Comparing Non-Steady State Emissions under Start-Up and Shut-Down Operating Conditions with Steady State Emissions

by

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AUTHOR’S DECLARATION

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

STATEMENT OF CONTRIBUTIONS

This thesis consists of material all of which I authored or co-authored.

The content of Chapter 2 is based on a paper published on February 4, 2017 in the journal "Energies" under the title "Comparing Non-Steady State Emissions under Start-Up and Shut-Down Operating Conditions with Steady State Emissions for Several Industrial Sectors: A Literature Review" by "Obaid et al.". The author specific contribution to this paper was: the investigation of the emissions of various industrial facilities under start-up, shut-down and normal operations, comparison of emissions under non-steady state to those under steady state, identification and analysis of trends, preparation of tables and results, and preparation of the draft manuscript with supervision from the study supervisors who are co-authors. This paper is co-authored by Dr. Ramadan, who prepared the final manuscript incorporating the reviewers' edits, and by Dr. Elkamel and Dr. Anderson, who supervised the study.

The content of Chapter 3 is based on a paper published in November 2014 in the "Journal of Renewable and Sustainable Energy" under the title "A study of the dispersion of vinyl chloride from a renewable energy facility located in Ontario, Canada" by "Obaid et al.". The author specific contribution to this paper was: the set-up and running of the simulations, analysis of the results, preparation of graphics, figures, tables and results, preparation of the draft manuscript, and preparation of the final manuscript incorporating the reviewers' edits with supervision from the study supervisors who are co-authors. This paper is co-authored by Dr. Abdul-Wahab, who supervised the simulations and edited the manuscript, and by Dr. Elkamel, who supervised the study.

The content of Chapter 4 is based on a paper published in November 2014 in the journal "Fuel" under the title "Modelling of greenhouse gas emissions from the steady state and non-steady state operations of a combined cycle power plant located in Ontario, Canada” by “Abdul-Wahab et al.”. The thesis author specific contribution to this paper was: the set-up and running of the simulations, analysis of the results, preparation of graphics, figures, tables and results, preparation of the draft manuscript, and preparation of the final manuscript incorporating the reviewers’ edits with supervision from the study supervisors who are co-authors. This paper is co-authored by Dr. Abdul-Wahab, who supervised the simulations and edited the manuscript, and by Dr. Elkamel, who supervised the study.

ABSTRACT

Although often neglected, the non-steady state operations of industrial facilities are more likely to result in increased emissions and process safety incidents compared to steady state operations. Regulatory authorities such as the United States Environmental Protection Agency and the Ontario Ministry of the Environment and Climate Change do not require industrial facilities to assess and report emissions under non-steady state operating conditions such as start-up and shut-down events.

It is demonstrated that emissions under non-steady state operation can be higher than those under steady state operation and that non-steady state emissions have the potential to exceed applicable regulatory emission limits.

A literature review has been conducted that compares non-steady state emissions under start-up and shut-down operating conditions with steady state emissions for several industrial sectors. Where available, trends have been developed to identify the circumstances, i.e. the industrial sector and contaminant, under which the assessment and consideration of emissions from start-up and shut-down events is necessary for each industry. The thesis also compares the two most commonly used air dispersion models: AERMOD and CALPUFF using a case study approach and recommends the use of CALPUFF as the more conservative approach. CALPUFF is then used to model the greenhouse gas emissions from the full load operation (steady state) and start-up conditions (non-steady state) of a combined cycle power plant to identify the worst-case emissions scenario.

The studies conclude that emissions under both, steady state and non-steady state operating conditions, must be modelled and assessed to ensure that the impacts of released emissions are modelled and studied in a conservative manner that takes into account all scenarios to determine the impacts of the worst-case scenario. The studies demonstrate that the worst-case operating condition may be different for each contaminant. Some contaminants have higher emissions during steady-state operating conditions, while others have higher emissions during non-steady state operating conditions. This was observed to depend on the nature of the industrial process and the type of contaminant. Considering these different operating scenarios is particularly important when emissions associated with non-steady state operation have the potential to exceed applicable regulatory emission limits, and to possibly cause an adverse impact on public health and the environment. Therefore, emissions under both, steady state and non-steady state, operating conditions must be assessed, controlled and reported to the regulatory authorities to ensure that emissions under the worst-case scenario are addressed, consequently preventing the emissions from adversely impacting public health and the environment.

The study recommends that regulatory authorities require industrial facilities to assess their emissions under non-steady state operating conditions as well as under steady state operating conditions to ensure that the emissions under both conditions are controlled below the applicable regulatory emission limits.

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DEDICATION

To my beloved son, Aadil Obaid Akhter

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LIST OF ABBREVRIATIONS

AERMOD	American Meteorological Society/ Environmental Protection Agency Regulatory Model
CALPUFF	California Puff
CEMS	Continuous emissions monitoring system
CO	Carbon monoxide
CO_2	Carbon dioxide
ESRL	Earth System Research Laboratory
GUI	Graphical user interface
HCl	Hydrogen chloride
HF	Hydrogen fluoride
H_2SO_4	Sulphuric acid
IGCC	Integrated gasification combined cycle
JSL	Jurisdictional screening level
LCC	Lambert conformal conic
LNG	Liquefied natural gas
LST	Local standard time
MOECC	Ministry of the Environment and Climate Change
NH_3	Ammonia
NOAA	National Oceanic and Atmospheric Administration
NO_2	Nitrogen dioxide
NO_x	Nitrogen oxides
O_2	Oxygen
PAHs	Polycyclic aromatic hydrocarbons
PCDD/Fs	Polychlorinated dibenzodioxins and polychlorinated dibenzofurans
PM	Particulate matter
$PM_{2.5}$	Particulate matter 2.5 micrometers or less in diameter
PM_{10}	Particulate matter 10 micrometers or less in diameter
SCR	Selective catalytic reduction
SNG	Substitute natural gas
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
TC	Transport Canada
U.S. EPA	U.S. Environmental Protection Agency
UTC	Universal time coordinates
UTM	Universal Transverse Mercator
VOCs	Volatile organic compounds
WMO	World Meteorological Organization

LIST OF SYMBOLS

^{o}C	degrees Celsius
g/s	grams per second
km	kilometer
km^2	kilometer squared
m	metre
m/s	metres per second
mbar	millibar
ppm	parts per million
t	tonnes
$\mu g/m^3$	micrograms per cubic metre

Chapter 1: Introduction

1.1 Background

To protect public health and the environment, the emissions of contaminants from industrial sources must be controlled below safe threshold values. The air permit framework in Ontario and the United States (U.S.) is based on defining and enforcing limits on the concentrations of contaminants that are emitted from a facility to the environment [1,2]. Concentration limits are different for each contaminant because different contaminants have the potential to cause an adverse impact to public health and the environment at different concentration values. Guidance provided by regulatory agencies in calculating emissions relies heavily on the use of the emission factors listed under AP-42, Compilation of Air Pollutant Emission Factors, developed and published by the United States Environmental Protection Agency (U.S. EPA) [1,3].

However, it should be noted that these emission factors were developed based on data collected from the testing of emissions under normal process operating conditions, such as steady state operation [4]. Furthermore, these emission factors do not account for short-term fluctuations in the process conditions, such as those encountered under non-steady state operation [4]. Thus, it can be concluded that the use of these emission factors in assessing worst-case scenario emissions from a facility does not capture emissions generated by the facility when it is operating under non-steady state conditions.

More accurate approaches need to be investigated and developed to predict the emissions of contaminants when a facility is operating under non-steady state conditions such as process start-ups and shut-downs, as well as process fluctuations and upsets where the operating conditions deviate from the normal operating conditions [5].

Due to the lack of clearly defined methods of quantifying and regulating emissions generated during start-up and shut-down events, the approaches taken by the states to limit and regulate these emissions have been inconsistent [1]. Some states allow facilities to use six to twelve months of Continuous Emissions Monitoring System (CEMS) data to develop site-specific emissions limits for start-up and shut-down events [1]. Other states apply emission limits for normal operating conditions only [1]. Furthermore, some states restrict the length of time that a facility takes during start-up and shut-down events to limit excess emissions during such events [6].

In response to a petition filed by a U.S.-based environmental organization called the Sierra Club, the U.S. EPA proposed a rule in February 2013, necessitating that the states develop plans to require that all industrial facilities comply with air pollution rules during plant start-ups, shut-downs and malfunctions [7]. This was further formalized in May 2015, when the U.S. EPA issued a final action that required the states to submit their revised state implementation plans, accounting for emissions under these non-steady state operating conditions [8]. No similar action has been made by the Ministry of the Environment and Climate Change (MOECC) within Ontario.

There are multiple challenges in predicting emissions that are generated during non-steady state operating conditions. Firstly, it is difficult to collect accurate and representative data during such events due to their relatively short time span and their dynamic process variables [5]. Additionally, many manufacturers do not have emissions data available for start-up and shut-down events [5]. Also, the U.S. EPA does not provide method tests that can be applied for dynamic process situations [5]. Furthermore, developing and processing dynamic models for facilities is often more challenging and costly than developing models that represent normal operating conditions [9]. Moreover, the integration of multiple process functions, such as reaction and heat transport operations, within the same process unit further complicates the prediction of emissions under non-steady state conditions [9].

Despite the challenges in predicting emissions from facilities under non-steady state conditions, investigating methods to predict these emissions is essential in ensuring that a facility does not adversely impact public health or the environment. Oftentimes, emissions are higher during the start-up and shut-down of a facility, compared to its steady state operation under normal operating conditions [6,10]. Additionally, most incidents that are related to the process carried out at the facility occur when the plant is operating under non-steady state conditions [9]. Furthermore, as emission limits become more stringent with time, it is important to investigate methods of predicting emissions associated with non-steady state events, to ensure that resources are adequately allocated to minimize emissions and thus to achieve compliance with these limits [1].

1.2 Motivation for this Thesis

The motivation for this thesis is to encourage regulatory authorities to require industrial facilities to assess their emissions under non-steady state operating conditions and ensure that these emissions are below the applicable regulatory emission limits. Regulating emissions that occur only under steady state operating conditions increases the potential for adverse impacts to public health and the environment resulting from emissions under non-steady state operating conditions.

1.3 Objectives of the Thesis

In this thesis, the author demonstrates that emissions under non-steady state operation can be higher than those under steady state operation and that non-steady state emissions have the potential to exceed applicable regulatory emission limits. Thus, emissions under both, steady state and non-steady state operating conditions, must be estimated and considered to ensure that emissions under the worst-case scenario are controlled to prevent adverse impacts on public health and the environment.

1.4 Outline of the Thesis

The thesis is comprised of three published papers arranged in separate chapters.

Chapter 2 is a literature review that compares non-steady state emissions under start-up and shut-down operating conditions with steady state emissions for several industrial sectors. Where available, trends have been developed to identify the circumstances, i.e. the industrial sector and contaminant, under which the assessment and consideration of emissions from start-up and shut-down events is necessary for each industry. The content of Chapter 2 is based on a paper published on February 4, 2017 in the journal “Energies” under the title “Comparing Non-Steady State Emissions under Start-Up and Shut-Down Operating Conditions with Steady State Emissions for Several Industrial Sectors: A Literature Review”.

The objective of Chapter 3 is to compare the two most commonly used air dispersion models: AERMOD and CALPUFF. In this Chapter, the study compares the results of modelling vinyl chloride emissions from a renewable energy generation plant located in the City of Kawartha Lakes, Ontario, Canada, using AERMOD and CALPUFF. The content of Chapter 3 is based on a paper published in November 2014 in the “Journal of Renewable and Sustainable Energy” under the title “A study of the dispersion of vinyl chloride from a renewable energy facility located in Ontario, Canada”.

In Chapter 4, the study focuses on modelling greenhouse gas emissions from the full load operation (steady state) and start-up conditions (non-steady state) of a combined cycle power plant using CALPUFF to identify the worst-case emissions scenario. The contaminants that have been modelled are nitrogen oxides, carbon dioxide, carbon monoxide and sulphur dioxide. Additionally, four different modelling scenarios have been considered: full load operation; a cold start followed by full load operation; a warm start followed by full load operation; and a hot start followed by full load operation. The content of this Chapter is based on a paper published in November 2014 in the journal “Fuel” under the title “Modelling of greenhouse gas emissions from the steady state and non-steady state operations of a combined cycle power plant located in Ontario, Canada”.

Chapter 5 concludes this thesis with conclusions and recommendations made as a result of the studies included within the aforementioned chapters. This chapter also includes recommendations for future research.

Chapter 2: Comparing Non-Steady State Emissions under Start-Up and Shut-Down Operating Conditions with Steady State Emissions for Several Industrial Sectors

The content of this chapter is based on a paper published on February 4, 2017 in the journal "Energies" under the title "Comparing Non-Steady State Emissions under Start-Up and Shut-Down Operating Conditions with Steady State Emissions for Several Industrial Sectors: A Literature Review" by "Obaid et al.". The author specific contribution to this paper was: the investigation of the emissions of various industrial facilities under start-up, shut-down and normal operations, comparison of emissions under non-steady state to those under steady state, identification and analysis of trends, preparation of tables and results, and preparation of the draft manuscript with supervision from the study supervisors who are co-authors. This paper is co-authored by Dr. Ramadan, who prepared the final manuscript incorporating the reviewers' edits, and by Dr. Elkamel and Dr. Anderson, who supervised the study.

2.1 Research Background

In the United States, the regulatory structure and framework pertaining to air permits is dependent on the requirement of a facility to meet emission limits for different contaminants as set out in the applicable regulations [1,2]. The described situation is also applicable outside the borders of the United States, e.g., Ontario in Canada. Thus, facilities must demonstrate compliance with these emission limits by calculating their emissions and comparing them to the limits. The emissions are most commonly calculated using the emission factors listed under AP-42, Compilation of Air Pollutant Emission Factors, published by the United States Environmental Protection Agency (U.S. EPA) [1,3]. The use of these emission factors to estimate emissions is encouraged by regulatory agencies [1,3]. It is noted that these emission factors are based on emissions data collected under normal, steady state process operating conditions [4]. Thus, these emission factors do not consider non-steady state operating conditions where the operating conditions may deviate from the steady state conditions [4]. Consequently, using these emission factors to calculate the worst-case emissions, a scenario which is very likely to occur under non-steady state conditions, is far from ideal. This demonstrates a need for the development and implementation of approaches that more accurately account for emissions attributed to non-steady state conditions. Non-steady state operation can include process start-ups and shut-downs, as well as process upsets [5].

In the United States, different states have adopted different methods of regulating the emissions associated with start-up and shut-down operation [1]. The inconsistencies in their method and regulatory approach are, in part, due to the absence of a clearly defined process of estimating and regulating emissions under such conditions [1]. For example, some states allow the development of site-specific start-up and shut-down emission limits based on a minimum of six months of CEMS data [1]. Alternatively, other states regulate emission limits for steady state operation only [1]. Yet other states control excess emissions generated during start-up and shut-down events by limiting the time period allowed for such events [6].

In February 2013, the U.S. EPA proposed a rule that mandated the states to develop plans that required industrial facilities to be in compliance with applicable emission limits during start-up, shut-down, and process malfunctions [7]. This rule was introduced as a result of a U.S. environmental organization, the Sierra Club, filing a petition for the consideration of emissions associated with these non-steady state operating conditions [7]. This was further formalized in May 2015, when the U.S. EPA issued a final action that required the states to submit their revised state implementation plans, accounting for emissions under these non-steady state operating conditions [11]. No similar action has been made by the Ministry of the Environment and Climate Change (MOECC) within Ontario.

Predicting emissions associated with non-steady state operations poses multiple challenges. Due to the variance in process variables and the relative short time span of start-ups and shut-downs, it can be challenging to obtain monitoring data that is accurate and representative [5]. In addition, manufacturer's emissions data relating to start-ups and shut-downs is often unavailable [5]. Moreover, the development and use of a non-steady state dynamic model is often more challenging and expensive than that of a steady state model [12]. Furthermore, the complex relationships between various process functions that are dynamic at the same time during non-steady state operation add to the difficultly in estimating non-steady state emissions [12].

Although the challenges described above may be cumbersome, time-consuming, and costly to address, developing and implementing methods to predict non-steady state emissions is vital in ensuring that industrial facilities do not exceed air emission limits during these short-term operations. In most cases, emissions associated with start-up and shut-down events are higher than those associated with normal, steady state operating conditions [6,13]. Methods of estimating these increased emissions need to be developed so that the facility can be designed such that an increase in emissions during start-up and shut-down does not result in an adverse impact on human health or the environment. Most incidents that are related to the facility's process operations occur when the facility is operating under non-steady state conditions [12]. Moreover, emission limits become more stringent with time. Thus, it is in the best interest of the permit applicants that methods to estimate emissions from start-up and shut-down events be developed, so that they can ensure compliance at the design stage rather than going through higher-cost retrofits. This would also help maintain compliance throughout the life of the facility [1].

This chapter focuses on comparing emissions from several industrial facilities under start-up, shut-down, and normal operating conditions from various industries. Where available, trends have been developed to assess the circumstances under which the consideration of emissions from start-up and shut-down events are necessary for each industry. These trends will help air permit applicants to effectively allocate their resources when assessing emissions related to non-steady state operations.

2.2 Methodology

As part of this study, journal articles, research papers, as well as reports prepared by industrial air applicants were researched with a focus on facilities that had assessed and reported their emissions under start-up, normal, and shut-down operating conditions.

The industrial sectors include power and/or heat generation, energy-from-waste generation, nuclear power generation, sulphuric acid production, ethylene production, petrochemical production, and waste incineration. Similar facilities were grouped together and categorized into industrial sectors for better organization and easy identification of emission characteristics by industry. Additionally, facilities within the same industrial sector are very likely to have the same chemical reactions and processes and, hence, have similar emission profiles and principles governing the processes. Any differences between facilities within an industrial sector that led to a different emissions profile were recognized and identified.

For facilities that had quantitatively assessed their emissions under start-up, normal, and shut-down operations, the emissions data was tabulated for each operating scenario. Since the facilities researched were from different countries, the emission variables measured, as well as their units, were different. For example, some papers listed the emission rates under the different operating conditions, others listed concentrations at the stack, whereas yet others listed the maximum off-property ground level concentration.

Since the emissions for any given facility had the same units, comparing the emissions pertaining to each operating condition for the same facility was not affected. However, the challenge came when the emissions data from different facilities within an industrial sector were grouped together to identify trends in emissions based on the operating scenario. The difference in emission variables and units made this comparison between facilities' emissions data difficult.

To deal with this difficulty, the emissions data was normalized to the emissions associated with the normal operating scenario. This means that the emissions pertaining to the normal operating scenario for each contaminant in each facility will be listed as '1', and the emissions for the start-up and shut-down events will be listed as the factor or multiplier of increase or decrease in emissions based on the normal operating scenario's emissions. This allows for a better comparison of emissions under each operating scenario for each facility, irrespective of the unit, scale, and measured parameter listed in each paper and/or report.

The range of normalized emission values was then tabulated into a single table for each industrial sector by contaminant type for easy analysis and identification of emission trends. These trends were then analysed, summarized, and reported to suggest the circumstances, i.e., the industrial sector and contaminant, under which the assessment of start-up and shut-down emissions should be performed.

2.3 Results and Discussion

2.3.1 Power and/or Heat Generation

Eleven different facilities were investigated under this industrial sector, including combined-cycle power plants, simple cycle gas turbines, reciprocating internal combustion engines, cogeneration power plants, and open-gas turbine power generations [11-20]. Geographically, the facilities were located in Canada, the United States, the United Kingdom (UK) and Australia. All eleven facilities provided emissions data related to the start-up and normal operating conditions. Only five of the eleven facilities also provided emissions data related to the shut-down conditions [11,12,15,17,18]. Table 1 summarizes the normalized emissions for each contaminant emitted in each of the facilities that comprise this industrial sector.

Table 1. Normalized emissions from power and/or heat generation facilities under start-up, normal, and shut-down operating conditions (number of facilities investigated shown in brackets).

Contaminants	Normalized Emissions			References
	Start-Up	Normal Operation	Shut-Down	
NO_x	0.47–16.67 (11)	1	1.13–9.26 (5)	[11–20]
CO	2.08–158.85 (11)	1	3.09–51.85 (5)	[11–20]
VOCs	1.57–156.84 (5)	1	2.80–94.86 (3)	[11–13,15,17]
SO_2	0.31–7.66 (9)	1	0.31–3.41 (4)	[11–18,20]
PM_{10}, $PM_{2.5}$	0.27–1.21 (9)	1	0.26–1.07 (4)	[11–18,20]
CO_2	1.15×10^{-4}–0.25 (2)	1	-	[13,16]
H_2SO_4	1 (2)	1	1 (1)	[11,13]
NH_3	0.78 (1)	1	-	[18]
formaldehyde	12 (1)	1	-	[20]

All facilities assessed the emission of NO_x under start-up and normal operating conditions. Five of the eleven facilities also assessed the NO_x emissions under shut-down conditions [11,12,15,17,18]. Nine facilities (i.e., approximately 82%) out of the eleven demonstrated that the NO_x emissions were approximately 1.7–16.7 times higher for the start-up conditions than for the normal operating conditions [11,12,13,15,16,17,18,20]. As for the NO_x emissions under shut-down, they were approximately 1.1 to 9.3 times higher than those under the normal operating scenario [11,12,15,17,18]. The increase in NO_x emissions during start-up is because during start-up, the temperature at the selective catalytic reduction (SCR) system is not high enough to activate the SCR [15,6]. Once the temperature of approximately 302 °C is reached, the SCR system is activated and the system enters a steady state [15,6]. The activation of the SCR decreases the emissions during the normal operation considerably [15,6]. Based on our above findings this decrease is somewhere between 41%–94%. During shut-down, the temperature continues to decrease until it drops below the SCR activation temperature and the SCR system is deactivated [15,6]. This, again, causes an increase in NO_x emissions during the shut-down of the plant [15,6]. Based on our findings, the increase in emissions during shut-down is between 10%–830%. The aforementioned figures demonstrate that an air permit applicant should assess the NO_x emissions during start-up and shut-down.

All eleven facilities assessed the emission of CO under start-up and normal operating conditions Five of the eleven facilities also assessed the CO emissions under shut-down conditions [11,12,15,17,18]. All eleven facilities demonstrated that the CO emissions were about 2.1–158.9 times higher for the start-up conditions than for normal operation while the five facilities demonstrated that the CO emissions during shut-down were about 3.1–51.9 times higher than the emissions under normal operations. The increase in CO emissions during start-up and shut-down is likely because the air-fuel ratio decreases at low load conditions, causing a decrease in flame temperature and, thus, incomplete combustion conditions [7]. Thus, an air permit applicant should, at minimum, assess CO emissions during start-up and shut-down due to the potential of these emissions to exceed those under normal operation by 110%–15,790% and 210%–5090% during start-up and shut-down conditions, respectively.

Five facilities assessed volatile organic compounds (VOC) emissions under start-up and normal operating conditions [11,12,13,15,17]. Three of the five facilities also assessed these emissions under shut-down conditions [11,12,17]. All five facilities demonstrated that the VOC emissions under start-up were approximately 1.6–156.8 times higher than under normal operating conditions while, for the shut-down conditions, the three facilities demonstrated that the VOC emissions were approximately 2.8–94.9 times higher than under normal operating conditions. Similar to the reason for the increase in CO emissions during start-up and shut-down events, it is likely that the increase in VOC emissions during these operating conditions is attributable to incomplete combustion. Thus, an air permit applicant should, at minimum, assess VOC emissions during start-up and shut-down due to the potential of these emissions to increase by 60%–15,580% and 180%–9390% under start-up and shut-down conditions compared to normal operations.

Nine facilities assessed the emissions of SO_2 under start-up and normal operating conditions [11-18,20]. Four of the nine facilities also assessed SO_2 emissions under shut-down conditions [11,12,17,18]. Approximately 89% of the facilities (eight out of nine facilities) demonstrated that SO_2 emissions under start-up conditions were lower than or equal to the SO_2 emissions under normal operation [12-18,20]. As for the shut-down conditions, two facilities demonstrated higher SO_2 emissions under shut-down conditions, while the other two facilities reported the opposite. The amount of SO_2 emitted is a function of the fuel composition and the fuel consumption [21]. Under normal operating conditions, the fuel consumption is higher than during start-up and shut-down and this conforms with the trend observed for SO_2 emissions. It should be noted that the SO_2 emission for one of the facilities is significantly higher under start-up and shut-down conditions than under normal operation [11]. What might appear to be a contradiction to the common trend observed (i.e., higher SO_2 emissions during normal operations due to higher fuel consumption) readily disappears when one realizes this facility has a sulphur recovery system consisting of a thermal oxidizer and a flare. The flare rarely operates under normal operating conditions and operates significantly under start-up and shut-down operation. Similarly, the oxidizer's operation during start-up and shut-down is much higher than during normal operation. The SO_2 emissions from this sulphur recovery system results in the SO_2 emissions being higher for the start-up and shut-down events than for the normal operation. It should be noted that the SO_2 emissions were the same for all operating conditions for the turbine sources, i.e., if the sulphur recovery system had not been a part of the plant, the SO_2 emissions would be the same under start-up, normal, and shut-down conditions. The exception in the observed trend should be emphasized because it portrays that the trends being observed and analysed here can be used as rules of thumb, but not as absolute rules. Each facility is unique and, although most facilities may follow a certain expected emission profile, diligence must be exercised on a case-by-case basis for each facility to ensure that the worst-case scenario for emissions is captured. Thus, taking into account the applicable exceptions, an air permit applicant does not necessarily need to assess SO_2 emissions during start-up and shut-down operations since these emissions are likely to be lower than those under normal operation.

Nine facilities assessed particulate matter (PM) emissions under start-up and normal operating conditions [11-18,20]. Four of the nine facilities also assessed these emissions under shut-down conditions [11,12,17,18]. Approximately 89% of the facilities (eight out of nine facilities) demonstrated that the PM emissions under start-up conditions were equal to or smaller than those under normal operation [12-18,20]. Similarly, 75% of the facilities (three out of four facilities) demonstrated that the PM emissions under shut-down conditions were equal to or smaller than those under normal operation [12,17,18]. PM emissions, like SO_2 emissions, are largely dependent on fuel composition [21]. Since normal operating conditions use higher quantities of fuel compared to start-up and shut-down events, the trend observed is consistent with higher PM emissions expected during periods of high fuel load combustion. However, it should be noted that the PM emission for one of the facilities is significantly higher under start-up and shut-down conditions [11]. This facility is the Great Bend integrated gasification combined cycle (IGCC) power plant, discussed above. Similar to the case of SO_2 emissions, considerable PM emissions are produced during the operation of the sulphur recovery system, which results in the rather uncommon observed trend. Thus, and similar to the comment made regarding SO_2, an air permit applicant may not need to assess PM emissions during start-up and shut-down. However, for facilities which have an unusual emission profile due to their unique source and operation characteristic configuration, it is important to exercise diligence to estimate the maximum emissions.

Two facilities assessed CO_2 emissions under start-up and normal operating conditions [13,16]. None of the facilities assessed CO_2 emissions under shut-down conditions. Although CO_2 is a major greenhouse gas, it is not a criteria pollutant. For this reason there has been less interest in the past in its monitoring. The two facilities demonstrate that the CO_2 emissions associated with start-up conditions are significantly lower than those associated with normal conditions. Primarily, CO_2 emission is a function of the amount of fuel that is combusted under complete combustion conditions. Since the normal operating conditions use higher fuel quantities, unlike start-up conditions, and because the operating conditions during normal operation are conducive to complete combustion, CO_2 emissions are much higher under normal operation. Thus, an air permit applicant may not need to assess CO_2 emissions during start-up. However, one should note that the trend observed for these two facilities might not be representative of the norm of the majority and accordingly, more facilities need to be investigated to validate the observed trend. Additionally, to develop a trend for CO_2 emissions during shut-down operation, more facilities need to be investigated.

Two facilities assessed H_2SO_4 emissions under start-up and normal operating conditions [11,13], and one of these facilities assessed these emissions under shut-down condition [11]. For both facilities, the H_2SO_4 emission remains fixed irrespective of the operating condition. Since the H_2SO_4 is a by-product of the SO_2 emission, it is likely that the emission of H_2SO_4, like the emission of SO_2, is also dependent on fuel properties. Thus, it would be expected that the H_2SO_4 emissions for start-up and shut-down operating conditions would be lower or equal to that for normal operation. Thus, an air permit applicant may not need to assess H_2SO_4 emissions during start-up and shut-down operation. Still, data from only two facilities is not enough to characterize the emissions trend and the emissions of more facilities need to be investigated to establish the correct trend.

One facility assessed the emissions of NH_3 under start-up and normal operating conditions and demonstrated that the NH_3 emissions under start-up were significantly lower than that for normal operation [18]. This is because NH_3 is added to the SCR to reduce NO_x emissions once normal operating conditions had been reached and the SCR had been activated [18]. The addition of NH_3 during normal operation results in higher emissions. The NH_3 emissions during start-up may have been from residual NH_3 leftover after shut-down. Only one facility was investigated for NH_3 emissions during start-up operations, which means our findings could not be conclusive. There is a need to investigate more facilities under start-up, normal, and shut-down conditions in order to establish the NH_3 emission trend.

One facility assessed formaldehyde emissions under start-up and normal operating conditions and demonstrated that the formaldehyde emissions during start-up were 12 times higher than under normal operation [20]. For this facility, the formaldehyde emissions for the start-up conditions were calculated empirically based on an adjustment factor from a previous report for a similar plant. As the case for H_2SO_4, more work is needed to establish the correct trend for emissions under different conditions.

2.3.2 Energy-from-Waste Generation

Two different facilities were investigated under this industrial sector. The first was an energy-from-waste thermal treatment facility, located in Durham, Ontario, Canada [22]. The second was the Oglethorpe Power Generation facility, which is a biomass-fuelled electricity generating facility, located in Warren County, Georgia, United States [21]. Table 2 summarizes the normalized (using normal operating conditions) emissions for each contaminant emitted in each of the facilities that comprise this industrial sector. The results show that for all contaminants emitted from the two plants, the emission of each contaminant was higher under start-up conditions than under normal conditions [21,22]. The contaminants emitted are as follows: NH_3, CO, hydrogen chloride (HCl), hydrogen fluoride (HF), NO_2, SO_2, metals, chlorinated polycyclic aromatics, chlorinated monocyclic aromatics, polycyclic aromatic hydrocarbons (PAHs), VOCs, NO_x, and PM_{10} (particulate matter 10 micrometers or less in diameter).

Table 2: Normalized emissions from energy-from-waste generation facilities under start-up and normal operating conditions (number of facilities investigated shown in brackets).

Contaminants	**Normalized Emissions**		**References**
	Start-Up	**Normal Operation**	
ammonia	10 (1)	1	[22]
CO	6.37–10 (2)	1	[21,22]
HCl	11 (1)	1	[22]
HF	13 (1)	1	[22]
NO_2	1.64 (1)	1	[22]
SO_2	8.14–14.5 (2)	1	[21,22]
Metals	8.33 (1)	1	[22]
Chlorinated polycyclic aromatics	10.00 (1)	1	[22]
Chlorinated monocyclic aromatics	10.67 (1)	1	[22]
PAHs	10.14 (1)	1	[22]
VOCs	10.00 (1)	1	[22]
NO_x	1.67 (1)	1	[21]
PM_{10}	2.24 (1)	1	[21]

Only two facilities were studied under this industrial sector [21,22]. Additionally, only two of the listed contaminants (CO and SO_2) were common contaminants emitted by both facilities. Hence, the emission values for most of the tabulated contaminants are based on one facility only. Additional facilities need to be investigated before developing an emission versus operation conditions trend, including shut-down conditions.

2.3.3 Nuclear Power Generation

Limited information was available on the start-up and shut-down emissions of nuclear power generation facilities. One facility was found and investigated under this industrial sector [23]. This facility is a proposed nuclear power plant to be located in Hinkley Point, Somerset, UK. The plant consists of two pressurized reactor units, each having four steam generators. The plant also includes backup diesel generators for power outages. The air quality modelling report for this nuclear power generation facility stated that start-up emissions include formaldehyde, CO, and NH_3. Table 3 summarizes the emissions of each of these contaminants during start-up operation.

Table 3: Emissions from a nuclear power generation facility under start-up and normal operating conditions (number of facilities investigated shown in brackets).

Contaminants	Normalized Emissions		References
	Start-Up	**Normal Operation**	
formaldehyde	0.0243 g/s (1)	-	[23]
CO	0.003 (1)	1	
NH_3	12.48 g/s (1)	-	

According to AMEC Environment & Infrastructure UK Ltd [23], formaldehyde is generated during the heating phase under start-up conditions, as a result of the thermal decomposition of a pipe insulation material that is used for piping in the reactor building. The thermal decomposition produces steam containing formaldehyde, which is discharged to the atmosphere by the ventilation extraction system. These formaldehyde emissions have the potential to decompose, producing CO emissions, which are also discharged to the atmosphere through the ventilation system.

Ammonia is also generated during the heating phase under start-up conditions [23]. When the steam generators are shut down for maintenance, they are filled with a lay-up solution consisting of demineralized water, hydrazine, morpholine, ethanolamine, and NH_3 to prevent corrosion and provide a biological barrier while they are turned off [23]. When the steam generators, and in turn the lay-up solution, are heated during start-up, NH_3 is generated and discharged to the atmosphere via exhaust stacks. The report assumes that all the hydrazine in the lay-up solution breaks down to NH_3. Since formaldehyde and NH_3 emissions are not generated under normal operation, the emissions of these contaminants are higher during start-up operation.

The CO emissions generated during start-up were approximately 0.3% of the total CO emissions produced during normal operation when the backup diesel generators are periodically tested [23]. Thus, the CO emissions generated during start-up can be considered negligible.

After investigating this nuclear power plant, it may be concluded that the air permit applicant should, at minimum, assess formaldehyde and NH_3 emissions during start-up operation.

Only one facility was studied under this industrial sector [23]. Emissions during start-up operation may differ significantly between different nuclear power plants. For example, another nuclear power plant may not use the same piping insulation and, thus, may not generate the formaldehyde emissions associated with the insulation's thermal decomposition. However, the same power plant may have other sources of start-up emissions. Thus, additional facilities need to be investigated prior to developing and validating a trend for this industrial sector. Emissions from the shut-down of nuclear power plants need to be further explored.

2.3.4 Sulphuric Acid Production

The search for information on the emissions from sulphuric acid production plants did not yield any quantitative case studies of plants. Thus, the trend observed is based on literature sources. A contact sulphuric acid production plant typically consists of fixed bed catalytic reactors, operated adiabatically [24]. Multiple cooling and heating exchange sections control the temperature of the reactors to ensure a maximum reaction rate is maintained [24]. The reaction that governs the production of sulphuric acid is as follows [24,25]:

$$SO_2 + \frac{1}{2}O_2 \longleftrightarrow SO_3$$

SO_2 emissions are significantly higher during start-up than during normal operation [9, 24-26]. This is due to several reasons. Firstly, the ratio of sulphur to air is fairly high at start-up, which reduces the reaction rate and consequently emits unreacted excess SO_2 [26]. Secondly, the low temperature at start-up also reduces the reaction rate, leading to the emission of unreacted, excess SO_2 during start-up [24].

Mann et al. (1986) developed a mathematical simulation model of SO_2 emissions for a sulphuric acid production plant under steady state and non-steady state conditions [25]. The model demonstrated increased SO_2 emissions during start-up, as high as 3000–4000 ppm while the steady state design value for SO_2 concentration was 500 ppm [25].

Despite the lack of quantitative emissions from facilities, the several literature sources explored conclude that SO_2 emissions increase significantly during the start-up of a sulphuric acid production plant. Thus, this can be adopted as a trend for this industrial sector such that an air permit applicant should, at minimum, assess SO_2 emissions from the start-up and normal operations of a sulphuric acid production plant. Further investigation is needed prior to developing a trend for shut-down operation.

2.3.5 Ethylene Production

Similar to the comment made on sulphuric acid production, quantitative information pertaining to case studies on ethylene production plants is somehow rare. Thus, literature sources were utilized instead. The start-up of an ethylene plant generates several contaminants in large amounts, particularly due to flaring operations [27]. The flaring can emit large amounts of CO_2, CO, NO_x, VOCs, highly reactive VOCs, and partially oxygenated hydrocarbons [27].

An ethylene plant having an annual production of 1.2 billion pounds can potentially flare approximately 50 million pounds of ethylene during one start-up event [28]. The emissions from the flare would comprise of a minimum of 18.1 t of CO, 3.4 t of NO_x, 6.8 t of hydrocarbons, and 45.4 t of highly-reactive VOCs [28].

Despite the lack of quantitative emissions from facilities, the literature sources explored conclude that flaring emissions increase significantly during the start-up of an ethylene production. Thus, this can be adopted as a trend for this industrial sector such that an air permit applicant should, at minimum, assess flaring emissions during start-up and normal operations. However, further investigation is required to better characterize common contaminants emitted during flaring operations, and also to develop a trend for shut-down emissions for ethylene production facilities.

2.3.6 Petrochemical Production

Two different facilities were investigated under this industrial sector. The first was a gas processing facility, comprised of two liquefied natural gas (LNG) process trains, located in Town Point, Barrow Island, Australia [29]. The second is a substitute natural gas (SNG) production facility, which relies on gasification of coal and coke and is located in Control City, Kentucky, U.S. [30]. Quantitative emissions data for start-up, normal and shut-down operation is available for the first facility only. Table 4 summarizes the normalized emissions for each contaminant emitted from the LNG processing facility. Emissions have been normalized with respect to the emissions of the normal operating conditions.

Table 4: Normalized emissions from an LNG processing facility under start-up, normal, and shut-down operating conditions (number of facilities investigated shown in brackets).

Contaminants	**Normalized Emissions**			**References**
	Start-Up	**Normal Operation**	**Shut-Down**	
NO_x	0.52 (1)	1	0.74 (1)	[29]
NO_2	0.59 (1)	1	0.78 (1)	
PM_{10}	18.00 (1)	1	110.00 (1)	

The results show that, for the LNG processing facility, the NO_x and NO_2 emissions were lower for start-up and shut-down than for normal operation, while the PM emissions had a reversed trend [29]. However, the results for the SNG production facility demonstrate that there is an increase in the emissions of CO, NO_x, SO_2, VOCs, PM, and lead during non-steady state conditions with the majority of these emissions being due to flaring [30]. The observations of the emissions from the two facilities are quite different, perhaps because the two investigated facilities are not similar enough to be grouped together to develop a trend. Additional facilities need to be investigated before an emission-operating conditions trend could be established.

2.3.7 Waste Incineration

Ten different facilities were investigated under this industrial sector [30-39]. These included continuously- and intermittently-operated incinerators located in Japan, Taiwan, Germany, the United States, Norway and Sweden. The incinerators under consideration combusted various sources of refuse, including municipal solid, organic, laboratory, industrial, liquid, and medical waste. Nine of the ten facilities provided emissions data related to the start-up and normal operating conditions [31-38,40], whereas only five provided data related to shut-down conditions [31,32,36,37,39].

Table 5 summarizes the emissions for each contaminant emitted in each of the facilities normalized with respect to the normal operating emissions.

Table 5: Normalized emissions from waste incineration facilities under start-up, normal, and shut-down operating conditions (number of facilities investigated shown in brackets).

Contaminants	Normalized Emissions			References
	Start-Up	Normal Operation	Shut-Down	
CO	2–69 (3)	1	30 (1)	[31,37,40]
NO_x	0.14–0.45 (1)	1	-	[31]
PCDD/Fs	0.80–2727.27 (8)	1	0.52–212.12 (2)	[31–36,38,40]
HCl	0.03–0.88 (2)	1	0.12–0.40 (1)	[32,39]
PCDD/F precursors (PAHs, chlorobenzene, chlorophenols)	1.81–95 (3)	1	1.07–21.28 (2)	[36,37,40]

Eight facilities assessed the emission of polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/Fs) under start-up and normal operating conditions [31-38, 40]. Two of these also assessed the PCDD/F emissions under shut-down conditions [31,36]. Approximately 88% of the facilities (seven out of eight) demonstrated that the PCDD/F emissions were approximately 2.3–2727 times higher under start-up conditions than under normal conditions [31-35,38,40]. As for the PCDD/F emissions under shut-down conditions, one of the two facilities reported approximately 5.5–212 times higher emissions [31], while the other reported approximately 5%–50% lower emissions compared to normal operating conditions [36]. The increase in PCDD/F emissions during start-up and shut-down is likely due to incomplete combustion during these conditions [32,33,34,39,41]. The reason behind one facility reporting lower PCDD/F emissions under start-up and shut-down conditions, is categorizing the feeding of waste as part of the normal operation. This is unusual as the feeding of waste is typically categorized as part of the start-up process of an incineration plant because the operating parameters do not reach steady state until later [31,32,36]. Thus, an air permit applicant should, at minimum, assess PCDD/F emissions during start-up due to the potential of these emissions to be higher. More facilities need to be investigated before a clear trend for PCDD/F emissions during shut-down operation for this industrial sector can be established.

Three facilities assessed the emissions of precursors of PCDD/F [36,37,40]. These precursors included PAHs, chlorobenzene and chlorophenols [35]. Two facilities assessed the emissions of PAHs under start-up, normal, and shut-down conditions [36,37], whereas one facility assessed the emissions of chlorobenzene and chlorophenol under start-up and normal conditions [40]. All three facilities reported that the emissions of the PCDD/F precursor contaminants were significantly higher under start-up (i.e., approximately 1.8–95 times higher) and shut-down (i.e., approximately 1.1–21.3 times higher) conditions. According to the results, an air permit applicant should, at minimum, assess emissions of the precursor contaminants of PCDD/Fs during start-up due to the potential of these emissions to exceed those under normal operation. Further facilities should be investigated prior to developing a representative trend for the emission of PCDD/F precursors for shut-down operation.

Three facilities assessed the emissions of CO under start-up and normal conditions [31,37,40], and only one of these also assessed the emissions of CO under shut-down conditions [37]. All three facilities demonstrated that the emissions of CO were 2–69 times higher under start-up conditions. The facility that assessed CO emissions under shut-down conditions also demonstrated that these emissions were 30 times higher for shut-down conditions. This increase in CO emissions during start-up and shut-down is likely attributable to incomplete combustion conditions. Thus, an air permit applicant should, at minimum, assess CO emissions during start-up and shut-down conditions due to the potential of these emissions to exceed those under normal operation. Additionally, more facilities need to be investigated to establish a more representative CO emissions trend for shut-down operation.

Two facilities assessed the emissions of HCl under shut-down and normal conditions [32,39], of which one facility also assessed HCl emissions for start-up conditions [32]. The results demonstrated that the HCl emissions under start-up and shut-down conditions were approximately 12%–97% and 60%–88% lower than those under normal operation, respectively [32]. It is likely that the HCl emissions were lower during start-up and shut-down due to less waste being combusted during these operating periods, i.e., a reduced amount of chlorine source [32]. Thus, an air permit applicant may not need to assess HCl emissions during start-up and shut-down. However, more facilities need to be investigated before one can reach a conclusive trend.

One facility assessed the emissions of NO_x under start-up and normal conditions and demonstrated that the NO_x emissions under start-up were approximately 55%–85% lower than those under normal operation [31]. As seen in Section 2.3.1, NO_x is usually expected to be higher under start-up and shut-down conditions in power generation since the temperature during these operating conditions is too low for the activation of the SCR. Thus, the reason behind this observation cannot be explained. Hence, more facilities need to be investigated in order to establish a more representative trend for NO_x emissions from waste incineration plants.

2.4 Conclusions and Recommendations

The results of this study are summarized in Table 6, which summarizes the circumstances under which emissions from start-up and shut-down operations should be assessed for each industry and contaminants that were investigated. Additionally, the table identifies when trends were inconclusive for specific contaminants and industries. When a trend was inconclusive, it is recommended that the emissions from start-up and shut-down operations be assessed to be conservative. This will ensure that emissions have been assessed for all operating conditions and, thus, will ensure that the emissions from the worst-case scenario have been assessed. Additionally, assessing and reporting the emissions under these non-steady state scenarios will increase the number of case studies that could serve as a basis for developing emissions trends under these operating conditions.

Table 6: Summary of when emissions from start-up and shut-down operations should be assessed for different industries and contaminants, based on aforementioned trends observed from case studies.
Legend: must assess emissions (Y); may not need to assess emissions (N); contaminant not studied (-); and inconclusive, i.e. further investigation necessary to develop a trend (Inc.).

Contaminants	**Power and/or Heat Generation**	**Energy-from-Waste Generation**	**Nuclear Power Generation**	**Sulphuric Acid Production**	**Ethylene Production**	**Petrochemical Production**	**Waste Incineration**
NO_x	start-up: Y shut-down: Y	Inc.	-	-	start-up: Inc. shut-down: -	Inc.	start-up: Inc. shut-down: -
CO	start-up: Y shut-down: Y	Inc.	Inc.	-	start-up: Inc. shut-down: -	Inc.	start-up: Y shut-down: Inc.
Highly reactive VOCs	-	-	-	-	start-up: Inc. shut-down: -	-	-
VOCs	start-up: Y shut-down: Y	Inc.	-	-	start-up: Inc. shut-down: -	Inc.	-
PAHs	-	Inc.	-	-	-	-	
PCDD/F precursors (PAHs, chlorobenzene, chlorophenols)	-	-	-	-	-	-	start-up: Y shut-down: Inc.
SO_2	start-up: N shut-down: N	Inc.	-	start-up: Y shut-down: -	-	Inc.	-
PM	start-up: N shut-down: N	Inc.	-	-	-	Inc.	-
Chlorinated polycyclic aromatics	-	Inc.	-	-	-	-	-
CO_2	start-up: Inc. shut-down: -	-	-	-	start-up: Inc. shut-down: -	-	-
metals	-	Inc.	-	-	-	-	-
H_2SO_4	start-up: Inc. shut-down: Inc.	-	-	-	-	-	-
NH_3	Inc.	Inc.	Inc.	-	-	-	-
Formaldehyde	Inc.	-	Inc.	-	-	-	-
PCDD/Fs	-	-	-	-	-	-	start-up: Y shut-down: Inc.
HCl	-	Inc.	-	-	-	-	start-up: Inc. shut-down: Inc.
HF	-	Inc.	-	-	-	-	-
NO_2	-	Inc.	-	-	-	-	-
Partially oxygenated hydrocarbons	-	-	-	-	start-up: Inc. shut-down: -	-	-

It is recommended that further case studies be explored for the industries that have been investigated in this study to further validate the observed trends and to develop trends where the trend was inconclusive. Additionally, emissions under start-up and shut-down operations should also be assessed for other industries such as polymer production, food production, agriculture, etc. Furthermore, emissions under other non-steady state operating conditions, such as process upsets and malfunctions, should also be investigated to aid in the control of such emissions.

The trends developed as part of this study will help air permit applicants to effectively allocate their resources when assessing emissions related to non-steady state operations. Additionally, it will ensure that emissions are assessed for the worst-case scenario. This is especially important when emissions under start-up and shut-down operations have the potential to exceed applicable emission limits. It is important to mention that the amount of time that a plant spends under non-steady state operating conditions is lower than the amount of time that it spends under steady state operating conditions, which consequently means that the total mass of contaminants emitted may be much higher during the latter. However, it should be noted that the value of concern is the concentration of the contaminant at the ground-level receptors, which has the potential to be higher under non-steady state operating conditions for several contaminants as demonstrated above. Thus, assessing emissions for the worst-case scenario help prevent the emissions from adversely impacting public health and the environment.

Chapter 3: A Study of the dispersion of vinyl chloride from a renewable energy facility located in Ontario, Canada

The content of this chapter is based on a paper published in November 2014 in the "Journal of Renewable and Sustainable Energy" under the title "A study of the dispersion of vinyl chloride from a renewable energy facility located in Ontario, Canada" by "Obaid et al.". The author specific contribution to this paper was: the set-up and running of the simulations, analysis of the results, preparation of graphics, figures, tables and results, preparation of the draft manuscript, and preparation of the final manuscript incorporating the reviewers' edits with supervision from the study supervisors who are co-authors. This paper is co-authored by Dr. Abdul-Wahab, who supervised the simulations and edited the manuscript, and by Dr. Elkamel, who supervised the study.

3.1 Background

The U.S. EPA identifies, in its Guidelines, a list of preferred or recommended air dispersion models to be used to predict and model the dispersion of airborne contaminants once they are emitted from a source. Amongst this list of dispersion models is the American Meteorological Society/Environmental Protection Agency Regulatory Model, AERMOD, and the California Puff Model, CALPUFF [42].

AERMOD is a steady state Gaussian plume model that is recommended to assess contaminant dispersion on a short-range transport basis. The U.S. EPA recommends that this model be used to estimate impacts on receptors that are located in the near field, i.e. less than 50 km from the source of the emission [42]. However, AERMOD has certain limitations. For example, this model assumes a straight-line trajectory for contaminant dispersion and does not incorporate curved or variable trajectories [43]. Additionally, AERMOD assumes a uniform atmosphere across the whole domain. Furthermore, it is not accurate when applied to calm conditions that are characterized by low wind speeds. AERMOD also does not retain the memory of any contaminant emissions that have occurred in the previous hours [43].

AERMOD has been used to model the dispersion of contaminant emissions in several studies and research papers. Examples include the modelling of the dispersion of polychlorinated dibenzodioxin emissions from a municipal solid waste bio-drying plant [44], particulate emissions from multiple coal mines [45], nitrogen oxide emissions from a commercial dairy facility [46], nitrogen dioxide and sulphur dioxide emissions from a power plant [47], and nitrogen dioxide emissions from a cement plant [48].

CALPUFF is a non-steady state Lagrangian puff model that can be used to assess contaminant dispersion on a long-range transport basis [43]. CALPUFF is recommended for use by the U.S. EPA when estimating impacts on receptors that are located more than 50 km from the source of the emission [42]. This model allows for non-straight line trajectories, does not assume a uniform atmosphere across the entire domain, is accurate for calm conditions, and retains the memory of contaminant emissions that have occurred in previous hours [43].

CALPUFF has been used to model the dispersion of contaminant emissions in several studies and research papers. Examples include the modelling of the dispersion of sulphur dioxide emissions from flaring activities in an oilfield [49], sulphur dioxide emissions from different refineries [50,51], nitrogen oxide emissions from a biomass energy power plant [52], carbon monoxide, nitrogen oxides and particulate emissions from an industrial complex [53], and hydrogen sulphide emissions from an accidental plant release [54].

Recent research papers have investigated the differences in modelling results when using CALPUFF and AERMOD to assess the dispersion of emitted contaminants. For example, Donaldson et al. (2008) modelled fugitive particulate emissions at aggregate handling facilities using both models and determined that the CALPUFF modelling resulted in lower pollutant concentrations at receptors in the near field than the AERMOD modelling [55]. Dresser et al. (2011) modelled sulphur dioxide emissions from two coal-fired power plants using both models and compared the results to collected monitoring data to determine that AERMOD almost always under-predicted the contaminant concentrations and that the results from CALPUFF generally agreed with the monitored data [56]. Busini et al. (2012) modelled emissions from hypothetical point and area sources using both models and determined that, although there was generally good agreement between the results of the two models for the point source, the AERMOD results were typically higher than those generated by CALPUFF for the area sources [57]. Li (2009) used both models to assess odour emissions from livestock and used various statistical analysis techniques to compare the results to monitoring data [58]. Varying results were obtained depending on the statistical analysis technique that was used to assess the models' performance against monitored data [58]. McDonald-Buller et al. (2010) assessed benzene and 1,3-butadiene emissions from two sites in Corpus Christi, Texas [59]. Maximum concentrations of benzene modelled by AERMOD were higher than those modelled by CALPUFF for one site and were lower for the other [59]. Varied results were seen for the maximum 1,3-butadiene concentrations [59]. Walker et al. (2002) modelled contaminant concentrations from a sour gas plant and determined that CALPUFF generated better results for a 400 km x 600 km domain, whereas AERMOD performed better for a 25 km x 25 km domain [60]. Schmidt et al. (2006) modelled hydrogen sulfide emissions near a head finishing site and determined that AERMOD gave larger and more conservative setback distances than CALPUFF [61]. Vieira de Melo et al. (2012) assessed odour emissions from a pig farm and demonstrated that AERMOD generated higher concentrations than CALPUFF and that

AERMOD performed better than CALPUFF in the near field [62]. Tartakovsky et al. (2013) modelled particulate emissions from a quarry and determined that AERMOD results were closer to the monitored data than the CALPUFF results [63]. Rood (2014) assessed the performance of several air dispersion models using the Winter Validation Tracer Study data and determined that steady state models such as AERMOD perform better in the near field and that CALPUFF should be used for long-range transport [64]. Pimente et al. (2010) assessed sulphur dioxide emissions in a metropolitan region of Brazil and determined CALPUFF to be more conservative since it predicted higher concentrations than AERMOD [65].

The intent of this study is to compare the results of modelling vinyl chloride emissions from a facility using AERMOD and CALPUFF within a large domain. The modelling has been performed for a day in the summertime and a day in the wintertime to better compare these modelling results.

3.2 Case Study

3.2.1 Description of Study Area

The study area is the City of Kawartha Lakes, located in Central Ontario, Canada. The facility that is the subject of this study is located in the community of Lindsay. The study area is shown in Fig. 1 and its terrain is shown in Fig. 2.

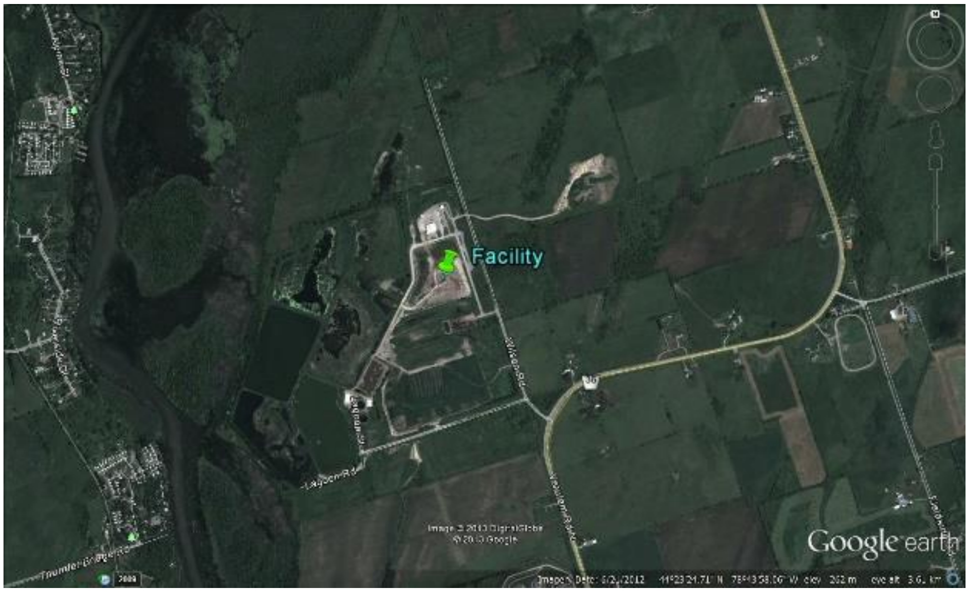

Figure 1: Study area shown by marker.

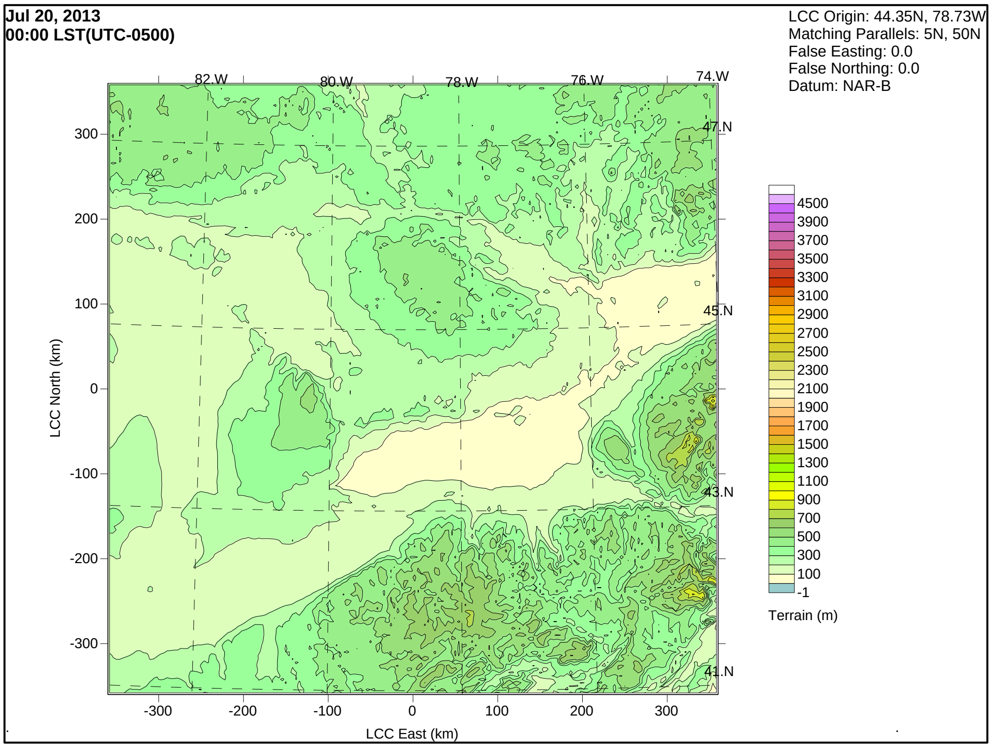

Figure 2: Terrain map of the domain of study.

3.2.2 Description of Facility

The facility is a renewable energy generation plant located at 51 Wilson Road, Lindsay, Ontario, K9V 4R3. The facility utilizes landfill gas emissions from the existing Lindsay/Ops landfill to fuel an on-site generator, and thus generate electricity. Emission sources located on the site include a landfill mound, an enclosed landfill gas flare and a generator stack. Approximately 70% of the landfill gas is captured by the gas collection system, of which about 62% is sent to the enclosed flare and 38% is sent to the generator. [66]

3.3 Materials and Methods

3.3.1 Calpro Modelling System

CALPro Plus version 6.9.10.25.2007 was used to model the dispersion of vinyl chloride emissions in this study. The CALPro software, developed by The Atmospheric Studies Group and adopted by the U.S. EPA, is a non-steady state meteorological and air quality modelling system. Also known as the CALPUFF Modelling System, it is the U.S. EPA's preferred model to assess the long range transport and impacts of contaminants. The model is highly effective in determining site-specific impacts of contaminant dispersion, specifically in areas that exhibit complex terrain and non-steady state flows. CALPro has the ability to account for coastal, overwater and wind conditions for a specific study area when analyzing contaminant dispersion. [67]

The main processors for the software include a pre-processing package, simulation models, and post-processing packages. The pre-processing package includes geophysical, surface meteorological, upper air meteorological, precipitation and overwater data processors. The simulation models include a meteorological model known as CALMET and an air quality dispersion model known as CALPUFF. The post-processing packages include PRTMET and CALPOST. All packages, processors and models discussed above include a graphical user interface (GUI). [67]

CALMET is a diagnostic meteorological model that utilizes geophysical, observational and prognostic data as inputs to model hourly meteorological results. Observational inputs include various kinds of meteorological data which must be processed using pre-processors prior to being inputted into CALMET. The inputs to CALMET vary with the site and study area. CALMET utilizes the inputs to generate wind and temperature results on a three-dimensional gridded domain on an hourly basis. [67]

CALPUFF is a non-steady state Lagrangian Gaussian puff model that utilizes the meteorological output from CALMET and the data pertaining to the emission source as inputs to model the dispersion and transformation of contaminants that are emitted from the sources. CALPUFF can accommodate multiple air layers, multiple species and multiple sources in its modelling. CALPUFF utilizes the inputs to generate concentrations of contaminants at specified receptor locations on a three-dimensional gridded domain on an hourly basis. [67]

PRTMET is a post-processor that utilizes the output file from CALMET to display portions of the meteorological data that are selected by the user onto the visual grid representation. CALPOST is a post-processor that utilizes the output file from CALPUFF to summarize the results of the simulation and to determine, identify and report the top hourly average concentrations of the emitted contaminants at each receptor. CALPOST also displays portions of the dispersion results that are selected by the user onto the visual grid representation. [67]

Table 7 summarizes the input data that was used for the model for this case study.

Table 7: Model input information for the domain of study.

Parameter	**Values Used**
Projection	LCC (CALPUFF) and UTM (AERMOD)
LCC latitude of origin	44.35°N
LCC longitude of origin	78.73°W
Latitude 1	5°N
Longitude 2	50°N
False Easting	0
False Northing	0
Continent/Ocean	North America

Geoid-Ellipsoid	North American 1983: GRS 80
Region	Canada
DATUM code	NAR-B
X (Easting)	-360 km
Y (Northing)	-360 km
Number of X grid cells	180
Number of Y grid cells	180
Grid spacing	4 km
Number of vertical layers	9
Cell face heights (m)	0-20, 20-50, 50-100, 100-150, 150-200, 200-300, 300-500, 500-1000, 1000-2000
Base time zone	UTC – 05:00
UTM zone	17
Hemisphere	Northern

3.3.2 AERMOD Modelling System

AERMOD version 12345 was used to model the dispersion of vinyl chloride emissions in this study. The AERMOD modelling system is the U.S. EPA's preferred model to assess the short range transport and impacts of contaminants. As described in Section 3.1, AERMOD is a steady state Gaussian plume model [42].

AERMOD consists of three primary components: a terrain pre-processor known as AERMAP, a meteorological pre-processor known as AERMET, and the modelling processor known as AERMOD [42]. Specific details about AERMAP, AERMET and AERMOD are discussed in the following paragraphs.

AERMAP is a terrain pre-processor that utilizes digital elevation data to generate a terrain file that is then used by AERMOD [68]. The terrain file that is generated includes elevation and scaling factors for all receptors that are located within the domain. AERMET is a meteorological pre-processor that utilizes surface and upper air meteorological data, land cover data and surface characteristics to generate a surface data file and a profile data file that are used by AERMOD.

AERMOD is the main modelling processor that utilizes the meteorological output from AERMET, the terrain output from AERMAP and the emission source information as inputs to model the dispersion of contaminants that are emitted from the sources [68]. AERMOD can accommodate multiple sources in its modelling. AERMOD utilizes the inputs to generate concentrations of contaminants at specified receptor locations on a two-dimensional gridded domain [68]. Table 7 above summarizes the input data that was used for the model for this case study.

3.3.3 Meteorological Data

The surface meteorological data was obtained from the Government of Canada website for climate data [69]. Data was obtained on an hourly basis for the Ottawa International Airport climate station for two separate meteorological conditions. The first data set was obtained for the time period from 00h00 Eastern Time on July 19, 2013 to 23h00 Eastern Time July 21, 2013, to represent the summertime. The second data set was obtained for the time period from 00h00 Eastern Time on November 16, 2013 to 23h00 Eastern Time on November 18, 2013, to represent the wintertime. The hourly data that was obtained for each meteorological condition included temperature (ºC), station pressure (mbar), relative humidity (%), wind direction (degrees) and wind speed (m/s). The Ottawa International Airport climate station is located relatively close to the emission sources. Information pertaining to this station is summarized in Table 8.

Table 8: Information about the surface station that was used to obtain surface meteorological data [69].

Parameter	Values Used
Station Name	Ottawa International Airport climate station
UTM Latitude	45.316667ºN
UTM Longitude	75.666667ºW
X location on grid	250 km
Y location on grid	100 km
Elevation	114 m
Climate ID	6106001
WMO ID	71628
TC ID	YOW

The upper air meteorological data was obtained from the Radiosonde Database website that has been developed and is run by the Earth System Research Laboratory (ESRL) at the National Oceanic and Atmospheric Administration (NOAA) [70]. Data was obtained for each twelve-hour interval for the Maniwaki upper air climate station for two separate meteorological conditions. The first data set was obtained for the time period from 00h00 Eastern Time on July 19, 2013 to 23h00 Eastern Time July 21, 2013, to represent the summertime. The second data set was obtained for the time period from 00h00 Eastern Time on November 16, 2013 to 23h00 Eastern Time on November 18, 2013, to represent the wintertime. The Maniwaki upper air climate station is located relatively close to the emission sources. Information pertaining to this station is summarized in Table 9.

Table 9: Information about the radiosonde station that was used to obtain upper air meteorological data [70].

Parameter	Values Used
Station Name/Location	Maniwaki, BQ, Canada
UTM Latitude	46.38°N
UTM Longitude	75.97°W
X location on grid	210 km
Y location on grid	200 km
Elevation	170 m
WBAN	04734
WMO ID	71722
INIT	YMW

3.3.4 Preparing the Meteorological Data Files

First, for each meteorological condition, the surface meteorological data was prepared in a format that was compatible for use with the surface meteorological pre-processor, SMERGE, which forms part of the CALPro model. For each meteorological condition, SMERGE processed the surface input file to generate the output file that was compatible for processing by CALMET. The output file for each meteorological condition was named “SURF.DAT”. For each meteorological condition, the upper air meteorological data was prepared in a format that is compatible for use with the upper air meteorological pre-processor READ62 that forms part of the CALPro model. For each meteorological condition, READ62 processed the input file to generate the output file that was compatible for processing by CALMET. The output file for each meteorological condition was named “UP.DAT”.

Second, for each meteorological condition, the meteorological data was prepared in a format that was compatible for use with the meteorological prep-processor, AERMET, which forms part of the AERMOD model. For each meteorological condition, AERMET processed the input file to generate a surface and a profile file that was compatible for processing by AERMOD. For the summertime meteorological condition, the surface output file was named “July.SFC” and the profile output file was named “July.PFL”. Similarly, for the wintertime meteorological condition, the surface output file was named “November.SFC” and the profile output file was named “November.PFL”.

3.3.5 Emission Data

This investigation utilizes the emission data taken from a case study that assesses the dispersion of contaminants that are emitted from the facility [66]. As described in Section 3.2.2, the sources of emission include: the flare (a point source), the generator stack (a point source) and the landfill mound (an area source). The contaminant of focus for this investigation is vinyl chloride, which is emitted from all three sources. The emission data was obtained from this case study and entered into the CALPUFF and AERMOD models. A summary of the emission data is included in Table 10. The models were run for each of the two aforementioned meteorological conditions (summertime and wintertime).

Table 10: Input data for emission sources [66].

Parameter	Source 1	Source 2	Source 3
Source description	Flare	Generator stack	Landfill mound
Source type	Point	Point	Area
Stack exit gas temperature (°C)	900	520	Not needed
Stack inner diameter (m)	1.12	0.2	Not needed
Stack exit velocity (m/s)	4.93	35.332	Not needed
Stack height above grade (m)	12.22	5.01	5
UTM Latitude	44.385°N	44.385°N	44.388°N
UTM Longitude	78.739°W	78.739°W	78.73777°W
Location on grid (km)	(10, 0)	(10, 0)	(25, 25) (25, -10) (20, -10) (22,25)
Initial vertical dimension (m)	-	-	2.33
Emission rate of vinyl chloride (g/s)	5.15E-05	2.88E-05	1.15E-03

3.3.6 Operation of CALPro

First, the meteorological and geophysical information was processed into a common file. The domain of the grid was chosen to be 360 km by 360 km, where the center of the grid was located at the facility. Data files pertaining to land use, coastline and terrain information was obtained from the Atmospheric Studies Group website [71]. These geophysical data files were utilized as inputs for the land use processing package called CTGPROC and the terrain processing package called TERREL to generate a land-use output file named “LU. DAT” and a terrain output file named “TERREL.DAT”, respectively. The output files generated by these two pre-processors were utilized as input files by the MAKEGEO pre-processor to generate the geophysical output file named “GEO.DAT” that would be compatible with CALMET. As described in the above sections, the surface and upper air meteorological data files for the two different meteorological conditions were prepared using the SMERGE and READ62 pre-processors. The geophysical and meteorological files named “GEO.DAT”, “SURF.DAT” and “UP.DAT” was utilized as inputs for the CALMET model. The output from the CALMET simulation was utilized as an input for the PRTMET post-processor to generate hourly wind field velocity vectors that were layered overtop of land use and terrain maps for the study area. This allowed the meteorological results to be viewed graphically along with the land use and terrain for the study area via CALVIEW.

The aforementioned emission data and the output files generated by the aforementioned pre-processing and simulations were utilized as inputs for the CALPUFF model to generate hourly concentrations of contaminants at the receptors. The output from the CALPUFF simulation was utilized as an input for the CALPOST post-processor to generate hourly concentration and plume trajectories that were layered overtop of the meteorological data, land use and terrain maps for the study area. This allowed the hourly concentration of contaminants (i.e., the dispersion of the plume) to be viewed graphically along with the meteorology, land use and terrain for the study area via CALVIEW.

The first vertical layer, from 0 m to 20 m, was selected when assessing the impacts of the dispersion and concentrations of vinyl chloride. Hourly wind direction and speed are represented by the direction and length of the arrows on the map, which change hourly. The trajectory of the vinyl chloride plume is represented by the contour lines on the map. The pre-processing, simulation and post-processing were performed twice, once for each meteorological condition.

3.3.7 Operation of AERMOD

First, the digital elevation data was used to generate a terrain file using AERMAP. The domain of the grid was chosen to be 360 km by 360 km, where the center of the grid was located at the facility. The terrain file that was generated was named “ROU.OUT”. As described in the above sections, the surface and upper air meteorological data files for the two different meteorological conditions were prepared using the AERMET pre-processor.

The terrain file, meteorological files and emission data described above were utilized as inputs for the AERMOD model to generate concentrations of contaminants at the receptor locations. The output from the AERMOD simulation was processed by the SURFER software to generate concentration contours for the study area. This allowed the concentration of the contaminant, i.e. the dispersion of the plume, to be viewed graphically. The trajectory of the vinyl chloride plume is represented by the contour lines on the map, where the numbers at each contour line are the highest concentration of vinyl chloride at each contour. The pre-processing and modelling were performed twice, once for each meteorological condition.

3.4 Results and Discussion

3.4.1 CALPUFF Modelling Results for July 20, 2013

Figures 3-5 depicts three of the twenty-four hourly contour maps of the wind vectors and concentration dispersion. The first contour map is for time 1:00 LST, which corresponds to the time at which the maximum highest concentration of vinyl chloride occurs. The second and third contour maps depict the concentration contours at 12:00 LST and 21:00 LST, respectively.

The wind vectors head towards the north-eastern direction from 0:00 LST to 9:00 LST, the eastern direction from 10:00 LST to 15:00 LST, the south-eastern direction from 16:00 LST to 20:00 LST, and the southern direction from 21:00 LST to 23:00 LST. The plume travels in the same general directions over time, dispersed over the distance by the wind.

It should also be noted that, at several instances, the concentration of vinyl chloride is higher at a receptor that is located further away from the emission source compared to receptors that are located closer to the source. The concentration of vinyl chloride is higher at receptors located closer to the emission source from 0:00 LST to 11:00 LST, and from 18:00 LST to 23:00 LST. However, from 12:00 LST to 17:00 LST, the concentration of vinyl chloride is higher at receptors that are located further away from the emission source. This can be seen by comparing the contour maps in Figs. 4 and 5, which depict concentration contours at 12:00 LST and 21:00 LST.

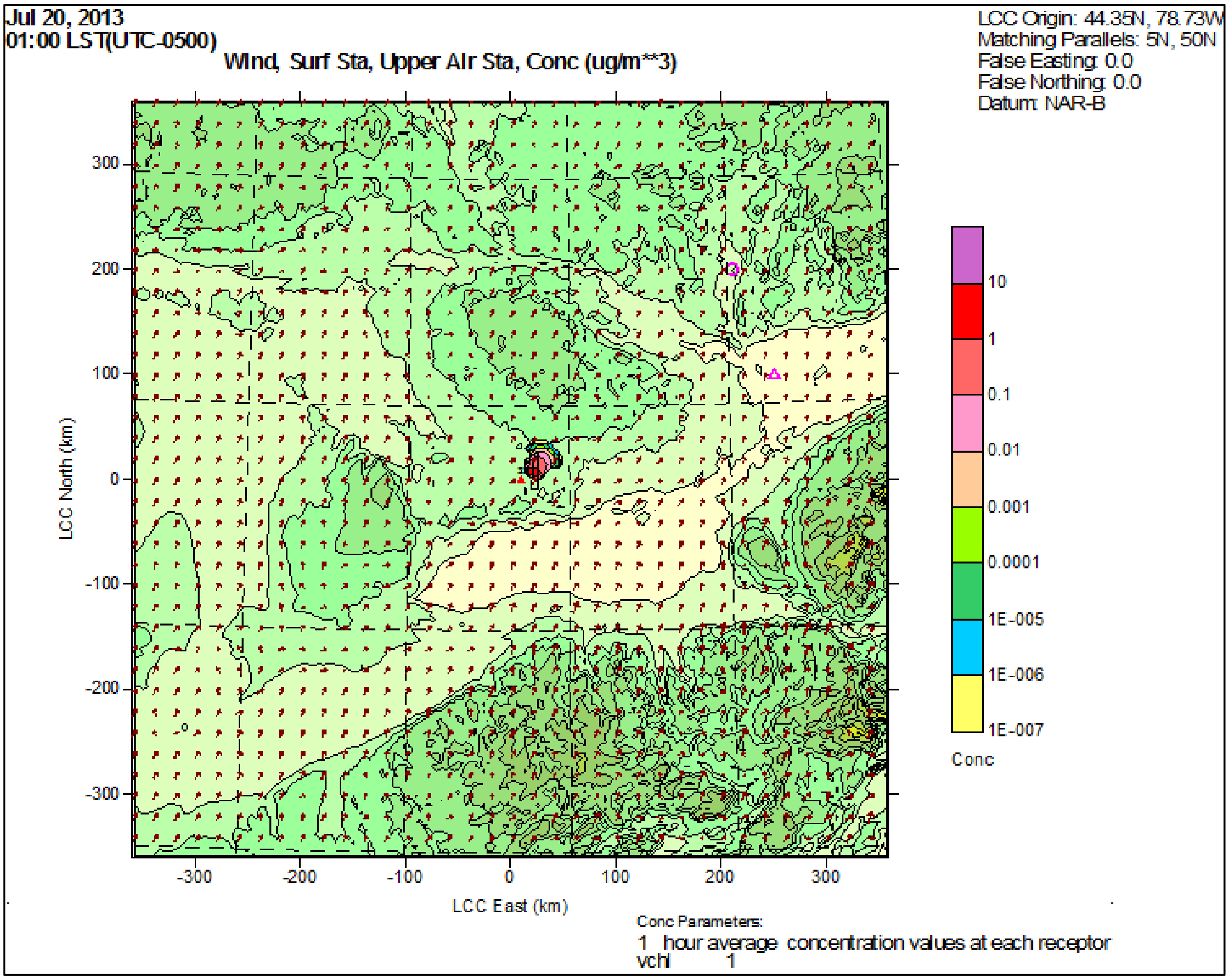

Figure 3: Concentration contour for 1:00 LST for July 20, 2013.

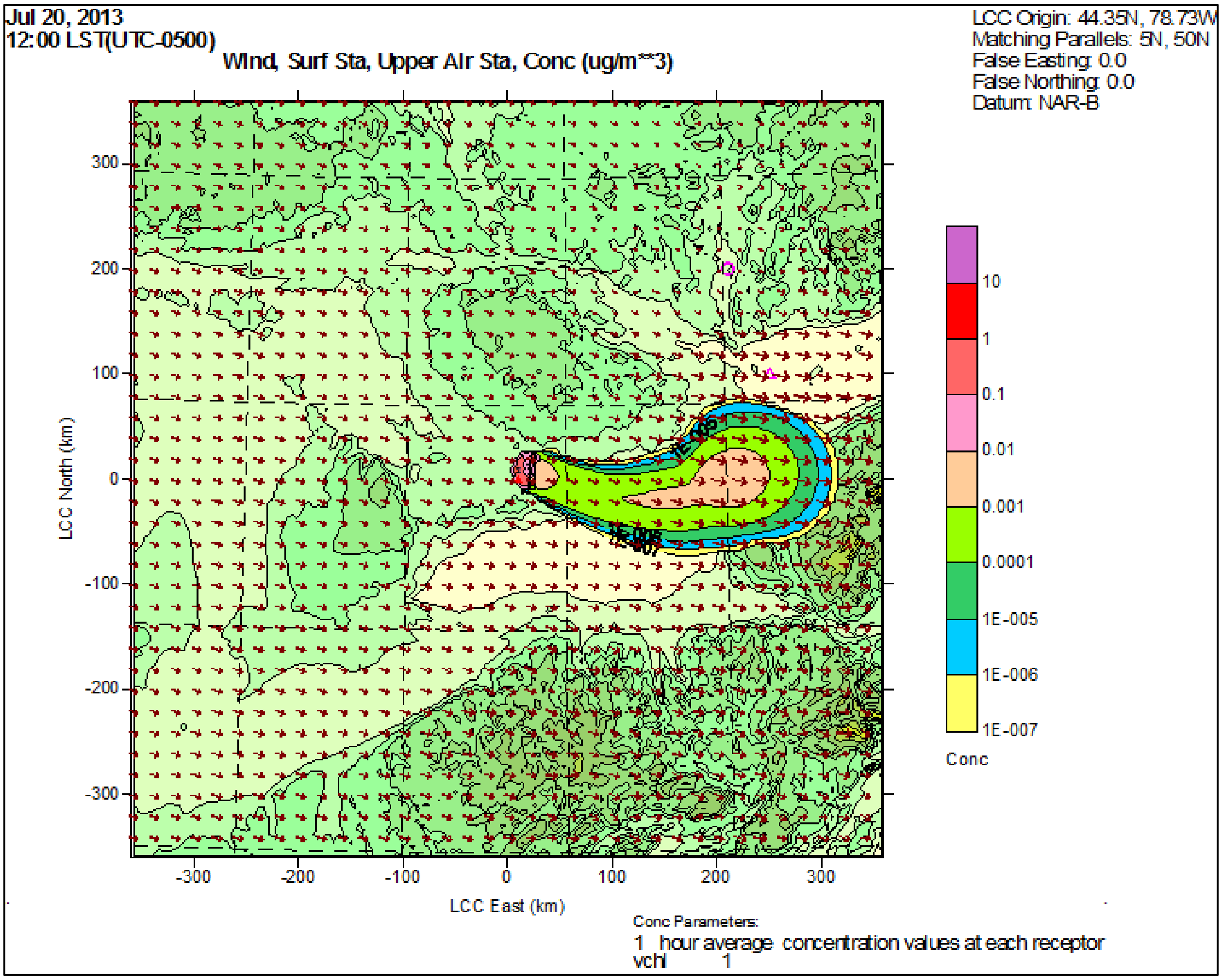

Figure 4: Concentration contour for 12:00 LST for July 20, 2013.

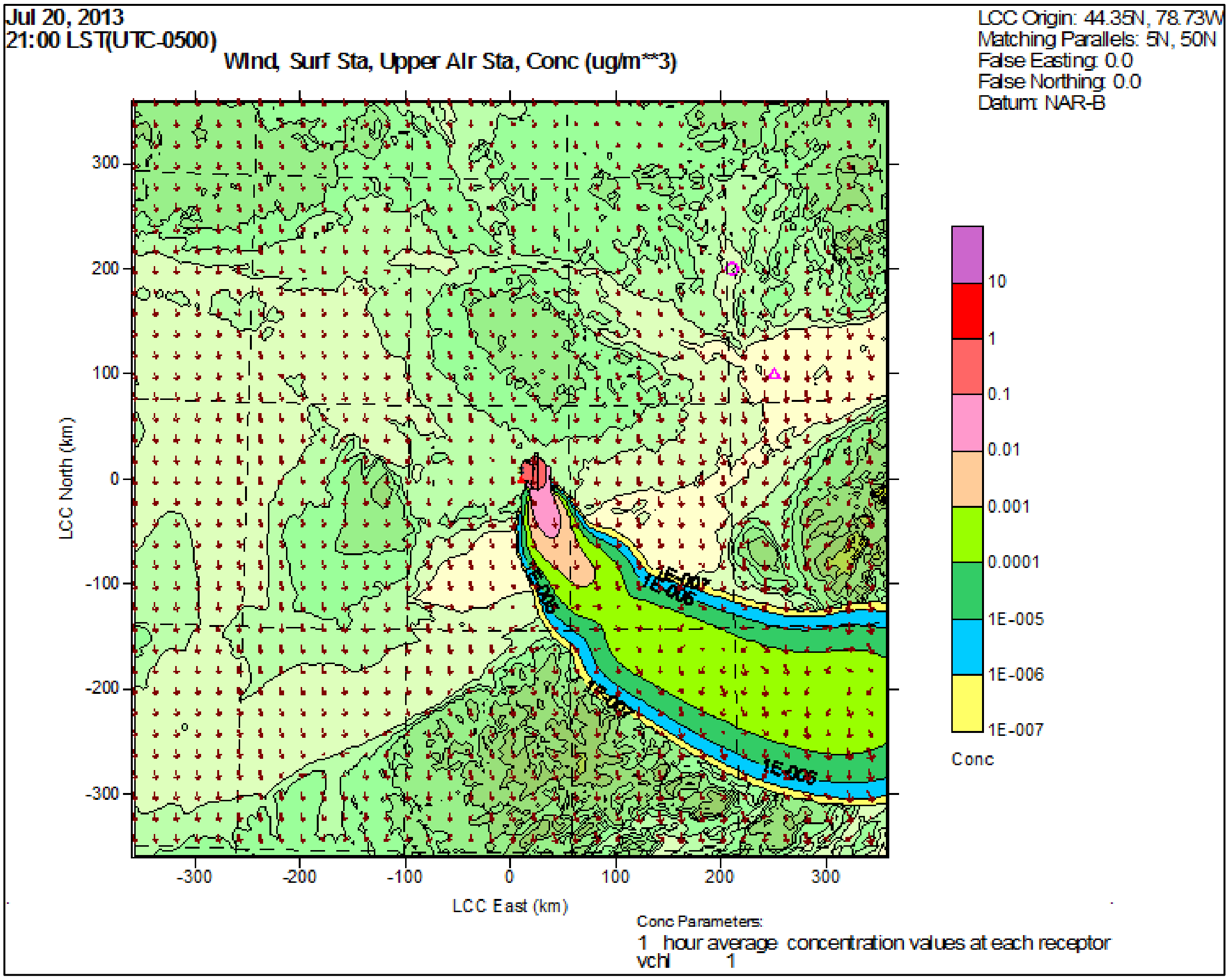

Figure 5: Concentration contour for 21:00 LST for July 20, 2013.

3.4.2 CALPUFF Modelling Results for November 17, 2013

Figures 6-8 depicts three of the twenty-four hourly contour maps of the wind vectors and concentration dispersion. The first contour map is for time 17:00 LST, which corresponds to the time at which the maximum highest concentration of vinyl chloride occurs. The second and third contour maps depict the concentration contours at 9:00 LST and 13:00 LST, respectively.

The wind vectors head towards the north-western direction, starting at 0:00 LST, and gradually move towards the northern direction as time passes. The plume travels in the same general directions over time, dispersed over the distance by the wind.

It should also be noted that, at several instances, the contours with the higher concentrations travel further away from the source compared to other times. These higher concentration contours travel further away from the source from 0:00 LST to 9:00 LST, and from 17:00 LST to 22:00 LST. However, from 10:00 LST to 16:00 LST, these higher concentration contours do not travel much further away from the source. This can be seen by comparing the contour maps in Figs. 7 and 8, which depict concentration contours at 9:00 LST and 13:00 LST.

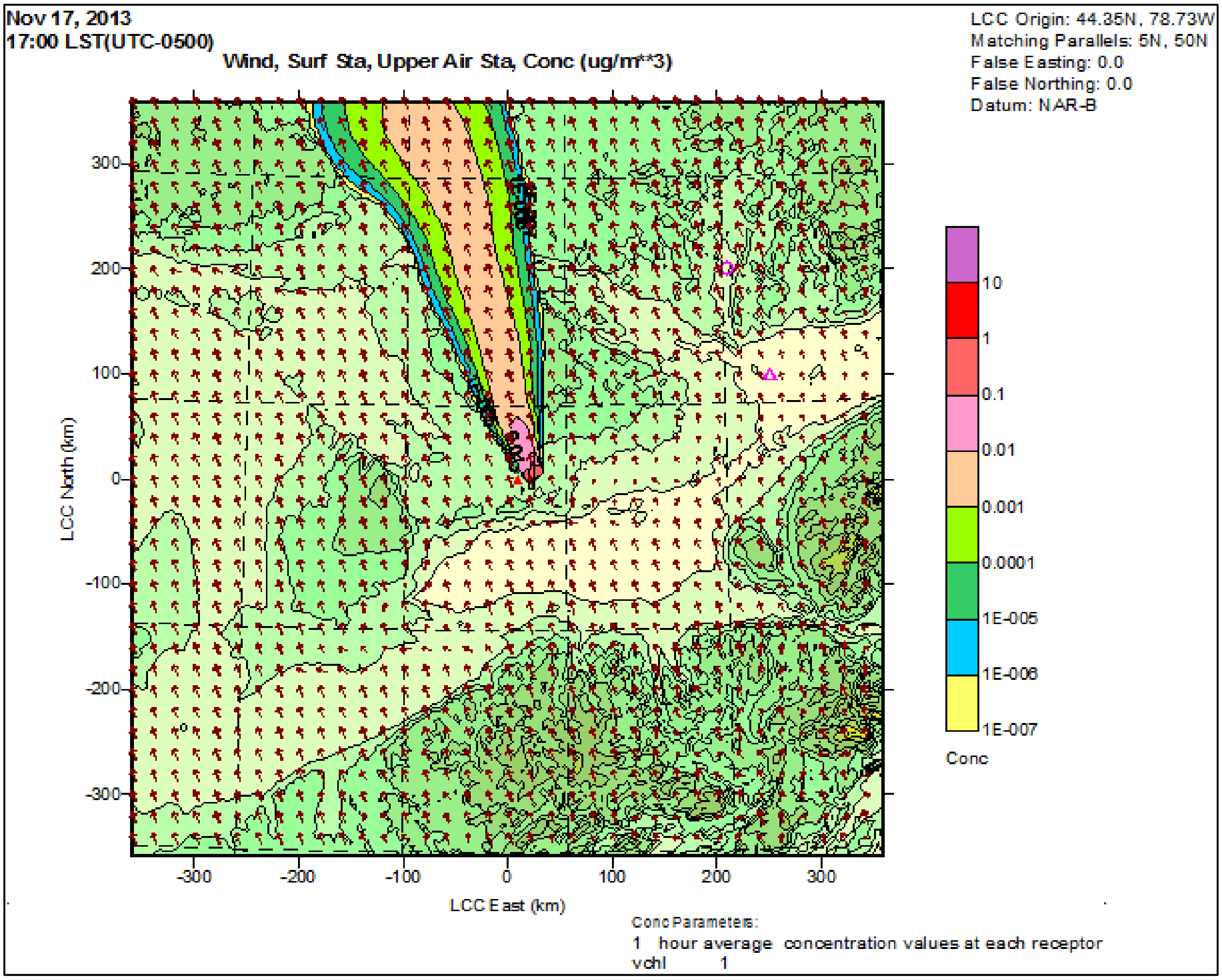

Figure 6: Concentration contour for 17:00 LST for November 17, 2013.

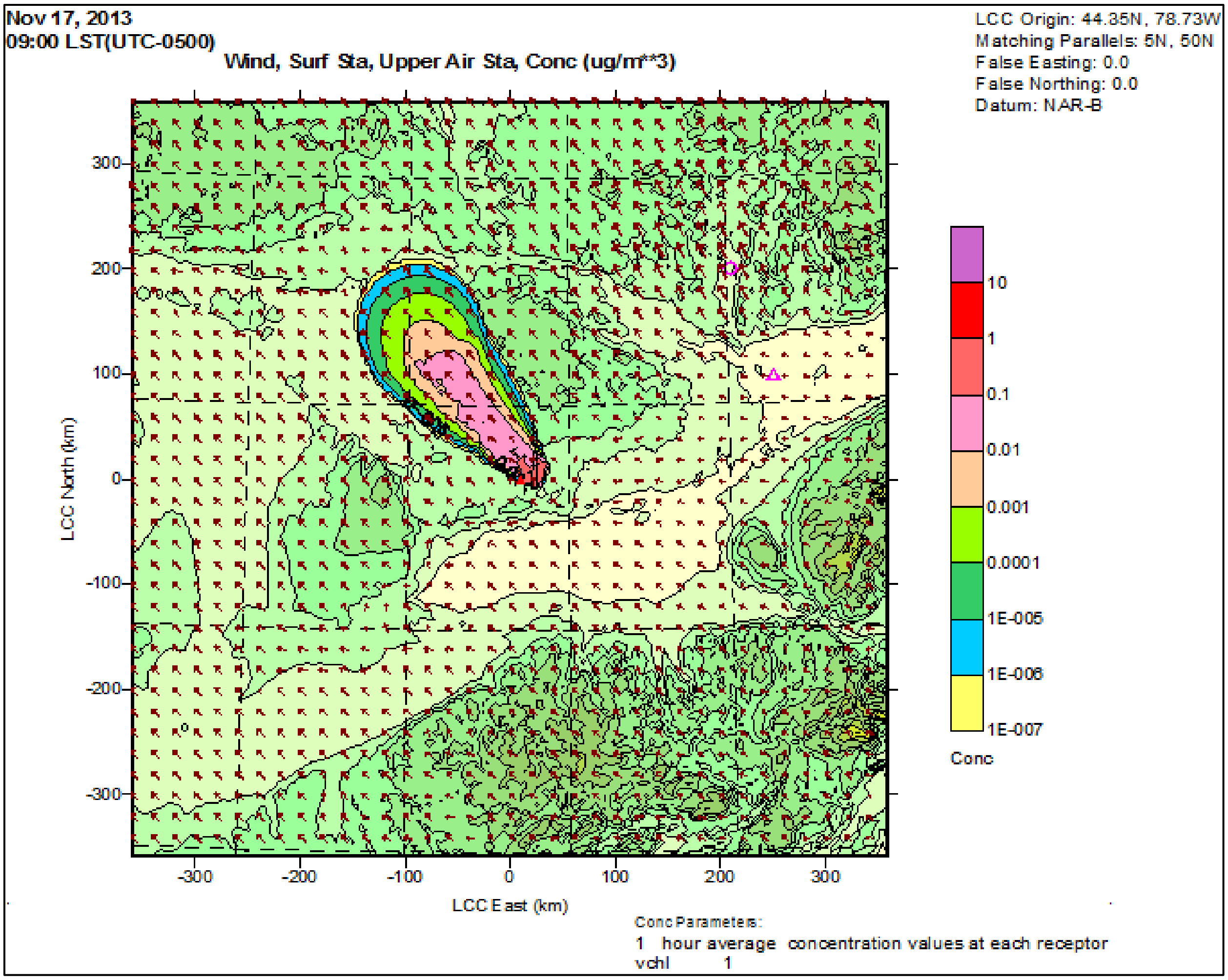

Figure 7: Concentration contour for 9:00 LST for November 17, 2013.

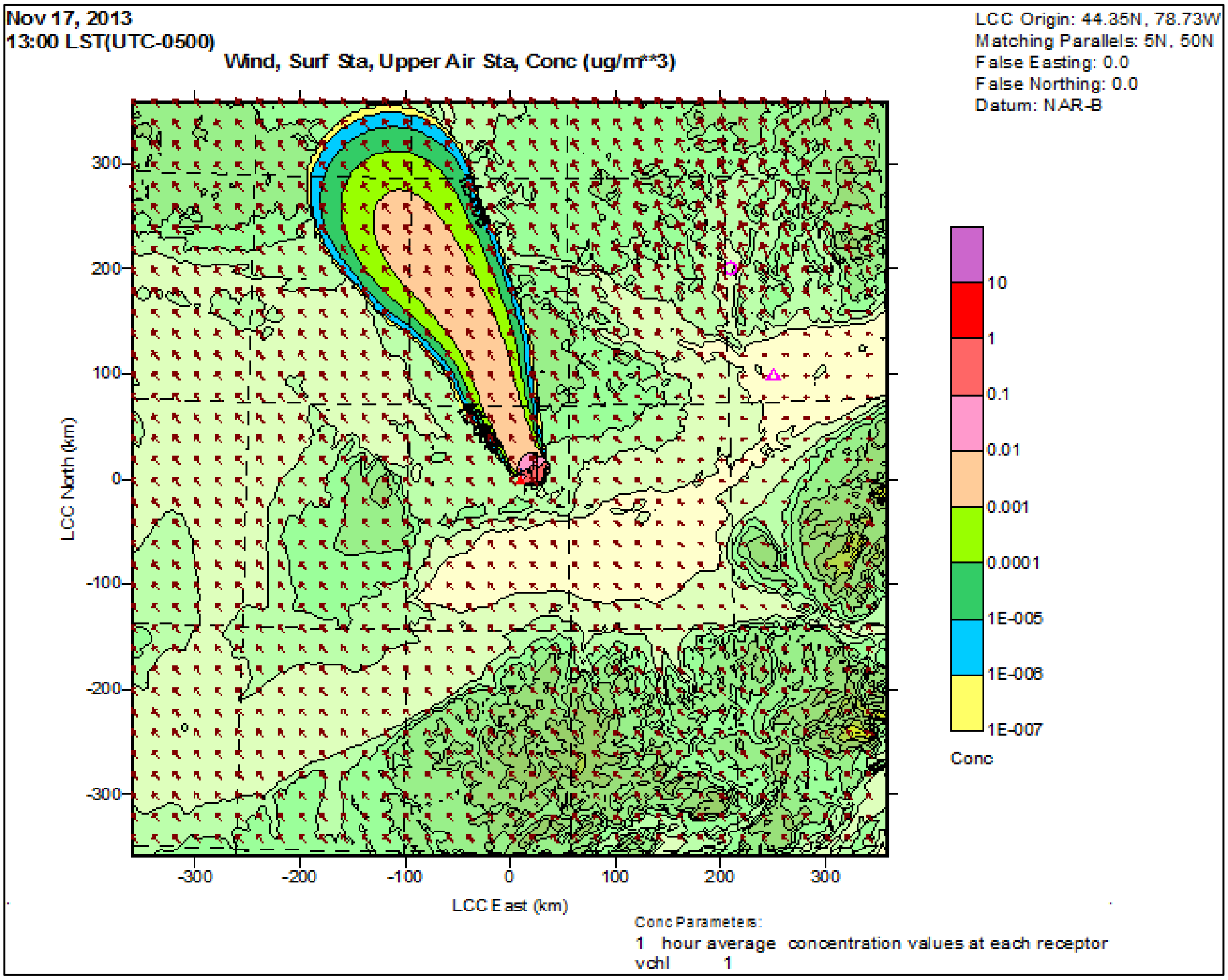

Figure 8: Concentration contour for 13:00 LST for November 17, 2013.

3.4.3 CALPUFF vs. AERMOD Modelling Results for July 20, 2013

Table 11 summarizes the three highest concentrations obtained from the AERMOD and CALPUFF modelling results for July 20, 2013. The table demonstrates that the resultant concentration values for the CALPUFF modelling are significantly higher than those outputted from the AERMOD modelling.

Table 11: CALPUFF vs. AERMOD modelling results for July 20, 2013.

	AERMOD			CALPUFF		
	1-h average concentration (μg/m^3)	Coordinates (UTM, km)	Time	1-h average concentration (μg/m^3)	Coordinates (LCC, km)	Time
1	0.0105	(680.9, 4,917.2)	16:00	5.37	(22, 6)	1:00
2	0.00896	(680.9, 4,917.2)	13:00	4.94	(22, 6)	1:00
3	0.00835	(680.9, 4,917.2)	14:00	3.10	(22, 10)	2:00

The highest 1-hour average concentration of 5.37 μg/m^3, modelled by CALPUFF, is at a receptor with coordinates (26 km, 6 km), which is located approximately 17 km away from the flare and generator stack and approximately 17 km away from the south-western corner of the landfill mound. The highest 1-hour average concentration of 0.0105 μg/m^3, modelled by AERMOD, is at a receptor which is located approximately 0.7 km away from the flare and generator stack and approximately 0.7 km away from the south-western corner of the landfill mound. Thus, it can be seen that the highest concentration modelled by CALPUFF occurs at a much greater distance from the emission source, compared to AERMOD.

3.4.4 CALPUFF vs. AERMOD Modelling Results for November 17, 2013

Table 12 summarizes the three highest concentrations obtained from the AERMOD and CALPUFF modelling results for November 17, 2013. The table demonstrates that the resultant concentration values for the CALPUFF modelling are significantly higher than those outputted from the AERMOD modelling. This is consistent with the trend seen in the modelling results for July 20, 2013.

Table 12: CALPUFF vs. AERMOD modelling results for November 17, 2013.

	AERMOD			**CALPUFF**		
	1-h average concentration (μg/m^3)	Coordinates (UTM, km)	Time	1-h average concentration (μg/m^3)	Coordinates (LCC, km)	Time
1	0.00766	(676.9, 4,917.2)	8:00	0.966	(22, 6)	17:00
2	0.00355	(676.9, 4,917.2)	6:00	0.954	(22, 6)	19:00
3	0.00214	(676.9, 4,917.2)	7:00	0.913	(22, 6)	20:00

The highest 1-hour average concentration of 0.966 μg/m^3, modelled by CALPUFF, is at a receptor with coordinates (22 km, 6 km), which is located approximately 10.4 km away from the flare and generator stack and approximately 16.1 km away from the south-western corner of the landfill mound. The highest 1-hour average concentration of 0.00766 μg/m^3, modelled by AERMOD, is at a receptor that is located approximately 3.3 km away from the flare and generator stack and approximately 3.3 km away from the south-western corner of the landfill mound. Thus, it can be seen that the highest concentration modelled by CALPUFF occurs at a much greater distance from the emission source, compared to AERMOD. This is also consistent with the trend seen in the modelling results for July 20, 2013.

3.4.5 Comparison of Modelling Results with Limits

Ontario Regulation 419/05 imposes a 24-hour limit of 1 μg/m^3 on the emission of vinyl chloride. To compare the concentration results of the modelling to this limit, the conversion method stated in the Regulation was used to convert the maximum highest concentrations mentioned above from a 1 hour averaging time to a 24 hour averaging time [2,3]. This conversion equation is as follows:

$$C_{24h} = C_{1h} \text{ x } (1 \text{ h}/24 \text{ h})^{0.28}$$

Table 13 compares these maximum highest concentrations with the limit. The results show that the concentration of vinyl chloride on July 20, 2013, as modelled by CALPUFF, exceeds the limit of 1 μg/m^3. This demonstrates that the selection of the model cannot only give different results, but that the difference in the results may be significant enough such that using one model may deem a facility compliant with contaminant emission limits, while the use of another model may deem the same facility non-compliant.

Table 13: Comparing 24-hour maximum highest concentrations with 24-hour limit.

Date	Maximum Highest 24-h Concentration, CALPUFF (μg/m^3)	Maximum Highest 24-h Concentration, AERMOD (μg/m^3)	24-h Limit (μg/m^3)
July 20, 2013	2.21	0.0043	1
November 17, 2013	0.397	0.00315	1

3.5 Conclusions and Recommendations

The results of this study demonstrated that, for the same facility and the same emission sources, modelling contaminant dispersion using the CALPro model resulted in higher concentrations than when modelling with AERMOD. This may be due to the several limitations of AERMOD which were discussed above, including its assumptions of straight line trajectory, steady state and a uniform atmosphere, its inaccuracy when determining long-range transport, and its inability to retain the memory of the emissions of previous hours.

The CALPro modelling results also demonstrated that, in many instances, the concentration of the contaminant could be higher at a receptor that is located further away from the source than at a receptor that is located close to the source. Due to such occurrences, it is advisable to use long-range models to assess contaminant dispersion to capture the impacts of the emissions on receptors that are located farther away from the sources of emission.

The difference in results may also be because AERMOD assumes that the entire modelling domain where the contaminant dispersion occurs is in a steady state condition. This assumption may be representative of the conditions within the near field since the smaller domain may not experience significant spatial and temporal variations in the winds. However, for a large modelling domain that is encountered in long-range transport assessments, such as in this case study, this assumption is likely not valid and winds typically vary spatially and temporally across the modelling domain. Thus, CALPUFF performs better in this instance due to its ability to accurately assess variations in contaminant concentration that may occur spatially and temporally.

The results of the study also showed that the maximum highest concentration was much higher for July 20, 2013 than for November 17, 2013. This may be due to several reasons, including meteorological anomalies, terrain effects and differences in the speed of the wind vectors.

As a result of this study, it is recommended that long-range transport models such as CALPro should be preferred over short-range transport models such as AERMOD when assessing the impacts of emissions from a facility. This will ensure that the impacts are studied more appropriately, and that the dispersion is assessed further away from the emissions sources as well as nearer to them. The appropriate selection of dispersion models is especially important when the results of one of the models may deem the facility's emissions non-compliant with the applicable regulatory limits. As per the previous studies discussed in Section 3.1, AERMOD was found to be more appropriate for receptors in the near field. Thus, this model could be an appropriate choice when studying a smaller domain.

Furthermore, it is recommended that the results of this study be compared to real emissions data from the facility to determine which model's results more accurately represent the emissions.

Chapter 4: Modelling of greenhouse gas emissions from the steady state and non-steady state operations of a combined cycle power plant located in Ontario, Canada using CALPUFF

The content of this chapter is based on a paper published in November 2014 in the journal "Fuel" under the title "Modelling of greenhouse gas emissions from the steady state and non-steady state operations of a combined cycle power plant located in Ontario, Canada" by "Abdul-Wahab et al.". The thesis author specific contribution to this paper was: the set-up and running of the simulations, analysis of the results, preparation of graphics, figures, tables and results, preparation of the draft manuscript, and preparation of the final manuscript incorporating the reviewers' edits with supervision from the study supervisors who are co-authors. This paper is co-authored by Dr. Abdul-Wahab, who supervised the simulations and edited the manuscript, and by Dr. Elkamel, who supervised the study.

4.1 Background

As discussed in Chapter 1, the air permit framework in Ontario and the United States is based on defining and enforcing limits on the concentrations of contaminants that are emitted from a facility to the environment [1,2]. Guidance provided by regulatory agencies in calculating emissions relies heavily on the use of the emission factors listed under AP-42, Compilation of Air Pollutant Emission Factors, developed and published by the U.S. EPA [1,3]. As mentioned in Chapter 1, these emission factors were developed based on data collected from the testing of emissions under normal process operating conditions, such as steady state operation [4]. Thus, the use of these emission factors in assessing worst-case scenario emissions from a facility does not capture emissions generated by the facility when it is operating under non-steady state conditions.

More accurate approaches need to be investigated and developed to predict the emissions of contaminants when a facility is operating under non-steady state conditions such as process start-ups and shut-downs, as well as process fluctuations where the operating conditions deviate from the normal operating conditions [5]. Due to the lack of clearly defined methods of quantifying and regulating emissions generated during start-up and shut-down events, the approaches taken by the states to limit and regulate these emissions have been inconsistent [1]. Chapter 1 outlines some of these approaches.

The U.S. EPA proposed a rule in February 2013, necessitating that the states develop plans to require that all industrial facilities comply with air pollution rules during plant start-ups, shut-downs and malfunctions [7]. This was further formalized in May 2015, when the U.S. EPA issued a final action that required the states to submit their revised state implementation plans, accounting for emissions under these non-steady state operating conditions [8]. No similar action has been made by the Ministry of the Environment and Climate Change (MOECC) within Ontario.

As discussed in Chapters 1 and 2, there are multiple challenges in predicting emissions that are generated during non-steady state operations. Firstly, it is difficult to collect accurate and representative data during such events due to their relatively short time span and their dynamic process variables [5]. Additionally, many manufacturers do not have emissions data available for start-up and shut-down events [5]. Also, the U.S. EPA does not provide method tests that can be applied for dynamic process situations [5]. Furthermore, developing and processing dynamic models for facilities is often more challenging and costly than developing models that represent normal operating conditions [9]. Moreover, the integration of multiple process functions, such as reaction and heat transport operations, within the same process unit further complicates the prediction of emissions under non-steady state conditions [9].

Despite the challenges in predicting emissions from non-steady state conditions, investigating methods to predict these emissions is essential in ensuring that a facility does not adversely impact human health or the environment. Oftentimes, emissions are higher during the start-up and shut-down of a facility, compared to its steady state operation under normal operating conditions [6,10]. Additionally, most incidents that are related to the process carried out at the facility occur when the plant is operating under non-steady state [9]. Furthermore, as emission limits become more stringent with time, it is important to investigate methods of predicting emissions associated with non-steady state events, to ensure that resources are adequately allocated to minimize emissions and thus to achieve compliance with these limits [1].

Chapter 2 discusses many case studies where the emissions of certain contaminants under non-steady state operating conditions exceeded the emissions of the contaminants under steady state operating conditions.

Chapter 3 utilizes a case study approach to compare the two most commonly used air dispersion models: AERMOD and CALPUFF and concludes that CALPUFF should be used to account for worst-case scenarios. The U.S. EPA specifically recommends the use of this Lagrangian puff model when assessing impacts on receptors that are located over 50 kilometres away from the emission source [42]. Thus, it is considered a long-range transport model [43]. A non-steady state model, CALPUFF has several advantages, including its allowance for non-straight line trajectories, its consideration of a non-uniform atmosphere across the domain, its accuracy in calm conditions, and its ability to retain the memory of contaminant emissions from previous hours [43]. Many studies have used CALPUFF to simulate the dispersal of contaminant emissions and assess their impacts at receptors within a domain.

As outlined in Chapter 3, CALPUFF has been used to model the dispersion of the emissions of sulphur dioxide from a flare located at an oilfield, sulphur dioxide from various refineries, nitrogen oxides from the operation of a power plant that converts biomass into energy, nitrogen oxides, carbon monoxide and particulates from an industrial plant, hydrogen sulphide from a hypothetical accidental release from a plant operation, odour from theoretical point and area sources, odour from livestock and benzene from different anthropogenic emission sources [49-54,57,58,59]. However, all of these papers focus on assessing the impacts of emissions during steady state operations. Very limited papers have assessed the dispersion of emissions from the non-steady state operation of a plant using dispersion models. Even fewer have used CALPUFF for this assessment. After extensive research, only one paper was found which used CALPUFF to assess the dispersion of emissions from the non-steady state operation of an energy-from-waste facility. This study concluded that the emissions associated with non-steady state operations were higher than the emissions associated with steady state operations [22].

This study focuses on modelling greenhouse gas emissions from the full load operation (steady state) and start-up conditions (non-steady state) of a future combined cycle power plant using CALPUFF. The contaminants that have been modelled are nitrogen oxides, carbon dioxide, carbon monoxide and sulphur dioxide. Additionally, four different modelling scenarios have been considered: full load operation; a cold start followed by full load operation; a warm start followed by full load operation; and a hot start followed by full load operation. Lastly, the modelling has been performed for one day in each of the following three seasons –winter, spring and summer – to better compare the modelling results.

4.2 Case Study

4.2.1 Description of Study Area

The study area is the Township of St. Clair, located along the eastern shores of the St. Clair River in Ontario, Canada. Covering an approximate land area of 619.32 km^2, the town had a population of about 14,515 in 2011 [72,73]. Since it is located in one of the most southerly parts of the country, the Town’s climate is one of the mildest in Canada [74]. Manufacturing, retail trade, agriculture, agriculture based industries and construction are the Town’s largest industries [75].

4.2.2 Description of Facility

The facility is a future combined cycle power plant that is fuelled by natural gas [16]. It consists of a turbine generator that exhausts through a heat recovery steam powered generator [16]. The main source of emission is the stack of the heat recovery steam generator [16]. The contaminants that are emitted are: NO_x, CO, SO_2 and CO_2.

4.2.3 Description of Operating Scenarios

The dispersion of emissions was modelled for four different operating scenarios. The first scenario is the steady state full load operation. The second scenario is the non-steady state warm start followed by the steady state full load operation. A warm start procedure is characterized by starting the gas turbine within 48 hours of shutdown [16]. The third scenario is the non-steady state hot start followed by the steady state full load operation. A hot start procedure is characterized by starting the gas turbine within 8 hours of shutdown [16]. The fourth scenario is the non-steady state cold start followed by the steady state full load operation. A cold start procedure is characterized by starting the gas turbine after it has been shut down for a minimum of 72 hours [16].

4.3 Materials and Methods

4.3.1 CALPro Modelling System

This study used CALPro Plus version 6.9.10.25.2007 to model the dispersion of greenhouse gas emissions from the facility. Developed by the Atmospheric Studies Group, the CALPro software models meteorology as well as contaminant dispersion [67]. As mentioned above, it is one of the models that the U.S. EPA recommends for use when assessing long-range impacts of emissions.

CALPro is especially effective in modelling the dispersion of emissions in areas that have a complex terrain and dynamic flows. The model also takes into consideration coastal effects, overwater conditions and wind parameters. [67]

Several pre-processors, simulation models and post-processors make up the CALPro software package. The pre-processors include the geophysical, surface and upper air meteorological, precipitation and overwater pre-processors. Two simulation models make up the software package –the first is a meteorological model called CALMET, and the second is an air quality dispersion model called CALPUFF. The post-processing package mainly consists of PRTMET and CALPOST post-processors. [67]

The pre-processors are used to process input data into a format that can be input into the simulation models. CALMET utilizes geophysical, observational and prognostic input data to model meteorological results on an hourly basis. It generates wind and temperature results on a three-dimensional gridded domain. CALPUFF utilizes the meteorological output from CALMET and the data that relates to the emission source to model the dispersion of emissions. It generates contaminant concentrations on an hourly basis at specified receptors on a three-dimensional gridded domain. [67]

PRTMET utilizes the output file from CALMET to display portions of the meteorological data that are selected by the user onto the visual grid representation. CALPOST utilizes the output file from CALPUFF to determine, identify and output the highest hourly average concentrations of the emitted contaminants at each receptor. CALPOST also displays portions of the dispersion results that are selected by the user onto the visual grid representation. [67]

The input data that was used for the model for this case study is summarized in Table 14.

Table 14: Model input information for the domain of study.

Parameter	**Values Used**
Projection	LCC (CALPUFF)
LCC latitude of origin	42.79°N
LCC longitude of origin	82.43°W
Latitude 1	5°N
Longitude 2	50°N
False Easting	0
False Northing	0
Continent/Ocean	North America
Geoid-Ellipsoid	North American 1983: GRS 80
Region	Canada
DATUM code	NAR-B
X (Easting)	-50 km
Y (Northing)	-50 km
Number of X grid cells	200
Number of Y grid cells	200
Grid spacing	0.5 km
Number of vertical layers	9
Cell face heights (m)	0-20, 20-50, 50-100, 100-150, 150-200, 200-300, 300-500, 500-1000, 1000-2000
Base time zone	UTC – 05:00
UTM zone	17
Hemisphere	Northern

4.3.2 Meteorological Data

The Environment Canada website for climate data was used to obtain the surface meteorological data [69]. Hourly data was downloaded for the London A climate station, located in Ontario, for data sets in each of the three aforementioned seasons. The first data set was obtained for the time period from 00h00 Eastern Time on January 19, 2013 to 23h00 Eastern Time on January 21, 2013, to represent the wintertime. The second data set was obtained for the time period from 00h00 Eastern Time on April 19, 2013 to 23h00 Eastern Time on April 21, 2013, to represent the springtime. The third data set was obtained for the time period from 00h00 Eastern Time on July 19, 2013 to 23h00 Eastern Time on July 21, 2013, to represent the summertime. For each data set, temperature (°C), pressure (mbar), relative humidity (%), wind direction (degrees) and wind speed (m/s) were obtained. The London A climate station is located relatively close to the emission sources. Table 15 summarizes information pertaining to this station.

Table 15: Information about the surface station that was used to obtain surface meteorological data [69].

Parameter	Values Used
Station Name	London A climate station
UTM Latitude	43.016667°N
UTM Longitude	81.15°W
Elevation	278 m
Climate ID	6144473
WMO ID	71623
TC ID	YXU

The Radiosonde Database website of NOAA was used to obtain the upper air meteorological data [70]. Data was obtained for the White Lake upper air climate station at twelve-hour intervals for the same time periods as described above. The White Lake upper air climate station is located relatively close to the emission sources. Table 16 summarizes information pertaining to this station.

Table 16: Information about the radiosonde station that was used to obtain upper air meteorological data [70].

Parameter	Values Used
Station Name/Location	White Lake, U.S.
UTM Latitude	42.7°N
UTM Longitude	83.47°W
Elevation	329 m
WBAN	04830
WMO ID	72632
INIT	DTX

4.3.3 Preparing the Meteorological Data Files

For each meteorological data set, the surface meteorological data was formatted such that it was compatible with SMERGE, which is CALPro's surface meteorological pre-processor. The surface input file was then processed by SMERGE to generate the output file, named "SURF.DAT", that is compatible for processing by CALMET. For each meteorological data set, the upper air meteorological data was formatted such that it was compatible with READ62, which is CALPro's upper air meteorological pre-processor. The upper air input file was then processed by READ62 to generate the output file, named “UP.DAT”, that is compatible for processing by CALMET.

4.3.4 Emissions Data

This study utilizes the emission data taken from the case study that is mentioned in Section 4.2. The source of emission is the stack of the heat recovery steam generator, which is modelled as a point source. The contaminants that are modelled in this investigation are NO_x, CO, SO_2 and CO_2. The emission rates for NO_x, CO and SO_2 under each of the operating scenarios described in Section 4.2.3 were obtained from this case study [16]. The emission rates for CO_2 were not calculated in the case study. As part of this investigation, the emission rates for CO_2 were calculated for each operating scenario using the manufacturer’s specifications provided and the calculations methodology shown in the case study. The emissions data was entered into the CALPUFF model as inputs. Tables 17 and 18 summarize the emission input data.

Table 17: Input data for emission source [16].

Parameter	Source
Source description	Heat recovery steam generator
Source type	Point
Stack exit gas temperature (°C)	87
Stack inner diameter (m)	5.5
Stack exit velocity (m/s)	13.06
Stack height above grade (m)	43
UTM Latitude	42.79°N
UTM Longitude	82.43°W
Location on grid (km)	(0, 0)

Table 18: Emission rates for contaminants under different operating scenarios [16].

Contaminants	Emission Rates (g/s)			
	Cold start followed by full load operation	Warm start followed by full load operation	Hot start followed by full load operation	Full load operation
NO_x	12.04	10.75	11.04	10.40
CO	13.88	18.82	10.85	9.76
SO_2	0.10	0.11	0.11	0.12
CO_2	19,478.98	20,427.80	20,161.70	21,172.60

4.3.5 Operation of CALPro

First, a common file was created that contained the processed meteorological and geophysical information. The grid domain was selected to be 100 km by 100 km, where the centre of the grid was situated at the facility.

The Atmospheric Studies Group website was used to obtain the geophysical data files for the domain [71]. The land use pre-processor, CTGPROC, utilized the geophysical data files as inputs to generate a land-use output file named “LU.DAT”. Similarly, the terrain pre-processor, TERREL, utilized the geophysical data files as inputs to generate a terrain output file named “TERREL.DAT”. The MAKEGEO pre-processor used these output files as inputs to generate the geophysical output file named “GEO.DAT”, which was compatible with CALMET. The surface and upper air meteorological data was prepared and processed in the manner that is explained in the sections above.

CALMET utilized the processed geophysical and meteorological files as inputs to generate an output that is compatible with the PRTMET post-processor. PRTMET utilized the CALMET output as an input to generate hourly wind velocity vectors for the domain, which were layered overtop of the land use and terrain maps. This gives a graphical representation of the meteorological results via CALVIEW.

CALPUFF utilized the emission data and the output files that were generated by the pre-processors and simulators as inputs to generate hourly concentrations of contaminants at the receptors. CALPOST utilized the CALPUFF output as an input to generate hourly concentration and plume trajectories that were layered overtop of the meteorological results, land use maps and terrain maps for the domain. This gives a graphical representation of the dispersion of the plume via CALVIEW.

The impacts of the dispersion of the greenhouse gases were assessed for the first vertical layer, which ranged from 0 m to 20 m. Hourly wind direction and speed are represented by the bearing and size of the arrows shown on the map. The trajectory of the plume is represented by the contour lines on the map. The numbers at each contour line are the highest concentration of the contaminants at each contour.

The CALPro simulations were performed for each of the four operating scenarios, each of the four contaminants and each of the three meteorological data sets.

4.4 Results and Discussion

4.4.1 Direction of Plume Dispersion

For January 20, 2013, the wind vectors bear north-east from 0:00 LST to 1:00 LST and fluctuate between the north-eastern and eastern directions from 2:00 LST to 23:00 LST. Carried by the wind, the plume is dispersed in the same directions.

For April 20, 2013, the wind vectors fluctuate between pointing east and north-east from 0:00 LST to 6:00 LST, and then between east and south-east from 7:00 LST to 23:00 LST. The plume is thus carried in the same directions by the wind.

For July 20, 2013, the wind vectors bear north-east from 0:00 LST to 1:00 LST, and north from 2:00 LST to 4:00 LST. From 5:00 LST to 23:00 LST, the wind fluctuates between the southern and south-eastern directions. Assisted by the wind, the plume is dispersed in the same directions.

4.4.2 Summarizing Modelling Results

Table 19 lists the highest 1-hour average concentration values for each of the four contaminants under each of the four operating scenarios, for each of the three seasons. The results depict that the average concentration values are the lowest for January 20, 2013 (wintertime) and the highest for July 20, 2013 (summertime). The results also demonstrate that the highest average concentration values occur under different operating scenarios for different contaminants.

Table 19: Highest average concentration values for each contaminant under each operating scenario and season.

1-hour highest average concentration values (µg/m^3) for January 20, 2013 (wintertime)				
Contaminants	Cold start followed by full load operation	Warm start followed by full load operation	Hot start followed by full load operation	Full load operation
NO_x	3.55	3.17	3.26	3.07
CO	4.09	5.55	3.20	2.88
SO_2	0.030	0.030	0.030	0.035
CO_2	5743.2	6023.0	5944.5	6242.6
1-hour highest average concentration values (µg/m^3) for April 20, 2013 (springtime)				
Contaminants	Cold start followed by full load operation	Warm start followed by full load operation	Hot start followed by full load operation	Full load operation
NO_x	5.18	4.63	4.75	4.48
CO	5.98	8.10	4.67	4.20
SO_2	0.043	0.043	0.043	0.052
CO_2	8387.0	8795.6	8681.1	9116.3
1-hour highest average concentration values (µg/m^3) for July 20, 2013 (summertime)				
Contaminants	Cold start followed by full load operation	Warm start followed by full load operation	Hot start followed by full load operation	Full load operation
NO_x	7.89	7.04	7.23	6.81
CO	9.09	12.32	7.10	6.39
SO_2	0.072	0.072	0.072	0.079
CO_2	1275.0	13372	13197	13859

Figures 9 and 10 depict the contour maps associated with the highest 1-hour average concentration scenarios for NO_x, CO, SO_2 and CO_2. These figures are all for time 13:00 LST on July 20, 2013 since the highest concentration values occur at this time and day for all contaminants. On the domain, the highest concentration for each contaminant occurs at the same location (101 km, 99 km), which is located approximately 141.43 km away from the source of emission.

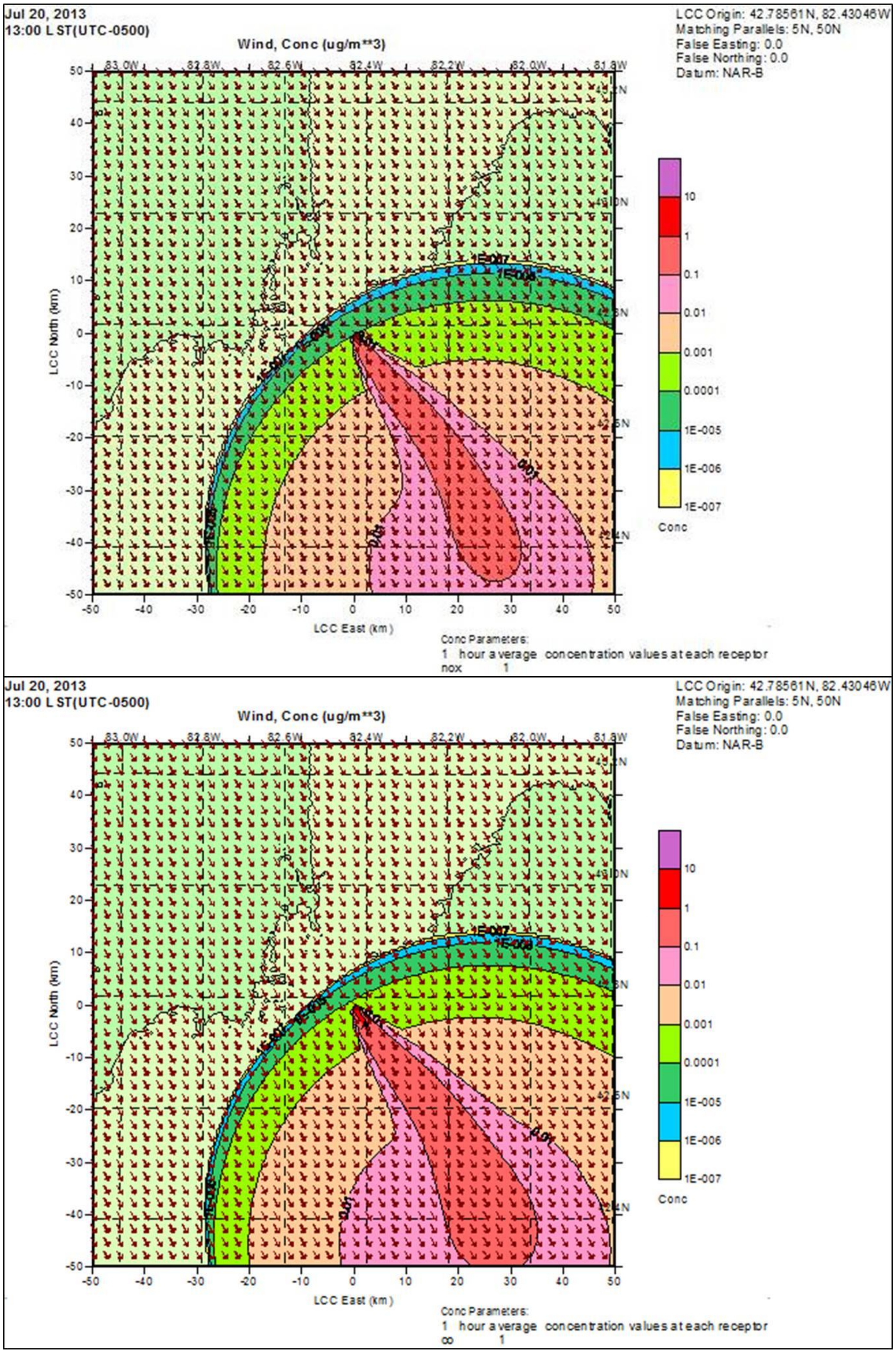

Figure 9: Concentration contours for 13:00 LST for July 20, 2013 for NO_x and CO emissions.

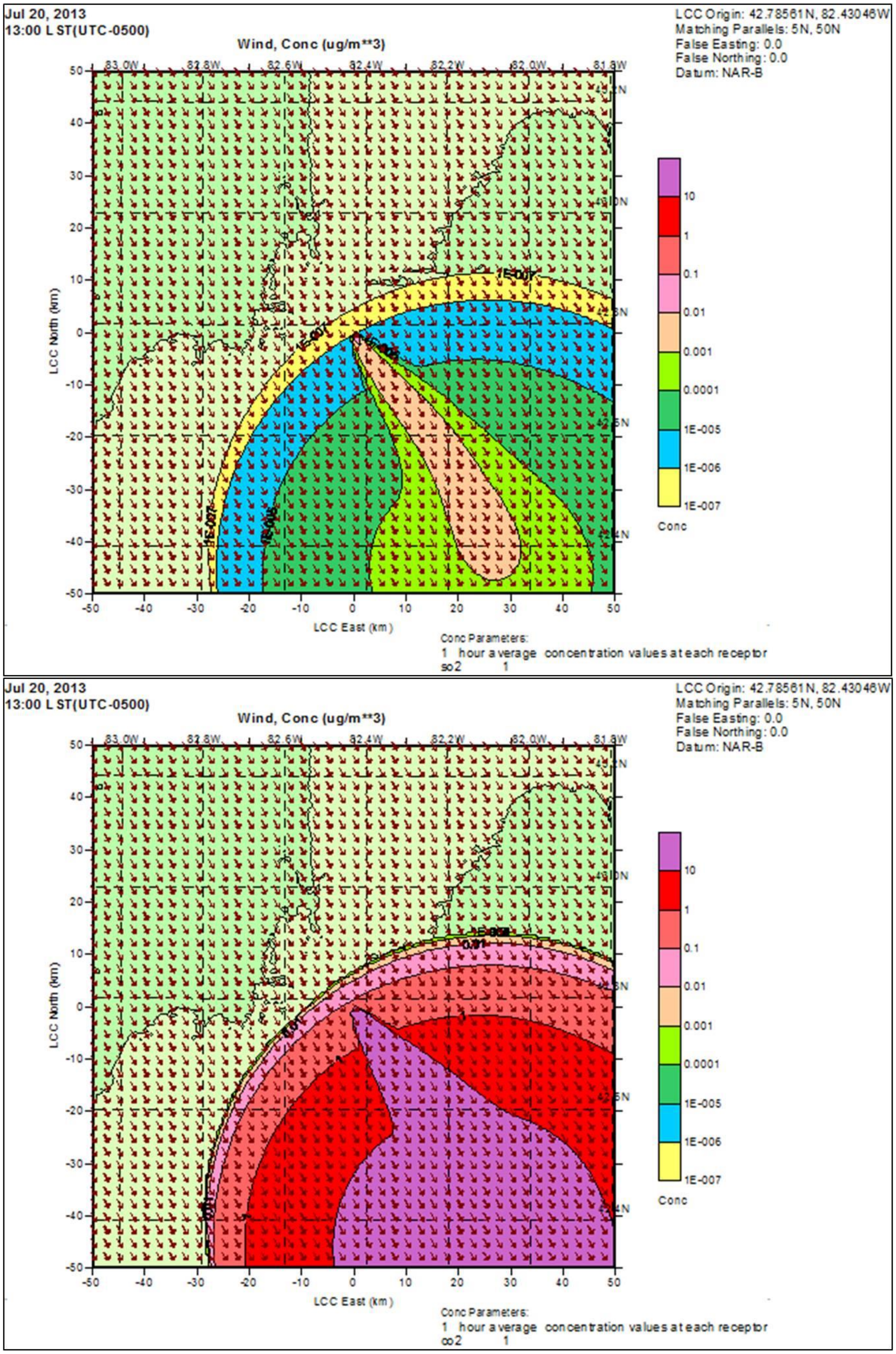

Figure 10: Concentration contours for 13:00 LST for July 20, 2013 for SO_2 and CO_2 emissions.

4.4.3 Analysis of Modelling Results for Each Contaminant

The results, summarized in Table 19, depict that the NO_x emissions are the highest for the scenario that is characterized by a cold start followed by full load operation, and are the lowest for the scenario that is characterized by full load operation without any start-up considerations. For CO, the results demonstrate that the emissions are the highest for a warm start followed by full load operation, and are the lowest for full load operation without any start-up considerations. This is likely because during start-up operation, the temperature may not be high enough to trigger the activation of control mechanisms that may be in place to reduce emissions [6].

The concentration for SO_2 is slightly higher at full load operation without consideration of start-up conditions, compared to the other operating scenarios. However, the emission rate and concentration for SO_2 hardly vary with the operating scenario. Thus, it can be assumed that the emissions do not depend significantly on the operating scenario.

The highest concentration for CO_2 is seen at the full load operation scenario which does not consider start-up. The lowest concentration is seen at the scenario that is characterized by a cold start followed by full load operation. This is likely because a higher amount of fuel is used, and therefore combusted, during full load operation than under start-up conditions.

4.4.4 Comparison of Modelling Results with Limits

Table 20 compares the highest average concentration values for each contaminant to the applicable limits imposed by the Ontario Ministry of the Environment and Climate Change (MOECC). The limits for NO_x, CO and SO_2 are listed in Ontario Regulation 419/05 [2]. The limit for CO_2 is listed in the MOECC’s Jurisdictional Screening Level (JSL) List [76].

Table 20: Comparison of maximum highest concentrations with the MOECC limits and guidelines.

Contaminant	Maximum highest concentrations (µg/m^3)	Averaging period (h)	Operating scenario	Date (2013)	Applicable MOECC limit (µg/m^3)	Averaging period for MOECC limit (h)
NO_x	7.89	1	Cold	July 20	400[a]	1
CO	14.96	0.5	Warm	July 20	6000[a]	0.5
SO_2	0.079	1	Full load	July 20	690[a]	1
CO_2	16828	0.5	Full load	July 20	63,000[b]	0.5

[a] *Limit obtained from Ontario Regulation 419/05.*
[b] *Limit obtained from the MOECC's JSL List.*

Since the MOECC limits for CO and CO_2 are based on a half hour averaging time, the highest concentration values that were modelled for these contaminants were converted from a 1 hour averaging time to a half hour averaging time using the conversion method stated in Ontario Regulation 419/05 [2]. The following equation is used for the conversion:

$$C_{0.5h} = C_{1h} \text{ x } (1h/0.5h)^{0.28}$$

The results show that the highest average concentration of each contaminant, as modelled by CALPUFF, is less than the applicable MOECC limit. However, it can be seen that the highest concentration of each contaminant can vary greatly with the operating scenario. In the case of NO_x, the highest concentration, which pertained to the cold start followed by the full load operation, was approximately 16% higher than the concentration that occurred at full load operation without consideration of start-up on the same day. Similarly, for CO, the highest concentration, which was for the warm start followed by the full load operation, was approximately 42% higher than the concentration that occurred at full load operation without consideration of start-up on the same day. Lastly, for CO_2, the highest concentration, which occurs at full load operation without start-up considerations, was approximately 3.6% greater than the highest concentration associated with start-up conditions, which is at the warm start followed by full load operation.

4.5 Conclusions and Recommendations

The results demonstrate that it is important to model and assess the dispersion of contaminants under both, steady state as well as non-steady state, operating conditions. In this case study, the emissions are sufficiently low such that the increase in the emissions of some contaminants under non-steady state operations does not result in an exceedance of the applicable MOECC limits. However, in cases where the emissions are high enough, such increases in emissions during non-steady state operations may result in an exceedance of the applicable limits.

Due to the results of the study, it is recommended that air quality impact assessments consider emissions from both, steady state and non-steady state operating conditions. This will ensure that the impacts of released emissions are modelled and studied in a conservative manner that takes into account all scenarios to determine the impacts of the worst-case scenario. As can be seen from the results of this study, the worst-case operating condition may be different for each contaminant. Considering these different operating scenarios is particularly important when emissions associated with non-steady state operation have the potential to exceed applicable emission limits, and to possibly cause an adverse impact on human health and the environment.

Chapter 5: Conclusion and Recommendations

5.1 Conclusion

To ensure that there is no adverse impact to public health and the environment, emissions from sources at industrial facilities must be considered under the worst-case scenario. This is to ensure that these facilities allocate resources adequately towards controlling emissions under the worst-case scenario. In addition, assessing emissions under the worst-case scenario allows regulatory authorities to focus their policy and regulatory efforts to address operating conditions under which emissions may cause an adverse impact. Furthermore, the requirement to address and control emissions under the worst-case scenario will lead to further innovation, research and development geared towards controlling emissions under such scenarios.

Currently, regulatory authorities such as the U.S. EPA and the MOECC in Ontario, Canada encourage the use of emission factors that were developed based on data collected under normal operating conditions, such as steady state operation. Although the U.S. EPA has recently required states to submit revised state implementation plans accounting for emissions under non-steady state operating conditions, it does not currently require facilities to assess emissions under operating conditions. Furthermore, due to the lack of clearly defined methods of quantifying and regulating emissions generated during start-up and shut-down events, the approaches taken by the states to limit and regulate these emissions have been inconsistent and ineffective. The MOECC does not require industrial facilities to assess emissions under non-steady state operating conditions.

As demonstrated through the findings of Chapters 2 and 4, it is important to model and assess the emission of contaminants under both, steady state as well as non-steady state, operating conditions. This will ensure that the impacts of released emissions are modelled and studied in a conservative manner that takes into account all scenarios to determine the impacts of the worst-case scenario. As can be seen from the conclusions drawn in these chapters, the worst-case operating condition may be different for each contaminant. Some contaminants have higher emissions during steady-state operating conditions, while others have higher emissions during non-steady state operating conditions. This was observed to depend on the nature of the industrial process and the type of contaminant. The trends developed in Chapter 2 can help industrial facilities effectively allocate their resources when assessing emissions related to non-steady state operations, consequently ensuring that emissions are assessed for the worst-case scenario. Considering these different operating scenarios is particularly important when emissions associated with non-steady state operation have the potential to exceed applicable regulatory emission limits, and to possibly cause an adverse impact on public health and the environment. Therefore, emissions under steady state and non-steady state operating conditions must be assessed, controlled and reported to the regulatory authorities to ensure that emissions under the worst-case scenario are addressed.

Based on the findings above, this thesis recommends that regulatory authorities require industrial facilities to assess their emissions under non-steady state operating conditions as well as under steady state operating conditions to ensure that the emissions under both conditions are controlled below the applicable regulatory emission limits.

5.2 Recommendations for Future Works

It is recommended that further case studies be explored for the industries that have been investigated in this study to further validate the observed trends and to develop trends where the trend was inconclusive. Additionally, emissions under start-up and shut-down operations should also be assessed for other industries such as polymer production, food production, agriculture, etc. Furthermore, emissions under other non-steady state operating conditions, such as process upsets and malfunctions, should also be investigated to aid in the control of such emissions. Assessing and reporting the emissions under these non-steady state scenarios will increase the number of case studies that could serve as a basis for developing emissions trends under these operating conditions.

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