOME-1 instrument (Global Ozone Monitoring Experiment, 1996-2003) aboard the ERS-2 satellite (Burrows et al., 1999) and has continued with SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY, 2002-2012) aboard the ENVISAT satellite (Bovensmann et al., 1999). Currently these measurements are made by the OMI (Ozone Monitoring Instrument, 2004-present) on the Aura satellite (Levelt et al., 2006) and the operational GOME-2 (2007-present) on the MetOP platform (Martin, 2008). The basic characteristics of these instruments are listed in Table 2.1. The satellites have been designed
to yield information on the lower tropospheric trace gas constituents by flying in near-polar, Sun-synchronous, low earth orbits; a typical orbit altitude is 705 km (Martin 2008). These trace gas constituents (e.g., NO$_2$ and SO$_2$), are processed as vertical column densities (VCDs) from an integrated column amount by measuring solar back-scattered UV-visible radiation commonly in nadir (down looking) geometry by these instruments. The determination of tropospheric VCDs from the calibrated spectra involves three main steps (Boersma et al., 2007): 1) a spectral fit to determine the slant columns densities (SCD), 2) elimination of the stratospheric contribution to the SCD; and 3) conversion of tropospheric SCD to tropospheric VCDs via an air mass factor (AMF), where the AMF accounts for the sensitivity of the instrument to the absorber (target species, such as: NO$_2$ and SO$_2$) (McLinden et al., 2014). The AMF describes the enhancement in absorption when light traverses a slant path through a layer and, therefore, it represents a basis of trace gas retrievals in the spectrum of UV-visible wavelengths. It is important to note that the AMF is the ratio of the SCD to the VCD and it is computed using a radiative transfer model because of the complex path of the scattered and reflected sunlight. The radiative transfer model simulates nadir radiances while accounting for all relevant physical factors such as: multiple scattering by molecules and aerosols, absorption by trace gases and reflection from the surface. The accuracy of the AMF calculation is largely governed by the accurate information of the absorber vertical profile including cloud and aerosol information, surface reflectivity and surface pressure (McLinden et al., 2014). The NASA OMI SO$_2$ product uses a spatially and temporally invariant AMF and it is 0.36.

These three sensors (SCIAMACHY, OMI, and GOME-2) differ in their horizontal resolution of each observation (pixel) and among these, OMI is finer (Table 2.1). However, unlike the
others, OMI’s across-track resolution varies noticeably due to its 2-D detector which can measure 60 across-track pixels simultaneously. Consequently, those pixels near the nadir are roughly 30 km wide (across track width) while pixels near the edge are larger than 100 km, however, the along track width of each OMI pixel is invariant (13km). Some pixels of OMI data products are affected by the “row anomaly” (RA) error which is an anomaly that affects the quality of the radiance data within a row of detectors (primary data that is collected by the instrument) at all wavelengths for a particular viewing direction of OMI (http://www.knmi.nl/omi/research/product/rowanomaly-background.php). The RA changes over time affecting radiance data and consequently impacting on the VCDs (OMI User’s Guide, 2012). The first RA occurred in June 2007, however, the origin of the RA remains unclear. The OMI team identified four probable reasons for the RA: 1) part of the incoming earthlight is blocked; 2) inhomogeneous illumination that causes a shifting of wavelength; 3) stray sun light is reflected into the field-of-view; and 4) stray earthshine is reflected into the field-of-view (Boersma et al. 2011a). Moreover, Boersma et al. (2011a) reported that various RA correction algorithms have been developed since the first occurrence but to date no correction algorithm works with reasonable agreement that effectively removes the anomalies. Therefore, the OMI team recommends that researchers not use the affected cross-track scenes; Table 2.2 lists the affected scenes to date.

Generally, all the satellite data products for both NO₂ and SO₂ offer the possibility to improve our understandings of lower tropospheric trace gas concentrations (Lamsal et al., 2008 and 2013; Lee et al., 2011), as well as helping with identification of emission sources (Fioletov et al., 2011 and 2013; Lu and Streets, 2012; Martin et al., 2003), and atmospheric
chemistry, through testing and improvements to emission inventories, using top-down
modeling techniques (Boersma et al., 2008).

Table 2.1. Basic characteristics of space-borne instruments (Adapted from Lu and Streets, 2012).

<table>
<thead>
<tr>
<th>Instrument</th>
<th>GOME</th>
<th>SCIAMACHY</th>
<th>OMI</th>
<th>GOME-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Satellite</td>
<td>ERS-2</td>
<td>Envisat</td>
<td>EOS-Aura</td>
<td>Metop-A</td>
</tr>
<tr>
<td>Agency</td>
<td>ESA</td>
<td>ESA</td>
<td>NASA</td>
<td>EUMETSAT/ESA</td>
</tr>
<tr>
<td>Type</td>
<td>Sun-synchronous</td>
<td>Sun-synchronous</td>
<td>Sun-synchronous</td>
<td>Sun-synchronous</td>
</tr>
<tr>
<td>Altitude</td>
<td>782 km</td>
<td>782 km</td>
<td>705 km</td>
<td>840 km</td>
</tr>
<tr>
<td>Time for one orbit</td>
<td>100.5 mins</td>
<td>100.5 mins</td>
<td>98.8 mins</td>
<td>101.7 mins</td>
</tr>
<tr>
<td>Inclination</td>
<td>98.52°</td>
<td>98.52°</td>
<td>98.2°</td>
<td>98.8°</td>
</tr>
<tr>
<td>Repeat time</td>
<td>35 days</td>
<td>35 days</td>
<td>16 days</td>
<td>5 days</td>
</tr>
<tr>
<td>Ascending or Descending</td>
<td>Descending</td>
<td>Descending</td>
<td>Ascending</td>
<td>Descending</td>
</tr>
<tr>
<td>Local equator overpass time</td>
<td>10:30</td>
<td>10:00</td>
<td>13:30</td>
<td>9:30</td>
</tr>
<tr>
<td>Spatial resolution</td>
<td>40×320 km²</td>
<td>30×60 km²</td>
<td>13×24 km²</td>
<td>40×80 km²</td>
</tr>
<tr>
<td>Global coverage time</td>
<td>3 days</td>
<td>6 days</td>
<td>1 day</td>
<td>1.5 days</td>
</tr>
</tbody>
</table>

Table 2.2. Cross-track raw anomalies (adapted from Boersma et al. 2011a).

<table>
<thead>
<tr>
<th>Anomaly</th>
<th>Date since its occurrence</th>
<th>Affected cross-track positions (0-based)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anomaly 1</td>
<td>Since June 25th, 2007</td>
<td>53-54</td>
</tr>
<tr>
<td>Anomaly 2</td>
<td>Since May 11th, 2008</td>
<td>37-44</td>
</tr>
<tr>
<td>Anomaly 3</td>
<td>Since January 24th, 2009</td>
<td>27-44</td>
</tr>
<tr>
<td>Anomaly 4</td>
<td>Since July 5th, 2011</td>
<td>42-45</td>
</tr>
<tr>
<td>Anomaly 5</td>
<td>Since August 9, 2011</td>
<td>41-45</td>
</tr>
</tbody>
</table>

2.2.3. Global Environmental Multi-scale – Modelling Air Quality and Chemistry (GEM-MACH) model

This section is synthesized from Anselmo et al. (2010). GEM-MACH, established by Environment Canada (EC) in November 2009, is the Canadian regional comprehensive air quality on-line model. This model is used operationally for forecasting the concentration of O₃, NO₂, and PM₂.₅ as well as a full description of atmospheric chemistry (including gas-phase, aqueous-phase, aerosol processes, and heterogeneous chemistry) and meteorological processes. GEM-MACH is currently integrated twice per day to provide 48-hour forecast on a 348×465 rotated latitude-longitude grid over North America with 15-km horizontal grid spacing (also known as GEM-MACH15) in 58 vertical levels extend from the surface to 0.1 hPa. This model uses the emissions inventory of the US EPA and EC to assess the source of
tropospheric ozone precursors. However, time-dependent meteorological lateral boundary conditions (LBCs) are taken from GEM15 which is the EC operational weather forecast model with a variable-resolution in global scale but found uniform 15-km grid spacing centered over North America. The chemistry fields of GEM-MACH are initialized by cycling the 12-h forecast of the previous model run. The time step for the integration of the chemical processes by the GEM-MACH is 15.0 minutes and meteorology is integrated with a 7.5 minutes time step, therefore, chemical processes have been integrated every second time step (i.e., 15 minutes) for the sake of reducing the model run time. No significant chemical degradation has been found in the chemistry forecast with this modification. Recently, McLinden et al. (2014) used the GEM-MACH output as a source of profile information for updating the AMF of OMI NO$_2$ and SO$_2$ data products over the Canadian oil sands area and they also reported that 15-km grid size of GEM-MACH was well suited for the OMI small pixels (across track width ~30km), therefore, no additional smoothing was applied.

2.2.4. Passive monitoring of air quality

Passive diffusive samplers have been widely used across North America and Europe for the assessment of atmospheric NO$_2$ and SO$_2$ concentrations (e.g., Bytnerowicz et al., 2010; Campos et al., 2010; Vardoulakis et al., 2009; Zbieranowski and Aherne, 2012a). Passive diffusion samplers can be broadly classified into tube, radial, badge and cartridge-type samplers (Krupa and Legge, 2000) and these samplers can have substantially different uptake rates, which make them more or less suitable to certain applications (Yu et al., 2008). For example, tube-type samplers have generally lower uptake rates due to longer axial diffusion path and smaller cross-sectional diffusion area, which makes them suitable for assessing relatively long-term (e.g., monthly mean) ambient air quality levels. In contrast, the badge-
type and radial samplers have typically higher uptake rates due to the shorter diffusion paths and larger diffusion areas and are suitable for assessing the relatively short-term (e.g., daily mean) personal/occupational exposure to air pollution (Vardoulakis et al., 2009). Furthermore, badge-type samplers are advantageous over tube-type since they have an entrance filter to create a diffusion area free from turbulence to avoid wind effects (Van Reeuwijk et al., 1998). The basic principle behind all the passive sampler measurements is Fick's law of diffusion of gases from the atmosphere into a sampler of defined dimensions onto an absorbing medium. The sampler's theoretical uptake rate is a function of the length, L (m), and the cross-sectional area, A (m²), of the stationary air layer within the sampler, and can be calculated provided that the diffusion coefficient, D (m²s⁻¹), of the gas of interest is known. In particular, tube and badge type passive samplers are used extensively to measure atmospheric NO₂ (Tang et al., 2001). The advantages of diffusive passive samplers include that they are inexpensive, easy to deploy and use in the field for long term assessments, do not require power, produce accurate results in both indoor and outdoor environments, and are reliable for monitoring ecosystem exposure to gaseous pollution (Cox, 2003; Hafkenscheid et al., 2009; Kot-Wasik et al., 2007; Namieśnik et al., 2005; Seethapathy et al., 2008; Zbieranowski and Aherne, 2012a and 2012b). However, passive samplers have some problems associated with the variability in environmental factors (e.g., temperature, relative humidity, wind, and rain), unsuitability for short term monitoring, and need to be validated with collocated continuous active monitors (Cox, 2003; Kot-Wasik et al., 2007; Krupa and Legge, 2000; Runeckles and Bowen, 1999; Seethapathy et al., 2008).
2.3. Methodology

2.3.1. Study area

Northeast B.C. is a region of plains, bordered by the Yukon and Northwest Territories to the north, the Rocky Mountains to the southwest and the province of Alberta to the east. It is the largest of B.C.'s ecological regions, representing 21.8% of the land area of the province (20,494,470 ha), but the least populated, with 1.6% of the total population (69,000 people). Of those residing there, approximately 13% self-identify to be of aboriginal (i.e., First Nations) descent. The Northeast region has one of the most active economies in B.C. which is mainly driven by oil and gas exploration and production. Due to this, the population of the northeast is expected to rise to almost 80,000 by 2030 (http://www.welcomebc.ca/Live/about-bc/regions/northeast.aspx). There are extreme differences in temperature between the warmest and coldest months of the year, in some areas, for example in Fort St. John, the average daily temperature can range from -21 °C in January to +14 °C in July. Major communities include Fort St. John, Fort Nelson, Taylor, Dawson Creek, Chetwynd and Hudson’s Hope. Due to the increase in natural gas development activities and the public concern about air quality in Northeastern B.C. this area analyzed in the present study covers the Heritage Field of the B.C. unconventional Montney formation (Fig. 2.1d, 2.2b, and also Fig. 2.3). This area is approximately bounded from 55°N to 57°N and the Alberta border to 122°W, which roughly encompasses Fort St. John, Taylor, Dawson Creek and Chetwynd. Therefore, this present study area covers not only the major gas development area but also most of the major communities of Northeastern B.C.
2.3.2. Satellite data products

In this analysis, NO\(_2\) data from three instruments (SCIAMACHY, OMI and GOME-2) from 2005-2013 were considered for analysis. While multiple OMI NO\(_2\) VCD data products currently exist, the two global primary products from the NASA standard product (SP) (Bucsela et al., 2013; http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/omno2_v003.shtml) and the Dutch OMI NO\(_2\) (DOMINO) (Boersma et al., 2011b; http://www.temis.nl/airpollution/no2.html) processed in near real time have been included in the analysis. The reason for two OMI NO\(_2\) data products in this analysis is to understand the differences in NO\(_2\) VCDs for the study area that arise from different algorithms used to eliminate the stratospheric SCD. The DOMINO product simulates the stratospheric NO\(_2\) by assimilating OMI SCDs in a chemical data assimilation system, whereas the SP executes a complex high-pass filtering approach (Dirksen et al., 2011). In addition, the algorithm of the SP product depends on monthly mean profiles from the Global Modeling Initiative (GMI) (Bucsela et al., 2013) while DOMINO uses daily output from the Tracer Model 4 (TM4) chemical transport model (Boersma et al., 2007). However, both of these models make use of emission inventories appropriate for the late 1990s (McLinden et al., 2014), when oil and gas activities in Northeastern B.C. were significantly lower than the current level. Accurate absorption profiles of trace gases (e.g., NO\(_2\)) substantially govern the accuracy of the AMF calculation, and the AMF plays a fundamental role in determining tropospheric VCDs from SCDs. Therefore, McLinden et al. (2014) recently recalculated the AMF (known as EC-AMF) for North America based on an updated and higher resolution absorption profile from a regional-scale (15 km × 15 km resolution) air quality model (the Global Environmental Multi-scale – Modeling Air Quality and Chemistry, GEM-MACH;
Anselmo et al., 2010) using emission inventories from the US EPA and EC data for 2006, high spatial and temporal surface reflectivity data, and an improved treatment of snow. Finally, two new OMI NO$_2$ data products from the tropospheric SCDs of SP and DOMINO divided by the EC-AMFs instead of the original AMFs have been created by the EC (McLinden et al., 2014) and these new data products (VCDs), EC-SP-NO$_2$ and EC-DOMINO-NO$_2$, were included in this analysis. Data from these two new products were collected from EC (Chris McLinden, EC, personal communication, 2014). In addition, NO$_2$ data products of SCIAMACHY between 2005 and 2011 were combined with the GOME-2 data products of 2012-2013 in this analysis (this combined data products named here as SCIA-NO$_2$ for simplicity) and this combination approach (Ghude et al., 2011) has been implemented for the comparison with the OMI data products between 2005 and 2013. The same retrieval techniques were used for NO$_2$ data products for both SCIAMACHY and GOME-2 instruments and the flight time of the satellites carrying these two instruments is almost identical (Table 2.1). Although multiple NO$_2$ data products have been included in this study, analysis of SO$_2$ data (2005-2013) was only limited to the OMI instrument (OMSO2 specific to the planetary boundary layer [PBL], version 3, http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/omso2_v003.shtml, this data product is named hereafter as NASA-SO$_2$ for simplicity). This product is retrieved based on the NASA Band Residual Method (BRM) using four wavelengths between 310 and 315 nm to quantify SO$_2$ absorption (Krotkov et al., 2006).

2.3.2.1. Satellite data filtering

Orbit based level 2 data products, in which the location of an observation is assigned to the co-ordinates of the pixel center, from all these instruments (SCIAMACHY, OMI, and
GOME-2) were used in this study. However, as OMI measures 60 cross-track positions (pixels), which are variable in size depending on the track position, 10 pixels on each swath edge were excluded from analysis to limit the across-track pixel width to ~40 km. In addition, some cross-track positions (Table 2.2), affected by RA since June 2007, were dynamically removed based on the RA flags in all OMI data products for both species. Daily OMI data products were also filtered to remove data with high cloud radiance fraction (>0.2) and large solar zenith angle (SZA), >75° and >60° for NO₂ and SO₂, respectively. The stringent SZA threshold of 75° for NO₂ results in about 75% of the data being allocated for April-September while the remaining 25% is for October-March. However, a 60° SZA threshold for SO₂ keeps 99% data between April and September of each year (McLinden et al., 2014). Surface albedo was limited to <0.3 for both SP and DOMINO data products from OMI. Although year round NO₂ data products from all these instruments were used, following the Fioletov et al. (2011) protocol, only summertime (May-August) NASA-SO₂ data were used, since data from this period have the best signal-to-noise ratio (SNR: the ratio between the mean values and the standard errors of the means). Furthermore, the data were also restricted to values between -10 and +5 DU (1 DU = 2.69 × 10²⁶ molecule/km²) to avoid spikes from transient volcanic plumes.

2.3.2.2. Pixel averaging approach

A pixel-averaging or oversampling approach was applied in this study to analyze the satellite data products of both gas species (Fioletov et al., 2011 and 2013). For this approach, a geographical grid is defined in the study area and the average of all pixels centered within a given radius from each grid point is calculated. For example, a grid of 224 km × 224 km with 1.2 km step and 1215 km × 1215 km with 6.0 km step is established for Northeast B.C. and a
larger regional area (most of B.C. and Alberta), respectively. An average of all valid pixel values of a sensor within a given time window and falling within the specified radius from the center of a grid cell is assigned to that grid point, where the pixel center is used as the location of the measurement. Therefore, this approach provides a detailed subpixel-resolution spatial distribution of mean values of the pollutant (Fioletov et al., 2011 and 2013). It is important to note that, the selection of an averaging radius determines the degree of smoothing; averaging with a large radius reduces the noise, but it also reduces the spatial resolution (Fioletov et al., 2013).

2.3.3. Passive monitoring network

Two-week average ambient concentrations of NO\(_2\) and SO\(_2\) were measured at 24 sites across Northeastern B.C. (Montney formation), Canada (Fig. 2.1d and Fig. 2.3) during the period August 2013-November 2013. The Taylor Town Site and Pine River Hasler, (Fig. 2.3) as well as an additional site in central B.C. (B.C. Environment Plaza 400 monitoring location in Prince George, B.C., Canada) were included in the study as they were part of an established B.C. air quality monitoring network, in order to assess the passive sampler performance. All other sites (Table 2.3) were selected to cover the region of oil and gas development activities in Northeastern B.C. (Fig. 2.1c), which corresponds to the Peace River region of B.C. (Fig. 2.3). All sites were chosen to be free of obstacles impeding wind flow and, with a few exceptions, most sites were also at least 3.0 kilometers from major industrial sources and from urban areas in order to provide a better estimate of the overall spatial pattern of ambient levels by avoiding the local impact of point source emissions (Table 2.3). A few sites were also placed at private homes to assess the ambient concentrations directly relevant to human exposure (Table 2.3).
Fig. 2.3. Study area with the locations of 24 passive monitoring stations (+ symbols). The study domain in northeast B.C. consists of 24 sites; Plaza 400 (in the Prince George air shed, not included in the figure) was selected in order to validate the passive sampler results with continuous monitoring data of NO₂ and SO₂. Besides Plaza 400, Site 14 and Site 16 were also chosen to collocate with continuous monitoring stations; each of these sites measures only SO₂ (except Plaza 400 which also measures NO₂) along with meteorology and data are archived by the B.C. Ministry of the Environment (available at: http://www.bcairquality.ca/readings/index.html). Each of the total of 25 stations are exposed to ambient conditions from 15 Aug. 2013 to mid Nov. 2013 with samplers being exchanged every two weeks (six measurements per site), major towns of the study area are also indicated with red circles. The B.C. - Alberta border is along 120°W longitude.
Table 2.3. Passive sampler deployment site IDs, nearest towns, location (latitude, longitude), elevation, sampling period, and site location description (see also Fig. 2.3).

<table>
<thead>
<tr>
<th>ID</th>
<th>Nearest town</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Elevation</th>
<th>Sampling period</th>
<th>Site description*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Dec. degrees</td>
<td>Dec. degrees</td>
<td>m</td>
<td>dd.mm.yyyy</td>
<td></td>
</tr>
<tr>
<td>F1</td>
<td>Dawson Creek</td>
<td>55.16375</td>
<td>-120.20661</td>
<td>965</td>
<td>17.08.2013-10.11.2013</td>
<td>Open field, near forested area</td>
</tr>
<tr>
<td>F2</td>
<td>Dawson Creek</td>
<td>55.30956</td>
<td>-120.12789</td>
<td>878</td>
<td>17.08.2013-10.11.2013</td>
<td>Open field, near forested area</td>
</tr>
<tr>
<td>F3</td>
<td>Dawson Creek</td>
<td>55.44800</td>
<td>-120.02722</td>
<td>963</td>
<td>17.08.2013-10.11.2013</td>
<td>Open field, 1 Gas plant in 200m</td>
</tr>
<tr>
<td>F4</td>
<td>Dawson Creek</td>
<td>55.54847</td>
<td>-120.10897</td>
<td>757</td>
<td>17.08.2013-10.11.2013</td>
<td>Open field, 3 Gas plants immediate after 5km</td>
</tr>
<tr>
<td>F5</td>
<td>Dawson Creek</td>
<td>55.57211</td>
<td>-120.60486</td>
<td>808</td>
<td>18.08.2013-11.11.2013</td>
<td>Open field, near Heritage Highway, 52</td>
</tr>
<tr>
<td>F6</td>
<td>Dawson Creek</td>
<td>55.85114</td>
<td>-120.37417</td>
<td>769</td>
<td>16.08.2013-10.11.2013</td>
<td>Open field, near agricultural crops</td>
</tr>
<tr>
<td>F7</td>
<td>Chetwynd</td>
<td>55.70142</td>
<td>-120.90508</td>
<td>865</td>
<td>18.08.2013-11.11.2013</td>
<td>Open field, near forested area</td>
</tr>
<tr>
<td>F8</td>
<td>Dawson Creek</td>
<td>55.91244</td>
<td>-120.50594</td>
<td>724</td>
<td>16.08.2013-10.11.2013</td>
<td>Open field, near agricultural crops</td>
</tr>
<tr>
<td>F9</td>
<td>Chetwynd</td>
<td>55.79628</td>
<td>-121.07164</td>
<td>758</td>
<td>18.08.2013-11.11.2013</td>
<td>Open field, near agricultural crops</td>
</tr>
<tr>
<td>F10</td>
<td>Taylor</td>
<td>56.03336</td>
<td>-120.63308</td>
<td>816</td>
<td>16.08.2013-10.11.2013</td>
<td>Private home lawn (open field)</td>
</tr>
<tr>
<td>F11</td>
<td>Chetwynd</td>
<td>55.82294</td>
<td>-121.60242</td>
<td>769</td>
<td>15.08.2013-09.11.2013</td>
<td>Forested area, near Road 29</td>
</tr>
<tr>
<td>F12</td>
<td>Taylor</td>
<td>56.12161</td>
<td>-120.61697</td>
<td>481</td>
<td>16.08.2013-10.11.2013</td>
<td>Private home lawn (open field)</td>
</tr>
<tr>
<td>F13</td>
<td>Fort John</td>
<td>56.28986</td>
<td>-120.10883</td>
<td>764</td>
<td>16.08.2013-10.11.2013</td>
<td>Open field, 3 Gas plants immediate after 5km</td>
</tr>
<tr>
<td>F14</td>
<td>Hudson Hoope</td>
<td>55.89094</td>
<td>-121.90462</td>
<td>735</td>
<td>15.08.2013-09.11.2013</td>
<td>Forested area, near Road 29</td>
</tr>
<tr>
<td>F15</td>
<td>Fort John</td>
<td>56.22453</td>
<td>-120.71636</td>
<td>694</td>
<td>16.08.2013-10.11.2013</td>
<td>Private home lawn (open field)</td>
</tr>
<tr>
<td>F16</td>
<td>Fort John</td>
<td>56.42047</td>
<td>-120.26722</td>
<td>769</td>
<td>16.08.2013-10.11.2013</td>
<td>Open field, near forested area</td>
</tr>
<tr>
<td>F17</td>
<td>Hudson Hoope</td>
<td>56.03253</td>
<td>-121.90086</td>
<td>515</td>
<td>15.08.2013-09.11.2013</td>
<td>Open field, near forested area</td>
</tr>
<tr>
<td>F18</td>
<td>Fort John</td>
<td>56.30503</td>
<td>-120.85406</td>
<td>692</td>
<td>16.08.2013-10.11.2013</td>
<td>Private home lawn (open field)</td>
</tr>
<tr>
<td>F20</td>
<td>Chetwynd</td>
<td>55.69753</td>
<td>-121.61836</td>
<td>627</td>
<td>15.08.2013-09.11.2013</td>
<td>Private home lawn (center of Chetwynd town)</td>
</tr>
<tr>
<td>F21</td>
<td>Chetwynd</td>
<td>55.56164</td>
<td>-122.01369</td>
<td>841</td>
<td>15.08.2013-09.11.2013</td>
<td>Open field, near forested area, 1 gas plant immediate after 3 km</td>
</tr>
<tr>
<td>Site 14*</td>
<td>Taylor</td>
<td>56.13028</td>
<td>-120.68647</td>
<td>513</td>
<td>16.08.2013-10.11.2013</td>
<td>Collocated in Taylor Town Site station, (Center of Taylor town) 2 gas plants in 1.5 km</td>
</tr>
<tr>
<td>Site 16*</td>
<td>Chetwynd</td>
<td>55.60544</td>
<td>-121.97347</td>
<td>635</td>
<td>16.08.2013-10.11.2013</td>
<td>Collocated in Pine River Hasler station, (forested area) 1 gas plant immediate after 3 km</td>
</tr>
<tr>
<td>Indus 1</td>
<td>Dawson Creek</td>
<td>55.95631</td>
<td>-120.15775</td>
<td>688</td>
<td>17.08.2013-11.11.2013</td>
<td>Open field, near agricultural crops, 2 gas plants immediate after 3 km</td>
</tr>
<tr>
<td>Indus 2</td>
<td>Dawson Creek</td>
<td>55.79222</td>
<td>-120.48333</td>
<td>809</td>
<td>18.08.2013-11.11.2013</td>
<td>Open field, near agricultural crops, 2 gas plants immediate after 3 km</td>
</tr>
<tr>
<td>Plaza</td>
<td>Prince George</td>
<td>53.91511</td>
<td>-122.74169</td>
<td>597</td>
<td>12.08.2013-06.11.2013</td>
<td>Collocated in Plaza 400 station, In the Downtown of Prince George, B.C.</td>
</tr>
</tbody>
</table>

Gas plants were identified according to the NPRI database (NPRI, NO2 and SO2 emissions for Canada, 2012, available at: http://www.ec.gc.ca/Ddb/websol/querysite/query_e.cfm).

2.3.3.1. Passive sampler preparation and analysis

The Willems badge diffusive passive samplers (Fig. 2.4a) were provided by the laboratory of Professor Julian Aherne, Trent University, Ontario, Canada. Once the passive samplers were
exposed at the field locations they were returned to Trent University by post (in resealable zip-lock plastic bags packaged in cardboard) for laboratory analysis. Exposed samplers before laboratory analysis and unexposed samplers before deployment were refrigerated at 4°C. Samplers were exposed in triplicate for each species, for a total of six samplers per site. A two-week sampling frequency at a height of 1.8 m was used (except Plaza 400 and Site 16, which were located on the roof-top of a 4 and a 1 storey building, respectively), which corresponds to the height of the active samplers they were collocated with. Each sampler was mounted using Velcro® under a 127 mm diameter plastic cap that acted as a precipitation and bird shield (Fig. 2.4b). There were a total of six exposure periods from August 15, 2013 until November 11, 2013. All NO₂ samplers in the ⁵th exposure period were not considered for analysis due to a problem with sampler preparation. Also, two thirds of all sites during first two exposure periods were monitored for both species with duplicate rather than triplicate passive samplers due to a shortage of samplers. During each exposure period, five unexposed samplers were retained as laboratory blanks. Besides laboratory blanks, travel blanks or lot blanks (for each return shipment from Peterborough, Ontario to Prince George, B.C.) and field blanks (for both species of each exposure) were also sent to and from sample sites periodically throughout the study and compared to laboratory blank samplers to ensure that the sampler cap and resealable bags were effectively protecting the samplers from contamination between preparation, shipment, exposure and analysis.

Analysis of NO₂ and SO₂ data followed the protocol developed by Zbieranowski and Aherne, (2012a and 2012b). The Willems badge passive sampler (Fig. 2.4a) has a cylindrical body (diameter 28 mm and length is 15 mm) in which a specially treated filter paper absorbs a specific gas from the air. A spacer ring separates the absorbent pad (Whatman 1820-090)
from a Teflon® membrane (Whatman 10 411 116) and this creates a stagnant air layer in which diffusion of the desired gas occurs from ambient air onto the absorbent pad. Both the Teflon® membrane and absorbent pad have the same cross-sectional area (5.309 × 10^{-4} \text{ m}^2).

An additional spacer ring holds the assembly together and a cap on the top creates an airtight seal when not sampling. The sampler body, spacer rings and cap of all the samplers were made from polystyrene vials (Greiner 214 111). The samplers were constructed at Trent University, Ontario, Canada to the exact specifications of the original Willems badge sampler for NO\textsubscript{2} (Van Reeuwijk et al., 1998) and the SO\textsubscript{2} sampler was a modified design from Bytnerowicz et al. (2005) (Zbieranowski and Aherne, 2012a and 2012b). Zbieranowski and Aherne (2012a and 2012b) also reported that Willems badge passive sampler has been tested to perform well against co-located active sampling methods. The passive samplers for NO\textsubscript{2} were assembled in a glove box connected to an air hose leading from a filtration pack (NO\textsubscript{2}: PVC tube ID 1 cm, length 80 cm stuffed with glass wool soaked in triethanolamine (TEA) solution). However, SO\textsubscript{2} sampler components were assembled without a filtration system. Before assembly, absorbent pads for NO\textsubscript{2} samplers were cleaned in a bath of Milli-Q water at a temperature of 95° C and then dipped in TEA solution (2 mL of TEA [CAS: 102-71-6] stirred in 48 mL of acetone [CAS: 67-64-1]) and left to dry for 15 min on a ribbed glass plate prior to assembly (Nylasorb filters for SO\textsubscript{2} did not require cleaning and coating as these filters directly absorb SO\textsubscript{2} from air). Teflon membranes for both species (NO\textsubscript{2} and SO\textsubscript{2}) samplers were cleaned in two baths of Milli-Q water and 95% ethanol (50:50, v:v) and a third bath of 95% ethanol; all other sampler components were washed in Milli-Q water. Samplers were capped and sealed inside sealed plastic bags and placed in a cardboard box.
prior to transfer to University of Northern British Columbia (UNBC), B.C., Canada, by post for deployment in the field.

![Diagram of passive sampler components](image_url)

**Fig. 2.4.** a) The 'Willem badge' passive sampler: 1) Velcro® for sampler deployment, 2) sampler body with opening at one end, 3) absorbent pad, 4) spacer ring, 5) Teflon® membrane filter, 6) spacer ring, and 7) cap, (adapted from Zbieranowski and Aherne, 2012a); b) Passive samplers were deployed in the field of this study.

After samplers were transferred to Trent University for analysis, each badge (sampler) was disassembled in a sealed glove box. Then the absorbent pad was placed in a vial containing 5 mL of Milli-Q water, shaken and left for 30 min. A two-times dilution was performed for analysis; 2.5 mL was removed and placed in a vial containing 1 mL of Milli-Q water to which 1.5 mL of reagent was added (total volume 5 mL). The reagent was prepared by 4.0 g of sulphanilamide [CAS: 63-74-1], 10.0 g of tartaric acid [CAS: 87-69-4] and 0.1 g of ethylene-diaminetetra-acetate (EDTA) [CAS: 6381-92-6] dissolved in 800 mL of Milli-Q water to which 0.1 g of N-1-naphthylethylene-diammonium dichloride [CAS: 1465-25-4] and 10 mL of acetone [CAS: 67-64-1] were added and diluted to a total volume of 1000 mL with Milli-Q water. Samples were left in dark conditions for 2-3 h and analyzed using a UV-VIS Spectrometer (Perkin Elmer Lambda XLS) at a wavelength of 540 nm. A standard calibration curve was developed from a set of six sodium nitrite [CAS: 7632-00-0] standards of known nitrite concentration (0.0, 26.6, 132.8, 265.6, 398.4 and 531.2 μg NO₂ L⁻¹).
Nylasorb filters without coatings were placed in the Willems badge samplers as Nylasorb directly absorbs SO\textsubscript{2} from the air. Each badge (sampler) was disassembled after exposure. The filter pad (Nylasorb filter) was placed in a 50 mL falcon tube containing 6 mL of Milli-Q water. The samples were then placed on a shaker table for 30 min after which 5.5 mL of the sample was taken in an IC (Ion Chromatography) vial. Finally, each sample was analyzed on a Dionex ICS-1100 Ion Chromatograph in a carbonate eluent through an IonPac AS22 analytical column.

2.3.3.2. Calculation of ambient concentrations from passive samplers

The calculation of ambient concentrations from passive samplers also follows the protocol developed by Zbieranowski and Aherne, (2012a and 2012b). The quantity of ambient NO\textsubscript{2} and SO\textsubscript{2} sampled on the absorbent pads was determined by subtracting the laboratory blank (n =5 per exposure period) from exposed field samples (n=3 per site per species) with the application of calibration and dilution factors:

\[ Q = (S_f - S_b) \times f \times df \]  

where Q is the total amount of NO\textsubscript{2} and SO\textsubscript{2} sampled (µg), S\textsubscript{f} is the average of the field samples (IC peak concentration [µg L\textsuperscript{-1}] for SO\textsubscript{2} and UV-VIS absorbance for NO\textsubscript{2}), S\textsubscript{b} is the average of the laboratory blanks, f is the calibration factor (slope between peak concentration [IC] or absorbance [UV-VIS] and standard concentration) and df is the dilution factor. The ambient concentration (C, µg m\textsuperscript{-3}) of atmospheric SO\textsubscript{2} was estimated from Q:

\[ C = \text{slope} \times \left(\frac{Q}{t}\right) \]  

Where slope is the conversion factor from amount sampled (SO\textsubscript{2}) to a dose (SO\textsubscript{2}) and t is the length of the sampler exposure period (hours).

The ambient concentration (C, µg m\textsuperscript{-3}) of atmospheric NO\textsubscript{2} was estimated from Q:
where \( R_t \) is the total resistance of the Willems badge, \( A \) is the absorbent pad surface area \((5.309 \times 10^{-4} \text{ m}^2)\) and \( t \) is the length of the sampler exposure period (s).

The method limit of detection (LOD) for NO\(_2\) and SO\(_2\) passive samplers were 0.3 ppb (0.54 \(\mu\)g m\(^{-3}\)) and 0.03 ppb (0.07 \(\mu\)g m\(^{-3}\)), respectively. These were estimated from three times the standard deviation of laboratory blanks of each corresponding species. No significant differences were obtained in lab blanks over field or travel blanks for both species \((p > 0.05\) in \(t\)-test of all cases). The lab blank mean value was subtracted during calculation of ambient concentrations of each species.

### 2.3.3.3. Accuracy and precision of Willems badge passive samplers

The accuracy of Willems badge passive diffusion samplers was assessed using the percentage relative error (\%) (also known as relative bias):

\[
\text{Accuracy} = \left( \frac{C_p - C_a}{C_a} \right) \times 100
\]

Where \( C_p \) is the air pollutant concentration measured with a Willems badge passive sampler, \( C_a \) is the concentration measured with the reference active method (i.e., automatic chemiluminescence and UV Fluorescence method applied for NO\(_2\) and SO\(_2\) measurement, respectively in the B.C. continuous air quality network, url: http://www.bcairquality.ca/assessment/monitoring-instruments.html, accessed on: 11 September 2014) and averaged over the same time period at exactly the same location. It should be noted that the percentage relative error is used here as a simplified indicator of accuracy and this method is also applied in other studies (e.g., Campos et al., 2010; Vardoulakis et al. 2009). In addition, to estimate accuracy, the least-squares regression equation coefficients of the passive diffusion measurements (dependent variable) against
automatic active measurements (independent variable) were also used as an indicator of linearity between these two methods. Finally, statistical significance (using a paired *t*-test to compare the means of two measurements) was carried out to determine whether the differences were significant between passive and active observations.

The precision of the Willems badge passive diffusion sampling measurements was evaluated from the triplicate (also from duplicate, see section 2.3.3.1) sets of NO₂ and SO₂ during each deployment at all sites. The relative standard deviation (RSD), which is a statistical measure of repeatability (also called coefficient of variation - CV), was calculated for each pollutant by dividing the standard deviation of the triplicate samples by the mean concentrations over the same time period and then multiplying by 100. This approach has also used to assess the suitability of passive diffusion samplers elsewhere (e.g., Vardoulakis et al. 2009; Zbieranowski and Aherne, 2012a and 2012b).
2.4. References


Cox, R.M., 2003. The use of passive sampling to monitor forest exposure to O$_3$, NO$_2$ and SO$_2$: a review and some case studies. Environmental Pollution 126, 301-311.


NO$_2$ and SO$_2$ over the Canadian oil sands and comparisons with surface measurements. Atmos. Chem. Phys. 14, 3637-3656, doi:10.5194/acp-14-3637-2014.


3. Satellite observations of Nitrogen dioxide and Sulfur dioxide over Northeastern B.C.,
Canada

Abstract
The Peace River district of Northeastern British Columbia (B.C.) Canada is a region of
natural gas production that has undergone rapid development since 2005. In order to assess
air quality implications of this a satellite air quality study in Northeastern B.C., using
multiple data products for Nitrogen dioxide (NO$_2$) and sulfur dioxide (SO$_2$), is presented. The
spatial distributions among all data products illustrate consistently high values in both
pollutants over the Montney formation which has experienced an increase in unconventional
natural gas activities. The Montney formation includes the communities of Taylor, Fort St.
John and Dawson Creek. The magnitude of these high values for both NO$_2$ and SO$_2$,
quantified in terms of tropospheric vertical column densities (VCDs) as well as surface
concentrations (except for SO$_2$), are approximately one fifth and half, respectively, of the
values found in the Canadian oil sands area, an area known as one of the largest non-urban
pollution sources in Canada. Furthermore, the temporal analysis of NO$_2$ data products
revealed higher values near Dawson Creek after 2007 with annual increment of 1.7% which
is coincident with the commencement of unconventional gas development activities.
However, a lack of available year round data limited the temporal analysis for SO$_2$.

Keywords: Northeastern B.C., Nitrogen dioxide (NO$_2$), Sulfur dioxide (SO$_2$), Taylor, GEM-
MACH, Natural gas, Volume mixing ratio (vmr), Montney formation.

3.1. Introduction
In 2012, the total production of natural gas in British Columbia (B.C.) was 40,482×10$^6$ m$^3$
(oil was 1,222×10$^6$ m$^3$) with total estimated reserves (proven plus probable recoverable) of
1,138×10^9 m^3 (oil was 19,108×10^6 m^3). This is a 146% increase over the natural gas reserves estimated in 2006 (OGC, 2012). The trend of increasing reserve estimates is largely due to the successful development of unconventional gas extraction including the application of horizontal drilling and hydraulic fracturing technology in the Montney formation and the Horn River Basin of Northeastern B.C. (OGC, 2012). The exploitation of these vast reserves of natural gas is a significant economic driver and revenue generator in the province, and as such the B.C. provincial government is planning on expanding this industry by promoting development of liquefied natural gas (LNG) for export. It is estimated that 84,951×10^6 m^3 per year will be produced in order to meet goals of developing three LNG facilities by 2020 (MEM, 2012). B.C. is currently the second largest natural gas producer in Canada, and Canada is the 5th largest in the world (CAPP, 2013).

Natural gas is a nonrenewable fossil fuel that develops naturally over millions of years from the carbon and hydrogen molecules of ancient organic matter trapped within geological formations. The two major geological formations in Northeastern B.C. are the Montney formation and the Horn River Basin. The Montney formation is an unconventional Lower Triassic aged formation that includes dry, liquid rich gas and oil in over-pressured siltstones that stretches toward northwest 200 km from the B.C.–Alberta border near Dawson Creek to the B.C. foothills of the Rocky Mountains. The unconventional mid-Devonian aged Horn River Basin is a shale play with dry gas over-pressured of the Muskwa, Otter Park and Evie Formations near Fort Nelson in Northeastern B.C. Currently, these two formations that utilize unconventional drilling which commenced extensively in 2007/2008, account for 60% of BC’s total production. Conventional drilling methods were predominantly applied before 2007 (OGC, 2012). It is expected that natural gas from unconventional sources will continue
to increase while conventional pools will be depleted in the next few years (OGC, 2012). Unconventional natural gas development consists of two main phases: well development and production. Individual well development involves three stages: pad preparation, well drilling and well completion (US EPA, 2010). Recently, the US EPA estimated that well completions involving hydraulic fracturing in an uncontrolled manner can vent natural gas to the atmosphere resulting in air pollution. This is done to guard against the over-pressuring of the well which results in approximately 230 times more natural gas being vented compared to wells without hydraulic fracturing (conventional well drilling) (US EPA, 2011). Therefore, people who lived within half a mile of the unconventional wells had a greater risk of developing non-cancer health effects from short-term exposure to the high emissions of hydrocarbons than those living further away (McKenzie et al., 2012). The well development phase is not the only source of air pollution; the production phase involving flaring (either purposefully or accidentally), processing, compressing, pipeline distribution, storage, etc. also may lead to air pollution. The leading air pollutants from natural gas development activities are hydrogen sulfide (H₂S), SO₂ from sulfur rich (or sour) gas, methane (CH₄), non-methane hydrocarbons typically volatile organic compounds (VOCs), and nitrogen oxides (NOₓ) (Lattanzio, 2013).

Concerns have arisen recently in Northeastern B.C. about increasing air pollution resulting from accelerating natural gas production (Fraser Basin Council, 2013; Krzyzanowski, 2012; MoE, 2014) without simultaneous implementation of available technological advances to control emissions (Krzyzanowski, 2009). According to the 2010 emissions data reported to Canada's National Pollutant Release Inventory (NPRI, http://www.ec.gc.ca/pdb/websol/quervsite/query_e.cfm), SO₂ and NO₂ are the dominant
species among all gaseous air pollutants in Northeastern B.C. which are emitted from various stages of oil and gas activities but mostly from the production phase such as processing (flares, engines, and compressors), distribution (leaks of pipelines and flanges), and also from storage tanks as vaporization (Krzyzanowski, 2012). However, oil and gas industries are not required to report to the NPRI the emissions during the well development phase (e.g., in pilot phase or in exploration or drilling phase) (http://ec.gc.ca/inrp-npri/default.asp?lang=En&n=02C767B3-C9FD-4DD7-8072). Therefore, it has been suggested that both of these gaseous species are under-reported (Krzyzanowski, 2009) and under-monitored (Krzyzanowski, 2011). Though significant emissions during production have been reported by the NPRI, there are only four permanent SO\textsubscript{2} monitors installed over the previous 15 years (Pine River Hasler and Pine River Gas Plant near Chetwynd, Taylor Townsite and Taylor South Hill near Taylor) and no monitoring of NO\textsubscript{2} except for occasional short term monitoring in some places in 2010 and 2011 using the B.C. MoE mobile air monitoring laboratory. However, SO\textsubscript{2} is also monitored at three additional industry operated sites, with data they are not publicly accessible (MoE, 2014). Due to this growing concern and high public demand, B.C. MoE recently has commissioned three new stations (Doig River, Farmington Community Hall and Tomslake) which were deployed in December 2013 and January 2014 to monitor SO\textsubscript{2} and total reduced sulfur (TRS) along with meteorology, as a pilot study (MoE, 2014).

NO\textsubscript{2} and SO\textsubscript{2} are gaseous species that undergo chemical and/or physical reactions in the atmosphere and contribute to acidic deposition in terrestrial ecosystems as dry-deposited gases or in dissolved form in precipitation, fog, and cloud (Cox, 2003) and also may impact on human health through a number of environmental pathways (Krzyzanowski, 2012). In
aerosol form, they can also impact visibility while NO$_2$ as a precursor to the formation of photochemical oxidants can also lead to direct impact on human health (Cox, 2003). Previous studies regarding air quality issues in northeastern B.C. and Alberta reported that elevated levels of SO$_2$ in this territory lead to direct injury to natural vegetation (Legge et al., 1998). Recently, as a result of the growing concern on potential negative impacts of gas extraction and processing, the B.C. provincial government has initiated a three-phase study on the health impacts of oil and gas activities in B.C.'s northeast region. Respondents during the Phase-1 preliminary study complained of personal health problems – such as asthma, bronchitis, cancer, stress and sleep deprivation associated with oil and gas activities (Fraser Basin Council, 2013). Besides the impact-oriented issues, some respondents were dissatisfied by what they saw currently as insufficient information available to them from both the government and the oil and gas sector, and a lack of transparency with respect to specific oil and gas activities. Consequently, it was suggested from the health impact study in Northeast B.C. that rigorous investigation and regulations are required for baseline assessments of air quality and also adequate communication with the public should be conducted prior to oil and gas resource development activities. This baseline information is not available from the current ambient monitoring network due to the limited number of monitoring sites, so new monitoring locations should be assessed. Decisions on where to install new stations should be based on background information such as which pollutants related to oil and gas development activities are changing over time in the ambient air.

Recently it has been suggested from the satellite observations of NO$_2$ and SO$_2$ over the Canadian oil sands in Alberta (McLinden et al., 2012 and 2014) and space-based ambient concentration of NO$_2$ in North America (Lamsal et al., 2008) that satellite observations
would be an alternative and complementary to surface-based measurements. Therefore, the overall purpose of this study is to assess air quality using satellite remote sensing observations of \( \text{NO}_2 \) and \( \text{SO}_2 \) over portions of Northeastern B.C. that are undergoing an expansion in natural gas production. To the best of our knowledge, there are no published articles available that describe the air quality of Northeastern B.C. using satellite observations. This chapter briefly introduces different satellite \( \text{NO}_2 \) and one \( \text{SO}_2 \) data products along with the importance of AMFs, particularly for this study area, in section 2. This section also describes the basic satellite data filtering criteria prior to obtain valid scenes. In section 3, spatial distributions of \( \text{NO}_2 \) VCDs of the study area in the context of known pollution sources over most of B.C. and Alberta have been analyzed by applying a pixel-averaging approach to different data products followed by space-based and model-simulated surface level \( \text{NO}_2 \) spatial distribution. \( \text{SO}_2 \) VCDs were analyzed over a small domain. This study also compares air quality in Northeastern B.C. with air quality in the Canadian oil sands area, which is known as one of the largest non-urban pollution sources in Canada (McLinden et al., 2012).

### 3.2. Satellite data products of air quality

Lower tropospheric pollutant observations from satellites began with the GOME-1 instrument (Global Ozone Monitoring Experiment, 1996-2003) aboard the ERS-2 satellite (Burrows et al., 1999) and has continued with SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY, 2002-2012) aboard the ENVISAT satellite (Bovensmann et al., 1999), and currently by the OMI (Ozone Monitoring Instrument, 2004-present) in the Aura satellite (Leviet et al., 2006) and the operational GOME-2 (2007-present) in the MetOP platform (Martin, 2008). The basic characteristics of these instruments
are listed in Table 2.1. The satellites have been designed to yield information on the lower tropospheric trace gas constituents by flying in near-polar, Sun-synchronous, low earth orbits; a typical orbit altitude is 705 km (Martin 2008). These trace gas constituents (e.g., NO\textsubscript{2} and SO\textsubscript{2}), are processed to yield vertical column density (VCD) from the integrated column amount by measuring UV-visible solar radiation in nadir (down looking) geometry. The tropospheric VCDs from the calibrated spectra involves three main steps (Boersma et al., 2007): 1) a spectral fit to determine the slant columns densities (SCD), 2) elimination of the stratospheric contribution to the SCD; and 3) conversion of tropospheric SCD to tropospheric VCDs via the air mass factor (AMF) where the AMF accounts for the sensitivity of the instrument to the absorber (target species, such as: NO\textsubscript{2} and SO\textsubscript{2}) (McLinden et al., 2014). The AMF describes the enhancement in absorption when light traverses a slant path through a layer and therefore it represents a basis of trace gas retrievals in the spectrum of UV-visible wavelength. It is noted that the AMF is the ratio of the SCD to the VCD and it is computed using a radiative transfer model because of the complex path of the scattered and reflected sunlight. The radiative transfer model simulates nadir radiances and accounts for all relevant physical factors such as: multiple scattering by molecules and aerosols, absorption by trace gases, and reflection from the surface. The accuracy of the AMF calculation is largely governed by the accuracy of information on the absorber vertical profile, cloud and aerosol information, surface reflectivity and surface pressure (McLinden et al., 2014).

In this analysis, NO\textsubscript{2} data from three instruments (SCIAMACHY, OMI and GOME-2) (2005-2013) were used for analysis. While multiple OMI NO\textsubscript{2} VCD data products currently exist, the two global, primary products from the NASA standard product (SP) (Bucsela et al., 2013; http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/omno2_v003.shtml) and the
Dutch OMI NO$_2$ (DOMINO) (Boersma et al., 2011; http://www.temis.nl/airpollution/no2.html) processed in near real time have been included in the analysis. The reason for using two OMI NO$_2$ data products in this analysis is to visualize how NO$_2$ VCDs particularly for the study area vary with data products. These two OMI NO$_2$ data products are derived from different separation techniques of stratospheric SCDs (Bucsela et al., 2013). The DOMINO product simulates the stratospheric NO$_2$ by assimilating OMI SCDs in a chemical data assimilation system whereas the SP executes a complex high-pass filtering approach (Dirksen et al., 2011). In addition, the SP algorithm depends on monthly mean profiles from the Global Modeling Initiative (GMI) (Bucsela et al., 2013) while the DOMINO product uses daily output from the TM4 (Tracer Model 4) chemical transport model (Boersma et al., 2007). However, both of these models make use of emission inventories appropriate for the late 1990s (McLinden et al., 2014), when oil and gas development activities in Northeastern B.C. were significantly lower than the current level.

An accurate absorption profile of trace gases (e.g., NO$_2$) substantially determines the accuracy of the AMF calculation whereas the AMF plays a fundamental role in the calculation of tropospheric VCDs from SCDs. Therefore, McLinden et al. (2014) recently recalculated the AMF (named as EC-AMF, EC stands for Environment Canada) for North America based on updated and higher resolution absorber profile from a regional-scale (15 km x 15 km resolution) air quality model (the Global Environmental Multi-scale – Modeling Air Quality and Chemistry, GEM-MACH; for more details refer to Anselmo et al., 2010) using emission inventories from the US EPA and EC data for the year 2006, high spatial and temporal resolution surface reflectivity from the Moderate Resolution Imaging Spectroradiometer (MODIS) satellite instrument, and an improved treatment of snow.
Finally, two new OMI NO\textsubscript{2} data products were calculated from each of the tropospheric SCDs of the SP and DOMINO by dividing them by the EC-AMFs instead of the original AMFs (McLinden et al., 2014). These new VCDs, named as EC-SP-NO\textsubscript{2} and EC-DOMINO-NO\textsubscript{2}, were also included in this analysis (2005-2013). Besides these OMI NO\textsubscript{2} data products, NO\textsubscript{2} data from SCIAMACHY between 2005 and 2011 were combined with the GOME-2 data for 2012-2013 in this analysis (the combined dataset is named as SCIA-NO\textsubscript{2}). The dataset created by this combination approach (Ghude et al., 2011) has been implemented for the comparison with OMI data products between 2005 and 2013. Note that the same retrieval techniques were used for NO\textsubscript{2} data products of both SCIAMACHY and GOME-2 instruments and flight time of the satellites carrying these two instruments is almost identical (Table 2.1). Although multiple NO\textsubscript{2} data products have been included in this study, analysis of SO\textsubscript{2} data (2005-2013) were only limited to the OMI instrument (OMSO2 specific to the planetary boundary layer [PBL], version 3, http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/omso2_v003.shtml, this data product is named here as NASA-SO\textsubscript{2} for simplicity). This product is retrieved based on the NASA Band Residual Method (BRM) using four wavelengths between 310 and 315 nm to quantify SO\textsubscript{2} absorption (Krotkov et al., 2006). Generally, all these satellite data products of both NO\textsubscript{2} and SO\textsubscript{2} offer the possibility to improve our understanding of lower tropospheric trace gas concentrations (Lamsal et al., 2008 and 2013; Lee et al., 2011), as well as helping with identification of emission sources (Fioletov et al., 2011 and 2013; Lu and Streets, 2012; Martin et al., 2003), and atmospheric chemistry, through testing and improvements to emission inventories, using top-down modeling techniques (Boersma et al., 2008).
Orbit based level 2 data products, in which the location of an observation is assigned to the co-ordinates of the pixel center, from all these instruments were used in this study. OMI measures 60 cross-track positions (pixels) during each along track scan. The across track width differs in size depending on the track position, however, along track width is constant (13 km). Therefore, 10 pixels on each swath edge were excluded from analysis to limit the across-track pixel width to ~40 km. In addition, some cross-track positions are affected by an error called the “row anomaly” (RA) since June 2007 (also see Table 2.2) due to the partial external blockage of the radiance port on the OMI instrument (http://www.knmi.nl/omi/research/product/rowanomaly-background.php), were dynamically removed based on the RA flags in all OMI data products of both species. Daily OMI data products were also filtered to remove data with high cloud radiance fraction (>0.2) and large solar zenith angle (SZA) (>75° for NO₂ and >60° for SO₂). Note that, the stringent SZA threshold of 75° for NO₂ means that about 75% data is from April-September and the remaining 25% is from October-March. However, using a 60° SZA threshold for SO₂ keeps 99% of the data between April and September of each year (McLinden et al., 2014). Surface albedo was limited to below 0.3 for both SP and DOMINO data products of OMI. Year round NO₂ data products from all these instruments were used but, following Fioletov et al. (2011), only summertime (May – August) NASA-SO₂ data were used in order to maximize the signal-to-noise ratio (SNR: the ratio between the mean values and the standard errors of the means) and also were restricted to values between -10 and +5 DU (1 DU = 2.69 × 10²⁶ molecule/km²) to avoid spikes from transient volcanic plumes.
3.3. Tropospheric NO\textsubscript{2} column densities over Northeastern B.C.

The nine year average (2005-2013) of tropospheric NO\textsubscript{2} VCDs over major parts of B.C. and Alberta, Canada, from different data products have been visualized in Fig 3.1 in an effort to provide the context for the satellite observed pollution levels across the Peace River region of Northeast B.C. Places with known large pollutant sources, including several urban areas, are included in this geographical area. Major pollutant sources in some of these urban areas (such as Vancouver, and Victoria) are primarily related to vehicle emissions while regions of large emissions particularly north of Fort McMurray but also Calgary and Edmonton also have significant emissions due to oil and gas activities. Fort St. John (\times symbol in Fig. 3.1), the main town located within the Montney formation of Northeastern B.C., has very small VCDs compared with larger emission regions (Fig. 3.1). The pixel averaging technique described by Fioletov et al. (2011 and 2013) was employed in this analysis to obtain a statistically significant signal. Initially a 6 × 6 km\textsuperscript{2} grid was defined for this larger area and all screened observations of SP and DOMINO NO\textsubscript{2} data products within 2005-2013 and falling within a radius of 24 km from the grid-cell center were averaged. However, a larger radius is required for analyzing GOME-2 or SCIAMACHY NO\textsubscript{2} products by pixel averaging technique due to these two data products having a coarser resolution (Table 2.1) (Fioletov et al., 2013). To remain consistent, a 60 km radius was used during the intercomparison between DOMINO-NO\textsubscript{2} and SCIA-NO\textsubscript{2} products. This long term averaging of VCDs from a large number of observations provides some advantages such as the center and shape of the enhancement of a given source location can be determined. All the plots in Fig. 3.1 illustrate consistently high values over the major known pollution sources in this larger region with some differences (DOMINO vs SCIA, and DOMINO vs SP) in the values mostly due to: i)
overpass times - OMI observes early afternoon while the others observe mid-morning; and ii) the separation of stratospheric contribution to the total SCDs. These findings show strong agreement with results from McLinden et al. (2012 and 2014) whose principal focus was to investigate the satellite observations of NO\textsubscript{2} over the Canadian oil sands, located near Fort McMurray, Alberta. Overall, Northeastern B.C. does not show any significant values of NO\textsubscript{2} VCDs in the context of the large area examined which suggests further investigation for greater detail considering a smaller domain.

The small domain, roughly 224 km × 224 km, spanning 54.8°N to 56.8°N latitude and 123.5°W to 120.0°W longitude was chosen as this area covers most of the Montney formation of Northeastern B.C. where substantial conventional and unconventional natural gas activities have been taking place. Owing to its superior resolution (Table 2.1), OMI allows for greater details in this small domain. All OMI NO\textsubscript{2} data products were analyzed using a 1.2 × 1.2 km\textsuperscript{2} grid and averaging over an 18 km radius. Plots of different OMI data products are shown in Fig. 3.2. The elongated ellipses in the north-south direction in the eastern side (near B.C.-Alberta border) of the small domain consistently were identified in all the plots of Fig. 3.2. Note that a similar pattern of distribution has been obtained with the tropospheric SCD (tropospheric VCDs of OMI NO\textsubscript{2} data products × corresponding AMFs) (see appendix, Fig. A1) that suggests the signals with the VCDs have not being created by the AMFs themselves. The highest value of VCD was found near Taylor (~15 km south of Fort St. John) where Station 1-Taylor (natural gas extraction station) is located and this is the significant source of NO\textsubscript{2} according to the NPRI database (https://ec.gc.ca/inrp-npri/default.asp?lang=en&n=1D892B9F-1). Besides the high values near Taylor, elevated levels were also captured in the northward direction toward Fort St. John, and also to the
south near Dawson Creek. These areas are close to regions of gas development, with unconventional drilling in the Montney formation, and processing activities based on the BC Oil and Gas Commission (OGC, 2012) and NPRI database. Although the places with elevated VCDs have been captured consistently by all the OMI NO\textsubscript{2} data products, significant differences in the values of VCDs were identified. The SP NO\textsubscript{2} (Fig. 3.2c) is larger than the DOMINO (Fig. 3.2a) by a factor of 2.6 over the community of Taylor and this is due to the different stratospheric VCD separation techniques involved in the algorithms of these two data products as well as the lower frequency of negative tropospheric VCDs in the SP data products (Bucsela et al., 2013). On the other hand, EC-DOMINO-NO\textsubscript{2} (Fig. 3.2b) data products differ from DOMINO products (Fig. 3.2a) by a factor of ~1.9, and this is due to the improved EC-AMFs. McLinden et al. (2014) reported that the improved EC-AMFs are predominantly driven by the accurate input information of the 2006 emission inventory based on an updated profile shape and accounted for over 90% of the average decrease in the original AMF. The same is true when comparing the SP (Fig. 3.2c) and EC-SP-NO\textsubscript{2} (Fig. 3.2d) over Taylor B.C.: the latter one is larger by a factor of 1.3. A similar degree of difference was also reported by McLinden et al. (2014) over the Canadian oil sands region. The reason for the difference between EC-DOMINO-NO\textsubscript{2} (Fig. 3.2b) and EC-SP-NO\textsubscript{2} VCDs of the small domain can be explained by the different algorithm used for stratospheric separation. It should be recognized that this region overall has much lower VCDs compared to other known polluted places such as the oil sands region north of Fort McMurray, Alberta (Fig. 3.1). From the NPRI data set it is found that maximum individual NO\textsubscript{x} emission over the oil sands region is roughly 15,000 tonnes per year (t/y) and the long-term (2005-11) averaged EC-SP-NO\textsubscript{2} tropospheric VCDs- reported $4.0 \times 10^{15}$ molecules/cm\textsuperscript{2} (McLinden et
al., 2014). However, the maximum NO\textsubscript{x} emission from the largest source of Northeast B.C., located in Taylor, is approximately 1,700 t/y which is approximately nine times less than in the oil sands region. It is therefore expected that the OMI VCDs over Northeast B.C. will also be lower than in the oil sands region by at least a factor of 9.0. The present study finds $8.0 \times 10^{14}$ molecules/cm\textsuperscript{2} as the maximum tropospheric VCD near the Taylor from EC-SP-NO\textsubscript{2} products (Fig. 3.2d) which is approximately five times less than in the oil sands region. This comparison puts the air quality near Taylor into an appropriate context.

In addition, the superior algorithm used for the SP NO\textsubscript{2} data products (Bucsela et al., 2013) along with corrected EC-AMFs (McLinden et al., 2014) suggest that the EC-SP-NO\textsubscript{2} data products will be used for temporal analysis. In this temporal analysis, NO\textsubscript{2} VCDs between 2005 and 2007 have been averaged, using the pixel averaging technique, and were compared with the average values between 2008 and 2013. The averaging time interval between the earlier and later periods was doubled as some of the cross-track positions were affected by RA since 2007 (Lu et al., 2013) (see also section 3.2). The dynamical RA flagging removes the affected pixels so that the number of valid observations in each pixel averaging radius (18 km) is decreasing with time, for example, valid observations in 2005-2007, 2008-2010 and 2011-2013 were found to be 394, 219, and 207, respectively. However, it was 422 in the doubling time interval (2008-2013) phase which is nearly consistent with the observation numbers between 2005 and 2007. Comparing the 2005-2007 (Fig. 3.3a) with the 2008-2013 (Fig. 3.3b) mean NO\textsubscript{2} VCDs, an increase in NO\textsubscript{2} with time is identified close to the community of Dawson Creek and this increment likely reflects the unconventional drilling commencement since after 2007 in the Montney formation (OGC, 2012). From these two figures (Fig. 3.3a and 3.3b), the maximum VCD of the NO\textsubscript{2} enhancement over the study area
is seen to be increasing at rates of 1.7%/y. This is calculated from the maximum values of these two time intervals, given that few months (December to February) of each year retain limited observations due to high pass filtering of satellite data (see also section 3.2). It is important to note that 60% of the total 2012's production comes from unconventional sources in B.C. and the Montney formation contributes 40% of the total 2012 unconventional production, however, southern Montney formation (or Heritage Montney field) which is located in the study area produces 60% of the total Montney production (see also section 2.2.1) (OGC, 2012).

The NO\(_2\) data products of different sensors have also been investigated for this small domain. The tropospheric VCDs from SCIA-NO\(_2\) (Fig. 3.4b) data products are nearly two times higher than the values of DOMINO data products (Fig. 3.4a). It is likely that photochemical loss of NO\(_2\) during the afternoon has resulted in a lower concentration of NO\(_2\) in the PBL during the OMI flight time, since the photochemical activity is not as strong in the morning (SCIAMACHY and GOME-2 flight time, also refer to Table 2.1). Besides the photochemical loss, diurnal variation in NO\(_2\) columns also may be driven by changing emissions throughout the day (Boersma et al., 2008), however, investigating this possibility is beyond the scope of this study. The SCIA-NO\(_2\) data products with coarse resolution (see also Table 2.1) cannot depict the maximum values as distinctly over the large source (Fig. 3.4b) particularly in a region having a cluster of sources (NPRI data base). This is due to the requirement of a larger radius in the pixel averaging technique for analyzing data products having a coarse resolution (Fioletov et al., 2013). The eastern boundary in the area of maximum value, previously identified in Fig. 3.2, also implies the presence of cluster of sources to the east of the B.C.-Alberta border near Dawson Creek and Fort St. John where the southern Montney formation
starts (for details refer to section 2.2.1). Thus, the maximum value over Taylor originally identified by all OMI data products (Fig. 3.2) has been shifted towards the east rather than west with 60 km averaging radius in OMI data (Fig. 3.4a).

3.4. Ambient NO₂ concentration

Although no in-situ ground-based instruments are currently available in the study domain it is necessary to represent the air quality of the study area in an easily understandable format rather than the less familiar vertically integrated quantities (VCDs). A thorough spatial coverage of ground-level NO₂ measurements is needed for exposure assessments (Lamsal et al., 2008). Currently, no stations are operating in Northeastern B.C. for this purpose. Lamsal et al. (2008) inferred surface-level NO₂ concentrations or surface volume mixing ratio-vmr (S) from OMI tropospheric VCDs (Ω) by applying the ratio of surface-level NO₂ concentrations (S₀) to vertical column densities (Ω₀) calculated by a global chemical transport model, usually by the GOES-Chem:

\[ S = \left( \frac{S₀}{Ω₀} \right) \times Ω \]  

(1)

Environment Canada researchers identified the general consistency of GEM-MACH with GOES-Chem (McLinden et al. 2014) during simulation of NO₂ and SO₂ in the PBL. Therefore, GEM-MACH could be an alternative for the well-established GOES-Chem model. Equation (1) was applied to the EC-VCDs using the same monthly mean profiles used in the calculation of the EC-AMFs (for detail refer to McLinden et al., 2014) and the ratio is obtained from the GEM-MACH (so ‘G’ in equation (1) stands for GEM-MACH). The output from equation (1) is referred to as EC-vmr for simplicity. For this analysis EC-vmr (based on EC-DOMINO-NO₂) and GEM-MACH-vmr were collected from EC (Chris McLinden, Environment Canada, personal communication, 2014). The 2005-2013 average surface NO₂
EC-vmr and GEM-MACH-vmr maps are illustrated in Fig. 3.5, and were calculated using the same pixel-averaging parameters as the VCDs in Fig. 3.2. The spatial distributions from EC-vmr (Fig. 3.5a) and GEM-MACH-vmr (Fig. 3.5b) generally mimic of spatial distribution of VCDs (Fig. 3.2), with a maximum NO$_2$ EC-vmr of nearly 0.4 ppbv (parts per billion by volume) and a maximum GEM-MACH-vmr of 0.6 ppbv. McLinden et al. (2014) reported the maximum long term average NO$_2$ EC-vmr of 2.3 ppbv over oil sands area to be 5.75 times higher than Northeastern B.C., which is consistent with the VCDs (also see section 3.3). The GEM-MACH map (Fig. 3.5b) shows similar spatial patterns to the EC-vmr map, GEM-MACH NO$_2$ where values are typically 50% larger than those of EC-vmr (Fig. 3.5a) through the area of higher concentration. The primary reason for this might be that it is associated with the large number of EC-DOMINO-NO$_2$ VCDs being removed due to high pass filtering, especially after 2007 due to the RA issue (Table 2.2). This can be seen in the 50% drop in valid signals of each pixel averaging circle (18 km radius) near to the area of high concentration in the EC-vmr map (Fig. 3.5c) compared to GEM-MACH-vmr map (Fig. 3.5d). However, NO$_2$ generally has a longer lifetime during winter with more shallow mixing depths than in summer due to the photochemical reactions in the PBL (Lamsal et al., 2008). Lamsal et al. (2008) also illustrated that the winter mean OMI tropospheric VCDs over the United States and southern Canada is 32% lower than the corresponding value from GOES-Chem which, in turn, may limit the value of ‘S’ in the equation (1).

3.5. Tropospheric SO$_2$ column densities over Northeastern B.C.

NASA-SO$_2$ tropospheric VCDs are presented in this section with a focus on the major emission sources in Northeastern B.C. This is done because previous studies report that elevated SO$_2$ column densities which have sufficiently high SNRs representing statistically
significant values will only be achieved within about 50 km of major emission sources using
the NASA-SO$_2$ data product (Fioletov et al., 2011). However, emission sources may affect
only 1-2 pixels (Fioletov et al., 2011) and the NASA-SO$_2$ VCDs have high noise levels
(Fioletov et al., 2011 and 2013; McLinden et al., 2012 and 2014). Therefore, NASA-SO$_2$ data
products with valid observations (see section 3.2) between May and August of each year
throughout 2005-2013 were taken for analysis. Fig. 3.2-3.5 clearly indicates the consistently
high values of NO$_2$ near Taylor throughout the study period, where Station 1-Taylor (natural
gas extraction industry) is a known large source of NO$_x$ emissions. However, this industry
emits very little SO$_2$, while the McMahon Gas Plant (gas processing industry) located very
close to the Station 1-Taylor is one of the largest sources of SO$_2$ emission (emission rate is
~3,500 t/y) in Northeastern B.C. (NPRI data base). Consequently, a 64 km $\times$ 64 km domain
with Taylor roughly in the center was selected and a pixel averaging approach was also used
taking 24 km as a pixel averaging radius in an effort to reduce noise (Fioletov et al., 2013). It
should also be noted that local bias correction (or background level), as suggested in previous
studies (Fioletov et al. 2011 and 2013), can be accomplished by calculating the average of all
NASA-SO$_2$ VCDs from pixels centered between 250 km and 300 km from the source
location and this average value (or local bias) was subtracted from all measurement near the
source. Due to the large distribution of oil and gas industries in the Northeastern B.C. (see
also Fig. 2.1), the NASA-SO$_2$ VCDs from pixels centered between 416 km and 466 km
(north east of Taylor) with no source have been averaged monthly and subtracted from the
monthly mean of each grid (1.2 $\times$ 1.2 km$^2$ grid) near the source. The high value (~0.18 DU)
of the long-term (2005-2013) average VCDs (Fig. 3.6a), after the local bias correction, is
seen to cover a large area with relatively weaker SNR (Fig. 3.6b) compared with that of the
NO₂ analysis (the SNR in all analysis of NO₂ data products remains >15 in all directions except west of the source, McMahon gas processing plant). The relatively large area of elevated SO₂ is partially a result of the pixel averaging approach, but may also indicate that SO₂ emitted from stacks (in the case of McMahon gas processing plant) is spread over a large area (McLinden et al., 2014). The longer lifetime of SO₂ than NO₂ (Lee et al., 2011) in the lower atmosphere also may influence this high value across a large area. In general, this high value is consistent with the recent air quality studies in Northeastern B.C. that reported large sources in Taylor, and SO₂ concentrations would likely be highest in Taylor (Krzyzanowski, 2011, MoE, 2014) and to the east of Taylor (MoE, 2014).

The available ground based in-situ SO₂ monitoring station located within few kilometers of the source (McMahon gas processing plant) along with SO₂ signals allows for a comparative analysis with that of the oil sands area of Alberta. The high values of SO₂ (2005-2013) over the Taylor area (or around the McMahon gas processing plant) in terms of NASA-SO₂ VCDs, and in-situ station (monitoring station name: Taylor Town Site, data is publicly available in the B.C. Ministry of Environment website, available at: http://envistaweb.env.gov.bc.ca/, accessed on: 06 September 2014) are 0.18 DU (Fig. 3.6a), and ~2 ppb, respectively. These are smaller than a factor of ~1.9 and 2.6, respectively in the corresponding parameters in the oil sands area (McLinden et al., 2014). The ratio of in-situ station to NASA-SO₂-VCDs in both sites is highly consistent, Oil sands area: 14.8 (or 10.4 with EC-AMFs based VCDs) (McLinden et al., 2014), and Taylor: ~11, which implies Taylor in Northeastern B.C. is approximately two times less polluted in terms of SO₂. However, the NASA-SO₂ VCDs in the oil sands area (due to annual SO₂ emission rate from Syncrude Canada Mildred Lake Plant Site ~ 80 kt/y) is as large as that from any other individual emissions source in Canada,
including the large base-metal smelting operations in Manitoba (Thompson Operations) and Ontario (Sudbury nickel smelter complex) (McLinden et al., 2012). Assuming the air quality data mentioned above is reliable, the large number of small sources in and around Taylor (NPRI data base) may cumulatively account for the higher value than the expected level. Another probable explanation is related to the geomorphological features of Taylor (in a valley) along with its industrial activities that may impede the efficient horizontal dispersion of pollutants and lead to a strong thermal inversion, which would limit vertical mixing mostly in the fall and winter (Ainslie and Jackson, 2009). Furthermore, the limited vertical mixing is confirmed from the long term (2005-2013) average ambient concentration (~0.9 ppb) of the Taylor South Hill monitoring station (data is publicly available in the B.C. Ministry of Environment website, available at: http://envisataweb.env.gov.bc.ca/, accessed on: 06 September 2014) which is located at 688 m above the mean sea level (MSL) and five km south of the McMahon gas plant, whereas this gas plant and the Taylor Town Site station are only one km apart in same elevation level (~ 470 m MSL) (Fig. 3.6). It should also be noted that the oil sands region is relatively flat and also located away from a large number of individual small sources. Since previous studies revealed that NASA-SO$_2$ data products can detect statistically significant signals only from the sources emitting SO$_2$ above 70 kt/y (Fioletov et al., 2011), therefore, further study is suggested to validate the present satellite SO$_2$ observation in the study area.

3.6. Conclusions

This study presents satellite data of NO$_2$ (OMI and combination of SCIAMACHY and GOME-2) and SO$_2$ (OMI) over the Northeastern B.C. and demonstrates a long term (2005-2013) spatial distribution using a pixel averaging approach with different data products from
these instruments (for SO\textsubscript{2} only NASA SP data product). All the data products of NO\textsubscript{2} VCDs indicate that the maximum value is confined to the vicinity of Taylor, Fort St. John, and Dawson Creek area where intensive natural gas development activities are taking place. In this vicinity the maximum long term average NO\textsubscript{2} VCDs have been identified consistently in Taylor owing to its position as a major source of emissions throughout the study period. However, temporal analysis revealed higher values near Dawson Creek after 2007 with annual increment of 1.7\% which implies that the commencement of unconventional gas development activities also lead to high NO\textsubscript{2} VCDs. Maximum reported values vary substantially with data products largely due to AMF, tropospheric VCDs retrieval algorithm, and possibly instrument observation time (satellite flight time). Notably, the NO\textsubscript{2} VCDs from SP are 2.6 times higher than those of DOMINO and with the new EC-AMFs the difference remains nearly the same, but values of both data products increased with the EC-AMFs. In addition to the VCDs, this area was also spatially examined with the surface level NO\textsubscript{2} concentrations taking data from both satellite and model simulations. These two different data sets reflect a similar spatial distribution of NO\textsubscript{2} concentrations compared to the NO\textsubscript{2} VCDs, however, GEM-MACH simulated ambient concentrations are two times larger than the satellite retrieval. Besides the multiple analysis of NO\textsubscript{2} in a relatively large area, SO\textsubscript{2} was analyzed only within few kilometers around the source (McMahon gas processing plant) also located in Taylor using NASA-SP products and an in-situ monitoring station data and it demonstrated that Taylor is half as polluted as Canada’s largest SO\textsubscript{2} emission sources area, the Canadian oil sands area, due to its morphological features along with large number of individual sources in close proximity. All these pieces of evidence in this previously less studied area suggest further investigation is required to directly validate the present satellite
investigation. This can be done using the high resolution air quality chemistry model (GEM-MACH or WRF-Chem) coupled with accurate emission estimation rather than relying on comparative analysis or in-situ stations without involving dispersion models (e.g., CALPUFF).

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3.7. References


Cox, R.M., 2003. The use of passive sampling to monitor forest exposure to O₃, NO₂ and SO₂: a review and some case studies. Environmental Pollution 126, 301-311.


OGC (BC Oil and Gas Commission), 2012. Hydrocarbon and By-Product Reserves in British Columbia; 2012 - BC Oil and Gas Commission. Available at: https://www.bcogc.ca/node/11111/download (accessed on: 15 May 2014).


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Fig. 3.1. OMI annual mean tropospheric NO$_2$ VCDs across a large area (B.C. and Alberta), averaged over 2005-13 shown on a 6.0 $\times$ 6.0 km$^2$ grid and calculated using different averaging radius. Plots a) and b) are showing tropospheric VCDs from DOMINO-NO$_2$ and SP-NO$_2$ data products, respectively with a 24 km averaging radius. An averaging radius of 60 km is used for the two NO$_2$ data products in c) DOMINO-NO$_2$ and d) SCIA-NO$_2$. Note pixels from the both edges of the swath of OMI data products were not removed for plots (a), (b), and (c). The locations of Victoria, Vancouver, Prince George, Fort St. John, Kamloops, Grande Prairie, Calgary, Edmonton and Fort McMurray are indicated by different symbols from left to right in each plot. The white rectangle of each plot indicates the present study area (Northeast B.C.).

Fig. 3.2. Average (2005-2013) tropospheric VCDs: (a) DOMINO-NO$_2$, (b) EC-DOMINO-NO$_2$, (c) SP-NO$_2$, and (d) EC-SP-NO$_2$. Marker notation of each plot from left to right: Chetwynd, Taylor, and Dawson Creek.

Fig. 3.3. Temporal variation of EC-SP-NO$_2$: (a) 2005-2007, and (b) 2008-2013. Marker notation of each plot from left to right: Chetwynd, Taylor, and Dawson Creek.

Fig. 3.4. Comparison of NO$_2$ data products (2005-2013): (a) DOMINO-NO$_2$, and (b) SCIA-NO$_2$. Here averaging radius is 60 km in both cases. Marker notation of each plot from left to right: Chetwynd, Taylor, and Dawson Creek.

Fig. 3.5. Average (2005-2013) EC-OMI spatial distributions of NO$_2$ vmr: (a) EC-vmr, (b) GEM-MACH-vmr, (c) number of signals from EC-OMI-vmr in each circle of 18 km radius, and (d) the same as (c) but using GEM-MACH-vmr.

Fig. 3.6. Average (2005-2013) tropospheric SO$_2$ VCDs: (a) NASA-SO$_2$-VCDs, (b) SNR of NASA-SO$_2$-VCDs. Marker notation of each plot: Taylor Town Site station (+), Taylor South Hill Station (×), Taylor (o), and McMahon gas processing plant (Δ).
Fig. 3.1. OMI annual mean tropospheric NO$_2$ VCDs across a large area (B.C. and Alberta), averaged over 2005-13 shown on a 6.0 $\times$ 6.0 km$^2$ grid and calculated using different averaging radius. Plots a) and b) are showing tropospheric VCDs from DOMINO-NO$_2$ and SP-NO$_2$ data products, respectively with a 24 km averaging radius. An averaging radius of 60 km is used for the two NO$_2$ data products in c) DOMINO-NO$_2$ and d) SCIA-NO$_2$. Note pixels from the both edges of the swath of OMI data products were not removed for plots (a), (b), and (c). The locations of Victoria, Vancouver, Prince George, Fort St. John, Kamloops, Grande Prairie, Calgary, Edmonton and Fort McMurray are indicated by different symbols from left to right in each plot. The white rectangle of each plot indicates the present study area (Northeast B.C.).
Fig. 3.2. Average (2005-2013) tropospheric VCDs: (a) DOMINO-NO₂, (b) EC-DOMINO-NO₂, (c) SP-NO₂, and (d) EC-SP-NO₂. Marker notation of each plot from left to right: Chetwynd, Taylor, and Dawson Creek.
Fig. 3.3. Temporal variation of EC-SP-NO$_2$: (a) 2005-2007, and (b) 2008-2013. Marker notation of each plot from left to right: Chetwynd, Taylor, and Dawson Creek.
Fig. 3.4. Comparison of NO$_2$ data products (2005-2013): (a) DOMINO-NO$_2$, and (b) SCIA-NO$_2$. Here averaging radius is 60 km in both cases. Marker notation of each plot from left to right: Chetwynd, Taylor, and Dawson Creek.
Fig. 3.5. Average (2005-2013) EC-OMI spatial distributions of NO$_2$ vmr: (a) EC-vmr, (b) GEM-MACH-vmr, (c) number of signals from EC-OMI-vmr in each circle of 18 km radius, and (d) the same as (c) but using GEM-MACH-vmr.
Fig. 3.6. Average (2005-2013) tropospheric SO$_2$ VCDs: (a) NASA-SO$_2$-VCDs, (b) SNR of NASA-SO$_2$-VCDs. Marker notation of each plot: Taylor Town Site station (+), Taylor South Hill Station (×), Taylor (o), and McMahon gas processing plant (Δ).
4. Passive monitoring measurements of Nitrogen Dioxide and Sulfur Dioxide concentrations over Northeastern B.C., Canada

Abstract

The Peace River district of Northeastern British Columbia (B.C.) Canada is a region of natural gas production that has undergone rapid expansion since 2005. In order to assess air quality implications of this, Willems badge passive samplers were deployed for six two-week exposure periods between August 15 and November 11, 2013 at 24 sites across the region to assess the ambient concentration of nitrogen dioxide ($\text{NO}_2$) and sulfur dioxide ($\text{SO}_2$). Site 14, located in Taylor, recorded the highest concentrations of both species ($\text{NO}_2$: 9.1 ppb, $\text{SO}_2$: 1.91 ppb) relative to other sites during the whole study period (except the 1st exposure period of both species) which is consistent with its location near major sources. However, high values from passive measurement of $\text{NO}_2$ at site F20 (deployed near the center of Chetwynd) indicate an origin of $\text{NO}_2$ from an urban setting as well. Observations of both species from other sites reflect relatively high concentrations near Fort St. John, Taylor and Dawson Creek where unconventional oil and gas development activities are quite high. Although a few sites in Northeastern B.C. recorded elevated concentrations of $\text{NO}_2$ and $\text{SO}_2$ during this investigation, the concentrations remain well below B.C. (Provincial) ambient air quality objectives. The average precision in terms of relative standard deviation (RSD) for the triplicate Willems badge passive samplers were 16.7% for $\text{NO}_2$ and 18.2% for $\text{SO}_2$. The analysis of results showed good agreement between ambient concentrations from $\text{NO}_2$ passive samplers and ambient concentrations from co-located chemiluminescence analyzers. Although, the average accuracies (percentage relative error) of three collocated passive $\text{SO}_2$
sites falls within the recommended values, the accuracy of each collocated site differ significantly, thus further investigation is suggested.

**Keywords:** Unconventional drilling, Oil and gas, Northeastern B.C., Willems badge, air quality, Nitrogen dioxide, Sulfur dioxide

### 4.1. Introduction

In 2012, the total production of natural gas in British Columbia (B.C.) was $40,482 \times 10^6$ m$^3$ (oil was $1,222 \times 10^6$ m$^3$) with total estimated reserves (proven plus probable recoverable) of $1,138 \times 10^9$ m$^3$ (oil was $19,108 \times 10^6$ m$^3$). This is a 146% increase over the natural gas reserves estimated in 2006 (OGC, 2012a). The trend of increasing reserve estimates is largely due to the successful development of unconventional gas extraction including the application of horizontal drilling and hydraulic fracturing technology in the Montney formation and the Horn River Basin of Northeastern B.C. (OGC, 2012a). The exploitation of these vast reserves of natural gas is a significant economic driver and revenue generator in the province, and as such the B.C. provincial government is planning on expanding this industry by promoting development of liquefied natural gas (LNG) for export. It is estimated that $84,951 \times 10^6$ m$^3$ per year will be produced in order to meet goals of developing three LNG facilities by 2020 (MEM, 2012). B.C. is currently the second largest natural gas producer in Canada, and Canada is the 5th largest in the world (CAPP, 2013).

Natural gas is a nonrenewable fossil fuel that develops naturally over millions of years from the carbon and hydrogen molecules of ancient organic matter trapped within geological formations. The two major geological formations in Northeastern B.C. are the Montney formation and the Horn River Basin. The Montney formation is an unconventional Lower Triassic aged formation that includes dry, liquid rich gas and oil in over-pressured siltstones.
that stretches toward northwest 200 km from the B.C.–Alberta border near Dawson Creek to the B.C. foothills of the Rocky Mountains. The unconventional mid-Devonian aged Horn River Basin is a shale play with dry gas over-pressured of the Muskwa, Otter Park and Evie Formations near Fort Nelson in Northeastern B.C. Currently, these two formations that utilize unconventional drilling which commenced extensively in 2007/2008, account for 60% of BC’s total production. Conventional drilling methods were predominantly applied before 2007 (OGC, 2012a). It is expected that natural gas from unconventional sources will continue to increase while conventional pools will be depleted in the next few years (OGC, 2012a). Unconventional natural gas development consists of two main phases: well development and production. Individual well development involves three stages: pad preparation, well drilling and well completion (US EPA, 2010). Recently, the US EPA estimated that well completions involving hydraulic fracturing in an uncontrolled manner can vent natural gas to the atmosphere resulting in air pollution. This is done to guard against the over-pressuring of the well which results in approximately 230 times more natural gas being vented compared to wells without hydraulic fracturing (conventional well drilling) (US EPA, 2011). Therefore, people who lived within half a mile of the unconventional wells had a greater risk of developing non-cancer health effects from short-term exposure to the high emissions of hydrocarbons than those living further away (McKenzie et al., 2012). The well development phase is not the only source of air pollution; the production phase involving flaring (either purposefully or accidentally), processing, compressing, pipeline distribution, storage, etc. also may lead to air pollution. The leading air pollutants from natural gas development activities are hydrogen sulfide (H\textsubscript{2}S), SO\textsubscript{2} from sulfur rich (or sour) gas,
methane (CH$_4$), non-methane hydrocarbons typically volatile organic compounds (VOCs), and nitrogen oxides (NO$_x$) (Lattanzio, 2013).

Concerns have arisen recently in Northeastern B.C. about increasing air pollution resulting from accelerating natural gas production (Fraser Basin Council, 2013; Krzyzanowski, 2012; MoE, 2014) without simultaneous implementation of available technological advances to control emissions (Krzyzanowski, 2009). According to the 2010 emissions data reported to Canada’s National Pollutant Release Inventory (NPRI, http://www.ec.gc.ca/pdb/websol/queriesite/query_e.cfm), SO$_2$ and NO$_2$ are the dominant species among all gaseous air pollutants in Northeastern B.C. which are emitted from various stages of oil and gas activities but mostly from the production phase such as processing (flares, engines, and compressors), distribution (leaks of pipelines and flanges), and also from storage tanks as vaporization (Krzyzanowski, 2012). However, oil and gas industries are not required to report to the NPRI the emissions during the well development phase (e.g., in pilot phase or in exploration or drilling phase) (http://ec.gc.ca/irnp-npri/default.asp?lang=En&n=02C767B3-C9FD-4DD7-8072). Therefore, it has been suggested that both of these gaseous species are under-reported (Krzyzanowski, 2009) and under-monitored (Krzyzanowski, 2011). Though significant emissions during production have been reported by the NPRI, there are only four permanent SO$_2$ monitors installed over the previous 15 years (Pine River Hasler and Pine River Gas Plant near Chetwynd, Taylor Townsite and Taylor South Hill near Taylor) and no monitoring of NO$_2$ except for occasional short term monitoring in some places in 2010 and 2011 using the B.C. MoE mobile air monitoring laboratory. However, SO$_2$ is also monitored at three additional industry operated sites, with data that are not publicly accessible (MoE, 2014). Due to this growing concern
and high public demand, B.C. MoE recently has commissioned three new stations (Doig River, Farmington Community Hall and Tomslake) which were deployed in December 2013 and January 2014 to monitor SO2 and total reduced sulfur (TRS) along with meteorology, as a pilot study (MoE, 2014).

NO2 and SO2 are gaseous species that undergo chemical and/or physical reactions in the atmosphere and contribute to acidic deposition in terrestrial ecosystems as dry-deposited gases or in dissolved form in precipitation, fog, and cloud (Cox, 2003) and also may impact on human health through a number of environmental pathways (Krzyzanowski, 2012). In aerosol form, they can also impact visibility while NO2 as a precursor to the formation of photochemical oxidants can also lead to direct impact on human health (Cox, 2003). Previous studies regarding air quality issues in northeastern B.C. and Alberta reported that elevated levels of SO2 in this territory lead to direct injury to natural vegetation (Legge et al., 1998).

Recently, as a result of the growing concern on potential negative impacts of gas extraction and processing, the B.C. provincial government has initiated a three-phase study on the health impacts of oil and gas activities in B.C.’s northeast region. Respondents during the Phase-1 preliminary study complained of personal health problems – such as asthma, bronchitis, cancer, stress and sleep deprivation associated with oil and gas activities (Fraser Basin Council, 2013). Besides the impact-oriented issues, some respondents were dissatisfied by what they saw currently as insufficient information available to them from both the government and the oil and gas sector, and a lack of transparency with respect to specific oil and gas activities. Consequently, it was suggested from the health impact study in Northeast B.C. that rigorous investigation and regulations are required for baseline assessments of air quality and also adequate communication with the public should be conducted prior to oil
and gas resource development activities. This baseline information is not available from the current ambient monitoring network due to the limited number of monitoring sites, so new monitoring locations should be assessed. Decisions on where to install new stations should be based on background information such as which pollutants related to oil and gas development activities are changing over time in the ambient air.

Therefore, the overall purpose of this study is to assess the spatial pattern of ambient concentrations of NO$_2$ and SO$_2$ over portions of Northeastern B.C. that are undergoing an expansion in natural gas production. Ambient concentrations of these species were measured using passive diffusive samplers, which have been widely used across America and Europe for the assessment of atmospheric NO$_2$ and SO$_2$ concentrations (e.g. Bytnerowicz et al., 2010; Campos et al., 2010; Cape et al., 2004; Cox, 2003; Hafkenscheid et al., 2009; Hagenbjörk-Gustafsson et al., 1999; Hsu, 2013; Kirchner et al., 2005; Legge et al., 1996; Tang et al., 1997; Tang et al., 1999; Tang et al., 2001; Van Reeuwijk et al., 1998; Vardoulakis et al., 2009; Zbieranowski and Aherne, 2012a) and for filling gaps in monitoring networks (Zbieranowski and Aherne, 2012a). To the best of our knowledge, there are no published articles available that describe the ambient air concentrations of Northeastern B.C. using passive diffuse samplers. However, a network of industry-run passive monitors exists in this region which is not publicly available (MoE, 2014). The advantages of diffusive passive samplers include that they are: inexpensive, easy to deploy in the field for long term assessment, easy to operate, do not require electricity, are able to produce accurate results in indoor and outdoor environments, and are reliable for monitoring ecosystem exposure to gaseous pollution (Cox, 2003; Hafkenscheid et al., 2009; Kot-Wasik et al., 2007; Namieśnik et al., 2005; Seethapathy et al., 2008; Zbieranowski and Aherne, 2012a and 2012b). Despite
having many advantages, passive samplers also have some problems associated with environmental factors (temperature, relative humidity, wind, and rain), unsuitability for short term monitoring, and need to be validated with collocated continuous active monitors (Cox, 2003; Kot-Wasik et al., 2007; Krupa and Legge, 2000; Runeckles and Bowen, 1999; Scethapathy et al., 2008).

The Methods section of this paper includes information on the study area and the study design followed by passive sampler preparation and analysis. The method to calculate accuracy and precision of passive diffusion sampler is also included in the Methods section. The ambient concentrations of NO\textsubscript{2} and SO\textsubscript{2} are described in the Results and Discussion section. Comparison of the data obtained from passive samplers with continuous monitoring is provided at the end of the Results and Discussion section, with the conclusions summarized at the end.

4.2. Methods

4.2.1. Study area and design

Northeast B.C. is a region of plains, bordered by the Yukon and Northwest Territories to the north, the Rocky Mountains to the southwest and the province of Alberta to the east. It is the largest of B.C.’s regions, representing 21.8% of the land area of the province (20,494,470 ha), but the least populated, with 1.6% of the population (69,068 people). Of those residing there, approximately 13% consider themselves to be of aboriginal (i.e., First Nations) descent. The Northeast region has one of the most active economies in B.C. and this active economy is mainly driven by oil and gas exploration and production. Due to this, the population of the northeast is expected to rise to almost 80,000 by 2030 (http://www.welcomebc.ca/Live/about-bc/regions/northeast.aspx). There are extreme
differences in temperature between the warmest and coldest months of the year, in some areas for example in Fort St. John, average daily temperature can range from -21 °C in January to +14 °C in July. Major communities are located in Fort St. John, Fort Nelson, Taylor, Dawson Creek, Chetwynd and Hudson’s Hope where oil and gas development activities are happening. In the present study, passive air quality sensors were deployed around each of these communities (Fig. 2.3), except Fort Nelson, which is geographically separated from the others.

Two-week average ambient concentrations of NO$_2$ and SO$_2$ were measured at 24 sites across Northeastern B.C., Canada (Fig. 2.3, Table 2.3) during the period August 2013-November 2013. Two sites were selected in existing air quality monitoring stations (Taylor Town Site and Pine River Hasler, Fig. 2.3; and an additional site in central B.C. collocated at the B.C. Environment Plaza 400 monitoring location in Prince George, B.C., Canada) as they were part of an established B.C. air quality monitoring networks in order to assess the passive sampler performance. Besides these, all other sites (Table 2.3) were selected to cover the region of oil and gas development activities in the Montney formation of Northeastern B.C., corresponding to the Peace River region of B.C., based on National Pollution Release Inventory data base (NPRI, Nitrogen oxide and sulfur oxide emissions for Canada, 2011, available at: http://www.ec.gc.ca/inrp-npri/default.asp?lang=en&n=1D892B9F-1). All sites were chosen to be free of obstacles impeding wind flow, and, with a few exceptions (Table 2.3), most sites were also at least 3.0 kilometers from major industrial sources and from urban areas in order to provide a better estimate of the overall spatial pattern of ambient levels by avoiding the local impact of point source emissions. A few sites (Table 2.3) were
also placed at private homes to assess the ambient concentrations directly relevant to human exposure.

4.2.2. Sampler preparation and analysis

The Willems badge diffusive passive samplers (Fig. 2.4a) were provided by the laboratory of Professor Julian Aheme, Trent University, Ontario, Canada. Once the passive samplers were exposed at the field locations they were returned to Trent University by post (in resealable zip-lock plastic bags packaged in cardboard) for laboratory analysis. Exposed samplers before laboratory analysis and unexposed samplers before deployment were refrigerated at 4°C. Samplers were exposed in triplicate for each species, for a total of six samplers per site. A two-week sampling frequency at a height of 1.8 m was used (except Plaza 400 and Site 16, which were located on the roof-top of a 4 and a 1 storey building, respectively), which corresponds to the height of the active samplers they were collocated with. Each sampler was mounted using Velcro® under a 127 mm diameter plastic cap that acted as a precipitation and bird shield (Fig. 2.4b). There were a total of six exposure periods from August 15, 2013 until November 11, 2013. All NO$_2$ samplers in the 5$^{th}$ exposure period were not considered for analysis due to a problem with sampler preparation. Also, two thirds of all sites during first two exposure periods were monitored for both species with duplicate rather than triplicate passive samplers due to a shortage of samplers. During each exposure period, five unexposed samplers were retained as laboratory blanks. Besides laboratory blanks, travel blanks or lot blanks (for each return shipment from Peterborough, Ontario to Prince George, B.C.) and field blanks (for both species of each exposure) were also sent to and from sample sites periodically throughout the study and compared to laboratory blank samplers to ensure that the sampler cap and resealable bags were effectively protecting the samplers from
contamination between preparation, shipment, exposure and analysis. Travel or lot blanks were not carried to and from the field.

Passive diffusion samplers can be broadly classified into tube, radial, badge and cartridge-type samplers (Krupa and Legge, 2000) and these samplers can have substantially different uptake rates, which make them more or less suitable to certain applications (Yu et al., 2008). For instance, tube-type samplers have generally lower uptake rates due to longer axial diffusion path and smaller cross-sectional diffusion area, which make them suitable for assessing relatively long-term (e.g., monthly mean) ambient air quality levels. In contrast, the badge-type and radial samplers which have typically higher uptake rates due to shorter diffusion paths and larger diffusion areas, are suitable for assessing relatively short-term (e.g., daily mean) personal/occupational exposure to air pollution (Vardoulakis et al., 2009). Furthermore, badge-type samplers are advantageous over tube-type since they have an entrance filter to create a diffusion area free from turbulence to avoid wind effects (Van Reeuwijk et al., 1998). The basic principle behind all passive sampler measurements is the principle of diffusion of gases from the atmosphere into a sampler of defined dimensions onto an absorbing medium, according to Fick's law. The sampler’s theoretical uptake rate is a function of the length, L (m), and the cross-sectional area, A (m²), of the stationary air layer within the sampler, and can be calculated provided that the diffusion coefficient, D (m²s⁻¹), of the gas of interest is known. In particular, tube and badge type passive samplers are used extensively to measure atmospheric NO₂ (Tang et al., 2001). In this particular study, ambient concentrations of gaseous NO₂ and SO₂ were measured with the Willems badge passive sampler which has been tested to perform well against co-located active sampling methods (Zbieranowski and Aherne, 2012a; 2012b). The Willems badge passive sampler has a
cylindrical body (diameter 28 mm and length is 15 mm) in which a specially treated filter paper absorbs a specific gas from the air (see also Fig. 2.4). Triethanolamine (TEA) coated filter paper was placed inside the Willems badge passive sampler to absorb NO\textsubscript{2} from ambient air while Nylasorb filters without chemical coating were used in the badge type passive samplers as Nylasorb directly absorbs SO\textsubscript{2} from the air. The methods of Willems badge passive sampler preparation, analysis and calculation are described in detail in Zbieranowski and Aherne, (2012a and 2012b) (also see sections: 2.3.3.1 and 2.3.3.2). The samplers for this study were constructed at Trent University, Ontario, Canada to the exact specifications of the original Willems badge sampler for NO\textsubscript{2} (Van Reeuwijk et al., 1998) and the SO\textsubscript{2} sampler was a modified design from Bytnerowicz et al. (2005) (Zbieranowski and Aherne, 2012a, 2012b). Samplers were capped and sealed inside zip-lock plastic bags and placed in a cardboard box prior to transfer to University of Northern British Columbia (UNBC), B.C., Canada by post for deployment in the field. It is noted that Zbieranowski and Aherne, (2012a and 2012b) did not measure SO\textsubscript{2}, however, design and analysis of SO\textsubscript{2} from the Willems badge type sampler is similar to that of H\textsubscript{3}NO\textsubscript{3} sampler except for the generation of a standard calibration curve during analysis with Ion Chromatography (Professor Julian Aherne, Trent University, Canada, Personal Communication). The method limit of detection (LOD) of NO\textsubscript{2} and SO\textsubscript{2} passive samplers were 0.3 ppb (0.54 µg m\textsuperscript{-3}) and 0.03 ppb (0.07 µg m\textsuperscript{-3}), respectively and these were estimated from three times the standard deviation of laboratory blanks of each corresponding species. It is also noted that no significant differences were obtained in lab blanks over field or travel blanks for both species ($p > 0.05$ in $t$-test of all cases). The lab blank mean value was subtracted during calculation of ambient concentrations of each species.
4.2.3. Accuracy and precision of Willems badge passive samplers

The accuracy of Willems badge passive diffusion samplers was assessed using the percentage relative error (%) (also known as relative bias):

\[
\text{Accuracy} = \left(\frac{C_p - C_a}{C_a}\right) \times 100
\]

(1)

Where \( C_p \) is the air pollutant concentration measured with a Willems badge passive sampler while \( C_a \) is the concentration measured with the reference active method (i.e. automatic chemiluminescence and UV Fluorescence method applied for NO\(_2\) and SO\(_2\) measurement, respectively in the B.C. continuous air quality network, url: http://www.bcairquality.ca/assessment/monitoring-instruments.html, accessed on: 11 September 2014) and averaged over the same time period at exactly the same location. It should be noted that the percentage relative error is used here as a simplified indicator of accuracy and this method is also applied in other studies (Campos et al., 2010; Vardoulakis et al. 2009). In addition to accuracy estimation, the least-squares regression equation coefficients of the passive diffusion measurements (dependent variable) against automatic active measurements (independent variable) were also used as an indicator of linearity between these two methods. Finally, statistical significance (using a paired \(t\)-test to compare the means of two measurements) was carried out to determine whether the differences were significant between passive and active observations.

The precision of the Willems badge passive diffusion sampling measurements was evaluated from the triplicate (also from duplicate, see section 4.2.2) sets of NO\(_2\) and SO\(_2\) during each deployment at all sites. The relative standard deviation (RSD), which is a statistical measure of repeatability (also called coefficient of variation - CV), was calculated for each pollutant by dividing the standard deviation of the triplicate samples by the mean concentrations over
the same time period and then multiplying by 100. Initially, RSD was calculated for each exposure period separately and then an average CV of each site over the whole sampling period was also provided (Table 4.1). This approach is also used to assess the suitability of passive diffusion samplers elsewhere (Vardoulakis et al. 2009; Zbieranowski and Aherne, 2012a and 2012b). Furthermore, CV was also obtained from calculated concentrations over the whole exposure period for each site of both species in order to evaluate the spatial and temporal variability across the study domain (Table 4.1).

4.3. Results and discussion

Ambient concentrations of NO\textsubscript{2} and SO\textsubscript{2} across the Peace River region of Northeastern B.C. are presented in this section with a focus on sites of higher concentrations. There are 6 periods of two-week exposures (the 5\textsuperscript{th} exposure period for NO\textsubscript{2} was not analyzed) between mid-August and mid-November, 2013 at 24 sites across the region of gas extraction in the Montney formation of Northeastern B.C.

4.3.1. Ambient concentration of NO\textsubscript{2} in Northeastern B.C.

Concentrations of NO\textsubscript{2} across the study area had high spatial variability during the study period (Fig. 4.1a, Table 4.1). Four locations (Site 14, F10, F20 and F15) (Fig. 4.1) had comparatively higher concentrations than the other twenty sites. The maximum concentration of NO\textsubscript{2} among all locations was recorded at Site 14 during the 2\textsuperscript{nd} exposure period at 9.1 ppb. This site also recorded the highest values among all sites across the whole period (except the 1\textsuperscript{st} exposures when F10 recorded the highest value) with values ranging from nearly 4.0 to 9.1 ppb. The F20 and F10 sites also documented high concentrations of NO\textsubscript{2} which were slightly lower than at Site 14; concentrations in these two places varied from 3.5 to 7.4 ppb and 2.7 to 8.1 ppb, respectively. NO\textsubscript{2} concentration at F15 was also high (2.2 to 4.9 ppb) but not as high as Site 14, F10 and F20 (Fig. 4.1a). In contrast, NO\textsubscript{2} concentrations at the other
20 sites (Fig. 4.1a) had lower values ranging from below the LOD to roughly 4 ppb with the following different pattern of variation across the whole period of exposures. Note that the four high concentrations sites (Site 14, F10, F20 and F15) show some temporal variation with a decrease during and after the 3rd exposure period (September 14, 2013 to September 28, 2013), while the highest values were captured by passive samplers during the 2nd exposure period (August 31, 2013 to September 14, 2013), which might be associated with the changes of source activities. However, this three months study is not long enough to justify the temporal variation; therefore, further study at least for one year is recommended. In general, NO$_2$ concentrations are higher when daytime sunlight is lower because there is decreased photo dissociation of ozone and hydroxyl radical formation leading to reduced conversion of NO$_2$ to HNO$_3$ (Hertel, 2011). Since the sampling period is in a period of decreasing sunlight from August through November, one might expect increasing NO$_2$ concentrations during this time, all else being equal. But, there was a sharp decrease in NO$_2$ concentrations after the temperature decreased from roughly 15°C to below freezing (-0.8°C) throughout the study period (local air temperature data were collected from an adjacent weather station [url: http://weather.gc.ca/city/pages/bc-78_metric_e.html] which were then corrected to estimate site specific air temperature using a lapse rate adjustment). This decrease on observed concentration may indicate reduced sampling efficiency of TEA (Triethanolamine) based passive samplers under colder temperatures and reduced humidity (Vardoulakis et al., 2009). TEA has been extensively used as a sorbent in passive samplers for assessing ambient NO$_2$ concentration since the mid 1970s with some studies suggesting that the sampling efficiency of TEA may be reduced at low humidity and temperature (Hafkenscheid et al., 2009). Zbieranowski and Aherne (2012a) during their Willems badge passive sampler-based study
of NO₂ in Southern Ontario, also noticed a sharp decrease in NO₂ concentrations across southern Ontario, Canada after temperatures fell below freezing. The application of correction factors for temperature and relative humidity following the method developed by Plaisance (2004) did not influence the results of the current study. However, again, this non-consistency might also be related to the fluctuation of emissions from sources which do fluctuate monthly (OGC, 2012b), as well as from changes in atmospheric dispersion.

Three of the sites (F10, F15 and F20) with relatively elevated concentrations were located at private homes (see Table 2.3), while Site 14 is also located close to private homes in Taylor. The levels at these sites as well as at all other sites remain well below the annual national Maximum Desirable Level (MDL) for NO₂ of 32 ppb (Table 4.2).

The average NO₂ of all exposures at each site is shown spatially in Fig. 4.2a. This indicates the highest average values are located near Taylor, Chetwynd, Fort St. John and Dawson Creek. These areas are close to regions of gas development with unconventional drilling in the Montney formation and processing activities based on the BC Oil and Gas Commission (OGC, 2012a) (also see 2.2.1 section for more details) and NPRI database (NPRI, Nitrogen oxide and sulfur dioxide emissions for Canada, 2011, available at: http://www.ec.gc.ca/pdb/websol/querysite/query_e.cfm). However, site F20 (in Chetwynd) with high values of NO₂ is not as close to Oil and Gas development activities. Since this site is located near the center of Chetwynd, vehicle emissions may be responsible for the elevated concentrations of ambient NO₂. Geddes et al. (2009) in their study reported that NO₂ concentrations were highest at Toronto West and Downtown, Toronto reflecting the importance of transportation as an emission source of NOx.
4.3.2. Ambient concentration of SO$_2$ in Northeastern B.C.

Ambient levels of SO$_2$ across the study area except the Site 14 did not have as much spatial variability as NO$_2$ during the study period (Fig. 4.1b, 4.2b, Table 4.1). In contrast, Site 14 (Fig. 4.1b), had the greatest variation and on average the highest concentrations among all 24 sites. Similar to NO$_2$, the maximum SO$_2$ concentration was recorded at this site (Site 14) during the 2$^{nd}$ exposure period with a value of 1.91 ppb (its lowest concentration was during the 6$^{th}$ exposure at 0.47 ppb, Table 4.1). Sites F13 and F10 had the highest SO$_2$ levels during the 1$^{st}$ exposure period (approximately August 15, 2013 to August 30, 2013; [see Table 2.3] as all sites were not deployed on the same day). Concentrations at these two sites varied from 0.43 to 1.47 ppb and 0.64 to 1.26 ppb, respectively. Although these three sites (Site 14, F10 and F13) recorded elevated concentrations of SO$_2$ during this study, the concentration remain well below Level A annual BC (Provincial) objectives of 10 ppb (Table 4.2).

SO$_2$ concentrations at the remaining sites (Fig. 4.1b) had low values ranging from below the LOD to roughly below 1 ppb with no clear pattern of variation across the whole period of exposures. Averaged values at all sites are shown spatially in Figure 4.2b. Similar to NO$_2$, the locations of high SO$_2$ levels are found near Fort St. John, Taylor and Dawson Creek, which are also in close proximity to locations of unconventional gas development in the Montney formation and processing according to the BC Oil and Gas Commission (OGC, 2012a) and the NPRI database.

Site 14 (Taylor) had the highest ambient concentrations of both NO$_2$ and SO$_2$ with less variation among all exposures compared to most other sites: it had a lower average CV (NO$_2$: 30.0% and SO$_2$: 43.8%, Table 4.1), suggesting consistent emissions and dispersion throughout the study period. According to the NPRI database (NPRI, Nitrogen oxide and sulfur oxide emissions for Canada, 2011, available at:
http://www.ec.gc.ca/pdb/websol/queriesite/query_e.cfm), two significant sources of NO₂ and SO₂ (Station 1-Taylor, McMahon Gas Plant) in Northeastern B.C. are located in Taylor which is the most likely cause of the relatively high NO₂ and SO₂ levels at Site 14 during the study period. A recent study (Hsu, 2013), conducted with passive samplers in the Athabasca Oil Sands Region of Alberta, Canada, found the highest concentration of passively sampled SO₂ and NO₂ (monthly exposure) were at 11.5 km from the largest stationary emission source with amounts of 2.2 ppb (SO₂) and 5.7 ppb (NO₂). These findings are consistent with those of the present study in terms of levels as well as proximity to sources (Fig. 4.2, Table 2.3). Furthermore, recent air quality studies in Northeastern B.C. also reported that due to large sources located in Taylor, SO₂ concentrations would likely be highest in Taylor (Krzyzanowski, 2011, MoE, 2014) and to the east of Taylor (MoE, 2014).

Box plots of both species at the 24 stations (Fig. 4.3) were produced in order to see the variation in levels at each station and between exposures. These box plots provide a visual impression of the location and shape of the underlying distributions. Box plots show a large spread in concentrations at Site 14 for both species (Fig. 4.3a and b). NO₂ had the greatest range in concentrations during the 2nd exposure period followed by the 3rd and 1st (Fig. 4.3c). Similarly, SO₂ concentrations at all sites during the 2nd exposure have the largest variation (Fig. 4.3d).

In the present study, the average precision in terms of RSD (CV) for the triplicate Willems badge passive samplers excluding Plaza 400 were: 16.7% for NO₂ (s.d. = 7.7, range: 7.4-37.5%), and 18.2% for SO₂ (s.d. = 7.5, range: 5.4-34.2%) (Table 4.1). Though individual outlier badges are statistically difficult to identify with 2 or 3 replicates (Vardoulakis et al., 2009), we eliminated a few very obvious outliers (5 for NO₂, n=122; 12 for SO₂, n=147)
from the dataset. The precision of the NO\textsubscript{2} diffusion badges in particular was very consistent with the values reported by Bush et al. (2001) for Palmes-type duplicate tubes exposed for 4-week periods in urban background sites in the UK, however, reported precision of NO\textsubscript{2} in this study is also different from some previous studies (Campos et al., 2010 [badge type samplers]; Vardoulakis et al., 2009 [tube type samplers]). Similar to NO\textsubscript{2}, precision of SO\textsubscript{2} measurements of this study (5.4-34.2%) is also comparable to the value (10-25%) reported by Ayers et al. (1998) where precision was expressed as mean percentage difference between duplicates of the specially designed passive diffusion samplers (very similar to the Willems badge samplers) in Australia. As noted before, there is no published study using passive samplers in Northeastern B.C. to compare with the passive data of the present study.

4.3.3. Comparison of passive with active (continuous) monitors at collocated sites

In this study, one site was collocated at the B.C. Ministry of Environment Plaza 400 continuous (active) NO\textsubscript{2} monitoring site in Prince George (Table 2.3 and 4.1), as there is no continuous monitoring of NO\textsubscript{2} in Northeastern B.C. Three sites (Site 14, Site 16, Plaza 400; Fig. 2.3, Table 2.3) were collocated with SO\textsubscript{2} continuous monitoring. Hourly continuous monitoring data corresponding to the exposure period were obtained from the B.C. Ministry of Environment (B.C. MoE) air quality website (available at: http://www.bcairquality.ca/readings/index.html, accessed on: 11 September 2014) and averaged for comparison with the passive data. The accuracy of NO\textsubscript{2} measurements with passive samplers following eq. (1) varied between 3.0% to 34.6%, with an average of 14.2% for the concentration ranges 6.4-11.9 ppb atmospheric NO\textsubscript{2}. The statistical analysis was also performed using the paired \textit{t}-test to compare the means of these two different measurements and has been found no significant difference between the results of the concentrations
obtained by both passive and chemiluminescence methods ($p=0.0722$ which is higher than the chosen 5% significance level). The correlation between the concentrations obtained with passive samplers for NO$_2$ and the continuous monitors (chemiluminescence method) is significantly strong (Fig. 4.4a) ($R^2=0.78$, $R=0.89$, $p=0.0439$ which is less than the chosen 5% significance level).

The accuracy of the SO$_2$ passive sampler measurements deployed in Site 14, Site 16, Plaza 400 was verified following eq. (1) against the measurements of the collocated continuous SO$_2$ analyzers at three sites. The accuracy of passive samplers for SO$_2$ ranged between 0 to 60.7% in the concentration range of 0.47 to 1.91 ppb at Site 14, -11.1% to 30.8% (except 2$^{nd}$ exposure period which reported 285.7% higher value than the active measurement) in the concentration range of 0.15 to 0.54 ppb at Site 16, and -58.0% to 20.0% in the concentration range of 1.41 to 2.22 ppb at Plaza 400, representing an average accuracy of 7.6% (or 23.0% if also considering the 2$^{nd}$ exposure period of Site 16). Fortunately, the average accuracies of diffusion passive samplers for both species satisfy the limit recommended by the European Union ($\pm25\%$) (Campos et al., 2010). In contrast, the statistical analysis (paired $t$-test to compare the means) shows that there is no significant difference between the concentrations obtained by passive diffusion samplers and continuous monitors in Site 16 and Plaza 400 while significant difference is attained for Site 14 ($p=0.0319$ under 5% significance level). But, the linear regression results for SO$_2$ show that a significant strong correlation is obtained between passive and continuous measurements at site 14 ($R=0.94$, $p=0.0057$) while a poor correlation exists at the other two sites (Site 16: $R=0.17$ and Plaza 400: $R=-0.42$) (Fig. 4.4b). The proper explanation for these inconsistencies is beyond the scope of this study. However, continuous and passive measurement techniques have different purposes and uses,
therefore it is suggested that the data from these two methods can be suitably compared for general trends rather than compared on an absolute basis (Hsu, 2013).

4.4. Conclusions

This air quality study using the Willems badge passive diffusion samplers in Northeastern B.C. indicated higher concentrations of NO$_2$ and SO$_2$ in the regions of high gas development activities. Among all sites, the highest concentrations of both these species were recorded (NO$_2$: 9.1 ppb, SO$_2$: 1.91 ppb) in Taylor where passive samplers were placed in close proximity to gas development and processing activities in this territory suggesting that these activities are an issue for air quality. Besides the gas processing areas, a site near a small urban centre (Chetwynd) also recorded higher than average NO$_2$ levels, likely due to emissions from vehicles. Although some of the sites in Northeastern B.C. sampled during this study recorded elevated concentrations of NO$_2$ and SO$_2$, the concentrations remain well below B.C. (Provincial) ambient air quality objectives.

The overall precision of this passive diffusion sampler is consistent with the precision found in other studies elsewhere. The accuracy of NO$_2$ passive samplers was verified by comparison with the collocated continuous monitoring station in Prince George, B.C. which showed no significant differences between the two methods, suggesting that the passive sampling of NO$_2$ is sufficiently accurate. Similar to NO$_2$, no significant differences in the means were also seen between passive and continuous SO$_2$ measurements at Plaza 400 (Prince George) and Site 16 (study area) while significant differences seen at Site 14. In contrast, Site 14 passive SO$_2$ measurements are strongly correlated ($R=0.94$) with the collocated continuous measurements. However, these inconsistencies in comparisons suggest further study, using a combination of different passive samplers (e.g., tube type) for
long term exposure, such as at least of one year, owing to validate the Willems badge passive samplers particularly for this study area and also to infer the temporal variation of concentrations.

Acknowledgements

The authors would like to express appreciation to the BC Oil and Gas Commission through a gift to UNBC for providing funding for this study. We also acknowledge the BC Ministry of Environment for providing access to air quality data from their continuous monitoring network.
4.5. References


Cox, R.M., 2003. The use of passive sampling to monitor forest exposure to O$_3$, NO$_2$ and SO$_2$: a review and some case studies. Environmental Pollution 126, 301-311.


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Fig. 4.3. Site and exposure specific box plots of both species. Values of all periods of exposures were considered for site specific box plot (a. NO₂, b. SO₂) while all sites values during each exposure period provide exposure specific box plot (c. NO₂, d. SO₂). The line across the box represents the median, whereas the bottom and top of the box show the locations of the first and third quartiles (Q₁ and Q₃). The whiskers are the lines that extend from the bottom and top of the box to the lowest and highest observations inside the region defined by Q₁-1.5(Q₃ - Q₁) and Q₃ + 1.5(Q₃ - Q₁). The hinges in ‘c’ and ‘d’ show the 95% confidence interval of the median. Individual points with values outside these limits (outliers) are plotted with ‘+’ signs.

Fig. 4.4. Comparison of passive with active (continuous) monitor at collocated sites. a) passive NO₂ vs active NO₂ (continuous data from Plaza 400 station in Prince George), b) passive SO₂ vs active SO₂ (three active stations over a total six period of exposures have been considered, see Table 2.3). The equation of the linear regression line (linear fit) of each plot is also included. 1:1 line is also provided in both figures for visual aid.
Table 4.1. Passive measurement of NO\textsubscript{2} and SO\textsubscript{2} concentrations (ppb) in Northeastern B.C., Canada. The CV is also provided in the parentheses.

<table>
<thead>
<tr>
<th>Site IDs</th>
<th>Exposures/ NO\textsubscript{2}</th>
<th>Exposures/SO\textsubscript{2}</th>
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<td></td>
<td>1\textsuperscript{st} (CV)</td>
<td>2\textsuperscript{nd} (CV)</td>
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<td>F2</td>
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Note: *concentrations are below the LOD. N/A indicates missing passive samplers during field exposures. Av (CV) stands for average passive concentration and average CV in the parenthesis. Columns Av (CV) under each section (NO\textsubscript{2} and SO\textsubscript{2}) were calculated from all exposures of each site, however, rows of Av (CV) were from all sites of each exposure. In addition, column Av under each section was calculated from the observed concentrations of each site across the whole study period. All CV values are reported here in percentages (detail in section 4.2.3).
Table 4.2. B.C. ambient air quality objectives.

<table>
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<td>A or lower</td>
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<tr>
<td></td>
<td></td>
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<td></td>
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<td>30</td>
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<tr>
<td></td>
<td>24 hour</td>
<td>60</td>
<td>A or lower</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>B or upper</td>
</tr>
<tr>
<td></td>
<td></td>
<td>140</td>
<td>C</td>
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<td></td>
<td>1 hour</td>
<td>170</td>
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<td>B or upper</td>
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<td></td>
<td></td>
<td>340</td>
<td>C</td>
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<tr>
<td></td>
<td>3 hour</td>
<td>140</td>
<td>Lower</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>53</td>
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<tr>
<td></td>
<td></td>
<td>532</td>
<td>MTL</td>
</tr>
</tbody>
</table>

Abbreviations: MDL=National Maximum Desirable Level; MAL=National Maximum Acceptable Level; MTL=National Maximum Tolerable Level; A, B and C=Provincial Level A, B and C Pollution Control Objectives (B.C.). "Lower" represents discharges as applying to sensitive environmental situations; and "Upper" represent discharges as applying to where it can be shown that unacceptably deleterious changes will not follow. Source: Provincial Air Quality Objective Information Sheet (available at: http://www.bcairquality.ca/reports/pdfs/aqotable.pdf, accessed on: 10 October 2013).
Fig. 4.1. Site and exposure specific concentrations: (a) NO₂; and (b) SO₂. NO₂ passive samplers were not analyzed for exposure 5. The horizontal dash line (red) in both figures represents the LOD.
Fig. 4.2. Spatial distribution of concentrations: (a) NO$_2$, and (b) SO$_2$. The units of both NO$_2$ and SO$_2$ in the color bar are ppb.
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5. Conclusions and Recommendations

5.1. Introduction

Satellite observations of NO\textsubscript{2} and SO\textsubscript{2} between 2005 and 2013 have been considered to investigate the air quality of Northeastern B.C. which has undergone rapid natural gas development since 2005. The satellite observations used in this study are vertically integrated column densities that extend up to few kilometers from the surface to the troposphere. In this study, space-based and model-simulated NO\textsubscript{2} ambient concentrations have also been investigated. In addition, Willems badge passive samplers were also deployed for six two-week exposure periods between August 15 and November 11, 2013 at 24 sites across this region to assess the ambient concentration of NO\textsubscript{2} and SO\textsubscript{2}. The study area is bounded from 55°N to 57°N and the B.C.-Alberta border to 122°W encompassing the towns of Fort St. John, Taylor, Dawson Creek and Chetwynd. The following section highlights the overall findings from this study.

5.2. Summary of results and conclusions

The findings of this study answer the research questions that are listed in chapter one. Question #1 “what are the levels of these pollutants in this region?” is answered through the satellite investigation as well as passive monitoring. All the data products of NO\textsubscript{2} VCDs indicate that the long-term average (2005-2013) of elevated pollutant levels are located in the vicinity of Taylor, Fort St. John, and Dawson Creek with maximum values of $8.0 \times 10^{14}$ molecules/cm\textsuperscript{2} (EC-SP-NO\textsubscript{2}) and the maximum value varies substantially with data products largely due to AMF, tropospheric VCDs retrieval algorithm, and instruments observation time (satellite flight time). Most notably, are the NO\textsubscript{2} VCDs from SP which are 2.6 times higher than those of DOMINO and with the new EC-AMFs the difference remains nearly the
same, but values of both data products increased with the EC-AMFs. Besides the multiple analysis of NO\textsubscript{2} in a relatively large area, SO\textsubscript{2} was analyzed only within few kilometers around the source (McMahon gas processing plant) also located in Taylor using NASA-SP products and is reported to be 0.18 DU SO\textsubscript{2} VCDs (May-August of 2005-2013). This relatively larger value implies Taylor is half as polluted as Canada's one of the largest non-urban SO\textsubscript{2} emission source areas (i.e., Canadian oil sands area). Willems badge passive monitoring of NO\textsubscript{2} and SO\textsubscript{2} also found larger values in the same area that were identified by the satellite observations. The three months average passive monitoring NO\textsubscript{2} and SO\textsubscript{2} maximum concentrations are reported in Taylor with 6.2 ppb and 1.19 ppb, respectively, while model-simulated and space-based nine year average NO\textsubscript{2} surface concentrations are 0.6 ppb and 0.4 ppb, respectively. However, two in-situ monitoring stations, installed these different altitudes in Taylor, reported nine years average SO\textsubscript{2} concentrations of 2 ppb (in the station located at the valley bottom) and 0.9 ppb (at a nearby location above the valley) which indicates possible trapping of pollutants due to less vertical mixing of SO\textsubscript{2} in Taylor. Passive and in-situ monitoring of SO\textsubscript{2} provides reasonable agreement, however, space-based and model-simulated NO\textsubscript{2} concentrations largely varies from passive monitoring might be due to substantial difference of area coverage by these two methods, such as: satellite-based concentration refers to an area of roughly 312 km\textsuperscript{2} (typical one small OMI pixel) while passive sensor takes the point observation. In addition, long-term average, short life time of NO\textsubscript{2} and also quick photolysis of NO\textsubscript{2} during the mid-day (inter-comparison of OMI and SCIA data products justify this quick photodissociation of NO\textsubscript{2}), particularly in summer may also explain the reason of differences between the concentrations obtained from satellite and passive observations.
Question #2 “are the trends in satellite air quality observations between 2005 and 2013 related to the increased trends in oil and gas development activities in this region?” is addressed by the two time intervals (2005-2007 and 2008-2013) EC-SP-NO\textsubscript{2} data products analysis. Note that limited valid SO\textsubscript{2} data products availability all the year round does not allow this study to investigate SO\textsubscript{2} trend analysis. Comparing the 2005-2007 with the 2008-2013 mean NO\textsubscript{2} VCDs, an increase in NO\textsubscript{2} with time (1.7\%/y) is identified close to the Dawson Creek and this increment likely reflects the unconventional drilling commencement since after 2007 in the Montney formation. 60\% of 2012 total production comes from unconventional sources in B.C. and the Montney formation contributes 40\% of the total 2012 unconventional production, however, the southern Montney formation (or Heritage Montney field) which is located in the study area provides 60\% of the total Montney production.

Question #3 “how do these pollutants vary spatially and temporally?” is answered by both satellite and passive observations. All satellite NO\textsubscript{2} data products, simulated model output of NO\textsubscript{2} and passive monitoring of NO\textsubscript{2} and SO\textsubscript{2} reflect almost the same pattern of spatial distributions and these distributions show that Taylor, Fort St. John, Dawson Creek and Chetwynd (not in order) are the most polluted areas of the study. Satellite SO\textsubscript{2} data products were not considered for large scale spatial analysis, however, these data products also found consistently high values in Taylor. Satellite NO\textsubscript{2} data products were also analyzed temporally and have revealed higher values near Dawson Creek since after 2007 due to the commencement of extensive unconventional natural gas development.

Question #4 “are satellite observations of NO\textsubscript{2} and SO\textsubscript{2} from different data products consistent?” is addressed by analyzing several satellite data products and comparing the spatial distribution of both satellite and passive monitoring observations. Passive monitoring
observations were also validated against collocated active (continuous) measurements. As mentioned before, satellite data products are represented by pixels while passive sensor reflects the in-situ observation, therefore, direct validation with passive monitoring is not feasible. However, the spatial distributions of both pollutants using these two measurement techniques have been found consistent distribution (Fig. 5.1). In addition, consistent spatial distributions from all kinds of satellite data reflect the consistency of satellite data products. Furthermore, consistent outcome in the previous investigation that is replicated in this study from the comparative analysis of satellite data products for the larger area (most part of B.C. and Alberta) using similar method of previous study also provides a strong indication of acceptability of present findings.

Fig. 5.1. Spatial distribution of satellite and passive observations of NO₂ and SO₂ in Northeastern B.C. a) Average passive NO₂ observations (Fig. 4.2a) and long-term average EC-SP-NO₂ VCDs (Fig. 3.2d); b) average passive SO₂ observations (Fig. 4.2b) and long-term average SO₂ VCDs (Fig. 3.6a). Note that all passive SO₂ locations are not included here since satellite SO₂ analysis was taken in a relatively small area. Also note that relative size of circle in each plot refers the variation of concentrations (not using the same scale of both plots).
5.3. Recommendations for future work

A number of developments would improve the usefulness of satellite observations of tropospheric trace gases, including a suitable technique being developed for year round valid NO\textsubscript{2} and SO\textsubscript{2} satellite data availability at high latitudes. Future work should also integrate the analysis of satellite observations with in-situ aircraft measurements to directly validate the satellite observations of NO\textsubscript{2} and SO\textsubscript{2} with a particular focus on the Northeastern B.C. and to provide information about other tropospheric constituents over the natural gas development area. The spatial and temporal coverage of the aircraft measurements are also important. Global models and updated emission inventory information will be essential in this integration. Air quality dispersion models in conjunction with the satellite data products should be considered for air quality study especially in this complex terrain area. Long-term passive monitoring of NO\textsubscript{2} and SO\textsubscript{2} with multiple passive sensors should be carried out to validate the passive sensors in respect of meteorology, geography and also concentration of particular pollutants.

Finally, it is suggested that a denser network of air quality stations in Northeastern B.C. with also including NO\textsubscript{2} monitoring facilities be established due to the recent extensive natural gas development activities. Quality assurances should be completed once the real time raw data has been taken. However, in general data older than three months from the current date available in the B.C. air quality data archive website have gone through a quality assurance review but the data are still subject to change. Oil and gas companies are also requested to share real time calibrated monitoring information publicly.
Appendix

Tropospheric slant column densities (SCD) in Northeastern B.C.

The SCD was calculated by multiplying the tropospheric VCD of four different OMI NO\textsubscript{2} data sets (DOMINO-NO\textsubscript{2}, EC-DOMINO-NO\textsubscript{2}, SP-NO\textsubscript{2}, and EC-SP-NO\textsubscript{2}) over Northeastern B.C. with the corresponding tropospheric AMF.

Fig. A1. Average (2005-2013) tropospheric SCD: (a) DOMINO-NO\textsubscript{2}, (b) EC-DOMINO-NO\textsubscript{2}, (c) SP-NO\textsubscript{2}, and (d) EC-SP-NO\textsubscript{2}. Marker notation of each plot from left to right: Chetwynd, Taylor, and Dawson Creek.