MODELLING PHOTOCHEMICAL AIR POLLUTANTS FROM INDUSTRIAL AND BIOGENIC EMISSIONS IN THE TERRACE - KITIMAT VALLEY: A CONSTRAINED COASTAL AIRSHED WITH COMPLEX TERRAIN

by

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Abstract

This study investigates the worst-case ambient concentrations of O$_3$ and its precursors (NO$_X$ and VOCs) that may occur from the construction of large industrial facilities in the Terrace-Kitimat valley airshed. This research is important as the Terrace-Kitimat valley naturally emits high levels of biogenic VOCs in the summer and many of the proposed facilities will, if constructed, emit high quantities of NO$_X$. To date, literature concerning O$_3$ production form industrial development in coastal airsheds with complex terrain is sparse.

The Comprehensive Air Quality Model with Extensions (CAMx) was used as the photochemical model for this research. Spring and summer periods were selected from 2010. Control and Test Case emission inventories were developed, the former for model evaluation and the latter to assess pollutant change. Model evaluation showed that CAMx was able to emulate daytime O$_3$ peaks in an adjacent valley for both periods though overnight titration by NO was less adequately replicated. Sensitivity tests revealed that this was due in part to inadequate Control Case emissions quantification; results improved with the addition of small scale area-based NO$_X$ emissions to account for missing sources in the original emissions inventory.

Results from the spring period suggest that increased industrial emissions, in general, would not contribute to valley-wide O$_3$ increases greater than 5 ppb, as biogenic VOC emissions are minimal throughout the airshed during this season. On the other hand, results from the summer period suggest that increased industrial emissions would, at times, contribute to a greater than 55% increase in O$_3$ concentrations, particularly downwind of Kitimat on days with high temperatures, low planetary boundary layer heights, differential heating of the land and ocean surface temperatures and consecutive days of horizontally recirculating wind.

This research also used the modelled O$_3$ - reactive nitrogen ratio during hours conducive to photochemistry to determine the O$_3$ sensitivity of the Terrace-Kitimat valley airshed. The
airshed is currently sensitive to NO$_X$ emissions however the full construction of all proposed industrial projects would likely change the O$_3$ sensitivity of a large portion of the valley to be sensitive to emissions of VOCs, especially in and around Kitimat.
Preface

This thesis contains the original research and analysis undertaken by the author Benjamin Ralph Weinstein, under the guidance of supervisors Douw Steyn and Peter Jackson.

This thesis contains many figures, some of which are maps. All maps were created by the author using the computer software QGIS, freely available for download from http://www.qgis.org/en/site/. Map base layers were obtained from: online sources (http://geogratis.cgdi.gc.ca/), Dave Amirault and Blair Ells at the B.C. Ministry of Forests, Lands and Natural Resource Operations, and Morgan Hite at http://hesperus-wild.org/.

For the purpose of this research WRF output was obtained from David Suita, a PhD student working at the Geophysical Disaster Computational Fluid Dynamics Centre at UBC.

Results from Chapters 3 and 4 of this thesis were presented at the International Technical Meeting on Air Pollution Modelling and its Application in Montpellier, France, in March 2015. The title of this presentation was: Modelling photochemical air pollutants from industrial emissions in a constrained coastal valley with complex terrain. The extended abstract from this presentation is forthcoming in: Air Pollution Modeling and its Application XXIV, published by Springer.
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List of Symbols

$\alpha$ one of two isomers of pinene

$\lambda$ wavelength

$\mu$ micro
List of Acronyms

AGL  above ground level
AQM  Air Quality Model
AQMS  Air Quality Management System

BC  British Columbia
BV  Bulkley Valley
BVLD  Bulkley Valley - Lakes District
bVOC  biogenic VOCs

CAAQS  Canadian Ambient Air Quality Standards
CAC  criteria air contaminants
CAMS  Community Modelling and Analysis System
CAMx  Comprehensive Air Quality Model with Extensions
CB05  Carbon Bond (2005 update)
CF  Coarse-Fine
CH₄  methane

CMAQ  Community Multiscale Air Quality Modelling System
CMU  Carnegie Mellon University
CO  carbon monoxide
CREATE-AAP  Collaborative Research and Training Experience - Atmospheric Aerosol Program

GREASED  Greatly Reduced Execution and Simplified Dynamics

ICs  Initial conditions

LFV  Lower Fraser Valley

LNG  liquefied natural gas

MAE  mean absolute error

MB  mean bias

MCIP  Meteorology-Chemistry Interface Processor

MEGAN  Model of Emissions of Gases and Aerosols from Nature

MLR  multiple linear regression

MOE  Ministry of Environment

MOZART  Model for Ozone and Related Chemical Tracers

NAAQO  National Ambient Air Quality Objectives

NAM  North American Mesoscale Forecast System

NCAR  National Centre for Atmospheric Research

NCEP  National Centre for Environmental Prediction

NCL  NCAR Command Language

NMB  normalized mean bias

NMHC  non-methane hydrocarbons
NN neural networks

NO nitric oxide

NO$_2$ nitrogen dioxide

NO$_X$ oxides of nitrogen

NOAA National Oceanic and Atmospheric Administration

NOy total reactive nitrogen

NPRI National Pollutant Release Inventory

NSERC Natural Sciences and Engineering Research Council of Canada

O$_3$ Ozone

OH hydroxyl radical

PAN peroxyacetyl nitrate

PBLH planetary boundary layer height

PiG Plume-in-Grid

PM particulate matter

PM$_{2.5}$ particulate matter with aerodynamic diameter less than 2.5 micrometers

ppb parts per billion

PPM Piecewise Parabolic Method

ppm parts per million

PST Pacific Standard Time

r correlation coefficient

RF random forests
**RH** relative humidity

**RMSE** root mean squared error

**RTA** Rio Tinto Alcan

**SMOKE** Sparse Matrix Operator Kernel Emissions Modelling System

**SO₂** sulphur dioxide

**TKV** Terrace - Kitimat Valley

**TKVA** Terrace - Kitimat Valley Airshed

**VOCs** volatile organic compounds

**WRF** Weather Research and Forecast Model
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Dedication

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Chapter 1

Introduction

1.1 Ozone and Ozone Chemistry

Ozone (O₃), a colourless molecule containing three oxygen atoms, plays two distinct roles in Earth’s atmosphere. In the stratosphere (approx 15 to 50 km above ground level (AGL)) O₃ is a valued greenhouse gas, protecting Earth’s surface from biologically-damaging UV-B radiation (Vallero, 2014). In the troposphere however (surface to 15 km), exposure to O₃ can be harmful to human health and vegetation (Krupa, 1997). O₃ is most plentiful in the lower part of the stratosphere commonly referred to as the O₃ layer (approximately 15-28 km) (Finlayson-Pitts and Pitts Jr, 2000). International treaties such as the Montreal Protocol and the Vienna Convention have been developed in order to protect and restore O₃ in this part of the atmosphere (see: Ozone Secretariat, 2015), while at Earth’s surface government standards exist to protect people and plants from exposure to O₃ in high concentrations.

O₃ is not emitted directly into the troposphere; it is either transported from the stratosphere or formed through the chemical reactions of its precursors in the presence of sunlight. For this reason O₃ is considered a secondary pollutant as opposed to a primary pollutant (those pollutants emitted directly into the atmosphere). Tropospheric O₃ chemistry is complex,
nonlinear and involves a multitude of competing reactions. The majority of tropospheric O₃ is produced through chemical reactions (3000 - 4600 Tg O₃ yr⁻¹), while a smaller amount is stratospheric in origin (400 - 1100 Tg O₃ yr⁻¹) (Jacob, 1999). Tropospheric O₃ is largely produced from the photolysis of nitrogen dioxide (NO₂):

\[ NO_2 + hv \xrightarrow{O_2} NO + O_3 \quad (\lambda < 420 \text{ nm}) \]  \( \{1.1\} \)

NO₂ is often combined with nitric oxide (NO) and referred to as oxides of nitrogen (NOₓ). These gases have a variety of tropospheric origins, the largest of which involve high temperature combustion (fossil fuels, biomass burning, etc.) (Jacob, 1999). In many respects, the question of O₃ formation is less about what is making O₃ and more about what is making NO₂.

O₃ photochemistry exhibits a cycling nature with NO and NO₂ based on the following return reaction:

\[ NO + O_3 \rightarrow NO_2 + O_2 \]  \( \{1.2\} \)

This cycle leads to a photostationary state where the O₃ concentration can be determined from the following expression:

\[
[O_3] = \frac{J_3 \cdot [NO_2]}{k_2 \cdot [NO]}\]

(1.1)

where \( J_3 \) is the rate of NO₂ photolysis and \( k_2 \) is the rate coefficient for reaction 1.2 (Jenkin and Clemitshaw, 2002). At night when there is insufficient solar radiation this balance shifts towards reaction 1.2, and O₃ concentrations decrease as a result (Sillman, 2012).

### 1.1.1 Production of Ozone in Polluted Air

In order to produce tropospheric O₃ in elevated concentrations, the presence of other gases is necessary. Interestingly, reactions that eventually produce O₃ all start with O₃ molecules themselves. O₃ is a key precursor to the hydroxyl radical (OH), an important molecule that
controls the oxidizing power of the troposphere through the reactions:

\[ O_3 + hv \rightarrow O^1D + O_2 \ (\lambda < 325 \text{ nm}) \]  \hspace{1cm} \{1.3\}

\[ O^1D + H_2O \rightarrow 2OH \]  \hspace{1cm} \{1.4\}

(Chin et al., 1994)

Once liberated, OH attacks many otherwise inert gasses such as carbon monoxide (CO) and methane (\text{CH}_4). CO is a product of incomplete combustion (typically of fossil fuels) (Fenger, 2002), while \text{CH}_4, a powerful greenhouse gas, has a variety of anthropogenic (natural gas leakage, coal mining and petroleum industries, landfills and the raising of livestock) and natural sources (wetlands are the largest) (U.S. Environmental Protection Agency, 2015a). In the presence of \text{NO}_X, oxidation of CO and \text{CH}_4 can lead to modest production of additional \text{O}_3 (Jacob, 1999).

In the presence of \text{NO}_X and non-methane hydrocarbons (NMHC), OH chemistry can lead to broad \text{O}_3 production and photochemical smog (Crutzen, 1995). Basic reactions involved with \text{O}_3 air pollution are presented below, while those concerning CO and \text{CH}_4 can be found in the literature (succinctly summarized in (Crutzen, 1995) and (Crutzen, 1979)).

Following the production of OH via reactions 1.3 and 1.4, where where \text{NO}_X and NMHC abound (NMHC are a subset of volatile organic compounds (VOCs)), additional \text{NO}_2 formation takes place as part of a five-sequence chain.

\[ RH + OH \rightarrow R + H_2O \]  \hspace{1cm} \{1.5\}

\[ R + O_2 + M \rightarrow RO_2 + M \]  \hspace{1cm} \{1.6\}

\[ RO_2 + NO \rightarrow RO + NO_2 \]  \hspace{1cm} \{1.7\}

\[ RO + O_2 \rightarrow R'CHO + HO_2 \]  \hspace{1cm} \{1.8\}

\[ HO_2 + NO \rightarrow OH + NO_2 \]  \hspace{1cm} \{1.9\}
Where the term $RH$ denotes an organic compound, $RO_2$ denotes the subsequent peroxy radical, $RO$ is a monoxy radical and $R’CHO$ denotes a radical aldehyde. Considering that each NO$_2$ molecule is subsequently photolized into NO and O$_3$ via reaction 1.1, the net reaction for this sequence is:

$$RH + 4O_2 \rightarrow R’CHO + 2O_3 + H_2O \quad \{1.10\}$$

O$_3$ production is complex and nonlinear. In areas with low NO$_X$, O$_3$ production varies linearly with increasing NO concentrations, while in areas with high NO$_X$, O$_3$ production varies linearly with increasing hydrocarbon concentrations but inversely with NO$_2$ concentrations (Jacob, 1999). Thus the emission of one precursor does not guarantee elevated ozone; at times increasing NO$_X$ emissions leads to reduced O$_3$ concentrations.

The cycling in reactions 1.5 through 1.9 ceases when the supply of HO$_X$ (OH + HO$_2$) runs out. This can happen in one of two ways:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad \{1.11\}$$

$$NO_2 + OH + M \rightarrow HNO_3 + M \quad \{1.12\}$$

Reaction 1.11 takes place when NO$_X$ concentrations are low, while 1.12 takes place when NO$_X$ concentrations are very high (Jacob, 1999).

### 1.1.2 Canadian Standards and Objectives for Ground Level Ozone

Acute exposure to elevated O$_3$ has been linked with negative health outcomes such as morbidity and mortality (Tiwary and Colls, 2010). In order to protect the public from exposure to O$_3$ (along with other air pollutants such as particulate matter with aerodynamic diameter less than 2.5 micrometers (PM$_{2.5}$)), the Canadian Council of Ministers of the Environment (CCME) has developed the Air Quality Management System (AQMS). This collaborative approach for improving air quality in Canada contains many elements, including: the Canadian Ambient Air Quality Standards (CAAQS), the concept of airsheds and air zones, industrial
emission standards, mobile source emission standards and monitoring/reporting requirements (Canadian Council of Ministers of the Environment, 2012b). Both the federal and provincial governments have roles in the implementation of the AQMS, outlined by the Canadian Council of Ministers of the Environment (2012c).

As part of the AQMS the federal government has developed the CAAQS for \( \text{O}_3 \) and PM\(_{2.5} \). The \( \text{O}_3 \) standard can be found in Table 1.1. In addition to the CAAQS, the British Columbia (BC) government also has a 1-hour advisory threshold of 82 parts per billion (ppb) which is based on an older set of national objectives, the National Ambient Air Quality Objectives (NAAQO) (British Columbia Ministry of Environment, 2014).

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Averaging Time</th>
<th>Standard</th>
<th>Metric</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_3 )</td>
<td>8-hour</td>
<td>63 ppb</td>
<td>2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>62 ppb</td>
<td>2020</td>
</tr>
</tbody>
</table>

3-year average of the annual 4th-highest daily maximum 8-hour average concentrations.

Within the context of the AQMS the above standards is not the starting point for air quality management purposes; a tiered approach is outlined by the Canadian Council of Ministers of the Environment (2012b) whereby a series of management actions are meant to occur as air quality begins to deteriorate (based on monitoring results).

These tiered levels, along with their respective ambient values are presented in figure 1.1. The metric associated with these threshold values is the same as the \( \text{O}_3 \) metric for the CAAQS (Canadian Council of Ministers of the Environment, 2012a), and is shown in table 1.1. The intent of this process is to keep clean areas clean and provide motivation for air quality management well before the CAAQS is exceeded.
1.2 Proposed Industrial Development in the Terrace - Kitimat Valley

One area which may require some form of air quality management related to the transitioning from the lowest category (green) to some other coloured category (unknown at this time) is the Terrace - Kitimat Valley (TKV), located at the head of the Douglas channel in central-west BC. The TKV stretches 55 km from Kitimat in the south to Lakelse Lake in the north and includes complex coastal terrain with a narrow valley bottom at sea level and mountains reaching 1500 m in elevation. Within the TKV is the District of Kitimat, pop. 8,300 (Statistics Canada, 2014a). To the southeast of Kitimat is Kitamaat Village, a small Haisla community. Just outside the northern edge of the TKV is the city of Terrace which lies along the Skeena river. Just east of Terrace is Thornhill, an unincorporated community. Together these communities have a population of approximately 11,500 (Statistics Canada, 2015a).

The TKV is the primary valley in the Terrace - Kitimat Valley Airshed (TKVA) which stretches from the small First Nations community of Hartley Bay in the south to Kalum Lake in the north. Aside from the locations listed above the airshed is sparsely populated. The airshed’s
complex topographical features along with the locations of its communities can be seen in
figure 1.2.

This valley is poised to undergo large-scale industrial expansion over the coming years; in
addition to the recently completed expansion of an existing aluminum smelter there is also
the potential for the construction of:

- a bitumen-condensate export-import terminal,
- four natural gas liquefaction facilities, and
- an oil refinery.

All of these facilities emit air pollutants, many of which (especially NO$_X$ from liquefied natural
gas (LNG) processing and shipping), are O$_3$ precursors. The current status of all proposed
projects is described in table 1.2.

Table 1.2: Status of proposed projects in Kitimat

<table>
<thead>
<tr>
<th>Industry</th>
<th>Project</th>
<th>Status (August 2015)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smelter</td>
<td>Rio Tinto Alcan Kitimat Primary Works</td>
<td>permit approved, pending appeal and review by BC environmental appeal board</td>
</tr>
<tr>
<td>Liquefied Natural Gas*</td>
<td>LNG Canada</td>
<td>EA certificate granted June 2015</td>
</tr>
<tr>
<td></td>
<td>Kitimat LNG</td>
<td>EA certificate granted originally as LNG import facility in October 2011, in permitting phase</td>
</tr>
<tr>
<td></td>
<td>Douglas Channel LNG</td>
<td>EA Process (final decision October 2015)</td>
</tr>
<tr>
<td></td>
<td>Other LNG (Triton LNG)</td>
<td>EA Process</td>
</tr>
<tr>
<td>Oil Refinery</td>
<td>Kitimat Clean</td>
<td>EA Process</td>
</tr>
<tr>
<td>Bitumen Import Export</td>
<td>Enbridge Gateway</td>
<td>EA Certificate granted pending completion of 125 tasks</td>
</tr>
</tbody>
</table>

*(British Columbia Ministry of Natural Gas Development, 2015b)*

1.2.1 Liquefied Natural Gas

At -162 °C natural gas (mainly CH$_4$) condenses into a liquid and occupies 1/600th of its
gaseous volume (Groupe International Des Importateurs de Gaz Naturel Liquifie, 2009). Once
liquefied, it can be loaded on to marine vessels and transported overseas for sale into export
Figure 1.2: The Terrace - Kitimat valley airshed. The green line outlines the Terrace - Kitimat valley airshed and the thin brown lines are 250 m contours. ⭐️, ⭐️, ⭐️, ⭐️ and ⭐️ identify the locations of Terrace, Thornhill, Kitimat, Kitamaat Village and Hartley Bay respectively. Parallel lines identify the locations of roads. Inset: The location of Kitimat within Canada. Grey lines show provincial and territorial borders. ⭐️ and ⭐️ identify the locations of Kitimat and Vancouver respectively
markets. Natural gas is extracted primarily in northeastern BC in areas such as the Horn River and Montney basins, and is proposed to be transported to the coast via pipelines (British Columbia Ministry of Natural Gas Development, 2015a).

The provincial government claims that countries such as Japan and China have a thirst for LNG as replacement for nuclear and coal in power generation (Canadian Press, 2013); this explains in part why there are four proposed LNG projects in the TKV. Thus on the surface there seems to be some global benefit from utilizing this energy source. However, LNG processing has also raised alarm in and around communities where facilities are proposed because its process is emissions-intensive.

Cooling natural gas to its condensation point requires tremendous energy; currently most proponents are proposing to power their refrigeration processes by burning some of their natural gas in gas-fired turbines which drive compressors (Hoffman, 2015). Occurring at high temperatures, natural gas combustion emits large quantities of NOX (for example, each LNG Canada refrigeration circuit requires two turbines, each emitting NOX at a rate of 32.1 kg/hr (Reid et al., 2014)). If all proposed projects in the TKV are built, NOX emissions will reach approximately 28 tonnes per day (refer to emissions chart - figure 2.11 in section 2.3.1, this includes the LNG facilities and their associated marine shipping emissions). To put this into context, correspondence with Environment Canada and Translink in June 2013 estimated that each tonne of emitted NOX per day is equivalent to the NOX emissions from approximately 22,000 vehicles in the Lower Fraser Valley (LFV) which includes the city of Vancouver and its surrounding communities, each driving an average of 37 km per day (this includes a mix of passenger cars, passenger trucks and heavy duty trucks). Thus the total projected daily NOX emissions in the TKV are the equivalent of approximately 616,000 vehicles (Vingarzan, 2013).

Assessing whether or not emissions of O3 precursor pollutants will actually lead to the production of O3 requires an air quality model capable of managing the complex chemistry presented in section 1.1. These models are often referred to as chemical transport models or photochemical models, and are described briefly in the following section.
1.3 Photochemical Models

Photochemical models are air quality models that simulate the production, loss and advection of photochemical pollutant concentrations using a series of equations which characterize the chemical and physical processes in the atmosphere. Most of these models employ an Eulerian-based fixed coordinate system with (respect to the ground) consisting of a three-dimensional series of cells. At each time step in the model period, emissions advect from one cell to another and are subjected to the physical and chemical processes quantified in the model’s code (U.S. Environmental Protection Agency, 2015b). Final concentrations within each grid cell are a function of six factors:

1. emissions within the cell,
2. deposition within the cell,
3. chemical production in the cell,
4. chemical loss inside the cell,
5. advection of pollutants into the cell from adjacent cells, and
6. advection of pollutants out of the cell into adjacent cells (Jacob, 1999).

Chemical production and loss are highly nonlinear, as reaction rates for many compounds depend on environmental conditions as well as ambient concentrations themselves (Jacob, 1999). A broad schematic of the photochemical grid modelling system is presented in figure 1.3.

1.3.1 Comprehensive Air Quality Model with Extensions

The Comprehensive Air Quality Model with Extensions (CAMx) is an Eulerian photochemical and dispersion air quality model currently in its sixth edition. It is built and maintained by Environ International Corp. (a global air quality consulting company) and is freely download-
Figure 1.3: A broad schematic of the Eulerian photochemical grid modelling system (Steyn et al., 2012).

able from the internet. Its FORTRAN code and input/output file formats are based on the Urban Airshed Model (UAM) convention. (ENVIRON, 2013). CAMx’s numerous data input requirements (many of which are also models) fall into five general categories: emissions, meteorology, photolysis, geographic and air quality. A schematic of the CAMx modelling framework including its pre and post-processors are presented in figure 1.4. Each category is colour-coded. More information on the sub-models are presented in chapter 2. CAMx, with its Eulerian nature and chemical processes, is capable of assessing O$_3$ and its precursors.
1.4 Research Motivation

The cumulative effects of airborne emissions from existing and potential sources in the TKVA were the subject of a recent government study, however, despite high projected emissions of photochemical precursors, it was limited in scope to sulphur dioxide (SO$_2$) and NO$_2$ exposure as well as sulphur and nitrogen deposition. Primary particulate matter (PM) and secondary pollutants were omitted. Yet without an understanding of the total change in atmospheric pollutant concentrations, it is not possible to make final conclusions regarding either the risk(s) from any combination of new sources or the future status of the airshed.

Research pertaining to photochemical modelling of O$_3$ in sparsely populated areas with complex coastal terrain at high latitudes, particularly in the context of industrial development, is limited. A list presented in Simon et al. (2012) of 69 peer-reviewed articles concerning the application of photochemical models in North America between 2006 and 2012 suggests that most applications are regional or continental in nature, and only a handful are applied on a
local scale. Very few relate to industrial development and those that do are regional in scale.

One similar study was conducted by Castell et al. (2010), who showed a range of potential increases to ambient O$_3$ caused by a hypothetical natural gas power plant in a coastal Spanish valley. Model output indicated O$_3$ increases 20 - 40 km and 80 - 140 km away during one episode, and 20 - 60 km away during another. Spatially, O$_3$ increases were greatest in NO$_X$-sensitive areas (nearby forests and hillsides), i.e.: locations with emissions of high biogenic VOCs (bVOC) and low NO$_X$ emissions. Note that this study was conducted in a location that was neither sparsely populated nor situated at high latitudes, but did pertain to complex coastal terrain and industrial development similar to those proposed for the TKVA.

The most similar physical environment to the TKV where O$_3$ has been extensively studied on a local scale is the LFV. The LFV is a temperate and triangular-shaped coastal valley bounded by the Coast mountains to the north, the Cascade mountains to the east and south and the Georgia straight to the west (Armstrong, 1990). Steyn et al. (2013) and Ainslie et al. (2013) used a combination of models, observations and emission inventories to better understand the relationships between reductions in precursor emissions and episodic O$_3$ concentrations. Model simulations indicated that O$_3$ concentrations were highest in tributary valleys on the northern edge of the LFV in locations with no ambient O$_3$ monitoring (Steyn et al., 2013). Furthermore, changes in valley-wide emissions over past decades have changed the O$_3$ sensitivity of certain communities within the LFV. For example, the town of Chilliwack has generally changed from being VOC-limited to NO$_X$-limited (Ainslie et al., 2013). Understanding this kind of change is important as it has implications for airshed management.

While the LFV is similar to the TKV in some respects they are also quite different. The TKV is much narrower and its terrain is more complex. As well, the population of the TKV is very small compared to the LFV (25,000 compared to approximately 2,500,000 (Statistics Canada, 2015b)). Anthropogenic emissions in the TKV are confined to two small urban areas as well as some mobile sources (roads and rail) while in contrast, anthropogenic emissions in the LFV occupy a significant percent of the domain. Lastly, studies in the LFV have been broad in
nature reflecting large-scale changes to airshed emissions while questions in the TKV concern industrial development from a handful of facilities and associated marine shipping emissions. Considering the lack of literature in this area there is currently an opportunity to apply a photochemical model to study industrial development on a scale not often used and to a physical environment that has received little attention. If successful, this approach can be applied to other airsheds with complex coastal terrain subject to industrial expansion where proposed projects emit photochemical precursor pollutants.

1.5 Proposed Research Questions

Given the discussion in the previous sections, the following three research questions have been developed:

1. Can spring and summer photochemical $\text{O}_3$ be replicated by a model in a manner that is fit for the purpose of investigating worst-case concentrations that may result from proposed industrial emissions in a constrained coastal airshed with complex terrain such as the Terrace - Kitimat valley?

2. Should all proposed industrial facilities in the Terrace - Kitimat valley airshed be constructed,

   (a) Where are the locations of the $\text{O}_3$ maxima, and what are the worst-case concentrations that could occur there?

   (b) What meteorological factors contribute to enhancing or reducing $\text{O}_3$ concentrations in the Terrace - Kitimat valley airshed?

3. What is the current and future $\text{O}_3$ sensitivity of the Terrace - Kitimat valley airshed to emissions of $\text{NO}_X$ and VOCs?

Question 1 is broad in nature while Questions 2 and 3 are more specific. Successfully answering Question 1 allows Questions 2 and 3 to be addressed. Question 1 involves the use of a control
case to demonstrate model fitness, i.e.: the modelling of known emissions and their level of agreement with measured values. Question 2 involves the modelling of a test case with projected emissions. The process of answering Question 2 includes not only an analysis of future concentrations but also an investigation into the changes in pollutant concentrations between control and test cases. This two step approach (whereby a model’s credibility in predicting future states is based on its ability to describe a current state) is not uncommon (Song et al., 2010). Question 3 will increase our understanding of the chemical sensitivity of the valley, and may inform O₃ reduction strategies in future airshed management planning initiatives.
Chapter 2

Methods

Running CAMx in order to answer Questions 1, 2 and 3 requires up-front groundwork, categorized into three groups:

1. Period selection.

   Period selection is the process of narrowing the model simulation to only those times considered necessary to address the research questions being asked, as computational resources are expensive. Conditions leading to worst-case $O_3$ must be identified based on some predictors and model runs must be constructed around those times.

2. Developing and evaluating input files.

   Developing and evaluating input files is the process of creating and evaluating all of the inputs used by CAMx. As displayed in figure 1.4, the CAMx modelling system relies on a number of inputs which must be carefully developed in order to obtain reasonable results. Developing inputs requires at least as much time as running CAMx itself as many of these inputs are also models. Output from these models can only be used as input to CAMx after some form of fitness evaluation; in this case some outputs were evaluated quantitatively while others were evaluated qualitatively.

Model settings are the various switches and parametrization schemes in CAMx that can influence the model’s outcomes. For example, the CB05 chemical mechanism in CAMx contains 51 chemical species and 156 reactions while the CB6 mechanism contains 77 gas phase species and 218 reactions (Yarwood et al., 2010). Professional experience often guides the selection of one scheme over another as well as the nature of the emissions inventory and research questions (UNC, 2013).

Completing this up-front groundwork comprises the *modelling approach*. This chapter describes the model approach for each group listed above.

## 2.1 Period Selection

Two periods were selected for this research, one in the spring and the other in the summer. A spring period was chosen because $O_3$ is naturally elevated during this time (Monks, 2000) and the result of adding additional NOX into the TKVA warranted some investigation. A summer period was selected as summer is a more traditional time of year for $O_3$ episodes due to increased production of the OH radical through reactions 1.3 and 1.4 (Jacob, 1999).

Figure 2.1 illustrates the annual $O_3$ cycle in Smithers, BC, the closest location to the TKV with ambient $O_3$ monitoring. The mean maximum daily $O_3$ mixing ratios for the years 2007 through 2013 along with daily maximum values form three select years, 2008, 2011 and 2012 are presented. The springtime $O_3$ peak is evident in this figure. Note that there is no summer peak in Smithers and it is probable that communities in the TKVA share this annual $O_3$ cycle.

The year 2010 was selected for this research due to the availability of emissions data from the Rio Tinto Alcan (RTA) aluminum smelter and the 2010 National Pollutant Release Inventory (NPRI) national emissions inventory. Finding a range of dates for each period was desired where either:

(a) $O_3$ was already elevated, or
Figure 2.1: Maximum daily O\textsubscript{3} mixing ratios at Smithers. Black line is the mean seven year period (2007-2013), red dotted line is 2008, blue dotted line is 2011 and orange dotted line is 2012.

(b) conditions conducive for photochemical O\textsubscript{3} production were present.

As no lengthy O\textsubscript{3} dataset exists for the TKV (permanent O\textsubscript{3} monitoring only began in Terrace in the spring of 2015), exact dates for the model period were informed by a random forests (RF) regression model which incorporated measured ambient meteorological and air quality variables as O\textsubscript{3} predictors. The model was trained with data from Smithers and was then applied to Kitimat. Note that while the climates of the TKV and Smithers are different (coastal and continental respectively), research suggests that the general O\textsubscript{3} climatology is similar across the northern hemisphere, particularly the presence of a springtime peak (Monks, 2000). A review of the limited 2015 springtime O\textsubscript{3} data in Terrace confirms the presence of the springtime peak while a review of summertime O\textsubscript{3} data in Kitimat (from a temporary monitoring program) suggests that afternoon peak mixing ratios are similar to Smithers, while overnight titration is not as prevalent (not shown).

A complete description of this process is presented in appendix A, where it is shown that the model estimated elevated O\textsubscript{3} in 2010 during two periods in the spring (April 14\textsuperscript{th} - 18\textsuperscript{th} and May 2\textsuperscript{nd} - 14\textsuperscript{th}), and two periods in the summer (July 29\textsuperscript{th} - Aug 6\textsuperscript{th} and Aug 12\textsuperscript{th} - 18\textsuperscript{th}). These days coincided with sunny weather and low relative humidity (RH). The final model
period for each season was selected to start at the beginning of the first period of the season and continue to the end of the second. The dates between were included for convenience however were not expected to be conducive to O₃ production. Table 2.1 shows the final dates for both the spring and summer periods.

<table>
<thead>
<tr>
<th>Season</th>
<th>Start Date</th>
<th>End Date</th>
<th>Number of Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>April 14</td>
<td>May 14</td>
<td>31</td>
</tr>
<tr>
<td>Summer</td>
<td>July 29</td>
<td>August 18</td>
<td>21</td>
</tr>
</tbody>
</table>

### 2.2 Developing Meteorological Inputs

As can be seen in figure 1.4, successfully running all other components of the photochemical modelling system requires completed meteorological files as inputs in some manner (with the exception of the photolysis component). Meteorological inputs are perhaps the most important inputs to any dispersion or chemical model as without reliable meteorological inputs they will fail to produce realistic results. This section concerns information related to the meteorological inputs used in this research.

#### 2.2.1 Weather Research and Forecast Model

Excluding data collection (from meteorological monitoring instruments, satellites, etc.), the first step in generating meteorological inputs for any photochemical model is usually to run a prognostic weather model. For this research, meteorological inputs were generated using the Weather Research and Forecast Model (WRF) model. WRF is a dynamical mesoscale prognostic numerical weather prediction model developed in an ongoing collaboration involving the National Centre for Atmospheric Research (NCAR) and the National Oceanic and Atmospheric Administration (NOAA)’s National Centre for Environmental Prediction (NCEP), with several other US government agencies and universities and its user community (National Oceanic & Atmospheric Administration, 2014). According to the WRF website
WRF has over 25,000 users globally in more than 130 countries.

For the purpose of this research WRF (ARW core, version 3.6) output was obtained from David Suita, a PhD student working at the Geophysical Disaster Computational Fluid Dynamics Centre at UBC. Each run consisted of a 34-hour run, initialized at 00:00 UTC (16:00 Pacific Standard Time (PST)). Output from the first eight hours was discarded as model spin-up, and the final two hours were also removed, leaving 31 (spring) and 21 (summer) 24-hour periods. (CAMx modelled each day separately and used final conditions from one day as input conditions for the following day.) WRF was initialized with 32 km North American Mesoscale Forecast System (NAM) gridded output. WRF output was developed for a parent and series of nested grids using a Lambert Conformal projection with horizontal resolutions of 36, 12, 4 and 1.333 km. Figure 2.2 shows the locations of the four grids and their positions relative to North America.

Each domain has a number of east-west and north-south cells (x and y-cells respectively), as well as vertical layers (z-cells). Table 2.2 lists the properties of each model domain.

<table>
<thead>
<tr>
<th>Domain</th>
<th>Name</th>
<th>Horiz. resolution</th>
<th>x-cells</th>
<th>y-cells</th>
<th>z-cells</th>
<th>Grid centre lat</th>
<th>Grid centre lon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent</td>
<td>d01</td>
<td>36 km</td>
<td>99</td>
<td>99</td>
<td>40</td>
<td>54.230</td>
<td>-128.620</td>
</tr>
<tr>
<td>1st nested</td>
<td>d02</td>
<td>12 km</td>
<td>99</td>
<td>99</td>
<td>40</td>
<td>53.883</td>
<td>-129.157</td>
</tr>
<tr>
<td>2nd nested</td>
<td>d03</td>
<td>04 km</td>
<td>120</td>
<td>105</td>
<td>40</td>
<td>54.012</td>
<td>-128.509</td>
</tr>
<tr>
<td>3rd nested</td>
<td>d04</td>
<td>1.333 km</td>
<td>120</td>
<td>159</td>
<td>40</td>
<td>54.117</td>
<td>-128.706</td>
</tr>
</tbody>
</table>

The smallest domain, d04, stretches 206.7 km in the north-south direction and 156 km in the east-west direction. This orientation reflects the orientation of the TKVA. Figure 2.3 shows an outline of d04 along with the locations of TKVA communities Terrace, Kitimat, and Hartley Bay.

From a north-south perspective, Kitimat is located in the middle of the domain while Terrace is located in the centre of the northern half. This was done intentionally to locate the majority of the emissions in the centre of the domain where they could advect north or south depending on wind direction. Hartley Bay, the small First Nations community at the southern edge of
Figure 2.2: All WRF domains. Green and red lines identify the 36 km and 12 km domains respectively, while the blue and black rectangles identify the 4 km and 1.333 km domains respectively.

the TKVA, is located near the southern end of the grid.

Model Settings

Some notable settings for the WRF model physics are provided in table 2.3. These were selected based on David Suita’s judgement and experience.
Figure 2.3: Outline and individual cell structure of the WRF d04. The maroon line is the domain outline and the thin black lines are the 1.333 km cells. ⭐️, ⭐️️ and ⭐️️ identify the locations of Terrace, Kitimat and Hartley Bay respectively. Parallel lines identify the locations of roads.

Table 2.3: Physics options used in WRF

<table>
<thead>
<tr>
<th>Physics Setting</th>
<th>WRF name</th>
<th>Option</th>
<th>Scheme name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longwave radiation</td>
<td>ra_lw_physics</td>
<td>1</td>
<td>RRTM</td>
</tr>
<tr>
<td>Shortwave radiation</td>
<td>ra_sw_physics</td>
<td>1</td>
<td>MM5 shortwave</td>
</tr>
<tr>
<td>Surface layer</td>
<td>sf_sfclay_physics</td>
<td>1</td>
<td>Monin-Obukhov similarity theory</td>
</tr>
<tr>
<td>Land/water surface</td>
<td>sf_surface_physics</td>
<td>2</td>
<td>Noah land surface model</td>
</tr>
<tr>
<td>PBL physics</td>
<td>bl_pbl_physics</td>
<td>1</td>
<td>YSU PBL scheme</td>
</tr>
<tr>
<td>Cumulus parameterization</td>
<td>cu Physics</td>
<td>1</td>
<td>New Kain-Fritsch</td>
</tr>
<tr>
<td>Microphysics</td>
<td>mp_physics</td>
<td>4</td>
<td>WSM 5-class</td>
</tr>
<tr>
<td>Turbulence / Diffusion</td>
<td>diff_opt, km_opt</td>
<td>1, 4</td>
<td>2nd order diffusion on model levels</td>
</tr>
</tbody>
</table>
2.2.2 Weather Research and Forecast Model Evaluation

WRF output was evaluated both quantitatively and qualitatively. The quantitative evaluation involved a comparison of modelled and observed parameters at three locations in the TKV, while the qualitative evaluation judged the spatiotemporal evolution of model output over the course of a single day. The complete evaluation can be found in Appendix C, where it is demonstrated that this WRF output is fit for use in CAMx to address the research questions from section 1.5. A summary of the evaluation methodology is presented in the following section.

Quantitative Evaluation

For the quantitative evaluation, modelled vs. observed variables were compared at three meteorological monitoring stations in the TKV. Only output from d04 was used. Properties of these stations are listed in table 2.4. Note that for all stations the actual elevation was greater than the elevation assigned to the station’s grid cell in WRF.

<table>
<thead>
<tr>
<th>Location</th>
<th>Lat</th>
<th>Lon</th>
<th>Elevation</th>
<th>Elevation (WRF)</th>
<th>x-cell</th>
<th>y-cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrace Access Centre</td>
<td>54.518</td>
<td>-128.598</td>
<td>68</td>
<td>62</td>
<td>66</td>
<td>111</td>
</tr>
<tr>
<td>CYXT Terrace Airport</td>
<td>54.471</td>
<td>-128.573</td>
<td>210</td>
<td>170</td>
<td>67</td>
<td>107</td>
</tr>
<tr>
<td>Kitimat Whitesail</td>
<td>54.069</td>
<td>-128.639</td>
<td>92</td>
<td>83</td>
<td>63</td>
<td>75</td>
</tr>
</tbody>
</table>

The locations of these stations are shown in figure 2.4. While the Terrace B.C. Access Centre and CYXT airport are not far each other (only 5 km), the difference in elevation between stations as well as the position of Terrace relative to the Skeena river valley led to very different results in the quantitative evaluation.

The parameters evaluated were temperature, RH, pressure, wind direction and wind speed. Many of these were proposed by Dennis et al. (2010) as being important from a meteorological evaluation perspective and have the advantage of having been measured at multiple locations.
Figure 2.4: Evaluation locations for WRF d04 output. ★, →, and ★ identify the locations of Terrace BC Access Centre, CYXT and Kitimat Whitesail respectively. The maroon line outlines the WRF d04 and the green line outlines the Terrace - Kitimat valley airshed. Parallel lines identify the locations of roads.

across the valley. Parameters measured at each station and used in the evaluation are listed in table 2.5.
Table 2.5: Parameters measured at meteorological monitoring stations in the Terrace - Kitimat valley airshed

<table>
<thead>
<tr>
<th>Location</th>
<th>Temp °C</th>
<th>RH %</th>
<th>Pressure Pa</th>
<th>Wind Speed ms⁻¹</th>
<th>Wind Direction deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrace Access Centre</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>CYXT Terrace Airport</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Kitimat Whitesail</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

As demonstrated in appendix C, the quantitative evaluation of WRF output shows that the model’s performance was fit for use in CAMx. Results were strongest for pressure and temperature and weakest for RH. Results for wind direction and wind speed were mixed. Despite overall strength of the model temperature output, one important limitation worth noting was the model's inability to recreate peak afternoon temperatures. On days where the measured temperature was greater than 30 °C, WRF was unable to recreate the highs of the diurnal cycles, typically falling short by 5 °C. As discussed later in section 4.2.3, this creates some uncertainty with respect to VOC emissions and resulting O₃ mixing ratios, as emissions of bVOC increase exponentially with increasing temperature, particularly isoprene (Guenther et al., 1993).

**Qualitative Evaluation**

The qualitative evaluation consisted of a spatiotemporal evaluation of wind streamlines and temperature evolution over a 24-hour period. This evaluation was based on personal experience with the TKV and flow in complex terrain. The day of July 31st was selected as this was a hot sunny day with a measured diurnal offshore-onshore wind. The qualitative evaluation showed that both wind streamlines and temperature evolved intuitively over the course of space and time for the chosen day in the evaluation. Streamlines were concentrated in overnight hours and there was evidence of katabatic flow on one side of the TKV. The offshore breeze shifted to become an onshore breeze around noon, about the time one would expect for a day in July in Kitimat, and the model was able to resolve flow around very fine-scale topographical features like tertiary valleys. The spatial and temporal evolution of temperature was as expected for a
summer day in complex coastal terrain, where the land 2 m temperature was originally cooler than the 2 m temperature of the nearby ocean though this reversed around noon. Temperatures at higher elevations also increased to some extent, albeit with a smaller amplitude than the valley bottom temperature.

### 2.2.3 Intermediate Programs: MCIP and WRFCAMx

The second step in developing meteorological inputs for a photochemical model involves translating the relevant outputs from the prognostic weather model into a format used by the photochemical model. This is done by taking the meteorological model output fields in their native formats and: performing horizontal and vertical coordinate transformations, diagnosing additional atmospheric fields, and defining gridding parameters (Otte and Pleim, 2010). The Meteorology-Chemistry Interface Processor (MCIP) (as described in Otte and Pleim (2010)) and WRFCAMx (as described in ENVIRON (2013)) fulfill this role. As some of the inputs to CAMx were built for use in Community Multiscale Air Quality Modelling System (CMAQ), CAMx requires both MCIP and WRFCAMx to be used. Table 2.6 sorts the components of the CAMx modelling system according to the translator program used (refer to 1.4 to view these in the overall context of CAMx).

<table>
<thead>
<tr>
<th>WRFCAMx</th>
<th>MCIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAMx</td>
<td>SMOKE (anthropogenic emissions model)</td>
</tr>
<tr>
<td>MOZART (boundary and initial conditions model)</td>
<td>MEGAN (biogenic emissions model)</td>
</tr>
<tr>
<td>MERGE_LULAI (merges land use and leaf area index files)</td>
<td></td>
</tr>
<tr>
<td>SEASALT (marine emissions (mainly aerosol phosphate) not used in this research)</td>
<td></td>
</tr>
</tbody>
</table>

In addition to the functions described above, MCIP and WRFCAMx also act to shrink the
WRF domain into the CAMx domain in both the horizontal and vertical directions. Typically CAMx domains are between 4 and 12 cells narrower (i.e.: between 2 to 6 cells per side) than WRF domains and contain fewer vertical levels. Table 2.7 lists the properties of the CAMx model domains defined in MCIP and WRFCAMx. An outline of the 1.333 km CAMx domain relative to the WRF domain can be seen in figure 2.5, while figure 2.6 displays the mapping of vertical layers from WRF to CAMx.

Table 2.7: Properties of the CAMx model domains

<table>
<thead>
<tr>
<th>Domain</th>
<th>Name</th>
<th>Resolution</th>
<th>x-cells</th>
<th>y-cells</th>
<th>Vertical Layers</th>
<th>Grid centre lat</th>
<th>Grid centre lon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent</td>
<td>grd01</td>
<td>12 km</td>
<td>93</td>
<td>93</td>
<td>23</td>
<td>53.883</td>
<td>-129.157</td>
</tr>
<tr>
<td>1st nested</td>
<td>grd02</td>
<td>04 km</td>
<td>116</td>
<td>101</td>
<td>23</td>
<td>54.012</td>
<td>-128.509</td>
</tr>
<tr>
<td>2nd nested</td>
<td>grd03</td>
<td>1.333 km</td>
<td>110</td>
<td>155</td>
<td>23</td>
<td>54.117</td>
<td>-128.706</td>
</tr>
</tbody>
</table>

Note that the 36 km domain was not included in CAMx. It was needed in order to develop the WRF input files (i.e.: to ensure large scale atmospheric processes trickled down to the finer grids) but was not required for the local-scale chemical modelling.

Also note that the 1.333 km CAMx domain is ringed by one extra set of cells (not shown), referred to as buffer cells. These cells hold internal boundary conditions between a finer grid and the coarser grid surrounding it. (The 4 km CAMx domain also contains a ring of buffer cells.)

As can be seen from figure 2.6, the transition from 40 to 23 vertical layers occurs gradually. The lower 10 layers of the WRFCAMx domain is structured identically to the lower 10 WRF layers. From layer 11 to 17, WRFCAMx layers occupy two WRF layers and above this WRFCAMx layers occupy three WRF layers (with the exception of the highest WRFCAMx layer which only occupies two WRF layers). This layer structuring was determined based on correspondence with ENVIRON staff (Wilson, 2014).
Figure 2.5: Outlines of the WRF d04 and CAMx grd03. The maroon line outlines WRF d04 and the steel blue line outlines the CAMx grd03. The green line outlines the Terrace - Kitimat valley airshed. ⭐️, ⭐️ and ⭐️ identify the locations of Terrace, Kitimat and Hartley Bay respectively. Parallel lines identify the locations of roads.
2.3 Developing Emissions Inputs

Once meteorological files are developed it is possible to move onto the next important set of inputs, emissions. As these research questions revolve around the effect of proposed emissions it is necessary to ensure they are adequately characterized. Two emissions models were used to calculate and process emissions for the TKVA airshed:

- The Sparse Matrix Operator Kernel Emissions Modelling System (SMOKE) and
- the Model of Emissions of Gases and Aerosols from Nature (MEGAN).

More information on both of these models is given in the following sections.

2.3.1 Anthropogenic Emissions

Anthropogenic emissions were processed in SMOKE, an emissions processor. SMOKE was created in order to prepare emission inventories for use in air quality and chemical models,
which involves transforming an inventory through temporal and spatial allocation as well as chemical speciation (UNC, 2013). SMOKE was created at the Microelectronics Centre of North Carolina’s Environmental Monitoring Centre and is now distributed through the Community Modelling and Analysis System (CAMS) operation (https://www.cmascenter.org/) at Chapel Hill in North Carolina. SMOKE processes all criteria air contaminants (CAC) as well as a variety of toxics (benzene, formaldehyde, etc.). It supports a variety of anthropogenic emission source types such as area, point, mobile as well as biogenic sources. The following subsections concern information regarding the temporal, spatial and chemical speciation of both the Control (used in addressing Questions 1, 2 and 3), and Test (used in addressing Questions 2 and 3) cases.

**Control Case**

The Control case (also referred to as 'Base') served two functions and was used for:

1. Model evaluation, and
2. Calculating percent change between Control and Test Cases

In the TKVA, where the Control case was needed for the second of the above functions, emissions from three source-types were modelled:

1. industrial sources
2. mobile sources, and
3. biogenic sources.

The industrial sources consisted of a single permitted facility, the RTA aluminum smelter, located to the southwest of Kitimat. Within this one facility were many point sources as well as some line sources (treated in SMOKE as area sources based on correspondence with other professionals (Henolson, 2014)). The location of anthropogenic sources can be seen in figure 2.7. In this image roads and rail lines should be considered as emission sources.
Figure 2.7: Emission locations in the Terrace - Kitimat valley airshed for the Control case. ◆ identifies locations of aluminum smelter sources while parallel lines and the solid black line indicate locations of mobile sources (roads and rail sources respectively). ★★★ and ★★★ identify the locations of Terrace, Kitimat and Hartley Bay respectively. The green line outlines the Terrace - Kitimat valley airshed. Inset: A closer look at emission locations in Kitimat.
Emissions information for RTA were obtained largely from the BC Ministry of Environment (MOE) (ESSA-Technologies et al., 2014). CO emissions (for some sources) were obtained from the NPRI, while VOC emissions were not available from either BC MOE or the NPRI. Omission of the smelter’s VOC emissions adds uncertainty to the Control case model scenario. Mobile sources consisting of road (highway only) and rail emissions were derived from the 2010 SMOKE-ready emissions inventory produced by the NPRI, available at http://www.epa.gov/ttnchie1/net/canada.html. Mobile emission totals were available for the Skeena region of BC and were allotted proportionately to cells with roads or rail lines based on the fraction of road or rail in the cell with the total length of roads and rail lines in the region. Daily CAC emissions from the above sources are presented in figure 2.8. (Note: NOX emissions are often apportioned a NO-NO2 split of 90%-10% (Swedish Environmental Protection Agency, 2009).)

![Figure 2.8: Daily criteria air contaminant emissions in the Terrace - Kitimat valley airshed for the control case.](image)

As there was insufficient O3 monitoring in either Kitimat or Terrace, model evaluation occurred in Smithers, the closest location with ambient O3 data. Smithers is located in the Bulkley Valley (BV), adjacent to the TKV and separated by the Coast Mountain range. The BV consists of five incorporated communities, the largest of which is Smithers, pop. 5400 (Statistics Canada, 2014b). Similar to the TKV, emissions from three source-types we modelled as part
of the model evaluation:

1. industrial sources
2. mobile sources, and
3. biogenic sources

The industrial sources consisted of two facilities within Smithers and two to the southeast in Houston (65 km away). Of the facilities in Smithers one was a sawmill and the other a particleboard plant. Sources in Houston included a sawmill and a pellet plant. The location of BV anthropogenic sources can be seen in figure 2.9.

Point source emissions data were obtained from the 2010 SMOKE-ready emissions inventory produced by the NPRI. Possibly due to a lack of reporting requirements, emissions from the permitted sources had disparities with those obtained from the BC MOE permit fee database (Pierce, 2015). Furthermore, these industrial point sources contained no stack information (height, exit velocity, exit temperature, etc.) and so were eventually treated by CAMx as area sources. Despite these differences, the NPRI emissions were used to maintain a level of consistency in the approach (i.e.: without stack testing for NO\textsubscript{X} it is hard to know which numbers to believe). The BV mobile source emissions inventory was developed in the same manner as for the TKVA. Daily CAC emissions form the above sources are presented in figure 2.10. Note that the point source emissions from Houston are omitted in this inventory.

**Test Case**

The purpose of the Test case was to investigate: worst-case O\textsubscript{3} concentrations, the locations of those maxima, the meteorological factors that contributed to enhancing or reducing O\textsubscript{3}, and the future O\textsubscript{3} sensitivity of the TKVA to emissions of NO\textsubscript{X} and VOCs. The Test case consisted of the same source types as the Control case (industrial, mobile and biogenic) though additional sources were included:

- an expanded aluminum smelter (RTA),
Figure 2.9: Outlines of the Bulkley and Terrace - Kitimat valley airsheds and emission source locations in the Bulkley valley for the Control case. The thick light blue line outlines the Bulkley valley airshed while the thick red line outlines the Terrace - Kitimat valley airshed. ● identifies locations of emission sources in Houston and ● identifies the location of an emission source in Smithers (there are two sources but their locations overlap in the larger map). ★, ★, ★ and ★ identify the locations of Terrace, Kitimat, Hazelton, Smithers and Houston respectively. Parallel lines identify the locations of roads while the solid black line identifies the locations of railways. Inset: emission source locations in Smithers for the control case. ● identifies the location of the sawmill while ● identifies the location of the particleboard plant. Parallel lines identify the locations of roads while the solid black line identifies the locations of railways. ★ identifies the location of the St. Josephs air quality monitoring station.
Figure 2.10: Daily criteria air contaminant emissions in the Bulkley valley airshed for the control case.

- four LNG facilities including:
  1. LNG Canada,
  2. Kitimat LNG,
  3. Douglas Channel LNG, and
  4. Triton LNG,
- an oil refinery, and
- marine emissions associated with shipping from all sources.

All industrial sources were input as point sources (SMOKE transforms some point sources to area sources in later processing). Information for the additional emissions was obtained for a variety of sources. For LNG Canada, emissions information was obtained from their Environmental Assessment application (Reid et al., 2014). For all other point sources emissions information was obtained from the BC MOE (ESSA-Technologies et al., 2014), with
the exception of CO and VOC emissions. These data had to be derived based on scaling of equivalent sources from the LNG Canada application, as that inventory was more complete. In some cases information from the NPRI was used to supplement missing information. If it was not possible to derive VOC or CO emissions they were set to 0. To simulate ship movement marine emissions were considered as a series of 27 stationary points within the Douglas channel (this same approach was used by ESSA-Technologies et al. (2014)). The locations of the new sources are not confined to the community of Kitimat and are spread up and down the TKV. The northernmost source is the oil refinery while the marine emissions are spread across the Douglas channel, reaching south past Hartley Bay. These locations are presented in figure 2.11.

Daily CAC emissions for the Test case are presented in figure 2.12. Emissions of all CACs increase relative to the Control case, some by over 700%. Of all the potential new sources to the TKVA, the largest emitters of the photochemical precursor NO\textsubscript{X} are the marine sources that transport LNG. As mentioned, marine sources are spread over the length of the Douglas channel and each individual source is 1/27th of the total emissions. Also recall that these emissions represent the combined emissions from all projects, as the marine emission inventory was developed in this manner by ESSA-Technologies et al. (2014) for the BC MOE. The project with the highest NO\textsubscript{X} emissions is the LNG Canada project.

2.3.2 Biogenic Emissions

Biogenic Emissions in the TKVA

Biogenic emissions, particularly bVOC, play a critical role in the photochemistry of the TKVA and indeed North America. In the USA annual bVOC emissions exceeded anthropogenic VOC emissions (Jacob, 1999). In the TKVA biogenic emissions are by far the largest source of VOCs (by two orders of magnitude). Isoprene, the largest bVOC emitted in the TKVA, is very reactive, with a lifetime of 0.2 days (Fall, 1999) and has been found to produce O\textsubscript{3} at 0.182 ppb/hr (rate coefficient against OH, $k_{OH} \times 10^{12} = 101$) in England (Derwent, 1999).
Figure 2.11: Emission locations in the Terrace - Kitimat valley airshed for the Test case. ● identifies locations of aluminum smelter sources, ○ identifies locations of liquefied natural gas sources, ◦ identifies locations of refinery sources and ● identifies locations of marine sources. Parallel lines and the solid black line indicate locations of mobile sources (roads and rail sources respectively). ★★★ and ★★ identify the locations of Terrace, Kitimat and Hartley Bay respectively. The green line outlines the Terrace - Kitimat valley airshed. Inset: A closer look at emission locations in Kitimat.
In order to appreciate the importance of biogenic emissions it is necessary to understand the factors that contribute to natural emissions, namely, the forest and land cover types in the TKVA. Forest type and landcover in the TKVA are themselves functions of the biogeoclimatic zones in which the valley is located.

The TKV bottom is located within the Coastal Western Hemlock Biogeoclimatic Ecosystem Classification zone of BC (Meidinger and Pojar, 1991), (Banner et al., 1993). As elevation increases there is a transition to the Mountain Hemlock Biogeoclimatic zone while at high elevations (above 1000 m) the Alpine Tundra zone is prevalent. These zones are depicted in figure 2.13 (a). The vegetation in this area ranges from coastal and valley-bottom wetlands and bog-forests, to floodplain shrubs and deciduous forests, to coniferous forests with understories that typically include well-developed shrub and moss layers in stands with open canopies, and finally subalpine scrublands. Forest communities vary with elevation and moisture availability, however overall forest productivity is high in the region. Low-lying coastal areas tend to include western red and yellow-cedar, western hemlock and Sitka spruce (ESWG, 1995). Forest harvesting has converted much of the valley bottom (approximately 97% (Douglas, 2012)) to 20-50 year old second growth western hemlock regeneration that typically creates a very dense
canopy and an impoverished understory. Floodplains include dense shrub cover of red-osier dogwood, red elderberry, salmonberry, horsetails and ferns (Demarchi, 2010). Red alder and black cottonwood are common in disturbed alluvial landforms. Western hemlock occurs up to approximately 460 m elevation with understory species such as blueberry, false azalea and devil’s club (ESSA-Technologies et al., 2013). At higher elevations a subalpine zone of yellow cedar, mountain hemlock and amabilis fir with an understory of blueberry and feather mosses are present. Wet meadows can also be found on perched benches that intercept groundwater. These species transition to stunted trees known as "krummholz", and beyond 1000 m elevation, to mountain heather hearthland and treeless alpine tundra (ESWG, 1995). Rock, snow and ice, with pockets of alpine vegetation characterize the highest elevations (ESSA-Technologies et al., 2013). The various land cover types in the TKV are shown in figure 2.13 (b).
Figure 2.13: Classification of the Terrace - Kitimat valley for: a) biogeoclimatic zones and b) landcover types. ★ and ★★ identify the locations of Terrace and Kitimat respectively.
Table 2.8: Biogenic volatile organic compound species output by the Model of Gases and Aerosols from Nature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Group Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD2</td>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>ALDX</td>
<td>Higher aldehydes</td>
</tr>
<tr>
<td>ETH</td>
<td>Ethene</td>
</tr>
<tr>
<td>EOTH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>FORM</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td>IOLE</td>
<td>Internal olefin carbon bond</td>
</tr>
<tr>
<td>ISOP</td>
<td>Isoprene</td>
</tr>
<tr>
<td>MEOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>NR</td>
<td>Nonreactive VOCs</td>
</tr>
<tr>
<td>OLE</td>
<td>Terminal olefin carbon bond</td>
</tr>
<tr>
<td>PAR</td>
<td>Paraffin carbon bond</td>
</tr>
<tr>
<td>TERP</td>
<td>Terpene</td>
</tr>
<tr>
<td>TOL</td>
<td>Toluene and other monoalkyl aromatics</td>
</tr>
<tr>
<td>XYL</td>
<td>Xylene and other polyalkyl aromatics</td>
</tr>
</tbody>
</table>

MEGAN

Biogenic emissions were developed and processed using MEGAN, a global biogenic emissions model with a base resolution of approximately 1 km (WSU, 2012). The MEGAN user’s manual offers an excellent description of its operation:

MEGAN is a semi-mechanistic model that accounts for the major known processes controlling biogenic emissions... Emissions of 150 chemical species are included in MEGANv2.1 and the model can output individual compounds or categories associated with various atmospheric chemistry schemes. The 150 compounds are lumped into 20 categories based on how emissions vary in response to changes in environmental conditions. Emission variations are first estimated for the 20 categories and then speciated into the 150 compounds or output in chemical categories associated with common atmospheric chemistry schemes (e.g., CB4, CB05, CB6, SAPRC99, MOZART, SOAX). Driving variables include land cover, weather, and atmospheric chemical composition. -MEGAN User’s Guide (WSU, 2012)

Daily airshed-wide biogenic emissions created by MEGAN are shown in figures 2.14 (a) and 2.14 (b) for the spring and summer model periods respectively. Table 2.8 lists the abbreviations and full compound grouping for each bVOC output by MEGAN.
Figure 2.14: Daily biogenic volatile organic compound emissions in the Terrace - Kitimat valley airshed for: a) spring and b) summer model periods.

As can be seen from figures 2.14 (a) and 2.14 (b), summer bVOC emissions are approximately one order of magnitude greater than spring emissions. Airshed-wide bVOC emissions increase with increasing temperature and exceed 300 tonnes per day when the temperature surpasses 29 °C. Emissions are dominated by isoprene and other multiples of the C_5H_8 chain (e.g.: terpenes). Isoprene emissions come largely from deciduous forest stands (aspen trees are particularly high emitters (Sharkey et al., 2008)) and shrubs, and isoprene is thought to be synthesized and emitted as protection against heat flecks, very rapid changes in leaf temperature caused by sunlight (Sharkey et al., 2008). Figure 2.15 shows that biogenic isoprene emissions occur in
high quantities on the west side of the TKV. Cross-referencing this figure with figure 2.13 (b), it is possible to confirm that isoprene emissions are highest in areas with broadleaf, wetland and scrubland land cover. Mature coniferous forest stands emit little isoprene in the TKVA, though there are high emissions on the southern edge of the domain which is designated as coniferous forest.

**Biogenic Emissions in the BV**

Similar to the TKV, biogenic emissions play a critical role in the photochemistry of the BV. The BV is comprised of four distinct biogeoclimatic zones. The Alpine Tundra zone is above 1500 m elevation while between 1000 m and 1500 m is the Engelmann Spruce - Subalpine Fir zone (Meidinger and Pojar, 1991). Below 1000 m elevation two zones split the valley with the northwestern quarter belonging to the Interior-Cedar Hemlock zone and the remainder belonging to the Sub-Boreal Spruce zone (Banner et al., 1993). The Sub-Boreal Spruce zone is characterized by cold winters and warm summers, deep snow cover and dense forests (Meidinger and Pojar, 1991). Coniferous tree species include hybrid white spruce, subalpine fir and lodgepole pines, while deciduous species include trembling aspen, black cottonwood and paper birch. Low elevation wetlands are common in this zone and consist of sedges, scrub birch and willows, with white and black spruce on treed sites. Marshes occur around lakes and streams, usually with horsetails, sedges, cattail and bulrush (British Columbia Ministry of Forests, 1998c). The ecology of the Interior-Cedar Hemlock zone is notably different and is well defined in the BV by the presence of western hemlock. Deciduous tree species include trembling aspen, and paper birch in dry areas. In the rough, steep terrain above these zones, forests of Engelmann spruce and subalpine fir comprise the Engelmann Spruce - Subalpine Fir zone. In the BV this begins approximately above 1000 m elevation. The zone contains few deciduous trees of any kind. Shrubs such as huckleberry and grouse berry are present in open areas and meadows (British Columbia Ministry of Forests, 1998b). Finally, the Alpine Tundra zone is at the highest elevations. This is a treeless environment with steep and rocky terrain and snow-capped peaks. Vegetation is scarce and occurs largely in the mid and lower
Figure 2.15: Isoprene emissions in the Terrace - Kitimat valley on August 15th, 2010 at 16:00 PST. The locations of Terrace and Kitimat are identified with ★, and ★ respectively.

elevations of the zone. Plants of the Alpine Tundra zone are small, close to the ground and snow-covered for up to 10 months of the year (British Columbia Ministry of Forests, 1998a). The delineation of these zones, along with the biogeoclimatic zones of the TKV are shown
in figure 2.16 (a). Lower elevations of the BV support extensive agricultural development, primarily cattle grazing and hay crops, resulting in land cover classification that differs considerably from the TKV where commercial agriculture is a minor land use component. This can be seen by comparing 2.16 (b) with 2.13 (b). Once prevalent throughout, forest harvesting in the BV is now concentrated in side-valleys as agricultural lands have replaced a large proportion of the historically forested lower elevations.
Figure 2.16: Outlines of the Bulkley and Terrace - Kitimat valley airsheds and classification of the region for: a) biogeoclimatic zones and b) landcover types (Bulkley Valley only). ★, ★, ★, ★ and ★ identify the locations of Terrace, Kitimat, Hazelton, Smithers and Houston respectively. Parallel lines identify the locations of roads.
Biogenic emissions developed and processed using MEGAN for the BV are presented in figures 2.17 (a) and 2.17 (b) for the spring and summer periods respectively. In both figures the ordinate has been scaled similarly to figures 2.14 (a) and 2.14 (b) for easy comparison with the TKV. Based on land cover, higher valley bottom elevation (i.e.: cooler temperatures) and a smaller geographic area, bVOC emissions in the BV are approximately 50% of those in the TKV.

Figure 2.17: Daily biogenic volatile organic compound emissions in the Bulkley valley airshed for: a) spring and b) summer model periods.

To emphasize the difference in biogenic emissions between the TKV and the BV, figure 2.18 shows isoprene emissions in both valleys for the same hour as figure 2.15. From this image
it is apparent that the land cover in the BV does not produce the same level of isoprene as the TKV. Indeed, Sharkey et al. (2008) explain that crop plants which are selected for rapid growth require open stomata, and that high stomatal conductance allows high rates of latent heat loss, buffering against heat flecks. Thus, crop plants should not, and generally do not emit isoprene. Also, a review of Smithers and Kitimat summertime temperatures (not shown) suggests that Kitimat experiences higher temperatures than Smithers on days where the maximum temperature is greater than 30 °C. Given that isoprene emissions increase exponentially with increasing temperature (for more see section 4.2.3), on hot days one would expect higher isoprene emissions from isoprene-emitting vegetation in the TKV than the BV. Note that in this image, the emissions scale has been adjusted to accommodate the increase in grid size for the 4 km domain (it takes 9 - 1.333 km cells to make 4 km cells so the emission rate has been scaled to 0 - 900 mol/hr from 0 - 100 mol/hr).

2.3.3 Other Emissions Processing

In sequential order, biogenic emissions were processed before anthropogenic emissions. This is because the final step of the SMOKE modelling system is the merging of anthropogenic and biogenic emissions. All non-point source emissions are output in a CAMx-usable format, and the final step in the emissions processing is to run the point source output files through a separate processor, the PiGSET program. The modeller uses this program to select and set the sources which will be treated with the Plume-in-Grid (PiG) submodel in CAMx. PiGSET also converts ASCII point source files commonly generated by emission models such as SMOKE to CAMx-ready binary format (ENVIRON, 2013). Once PiGSET has completed processing the point sources, all emissions output is ready to be used as input to the photochemical model. (Note that a discussion on plume-in-grid modelling occurs in section 2.6.4.)
Figure 2.18: Isoprene emissions in the Bulkley and Terrace - Kitimat valleys on August 15\textsuperscript{th}, 2010 at 16:00 PST, and outlines of the Bulkley and Terrace - Kitimat valley airsheds. The thick light blue line outlines the Bulkley valley arished while the thick red line outlines the Terrace - Kitimat valley airshed. ★, ★, ★, ★ and ★ identify the locations of Terrace, Kitimat, Hazelton, Smithers and Houston respectively.
2.4 Developing Boundary and Initial Conditions Inputs

Boundary and Initial conditions (ICs) were generated from the Model for Ozone and Related Chemical Tracers (MOZART), a global chemical transport model independent of other chemical models. Detailed information about MOZART is published in Emmons et al. (2010). MOZART output includes 85 gas-phase species and 12 bulk aerosol compounds. 6-hour output can be downloaded for free from http://www.acom.ucar.edu/wrf-chem/mozart.shtml and customized for any domain. MOZART includes 39 photolysis and 157 gas phase reactions in its chemical process. The freely available output uses anthropogenic emissions based on the ARCTAS global emissions inventory (http://bio.cgrer.uiowa.edu/arctas/emission.html), fire emissions from FINN-v1 (Wiedinmyer et al., 2011), as well as biogenic emissions based on MEGAN.

For both spring and summer model periods, output was downloaded for a wide swath of the globe (20°N to 80°N latitude (31 cells) and -90°W to -180°W longitude (37 cells)). MOZART output contains 56 vertical cells. Output was passed through the program MOZART2CAMx, which reads MOZART files and horizontally and vertically interpolates the data onto a CAMx domain to generate date-specific initial and/or boundary conditions. Boundary and ICs were generated only for the outermost domain, grd01.

2.5 Developing Other Model Inputs

Two remaining input categories required for CAMx also consist of models, albeit smaller than WRF, SMOKE, MEGAN and MOZART. These are the photolysis rate models and the land use-leaf area index merging tool. Photolysis rate inputs are critical for the function any photochemical model. Final photolysis inputs were processed by two sub-models, O3MAP (which defines the atmospheric ozone column intervals for CAMx) and the TUV (which is a radiative transfer model developed and distributed by NCAR that develops clear-sky photolysis rate inputs (ENVIRON, 2013)). MERGE_LULAI merges independently-developed landuse
and/or leaf area index fields (taken from MEGAN input) with an existing CAMx surface file generated by WRFACMx.

2.6 CAMx Model Settings

Model settings refers to the various switches and parametrization schemes used in CAMx. Model settings unique to this research are briefly presented below.

2.6.1 Advection

The Piecewise Parabolic Method (PPM), developed by Colella and Woodward (1984), was selected as the horizontal advection solver. This scheme is one of two options available in CAMx and was selected because, despite increasing model runtime, it is considered to have increased accuracy over the area-preserving flux-form advection solver developed by Bott (1989).

2.6.2 Chemical Mechanism

The Carbon Bond (2005 update) (CB05) mechanism was selected for this research. CB05 employs 51 species in 156 reactions, and is suitable for computer modelling studies of O\textsubscript{3}, PM, visibility, acid deposition and air toxics (Yarwood et al., 2005). This is the default option of the SMOKE emissions processor and was chosen mainly out of convenience. It is described in detail in Yarwood et al. (2005) (including a list of all reactions and rate constants).

2.6.3 Aerosol Option

The Coarse-Fine (CF) aerosol scheme was selected for this research. The CF scheme divides the PM size distribution into two static modes (coarse and fine). Primary species can be modelled as fine and/or coarse particles, while all secondary species are modelled as fine particles only.
(ENVIRON, 2013). This scheme was chosen for simplicity, though aerosols are not the focus of this research.

2.6.4 Plume in Grid Option

Grid resolution plays a critical role in resolving emissions advection, yet practical and theoretical considerations suggest 1000 m as the limit to the resolution of Eulerian air quality models (ENVIRON, 2013). This is an important limitation of the Eulerian-based modelling system as it affects their ability to treat point sources. In order to properly model point sources, sub-models referred to as PiG models were developed (Karamchandani et al., 2011). These sub-models track point source plumes outside of the main Eulerian model (using Lagrangian physics and individual plume segments) and only return the plume (also referred to as ‘dumping’) to the Eulerian model when:

- the size of the puff is approximately the same size as the grid, or
- the puff has reached a state of chemical maturity.

The Greatly Reduced Execution and Simplified Dynamics (GREASED) PiG option was selected for this research. This option is described as ideal for treating the early chemical evolution of large NO$_X$ plumes (ENVIRON, 2013) which matches the emissions profiles of LNG and marine sources. Also, this option is compatible with aerosol chemistry and the O$_3$ source apportionment tools available in CAMx. All stacks greater than 20 m were allotted for plume in grid treatment. While PiG treatment is generally reserved for large sources, a low threshold of 0.01 tonnes per day was selected for this research. The result from using such a low threshold was that many NO$_X$ sources were immediately diluted and returned into the grid the following time step.
2.6.5 Wet and Dry Deposition

Wet and dry deposition are important scavenging processes for both aerosols and soluble gaseous pollutants. Both wet and dry deposition options were used in this research. The Zhang et al. (2003) scheme was selected for dry deposition as it is described by ENVIRON (2013) as a state-of-the-science method that has been shown to reproduce observed fluxes of $O_3$ with reasonable accuracy.
Chapter 3

Results and Discussion I: Answering Question 1

Recall Question 1 from section 1.5:

Can spring and summer photochemical $O_3$ be replicated by a model in a manner that is fit for the purpose of investigating worst-case concentrations that may result from proposed industrial emissions in a constrained coastal airshed with complex terrain, such as the Terrace - Kitimat valley?

The nature of answering this question lies in the numerous smaller decisions and settings that comprise a modelling approach, as outlined in chapter 2. Recreating worst-case photochemical $O_3$ generally refers to the magnitude of afternoon maxima, however the model would be somewhat inadequate if it could not also broadly recreate time series consistent with the overall diurnal pattern that $O_3$ exhibits. Also, while $O_3$ is stated explicitly in the above question, some attention must also be given to NO and NO$_2$ because of the important relationship between these gases and $O_3$ as described by reactions 1.1 and 1.2. Therefore, model fitness tests concerning $O_3$ must also include the fitness of the gases that comprise NO$_X$. 
The remainder of this chapter contains an evaluation of model fitness and ultimately conclusions regarding the appropriateness of the modelling approach as described in the previous chapter for recreating worst-case spring and summer O$_3$. This chapter is limited to the O$_3$ portion of the evaluation while the NO and NO$_2$ portions located in appendices D and E.

3.1 Model Fitness Evaluation Description

As ambient monitoring of O$_3$, NO and NO$_2$ is not routine in Kitimat and is limited to two brief periods which do not coincide with either spring or summer model period, modelled output was instead evaluated at the St. Josephs air quality monitoring station in Smithers where ambient observations were available for comparison. Smithers is outside the 1.333 km domain but is within the 4 km domain; its location relative to Kitimat and Terrace can be seen in figure 2.9. Properties of this station are listed in table 3.1 below.

Table 3.1: Location of Smithers St. Josephs air quality monitoring station and corresponding x and y-grid cells in the 4.0 km domains, d03 (WRF) and grd02 (CAMx).

<table>
<thead>
<tr>
<th>Name</th>
<th>Lat</th>
<th>Lon</th>
<th>Elevation</th>
<th>Elevation (WRF)</th>
<th>x-cell</th>
<th>y-cell</th>
<th>x-cell</th>
<th>y-cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smithers St. Josephs</td>
<td>54.783276</td>
<td>-127.177340</td>
<td>497</td>
<td>626</td>
<td>82</td>
<td>73</td>
<td>80</td>
<td>71</td>
</tr>
</tbody>
</table>

The model evaluation consisted of three components:

1. a qualitative evaluation of modelled and observed time series to check their general agreement,

2. a quantitative evaluation of overall and maximum modelled vs. observed mixing ratios using various statistical metrics, and

3. a qualitative evaluation of modelled vs. observed scatterplots to visualize their correlation and determine whether the model output fall in the 2:1 or 1:2 ratio which is commonly accepted as a measure of performance for air quality models (Chang and Hanna, 2004).

Dennis et al. (2010) describe this evaluation as an *operational evaluation*, where statistical and
graphical analyses are aimed at determining whether model estimates are in agreement with the observations in an overall sense. The approach to model fitness is similar to those used in the past (Steyn et al., 2013). The statistical part of the model evaluation was guided by Willmott (1982), Dennis et al. (2010) and Simon et al. (2012). Willmott argued that the best metrics for model evaluation are difference measures as opposed to correlation measures (Willmott, 1982). The strength of these metrics are reinforced by Simon et al. (2012), who listed all statistical metrics used in evaluating photochemical model performance. Metrics selected for this evaluation include normalized mean bias (NMB), mean bias (MB), root mean squared error (RMSE), mean absolute error (MAE), and the correlation coefficient (r). Equations for these metrics are presented in appendix B. The above were selected as a suite to succinctly inform model performance based on the following rationale:

- NMB allows the bias of various parameters to be compared against each other.
- MB is an important element to understanding the performance of any model and was the most commonly used metric in Simon et al. (2012).
- RMSE is a popular choice in many sciences. It penalizes outliers and gives a good indication of whether there were many of these in the dataset.
- According to Willmott and Matsuura (2005), MAE offers a natural measure of average error as it “avoids the physical artificial exponentiation that is an artifact of the statistical-mathematical reasoning from which RMSE comes” (Willmott, 1982).
- While r is not a difference measure and is not recommended by Willmott (1982), it is nevertheless popular (as documented by Simon et al. (2012)), and adds clarity to modelled vs. observed scatterplots.

Consistent with Dennis et al. (2010), statistical confidence levels are not presented. It should also be noted that there is no pass or fail point for any of these metrics (though Chang and Hanna (2004) indicate a NMB < 30% constitutes a ‘good’ outcome), rather the model’s fitness is evaluated based on the cumulative evidence of all metrics.
Dates Omitted

Not all dates from the model periods were included in the evaluation. Those removed from the analysis are listed in table 3.2, along with the rationale for their exclusion.

Table 3.2: Dates removed from model evaluation

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Season</th>
<th>Date</th>
<th>Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_3$</td>
<td>Spring</td>
<td>April 14</td>
<td>First day of model run - spinup</td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>May 14</td>
<td>Final day of model, run incomplete</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>July 29</td>
<td>First day of model run - spinup</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>August 10</td>
<td>Incomplete observation record</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>August 15 - 17</td>
<td>Forest fire</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>August 18</td>
<td>Final day of model run incomplete</td>
</tr>
<tr>
<td>NO and NO$_2$</td>
<td>Spring</td>
<td>April 14</td>
<td>First day of model run - spinup</td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>May 2 - 3</td>
<td>Incomplete observation record</td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>May 14</td>
<td>Final day of model run incomplete</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>July 29</td>
<td>First day of model run - spinup</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>August 15 - 17</td>
<td>Forest fire</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>August 18</td>
<td>Final day of model, run incomplete</td>
</tr>
</tbody>
</table>

3.2 Evaluation Results

3.2.1 Ozone

As can be seen in figures 3.1 (a) and 3.1 (b), modelled O$_3$ and observed mixing ratios show general agreement during daytime hours. Maximum modelled O$_3$ is similar to maximum measured O$_3$ on most days in the spring, while the summer performance is slightly poorer. Overnight however, the model was unable to capture low O$_3$ values. The observed mean difference between maximum and minimum O$_3$ mixing ratios were 36.8 $\pm$ 1.6 ppb in the spring and 28.2 $\pm$ 1.8 ppb in the summer, while the modelled mean difference was only 6.9 $\pm$ 0.6 ppb in the spring and 8.8 $\pm$ 1.3 ppb in the summer (note: $\pm$ values represent standard error).
Evaluation statistics are listed in tables 3.3 and 3.4. Table 3.3 refers to all model-observed hours, while table 3.4 refers to a 12 hour period from 10:00 to 21:00 (the last hour refers to data from 21:00 to 22:00). Considering all paired hours (top line of table 3.3), statistical metrics indicate a clear high bias in both spring and summer, with a MAE of 15.4 and 12.1 ppb respectively. Considering maximum modelled vs. maximum observed values (middle line of table 3.3), statistical metrics are much better. A comparison of the maximum daily modelled mixing ratio and the value of its paired observed value (bottom line of 3.3) indicate CAMx is not able to predict the correct hour of maximum observed O$_3$. 

Figure 3.1: Observed and modelled O$_3$ time series at Smithers for: a) spring and b) summer model periods. Black lines are observed and red lines are modelled Control Case.
Table 3.3: O₃ model evaluation statistics for the Control case - (all hours)

<table>
<thead>
<tr>
<th>Description</th>
<th>Spring</th>
<th></th>
<th></th>
<th>Summer</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>NMB (%)</td>
<td>MB (ppb)</td>
<td>RMSE (ppb)</td>
<td>MAE (ppb)</td>
<td>r</td>
</tr>
<tr>
<td>Paired mixing ratios</td>
<td>662</td>
<td>51.672</td>
<td>13.989</td>
<td>19.921</td>
<td>15.396</td>
<td>0.108</td>
</tr>
<tr>
<td></td>
<td>344</td>
<td>63.834</td>
<td>11.072</td>
<td>15.706</td>
<td>12.095</td>
<td>0.189</td>
</tr>
<tr>
<td>Max model / max obs</td>
<td>29</td>
<td>2.543</td>
<td>1.097</td>
<td>4.857</td>
<td>3.862</td>
<td>0.593</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>5.203</td>
<td>1.622</td>
<td>6.169</td>
<td>4.885</td>
<td>0.235</td>
</tr>
<tr>
<td>Max model w/ paired obs</td>
<td>29</td>
<td>63.027</td>
<td>17.104</td>
<td>22.514</td>
<td>17.811</td>
<td>0.209</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>46.975</td>
<td>10.482</td>
<td>16.174</td>
<td>11.706</td>
<td>-0.289</td>
</tr>
</tbody>
</table>

Statistical metrics improved when data from only the 12 hour period from 10:00 to 21:00 were used. When considering all paired modelled vs. observed values spring and summer biases decreased from 51.7 to 12.8% and 63.8 to 18.9% respectively, RMSE decreased from 19.9 and 15.7 ppb to 10.2 and 9.2 ppb (spring and summer respectively) while MAE decreased from 15.4 and 12.1 ppb to 7.4 and 6.6 ppb (spring and summer respectively). These biases are well below the 30% value presented by Chang and Hanna (2004) as 'good'. The metrics for daily maximum modelled vs. maximum observed mixing ratios also improved, with a MB of less than 1 ppb and a reasonable r value (0.65) in the spring.

Table 3.4: O₃ model evaluation statistics for the Control case - (10:00 to 21:00)

<table>
<thead>
<tr>
<th>Description</th>
<th>Spring</th>
<th></th>
<th></th>
<th>Summer</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>NMB (%)</td>
<td>MB (ppb)</td>
<td>RMSE (ppb)</td>
<td>MAE (ppb)</td>
<td>r</td>
</tr>
<tr>
<td>Paired mixing ratios</td>
<td>333</td>
<td>12.791</td>
<td>4.693</td>
<td>10.219</td>
<td>7.415</td>
<td>0.265</td>
</tr>
<tr>
<td></td>
<td>174</td>
<td>18.923</td>
<td>4.665</td>
<td>9.214</td>
<td>6.568</td>
<td>0.371</td>
</tr>
<tr>
<td>Max model / max obs</td>
<td>29</td>
<td>1.597</td>
<td>0.683</td>
<td>4.787</td>
<td>3.772</td>
<td>0.649</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>2.332</td>
<td>0.727</td>
<td>4.871</td>
<td>4.071</td>
<td>0.523</td>
</tr>
<tr>
<td>Max model w/ paired obs</td>
<td>29</td>
<td>30.441</td>
<td>10.145</td>
<td>15.939</td>
<td>11.315</td>
<td>0.270</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>20.774</td>
<td>5.487</td>
<td>9.216</td>
<td>7.738</td>
<td>0.342</td>
</tr>
</tbody>
</table>

Figure 3.2 is a scatter plot of all 10:00 to 21:00 spring (red dots) and summer (blue dots) paired observed and modelled maximum mixing ratios, along with observed maximum and modelled values for the spring (red diamonds) and summer (blue circles). This figure demonstrates the strength of the Control case output, which is that maximum modelled O₃ mixing ratios are similar to maximum observed. Given the intent of research question 1, agreement between maximum modelled and observed values is crucial.

On the other hand, better agreement between modelled and observed O₃ over all hours would improve model fitness and better demonstrate the appropriateness of the model approach for answering Question 1. Among all the reasons for the inability of CAMx to successfully reproduce overnight O₃ mixing ratios, two were investigated:
Figure 3.2: Observed vs. modelled O\textsubscript{3} scatterplot at Smithers for spring and summer model periods. Small red diamonds small blue dots are daytime (10:00 - 21:00) hourly paired values for spring and summer Control Case model periods respectively. Large red diamonds and large blue circles are maximum daytime modelled vs. maximum daytime observed mixing ratios for spring and summer Control Case model periods respectively.

1. emissions were improperly characterized, and

2. emissions diffused out of the surface layer to higher layers in the model overnight, reducing NO\textsubscript{X} available for titration.

The complete evaluation of NO and NO\textsubscript{2} model output assisted in addressing the first point and an examination of output through vertical layers addressed the second point. Other possible causes of the lack of agreement between overnight modelled and observed mixing ratios, include: the failure of WRF to adequately characterize some meteorological parameters and potentially CAMx’s inability to adequately characterize nocturnal chemistry in rural areas. These were not investigated, as the NO and NO\textsubscript{2} time series, as presented in appendix D, clearly indicate that emissions were a large contributor to the problem. Vertical NO and NO\textsubscript{2} plots presented in appendix D for Smithers also demonstrate that diffusion did not contribute to the poor results overnight.
3.2.2 Fitness of Control Case

As seen from the time series plots, O$_3$ scatter plot and statistical metrics, the control case emissions as described in section 2.3.1, captured afternoon peak O$_3$ values reasonably but failed to recreate the diurnal O$_3$ pattern that was measured in Smithers. Also, as shown in appendix D, the model failed to replicate NO and NO$_2$ mixing ratios at all hours of the day. Indeed, it appeared as though CAMx acted independent of the anthropogenic NO$_X$ emission inventory. Given that the desired outcome of this research was to investigate not only peak O$_3$ but also the complete spatiotemporal O$_3$ distribution, the model’s original emissions inventory caused CAMx to be unfit for research purposes. A series of sensitivity model runs was conducted to determine a more appropriate baseline emission inventory, which is the subject of the next section.

3.3 CAMx Sensitivity to Mobile and Point Source Emissions Perturbations

3.3.1 Sensitivity Case Studies

A series of sensitivity tests were conducted as part of the model evaluation to gauge whether improvements to model fitness could be attained for O$_3$, NO and NO$_2$ by perturbing NO$_X$ emissions. Sensitivity cases can be considered a form of top-down emission inventory development, where the final concentrations are known and the inventory is built to match what was observed. Five scenarios were selected for the sensitivity study, and are listed and described in table 3.5. Emissions for a single cell in Smithers are listed, along with emissions for Smithers and the surrounding cells. The final column lists valley-wide NO$_X$ emissions in tonnes per day. It should be noted that only NO$_X$ emissions were perturbed and that no other CAC was modified.

Three different approaches to emissions perturbations were investigated:
Table 3.5: Sensitivity test names and totalled NOX emissions in Smithers

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Name</th>
<th>One Cell Emissions</th>
<th>One Cell All Smithers Emissions</th>
<th>Approx Smithers Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mobile Point Bio</td>
<td>(moles NO/hr)</td>
<td>Mobile Point Bio</td>
</tr>
<tr>
<td>Base</td>
<td></td>
<td>351.1</td>
<td>103.1</td>
<td>141.2</td>
</tr>
<tr>
<td>10x Mobile</td>
<td>Base Point</td>
<td>381.2</td>
<td>103.1</td>
<td>484.3</td>
</tr>
<tr>
<td>20x Mobile</td>
<td>Mobile Point</td>
<td>38.1</td>
<td>205.7</td>
<td>2065.8</td>
</tr>
<tr>
<td>30x Mobile</td>
<td>Mobile Point</td>
<td>38.1</td>
<td>205.7</td>
<td>2065.8</td>
</tr>
<tr>
<td>50x Mobile</td>
<td>Mobile Point</td>
<td>38.1</td>
<td>205.7</td>
<td>2065.8</td>
</tr>
<tr>
<td>100x Mobile</td>
<td>Mobile Point</td>
<td>38.1</td>
<td>205.7</td>
<td>2065.8</td>
</tr>
</tbody>
</table>

1. perturbing mobile, time varying emissions,
2. perturbing point, time invariant emissions, and
3. perturbing both mobile and point sources.

Three of the five cases (10xm, 20xp and 10xm20xp) represent modest emissions perturbations (relative to the original emissions inventory), while two (50xm and 100xm20xp) represent extreme cases that are unrealistic in magnitude. These emission perturbations were chosen for a variety of reasons. Time invariant point source emissions were perturbed by 20 times to investigate the model’s ability to titrate O3 overnight. Recall that the point sources listed by the NPRI for Smithers had no stack information and thus were treated as area sources by CAMx. Thus these increases in NOX can be considered to account for any and all sources which are constant throughout the day (such as industrial emissions unaccounted for by the NPRI). Mobile emissions were perturbed by a variety of magnitudes (10, 50 and 100 times) to investigate the model’s response to emissions occurring throughout the length of the entire BV.

The diurnal weighting of the time-varying emissions is presented in figure 3.3. From this it can be seen that mobile emissions are greatest in the morning and evening hours, with minimal emissions overnight.

O3 results from the sensitivity tests are presented in the following subsections while the results for NO and NO2 are presented in appendix E. Results for O3 demonstrate improved model fitness with increasing emissions. CAMx had difficulty matching the timing of peak NO values which led to poor statistical outcomes for that pollutant and NO2 even though the magnitudes of peak values for improved noticeably.
3.3.2 Ozone Sensitivity Results

As can be seen from the figures 3.4 (a) and 3.4 (b), nighttime titration was best emulated by the most extreme case, 100xm20xp. The 50xm case also led to overnight titration though its performance was inconsistent (not surprising as this case had reduced emissions overnight). Emissions from the 20xp and 10xm20xp cases also led to some reduced overnight O$_3$ while the 10xm case made little difference to overnight O$_3$. Daytime O$_3$ maxima were increased in all cases, at times bringing the maxima closer to the observed maxima and at times doing the opposite.

Based on the statistical metrics listed in tables 3.6 and 3.7 it is evident that for O$_3$, model performance improved with increasing NO$_X$ emissions. Comparing the Base case to the 100xm20xp case, in the spring model bias decreased from 51.7% to 14.2% (all hours, table 3.6) and from 12.8% to 2.3% (daytime hours, table 3.7). In the summer, model bias decreased from approximately 63.8% to 14.8% (all hours, table 3.6) and from 18.9% to 4.0% (daytime hours, table 3.7). The r also increased with each case of increasing emissions, from 0.11 to 0.62 (spring Base to 100xm20xp, table 3.6) and from 0.19 to 0.71 (summer Base to 100xm20xp,
Figure 3.4: Observed and modelled O$_3$ time series at Smithers for: a) spring and b) summer model periods. Black lines are observed and red lines are modelled Control Case. Green, blue, purple, orange and light blue lines are the modelled sensitivity test cases: 10xm, 20xp, 10xm20xp, 50xm and 100xm20xp respectively, as defined in table 3.5.
Considering all cases, springtime bias metrics were lower than summertime bias metrics, while error metrics were lower in the summer than the spring. Correlation was also better in the summer period (all cases). For O\textsubscript{3}, increased emissions led to improvements in model fitness for all cases except for the 10xm case, which did little to reduce overnight O\textsubscript{3} and led to poorer performance statistically due to increased daytime O\textsubscript{3} mixing ratios.

| Table 3.6: O\textsubscript{3} model evaluation statistics for the sensitivity tests - (all hours) |
|-----------------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Description                               | n | NMB  | MB     | RMSE    | MAE      | r   | NMB  | MB     | RMSE    | MAE      | r   |
|-----------------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Base                                        | 662 | 51.672 | 13.989 | 19.921 | 15.396 | 0.108 | 344 | 63.834 | 11.072 | 15.706 | 12.095 | 0.189 |
| 10x Mobile base Point                       | 662 | 51.683 | 13.992 | 19.404 | 15.133 | 0.270 | 344 | 69.323 | 12.024 | 16.012 | 12.611 | 0.345 |
| Base Mobile 20x Point                      | 663 | 48.820 | 13.230 | 18.595 | 14.537 | 0.352 | 344 | 52.369 | 9.084 | 13.136 | 10.250 | 0.467 |
| 10x Mobile 20x Point                        | 662 | 42.245 | 11.437 | 17.139 | 13.141 | 0.390 | 344 | 60.170 | 10.437 | 13.897 | 11.115 | 0.522 |
| 50x Mobile base Point                       | 664 | 45.638 | 12.370 | 17.295 | 13.775 | 0.509 | 344 | 58.364 | 10.123 | 13.480 | 10.846 | 0.599 |
| 100x Mobile 20x Point                       | 664 | 14.170 | 3.841 | 12.027 | 9.353 | 0.624 | 344 | 14.822 | 2.571 | 8.656 | 6.527 | 0.706 |

| Table 3.7: O\textsubscript{3} model evaluation statistics for the sensitivity tests - (10:00 to 21:00) |
|-----------------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Description                               | n | NMB  | MB     | RMSE    | MAE      | r   | NMB  | MB     | RMSE    | MAE      | r   |
|-----------------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 10x Mobile base Point                       | 334 | 15.467 | 5.675 | 10.612 | 7.862 | 0.315 | 174 | 27.440 | 6.765 | 10.524 | 7.811 | 0.431 |
| Base Mobile 20x Point                      | 335 | 14.871 | 5.462 | 10.153 | 7.779 | 0.408 | 174 | 14.382 | 3.546 | 7.408 | 5.664 | 0.602 |
| 10x Mobile 20x Point                        | 333 | 10.822 | 3.970 | 9.477 | 7.062 | 0.385 | 174 | 23.278 | 5.739 | 8.879 | 6.24 | 0.587 |
| 50x Mobile base Point                       | 335 | 19.141 | 7.023 | 11.447 | 8.938 | 0.428 | 174 | 29.945 | 7.383 | 10.501 | 8.390 | 0.601 |
| 100x Mobile 20x Point                       | 335 | 2.328 | 0.854 | 9.378 | 7.225 | 0.503 | 174 | 4.011 | 0.989 | 6.825 | 5.339 | 0.749 |

Finally, figure 3.5 shows an O\textsubscript{3} scatter plot of the 20xp case. This case was chosen to demonstrate how, when emissions are increased in a modest fashion, the strength of the original model results (reasonable recreation of maximum mixing ratios) is not compromised. Included are all 10:00 to 21:00 spring (red dots) and summer (blue dots) paired observed - modelled mixing ratios along with observed maximum and modelled values for the spring (red diamonds) and summer (blue circles). Considering how overnight O\textsubscript{3} titration is increased with this case, the addition of a constant low-level NO\textsubscript{X} area source is seen as improving model fitness.

These additional emissions could conceivably represent two potential NO\textsubscript{X} sources in Smithers that were unaccounted in the original emissions inventory:
Figure 3.5: Observed vs. modelled O\textsubscript{3} scatterplot at Smithers for spring and summer model periods. Small red diamonds small blue dots are daytime (10:00 - 21:00) hourly paired values for spring and summer 20xp sensitivity case model periods respectively. Large red diamonds and large blue circles are maximum daytime modelled vs. maximum daytime observed mixing ratios for spring and summer 20xp sensitivity case model periods respectively.

- Residential and commercial heating.

Residential and commercial heating in the form of natural gas (or wood) combustion is a source of NO\textsubscript{X} emissions not included in the emissions inventory. Particularly for the spring period when overnight temperatures in Smithers often fall below 0 °C, it is not unreasonable to assume that these emissions occur overnight and contribute to O\textsubscript{3} titration.

- Other Industrial sources unaccounted for in the NPRI.

The NPRI contained one emission source for each Smithers-based industry, however in reality these facilities were comprised of numerous emission sources. For example, actual emissions at the sawmill included natural gas-fired kilns (Pierce, 2015), yet these were not identified in the NPRI. Also, the particleboard plant contained two wood-fired drying stacks (which emit NO\textsubscript{X}) however the NPRI only listed one entry for that facility. Both
of these facilities were located upwind of Smithers at night (when the planetary boundary layer is stable). Discrepancies in emissions from industrial facilities could explain why increasing low-level emissions increased model fitness, as these sources should have been included in the NPRI’s original emission inventory.

The results of the NO and NO$_2$ sensitivity tests can be found in appendix E, along with scatterplots for each sensitivity test. In this appendix it is shown that NO and NO$_2$ results also improved with increasing emissions, however statistical results for NO$_2$ were most improved for the 20xp and 10xm cases, as excess NO emissions let to overproduction of NO$_2$ for the 50xm and 100xm20xp cases.

### 3.4 Question 1 Summary and Conclusion

The following is a summary of the salient outcomes of the five sensitivity model runs.

- The emission inventory for Smithers, taken from the NPRI did not adequately capture NO$_X$ emissions in Smithers. This was evident from the Control case model run where O$_3$ output had little diurnal variability and from NO output which, as shown in appendix D, rarely exceeded 2 ppb.

- CAMx was capable of titrating O$_3$ overnight given additional NO emissions. As shown in appendix E, overnight O$_3$ mixing ratios decreased with increasing NO emissions.

- As shown in appendix E, when NO emissions were very high, overnight NO$_2$ production was elevated and became unrealistically high.

- Modest increases in NO$_X$ emissions from the 10xm and 20xp scenarios led to improved statistical metrics for all gases (O$_3$, NO and NO$_2$) when compared with the Base case.

- With the exception of April 21, none of the modest increase scenarios resulted in greater than 25% elevated O$_3$ when compared with the Base case, suggesting that daytime maxima for these cases were similar with the Base case.
• Of the modest-increase scenarios, the 20xp scenario was better able to titrate overnight

\( O_3 \) than the 10xm case.

Based on the above, the following conclusion can be drawn:

• A top-down emission inventory approach can be a reasonable method for estimating

emissions for the BV, though a well-developed spatial and temporal emissions inventory

would have been ideal. Care must be taken to ensure a balance between elevated emis-

sions (which improves \( O_3 \) and NO) and elevated titration (which produces too much

\( NO_2 \)).

Considering the above, an affirmative answer can be assigned to Question 1. With the inclusion

of an updated emissions inventory, photochemical \( O_3 \) was replicated by a model in a manner

fit for the purpose of investigating worst-case concentrations. The emission inventory for both

Test and Control cases in Kitimat was subsequently amended to incorporate the results of the

model evaluation. In addition to all proposed sources in Kitimat a low-level emission source

was added to the inventory in order to facilitate overnight \( O_3 \) titration. This approach does

not change maximum daytime \( O_3 \) (which forms downwind of \( NO_X \) emissions (Sillman, 2012))

and creates more realistic results overnight, as seen in the above sensitivity tests. In order

to prevent over-titration of \( O_3 \) the new source was minimal, approximately 50% of the 20xp

case (~1.5 tonnes of \( NO_X \) per day). These emissions were uniformly distributed throughout

the urban community of Kitimat and had no diurnal variability. This change to the emission

inventory was a top-down approach to account for all unaccounted sources in the original

emissions inventory. This additional source, when contrasted with the all proposed \( NO_X \)

sources in Kitimat, is minor in magnitude, as seen from the small purple addition to the

\( NO_X \) column in figure 3.6. Also, an updated image showing emission sources near Kitimat is

presented in figure 3.7.
Figure 3.6: Updated daily NO\textsubscript{X} emissions in the Terrace - Kitimat valley for the Test case. Other emissions remain unchanged.
Figure 3.7: Updated emission locations in Kitimat for the Test case. ◈ identifies locations of aluminum smelter sources, ◈ identifies locations of liquefied natural gas sources and ◈ identifies locations of marine sources. ◈ identifies the locations of new low-level area NOX sources. Parallel lines and the solid black line indicate locations of mobile sources (roads and rail sources respectively). Note that local roads are identified with thin brown lines though these are not associated with mobile emissions.
Chapter 4

Results and Discussion II: Answering Question 2

Question 2 has two parts, both of which are useful in deepening our understanding of worst-case $O_3$ production in the TKVA. The exact questions is: should all proposed industrial facilities in the TKVA be constructed,

(a) Where are the locations of the $O_3$ maxima, and what are the worst-case concentrations that could occur there?

(b) What meteorological factors contribute to enhancing or reducing $O_3$ concentrations in the Terrace - Kitimat valley airshed?

Because of averaging times and statistical metrics a number of meanings could be assigned to the words worst-case. In this research worst-case is thought of as hourly maxima, though as $O_3$ research evolves in the TKVA other forms of worst-case may be considered. An important threshold for this analysis is the one-hour mixing ratio of 82 ppb, the level at which the provincial government issues $O_3$-based air quality advisories (British Columbia Ministry of Environment, 2014).
This section follows the following format: section 4.1 looks at the results of the Test case for the spring period. Time series for the three TKVA communities are presented. Spatial and temporal maxima and minima are explored, along with an analysis of the meteorological conditions contributing to the greatest change in O₃ mixing ratios. Section 4.2 is similar in nature to 4.1, though instead of presenting time series at all communities, time series are presented for Kitimat and the locations of the spatial maxima. An analysis of the meteorological conditions contributing to the greatest change in O₃ mixing ratios is included, as well as an example of how varied initial conditions can affect model results.

4.1 Springtime

4.1.1 Time Series: Communities in the Terrace - Kitimat Valley Airshed

Community time series plots tell one part of the spring model period’s story. The spring model period was selected to investigate whether increased NOₓ emissions would exacerbate O₃ formation during the springtime peak which is measured across mid and high latitudes in the northern hemisphere (Monks, 2000). Test Case results for the communities of the TKVA indicated that in the spring elevated NOₓ emissions often led to the opposite, and contributed to broad O₃ titration and NO₂ production. This scavenging was most prevalent in the valley bottom overnight and was shown to, at times, decrease O₃ mixing ratios by 50%.

Figure 4.1 contains spring period O₃ time series for Terrace, Kitimat and Hartley Bay. Included in these plots are planetary boundary layer height (PBLH) and temperature time series. The shaded areas indicate a south wind, while the non-shaded areas indicate a north wind. As can be seen from these plots, Test Case emissions made little difference to O₃ mixing ratios in Hartley Bay (fig 4.1 (a)). Closer to the emission sources in the community of Kitimat, excess (fig 4.1 (b)) O₃ was also rarely produced. Indeed during the model period O₃ was often scavenged, particularly when the wind was from the south. Reductions in O₃ came at the expense of NO₂ production (not shown). O₃ titration was amplified from April 15ᵗʰ - 18ᵗʰ
when there were horizontally recirculation winds over the course of several days. As shown by the alternating shaded and non-shaded backgrounds of the time series, one can imagine the 'sloshing' of air up and down the valley with this repeated wind pattern. Lastly, O$_3$ mixing ratios in Terrace were largely unchanged by the addition of new industrial emissions, except for April 16$^{th}$ and 17$^{th}$, when there was some overnight O$_3$ scavenging by the NO$_X$ plume that stretched the entire length of the TKV (fig 4.1 (a)).

4.1.2 Locations of Minima and Maxima

Spatially the results are more nuanced. Overnight O$_3$ titration was often prevalent at low elevations along the entire length of the TKV when winds were southerly. This is explained by the large-scale NO$_X$ sources and the shallow boundary layer which trapped these plumes when mixing was at a minimum. As an example, figure 4.2 (a) displays an 80 km zone of reduced O$_3$, while figure 4.2 (b) relates these mixing ratios as a percent change from the Control case. Because the marine emission sources stretch the length of the Douglas channel, O$_3$ is scavenged along the entire length of the CAMx grd03 domain (with the exception of the far-north section).
Figure 4.1: Planetary boundary layer depth, O₃ and temperature time series for the spring model period. Model output at: a) Terrace, b) Kitimat and c) Hartley Bay. Black lines are the Control case and red lines are the Test case. Purple shading indicates southerly wind as output from the WRF in Kitimat.
Figure 4.2: CAMx spatial output for the Terrace - Kitimat valley airshed on April 17th, 2010 at 00:00 PST showing: a) Test Case modelled O$_3$ mixing ratios, and b) percent change from the Control case. The green line outlines the Terrace - Kitimat valley airshed. ⭐, ⭐️ and ⭐️ identify the communities Terrace, Kitimat and Hartley Bay respectively, while ⬤ and ⬤️ identify hotspot locations Lakelse Lake and Miskatla Inlet. Parallel lines identify the locations of roads.
On the other hand, daytime production of O$_3$ also occurred, albeit in modest quantities. The hours with the greatest O$_3$ production were 12:00 - 16:00 PST, with 14:00 PST being the hour with greatest O$_3$ differences between Test and Control cases. Locations of this production varied with wind direction but were typically along valley walls, downwind of emissions and outside the fresh NO$_X$ plume. In absolute terms, the change in ambient O$_3$ mixing ratios was limited in magnitude to a maximum of 5 ppb (and often less) though spatially these increases occurred over broad sections of the domain. As the spring O$_3$ peak diminished over the month of April and into May these modest increases in O$_3$ led to a greater overall percent change in O$_3$. Figure 4.3 (a) contains an image showing O$_3$ mixing ratios at 16:00 PST on May 4$^{th}$, while figure 4.3 (b) shows the percent difference between these mixing ratios and the Control case.
Figure 4.3: CAMx spatial output for the Terrace - Kitimat valley airshed on May 4th, 2010 at 16:00 PST showing: a) Test Case modelled O₃ mixing ratios, and b) percent change from the Control case. The green line outlines the Terrace - Kitimat valley arished. ★, ★★ and ★★★ identify the communities Terrace, Kitimat and Hartley Bay respectively, while ⚫ and ⚫ identify hotspot locations Lakelse Lake and Miskatla Inlet. Parallel lines identify the locations of roads.
4.1.3 Ingredients for Reduced Ozone

The meteorological factors which contributed to the greatest change in O$_3$ over the spring period were the coupling of low PBLHs with diurnal horizontal recirculation, particularly on the longer nights early in April. These variables, which contributed to O$_3$ production in the summer (with the exception of night length, see section 4.2), led to long-lasting titration of O$_3$ along the TKV bottom in the spring. Figure 4.4 displays spring PBLH at four locations in the TKV along with generalized mountain peak elevations (as determined from contour plots).

![Figure 4.4: Planetary boundary layer depth time series for the spring model period in the Terrace - Kitimat valley airshed. Model output at: Terrace (yellow lines), CYXT (orange lines), Kitimat (blue lines) and Hartley Bay (green lines). Static lines indicate nearby mountain peak elevations, coloured for the respective communities.](image)

As can be seen from this image in conjunction with the time series in figure 4.1, the days with low PBLH corresponded to days with increased differences between the Control and Test case O$_3$ mixing ratios. This was amplified on days with low PBLH as well as horizontal recirculation, exemplified for the period of April 15$^{th}$ - 19$^{th}$. As can be seen by the shaded sections in figure 4.1, there was a 5-day diurnal onshore-offshore wind pattern which advected pollutants up and down the valley. During this time the low PBLH acted like a lid and limited dispersion vertically. However, despite contributing to an environment for increased O$_3$ as
occurred during the summer (see section 4.2), this created an environment for long-lasting O₃ titration. These dates in the mode period have the longest nights and fewest hours of daylight, another possible contributor. (In fact, these are the shortest days of either model period.) It is also possible that despite ever increasing NO₂ concentrations, the valley lacked sufficient VOC emissions to lead to meaningful O₃ production as occurs in reactions 1.5 through 1.9. As seen in figure 2.14 (a), isoprene emissions were minimal during this time (owing to the absence of leaves on shrubs and deciduous trees) and while terpene emissions were dominant, the rate coefficient of α-Pinene (an example terpene) against OH is 50% of isoprene’s (Derwent, 1999). Thus, in the absence of VOC emissions, those factors which create O₃ can also lead to reduced O₃.

4.2 Summertime

4.2.1 Time Series: Hotspots in the Terrace - Kitimat Valley Airshed

The summer period resulted in increased O₃ production in certain locations of the TKVA under certain meteorological conditions, often in the 12 - 20 ppb range. A spatial examination of the results shows two two prevalent 'hotspots' (i.e.: areas with the greatest increase over the Control case), one to the south of the emission sources and the other to the north.

To the south, the location with the greatest O₃ increase was Miskatla Inlet, a small bay 30 km south of Kitimat along the Douglas channel. Miskatla Inlet was not a location with high VOC emissions; instead this location seemed to trap recirculating air which had advected southward (from Kitimat) earlier in the day and was returning north under an onshore wind. As seen in figure 4.5 (c), Test Case O₃ at this location was at times 50% higher than the control case.

To Kitimat’s north the location of the greatest O₃ increase was Lakelse Lake, 13 km south of Terrace. As seen in figure 4.5 (a), the difference in Control and Test Case O₃ at this location reached over 55% on one instance, and is the subject of further analysis in section 4.2.3. As seen in figure 4.5 (b), O₃ increases did not occur (in any meaningful way) in the community of
Kitimat itself because, as discussed earlier, this pollutant manifests downwind of the emissions of its precursors (Sillman, 2012).

### 4.2.2 Locations of Minima and Maxima

While the locations of greatest increase were within the 1.333 km domain, the spatial extent of O₃ production extended beyond its boundaries on dates which were conducive to O₃ development. Nevertheless only results for the 1.333 km domain are presented. O₃ production occurred throughout the Douglas channel as well as the lower TKV, depending on wind direction. Under a north wind, air masses advected south through the Douglas channel. Under a pattern of horizontally recirculating wind (as exhibited during the first 5 days of the summer period), as these air masses returned northward, pollutants were funneled into and trapped in Miskatla Inlet, explaining why this location to the south of Kitimat is the location of the southern maximum O₃. Figures 4.6 (a) and 4.6 (b) show the accumulation of O₃ there (coloured with a blue circle) as well as the percent increase from the Test case over the Control case.
Figure 4.5: Planetary boundary layer depth, O₃ and temperature time series for the summer model period. Model output at: a) Lakelse Lake, b) Kitimat and c) Miskatla Inlet. Black lines are the Control case and red lines are the Test case. Purple shading indicates southerly wind as output from WRF in Kitimat.
Figure 4.6: CAMx spatial output for the Terrace - Kitimat valley airshed on August 4th, 2010 at 15:00 PST showing: a) Test Case modelled O3 mixing ratios, and b) percent change from the Control case. The green line outlines the Terrace - Kitimat valley airshed. ★, ★★ and ★★★ identify the communities Terrace, Kitimat and Hartley Bay respectively, while ● and ○ identify hotspot locations Lakelse Lake and Miskatla Inlet. Parallel lines identify the locations of roads.
Under a south wind, pollutants advected northward towards Terrace. The location of the northern maximum was adjacent to Lakelse Lake, approximately 13 km south of Terrace and close to the CYXT airport. Areas surrounding Lakelse Lake have land cover conducive to isoprene emission, as illustrated in figure 2.15. These findings are in general agreement with those of Castell et al. (2010), who found O$_3$ maxima between 40 and 140 km away from the hypothetical emission source, and who also found that increases were greatest in locations with high bVOC and low NO$_X$ emissions. Lakelse Lake is not a community itself though both the eastern and western shores are inhabited.

Figures 4.7 (a) and 4.7 (b) show the accumulation of O$_3$ at this location (coloured with a purple circle), as well as the percent increase from the Test case over the Control case. More information on this event is discussed in later sections. It should be stated that at no time did O$_3$ mixing ratios exceed the provincial one-hour objective of 82 ppb. The eight-hour objective of 63 ppb was also not exceeded (ignoring the 99$^{th}$ percentile metric shown in table 1.1) either at any particular location or following the plume as it advected down then up the valley.
Figure 4.7: CAMx spatial output for the Terrace - Kitimat valley airshed on August 15th, 2010 at 16:00 PST showing: a) Test Case modelled O₃ mixing ratios, and b) percent change from the Control case. The green line outlines the Terrace - Kitimat valley arised. ⭐️, ⭐️ and ⭐️ identify the communities Terrace, Kitimat and Hartley Bay respectively, while ⚫ and ⚫ identify hotspot locations Lakelse Lake and Miskatla Inlet. Parallel lines identify the locations of roads.
4.2.3 Ingredients for Elevated Ozone

This section provides an in-depth examination of the elevated $O_3$ as modelled from August 14$^{th}$ to August 15$^{th}$. During this time it is proposed that the cause of the elevated concentrations were warm temperatures (which led to high biogenic emissions), low mixing heights (PBLH lower than the height of the surrounding mountain peaks), differential land and water surface heating and a two-day period of horizontal recirculation.

Warm Temperatures (High Biogenic Emissions)

As can be seen from the WRF evaluation and figure C.1 (b) in appendix C, maximum modelled temperature increased daily from the afternoon of August 9$^{th}$ through the afternoon of August 14$^{th}$ (with the exception of August 12$^{th}$ which was modelled as slightly warmer than the 13$^{th}$), exceeding 29 °C in Kitimat and also in the TKV. This increase in temperature corresponded with an increase in overall biogenic emissions in the TKV, as shown in figure 2.14 (b). Interestingly, valley-wide bVOC emissions on August 14$^{th}$ were 100 tonnes higher than August 13$^{th}$ even though the maximum temperature only increased by 5 °C between those two days. A large increase in biogenic emissions also occurred from August 3$^{rd}$ to 4$^{th}$ when maximum modelled temperature exceeded 29 °C, suggesting that 29 degrees is a good trigger for high biogenic emissions in the summertime. Figure 4.8 (a) is a linear scatterplot of daily biogenic emissions vs. maximum modelled temperature for both spring and summer periods. When considered on a seasonal basis, the relationship between maximum temperature and bVOC emissions appear linear, with the summer maximum temperature explaining over 93% of the variability in VOC emissions. However, when both seasons are considered together the relationship appears exponential. Figure 4.8 (b) shows the same points as 4.8 (a) though with a logarithmic-scaled ordinate. From this plot the exponential dependence of bVOC emissions with temperature is evident, where temperature explains over 95% of the variability in bVOC emissions. This curve matches general results found by Guenther et al. (1993). (Note: above 40 °C emissions do begin to decrease)
Figure 4.8: Maximum daily temperature vs. bVOC emissions scatterplots in the Terrace - Kitimat valley airshed for spring and summer model periods presented on: a) linear axes and b) semi-log axes with best fit lines. Blue dots are spring model period and red dots are summer model period. Individual linear fits for both periods are shown in a) and a combined exponential fit is shown in b). $r^2$ values are: 0.66 for the spring period, 0.93 for the summer period and 0.95 for both periods combined.

Low Mixing Heights (PBLH Lower than Surrounding Mountains)

Figure 4.9 shows modelled PBLH at four locations in the TKVA for the entire summer period, along with generalized mountain peak elevation (as determined from contour plots). As can be seen in this figure, summertime mixing heights rarely exceeded the height of the surrounding mountain peaks. This led to the accumulation of pollutants, as the only effective outlets during these times were the north or south ends of the valley. Unfortunately, as the nearest radiosonde is hundreds of kilometres away it was not possible to evaluate modelled PBLH with actual observations.

As can be seen, in figure 4.9, PBLHs were low on August 14th and 15th, with maxima of 550 m in Kitimat, 1000 m at CYXT and 1200 m in Terrace on the 15th, the day with the highest O$_3$ mixing ratios.
Figure 4.9: Planetary boundary layer depth time series for the summer model period in the Terrace - Kitimat valley airshed. Model output at: Terrace (yellow lines), CYXT (orange lines), Kitimat (blue lines) and Hartley Bay (green lines). Static lines indicate nearby mountain peak elevations, coloured for the respective communities.

**Differential Surface Heating and Horizontal Recirculation**

Over the course of August 14th and 15th differential surface heating over land and water occurred along with a repeated pattern of onshore - offshore wind. Differential surface heating was prevalent throughout most of the model period, while the repeated onshore - offshore wind occurred in late July and early August, and then again on August 10th, 14th and 15th. While it has not been established that a sea breeze circulation was present over these days, differential heating and onshore - offshore wind are two of the main ingredients of a sea breeze, which are known to coincide with and indeed intensify air pollution episodes (Steyn, 2003). Figure 4.10 shows the difference between 2 m land and 2 m sea temperature for the entire summer model period, as output by WRF. The shaded periods indicate a south wind while the non-shaded periods indicate a north wind. Interestingly, the difference in land and sea temperature was greater in early July than in mid August, however the maximum daily temperatures were only in the mid 20’s (refer to figure 4.5). This underscores the importance of the presence of all O₃-generating ingredients.

In the absence of formally declaring this as an occasion where a sea breeze occurred, it is rea-
Figure 4.10: 2m temperature difference between Kitimat and the Douglas channel as modelled by WRF for the summer model period. Purple shading indicates southerly wind as output from WRF in Kitimat.

reasonable to label this period as one with horizontal recirculation based on the onshore - offshore wind that can be seen in figures 4.11 and 4.12. This pattern recirculates pollutants throughout the valley, exacerbating air pollution problems. Figures 4.11 and 4.12 show streamlines (red) in the 1.333 km domain on August 14\textsuperscript{th} (14:00 through 20:00) and 15\textsuperscript{th} (10:00 through 16:00) respectively, at two hour intervals. These figures also show wind barb cross sections along the TKV at 54.1 and 54.4\textdegree (the approximate locations of Kitimat and the CYXT airport).

These hours were selected to highlight the shift from offshore to onshore wind. Using the combination of streamlines (which show the general anabatic and katabatic flow within the valley and other tributary valleys) along with the wind barbs (which provide additional information about wind speed and direction within the TKV itself), one can see the timing of the transition (16:00 on August 14\textsuperscript{th} and 12:00 on August 15\textsuperscript{th}) and appreciate how on those days air would have ‘sloshed’ up and down the valley. Figure 4.10 suggests that onshore breezes commence around the time where $T_{\text{land}} - T_{\text{sea}}$ is at a maximum and persist until $T_{\text{land}} - T_{\text{sea}}$ is approximately 0 (i.e.: the land has cooled to below the temperature of the nearby ocean).
Figure 4.11: Modelled wind streamlines and wind barb cross sections in the Terrace - Kitimat valley on August 14th at: a) 14:00, b) 16:00, c) 18:00, and d) 20:00 PST. Red lines are streamlines and white lines are wind barbs. Grey triangles along the wind barb cross sections indicate the midpoint of the cross section.
Figure 4.12: Modelled wind streamlines and wind barb cross sections in the Terrace - Kitimat valley on August 15\textsuperscript{th} at: a) 10:00, b) 12:00, c) 14:00, and d) 16:00 PST. Red lines are streamlines and white lines are wind barbs. Grey triangles along the wind barb cross sections indicate the midpoint of the cross section.
Spatiotemporal O₃ Evolution

Based on the above it is proposed that warm temperatures, low mixing heights, differential land and water surface heating and a two-day period of horizontal recirculation in combination provide the necessary ingredients for elevated O₃ mixing ratios in the TKVA. Considering that O₃ was not produced during periods where one ingredient was missing (e.g.: August 4th - August 5th which was missing horizontal recirculation or April 15th - 19th which was missing warm temperatures), the importance of all these factors acting in concert becomes clear. Figures 4.13 and 4.14 show the spatiotemporal evolution of O₃ on August 14th and August 15th respectively.
Figure 4.13: CAMx spatial O₃ output in the Terrace - Kitimat valley airshed for the Test case on August 14ᵗʰ, 2010 at: a) 08:00, b) 10:00, c) 12:00, d) 14:00, e) 16:00, f) 18:00, g) 20:00 and h) 22:00 PST. The green line outlines the Terrace - Kitimat valley airshed. ⭐, ⭐️ and ⭐️ identify the communities Terrace, Kitimat and Hartley Bay respectively, while ⚫ and ⚪ identify hotspot locations Lakelse Lake and Miskatla Inlet. Parallel lines identify the locations of roads.
Figure 4.14: CAMx spatial O₃ output in the Terrace - Kitimat valley airshed for the Test case on August 15ᵗʰ, 2010 at: a) 08:00, b) 10:00, c) 12:00, d) 14:00, e) 16:00, f) 18:00, g) 20:00 and h) 22:00 PST. The green line outlines the Terrace - Kitimat valley arished. ⭐️, ⭐️ and ⭐️ identify the communities Terrace, Kitimat and Hartley Bay respectively, while ● and ○ identify hotspot locations Lakelse Lake and Miskatla Inlet. Parallel lines identify the locations of roads.
From these figures one can see how on the morning of August 14th a northerly wind (outflow) advected emissions from land over water where photochemistry began to occur around noon (see figure 4.13 (c)). Between 14:00 and 16:00 PST the flow reversed and air began to advect northward though elevated mixing ratios were limited to the southern portion of the valley. On August 15th the onshore wind commenced at 12:00 (see figure 4.14 (c)), and the airmass once again passed over the main emission sources in Kitimat and was advected further up the TKV where it encountered elevated biogenic VOC emissions. Given the shallow PBLH there was a limited volume in which to disperse these pollutants and the result was elevated O₃ near Lakelse Lake at 16:00 PST (figure 4.14 (e)). The maximum mixing ratio at this location reached 67.6 ppb, which was a 55.8% increase compared with the control-case emissions.

Multiday recirculation has been hypothesized in other areas (Vancouver, Los Angeles, Spain and Israel) and these photochemically-aged air masses are more likely to be sensitive to NOₓ emissions (Sillman, 2002). Given the nature of the proposed emissions, it is thus not surprising that this combination of meteorology and emissions are the ingredients for elevated O₃ in the TKVA. While at no time did these elevated mixing ratios exceed the provincial one-hour ambient O₃ objective, some sources of uncertainty exist from the model results which may have led to under-predicting O₃ mixing ratios:

- In reality temperatures from August 13th through August 16th were much warmer than WRF-modelled temperatures, exceeding 35 °C on August 14th in the TKV (see appendix C), and
- in reality, wind direction had an onshore-offshore diurnal variation from August 14th through August 17th, however WRF output only shows this exchange from August 14th through August 15th.

Based on this information bVOC emissions would have been even higher than those output by MEGAN. Also, horizontal recirculation has been shown to lead to increased O₃ air pollution (Steyn, 2003). The combination of extra bVOC emissions with additional days of recirculation may have led to even greater O₃ production during this time. Additional research is warranted
to investigate whether this would have happened.

**Historical Frequency of Meteorological Factors Which Contribute to Elevated O\textsubscript{3}**

Two of the above ingredients were parameters measured at meteorological monitoring stations in Kitimat, namely temperature and wind direction. Monitoring data from January 2001 until August 2015 was reviewed and dates meeting the criteria of two or more consecutive days with daily maximum temperatures greater than 29 °C and onshore-offshore wind patterns are listed in table 4.1. It is not possible to know what the sea surface temperature was on those days as well as the height of the PBLH, as those were not measured.

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<td></td>
</tr>
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</tr>
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<td>2003</td>
<td>July 28 - 30</td>
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</tr>
<tr>
<td>2004</td>
<td>Jun 16 - 23</td>
<td>8</td>
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<td>2013</td>
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<td>2014</td>
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<td>2015</td>
<td>July 4 - 9</td>
<td>6</td>
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<tr>
<td></td>
<td>July 17 - 19</td>
<td>3</td>
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</tbody>
</table>

The results from this brief analysis suggest that the median frequency meeting the above criteria is 1 occurrence per year with a median length of 3 days. The previous three summers have each met this criteria twice, with a median length of 3.5 days (mean of 3.8 days). From
this information is plausible to assume that elevated O$_3$ ingredients present themselves annually. More research is needed to confirm the PBLH for those periods, as well confirm whether there was a differential in sea and land surface temperature.

4.2.4 Effect of a Wildfire on Ozone Production

Changing the emissions inventory in SMOKE is not the only method to modify emissions input to CAMx. The other method, used in this section, is modification of the model’s ICs. Modifying the ICs provides a one-time opportunity to change the model outcomes, potentially influencing up to 84 hours of the model run.

The rationale for the importance of investigating ICs is provided in this section. Only industrial, mobile and biogenic emissions were included in the emission inventory though in reality there were a host of uncounted emissions emitted into the model domains during both periods. The addition of low-level area sources was intended to account for any and all other NO$_X$ emissions within Kitimat itself, though other sources were not represented. One of these was a forest fire within the 4 km model domain which had elevated emissions on August 14$^{th}$ - 16$^{th}$, 2010 and led to high concentrations of PM$_{2.5}$ in Smithers on those days. Images taken from a viewpoint near Smithers on August 14$^{th}$ and 15$^{th}$ (see figures 4.15 (a) and 4.15 (b)) illustrate the polluted nature of the BV.

The forest fire’s emissions were not captured in the SMOKE emissions inventory, and, as they occurred within the domain, they were also not captured as part of the model’s boundary conditions. The only method to investigate their effect was to initiate the model on the dates leading up to August 15$^{th}$ and analyze the output. Changes to resulting ambient concentrations could then be attributed to the forest fire.

Method for Incorporating Forest Fire Emissions into the CAMx Model Runs

As mentioned in section 2.4, boundary and ICs were provided to CAMx from MOZART. This model relies on a variety of emission inputs including anthropogenic emissions based on
the ARCTAS global emissions inventory (http://bio.cgrer.uiowa.edu/arctas/emission.html), fire emissions from FINN-v1 (Wiedinmyer et al., 2011) as well as biogenic emissions developed using MEGAN. Fire emissions from FINN-v1 include emissions of trace gas and particles from wildfires, agricultural fires and prescribed burning but exclude biofuel use and garbage burning (Wiedinmyer et al., 2011). Emissions are satellite derived, based on observations from MODIS instruments onboard the NASA Terra and Aqua polar-orbiting satellites and have a global resolution of 1 km$^2$. Forest fire information is available for download at http://bai.acom.ucar.edu/Data/fire/. Fire emissions which occurred within the various domains are illustrated in figure 4.16.

IC images for NO, NO$_2$, and O$_3$ are presented in figures 4.17, 4.18 and 4.19 respectively for July 29$^{th}$ and August 12$^{th}$ - 14$^{th}$. From these images it is possible to see how forest fire emissions captured by FINN-v1 change ICs in MOZART and ultimately those of CAMx.
Figure 4.16: Forest fire locations within the 12 km model domain on August 14th 2010. ● indicate forest fire locations. The red line outlines the CAMx 12 km domain, the green line outlines the Terrace - Kitimat valley airshed and the purple line outlines the Bulkley valley airshed. ★, ★★ and ★★★ identify the locations of Terrace, Kitimat and Smithers respectively.
Figure 4.17: Spatial NO fields generated by the Model of Ozone and Related Chemical Tracers for use as initial conditions to CAMx for: a) July 29th, b) August 12th, c) August 13th and d) August 14th. Forest fire locations are shown on August 14th. The red line outlines the CAMx 12 km domain, the green line outlines the Terrace - Kitimat valley airshed and the purple line outlines the Bulkley valley airshed. ★, ★★ and ★★★ identify the locations of Terrace, Kitimat and Smithers respectively.
Figure 4.18: Spatial NO$_2$ fields generated by the Model of Ozone and Related Chemical Tracers for use as initial conditions to CAMx for: a) July 29$^{th}$, b) August 12$^{th}$, c) August 13$^{th}$ and d) August 14$^{th}$. Forest fire locations are shown on August 14$^{th}$. The red line outlines the CAMx 12 km domain, the green line outlines the Terrace - Kitimat valley airshed and the purple line outlines the Bulkley valley airshed. ★, ★★★ and ★★★ identify the locations of Terrace, Kitimat and Smithers respectively.

Figure 4.19: Spatial O$_3$ fields generated by the Model of Ozone and Related Chemical Tracers for use as initial conditions to CAMx for: a) July 29$^{th}$, b) August 12$^{th}$, c) August 13$^{th}$ and d) August 14$^{th}$. Forest fire locations are shown on August 14$^{th}$. The red line outlines the CAMx 12 km domain, the green line outlines the Terrace - Kitimat valley airshed and the purple line outlines the Bulkley valley airshed. ★, ★★★ and ★★★ identify the locations of Terrace, Kitimat and Smithers respectively.
Temporal Results

Figure 4.20 shows how initializing CAMx using ICs from August 12\textsuperscript{th} - 14\textsuperscript{th} changes ambient O\textsubscript{3} at Lakelse Lake, the location with the highest mixing ratio only for the model initialized on August 14\textsuperscript{th}. O\textsubscript{3} mixing ratios for the model run initialized on August 12\textsuperscript{th} are identical to those from the July 29\textsuperscript{th} initialization after only 24 hours. It takes approximately 48 hours for this to happen to the run initialized on August 13\textsuperscript{th}. Neither of these runs incorporate the forest fire’s emissions, and resulting O\textsubscript{3} mixing ratios on August 15\textsuperscript{th} are identical to those from the July 29\textsuperscript{th} initialization. MOZART’s inclusion of forest fire emissions in the ICs on August 14\textsuperscript{th} adds a further 10 ppb O\textsubscript{3}, leading to a peak mixing ratio just under 80 ppb. Differences in ambient mixing ratios persist for an additional 24 hours with final convergence to the original time series approximately 84 hours after initialization. It should be noted that the provincial air quality advisory threshold for O\textsubscript{3} is a one-hour mixing ratio of 82 ppb. Therefore, the combination of industrial emissions with the ingredients required for elevated O\textsubscript{3} and wildfires came close to, but did not exceed this provincial objective.

Figure 4.20: O\textsubscript{3} time series at Lakelse Lake with varied initial conditions. Test Case time series initialized on July 29\textsuperscript{th}, August 12\textsuperscript{th}, August 13\textsuperscript{th} and August 14\textsuperscript{th} are shown as dashed red, purple, blue and turquoise lines respectively. Control case time series for all dates are shown as dotted black lines. Initial O\textsubscript{3} mixing ratios for each run are shown as coloured triangles.
Spatial Results

CAMx output suggests that for a case such as a wide-spread forest fire, increased O$_3$ would not be limited to the point of maximum mixing ratio. Indeed, O$_3$ mixing ratios were increased across the entire model domain. Figure 4.21 shows ambient O$_3$ at 16:00 PST on August 15$^{th}$ for the test case initiated on July 29$^{th}$ and also for the Test case initiated on August 14$^{th}$. 
Figure 4.21: CAMx spatial O₃ output for the Terrace - Kitimat valley airshed on August 15th, 2010 at 16:00 PST for Test Case model initialization on: a) July 29th and b) August 14th. The green line outlines the Terrace - Kitimat valley arished. ★, ★ and ★ identify the communities Terrace, Kitimat and Hartley Bay respectively, while ● and ○ identify hotspot locations Lakelse Lake and Miskatla Inlet. Parallel lines identify the locations of roads.
Chapter 5

Results and Discussion III: Answering Question 3

The cycling of reactions 1.5 through 1.9 terminates through either reaction 1.11 or 1.12. Based on which terminal reaction dominates it is possible to determine the sensitivity of O$_3$ production to emissions of NO$_X$ or VOCs. In low-NO$_X$ environments 1.11 dominates and O$_3$ production varies linearly with increasing NO, while in high-NO$_X$ environments 1.12 dominates and O$_3$ production varies linearly with increasing VOCs but inversely to increasing NO$_2$ (Jacob, 1999).

These sensitivities are applicable both spatially and temporally. For example, in urban centres (or large NO$_X$ producing areas) production of O$_3$ is generally VOC-limited while in less urban areas O$_3$ production is limited by emissions of NO$_X$ (Jacob, 1999). Locations which are NO$_X$-sensitive at one time of day can be VOC-sensitive at other times of the day (Sillman and West, 2009), and NO$_X$-sensitive locations in the summer can transition to be VOC-sensitive in the autumn (Jacob et al., 1995). The final question in this research is aimed at understanding the present and futures sensitivity of O$_3$ in the TKVA to emissions of NO$_X$ and VOCs:

- What is the current and future O$_3$ sensitivity of the Terrace - Kitimat valley airshed to
emissions of NO$_X$ and VOCs?

As management strategies for O$_3$ must take into account the complexities and non-linear nature of its production, this question is often asked when policy makers are attempting to maximize O$_3$ reduction strategies (Sillman and He (2002), Jacob (1999)). In this application NO$_X$-VOC sensitivity is assessed to better understand the future state of the TKV and whether or not further increases in NO$_X$ would lead to additional O$_3$.

5.1 Method for Determining NO$_X$-VOC Sensitivity

Only model output from the summer period was used to assess the sensitivity of O$_3$ formation in the TKVA to emissions of NO$_X$ and VOCs. The spring period was omitted as O$_3$ was not generated in meaningful quantities along the valley bottom. Sensitivity designations are often based on modelled change in O$_3$ relative to decreases in NO$_X$ or VOCs from various emission scenarios (Sillman and He, 2002). An important parameter for this analysis is total reactive nitrogen (NO$_y$), which includes the gases in NO$_X$ as well as NO$_3$, HNO$_3$, HONO, N$_2$O$_5$, HO$_2$NO$_2$, peroxyacetyl nitrate (PAN) and organic nitrates, but excludes NH$_3$ (Neuschuler, D., 2006). Ainslie et al. (2013) demonstrated how, in the LFV, the ratio of $[O_3]/[NO_y] \approx 7$ can be used to differentiate NO$_X$ and VOC-sensitive areas, where $[O_3]/[NO_y] < 7$ is sensitive to VOCs and $[O_3]/[NO_y] > 7$ is sensitive to NO$_X$. This result is similar to a result from (Castell et al., 2009) who found that 6.11 was an appropriate ratio considering an O$_3$ response of at least 3 ppb to changes in NO$_X$ emissions in an airshed with a natural gas power plant emitting 4.45 tonnes of NO$_X$ per day. Sillman and He (2002) proposed a range of 11-15 as the transition range for areas with O$_3$ mixing ratios less than 80 ppb. Given the above findings, this research applies a broad transition range of 7 - 15 for the TKVA; one area for further study could be to reduce this range based on localized findings and further sensitivity tests.

In order to facilitate this analysis, a transect of the TKV was created. This transect follows the main trajectory of the large industrial plumes, both to the north (when the wind is onshore), and to the south (when the wind is offshore). The domain was also divided into north and
south sections. This enabled separate analysis of each section, depending on the dominant wind direction. Figure 5.1 shows the transect and north-south divide.

![Figure 5.1: The north-south transect and north-south divide of the Terrace-Kitimat valley. The orange line indicates the transect and the yellow line identifies the divide. The green line outlines the Terrace-Kitimat valley arified. ⭐️, ⭐️ and ⭐️ identify the communities Terrace, Kitimat and Hartley Bay respectively, while ⬜️ and ⬜️ identify hotspot locations Lakelse Lake and Miskatla Inlet.](image)

For each half of the domain, the $\frac{[O_3]}{[NO_y]}$ ratio was extracted for the hours where the difference between Control and Test Case modelled $O_3$ was 4 ppb or greater. This enabled the analysis of only those hours where $O_3$ was produced. These differences were calculated at Lakelse Lake (to the north) and Miskatla Inlet (to the south). In other studies the hours selected have been in the afternoon, typically between 1300 and 1600 local time (Steyn et al. (2012), Stein et al. (2005), Torres-Jardon and Keener (2006)), though in the TKVA $O_3$ production often commenced earlier (noon) and continued later (until 1800). Thus it was more relevant to use hours where the difference was 4 ppb or greater rather than a set time. The
dates and hours used for analysis of both the northern and southern halves of the domain are listed in table 5.1. As the dominant wind direction was northerly for this period, there were only two days that satisfied the criteria for the northern half. (See the time series of control and test cases for Lakelse Lake and Miskatla Inlet in figure 4.5)

Table 5.1: Hours used for $[O_3]/[NO_y]$ analysis.

<table>
<thead>
<tr>
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<th>North</th>
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<tbody>
<tr>
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<tr>
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<td>14:00 - 16:59</td>
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<td>11:00 - 21:59</td>
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<tr>
<td>Aug 15</td>
<td>08:00 - 15:59</td>
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</tbody>
</table>

5.2 Sensitivity Results

The mean and median $[O_3]/[NO_y]$ ratios were calculated for each half of the domain, along with the 5th and 95th percentiles. Sillman and He (2002) identify the transition zone between VOC and NOX-sensitive regions to be the area between the 95th percentile of the VOC-sensitive area and the 5th percentile of the NOX sensitive area. In this analysis the 7 - 15 range is used because of its breadth. Transect results from both halves were stitched together and are presented in figure 5.2 for both the Control and Test cases. Also presented are box-whisker plots at five locations along the TKV: Hartley Bay, Miskatla Inlet, Kitimat, Lakelse Lake and Terrace.

As can be seen from these figures, the full construction of all industrial projects in the TKVA would result in a change in sensitivity of large sections of the TKV on O3-producing days from NOX to VOC-sensitive, particularly from Miskatla Inlet to 10 km south of Lakelse Lake. The transect passing through Kitimat shows the median $[O_3]/[NO_y]$ ratio decreasing from 11 to 1, indicating that without additional VOC emissions, model output represents a worst case representation of O3 concentrations in this area. At Lakelse Lake the median $[O_3]/[NO_y]$
Figure 5.2: Median, mean, 5th and 95th percentile \([O_3]/[NO_y]\) ratios along the Terrace - Kitimat valley transect defined in figure 5.1 during hours identified in table 5.1 for the: a) Control and b) Test cases. Red line is the median while black line is the mean. Light shading indicates areas where \([O_3]/[NO_y]<7\) (sensitive to emissions of VOCs), violet shading indicates areas where \(7<[O_3]/[NO_y]<15\), and purple shading indicates areas where \([O_3]/[NO_y]>15\) (sensitive to emissions of NO\(_X\)). The vertical yellow line represents the north-south divide. Box plots showing the interquartile range and outliers for transect cells matching the same latitude as Hartley Bay, Miskatla Inlet, Kitimat, Lakelse Lake and Terrace are shown in green, cyan, blue purple and yellow shading respectively.

Ratio decreases from 45 to 12, suggesting that in this area additional NO\(_X\) would still lead to additional O\(_3\). Similar to Lakelse Lake, south of Miskatla Inlet to Hartley Bay the sensitivity
also changes from NO\(_X\)-sensitive to a transitional sensitivity. Note that photochemically aged plumes are increasingly more NO\(_X\)-sensitive (Sillman, 2002); additional research is needed to investigate the balance between predicted NO\(_X\)-insensitive (and transitional) areas with NO\(_X\)-sensitive plumes.

Figure 5.3, presents domain-wide renderings of the median [O\(_3\)]/[NO\(_y\)] ratio for (a) Control and (b) Test Cases. This figure illustrates how the change in sensitivity from NO\(_X\) to VOCs is greatest in and around Kitimat (approximately 25 km to the north and 25 km to the south) and while the changes are greatest along the trajectory of the emissions plume, the decrease is spread over the entire width of the TKV where it is narrow. Areas with [O\(_3\)]/[NO\(_y\)] < 7 are insensitive to NO\(_X\) emissions, suggesting that further NO\(_X\) would not lead to increased O\(_3\) in those areas. Purple areas are still NO\(_X\)-sensitive, indicating that additional NO\(_X\) would still lead to increased O\(_3\). The violet area is sensitive to both NO\(_X\) and VOCs though it is unclear how much O\(_3\)-generating potential remains in this zone. Additional research is warranted to further our understanding of the 7 < [O\(_3\)]/[NO\(_y\)] < 15 area, as this zone occupies a large percentage of the TKV bottom.
Figure 5.3: Median $[O_3]/[NO_y]$ ratios in the Terrace - Kitimat valley airshed during hours identified in table 5.1 for the: a) Control and b) Test cases. Light shading indicates areas where $[O_3]/[NO_y] < 7$ (sensitive to emissions of VOCs), violet shading indicates areas where $7 < [O_3]/[NO_y] < 15$ (zone of transition), and purple shading indicates areas where $[O_3]/[NO_y] > 15$ (sensitive to emissions of NOX). The green line outlines the Terrace - Kitimat valley airshed and ★, ★ and ★ identify the communities Terrace, Kitimat and Hartley Bay respectively, while ● and ○ identify hotspot locations Lakelse Lake and Miskatla Inlet.
Chapter 6

Summary and Conclusion

The WRF, SMOKE, MEGAN, MOZART and CAMx models were run for two periods in 2010 in order to assess the potential change in ambient mixing ratios of O$_3$ and its precursors that may arise from the construction of large industrial facilities in the TKVA. Control and test cases were developed and applied for each period, the former for model evaluation and the latter to assess pollutant change. The current and future O$_3$ sensitivity in the TKVA to emissions of NO$_X$ and VOCs was also assessed.

6.1 Findings: Research Questions Revisited

The findings of this research are put in the context of the original research questions:

1. Can spring and summer photochemical O$_3$ be replicated by a model in a manner that is fit for the purpose of investigating worst-case concentrations that may result from proposed industrial emissions in a constrained coastal airshed with complex terrain, such as the Terrace - Kitimat valley?

Photochemical O$_3$ was replicated by a model in a manner that was fit for the purpose of investigating worst-case concentrations albeit not without some difficulties initially.
While not explicitly mentioned in the question, NO and NO\textsubscript{2} were included in the analysis because of the important relationship between these gases and O\textsubscript{3} as described by reactions 1.1 and 1.2. Model fitness was evaluated based on a combination of the overall modelled and observed time series, scatterplots and five statistical metrics (NMB, MB, RMSE, MAE and r). Daytime O\textsubscript{3} maxima were replicated reasonably however the model was originally unable to recreate overnight O\textsubscript{3} titration by NO. NO and NO\textsubscript{2} time series and statistical metrics were originally poor when compared with observed mixing ratios. Because of this the original CAMx Control Case output was deemed unfit. Sensitivity tests were developed to investigate the cause of the lack of overnight O\textsubscript{3} titration. It was deemed that the original emissions inventory was inadequate to characterize overnight O\textsubscript{3}, NO and NO\textsubscript{2} mixing ratios. Results improved with the addition of low-level NO\textsubscript{X} sources to account for sources absent in the emissions inventory, as these sources allowed overnight titration to occur without affecting daytime O\textsubscript{3} production. The model was then determined to be fit for the purpose of investigating worst-case O\textsubscript{3} concentrations and thus the approach described in chapter 2 was deemed to be an appropriate modelling approach.

2. Should all proposed industrial facilities in the Terrace - Kitimat valley airshed be constructed,

   (a) Where are the locations of the O\textsubscript{3} maxima and what are the worst-case concentrations that could occur there?

   (b) What meteorological factors contribute to enhancing or reducing O\textsubscript{3} concentrations in the Terrace - Kitimat valley airshed?

Results for the spring period illustrated that, despite the naturally elevated O\textsubscript{3} in the spring, the addition of NO\textsubscript{X} from industrial sources led to O\textsubscript{3} titration overnight and also during some daytime hours along low elevations of the TKV. This was most prevalent in the near-field around Kitimat but occurred upwards of 80 km downwind, occasionally in Terrace. The meteorological conditions which led to the greatest change (i.e.: decrease)
in springtime O$_3$ were low PBLHs and consecutive days of recirculating wind. Modest O$_3$ production was found during afternoon hours outside of this main plume and on valley walls.

Results from the summer period illustrated how the addition of O$_3$ precursors contributed to an overall increase in O$_3$ downwind of Kitimat. O$_3$ production varied with wind direction. To the south the hotspot was determined to be Miskatla Inlet, which acted as a trap for pollutants returning northward after advecting southward earlier in the morning hours. To the north the hotspot was Lakelse Lake, a location surrounded by vegetation that emitted high quantities of isoprene when temperatures were greater than 29 °C. These findings are in general agreement with those of Castell et al. (2010), who found O$_3$ maxima between 40 and 140 km away from the hypothetical emission source, and who also found that increases were greatest in NO$_X$-sensitive areas, i.e.: locations with high bVOC and low NO$_X$ emissions.

In the summer the meteorological conditions which led to the greatest change (i.e.: increase) in O$_3$ were high temperatures (these led to high bVOC emissions), low PBLHs, differential heating of the land and ocean surface temperatures and consecutive days of recirculating wind. These conditions led to a greater than 55% increase in O$_3$ production at both Miskatla Inlet and Lakesle Lake. The frequency of these meteorological conditions was estimated to be one per year with a median length of three days based on an analysis of meteorological monitoring data in Kitimat over the past 15 years. When emissions from a nearby forest fire were included in the emissions inventory (through the ICs input file) the maximum O$_3$ at these locations increased by 10 ppb and approached the provincial threshold for O$_3$-based air quality advisories.

3. What is the current and future O$_3$ sensitivity of the Terrace - Kitimat valley airshed to emissions of NO$_X$ and VOCs?

The modelled [O$_3$]/[NO$_y$] ratio during hours conducive to photochemistry was used to determine the O$_3$ sensitivity of the TKVA. The TKVA is currently very sensitive to NO$_X$
emissions however the full construction of all proposed industrial projects would likely change the sensitivity of the large portions of the valley. From Miskatla Inlet to 10 km south of Lakelse Lake the change would be from NO\textsubscript{X} to VOC-sensitive (especially in and around Kitimat). South of Miskatla Inlet and in the area surrounding Lakelese Lake the change would be from NO\textsubscript{X}-sensitive to a transitional sensitivity. In VOC-sensitive areas further NO\textsubscript{X} emissions would not likely lead to increased O\textsubscript{3}, though in the the zone of transition there may still be some O\textsubscript{3} production potential.

6.2 Future Study

An interesting outcome of this research was the determination of the ingredients of elevated O\textsubscript{3} production in the TKV. It is startling that the ingredients are almost the same for spring and summer periods, yet the predicted outcomes are vastly different, based on higher summer temperatures leading to increased biogenic emissions. Some confirmation of this seems required, i.e. can high biogenic emissions in the TKV be confirmed (perhaps through another model, an evaluation of landcover, or (even better) through monitoring). An ideal location for this would be Lakelse Lake where there is currently a wet deposition station operated by the aluminum smelter. This seems prudent as measured temperatures during the summer model period exceeded those from WRF output and it is possible that bVOCs emissions were even higher.

Reducing uncertainty related to model inputs is also warranted. With respect to meteorological inputs, the RF statistical model identified RH to be an important predictor for O\textsubscript{3} in the TKV, yet it was also the parameter that performed poorest in the WRF evaluation. It is unclear how this affected model results though improvements to modelled humidity seem warranted. Also, improving WRF temperature output should be attempted, potentially using the nudging technique in WRF’s initialization.

With respect to the emissions inputs, a thorough emissions inventory is warranted for future modelling studies. As many local emission sources as possible should be included, even though
the time required to complete this task could be daunting. NPRI data should be supplemented with other local data where possible.

Future modelling studies would benefit by taking a focused approach and only investigating those times identified as meeting the criteria for elevated O$_3$. Modelling the spring period demonstrated how the spring O$_3$ peak was insensitive to NO$_X$ emissions in this area as VOC emissions are low. The summer provided much more interesting results and future work can focus on those periods where production is likely, especially extended warm periods with horizontal recirculation.

It must be noted that as of spring 2015, O$_3$ monitoring commenced in Terrace, operated by the BC MOE. Therefore, future model evaluation could occur within the TKVA and not in neighbouring airsheds.

Lastly, scientific study has moved from studying single pollutants to studying multiple pollutants. Without an understanding of the total change in atmospheric pollutant concentrations, it is not possible to make final conclusions about the total human and environmental risks from any combination of these potential new sources. Future iterations may desire to calculate the Air Quality Health Index for different areas in the TKV to begin a true effects assessment, as that was not the role of this research.
References


Appendix A

Random Forest Regression Method for Modelling Ozone in Kitimat

This chapter contains a brief description of the regression model that was used to select dates for the spring and summer model periods.

A.1 Background

Two periods were selected for this research, one in the spring and one in the summer. A spring period was chosen because O\textsubscript{3} is naturally elevated during this time (Monks, 2000) and the result of adding additional NO\textsubscript{X} into the TKV warranted some investigation. A summer period was selected as summer is a more traditional time of year for O\textsubscript{3} episodes due to increased production of the OH radical through reactions 1.3 and 1.4 (Jacob, 1999). Because computational resources are expensive, running CAMx for the entire spring and summer was not possible. Instead, finding a range of dates was desired where either:

(a) O\textsubscript{3} was already elevated, or

(b) conditions conducive for photochemical O\textsubscript{3} production were present.
A.2 Methods

A statistical regression model was used to determine, in a scoping capacity, date ranges that met the above criteria. As O₃ data is limited to two short periods in Kitimat (Sept 16th - Dec 1st, 2010 and May 20th - Nov. 21st, 2011), the model was developed (trained and tested) using air quality and meteorological observations from Smithers. Input predictors originally included: temperature, RH, wind speed, NO, NO₂, CO and PM₂.₅.

Three different regression models were tested for both spring and summer to investigate which could best emulate an O₃ time series using the above predictors.

1. multiple linear regression (MLR),
2. neural networks (NN), and
3. RF (ensemble of Classification and Regression Trees).

Background information on all these models can be found in Hsieh (2009) and Hastie et al. (2009).

As complete time series are required for both predictor and response variables, only data from 2007, 2010 and 2011 were used for the spring while and 2007, 2009, 2010 and 2011 were used for the summer (other years have large data gaps for one or more variable). Predictors were initially trained to model O₃ for the same year, and regression coefficients were developed. (Note that NN and RF models do not develop regression coefficients; for extreme simplicity the term is used in the context of NN and RF to describe what those models use to predict response variables.) Thus each year constituted its own model. Metrics chosen to evaluate model performance and fitness were: RMSE, MAE and r. Equations for these metrics are presented in appendix B.
A.3 Results

Tables A.1, A.2 and A.3 list the evaluation result statistics for each model type and year based on its ability to recreate observed O$_3$ for the same year. As can be seen, for all metrics in all years the RF model outperformed the other two model types and it was chosen to be the statistical model for predicting O$_3$ in Kitimat.

Table A.1: Model evaluation statistics for spring and summer periods at Smithers: multiple linear regression model

<table>
<thead>
<tr>
<th>Model Year</th>
<th>n</th>
<th>RMSE (ppb)</th>
<th>MAE (ppb)</th>
<th>r</th>
<th>n</th>
<th>RMSE (ppb)</th>
<th>MAE (ppb)</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td>2080</td>
<td>8.324</td>
<td>6.722</td>
<td>0.823</td>
<td>1640</td>
<td>4.759</td>
<td>3.589</td>
<td>0.883</td>
</tr>
<tr>
<td>2009</td>
<td>1570</td>
<td>4.287</td>
<td>3.289</td>
<td>0.908</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010</td>
<td>2310</td>
<td>6.969</td>
<td>5.541</td>
<td>0.871</td>
<td>1640</td>
<td>4.196</td>
<td>3.181</td>
<td>0.915</td>
</tr>
<tr>
<td>2011</td>
<td>2360</td>
<td>6.675</td>
<td>5.179</td>
<td>0.883</td>
<td>1250</td>
<td>4.025</td>
<td>3.138</td>
<td>0.888</td>
</tr>
</tbody>
</table>

Table A.2: Model evaluation statistics for spring and summer periods at Smithers: neural network regression model

<table>
<thead>
<tr>
<th>Model Year</th>
<th>n</th>
<th>RMSE (ppb)</th>
<th>MAE (ppb)</th>
<th>r</th>
<th>n</th>
<th>RMSE (ppb)</th>
<th>MAE (ppb)</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td>2080</td>
<td>8.746</td>
<td>6.831</td>
<td>0.804</td>
<td>1640</td>
<td>4.680</td>
<td>3.288</td>
<td>0.887</td>
</tr>
<tr>
<td>2009</td>
<td>1570</td>
<td>4.592</td>
<td>3.483</td>
<td>0.881</td>
<td>1640</td>
<td>4.507</td>
<td>3.389</td>
<td>0.902</td>
</tr>
<tr>
<td>2010</td>
<td>2310</td>
<td>6.720</td>
<td>5.199</td>
<td>0.881</td>
<td>1640</td>
<td>4.507</td>
<td>3.389</td>
<td>0.902</td>
</tr>
<tr>
<td>2011</td>
<td>2360</td>
<td>6.439</td>
<td>4.977</td>
<td>0.891</td>
<td>1250</td>
<td>4.011</td>
<td>3.035</td>
<td>0.889</td>
</tr>
</tbody>
</table>

Table A.3: Model evaluation statistics for spring and summer periods at Smithers: random forest regression model

<table>
<thead>
<tr>
<th>Model Year</th>
<th>n</th>
<th>RMSE (ppb)</th>
<th>MAE (ppb)</th>
<th>r</th>
<th>n</th>
<th>RMSE (ppb)</th>
<th>MAE (ppb)</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td>2080</td>
<td>6.571</td>
<td>4.884</td>
<td>0.895</td>
<td>1640</td>
<td>3.998</td>
<td>2.796</td>
<td>0.919</td>
</tr>
<tr>
<td>2009</td>
<td>1570</td>
<td>3.867</td>
<td>2.916</td>
<td>0.926</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010</td>
<td>2310</td>
<td>5.832</td>
<td>4.372</td>
<td>0.912</td>
<td>1640</td>
<td>3.916</td>
<td>2.917</td>
<td>0.927</td>
</tr>
<tr>
<td>2011</td>
<td>2360</td>
<td>5.401</td>
<td>3.969</td>
<td>0.925</td>
<td>1250</td>
<td>3.585</td>
<td>2.687</td>
<td>0.913</td>
</tr>
</tbody>
</table>

Using regression coefficients determined by particular models for particular years, the RF models were then used to predict O$_3$ from different years as well as O$_3$ in Kitimat for the brief period with available monitoring data. An ensemble model was also used. Because not all the predictor variables available in Smithers were available in Kitimat, the number of predictors was reduced to only those monitored in Kitimat. These included: temperature, RH, wind
speed and PM$_{2.5}$. It was determined that while all predictors added value to modelling O$_3$ in the spring, the models performed better in the summer using only RH and wind speed as inputs. Of all predictors (in both spring and summer), RH was the most important. This was determined by removing each predictor from the model and measuring the increase in RMSE and MAE, and decrease in $r$. Model results from the RF prediction of O$_3$ in Kitimat are listed in table A.4.

Table A.4: Model evaluation statistics for spring and summer periods at Kitimat using model coefficients developed from Smithers: random forest regression model

<table>
<thead>
<tr>
<th>Model Year</th>
<th>Spring</th>
<th>Summer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RMSE (ppb)</td>
<td>MAE (ppb)</td>
</tr>
<tr>
<td>2007</td>
<td>6.239</td>
<td>5.067</td>
</tr>
<tr>
<td>2009</td>
<td>4.897</td>
<td>3.863</td>
</tr>
<tr>
<td>2010</td>
<td>6.562</td>
<td>5.339</td>
</tr>
<tr>
<td>2011</td>
<td>6.501</td>
<td>5.222</td>
</tr>
<tr>
<td>Ensemble</td>
<td>6.403</td>
<td>4.879</td>
</tr>
</tbody>
</table>

As can be seen from table A.4, for all metrics the summer period outperforms the spring period. The ensemble RF model outperforms the individual models for the spring period though the 2009 RF model outperforms the other years, including the ensemble. The cause of the high performance for the 2009 summer model is not known. Based on these results the ensemble model was selected for predicting springtime O$_3$ for 2010, while the 2009 model was selected to model 2010 summertime O$_3$. The resulting O$_3$ time series for the year 2010 for both spring and summer model periods are shown in figure A.1 (a) and A.1 (b) respectively.

The models estimated elevated O$_3$ in 2010 during two periods in the spring (April 14$^{th}$ - 18$^{th}$, May 2$^{nd}$ - 14$^{th}$), and two periods in the summer (July 29$^{th}$ - Aug 6$^{th}$ and Aug 12$^{th}$ - 18$^{th}$). These corresponded to days with low RH, as model results show this to be the most important predictor for elevated O$_3$ in the TKV and Smithers. The final model period for each season was selected to start at the beginning of the first case of elevated O$_3$ for each season and continue to the end of the second, and are listed in table A.5.

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Figure A.1: Modelled O$_3$ time series at Kitimat using RF model coefficients developed in Smithers for: a) spring and b) summer model periods. Final spring model period is from April 14$^{th}$ - May 14$^{th}$, and summer period is from July 29$^{th}$ to August 18$^{th}$.

Table A.5: Dates for the spring and summer model periods (2010).

<table>
<thead>
<tr>
<th>Season</th>
<th>Start Date</th>
<th>End Date</th>
<th>Number of Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>April 14</td>
<td>May 14</td>
<td>31</td>
</tr>
<tr>
<td>Summer</td>
<td>July 29</td>
<td>August 18</td>
<td>21</td>
</tr>
</tbody>
</table>
Appendix B

Statistical Metrics Used for Model Evaluation

Note that in each equation, $M_i$ represents the $i^{th}$ model output and $O_i$ represents the corresponding $i^{th}$ observed output. The difference between $M_i$ and $O_i$ is the error, $E_i$.

Normalized mean bias

$$NMB = 100\% \cdot \frac{\sum (M_i - O_i)}{\Sigma O_i} \quad (B.1)$$

Mean bias

$$MB = \frac{1}{N} \cdot \sum (M_i - O_i) \quad (B.2)$$

Root mean squared error

$$RMSE = \sqrt{\frac{\sum (M_i - O_i)^2}{N}} \quad (B.3)$$

Mean absolute error

$$MAE = \frac{1}{N} \cdot \sum |M_i - O_i| \quad (B.4)$$
Correlation coefficient

\[ r = \frac{\sum_{i=1}^{N} ((M_i - \bar{M}) \times (O_i - \bar{O}))}{\sqrt{\sum_{i=1}^{N} (M_i - \bar{M})^2 \sum_{i=1}^{N} (O_i - \bar{O})^2}} \]  

(B.5)
Appendix C

WRF Evaluation

C.1 Quantitative Evaluation

Note that all figures provided in this section are in Pacific Standard Time (UTC - 8).

Temperature

Spring and summer time series of modelled and observed temperature at the three evaluation locations can be found in figures C.1 (a) and C.1 (b) respectively.

These plots show that WRF does a reasonable job modelling temperature. Output is almost always within the diurnal range measured at each station but is unable to capture the daily peaks and troughs. Maximum error at all stations occurs around May 9\textsuperscript{th} and August 15\textsuperscript{th}. At Terrace the model temperature is consistently near the warmer end of the observed values whereas in Kitimat the modelled temperature is in the middle of the observed values. From these time series it is apparent that model performance is strongest at the airport. Statistical metrics are listed in table C.1 below.

With the exception of CYXT in the summer period, the overall tendency of WRF is a warm
Figure C.1: Observed and modelled temperature time series at Terrace (top), CYXT (middle) and Kitimat (bottom) for: a) spring and b) summer model periods. Black lines are observed while yellow, orange and blue lines are modelled.

Table C.1: Modelled - observed temperature statistics from the WRF evaluation.

<table>
<thead>
<tr>
<th>Location</th>
<th>Spring</th>
<th>Summer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NMB</td>
<td>MB</td>
</tr>
<tr>
<td>Terrace B.C. Access Centre</td>
<td>6.136</td>
<td>0.601</td>
</tr>
<tr>
<td>CYXT Terrace Airport</td>
<td>3.980</td>
<td>0.335</td>
</tr>
<tr>
<td>Kitimat Whitesail</td>
<td>4.304</td>
<td>0.362</td>
</tr>
</tbody>
</table>
bias between 0.3 and 0.9 °C. Considering only bias, WRF had the greatest difficulty modelling temperature in Terrace and performed best at the airport. On the other hand, in the spring both the RMSE and MAE are lowest for Terrace and highest at the airport. Results for Kitimat are somewhere in the middle, with the model having a warm bias (0.3 and 0.5 °C for the spring and summer periods respectively) and in the summer the highest RMSE and MAE.

One possible explanation for the model’s inability to capture the highs and lows of the diurnal cycle in Kitimat is that WRF is unable to master the transition from water to land. Indeed, a look at the Landmask variable shows that Kitimat Whitesail is located in a cell adjacent to a water cell (the Kitimat river) even though this feature is 2 km away. This sub-grid scale effect is an example of an incommensurability problem, described by Swall and Foley (2009).

Relative Humidity

RH data is not a direct output from WRF and was calculated by the program NCAR Command Language (NCL) using the temperature, pressure and water vapour mixing ratio variables. More information on this process can be obtained from the NCL website: https://www.ncl.ucar.edu/Document/Functions/Built-in/relhum.shtml. (Note that a formula is not given but RH can be determined using guidance from Roland Stull’s online textbook: Practical Meteorology, Chapter 4: http://www.eos.ubc.ca/books/Practical_Meteorology/Chapters/Ch04-Moist.pdf (Stull, 2014)). In 2010 RH was measured at Terrace and the CYXT airport but not at Kitimat Whitesail. Interestingly, while WRF was able to model temperature adequately, as can be seen in figures C.2 (a) and C.2 (b), it had a more difficult time with RH.

The level to which RH was under-modelled in Terrace is quite apparent in both figures of C.2 (a). RH troubles are not isolated to the B.C. Access Centre; looking at the airport time series, it is evident that timing of the modelled diurnal RH pattern is not aligned with the timing of the observed RH pattern and appears consistently out of sync by two hours. It is unclear what this means from a photochemical perspective, however during the statistical analysis of
O$_3$ production in Smithers high O$_3$ was correlated with low RH values. These issues affect the statistical metrics, as listed in table C.2.

Table C.2: Modelled - observed relative humidity statistics from the WRF evaluation.

<table>
<thead>
<tr>
<th>Location</th>
<th>Spring</th>
<th>Summer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NMB</td>
<td>MB</td>
</tr>
<tr>
<td>CYXT Terrace Airport</td>
<td>-5.112</td>
<td>-3.458</td>
</tr>
</tbody>
</table>

At the B.C. Access Centre in Terrace, RH is under-predicted by approximately 12% in both spring and summer seasons (MB). This corresponds with an 18.2 and 19.2% NMB for spring
and summer respectively. This is a much poorer showing when compared with the normalized temperature biases. The RH RMSE and MAE in Terrace are also quite high, indicating that there were some strong discrepancies between modelled and observed values. Despite the time lag, evaluation metrics fare better at the airport. It is interesting that results vary so greatly over such a short distance given that the airport is less than 5 km from the Access Centre. It is possible that the difference in elevation between the two stations plays a role in the model output performance (elevation of the airport is over 200 m while the elevation of the Access Centre is 68 m).

**Pressure**

In the TKV pressure is only measured at the CYXT airport. Modelled vs. observed pressure time series are presented in figures C.3 (a) and C.3 (b). As can be seen, WRF performs optimally for this parameter at this location.

Evaluation metrics for pressure are listed in table C.3. WRF does a satisfactory job modelling atmospheric pressure. Springtime normalized mean bias was less than 0.1% and summertime bias was just over 0.2%. Considering that the these metrics are calculated in Pascals (as opposed to kPa) they stand out as being remarkably low.

<table>
<thead>
<tr>
<th>Location</th>
<th>Spring</th>
<th></th>
<th></th>
<th>Summer</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NMB (%)</td>
<td>MB (Pa)</td>
<td>RMSE (Pa)</td>
<td>MAE (Pa)</td>
<td>NMB (%)</td>
<td>MB (Pa)</td>
</tr>
<tr>
<td>CYXT Terrace Airport</td>
<td>0.081</td>
<td>80.51</td>
<td>191.73</td>
<td>154.42</td>
<td>0.220</td>
<td>218.28</td>
</tr>
</tbody>
</table>

**Wind Direction**

From an evaluation perspective, wind direction is a very important parameter. Without properly modelling wind direction a model loses its credibility. Usually the U and V wind vectors are evaluated as opposed to wind direction as it is not output directly from WRF and must be calculated from the U and V vectors at 10 m using the following formula:
Figure C.3: Observed and modelled pressure time series at CYXT for: a) spring and b) summer model periods. Black lines are observed and orange lines are modelled.

\[ WDIR = \text{atan2}(-U, -V) \times \left( \frac{180}{\pi} \right) \]  \hspace{1cm} (C.1)

Given the north-south orientation of the TKV it was determined that the calculated wind direction could be evaluated as opposed to the U and V vectors themselves. Model and observed wind direction are presented for the spring and summer periods in figures C.4 (a) and C.4 (b) respectively. From these it is possible to see that WRF does a reasonable job in Kitimat and at the CYXT airport but seems to have some difficulty at Terrace. It should be noted that given the dominant north-south wind pattern in this valley, wind directions less than 90° were added to 360, thus 405° is equivalent to a northeast wind while 450° is equivalent to an east wind.

As is seen in the above figures, WRF’s performance is reasonable, especially in Kitimat where,
Figure C.4: Observed and modelled wind direction time series at Terrace (top), CYXT (middle) and Kitimat (bottom) for: a) spring and b) summer model periods. Black lines are observed and yellow, orange and blue lines are modelled. Note that to reduce clutter in the figures, wind from directions 0° - 90° were moved to the 360° - 450° range. Therefore, 405° is equivalent to a northeast wind while 450° is equivalent to an east wind.

despite the obvious bias, the diurnal flow is adequately captured. Records of Kitimat Whitesail’s wind vane maintenance were recently checked to confirm that observational error was not a problem (20° is the approximate difference between true north and magnetic north in Kitimat) and in looking at the detailed topography of the location of Kitimat Whitesail it is
possible to explain why, when there is a southerly wind, this station measures a south-southeast wind at 10 m above ground (the slope of the terrain faces the south-southeast).

Output for the airport is also reasonable. Environment Canada records wind direction in 10 degree increments, which explains why the observed values look “chunky” (see around the 360° line on August 16th) when plotted. The model does poorest in in Terrace though this should not come as a surprise. Terrace, located at the confluence of the Terrace - Kitimat valley as well as the Skeena and Kalum rivers, is known by locals as “the bowl” because of the tendency for wind to blow from a multitude of directions. Annual wind roses (not shown) show that the dominant wind direction in Terrace is south yet in the spring and summer this is not the case, as shown by observations in figure C.4. Statistical metrics confirm these observation, as listed in table C.4.

Table C.4: Modelled - observed wind direction statistics from the WRF evaluation.

<table>
<thead>
<tr>
<th>Location</th>
<th>Spring MB (deg)</th>
<th>Spring MAE (deg)</th>
<th>Summer MB (deg)</th>
<th>Summer MAE (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrace B.C. Access Centre</td>
<td>22.603</td>
<td>67.736</td>
<td>26.230</td>
<td>60.731</td>
</tr>
<tr>
<td>CYXT Terrace Airport</td>
<td>14.232</td>
<td>58.595</td>
<td>14.477</td>
<td>42.945</td>
</tr>
<tr>
<td>Kitimat Whitesail</td>
<td>23.946</td>
<td>52.158</td>
<td>14.716</td>
<td>50.113</td>
</tr>
</tbody>
</table>

Wind direction is a difficult parameter to evaluate statistically as the analysis requires careful attention to detail. Given the equation for NMB it does not make sense to use this metric, as the sum of observed wind directions in the denominator does not have informational value. RMSE is also not presented, as the square of the error leads to very high values which are out of place given the mostly positive results of figure C.4. Error values (model - observed) greater than 180° or less than -180° were processed to confine the errors between -180° and 180°. The following is an example of the method used: If the modelled wind direction was 10 degrees and the observed wind direction was 350 degrees, modelled - observed yields a difference of -340°. The correction changed this to be a +20 degree overestimation as opposed to an -340 degree underestimation.

As can be seen there is a clockwise bias in the wind direction data, of between 14 and 26
degrees. This is best illustrated by figure C.4 (a) showing Kitimat’s modelled vs observed wind direction. A 20 degree clockwise bias means that if the observed wind were blowing from the north (360°) then the modelled wind would be blowing from the north-northeast (20°), and if the wind was observed as blowing from the south (180°) then the model would output wind from the south-southwest (200°). MAE is high at all stations. This may be considered a poor result, yet the overall picture from the plots of Kitimat and the CYXT airport suggest the modelled wind direction output does not appear to be unreasonable.

**Wind Speed**

The last parameter in the evaluation, wind speed, is also not produced directly by WRF and is calculated using the combination of U and V-wind vectors at 10m. This is done with the following formula:

\[
WSPD = \sqrt{(U^2 + V^2)}
\]  

(C.2)

Model and observed wind speed are presented below for the spring and summer periods in figures C.5 (a) and C.5 (b) respectively.

WRF often over predicted wind speed for Terrace (especially for the summer). The wind speeds at the airport are under-predicted but the high observed wind speeds there are also unusual given the speeds in Kitimat (closer to the water) for the same hour. The model performs best in Kitimat.

<table>
<thead>
<tr>
<th>Location</th>
<th>NMB</th>
<th>MB</th>
<th>RMSE</th>
<th>MAE</th>
<th>NMB</th>
<th>MB</th>
<th>RMSE</th>
<th>MAE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrace B.C. Access Centre</td>
<td>27.212</td>
<td>0.573</td>
<td>1.704</td>
<td>1.331</td>
<td>40.482</td>
<td>0.854</td>
<td>1.825</td>
<td>1.386</td>
</tr>
<tr>
<td>CYXT Terrace Airport</td>
<td>-27.242</td>
<td>-0.969</td>
<td>2.401</td>
<td>1.885</td>
<td>-20.802</td>
<td>-0.672</td>
<td>2.133</td>
<td>1.619</td>
</tr>
<tr>
<td>Kitimat Whitesail</td>
<td>-5.760</td>
<td>-0.167</td>
<td>1.614</td>
<td>1.270</td>
<td>-5.409</td>
<td>-0.175</td>
<td>1.639</td>
<td>1.285</td>
</tr>
</tbody>
</table>

As can be seen in table C.5, from the perspective of the MB, RMSE and MAE, WRF performs best in Kitimat for wind speed. A different story is told by the NMB where speeds were over
predicted in Terrace (both seasons) by up to 40.5%, and under predicted at the airport by up to 27.2%. As well, RMSE is largest at the airport suggesting that there were occasions where the error was quite high, and this is confirmed by both figures C.5 (a) and C.5 (b). It is possible that the high error values at the airport are due to measurement error, given the unusually high wind speeds measured there.
Figure C.5: Observed and modelled wind speed time series at Terrace (top), CYXT (middle) and Kitimat (bottom) for: a) spring and b) summer model periods. Black lines are observed while yellow, orange and blue lines are modelled.
C.2 Qualitative Evaluation

The qualitative evaluation consists of a spatiotemporal evaluation of wind streamlines and temperature evolution over a 24-hour period. The day of July 31st was selected because there is a diurnal cycle in both wind direction and temperature, and the evolution of these two parameters is predictable based on a basic understanding of meteorology. For the wind streamlines an offshore wind along with katabatic flow down the valley walls and in tributary valleys is expected in the morning. This must change at some point to an onshore wind with anabatic flow up the valley walls and in tributary valleys. For temperature, it is expected that the amplitude of the diurnal cycle will be greater on land than over the Douglas Channel (with respect to both heating and cooling). Mountain peaks are expected to warm as well however not to the extent of the valley bottom. A more sophisticated (and quantitative) spatial evaluation is possible, however given that the concern in the TKV is advection of pollutants up and down the valley, WRF will be deemed fit for use if it is capable of reproducing the 'sloshing' that is known to occur in the TKV from the advection of pollutants up and down the valley over the course of one day. Differential heating of land and sea surface temperatures as well as onshore - offshore winds are two of the main ingredients of a sea breeze, which are known to coincide with and indeed intensify air pollution episodes (Steyn, 2003). Note that a successful spatial evaluation does not mean that the model performs optimally at all times for all locations, just that is capable of doing so. This approach is justified given the intended use of the WRF dataset and the focus on the TKV which does have monitoring stations.

The locations of the Kitimat, CYXT airport and Terrace monitoring stations are not included in the figures below so as to not obscure any of the figures. For reference on the streamline figure, the main north - south valley is the TKV which runs from the head of the Douglas channel (the tip of the coastline marked in green) to approximately 3/4 up the middle of the plot. Terrace is located at the end of the TKV, at the confluence of the Skeena and Kalum rivers. The Skeena river runs from the coast through Terrace and up towards the northeast corner of the plot. The valley that runs north from Terrace is the Kalum river valley.
detail can be found in figure 2.3. Seven figures are included in each section spanning midnight on the 31st to midnight on the 1st in 4-hour intervals. All times are in PST.

**Streamlines**

As can be seen from the first figures (especially C.6 (a)), streamlines are highly organized. Over open water (SW corner) wind is from the northwest. There are concentrated streamlines moving up the Skeena river, around the corner and then down the TKV. On the west side of the valley wind is advecting up some tributary valleys while on the east side there is katabatic movement down valley walls and south towards the Douglas channel where it eventually meets the open ocean of Hecate straight. This organized pattern begins to break down by 08:00 PST and by noon PST the arrangement of streamlines has completely reversed. At this point wind is blowing down all tributary valleys and up the TKV towards Terrace. The ability of WRF to resolve fine-scale topographical features can is apparent from streamlines of narrow secondary and tertiary valleys in the domain. It is clear that 1.333 km grid spacing is required to accomplish this level of resolution.

By the latter hours of the day streamlines have again begun to organize themselves though it comes together in the form of strong output down the Skeena river valley (see fig C.7 (b)). In the TKV wind is still onshore and chaotic, especially up the valley where there appears to be a large eddy in the vicinity of the airport. Flow does not completely settle down by midnight (i.e.: became as organized as midnight the day before) but has once again turned into flow down the TKV and Douglas Channel towards Hecate Straight.

**Spatiotemporal Temperature Evolution**

From a spatial perspective the temperature resolves nicely. At midnight, as expected, the warmest parts of the plot are all over water, while the coolest areas are over the mountain ranges. Cooling continues through 04:00 PST but somewhere between C.8 (b) and C.8 (c) this pattern changes due to the early sunrise in the summer. Low-lying areas of near Kitimat
Figure C.6: Wind streamlines in the Terrace - Kitimat valley on July 31st, 2010 at: a) 00:00, b) 04:00, c) 08:00 and d) 12:00 PST. Red lines are streamlines.
Figure C.7: Wind streamlines in the Terrace - Kitimat valley on July 31st, 2010 at: a) 16:00, b) 20:00 and c) 00:00 (August 1st) PST. Red lines are streamlines.
and Terrace (Terrace is only 68 m asl) begin to heat up first as reflected in C.8 (c). Note that the entire Skeena river valley does not warm. This is reasonable given that the valley between Terrace and the ocean is almost entirely water. There is very little land that is not mountain jutting out of the river and so it seems reasonable that the land around Terrace would warm faster than the Skeena river valley. By noon (fig C.8 (d)), tributary valleys have begun to warm and the land and surrounding water are in the same temperature range, while mountainous areas are warming but are still cool.

The warmest part of the day occurs around 16:00 PST, as seen in figure C.9 (a). At this time temperatures have reached the mid twenties in Kitimat and high twenties in Terrace. The entire valley is warm and the land is warmer than the surrounding water. Over Hecate Straight temperatures are still cooler which is reasonable and mountaintop temperatures remain the coolest in the domain. The spatial graduation of temperatures from mountain top to valley bottom to ocean is reasonable. Temperatures begin to cool by 20:00 PST and by midnight temperatures have reverted to the way they were at the start of the day with the warmest temperatures over the Douglas channel.
Figure C.8: Spatial temperature fields for the Terrace - Kitimat valley on July 31st, 2010 at: a) 00:00, b) 04:00, c) 08:00 and d) 12:00 PST.
Figure C.9: Spatial temperature fields for the Terrace - Kitimat valley on July 31st, 2010 at:
a) 16:00, b) 20:00 and c) 00:00 (August 1st) PST.
C.3 WRF Evaluation Summary and Conclusion

This section is concluded by stating that the WRF output prepared by David Suita is acceptable for use in CAMx for the three research questions. This statement is made based on the following summary:

- The quantitative evaluation of WRF output showed that it performed optimally with pressure and temperature, moderately optimal for wind direction and wind speed, and worst for RH (depending on the metrics used one could also argue for a poor performance for wind speed output). For temperature the model was unable to recreate the peaks and lows of the diurnal cycles, and for wind direction there was a constant clockwise bias to the modelled output. For wind speed the model was biased very high in Terrace (by as much as 40%) though in Kitimat the bias was low (by 5% which works out to be -0.167 ms$^{-1}$). Humidity output was greatly under predicted in Terrace by 19% in the summer (NMB). Still, even for its weakest overall performers, there were times when the output was reasonable and, except for RH in Terrace, the model was never truly unreasonable at any location for any parameter. The errors do create a level of uncertainty, yet this is well within the realm of acceptable uncertainty.

- The qualitative spatial evaluation showed that both wind streamlines and temperature evolve as expected over the course of space and time for the chosen day in the evaluation. Streamlines were concentrated in overnight hours and there was evidence of katabatic flow on one side of the Terrace - Kitimat valley. The offshore breeze shifted to become an onshore breeze about the time one would expect for a day in July, and the model was able to resolve flow around very fine-scale topographical features like tertiary valleys. The spatial and temporal evolution of temperature was as expected for a summer day in complex coastal terrain.
Appendix D

Control Case Model Evaluation for NO and NO₂

D.1 Nitric Oxide

From figures D.1 (a) and D.1 (b) it is clear for both periods that modelled Control Case NO failed to recreate observed NO for either period. This lack of characterization likely explains why O₃ mixing ratios remain elevated overnight as there was insufficient NO to titrate O₃ as per reaction 1.2. Mixing ratios are so low they are barely visible in figure D.1 and insets are required to magnify the modelled NO time series.

The poor performance of the model is mirrored in the statistics presented in table D.1. Despite a MB of only -2.2 and -1.8 ppb for spring and summer respectively, modelled concentrations were biased low by nearly 100% (NMB, both seasons) and there was little linear relationship between modelled and observed values. These results point strongly to an improper characterization of NOₓ emissions in Smithers.
Figure D.1: Observed and modelled NO time series at Smithers for: a) spring and b) summer model periods. Black lines are observed and red lines are modelled Control Case. Insets in each figure allow the modelled NO to be seen.

Table D.1: NO model evaluation statistics for the Control case - (all hours)

<table>
<thead>
<tr>
<th>Description</th>
<th>Spring</th>
<th></th>
<th></th>
<th></th>
<th>Summer</th>
<th></th>
<th></th>
<th></th>
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<tr>
<td></td>
<td>n</td>
<td>NMB (%)</td>
<td>MB (ppb)</td>
<td>RMSE (ppb)</td>
<td>MAE (ppb)</td>
<td>r</td>
<td>n</td>
<td>NMB (%)</td>
</tr>
<tr>
<td>Paired mixing ratios</td>
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<td>-98.386</td>
<td>-2.183</td>
<td>4.614</td>
<td>2.183</td>
<td>0.020</td>
<td>367</td>
<td>-97.738</td>
</tr>
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<td>2.219</td>
<td>0.269</td>
<td>16</td>
<td>-96.596</td>
</tr>
</tbody>
</table>
D.2 Nitrogen Dioxide

Given the low NO mixing ratios is is not surprising that NO\textsubscript{2} mixing ratios also did not agree with observed values. At nighttime when there is no photolysis of NO\textsubscript{2} reaction 1.2 leads to the removal of O\textsubscript{3} (Sillman, 2012), however without NO this is not possible. (In unpolluted environments such as Smithers it is common for NO\textsubscript{2} to peak overnight or in the early morning hours, as shown in figure D.2.) During the day, reactions involving HO\textsubscript{2} and other peroxy radicals also contribute to NO\textsubscript{2} formation (Crutzen, 1979), so the lack of NO\textsubscript{2} during afternoon hours cannot be wholly explained by the absence of NO.

The performance of NO\textsubscript{2} was not as poor as NO yet the statistical metrics are not encouraging. While both spring and summer RMSE were less than 5.0 ppb, modelled NO\textsubscript{2} was biased low by 91.3 and 87.1% respectively. The maximum modelled mixing ratio was negatively correlated to the maximum observed mixing ratio, reinforcing that, since the maxima occurred during overnight hours, emissions were improperly characterized.

Table D.2: NO\textsubscript{2} model evaluation statistics for the Control case - (all hours)

<table>
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<tbody>
<tr>
<td></td>
<td>n</td>
<td>NMB (%)</td>
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<td>Paired mixing ratios</td>
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</table>
Figure D.2: Observed and modelled NO$_2$ time series at Smithers for: a) spring and b) summer model periods. Black lines are observed and red lines are modelled Control Case.

D.3 Vertical layers

Investigating model output through vertical layers in CAMx was conducted to examine if and when pollutants leave the surface layer and enter other layers. Figure D.3 presents plots of PBLH, wind speed as well as contours of NO$_2$ and NO mixing ratios for the lowest eight layers of the model from May 6$^{th}$ to 12$^{th}$, 2010. Note that the scales for both pollutants (located on the right hand side) have similar colours but are different in magnitude. It is clear from this image that all NO emitted during the day is mixed into upper layers in the model.
corresponding with an increased PBLH. Overnight mixing ratios of NO and NO$_2$ are very low, and what is present does not appear to diffuse out of the model’s surface layer. This strongly reinforces the idea that lack of overnight O$_3$ titration is occurring due to mischaracterization of NO$_X$ emissions as opposed to diffusion into non-surface layers.
Figure D.3: Modelled planetary boundary layer height (top) and wind speed (second from top) time series as well as vertical NO$_2$ (second from bottom) and NO (bottom) profiles at Smithers from May 6$^{th}$ - 12$^{th}$, 2010. Only the lowest eight layers are included in the vertical profiles. Note that while the colour profiles of the lower plots are the same the mixing ratio scale is not.
Appendix E

Sensitivity Test Results for NO and NO\textsubscript{2}

E.1 Nitric Oxide

As seen in figures E.1 (a) and E.1 (b), the scenario which seemed to replicate the general range of observed NO mixing ratios (especially in the spring) was the 100xm20xp case. While the timing was somewhat misplaced, this high-emitting scenario was able to produce ambient mixing ratios in the 20 - 30 ppb range, which matched what was observed on some evenings (though in the summer there were two days with erroneously high mixing ratios). The 50xm scenario was also able to produce elevated NO in the spring, while the 10xm20xp and 20xp scenarios were able to produce elevated NO, particularly in the summer (note the 10xm20xp line is directly behind the 20xp line for much of both figures). The 10xm scenario, because overnight emissions in this case were low, was unable to produce elevated NO.

No case was able to replicate the exact timing of overnight emissions, and this affected the statistical performance of all cases (all metrics). None of the scenarios were able to produce meaningful correlation with the observed values. All biases were low except for the 100xm20xp case which was biased very high, with a 179% high bias in the summer period. The MAE was only 2 ppb or less for all cases except the 100xm20xp case, indicating that on average model
output was close to observed values (which makes sense as NO mixing ratios are near zero for large portions of the day) though the RMSE of 3.1 - 4.5 ppb (including spring and summer and ignoring 100xm20xp) indicates that there were some misses with peak values. Despite the large negative biases however, all scenarios produced improved statistics compared to the Base case, and the NO magnitudes of the 100xm20xp case match the magnitudes of the observations (with two exceptions in the summer period on April 4th and 5th). For the two modest cases with increased point source emissions (20xp and 10xm20xp), the biases improved from -98.4 and -97.7% (spring and summer respectively) to -72.1 and -56.0%. The MAE of these two cases also improved compared to the base case, decreasing from 2.1 to 1.8 ppb in the spring and 1.7 to 1.5 ppb in the summer. The complete results from this case are listed in table E.1.

Table E.1: NO model evaluation statistics for the sensitivity tests - (all hours)

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<td>n</td>
<td>NMB</td>
<td>MB</td>
<td>RMSE</td>
</tr>
<tr>
<td></td>
<td>(%)</td>
<td>(ppb)</td>
<td>(ppb)</td>
<td>(ppb)</td>
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Figure E.1: Observed and modelled NO time series at Smithers for: a) spring and b) summer model periods. Black lines are observed and red lines are modelled Control Case. Green, blue, purple, orange and light blue lines are the modelled sensitivity test cases: 10xm, 20xp, 10xm20xp, 50xm and 100xm20xp respectively, as defined in table 3.5.
Nitrogen Dioxide

NO₂ is an important gas when considering the performance of these sensitivity case studies as NO₂ is the product of the titration reaction between O₃ and NO as per reaction 1.2. It is possible for models to properly model O₃ and NO, but produce elevated NO₂; this can be thought of getting O₃ and NO right for the wrong reasons. An example of great O₃ and NO results but poor NO₂ results is the 100xm20xp scenario, as shown in E.2 (a) and E.2 (b). These plots indicate that NO₂ mixing ratios are many times higher than those observed for this extreme case. The 50xm case also produced NO₂ mixing ratios well above those observed, illustrating how emissions of such magnitudes are unrealistic. A visual inspection of the time series show that the performance of the remaining scenarios was not uniform across both seasons, with the 10xm20xp and 20xp scenarios matching the range of observed values in the spring and the 10xm scenario matching the range of observed values in the summer.

Based on the statistical metrics listed in table E.2, it can be seen that the 20xp scenario has the smallest bias (only 8.0%) in the spring and the 10xm has the smallest bias in the summer as well as the smallest error for both seasons. These are a considerable improvement over the base case and a marked indicator of improved fitness. Excluding the r, these scenarios were the best performers with respect to NO₂. The 100xm20xp and 50xm scenarios produced extreme bias and errors, while the 10xm20xp case did not perform as well as the other modest cases.

<table>
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<th>RMSE</th>
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<td>NMB (%)</td>
<td>MB (ppb)</td>
<td>RMSE (ppb)</td>
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<td>17.861</td>
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Figure E.2: Observed and modelled NO\textsubscript{2} time series at Smithers for: a) spring and b) summer model periods. Black lines are observed and red lines are modelled Control Case. Green, blue, purple, orange and light blue lines are the modelled sensitivity test cases: 10xm, 20xp, 10xm20xp, 50xm and 100xm20xp respectively, as defined in table 3.5.
E.3 Scatterplots

The scatterplots shown in figures E.3 and E.4 depict hourly paired mixing ratios of observed vs. modelled O$_3$, NO and NO$_2$ for both the spring and summer cases. The 50xm scenario was omitted to allow the remaining 5 sets of model output to fit on one line. A linear fit is also shown. For the O$_3$ scenarios, daytime paired values are included and are indicated by a black dot in the middle of the coloured circle. The strongest model performer, as indicated by the results of the previous sections and section 3.3.2, is outlined with a blue square. As is apparent, the 100xm20xp scenario performs well for O$_3$ and NO but poorly for NO$_2$. The 10xm, 20xp and 10xm20xp scenarios appear to be an improvement over the base case with respect to paired values for all gaseous pollutants (both seasons). For O$_3$, it is clear, especially in the spring, that increasing emissions improves the model output, placing more and more paired values within the 1:2 ratio lines. Daytime mixing ratios are mostly within these limits.

The NO scatterplots indicate that no model scenario correctly captured emissions in Smithers, though the 100xm20xp scenario did result in elevated NO mixing ratios. The NO$_2$ plots indicate that the best performers were the 20xp scenario for the spring and 10xm scenario for the summer. In order to avoid over-titration, it is proposed that model fitness is sufficiently improved with the inclusion of additional low-magnitude, area-based NO$_X$ increases, such as those from the 20xp case.
Figure E.3: Observed vs. modelled O₃, NO and NO₂ scatterplots at Smithers for the spring model period. a), b), c), d) and e) show observed vs. modelled O₃ (Control and sensitivity cases: 10xm, 20xp, 10xm20xp, and 100xm20xp respectively). f), g), h), i) and j) show observed vs. modelled NO (Control and sensitivity cases: 10xm, 20xp, 10xm20xp, and 100xm20xp respectively). k), l), m), n) and o) show observed vs. modelled NO₂ (Control and sensitivity cases: 10xm, 20xp, 10xm20xp, and 100xm20xp respectively). Hollow dots (e.g.: ◊) indicate all paired values while filled dots (e.g.: ●) indicate daytime hours (only for O₃ figures). A linear best fit is shown as a solid black line while a dashed line represents the daytime best fit (O₃ row only). 2:1, 1:1 and 1:2 ratios are shown as thin dotted lines. The best performing sensitivity case (based on a combination of all statistical metrics) is outlined in blue.
Figure E.4: Observed vs. modelled O$_3$, NO and NO$_2$ scatterplots at Smithers for the summer model period. a), b), c), d) and e) show observed vs. modelled O$_3$ (Control and sensitivity cases: 10xm, 20xp, 10xm20xp, and 100xm20xp respectively). f), g), h), i) and j) show observed vs. modelled NO (Control and sensitivity cases: 10xm, 20xp, 10xm20xp, and 100xm20xp respectively). k), l), m), n) and o) show observed vs. modelled NO$_2$ (Control and sensitivity cases: 10xm, 20xp, 10xm20xp, and 100xm20xp respectively). Hollow dots (e.g.: o) indicate all paired values while filled dots (e.g.: •) indicate daytime hours (only for O$_3$ figures). A linear best fit is shown as a solid black line while a dashed line represents the daytime best fit (O$_3$ row only). 2:1, 1:1 and 1:2 ratios are shown as thin dotted lines. The best performing sensitivity case (based on a combination of all statistical metrics) is outlined in blue.