ON THE CHEMICAL MIXTURE METHODOLOGIES FOR ESTIMATION OF THE INTEGRATED HEALTH EFFECTS

A Thesis

by

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ABSTRACT

It is very worthwhile for the regulatory agencies to have an understandable method to evaluate the health effects for humans who may be exposed to several mixtures of emitted chemicals, due to continuous regulated releases from industries. Several scientific studies and approaches were developed by international environmental agencies to estimate the combined effects from exposure to a mixture of chemicals.

Usually, the developed approaches focus on predicting the impact from non-routine chemical releases in the atmosphere. However, even regulated routine releases could pose significant threat to human health when one considers the integrated effects. Present study examines the available methods to estimate the impact of air pollutants mixture and in the case of continuous airborne releases from several industries (industrial cities).

The Chemical Mixture Methodology (CMM) is extensively used for emergency preparedness in the U.S. (Department of Energy, DOE). CMM uses the Hazard Index (HI) method which is also one of the recommended simple approaches to conduct a health risk assessment of chemical mixtures by both the Environmental Protection Agency (EPA) and Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulations. Therefore the study deals with the necessary tools in order to sustain the original CMM applicable for continuous releases in the atmosphere.

These tools include: a) models to predict the emission rates of the released pollutants, b) a dispersion model (AERMOD) to predict the concentrations of the pollutants at several receptor points and c) an in-house algorithm that deploys the various realizations of the CMM. A hypothetical scenario, based on an industrial city in State of Qatar, was built using an appropriate methodology. The outcomes demonstrate the applicability of the developed CMM methodology and tools to account for continuous releases. Finally, the results for the scenario revealed two important aspects. First, that the likelihood of severe impacts – hazard – increase in the case of a mixture of pollutants than a single one. Secondly, the selection of the exposure limits is a critical factor that can drastically change the conclusions of the CMM method, in other words the assessment of risk.

DEDICATION

To my parents

ACKNOWLEDGEMENTS

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NOMENCLATURE

ACGIH	American Conference of Governmental Industrial Hygienists
ADI	Acceptable Daily Intake
ALOHA	Areal Locations Of Hazardous Atmospheres
API	Air Pollution Index
AQI	Air Quality Index
ATSDR	Agency for Toxic Substances and Disease Registry
BAT	Best Available Technology
BMC/BMD	Benchmark Concentration or Dose
BREF	Best Reference document
CDO	Climate Data Online
CEC	Commission of the European Communities
CMM	Chemical Mixture Methodology
CSV	Comma Separated Values
DOE	Department Of Energy
EEA	European Environmental Agency
EET	Emission Estimation Technique
EMEP	Emission Monitoring and Evaluation Program
EPA	Environmental Protection Agency

ERPG	Emergency Response Planning Guidelines
HAP	Hazardous Air Pollutants
HCNs	Health Code Numbers
HEIDI	Health Effects Indicators Decision Index
HI	Hazard Index
ILO	International Labor Organization
IPCS	International Program on Chemical Safety
MIC	Mesaieed Industrial City
MM5	5^{th} Mesoscale Model
MRLs	Minimal Risk Levels
NCDC	National Climate Data Center
NERAM	Network for Environmental Risk Assessment and Management
NIOSH	National Institute of Occupational Safety and Health
NOAA	National Oceanic and Atmospheric Administration
NOAL	No- Observed-Adverse-effect-Level
NPI	National Pollutant Inventory
OSHA	Occupational Safety and Health Association
PAC	Protective Action Criteria
PEL	Permissible Exposure Limit
PI	Pollution Index

PODI	Point Of Departure Index
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RPF	Relative Potency Factor (RPF)
SCAPA	Sub-Committee on Consequence Assessment and Protective Actions
TE	Toxic Equivalency
TEEL	Temporary Emergency Exposure Limit
TEF	Toxic Equivalency Factor
UNEP	United Nations Environment Program
WFs	Weighting Factors
WHO	World Health Organization

TABLE OF CONTENTS

Page

Page

Page

LIST OF FIGURES

Page

Page

LIST OF TABLES

Page

Page

1. INTRODUCTION

Human health risk assessment is considered as one of the crucial topics in risk assessment field. The Environmental Protection Agency (EPA) defined the human health risk assessment as: “the process to estimate the nature and probability of adverse health effects in humans who may be exposed to chemicals in contaminated environmental media, now or in future" [1]. Various scientific studies used different human health risk assessment methods to assess the potential health effects from exposure to the emitted chemicals in the atmosphere [2]. The primary studies were focused on assessing the potential health effect of the individual substances. Further attention is presented recently to account for the combined effects of a mixture of chemicals emitted from several industries to the atmosphere [3]. The aim of such assessments is to study the relation between human health and air pollution levels, in order to identify air pollution circumstances and to plan reduction strategies [4]. In addition, to collect reliable emissions inventory information and health effects records, in order to improve the existing environmental management systems and the policy-making resolutions [5]. The United Nations Environment Program (UNEP), the International Labor Organization (ILO) and the World Health Organization (WHO) have established the International Program on Chemical Safety (IPCS) in 1980 to set the scientific basis for human health and environmental risk assessments as a result of exposure to chemicals.

The program is also created to promote chemical safety measures in different industries [6]. Figure 1 shows the four basic required steps to carry out a human health risk assessment based on EPA recommendations:

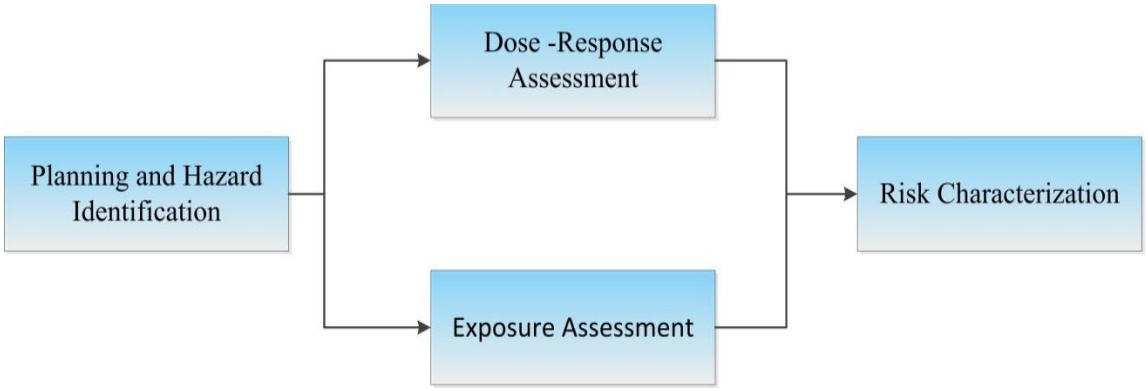

Figure 1: The recommended steps for human health risk assessment by EPA [1].

The preliminary step according to EPA is the planning and hazard identification where a scope and purpose for the assessment is stated with all required technical judgments for the situation, the next measure is to identify the potential health effects with the possible impacts on the ecological systems that may be caused by the pollutant (stressor), in additions to the expected conditions for the risk to be likely occurred. The second step of the assessment is to investigate the possible relations between the exposures (doses) and the toxic effects numerically. The third step is to evaluate the frequency (likelihood) and the severity (level) of contacting the stressor.

The final step in the assessment is to summarize the findings and results from the previous steps to create a complete conclusion about the risk of exposure to such stressor [1]. The conclusion may include the nature and extent of an exposure to such stressor and the mitigation measure to reduce or avoid unnecessary exposure to it. The same steps were recommended by the European Environmental Agency (EEA) for all human health risk assessments studies with further release assessments procedures for some specific scenarios for non-routine or accidental releases [7]. In addition, EEA defined the human exposure major routes for air pollutants as shown in Figure 2 , the figure illustrates the possible routes of exposure by inhalation to chemicals. Generally, the exposure can be in a direct manner (produced emissions to air, land or water through industrial fabrication, usage or disposal) or by indirect way (through another transportation medium like drinking water) [7].

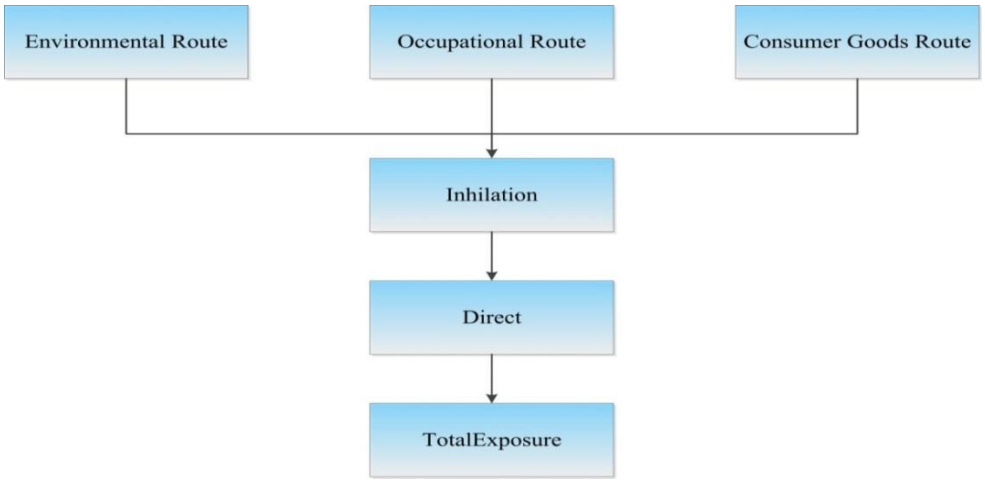

Figure 2: Main routes for human exposure (by inhalation) to emissions by EEA [7].

Several dozens of researches have been conducted to investigate the effect of the released chemicals to atmosphere, water or soil on the living organisms. The main aim of such studies was to establish acceptable legislations and regulations internationally to enhance the inventory processes for the chemicals which are released to the environment. In 2008, REACH has registered around 150,000 chemicals that might be released to atmosphere, soil or water as a sequence of normal life cycle of the chemical, unplanned releases or regular releases from indoor and outdoor activities [3]. The majority of the analysis methods was subjected to intensive studies on the human organs/tissues or from environmental partitions, and most of the studies concluded the importance of studying combined effects of multi chemicals exposure situations [3]. Previously, most of the conducted assessments are based on a toxicological consideration for single chemicals, while in reality the public are exposed to combined mixtures of components which might reflect a serious hazardous situation either by the additivity of the components effects, interactions between the components or both. One of the first stages in such risk assessment is to define the category of the concerned chemical mixture. For example if it is final product like gasoline and pesticides or a process emission such as: emissions from fuel combustions [8]. Frequently, the chemical mixtures are consisting of variety range of chemicals which may be unrelated or from different sources, and the common factor between the concerned chemicals is the receptor point or population [8].

The actual exposure to such chemicals may depend strongly on several conditions like: time or period of the release, delayed and acute effects of the chemicals in the mixtures, distance from the sources, the meteorological conditions and dynamics of chemicals concentrations [3,4]. Therefore, the relation between the toxicological effects and the exposure to a mixture of chemicals is considered as a challenging issue while applying the cumulative risk assessment for such cases.

There are two types of assessments widely used to perform the required exposure assessment for the mixture of chemicals; the first assessment is the macro assessment type which is strongly depending on the bio-monitoring information. The collected results from living organisms and blood samples are used to assess the exposure to such mixture of chemicals in specific area. The second type of assessment is the micro assessment method which is predicting the exposure of the chemical mixtures using modeling concepts. In such assessment the steps include detailed quantification for the different sources of emissions and the actual exposure to the chemicals. Frequently, this method is used to regulate the necessary standards and limitations for environment and human health [3].

"Are chemical mixtures more toxic than their individual components? " this question is posing a challenge for risk assessment experts and organizations all over the world, many scientific studies and technical reports are conducted to evaluate the cumulative risk of exposure to mixtures of chemicals and compare it with the risk of exposure to same chemicals individually.

It is stated clearly in hazard and risk assessments under REACH that "The mixture toxicities need to be specifically considered in chemical regulation" and "The joint toxic effect of chemical mixtures is always higher than the individual effects of each of its components" [2, 8]. In addition, scientific researches proved that the effect of a mixture of chemicals existing in low concentrations might still posing a significant risk to the living organisms, however the low concentrations of the same chemicals won't create any significant effect individually. This evidence was delivered from several studies for different groups of chemicals in REACH guidelines [2, 9, 10].

Many efforts have been made aiming to find the appropriate approaches to conduct the required risk assessments for multi chemicals or even a group of mixtures. According to EPA, ATSDR and REACH, there are three established general methods to conduct the risk assessments for the multi chemicals or chemical mixtures [2, 7, 11]:

1- Whole mixture assessments or (actual mixture of concern).

2- Similar mixture assessments.

3- Component by component assessments.

The usage of each method strongly depends on the availability of the basic required information and inventory data for each situation or scenario. Therefore, recommended guidelines were established by EPA for selecting the applicable method to conduct the desired risk assessment. An overall idea about the published chemical mixture risk assessments approaches by the international agencies is available in appendix A. Figure 3 shows the suggested criteria for selecting the applicable approach.

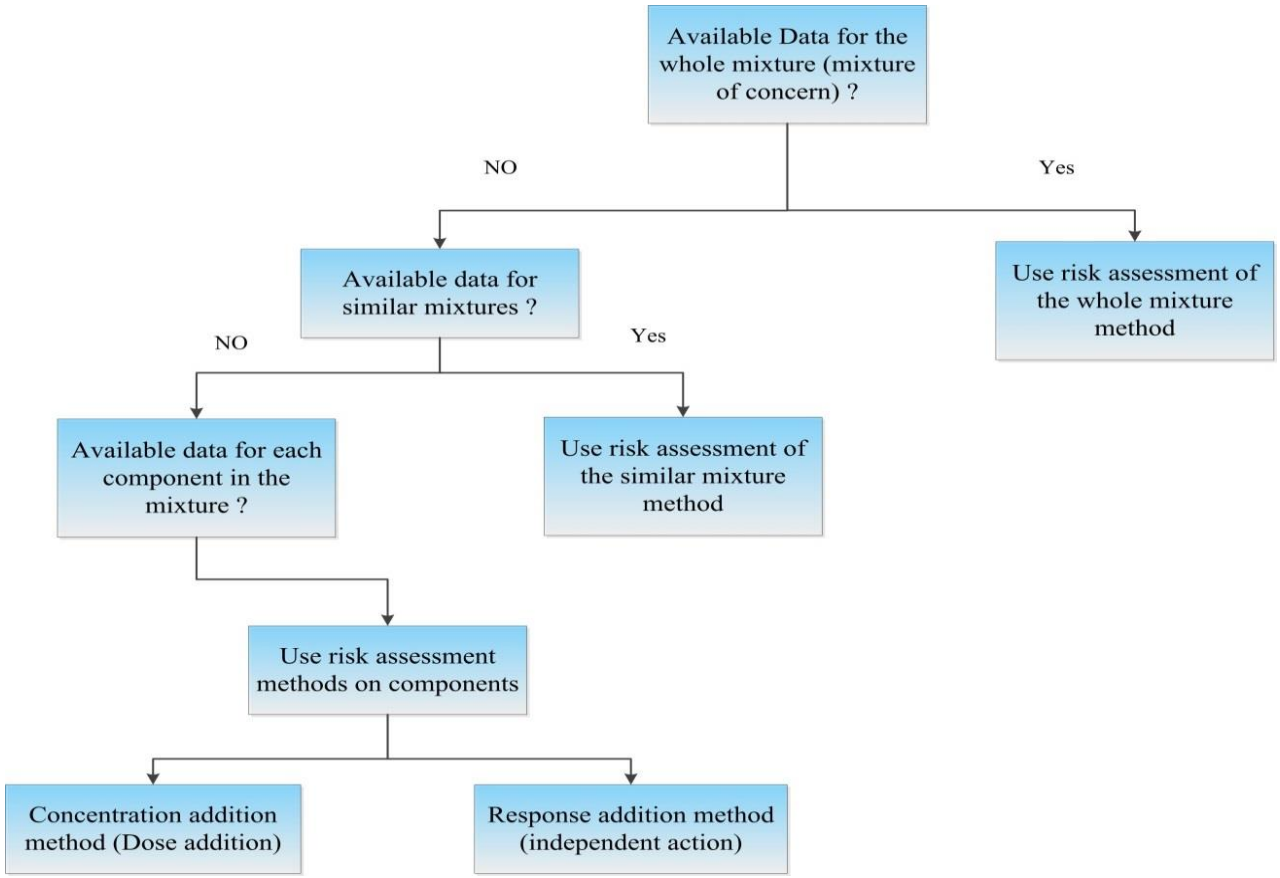

Figure 3: Risk assessment guidelines and approaches for mixtures of chemicals [8].

1.1. Hazard Index Method

HI is considered as the most applied method for component by component risk assessment approach under concentration addition methods [3, 7], if the toxicological data showed relative similarities for each component within the mixture.

HI is applying a simple mathematical model to sum the individual HI according to the following simple equation [12]:

$$HI = \sum_{i=1}^{n} \frac{E_i}{AL_i} \qquad \text{Equation (1)}$$

Where: HI is hazard index, n is the number of components in the concern mixture, E_i is the exposure level of component i and AL is the recommended or acceptable exposure level. The above equation is describing the ratio between the exposure levels –which might be the concentration– to the acceptable exposure level of this component. The concern of a potential hazard from the mixture is raised when the hazard index of the mixture exceeds the unity (HI > 1). Consequently, several mitigation measure will be required to reduce the effects of the mixture of concern [3, 4].

The assumption of dose additivity is used in the above simplified form of hazard index, and accounting for the interactions between the components in the mixture are assumed to be neglected [7, 12]. This assumption simplified the approach and makes it wieldy accepted as a first screening measure for the associated hazards with the

chemicals in the mixture of concern. In some preliminary studies the simplified HI might be applicable even for components with different mechanism of actions or target organs, to initially examine the situation but taking in consideration that the model will be conservative to some extent [8]. There are several allowable exposure levels used in literature and accepted by different agencies to conduct the necessary risk assessment of the studied mixtures. RFD & RFC are used by EPA 2000 [4, 5], MRLs is used by ATSDR, TLVs is used by ACGIH, OSHA is using PELs and WHO is using ADIs. A brief discussion is given in appendix A for using different limits and standards with HI method.

1.2. Determining an Approach for Chemical Mixture Risk Assessment

The amount of the available information and inputs data will strongly determine the suitable approach for a chemical mixture in a specific study. Since the toxicological data of the studied mixture are rarely available for whole mixture groups, and even for similar mixtures approaches. The component based approach is widely selected to conduct the preliminary risk assessment for a group of chemicals. Figure 4 was suggested by L.Teuschler in 2007 to summarize the way of selecting the most applicable compnents based approach depending on the available information for a specific group of chemicals [14]. Level and likelihood of knowledge are the main factors for selecting the optimum approach according to L.Teuschler [14].

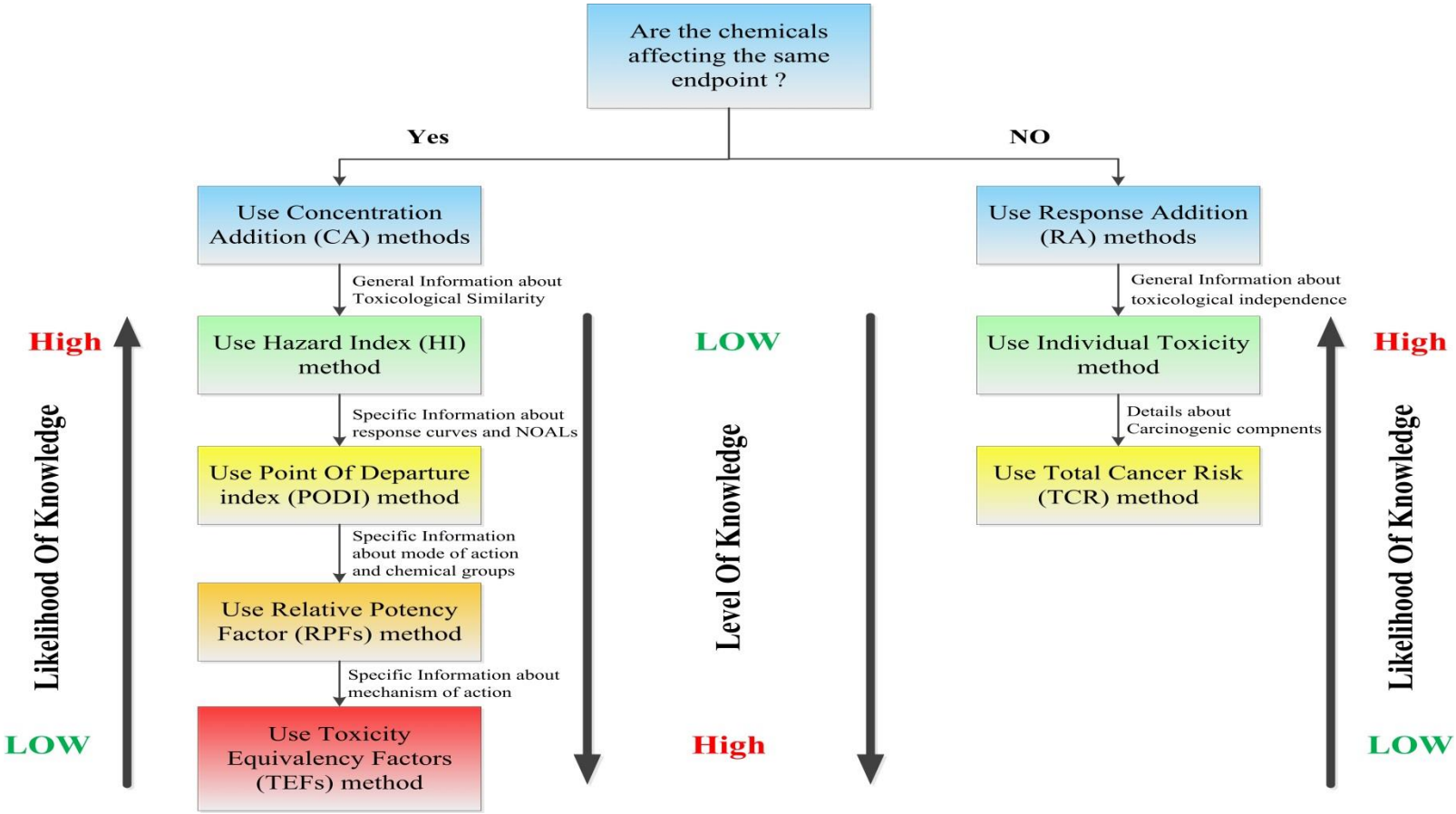

Figure 4: Selection criteria for the applicable method in components based approach[1].

[1] The original L.Teuschler flow diagram is modified to include other methods like PODI and RA methods in order to give an overall idea about the selection criteria.

Table 1 shows a benchmarking analysis method for several studies used to assess the health effects from the emitted pollutants to the atmosphere. The main target of this analysis is to select the best available method to study the health effects of the regulated emitted releases to the atmosphere from different industries. Table 1 also shows several factors used to validate the selection criteria of a method to be used in this study. The selected assessment method is the Chemical Mixture Methodology (CMM), this method was selected due to:

1- Availability of guidance and inputs information.

2- Dealing with various types of chemicals in a mixture.

3- Accounting for the combined effect of the mixture of emissions to atmosphere.

4- Counting the health effects in a quantitative manner.

The following section is giving a brief idea about CMM uses and assumptions.

1.3. Chemical Mixture Methodology (CMM)

The Chemical Mixture methodology (CMM) is developed by the emergency planning and hazard assessment office in the U.S. Department Of energy. The first attempt to create the CMM was officially established in 1999 by D.K.Craig and others [15]. The default CMM was used to assess the exposure to several mixtures of chemicals emitted to the atmosphere in emergency or non-routine releases.

Table 1: Benchmarking analysis between different assessment methods.

Method Name	Health effect priority ranking system		Chemical Mixture Methodology		Air Quality Indices	
Approaches	HEIDI I, HEIDI II	--	CMM (HI)	--	AQI, API ,PI	--
Developer	Network for Environmental Risk Assessment and Management (NERAM), Canada	--	Emergency planning and hazard assessment of U.S Department of energy (U.S. DOE)	--	AQIs researchers from agencies guides (ex.: EPA, EC and WHO)	--
References	(NERAM final report, 2004) [16], (L. Gowar, 2008) [17],	--	(D.K. Craig, 1999) [15], (Xiao- Ying Yu, 2010) [18], (Xiao- Ying Yu, 2012) [19]	--	(Murena, 2004) [20], (Kyrkilis, 2007)[4], (Caircross, 2007) [21], (Dimitriou, 2012) [22]	--
Scenarios' duration	Continuous Releases	↑	Emergency Releases	↓	Emergency Releases and Continuous Releases	↑
Guidance availability	General guidelines are available	—	Step by step guidelines are available	↑	Different guidelines are available	—
Inputs Data Availability	Quite available	—	Available in a good quantity	↑	Quite available	↓

Table 1: Continued

Method Name	Health effect priority ranking system		Chemical Mixture Methodology		Air Quality Indices	
Counting health effects	General health effects (DALYS)	↓	Detailed information about health effects and targeted organs (HCNs)	↑	General health effects (mortality, morbidity)	↓
Included chemicals, pollutants	Various range of pollutants Such as: PAHs,BTEX etc…	↑	Various range of pollutants Such as: SOx, NOx, VOCs, PAHs etc…	↑	Generally for common air pollutants such as: PM, NO2, SO2, CO etc….	↓

The following equations were used to estimate the hazard index for the individual compnents in the mixture and sum the hazard indices to get the overall hazard index of the mixture [15]:

$$HI_i = \frac{C_i}{Limit_i} \qquad \text{Equation (2)}$$

$$\sum_{i=1}^{n} HI_i = HI_1 + HI_2 + HI_3 + ... + HI_n \qquad \text{Equation (3)}$$

Where, C_i is the individual concentration of each chemical in the mixture, if the summation of $HI \geq 1$ this indicates that limits have been exceeded.

1.4. NERAM Health Effect Assessment Project

Another attempt to use the environmental risk assessment approaches was conducted from 2002 to 2004 by the Network for Environmental Risk Assessment and Management team (NEARM) in Canada with corporation of the institute of risk research. The aim of the project was to develop a health effect based priority ranking system for the air emissions from 20 oil refineries in Canada. The team developed an excel sheet and called it Health Effects Indicators Decision Index (HEIDI), the spread sheet has the ability to help policymakers in prioritizing reductions measures for air emissions from the studied refiners [16].

The contribution of each pollutant from each refinery to ambient air concentration in Canada was accounted in the study [17]. The exposed population was estimated using ArcMap GIS software for the 20 zones. The incident cases were predicted according to the several equation available in appendix B [16].

In order to assess the health impacts of the emitted pollutants, a series of simplified and complex Disability Adjusted Life Years (DALYs) values were estimated. The NERAM team concluded the outcome that HEIDI has the ability to provide the policymakers a screening level based ranking for the contributed refineries in Canada. In addition extra care is required while comparing the health impact across different chemical classes, since there are several valid assumptions used in each module in the project and the uncertainties are likely to occur [16]. A flow structure figure –available in appendix B– was published in the NERAM final report in 2004 and it provides an overall idea about the HEIDI II project steps and the expected result from each module [17].

2. RESEARCH PROBLEM AND OBJECTIVE

This study aimed to use one of the applied health effects assessment methods to estimate the integrated health effects for a mixture of chemicals. According to the available data and information, the selected assessment method is the Chemical Mixture Methodology (CMM). The thesis is focusing on determining the expected health effects on individuals from the continuous exposure to various emitted releases from industries.

The main objective of this thesis is to use several tools in order to make the original CMM applicable for continuous releases to the atmosphere, and to estimate the integrated health effects for a wide range of receptor points around the sources of emissions. The following tasks are accomplished to deliver the stated objective:

1. Build a virtual industrial city and estimate the releases from the facilities based on a selected layout for an existing industrial city (MIC in Qatar).
2. Estimate the emission rates for each industry using emission factors approaches.
3. Assemble and simulate the meteorological conditions of the studied location based on the available weather conditions information.
4. Introduce a dispersion model to estimate the concentration contours at the receptor points for different geographical locations in a selected base map.
5. Apply the latest developed CMM approaches to evaluate the associated health impacts from the emitted chemicals.

3. METHODOLOGY

In this section, the required steps to carry out the health effects study are discussed in details with the related assumptions and justifications. The methodology is constructed according to the stated tasks in the research objective. A brief background review is given about the CMM topic at the beginning of the methodology and a short overview is given for each required tool in the study at the beginning of each topic.

3.1. Background on the Chemical Mixture Methodology CMM Topic

Craig suggested the use of default hazard index method to predict the potential health effects from the exposure to a mixture of chemicals emitted to atmosphere from anthropogenic sources [15]. The chemicals were classified in this study according to their toxic consequences in order to sufficiently use the outcomes of this method. Health code numbers were used to define the toxic consequences of the studied mixtures by the committee. The published article in 1999 described the default methodology used to the find the hazard indices of several mixtures available from DOE facilities in U.S.

The concentrations of the individual chemicals are calculated at the desired receptor points and the exposure limits were mainly extracted from ERPGs and TEELs. The article is specified that if the chemicals are affecting the same “target organs” or “modes of action”, the hazard index summation should be done for the similar groups of effects or actions [15].

The used Health Code Numbers HCNs for “target organs” and “modes of action” in the default CMM –attached in appendix C– are originally published by Patty’s industrial hygiene and toxicology in 1985 and SAX’s dangerous properties of industrial materials in 1996. HCNs are categorized in a way to understand the different potential effects on humans over a specific period for example (acute effects and chronic effects). The default methodology focused on the accidental scenarios from DOE facilities for example: sudden releases of chemicals, violent reactions or even explosions. The assumption of neglecting the interaction effects (synergism, antagonism) were used to conduct the hazard index method for chemicals that have similar effect on specific organs. Figure 5 shows the recommended published methodology in 1999 by .D. Craig to assess the risk from exposure to chemical mixtures. The default method concluded that using the recommended methodology is better than studying each pollutant independently in the mixture and proved that using the assigned HCNs for the “target organs” or “mode of action” method is more precise than the simple summation the hazard indices of all chemicals within the mixture [15].

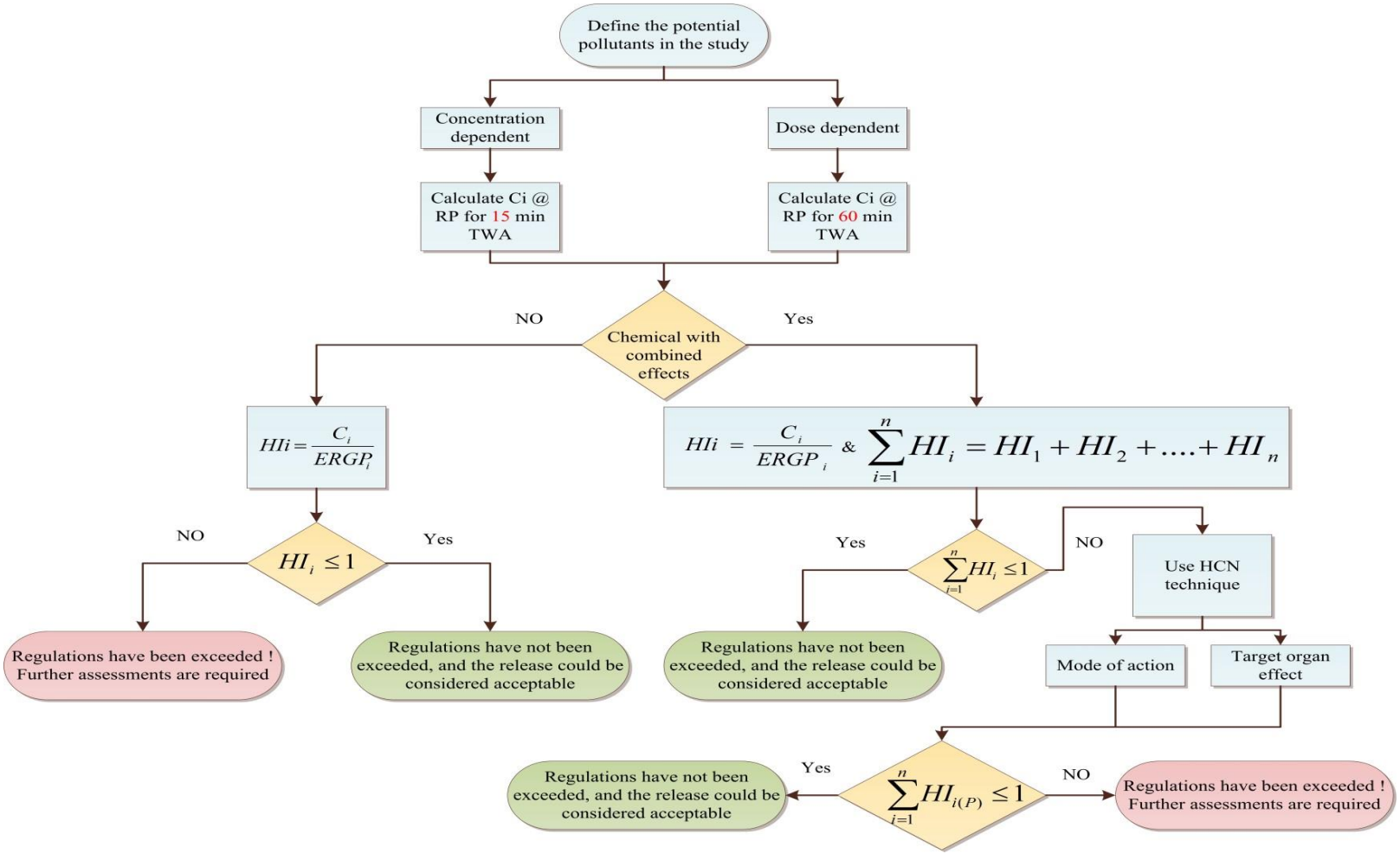

Figure 5: Default methodology for CMM in 1999 [15].

3.1.1. The development of CMM

In 2010, the Sub-Committee on Consequence Assessment and Protective Actions SCAPA members in the U.S DOE published an article to describe the new modifications and applications of the CMM in evaluating the expected impacts from the emergency or the unplanned releases to atmosphere.

The study validated the same initial assumption used in 1999 and didn't account for any chemical reactions that taking place after releasing the mixture to atmosphere. The SACPA team created an excel workbook to account for maximum 30 chemicals in a single mixture. The spreadsheet has the ability to define the impacts of each chemical and categorizes them upon their endpoints (target organ and /or mode of action). It also provides the required hazard indices for each case in an output sheet with attention signs if the limits are exceeded. The spreadsheet contains the background information of more than 3300 chemicals including their CASRNs, several levels of limits and the associated HCNs for each chemical. The SCAPA team introduced the use of dispersion models to predict the concentrations of the emitted releases to atmosphere at the desired receptor points [18]. The suggested models for an emergency releases were EPI code and ALOHA dispersion models.

The developed approach of CMM suggested the use of protective action criteria (PAC) values which are established by U.S DOE and updated in 2012. The health code

numbers were improved from the last published default methodology in 1999, and the HCNs concept were recommended to be used again in the developed methodology. There are 60 HCNs used to characterize the potential impacts of the chemicals on human organs. The used HCNs and PAC values are tabulated in appendix C. Figure 6 shows the methodology used in the developed approach where the stated modifications are suggested, the methodology clearly showed that all chemicals within the studied mixtures are routed to the HCNs approach even if the hazard index summation is not exceeding the unity. This modification will ensure all the associated impacts of the chemicals in the mixture are considered for each target organ.

The study concluded that the major changes in the CMM approach leads to significant improvements in the performance of the methodology in emergency management and response applications. The new added HCNs enhanced the CMM to predict more accurate results on each target organs from the releases of the mixture [18]. The SCAPA team recommended the use of more powerful atmospheric dispersion model that generates a grid of concentration profile at different receptor points. Also, it is advisable to use a more compact form of CMM for the acute HCNs in the emergency situations or applications. A more expanded CMM approach which includes all HCNs (acute and chronic) is recommended to be used in other types of safety investigations [18].

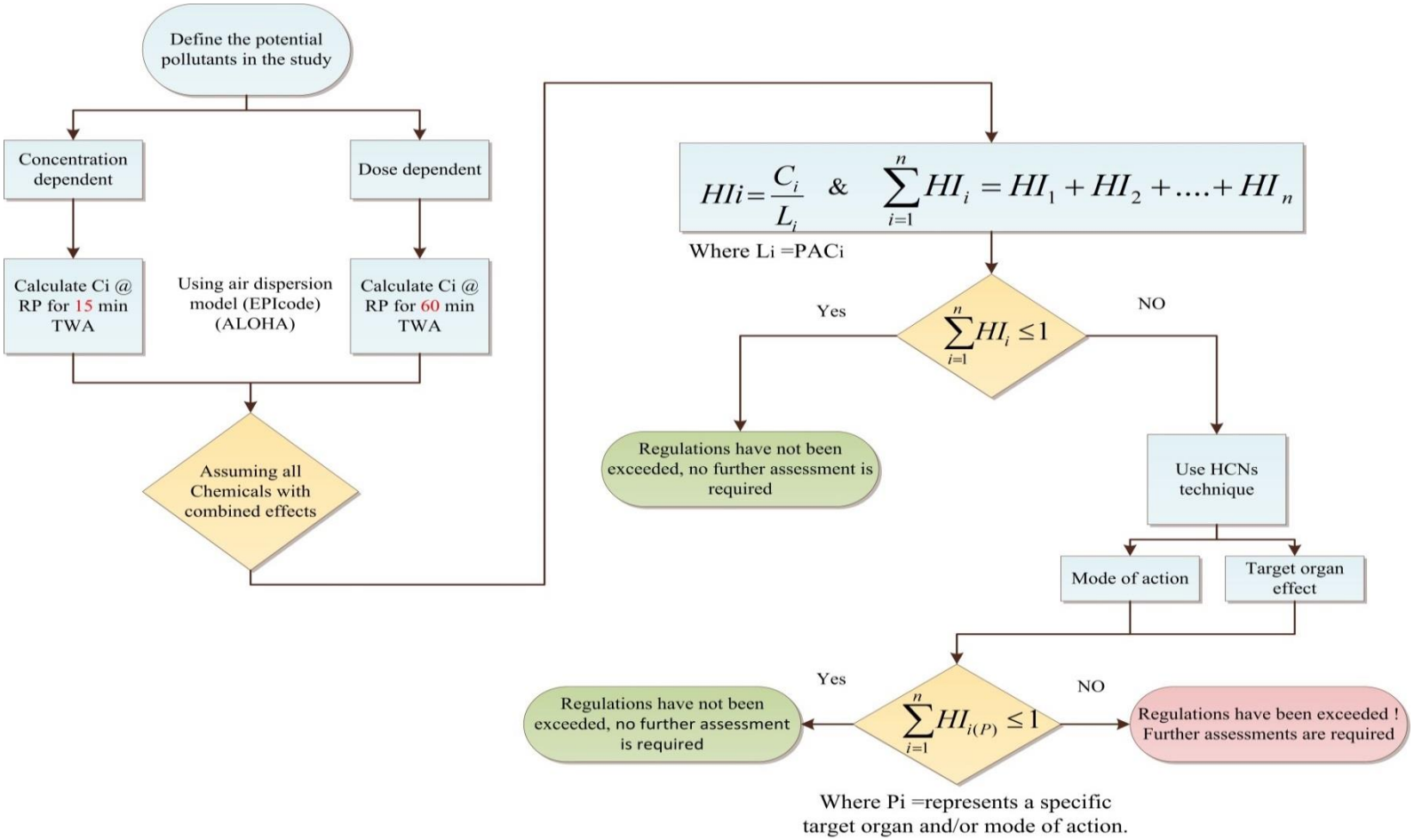

Figure 6: The suggested steps for the developed CMM Approach in 2010 [18].

3.1.2. Enhancing the developed CMM

In 2012, the CMM was enhanced by introducing several HCNs weighting factors approaches in order to improve the effectiveness of the CMM and reduce the conservative aspects of the default approach [19]. Although the introduced HCNs approach in 2010 resulted in more realistic outcomes from the default CMM, the approach is still conservative to some extent and requires some enhancements [19]. The suggested enhancement in this study was: introducing several weighting factors approaches to decrease the HIs results from HCNs approach for the insignificant affected target organs. The main benefit of using such factors was to reduce the HIs for the target organs that are unlikely to be affected at the selected concentration limits. There are three different weighting factors approaches used to reduce the associated HIs:

Approach 1

This approach is based on multiplying the HI of the target organ by a numerical value ranged from 1.0 to 0.1 for the top ten associated HCNs for that chemical. The ranking of the HCNs are used to select the top ten HCNs for each chemical. The ranking table is provided in appendix C with an illustrated example.

Approach 2

This approach is also suggested to be applied for the CMM approaches, and it consists of two methods (Alpha & Beta). The alpha method is based on a percentile weighting factors while the Beta scheme is based on a step wise weighting factors. The

Alpha approach is dividing the ranking table of HCNs to four quarters and the following weighting factors for them (1.0, 0.75, 0.5, and 0.25). The Beta approach is mainly giving more attention to the selected PAC level in the study (PAC-2) [19]. The assigned factors by both types are given in details in appendix C.

Approach 3

This approach is based on the route of exposure to the chemicals in the mixtures, by using two ways to indicate the required WF. The first method is using the documented route of exposures in the toxicity studies based on a priority ranking criteria given in appendix C. The second method in approach 3 is based on multiplying the route of exposure factors by the stepwise factors used in approach 2 Beta [19].

The differences between the three approaches is discussed in the study, the first approach is considered as conservative to some extent because of the using of the top ten highest ranking method to assign the WFs for each HCNs. The second approach overcomes this problem by using ranking of health effects and HCNs. This approach did not depend on the ranking of each chemical individually. The use of approach 3 requires more data and literature review to understand the exposure routes of each chemical in the mixture. The use of the WFs approaches shows a significant improvement for the outcomes of the CMM HCNs approach, and it was concluded that: ranking the HCNs according to their significance with the assigned WFs for each HCNs appeared to be the most promising method to enhance the CMM approach. [19].

3.2. Building a Virtual Industrial City

The study is started by defining a scope of the work and creating a hypothetical scenario including six main facilities (large scale industries). The selected industries are presented in Table 2 and located in a map extracted from google earth program for the nominated location in Figure 7:

Table 2: The production rates of the selected facilities for the virtual industrial city.

#	Industry	Production rate (Thousand tons/annum)
1	Aluminum	585
2	Steel	3200
3	Ammonia/Urea	3800/5600
4	Ethylene	1300
5	EDC/VCM	200/330
6	Fuel additives	610

The actual production rates of the plants in the real industrial city were used to find the contribution of each industry to the discharged emissions to atmosphere. The number of days in each year is assumed to be 365 days wherever it is applicable or required in the calculations, the production rate is assumed to be constant over the year. In addition, the study evaluated the health effects due to the emitted continuous releases for a period of three years, starting from 2011 until the end of 2013 according to the availability of information.

Figure 7: The base map for the hypothetical scenario located in MIC.

The required base maps for the geographical location of the real city were extracted from google earth software, the location of each facility was identified on the maps with the required stacks locations (sources of releases). A brief literature review about each plant was conducted to understand the technology and the various units inside each facility.

Note: The geographical maps and source locations are used only to quantify the objective of the thesis and don't reflect any actual results or conclusions for the real industrial city or facilities. MIC was only nominated due to the availability of the required information to carry out the study; the aim of the thesis is not related to any authorized environmental impact assessments for the industrial city.

3.3. Dispersion Modeling Methodology

The use of atmospheric dispersion models is truly required to predict the concentrations level of each chemical within the mixture at the desired receptor point. Several models are widely accepted to be used in risk assessment studies, depending on the required outcomes and the nature of the study. In this section, the main concepts of dispersion modeling are given with several examples of widely used dispersion models in chemical mixture risk assessments studies. In order to estimate the concentration profile of the continuous industrial releases, we need to select the appropriate dispersion model which is applicable to estimate the concentrations profiles for continuous emissions.

Previous studies showed that ALOHA and EPI code are usually used for the emergency or unplanned situations, both models are recommended for such scenarios in several researches conducted by SCAPA [8, 9]. For continuous releases, NERAM team used the recommended dispersion model (AERMOD) by EPA to predict the concentrations for the released pollutants from 20 refineries in Canada under a project conducted by CCME to reduce the emissions of the selected refineries [17]. Since the target of this research is to investigate the health effects of contusions releases, AERMOD was the best available option to estimate the concentration profile at different receptor points around studied regional area.

3.3.1. Basics of atmospheric dispersion calculations

The atmospheric dispersion models are founded to estimate the dispersion calculations of the emitted pollutants to the atmosphere. The model is predicting the downwind concentration of the pollutant which is released from a specified source. The release may include: accidental releases, regular releases from industrial plants or vehicles emissions and indoor activities. These models are extensively used by air quality teams and emergency planning departments to study the following points:

1. Studying the existing facilities emissions and evaluate the effects and impacts to the surroundings.
2. Proposing new facilities or industries in specified area.

3. Simulating some hypothetical scenarios of accidental releases and estimating the severity of them.

Such models can help decision makers to set the necessary regulations to protect surrounded communities and environment from any regular or unplanned emissions. The available dispersion models usually use the Gaussian dispersion model as the basis of the calculations; the Gaussian equation is given in appendix D with the required terminologies and steps to estimate the concentration at a specific receptor point [23].

The basic inputs for any dispersion model are:

1. Meteorological conditions such as: wind speed, direction, temperature, cloud coverage and solar radiation.
2. Source term (pollutant) and its properties and parameters.
3. Source location and geographical maps.
4. Terrains elevations.
5. Receptor point properties such as location, height and surface roughness.

A brief review is given in appendix D for the previously used dispersion models in the discussed assessments methods.

3.3.2. AERMOD dispersion model

The AMS/EPA Regulatory Model (AERMOD) is one of the leading atmospheric dispersion models used by U.S. EPA to estimate the concentrations of air pollutants in the atmosphere and the amount of deposition from different sources.

The model is improved by Lakes environmental group under the name of [AERMOD VIEW] package and uses the concepts of the steady state Gaussian plume rise and dispersion equations to perform the concentration calculations [24]. The AERMOD package consists of several preprocessors such as AERMET and AERMAP. The meteorological preprocessor program AERMET is responsible for creating the required surface scalar parameters and the vertical profile files which are necessary to AERMOD. These files are generated in AERMET using the meteorological data and inputs defined by the user. The AERMAP preprocessor program is responsible to generate the required terrain profile files for AERMOD; the data may extract from digital terrain data and GIS resources such as: WebGIS or WebMET webpages [25]. The following features are available for the AERMOD user:

1. A friendly graphical interface for the user with various tools of display options.
2. Automatic ordering of the required inputs and objects in the interface.
3. The availability of several formats to import the base maps for better geographical representations of the user's projects.
4. Ability of using 3-D visualization in the interface.
5. Carrying out the building downwash analysis, meteorological and terrain processing data in an effective, step by step and quick manner.
6. Comparing several models option is available.

7. Multiple options are available for post-processing analysis.
8. Creating professional reports for the inputs and outcomes of the projects.
9. Ability to use AERMOD for continuous releases from the industries and process unlimited years for the meteorological data to use it for statistical results.

The AERMOD model has some limitations such as [26]:

1. It is a steady state model and accounts only for straight line plume models.
2. The assumption of uniform atmosphere across domain is used in the model.
3. The studied areas are limited in the model (up to 50 km^2).
4. It is only applicable for continuous releases scenarios like regular air emissions from industries.
5. The model is not applicable for any photochemical transformation (degradation) or secondary pollutants calculations.

The following sections are presenting the necessary prerequisites for the nominated air quality dispersion model:

3.3.3. Meteorological data collection and analysis

The first requirement for any dispersion model is the meteorological data for the selected area of interest. Meteorological data includes any information which is related to climate or weather conditions and can support the dispersion model by the necessary

data to compute the required boundary layer parameters in addition to the wind, temperature and turbulence profiles.

Meteorological data collection from NCDC

The first step to find the meteorological data in the project was a review of the documented data in NCDC/ NAOO centers to understand the weather conditions in the region and check the availability of historical data in NCDC archive. A free access for the historical climate data in NCDC was used through the climate data online CDO feature in NCDC website. The website provides the user the available stations in the selected area and generates the required data in a text files format. There are several weather stations available in Qatar and documented in hourly global data for NCDC archive. Mesaieed weather station and Doha International Airport (DIA) weather station were selected to check the availability of weather conditions information and the meteorological data for both locations. The required information were extracted for the selected stations from the NCDC hourly collected data, then the data was tabulated in a spreadsheet with a specific arrangement to cope with the required format style for the meteorological preprocessor program. The extracted measurements from NCDC were: wind direction, speed, ceiling height, visibility, station pressure, dew point temperature, precipitation amount and relative humidity. The required format style for the meteorological input files is available in the meteorological resource center web page for AERMET data guidelines [27].

The missing hours were flagged for both stations and the percentage of the overall missing data for each year was calculated to ensure the availability of the minimum required data for the preprocessor meteorological program. The total amount of hourly data collected for each year should be around 8760 cell for each extracted meteorological parameter from NCDC. The next step was to convert the generated excel file in to a CSV format to make it readable for the meteorological preprocessor program AERTMET. Several attempts were carried to convert the spreadsheets in to a suitable format for the preprocessor program, but AERMET was not able to process the generated files. Another methodology was suggested at that stage to overcome this issue by using a generated MM5 data from another meteorological processor. Although AERMET was not able to read the entire generated files (hourly data files), the data was used to perform the wind roses and the wind class frequency distribution graphs using WRPLOT program. The generated wind roses and frequency distribution graphs are available in the first section of the results.

Meteorological data estimation by mesoscale meteorological models

Another way to generate the required meteorological files is using numerical weather prediction (NWP) method with higher resolution models like (Mesoscale model) to estimate the meteorological data for the studied area if one of the following limitations is existing in the study [28]:

1. No weather station data available for the studied area or even a representative data available for the selected site.

2. The available weather station data is out of date.
3. The existing weather station data are reported in long intervals (every 3 or 4 hours).

In this study the fifth generation of Penn state/NCAR Mesoscale model (MM5) was used in addition with CALMET (meteorological processor), CALPUFF (dispersion model) and CALPOST (post-processor model) –brief description for each program is available in appendix D– to simulate the meteorological conditions of Qatar state. CALMET is first initialized with Mesoscale Model data (MM5) which is used for creating weather forecasts and climate projections. The meteorological domain extended 441 km horizontally and 2708 km vertically with 11 vertical layers along the elevation. MM5 data with a 4 km spatial resolution is used as an input to CALMET.

Meteorological data post-processing

Another direct method is used to convert the MM5 data to meet the required format style for our post processing program AERMET, this method includes adjusting the format of the files to generate the desired format style for AERMET. The collected hourly surface data and upper air files are used subsequently in AERMET file to generate the required boundary layer parameters files for AERMOD program. The AERMET program is processing the given meteorological data in three stages -presented in Figure 8- to give the user the required preprocessed files for AERMOD.

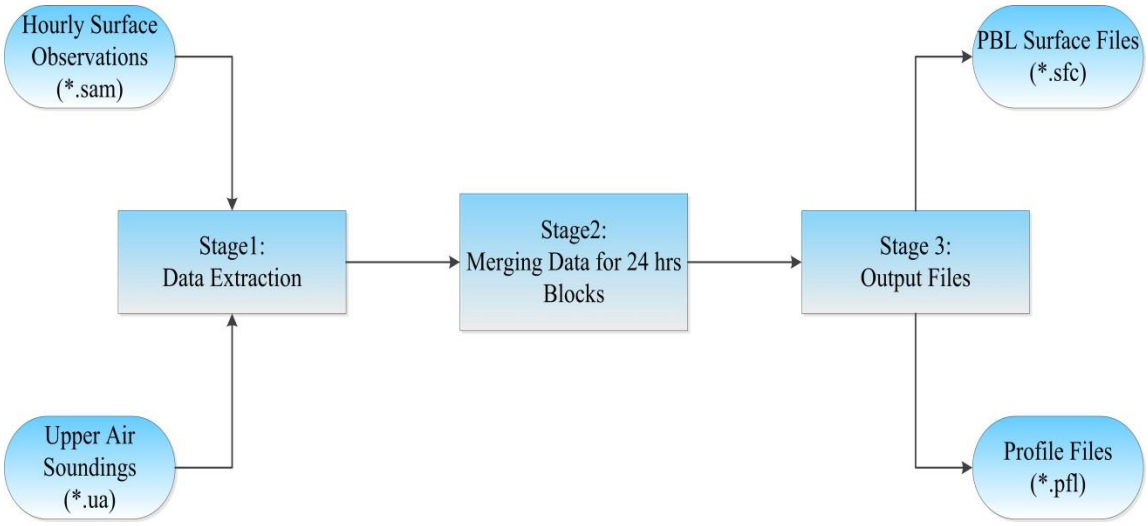

Figure 8: Data processing steps in AERMET.

The hourly surface observations file is introduced to the AERMET program to extract the necessary information for data processing; the station ID and location information are extracted from the input file automatically with the base elevation of the station. The onsite data can be defined if it is available for the user, in our case only the hourly surface generated data are founded for a period of three years (2011 to 2013) and processed in this project due to the lack of the onsite information. The upper air data file is introduced also to the program and it is following the same previous steps for hourly surface data. The reported time is clearly identified in the project to be in the Local Standard Time (LST).

The sectors were defined in the processing options tab for better surface characterizations, the characterizations parameters are automatically estimated when the following requirements are defined:

1. Number of sectors (two sectors were defined).
2. Land use type (1: Urban, 2: water) since the selected area is located near the sea, two sectors were defined as above.
3. Precipitation (average).
4. Season (annual average was selected).

The generated surface files (*.sfc) are containing the hourly boundary layer parameters while the profile files have the observations for wind directions, wind speeds, deviation calculations for winds components and temperature. Both files are used later in AERMOD program to build the required model for our hypothetical scenario. The next step after processing the meteorological data is to insert the required inputs for AERMOD program; the following section is explaining the required basic steps to achieve this task.

3.4. AERMOD Processing

The first step to build an AERMOD model is to introduce the basic information about the selected area to carry the dispersion modeling study. The project coordinates system and reference points of the project were inserted with the extracted base maps for MIC and Qatar.

A high resolution map for MIC area was used with another medium resolution image for Qatar's map; both maps were used together in the AERMOD interface. The benefit of using such arrangement is to focus more in MIC areas and to clearly define sources of the releases on the map, while the bigger map for Qatar is just used to extend the dispersion profile to cover most of the country for concentration gradient visualization.

3.4.1. Releases and sources estimations

The second step in AERMOD is to define the releases and introduce all the required emissions sources information, for example: emissions rates, stacks highest, releases temperature, etc... .

Overview about the emission factors

When the emission rates or concentrations are not available directly from the studied facility, the use of other engineering tools or estimations are recommended. The emission rates might be derived from material balance of the facility (large scale), experimental measures for the mixture in the lab (limited scale) or using the recommended emission factors established by well-known agencies. The emission factors (EFs) have been widely used to predict the quantities of the released pollutants to environment. They are used extensively by the air quality and emergency response management teams in addition to local and international regulatory inventories to set the guidelines for emissions control plans, environmental management programs and related decisions.

The emission factors represent the ratio between the amount of the released pollutant to the activity or production weight, volume, area or duration. The factors are originated from the available and monitored previous releases under same conditions or similar acceptable quality data from different facilities all over the world. The uncertainty topic is likely to occur in estimating the emission factors and might depend on the type of emission, quality of the collected data and similarities of the conditions [29]. There are enormous amount of published researches and guidelines to establish the required methodology carried for emission factors estimations. Several national and international agencies quantified the emission factors and categorized them according to several conditions such as: emission sources, type of industry or chemical groups. In addition, the use of engineering estimates and material balance techniques were recommended if the onsite observations are missing. The quality of the emission factor is measured by the available information and the number of conducted and documented observations. A rating procedure is used in AP42 by U.S. EPA to evaluate the reliability of the observed emission factors and the representative characteristics of them. The rating letters A to E were established by U.S.EPA for the collected AP42 EFs to quantify the ratability of them, being that A represented the excellent factor and E the poor observed factor (additional details about rating meanings are illustrated in appendix E) [29]. The EPA quantified more than 200 air pollution source categories since 1972, and the following equation is generally used to find the emission rate of a pollutant [20]:

$$E = A \times EF \times \left(1 - \frac{ER}{100}\right) \qquad \text{Equation (4)}$$

Where, E is the emission rate (quantity /time), A is the Activity rate (quantity of the activity /time), EF is the emission factor (quantity of the emission/ quantity of the activity), ER is overall emission reduction efficiency (%). The overall emission reduction efficiency is also defined as the removal efficiency of the control system in the equipment.

EMEP established specific tiers for the emission factors rating depending on the available information and the level of complexity of the studied case. A brief description is given in appendix E. The emission factors are available in BAT and BREF files for different activities and industries and required to be reviewed while selecting the best available technology for designing or controlling the processes [30]. Furthermore, EPA establish an online emissions factor development tool (WEBFIRE) to find the desired emission factors from the EPA emission inventory and database. The WEBFIRE tool contains the hazardous air pollutants (HAP) for industrial and non-industrial processes and has the ability to generate spreadsheets for the required factors [31].

The emitted releases from the selected 6 industries in MIC are found to be around 28 emissions in the literature. The used documents to identify these pollutants are:

1. BAT and BREF or reference documents for several industries published by the European Integrated Pollution Preventive and Control (IPPC) and institute for prospective technologies studies (IPTS) [30].
2. AP-42, Compilation of Air Pollutant Emission Factors, volume 1, fifth edition published by EPA [29].
3. The EMEP/EEA air pollutant emission inventory guidebook [32].
4. The Emission Estimation Technique (EET) manuals published by National Pollutant Inventory (NPI) [33].

Emissions rate calculations

The emission rate for each pollutant is estimated using the available emission factor from literature according to the following simplified equation:

$$E = A \times EF \qquad \text{Equation (5)}$$

A is assumed to be the annual production rate of each industry, the production rate of each facility was assumed to be constant over the period of the study. The emission factors were primarily extracted from BAT & BREF files then from EMEP, EPA and NPI inventory files depending on the available documented factors from similar industries and technologies from various plants in the world.

The extracted emissions factors from BAT & BREF files are adjusted whenever the production rate is different or other scaling factors are required. The highest available quality rating factors were used for EPA factors and tier 1 was assumed for the factors extracted from EMEP documents. The total number of the founded releases in emission inventory guides is 28 air emissions for the selected industries. Each industry along with the production rate and the potential emissions are given in Table 3, the selected emissions factors are tabulated in appendix F. Each pollutant is introduced separately in AERMOD model to simulate the expected dispersion model individually. An attempt to simulate all the pollutants together was implemented but the desired output files were not delivered by AERMOD and the model was not successful running. As a result 28 models were simulated for the study and the hourly averaging output files for concentration profiles at different receptors points were extracted from the models. AERMOD has especial arrangements and modification for the governing dispersion equation and calculations for the following pollutants: SO_2, CO, NO_x, NO, Lead and several types of PM. These arrangements were used for SO_2, CO, NO_x and Lead pollutants in the study while the other 24 pollutants were defined under others selection option in pollutant type tab.

Table 3: The predicted emissions from the selected industries in MIC.

#	Industry	Production rate (Thousand tons/annum)	Available emissions in literature	Emitted pollutants[1]
1	Aluminum	585	11	NO_x[2], SO_2, CO, HF, C_2F_6, CF_4, COS, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene
2	Steel	3200	10	NO_x, SO_2, CO, Pb, Cr, Ni, Zn, HF, HCl, Benzene
3	Ammonia/Urea	3800/5600	9	NO_x, SO_2, CO, NH_3, n-hexane, Cyclohexane, Toluene, Formaldehyde, Benzene
4	Ethylene	1300	3	NO_x, SO_2, CO
5	EDC/VCM	200/330	9	NO_x, SO_2, CO, CL_2, EDC, VCM, HCL, Chloroform, C_2H_4
6	Fuel additives	610	1	NO_x

[1] The tabulated emissions have well defined emission factors and reported clearly in literature reviews. There are several other emissions from each industry can be found in literature but with unknown factors or less quality collected data.
[2] NO_x is simulated in AERMOD and assumed to be mainly NO_2 for the rest of calculations in the study.

The study focused on the primary pollutants from the industries and neglected the formation of secondary pollutants in the atmosphere. The reasons for using such assumption are:

1. The limitation of AERMOD dispersion model: since the simulation is not supporting the interactions and chemical reactions that took place after emitting the pollutants to atmosphere and also the photochemical degradation for the pollutants.
2. To validate the selected risk assessment method (CMM based on HI): where the interaction of emitted chemicals to atmosphere is neglected due to the complicity of predicting the nature of interactions.
3. The lack in information about the secondary pollutants which might be created from such combination of chemicals (such as: rate laws for degradation or photochemical reactions and rate law constants).

As a result of the previous assumptions, the PM and secondary pollutants calculations are not considered in this study.

The main common pollutants between all industries were NO_x, SO_2 and CO. The total number of the other releases from the six industries is 24 pollutants with a different contribution of each industry for some releases. The AERMOD simulation files are based on type of pollutants as stated previously. The dispersion coefficient was selected to be urban for all simulations files and the averaging time is based on hourly observations from the generated meteorological files.

The terrain height option was assumed to be based on elevated terrains with the support of AERMAP to process the terrain files for the selected area. The rate of each emitted release is introduced for each industry along with the associated stacks or areas. The quantity of the released emission is assumed to be equally distributed and emitted from the assigned stacks, for example: it is found that 18.5 g/s of NO_x emissions are released from 22 stacks in the aluminum facility, the emission rate of the individual stack is assumed to be 0.843 g/s using the assumption of equal distribution emission rate releasing. The gas exit temperature, stack inside diameter and gas exit velocity are estimated using some available information from MIC plants, the unknown parameters were scaled from the available data for other industries. A spreadsheet was developed for each pollutant with all sources inputs parameters and it was imported to AERMOD simulation file. The sources are grouped whenever it is possible to develop different concentration profiles for each industry within the same simulation file. The grouping option in AERMOD provides the user several choices to present a concentration profile for each group of sources separately in the interface map and also generates separate PLT and POS files for each group. Figure 9 concludes the basic required information for each source. The following sections are illustrating the main steps carried to find the remaining sources inputs for AERMOD.

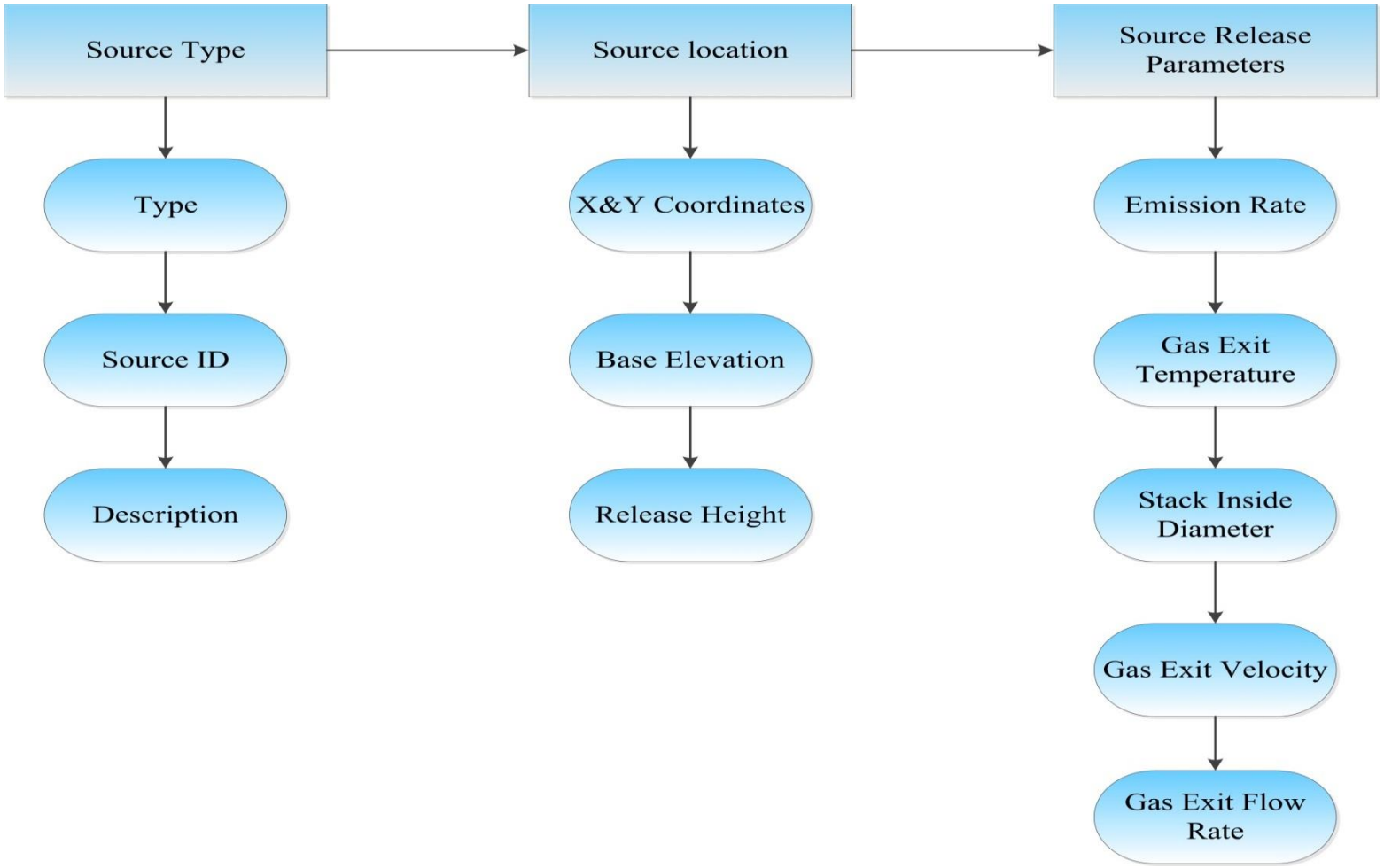

Figure 9: The required inputs for emissions sources in AERMOD.

Source type

The studied releases were mostly assumed to be emitted from stacks located within the facilities. The stacks are identified as point sources in each simulation while the emitted releases from a specific fugitive source are considered as volume sources. An identification tag was given for each stack depending on the assigned industry for it, for example: in the aluminum plant the stacks are assigned to have the following tags identification (AL-*), for ammonia plant (NH_3-*) where the star indicates the given number for each stack. A brief discerption is mentioned whenever it is applicable for each stack to clarify the source of the emitted releases from the real process, for example: AL-1 is assigned for the expected releases from aluminum prebaked cells unit in the plant. The details of sources parameters are tabulated for each industry in appendix F.

Source location

The sources locations were identified by using google earth maps for the real locations of the stacks in MIC. X and Y coordinates are reported by using the Universal Transverse Mercator (UTM) system. The release height is assumed to be the stack height, and it is predicted for each stack from similar available documented heights in literature. The coordinates and stacks heights are available in appendix F for each industry.

3.4.2. Receptor points identifications

The receptors points were defined in AERMOD to predict the concentration profile for the emitted releases at the surrounded areas. A uniform Cartesian grid is used for MIC map and extended to include Qatar base map. The total number of the selected receptors points (RPs) are around 1764, and covering an area equal to 16,810 km^2 approximately.

3.4.3. Introducing meteorological data for AERMOD

The meteorological data were introduced to AERMOD using the generated profile file (*.pfl) and surface file (*.sfc) for a period from 2011 to 2013. These files include the processed MM5 data for the hourly boundary layer, wind speed, direction, temperature and deviation of fluctuating wind compnents. The anemometer base elevation is assumed to be the default given elevation in AERMOD which is 10 meters. In addition the default given values for wind speed categories in AERMOD are used.

3.4.4.Terrain files processing

The terrain elevation files were extracted from WEBGIS files and used for all sources and receptor points. The third version of Shuttle Radar Topography Mission (SRTM3) is selected with 90 m global resolution data for elevation files in this project; this will assure the highest available accuracy for terrain calculations in the study. The studied area is covered by 4 terrain files with the following datum and files names:

- N24E050 with a horizontal datum: WGS84
- N24E051 with a horizontal datum: WGS84
- N25E050 with a horizontal datum: WGS84
- N25E051 with a horizontal datum: WGS84

3.4.5. Output files options

The plot files (*.plt) and post processing files (*.pos) were decided to be the main outputs from the created dispersion models. The maximum values option is selected to represent the total number of hours per a year – assuming one year has 365 days so the total number is 8760 hrs – with 1 hour averaging time for the selected three years of the study. The contour plot files and Post processing files are generated for the same selected options. Furthermore, a percentile value is assigned for the simulation with a value equal to 98 % to report the highest predicted concentration within the simulation.

3.5. CMM and Health Effects Calculations

The study was mainly carried out to investigate the applicability of CMM method to be used for the continuous releases to atmosphere, and also to check if the resulted health impacts have significant acute or delayed (chronic) effects on the individuals if they exposed to such mixture continuously.

3.5.1. CMM Requirements

The following requirements are necessary to conduct CMM for a specific number of chemicals in a mixture:

Concentrations of the chemicals

According to D.K.Craig, the used concentrations were given for some reported values from DOE facilities in U.S. However, Craig recommended the use of dispersion models such as ALOHA or EPIcode to estimate the concentrations [15]. Xiao-Ying Yu with SCAPA team predicted the concentrations using the recommended Gaussian dispersion models from Craig in 1999. Since the purpose of this study is to examine the applicability of using CMM in continuous releases, AERMOD was the best available choice to estimate the required concentrations of each chemical in the mixture at different receptor points surrounding the source of the continuous release.

Recommended exposure limits

In 1999, Craig recommended the use of ERPG and TEEL values as a guideline limits for the chemicals in the studied mixture, he used the second level of ERPG and TEEL to examine the default methodology for two receptor points at a distance of 30 meters (inside the facility) and 100 meters (outside the facility) from the source of release [15]. Xiao used the protective action criteria limits as enhanced levels for the used values in 1999. In addition he recommended the use of PAC-2 values in order to provide the risk assessor with some useful information about the ability of individuals to

take the required protective actions if such chemical mixture is emitted to atmosphere in unplanned situation [18]. Since both studies focused on the emergencies or unplanned situations the use of ERPG, TEEL and PAC values were the optimum choice. However if the study is focusing on the continuous releases from normal daily activities from the industrial cities, the regulations should reflect lower exposure limits for individuals. Several options are recommended to be used in such continuous releases cases if the limits are documented for the selected chemicals in the mixture, for example: NOAL, TEEL-0, RFCs, PELs, MRLs and TEEL-0 vallues. Since the aim of studying continuous releases to atmosphere is to identify whether the released amounts are not expected to cause any observed adverse health effects for individuals, TEEL-0 is used initially due to their availability for all chemicals in the concerned mixture. The database for the selected TEEL-0 values are extracted from the latest versions available in DOE protective action criteria (PAC) web page [34]. TEEL-0 values are recommended to be used since they are presenting no adverse health effects on individuals if they exposed to such concentrations within one hour. TEEL-0 values are only documented in the DOE webpage until the 26^{th} revision in 2010. In addition, MRLs values were also used and compared with TEEL-0 results for selected scenarios. MRLs are extracted from ATSDR guidelines and only available for 11 chemicals of the selected ones in this study [35]. Appendix G is giving the stated exposure limits for each chemical in the study upon their availability in literature.

3.5.2. Implementing CMM

The following equation is used to obtain the hazard index for the individual chemicals within the mixture of the selected chemicals:

$$HI_i = \frac{C_i}{L_i} \qquad \text{Equation (6)}$$

Where: HIi is the Hazard index for a specific chemical, C_i is the estimated concentration at the desired RP using AERMOD simulation and L_i is the recommended limit for the chemical (TEEL-0 or MRLs).

After finding the hazard index for each chemical in the mixture, it is assumed that all chemicals in the mixture are showing combined effects outcomes. The required summation of the hazard indices are achieved by the following two approaches.

HCNs and mode of action approaches

HCNs and mode of action approaches are recommended by SCAPA committee to be carried out instead of the simple summation of the hazard indices for the chemicals in the mixture. Although the simple used summation method for HIs is expected to give conservative results, HCNs approaches have the advantage of showing the associated HIs for the affected organs separately; the same benefit is applicable for modes of action approach.

The following equations present an appropriate way to sum the hazard indices for both approaches to get the desired outcomes:

$$\sum_{i=1}^{n} HI_{i(M)} = HI_{1(M)} + HI_{2(M)} + HI_{3(M)} + ... + HI_{n(M)} \qquad \text{Equation (7)}$$

$$\sum_{i=1}^{n} HI_{i(M)} = HI_{1(M)} + HI_{2(M)} + HI_{3(M)} + ... + HI_{n(M)} \qquad \text{Equation (8)}$$

Where (M, T) are representing the mode of action and the target organ respectively. The provided HCNs and modes of action categories are tabulated in Appendix H according to the latest published user guide for CMM by SCAPA [36]. Since the time scale is different between the chronic effects and acute effects, it is important to distinguish between both effects while using these equations, chronic effects should be summed together separately than acute effects. The following example illustrates the way of summing different HIs: the including HCNs from 1.00 until 2.99 are considered as chronic carcinogens. As a result, if the selected chemicals have any HCNs within this range, all HIs for these chemicals should be summed together to give an indication of the selected mode of action (carcinogens). The same concept is applied for other HCNs. Additionally, this approach can be used for specific targeted organ if the chemicals have the same HCN and affect the same organ. For example if several chemicals have the

HCN 1.01 (bladder carcinogen). Table 4 and Table 5 are presenting the modes of action & target organs categorization.

Table 4: Modes of action categorization table.

HCNs based on mode of action			
HCN = 1 or 2 Carcinogens	HCN = 3 Chronic Systemic Toxins	HCN = 4 Acute Systemic Toxins	HCN = 5 Reproductive Toxins
HCN = 6 Cholinesterase Toxins	HCN = 7 Nervous System Toxins	HCN = 8 Narcotics	HCN = 9 Respiratory Sensitizers
HCN = 10 Chronic Respiratory Toxins	HCN = 11 Acute Respiratory Toxins	HCN = 12 Blood Toxins – Anemia	HCN = 14, 15, or 16 Irritants
HCN = 13 Blood Toxins-Methemo-globinemia	HCN = 17 Asphyxiants	HCN = 18 Explosive flammable, safety	HCN = 19 & 20 Other & Nuisance

Both tables were used to gather the necessary data for the 28 exiting pollutants in our hypothetical mixture. The latest published CMM approach (Rev.27) workbook spreadsheet was used to understand the calculation procedures. A simplified excel sheet was developed to tabulate only the required information about the concerned chemicals in this study.

Table 5: HCNs categorization table.

HCNs based on target organ			
Carcinogen-unspecified target organ (C)	Carcinogen-bladder (C)	Carcinogen- Kidney (C)	Carcinogen-Liver (C)
HCN = 1.00, 2.00	HCN = 1.01, 1.00, 2.00	HCN = 2.01, 1.00, 2.00	HCN = 1.02, 2.02, 1.00, 2.00
Bladder toxin (C)	Bladder toxin (A)	Hematological system, unspecified effects (C)	Hematological system, unspecified effects (A)
HCN = 3.01, 3.00	HCN = 4.03, 4.00	HCN = 3.02, 3.00	HCN = 4.06, 4.00
Bone toxin (C)	Bone toxin (A)	Bone marrow toxin (C)	Bone marrow toxin (A)
HCN = 3.03, 3.00	HCN = 4.13, 4.00	HCN = 3.04, 3.00	HCN = 4.04, 4.00
Brain toxin (C)	Brain toxin (A)	Eye toxin (chronic ocular effects) (C)	Eye toxin (acute, other than irritation) (A)
HCN = 3.05, 3.00	HCN = 4.05, 4.00	HCN = 3.06, 3.00	HCN = 4.01, 4.00
Gastrointestinal tract toxin (C)	Gastrointestinal tract toxin (A)	Heart, Cardiovascular system toxin (C)	Heart, Cardiovascular system toxin (A)
HCN = 3.07, 3.00	HCN = 4.07, 4.00	HCN = 3.08, 3.00	HCN = 4.08, 4.00
Kidney toxin (C)	Kidney toxin (A)	Liver toxin (C)	Liver toxin (A)
HCN = 3.09, 3.00	HCN = 4.09, 4.00	HCN = 3.10, 3.00	HCN = 4.10, 4.00
Skin toxin, including dermatitis & sensitization (C)	Skin toxin, other than irritation (A)	Skin perforation (C)	Skin perforation (A)
HCN = 3.11, 3.00	HCN = 4.11, 4.00	HCN = 3.12, 3.00	HCN = 4.12, 4.00

Table 5: Continued

HCNs based on target organ			
Nose toxin, other than irritation (A)	Reproductive system toxin (C)	Reproductive system toxin (A)	Nervous system, including CNS, narcosis and cholinesterase toxin (A)
HCN = 4.02, 4.00	HCN = 5.10, 3.00	HCN = 5.00, 4.00	HCN = 7.00, 7.01, 8.00, 6.00, 4.00
Nervous system, including CNS (C)	Respiratory system toxin, including sensitizers (C)	Respiratory system toxin, including severe and moderate irritation (A)	Blood toxin, anemia (C)
HCN = 7.10, 7.11, 3.00	HCN = 9.00, 10.00, 3.00	HCN = 11.00, 11.01, 4.00	HCN = 12.00, 3.02, 3.00
Blood toxin, methemoglobinemia and asphyxiants (A)			
HCN = 13.00, 17.00, 4.06, 4.00			

Table 6 shows the assigned top ten HCNs for each chemical along with CASRN and TEEL-0 values. TEEL-0 limits are extracted from the Protective Action Criteria (PAC) Rev 26 in 2010 based on applicable TEELs for 60-munites for TWA concentrations calculations [37]. The published CMM workbook by SCAPA was used to deliver the priority ranking for the assigned HCNs in Table 6 for each pollutant in the mixture, the workbook is using the ranking table which was recommended by Craig in 1999 and updated later by SCAPA team in 2007 [15, 18]. The latest priority ranking table for HCNs is available in appendix C [19].

3.5.3. Introducing weighting factors for CMM

The use of Weighting Factors (WFs) approaches were introduced to the CMM as recommended by Xiao in 2012, two approaches out of the three approaches were examined in this study to reduce the level of conservativity associated to HCNs approaches [19]. The selected approaches in this study were: Approach 1and Approach 2 alpha.

Approach 1: applying WFs to the top ten HCNs starting from 1 to 0.1 according to their priorities. Approach 2-Alpha: dividing the priority ranking table in to four quarters with the following 4 percentile WFs: (1.0, 0.75, 0.5, and 0.25) [19].

Table 6: Top 10 HCNs values for 28 chemicals.

Chemical Compound	Nitric oxide	Nitrogen dioxide	Sulfur dioxide	Carbon monoxide	Hydrogen fluoride; (Hydrofluoric acid)	Hexafluoroethan (Freon 116; Perfluoroethane)	(Tetrafluoromethan) Carbon tetrafluoride;
CASRN	10102-43-9	10102-44-0	7446-09-5	630-08-0	7664-39-3	76-16-4	75-73-0
TEEL-0[1] (mg/m^3)	0.61	0.94	0.52	60	0.4	NA[2]	NA
HCN-1	13.00	14.01	14.01	17.00	3.02	6.00	8.00
HCN-2	6.00	11.01	11.01	13.00	17.00	14.01	17.00
HCN-3	14.01	14.02	14.02	4.01	4.08	4.01	4.11
HCN-4	4.01	13.00	4.08	11.01	4.07	11.01	7.01
HCN-5	11.01	6.00	4.05	4.08	7.01	14.02	4.08
HCN-6	14.02	4.01	7.01	4.05		4.08	4.07
HCN-7	4.08	4.05	7.00	7.01		4.05	
HCN-8	4.05	7.01	11.00	8.00		7.01	
HCN-9	7.01	8.00	4.02	7.00		7.00	
HCN-10	11.00	7.00	4.09	11.00		11.00	

[1] Extracted from revision 26 in 2010.
[2] NA means the reported TEEL-0 value in 2010 is exceeded the published PAC-1 value in 2012, As a result these values are excluded and PAC-1 values from 2012 will be used instead.

Table 6: Continued.

Chemical Compound	Carbonyl sulfide	Benzo(a)pyrene; (Coal tar pitch volatiles)	Benzo(b) fluoranthene	Benzo(k) fluoranthene	Indeno (1,2,3-cd)pyrene	Lead	Chromium
CASRN	463-58-1	50-32-8	205-99-2	207-08-9	193-39-5	7439-92-1	7440-47-3
TEEL-0[1] (mg/m^3)	NA[2]	0.2	NA	NA	NA	0.05	1
HCN-1	13.00	4.05	15.01	2.00	2.00	4.01	15.01
HCN-2	15.01	11.00	11.01	4.06	15.01	4.08	11.01
HCN-3	11.01	4.06	15.02	4.10	11.01	7.01	15.02
HCN-4	15.02	4.10	4.01	5.00	15.02	7.00	11.00
HCN-5	4.05	2.00	4.05			4.09	4.01
HCN-6	7.01	3.05	7.01			4.06	10.00
HCN-7	8.00	10.00	11.00			4.10	3.06
HCN-8	7.00	3.09	4.09			4.07	3.02
HCN-9	11.00	3.02	4.06			2.00	
HCN-10	4.07	3.10	4.10			3.05	

[1] Extracted from CMM workbook revision 26 in 2010.
[2] NA means the reported TEEL-0 value in 2010 is exceeded the published PAC-1 value in 2012, As a result these values are excluded and PAC-1 values from 2012 will be used instead.

Table 6: Continued.

Chemical Compound	nickel	Zinc	Hydrogen chloride; (Hydrochloric acid)	Benzene	n-Hexane	Cyclohexane	Toluene
CASRN	7440-02-0	7440-66-6	7647-01-0	71-43-2	110-54-3	110-82-7	108-88-3
TEEL-0[1] (mg/m^3)	1	1	0.75	3	150	NA[2]	75
HCN-1	15.01	18.00	6.00	14.01	17.00	15.01	15.02
HCN-2	4.01	11.01	14.01	4.01	14.01	15.02	16.01
HCN-3	11.01	15.02	4.01	11.01	4.01	4.08	7.01
HCN-4	15.02	4.05	11.01	15.02	11.01	7.01	4.01
HCN-5	4.08	7.01	14.02	4.08	15.02	8.00	3.02
HCN-6	8.00	7.00	4.08	4.05	4.08	7.00	5.10
HCN-7	11.00	11.00	7.00	7.01	4.05	11.00	3.08
HCN-8	4.09	4.09	11.00	8.00	7.01	4.07	11.00
HCN-9	4.06	4.06	4.02	7.00	8.00	3.05	3.10
HCN-10	4.10	4.10	4.09	4.09	7.00	3.09	8.00

[1] Extracted from CMM workbook revision 26 in 2010.
[2] NA means the reported TEEL-0 value in 2010 is exceeded the published PAC-1 value in 2012, As a result these values are excluded and PAC-1 values from 2012 will be used instead.

Table 6: Continued.

Chemical Compound	Formaldehyde	Ethylene dichloride; (1,2-Dichloroethane)	Vinyl chloride monomer VCM	Chloroform	Ethylene	Chlorine	Ammonia
CASRN	50-00-0	107-06-2	75-01-4	67-66-3	74-85-1	7782-50-5	7664-41-7
TEEL-0[1] (mg/m^3)	0.35	40	2.5	9.8	200	1.4	15
HCN-1	6.00	14.01	14.01	15.01	17.00	14.01	14.01
HCN-2	14.01	4.01	11.01	4.01	6.00	4.01	4.01
HCN-3	4.01	11.01	14.02	11.01	4.08	11.01	11.01
HCN-4	11.01	14.02	4.08	4.08	4.05	14.02	14.02
HCN-5	14.02	4.08	4.05	7.01	7.01	4.08	4.08
HCN-6	4.08	4.05	7.01	8.00	8.00	4.05	4.05
HCN-7	7.01	7.01	8.00	7.00	7.00	7.01	7.01
HCN-8	8.00	8.00	7.00	4.02	11.00	7.00	11.00
HCN-9	7.00	7.00	11.00	4.09	4.10	11.00	4.02
HCN-10	11.00	11.00	4.09	4.06	4.07	4.02	4.07

[1] Extracted from CMM workbook revision 26 in 2010.

The priority ranking table with the assigned WFs for Alpha type is available in appendix C. The HI for each chemical in the mixture is multiplied by the assigned WF and the summation is carried on as following:

- Summation of same targeted organs and same mode of actions separately.
- Summation of acute effects and chronic effects separately.

Figure 10 gives an overall idea about the required steps to carry the CMM analysis in this study.

3.6. Presenting the results in AERMOD

The generated post processing files for each release (*.pos) were generated as binary files by AERMOD. It was necessary to convert the files to a more fixable format such as ASCII by using simple programing language. The estimated number of hours for the studied period is around 26304 hours for 1764 receptor points. Such enormous data require a numeric computing program that is capable to analyze the inputs and compute the calculations in an efficient manner; this was the main reason of using FORTRAN software in the study. A simple code was written to carry the calculations of the CMM approaches for each mode of action or target organ separately. The outcomes of the code are presented in text files, and the generated text files are applicable to be imported back to AERMOD model.

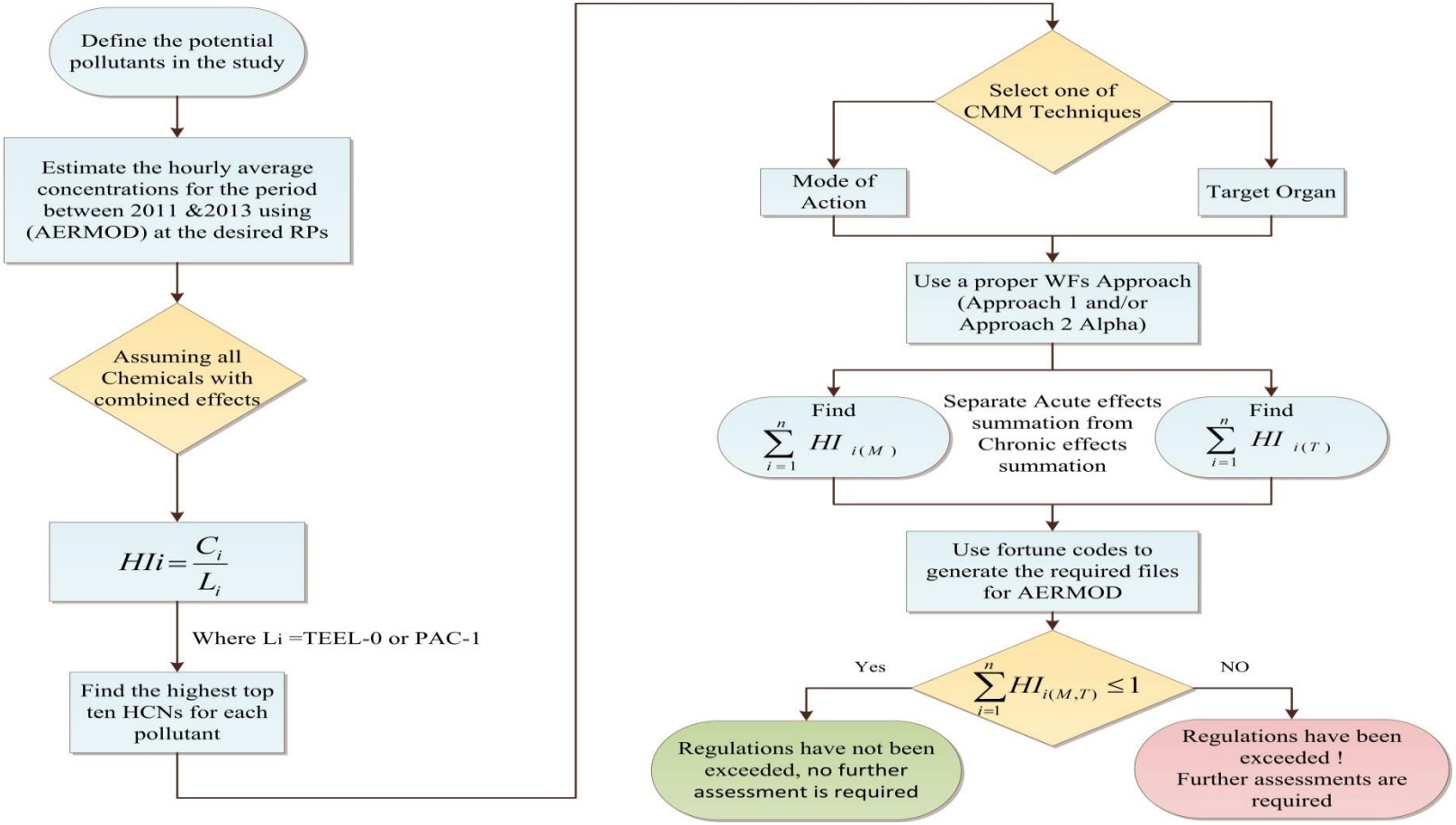

Figure 10: The proposed steps to use CMM for continuous releases.

The Chemical Mixture Methodology (CMM) steps were introduced to the code as following:

1. A text file (Chemicals.ini) for each HCN is built according to specific spacing style and format, the file includes: CASRN number of each chemical, defined limit value and the path of the post processing files in the computer. Figure 11 shows an example of the created text files.
2. A text file for HCNs is defined for each chemical text file; it includes the number of the chemical with the assigned weighting factor value.
3. The generated *Pos file from AERMOD are introduced to the code.
4. The number of receptors points and hours in the study are defined in the interface window of the code. Figure 12 shows the code window with the required inputs.
5. The FORTRAN codes use the inputs and calculate the HIs for each concentration in the generated *Pos file at different receptor points.
6. The output files has specific formatting style, with the following associated names:
   a) 01H1GALL.PLT: plot file for the concentration values from AERMOD.
   b) PE00GALL.PLT: plot file for the percentile values from AERMOD.
7. The code generate two output files:
   a) HCN_xx.xx_A.PLT: represents the averaging HI value for each receptor point.
   b) HCN_xx.xx_M.PLT: represents the maximum value for each receptor point.

   (xx.xx) is the number of the studied HCN.
8. The resulted plot files are imported after to AERMOD interface to visualize the affected locations (where HI $\geq$ 1).

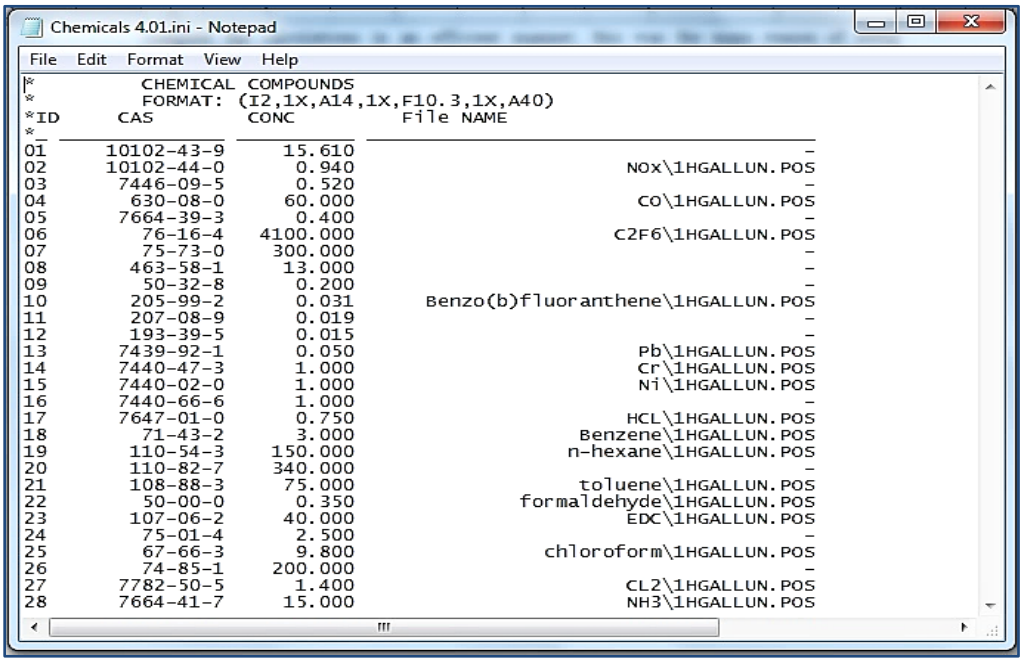

Figure 11: Structure of the chemicals text file for Fortran code.

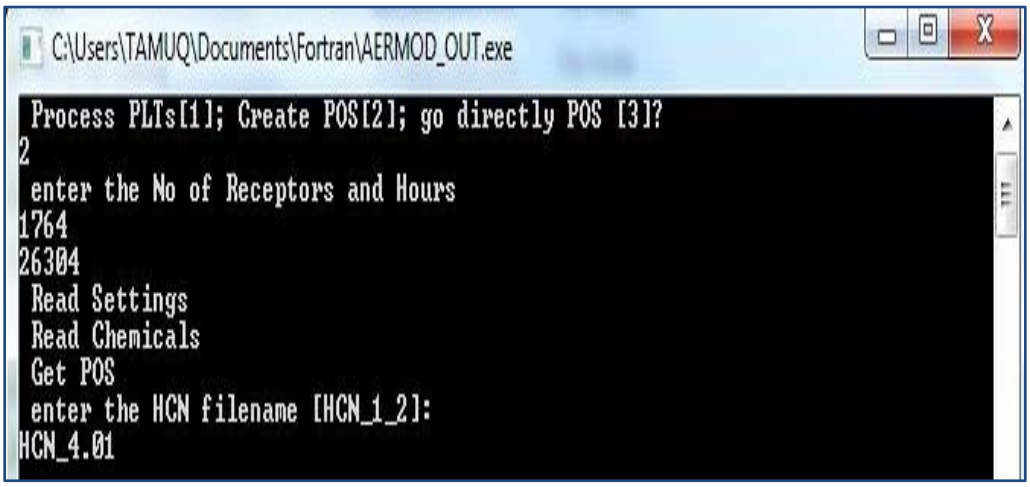

Figure 12: Fortran code screen inputs.

4. RESULTS AND DISCUSSION

The results and discussion section is presenting the outcomes of the recommended methodology. The results are divided in to four sections, following the steps of the methodology:

1. Meteorological data processing.
2. Dispersion - AERMOD - concentration contour graphs.
3. Health effects estimation.
4. Impacts of selecting different exposure limit

The results of each step are presented along with a detailed discussion.

4.1. Meteorological Data Results

The collected meteorological data from NCDC/ NAOO (for the Doha Airport station) were compared with the MM5 model runs. The main reasons for conducting such a comparison are: a) to address the impact of the missing airport data b) to assess the deviation between the airport data and the location of the industrial city (~50km Southern following the shoreline). Another critical point is the missing data in the airport data files. When the missing data are exceeding the stated limits in AERMET, the input files cannot be processed and warning errors will be massaged. The WRPLOT tool was used to estimate the amount of the missing data from NCDC/NAOO meteorological files.

The same tool was also use to build the corresponding wind roses for the period of study. The wind roses are presented in Figure 13 for both meteorological files, they give an overview about the variances in wind directions between NCDC and MM5. The roses also clearly show the wind velocity classes and frequencies for the studied periods. The NCDC data show prevalence for the North Western winds and a lack of any other significant direction. On the other hand the MM5 data show again the frequent North Western winds but in this case there also significant Eastern winds. These differences are quite important and should be the main scope of a future work. Table 7 presents the characteristics for each meteorological.

Table 7: WRPLOT outcomes for MM5 and NCDC meteorological data.

Description	**MM5 2011**	**MM5 2012**	**MM5 2013**
Total number of hours	8760	8784	8760
Data availability (%)	100	100	100
Incomplete/missing records	0	0	0
Total records used	8760	8784	8760
Average wind speed	4.18	4.18	4.15
Description	**NCDC 2011**	**NCDC 2012**	**NCDC 2013**
Total number of hours	8760	8784	8760
Data availability (%)	91	90	91
Incomplete/missing records	722	842	821
Total records used	8038	7942	7939
Average wind speed	4.26	4.04	4.15

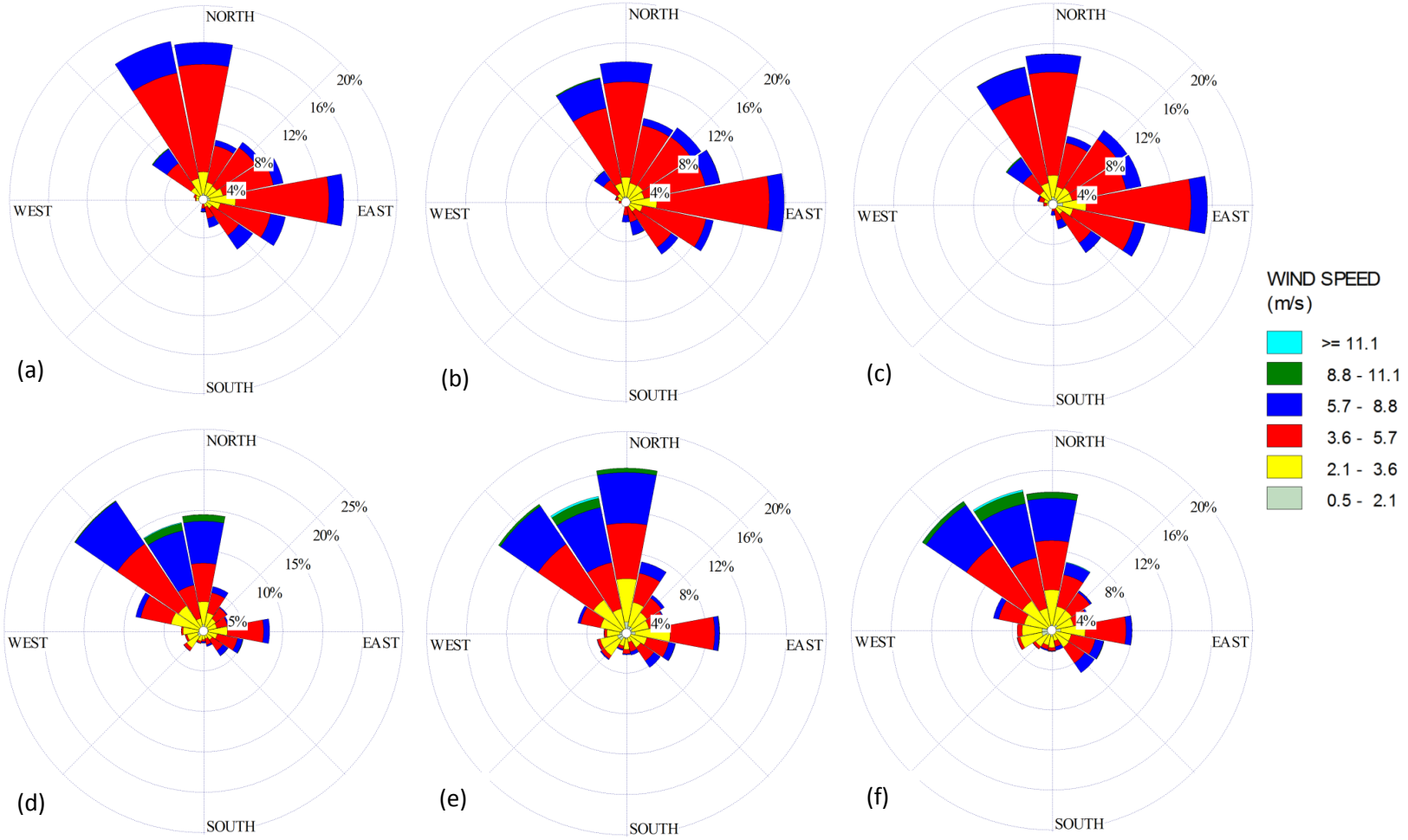

Figure 13: Wind roses for: MM5 (a, b, c) and NCDC (d, e, f) for (2011 to 2013).

The wind class frequency distribution is also compared for each year separately in Figure 14, Figure 15 and Figure 16. The differences in velocity frequency distribution are between MM5 and NCDC data. These variances could be attributed to a number of reasons but this is out of the scope of this study. In general, the NCDC data showed wider range of data and concentrated frequency distribution percentage between 3.6- 5.7 m/s. MM5 data showed a narrower range of data, this leads to higher average wind speeds for the MM5 dataset and concentrated frequency distribution percentage between 3.6- 5.7 m/s.

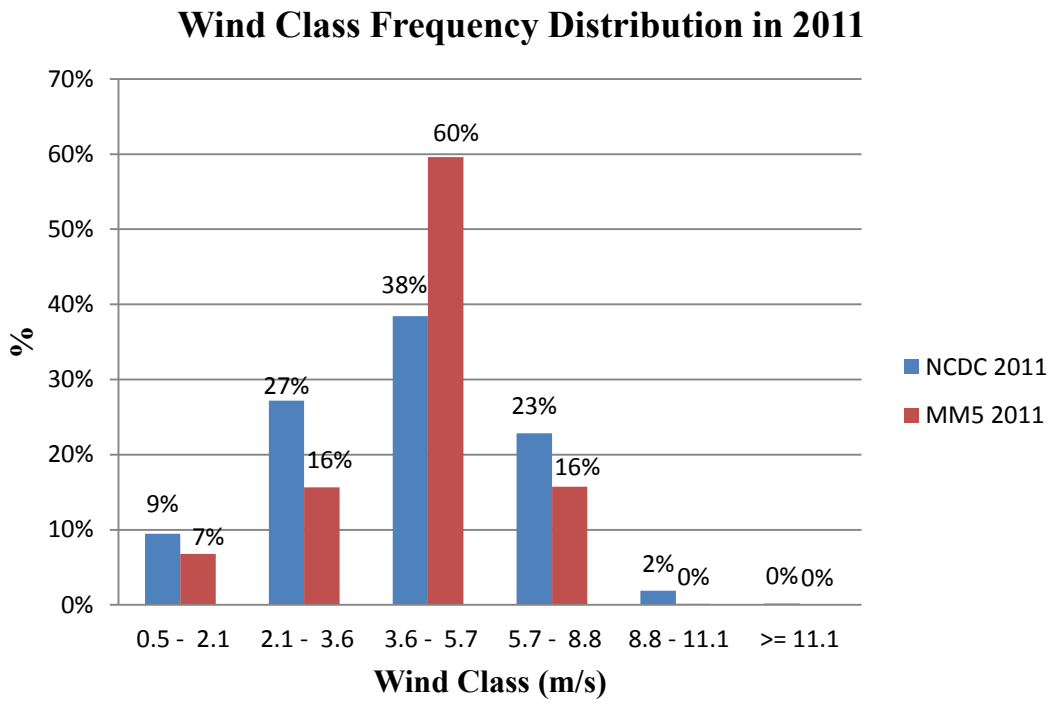

Figure 14: Wind class frequency distribution in 2011 for NCDC & MM5.

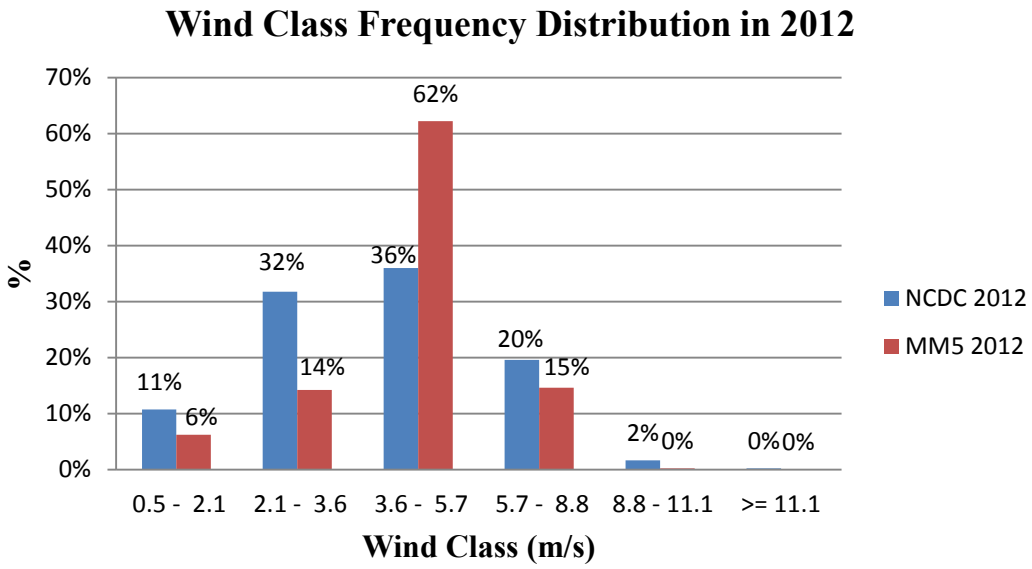

Figure 15: Wind class frequency distribution in 2012 for NCDC & MM5.

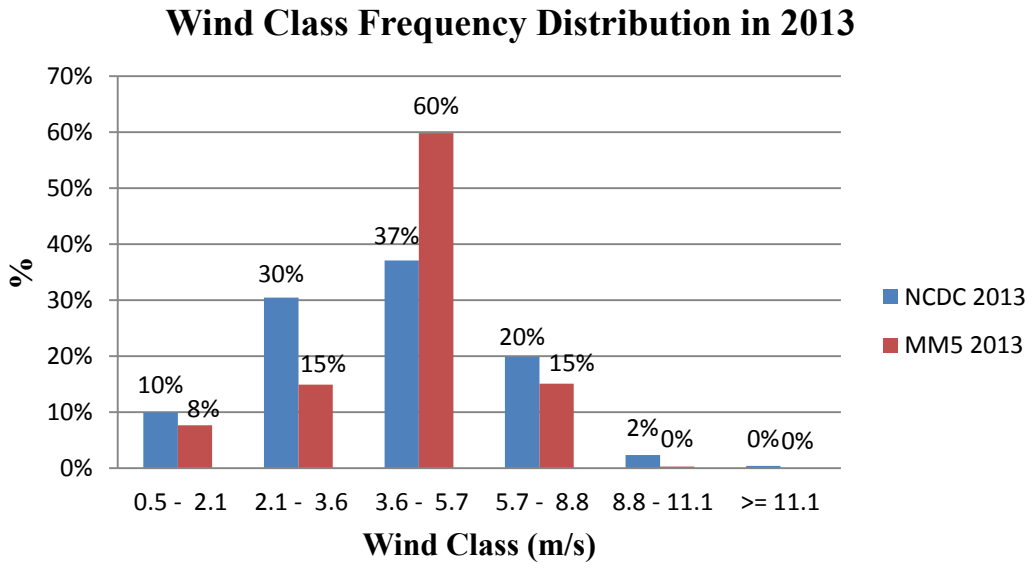

Figure 16: Wind class frequency distribution in 2013 for NCDC & MM5.

Taking in consideration the discussion on the meteorological data, their differences and the level of missing or incomplete data, the recommended meteorological data to be used in this thesis was selected the MM5 one. The details on the preparation of the MM5 data are described in the methodology chapter.

4.2. Dispersion Modelling Results

The ground level concentrations of the emitted releases from the selected facilities were estimated using the AERMOD modelling system. Each pollutant was modeled separately due to some limitations of the input file when dealing with multiple chemicals. The concentration contours graphs visualize the affected areas and the distribution of each pollutant. All 28 selected chemicals were modelled with the same configurations but here are illustrated only the most significant pollutants. In other words (the pollutants that have the highest concentrations compared exposure limits). The selected contours are presented in two graphs as following:

1. A base Map of the whole area to demonstrate the range and traveled distance of each case.
2. A closer view map for the facilities (sources locations) to focus on the areas with the highest values.

Figure 17 and Figure 18 present the concentration contours for NO_x emissions (as stated previously, NO_x are assumed to be NO_2) as a characteristic example for the graphs.

The concentration is varying along the base map; as expected the highest concentration values are located near the emissions sources, however the values are decreasing gradually as the emissions travel away from the sources points. Figure 18 shows a limit exceeding condition for the emitted NO_2, the assigned TEEL-0 value for NO_2 is 0.94 mg/m^3. The exceeded concentrations are located in a circle with a radius of 2000m from the virtual industrial city. The northeastern side of the industrial city is more affected than the other sides because of the locations of the emission sources and obviously the prevailing wind directions. The concentration contours for other selected emissions are available in appendix I. Moreover, Figure 17 shows a waiving pattern for the concentrations gradient at different RPs. The reason for this pattern is due to the grid resolution and wind resolution in AERMOD. The dispersion model is estimating the concentration using a single point methodology, and the plume estimation is based on averaged hourly calculations (one direction for the plume per hour). Due to the use of small sizes for the girds, the directions of the grouped wind resolutions are clear at far distances from the emissions sources. The simulated concentrations contours in AERMOD are limited to the hourly averaging values for the selected receptor points; and further data processing is required to estimate the maximum concentration at each receptor point. In addition, concentrations contours represent the situation of each pollutant individually. Consequently, the post processing files are used for calculating the hazard indices and estimate the integrated health effects of the mixture of chemicals instead of presenting individual results for each emission.

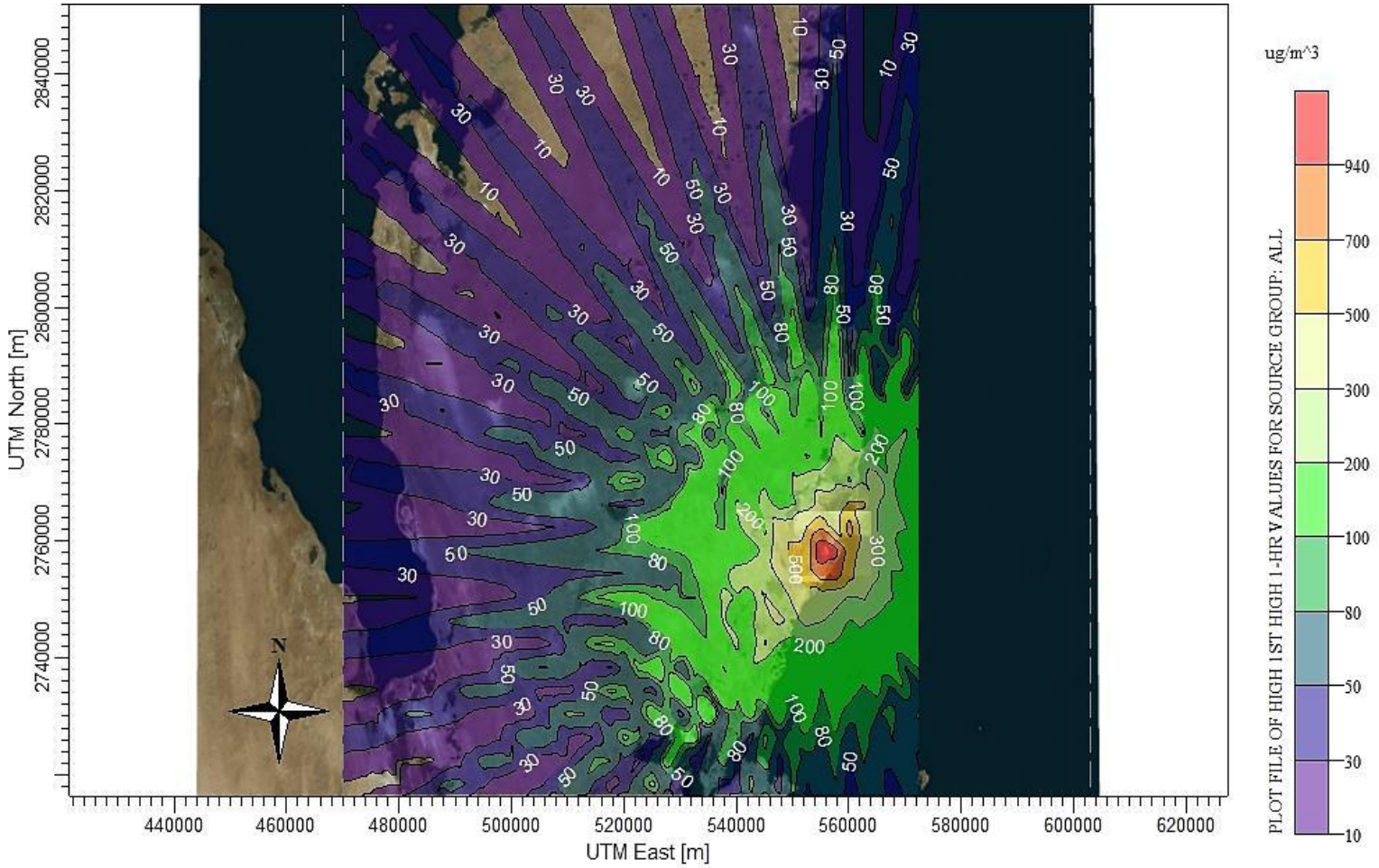

Figure 17: NO_2 concentration contours for the whole simulated area.

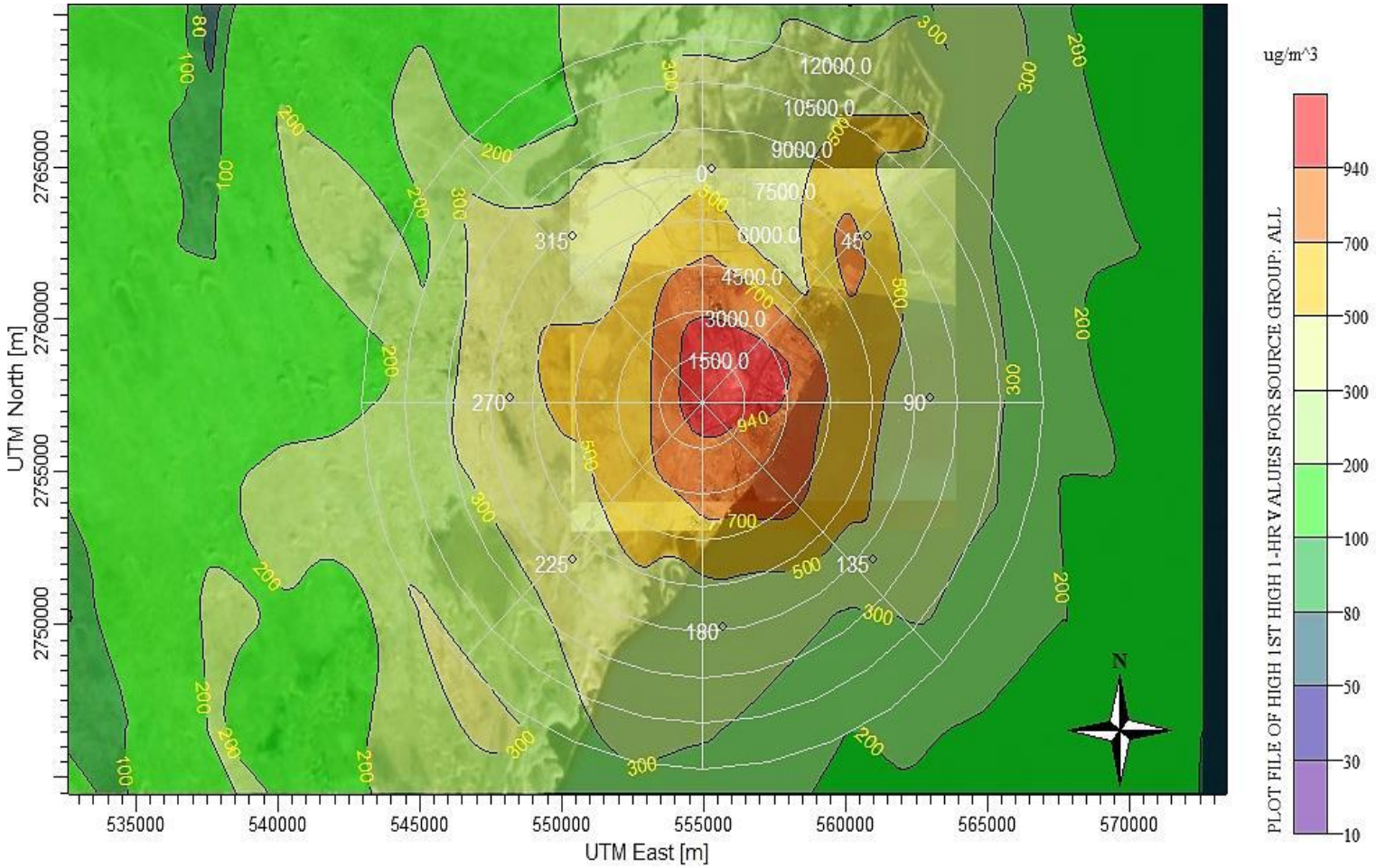

Figure 18: NO_2 concentration contours for industrial city.

4.3. Health Effects Estimation Results

The results of the discussed CMM approaches, to estimate the health effect from exposure to a mixture of pollutants, are presented in this section. These calculations are based on the dispersion results from AERMOD. The 28 chemicals of this study include more than 40 HCNs. The CMM approaches have been applied for all of them but the following paragraphs present the highest hazard indices for various HCNs.

4.3.1. Modes of action

Table 8 describes the summary of the "mode of action" results for the exceeded hazard indices. Both discussed approaches have been used to estimate the hazard indices for the specific mode of actions. It is observed that approach 2-alpha showed an exceedance of the hazard index limit for HCN 4, 6 and 13 at specific receptor points within the borders of the virtual industrial city.Approach-1 showed lower values and the hazard index is not exceeding the limit). The reasons for this outcome are:

1- Approach -1 uses simple ranking for HCNs and depends on the priorities of each chemical. For example: according to approach -1, the weighting factor (WF) for HCN 4 for NO_2 is 0.5 while approach 2-alpha is assigning a WF equal to 1 for the same HCN.

2- Approach 2 considers priority ranking for acute effects regardless the ranking of the health code number for each chemical. The WFs are tabulated in appendix C.

Table 8: The approaches that showed a higher HI for the specific mode of actions.

#	HCNs	Mode of action	The exceeded approach
1	4	Acute Systemic Toxins	Approach 2 -alpha
2	6	Cholinesterase Toxins, acute effects	Approach 2-alpha
4	11	Acute Respiratory Toxins other than irritants	Approach 1
5	13	Blood Toxins-Methemo-globinemia, acute effect	Approach 2-alpha
6	14	Severe Irritants	Approach 1 Approach 2-alpha

According to Table 8, HCN 14 (severe irritants) is exceeding the hazard index limits for the two approaches. The main causes for this are:

1- Both approaches assign high WFs (1, 0.9, 0.8 …) for the studied chemicals, for example: approach 2-alpha assigned a WF equal to 1 for HCN 14; similarly HCN 14 was given a higher priority in 12 chemicals according to approach 1.

2- The NO_2 high concentrations strongly affect the hazard index calculation; in comparison to all other chemicals. Therefore, it is expected whenever NO_2 participates in a mode of action at higher ranking order, the hazard index will exceed the limits.

Figure 19 and Figure 20 present the affected areas as a result of the summation of chemicals that have the same mode of action for HCN 14 (Severe Irritants).

Another example is, HCN: 11 (acute respiratory toxins other than irritants) is exceeding the hazard index limits when using approach 1. Again, the higher ranking of NO_2 for HCN 11 and the same for some other chemicals is the main reason for this finding. Approach 2-alpha has in general lower WFs value for HCN 11 (WF=0.75) than approach 1.

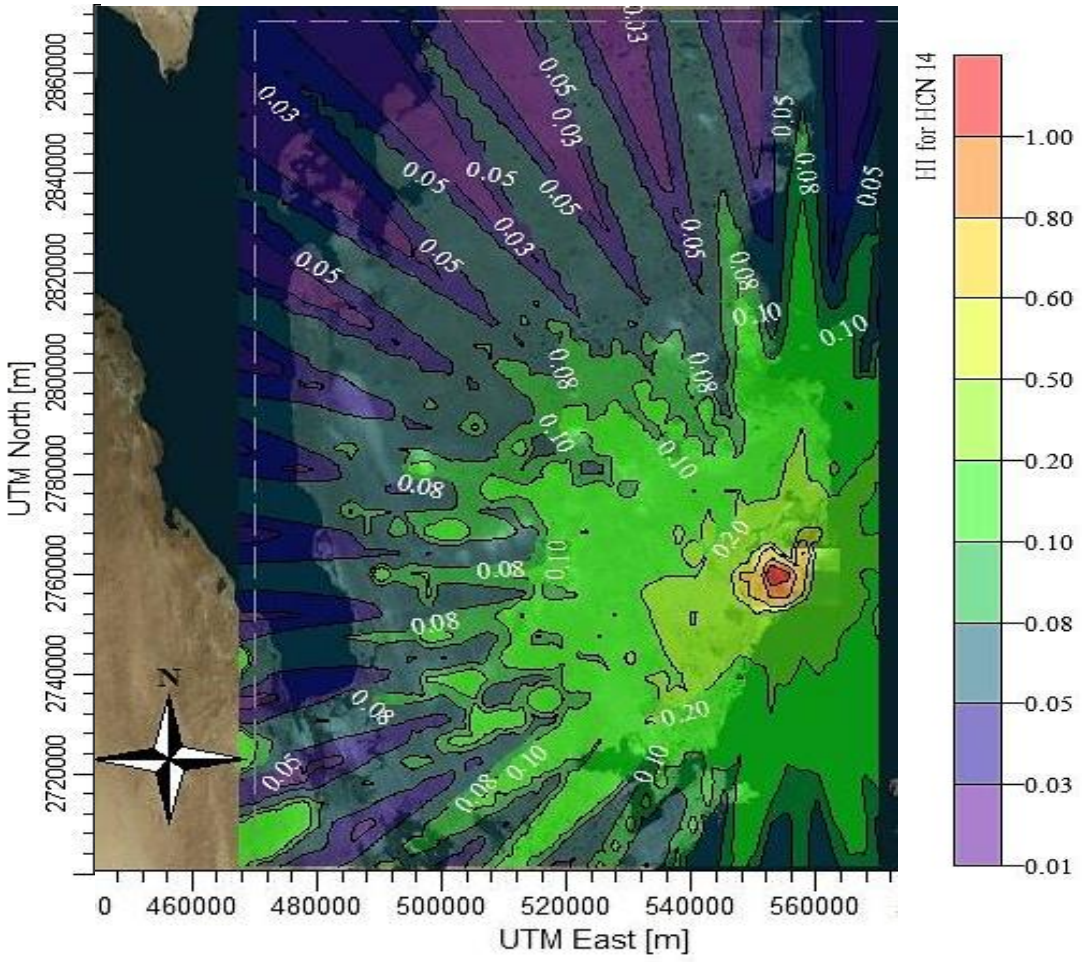

Figure 19: Hazard index estimations contour for HCN 14 using approach-2.

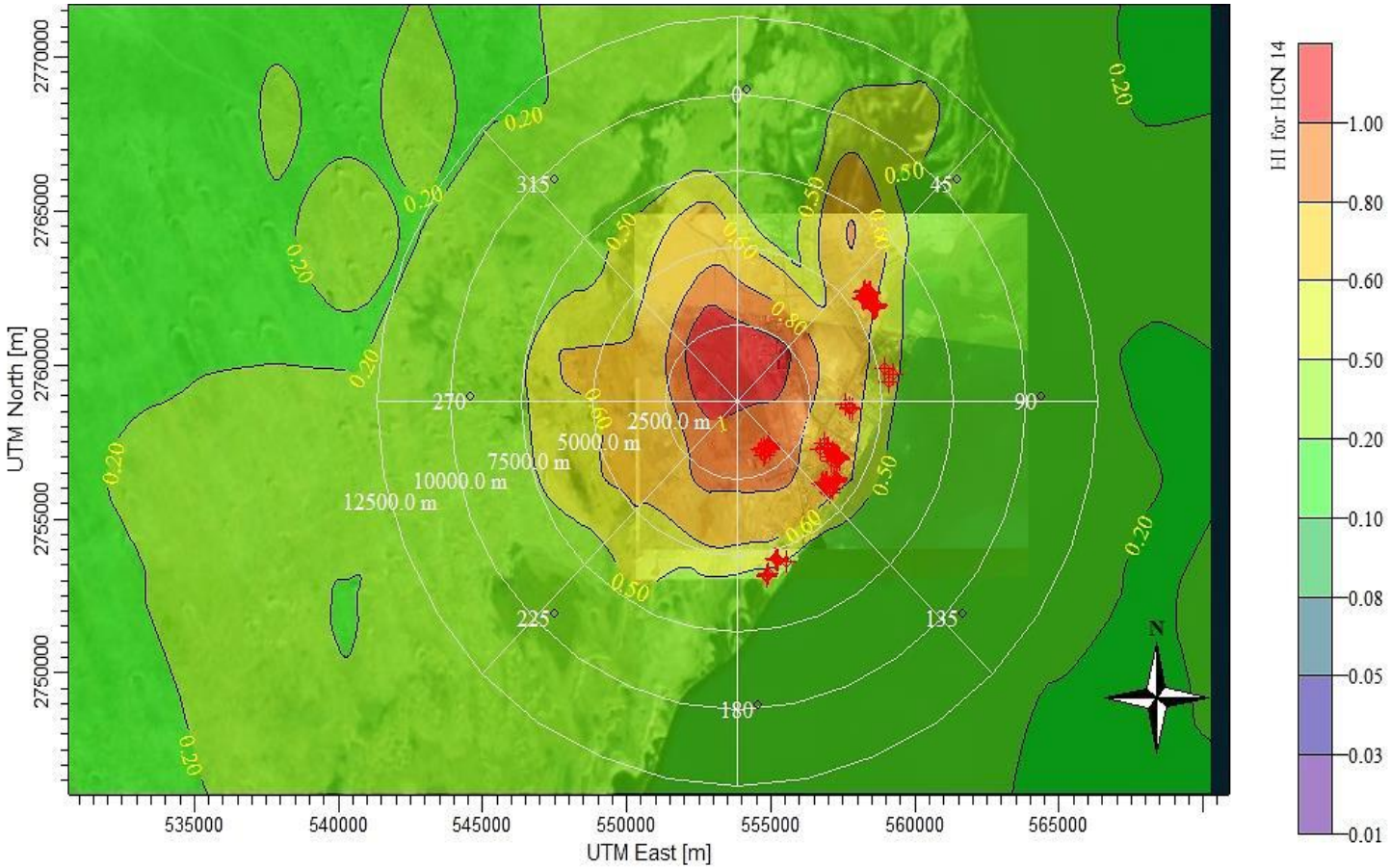

Figure 20: Hazard index contour for HCN 14 in MIC.

4.3.2. Specific target organs

The previous paragraph discussed the "modes of action" results which provide an overview about the expected overall health effects from the exposure to the mixture of chemicals. In this paragraph, the target organs HNCs are studied to predict the most affected organs from the emissions. Because of the link between the two approaches - mode of action and the target organs – a similar behavior is expected. For example: Table 9 shows the most affected organs when the CMM approaches are applied for each HCN; that previously showed exceedances:

Table 9: The affected organs according to CMM approaches that show exceedances.

#	HCNs	Target organ/effect	The exceeded approach
1	4.01	Eye—acute, other than irritation	Approach 2-alpha
2	4.05	Brain—acute effects	Approach 2-alpha
3	11.01	Respiratory irritant, acute severe or moderate	Approach 1 Approach 2-alpha
4	14.01	Eye irritant— severe	Approach 1 Approach 2-alpha

Table 9 shows the expected approaches to demonstrate affected organs. However, HCN 11.01 shows a different behavior from HCN 11. The main reason is the higher priority ranking for HCN 11.01 in approach 2-alpha than HCN11.00. According to the given ranking table for approach 2–alpha in appendix D, HCN 11.01 assigns WFs equal to 1, while the WF for HCN 11.00 is equal to 0.75.

According to Table 9, the most affected organ is the eye, acute severe irritants are expected and the individuals will start suffering mild or temporary symptoms; based on the TEEL-0 limit values. The respiratory system is also affected and individuals are expected to moderate

4.3.3. Differences between CMM approaches

According to the presented results, the use of CMM approaches for continuous releases and thus their outcomes depend on the following factors:

1. Selection of approach:
    a) Approach 1 gives a priority for HCNs according to their ranking for each chemical in the mixture.
    b) Approach 2-alpha gives a priority for HCNs according to their acute effects and severity. (HCNs associated with vision, cardiovascular, respiratory and nervous systems are assigned higher rankings).
2. Contribution of the chemical:

    NO_2 shows significant contribution at the results for all modes of action and target organs hazard indices due to the relatively high ground level concentrations. This result is probably attributed to the fact that all facilities in the virtual industrial city release this pollutant.

Additionally, the majority of the contributed chemicals pose higher hazard indices for acute effects than chronic effects.

Moreover, the observed exceeded values for hazard indices limits are frequently related to acute HCNs. As a result for the previous observations, several attempts are suggested to enhance the outcomes of the study and to cope with the objectives. The used standards and limits are one of the main factors that affect the outcomes of the CMM approaches. The specific limit value dictates the level of HI for each pollutant and consequently drives the total HI to higher or lower values. Especially to demonstrate the impact of this last factor, an extra case is discussed in the next paragraph where several exposure limits from various international agencies are discussed for applying CMM for continuous releases.

4.3.4. The impact of the selected exposure limits

The most affected organ – the eye – in the previous results is selected for this case study. Several limit values are examined and Table 10 shows the suggested values for the proposed limit values.

Table 10: The recommended exposure limits.

#	Standards	Time scale	Agency or institute[1]
1	RFC,RFD, MRL	Daily or continuously exposure	EPA,EPA,ATSDR
2	PEL, REL, TLV, WEEL	8 to 10 hours/day for 40 hours /week	OSHA, NIOSH, ACGIH, AIHA
3	TEEL, ERPG, AEGL	Generally 1 hour or different periods in emergencies	DOE SCAPA, AIHA, ACGIH

[1] Agencies or institutes in column 4 are ordered respectively according to standards durations in column 2.

The RFC/MRL standards have the lowest exposure values between the other standards. Also they could be more appropriate standards for this study because both address the daily exposure rather than in the case of emergencies. Unfortunately, the availability of this kind of standards was limited for the chemicals of this study. RFC limits from the EPA ISIR system were found for only 5 out of 28 chemicals, while the MRL values from ATSDR were observed for 11 out of 28 chemicals. PELs could be considered as another alternative option to be used; the exposure duration is considerably higher than TEEL-0 limits but lower than MRLs. PELs were found for 19 out of the 28 chemicals. All standards and limit values are tabulated in appendix G. MRLs are selected for this example and to demonstrate the impact of the limit values on the CMM results. Table 11 shows a comparison between the affected receptor points if TEEL-0 limits are used and if MRLs are used for HCN 14.01.

Table 11: The CMM results for the two different exposure standards.

Criteria	**(TEEL-0) Standards**	**(MRL)[1] Standards**
Total affected area[2] (Km^2)	14.5	8120
Maximum HI[3]	1.2	7.8
RPs location for max HI[4] (m)	X=552785 Y=2760343	X= 557785 Y= 2756343
Average HI[5]	0.01	0.19

[1] MRLs values are found for 11 chemicals out of 28 in this study, the values are extracted from ATSDR.
[2] The affected area is estimated approximately from AERMOD interface maps.
[3] The maximum HI is extracted from the plot file outputs for HCN 14.01.
[4] Receptor point location is extracted from the plot file outputs for HCN14.01.
[5] The average HI is extracted from the plot file outputs for HCN 14.01.

Figure 21 and Figure 22, present the maximum and the average HIs results for the 1764 receptor points using TEEL-0 standards, while Figure 23 and Figure 24 show the maximum and the average HIs results if MRLs limits are used. This example showed a significant change in the affected areas when the minimal risk levels (MRLs) are used as the standard exposure limits for the CMM approaches. The affected area is increased considerably due to the reduction in the used limits to estimate the HIs. The maximum hazard index is also higher due to the increasing number of the exceeded specific HIs for several chemicals as a result of the using MRLs. The average values of the HIs at each RP are also raised significantly compared to when using the TEEL-0 limits. However, the average values are still relatively low. This important observation was related to the frequency of exceeding the hazard indices for the studied mixture. The estimated average values for HIs summations showed relatively low HIs ($HIs_{estimated} \ll 1$). This outcome proved that HIs are exceeded only in few several times during the period of the study for both exposure limits. Consequently, the stated limits are expected to be exceeded occasionally and individuals are not regularly exposed to such concentrations all over the year.

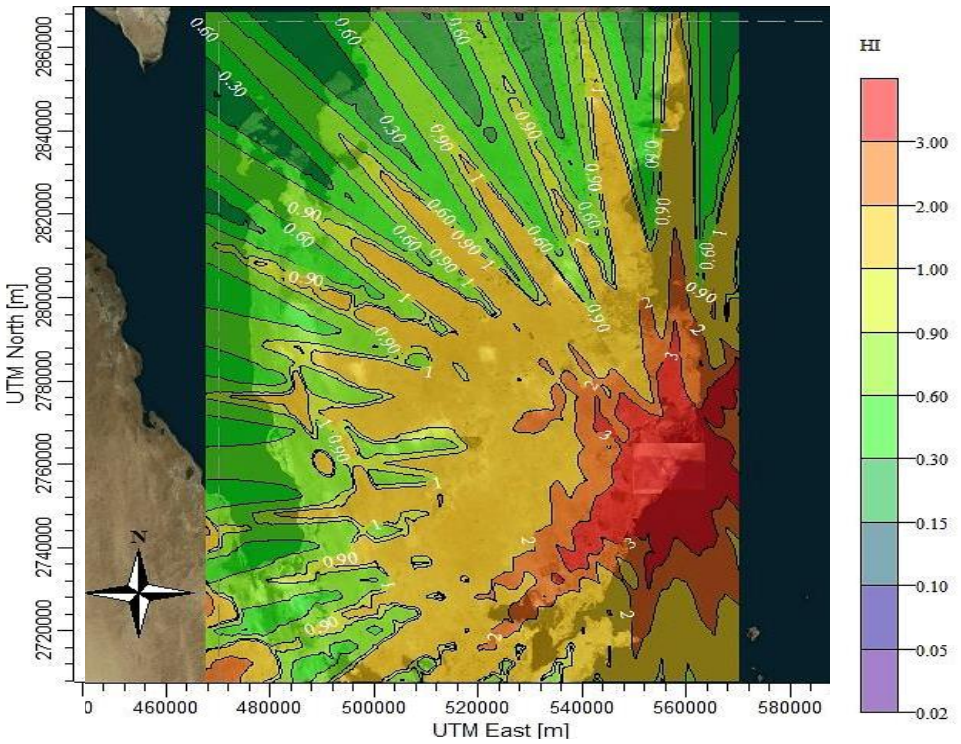

Figure 21: The maximum values for HIs results using MRLs standards.

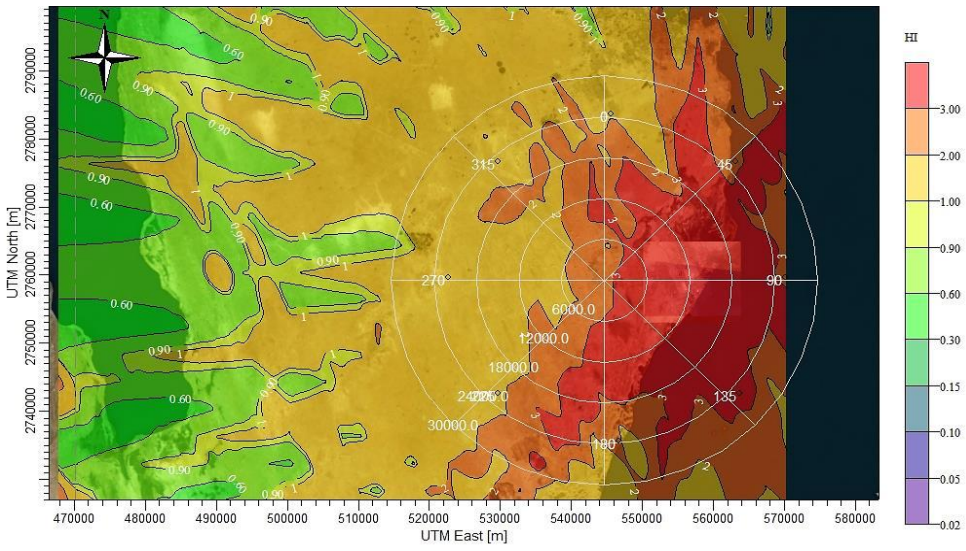

Figure 22: Closer view for max.values of HIs results using MRLs standards.

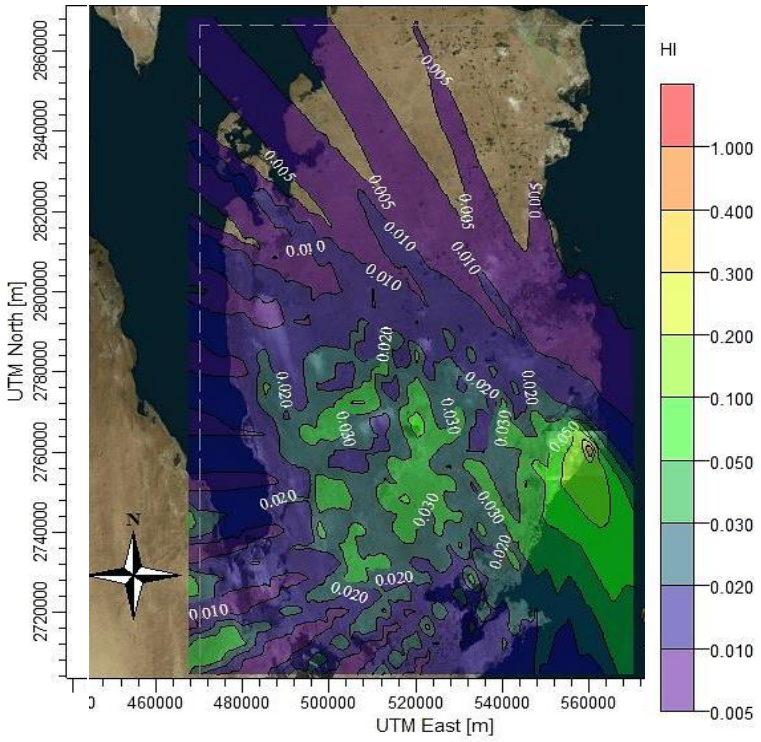

Figure 23: The average values of HIs results using MRLs standards.

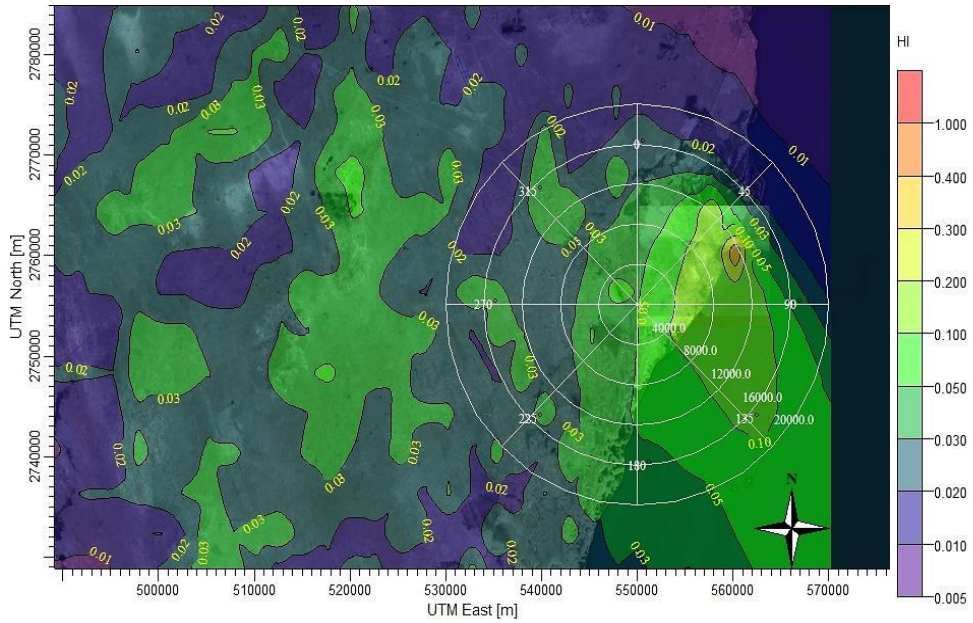

Figure 24: Closer view for average values of HIs results using MRLs standards.

4.4. General Discussion and Observations

The recommended meteorological data used in this thesis (MM5) showed useful outcomes for the studied region over the selected three years. The meteorological data may be enhanced if a reliable and complete inventory is used for the meteorological conditions from local weather stations in selected area, and compared with the simulated MM5 files. .

Moving to the concentrations estimations of the selected group of chemicals, the study introduced the Emission factors (EFs) method to deliver the required emission rate for each chemical. Such outcomes may vary significantly in reality due to several circumstances related to process or hazards controlling measures in each plant. Various improvements are available to be implemented in this field to get better estimations. One of the suggested improvements is using actual emissions inventory documents from the selected facilities, or reliable emissions rates for the atmospheric releases from the monitoring systems in industries. This method was used by SCAPA team to conduct CMM approaches in emergency situations, and also used by NERAM researchers to estimate the potential risk from continuous exposure to refineries releases in Canada.

The CMM was significantly enhanced due to the use of AERMOD simulation program; SCAPA team stated the benefits of using dispersion models in order to get wider range for the affected receptor points. In this study, the use of AERMOD achieved SCAPA recommendations and delivered the hazard indices for multi RPs instead of single scattered RPs.

The study discussed extensively the use of CMM approaches and delivered variety range of outcomes for the potential health effects. The use of several exposure limit standards was addressed in the study and examined for the selected group of chemicals. According to the provided outcomes in this thesis, the highest expected mode of action was acute eye irritation and accordingly the most affected organ was the eye. TEEL-0 and MRLs values provided the same findings with different extent of hazard indices and affected RPs. The use of MRLs showed a higher number of exceeded HIs and a wider range of the affected RPs. The results were reasonable enough due to the low concentration limit values of MRLs. Although the hazard indices results showed an exceedance for the stated criteria in several cases, the HI average values at each RP showed relatively low values during the studied periods. As a result, the portability of exposing to such conditions are expected to be low and occasionally for individuals. This also validates the use of TEEL-0 as an acceptable exposure limit for the aim of this study.

The main factors that affect the CMM results are:

1. The contribution of the chemicals in the mixture, relatively to their exposure limits.
2. The selected exposure limits for conducting HI calculations.
3. The frequency of exceeding the stated index for HI summation.

5. CONCLUSIONS

In conclusion, this study presented the Chemical Mixture Methodology CMM approaches as a tool to predict the associated hazard index from continuous exposure to a mixture of atmospheric pollutants. A proposed methodology was suggested to adapt the original CMM method to account for continuous releases situations and not just in emergency cases. A virtual industrial city was developed as a basis and the atmospheric emissions were estimated for several large scale industries based on literature data. The meteorological data were collected from the local airport and a mesoscale meteorological model for a period of three years (from 2011 to 2013). The EPA-AERMOD dispersion modelling system was used to calculate the concentration contours of the 28 contributed chemicals. Various exposure standard limits were examined to select the most appropriate one to obtain the hazard index summation for the chemical mixture. The CMM was applied for different "modes of action" (e.g. respiratory system, severe irritants and others) and for "specific target organs" (e.g. eyes, brain and others).

Finally, the study demonstrated that even in the case where all individual pollutant releases are lower than the recommend values there is a potential impact because of the integrated health effects. More specifically, the associated health code numbers for the studied chemicals and sources showed that there will be exceeding cases, mainly irritations for respiratory system or eyes. Another aspect is the use of the

appropriate threshold limit value. The use of minimal risk levels MRLs showed a higher number of exceeding HIs and a wider range of affected RPs than using the temporary emergency exposure limits TEEL-0. However, the results generally showed low average values for the hazard index for the studied period.

6. RECOMMENDATIONS

This section proposes a number of recommendations in order to improve the outcomes of the CMM approaches to assess the associated integrated health impacts from continuous exposure to industrial releases. The recommendations are divided in to three categories:

- Suggestions for the proposed methodology:
  1- The meteorological data play a significant role and is recommended to further study the variations between the airport data and the MM5 simulations. In general, it is also suggested to be collected from local weather stations for the selected geographical location to ensure the reliability of the AERMOD meteorology profile.
  2- An actual emission inventory data are suggested to be used for continuous industrial releases and to be compared with the estimated rates from EFs method. This suggestion will eliminate the associated uncertainty with the use of emission factors to estimate emission rates.
  3- MRLs and RFCs limits are recommended to be investigated more to check the applicability of using such limits with CMM approaches.

- Suggestions for HCNs List

  4- An extension for the HCNs list is required to include more affected organs due to the inhalation of industrial emitted pollutants.

- Future directions for the study

  5- It is advisable to study the neighorbing industrial cities in the region, and find the contribution of each industrial city to the ambient air concentration for each pollutant.

  6- In that case a long range dispersion model is suggested to be used for better concentrations estimations.

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APPENDIX A: CHEMICAL MIXTURE RISK ASSESSMENT APPROACHES

Whole mixture method

This approach is considered as the first applicable method to conduct the risk assessment of chemical mixtures. It deals with the mixture as a whole and uses the available data for exposure and health effect of the concern mixture. Same approach is used in several literatures and studies but under different names such as: mixture of concern or original mixture studies. It is observed that this approach requires intensive data about the mixture of concern and most of the time these data are rarely available in literatures [8]. The established studies using such approach are mainly concerned on the surrounded area of the emitted pollutants (near the sources). Some examples for such studies are: coke oven emissions [38], Natural gas emissions[39], ground water contaminants and pesticides [1, 4]. The benefit of using such approach is: the health effects data are accounting for the interactions among the components of the concerned mixture. On the other hand, the studied mixture may be quietly different than the original hypothetical mixture used to deliver the basic risk assessment or the one used to determine the health effects; because of mixture compositions changes due to the duration of releases (time factor) or the distance travelled before reaching the receptor points [8].

As a result, the reliability of the studied mixture in a real environment or scenario will strongly support the required decision to use the observed effects from the original hypothetical studied mixtures [12]. The basic required data for this approach is the collected toxicity information and results from animal toxicity studies and experiments , human epidemiologic and clinical data [12].

Similar mixture method

This approach is using the available data and health effects of an original studied mixture and applies them to similar (sufficiently) mixtures. Those similar mixtures may have the same or most chemicals of the studied original mixture but in a little different proportion. Also they should display the same health effects, way of transport, outcomes or act in a similar toxicologically modes. Some scaling factors or extrapolating data are used to assess the similar mixture risks in some cases like: the human cancer risk studies which were conducted to assess the potential risk from various sources of combustion emissions [4, 5]. The scaling factors (comparative potency) approach requires several comparisons on the data collection, potency relations and dose responses steps to valid the similarity assumption [12].

Component by component approach

Chemical mixtures assessments frequently use this useful approach in the absence of the required basic information about the concern mixture or similarities. The

total toxicity of the mixture is calculated from the individual toxic data for its components [3]. One of the main assumption that is usually used in this approach is considering the exposure to the doses or the responses of each component in mixture to be additive [8]. This simply allows the risk assessor to sum the does effects or responses to evaluate the risk of exposure for such components in the environment. Consequently, this approach is recommended to be use from EPA supplementary guideline for conducting health risk assessment of chemical mixture if the interactions information are missing [12]. There are mainly two concepts used to estimate the health effect in component based approach, the first concept is the concentration addition or (dose addition) and the second concept is the independent action or (response addition) [3, 4]. The main condition to select one of these concepts is the toxicological similarities for chemicals in the mixtures [12]. Therefore, the information of mode of action of each component in the mixture is required for easily selecting the optimum approach for the studied mixture of chemicals [5].

Dose Addition

The dose addition concept is clearly used the assumption of the same joint action of the mixture components, in other words the mixture's components are affecting the same endpoint (toxicologically similar) [12]. The following general formula is used to evaluate the dose addition:

$$\sum_{i=1}^{n} \frac{C_i}{EC_{xi}}$$ Equation (9)

Where C_i is the individual concentration of each component in the mixture, and EC_{xi} is the effective concentration of each component with the fractional effect (x) [3]. This simply means the dose addition is using the summation of the individual doses to predict the response to the mixture, and each chemical is acting as a dilution for each other chemical in the mixture [12]. There are several methods used in literature to apply the dose additive model, for example: the Hazard index method, toxic equivalency (TE) and point of departure index (PODI) [5]. There are several evidences and studies supporting the use of dose addition methods. ACIGH, EPA, NAS and Mumtaz recommended the use of HI methods in several articles for different types of exposure[8, 9, 10]. The supported evidences are mentioned in the guidance manual for assessment of joint toxic action of chemical mixtures which is published by the U.S department of health and human services in 2004 [8].

Response Addition (Independent action)

Unlike the dose addition assumption, the response addition method is assuming that each component in the mixture is acting independently from each other chemical; the influence of the produced effects of each chemical is different than others in the same mixture. As a result, the response of exposure to such mixture is depending more on the contribution of each chemical in the concerned mixture [8]. For example:

chemical A is affect a specific target X and Chemical B is affecting the same organ, if chemical B is existing or not existing the target organ response from A is the same. This method requires a reliable data for toxicity, dose response and exposure data for the components in the mixture. The interactions between the components at the low level are unlikely to occur and most of the time is neglected. The response addition method is also limited to the low exposure concentrations scenarios and the uncertainty in this method is mainly from the accuracy of the collected exposure data and independence of the mode of action of each component in the mixture [12]. This method is used extensively for total cancer risk assessment for chemical mixtures and also in ACGIH's approach for independent agents [8]. Table 12 is summarizing the differences between the dose addition methods and response addition method:

Table 12: Comparison table between CA and RA methods.

#	Criteria/ description	Concentration Addition	Response Addition
1	Contribution to endpoints	Same mechanism of action, all components are affecting the same endpoint	Unique mechanism of action, independently contribution
2	Requirements	Individual Components' concentrations Effects of all components to the endpoint	Toxicity data, exposure data and response data Relative effects of single components
3	Limitations	Requires low level concentration when interaction effect is not counted.	Using low exposure concentrations Limited to independence of actions
4	Uncertainties	The accuracy of both toxicological similarities and exposure data	The accuracy of exposure data and the certainty of independent actions.
5	Examples	Hazard index (HI) Point of departure index (PODI) Toxic equivalency factor (TE) Relative potency factor (RPF)	Cancer risk assessment for chemical mixtures ACGIH's approach for independent agents

Concentration addition Methods

HI method

The use of HI is recommended by many agencies like ACGIH, OSHA, NIOSH and EPA. For a chemical mixture of two or more components ACGIH is recommended the use of HI approach if the chemicals are affecting the same endpoint (target organ). The acceptable limits used within this approach by ACGIH are TLVs and the interactions between the components can be neglected at low concentrations cases. OSHA is also recommending the use of HI with the PELs values for the chemicals which are available in the concerned mixture. Unlikely ACGIH, OSHA didn't put any restriction to use this specific approach with chemicals that affecting the same endpoint (toxicologically similar). EPA is recommended the use of compnents based approaches and to assess the interactions data if available. Detailed explanation was previously given for EPA compnents based approaches [8].

The modified HI method

HI is exposed to several modifications to account for the interaction between the chemicals in the mixture; the modified version of HI is called Interaction Based HI and mentioned in EPA 2000 guidance [12]. The modified method is using a defined factor to account for the interaction among the components within the chemical mixture. The following general equation shows the suggested modification of the original HI equation by EPA 2000 guidance:

$$HI_I = HI_{ADD} \times UF_I^{WOE}$$ Equation (10)

Where HI_I is the modified hazard index which counting the interactions, HI_{ADD} is the hazard index derived from dose addition (non-interactive HI), UF_I is the uncertainty factor for interaction and WOE is weight of evidence of the interaction.

The previous equation is Cleary describing the required procedure to account for interaction with the chemicals in the mixture, however the steps to determine the UF and WOE is not straight forward and require an extensive knowledge about the interaction mechanisms between the contributed chemicals with some experimental measures which might be inapplicable for some mixtures. Several modifications for the interaction based HI are stated in the EPA guidance and other studies to establish a defined criteria for the uncertain factors and WOEs [12].

Point of departure index (PODI)

PODI is a simple CA approach used by EPA and similar to the HI method, the only difference is PODI is using the Point of departure level instead of AL. the following equation is describing the concept of PODI method:

$$PODI = \sum_{i=1}^{n} \frac{EL_i}{POD_i}$$ Equation (11)

Where PODI is the point of hazard index, EL_i is the exposure level of chemical I and PODi is the point of departure of chemical i. The point of departure index is the summation of the individual fractions of the exposure levels to point of departure for each chemical in the mixture. POD_i is representing the No- Observed-Adverse-effect-Level (NOAL) or the Benchmark Concentration or Dose (BMD) [3]. This method is also neglecting the effect of the interactions between the components within the mixture [6].

The advantage of this method is the removing of the uncertainty factors associated with AL in HI method since HI is comparing the exposure level to a concentration level redirected from toxicity data [5]. The NOAL levels is derived from the response curves of the concern chemicals, the response curve represents the relation between the different concentrations of chemical used in the toxicity tests verses the frequency of hazard to occur. Such data requires intensive experiments for each chemical in the mixture to observe the desired limits.

Toxic equivalency (TEQ)

The toxic equivalency method is one of the components based approach to assess the health effect of a mixture using the assumption of dose additivity. The following equation is showing the method to find the TEQ based on TEF:

$$TEQs = \sum_{i=1}^{n} C_i \times TEF_i \qquad \text{Equation (12)}$$

Where TEQ is the toxic equivalency index, C_i is the concentration of chemical I and TEF_i is the toxic equivalency factor of chemical i. Literature review shows that TEF approach is mainly used to explain the toxicity of PCDDs, PCDFs, dioxins and PAHs mixtures. As a result this approach is applied to specific classes of chemicals with sufficient health effects information for at least one component in the mixture [8].

Relative Potency factor (RPF)

RPF is considered as the general form of TEQ which is applicable to be used to other mixtures of concern. This method is using the dose addition assumptions and examined to several mixtures such as pesticides [6]. The following equation describes the RFP approach:

$$C_m = \sum_{i=1}^{n} C_i \times RPF_i \qquad \text{Equation (13)}$$

Where C_m is mixture concentration, C_i = concentration of individual chemicals in the mixture and RPF_i = the relative potency factor of each chemical in the mixture. This method is simply applying a scaling factor (RPF) to the individual chemicals in the mixture in order to assess the toxicity of the compnents. In addition it is predicting the toxicity of the related compnents from the index compound of the mixture. The index compound of the mixture is defined as the exiting compound in the mixture where all toxicological and dose response data are available.

A simplified example to explain the way of applying the RPF is: compound A is considered to be one –eighth as toxic as the selected index compound in the mixture, this means we need eight times of exposure to compound A to cause same effect of the selected index compound in the concerned mixture. As a result the RPF of compound A is 0.125. if all compnents in the mixtures are considered to cause same effects or equivalent effects, then all RPFs will be equal to 1.0, if the effect of some compnents in the mixture are neglected the RPF of such compnents will be equal to zero. EPA established three studies using such approach in literature; the approach is applied to dioxins, polychlorinated biphenyls (PCBs) and PAHs mixtures. The efforts in the three studies didn't achieve the desired scientific acceptance, because the toxicological data and mechanism of actions for the studied groups are different [12].

Response Addition Methods

Individual Toxicity Method

As described before, the RA approach is valid when the information about the toxicological independence is available for the mixture of concern. The used methods in this approach are based on measuring the probability of specific toxic effects [12]. The following equations explains the individual toxicity method in applying such approach [3].For binary mixture:

$$E(C_{mix}) = E(C_1) + E(C_2) - E(C_1) \times E(C_2) \qquad \text{Equation (14)}$$

For extended model:

$$E(C_{mix}) = 1 - \prod_{i=1}^{n}(1 - \quad E(C_i)) \qquad \text{Equation (15)}$$

Where C_i is the concentration of each chemical in the mixture and $E(C_i)$ is the fractional effect or the risk associated with each chemical in the mixture.

For example:

If we have 28 chemicals in a mixture where all chemicals are posing an individual risk of (5×10^{-3}).

Then:

The number of chemicals = 28

Individual chemical risk =(5×10^{-3}).

The mixture risk using the RA approach is equal to:

$$E(C_{mix}) = 1 - (1 - (5 \times 10^{-3}))^{28}$$

$$E(C_{mix}) = 0.1309$$

Total Cancer Risk

Another method has been used for RA approach and recommended by EPA is the total cancer risk TCR method. TCR is applied to assess the expected risk from a mixture of carcinogenic compnents [8]. The following equation is given the response risk for mixtures as a sum of the individual risks for the compnents:

$$Risk = \sum_{i=1}^{n} Risk_i = \sum_{i=1}^{n} d_i B_i \qquad \text{Equation (16)}$$

Where d_i is the dose of concentration of chemical i and B_i is the slope factor, potency of parameter or the unit risk for chemical i. B_i can be found from the IRIS values established by EPA, and the equation is limited to carcinogen chemicals which have an individual risk below 0.01 and a summation below 0.1 [1, 12].

APPENDIX B: HDIDI II STEPS ACCORDING TO NERAM FINAL REPORT

The NERAM team used three classes for air emissions to prioritize the impacts of the releases amounts of pollutants, the classes were: carcinogenic toxics, non-carcinogenic toxics and criteria air contaminants (CACs) [17]. The study included 29 releases from the 20 oil refineries in different geographical locations in Canada. The pollutants were mainly polycyclic aromatic hydrocarbons (PAH), benzene, toluene, ethylbenzene, and xylene. HEIDI II was developed to predict the incidence of relevant disease endpoints from each chemical emitted from the refineries. The NERAM team has divided the project to three modules, the first module was created to estimate the concentration profile using a U.S. EPA air dispersion model (AERMOD) to estimate ambient concentrations of the carcinogenic toxics, non-carcinogenic air toxics and particulate matters (PM) in the study [17]. A generic meteorological profile was simulated for the southwestern side of Ontario City; it was used as a default scenario to get the required terrain and physical air distribution parameters for metrological preprocessing for AERMOD [16]. The secondary pollutants were considered in this study and more specifically for NO_x, SO_2 and PMs.

A health effect module was used to estimate the predicted incidence in each geographical location for different kind of diseases such as: Cancer diseases, cardiopulmonary disease, or other systemic disease incidences.

Figure 25 is giving the steps used to deliver HEIDI II in the final report of NERAM team in 2004.

The incident cases were predicted according to the following equation [16]:

$$IC = IC_{B+R} - IC_B \qquad \text{Equation (17)}$$

Incident cases were calculated using concentration-response function as following [16]:

$$IC = inhalation\ unit\ risk * conc.* exposed\ population \qquad \text{Equation (17)}$$

Where IC is the incident case, B is the background and R is refinery. The simplified DALYs were published by the International Life Science Institute (ILSI) and the complex DALYs were extracted from WHO (global burden of diseases approach) [16]. The definition and the calculation of DALYs were documented in the NAREM published final report in 2004 [16]. The outputs of HEIDI were mainly:

1. Ranking of the contributed pollutants based on the estimated number of cases per annum.
2. Ranking of the contributed pollutants based on simplified and complex DALYs calculations.

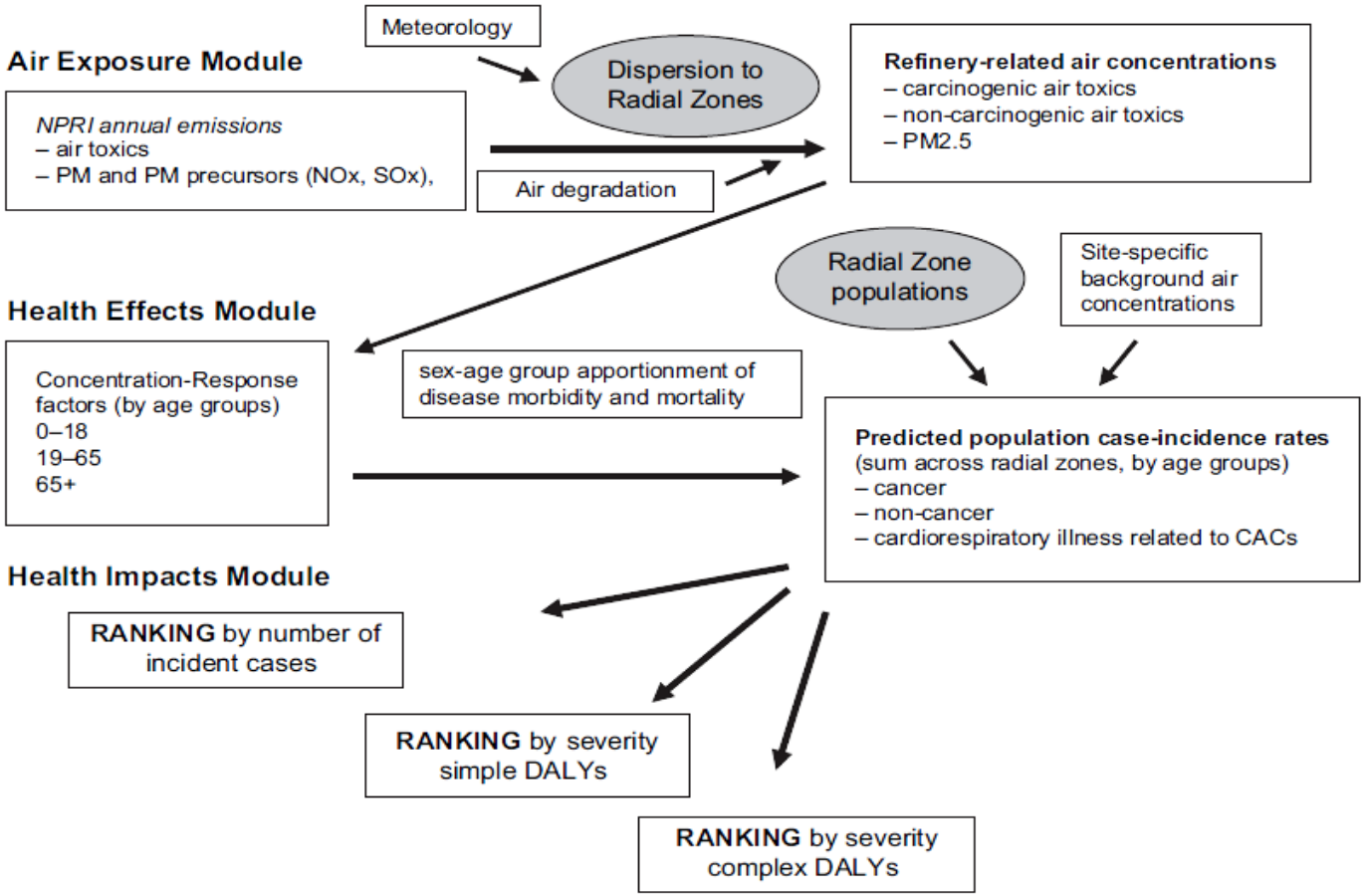

Figure 25: HEIDI II modules and outcomes flowchart from NERAM report [14].

APPENDIX C: BACKGROUND ON CMM

Default chemical mixture methodology CMM information (1999)

Three different receptor points (RPs) used to predict the concentrations of the chemicals in the mixtures and three emergency classes are established to predict necessary limits (ERPGs) for each RP [15]. Table 13 presents the RPs with the applicable emergency response class.

Table 13: Guidelines for different emergency planning for default CMM [15].

Receptor Point	Emergency Class		
	Alert	site	general
Within the facility (or30 m)	≥ERPG-2		
Facility boundary (or 200 m from facility structure)		≥ERPG-2	
Site boundary (or on –site location accessible to public)			≥ERPG-2

The estimated periods for releases of the selected scenarios were 15 minutes for concentration dependent chemicals and around 60 minutes for dose dependent chemicals. Table 14 shows the different classifications used in the default CMM by Craig in 1999:

Table 14: Chemicals categories for CMM in 1999 [15].

Category	Conc. Limit classification	Exposure duration
1A	Ceiling standard	Conc. dependent
1B	Irritants	Conc. dependent
1C	Technological feasibility	Conc. dependent
2	Acute toxicants	Does dependent (8hr/day)
3	Cumulative toxicants	Does dependent (40hr/week)
4	Both acute and cumulative	Does dependent (8hr/day & 40 hrs /week)

The results of the primary study tabulated the estimated HIs according to their toxic consequences in to three main categories (Chronic, Narcosis and irritation). The study strongly supported the use of addition method of and more specifically (hazard index) and validated the assumption of neglecting the interaction effects if the knowledge about (synergistic or antagonistic effects) is unavailable [15].

Development for CMM method in 2010

According to the developed method for the default CMM method by SCAPA team in 2010, the guideline concentrations (PAC) are extracted from following guidelines [18]:

1. AEGL, Acute Exposure Guideline Levels.
2. ERPG, emergency Response Planning Guidelines.
3. TEEL, temporary Emergency Exposure limits.

The PAC values were categorized to 4 main groups [18]:

1. TEEL-0: No adverse health effects are expected.
2. PAC-1: Mild or transient health effects are expected.
3. PAC-2: Serious or irreversible effects are expected that might prevent the person to take any protective action.
4. PAC-3: life –threatening health effects are expected.

The study compared the outcomes of the developed method and the default one in a proposed case from DOE facility in U.S to validate the results. The increasing in the HCNs leads to a better representation for the impacts on each organ for both acute and chronic effects. In addition, the new HCNs delivered varied analytical toxic consequences to predict the most affect human's systems from the exposure to such releases [18]. The modified HCNs are available in Table 15; the new added HCNs are tabulated in bold font, also the rank for each HCN to indicate the importance of them in any planning study for emergency response.

Table 15: Modified HCNs for CMM in 2010 [18].

Rank	HCN	Target organ	Rank	HCN	Target organ
29	1.00	OSHA carcinogen (29 CFR 1910.1000)-chronic effects	9	4.01	Eye (acute, other than irritation)
30	1.01	Bladder carcinogen-)-chronic effects	**20**	**4.02**	**Nose-acute effects other than irritation**
31	1.02	Liver carcinogen-)-chronic effects	**26**	**4.03**	**Bladder – acute effects**
32	2.00	Suspect carcinogen or mutagen-)-chronic effects	**23**	**4.04**	**Bone marrow – acute blood-forming system and other acute effects**
33	2.01	Kidney carcinogen-)-chronic effects	**15**	**4.05**	**Brain – acute effects**
34	2.02	Liver carcinogen-)-chronic effects	**22**	**4.06**	**Hematological effects – acute, unspecified**
55	3.00	Chronic systemic toxin-)-chronic effects	**25**	**4.07**	**Gastrointestinal tract – acute effects**
45	3.01	Bladder-)-chronic effects	**14**	**4.08**	**Heart, Cardiovascular system – acute effects**
41	3.02	Unspecified hematological effects)-chronic effects	**21**	**4.09**	**Kidney – acute effects**
46	3.03	Bone)-chronic effects	**24**	**4.10**	**Liver – acute effects**
42	3.04	Bone marrow)-chronic effects	**51**	**4.11**	**Skin – acute effects other than irritation**
35	3.05	Brain)-chronic effects	**53**	**4.12**	**Skin perforation – acute effects other than skin absorption**
47	3.06	Eye -chronic ocular) effects	**27**	**4.13**	**Bone – acute effects**
44	3.07	Gastrointestinal tract)-chronic effects	49	5.00	Reproductive toxin – acute effects
28	3.08	Heart)-chronic effects	50	5.10	Reproductive toxin – chronic effects
40	3.09	Kidney)-chronic effects	4	6.00	Cholinesterase toxin – acute effect
43	3.10	Liver)-chronic effects	18	7.00	Nervous system toxin – acute effects

Table 15: Continued

Rank	HCN	Target organ	Rank	HCN	Target organ
52	3.11	Skin-chronic effects including dermatitis and sensitization	16	7.01	Central nervous system – acute effects
54	3.12	Skin perforation-chronic effects including dermatitis and sensitization	37	7.10	Nervous system toxin – chronic effects
13	4.00	Acute systemic toxin - Short-term high hazard effects	36	7.11	Central nervous system – chronic effects
17	8.00	Narcotic – acute effect	8	15.00	Moderate irritant
39	9.00	Respiratory sensitizer – chronic effect	7	15.01	Eye irritant - moderate
38	10.00	Respiratory toxin – chronic effects	12	15.02	Skin irritant - moderate
19	11.00	Respiratory toxin – acute effects other than irritation	57	16.00	Mild irritant
10	**11.01**	**Respiratory irritant – acute severe or moderate but not mild irritant effects**	56	16.01	Eye irritant - mild
48	12.00	Blood toxin, anemia – chronic effect	58	16.02	Skin irritant - mild
3	13.0	Blood toxin, methemoglobinemia – acute effect	1	17.00	Asphyxiants, anoxiants – acute effect
6	14.00	Severe irritant	2	18.00	Explosive, flammable safety (no adverse effects with good housekeeping)
5	14.01	Eye irritant - severe	59	19.00	Generally low-risk health effects-nuisance particles, vapors or gases
11	14.02	Skin irritant - severe	60	20.00	Generally low-risk health effects-odor

The enhanced CMM

In 2012, the SCAPA team examined the effectiveness of using the HCNs approach. The benefit term used to describe the reduction percentage was given as following [19]:

$$Benefit(p) = \frac{\sum_{i=1}^{n} HI_i - \sum_{i=1}^{n} HI_{i(P)}}{\sum_{i=1}^{n} HI_i} \times 100\% \qquad \text{Equation (18)}$$

Where: $\sum_{i=1}^{n} HI_i$ is the simple hazard index summation of the individual chemicals and $\sum_{i=1}^{n} HI_{i(P)}$ is the hazard index summation based of the specified target organs.

WFs approaches for the enhanced CMM

An example in Table 16 illustrates the use of Approach 1.

Table 16: An illustrated example for applying weighting factor approach-1.

Ranking	HI	Top 10 HCNs	Assigned WFs (Approach 1)	New HIs (HI*WF)
1	0.10	17.0	1	0.1
2		13.0	0.9	0.09
3		15.0	0.8	0.08
4		8.0	0.7	0.07
5		7.0	0.6	0.06
6		2.00	0.5	0.05
7		3.05	0.4	0.04
8		12.0	0.3	0.03
9		5.00	0.2	0.02
10		3.00	0.1	0.01

Table 17: Weighting factor approach -2 (Alpha) values [19].

Rank	HCN	WF	Rank	HCN	WF
1	17.00	1	31	1.02	0.5
2	18.00	1	32	2.00	0.5
3	13.00	1	33	2.01	0.5
4	6.00	1	34	2.02	0.5
5	14.01	1	35	3.05	0.5
6	14.00	1	36	7.11	0.5
7	15.01	0.5	37	7.10	0.5
8	15.00	0.5	38	10.00	0.5
9	4.01	1	39	9.00	0.5
10	11.01	1	40	3.09	0.5
11	14.02	1	41	3.02	0.5
12	15.02	0.5	42	3.04	0.5
13	4.00	1	43	3.10	0.5
14	4.08	1	44	3.07	0.5
15	4.05	1	45	3.01	0.5
16	7.01	0.75	46	3.03	0.25
17	8.00	0.75	47	3.06	0.25
8	7.00	0.75	48	12.00	0.25
19	11.00	0.75	49	5.00	0.25
20	4.02	0.75	50	5.10	0.25
21	4.09	0.75	51	4.11	0.25
22	4.06	0.75	52	3.11	0.25
23	4.04	0.75	53	4.12	0.25
24	4.10	0.75	54	3.12	0.25
25	4.07	0.75	55	3.00	0.25
26	4.03	0.75	56	16.01	0.25
27	4.13	0.75	57	16.00	0.25
28	3.08	0.75	58	16.02	0.25
29	1.00	0.75	59	19.00	0.25
30	1.01	0.75	60	20.00	0.25

Table 18: Weighting factor approach -2 (Beta) values [19].

Rank	HCN	WF	Rank	HCN	WF
1	17.00	1	31	10.00	0.4
2	18.00	1	32	9.00	0.4
3	11.01	1	33	7.11	0.4
4	11.00	1	34	7.10	0.4
5	7.01	1	35	12.00	0.4
6	7.00	1	36	3.01	0.4
7	8.00	1	37	3.02	0.4
8	14.01	1	38	3.03	0.4
9	4.08	1	39	3.04	0.4
10	4.05	1	40	3.05	0.4
11	4.01	1	41	3.06	0.4
12	6.00	1	42	3.07	0.4
13	14.00	1	43	3.08	0.4
14	14.02	1	44	3.09	0.4
15	13.00	1	45	3.10	0.4
16	15.01	0.8	46	3.00	0.4
17	15.00	0.8	47	1.00	0.4
8	15.02	0.8	48	1.01	0.4
19	4.00	0.8	49	1.02	0.4
20	4.02	0.8	50	2.00	0.4
21	4.03	0.8	51	2.01	0.4
22	4.06	0.8	52	2.02	0.4
23	4.07	0.8	53	16.01	0.2
24	4.04	0.6	54	16.00	0.2
25	4.09	0.6	55	16.02	0.2
26	4.10	0.6	56	5.10	0.2
27	4.11	0.6	57	3.11	0.2
28	4.12	0.6	58	3.12	0.2
29	4.13	0.6	59	19.00	0.1
30	5.00	0.6	60	20.00	0.1

Table 19 gives the priority ranking for selection the exposure route from different literature which is used in approach 3:

Table 19: Priority ranking table for Approach 3[19].

priority	References (toxicity data)
1	AEGL
2	ERPG
3	HSDB
4	RTECS, TLVs or BELs
5	NIOSH
6	CHIRS
7	SAX
8	MSDS

If it is observed that multiple routes are specified, the highest weighting factor should be used. Table 20 shows the different assigned WFs for each mode of action or target organ based on the toxicity data references. It was recommended to assign specific ranking for the associated HCNs for irritant conditions by Craig in 1999 depending on their severity level [15], for example: a weighting factor equal to 1 is assigned to severe while 0.5 is assigned to moderate (Check table 18) and 0.25 to mild conditions. Same WFs were used in this study for irritants as recommended by Xaio in 2012 for Alpha approach [19].

Table 20: WFs for approach 3 based on the route of exposure studies.

Route of exposure	**WFs**
Inhalation	1
Skin or eye contact	1
Oral	0.75
Other exposure route but primary target organs	0.5
Other unspecified route but not primary target organs	0.25

APPENDIX D: DISPERSION MODELING BACKGROUND

Basic terminologies

Datum: is well-known coordinate system some time it is called (geodetic system), used for setting references points and locating the required place on the earth. WGS84 is a type of datum which is accurately defined the sea level from 1984.

Mesosocale model: is a technique to use numerical weather predication methods (NWP) for weather forecasting, the model is using a set of equation to numerically represnt the evolution of the atmospheric conditions and data. Temperature, wind parameters, humidity percentage and atmospheric pressure are used intensively in such model.

CALMET is an interactive model to perform wind fields calculations; it has micro-meteorological elements for overwater or overland boundary layers. In addition, CALMET has the ability to simulate a prognostic wind field.

CALPUFF is basically used for non-steady-state Gaussian puff dispersion models; it has the ability to simulate the effects of time and space-varying meteorological parameters. It includes multi-layer, multi-species options for un-steady state models.

CALPOST is software contains post processing modules for the output fields of meteorological data.

The general form of Gaussian dispersion model [23]:

$$X(x,y,z) = \frac{Q}{2\pi\sigma_y\sigma_z u}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \times \left\{\exp\left[-\frac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right]\right\}$$

Equation (19)

Where: X is the concentration of the pollutant at x,y,z distance (mg/m^3), Q is the rate of the release from the source (mg/s), H is the stack height and x, y & z= are the distances in three dimness from the source.

The following parameters are required in order to estimate the concentration at the targeted location:

3- Define the transport method and dispersion pattern.

4- Identify the natural of the studied geographical location: urban or rural.

5- Find the downwind, lateral and vertical distances from the source point.

6- Wind speed and atmospheric stability estimations.

7- Finding σ_y & σ_z according to several methods available in literature.

The following section is giving a brief description for several dispersion models recommended or used in CMM approaches.

AERMOD dispersion model

A detailed description was given for AERMOD model in the thesis text; the following points are covering the preprocessor software used for meteorological data processing. The following inputs are the minimum requirements for the AERMET preprocessor to generate the required hourly surface data file:

- Hourly surface observations like:
    a) Wind speed
    b) Wind direction
    c) Dry bulb temperature
    d) Cloud coverage
- Upper air data

The AERMAP program requires the GIS resources and terrain data to perfume the required terrain file for AERMOD. The generating meteorological file in AERMET program and terrain file in AERMAP are used after in AERMOD interface with the following inputs to build up the project case [44]:

1. Control pathways:

   Pollutant type, dispersion coefficient, averaging time and terrain height option are defined.

2. Source pathway:

   All the required parameters for the pollutant sources and buildings down wash values are inserted.

3. Receptors:

   The available information about the receptor points and grids are defined.

4. MET pathway:

   The generated Met files from AERMT (hourly surface and upper air data files) are specified with any required additional data period.

5. Terrain:

   The generated files from AERMAP are used here to extract the terrain data and represented on the defined base map for the project (location and height data for each RP).

6. Building

   The user can define several buildings in the project and provide the model with the height and coordinates of each.

The main output data of AERMOD are consisting of the estimated high values concentrations (highest, second highest …) by each defined receptor point for the selected averaging time periods or source groups. In addition, the model has the ability to provide the user by the maximum values and the raw concentration values in binary files to be used for other coding programs for further results processing [44].

ALOHA dispersion model

Areal locations of hazardous atmospheres (ALOHA) model was developed by NOAA and EPA together. It is used to evaluate the likely emissions of the hazardous chemicals and pollutants to atmosphere. The model is using the toxicological and physical properties of the released chemicals to estimate the downwind concentration at the desired receptor point. The model has the ability to estimate the dangerous zones of several specific circumstances such as fire, explosions chemical spills and toxic gas clouds. The outputs are presented on displayed maps and model has the ability to export the plots to google earth program to evaluate the degree of the hazard to the adjacent communities [45]. The basic inputs for ALOHA are [46]:

1. Information about the geographical location, time and date.
2. Selecting the pollutant and specifying the sources.
3. Current meteorological conditions.
4. Details about the transporting method to atmosphere (fire, explosion …).

The following limitations are stated in the model and required the attention of the user while simulating the concerned chemical [46]:

2. ALOHA is not applicable for the following cases:
    a. Effects of chemical reactions or by products and secondary pollutants.
    b. Particulates.
    c. Chemical mixtures.
    d. Terrains.

e. Hazardous fragments.

3. ALOHA may simulate unreliable outputs for the following cases:

    a. Very low wind speed.

    b. Very stable atmospheric condition (no mixing).

    c. Wind shifts and terrain steering effects.

    d. Concentration patchiness, particularly near the release source.

EPI code dispersion model

The EPI code software is another dispersion model used to predict the outcomes and consequences of unplanned releases to the atmosphere. It perfumes the required calculations for the given source terms and estimates the time averaged downwind concentration of the released pollutant [47]. The EPI library contains around 2000 chemicals with the standard limits and the acceptable exposure levels which are stated from several regulatory agencies such as: ACGIH, ERPGs, TEELs, IDLH and AEGLs [48]. The model has the ability to simulate different types of releases such as: unplanned releases, continuous releases, liquid spill releases, fire release and explosive releases [47].

The basic requirements for the model are: chemical properties, meteorological conditions and sources data. The EPI user is required to have enough information about:

- Source Term Rate, source Term Quantity and Release Duration.

- Release Height and source Dimensions.

- Terrain Factor (Dispersion Coefficient Set).
- Atmospheric stability Class.
- Wind speed and wind speed height.
- Stack Height / Effective Plume Rise.

The following additional inputs are required for specific scenarios:

- Fire Heat Emission Rate for fires scenarios.
- Explosion Strength for explosion scenarios.
- Liquid Spill Release for liquid spill scenarios.
- Inversion Layer (or Mixing Layer) Height.
- Sample (or Averaging) Time.
- Deposition Velocity.
- Receptor Height.

The output file of EPI code is consisting of tabulated values for the calculated downwind concentrations for the released pollutant. It also provides the desired graphical representations for the concretion as a function of the downwind distances [47]. The following limitations are mentioned in the guidelines of using EPI code model and require the attention of the user [47]:

1. The outcomes of using low wind speed or very stable atmospheric conditions are expected to be less reliable.
2. The EPI code doesn't have the ability to model the dense gas releases.

3. There is no counting for the terrain steering effects or building wakes dispersion effects in EPI code model.
4. A high level of uncertainty is likely to occur for the selected receptor points very close to the sources.
5. The model doesn't have the ability to process one year or more of meteorological data. (Statistical methods cannot be applied to estimate the median and unfavorable concentrations).

APPENDIX E: EMISSIONS FACTORS RATING CRITERIA

The rating letters A to E were established by U.S.EPA for the collected AP42 EFs to quantify the ratability of them, being that A represented the excellent factor and E the poor observed factor, AP-42 emission factor quality ratings definitions are [29]:

- A= (Excellent). Factor is developed by a sound methodology, and test data are used from many reliable selected facilities in the industry. The details are sufficiently reported for any required validation.
- B= (Above average). Factor is developed by a generally sound methodology, and test data are used from a “reasonable number" of facilities. The details are lacking some information for the required validation.
- C= (Average). Factor is developed by an unproven or new methodology, and test data are used from a reasonable number of facilities. The details are lacking significant information for the required validation.
- D= (Below average). Factor is developed by a generally unreliable method with just providing an order for the magnitude value for the source. Test data are used form a small number of facilities, and there may be reason to suspect that these facilities do not represent a random sample of the industry.
- E= (Poor). Factor is developed by a generally unacceptable method, and test data are may be not collected from random samples from the industry.

Figure 26 shows the wildly used emissions estimation approaches. The required costs are directly proportional to the reliability of the approach used to estimate the factor.

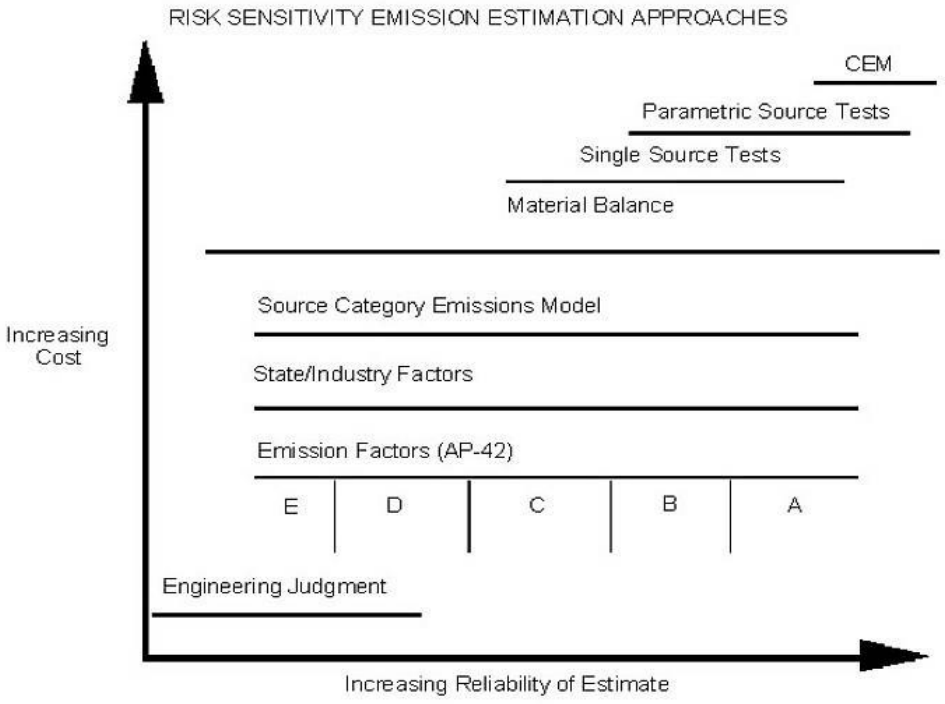

Figure 26: Emission factors estimations approaches [29].

The following tiers are mentioned in the guidelines of the EMEP emission factors literature [49]:

1. Tier 1: the simplest method to be used by EMEP, where the default emission factors are derived from a liner relation between the releasing emission and the intensity of the process. The required knowledge about the details of the process is less but the uncertainty is high in this tier.
2. Tier 2: the concepts of tier 2 are similar to tier one with replacing the default emission factors with technology, licensor, designer or supplier emission factors estimations based on previous conducted engineering calculations or other experimental methods. The factors may cope with the sated legislations and regulation of manufactured country of the technology or the equipment.
3. Tier 3: a wide range of scientific evidences and knowledge were applied for the approach, dynamic models or more sophisticated approaches were used to reduce the uncertainty of the EFs findings.

APPENDIX F: SOURCES OF EMISSIONS DETAILS

The sources locations were identified by using google earth maps for the real locations of the stacks in MIC according to the following procedure:

1. The sites of the plants and facilities were located.
2. The available stacks in the plant were defined.
3. Generally, the major stacks for continuous releases are the only stacks required in the study.
4. X and Y coordinates were reported by using the Universal Transverse Mercator (UTM) system.
5. The release height was assumed to be the stack height, and it was predicted for each stack from visual observations for some stacks in the field or from similar available documented heights for the adjacent stacks in the area.

Table 21 and Table 22show the source parameters used for each stack in the AERMOD calculations for each industry.

Table 21: Sources locations and base elevation details.

Type	ID	Descrip.	Base_Elev	Height	Diam	Exit_Vel	Exit_Temp	Release Type	Num_Coords	X1	Y1
			[m]	[m]	[m]	[m/s]	[K]			[m]	[m]
POINT	AL_01	AL Cells	3.80	70.00	3.00	4.00	473.15	VERTICAL	1	557992	2762179
POINT	AL_02	AL Cells	3.64	70.00	3.00	4.00	473.15	VERTICAL	1	557995.35	2762199
POINT	AL_03	AL Cells	4.07	70.00	3.00	4.00	473.15	VERTICAL	1	557996.79	2762164
POINT	AL_04	AL Cells	4.07	70.00	3.00	4.00	473.15	VERTICAL	1	557988.69	2762143
POINT	AL_05	AL Cells	3.68	70.00	3.00	4.00	473.15	VERTICAL	1	557433.66	2762265
POINT	AL_06	AL Cells	3.91	70.00	3.00	4.00	473.15	VERTICAL	1	557444.91	2762291
POINT	AL_07	AL Cells	3.58	70.00	3.00	4.00	473.15	VERTICAL	1	557431.72	2762253
POINT	AL_08	AL Cells	3.32	70.00	3.00	4.00	473.15	VERTICAL	1	557440.46	2762232
POINT	AL_09	AL Cells	5.03	70.00	3.00	4.00	473.15	VERTICAL	1	557641.09	2762356
POINT	AL_10	AL Cells	5.33	70.00	3.00	4.00	473.15	VERTICAL	1	557651.78	2762375
POINT	AL_11	AL Cells	4.91	70.00	3.00	4.00	473.15	VERTICAL	1	557639.73	2762342
POINT	AL_12	AL Cells	4.84	70.00	3.00	4.00	473.15	VERTICAL	1	557644.5	2762321
POINT	AL_13	AL Cells	3.33	70.00	3.00	4.00	473.15	VERTICAL	1	557818.41	2762380
POINT	AL_14	AL Cells	3.42	70.00	3.00	4.00	473.15	VERTICAL	1	557823.48	2762410
POINT	AL_15	AL Cells	3.13	70.00	3.00	4.00	473.15	VERTICAL	1	557810.28	2761864
POINT	AL_16	AL Cells	2.69	70.00	3.00	4.00	473.15	VERTICAL	1	557815.08	2761827
POINT	AL_17	Furnaces	5.13	30.00	2.00	9.00	423.15	VERTICAL	1	557450.18	2761852
POINT	AL_18	Furnaces	5.07	70.00	3.00	9.00	423.15	VERTICAL	1	557486.63	2761888
POINT	AL_19	Furnaces	5.35	30.00	2.00	9.00	423.15	VERTICAL	1	557672.33	2761943

Table 21: Continued.

Type	ID	Descrip.	Base_Elev	Height	Diam	Exit_Vel	Exit_Temp	Release Type	Num_Coords	X1	Y1
			[m]	[m]	[m]	[m/s]	[K]			[m]	[m]
POINT	AL_20	Utility	3.57	50.00	6.00	22.00	523.00	VERTICAL	1	558188.29	2762179
POINT	AL_21	Utility	3.22	50.00	6.00	22.00	523.00	VERTICAL	1	558218.64	2762199
POINT	AL_22	Utility	3.55	50.00	6.00	22.00	523.00	VERTICAL	1	558243.08	2762164
POINT	AL_23	Utility	4.31	50.00	6.00	22.00	523.00	VERTICAL	1	558214.05	2762143
POINT	AL_24	Utility	3.04	50.00	6.00	22.00	523.00	VERTICAL	1	558310.72	2762265
POINT	AL_25	Utility	3.36	50.00	6.00	22.00	523.00	VERTICAL	1	558329.11	2762291
POINT	AL_26	Utility	2.91	50.00	6.00	22.00	523.00	VERTICAL	1	558360.95	2762253
POINT	AL_27	Utility	2.72	50.00	6.00	22.00	523.00	VERTICAL	1	558330.74	2762232
POINT	AL_28	Utility	4.11	50.00	6.00	22.00	523.00	VERTICAL	1	558427.81	2762356
POINT	AL_29	Utility	4.22	50.00	6.00	22.00	523.00	VERTICAL	1	558455.01	2762375
POINT	AL_30	Utility	5.13	50.00	6.00	22.00	523.00	VERTICAL	1	558478.62	2762342
POINT	AL_31	Utility	4.75	50.00	6.00	22.00	523.00	VERTICAL	1	558450.16	2762321
POINT	AL_32	Utility	3.79	50.00	3.00	22.00	523.00	VERTICAL	1	558207.92	2762380
POINT	AL_33	Utility	3.16	50.00	3.00	22.00	523.00	VERTICAL	1	558249.14	2762410
POINT	AL_34	Utility	5.67	50.00	6.00	22.00	523.00	VERTICAL	1	558527.4	2761864
POINT	AL_35	Utility	4.16	50.00	6.00	22.00	523.00	VERTICAL	1	558555.66	2761827
POINT	AL_36	Utility	3.69	50.00	6.00	22.00	523.00	VERTICAL	1	558582.88	2761852
POINT	AL_37	Utility	5.06	50.00	6.00	22.00	523.00	VERTICAL	1	558555.94	2761888
POINT	AL_38	Utility	4.00	50.00	6.00	22.00	523.00	VERTICAL	1	558625.8	2761943
POINT	AL_39	Utility	3.02	50.00	6.00	22.00	523.00	VERTICAL	1	558653.34	2761906
POINT	AL_40	Utility	2.59	50.00	6.00	22.00	523.00	VERTICAL	1	558685.14	2761930
POINT	AL_41	Utility	3.68	50.00	6.00	22.00	523.00	VERTICAL	1	558653.07	2761967

Table 21: Continued.

Type	ID	Descrip.	Base_Elev	Height	SigmaY	SigmaZ	Length_X	Num_Coords	X1	Y1
			[m]	[m]	[m]	[m]	[m]		[m]	[m]
VOLUME	STEEL_1	FURNACE-1	5.85	20.00	21.04	2.36	90.46	1	559273.41	2759722
VOLUME	STEEL_2	FURNACE-2	8.85	20.00	65.78	2.32	282.88	1	558982.21	2759570

Type	ID	Descrip.	Base_Elev	Height	Diam	Exit_Vel	Exit_Temp	Release_Type	Num_Coords	X1	Y1
			[m]	[m]	[m]	[m/s]	[K]			[m]	[m]
POINT	STEEL_5	near furnace	11.92	40.00	2.50	7.00	533.15	VERTICAL	1	559264.54	2759585
POINT	STEEL_6	heater		50.00	1.50	4.00	693.15	VERTICAL	1	559228.51	2759717
POINT	STEEL_7	casting		30.00	1.00	4.00	693.15	VERTICAL	1	559105.82	2759470

Type	ID	Descrip.	Base_Elev	Height	Diam	Exit_Vel	Exit_Temp	Release Type	Num Coords	X1	Y1
			[m]	[m]	[m]	[m/s]	[K]			[m]	[m]
POINT	MTBE_1	Fuel Add furnace	10.99	50.00	2.00	7.00	563.15	VERTICAL	1	557604.98	2758700
POINT	MTBE_2	Fuel Add boiler	6.84	35.00	2.00	12.00	523.15	VERTICAL	1	557730.53	2758615
POINT	MTBE_3	Fuel Add boiler	7.15	35.00	2.00	12.00	523.15	VERTICAL	1	557720.39	2758593
POINT	MTBE_4	Fuel Additive	7.20	50.00	3.00	10.00	473.15	VERTICAL	1	557826.78	2758570

Table 21: Continued.

Type	ID	Descrip.	Base_Elev	Height	Diam	Exit_Vel	Exit_Temp	Release_Type	Num_Coords	X1	Y1
			[m]	[m]	[m]	[m/s]	[K]			[m]	[m]
POINT	ETHY_1	ethylene	9.90	70.00	2.80	6.33	563.15	VERTICAL	1	557235.98	2757008
POINT	ETHY_2	ethylene	10.64	70.00	2.80	6.33	563.15	VERTICAL	1	557251.57	2756999
POINT	ETHY_3	ethylene	11.31	70.00	2.80	6.33	563.15	VERTICAL	1	557267.11	2756990
POINT	ETHY_4	ethylene	11.86	70.00	2.00	6.20	563.15	VERTICAL	1	557281.38	2756982
POINT	ETHY_5	ethylene	12.39	70.00	3.00	7.54	533.15	VERTICAL	1	557298.22	2756973
POINT	ETHY_6	ethylene	11.88	70.00	2.10	7.70	533.15	VERTICAL	1	557315	2756963
POINT	ETHY_7	ethylene	9.00	44.00	1.93	9.04	423.15	VERTICAL	1	557224.75	2757022
POINT	ETHY_8	ethylene	8.85	44.00	1.93	9.04	423.15	VERTICAL	1	557221.99	2757024
POINT	ETHY_9	ethylene	11.82	40.00	0.75	4.10	693.15	VERTICAL	1	557287.34	2756988
POINT	ETHY_10	ethylene	8.07	75.00	2.42	22.20	1073.15	VERTICAL	1	557376.61	2756914
POINT	ETHY_11	ethylene	6.04	40.00	2.90	20.36	973.15	VERTICAL	1	557080.91	2756860
POINT	ETHY_12	ethylene	7.16	34.00	1.25	12.91	513.15	VERTICAL	1	557085.18	2757024
POINT	ETHY_13	ethylene	8.23	30.00	3.51	17.20	450.15	VERTICAL	1	557264.24	2757083
POINT	ETHY_14	ethylene	9.52	30.00	3.51	17.20	450.15	VERTICAL	1	557290.8	2757067
POINT	ETHY_15	ethylene	10.03	30.00	1.50	12.69	473.15	VERTICAL	1	557303.86	2757060
POINT	ETHY_16	ethylene	9.98	30.00	1.50	12.69	473.15	VERTICAL	1	557313.55	2757054
POINT	ETHY_17	ethylene	8.19	30.00	1.70	15.00	429.15	VERTICAL	1	557380.82	2756989
POINT	ETHY_18	ethylene	7.96	30.00	2.40	22.00	523.15	VERTICAL	1	557257.82	2757087
POINT	ETHY_19	ethylene	9.19	30.00	2.40	22.00	523.15	VERTICAL	1	557284.38	2757071
POINT	ETHY_20	ethylene	9.61	30.00	2.40	41.67	523.15	VERTICAL	1	557339.86	2757039
POINT	ETHY_21	ethylene	6.5	30.00	3.30	22.04	523.15	VERTICAL	1	557170.29	2757138
POINT	ETHY_22	ethylene	6.65	30.00	3.30	22.04	523.15	VERTICAL	1	557141.57	2757155

Table 21: Continued.

Type	ID	Descrip.	Base_Elev	Height	Diam	Exit_Vel	Exit_Temp	Release_Type	Num_Coords	X1	Y1
			[m]	[m]	[m]	[m/s]	[K]			[m]	[m]
POINT	ETHY_23	ethylene	1.49	30.00	2.00	15.00	398.15	VERTICAL	1	555551.57	2753606
POINT	ETHY_24	ethylene	4.32	50.00	1.50	20.00	498.15	VERTICAL	1	555259.1	2753673
POINT	ETHY_25	ethylene	4.18	50.00	2.20	17.00	423.15	VERTICAL	1	555219.46	2753648
POINT	ETHY_26	ethylene	4.03	50.00	2.20	17.00	423.15	VERTICAL	1	555211.82	2753653
POINT	ETHY_27	ethylene	4.97	30.00	3.00	20.00	498.15	VERTICAL	1	555178.87	2753730
POINT	ETHY_28	ethylene	5.46	30.00	3.00	20.00	498.15	VERTICAL	1	555168.36	2753714
POINT	ETHY_29	ethylene	5.80	30.00	3.00	20.00	498.15	VERTICAL	1	555157.8	2753699
POINT	ETHY_30	ethylene	7.28	25.00	1.50	12.00	398.15	VERTICAL	1	554886.58	2753203
POINT	ETHY_31	ethylene	6.98	40.00	2.50	15.00	503.15	VERTICAL	1	554874.06	2753151
POINT	ETHY_32	ethylene	6.86	35.00	3.50	22.00	523.15	VERTICAL	1	554858.31	2753162

Type	ID	Descrip.	Base_Elev	Height	Diam	Exit_Vel	Exit_Temp	Release Type	Num_Coords	X1	Y1
			[m]	[m]	[m]	[m/s]	[K]			[m]	[m]
POINT	NH3_1	Ammonia	6.55	30.00	3.00	18.00	523.15	VERTICAL	1	557274.41	2756327
POINT	NH3_2	Ammonia	7.01	40.00	3.00	9.00	533.15	VERTICAL	1	557308.54	2756298
POINT	NH3_3	Ammonia	7.95	50.00	1.00	10.00	573.15	VERTICAL	1	557288.31	2756261
POINT	NH3_6	Ammonia	6.72	25.00	2.50	25.00	423.15	VERTICAL	1	557216.9	2756325
POINT	NH3_7	Ammonia	9.60	40.00	2.50	9.00	543.15	VERTICAL	1	557235.84	2756204
POINT	NH3_8	Ammonia	9.83	40.00	2.50	9.00	543.15	VERTICAL	1	557228.95	2756211
POINT	NH3_9	Ammonia	8.32	30.00	2.50	18.00	523.15	VERTICAL	1	557196.33	2756241
POINT	NH3_19	Ammonia	8.73	40.00	2.50	9.00	543.15	VERTICAL	1	557123	2755997
POINT	NH3_20	Ammonia	9.28	40.00	3.50	9.00	543.15	VERTICAL	1	556953.46	2756087

Table 21: Continued.

Type	ID	Descrip.	Base_Elev	Height	Diam	Exit_Vel	Exit_Temp	Release Type	Num_Coords	X1	Y1
			[m]	[m]	[m]	[m/s]	[K]			[m]	[m]
POINT	NH3_21	Ammonia	8.68	40.00	2.50	9.00	543.15	VERTICAL	1	556950	2756151
POINT	NH3_22	Ammonia	7.63	35.00	2.50	15.00	493.15	VERTICAL	1	556931.33	2756179
POINT	NH3_23	Ammonia	7.47	35.00	3.50	15.00	503.15	VERTICAL	1	556917.24	2756164
POINT	NH3_24	Ammonia	5.87	30.00	2.50	17.00	503.15	VERTICAL	1	556883.45	2756211
POINT	NH3_25	Ammonia	1.69	40.00	3.50	9.00	543.15	VERTICAL	1	556785.39	2756172
POINT	NH3_26	Ammonia	2.02	40.00	3.50	9.00	543.15	VERTICAL	1	556756.81	2756144
POINT	NH3_27	Ammonia	6.08	40.00	3.50	9.00	543.15	VERTICAL	1	556870.16	2756107
POINT	NH3_28	Ammonia	6.85	40.00	3.50	9.00	543.15	VERTICAL	1	557065.06	2755870
POINT	NH3_29	Ammonia N	0.54	30.00	2.00	18.00	523.15	VERTICAL	1	554925.41	2757442
POINT	NH3_30	Ammonia N	0.27	30.00	2.50	17.00	523.15	VERTICAL	1	554889	2757428
POINT	NH3_31	Ammonia N	-0.06	30.00	2.00	18.00	523.15	VERTICAL	1	554940.66	2757396
POINT	NH3_32	Ammonia N	-0.46	30.00	2.50	19.00	523.15	VERTICAL	1	554906.38	2757382
POINT	NH3_33	Ammonia N	-0.30	30.00	2.00	19.00	523.15	VERTICAL	1	554955.44	2757350
POINT	NH3_34	Ammonia N	-0.59	30.00	2.50	19.00	523.15	VERTICAL	1	554922.37	2757337
POINT	NH3_35	Ammonia N	0.50	35.00	3.00	15.00	503.15	VERTICAL	1	554972.9	2757288
POINT	NH3_36	Ammonia N	0.23	35.00	3.00	15.00	503.15	VERTICAL	1	554953.73	2757284
POINT	NH3_37	Ammonia N	3.09	40.00	2.50	9.00	533.15	VERTICAL	1	554760.55	2757327
POINT	NH3_38	Ammonia N	1.27	30.00	1.00	17.00	523.15	VERTICAL	1	554685.02	2757252
POINT	NH3_39	Ammonia N	2.37	40.00	2.50	9.00	533.15	VERTICAL	1	554820.1	2757159
POINT	NH3_40	Ammonia N	0.97	30.00	1.00	17.00	523.15	VERTICAL	1	554746.47	2757083

Table 21: Continued.

Type	ID	Descrip.	Base_Elev	Height	Diam	Exit_Vel	Exit_Temp	Release Type	Num_Coords	X1	Y1
			[m]	[m]	[m]	[m/s]	[K]			[m]	[m]
POINT	FURNACE	VCM	6.94	40.00	1.70	7.00	533.15	VERTICAL	1	556842.2	2757446
POINT	TR_1	VCM	5.52	30.00	3.00	20.00	523.15	VERTICAL	1	557008.25	2757291
POINT	TR_2	VCM	5.38	30.00	3.00	20.00	523.15	VERTICAL	1	556989.25	2757300
POINT	TR_3	VCM	5.10	30.00	3.00	20.00	523.15	VERTICAL	1	556967.9	2757311
POINT	TR_4	VCM	5.45	30.00	3.00	20.00	523.15	VERTICAL	1	556947.18	2757324
POINT	INC_1	VCM	4.78	30.00	1.20	21.00	573.15	VERTICAL	1	556712.07	2757244

Type	ID	Descrip.	Height	SigmaY	SigmaZ	Length_X	Num_Coords	X1	Y1
			[m]	[m]	[m]	[m]		[m]	[m]
VOLUME	VCM_1	EDC/VCM	10.00	69.77	2.33	300	1	556819.87	2757307

Table 22: Emission factors & rates for the selected atmospheric releases.

industry	Prod. Rate (Ton/hr)	pollutant	EF	unit	Ref.	Rate Kg/hr	g/s	No. stacks	flow rate for each
AL	66.78	NOx	1,00	Kg/ton	EMEP[50], BREF[51]	66.78	18.55	22	0.84
Steel	365.3	NOx	0.50	Kg/ton	EMEP[52], BREF[53]	181.20	50.30	4	6.29
NH3	433.79	NOx	0.32	Kg/ton	EMEP[54], BREF[55]	136.64	37.96	29	1.31
C2H4 (1)	91.32	NOx	2.80	Kg/ton	BREF[56]	255.71	71.03	22	3.23
C2H4 (2)	57.08	NOx	2.80	Kg/ton	BREF[56]	159.82	44.39	10	4.44
EDC/VCM	37.67	NOx	242.60	g/ton	BREF[56]	9.13	2.53	6	0.42
Fuel Add	69.63	NOx	0.28	Kg/ton	BREF[56]	19.87	5.52	4	1.38

Industry	Prod. Rate (Ton/hr)	pollutant	EF	unit	Ref.	Rate kg/hr	g/s	No. stacks	flow rate for each
AL	66.78	SO2	10.00	Kg/ton	EMEP[50], BREF[51]	667.80	185.50	41	4.52
Steel	365.30	SO2	0.11	Kg/ton	EMEP[52], BREF[53]	40.00	11.16	5	2.20
NH3	433.79	SO2	0.10	Kg/ton	EMEP[54], BREF[55]	43.38	12.05	22	0.55
C2H4 (1)	91.32	SO2	3.30	Kg/ton	BREF[56]	301.37	83.71	22	3.81
C2H4 (2)	57.08	SO2	3.30	Kg/ton	BREF[56]	188.36	52.32	10	5.23

Industry	Prod. Rate (Ton/hr)	pollutant	EF	unit	Ref.	Rate kg/hr	g/s	No. stacks	flow rate for each
AL	66.78	CO	120.00	Kg/ton	EMEP[50], BREF[51]	8013.60	2226.00	19	117.16
Steel	365.3	CO	2.27	Kg/ton	EMEP[52], BREF[53]	829.20	230.30	5	46.00
NH3	433.79	CO	7.90	Kg/ton	EMEP[54], BREF[55]	3426.94	951.93	20	47.60
C2H4 (1)	91.32	CO	1.00	Kg/ton	BREF[56]	91.32	25.37	22	1.15
C2H4 (2)	57.08	CO	1.00	Kg/ton	BREF[56]	57.08	15.86	10	1.59
EDC/VCM	37.67	CO	79.20	g/ton	BREF[56]	2.98	0.83	1	0.83

Table 22: Continued.

#	Industry	Prod. rate (ton/hr)	Pollutant	EF	unit	Ref.	Rate kg/hr	g/s	No. stacks	flow rate for each
1	AL	66.78	HF	1.60	kg/ton	BREF[51]	106.85	29.68	16.00	1.86
2	AL	66.78	C2F6	0.01	kg/ton	EMEP[50]	0.61	0.17	16.00	0.01
3	AL	66.78	CF4	0.09	kg/ton	EMEP[50]	6.07	1.69	16.00	0.11
4	AL	66.78	COS	2.00	kg/ton	EMEP[50]	133.56	37.10	16.00	2.32
5	AL	66.78	Benzo(a) pyrene	6.00	g/ton	EMEP[50]	0.40	0.11	3.00	0.04
6	AL	66.78	Benzo(b) fluoranthene	7.00	g/ton	EMEP[50]	0.47	0.13	3.00	0.04
7	AL	66.78	Benzo(k)fluoranthene	7.00	g/ton	EMEP[50]	0.47	0.13	3.00	0.04
8	AL	66.78	Indeno(1,2,3-cd)pyrene	1.00	g/ton	EMEP[50]	0.07	0.02	3.00	0.01

#	Industry	Prod. rate (ton/hr)	pollutant	EF	unit	Ref.	Rate kg/hr	g/s	flow rate g/s	per volume
1	Steel	365.30	Pb	2.85	g/ton	BREF[53]	1.04	0.29	0.14	0.07
2	Steel	365.30	Cr	2.80	g/ton	BREF[53]	1.02	0.28	0.14	0.07
3	Steel	365.30	Ni	2.00	g/ton	BREF[53]	0.73	0.20	0.10	0.05
4	Steel	365.30	Zn	24.00	g/ton	BREF[53]	8.77	2.44	1.22	0.61
5	Steel	365.30	HF	15.00	g/ton	BREF[53]	5.48	1.52	0.76	0.38
6	Steel	365.30	HCl	35.25	g/ton	BREF[53]	12.88	3.58	1.79	0.89
7	Steel	365.30	Benzene	4.40	g/ton	BREF[53]	1.61	0.45	0.22	0.11

Table 22: Continued.

#	industry	production (ton/hr)	pollutant	EF	unit	Ref.	Rate kg/hr	g/s	No. stacks	flow rate for each
1	NH3	433.79	NH3	5.00E-02	kg/t	EMEP[54]	21.69	6.02	1.00 (volume)	6.02
2	NH3	433.79	n-hexane	5.72E-03	kg/t	NPI[57]	2.48	0.69	20.00	3.45E-02
3	NH3	433.79	cyclohexane	6.00E-05	kg/t	NPI[57]	0.03	0.01	20.00	3.61E-04
4	NH3	433.79	toluene	1.00E-04	kg/t	NPI[57]	0.05	0.01	20.00	7.23E-04
5	NH3	433.79	formaldehyde	5.00E-04	kg/t	NPI[57]	0.21	0.06	20.00	2.89E-03
6	NH3	433.79	Benzene	2.00E-04	kg/t	NPI[57]	0.10	0.03	20.00	1.45E-03

#	industry	production (ton/hr)	pollutant	EF	unit	Ref.	Rate kg/hr	g/s	No. stacks	flow rate for each
1	Urea	639.27	NH3	0.73	kg/t	BREF[55]	466.67	129.63	1.00	129.63

#	industry	production (ton/hr)	pollutnat	EF	unit	Ref.	Rate kg/hr	g/s	volume
1	CL2/EDC	85.62	CL2	0.02	kg/t	BREF[56]	1.37	0.38	0.38
1	EDC/VCM	37.67	EDC	0.64	kg/t	BREF[56]	24.15	6.71	7.77
2	EDC/VCM	37.67	VCM	0.01	kg/t	BREF[56]	0.20	0.06	
3	EDC/VCM	37.67	HCL	0.02	kg/t	BREF[56]	0.57	0.16	
4	EDC/VCM	37.67	Chloroform	3.60E-03	kg/t	BREF[56]	0.14	0.04	
5	EDC/VCM	37.67	C2H4	0.08	kg/t	BREF[56]	2.93	0.81	

APPENDIX G: EXPOSURE LIMITS FOR THE 28 CHEMICALS

Terminologies

RFC: the acceptable continuous inhalation exposure limits for a chemical, which is likely to be without any risk or effects during a lifetime for individuals[58].

MRL: the acceptable daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse non-cancer health effects over a specified duration of exposure, used by ATSDR health assessors [35].

PEL: the acceptable occupational exposures levels for workers or exposed people in industry, used mainly by OSHA for a period of (8 hrs working/day for 40 hrs per week) TWA [59].

TEEL: temporary Emergency Exposure limits, used for emergency scenarios by DOE, applicable for (15 mins to 60 mins TWA releases).

PAC: Protective action criteria limits developed by DOE based on several guidelines such as: AEGL, ERPG and TEEL, used mainly for emergency scenarios (15 mins to 60 mins TWA releases).

Note: the exposure limits are tabulated in Table 23 according to their availability in literatures.

Table 23: Exposure limits for the selected chemicals in the study.

No.	Chemical Compound	CASRN	Limits (mg/m^3)	References
1	Nitric oxide	10102-43-9	PEL: 30.00 TEEL-0: 0.61 PAC-1: 0.61	PELs, OSHA Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
2	Nitrogen dioxide	10102-44-0	PEL: 1.00 TEEL-0: 0.94 PAC-1: 0.94	PELs, OSHA Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
3	Sulfur dioxide	7446-09-5	PEL: 13.00 MRL: 0.026 TEEL-0: 0.52 PAC-1: 0.52	PELs, OSHA Minimal risk level ATSDR, 1998 Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
4	Carbon monoxide	630-08-0	PEL: 55.00 TEEL-0: 60.00 PAC-1: 95.00	PELs, OSHA Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
5	Hydrogen fluoride; (Hydrofluoric acid)	7664-39-3	PEL: 3.00 MRL: 0.0164 TEEL-0: 0.40 PAC-1: 0.82	PELs, OSHA Minimal risk level ATSDR, 2003 Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
6	Hexafluoroethane; (Freon 116; Perfluoroethane)	76-16-4	PAC-1: 4100.00	Rev 27, SCAPA (DOE) PAC website, 2012
7	Carbon tetrafluoride; (Tetrafluoromethane)	75-73-0	PAC-1: 300.00	Rev 27, SCAPA (DOE) PAC website, 2012
8	Carbonyl sulfide	463-58-1	PAC-1: 13.00	Rev 27, SCAPA (DOE) PAC website, 2012
9	Benzo(a)pyrene; (Coal tar pitch volatiles)	50-32-8	TEEL-0: 0.20 PAC-1: 0.60	Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012

Table 23: Continued.

No.	Chemical Compound	CASRN	Limits (mg/m^3)	References
10	Benzo(b)fluoroanthene	205-99-2	PAC-1: 0.031	Rev 27, SCAPA (DOE) PAC website, 2012
11	Benzo(k)fluoranthene	207-08-9	PAC-1: 0.019	Rev 27, SCAPA (DOE) PAC website, 2012
12	Indeno(1,2,3-cd)pyrene	193-39-5	PAC-1: 0.015	Rev 27, SCAPA (DOE) PAC website, 2012
13	Lead	7439-92-1	PEL: 0.05 TEEL-0: 0.05 PAC-1: 0.15	PELs, OSHA Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
14	Chromium	7440-47-3	PEL: 0.05 RFC: 0.0001 MRL: 0.005 TEEL-0: 1.00 PAC-1: 1.50	PELs, OSHA EPA, IRIS, 1998 Minimal risk level ATSDR, 2012 Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
15	nickel	7440-02-0	PEL: 1.00 MRL: 0.0002 TEEL-0: 1.00 PAC-1: 4.50	PELs, OSHA Minimal risk level ATSDR, 2005 Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
16	Zinc	7440-66-6	TEEL-0: 1.00 PAC-1: 1.90	Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
17	Hydrogen chloride; (Hydrochloric acid)	7647-01-0	PEL: 7.00 TEEL-0: 0.75 PAC-1: 2.70	PELs, OSHA Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
18	Benzene	71-43-2	PEL: 3.19 RFC: 0.03 MRL: 0.02 TEEL-0: 3.00 PAC-1: 170.00	PELs, OSHA EPA,IRIS, 2003 Minimal risk level ATSDR, 2005 Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012

Table 23: Continued.

No.	Chemical Compound	CASRN	Limits (mg/m3)	References
19	n-Hexane	110-54-3	PEL: 1800.00 MRL: 2.112 TEEL-0: 150.00 PAC-1: 1100.00	PELs, OSHA Minimal risk level ATSDR, 1999 Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
20	Cyclohexane	110-82-7	PEL: 1050.00 PAC-1: 340.00	PELs, OSHA Rev 27, SCAPA (DOE) PAC website, 2012
21	Toluene	108-88-3	PEL: 37.70 MRL: 3.77 TEEL-0: 75.00 PAC-1: 750.00	PELs, OSHA Minimal risk level ATSDR, 2000 Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
22	Formaldehyde	50-00-0	PEL: 0.925 MRL: 0.0369 TEEL-0: 0.35 PAC-1: 1.10	PELs, OSHA Minimal risk level ATSDR, 1999 Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
23	Ethylene dichloride; (1,2-Dichloroethane)	107-06-2	PEL: 40.40 RFC: 0.005 MRL: 2.42 TEEL-0: 40.00 PAC-1: 200.00	PELs, OSHA US EPA, 2004 Minimal risk level ATSDR, 2001 Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
24	Vinyl chloride	75-01-4	PEL: 2.55 MRL:1.27 TEEL-0: 2.50 PAC-1: 640.00	PELs, OSHA Minimal risk level ATSDR, 2006 Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012

Table 23: Continued.

No.	Chemical Compound	CASRN	Limits (mg/m3)	References
25	Chloroform	67-66-3	PEL: 240.00 RFC: 0.05 MRL: 0.488 TEEL-0: 9.80 PAC-1: 9.80	PELs, OSHA US EPA 2004 Minimal risk level ATSDR, 1997 Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
26	Ethylene	74-85-1	TEEL-0: 200 PAC-1: 690.00	Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
27	Chlorine	7782-50-5	PEL: 3.00 MRL: 0.0174 TEEL-0: 1.40 PAC-1: 1.40	PELs, OSHA Minimal risk level ATSDR, 2010 Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012
28	Ammonia	7664-41-7	PEL: 35.00 MRL: 1.70 TEEL-0: 15.00 PAC-1: 21.00	PELs, OSHA Minimal risk level ATSDR, 2004 Rev 26, SCAPA (DOE) PAC website, 2010 Rev 27, SCAPA (DOE) PAC website, 2012

APPENDIX H: THE USED HCNS TABLE

HCNs are used by SCAPA research team in CMM methods to classify the toxic effects by either mode of action or target organs [60].

The associated HCNs with acute effects are tabulated in Table 24 in a red color font while for chronic effects the HCNs are tabulated in a black color**.**

Table 24: HCNs idetification for chronic and acute effects [60].

HCN number	Description	HCN number	Description
1.00	OSHA carcinogen — chronic effect	3.01	Bladder—chronic effects
1.01	Bladder carcinogen — chronic effect	3.02	Hematological effects—chronic, unspecified
1.02	Liver carcinogen — chronic effect	3.03	Bone—chronic effects
2.00	Suspect carcinogen or mutagen — chronic effect	3.04	Bone marrow—chronic blood-forming system and other chronic effects
2.01	Kidney carcinogen — chronic effect	3.05	Brain—chronic effects
2.02	Liver carcinogen — chronic effect	3.06	Eye—chronic ocular effects
3.00	Systemic toxin—chronic effects	3.07	Gastrointestinal tract—chronic effects

Table 24: Continued.

HCN number	Description	HCN number	Description
3.08	Heart, Cardiovascular system—chronic effects	4.08	Heart, Cardiovascular system—acute effects
3.09	Kidney—chronic effects	4.09	Kidney—acute effects
3.10	Liver—chronic effects	4.10	Liver—acute effects
3.11	Skin—chronic effects including dermatitis and sensitization	4.11	Skin—acute effects other than irritation
3.12	Skin perforation—nasal septum perforation and other chronic effects other than skin absorption	4.12	Skin perforation—acute effects other than skin absorption
4.00	Systemic toxin—acute short-term high hazard effects	4.13	Bone—acute effects
4.01	Eye—acute, other than irritation	5.00	Reproductive toxin—acute effects
4.02	Nose—acute effects other than irritation	5.10	Reproductive toxin—chronic effects
4.03	Bladder—acute effects	6.00	Cholinesterase toxin—acute effect
4.04	Bone marrow—acute blood-forming system and other acute effects	7.00	Nervous system toxin—acute effects
4.05	Brain—acute effects	7.01	Central nervous system—acute effects
4.06	Hematological effects—acute, unspecified	7.10	Nervous system toxin—chronic effects
4.07	Gastrointestinal tract—acute effects	7.11	Central nervous system—chronic effects

Table 24: Continued.

HCN number	Description	HCN number	Description
8.00	Narcotic — acute effect	15.00	Moderate irritant
9.00	Respiratory sensitizer — chronic effect	15.01	Eye irritant — moderate
10.00	Respiratory toxin — chronic effects	15.02	Skin irritant — moderate
11.00	Respiratory toxin — acute effects other than irritation	16.00	Mild irritant
11.01	Respiratory irritant — acute severe or moderate but not mild irritant effects	16.01	Eye irritant — mild
12.00	Blood toxin, anemia — chronic effect	16.02	Skin irritant — mild
13.00	Blood toxin, methemoglobinemia — acute effect	17.00	Asphyxiants, anoxiants — acute effect
14.00	Severe irritant	18.00	Explosive, flammable safety (no adverse effects with good housekeeping)
14.01	Eye irritant— severe	19.00	Generally low risk health effects—nuisance particles, vapors or gases
14.02	Skin irritant — severe	20.00	Generally low risk health effects—odor

APPENDIX I: CONCENTRATIONS CONTOURS FOR SELECTED POLLUTANTS

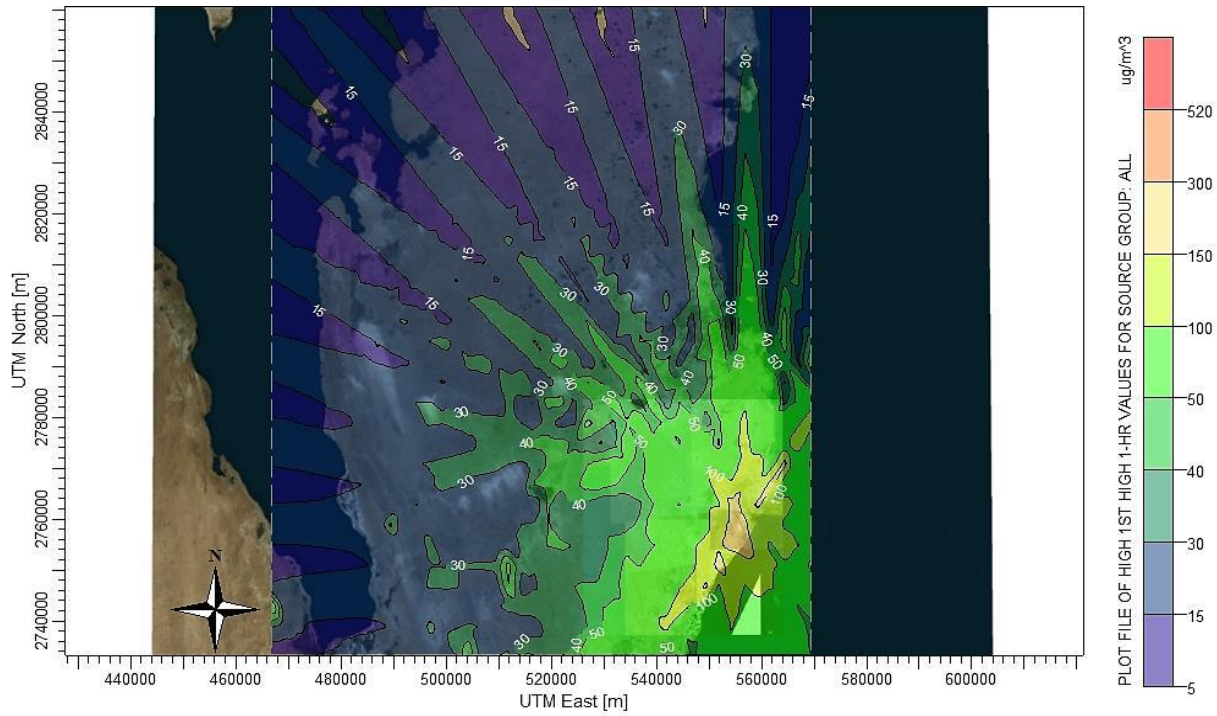

Figure 27: SO_2 concentration contours for the whole simulated area.

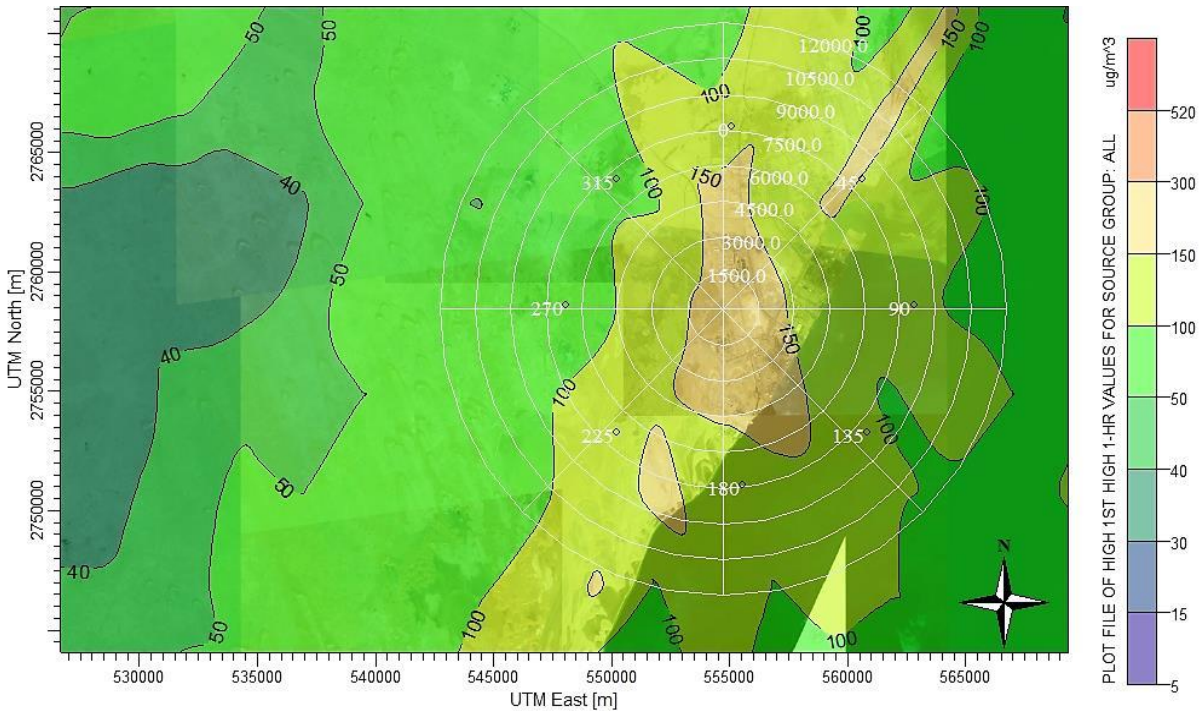

Figure 28: SO_2 concentration contours for industrial city.

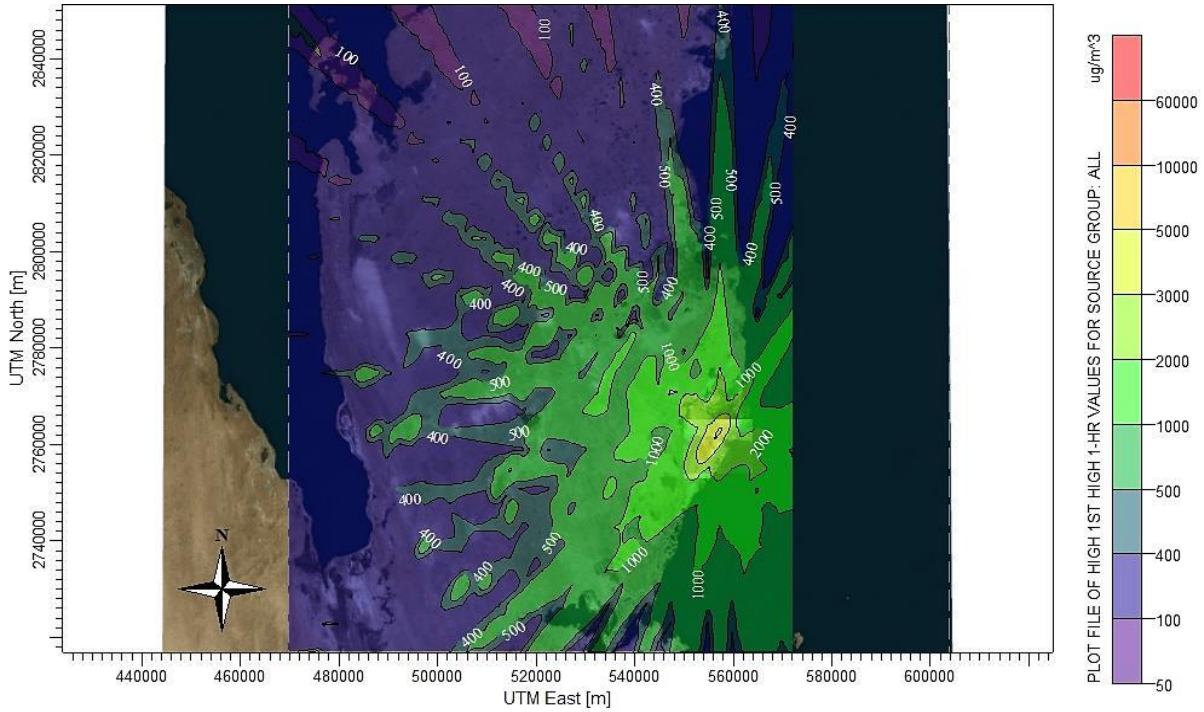

Figure 29: CO concentration contours for the whole simulated area.

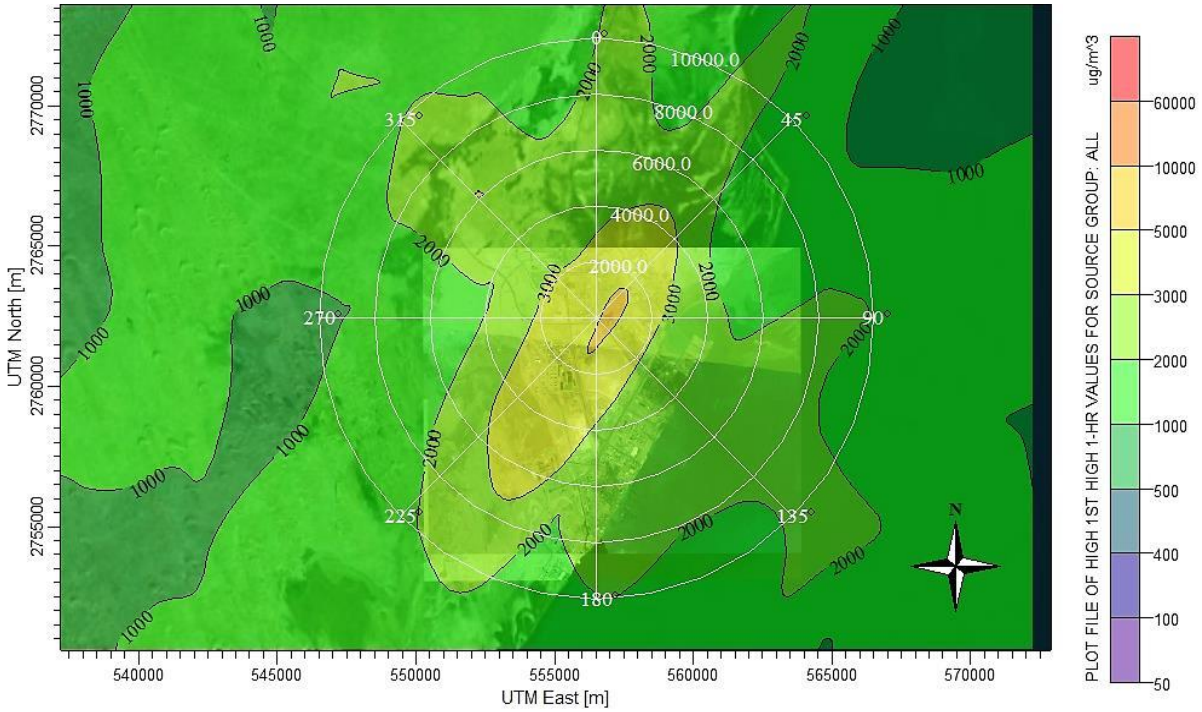

Figure 30: CO concentration contours for industrial city.

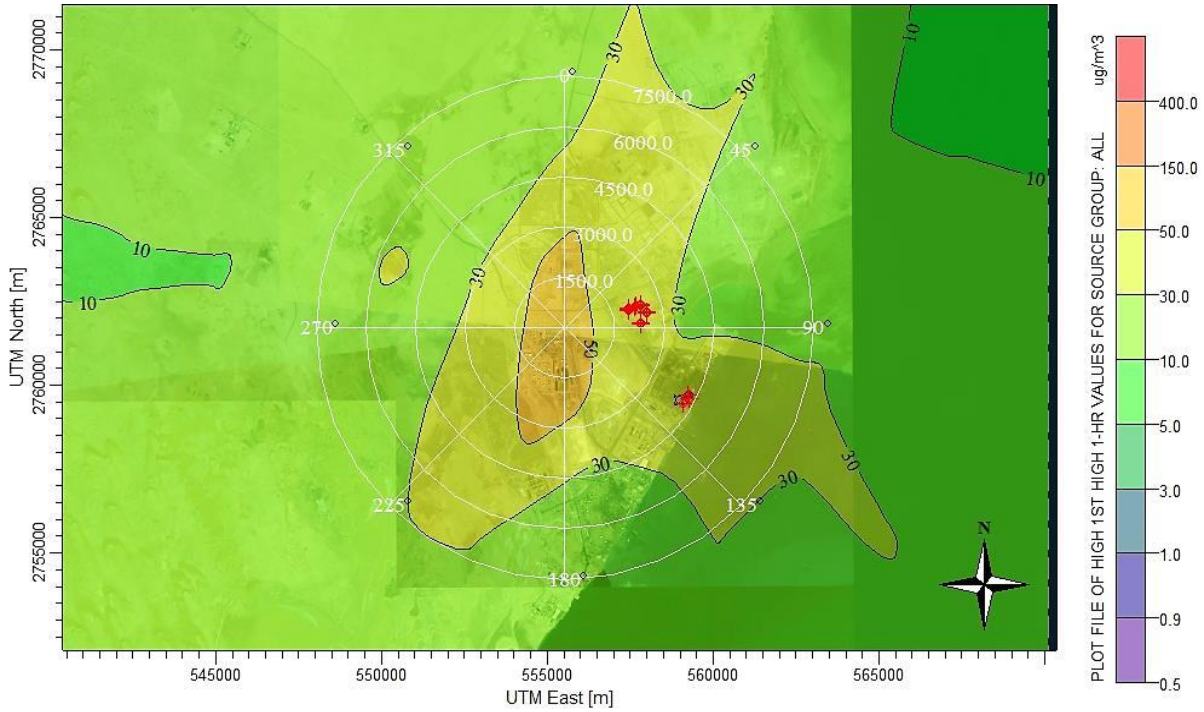

Figure 31: HF concentration contours for industrial city.