Economical and Environmental Impacts of Emission Mitigation in Petroleum Refineries

by

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Abstract

Despite the large number of products produced by oil refineries, they are considered to be one of the main source of air contaminants including, sulphur oxides SO_x, hydrocarbons, nitrogen oxides NO_x and carbon oxide CO_2, which are primarily caused by fuel burning. Gases emanated from fuel burning in oil refinery need to be tumbled down as they create a critical environmental issue in the developed world. A number of control strategies can be applied in order to mitigate emissions and meet certain environmental regulations.

This thesis addresses the development of a mathematical model for an oil refinery with consideration to multiple pollutants reduction alternatives. The objective of this study is to help decision makers of oil refineries to select the best pollution control strategies for a given emission reduction target. The model is demonstrated by an industrial scale refinery with three emissions including nitrogen oxides (NO_x), sulphur dioxide (SO_x) and carbon dioxide (CO_2). Furthermore, this research studies the dispersion of air pollutants that are potentially released from oil refinery. As a test case, we used a potential site for oil refinery in the northern area of Toronto, Ontario, Canada. In order to predict pollutants concentrations, dispersions and transports, we used a screening model (SCREEN3), and a non-steady state Lagrangian puff model (CALPUFF), which use topographical and meteorological conditions on concentration of pollutant emissions to examine the impacts at receptor locations.

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Table of Contents

List of Tables x

List of Figures xii

1 Introduction 1

1.1 Background and motivation . . . 1

1.2 Research Objectives . . . 5

1.3 Organizations of the thesis . . . 6

2 Background and Literature Review 7

2.1 Introduction . . . 7

2.2 Oil refinery Overview . . . 9

2.2.1 System Configuration of Refinery . . . 13

2.2.2 Fractionation or Distillation . . . 15

2.2.3 Hydrotreating . . . 17

2.2.4 Product Blending 18

2.2.5 Upgrading 19

2.3 Refinery Emissions 20

2.3.1 Potential Emissions Impacts 20

2.4 Emission Control Plans 21

2.4.1 NO_x/SO_x Mitigation Through Decreasing Carbon Emission 22

2.4.2 Source Emission Limits 23

2.4.3 CO_2 Capture 24

2.5 Air Quality Dispersion Models 24

2.5.1 Steady State Model 25

2.5.2 Non-Steady State Models 26

2.5.3 Factors Affecting Air Dispersion 27

3 Cost Optimization Model with Emissions Mitigation Targets **29**

3.1 Introduction 29

3.2 Mathematical Optimization Model 30

3.3 Air Emission Optimization Model 35

3.4 Results and Discussion 40

3.4.1 Base Case Scenario 42

3.4.2 Independent Emission Reduction 43

3.4.3 Simultaneous Emissions Reduction 44

3.5 Conclusion 46

4 Air Pollution Dispersion Models 49

4.1 Introduction 49

4.2 CALPUFF Dispersion Model 49

4.2.1 Data collection 51

4.3 Screen 3 Dispersion Model 55

4.4 Results and Discussion 56

4.4.1 CALPUFF 56

4.4.2 SCREEN3 66

4.5 Conclusion 72

5 Conclusion and Future Work 73

5.1 Summary of Contributions 74

5.2 Future Directions 74

References 76

Appendices 86

A Cost Versus Reduction 87

B National Ambient Air Quality Standards and Guidelines 94

C Screen3 Results **98**

List of Tables

3.1 Nomenclature 36

3.2 Unit capacity constraints within refinery 41

3.3 Domestic demand for final products 42

3.4 SO_x emission reduction for each unit 44

3.5 NO_x emission reduction for each unit 45

3.6 CO_2 emission reduction for each unit 46

3.7 Cost compared to reduction in SO_x NO_x and CO_2 emissions, all together . 47

4.1 The model information for the meteorological domains 52

4.2 Surface stations information 53

4.3 Radiosonde stations information 54

4.4 Source parameters information for the case study 54

4.5 Emission rate reduction used for CALPUFF 55

4.6 The maximum and minimum monthly average concentrations of CO_2 for six reduction plans in the period of January 2014 58

4.7 The maximum and minimum monthly average concentrations of CO_2 for six reduction plans in the period of May 2014 60

4.8 The maximum and minimum monthly average concentrations of SO_2 for six reduction plans in the period of January 2014 62

4.9 The maximum and minimum monthly average concentrations of SO_2 for six reduction plans in the period of May 2014 64

4.10 The maximum and minimum monthly average concentrations of NO_2 for six reduction plans in the period of January 2014 66

4.11 The maximum and minimum monthly average concentrations of NO_2 for six reduction plans in the period of May 2014 69

B.1 Summary of International Ambient Air Quality Standards (data in $\mu g/m^3$) 96

B.2 Cont. Summary of International Ambient Air Quality Standards (data in $\mu g/m^3$) 97

List of Figures

1.1 Greenhouse gas effect [1] 2

1.2 Emission contribution by sector [1] 3

2.1 Simplified refinery process flow diagram [2] 11

2.2 Diagram of standard refining configuration [3] 14

2.3 Crude distillation [4] 16

3.1 A schematic diagram of the refinery using SEN representation 31

3.2 The total emissions from each refinery unit 43

3.3 Cost compared to reduction in SO_x 48

3.4 Cost compared to reduction in NO_x 48

4.1 CALPUFF Modelling System [5] 51

4.2 Characteristics of study area 57

4.3 CO_2 Dispersion over January 2014 59

4.4 CO_2 Dispersion over May 2014 61

4.5 SO_x Dispersion over January 2014 63

4.6 SO_x Dispersion over May 2014 65

4.7 NO_x Dispersion over January 2014 67

4.8 NO_x Dispersion over May 2014 68

4.9 Maximum SO_x concentration vs. downwind distance (m) using *SCREEN3* over multiple reduction plans 70

4.10 Selected results for maximum SO_x concentration vs. downwind distance (m) for A,D and F stability classes 71

A.1 Cost compared to reduction in CO_2 88

A.2 Cost compared to reduction in CO_2 89

A.3 Cost compared to reduction in SO_x 90

A.4 Cost compared to reduction in SO_x 91

A.5 Cost compared to reduction in NO_x 92

A.6 Cost compared to reduction in NO_x 93

C.1 Maximum NO_x concentration vs. downwind distance (m) using *SCREEN3* over multiple reduction plans 99

C.2 Maximum CO_2 concentration vs. downwind distance (m) using *SCREEN3* over multiple reduction plans 100

Chapter 1

Introduction

1.1 Background and motivation

The risks connected with global warming have been the focus of great debates in recent decades. Climate change has been considered as an important ecological concerns faced by the world today [1]. Though further environmental dangers can be extremely important to explicit sectors, climate risk differentiates itself through its extensive potential for influence on distinct corporations. The influence of climate change will be sensed straight (in the form of harm to agriculture, water and forestry), and will also have grave concerns for the areas impacted by policy driven schemes to alleviate climate change.

Distress is rising because average global temperatures are increasing. It seems to be happening since an upsurge in greenhouse gases, that absorb heat in atmosphere is called the greenhouse effect (see Figure 1.1). The natural greenhouse effect has rendered life on the earth promising. It is extra greenhouse gases that creates concern. Modernization

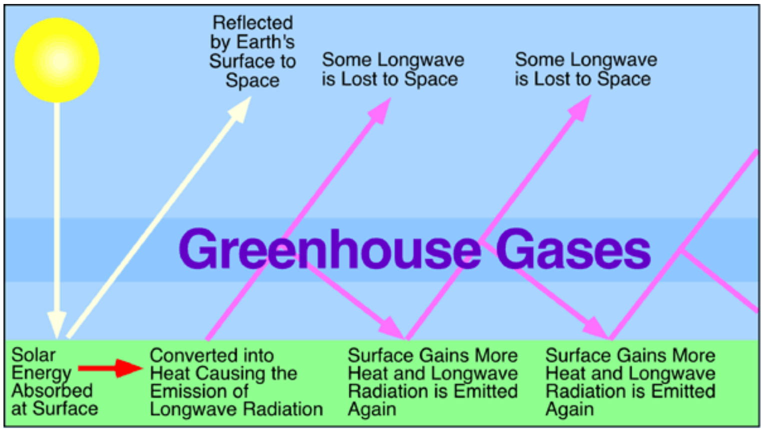


Figure 1.1: Greenhouse gas effect [1]

and technological human activities have ran to the danger of global warming and thus bad impacts on our normal life [1]. The international policy to climate change began with the cooperation of the United Nations Framework Convention on Climate Change (UNFCCC) [6] and its decisive objective is to attain equilibrium of greenhouse gas absorptions in the atmosphere at a degree that would avert unsafe human-caused meddling with the climate system. The UNFCCC offers a legal outline for global stroke to cut greenhouse gas (GHG) emissions. The UNFCCC agreed on the necessity for a supplementary accord to set lawfully obligatory targets and timelines for the GHG releases of developed countries. The decorum sets officially binding GHG emission targets for each of 38 industrialized countries, including Canada. The protocol had been approved by many countries to arrive into power as international law on February 16, 2005. Canada endorsed the Kyoto Protocol in December 2002, thereby supportive to be lawfully assured to meet a mark of tumbling its GHG discharges to 6%.

There are six greenhouse gases enclosed under the Kyoto Protocol; carbon dioxide (CO_2), CH_4, nitrous oxide-N2O, perfluorocarbons, hydrofluorocarbons HFCs and sulphur

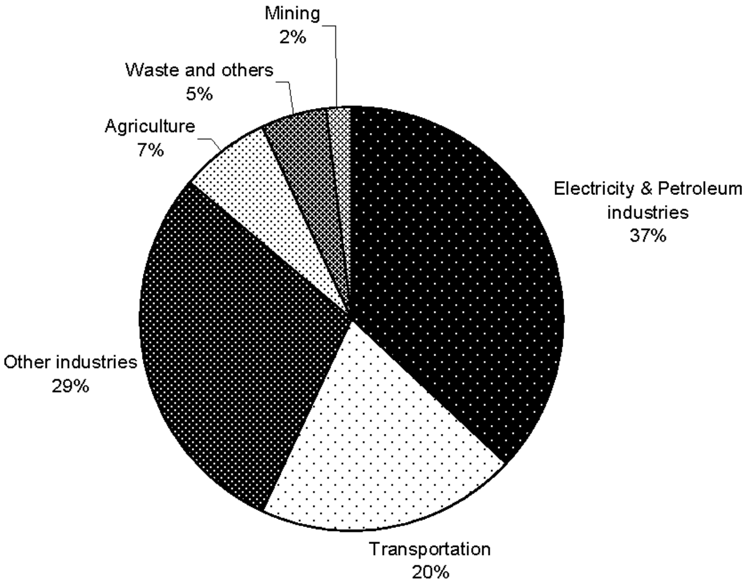


Figure 1.2: Emission contribution by sector [1]

hexafluoride (SF6). CO_2 forms up the major portion of greenhouse gas discharges and has converted the utmost significant anthropogenic greenhouse gas. Methane backed 13% and nitrous oxide 7% to the entire 2004 greenhouse gas emission. The highest contributions to GHG releases in 2004 were from the power and petroleum industries, which accounted for 37% of whole countrywide emissions monitored by further industries that contributed around 29% and the transportation area, which contributed 20% as shown in Figure 1.2. These divisions are also accountable for approximately all of the development in Canadian discharges since 1990. Since the power and petroleum industries contribute to whole GHG releases.

Oil refineries are considered to be one of the significant source of air contaminants including, sulphur oxides SO_x, hydrocarbons, nitrogen oxides NO_x, particulate matter PM_x, volatile organic compounds (VOC), and carbon oxide CO_2, which are primarily caused by fuel burning [1]. Petroleum plant processes extend from the receiving and storing of crude oil at the plant to petroleum management and purifying processes and, lastly, to storing and shipping of the completed products. A refinery's processing system is found mainly by the configuration of the crude oil contribution and the selected mixture of petroleum yields. The combination and preparation of refining processes will differ amongst refineries.

Gases such as CO_2, NO_x and SO_x emanated from fuel burning to supply heat to units inside an oil refinery, need to be tumbled down. A number of control strategies can be applied in order to mitigate emissions and meet certain environmental regulations. For example, installing additional control measures for existing pollution sources including chemical capture process such as MEA, physical adsorption in solid and liquid, membrane separation [7, 8, 6, 7]. Another strategy that can be applied is related to increasing production from sources that emit less emissions. For instance, one option to reduce CO_2 emissions is by considering non fossil fuel, such as Biofuels. Another method worth noting is load shifting which considers refitting production throughput across the refinery units for the seek of emissions reduction [9].

It has become a visible fact that preserving an appropriate air quality generally involves use of various complex methods of management to deal with diverse interrelated air quality concerns [10]. In this regard, there have been a number of air dispersion models that are have been developed to envisage the diffusion of industrial air discharges and the successive pollutant concentrations in nearby regions, such as AERMOD [11], Lagrangian puff (CALPUFF [5])and Industrial Source Complex (ISC3 [12]) models.

Typically, complexity of the management methods may get through a considerable time and cost elements. As an outcome, the dispersion models are used as substitute tools to assess diverse emanation control settings. Those may be applied for approximation of the whole contaminant concentrations for precise geographic locations and time zones. In addition, these can be worn to comprehend the interfaces of an emission resource and geophysical conditions. Furthermore, we can obtain benefit of those models to find out the ecological exposure to the contaminants and evaluate the health measures related to it [13].

It is considered important to decide the model that may satisfy the prerequisites of the study since no certain model can deal with all the situations and the relevant implementations [14, 15]. This project is aimed at using three different air dispersion models (SCEEN3, Gaussian, and CALPUFF) to foresee the concentration of unintended discharged from an oil refinery.

1.2 Research Objectives

This research aims to determine the best strategy for a refinery to comply with a given CO_2, N_Ox, and SO_x reduction targets while keep the cost to a minimum and meet a desired production level. We implement this idea for multiple pollutants management and mitigation plans on a single site industrial-scale refinery planning problem.

By using air dispersion models, we can estimate the concentration of pollutants released from oil refinery, identify the effect of meteorological conditions on pollutant dispersion, and compare the different dispersion models as tools for estimating concentration and dispersion.

1.3 Organizations of the thesis

The remainder of this thesis is organized as follows. Chapter 2 provides a general overview of oil refineries and their operations modeling, presents previous studies conducted on emission mitigation strategies, and mentions pervious efforts in developing air dispersion models. Chapter 3 presents the development of a mathematical model for an oil refinery with consideration to multiple pollutants reduction alternatives and demonstrates the performance of the model through various emission reduction levels. In Chapter 4, we investigate the dispersion of air pollutants that are omitted from oil refinery. Finally, we draw our conclusions and discuss potential future work in Chapter 5.

Chapter 2

Background and Literature Review

2.1 Introduction

The major greenhouse gases are generated by diverse sources and different industrial sites. Stationary resources symbolize a chief supplier to carbon dioxide release in Canada. These immobile sources include burning of any carbon loaded fuel, either to produce electricity or to provide energy for various different units in a plant, such as an oil refinery. The oil refinery and power generation industries yield about 37% of total CO_2 emissions in Canada [1]. Petroleum production and refining play a principal role in the recent world economy. It provides a stand to convert raw resources into many indispensable products for our daily life necessities, extending from transportation to elementary components for synthetic rubbers, plastics and many other products. The financial evolution and amassed populations is likely to retain the global requirement for such products great for the predictable forthcoming ages. As per the International Energy Agency [16], petroleum forms up 42.3 percent of the entire world energy consumption. Almost, a half of the petroleum consumption will be in the transportation sector during the period of 2003 to 2030. The industrial sector, accounts for a 39% of the projected increase in world oil utilization, typically in chemical and petrochemical developments [16]. In order to meet such claim, one will need great savings and appropriate optimization tools for the planned development of these productions.

The race in the marketplace is another demanding reason for corporations to chase reliable plans obtaining a viable edge, with the pursuit for prospects to advance their coordination and collaboration. Authors in [17] demarcated two different types of coordination, called: a general Coordination and Multi-plant Coordination. The former class reflects the issue of incorporating different happenings of the manufacture and delivery.

The Multi-plant Coordination primarily addresses manufacture scheduling complications. Those strained the importance and necessity to advance the development and design all-purpose and perfect frameworks for Multi-plant Coordination. The earnings anticipated after the coordination of manifold spots are in terms of expenditures and in the form of marketplace efficiency and responsiveness. Many of the preceding plans development researches have concentrated principally on limited supply chain grids and did not deliver a full analysis of an business as a total [18]. Additionally, they concentrated on the coordination of the numerous scheme levels of a enterprise with a few care on providing with an outline for the coordination of the scheduling level at various locations through procedural system incorporation.

Though, bearing in mind such extraordinary planning decisions, particularly with the present instable marketplace situation, needs understanding of uncertainties influence. In production scheduling, bases of the uncertainties is characterized as short term and long-term based on the degree of time horizon [19]. The short term uncertainties mostly refer to operative dissimilarities, apparatus failure and etc. While, the latter uncertainty involves supply and demand relation changeability and value variations [20].

Scientific uncertainty in the amounts, which can be seen on the basis of forecasts of production and inconsistency in the implementation of revenues, is an additional feature significant uncertainty [20, 21, 22, 23]. Alqhatani [20] studied the growth of the overall planning and related issues, said that the greatest challenges in the future; i) the development of genuine integration and harmonization between the different models of planning and forecasting in a multi-site / single, ii) uncertainty in modelling systems random processes satisfying and models, and iii) development the organization algorithms well organized and developed expressly to provide the proper planning techniques resulting and associated problems.

The Canadian Regulatory Analysis Guide [24] outlines the all-purpose methodology and analytical ladder to carry out a cost-benefit analysis of oil refineries using pollutants emission reduction strategies. To make the Guide operational, a case study has been organized following the methodical approach given by the Guide. The case study enables to identify the substitute choices and then a cost-benefit analysis is performed to assess the alternatives.

2.2 Oil refinery Overview

Initially a refinery plant was erected in Titusville, United State, in 1860 [25]. At that time, Refineries used batch distillation in order to distinct fuel, heating oils and fuel from crude fractions. Through the years, refining distillation was achieved by batch system. Nonetheless, beside the rise in oil production and its demands, constant refining turned to be a need. The first extensively documented refining plants arose about 1912 [26]. Beside the multiplicity and complication of oil production demands, refining processes have advanced from a straightforward treating units to more complicated fabrication plant. The contemporary oil refinery is an extremely sophisticated engineering site. Generally, the classic petroleum refinery looks like a maze of pipes with dispersed procedure components covering extremely high apparatus and huge storage tanks. Petroleum refining has advanced unceasingly in reaction to altering customer need to improved as well as diverse products. There are usually no two oil refineries are undistinguishable. It is exclusivity restricts largely by the topographical site of the refinery, and jointly with the refinery course configuration, defines how capably crude oils is transported to the plant and harvests to the marketplaces. The numerous procedures that combined to the present oil refinery is discussed here. A simple flow diagram of an oil refinery is shown in Figure 2.1 [25].

An important purpose of refining process is to upshot chemical reactions of the treated hydrocarbons. Usually, the affect are done at great temperatures in the 300-550^{o}C (600-1000^o F) range based on the method, and at high pressures, e.g., 3,000 psi (20 MPa). The methods containing reactions will characteristically integrate a fraction to separate the reactor waste into different product paths. One of the main refinery processes is a crude distillation which is for fractionation only [27]. A broad explanation of a refinery treating component is that the feedstocks are driven, warmed through heat with reactor effluent, and lastly exited through heat exchange in a furnace before inflowing the distillation tower. The distillation waste is air-conditioned via heat exchange, fractionated into the anticipated products via distillation. [27, 28].

A detailed explanation of crude oil is set before discussing refining processes. Crude oil is a mixture of organic molecules of hydrocarbons of 1 to 60 carbon atoms restrictions.

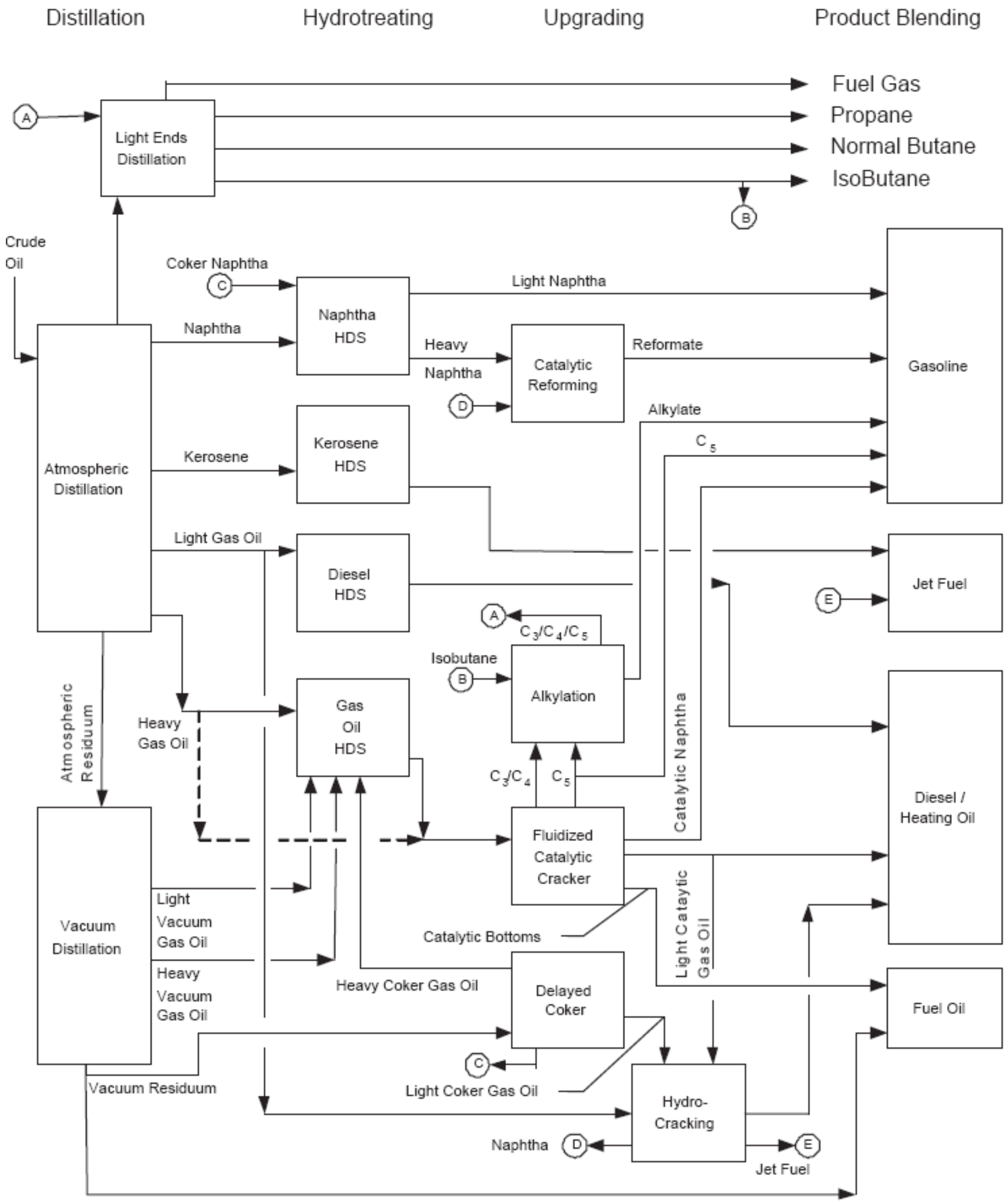


Figure 2.1: Simplified refinery process flow diagram [2]

The refining process uses elements, catalysts and pressure for different groups of similar molecules. The refining process also rearranges its assemblies and connection standard in various hydrocarbon compounds. Thus, instead of the hydrocarbon type whole specific chemical which is important in the refining process. Compounds of paraffinic hydrocarbons are saturated compounds based on carbon, without double bonds. They are long and restrictions isomers. Compounds of aromatic hydrocarbons are organic compounds that have the type of ring structure. All complexes have at least one aromatic benzene ring. Naphthenic hydrocarbon groups are immersed settled in the formula closed rings and in all parts of crude, excluding the lighter. These are the three series of naturally fall in crude oil. Other hydrocarbon moleculess are formed during the refining process (cracks), such as alkenes (ethylene, or ethylene) and alkynes. All of these compounds are unsaturated. Other substances other than oil or molecules that can exist in crude oil are sulfur compounds, oxygen compounds, nitrogen compounds, trace metals, salts (such as NaCl) and carbon dioxide.

Elements in crude oil such as non-carbon/hydrogen are the most unwanted in refinery processing, which as detached in whole or in part from hydrocarbons are separated. One of the key properties of hydrocarbons, including crude oil is heated to boiling point [28] . A real boiling point curve at atmospheric pressure has been chosen where the liquid evaporates at different temperatures to tabulates percent by volume of crude oil. Generally hydrocarbons elements is separated boiling points by at least 60^oF (15^oC) and more than 1200^oF (650^oC).

Crude oil is assembled into broad categories, is generally restricted on geographic location of origin, the sulphur content in the crude or based the density of the crude oil. For example, sulphur crudes scars more than smaller sulphur oil. In order to ensure adequate life expectancy for the treatment of advanced herds sulphur unit is to identify the device from the refineries expensive mixture having a corrosion resistance higher than raised [2]. If you combine two herds, a higher bulk density is a low API gravity degree compatibility. For example, crude oil at 35 API is denser than 40 API crude oil. The Elders of crude oil are the results of laboratory tests showed many segments around the crude oil or crude oil [28]. These tests describe a crude and allow refineries to assess the feasibility and cost-effectiveness of processing certain crude oil refinery. The elders of crude oil vary greatly in the level of detail. However, the potential interest in the product and raw full various fractions of the crude oil are presented in the essay. All divisions within an oil refinery, may fall into the following categories [2].

2.2.1 System Configuration of Refinery

A refinery is composed of numerous different components that constitute whole production system, as shown in Figure 2.2 .

Crude Supply and Blending This part contains receiving amenities and a container area where all crude oil kinds are expected and blended or sent straight to the production system.

Production Units Production units separate crude oil into diverse fractions, upgrade and cleanse some of these cuts, and convert heavy portions to light, more valuable fractions. It also embraces the utilities which deliver the plant with fuel, flaring capability, steam, cooling water, sweet water, compressed air, nitrogen, etc, all of which are essential for the refinerys safe process.

Product Blending and Transportation In this part ultimate products are treated

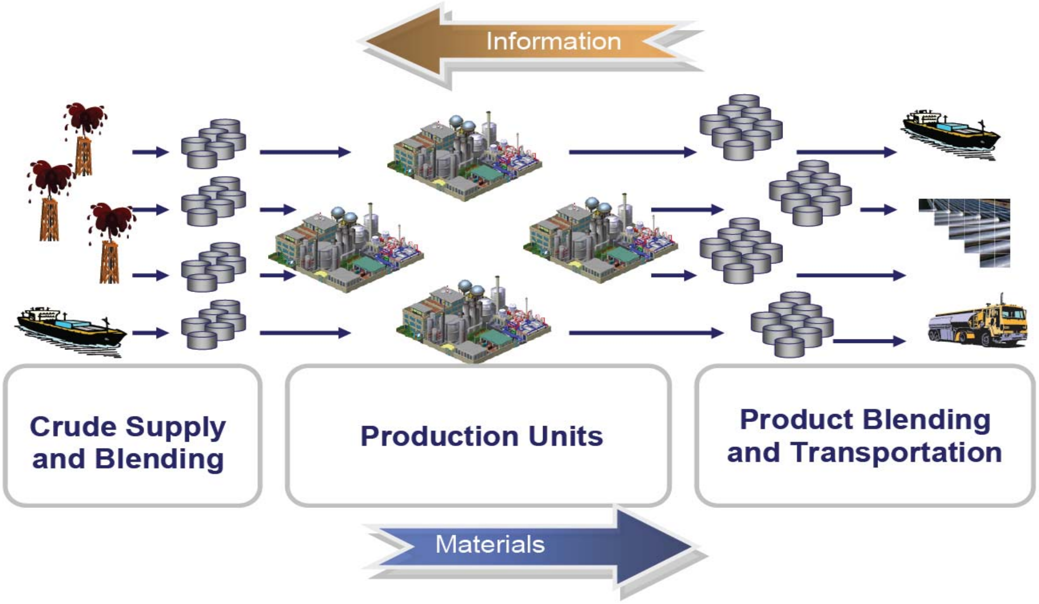


Figure 2.2: Diagram of standard refining configuration [3]

according to either a prearranged formulae or to a definite product specifications. This facility also includes the dispatch of finished products to the clients.

All components inside an oil refinery can fall into one of the following four classes [2]:

- Fractionation or Distillation
- Hydrotreating
- Upgrading
- Product Blending

2.2.2 Fractionation or Distillation

Splitting uses a mass separation process called distillation, in which distilled the raw material in several areas of cuts or freestanding different hydrocarbon compounds boiling point. Distillation usually by hitting a temperature profiles through the tower so that variations in the compositions of the symmetry of the mist and the liquid phase to the structures done to change in the distillation column [28],

Distillation consider on materials that has lower boiling points which are reside below the top of the tower. Lowest boiling point products are vapor above the tower and are condensed into a distillates. High boiling point materials exist along down the tower. The liquid phase flows through the tower by gravity. Additional boiling streams may be reserved at different levels of the tower as a side stream products. The maximum boiling range products are taken over the bottom of the tower [25].

The primary refinery procedure component is a crude distillation component. It contains a distillation tower, which is also called a vacuum distillation unit. The crude oil (or mixture) that exemplifies the feedstock to the distillation tower is sent from storage containers to heat exchangers in order to pre-heat it to around 250^{o}F (120^{o}C). Crude oils comprise considerable quantities of inorganic salts, which may trigger downstream decomposition. Emulsifying the crude oil with water to desalt the crude oil. The salts will dissolve in water and the saltwater stage will then separate after the oil stage and reserved. More preheated is done to the crude oil to the extreme temperature (500-550^{o}F or 260-290^{o}C). Lastly, the temperature reaches almost 750^{o}F (400^{o}C) in a furnace and supply the curd oil to the distillation unit. The mutual portions reserved from the distillation tower are diesel, naphtha, kerosene, gas oils, and residual.

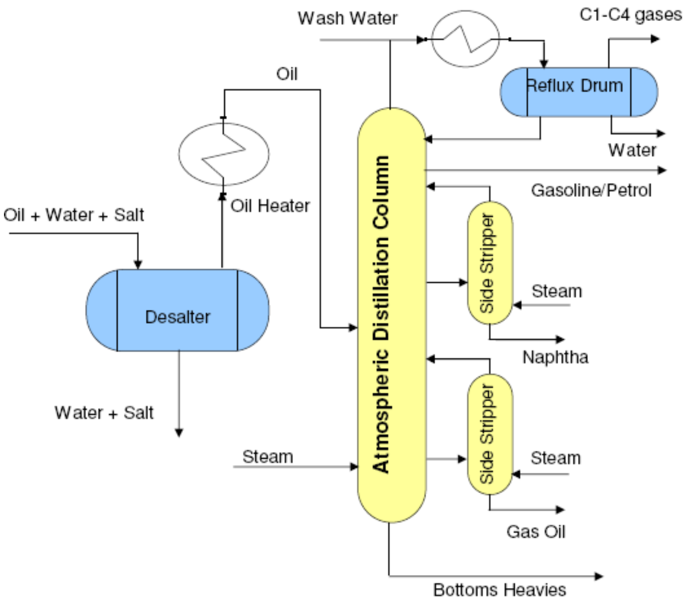


Figure 2.3: Crude distillation [4]

Figure 2.3 gives a sketch of a crude distillation unit with the chief products. An atmospheric distillation unit works usually at atmospheric pressure. The maximum process temperature in the atmospheric distillation unit is approximately 750^{o}F (400^{o}C). At temperatures above 750^{o}F (400^{o}C), thermal cracking of the petroleum into light gases and coke occurs [2]. Coke is essentially pure carbon in a solid form. The presence of coke is undesirable in refinery process units because solid coke formation fouls refinery process equipment and severely reduces equipment performance. The residual stream is usually further fractionated in a vacuum distillation tower. Hydrocarbons existing as a liquid at a given temperature at atmospheric pressure will boil at a lower temperature when the pressure is sufficiently reduced.

Figure 2.3 is a chart of a crude distillation unit with the fundamental items. A atmospheric refining unit for the most part works at atmospheric pressure. The most extreme procedure temperature in the atmospheric refining unit is around 750^{o}F (400^o C). At temperatures above 750 ^{o}F (400 ^{o}C) heat splits petroleum into light gases [2]. The presence of coke -coke is basically pure carbon in solid form- in the refinery process unit is undesirable due to the equipment performance limitations. Hydrocarbons existing as a fluid at certain temperature at atmospheric pressure[27, 28].

Refining/fractionation does not deliver alluring refined products in light of the fact that impurities have not yet been removed. Henceforth, the items from refining are changed into more useable products however different transformation processes occur. This is done after treatment routines, for example, hydrotreating to evacuate impurities to enhance products quality. Lastly, a mixing operation is completed to add additives substances to with particular properties. Numerous operations can be performed on the products to have compounds that meet particular requirements. Thusly, there are no end limitations in the refining procedure [27, 28].

2.2.3 Hydrotreating

Hydrotreating is an operation that is carried out to eliminate 90% of pollutants like nitrogen, sulphur and metals by liquid petroleum segments. If these are not taken out from the fuel via the refinery dispensation units, may have harmful impacts on the apparatus, the catalysts, and the eminence of the ended production [27]. Hydrotreating is the a mutual procedure configuration used to eliminate the sulphur from the transitional creek. It may similarly decrease the stages of nitrogen limited in the stream [2]. Additionally, some metals can be detached after the hydrocarbon stream through the hydrotreating process.

Hydrotreaters might be chosen to unceasingly process or an alternate dispensation of diverse feed streams. In hydro-treating process, hydrogen is diversified with hydrocarbon and contacted with catalyst in a reactor container at a adequately great temperature to influence the hydro-desulfurization reactions [27].

2.2.4 Product Blending

Refinery products are the outcome of a blend of numerous parts found. Much of the time, the product blend is affected by controlling the measure of blend parts of each of the storing tank segments, which are blended into the completed product storing tank. Samples of the last blend are then checked by lab tests for all product specification before delivery. Specifications differ by product, yet more often are density and sulfur content specification [2].

Taking fuel as a sample since it is the real product from an oil refinery, engine gas has various specifications that must be fulfilled to enhance the functioning of our engine vehicles. The most generally perceived gas specification is the octane number. Gas is normally retailed in ordinary evaluations, mid and premium, which are separated by the posted octane number. Tragically, the desulphurized light and substantial naphtha divisions of rough oils have low octane numbers. The naphtha part is around 50 (R+M)/2. Illustrations of other product particulars incorporate Cetane number, Reid Vapor Pressure, Smoke Point, and so on. Large portions of these item specification do not mix directly by part volumes. In these circumstances, the completed mix properties are anticipated utilizing knowledge-based calculations for the material blendstock parts. These calculations are extremely refined and their accuracy is completely basic for in line mixing [2].

2.2.5 Upgrading

Upgrading is a term related to refinery handling which altogether increases the market revenue of the hydrocarbons processed. This is achieved through synthetic responses to yield more attractive hydrocarbon mixes. The upgrading responses result in either enhancing product specification qualities or reorganizing the molecular structure so that the hydrocarbons boiling in a more attractive boiling range. The upgrading units include catalytic reforming, fluidized catalytic cracking, hydrocracker, Isomerization, polymerization, and alkylation. The catalytic reforming is the procedure to change the structure of molecular for naphtha to enhance the high-octane components while lowering the rate of low-octane components [2, 29, 30]. The fluidized catalytic cracking (FCC) procedure changes over heavy gas oils into lighter products which are then utilized as blendstocks for gas and diesel fuels [2, 25]. The hydrocracker is a similar procedure to FCC to the degree that this procedure chemically breaks the substantial atoms that include gas oils by separate them into littler particles which boil in the gas, plane fuel, and diesel fuel boiling reaches [27]. Isomerization is identical to catalytic restructuring; the hydrocarbon are reorganized, but dissimilar from catalytic reforming, isomerization only changes usual paraffins to iso-paraffins [27, 25]. Polymerization in oil refinery is the process of changing olefin, for example, ethylene and butylene into the hydrocarbons with more molecular weight [27, 2]. Alkylation joins low-molecular-weight olefins with isobutene in occurrence of a catalyst. The product is named as alkylate and is consists of a blend of higho-ctane, paraffinic hydrocarbons, which is considered a premium combination stock since it has extraordinary antiknock possessions and burns fine [27, 2].

2.3 Refinery Emissions

Refinery air emissions can be categorized as either hydrocarbons, for example, fugitive and volatile organic compounds (VOC), or combustion products, for example, NO_x, SO_x, H2S, CO_2 , PM and others. At the point when taking care of hydrocarbon materials, there is a potential for emanations through seal leakage or by evaporation from any contact of the material with the outside environment. Consequently, the essential hydrocarbon discharges originate from piping system fugitive escapes, product stacking, atmospheric capacity tanks and wastewater gathering and treatment. A refinery utilizes extensive amounts of energy to heat process streams, advance compound reactions, and give steam and create power. This is normally proficient by burning of fuels in boilers, heaters, heaters gas turbines, generators and the catalytic cracker [31]. This results in the emission of product burning. Nevertheless hydrocarbon losses and centre combustion emissions, refineries emit little amounts of particular compounds maybe that ought to be reported if threshold limits are exceeded. Controls on core emissions might be efficient in this respect. For instance, dust controls are successful for decreasing emissions of heavy metals, VOC controls are viable for particular hydrocarbons, for example, benzene) [32] .

2.3.1 Potential Emissions Impacts

Administration of refinery emissions is attentive around meeting local and national air quality standards and guidelines. Air quality standards and guidelines are expressed as concentration limit values for specific averaging periods. The real concentrations created rely on upon the attributes of particular site emission and on the nearby meteorological conditions. Standards limit might similarly apply where long range or local contamination is of concern. Here, the particulars of the site emission are irrelevant however the total site emission of specific pollutants may be subject to a national or regional emission reduction plan. The reason for air quality standards and guidelines is to protect the human population from aggressive effects of contamination from all sources. The justification behind particular standard qualities can be found in, for instance, the specialized documentation for the World Health Organization Air Quality Standards [33]. Not every single pollutant concentrations can be straightforwardly connected to basic source emissions. NO_x and unstable natural mixes (VOCs) can respond in the lower air under suitable conditions to make higher than natural environmental concentrations of ozone. A provincial or national emission control plan is expected to manage such long-winded ozone occasions.

2.4 Emission Control Plans

Administrative organizations can determine air contamination emission limits and control requirements in different ways. These incorporate limits on the amount of a pollutant that may be emitted, the acceptable concentration of the emission, the resultant local ambient concentration, objective emission reduction, and particular monitoring techniques, etc. In some cases, more than one of these emission limits and control requirements are connected to the same source. Regulation on emission control strategies might likewise be given, for instance data on effectiveness, expense and applicability.

Much of the time, the control situations are not one of a kind. They are frequently taken from different countries that have entrenched national air pollution reduction programs [34]. It is common that the more stringent control requirements have a tendency to be propagated. In various areas, facilities must apply what is frequently called best available technology (BAT) and best environmental practice (BEP). The meaning of BAT and BEP can vary from office to office, yet it for the most part refers to advanced economically available control equipment, plans, standards or practices that are technically and economically applicable. The expense adequacy of executing a particular control ought to be evaluated, especially where a retrofit to a current unit is concerned.

2.4.1 NO_x/SO_x Mitigation Through Decreasing Carbon Emission

For the most part, two situations are considered to check CO_2 emissions. The Organization for Economic Cooperation and Development (OECD) [35] mutually balance out carbon emissions at countries$'$ 1990 levels. The second situation relates to the joint adjustment of emissions by the major CO_2 emitters: the OECD locales, the previous Soviet-Union and Eastern Europe, China and India. The adjustment of carbon emissions in the OECD obliges a carbon tax rising from approximately 80 dollars for every ton of carbon in 2000 to 170 dollars by 2050. In OECD countries/regions, carbon emissions are decreased by around 50 per cent with respect to Baseline levels toward the end-period. This speaks to a 18 per cent cut in world carbon emissions. The induced changes in local NO_x and SO_x emissions extent somewhere around 37 and 65 per cent decreases with respect to baseline.

Emission reductions for SO_x are to some degree higher than for NOx. The clarification of the diverse overflow is identified with the relative effect of the energy substitution and conservation impacts. NOx emissions are mainly found in the transportation sector where there are little substitution potential outcomes among powers. Emission cuts are then for the most part determined by the general decrease of energy consumption. For SOx, the key division is power era. In this segment, there is a bigger capability of substitution from high-sulfur fuels, similar to coal, towards oil and natural gas. This impact cumulated with energy conservation clarifies why there is a higher emission overflow in the case of SOx. The adjustment of carbon emissions in the group of significant emitters induces a decrease of 45 per cent of world carbon emissions by 2050. NO_x emissions are cut by roughly the same amount. SO_x emission reduction reaches 55 per cent with respect to baseline. It is important that, as on account of CO_2 , a critical reduction of NOx/SOx at the world level must be achieved by the participation of the main non-OECD emitters [36] .

2.4.2 Source Emission Limits

Regulating emissions by putting a on the cumulative amount of a pollutant released in a given time can unclear environmental performance in light of the fact that correlation of diverse facilities of distinctive sizes or capacity is not effortlessly made. It is desirable to put a concentration limit where it is stated at some standard condition. The limit can be set for an individual source, a group of similar sources or for the whole facility. Normal applications of this kind of limit are for SO_x, NO_x and particulate matter (PM) from burning sources and for hydrocarbons from procedure vents or from product stacking operations.

Consideration must be taken to control units for ambient air concentration limits in light of the fact that documentation can be befuddling, especially if estimations are referred to in volume units and the standards in mass units. Mass units are essentially stated at one atmosphere and 0^oC, and a scale is utilized. An averaging time must be determined, and a few standards have more than one period indicated. Regular periods are hourly, daily, and yearly. As coupling to the limit, and perceiving that concentrations in the air are exceedingly variable, a certain number exceedances may be permitted. The limit of confinement may be identically stated as a percentile of suitably averaged concentrations instead of a general maximum. Dispersion modeling can be utilized to perform an ambient air quality impact evaluation to foresee how the maximum expected concentrations from a source will contrast with ambient concentration standards. Air quality monitoring can be utilized to clarify on real concentrations, particularly where sources separated from a refinery, for instance movement, are available and overwhelming.

2.4.3 CO_2 Capture

Since oil refineries add to around 37% of Canada CO_2 emissions, CO_2 capture and storage processes have been seen as a potential answer for accomplish profound reduction of CO_2 from these areas. The objective of CO_2 capture and storage is to isolate the CO_2 from its sources in suitable structures for transportation and sequestration. When CO_2 is capture, it should be pipelined and put away safely and for all time. In this way, the relevance of CO_2 capture innovations to power plants must be assessed in an absolute's setting framework including capture, transportation and storage. A large portion of the research found in the literature has concentrated on CO_2 capture from power plants however the innovation would not change if it is connected to flue gas from an oil refinery.

2.5 Air Quality Dispersion Models

Dispersion models are mathematical models of the behavior of air pollutants in the atmosphere. The fundamental aim of the dispersion models is to accurately estimate the pollutant concentration downwind of any source for a wide range of meteorological conditions [37]. There is a range of air dispersion models that have been used in different jurisdictions around the world to treat a wide array of modelling circumstances. They have been constructed to assess various source kinds including point, area, and volume, various terrain, various locales such as urban, rural, various emission rates include plume, puff and various meteorological conditions. Air dispersion models have many features that cause them to be used in different investigations of air quality. They have the ability to elucidate the interactions of emission sources and the geophysical and meteorological conditions [38]. Moreover, using the dispersion models, it is possible to: determine whether a permissible facility is obeying with state or federal necessities, evaluating where the best location site for an air monitor that reads actual data, etc. (MDCA, Citizens Guide to Air Dispersion Modeling, 2002), and finally, to estimate the possible environmental and health effects due to releases from industrial or trade locations .

There are two types of dispersion models used in air quality studies: steady state and non steady state.

2.5.1 Steady State Model

Steady-state models are usually called Gaussian plume models. These are constructed on the mathematical approximation of the plume conduct and are the simplest models to use [39]. They estimate the pollutant concentrations for each hour, supposing that the meteorological conditions are even through the modeling domain. They assume that the plume center line moves straight to the end of the modeling region despite if it could really do that at the specified wind speed [40]. For instance, if the wind velocity is 6 km/h, the plume has to tour a distance of 6 km in an hour simulation period. However, a plume dispersion model presumes that the traveling distance of plume to the end of the modeling location could be 20 or 30 km. They also do not have memory of former hour's emission.

Thus a plume traveling in a windy route over several hours cannot be simulated [38]. As a result of the steady state, and straight-line features of these models, they obviously do not account for the bent plume trajectories and inconstant wind conditions that occur in complex flow circumstances. Furthermore, these models have a limited capacity to handle low wind speeds.

Although the limitations of the steady-state models, they can deliver realistic outcomes when used properly. Lately, superior methods of depicting the spatially changing turbulence and dispersion properties within the mesosphere have been developed. The recent dispersion models embrace an additional advanced way to describe dissemination and dispersion using the basic characteristics of the atmosphere instead of depending on general mathematical calculation. This allows for better management of challenging circumstances such as steep rugged topography and far transportation [41]. There are numerous steady-state models that are commercially accessible for air dispersion model.

2.5.2 Non-Steady State Models

Non-steady state dispersion models are usually called puff models advanced models (unsteady-state models). Puff models can handle the two drawbacks of plume models . Puff models discharge emissions independent of the source, allowing the puff to counter the meteorology directly around it. This also permits puffs to be traced through multiple testing periods until they have either totally diluted or have been tracked throughout the entire modeling area and out of the computational zone[42, 43]. In addition, they can describe the accumulation of pollutants during tranquil conditions, the bent paths of plumes, and the effects of causality (where the former location of the plume is accounted for to define the present plume location). Although these models have the advantage of permitting meteorological conditions (winds, turbulence, vertical temperature construction) to alter across the modeling domain, they demand more computing power because they trace puffs that represent incoherent quantities of pollutants over time. In this way, puff models have a more accurate display of dispersion than plume models. There are models that treat emissions as a series of puffs such as the CALPUFF model and advanced model [37].

2.5.3 Factors Affecting Air Dispersion

Odor dispersion is affected by many factors that include: 1) meteorological conditions; 2) geography; 3) source of odor release; 4) the position of the receptors to the source including distance and direction; and 5) the odor sensibility and the acceptance of the receptors [44, 45]. However, the weather conditions, including, wind speed; wind direction; temperature; and atmospheric stability classes, and the topography of area are the dominant factors for air dispersion. Because the weather condition is variable and an essential input of air dispersion models, it attracted scientists attention when performing researches associated to odor dispersion. There are several studies that have been conducted using atmospheric dispersion models to investigate the effect of weather parameters on the dispersion of different contaminants. Authors in [46, 47] used the CALPUFF model to investigate the effect of geophysical and meteorological conditions on the dispersion of nitrogen dioxide (NO2). Author in [48] identified the impact of the meteorological variability on O3 and SO4 2 NO3 NH4 plus concentrations in East Asia using the 3-D global chemical transport model. Authors in [49, 50] explained the role of turbulence on the carbon monoxide (CO) pollutant distribution in their study; they used the Chilean Air Pollution Dispersion Model (CADM). Also, [51] evaluated the performance of two dispersion models AERMOD and CALPUFF to examine the impact of wind direction on the odor dispersion around a pig farm-building complex. However, very limited studies have been performed to investigate either the dispersion of pollutant emissions that accidently release from biofilters or the impact of the atmospheric and topographic conditions on the pollutant concentration.

Chapter 3

Cost Optimization Model with Emissions Mitigation Targets

3.1 Introduction

This chapter addresses the development of a mathematical model for an oil refinery with consideration to multiple pollutants reduction alternatives. The objective of this study is to help decision makers of oil refineries to select the best pollution control strategies that can be achieved for a given emission reduction target. Furthermore, the model is useful for selecting alternative plans in various conditions, such as proposing new sources of emissions or changes in environmental regulations. The model is demonstrated by a refinery with industrial scale operations and has three emissions including nitrogen oxides (NO_x), sulphur dioxide (SO_x) and carbon dioxide (CO_2). To summarize, the ideal strategy is controlled by economic and market sector analysis (to maximize the profit), but should take into account compliance with environmental regulations (air quality standards).

The remainder of the chapter is organized as follows. In the next section, the problem statement of the petroleum refinery planning problem is presented with detailed mathematical formulation. In section 3.3, an air emission sub-model is developed to optimize the overall costs when controlling pollutants. Finally, several experiments have been conducted and presented in section 3.4, to validate the performance of this model.

3.2 Mathematical Optimization Model

The representation of the oil refinery considered in this study is based on the state equipment network (SEN) as shown in Figure 3.1 [52], which is adapted from the work done by Elkamel and Al-Qahtani [53, 54]. Three elements categorized this representation, including state, task and equipment. State represents all streams in a process, which can be categorized quantitatively (i.e. flow-rate, temperature and pressure), qualitatively (i.e., phases of the streams), or in both ways. Any physical or chemical transformation that occurs in consecutive states is represented by a task. Finally, equipment represents any physical device that performs a given task.

The refinery model adapted in this dissertation is based on a single refinery site and uses only one type of curd oil source. The material streams used in this model are divided into four types, namely: raw, intermediates, final products, and fuel. Mass balances are assumed to be applied for all material balances. However, volumetric flow rates are carried out in the case where quality attributes for some streams only blend by volume. The refinery model is initially formulated as a mixed integer linear program (MILP). Selecting the ideal pollutants control strategies are achieved using binary variables, which add nonlinearity to the model, and linearized by defining components' flows instead of individual

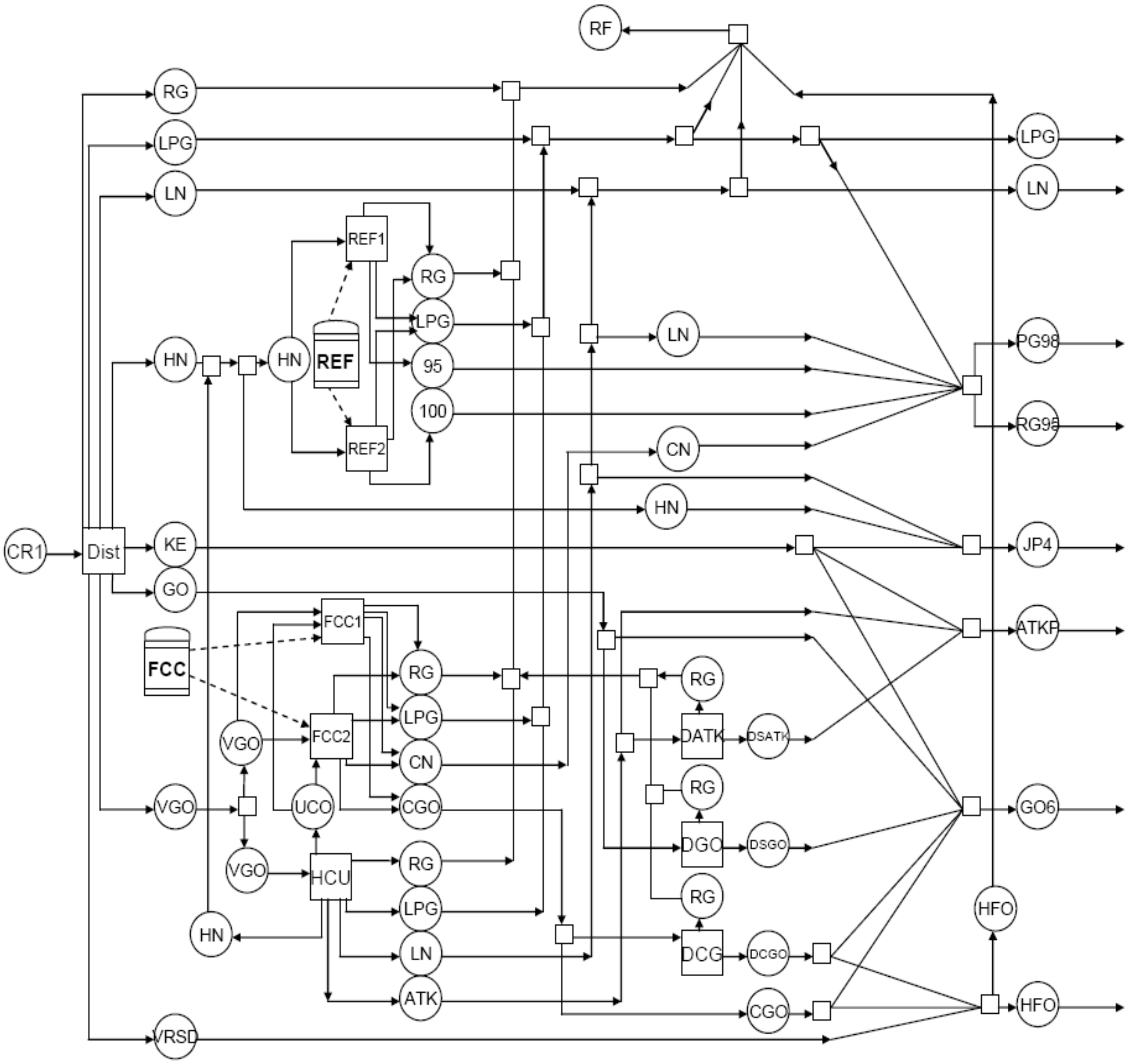


Figure 3.1: A schematic diagram of the refinery using SEN representation

flows [54].

Before introducing the mathematical model for the oil refinery that selects the best pollution control strategies for a given emission reduction target, we first start with the development of refinery processing units. In order to make the operation of a refinery profitable, optimization of different intermediate and final products are required. The model attempted in this chapter aims to minimize the annualized cost associated with raw material costs and operating costs with specific properties constraints.

The refinery modeling problem addressed in this chapter can be stated as follows: *What is the minimal annual cost of the oil refinery in order to meet a given product demand and specifications?* The mathematical statement of the problem above consists of minimizing an objective function while observing equality and inequality constraints. This problem is modeled mathematically as follows:

Objective Function:

The objective function of this model is to minimize the annual refinery cost including crude oil cost, refineries operating cost, and export revenue, and is expressed as follow.

$$Minimize \sum_{cr} \sum_{1} SR\, cost_{cr} + \sum_{p} WOcost_{p} \sum_{cr} \sum_{1} z_{p} - \sum Xpr_{cfr} ex_{cfr} \tag{3.1}$$

The given objective function represents a minimization of the annual cost which is consist of oil cost $cost_{cr}$, operating cost $WOcost_{p}$, and the revenue of exports $Xpr_{cfr}ex_{cfr}$. The operating cost is assumed to be proportional to the inlet flow process and it is given on per annum basis.

The constraints related to this objective function are divided into equality and inequality constraints and are explained bellow:

Equality constraints:

The first equality constraint is related to the intermediate material balances which can be expressed in expression 3.2.

$$\sum_{p} \alpha_{ip,p}\; z_p - \sum_{cfr} w_{ip,cfr} - \sum_{rf \in Fuel} w_{ip,rf} = 0 \;\forall\; p = 1,\; and\, crude = 1 \tag{3.2}$$

The coefficient, α_{ip} can either be a positive, if it is an input to a unit or a negative, if it is an output. It will ensure that the intermediate streams are either consumed in the in the refinery fuel system $w_{ip,rf}$ or final product pool $w_{ip,rfr}$.

Another equality constraint is related to the throughput of raw materials, it demonstrates the refinery raw materials balance in which throughput to each refinery crude distillation, considering one plant and one crude type that is equal to supply $S_{cr=1,\,p=1}$, as given in Eq.3.3

$$z_p = S_p \qquad \forall\; p = 1,\; and\, crude = 1 \tag{3.3}$$

The material balance of the products af_{cfr} in a refinery is defined as the difference between flow rates from intermediate steam $w_{ip,cfr}$ that contribute to the final product and the streams that contribute to fuel system as given in constraint C given in Eq.3.4.

$$\sum_{cr}\sum_{pi} w_{ip,cfr} - \sum_{cr}\sum_{rf \in Fuel} w_{rf,crf} = af_{cfr} \;\forall\; p = 1,\; and\, crude = 1 \tag{3.4}$$

The mass flow rate xf_{cfr} is converted to volumetric flow rate ,avf_{cfr} and dividing it by individual specific gravity $g_{ip}$for ip (intermediate stream). As a few quality attributes blend only by volume in the products pools. This constraint is expressed in Eq. 3.5 as follow:

$$\sum_{cr}\sum_{pi}\frac{w_{ip,cfr}}{g_{ip}} = avf_{cfr}\ \forall\, all\ cfr \tag{3.5}$$

In the next Constraint in Eq. 3.6 the fuel system material balance is represented. The term is the caloric value equivalent for pi used in the fuel system at the considered plant. The fuel production system may composed of a single or a combination of different products. The relevant $\beta_{rf,p}$ matrix represents the consumption of a processing unit at plant under study.

$$\sum_{pi,Fuel} cv_{ip,rf}\, w_{ip,cfr} + \sum_{cfr,\,Fuel} w_{ip,cfr} - n_1 \quad = 0 \quad \forall\ cr = 1\, all\, Fuel \tag{3.6}$$

where, $n_1 = \sum_p \beta_{rf\ ip} z_p$

Inequality constraints:

The lower and upper bound on quality constraints for all products are consider to be one of inequality constraints and are represented in Equations (3.7 and 3.8), for all products, blend by volume $R = Q_{vol}$ or mass $R = Q_m$.

$$\sum_{cr}\sum_{pi}\left[atb_{pi,R=Q_{vol}}\frac{w_{ip,cfr}}{g_{ip}} + m_a\right] \quad \forall \geq q^k_{cfr},\ avf_{cfr} + q^k_{cfr},\ af_{cfr} \tag{3.7}$$

where, $n_a = atb_{pi,R=Q_m}\left(w_{ip,cfr} - \sum_{rf,\,Fuel} w_{ip,cfr}\right)$

$$\sum_{cr}\sum_{pi}\left[atb_{pi,R=Q_{vol}}\frac{w_{ip,cfr}}{g_{ip}} + n_b\right] \quad \forall \geq q^k_{cfr},\ avf_{cfr} + q^k_{cfr},\ af_{cfr} \tag{3.8}$$

where, $n_b = atb_{pi,R=Q_m}\left(w_{ip,cfr} - \sum_{rf,\,Fuel} w_{ip,cfr}\right)$

Maximum and minimum flow rate for each processing unit are expresses in Eq. 3.9. a zero-one matrix is shown by the coefficient δ_{op} for the assignment of production unit for $\mu\epsilon U$ for an operating mode $o\rho\epsilon OP$. As an example, the reformer is a production unit that can operate at high or low severity modes.

$$Min\, C_m \leq \sum_{p} \delta_{op} \sum_{cr} z_p \leq Max\, C_m \quad \forall\, \mu \in U \tag{3.9}$$

The final products is stipulated in Eq. 3.10 for each refinery af_{cfr} minus the exported amount E_{cfr} for each product.

$$\sum (af_{cfr} - E_{cfr}) \geq D_{cfr} \tag{3.10}$$

An upper and lower bound is set by the imports or resources as given in Eq. 3.11 as per available feed-stock to the refineries. Its lower bound is useful for a situation where there is a protocol to exchange or supply oil (crude) between different countries.

$$IM^k \leq \sum S_p \leq IM^u \quad \text{for all}\, cr \tag{3.11}$$

3.3 Air Emission Optimization Model

The air emission sub-model is developed to optimize the overall costs of oil refinery when controlling pollutants that are generated during process unit operation. In this study three different mitigation techniques are covered for air emission reduction, as follows:

Table 3.1: Nomenclature

Symbol	Names	Symbol	Names
$w_{ip,rfr}$	final product pool	δ_{op}	coefficient
$w_{ip,rf}$	refinery fuel system	Ex	exportable product
α_{ip}	coefficients	E_{cfr}	exported amount
af_{cfr}	products of material balance	$n\epsilon N$	mitigation methods
$w_{ip,cfr}$	intermediate steam	EF_{rf}	emission factor
avf_{cfr}	volumetric flow rate	CF_m	fuel consumption
g_{ip}	specific gravity for *ip*	E_u	upper bound on emission
δ_{op}	matrix coefficient	$G_{u,t}$	binary number
Q_{vol}	products, blend by volume	$\varepsilon_{(cap.)}$	efficiency of capturing process
Q_m	products, blend by mass	$\phi_{u,t}$	upper bound cost
atb	attributes	$HC^{mi}_{u,t}$ and $HC^{pl}_{u,t}$	selected for cost $cost_{capture}E_{u,t}$
$o\rho\epsilon OP$	operating mode	$\varphi_{u,t}$	annual cost
$\mu\epsilon U$	production unit		

- fuel switching to reduce emissions from one type of fuel to another type of fuel, (typically shifting from fuel oil to natural gas).
- process load shifting to adjust the production across the refinery units for reducing emissions.
- implementation of various air emission capture technologies.

In particular, formulation of emission flow rate of a production unit $\mu \in U$ of a certain $t \in T$ pollutant over multiple mitigation methods $n\epsilon N$ can be given as:

$$E_{u,t} = \sum E_{u,t}\, G_{u,t} \quad \forall\, \mu \in U,\, t \in T \tag{3.12}$$

where, $G_{u,t}$ is a binary number that represents different mitigation schemes. The emission of all unit $\mu \in U$ is computed by multiplying the emission factor of each fuel by fuel consumption in unit that is related to inlet flow rate. Nonetheless, this formulation gives a mixed integer nonlinear program (MINLP) due to the multiplication of a binary by a continuous variable. Here, we again define $G_{u,t}$ in terms of switching or consuming with a bound on various emissions. Thus, the above equation 3.12 can be expresses as a set of inequality constraints. Furthermore, for the three mitigation a set of inequality constraints are found and in case of the load shifting alternatives the constraints are written as:

$$E_{u,t} \leq EF_{rf}\, CF_m + E^{pl}_{u,t} \sum_{switch} G_{u,t(switch)} + b \;\; \forall\, \mu \in U,\, t \in T \tag{3.13}$$

where, $b = E^{pl}_{u,t} \sum_{capture} G_{u,t(capture)}$

$$E_{u,t} \geq EF_{rf}\, CF_m - E_{u,t} \sum_{switch} G_{u,t(switch)} - g \;\; \forall\, \mu \in U,\, t \in T \tag{3.14}$$

where, $g = E_{u,t} \sum_{cap.} G_{u,t(cap.)}$

EF_{rf}, CF_m, E_u are the emission factor of each fuel and fuel consumption in unit and upper bound on emission respectively and the relevant constraints can be expresses as in Eqs. (3.15 and 3.16).

$$E_{u,t} \leq EF_{rf'}\, CF_m + E^{pl}_{u,t} \left[1 - \sum_{switch} G_{u,t(switch)} \right] + h \;\; \forall\, \mu \in U,\, t \in T \tag{3.15}$$

where, $h = E^{pl}_{u,t} \sum_{cap.} G_{u,t(cap.)}$

$$E_{u,t} \geq EF_{rf'}\, CF_m - E_{u,t} \left[1 - \sum_{switch} G_{u,t(switch)} \right] - I \;\; \forall\, \mu \in U,\, t \in T \tag{3.16}$$

where, $I = E_{u,t} \sum_{cap.} G_{u,t(cap.)}$

By applying a process of capture for a given production unit u can be written as:

$$E_{u,t} \leq EF_{rf'}\, CF_m \left(1 - \varepsilon_{(cap.)}\right) + E_u \sum_{switch} G_{u,t(switch)} + x_a \;\; \forall \mu \in U,\, t \in T \tag{3.17}$$

where, $x_a = E_{u,t} \left[1 - \sum_{cap.} G_{u,t(cap.)}\right]$

$$E_{u,t} \geq EF_{rf'}\, CF_m \left(1 - \varepsilon_{(cap.)}\right) - E_u \sum_{switch} G_{u,t(switch)} - x_b \;\; \forall \mu \in U,\, t \in T \tag{3.18}$$

where, $x_b = E_{u,t} \left[1 - \sum_{cap.} G_{u,t(cap.)}\right]$

$\varepsilon_{(cap.)}$ stands for the efficiency of capturing process. It is to be noted that for a certain production unit only one refinery fuel, one single mitigation method and a single capture process and is applied pollutant t and it can be, expressed as in equations below:

$$\sum_{switch} G_{u,t(switch)} \leq 1 \;\; \forall\, \mu \in U,\, and\, t \in T \tag{3.19}$$

$$\sum_{cap.} G_{u,t(cap.)} \leq 1 \;\; \forall\, \mu \in U, \text{ and}\, t \in T \tag{3.20}$$

$$\sum_{switch} G_{u,t(switch)} + \sum_{cap.} G_{u,t(cap.)} \leq 1 \;\; \forall \mu \in U,\, and\, t \in T \tag{3.21}$$

The nonlinear terms are uncured by the objective function because of the multiplication of process emissions $E_{u,t}$ with respect to binary variables. With introduction of additional variables and new set of constraints a set of bounding constraints for capture cost $\phi_{u,t}$ (for upper bound) can be expresses as in Eq. (3.22 and 3.23) when $HC_{u,t}^{mi}$ and $HC_{u,t}^{pl}$ properly selected on for cost $cost_{capture}E_{u,t}$:

$$HC_{u,t}^{mi}\sum_{cap.}G_{u,t(cap.)} \leq \phi_{u,t} \;\; \forall\, \mu \in U,\, and\, t \in T \tag{3.22}$$

$$\phi_{u,t} \leq HC_{u,t}^{pl}\sum_{cap.}G_{u,t(cap.)} \;\; \forall\, \mu \in U,\, and\, t \in T \tag{3.23}$$

$$cost_{cap.}E_{u,t} - x_c \leq \phi_{u,t} \;\; \forall\, \mu \in U,\, and\, t \in T \tag{3.24}$$

where, $x_c = HS_{u,t}^{pl}\left[1 - \sum_{cap.}G_{u,t(cap.)}\right]$

In the same way, another set can be reformulated through introduction of additional variables and new set of constraints. Thus, we get following expressions (3.25 and 3.26):

$$HS_{u,t}^{mi}\sum_{switch}G_{u,t(switch)} \leq \varphi_{u,t} \;\; \forall\, \mu \in U,\, and\, t \in T \tag{3.25}$$

$$\varphi_{u,t} \leq HS_{u,t}^{pl}\sum_{switch}G_{u,t(switch)} \; \forall\, \mu \in U,\, and\, t \in T \tag{3.26}$$

$$cost_{switch}E_{u,t} - x_d \leq \varphi_{u,t} \; \forall\, \mu \in U,\, and\, t \in T \tag{3.27}$$

where, $x_d = HS_{u,t}^{pl}\left[1 - \sum_{switch}G_{u,t(switch)}\right]$

where, $\varphi_{u,t}$ represents annual cost of fuel switching and $HS_{u,t}^{pl}$ and $HS_{u,t}^{mi}$ provide upper and lower bounds respectively. Having added set of costs, the objective function may be reformulated as follow:

$$\begin{aligned} Minimize \qquad & \sum_{cr}\sum_{1} SR\,cost_{cr} * S_1 + \sum_{p} WOcost * \sum_{cr}\sum_{1} z_p \\ & + \sum_{u}\sum_{t} \varphi_{u,t} + \sum_{u}\sum_{t} \phi_{u,t} - \sum_{cfr}\sum_{1} Xpr_{cfr} * ex_{cfr} \end{aligned} \tag{3.28}$$

The above objective function helps selecting the best emission control strategies for a given reduction target. Each emission can be controlled by the following constraint:

$$E_{u,t} = (1 - Reduction_Target\%) \times Total_Emission \vee t \in T \tag{3.29}$$

where $Total_Emission$ is obtained when no reduction plan is applied of a given refinery.

The model was coded using GAMS - the General Algebraic Modeling System [55] - and solved by CPLEX [56]. The experiments were ran on a Pentium 4 processor 3.0 GHz.

3.4 Results and Discussion

Petroleum refineries are complex plants that involve many different processing units including: Distillation unit (CDU), Reforming (REF), Fluid cat cracker (FCCU), Hydrocracker (HCU), Des gas oil (DGO), Des cycle gas oil (DCGO), and Des ATK (DATK). The oil refinery flow diagram considered in our case studies is shown in Figure 3.1 and the major units capacity constraints are shown in Table 3.2. We assume that the planning period of this model is set to one year and the feedstock to the refinery is a single type (e.g. Arabian light crude), and the total flow rate is 12000 Kton/year in order to produce different final products. These parameters are inspired by the work done by Alqhatani [3].

The pollutants included in this study are SO_x and NO_x whereas the greenhouse gases will be in terms of CO_2. Several emission mitigation alternatives are considered here for the purpose selecting the best ones. Among these alternatives is fuel switching which represents switching from the current fuel (fuel oil) to natural gas. The SO_x capture process considered in this study is wet scrubber (WS) (fuel-gas desulphurisation; FGD) technology and the NO_x capture process will be in terms of retrofitting current burners with low NO_x burner technology (LNB). The CO_2 capture process used will be monoethanolamine absorption technology (MEA). CO_2 emissions are based on [57] whereas Emissions data of the pollutants are based on [58]. Fuel switching and MEA capture process economics are based on [59] while economics of the SO_x and NO_x capture processes were taken from a report by the World Bank [60].

Table 3.2: Unit capacity constraints within refinery

Unit	**Capacity (Kton/year)**
Distillation	12000
Reforming	2000
FCCU	1000
Hydrocracker	2000
Des gas oil	3000
Des cycle gas oil	70
Des ATK	1200

Three case studies are considered in this chapter in order to illustrate the validity of the model discussed in the previous section. The first case study involves solving the planning model without any emissions mitigation plan. This case study is considered to be the base case scenario. The second case study is related to reducing a particular emission (i.e., CO_2) without considering other emissions (i.e., SO_x and NO_x). That is, we reduce each pollutant in an independent manner. Finally, the third case study is related to the examination of reducing different emissions together in a general dependent manner.

Table 3.3: Domestic demand for final products

Product	**Demand (K ton/year)**
LPG	150
LN	90
PG98	30
PG95	1600
JP4	1300
GO6	2500
ATKP	1000
HFO	700

3.4.1 Base Case Scenario

The objectives of this base case scenario are i) to minimize the overall annualized cost which is the total of the crude oil cost, refinery operating cost, and export revenue, and ii) to meet the demands of each product with quality specifications *without considering any emissions mitigation option*. The market demands and specifications for different products that the refinery has to meet are shown in Table 3.3, and this is applied for all case studies.

The results of the base case scenario where no emission reduction plans are considered are shown in Figure 3.2. The figure shows emissions generated by each unit which are primarily from the fire heater when using fuel oil. The sum of emissions from all the units for SO_x, NO_x, and CO_2 were 8170.6, 2826.9 and 1342.3 Kton/year; respectively. The total annual production cost of this refinery is \$3,295,058.

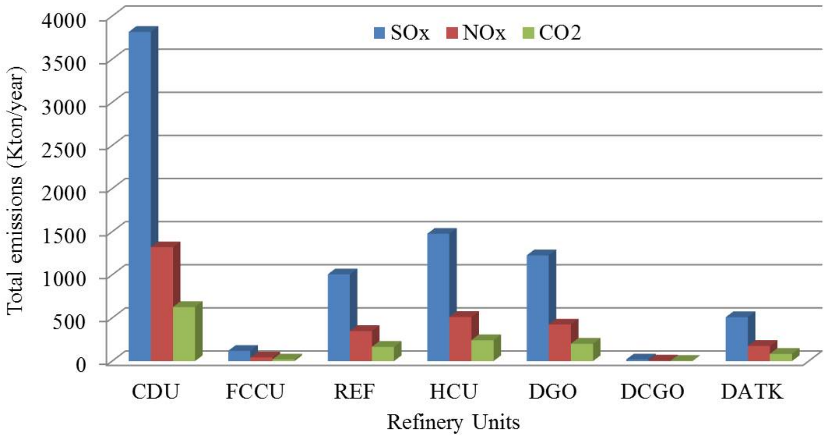


Figure 3.2: The total emissions from each refinery unit

3.4.2 Independent Emission Reduction

In this case study, we focus on reducing one emission at a time without considering other pollutants such as NO_x and CO_2. Our interest in this study is to analyze the impact of reducing each emission independently and to figure out the overall refinery cost correspondingly.

Comparisons of cost increment when reducing SO_x, NO_x, and CO_2 emissions are given in Tables 3.4, 3.5 and 3.6 respectively. For the SO_x reduction scenario, it has been given that -with only a 6.6% increment in price, almost 60% of SO_x releases can be alleviated by installing a wet scrubber capture process (WS) or through switching of fuels. On the other hand, NO_x discharge may be reduced by retrofitting the existing burners with low NO_x burners (LNB). There may be a maximum emissions reduction of 60% at a cost increment of 6.9% according to Table 3.5. The NO_x release is higher when no fuel switching was selected over the present fuel. Table 3.6 shows that a reduction of 60% of CO_2 emissions can be gained with an enhancement on the whole cost of 6.7%. Furthermore, it may

Table 3.4: SO_x emission reduction for each unit

Reduction	**Base case**	**10%**	**20%**	**30%**	**40%**	**50%**	**60%**
Unit	**Emission rate (Kton/year)**						
CDU	3816.0	3434.4	3035.4	2760.0	2346.0	1904.4	1439.6
FCCU	119.3	107.3	85.5	89.6	76.2	61.8	57.7
REF	1005.7	905.1	714.4	702.3	597.0	484.6	314.1
HCU	1475.8	1328.3	1294.3	984.2	836.5	679.1	584.2
DGO	1226.0	1103.4	964.1	851.8	724.0	587.7	549.2
DCGO	18.8	16.9	21.1	11.0	9.4	7.6	7.2
DATK	508.8	457.9	429.0	339.3	288.4	234.1	239.3
Total emission	8170.5	7353.4	6543.8	5738.1	4877.4	3959.3	3191.3
Cost ($/year)	3295058.9	3302704	3338273	3360812	3415168	3486346	3513680
Cost increase (%)	0.0	0.2	1.3	2.0	3.6	5.8	6.6

be observed that a decrease in the CO_2 discharge from 25% to 10% has been achieved without shifting units to the natural gas or by setting up extra MEA capturing practices (Table 3.6). The decreasing has been attained through load shifting and additionally the emissions reduction actions are recommended at 10% with a minor increase in cost. These examples offer a better demonstration of flexibility of model while proposing diverse emission reduction actions with different targets.

3.4.3 Simultaneous Emissions Reduction

In this case study, the mitigation strategies for SO_x, NO_x, and CO_2 emissions are considered simultaneously. In particular, we are interested in reducing SO_x, NO_x, and CO_2 together by various levels, and comparing the overall costs for each mitigation plan. Table 3.7 provides a summary of selected experiments when varying reduction targets for all emissions including SO_x, NO_x, and CO_2 and the corresponding annual cost for each plan. For instance, reducing SO_x, NO_x, and CO_2 by 10% each, results in increasing the annual

Table 3.5: NO_x emission reduction for each unit

Reduction	**Base case**	**10%**	**20%**	**30%**	**40%**	**50%**	**60%**
Unit	**Emission rate (Kton/year)**						
CDU	1320.3	1188.3	1056.2	1031.2	1042.8	583.3	401.2
FCCU	41.3	37.1	33.0	42.4	17.7	16.3	14.6
REF	348.0	313.2	278.4	265.3	151.3	155.0	135.0
HCU	510.6	459.6	408.5	340.5	223.3	236.8	205.1
DGO	424.2	381.8	339.4	182.1	184.1	340.5	306.5
DCGO	6.5	5.9	5.2	4.3	2.3	1.6	1.2
DATK	176.0	158.4	140.8	117.4	77.0	81.6	69.1
Total emission	2826.9	2544.2	2261.5	1983.2	1698.5	1415.1	1132.7
Cost ($/year)	3295058.9	3311068	3338273	3465016	3503746	3510880	3522880
Cost increase (%)	0.0	0.5	1.3	5.2	6.3	6.5	6.9

cost by 3.2%, reducing them by 30% raises the overall cost to 9.2%, and reducing them all by 60% causes an increase of 10.7%.

Figures A.4, A.6 and A.2 show the overall cost when reducing emissions by certain percentage. We observe that the overall cost incenses linearly with the emission reduction. For instance, Figure A.3b shows the annual cost when reducing SO_x from 0% to 60% with varying CO_2 and fixing NO_x to 10%. Similarly, Figure A.3d represent the case when varying SO_x and CO_2 while fixing NO_x to 30%. Figure A.6 plots the annual cost as a function of increasing both SO_x and NO_x reduction rates. We are interested in understanding the impact of the reduction rates on the annual cost. Figures A.6a shows the impact of varying SO_x and NO_x on the overall cost while fixing CO_2 to 40% while A.6c represents the results when fixing the reduction rate of CO_2 to 60%. We refer the reader to Appendix A for more results on independent and simultaneous emissions reduction case studies.

Table 3.6: CO_2 emission reduction for each unit

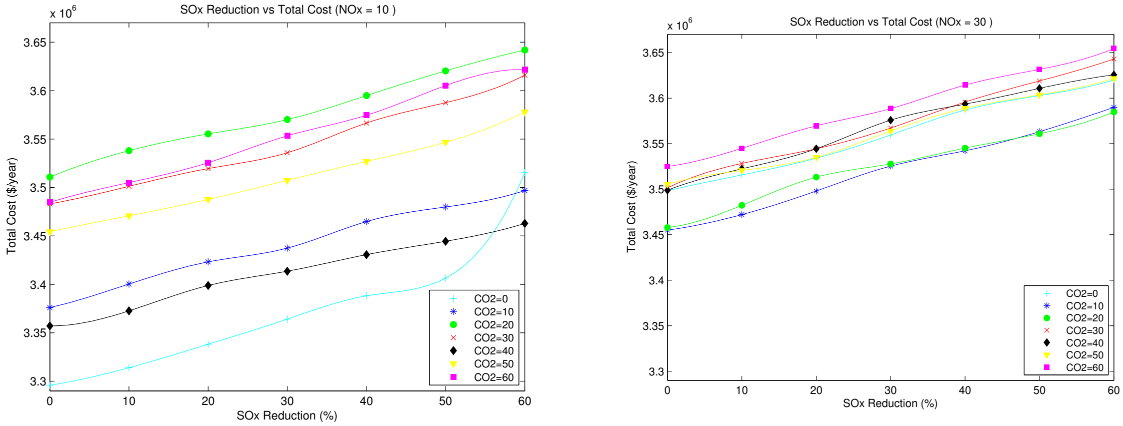
Reduction	**Base case**	**10%**	**20%**	**30%**	**40%**	**50%**	**60%**
Unit	**Emission rate (Kton/year)**						
CDU	626.9	590.5	531.4	457.0	376.2	283.8	192.6
FCCU	19.6	18.6	16.8	14.4	13.1	14.6	7.7
REF	165.2	143.9	129.5	111.4	107.1	96.0	50.0
HCU	242.5	204.1	183.7	158.0	137.4	116.8	161.7
DGO	201.4	176.6	159.0	136.7	123.6	113.6	62.4
DCGO	3.1	4.9	4.4	3.8	2.1	1.9	1.4
DATK	83.6	70.4	63.3	54.5	47.4	40.3	55.7
Total emission	1342.3	1208.9	1088.0	935.7	807.0	666.9	531.5
Cost ($/year)	3295058.9	3311068	3338273	3360812	3379316	3397771	3515168
Cost increase (%)	0.0	0.5	1.3	2.0	2.6	3.1	6.7

3.5 Conclusion

In this chapter we studied the problem of selecting the best pollution control strategies in oil refinery that can be achieved for a given emission reduction target. We formulated the problem based on a mixed integer linear program (MILP) and solve it using GAMS. The model was tested on an industrial scale refinery case study. We consider three pollutants (SO_x, NO_x and CO2) and three mitigation alternatives (fuel switching, sulphur oxides capturing, and nitrogen oxides capturing). The results showed that with only a 6.6% increment in price, almost 60% of SO_x releases can be alleviated by installing a wet scrubber capture process (WS) or through switching of fuels. Furthermore, reducing NO_x by 60% increases the cost by 6.9%. We showed that a reduction of 60% of CO_2 emissions can be gained with an enhancement on the whole cost of 6.7%. The ultimate goal of this study is to provide a tool to decision makers in oil refineries to help them in selecting the best pollution control strategies for a given emission reduction target.

Table 3.7: Cost compared to reduction in SO_x NO_x and CO_2 emissions, all together

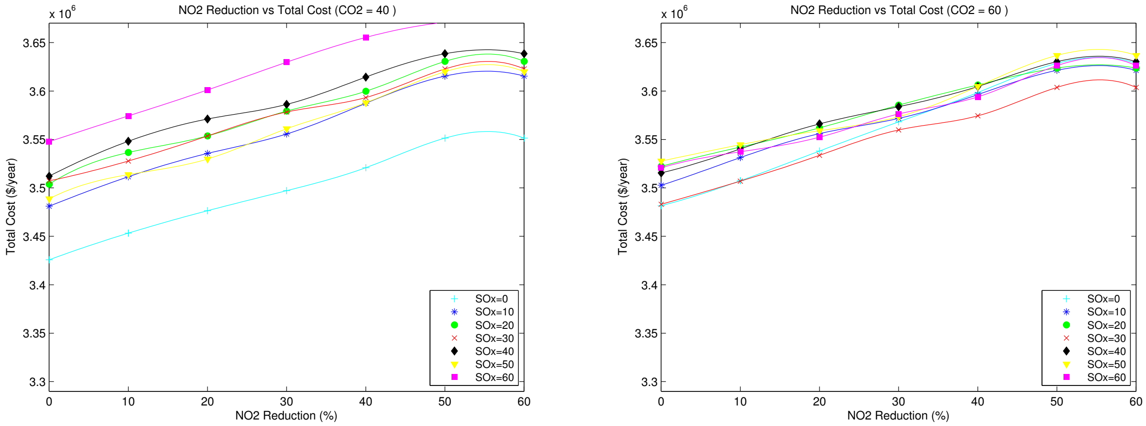
Scenario	**SOx (%)**	**NOx (%)**	**CO2 (%)**	**Total Cost (K$)**	**Cost increase (%)**
1	10	10	10	3399494.097	3.2
2	30	10	10	3406170.124	3.4
3	10	30	10	3436589.846	4.3
4	30	30	10	3453074.546	4.8
5	10	60	10	3479067.41	5.6
6	10	10	30	3494009.764	6.0
7	10	30	30	3503489.963	6.3
8	30	10	60	3506966.401	6.4
9	60	10	30	3511469.457	6.6
10	10	10	60	3531285.046	7.2
11	60	10	10	3535160.451	7.3
12	60	10	60	3537302.721	7.4
13	60	60	10	3547596.202	7.7
14	60	30	30	3554675.24	7.9
15	30	10	30	3557440.002	8.0
16	30	30	60	3559830.952	8.0
17	60	30	10	3570190.229	8.3
18	10	30	60	3571728.303	8.4
19	60	30	60	3576363.652	8.5
20	10	60	30	3585730.425	8.8
21	30	30	30	3596704.69	9.2
22	60	60	30	3597380.461	9.2
23	30	60	60	3603730.205	9.4
24	10	60	60	3621384.8	9.9
25	30	60	10	3622379.528	9.9
26	30	60	30	3626200.694	10.0
27	60	60	60	3648820.139	-



(a) At NO_x =10

(b) At NO_2 =30

Figure 3.3: Cost compared to reduction in SO_x



(a) At CO_2 =40

(b) At CO_2 =60

Figure 3.4: Cost compared to reduction in NO_x

Chapter 4

Air Pollution Dispersion Models

4.1 Introduction

This chapter outlines various air dispersion models that describe how air pollutants, emitted by a source, disperse in the ambient atmosphere. In particular, we consider *CALPUFF* and *SCREEN3* to estimate the overall concentration of SO_x, NO_x, and CO_2 within the area of study. The chapter will conclude by modeling the data based on the chosen model and then displaying the results.

4.2 CALPUFF Dispersion Model

In this thesis, a proposed oil refinery site is assumed to be located in the north area of Toronto, Ontario, Canada. This refinery has similar processes to the one mentioned in Chapter 3. The location of this refinery is 50 km away from the urban area of Toronto, hence the need for providing a screening analysis to gauge the possible extent of potential impacts on the surrounding area of Toronto. *CALPUFF* and *SCREEN3* will be used as modeling tools to estimate the overall concentration of SO_x, NO_x, and CO_2 within the area of study.

CALPUFF is a computer based tool for air dispersion modeling which has been developed by the United States Environmental Protection Agency [5]. It consists of a meteorological, a non-steady-state puff dispersion, and a post-processing modules and it simulates the effects of temporally and spatially changing meteorological conditions on air pollutant movement. CALPUFF is considered to be used for modeling areas that are 5km to 300km away from the source. CALPUFF makes provision for point, area, line, and volume sources and assesses the mesoscale transport of pollutants as well as their dispersion in the surrounding complex terrain. For instance, the puffs emitted from a stack point are modeled individually based on conditions of wind direction and speed in an hourly basis, where the concentration of pollutants is calculated as each puff passes over a receptor point.

As shown in Figure 4.1, the CALPUFF modeling system is divided into three main modules namely: CALMET, CALPUFF, and CALPOST. CALMET is a meteorological model that requires geophysical data such as gridded fields of terrain elevation and land use and meteorological data including atmospheric temperature, wind speed, wind direction, cloud cover, relative humidity, and atmospheric pressure (i.e. surface, upper air, precipitation, and over water). The purpose of CALMET is to generates 3-dimensional wind fields that are used in CALPUFF, and CALPOST modules. CALPUFF is a Gaussian puff model with different effects such as chemical removal, wet and dry deposition, and complex terrain algorithms. CALPOST is the post- processing package, which is used to process the output models generated by CALMET and CALPUFF for plotting on modeling domain

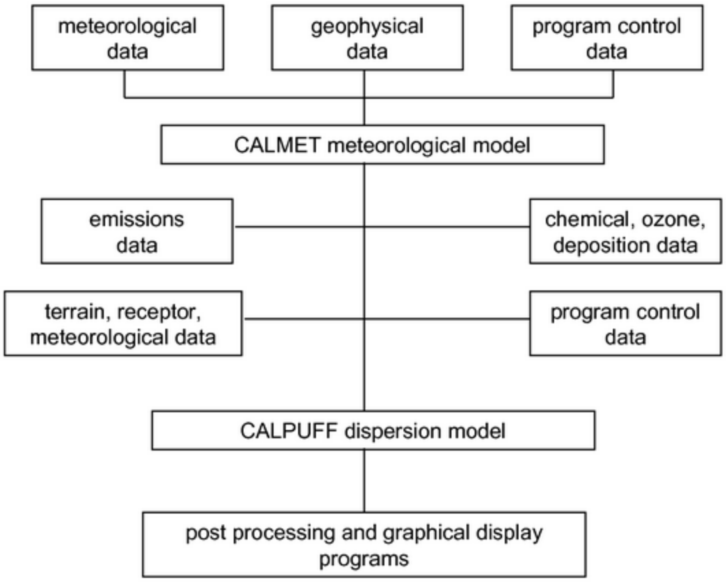


Figure 4.1: CALPUFF Modelling System [5]

maps. The process and information flow needed to carry out the air dispersion study is represented below

The CALPUFF model is an internationally approved model that is used by the USEPA for regulatory purposes (United States Environmental Protection Agency). The CALPUFF model has gained regulatory approval for air dispersion modeling of medium to long range transport of pollutants [61]. Due to the capability of CALPUFF to evaluate both short and long range pollutant transport, the impacts of pollutants can be measured around an industry's fence line to the nearest populated areas situated kilometers away.

4.2.1 Data collection

The first step in processing the models is by identifying the meteorological domain information for the case study region (Table 4.1).

Table 4.1: The model information for the meteorological domains

Parameter	**North of Toronto**
Map Projection	UTM
Latitude of origin	594.237 km
Longitude of origin	4877.678 km
Continent/Ocean	Global
Region	84
DATUM Code	WGS-84
X (Easting)	75 km
Y (Northing)	75 km
Number of X grid cells	75
Number of Y grid cells	75
Grid spacing	2 km
Number of vertical layers	10
Number cell face heights (m)	0, 20, 40, 80, 160, 320, 640, 1200, 2000, 3000

Surface data

The hourly surface observations for the Toronto area were acquired from the historical weather records in the Canadian government website (climate.weather.gc.ca). The surface stations were chosen based on their proximity to the source point and upper air stations. For each station, each hourly record contains the date and the time, temperature, wind speed, wind direction, ceiling height, cloud cover, and station pressure. The hourly data for two modeling periods from (i) January 1, 2014 at 0000h to January 31, 2014 at 2300h; (ii) May 1, 2014 at 0000h to May 31, 2014 at 2300h were extracted and organized in a certain layout that is suitable for use in SMERGE to create a formatted file SURF.DAT, which is compatible for usage with CALMET. The information of the surface meteorological station selected in each of the region of study is shown in Table 4.2.

Table 4.2: Surface stations information

Parameter	North of Toronto
Station Name	Toronto Buttonville
Latitude	43 51 44
Longitude	79 22 12
Elevation	198.1
Climate ID	615HMAK
WMO ID	71639
TC ID	YKZ

Upper air data

The upper air meteorological information for the location was obtained from the radiosonde station records in the NOAA/ESRL radiosonde database (esrl.noaa.gov/raobs/). These data records contain the station ID number, date and time, and information of the sounding level followed by pressure, temperature, elevation, wind direction, and wind speed for each sounding level. The hourly data for the Toronto area was taken from one radiosonde station that is close to these study sites for the two modeling periods mentioned above and was then prepared in a format suitable to use in READ62 to generate the UP.DAT file that will be used later in the CALMET program. Table 4.3 lists information about the radiosonde station from which upper air meteorological data were extracted.

Geophysical data

The geophysical data, including land use and terrain, were obtained from the Geographic Information Systems Resource website (www.webgis.com) and used as input files in CTG-PROC and TERREL to produce LU.DAT and TERREL.DAT respectively. This data is then compressed together by a MAKEGEO program to generate the output file GEO.DAT,

Table 4.3: Radiosonde stations information

Parameter	North of Toronto
Station Name/Location	Moosone PQ
UTM latitude	51.27
UTM longitude	80.65
X location on grid	808.3 km
Y location on grid	1 km
Elevation	10 m
WBAN	15803
WMO ID	71836

which can later be used in the CALMET program.

Emission rates and source parameters

The pollutant emission rates for the case study were obtained from the mathematical modeling mentioned earlier in Chapter 3. Table 4.4 and 4.5, contain the values of source parameters, and emission rates of pollutants at various reduction plans, respectively. These values were used in the CALPUFF model and specified for the two modeling periods.

Table 4.4: Source parameters information for the case study

Source Parameters	North of Toronto
X Coordinate (km)	592.430km
Y Coordinate (km)	4877.631 km
Base Elevation (m)	256.6
Stack Height (m)	75
Stack Diameter (m)	6
Exit Velocity (m/s)	20
Exit Temperature (K)	418

Table 4.5: Emission rate reduction used for CALPUFF

Reduction	Base case	10%	20%	30%	40%	50%	60%
CO_2 (Kton/year)	1342.3	1208.1	1087.3	978.5	880.7	792.6	713.4
NO_x (Kton/year)	2826.9	2544.2	2289.8	2060.8	1854.7	1669.3	1502.3
SO_x (Kton/year)	8170.6	7353.5	6618.2	5956.4	5360.7	4824.7	4342.2

4.3 Screen 3 Dispersion Model

In order to identify the emissions concentration that is derived from the oil refinery and approaching surrounding cities, we sought a model that would be able to assist in the measurement and estimation dispersion of pollutants by atmospheric air. The model chosen for this purpose is Screen View version 3.0 (*SCREEN3*), which is recommended by the USEPA. Among the programs recommended by the American agency, *SCREEN3* was the only one available for free. It is free because it has some limitations, which will be presented below, but they do not interfere with this study.

SCREEN3 is designed to provide a simple way to get the concentration of pollutants based on simple tracking information available to a large number of users. *SCREEN3* uses a Gaussian plume model, taking into account meteorological factors to calculate the concentration and dispersion of contaminants from stationary sources. *SCREEN3* examines a number of classes and stable wind speed identifies the turbulence of the atmosphere, which greatly influences the spread of pollutants. Stability conditions are divided into six classes, with Class A extremely unstable, class B unstable, slightly unstable class C, class D neutral, Class E slightly stable and stable F class. The stability condition occurs when there is an absence of solar radiation, no clouds and the presence of mild winds. This condition is less favorable for the dispersion of pollutants. The mixing time is a measure of where the atmosphere is at a higher process turbulence, thus favoring the dispersion of pollutants.

One of the limitations found in the Screen is that it is unable to determine the impacts from multiple sources and merge them into a single representation. To make such a representation, it is necessary to make separate simulations, then manually superimpose the results obtained. Another limitation is that the program presents the results only linearly and at a maximum distance of 50 kilometers. To overcome these situations, it is recommended to use some paid program, e.g., ISCST3.

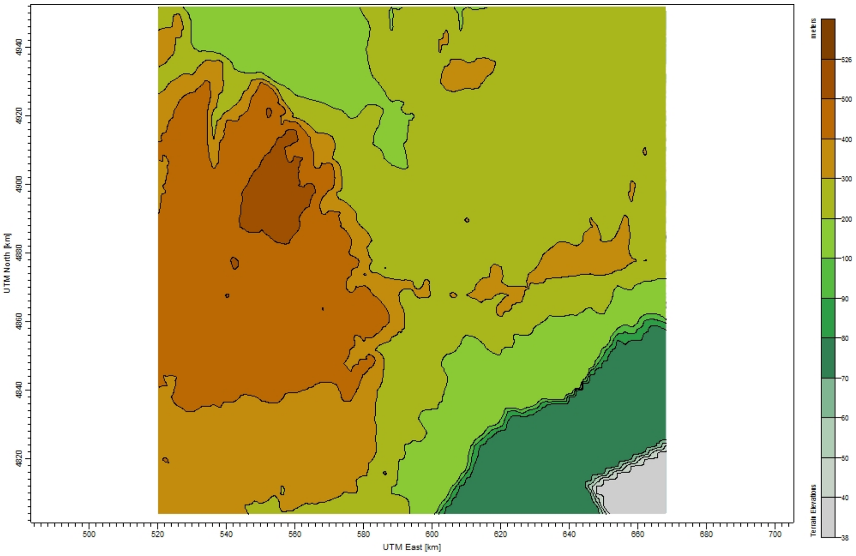
4.4 Results and Discussion

4.4.1 CALPUFF

The CALPUFF model was used to predict the concentration of pollutants released from the oil refinery , as well as to simulate the transport and dispersion of these pollutants during two months' modeling periods, January and May of 2014. The CALPOST post-processor was used to show the spatial distribution of predicted concentrations. Figure 4.2 represents the characteristics of the study area. In this figure, the capability of the CALPUFF model to simulates the geographical condition of the area of interest can be seen. Table 4.6 illustrates the maximum monthly CO_2 average concentrations.

Figure 4.3 shows the CO_2 plume distributed significantly in the Toronto area in January 2014. The highest monthly CO_2 concentration calculated by CALPUFF view model is 216 $\mu g/m^3$ and the lowest is 2 $\mu g/m^3$ when considering the base case scenario as shown in Figure 4.3a and the plume affecting Toronto residential area concentration is 20 $\mu g/m^3$. In

(a) Street View



(b) Terrain View

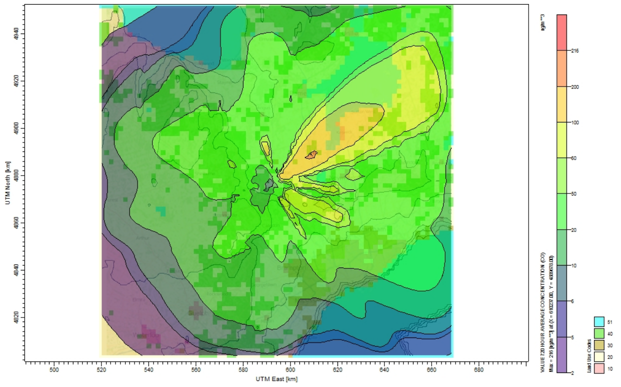
Figure 4.2: Characteristics of study area

redaction of 10%, the maximum monthly average concentration of CO_2 was 194 $\mu g/m^3$, and the minimum average concentration was $2\mu g/m^3$ as seem in Figure 4.3b. Also, the pollutant dispersed in all directions, especially in the northwest direction as seen in Figure 4.3c. When reducing 50% of emission CO_2, the maximum monthly concentration was 127 $\mu g/m^3$ at the distance of 2 km from the source as shown in Figure 4.3e. The dispersion of CO_2 was heading drastically in the south and northeast direction as presented in Figure 4.3d, thus affecting people in that area. As displayed in Figure 4.3f, the plume dispersed significantly toward the northwest and it shows that the maximum monthly average concentration of CO_2 obtained in the 60% redaction reached 115 $\mu g/m^3$ within 2 km northeast of the source. It is clear how the plumes are covering the Toronto residential area and from the color code the range of the plumes concentration of the subject pollutant is changing gradually from 216 to 1 $\mu g/m^3$.

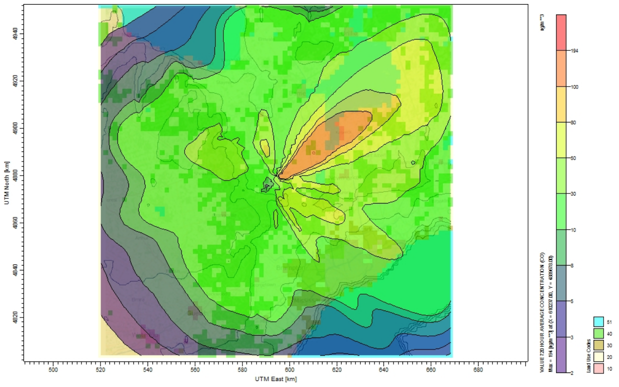
Table 4.6: The maximum and minimum monthly average concentrations of CO_2 for six reduction plans in the period of January 2014

Reduction plan	Maximum Average monthly concentration $\mu g/m^3$	Minimum Average monthly concentration $\mu g/m^3$
Base case	216	2
10%	194	2
30%	157	2
40%	141	1
50%	127	1
60%	115	1

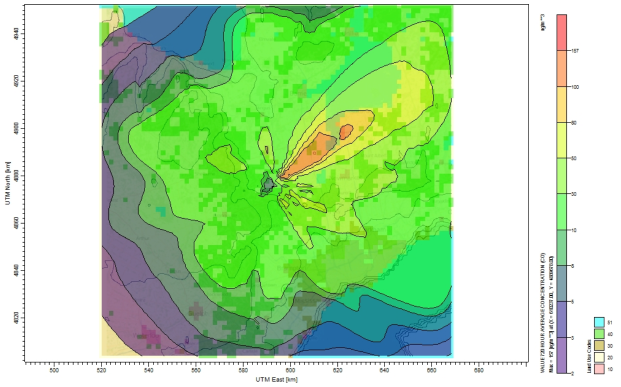
Now we consider the month of May for this case study. Table 4.7 shows the maximum monthly average concentrations of CO_2 for the six reduction plans. Figure 4.4 shows the dispersion of CO_2 emission for different plans to the surrounding area of Toronto at



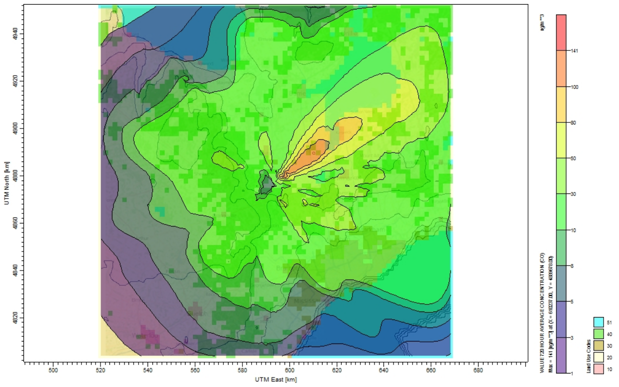
(a) Base Case



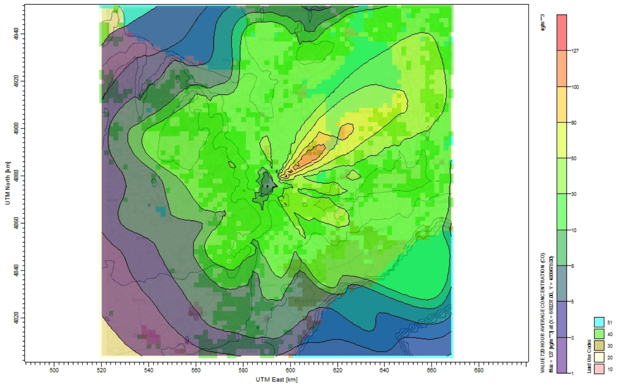
(b) 10% Reduction



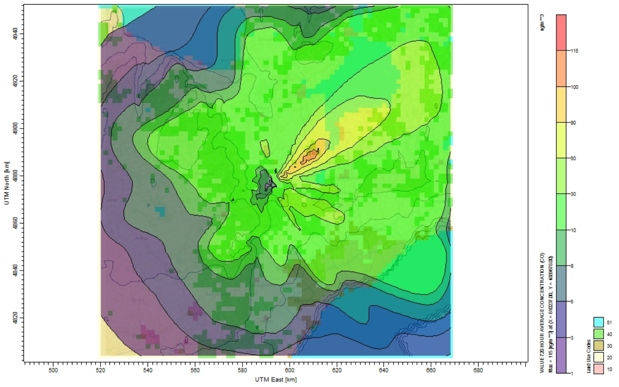
(c) 30% Reduction



(d) 40% Reduction



(e) 50% Reduction



(f) 60% Reduction

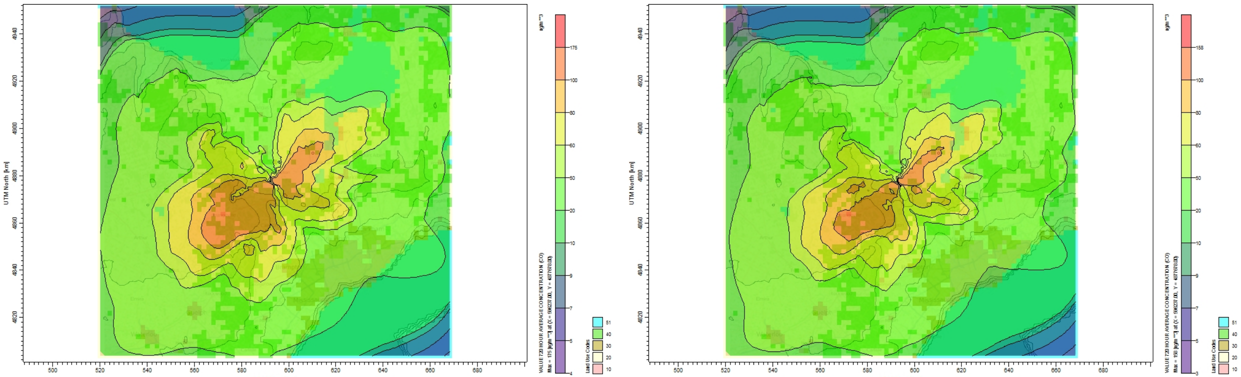
Figure 4.3: CO_2 Dispersion over January 2014

the southwest of Ontario. The maximum monthly CO_2 concentration calculated by the CALPUFF model for the base case scenario is $175 \mu g/m^3$ and the lowest is $4 \mu g/m^3$. The plume affecting the Toronto residential area has a concentration of $20 \mu g/m^3$ as depicted in Figure 4.4a. The maximum CO_2 monthly average concentration became 158 $\mu g/m^3$ once the oil refinery site reduces its omission by 10% as shown in Figure 4.4b. In the case of 30% CO_2 reduction, Figure 4.4c shows that the maximum average concentration reduced to 128 $\mu g/m^3$ and the minimum concentration became 3 $\mu g/m^3$. Furthermore, Figure 4.4f shows that reducing the CO_2 pollutant by 60% results in reducing the monthly average concentration to 93.1 $\mu g/m^3$. The highest monthly average concentration of CO_2 for all reduction plans that affect the Toronto area are between 2 and 30 $\mu g/m^3$. No health symptoms are associated with this range of concentration values according to air quality standard and guideline (Appendix B).

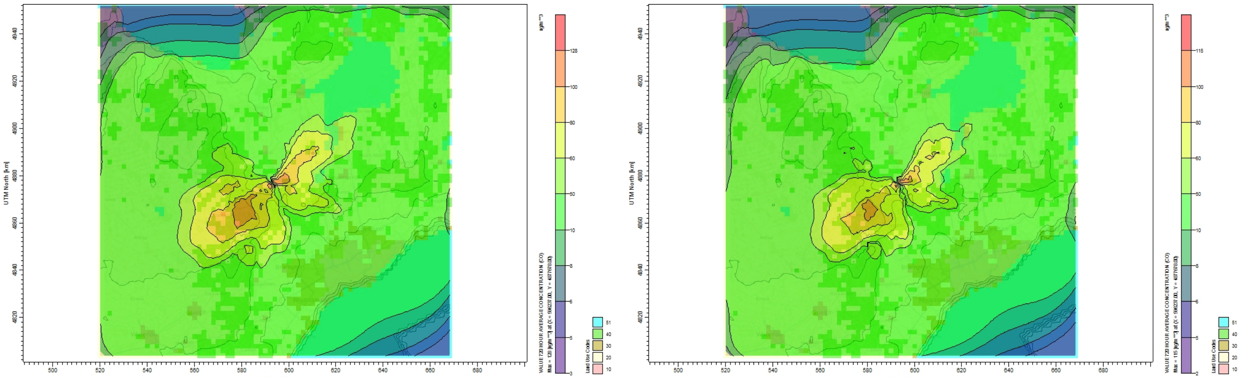
Table 4.7: The maximum and minimum monthly average concentrations of CO_2 for six reduction plans in the period of May 2014

Reduction plan	Maximum Average monthly concentration $\mu g/m^3$	Minimum Average monthly concentration $\mu g/m^3$
Base case	175	4
10%	158	3
30%	128	3
40%	115	2
50%	103	2
60%	93.1	2.0

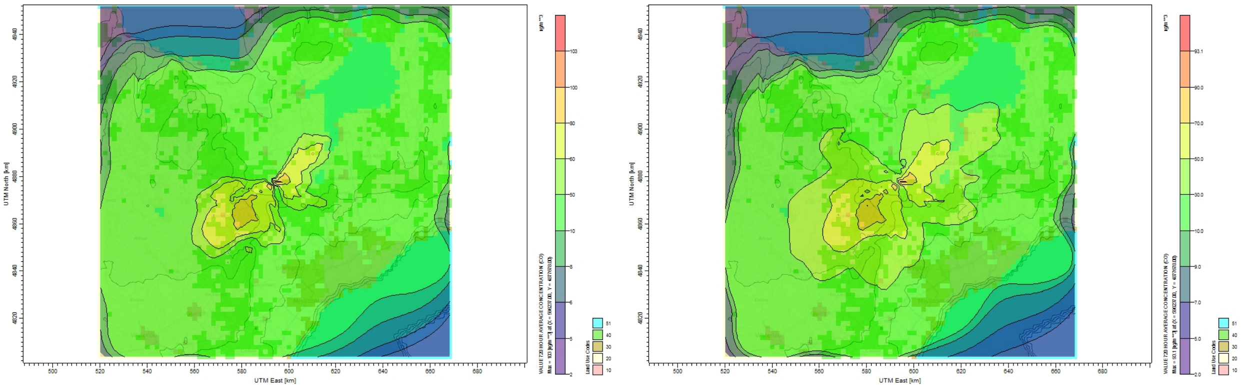
The following set of experiments are related to the dispersion of SO_2 in the month of January 2014. Table 4.8 summaries the maximum and minimum average monthly concentrations of SO_2 for all reduction plans. The maximum monthly average concentration of



(a) Base Case (b) 10% Reduction



(c) 30% Reduction (d) 40% Reduction



(e) 50% Reduction (f) 60% Reduction

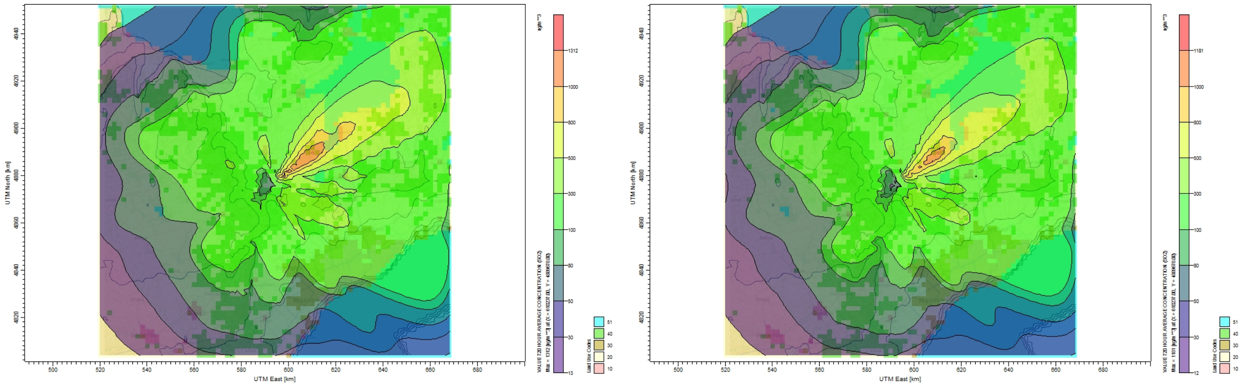
Figure 4.4: CO_2 Dispersion over May 2014

SO_2 when no reduction plan is applied to the refinery was 1312 $\mu g/m^3$ as seen in Figure 4.5a and the plumes dispersed 5 km north east of the source. Figure 4.5b illustrates that the maximum and minimum average monthly concentrations of SO_2 were 1181 and 12 $\mu g/m^3$ when reducing the emission by 10%. One can clearly notice that when reducing the pollutants from the source by certain percentages, the concentration of the pollutants in the receptor area will reduce accordingly. Therefore, reducing the SO_2 by 30%, 50%, and 60% results in reducing the maximum monthly average concentration to 956.5, 775, and 697$\mu g/m^3$ respectively as shown in figures 4.5c, 4.5e, and 4.5f.

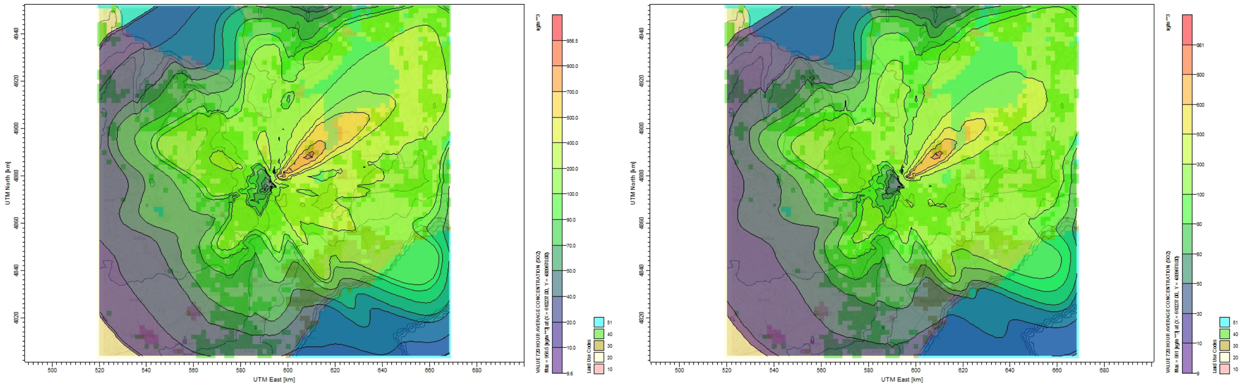
Table 4.8: The maximum and minimum monthly average concentrations of SO_2 for six reduction plans in the period of January 2014

Reduction plan	Maximum Average monthly concentration $\mu g/m^3$	Minimum Average monthly concentration $\mu g/m^3$
Base case	1312	13
10%	1181	12
30%	956.5	9.6
40%	851	9
50%	775	8
60%	697	7

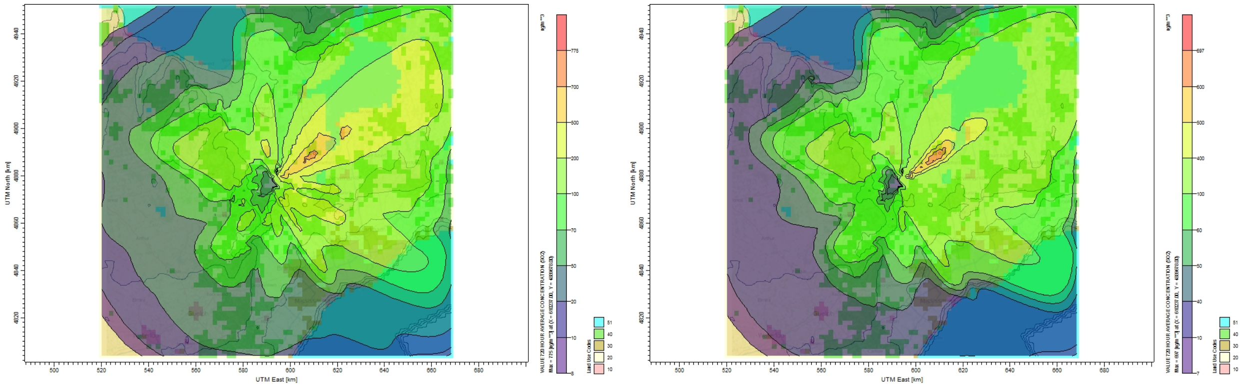
Table 4.6 presents the values of the maximum and minimum average monthly concentration of SO_2 for all reduction plans in May 2014. Figure 4.6 shows the SO_2 overall plume dispersion of January 2014. For the base case scenario, the maximum and minimum average monthly concentrations of SO_2 as depicted in Figure 4.6a is 1066 and 22$\mu g/m^3$, whereas the plume affecting the Toronto residential area has a concentration of 100$\mu g/m^3$. Reducing 10% of SO_2 in the oil refinery decreases the maximum and minimum monthly average concentration of SO_2 to 960 and 20$\mu g/m^3$ respectively as seem in Figure 4.6b. From



(a) Base Case (b) 10% Reduction



(c) 30% Reduction (d) 40% Reduction



(e) 50% Reduction (f) 60% Reduction

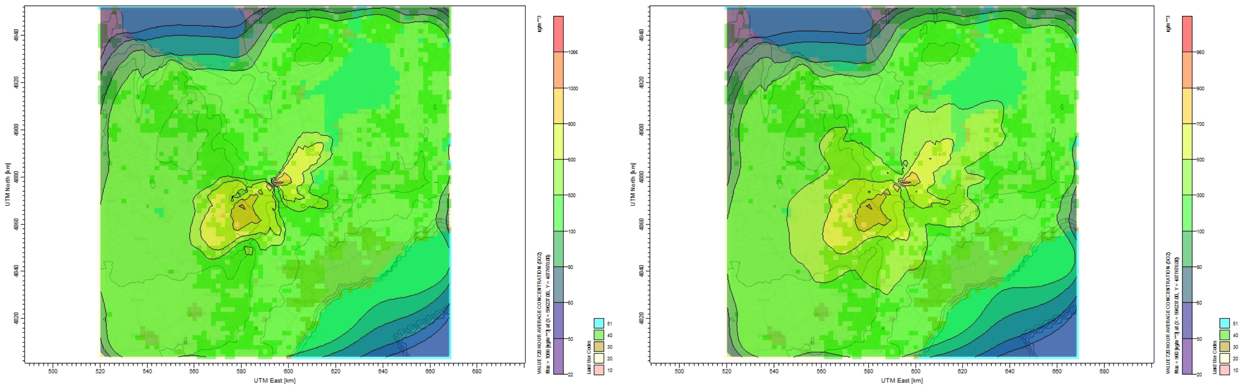
Figure 4.5: SO_x Dispersion over January 2014

Figure 4.6c, the highest monthly SO_2 concentration computed by CALPUFF when reducing the SO_2 emission by 30% is 777 $\mu g/m^3$ and the lowest is 16 $\mu g/m^3$ and the monthly concentration of plume covering the Toronto residential area is 80 $\mu g/m^3$. Figures 4.6c, 4.6e and 4.6f illustrate the maximum and minimum average monthly concentrations of SO_2 when reduction plans of 40%, 50%, and 60% are applied respectively.

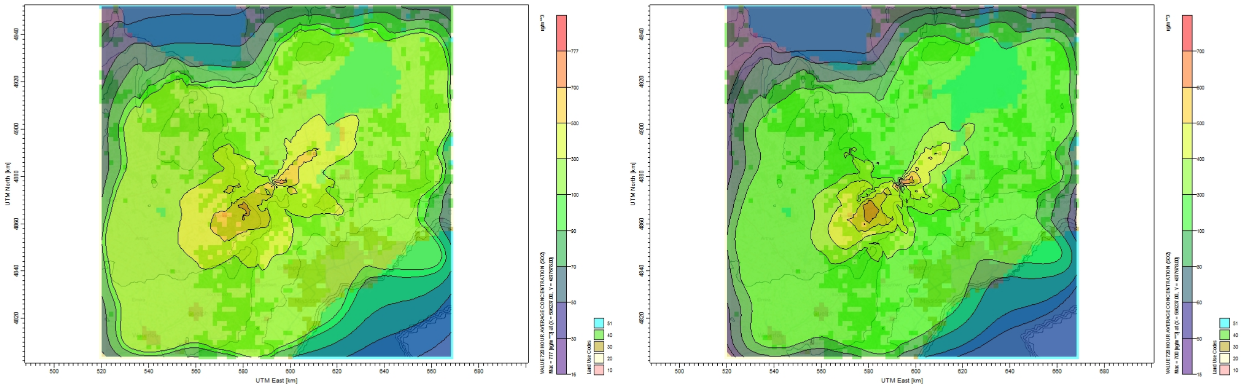
Table 4.9: The maximum and minimum monthly average concentrations of SO_2 for six reduction plans in the period of May 2014

Reduction plan	Maximum Average monthly concentration $\mu g/m^3$	Minimum Average monthly concentration $\mu g/m^3$
Base case	1066	22
10%	960	20
30%	777	16
40%	700	15
50%	630	13
60%	567	12

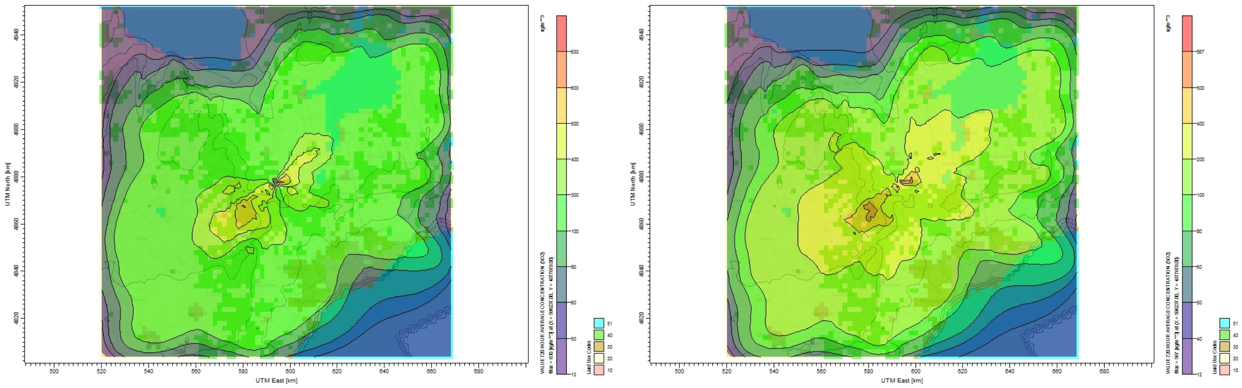
Table 4.10 presents the values of the maximum and minimum average monthly concentration of NO_2 for all reduction plans in January 2014. Figure 4.7 shows the typical NO_2 dispersion of 1-month average from the stack of the oil refinery for the base case scenario and various reduction plans. The maximum NO_2 concentration for the month of January for the oil refinery was about 454 $\mu g/m^3$ when no reduction plan is applied as shown in Figure 4.7a. From Figure 4.7b, NO_2 was dispersed from the north western to the north eastern of the Toronto area with maximum and minimum average monthly concentrations of 409 and 4 $\mu g/m^3$ respectively when applying the 10% reduction plan. The maximum SO_2 concentration of monthly average for the plant was about 331 $\mu g/m^3$ when reducing the emission by 30% as shown in Figure 4.7c. The monthly average of SO_2 concentration



(a) Base Case (b) 10% Reduction



(c) 30% Reduction (d) 40% Reduction



(e) 50% Reduction (f) 60% Reduction

Figure 4.6: SO_x Dispersion over May 2014

for 40%, 50% and 60% reduction plans was 298, 268 and 241 $\mu g/m^3$ as depicted in Figures 4.7d, 4.7e, and 4.7f respectively.

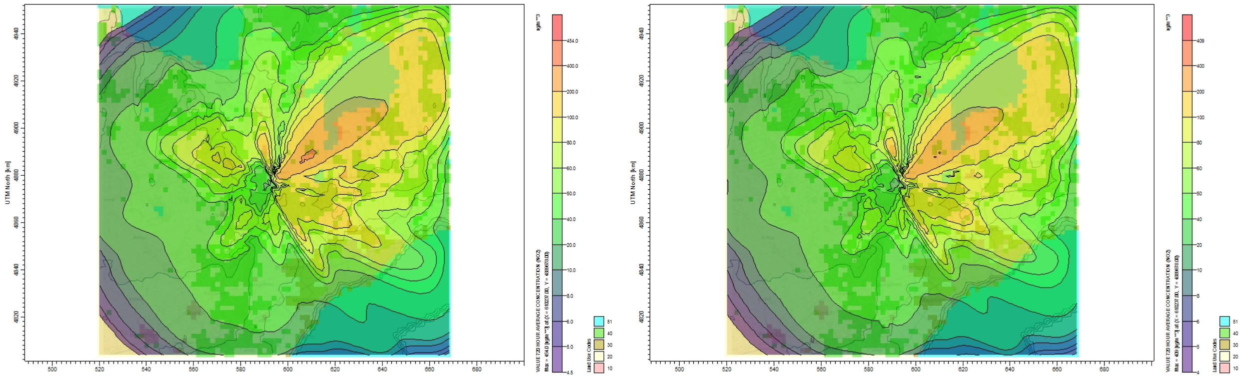
Table 4.10: The maximum and minimum monthly average concentrations of NO_2 for six reduction plans in the period of January 2014

Reduction plan	Maximum Average monthly concentration $\mu g/m^3$	Minimum Average monthly concentration $\mu g/m^3$
Base case	454	4.5
10%	409	4
30%	331	3
40%	298	3
50%	268	3
60%	241	2

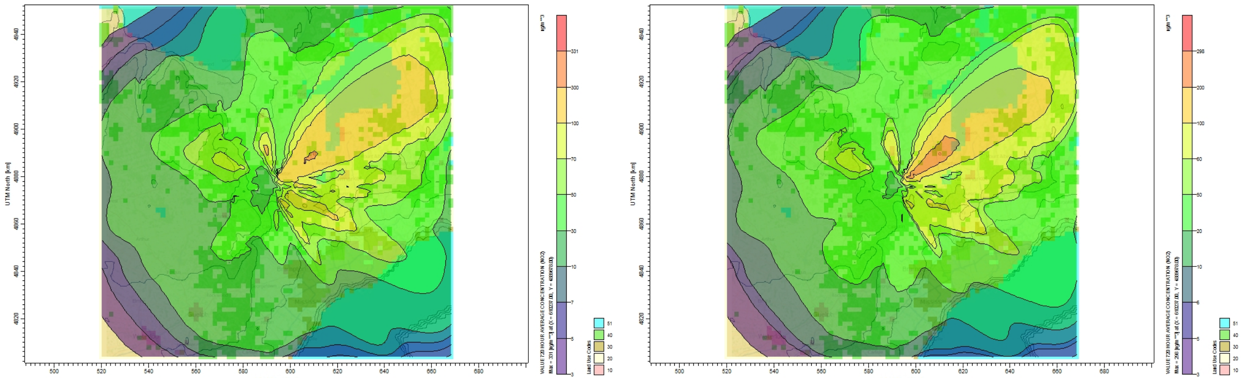
For the month of May in 2014, Table 4.11 shows the maximum and minimum monthly average concentrations of NO_2 for the base case scenario and all reduction plans. Figure 4.8 shows the typical NO_2 dispersion of one month (May) from the oil refinery for the base case scenario and all reduction plans. The typical NO_2 dispersion of 1-month average in the Toronto area was shown in Figure 4.8b when applying the 10% reduction plan. The maximum monthly average of NO_2 was dispersed with concentration of 332 g/m3 as a 30% reduction plan is applied (see Figure 4.8c). Finally, Figures 4.8d, 4.8e, and 4.8f, illustrate the maximum and minimum average monthly concentration of SO2 when reduction plans of 40%, 50%, and 60% are applied.

4.4.2 SCREEN3

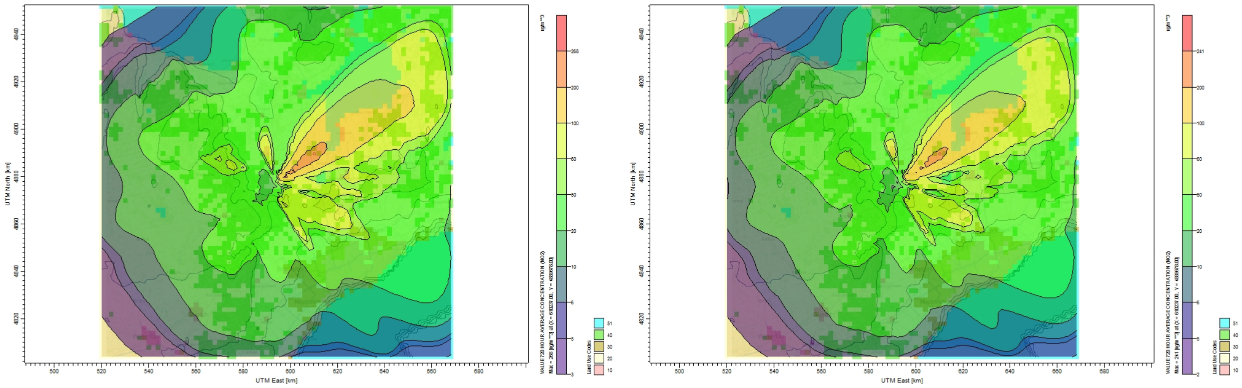
For *SCREEN3* modelling, we considered atmospheric emissions of SO_2, NO_x and CO_2 omitted from the oil refinery as the input data. The results of *SCREEN3* are expressed



(a) Base Case (b) 10% Reduction

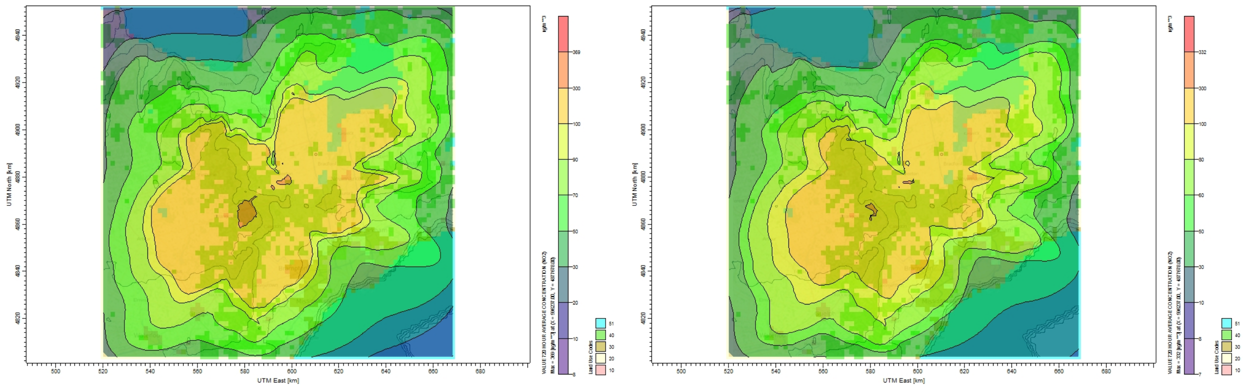


(c) 30% Reduction (d) 40% Reduction

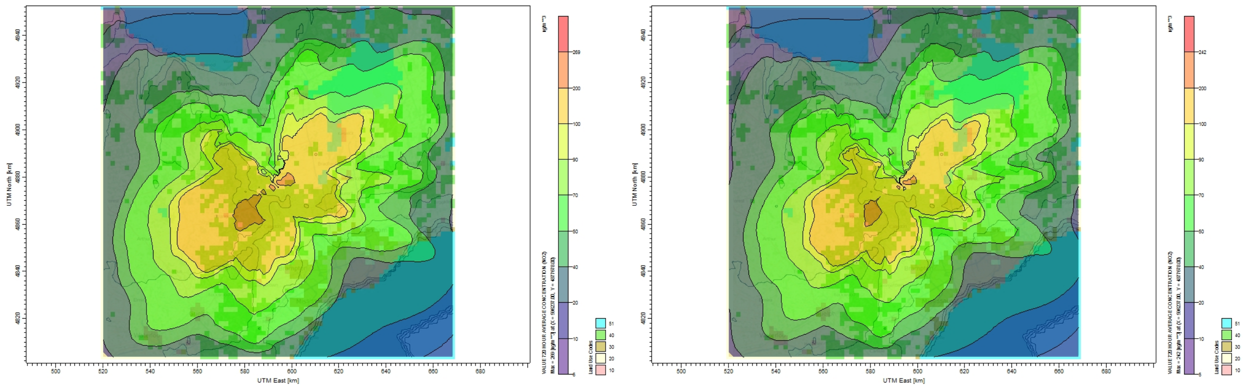


(e) 50% Reduction (f) 60% Reduction

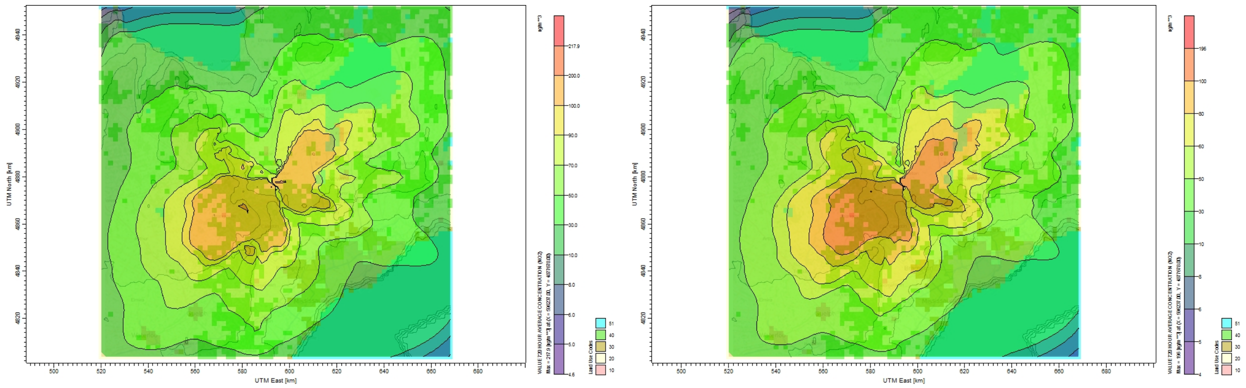
Figure 4.7: NO_x Dispersion over January 2014



(a) Base Case (b) 10% Reduction



(c) 30% Reduction (d) 40% Reduction



(e) 50% Reduction (f) 60% Reduction

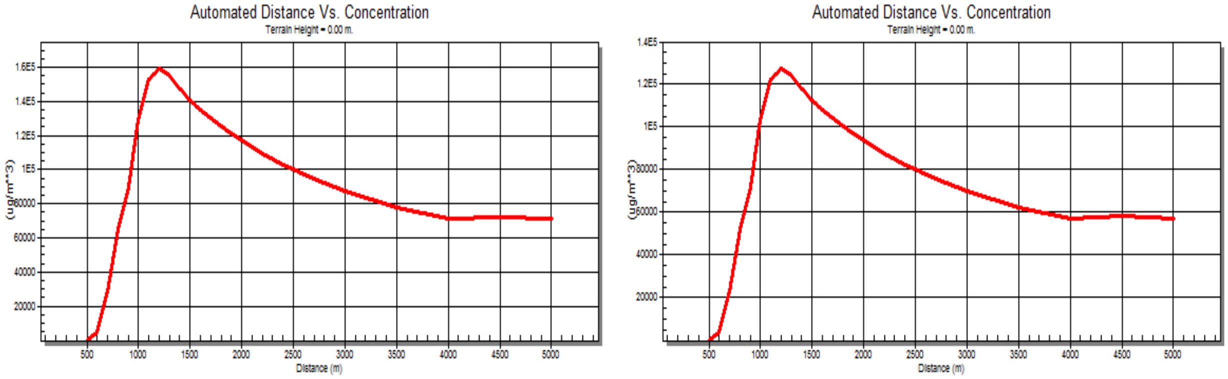
Figure 4.8: NO_x Dispersion over May 2014

Table 4.11: The maximum and minimum monthly average concentrations of NO_2 for six reduction plans in the period of May 2014

Reduction plan	Maximum Average monthly concentration $\mu g/m^3$	Minimum Average monthly concentration $\mu g/m^3$
Base case	369	8
10%	332	7
30%	269	6
40%	242	5
50%	217	4.6
60%	196	4

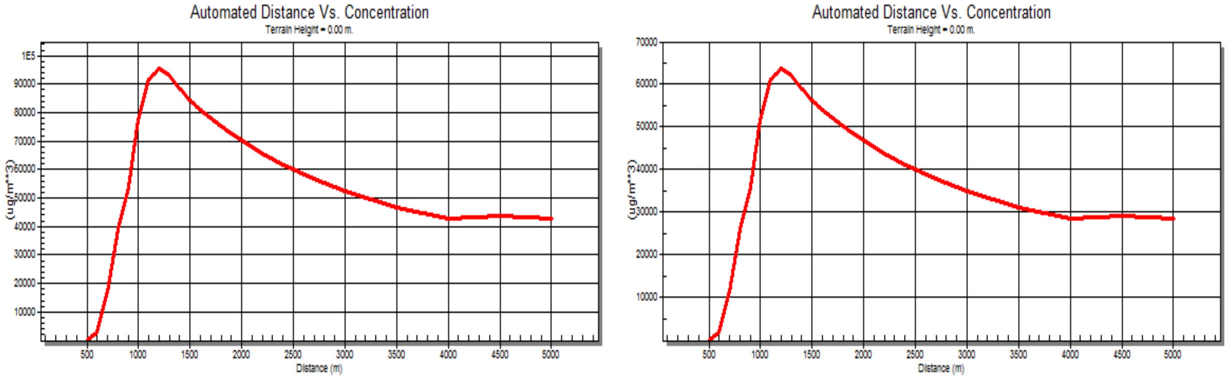
in concentration units ($\mu g/m^3$) and distance (m). The first group of simulations were performed considering the option of *Full Meteorology*. That is, we omitted defining the type of atmospheric stability class where the program assumes the "C" class. Figure 4.9 shows the maximum concentration calculated for SO_x for the base case and various mitigation plans. The figure depicts that the maximum concentration was found 1200 meters away from the source for all scenarios and the emission concentrations were 1.6E5, 1.3E5, 9.5E4 and 6.4E4 ug/m^3 for the base case, 20%, 40% and 60% reduction plans respectively. Other results of the program are found in Appendix C.

The second set of simulations were performed for each type of atmospheric stability. Figure 4.10 shows the concentration of emissions of SO_x for Type A, D and F stability classes. We choose to present the base case scenario and a 40% reduction plan for these stability classes. Other pollutants' results can be found in Appendix C.



(a) Base Case

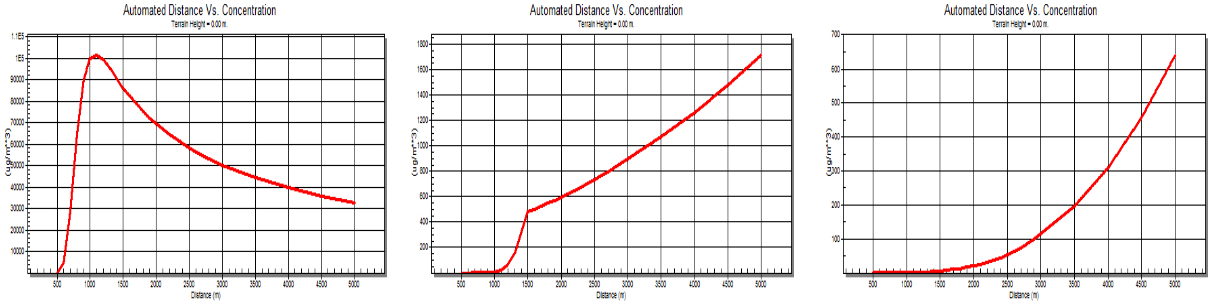
(b) 20% Reduction



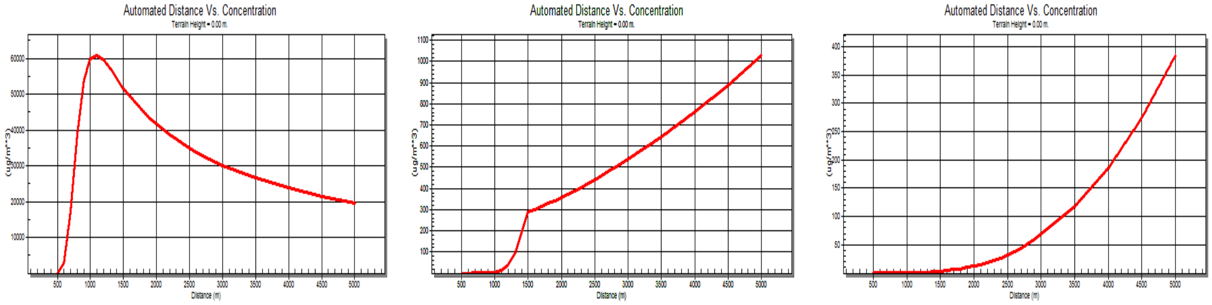
(c) 40% Reduction

(d) 60% Reduction

Figure 4.9: Maximum SO_x concentration vs. downwind distance (m) using *SCREEN3* over multiple reduction plans



(a) Class A, base case scenario (b) Class D, base case scenario (c) Class F, base case scenario



(d) Class A, 40% Reduction (e) Class F, 40% Reduction (f) Class F, 40% Reduction

Figure 4.10: Selected results for maximum SO_x concentration vs. downwind distance (m) for A,D and F stability classes

4.5 Conclusion

In this chapter we used air dispersion models to study how air pollutants, emitted by a source, disperse in the ambient atmosphere. We used *CALPUFF* and *SCREEN3* to estimate the overall concentration of SO_x, NO_x, and CO_2 within the area of study. We calculated emission concentrations, dispersion and transport of pollutants released from the oil refinery in order to evaluate their impacts on receptor locations.

Chapter 5

Conclusion and Future Work

The refinery sector is one of main contributors to SO_x, NO_x and CO_2 emissions in Canada. Optimization models were used for refinery sector to solve the problem of meeting local demand at a given emission reduction plan. The model manipulates three mitigation options and chooses the optimal set to meet a certain emission reduction goal with the minimum annual cost ensuring that the demand and quality specifications were met. The formulation of the model was developed in the form of a mixed integer linear program (MILP) and demonstrated using different case studies. Furthermore, two air dispersion models were investigated for pollutants released the potential oil refinery located in northern area of Toronto, Ontario, Canada. in particular, a screening model (*SCREEN3*) and a non-steady state Lagrangian California Puff Model (*CALPUFF*), were used to calculate emission concentrations, dispersion and transport in order to evaluate their impacts on receptor locations.

5.1 Summary of Contributions

The contributions of this dissertation can be summarized as follows:

- The development of a mathematical model for an oil refinery with consideration to multiple pollutants reduction alternatives was addressed.
- Two air quality dispersion models (SCEEN3, and CALPUFF) were used to predict the concentrations of pollutants omitted from oil refinery.
- several simulations were conducted to illustrate the validity of both models.

5.2 Future Directions

In the current state of our work, possible future research avenues can be followed:

- It is interesting to study the impact of reducing the ambient air pollution concentrations released for oil refineries on the economic and on human health. Although, the oil refinery pays extra costs when reducing emissions concentration; however, the heath benefit is found to be significant. Conducting a cost-benefit analysis for oil refinery is therefore crucial to compare the cost of reducing the emissions concentration and the health benefit due to this reduction.
- The cost optimization model used in this dissertation considered only one refinery and three emission reduction strategies. It is interesting to study multiple refineries as well as more emissions mitigation options such as biofilter systems.

- Conduct an empirical analysis for actual oil refinery site and compare both results to investigate the accuracy of these models .

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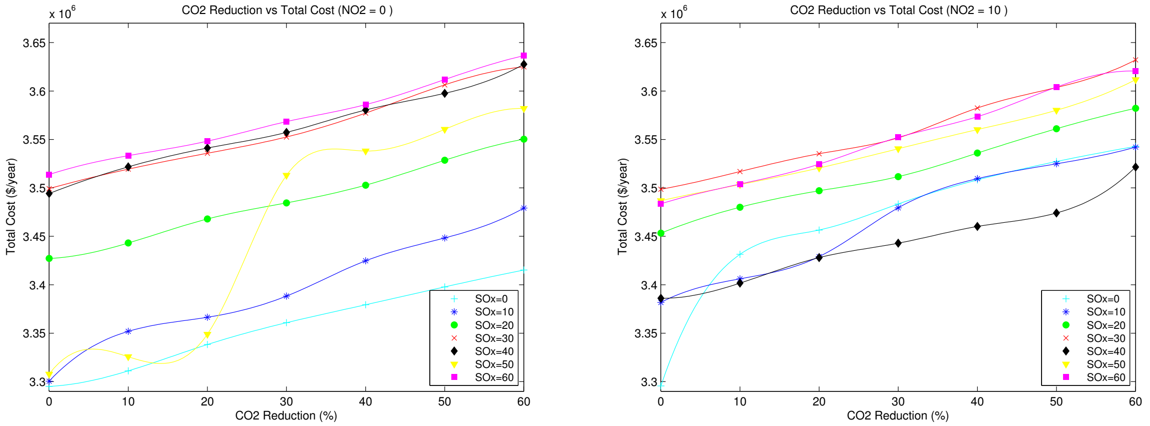
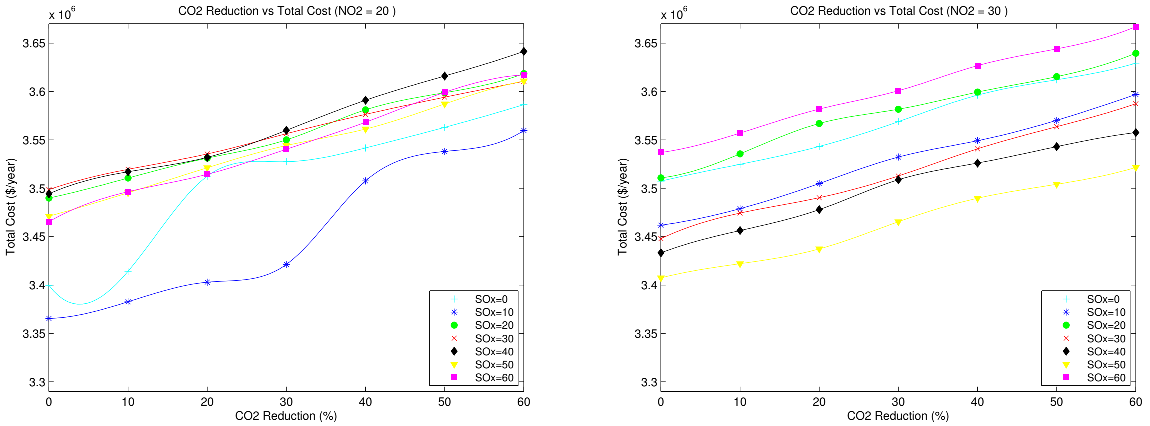
Appendices

Appendix A

Cost Versus Reduction

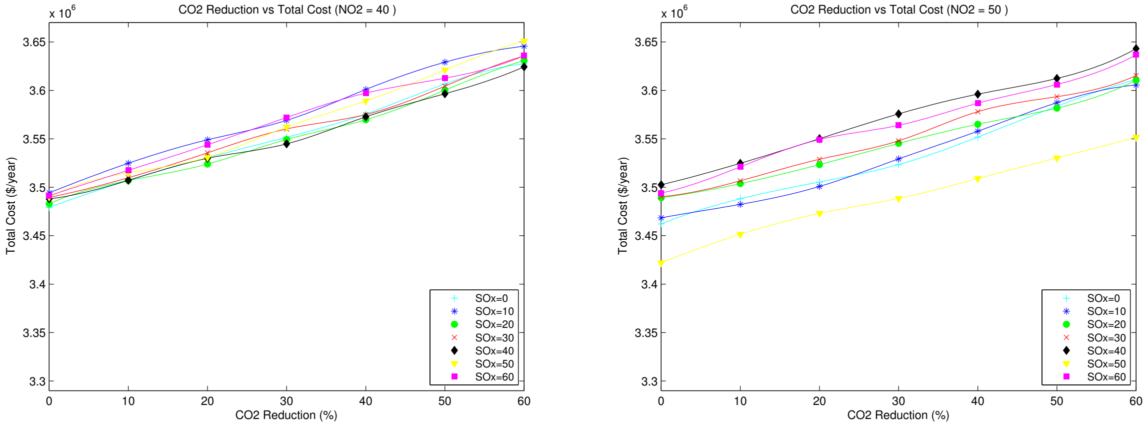


(a) At NO_x =0 (b) At NO_x =10

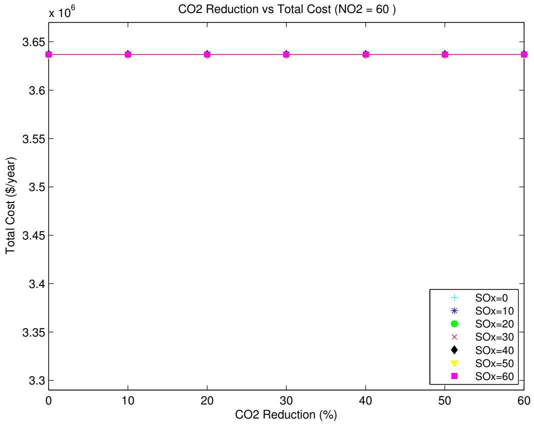


(c) At NO_x =20 (d) At NO_x =30

Figure A.1: Cost compared to reduction in CO_2

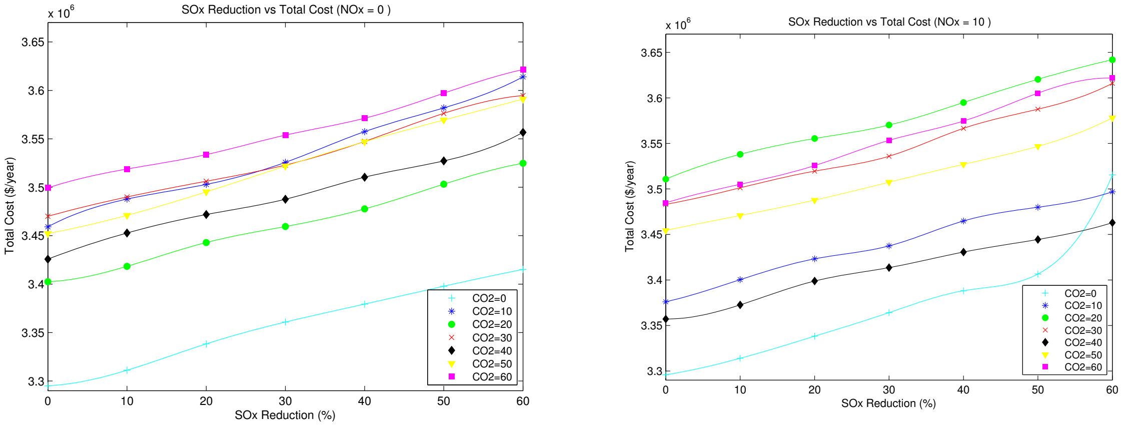


(a) At NO_x =40 (b) At NO_x =50



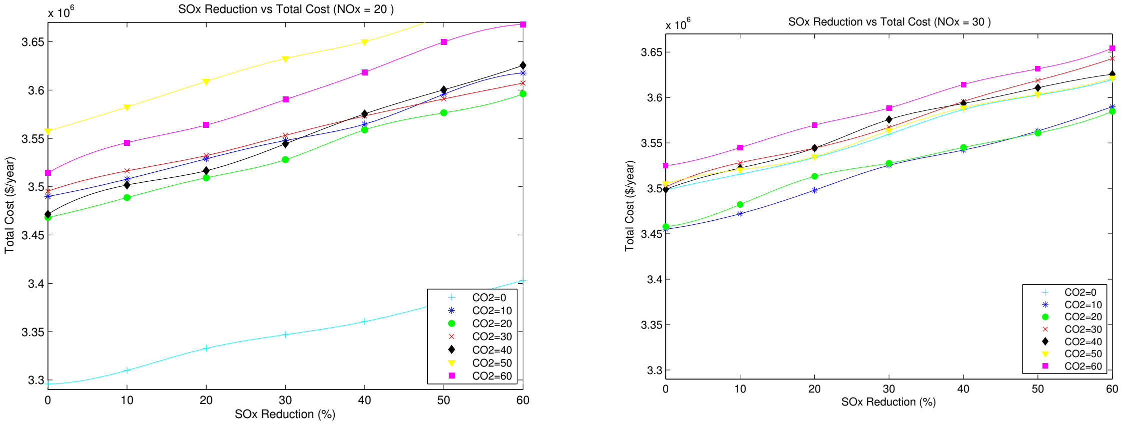
(c) At NO_x =60

Figure A.2: Cost compared to reduction in CO_2



(a) At NO_x =0

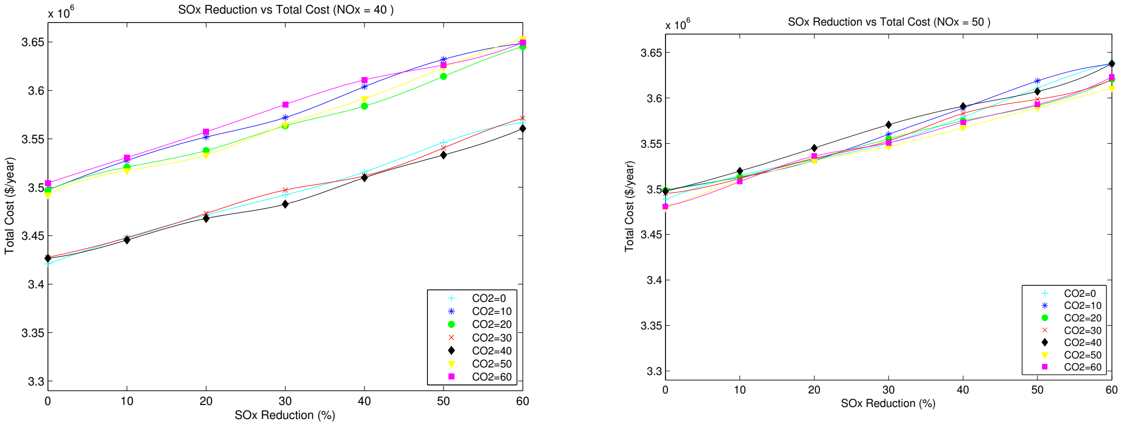
(b) At NO_2 =10



(c) At NO_x =20

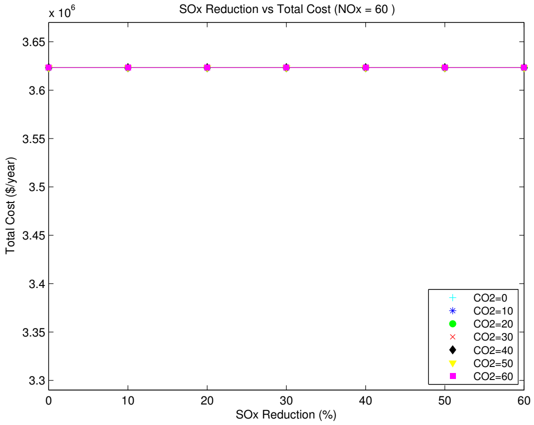
(d) At NO_2 =30

Figure A.3: Cost compared to reduction in SO_x



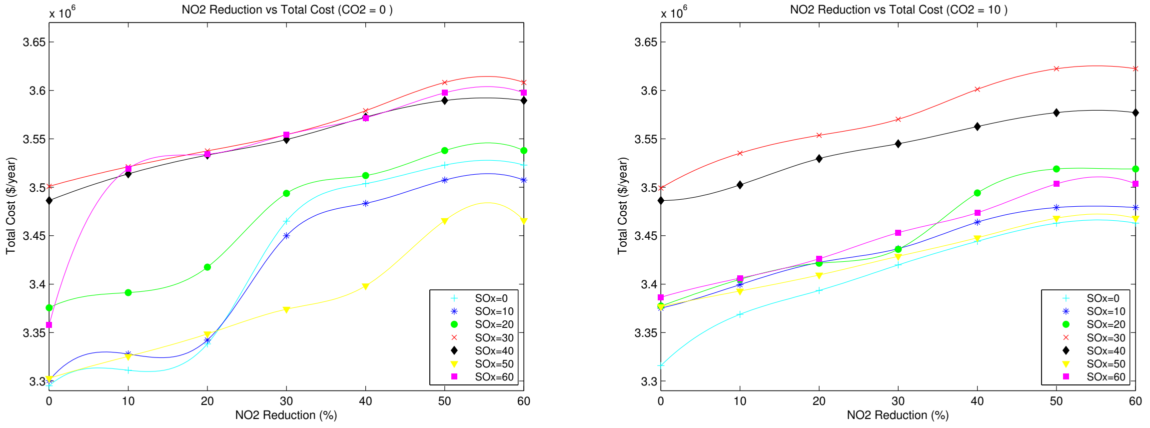
(a) At NO_x =40

(b) At NO_2 =50



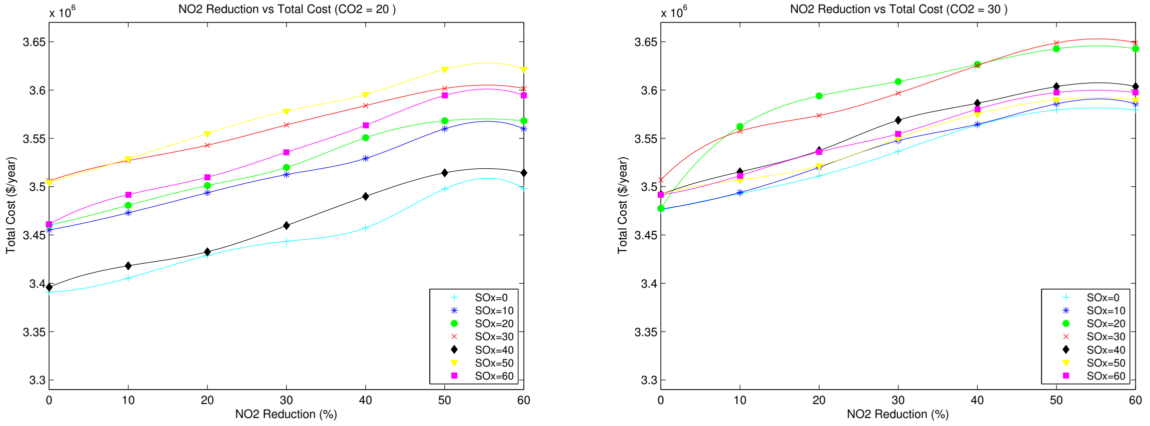
(c) At NO_x =60

Figure A.4: Cost compared to reduction in SO_x



(a) At CO_2 =0

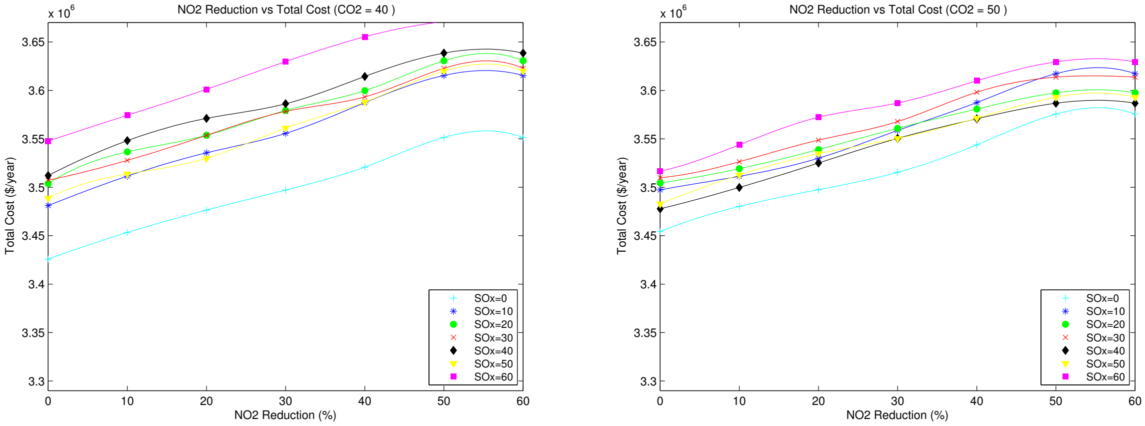
(b) At CO_2 =10



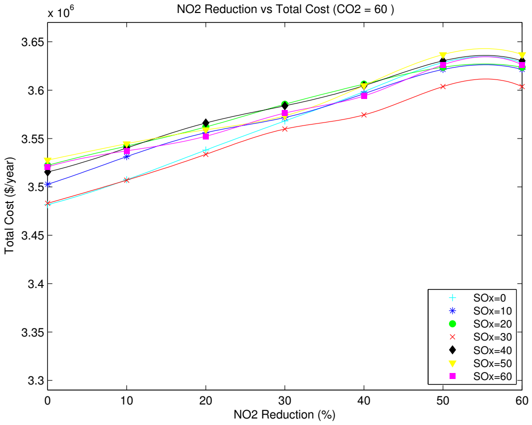
(c) At CO_2 =20

(d) At CO_2 =30

Figure A.5: Cost compared to reduction in NO_x



(a) At CO_2 =40 (b) At CO_2 =50



(c) At CO_2 =60

Figure A.6: Cost compared to reduction in NO_x

Appendix B

National Ambient Air Quality Standards and Guidelines

Sulphur dioxide (SO_2), nitrogen dioxide (NO_x), and carbon monoxide (CO_2) are considered to be the major pollutants by many countries and organizations [1]. Setting air quality limits and thresholds for these criteria pollutants is very essential in protecting public health.

Ambient air quality standards are essential for air quality management. To protect people and the environment from harm, designing ambient air quality standards that control concentrations level of air pollutants [2]. The assurance of the air quality standards comes through Laws and regulations governing air quality [3]. In fact, it is a challenging task to precisely set a standard for an air pollutant, which requires inputs from two main sources including observations of the short-term and long-term impact of environmental pollutants and specific experiments under controlled conditions 4. Ambient air quality standards are sometimes different for the same air pollutant that is due to that different organizations have independently evaluated the evidence on the same air pollutant [4].

In this appendix, we investigate the ambient air quality standards through official publications, relevant responsible government documents, and literature surveys. However, several nations do not have air quality standards at all and sometimes we face difficulties to report the standard due to the language issues. As we mentioned earlier, there is significant difference in the ambient air quality standards implemented by different countries. This results in presenting only a total of fifty countries and organizations as shown Table 1. It worth noting that World Health Organization's (WHO) recommendations for air quality is well accepted for many countries [5,6]. For instance, Singapore has standards that are generally adopted from the WHO guidelines [7].

Table B.1: Summary of International Ambient Air Quality Standards (data in $\mu g/m^3$)

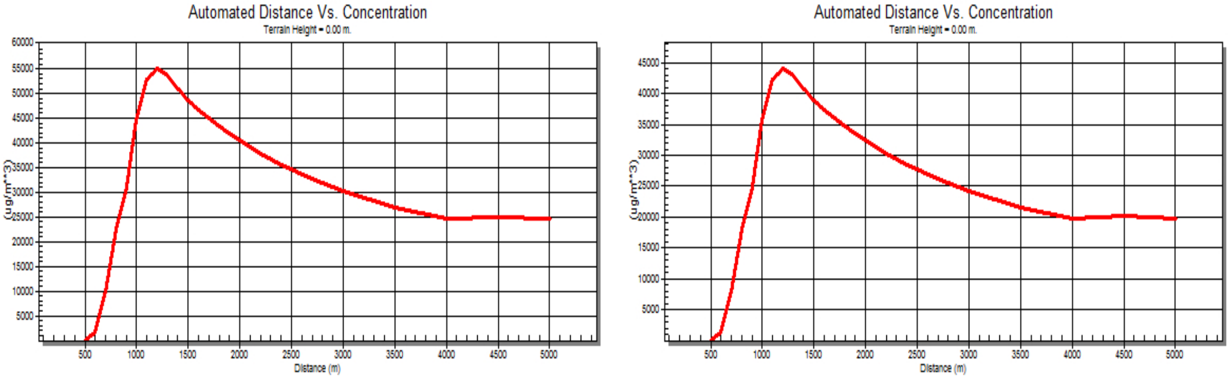
		SO2			NO2			CO (mg/m^3)		
Area	Country/ Organization	1h	24h	1 yr	1 h	24h	1yr	1 h	8h	24h
World	WHO	500d	20		200		40			
Europe	EU	350	125	-	200	-	40	-	10	-
Asia	Bangladesh	-	366	78	-	-	100	40	10	-
	Bhutan									
	Industrial	-	120	80	-	120	80	10	5	-
	Mixed	-	80	60	-	80	60	4	2	-
	Sensitive	-	30	15	-	30	15	2	1	-
	Cambodia	500	300	100	300	100	-	40	20	-
	China 1									
	Grade I	150	50	20	120	80	40	10	-	4
	Grade II	500	150	60	240	120	80	10	-	4
	Grade III	700	250	100	240	120	80	20	-	6
	China 2									
	Grade I	150	50	20	200	80	40	10	-	4
	Grade II	500	150	60	200	80	40	10	-	4
	Hong Kong									
	HK1	800	350	80	300	150	80	30	10	-
	HK SAR	-	125	-	200	-	40	-	-	-
	India									
	Area 1	-	80	50	80	40	50	4	2	-
	Area 2	-	80	20	80	30	20	4	2	-
	Indonesia	900	365	60	400	150	100	30	10	-
	Iran	210	-	-	-	100	-	-	50	10
	Japan	282	113							
	Korea	393	131	52	188	113	56	29	10	-
	Kuwait	800	500	-	200	100		40	9	-
	Malaysia	350	105	-	320	-	90	35	10	-
	Mongolia		30	10	85	40	30	-	-	-
	Nepal	-	70	50	-	80	40	-	10	-
	Oman	130b	-	-	-	-	100	40	-	-
	Pakistan									
	2009		120	80	-	80	40	10	5	-
	2012		120	80	-	80	40	10	5	-

Table B.2: Cont. Summary of International Ambient Air Quality Standards (data in $\mu g/m^3$)

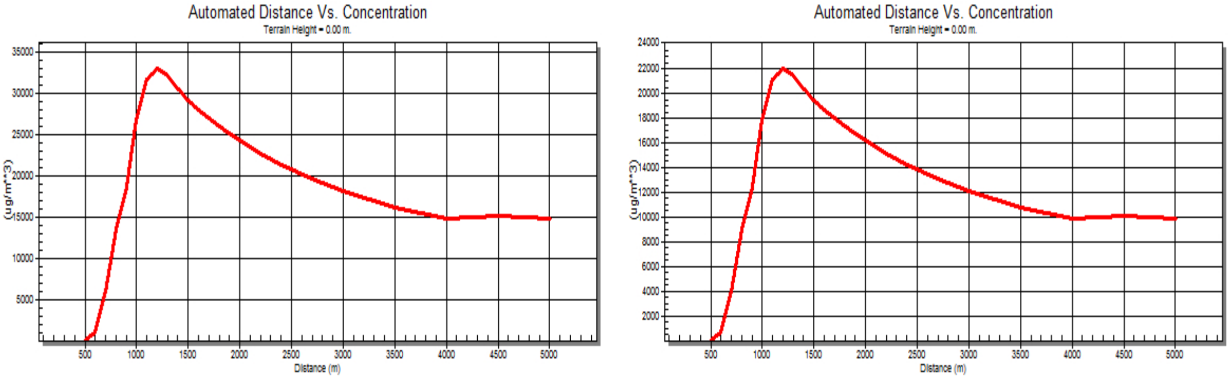
		SO2			NO2			CO (mg/m^3)		
Area	Country/ Organization	1h	24h	1 yr	1 h	24h	1yr	1 h	8h	24h
Asia	Philippines	-	180	80	-	150	-	35	10	-
	Qatar	-	365	80	400	150	100	40	-	-
	Saudi Arabia	730	365	80	660		100	40	10	-
	Singapore	196	365	80	188	-	100	40	10	-
	Sri Lanka	200	80	-	250	100	-	30	10	-
	Thailand	784	314	104	319	-	-	34	10	-
	Viet Nam	350	125	50	200	100	40	30	10	5
Africa	Egypt	350	150	60	400	150	-	-	-	-
	Tunisia	-	365	80	660	-	200	40	10	-
	Ghana									
	Industrial	900	150	80	-	-	400	30	10	-
	Residential	700	100	50	-	-	-	30	10	-
	Tanzania	-	100	60	120d	150	-	30	10	-
	Senegal	-	125	50	200	-	40	-	-	30
	South Africa	350	125	50	200	-	40	-	-	-
North America	Canada									
	NAAQO	875	300	60	400	200	100	35	15	-
	CWS	-	-	-	-	-	-	-	-	-
	CAAQS	-	-	-	-	-	-	-	-	-
	Mexico	524	288	66	395	-	100	-	13	-
	United State									
	Primary	196	-	-	190	-	100	40	10	-
	Secondary	-	1300g	-	-	-	100	-	-	-
Latin America	Argentina	2620	780d	80e	847	282	-	57	11	-
	Bolivia	-	365	80	400	150	-	40	10	-
	Brazil	365	-	80	320	-	100	40	10	-
	Chile	-	250	80	400	-	100	30	10	-
	Colombia	-	250	80	200	150	100	40	10	-
	Costa Rica	-	365	80	400	-	100	40	10	-
	Ecuador	-	350	80	-	150	100	40	10	-
	El Salvador	-	365	80	-	150	100	40	10	-
	Jamaica	700	365	80	100	-	-	40	10	-
	Nicaragua	-	365	80	400	-	100	40	10	-
	Puerto Rico	-	367	79	188	-	100	40	10	-
	Pure	-	80	-	200	-	100	30	10	-
	Rep. Dominican	450	150	100	400	300	100	40	10	-
	Venezuela	-	365	80	367	300	100	35	10	-
Oceania	Australia	524	210	52	225	-	56	-	10	-

Appendix C

Screen3 Results

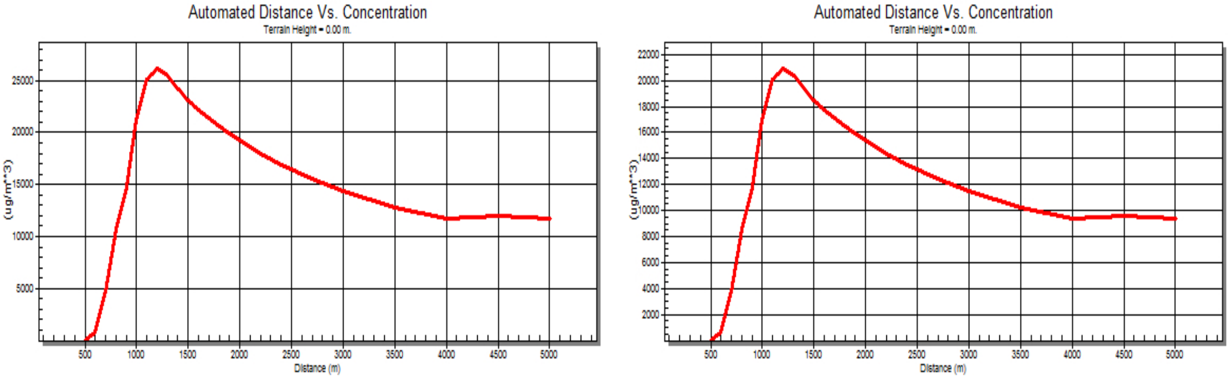


(a) Base Case (b) 20% Reduction



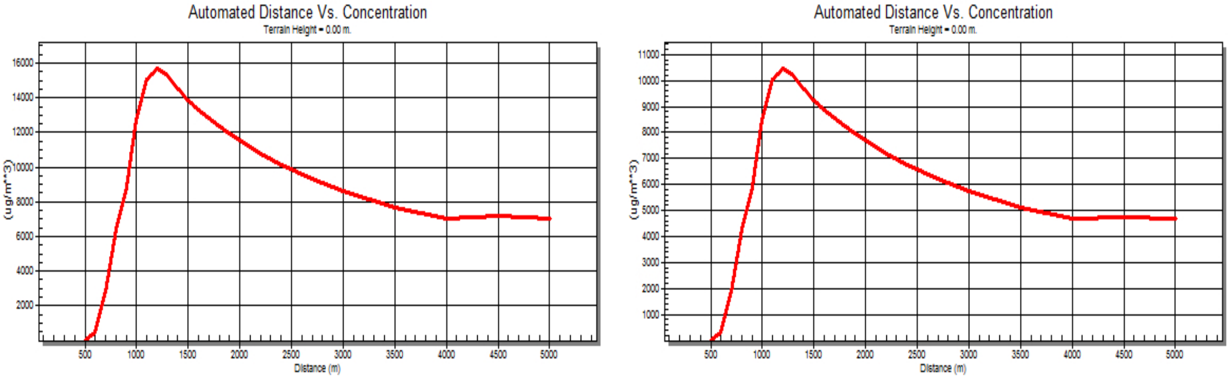
(c) 40% Reduction (d) 60% Reduction

Figure C.1: Maximum NO_x concentration vs. downwind distance (m) using *SCREEN3* over multiple reduction plans



(a) Base Case

(b) 20% Reduction



(c) 40% Reduction

(d) 60% Reduction

Figure C.2: Maximum CO_2 concentration vs. downwind distance (m) using *SCREEN3* over multiple reduction plans