Peninsula Technikon

Research Thesis

Submitted in fulfillment of the requirements
for the degree of

Master of Technology in Chemical Engineering

Title: *The use of Monte Carlo Simulation to quantify the uncertainty in modeled estimates of toxic, radiation and overpressure impacts resulting from accidents in large chemical plants.*

Candidate: *Heinrich Francois Amsterdam*
BTech (Chemical Engineering)

Internal Supervisor: *Prof. E.K. Cairncross*
B.Sc., (Chem. Eng.), PhD
Senior Lecturer: Physical Science
(Chemical Engineering)
Peninsula Technikon

Statement

I declare that the content of this thesis represents my own work, with the exception of those particular cases that are referred in the text of the thesis. I also declare that this thesis has not been submitted to any other educational institution for the purpose of the awarding of an academic qualification.

H.F. Amsterdam

This thesis is dedicated to my loving mother who through of ten stormy and rough times supported me both financially and emotionally, and supported my career choice(s) throughout, thanks Mommy. Finally praise goes out to our heavenly father for all the blessing brought upon me.

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Abstract

Current Risk Assessment procedures for the estimation of the acute health impacts resulting from the accidental release of toxic chemicals into the atmosphere involve the definition or construction of a representative accidental release scenario and the use of one or other air quality or dispersion model to estimate ambient air concentrations and exposure durations in the vicinity of the source. Legislation such as the South African Occupational Health and Safety Act, 1993, Major Hazard Installation Regulations, United States Risk Management Plan Rule and the European Union Seveso II, to prevent and or minimize impacts of such events require owners of installations to perform a Risk Assessment if they handle hazardous substances above specified threshold quantities. Mathematical modeling has been widely used to assist with the Exposure Assessment to perform off-site worst-case release analysis. Governmental departments, agencies and local authorities increasingly (but not exclusively) rely on air pollution models for making decisions related to air quality, traffic management, urban planning, and public health. As a result, the model users' community is becoming larger and more diverse. Most of the air quality modeling work has so far been based on the "deterministic" approach of using only set input parameters and specific applications. The selected model provides estimates of averaged concentrations using specific meteorological and emission data sets. A serious weakness of this method lies in the fact that many uncertainties, not related to the calculations and input variables, but also to the very nature of atmospheric processes, are ignored. This might have serious implications for exposure studies. Dispersion modeling, accident scenarios and dose-response relationships are by no means the only (or necessarily the major) sources of uncertainty. Yet the results of such accident consequence studies are frequently presented with little regard to quantifying the uncertainty inherent in the Risk Assessment procedure, other than the possible application of an arbitrary 'safety factor' to risk estimates. Clearly decisions made on the basis of such risk assessments may be fundamentally flawed, and compliance or non-compliance with regulatory 'acceptable risk' criteria (if they exist) may well be challenged. The problem of the uncertainty in 'consequence analysis' is compounded by the availability of a number of dispersion models that may be used in the analysis, uncertainty in the meteorology that may have been applicable at the time of the accident,

and uncertainty as to the details of release scenario. Monte Carlo Simulation has been increasingly used to quantify uncertainties inherent in various situations. The method characterizes the uncertain input parameters via applicable probability distributions, and samples input parameter values randomly from these distributions. The user now has a number of release scenarios where uncertain input parameters have been changed simultaneously. Outputs approximate a full range of possible outcomes and the likelihood of each, which often is presented as a frequency distribution graph, which gives the ability to present output with confidence intervals. A case study approach was used to explore the range of predicted impacts that occur using applicable models to determine the various endpoints from accidental releases, which occurred in the past. Chemical production, usage and accidental frequency and to a lesser extent its toxicity served as a basis for selecting a particular substances for investigation in this study. SO_2 (dilute phase), Cl_2 (dense phase) and C_3H_8 (fire & explosion) releases were investigated, for they are constantly ranked in the top 15 in one or the other category previously mentioned for substance selection. Representative and as far as possible accurate release scenarios were constructed to explore the probable impacts (exposure concentration, overpressure and radiation effects) accidents might have had on the environment and the health of humans. This was done via modeling initially disregarding any from of parameter uncertainty present. Uncertain parameters were identified and further investigated to apply or assign relevant probability distributions to perform a probabilistic analysis of impacts. Monte Carlo Simulation technique was used in this regard and was implemented with the @ Risk[1] software tool. Each of the simulation runs consisted of a 50-iteration run to obtain frequency distributions for each of the impacts, which varied for individual case studies. The outcome from the probabilistic method differed from output generated via the deterministic method. The variation for SO_2 was exceptional, and marginal for the other two (chlorine and propane) cases. Results included both frequency distributions and a statistical analysis of the range of outcomes obtained, following the incorporation of Monte Carlo Simulation. Relevant conclusions were drawn from the output as to what the most likely impacts were from each of the accidental releases. A quantitative assessment

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[1] . This tool was purchased online from the Palisade Corporation, 31 Decker Road Newfield, NY 14867, sales@palisade.com

of uncertainty may improve the objectivity of decision-making based on the estimated risk.

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Nomenclature

Symbol	***Description***	***Units***
LD_{50}	The dose of a chemical, which kills 50% of a sample population.	ppm
t	Time elapsed after a release of pollutant	s
x	Downwind distance of receptor	m
y	Horizontal distance from plume centerline to receptor	m
z	Elevation of receptor	m
Q	Emission rate from a point source	g/s
U	Mean wind speed affecting the plume	m/s
$\delta_{X,Y}$	Crosswind standard deviation of plume at distance y	m
$\delta_{X,Z}$	Vertical standard deviation of plume at distance z	m
$\delta_{X,X}$	Downwind standard deviation of plume at distance x	m
M	Emission as mass released from point source	g/s
$C_{x,y,z}$	Pollutant concentration at distances x, y and z from the source	$\mu g/m^3$
K	First order rate constant	1/s
R	Radius affected by an explosion	m

List of Abbreviations

ABL	Atmospheric Boundary Layer
ACGIH	American Conference of Governmental Industrial Hygienists (US)
ADI	Acceptable Daily Intake
AFTOX	Air Force Toxic Chemical Dispersion Model
ALOHA	Aerial Location of Hazardous Atmospheres
BLEVE	Boiling Liquid Expanding Vapor Explosion
CAIA	Chemical and Allied Industries' Association (SA)
CFD	*Cumulative Frequency Distribution*
DEGADIS	Dense Gas Dispersion
EPCRA	Emergency Planning and Community Right-to-Know Act (US)
ERPG (2)	Emergency Response Planning Guideline 2 (US)
HAP's	Hazardous Air Pollutants
IARC	International Agency for Research on Cancer
IDLH	Immediately Dangerous to Life or Health
IPCS	International Program on Chemical Safety
LOAEL	Lowest Observed Adverse Effect Level
LPG	Liquefied Petroleum Gas
MHI	Major Hazards Installations
MIC	Methyl Isocyanate
MOS	Margin of Safety
NAEL	No Adverse Effect Level
NAS	National Academy of Science (US)
NTP	National Toxicology Program (US)
NOAA	National Oceanic and Atmospheric Administration
OHS	Occupational Health and Safety
PFD	Probability Frequency Distribution

RA	Risk Assessment
RMP	Risk Management Program (US)
SA	South Africa
SCRAM	Support Center for Regulatory Air Models
STEL	Short Term Exposure Limit
TCDD	Tetrachlorodibenzodioxin
TLV-TWA	Threshold Limit Value - Time Weighted Average
TNT	2,4,6 trinitrotoluene
UK	United Kingdom
US	United States of America
USDOH	United States Department of Health
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

Chapter 1: Introduction

In many areas of technology, particularly industrial technology, major accidents can have catastrophic effects on the environment and humans. Since the industrial revolution, processing industries have grown and developed and with it accidents have occurred [1]. Since the industrial revolution chemical production and usage figures had been at excessive quantities, with a corresponding increase of accidental releases into the atmosphere. The 1974 Flixborough disaster in the UK made governments aware of chemical Major Hazard Installations (MHI). This awareness increased shortly afterwards in 1976 with the Seveso incident and was even further magnified by the Bhopal disaster in 1984. Increased loss of life or property were highlighted with incidents such as the Seveso (Italy) dioxin release (1976), Bhopal (India) methyl isocyanate release (1984), Mexico City (Mexico) fire and explosion at a LPG storage facility (1984) and the Pasadena (USA) polyethylene plant fire and explosions (1989). South Africa has also been affected by such occurrences, such as the sulfur stockpile fire and subsequent SO_2 release in Macassar (1995) [2], which in addition exemplified the reality of the risks associated with MHI's. The most recent incident in South Africa was the explosion at the ethylene plant at Sasol, Secunda (01 September 2004), which resulted in 6 deaths and the hospitalization of 20 people, of which 5 were booked into the intensive care unit of the Highveld Medi Clinic.

It is realized that after many years of improvements in safety methods and system design, that accident rates and system losses have reached a plateau beyond which further improvement seems impossible to achieve [3]. The public has been justifiably concerned with the presence of large industrial plants close to populated areas. Severe industrial accidents, which have happened in the past decades, have raised the awareness of the public regarding the negative effects of technology and raised demands for more effective controls [4]. Chemicals like hydrogen sulfide and sulphur dioxide are discharged as a result of manufacturing and in some cases a chemical like dioxin can be accidentally released into the environment [5]. Other mechanisms for accidental releases range from tornados and earthquakes to accidents during transportation via truck or railroads.[6]

These cases trigger the public's concern about the short-term and long-term effects of such chemical exposures. Even in organizations with good general safety records, occasional large-scale disasters do occur and shake public confidence in modern technological systems. The public concern in one form or the other led to legislation aimed at the regulation of chemical concentrations in the atmosphere and inventories on site.

Responses to accidents, and in particular the Bhopal and Seveso incidents, resulted in government introduction of legislation to regulate Major Hazard Installations to protect the public and the environment. First was the Seveso I directive (1984) in Europe, subsequently upgraded to the Seveso II Directive (December 1996) [7]. It was a direct result of the Seveso disaster [4], thus referring to it as the 'Seveso Directive'. The US developed the Risk Management Plan (RMP) otherwise known as the RMP Rule (Promulgated June 1996, and facilities to comply by June 1999) [8]. With minor differences i.e. structure, these two policies call for similar outputs, which are: the reporting/notification of accidents, risk assessment to be performed by the operators/owners of an installation including a thorough risk management to make decisions about what actions should or will be taken to control pollution or accidental releases, and the implementation of an Emergency Response Plan. It was in line with these overseas developments that the authorities in South Africa promulgated the Major Hazards Installations (MHI) Regulations [1] under the Occupational Health and Safety (OHS), Act No. 85 of 1993 during 1998 to deal with such installations.

The common feature of these regulations is that it requires owners of installations to perform a Risk Assessment (RA) for probable accidental releases. The RA procedure plays a significant role in the regulation of the process industries, in particular determination of probable receptor exposure, land-use planning and in the prevention of accidents (explosion, fire, leaks of hazardous substances). It's also used by environmental agencies to further its environmental mandate and environmental goals [9]. The RMP Rule, SEVESO II and the South African Major Hazard Installations Act under the Occupational Health and Safety Act of 1993 all call for Risk Assessments.

Current Risk Assessment procedures for the estimation of the acute and possible long term health impacts resulting from the accidental release of toxic chemicals into the atmosphere involve the definition or construction of an accidental release scenario and the use of one or other air quality or dispersion model to estimate ambient air concentrations and exposure durations in the vicinity of the source. It also involves estimating the consequences of a possible release [10]. However uncertainty is present in all exposure assessment (therefore too in risk assessment) in which mathematical models are applied to predict information not obtainable via observations (Hoffman & Kaplan, 1999 [11]; Korving et al., 2002 [12]).

Uncertainty is inherent in the process of Exposure Assessment even if the most accurate data with the most sophisticated models are used. A common approach dealing with uncertainty in exposure assessment is to use a conservative assumption (e.g., "most exposed individual" or "highly exposed individual") and to calculate a point (single) estimate of likely exposure accordingly. An error in the exposure assessment, which occurs relatively early in the RA process may over or underestimate the outcome and ultimately the quality of decisions made based on the estimated outcome. Uncertainty exists because models are imperfect mimics of reality (Hoffman & Kaplan, 1999), and users are often unsure about the values for input parameters. Uncertainty may also be apparent and often unsighted in the construction of a representative release scenario of the actual accident, due to the deficiency in the human knowledge about the event that occurred.

Risk Assessment is uncertain by its very nature. With the adoption of risk assessment as an important input for reaching risk management decisions, the concept of risk acceptance was introduced to the environmental community. In the US, gaps in the scientific databases, led to the EPA's to err on the side of public safety (*i.e. intentionally insert public health protective parameter values in the place of data gaps*). While this approach promoted the acceptability of risk-based decision-making [13], this *policy decision* of risk assessment practices which, in large provided scientific assessments with a "public health protective" or "conservative" bias are likely to overestimate risk [14].

Furthermore when many parameters exist for which such assumptions are made, the compounding effect of the conservative assumptions is often not quantitatively understood. In short risk assessment in the US was originally intended to overestimate the magnitude of the public health problem, at least for carcinogenic risk where quantification was usually undertaken.

Clearly not all risk assessments are created according to equal standards, and this necessitates that tools be employed for describing the degree of bias and uncertainty in the assessment. The above indicates that it is very difficult to select a distinct value for risk that can be regarded as fully protective for the entire population. This problem is compounded by the variability in exposure susceptibility in the human species. At present controversies are ongoing over the appropriateness of the exposure levels that the EPA has proposed for resetting the ozone and particulate matter national ambient air quality standards (USEPA, 1996) [15]. Since it is impossible (and perhaps not desirable) to avoid a public health protective policy, systematic means of expressing the degree of certainty for potentially important (high health hazard, high cost) management decisions is long overdue. For this very reason the need of methods for the identification and quantification of uncertainty is as significant as modeling the release itself.

Dispersion modeling, accident scenarios and dose-response relationships are by no means the only (or necessarily the major) sources of uncertainty. Yet the results of such accident consequence studies are frequently presented with little regard to quantifying the uncertainty inherent in the Risk Assessment procedure, other than the possible application of an arbitrary 'safety factor' to risk estimates. Clearly decisions made on the basis of such risk assessments may be fundamentally flawed, and compliance or non-compliance with regulatory 'acceptable risk' criteria (if they exist) may well be challenged. Propagation of uncertainties in models has been studied by means of first order variance (uncertain input parameters are independent) propagation or Monte Carlo Analysis [12]. Over the years Monte Carlo simulation increasingly played an integral part in the field of environmental health and safety risk assessments (Poulter, 1998) [16]. When assessing uncertainty and/or variability Monte Carlo Simulation Analysis has been readily applied to quantify the uncertainty in environmental fate and effects models [17]. Previous research has employed Monte Carlo methods to investigate uncertainty in air modeling estimates (Hanna *et al.*, 1998 [18]; Jaarsveld *et al.*, 1997 [19]; Smith *et al.*, 1999 [20]; Guensler and Leonard, 1995). The use of Monte Carlo Simulation has been supported by the USEPA who recently adopted a policy (USEPA, 1997) [21], indicating their approval of Monte Carlo simulation and other probabilistic analytical tools. The USEPA and US National Academy of Science (USNAS) recognized the important role of probabilistic analysis. In March 1997, USEPA issued a "Guiding Principles for Monte Carlo Analysis (EPA, 1997b) [22]. The policy supports "good scientific practices" in quantifying variability and uncertainty (Frey, 1998) [23].

Monte Carlo Simulation is a widely used computational method for generating probability distribution (output) on variables that depends on other variables or parameters (input) represented as Frequency Probability Distributions. The availability and use frequency of Monte Carlo Simulation has rapidly gained momentum with an increasingly dissatisfaction with the deterministic or point estimate calculations typically used in Risk Assessment (Poulter, 1998). Monte Carlo Simulation does not dictate any particular degree of protectiveness or conservatism, but provides more information for implementation of policy choices and decision-making.

Alternative methods for the identification and quantification of uncertainty have been used in the field of exposure assessment. Frey and Burmaster (1999) [24] applied Bootstrap Simulation and Maximum Likelihood estimation to quantify uncertainties in the measurements of PCB concentrations in leafy produce in three databases. Results for these two approaches yielded comparable outcomes in most cases. The Bayesian statistical approach (reverse of bootstrap simulation) is another method readily applied.

This research will address aspects of quantification of uncertainty inherent in exposure assessment. We will be focusing on exploiting the promise of Monte Carlo Simulation in the field of exposure assessment in particular in air quality modeling. Three substances of which have been involved in accidents will be utilized to propagate uncertainty in modeling output. Results obtained from these analyses should instill more confidence in the decisions made based on such outputs, and it will give consideration to the influence that uncertainty has on decisions. This research will focus on the impact uncertainty has on model estimates. The question this research will be looking to answer is whether estimations acquired without giving weight to uncertainty and those generated giving consideration to uncertain input parameters are significantly different to affect an impact on decision-making.

1.1 Objectives of Project

- The main objective is to show that Monte Carlo Simulation can be used to quantify uncertainty inherent in the analysis of the impact of accidental releases of toxic and flammable substances, and that the output in the form of a probability histogram and confidence intervals, is more useful than a point estimate or sensitivity analysis.

1.1.2 Sub-Objectives

- To use models to perform receptor exposure assessments based on selected accidents scenarios.

- To acquire figures of production, usage and accident frequency of hazardous chemicals, to select three substances based on their rankings in one or the other category and their dispersion (dilute or dense phase) and hazardous (toxic or flammable) characteristics. An analysis of reported accidents involving these substances will form the foundation for demonstrating the proposed Monte Carlo Simulation methodology.

- To identify and investigate the uncertainty associated with the input parameters or data necessary to perform such analysis.

This study does not include a detailed but a rather limited characterization of assigned input parameter distributions due to the limited availability of input parameters datasets in studies of this nature.

1.2 Thesis Chapter Content

The outline of this thesis is as follows: Chapter 2 provides a background to the topic; Chapter 3 deals with the use of Dispersion Modeling in the analysis of consequences of accidental releases and the types of releases that might need to be treated; Chapter 4 outlines the methods implemented to perform a probabilistic analysis of accidental releases; Chapter 5 displays the results obtained, Chapter 6 discusses these results and Chapter 7 outlines conclusion drawn and some recommendations for use of Monte Carlo Simulation. The Appendices follow which displays the figures and tables referred to, where applicable, throughout the document. Finally, the list of references used is displayed at end of the thesis.

Chapter 2: Background

A variety of research areas will be utilized to support the research objectives stated previously. We will have a look at some of the most documented industrial accidents, which made people aware of the dangers of Major Hazard Installations. These accidents largely led to the introduction of legislation to regulate Major Hazard Installations and ultimately purposefully lessening potential accidental releases of hazardous substances into the atmosphere. These regulations with minor differences in structure require similar outputs, of which performing a Risk Assessment is one. The concepts of RA will be reviewed on; including its potential uncertainties and the impact such uncertainty may have on desired outcomes. Monte Carlo Simulation will be applied to provide a method to quantify such uncertainty, and we will therefore look at this technique in more detail, and some corresponding studies, which were undertaken in the past.

2.1 Survey of Industrial Accidents

2.1.1 SEVESO [4,25]

On July 10, 1976 in Seveso a small town of approximately 17,000 inhabitants and 15 miles from Milan (Italy), a hexachlorophene manufacturing plant owned by the Icmesa Chemical Company experienced a loss in temperature control in one of it's process reactors. The result, an uncontrolled increase in the formation of a byproduct known as Tetrachlorodibenzodioxin (TCDD), perhaps the most potent toxin known to man. Animal studies have shown TCDD to be fatal in doses as small as 10^{-9} times the body weight. It was estimated that approximately 3-10 kg. of TCDD was released via an implemented reactor relief system and dispersed over Seveso. TCDD is a highly toxic ($LD_{50} = 10^{-9}$ kg/kg for rats) [26] substance, environmentally persistent and very insoluble in water. Approximately 600 people were evacuated and an area of 25 km^2 contaminated. This contamination resulted in certain areas remaining abandoned to date. Approximately 300 Cases of chloroacne resulted due to this exposure, enlarged livers in 8% of the population including nerve damage to a minor extent. Damage to vegetation and animals in the area however, were severe.

2.1.2 BHOPAL [27]

December 3, 1984, the worst industrial accident on record took place in Bhopal, India [28]. The plant produced pesticides. An intermediate compound in the process was methyl isocyanate (MIC). A sequence of failures resulted in the accidental atmospheric release of approximately 40 tons of methyl isocyanate (MIC). Methyl isocyanate is extremely toxic to humans. Acute (short-term) exposure has an LC_{50} of 5.9 ppm and the maximum exposure concentration to MIC for workers over an eight-hour period is 0.02 ppm. MIC demonstrates a number of hazardous physical properties. Its boiling point at atmospheric pressure is 39.1°C; its vapor pressure is 348 mmHg @ 20°C [29]. The vapor is about twice as heavy as air, ensuring that vapors stay close to the ground once released. It was estimated that the MIC killed 2,000-3,000 people immediately and injured ~170,000.

Pulmonary edema was the probable cause of death in most cases, with many deaths resulting from secondary respiratory infections. Survivors continue to exhibit damage to the lungs and eyes. Reproductive effects and increased number of stillbirths and spontaneous abortions were noted in the survivors of the Bhopal, India accident. Estimates of total deaths exceeded 5,500, and with some 120,000 chronically ill survivors.

2.1.3 MEXICO CITY [30]

At approximately 05:35 hours on 19 November 1984 a major fire and a series of catastrophic explosions occurred at the government owned and operated PEMEX LPG Terminal at San Juan Ixhuatepec, Mexico City. As a consequence of these events some 500 individuals were killed and the terminal was destroyed. A pressure drop was noticed in the control room and also at a pipeline pumping station. The pressure drop was due to the rupture of an 8-inch pipe between a sphere and a series of cylinders. Unfortunately the operators could not identify the cause of the pressure drop. The release of LPG continued for about 5-10 minutes. The gas cloud, estimated at 200 m x 150 m x 2 m high, drifted to a flare stack. It ignited, causing violent ground shock, resulting in a number of ground fires. Approximately fifteen minutes after the initial release the first Boiling

Liquid Expanding Vapor Explosion (BLEVE) occurred. A series of BLEVE's followed for the next hour and a half as the LPG vessels violently exploded. LPG was said to rain down and surfaces covered in the liquid were set alight.

2.1.4 PASADENA [31]

October 23, 1989 shortly after 1:00 pm an accidental release on a polyethylene plant at the Phillips 66 Company's complex at Pasadena, near Houston, Texas transpired. This resulted in the formation of a vapor cloud, which ignited and caused a massive vapor cloud explosion followed by a series of explosions and fires. A total quantity of 85,200 pounds of a mixture of ethylene, isobutane, hexane and hydrogen was estimated to have escaped within seconds. Approximately 90 – 120 seconds after the initial release the vapor cloud formed ignited. Two other major explosions followed, one in which a 20,000 US gal isobutane storage tanks exploded and another when a second polyethylene plant reactor failed. These explosions occurred 10-25 and 25-45 minutes, respectively after the initial explosion. The death toll was 23 (22 on site and 1 died later on due to the severity of injuries sustained), and a total of 103 injuries.

2.1.5 MACASSAR [2]

After several days of brush fires in the vicinity, a huge sulphur stockpile (owned by AECI, the largest manufacturer of chemicals and explosives in South Africa) caught fire late on a Saturday afternoon (13 December 1995). The fire could not be extinguished due to strong and persistent winds which resulted in a total of about 7000 tons of sulphur be burned over a 21 hour period. While the fire site was several kilometers away from large population areas, the township of Macassar (population 40,000 at the time) is 2.5 km downwind, and many suburbs of Cape Town (population 1.5 million at the time) are 10-30 km distant. From about 21:00 on Saturday to 01:00 on Sunday morning, (the most intense period of burning) the prevailing winds blew to the west-north-west (in the direction of the Macassar suburb). Symptoms among residents near/in Macassar increased in prevalence and intensity up to midnight and beyond. Residents, mostly black, working class and poor, reported a number of irritative affects including burning and irritation of eyes, nose and throat, coughing, shortness of breath, chest pain, stomach cramps and vomiting.

The above survey included the most common types of incidents in industry. These include the

- dilute (neutrally bouyant) phase release of hazardous chemicals, exemplified by the Macassar sulfur dioxide release
- dense (heavier than air) phase release exemplified by the methyl isocyanate release in Bhopal, and
- the releases of flammable gases and liquids resulting in fire and explosions exemplified by Pasadena and Mexico City.

2.2 Uncertainty in the analysis of the above accidents.

For all of these incidents attempts were made to determine the impacts via computational modeling. This presented some degree of uncertainty as to what the true outcome from these accidents were. We will briefly summarize some of the uncertainties that were encountered and the effect it may have had on decisions made.

2.2.1 SEVESO

There was considerable uncertainty determining which toxin/poison was released. Laboratory tests had to be performed which concluded that the substance released was tetrachlorodibenzodioxin (TCDD). Confirmation as to which substance was released was only established 10 days after the release occurred, which resulted in evacuation only occurring after 16 days. Temperatures reached by the reactor and thus the substance release temperature was unknown. Estimates of the amounts of TCDD generated in this particular reactor and eventually dispersed over Seveso were uncertain? Estimated amounts ranged from 0.45 to 3kg released. From a modeling point a view, they assumed an amount of 2kg being released. Agreement between predicted and measured concentrations confirmed that the amount released might have been 2kg. This statement might still have been wrong since other uncertain parameters may have played a significant role in this aspect. Data such as the rupture pressure, vent diameter and discharge height above the ground were used to obtain vapor exit velocity. Unfortunately two cases were considered. Case A: That a pure vapor ($\rho = 1.61$ kg/m^3) was released, and Case B: That a two-phase vapor – liquid mixture ($\rho = 8.99$ kg/m^3) was released. According to eyewitnesses the actual case was an intermediate of the above two extreme cases.

2.2.2 BHOPAL

For some days after the release it was unknown what the gas was that were released. This made treatment of casualties very difficult. For days speculation about the gas included suggestions that it was phosgene, continued in the world press. During the investigations a lot of parameters were believed to be uncertain:

The release duration, which ultimately had an effect on the release rate, was uncertain. The release pressure, which investigators found to be at least 180 psig to obtain a certain release rate, had some uncertainty. The temperature reached due to the exothermic reaction of water with MIC was estimated to be in excess of 200°C. The effect of this parameter on the outcome should not be underestimated. The precise number of the dead and injured at Bhopal was uncertain too. The scale of the accident led to much confusion. People continued to die of the effects over a period of years. The Indian Government estimates of the death toll about 2 years after the event was 1,754 and by 1989 figures had risen to 3,150 and by 1994 numbers added up to 5,500 deaths.

2.2.3 MEXICO CITY

The dynamics of the characteristics of a BLEVE alone presents a considerable degree of uncertainty. The fact that there were some 15 explosions over 90 minute period compounds the problem of constructing a representative scenario of the event. Uncertainty in determining the actual release duration of LPG existed. It was estimated to be 5 – 10 minutes. At the time of the incident the wind speed was 0.4 m/s and modeling with calm wind conditions such as this is always uncertain, because in general low wind speeds lead to higher toxic concentrations and larger flammable gas clouds [32]. Main issue is that uncertainty lies in the applicability of dispersion models when low wind speed conditions prevailed at the time of the incident.

2.2.4 PASADENA

Massive vapor cloud explosions were the major cause of harm in the release, and estimating the impacts of these explosions on it own present a great deal of uncertainty. The TNT equivalent of the explosion was estimated in the OSHA report as 2.4 tons, but alternative estimates from seismograph records indicated 10 tons.

2.2.5 MACASSAR

Attempts were made to determine SO_2 concentrations in especially the Macassar suburb (Batterman & Cairncross, 1999) [2]. It was assumed that only SO_2 was released from the fire, naturally the release of SO_3 and H_2SO_4 both of which are more toxic than SO_2 would also be expecting. Meteorological data used for modeling may have been the most unreliable. Met data were obtained form Cape Town International Airport situated approximately 20 km WNW from the site.

2.3 The Regulation of Major Hazards Installations

In response to these accidents and in particular the Bhopal and Seveso incidents led to much greater awareness of process industry hazards on the part of the public and demanded for more effective controls [4]. Governments introduced legislation to regulate Major Hazard Installations in order to protect the public and the environment.

The first was the Seveso I directive in 1984 in Europe eventually upgraded to the Seveso II Directive (December 1996) [7] was a direct result of the Seveso disaster [4], thus referring to it as the 'Seveso Directive'.

The US developed a policy, the Risk Management Plan (RMP) otherwise known as the RMP Rule (Facilities to comply by June 1999) [8]. With minor differences in terms of structure, these Seveso II and RMP Rule call for similar outputs such as the reporting/notification of accidents, risk assessment to be performed by the operators/owners and requires implementation of an Emergency Response Plan. It was in line with these overseas developments that the authorities in South Africa promulgated the Major Hazards Installations (MHI) Regulations [1] under the Occupational Health and Safety (OHS) Act No. 85 during 1993 [33] to deal with such installations here.

2.3.1 Legislations and Guidelines

2.3.1.1 South Africa-Major Hazards Installations

South Africa promulgated the Major Hazards Installation (MHI) Regulations under the Occupational Health and Safety (OHS) Act No. 85 of 1993 to deal with installations that might pose threat to humans and animals [1]. The regulations apply to employers and self-employed persons and users who have on their premises, either permanently or temporarily, a major hazard installation or a quantity of a substance which may pose a risk that could affect the health and safety of employees and the public. Nuclear installations, civil works (dams and buildings), food processing & mining operations are excluded.

Classifications of a Major Hazards Installation:

In South Africa it is left to the owner to decide whether the installation is a major hazard opposite to the toxicity of chemical and quantities stored criteria used in the US (APPENDIX B1 and B2) and EU (APPENDIX C1 and C2). This decision has no immediate implications, except that, if an incident occurred and it is proven that it was a major hazard installation, there could be legal repercussions.

Approaches used to classify an installation as a MHI:

1. Handling a listed or scheduled substance

If on an installation the chemical and its inventory which is handled, processed or stored in one single container constitutes a listed substance as identified in schedule A (APPENDIX A) of the General Machinery Regulations [34] under the Occupational Health and Safety (OHS) Act No. 83, then the installation is classified a MHI.

2. Potential to harm the public:

Installations not classified were explosive plants with the so-called safety circles, and installation built in isolated areas e.g. open field, deserts, sea and underground mines [1]. It is common for chemicals to cause an immediate major harm to the public via explosion, fire and toxic release, thus only overpressure, radiation and concentration needs to be considered.

2.3.1.2 U.S. Risk Management Plan

For the US the Bhopal accident served as the main impetus for the establishment of legislation securing the public's right-to-know how much of certain toxic substances are emitted from each factory, and how much may be stored on-site at any one time. In 1986 the Emergency Planning and Community Right-to-Know Act (EPCRA), was passed as part of the amendments to the "Superfund" hazardous waste cleanup program. The RMP was promulgated on June 21, 1996 under the Clean Air Act as Amended in 1990 [8].

As of June 21, 1999, affected facilities were expected to be in compliance with the USEPA Risk Management Program (RMP) Rule (40 CFR 68) under section 112(r)(7) [8]. A company is required to comply with the rule if it manages a regulated substance above the listed threshold quantity in 40 CFR 68.130 within a given process. Regulated substances include 77 toxic substances (threshold quantities of 500 to 20,000 lbs.) [Full list in APPENDIX B1], and 63 flammable substances (threshold quantities of 10,000 lbs.) [Full list in APPENDIX B2], published in the July 1, 1998 Federal Register[35].

The RMP Rule requires facilities to develop and implement appropriate Risk Management Programs to minimize the frequency and severity of plant accidents. Three levels of implementation are required by the EPA RMP Rule based on the level of risk presented by a covered process.

Program 1: Minimal for facilities with no history of off-site accidents, no public receptors in the worst-case circle, and emergency response has been coordinated with local authorities.

Program 2: Expanded program for facilities that are not required to implement Program 3, but do not qualify for Program 1.

Program 3: Most stringent of the three programs, requires a "worst-case release scenario" analyses, "alternative case" analyses, an accident prevention program and an emergency response plan. Owners is required to submit a risk management plan which includes the offsite consequence analysis, 5 year accident history, accident prevention plan and the emergency response program.

The RMP Rule has five major components

1. Management System (40 CFR 68.15)
Assigns responsibility and the approach to implementing the components of the RMP Rule.

2. Hazard Assessment (40 CFR 68 Subpart B)
Includes worst-case release analysis, alternative release analysis, five-year accident history, and identification of receptors.

3. Risk Management Plan (40 CFR 68 Subpart G)
Comprised of an executive summary, registration, off-site consequence analysis, five-year accident history, prevention program 2 or 3, emergency response program and certification.

4. Emergency Response Program (40 CFR 68.90 and 95)
Written plan implemented to protect public health and the environment should an emergency occur?

5. Prevention Program (40 CFR 68 Subpart C & D)
The Clean Air Act requires the risk management program to include a prevention program that covers safety precautions and maintenance, monitoring and employee

training measures. This program includes nine elements: process hazards analysis, process safety information, operating procedures, training, maintenance, re-startup review, management of change, safety audits and accident investigation.

2.3.1.3 European Regulation: Seveso II

Both the Seveso (1976) and Bhopal (1985) accidents had a considerable influence on the development of European regulations for the control of Major Hazard Installations. The original European Union (EU) Council Directive of 1982 (Seveso I) was revised and replaced by the Seveso II Directive of December 1996 [7], of which was amended in December 2003 [36]. The Directive emphasizes the development of a safety management system, emergency plans, accident reporting, inspection of plants and provision of information to the public.

The Seveso II Directive requires operators of installations producing or using hazardous substances to take all necessary measures to prevent major accidents and to limit the consequences to man and the environment to those that do occur. Member States of the European Union (EU) had up to two years, after the Directive was adopted to comply with these new regulations (Kirchteiger, Chritou & Papadikas, 1997) [25].

The Directive specifies that operators of installations producing or using hazardous substances must:

- Send a "notification" about their operations to a Competent Authority (Article 6)
- Draw up a Major Accident Prevention Policy, and ensure it is properly implemented (Article 7).
- Above a certain threshold of dangerous substance, produce a Safety Report and Risk Assessment (Article 9).
- Draw up an internal emergency plan and submit it to the Competent Authority, which would then draw up external emergency plans (Article 11).

The Directive applies to establishments using or producing qualifying quantities (Substances and quantities in APPENDIX C1) of certain named substances or categories of substances. There are two threshold quantities. The lower threshold: quantity above which the establishment must notify the Competent Authority of its operation and provide a Major Accident Prevention Policy. The upper threshold: quantity above which the establishment must provide a Safety Report in addition.

The Safety report must include the identification and analysis of accident risks and prevention methods for potentially identified accidents. The report should provide a detailed description of possible major accident scenarios and their probability under which they occur, including a summary of the events that may play a role in triggering each of these scenarios. The Safety Report must also include an assessment of the extent and severity of the consequences of identified major accidents.

The Safety Report should discuss general criteria assumed (i.e. best available technology, good engineering practice and quantitative risk criteria) in the assessment of risk, and should justify the selection of a particular method (Papadakis & Amendola, 1997) [37].
The Directive includes specific provisions for providing information to the public. The new directive has a sharper focus on Management Systems. In addition the number of substances named in Seveso I has been reduced from 178 to 37 through the use of generic categories such as toxic, oxidizing and dangerous to the environment.

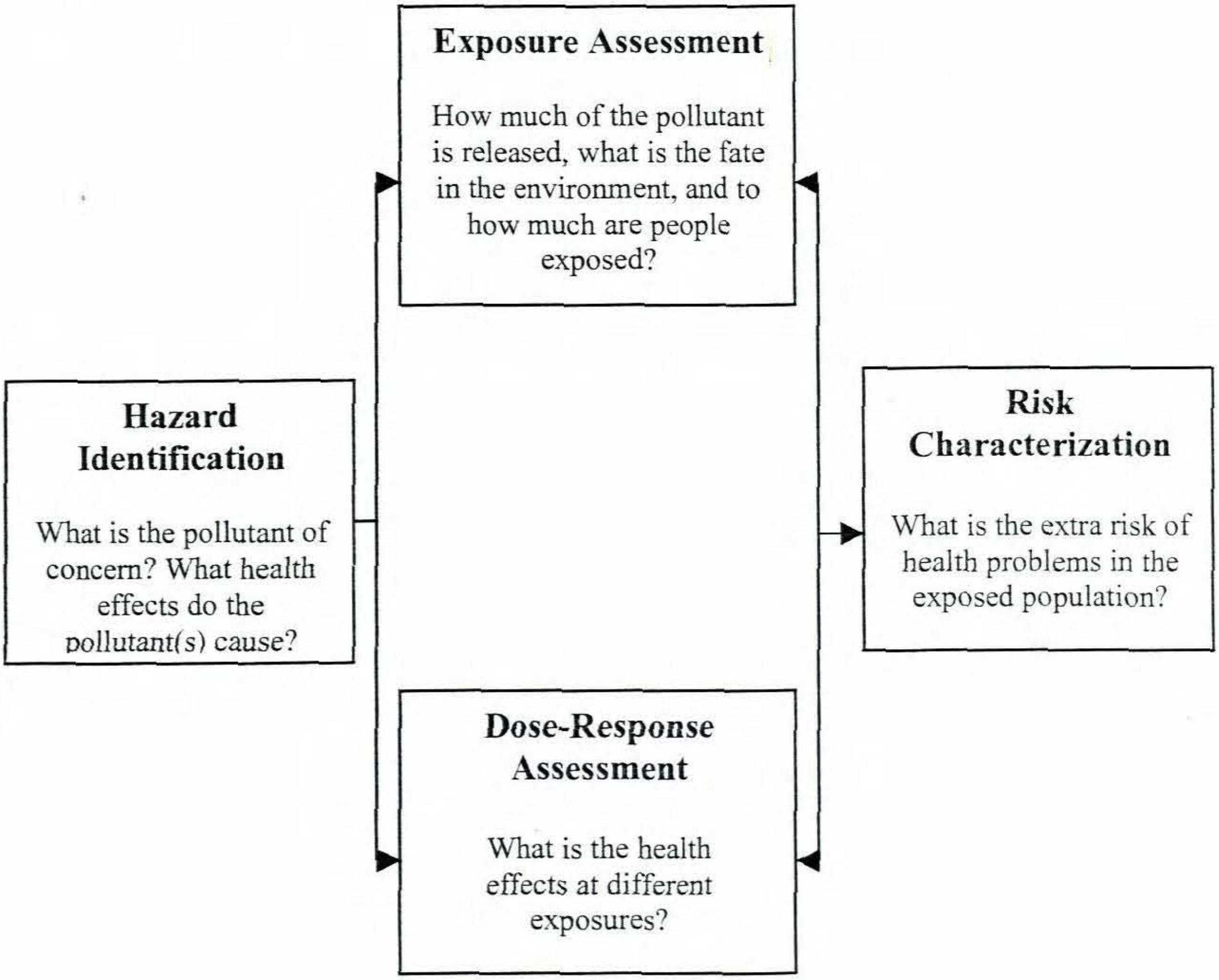
2.4 Concepts of Risk Assessment (RA)

Risk Assessment methodologies and in particular Environmental Risk Assessment (ERA) have been a developing technique since the 1970's [38], and is demonstrating benefit in many applications of risk assessment [39]. Risk Assessment is an extensively used procedure to assess risks associated with various processes and new developments. It has been used by many agencies to further environmental mandates and environmental goals [40].

As previously noted accidental releases often have detrimental effects such as the loss of human life and the contamination of the immediate environment, which may persist for several years after the release (Bhopal, India). The RMP Rule, Seveso II Directive and the SA MHI regulations require process industries to perform a detailed Risk Assessment if determined installations and its operating conditions fall under these policies [38]. Control of risks from exposure to chemicals requires a scientific, ideally quantitative, assessment of potential effects/consequences (Melhem & Stickles, 1997) [10] at given exposure levels (risk assessment). Based upon the results of risk assessment, and taking into consideration other factors, a decision-making process aimed at eliminating or, if this is not possible, reducing to a minimum the risk to the chemical(s) under consideration (risk management), can be initiated (Freeman, 1989) [41].

Risk Assessment (RA) is a conceptual framework that provides the mechanism for a structured review of information relevant to estimating health or environmental outcomes. The National Academy of Sciences risk assessment paradigm has proven to be a useful tool (US NAS, 1983) [42] for conducting risk assessments. This paradigm divides the risk assessment process into four distinct steps: Hazard Identification, Dose-Response Assessment, Exposure Assessment and Risk Characterization illustrated in the following flowchart (Figure 2-1).

Figure 2-1: Flowchart of the four steps of Health Risk Assessment



2.4.1 Hazard Identification

The purpose of hazard identification is firstly to identify the pollutants/substances that may be released, and to evaluate the weight of evidence for adverse effects in humans based on assessment of all available data on the toxicity and mode of action of a particular substance (which organs are affected). It is designed to address primarily two questions: (a) whether an agent may pose a health hazard to humans, and (b) under what circumstances an identified hazard may be expressed. Hazard identification is based on analysis of a variety of data that may range from observations in humans to analysis of structure–activity relationships.

In hazard identification, we judge the likelihood of a pollutant causing various health effects in humans by considering what is known about how the pollutant will behave when it enters the body and what harm it can cause. This entails rigorous examination of the quantity, quality and nature of the results of available toxicological and epidemiological studies and information on mechanisms of toxicity. The latter is particularly important with respect to assessment of relevance to humans.

Several classification schemes provide a framework for assessment of the weight of evidence for various toxicological end-points (IPCS, 1986 (neurotoxicity) [43]; US EPA, 1986 [44], 1996 [45]; IARC, 1987 [46]; IPCS, 1996 (immunotoxicity); [47].

2.4.2 Dose-Response Modeling - What type and how much exposure may be harmful? [48]

Dose-response assessment provides a numerical basis for translating exposure information into an evaluation of risk. The dose-response assessment answers two questions about a substance's potential to cause adverse health effects. First, what is the adverse effect (*i.e.*, "response") that occurs at the lowest exposure (or dose) at which an effect is observed? This response is called the "critical" effect. Second, what is the quantitative relationship between exposure and adverse effects? This association is termed the "dose response" relationship. It is often expressed as a graph that shows exposure (*i.e.*, "dose"), on the horizontal axis and proportion of individuals (either humans or laboratory animals) showing the critical effect on the vertical axis. With increasing dose more individuals will show the effect and the rate of this increased response with increased dose is the slope of the "dose-response". Alternatively, we may graph the different levels of effect such that increasing dose results in increasingly more severe effects. Toxicologists often fit a mathematical model to the dose-response graph in order to make predictions of effects for doses that have not been tested. For risk assessment, we use the dose-response for the "critical" effect to estimate the exposure level at which adverse effects would not be expected to occur in people.

2.4.3 Exposure Assessment – How are we exposed to Hazardous Air Pollutants (HAPs)? [49]

Exposure to environmental pollutants is determined by the concentration of that pollutant in various environmental media (i.e., air, soil, water, food), and the contact of an individual with that media. Through dispersion modeling and monitoring, the ambient concentrations of the pollutants can be estimated geographically and temporally in air. Actual exposure (or dose) is principally defined by the concentration to which the individual is exposed; time spent in various microenvironments[1], exposure duration, and an individual's activity pattern, which may influence such things as inhalation rate.

2.4.4 Risk Characterization [49]

Risk characterization, the final step in risk assessment, is primarily used to integrate the information from the other three components and describes the nature and magnitude of human or nonhuman risk and the attending uncertainties. Risk characterization describes why risk was assessed the way it was in terms of choices made. Every risk assessment involves a multiplicity of choices and options. In the risk characterization, the key strengths and weaknesses of the assessment are described. Two elements are required for full characterization of risk. First, the characterization must address qualitative and quantitative features of the assessment. That is, along with quantitative estimates of risk, full risk characterization must clearly identify all assumptions, their rationale and the effect of reasonable alternative assumptions on the conclusions and estimates. Second, it must identify any important uncertainties in the assessment as part of a discussion on confidence in the assessment. This statement on the confidence of the assessment must identify all major uncertainties and comment on their influence on the assessment. Risk characterization often serves as the link with risk management and the uncertainty statement is important for several reasons, discussed in the following sections.

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[1] A microenvironment is a place where the pollutant concentration is considered uniform.

2.5. The Problem of Uncertainty in Risk Assessment

2.5.1 Technical Issues with Uncertainty

The RA procedure plays a significant role in the process industries, in particular determination of probable receptor exposure, in the analysis of accidents, land-use planning and in the prevention of accidents (explosion, fire, leaks of hazardous substances). It's also used by environmental agencies to further their environmental mandate and environmental goals [9]. Risk Assessments are required under the RMP Rule, SEVESO II and the South African Major Hazard Installations Act.

Current Risk Assessment procedures for the estimation of the acute and possible long term health impacts resulting from the accidental release of toxic chemicals into the atmosphere involve the definition or construction of an accidental release scenario and the use of one or other air quality or dispersion model to estimate ambient air concentrations and exposure durations in the vicinity of the source. It also involves estimating the consequences of a possible release [10].

However uncertainty is present in all exposure assessment (therefore too in risk assessment) in which mathematical models are applied to predict information not obtainable via observations (Hoffman & Kaplan, 1999 [11]; Korving et al, 2002 [12]). An error in the exposure assessment, which occurs relatively early in the RA process may be detrimental to the outcome and ultimately the decisions made based on the outcome. Uncertainty at this stage exists because models are imperfect mimics of reality (Hoffman & Kaplan, 1999), and users are often unsure about the values for input parameters.

Uncertainty may also be apparent and often unsighted in the construction of a representative release scenario of the actual accident, due to the deficiency in the human knowledge about the event that occurred.

Uncertainty arises due to the lack of knowledge regarding the true value of a quantity. Frey, 1998 [23], Frey & Burmaster, 1999 [24]), and Finkel (1990) [50] define uncertainty as knowledge about the limits of our knowledge. Minimizing uncertainty in risk assessment has been a 20-year process (Hattis et al., 1999) [13].

Uncertainty is inherent in the process of Exposure Assessment even if the most accurate data with the most sophisticated models are used. In Exposure Assessment a common approach dealing with uncertainty is to use a conservative assumption (e.g., "most exposed individual" or "highly exposed individual" or "worst-case") and to select a point estimate accordingly, or sensitivity analysis may be used to evaluate outcomes for outcomes for different input parameters

2.5.2 Types of Uncertainty

Several forms of uncertainty in exposure assessment can exist. Three forms of uncertainty in exposure modeling were suggested by Hattis, Mckone and Pease, 2000 [51], Finkel, 1990 [50] and Frey, 1993 [52].

2.5.2.1 Decision Rule Uncertainty

This form of uncertainty arises whenever there is controversy about how to quantify or compare social objectives. This form of uncertainty may include a series of potentially controversial value judgments, which need be made based on outputs of a risk assessment in order to reach a decision. Although rarely considered as a form of uncertainty (Hertwich et al., 2000), due to the issue of preference are not seen as a scientific question and particularly since decision makers are uncomfortable making this value judgment. Decision rule uncertainty also arises in response to other uncertainties, such as how parameter uncertainty should be included in the decision-making. Should point estimates, mean exposure or the 95th percentile be used? Should an "average" person be considered, or one that is highly exposed?

2.5.2.2 Model Uncertainty

Introduced through the simplification of reality via representative models. Any real world situation contains phenomena or behaviors that cannot be reproduced by even the most detailed model (Hertwich et al., 2000). The most important issue to address is whether a particular model adequately addresses those aspects of reality that are of concern to the decision maker.

2.5.2.3 Parameter Uncertainty and Variability

This form of uncertainty necessitates the distinction between variability vs. true uncertainty of a predicted outcome (Hattis & Burmaster, 1994) [14]. Variability refers to statistical variance that originates from random or heterogeneous factors such as human exposure factors, rainfall, soil characteristics and climate factors (Hetwich et. al., 2000; Frey, 1998). It may arise for example due to differences in design from one emitter to another, and in operating conditions from one time to another. Spatial and temporal difference mainly accounts for variability. True uncertainty as mentioned previously is due to the lack of knowledge regarding a certain parameter.

2.6 Sources of Uncertainty in Risk Assessment

By now its common knowledge that uncertainty in risk assessment results form the lack of knowledge in any particular area of the process being investigated. This thesis will solely focus on the uncertainty present in Exposure Assessment. However, uncertainty is also present in the other areas of health risk assessment, and in particular the Dose Response Modeling where data gaps are often encountered and generally accounted for using mathematical modeling.

2.6.1 Uncertainty in the Toxicology

Uncertainty in toxicological risk assessment results from the lack of knowledge of the toxicity of a substance to the target population. The current approach for development of dose-response values yields human limit values, which rely heavily on the traditional uncertainty (safety) factor or Margins of Safety (MOS) approach to convert empirical evidence into acceptable exposure levels for, the human population without quantitative measurement of uncertainty [53,54]. However this is not true for the classical pollutants such SO_2 etc., where exposure-response values are largely based on epidemiological studies. For most of the chemical substances that are subject to regulatory and industrial decision-making, important toxicological data are missing, and the available datasets is often difficult to interpret [55]. Knowledge gaps causing uncertainty in risk assessment are usually overcome by extrapolation (Kalberlah et al, 2003).

Toxicological studies usually result in point estimates for human limit values e.g. Acceptable Daily Intake (ADI) or Reference Dose. Information provided by these point estimates is simple: exposures above the limit value may be regarded as "unsafe", and exposures below as "safe". These procedures resulting in point estimates are called deterministic approaches, which exclude dealing with the uncertainty inherent in estimation. Historically the application of some arbitrary safety factor was at the order of the day, which ranges for a factor of 10 to 100 fold of which these factors remains unproven up to the present [56].

Several forms of uncertainty are present in toxicological risk assessment:

- **Dose-Response Relationships** – Extrapolation systems use a default factor of 10 or 3 to obtain a "No Adverse Effect Level" (NAEL) from a Lowest Observed Adverse Effect Level (LOAEL). These factors are usually not well supported by biological or statistical background data (Kalberlah *et al*, 2003).
- **Time Extrapolation** – This is extrapolation from less-than-lifetime exposures to lifetime exposure scenarios thus time extrapolation. The extent of uncertainty can be characterized by the empirical data evaluation.
- **Interspecies Extrapolation** – Allometric principles suggest that bigger species should appear more susceptible than smaller ones, if dose is related to body weight and expressed as mg per kg body weight. Factors correcting for the regular behavior are called scaling. Current scaling factors are about 7 for mice and 4 for rats [57].
- **Intraspecies Extrapolation** – A factor of 10 is usually applied for consideration of intraspecies variability (Kalberlah et. al. 2003).

Many forms of uncertainty do exist in current deterministic Risk Assessment procedures. The toxicological uncertainty is one of the major contributors to uncertainty, which ultimately affects decision-making and may flaw the purpose of Human Risk Assessment.

2.7 The Need to Estimate

There is considerable expense and technical difficulties in conducting detailed exposure assessments using ambient air and personal exposure monitoring. Due to differences in chemical properties, a fixed site monitor cannot often measure all pollutants. As a result, even when monitoring occurs, we typically do not have coverage across all hazardous air pollutants (HAPs). Therefore, modeling is the most common approach to estimate exposures within a population. Exposure assessment using modeling has four major components: emissions or source characterization, environmental fate and transport, characterization of the study population, and exposure calculation.

2.8 Monte Carlo Simulation and its Application

Propagation of uncertainties in models is usually studied by means of first order variance[1] propagation or Monte Carlo Analysis [12]. Over the years Monte Carlo simulation has become widely used in the field of environmental health and safety risk assessments (Poulter, 1998) [16]. The use of this approach has been supported by the USEPA who adopted a policy (USEPA, 1997) [21], indicating their approval of Monte Carlo simulation and other probabilistic analytical tools. The USEPA and US National Academy of Science (NAS) recognized the important role of probabilistic analysis. In March 1997, EPA issued a "Guiding Principles for Monte Carlo Analysis (USEPA, 1997b) [22]. The policy supports "good scientific practices" in quantifying variability and uncertainty (Frey, 1998) [23].

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[1] . Uncertain input parameters are independent, meaning it is not affected by changes in any other input parameter, which also may be uncertain.

Monte Carlo Simulation is a widely used computational method for generating a probability distribution (output), represented as a Frequency Distribution, on variables that depends on other variables or parameters (input). The availability and use frequency of Monte Carlo Simulation rapidly gained momentum with an increasingly dissatisfaction with the deterministic or point estimate calculations typically used in Risk Assessment (Poulter, 1998).

Monte Carlo simulation techniques have been readily applied to propagate uncertainty in a model's outcome. This method has been used in the field of water quality [28], environmental fate and exposure models [16, 23, 51, 58].

This technique has already been extensively applied to fields outside of a public health perspective. It has been readily applied to economic modeling for performing risk analysis [59], including the determination of pricing fluctuations considering past and current exchange rates [60]. Other disciplines also makes use of this useful technique for example its been applied to chemical engineering research where it was attempted to simulate turbulent drop dispersion behavior [61], and also for analyzing the effect of crystallite size in catalytic reactions, where the proportion of corners, edges, base and face atoms varies with crystallite size of which cannot be accounted with traditional continuous models [62]. In this case Monte Carlo Simulation has been applied to account for surface structure and rate processes associated with them. Monte Carlo Simulation has thus been applied to a number of fields including Engineering, Science and Business.

2.8.1 Motivation for Using Monte Carlo Simulation

There are several advantages for making use of Monte Carlo Simulation for probabilistic analysis. Output provides more information than available form point (deterministic) estimates, since output estimates (risk/concentrations) is in the form of a frequency distribution of the output that reflects the probability of the output value. These distributions display the location of any particular risk estimate within the probable range of risks. This enables decision-makers to determine that a particular risk or exposure level presents the 50th-95th or some other percentile level of risk (Poulter, 1998). The

generation of probability distributions of exposure or risk avoids the problem of compounding conservative values of input variables. Monte Carlo simulation is very useful in providing the user (s) with a sensitivity analysis on uncertain input parameters. It enables one to identify which parameters affects the outcome and which are worthwhile estimating with more precision, in order to have a more accurate assessment of risks. Monte Carlo simulation can have a huge impact in regulatory and cleanup standard determination (Smith, 1994) [63]. For example, Burmaster and Harris (1993) [64] reported that the New Jersey Department of Environmental Protection's choice for upper bound values for three exposure factors in soil ingestion risk assessment for chloroform resulted in a cancer risk estimate of
$8.3*10^{-6}$, Monte Carlo simulation in contrast results in a 95th percentile risk of $9.5*10^{-7}$, almost a factor of 10 lower.

However the need to acknowledge limitations of the Monte Carlo simulation method does exist. It requires more data; otherwise uncertainties in input parameters may result in large uncertainties in resulting risk or exposure estimates. This method requires more computer sophistication than point source calculations [16] with corresponding increases in computer costs [65]. In its most straightforward form Monte Carlo simulation usually assumes that input parameters are independent. In essence this means that the input parameters are not dependant of any other parameter that might influence it.

Monte Carlo does not dictate any particular degree of protectiveness or conservatism; it rather provides more information for implementation of policy choices. The use of Monte Carlo simulation to propagate uncertainty in the values of input variables to the output is also relatively straightforward and may be valuable to the user of the information, particularly if such techniques are combined with sensitivity analysis to determine the major and perhaps reducible sources of uncertainty, such as sampling and measurement uncertainty, that can be estimated with a reasonable degree of confidence, and thus, their incorporation in probabilistic calculation seems relatively uncontroversial. Monte Carlo simulation using probability distributions for input variables can give a measure of the overall uncertainty in the output that is attributable to the uncertainties in the input parameters.

2.9 Alternative Methods of Addressing Uncertainty in Accident Impact Analysis

Three methods for identification and quantification of uncertainty have been readily used in the field of exposure assessment. Frey and Burmaster (1999) [24] applied Bootstrap Simulation and Maximum Likelihood estimation to quantify uncertainties in the measurements of PCB concentrations in leafy produce in three databases. Results for these two approaches yielded comparable outcomes in most cases. The Bayesian statistical approach (reverse of bootstrap simulation) is another method, which is readily applied.

2.9.1 Bootstrap Simulation

Bootstrap Simulation has been frequently used in recent years for the purpose of quantifying both variability and uncertainty in energy and environmental system models (Frey, 1998) [23]. Given a data set of sample size n, the general approach in bootstrap simulation is to assume a nonparametric or parametric distribution which describes the quantity of interest to perform r replications of the original data set by randomly drawing from the distributions, with replacement, n values, and then calculating r values of the statistic (mean, standard deviation, 95th percentile or skewness of the sampling distribution for the mean) of interest [23]. Each random sample of size n is referred to as a bootstrap sample.

2.9.2 Bayesian Approach

This method reverses the role of sample and model: the sample is fixed and unique, and the model itself is uncertain. This statistical viewpoint corresponds better to the practical situation a researcher may be facing: there is only one sample and there are doubts what model to use, or, if the model is chosen, what values the parameter will take. The uncertainty of the model is modeled by assuming that the parameters of the model are distributed.

2.9.3 Maximum Likelihood Estimation (MLE)

Developed by Sir Ronald A. Fisher for fitting parametric distributions to data [40]. In general an estimator is chosen for the parameter(s) in a distribution to maximize a function of the sample observation [66].

Chapter 3: The use of Dispersion Modeling in the Analysis of Consequences of Accidental Releases

Accidents involving the release of hazardous substances continue to occur in the chemical process industries, necessitating the determination whether such incidents posed increasing risks to the well being of humans and the immediate surroundings. As already mentioned accident analyses are also required for installations, which need to comply with regulations irrespective of the country or region (SA, EU or US) where it's situated. The assessor appointed to perform these analyses should have the following information at their disposal before initiated such tasks. The release configuration either plume (continuous) or a puff (instantaneous) release, and the constructing a representative release scenario to approximate the actual process is also necessary. This is necessary to decide which type of model to employ for the determination of impacts due to the incident. The relevant input parameters can be extracted from the release scenario and local meteorological data. The model will be used to estimate the impacts providing all the relevant information has been gathered beforehand.

3.1 Dispersion Modeling

Dispersion models describe the airborne transport of toxic materials away from the accident site and into the plant and community. Air dispersion models are used to estimate the downwind concentration of pollutants emitted by various pollution sources such as industrial facilities and regional public traffic. Dispersion models play an important role in the industrial and regulatory communities. They are typically used to demonstrate compliance with National Ambient Air Quality Standards as part of new source review. After a release the pollutant is carried away from the source by the wind in a characterizing plume (Figure 3-1) and puff (Figure 3-2) manner.

Figure 3-1: Characteristic plume formed by a Continuous release of material

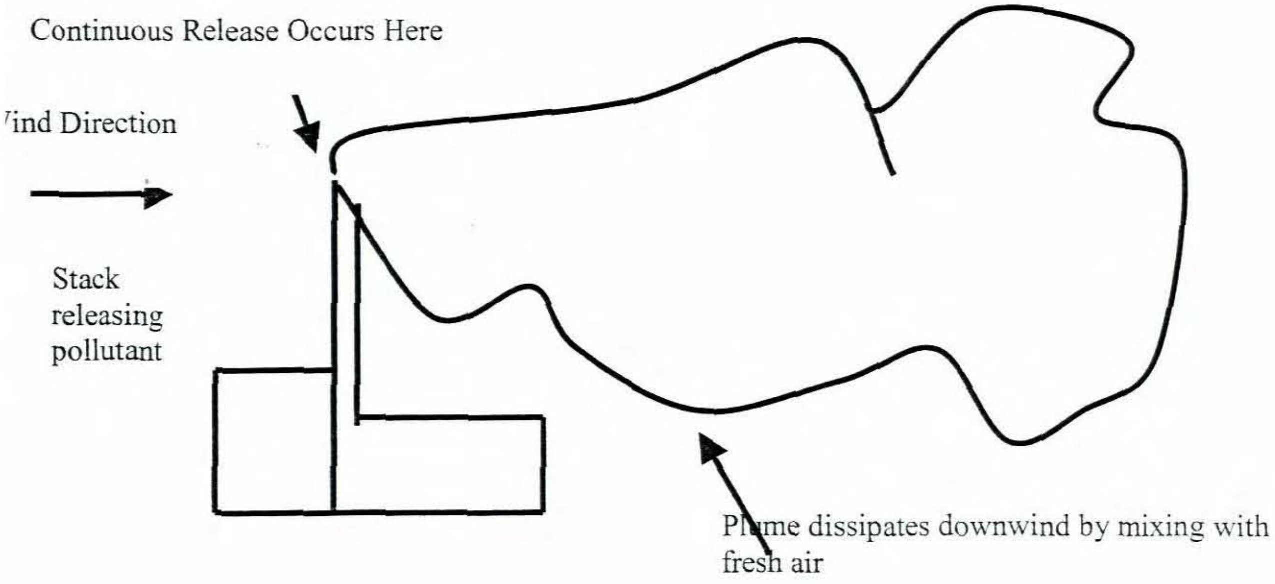
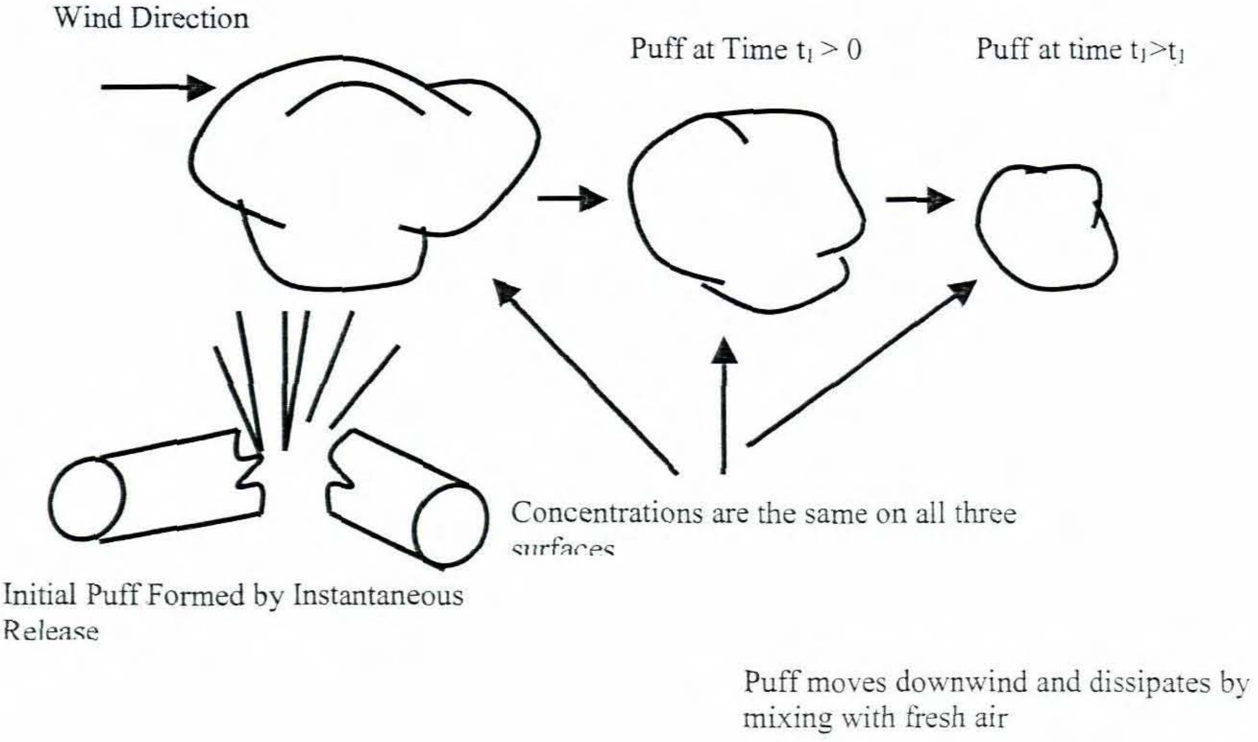


Figure 3-2: Characteristic puff formed by an Instantaneous release of material



The maximum concentration of toxic material in the atmosphere occurs at the release point (which may not be at ground level). Concentrations downwind are less, due to turbulent mixing with fresh air and dispersion of toxic substances.

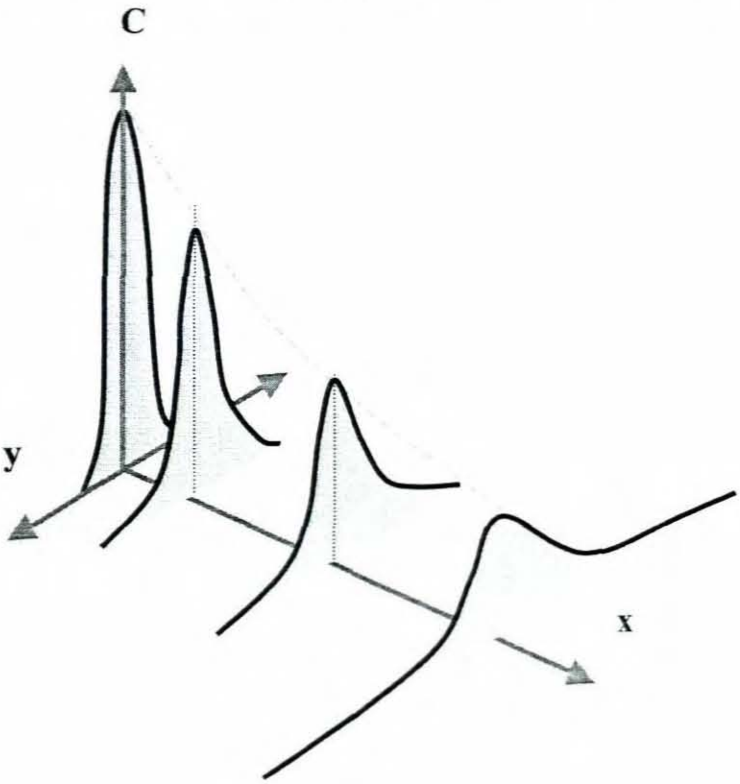
A wide variety of parameters affect atmospheric dispersion of toxic materials:

1. Wind speed - Increase in wind speed results in the plume (Figure 3-1) becoming longer and narrower, substance is carried downwind faster and subsequently diluted faster by a larger quantity of air subsequently decreasing ground level pollutant concentrations. An increase in wind speed may limit plume rise and have the reverse effect on ground level concentrations.
2. Atmospheric Stability-Relates to vertical mixing of the air. During the day the air temperature decreases rapidly with height, encouraging vertical motion, and with usual higher wind speeds at daytime, we refer to the atmosphere as unstable. This decrease in temperature in the evening is of a lesser extent (temperatures may be increasing rather than decreasing), and with lower wind speeds, vertical motion of substances is limited, presenting a stable environment.
3. Ground condition, buildings, water, trees - Ground conditions (surface roughness) affect the mechanical mixing at the surface. Trees and buildings increase mixing while lakes and open areas decrease mixing.
4. Height of release above ground level - The release height significantly affects ground level concentrations. As the release height increases, ground level concentrations are reduced since the plume must disperse over a greater distance vertically.
5. Momentum (result of the pollutant release velocity) and buoyancy (result of the release temperature) of the initial material released -These parameters affects the effective height of the release.

Two types of neutral buoyancy pollutant dispersion models are commonly used: the plume and puff models. The plume model describes the steady-state concentrations of material released from a continuous source of which a typical example is the release of gases from industrial smokestacks. The puff model describes the temporary concentration of material from a single release of fixed amount of material: sudden release of material from a rupture of a storage vessel.

Models to be used in this research are based on the Gaussian Dispersion Equations (Equations 3-1 and 3-2). [For derivation see Appendix D] The statistical assumption associated with these equations is that the material released takes on the format of a Gaussian distribution ("normal" distribution) and as it moves further away from the source the profile becomes wider and flatter (Figure 3-3).

Figure 3-3: Pollutant discharged has an average concentration that is approximately Gaussian



where 0;0;0 = pollutant source

x = wind direction

y = crosswind direction, and

C = pollutant concentration

3.3.1 Continuous Release - Plume Model [67]

The basic assumptions, which are associated with this model:

- Steady-State conditions are assumed -concentrations only average over a certain time period.
- Pollutant take on neutrally buoyant characteristics
- Constant wind speed at all locations.
- Vertical and crosswind distributions are known and Gaussian.
- Negligible mass diffusion in the x direction.
- No deposition and gravitational settling of pollutant.

Model equations if dispersion occurs in all three directions with negligible mass diffusion in the x direction as per assumption [67]

$$C_{x,y,z} = \frac{Q}{(2\pi)*U*\delta_{xy}\delta_{xz}}\exp\left[-\frac{(y)^2}{2\delta xy^2} - \frac{(Z-H)^2}{2\delta xz^2} - kt\right] \qquad \ldots\ldots \text{(3-1)}$$

Equation 3-1: Model equation for a plume (continuous) release

where: x = downwind distance from receptor (m)

y = horizontal distance from plume centerline to receptor (m)

z = elevation of receptor (m)

Q = emission rate (g/s) for a point source

U = mean wind speed affecting the plume (m/s)

δ_{xy} = horizontal standard deviation of plume at distance x (m)

δ_{xz} = vertical standard deviation of plume at distance x (m)

$C_{x,y,z}$ = pollutant concentration at point x, y and z

k = first order rate constant (decay fraction/time) (1/s)

t = time after initial release (s)

H = effective height of plume (meters)

3.3.2 Instantaneous Release - Puff Model [5]

The basic assumptions, which are associated with this model:

- Gaussian profile (Figure 3-3) is all directions: X (downwind), Y (crosswind) and Z (vertical).
- Instantaneous point source located at X=0, Y=0 and Z=0.

Model equations if dispersion occurs in all three directions

$$C_{x,y,z,t} = \frac{M}{(2\pi)^{3/2} * \delta_{xx}\delta_{xy}\delta_{xz}} \exp\left[-\frac{(x-Ut)^2}{2\delta xx^2} \quad -\frac{(y-Ut)^2}{2\delta xy^2} \quad -\frac{(z-Ut)^2}{2\delta xz^2} \quad -kt\right] \ldots (3\text{-}2)$$

Equation 3-2: Model equation for a puff release if dispersion is in all three (x, y, z) dispersing directions

where: x, y, z = location of interest relative to source (m)

x-Ut = downwind distance from puff center (m)

y-Ut = crosswind distance from plume centerline (m)

z-Ut = vertical distance from plume centerline (m)

M = emission as mass released from point source (grams/second)

U = mean wind speed affecting the plume (m/s)

δ_{xx} = downwind standard deviation of plume at distance x (m)

δ_{xy} = horizontal standard deviation of plume at distance x (m)

δ_{xz} = vertical standard deviation of plume at distance x (m)

k = first order decay (1/s)

3.4 Atmospheric Dispersion of Dense Gases

It is commonly the case that hazardous industrial material, be they flammable or toxic, produce a cloud, upon release into the atmosphere, that is denser than the atmosphere (air). The information on dense-gas dispersion that is of interest to the hazards analyst is contained in the distribution of concentration as a function of the spatial coordinates and time similar to the dilute phase dispersion expanded on in the previous section. The relatively recent research on dense – that is negatively buoyant gas dispersion should be contrasted with the far more extensive and detailed study of the dispersion of neutrally and positively buoyant pollutants [68].

3.4.1 Dense-Gas dispersion vs. Neutrally buoyant dispersion

The assessment of the dispersion of dense gases is quite different to conventional dispersion problems for the following reasons:

- Unlike chimney emissions, the modes of release are very diverse in terms of geometry and source specification,
- Because the released material is typically stored in a liquid phase, the volumes of gas released may be very large,
- The release may be a gas liquid mixture,
- The release is usually transient,
- The formation of the gas cloud typically involves phase changes, and
- There may be heat and/or mass transfer within the underlying surfaces

In addition, the dispersing gas forms a low-level cloud that is sensitive to the effects of both-man made and natural obstructions and topography.

3.4.2 Formation of Dense-Gas Clouds

The density of the cloud results not only from the properties of the material released, but also from the methods of storage and of release. Most cases of interest are covered by the following broad categories.

- Materials with a high molecular weight compared with that of air (e.g. chlorine);
- Materials with a low molecular weight that may be at a low temperature [e.g. cold methane evolving from the boiling of refrigerated liquefied natural gas (LNG) following a spill onto a warmer surface];
- Materials with low molecular weight and whose vapor at the boiling temperatures is less dense than the environment, but which as a result of the release type

produce a cloud including material droplets. The cloud-borne droplets increase the cloud density, as does the cooling resulting from their subsequent evaporation [69].

- Materials in which a chemical transformation takes place as a result of reaction with water vapor in the ambient atmosphere [e.g. nitrogen teroxide (N_2O_4), hydrogen fluoride (HF) (Britter, 1989)]

3.4.3 Dispersion models for Dense Gases

Earlier attempts to modifying conventional Gaussian dispersion models was found to be inadequate when experimental results became available in the 1970's (Britter, 1989). Their use had, in part led to uncertainty in predictions of nearly two orders of magnitude [70]. Subsequent model development has been along two distinct lines.

1. Referred to as three-dimensional, time dependant models, addresses the Reynolds's-averaged, three-dimensional, time dependant conservation equations. The most common of these use empirical *K*-theory for turbulent closure. With these models "severe numerical problems may be encountered".
2. The second and simplest approach is basically and integral formulation, with any variations in the cloud or plume in the vertical or lateral direction integrated out and if appropriate, later reincorporated through empirically determined profiles; this a common approach for many applied problems in fluid mechanics [68]. These models are referred to as box models. Though limited in their flexibility, they have only a small number of adjustable constants, whose effects may be easily interpreted physically.

Chapter 4: A Methodology for the Quantification of Uncertainty in Exposure Assessment for Accidental Releases of Hazardous Substances

Hazardous substances will be selected based on its ranking in terms of production, usage, toxicity and frequency of involvement in accidental releases. A substance should be ranked high up the order in one or the other category. It should also be representative of the three most common types of releases, thus selecting three substances. Three case studies drawn from real life accidental releases, will serve as a basis for modeling to firstly estimate the likely impacts at the time of the incidents, disregarding the possibility of uncertainty (deterministic approach), and secondly taking these uncertainty of modeling inputs into consideration, and quantifying the uncertainty (probabilistic approach). One of the incidents occurred in South Africa and the remainder from abroad. Models to estimate impacts from accidental releases were selected based on applicability, desired outcome and availability. A discussion of the model's capabilities, output options and limitations follow, including its various input parameter requirements. The incorporation of Monte Carlo Simulation using @ Risk to quantify uncertainty follows.

4.1 Criteria for the selection of hazardous substances

Three substances, and releases (pollutant) types representative of neutrally buoyant dispersion, dense phase dispersion and a fire and explosion event, will be selected for the purpose of quantifying the uncertainty inherent in the determination of receptor exposure levels. Release scenarios will be constructed based on real life accidental releases.

4.1.1 Basis for selecting hazardous substances

- Production/Usage rates in South Africa, UK and US. This should support the likelihood that accident frequency is coupled to production volumes and will serve as a guideline for hazardous substance selection.
- Frequency of involvement in accidents. The more frequently the substance is involved in an accidental release, the more likely it will surface again in the future.

- Severity (deaths, injuries etc.) of accidents. The severity of past accidents i.e. deaths, injuries and the loss of property serves as a guideline as to which substance will be selected for investigation.
- Toxicity of chemicals. The more toxic, the more likely the substance may be used in this research

Finally the substances and its corresponding release characteristics should be representative of the three major forms of dispersion dynamics, which are:

- Neutrally buoyant (substance density similar to that of air) type of release.
- Dense (gas substance density higher than air density) release.
- A release of a flammable substance, ignition and an explosion.

Chemicals already been selected based on the above criteria, will be subject to a hazards assessment, to give an indication of its potential harmful effect due to possible human exposure.

4.2 Model Selection

The model selection will be based on the desired output, model's applicability, and availability and user friendliness. The research will not focus on model accuracy but rather attend to the introduction of a probabilistic method for exposure assessment. Three well-established USEPA supported models will be selected and used in this application to quantify uncertainty, and it should be capable of handling puff releases, since this is the most likely type of release for accidental scenarios.

4.2.1 Air Force Toxic Chemical Dispersion Model (AFTOX)

The latest version of the US Environmental Protection Agency's Air Force Toxic Chemical Dispersion Model (AFTOX) was downloaded from the US EPA's Support Center for Regulatory Air Models (SCRAM) [71].

4.2.1.1 Capabilities

- AFTOX is a Gaussian model capable of simulating both puff and plume releases.
- It was developed by the U.S. Air Force to model neutrally buoyant gaseous releases.
- Both gas and liquid (evaporating to a neutrally buoyant gas) sources can be modeled with AFTOX.
- Source types include point, area, and liquid spill sources.

4.2.1.2 Output options

- Output consists of concentration contour plots,
- concentration at a specified location, and
- maximum concentration at a given elevation and time (Kinkel, 1991) [72].

4.2.1.3 AFTOX Limitations

- AFTOX is not capable of modeling dense (heavier than air) gas dispersion.
- Model output may be very unreliable if releases in low wind speed (, < 1.5 m/s) conditions are modeled, and
- it is not able to models releases where substances undergoes chemical reactions in the atmosphere, and thus neglects the decay variable in the modeling equations (equations 3-1 and 3-2).

4.2.2 Aerial Location of Hazardous Atmospheres (ALOHA) (NSC, 1996) [73]

4.2.2.1 Capabilities

- ALOHA is an air dispersion model, which can be used for predicting the movement and dispersion of gases.
- It can account for both neutrally buoyant and dense gas releases.
- Predicts pollutant concentration downwind and if necessary crosswind variation may be included from the source or spill, taking physical characteristics of the material, the physical characteristics of the site, weather conditions and release circumstances into consideration.

4.2.2.2 *Output options*

- ALOHA simulates the dispersion of a cloud of pollutant gas in the atmosphere. The main output is a diagram that shows a plan view of the area within which it predicts the gas concentration in air will reach hazardous levels. This is known as the hazardous footprint. This footprint indicates that the user defined hazardous concentration (e.g. IDLH) will be exceeded for that particular footprint width and length at some time after the release. ALOHA will be utilized to model a possible heavy gas (Cl_2) release.

4.2.2.3 ALOHA *Limitations*

ALOHA results can be unreliable when the following conditions exist:

- Very low wind speed. The lowest wind speed acceptable is 1m/s
- Very stable atmospheric conditions. This condition is normally associated with low wind speeds and late at night and early mornings.
- Wind shifts and terrain steering effects. ALOHA assume wind speed and direction remain constant throughout the footprint distance, and the model ignores obstacles that might affect the direction in which the plume moves.

ALOHA does not account for the effects of:

- fires and chemical reactions.
- particulates (Small particles that are light enough to float suspended in air), and
- chemical solutions and mixtures

4.2.2.4 ALOHA Validation

Its heavy gas dispersion calculations are based on those used in the DEGADIS (Dense Gas Dispersion) models (Spicer and Havens, 1989) [74], hence the ALOHA heavy gas model is known as the ALOHA-DEGADIS model. The DEGADIS model algorithm was selected because of its general acceptance and the extensive testing carried out by its authors.

A few simplifications were introduced in the ALOHA-DEGADIS model, which makes it different from the original DEGADIS model. These are:

- Does not use the OOMS model [70] for elevated sources to account for the initial momentum of a Jet release-assume Heavy Gas release originates at ground level.
- The mathematical approximation procedures used for solving the model's equations are faster, but less accurate than those used in DEGADIS.

Throughout the creation of ALOHA-DEGADIS, the National Oceanic and Atmospheric Administration (NOAA) worked closely with the original authors of the DEGADIS to ensure a faithful representation of the DEGADIS model dynamics. These two models were checked against each other to ensure that only minor differences existed in results obtained from both [73].

4.2.3 RMP*COMP

Can be downloaded from http://yosemite.epa.gov/oswer/ceppoweb.nsf/content/comp-dwn.htm free of charge.

RMP*Comp is a free program which can be used to perform offsite consequence analyses required under the EPA's Risk Management Planning (RMP) rule, which implements Section 112(r) of the 1990 Clean Air Act [8]. Results obtained using RMP*Comp may not closely match the results generated by running the same release scenario in a more sophisticated air dispersion model such as ALOHA or DEGADIS. That's because of a fundamental difference in purpose between those models and RMP*Comp. RMP*Comp is a planning tool designed to help you to easily identify high-priority hazards at a facility. It relies on very simplified and generalized calculations. In contrast, models like ALOHA and DEGADIS are intended to give you as accurate an estimate as possible of the extent and location of the area that might be placed at risk by a particular chemical release. It account for many more of the factors that influence the dispersion of a hazardous chemical. (For this reason, when you need to make decisions during an actual response, use only models like ALOHA or DEGADIS, not RMP*Comp.)

4.2.3.1 Capabilities

This model contains some capabilities of which may not be present in some of the more sophisticated models. It however consists of capabilities generally associated and expected of models used whether for prevention, planning or analysis application.

- The chemical list contains all the substances stipulated under the RMP Rule {Appendix B1 and B2] and it includes both toxic (dilute/dense) and flammable substances.
- It has the ability to model more than one flammable substance released simultaneously.
- Can model release types such as a BLEVE, Vapor Cloud Explosion and a Pool Fire, which is often difficult to construct.
- Provision was made to model possible releases with mitigation measures that may be in place at a particular facility.
- The facility's immediate surroundings are also taken into consideration via an urban/rural check box.
- Determines hazard distances up to a maximum distance of 40km (25 miles).

4.2.3.2 Output options

- For toxic substances, estimates the maximum distance to the toxic endpoints specified, which in most cases is the ERPG (2).
- The maximum distance to 1psi over pressure as stipulated by the RMP Rule is the quantitative measure used for the flammable substances, and also estimates the maximum distance at which 2nd degree burns will be experienced.

4.2.3.3 RMP*COMP Limitations

Perhaps the most limiting aspect of this model is that the user does not have access to specify applicable meteorological data. The model selects wind speed, stability class and ambient temperature based on location (longitude and latitude), the time of year and the applicable time zone. RMP*Comp is based on a series of look-up tables. The model provides no calculations. Model outputs are incremental, not continuous and the increments, irrespective of the desired endpoint, are in the order of 100 units.

4.3 Input Parameter Requirements

4.3.1 AFTOX

Table 4-1: Input parameter requirements and possible ranges of these parameters for the AFTOX model

Input variable	Range of possible values	Comments
Wind speed	1.5 – x m/s	The upper limit to the wind speed is not known, but a wind speed below 1.5 m/s results in dispersion modeled in all directions. In other words the direction in which the plume will be moving is unknown due to the uncertainties surrounding low and calm wind speeds.
Wind direction	0 – 359 °	0° represents a southerly (south to north) wind and 90° a westerly (west to east) wind etc
Ground roughness	0 –100 cm	AFTOX has 5 values, which describes the surrounding area, and its orientation (rural/urban). 0 denotes flat areas such as snowy areas and water bodies with relative little obstacles. 100 represent an urban like configuration. This parameter is continuous thus any value between 0 and 100 cm may be selected.
Release duration	1 – 60 min or continuous release	The model has a default setting of 1 min. incorporated into it. It is however possible

		to modify this setting to the desired release duration (<1min. and up to 60min).
Input variable	**Range of possible values**	**Comments**
Inversion Height	No range	No limits have been set on this parameter
Ambient temperature	No range	No limit is been set on this parameter
Concentration averaging times	1 – x value	The model is capable of handling any averaging time above 1 min. but if the pollutant source is modest in case of a puff release, too high an averaging time will be disregarded by the model and reverted back to the default setting of 1 min.
Height of release above ground (m)	0 – x value	This parameter does not have any limit. If it exceeds that of the inversion layer height, a parameter such as ground roughness is not considered in dispersion calculations.
Release quantity (kg)	No range	AFTOX is capable of modeling any given quantity of pollutant released.
Cloud cover (eights)	1/8 to 8/8	The cloud cover can be categorized into 8 different possible combinations. 1/8 being the least amount of clouds in the immediate area and 8/8 suggesting a cloudy day.

4.3.2 ALOHA

Source Data: Physical characteristics of the release (Tank, direct, pipe or from a puddle including its dimensions), contaminant name, release temperature of contaminant (^{o}C), release rate (kg/s) or quantity released (kg), source height and diameters in meters (e.g. hole size).

Meteorological Data: Ambient atmospheric temperature (^oC), wind velocity (m/s), wind direction (deg.), anemometer height (m), stability class (A-F), surface temperature if heavy gas release (^oC), relative/absolute humidity (%), Cloud Cover (tenths).

Topography: Ground Roughness (m)

Output Options: Hazardous Footprint, Peak concentration at a specified location for the first hour after the release or spill and the dose (time-concentration integral), which possible receptors might receive for the first hour after the release.

4.3.3 RMP*COMP

Source Data: Contaminant name, Quantity released (M) or it estimates the Release rate (M/T) via the hole area and height of liquid column above the hole.

Topography: Rural/Urban configuration

Output Options: Maximum distance to the toxic endpoint for toxic substances and the maximum distance to 1psi overpressure for the flammable substances especially where an explosion might occur.

4.4 Justification for using 50 samples

Previous studies incorporating Monte Carlo simulation had a variety of sample sizes ranging from as little as 500 to 5000 different scenarios [32,75]. It is common knowledge that the bigger the sample sizes the more representative estimates is of the true population. Studies where statistical methods are utilized may require an infinite number of samples or input combinations for estimation to be representative of the true population.

This necessitated determination of the required sample size, significance of 0.005 and an applicable tolerable error for each individual case. Sample size required to achieve a 99% confidence in estimates were calculated at 30 samples for the SO_2 release. A consistent factor for the tolerable error was used, which was selected to be 10% of the computed standard deviation for individual case studies.

4.4.1 Sample Calculation of sample size requirement

A preliminary study of 10 iterations was performed to determine a mean and standard deviation for the SO_2 concentration at the school, making use of the same probability distributions that will be used in the final assessment of concentrations. Results are presented in Table 4-2 below.

Table 4-2: Preliminary SO_2 concentrations

Iteration Number	1	2	3	4	5	6	7	8	9	10
Peak SO_2 Concentrations (ppm)	3.2	2.2	4.5	5.8	5.2	4.9	7.5	3.1	5.1	1.9

The mean for the above was calculated at 4.4 ppm with a standard deviation of 1.63 ppm. The equation used to determine sample size requirements was as follows:

$$n = \left(\frac{z_{\alpha/2} \times \sigma}{E} \right)^2 \qquad \text{...eqn. 4-1[76]}$$

where:

n = sample size required

$z_{\alpha/2}$ = level of confidence

σ = standard deviation (ppm)

E = tolerable error (ppm)

The z value is obtained from tables of normal distribution at various confidence levels e.g. at 99% confidence (used in this study) it takes on the value of 2.58. The tolerable error is one the user decides on. In this case it was selected that 99% of estimates only deviate from the mean by 0.44 (50% of the preliminary mean) or less for the sample size to be calculated, the same will account for the other cases.

Calculation:

$$n = \left(\frac{2.58 * 1.63}{0.82} \right)^2 = 26$$

4.4.2 Sample size requirements for all three cases

The table below illustrates the required sample for each substance and its various endpoints. The method is making use of a tolerable error, which is calculated, at 10% of the preliminary computed mean. In this thesis 50 samples will be used for each of the 3 assessments.

Table 4-3: Summary of sample size requirement for each case study

Variables	**Chlorine**		**Propane**	
	Distance to toxic endpoint	Outdoor Concentration	Distance to 1psi overpressure	Radiation endpoint
Level of Confidence (%)	99	99	99	99
Preliminary Computed mean	1.45 km	10.9 ppm	464 meters	479 meters
Standard deviation	0.35 km	2.80 ppm	67 meters	70 meters
Tolerable error	0.145 km	1.09 ppm	46.4 meters	47.9 meters
Sample Size Required	39	44	14	14

4.5 Monte Carlo Simulation using @ Risk

This software program is based on a technique in computational mathematics called Monte Carlo simulation. @RISK allows decision-makers to explore the *range of possible outcomes* for any decision by using probability distribution functions to represent uncertain parameters in models set-up via spreadsheet models only. During a simulation,

@RISK randomly samples from the probability distribution functions specified by the user, and records the resulting outcomes. This enables the users to look at literally thousands of scenarios [77]. @ Risk operates via Microsoft™ Excel. Uncertain input parameters have to be identified, and characterized by user-defined probability distributions. These distributions should describe the general trend of the particular input parameter i.e. most likely, maximum, minimum values.

4.6 Uncertainty Investigation

In the majority of accidental or routinely released substances uncertainty regarding some if not all of the input parameters exists. This corresponds to uncertainty in the exposure estimates. The value of modeling outputs can be greatly enhanced if uncertainty in the exposure estimates can be identified and quantified. In this thesis this procedure is developed and illustrated through generating a frequency histogram or curve representing the probability of occurrence of a given output value or range of values by the application of Monte Carlo simulation.

4.6.1 How Monte Carlo Simulation will be used?

Three accidental releases will be constructed into case studies to determine the impacts (pollutant concentrations, radiation and overpressure) at which possible receptors might have been exposed to. Uncertain parameters will be identified. Distributions representative of particular parameters will be assigned to those parameters. @Risk will generate a minimum of 50 iterations (randomly changing input parameters simultaneously taking the assigned distribution in consideration). Since @Risk is unable to interact directly with the AFTOX, ALOHA and RMP*Comp models, which are either MS Dos based or interactive programs the following method was followed. We extracted all the iterations from the @ Risk program via Microsoft™ Excel, thus allowing the user to have 50 different release scenarios for which the uncertain input parameters have been randomly selected and changed simultaneously. This approach should generate similar results if compared to the common approach applying the @Risk software, which is driving the software as an add-in through Microsoft™ Excel. A re-run of the models for that number of iterations specified (50) commenced and desired output (impacts) extracted. A flowchart of this method can be viewed in **APPENDIX E**.

4.6.2 Methods used to quantify uncertainty

Output from Monte Carlo simulation will be in the form of a Probability Frequency Distribution (PFD). A Cumulative Frequency Distribution (CFD), which enables us to express impacts in terms of probabilities, will be derived from the PDFs (see **APPENDIX F** for a demonstration how the PDFs and CFDs were derived). Confidence intervals in estimates can be extracted from the CFDs, which allow decision makers to evaluate impact estimates based on a range of possible values, and the confidence level associated with the range.

The mean and standard deviation will be computed for the exposure concentrations. This will be compared to the initial point/deterministic estimates, which did not take uncertainty into consideration.

Chapter 5: Results

Data from three major countries (US, UK and SA) were collected to determine which chemicals would serve as the basis for modeling and quantification of uncertainty in input parameters. Data categories range from production, usage and accidental frequency in the respective countries. These chemicals were subjected to a brief hazards assessment to indicate the potential risks posed at the time of the incidents. Descriptions of real life accidents involving these substances were obtained from various sources. The models consistent with and applicable to the release types were selected from the three modeling tools formerly identified. The necessary input requirements for the various models were extracted for usage in model predictions. Initially modeling predictions for these releases did not incorporate uncertainty, which followed directly afterwards. Uncertain input parameters were identified and a distribution assigned to each. The re-run (50 iterations) of the model followed, which resulted in a range of outputs enabling us to derive Frequency Distributions and Cumulative Frequency Distributions, and carry out a Statistical Analysis of results. At this stage results incorporating uncertainty and those excluding uncertainty estimates were compared.

5.1 Selection of Hazardous Substances

5.1.1 South African data: Usage Annually (C&AIA) [78]

Table 5- 1: Annual chemical usage figures per annum (1993/1994) in South Africa (SA)

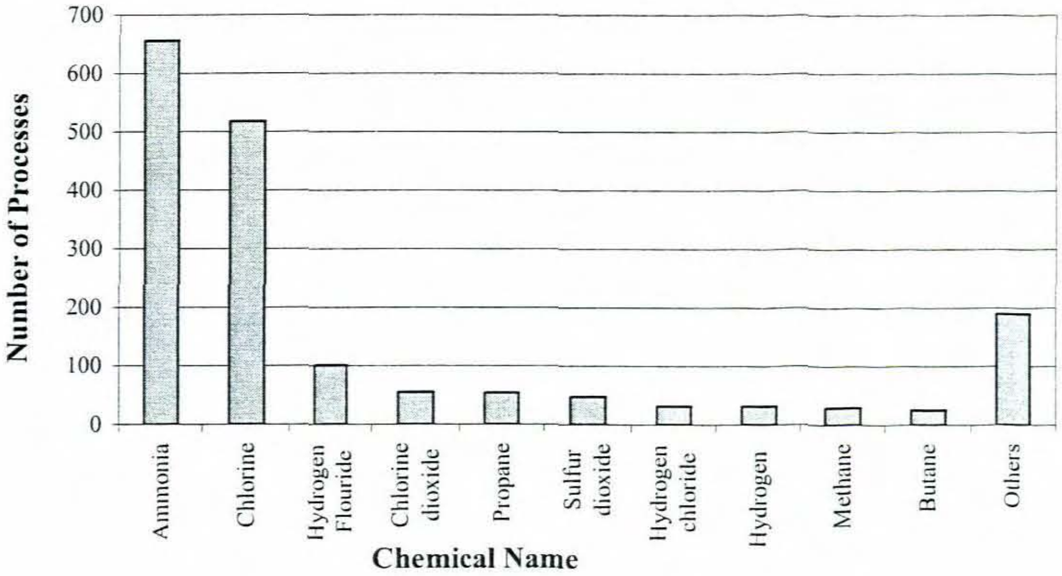
Chemical	Annual usage in SA (tons)	Order Ranking per Usage
Sulphuric acid	3 000 000	**1**
Calcium oxide (quick-lime)	*1 950 000*	**2**
Ammonia	596 000	**3**
Nitric acid	470 000	**4**
Sodium chloride	400 000	**5**
Sodium carbonate (Soda ash)	340 000	**6**
Solvents e.g. acetone	340 000	**6**
Sulfur	340 000	**6**
Propylene	330 000	**7**
Ethylene	280 000	**8**
Calcium hydroxide	250 000	**9**
Phosphoric acid	240 000	**10**
Sodium hydroxide	240 000	**10**
Potassium chloride	190 000	11
Chlorine	160 000	12
Polyethylene (low density and linear low density)	150 000	13
Manganese dioxide	150 000	13
Alpha-olefins e.g. 1-hexene	120 000	14
Polyvinyl chloride (PVC)	120 000	14
Hydrochloric acid	110 000	15
Polyethylene (high density HDPE)	105 000	16
Sodium sulfate (Salt cake)	90 000	17
Calcium carbonate	80 000	18
Polypropylene	75 000	19
Aluminium sulphate	74 000	20
Ethyl alcohol	60 000	21
Sodium tripolyphosphate	46 000	22
Carbon black	45 000	23
Calcium cyanide	36 000	24
Ethylene glycol	35 000	25
Methyl alcohol	10 000	26

5.1.2 United States of America

Figure 5 -1 reports accidents by listed chemical involved in accidents for the 10 most frequently involved for the period 1994 to 1999. Appendix G1 gives the full list of 24 chemicals. Accident frequency ranged from 656 for anhydrous ammonia to 8 accidents for Acrylontrile for the reporting period.

5.1.2.1 Chemical Accident Frequency: (Belke, 2000) [79]

Figure 5-1:Frequency Distribution of Accidents Reported in the period 1994-1999



5.1.2.2 Top 20 Chemical Production Figures Annually (USA)

The annual production of various chemicals in millions of tons in the years 1994 and 1995 can be seen in Table 5 –2, and is presented in descending order.

Table 5 - 2: Chemical Production per chemical in millions of tons in the US (1994 and 1995)

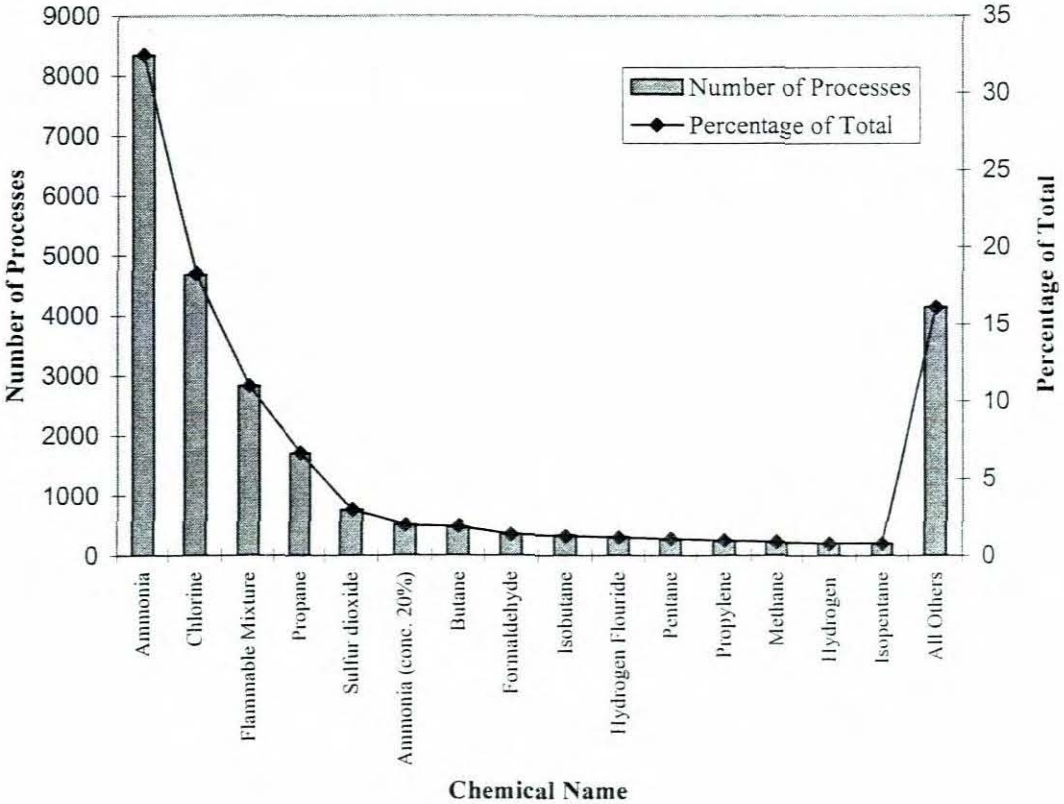
Rank		Chemical Name	millions of tons.	
1995	1994		1995	1994
1	1	Sulfuric acid	43.26	40.66
2	2	Nitrogen	30.86	28.99
3	3	Oxygen	24.26	22.72
4	4	Ethylene	21.31	20.23
5	5	Lime (b)	18.70	17.40
6	6	Ammonia	16.15	15.65
7	7	Phosphoric acid	11.88	11.60
8	8	Sodium hydroxide	11.88	11.39
9	10	Propylene	11.65	10.86
10	9	Chlorine	11.38	11.05
11	11	Sodium carbonate(c)	10.11	9.33
12	18	Methyl *tert-butyl* ether	7.99	6.17
13	14	Ethylene dichloride	7.83	7.60
14	12	Nitric acid	7.82	7.81
15	13	Ammonium nitrate (d)	7.25	7.72
16	16	Benzene	7.24	6.93
17	15	Urea (e)	7.07	7.21
18	17	Vinyl chloride	6.79	6.28
19	22	Ethylbenzene	6.20	4.88
20	21	Styrene	5.17	5.12

The full list of figures can be viewed in **Appendix G2**

5.1.2.3 Frequency Distribution of RMP Chemicals used in various Processes: (Belke, 2000)

Figure 5-2 illustrates the distribution of chemicals present in all of RMP processes reported up to the year 2000. Processes are defined as a facility processing the chemical e.g. ammonia is used in its daily operation by more than 8,000 facilities. The percentage of the total per chemical is also presented on the figure below. Annual usage of RMP chemicals in various processes can be obtained from Figure 5-2.

Figure 5-2: Graphical Distribution of Chemical Usage in Various Processes



Full list of figures can be viewed in **Appendix G3**

5.1.2.4 Accidents Rate by Chemical Type: (Belke, 2000)

Table 5 –3 indicates the rate of accidents for each chemical divided by the total number of processes in which the chemical is either used or stored, and the rate of accidents for that chemical divided by the total quantity of the chemical in all processes containing it. This table contains information on all those RMP chemicals involved in more than 10 accidents over the 5-year period.

Table 5 - 3: Normalized Accident Rates for RMP Chemicals, 1994-1999

Chemical Name	Number of accidents per process per Year	Rank	Number of Accidents per million of kgs stored per year	Rank
Chlorine Dioxide	0.155	1	4.334	2
Hydrogen Sulfide	0.067	2	1.100	3
Hydrogen Fluoride	0.064	3	0.594	4
Hydrogen Chloride	0.06	4	0.550	5
Titanium tetrachloride	0.056	5	0.198	9
Phosgene	0.044	6	5.478	1
Vinyl Chloride	0.042	7	0.011	19
Nitric Acid	0.038	8	0.103	10
Trichlorosilane	0.034	9	0.220	8
Hydrogen	0.031	10	0.528	6
Methane	0.027	11	0.014	17
Ethylene Oxide	0.027	12	0.099	11
Chlorine	0.022	13	0.352	7
Oleum	0.022	14	0.024	16
Ammonia (aqueous)	0.017	15	0.040	13
Ammonia	0.016	16	0.031	14
Ethane	0.014	17	0.002	25
Ethylene	0.014	18	0.002	22
Pentane	0.013	19	0.011	18
Sulfur Dioxide	0.013	20	0.024	15
Butane	0.011	21	0.002	23
Isobutane	0.01	22	0.024	21
Formaldehyde	0.009	23	0.053	12
Flammable Mixture	0.007	24	0.002	24
Propane	0.006	25	0.003	20

5.1.3 United Kingdom

5.1.3.1 UK Annual Production Figures

The annual production figures in the UK for the period 1992 to 1995 can be viewed in descending order for the year 1995 in Table 5 –4 [80].

Table 5 - 4: Annual production figures per chemical in the United Kingdom (UK)

Millions of kilograms.	1992	1993	1994	1995
Ethylene	4,263	2,557(l)	2,847	2,571
Sulfuric acid	2,170	2,699	2,134	2,153
Polyethylene (i)	693	658(l)	1,598	1,720
Sodium hydroxide	1,993	na	1,775	1,704
Propylene	1,835	632	1,701	1,432(m)
Benzene	1,717	818(l)	1,149	1,462
Synthetic rubber	558	762(l)	979	945
Polyvinyl chloride	647	724(l)	799	854
Chlorine	1,980	1,980	832	607
Hydrochloric Acid	328	463	381	437
Carbon black	na	361	395	413(k)
Polypropylene	721	821(l)	484	394
Calcium carbonate	na	na	357	361
Formaldehyde	131	214(l)	187	265
Toluene	na	257(m)	185	226

a C&EN estimate based on 10 months' data. **b** As N. **c** As P_2O_5. **d** Data for 1992 are for West Germany only, subsequent years are for unified Germany. The classification system changed in 1995, and data are not necessarily directly comparable. **e** C&EN estimate based on nine months' data. **f** High density.

g Compounded nitrogen fertilizers, as N. **h** Includes C&EN estimates based on 6 months' data.

i Compounded phosphate fertilizers. **j** U.K. data collection revised in 1993 to be based on manufacturers' sales; previous years' data are not comparable unless shown as revised; 1995 data are C&EN estimates based on nine months' data. **k** C&EN estimate based on three months' data. **l** Revised. **m** C&EN estimate based on six months' data. **na** = not available.

5.1.4 Comparison of Chemical production and usage figures on an annual basis: Summary Table for all three countries

The table below is an extract from tables presented above and represents the top 15 chemical production and usage figures in different categories. Chemicals are ranked in descending order.

Table 5 -5: Top 15 chemicals produced and used annually in each of the three countries

Order Ranking	South African Usage per year	US Chemical Production per year	UK Chemical Production per year
1	Sulphuric acid	Sulfuric acid	**Ethylene**
2	Calcium oxide (quick-lime)	Nitrogen	Sulfuric acid
3	**Ammonia**	Oxygen	Polyethylene (i)
4	Nitric acid	**Ethylene**	Sodium hydroxide
5	Sodium chloride	Lime (b)	Propylene
6	Sodium carbonate (Soda ash)	**Ammonia**	Benzene
7	Solvents e.g. acetone	Phosphoric acid	Synthetic rubber
8	Sulfur	Sodium hydroxide	Polyvinyl chloride
9	Propylene	Propylene	**Chlorine**
10	**Ethylene**	**Chlorine**	Hydrochloric Acid
11	Calcium hydroxide	Sodium carbonate(c)	Carbon black
12	Phosphoric acid	Methyl *tert-butyl* ether	Polypropylene
13	Sodium hydroxide	Ethylene dichloride	Calcium carbonate
14	Potassium chloride	Nitric acid	Formaldehyde
15	**Chlorine**	Ammonium nitrate (d)	Toluene

5.2 Chemicals to be used as a basis for modeling

The following substances were selected for modeling and estimation of exposure parameters, and to illustrate the usage of probabilistic analysis in Air Pollution Modeling. Justification for usage is that in one or the other category (usage, production, accident frequency) it features in a high ranking, and it should also be representative of all three common different types (dilute, dense & flammable) of release scenarios. The toxicity to humans also played a critical role in selection.

5.2.1 Chlorine

Chlorine's usage in South Africa is ranked 12th overall with an annual usage of 160,000 tons in all of the chemical industry (Table 5-1). Table 5-5 represents it as being ranked 15th, this because some chemicals above chlorine is ranked having similar usage volumes. In the US Chlorine is ranked 2nd in terms of it's accidental frequency from the years 1994 to 1999 with a gross total of 518 accidents reported in this time period (Figure 5-1). It's extensively used or stored at various facilities (Figure 5 - 2) and represents 18.3 % of facilities in the US either use or store chlorine. Ammonia is predominant due to its widespread uses, including fertilizer production, refrigeration and land application as an agricultural nutrient. The high number of chlorine processes is mainly due to the common uses of chlorine for water disinfection. Production figures (Table 5 -2) reveals that chlorine is the 10th highest chemical produced within the US, and is ranked 13th and 7th i.t.o. the number of accidents per process per year and per million lb. stored per year (Table 5 – 3) respectively for chemicals listed under the US. EPA Risk Management Plan. In the UK a considerable decrease in chlorine production volumes were experienced within a 4-year period, it was ranked in the top 4 for 1992 and 9th by the year 1995. Table 5 –5 reveals that chlorine is ranked within the top 15 in terms of production for the US and UK, and is ranked high up the order for usage amounts in South Africa.

The well-documented toxicity of chlorine also supports further investigation into accidental release impacts. Chlorine gas released under specific conditions and due to its physical properties may represent a typical dense (heavier-than-air) gas dispersion type necessary for this research.

5.2.2 Sulfur Dioxide

SO_2 is produced as a by-product in many processes, thus the determination of annual production is not possible. Involvement in accidents (6th i.t.o. number of accidents only) in the US and the frequent emissions of SO_2 gas into the atmosphere by a variety of industries makes it viable to be selected it as one of the pollutants be investigated. SO_2 is ranked 20th and 15th in terms of the number of accidents per process per year and number of accidents per million of kilograms stored per year respectively listed under the USEPA Risk Management Plan. (Table 5 -3). SO_2 is also selected to represent a typical neutral buoyant (dilute) gas type of release and dispersion characteristics.

5.2.3 Propane

The selection of propane is mainly based on its representation of an unstable type of release. It has the ability to cause several types of outcomes, such as a BLEVE, a vapor cloud explosion or may result in a minor toxic cloud with all sorts of repercussions.

In the US propane is ranked 5th in terms of it's accidental frequency from the years 1994 to 1999 with a gross total of 54 [see **Appendix G1**] accidents reported in this time period (Figure 5-1) and is ranked above some other very important flammable liquids which belongs to the LPG family such as butane. It's extensively used or stored in several of facilities (Figure 5 - 2) and represents 6.7 % [see **Appendix G3**] of total chemical usage in the US ranked 4th overall. Propane is ranked 25th and 20th in terms of the number of accidents per process per year and number of accidents per million lb. stored per year respectively listed under the US. EPA Risk Management Plan. (Table 5 –3).

5.3 Hazard Assessment

5.3.1 Chlorine

5.3.1.1 Acute Effects

Chlorine is a commonly used household cleaner and disinfectant. Chlorine gas is irritating and corrosive to the respiratory tract, eyes, and skin. The effects depend on the concentration you are exposed to and for how long. Exposure to low concentrations of chlorine gas (1 to 10 ppm) may cause sore throat, and eye and skin irritation and coughing. Exposure to higher levels could cause burning of the eyes and skin, rapid breathing, narrowing of the bronchi, wheezing, blue coloring of the skin, accumulation of fluid in the lungs, and pain in the lung region. Exposure to even higher levels can produce severe eye and skin burns, lung collapse, and death. (US HHS, 1999) [81].

5.3.1.2 Chronic Effects (No cancer)

Chronic (long-term) exposure to chlorine gas in workers results in respiratory effects, and airflow obstruction (CalEPA, 1999) [82]. No information is available on the carcinogenic effects of chlorine in humans from inhalation exposure.

5.3.1.3 Reproductive/Developmental Effects

No information is available on the developmental or reproductive effects of chlorine in humans or animals via inhalation exposure.

5.3.1.4 Cancer Risk

No information is available on the carcinogenic effects of chlorine in humans from inhalation exposure. An NTP study reported no evidence of carcinogenic activity in male rats or male and female mice, and equivocal evidence, based on an increase in mononuclear cell leukemia, in female rats, from ingestion of chlorinated or chlorinated water (National Toxicology Program, 1992) [83]. EPA has not classified chlorine for carcinogenicity (USEPA, 1999) [84].

The following table summarizes the standards and guidelines applicable to Cl_2 (Table 5-6)

Table 5 - 6: Summary of Cl_2 Standards and Guidelines

Type	Name	Averaging time	Concentration (ppm)
Occupational	U.S. NIOSH/OSHA STEL[2]	15 min	1.0
Occupational	U.S. ACGIH/TLV-TWA[2]	8 h	0.5
Emergency	Immediately Dangerous to Life and Health (IDLH)[3]	30 min	10.0
Emergency	Emergency Response Planning Guideline-2 /ERPG (2)[4]	1 h	3.0

5.3.2 Sulfur Dioxide [85]

Colorless gas with a pungent, irritating odor similar to burning sulfur. Colorless liquid below -10 deg C. Will not burn. Cylinders or tanks may rupture and explode if heated. Very Toxic. May be fatal if inhaled. Extremely irritating to eyes and respiratory tract.

Causes lung injury, effects may be delayed. Liquid chlorine may cause frostbite.

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[2] NIOSH/OSHA (ACGIH, 1980): The maximum concentration to which workers can be exposed for a short period of time (15 minutes) for only four times throughout the day with at least one hour between exposures.

[2] US ACGIH/TLV-TWA: Airborne concentrations of substances devised by the ACGIH that represents conditions under which it is believed that nearly all workers may be exposed day after day with no adverse effect.

[3] IDLH: Immediately dangerous to life or health concentrations represent the maximum concentration from which one could escape within 30 minutes without a respirator and without experiencing any escape-impairing (e.g., severe eye irritation) or irreversible health effects.

[4] ERPG (2): The maximum airborne concentration [of a toxic gas] below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms, which could impair an individual's ability to take protective action.

5.3.2.1 Acute Effects

Sulfur dioxide (SO_2) is a moderate to strong irritant. Most inhaled SO_2 only penetrates as far as the nose and throat with minimal amounts reaching the lungs unless the person is breathing heavily, breathing only through the mouth or the concentration of SO_2 is high. Sensitivity varies among people, however, short exposure (1-6 hours) to concentrations as low as 1 ppm may produce a reversible decrease in lung function. A 10 to 30 minute exposure to concentrations as low as 5 ppm results in the constriction of the bronchiole tubes, so objectionable that a person cannot inhale a single deep breath. In severe cases where very high concentrations of SO_2 have been produced in closed spaces, SO_2 has caused severe airways obstruction, hypoxemia (insufficient oxygenation of the blood), pulmonary edema (a life threatening accumulation of fluid in the lungs), and death in minutes. The effects of pulmonary edema include coughing and shortness of breath, which can be delayed until hours or days after the exposure. These symptoms are aggravated by physical exertion. As a result of severe exposures, permanent lung injury may occur.

5.3.2.2 Chronic Effects (No cancer)

Several human studies have shown that repeated exposure to low levels of SO_2 (below 5 ppm) has caused permanent pulmonary impairment. This effect is probably due to repeated episodes of broncho constriction. One study has found a decrease in lung function in smelter workers exposed for over 1 year to 1-2.5 ppm SO_2 [82]. No effect was seen in the same study in workers exposed to less than 1 ppm.

5.3.2.3 Reproductive/Developmental Effects

A number of epidemiological studies have suggested that exposure to SO_2 may be related to adverse reproductive effects. However, it is not clear that SO_2 caused the effects observed in any of these studies. There are no relevant results from animal studies [85].

5.3.2.4 Cancer Risk

Several epidemiological studies have examined the possibility that sulfur dioxide may cause cancers such as lung cancer, stomach cancer or brain tumors. In all of the studies, there were uncontrolled confounding factors, such as concurrent exposure to other chemicals. The International Agency for Cancer (IARC) has reviewed these studies and concluded there is inadequate evidence for carcinogenicity in humans [85].

Since SO_2 is one of the six criteria pollutants, and had been subject to much research, do we find additional guidelines. These include in particular ambient guidelines due to the routine nature of emissions into the atmosphere on a daily basis.

Proposed guidelines by the World Health Organization (WHO), South Africa and the US can be found in Table 5 –7. Occupational and accidental standards are also presented.

Table 5 - 7: Summary of SO_2 Standards and Guidelines

Type	Name	Averaging time	Concentration (ppm)
Ambient	WHO Guidelines	24 h	0.06
	WHO Guidelines	1 h	0.16
	WHO Guidelines	10 min	0.24
Ambient	South African	Annual	0.03
	South African	24 h	0.10
Ambient	U.S. National Ambient Air Quality Standards (NAAQS)	Annual	0.03
	U.S. National Ambient Air Quality Standards (NAAQS)	24 h	0.14
	U.S. National Ambient Air Quality Standards (NAAQS)	3-h peak	0.50
Occupational	U.S. NIOSH/OSHA STEL	15 min	5.0
	U.S. ACGIH/TLV-TWA	8 h	2.0
Emergency	Immediately Dangerous to Life and Health (IDLH)	30min	100
Emergency	Emergency Response Planning Guideline-2 /ERPG (2)	1 h	3

5.3.3 Propane

Propane is normally stored and transported in the liquid phase and under sufficiently high pressures (less than 10 bar) to maintain the liquid state at ambient temperatures. Such a tank may be damaged; an abrupt pressure drop may release enormous quantities of evaporative gas and energy, which normally has a destructive effect on the tank and its surroundings [86].

The degree of hazard depends on many factors such as the mass of the substance released, the rate of gas released, physio-chemical properties of the substance at the moment of release, flammability and the toxicity of the medium being released [87]. Sometimes the release is calm and does not present a menace to the environment. It happens however that its result can be disastrous. The most dangerous is a Boiling Liquid Expanding Vapor Explosion (BLEVE). Birk et al. (1995) [88] performed a study, which concluded that out of 40 fire tests of propane tanks 13 resulted in BLEVE's. Hazards from these included Fireballs, Projectiles and Blast.

A BLEVE come about when a liquid of temperature higher than its boiling point under normal pressure suddenly flows out. The most common BLEVE occurs when a pressure vessel partially filled with liquid is exposed to a fire or ignition source [89]. Pressure thus increases in the tank due to the increased temperature and vaporization pressure. The thermally induced stresses in the tank shell, the heat weakened tank, and high internal pressure combine to cause a sudden violent rupture of the tank also known as a BLEVE. As already mentioned direct hazards from a BLEVE are Projectiles, and Blast wave. Upon ignition a fireball may be formed and heat radiation, directly associated to it as well as secondary fires may be the consequence.

Propane has a variety physical properties of which users need to be aware of. It has an auto-ignition temperature [the temperature at which, in the presence of sufficient oxygen, a material will ignite on its own and burn (spontaneous ignition)] of 470 ^{0}C, and its flammability range [the concentration range in which a flammable substance can produce a fire or explosion when an ignition source (such as a spark or open flame) is present] is 2.2 to 9.5-volume % in air. Any concentration between these limits can ignite or explode.

5.3.3.1 Fireballs

Safe distances away from the source are used as indicators or guidelines for safety purposes to the public and usually firemen. Moorehouse *et al.* (1982) [90] determined the hazard radius (circular distance affected around the source) from the source to be $R = 3m^{0.33}$ (meters), with m the mass of the substance in pounds. Subsequently the duration of the fireball can be determined via $t = 0.15R$, where t is in seconds. Associated with a fireball is the Target Flux. Humans can endure a flux of 21 kW/m^2 for 2 seconds, before experiencing pain. Exposure beyond this time limit and corresponding intensity may lead to severe burns. Similarly a flux of 6.5 kW/m^2 can produce pain in 1 second and burn the skin if exposed continually for 20 seconds [90]. Target distance for these fluxes is 3.8R and 7.1R respectively. Safe distance of 3.2 – 3.6 fireball radii when only considering fireball thermal effects was also suggested [90]. The endpoint considered safe relevant to radiation effects of fireballs are 5 kW/m^2, and is also used as an endpoint by the RMP*Comp model for its calculation of distances at which 2nd degree should occur.

5.3.3.2 Blasts

There's very little data available on potential hazards from blasts. However the literature generally suggests/states that blasts from the vapor space and liquid flashing are relatively localized and therefore not as far-reaching as fireball and projectile effects [90].

5.3.3.3 Projectiles

Projectiles are potentially the furthest reaching immediate hazard from a BLEVE. Is one of the hazards, which are complex to quantify accurately, because of its random behavior. There are basically two kinds of projectiles from a BLEVE.

1. Primary projectile: Major pieces of the tank.
2. Secondary projectiles: Generated by acceleration of nearby objects.

In a study by Birk (1995) the projectile range was 0 – 200m in distances from the source with primary projectiles projected the furthest.

5.4. Release Scenarios

5.4.1 Sulfur Dioxide (SO_2) release

At approximately 10h30 September the 16th 1999 an SO_2 release occurred due to an accidental opening of the pulp discharge valve at the bottom of a digester. This incident occurred at SAPPI – SAICCOR in KwaZulu-Natal [91]. This case study will attempt to determine the pollutant concentration at a school 3km downwind, taking uncertainty into consideration and employing Monte Carlo simulation in order to present results with desired levels of confidence.

A study [91] of this incident estimated that approximately 3.2 – 4,5 tons of SO_2, which flashed of the boiling liquid (see section 5.4.1.1) was discharged. This release lasted approximately 10 minutes. It has been suggested that this incident might have had an effect on the students at a school located south – southwest of the plant.

5.4.1.1 Accident Chronology

The incident was caused by a malfunction of the normal operating cycle. The pulp discharge valve at the bottom of the digester was opened by error. The digester still contained wood chips and cooking liquor impregnated in wood at this point in time. Between 70,000 and 100,000 liters of cooking liquor was discharged into the blow-tank, resulting in the sudden release (flash-off) of sulfur dioxide from the liquor. The increased amount of gas led to a pressure build-up in the blow-tank. The pressure relief bypass system was activated, releasing the majority of the gas to the atmosphere via a stack, with the balance via a scrubber.

5.4.1.2 Modeling Parameters

Table 5 -8: SO_2 Source input parameters

Parameter	**Input Range**
Release Quantity (kg)	3200-4500
Release Time (min)	1-3
Release Height (m)	1-10

Table 5 -9: Meteorological input parameters at time of the SO_2 accidental release

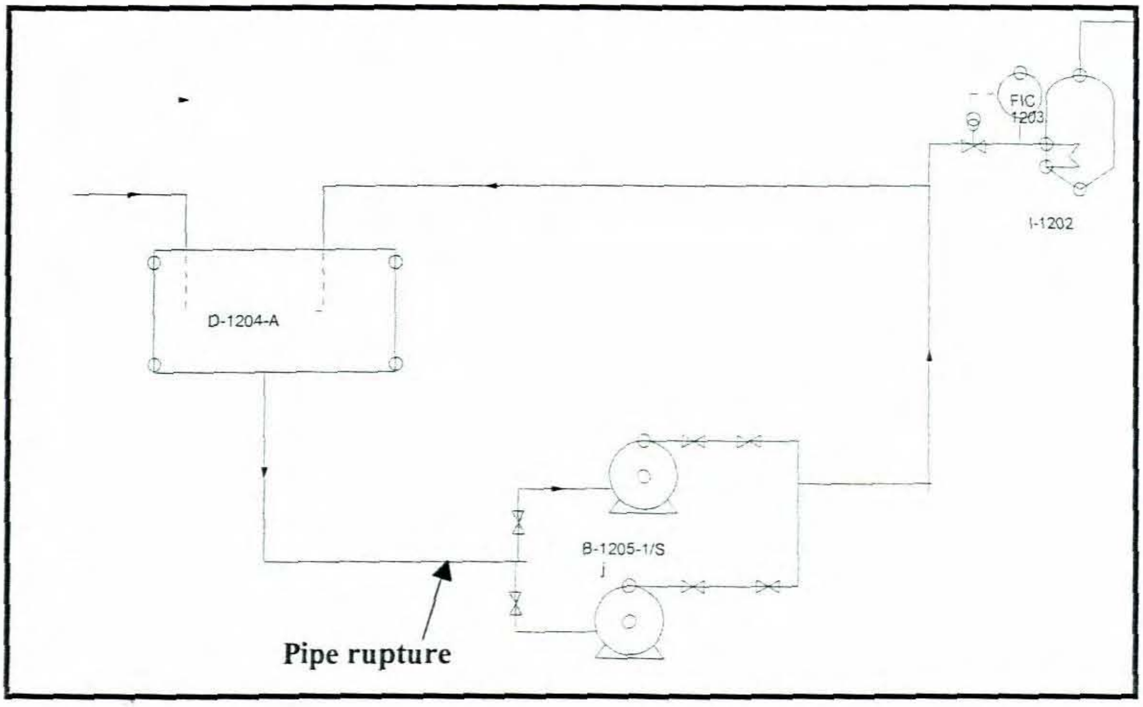
Parameter	**Input Range**
Ambient Temperature (^{o}C)	25
Wind Speed (m/s)	1.2-2.2
Wind Direction (degrees)	70-110
Relative Humidity (%)	50-100
Atmospheric Pressure (atm)	1
Ground Roughness (0 /rural-100/urban)	60-100

The AFTOX model will be utilized to determine peak concentrations at the school.

5.4.2 Chlorine (Cl_2) Release

On January 21st 1996 at around 2.10am a pipe carrying liquid chlorine in the plant for production of chloromethanes owned by Erkimia at Flix (Tarragona, Spain), ruptured, releasing the contents (5000-6000kg) of an intermediate storage tank, and giving rise to the formation of a dense toxic cloud with a high chlorine concentration. The cloud moved in the direction of a nearby residential area in Flix (population ca. 5000), about one kilometer away (Marco et al., 1998) [92]. Fortunately, as a consequence of the time of release (early morning), and the cold ambient temperature (around 4°C at the time of release), residents were at home with windows closed, no major injuries resulted. Only 12 people needed medical attention, with two of them taken into hospital for a 24-h observation period (Marco et al., 1998).

Figure 5 - 3: Schematic representation of the process in the immediate vicinity of the pipe rupture



5.4.2.1 Accident Chronology

The operator observed a high current intensity in Pump B1205-1/S. At the time the flow of liquid chlorine to the vaporizer dropped to zero. A few seconds later the, reading of the current meter of pump B-1205-1/s was zero, indicating pump (the amperage readings for the pump stator circuit after pump blockage were equivalent to a heat generation rate of 130 kW) stoppage. The most likely cause of pump stoppage was internal friction in the pump, eventually leading to blockage of the impeller, and heating the chlorine inside the pump (Marco et al., 1998). When the temperature was high enough, steel ignited and a reaction with liquid chlorine rapidly propagated the heat upstream in the chlorine filled pipe. The final consequence was the rupture of the pipe (Figure 5 – 3), at a short distance from the pump inlet.

5.4.2.2 Modeling Parameters

Table 5-10: Cl_2 Source input parameters

Parameter	Input Range
Release Quantity (kg)	5000-6000
Release Time Instantaneous (min)	<3
Tank pressure (bar-g)	7.8

Table 5 - 11: Meteorological Input Parameters at the time of accidental release of Chlorine

Parameter	Input Range
Ambient Temperature (°C)	4
Wind Speed (m/s)	<2
Wind Direction (degrees)	315 in the direction of the residential area
Relative Humidity (%)	97
Atmospheric Pressure (atm)	1
Ground Roughness (0 /rural-100/urban)	60-100

A chlorine release of this magnitude usually results in a dense cloud being formed at the point of release. The ALOHA model developed with an alternative option to model dense cloud releases will be used to determine concentrations in the Flix community 1.5 km downwind.

5.4.3 Propane Release

On April 9, 1998, at approximately 11:28 pm, an 18,000-gallon propane tank exploded at the Herring Brother Feather Creek Farm in Albert City, Buena Vista County Iowa (US) [93]. The propane was stored below its boiling point (-42.1°C) in a liquid state. Two volunteer fire fighters were killed and seven emergency response fire fighters personnel were injured. Several buildings were also damaged by the blast.

5.4.3.1 Accident Chronology

The farm raised turkeys housed in seven barns. Heating in barns were provided via space heaters and furnaces, of which fuel was supplied by a propane storage and handling system that included the propane tank that exploded.

On the evening of the incident, eight secondary-school-aged-teens gathered at the farm for a party. At approximately 11:00 pm, one of the youth began driving an all-terrain vehicle (ATV) around the farm. The automobile was heading east between the propane tank and a turkey barn when it struck two propane pipes (liquid and vapor lines). Both the liquid and vapor lines were damaged. These two lines ran parallel to one another from the propane tank to direct-fired vaporizers approximately 12 meters to the north of the tank. The liquid line (3/4-inch) was completely severed from the tank where it was connected to a manual shut-off valve directly beneath the tank. Propane leaked out of the tank at the point of the break. The liquid propane spraying out of the tank rapidly changed to vapor. The propane ignited within a few minutes most likely when it reached the vaporizers 12 meters away. This fire fed by the liquid line began burning vigorously under the tank.

At about 11:21 pm, fire fighters observed flames originating from two primary locations:

1. from under the west-end of the tank, and
2. from the pressure relief valves located on top of the tank

One fire fighter reported that the west end of the tank was engulfed in flames.

At approximately 11:28 pm the tank exploded, scattering metal tank fragments in all directions one large piece traveled in a northwesterly direction, striking and killing two volunteer firemen. Seven other emergency personnel sustained injuries as a result of the explosion.

5.4.3.2 Modeling Parameters

Table 5-12: Propane Source input parameters

Parameter	Input Range
Release Quantity (kg)	19,000 – 35,407
Release Time (min)	18
Release Height above the ground (meters)	0.98
Liquid pipe diameter (cm)	0.02
Tank Diameter (meters)	2.9
Tank Length (meters)	13.6

Table 5-12: Meteorological input parameter at time of accidental release of Propane

Parameter	Input Value
Ambient Temperature (°C)	2.8
Wind Speed (m/s)	4.4
Wind Direction (degrees)	Unknown
Relative Humidity (%)	86
Atmospheric Pressure (atm)	1
Cloud Cover (tenths)	Unknown
Ground Roughness (0 /rural-100/urban)	Unknown

RMP*Comp will be used to model the propane release, since it has the option of modeling Vapor Cloud Explosions and a BLEVE's.

5.5 Modeling Results

5.5.1 SO_2 release

5.5.1.1 SO_2 Concentration at the school-no uncertainty consideration

AFTOX was used to predict the ambient concentrations at the school. The school is located approximately 3 kilometers from the SO_2 source. It is assumed that the school is downwind relative to the source, and that it is located on the plume centerline since it is very difficult to determine whether the school is directly in the path of the plume or not. The concentration corridor (hazard footprint) indicated the SO_2 concentration at the school 3000 m downwind marginally exceeded the 3ppm Emergency Response Planning Guideline (ERPG) – 2. The footprint (the area covered by SO_2) indicates the distances downwind from the source and the contour half width the area covered at that particular distance. The table can be understood as follows: Column 1: the distances away from the source as the pollutant moves downwind. Column 2: the crosswind distance covered by the pollutant in other words how wide the plume became at 10 meters height above the ground relative to the plume centerline, and Column 3 is the peak SO_2 concentration at the plume centerline, at a time calculate via the wind speed at the time and the distance the plume had to travel. The bold values indicate those concentrations 3000m downwind relative to the source.

Table 5 -14: SO_2 concentration at the School in ppm

DIST (M)	CONTOUR HALF [WIDTH (M)]	PEAK (CENTRELINE) CONC (PPM)
2686	0	2.8
2786	120	3.1
2886	160	3.2
2986	**110**	**3.1**
3019	**0**	**3.0**

5.5.1.2 Uncertainty present in input parameters

Uncertainty arises in the release rate due to uncertainty in release duration. It is estimated that the duration could have been in the vicinity of 1 to 3 minutes. The ALOHA model also available from the EPA computed the release duration to be 2 minutes, and this time was used as a basis for the AFTOX modeling. The SO_2 was released from an accidental opened discharge valve, which adds to the uncertainty surrounding the total time duration for which the substance has been released.

The wind speed issue was identified since 4 different weather stations, which are located in close proximity to each other and to the SO_2 source, indicate variation in this parameter. This range is between 1.2 – 2.2 m/s. An eyewitness mentioned that the plume went in the direction of the school, which is in a south - southwestern direction from the plant. The weather stations contradict this and suggested that the predominant wind direction was in a northeasterly direction. The uncertainty surrounding the determination of dispersion coefficients especially at low wind speeds mainly because under light winds and especially during stable stratification the turbulence structure of the atmospheric boundary layer (ABL) is poorly known (Crowl & Louva, 1990) [94] further escalated the problem of uncertainty. This problem is compounded by the fact that if Pasquill stabilities and Pasquill-Gifford dispersion parameters are used for meteorological conditions we are considering the atmosphere in only six classes while, in reality, it is a continuum (Turner, 1994) [95].

The ground roughness and its orientation also add to uncertainty in the output. The area is believed to be densely populated, but the roughness of the immediate area surrounding the plant is not known. Other sources of uncertainty may also be present but excluded from this study. For example small shifts in wind direction would make a big difference. The wind direction was assumed constant blowing in the direction of the school with no variations.

In Table 5 -15 distributions used and comments on justification for using a particular distribution is included. Since the distribution of input parameters is unknown, distribution types were assumed to be of the more general forms such as normal, triangular and uniform.

Table 5-15: Identification of uncertain input parameters, distributions used and its justification

Uncertain input variable	**Uncertainty range**	**Probability Curve**	**Comments**
Quantity released (tons)	3.2 – 4.5	Uniform	The uniform distribution best represents this parameter since any amount of SO_2 within this range is likely to occur.
Release duration (min)	A release duration of 1 – 3 min with 2 minutes the most likely	Triangular	The reason for using this distribution is because any value within this range is likely to materialize but 2 minutes are the most likely
Wind speed (m/s)	1.2 -2.2	Uniform	Continuous wind fluctuations makes any wind speed between 1.2 and 2.2 likely
Ground roughness (cm)	50 – 100	Triangular	Any value between 0 and 100 cm is possible, but the most likely is in the range of 50 – 100cm.

5.5.1.3 Estimates of SO_2 concentration at school, uncertainty incorporated

Uncertainty analysis was performed and 50 random iterations were generated for the wind speed, ground roughness and release quantity input parameters with the aid of the @Risk Software Package (Table 5 –16).

For full list of 50 iterations refer to Appendix H1

Table 5-16: Simultaneous iterations of input parameters, and the resulting peak concentrations

Iteration Number	Wind Speed (m/s)	Release Quantity (kg)	Ground Roughness (cm)	Peak concentrations at school (ppm)
1	1.39	3240	100	1.7
2	1.81	3451	50	5.3
3	1.69	4327	50	6.5
4	1.98	3523	50	6.4
5	1.83	4279	100	3.9
6	1.79	3694	100	3
7	2.17	4123	100	6.2
8	1.77	3271	100	5.3
9	1.64	3347	50	3.5
10	1.56	3961	100	2.5
11	1.60	3572	50	3.6
12	1.32	4348	100	2.1
13	2.00	3491	100	4.3
14	1.49	4008	50	3.7
15	1.68	3853	50	5.8
16	1.31	3403	100	1.5
17	1.46	4472	100	5.2
18	2.09	3219	50	6.9
19	1.21	3809	50	2.3
20	1.38	3980	50	3.1

The results will be best described with the visual aid of a Frequency - and Cumulative Frequency Distribution (CFD). **[Distribution derived corresponding to the method described in APPENDIX F]** These two plots give an indication of the most likely exposure level at the school from the accidental SO_2 release.

Peak concentration at the school

Figure 5 - 4:% Frequency Distribution of calculated SO_2 Concentration at the School

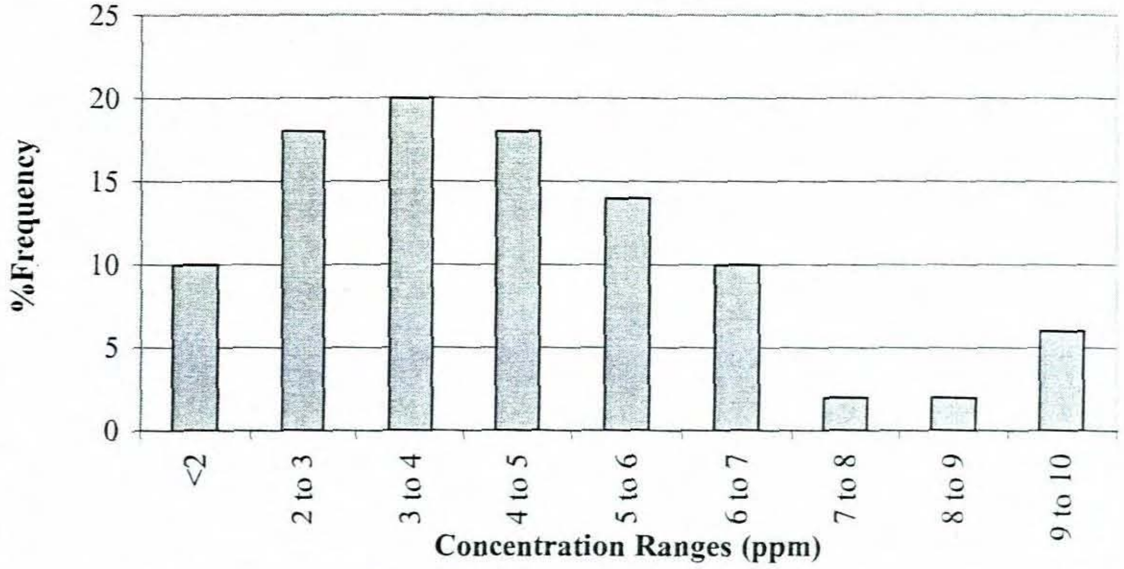
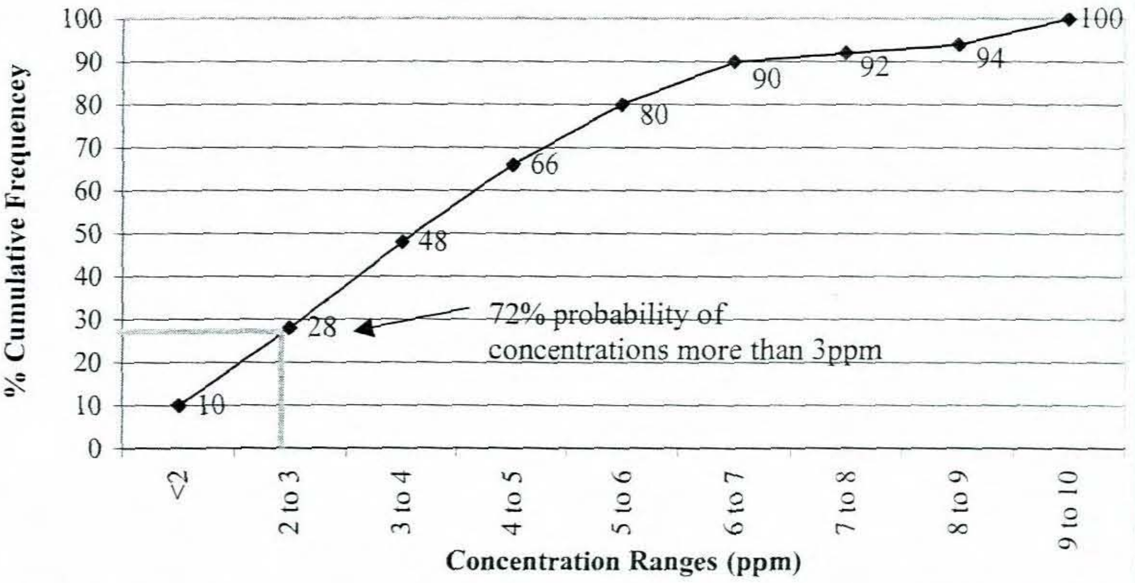


Figure 5 -5: %Cumulative Frequency Distribution of SO_2 Concentration at the School



Referring to table 5-4 and figures 5-4 and 5-5 we could observe a concentration range from as little as 1.5 ppm up to a maximum of 10 ppm. Likely concentrations from charts are in the region of 2 to 5 ppm (Figure 5 –4) and are supported by a mean of 4.5 ppm (Table 5 –16). Figure 4 –5 and Table 5-16 indicates that there is a 95% probability that the peak concentration at the school was less than 9 ppm.

5.5.1.4 Statistical Analysis

Table 5 - 17: Resultant Statistics for SO_2 Peak Concentrations

Statistic	Value
Mean	4.5ppm
Median	4.2ppm
Mode	5.3ppm
Standard Deviation	2.12ppm
Variance	4.5ppm
95% Confidence Limit	8.6ppm
5% Confidence Limit	0.3ppm

This statistical analysis supports what's been indicated by the two frequency distributions, that there is a 95% chance/probability that the SO_2 concentration at the school was less than 9ppm. The mean 4.5 ppm, (measure of central tendency) as a result of this analysis can be considered the most likely concentration at the school. Considering the ERPG (2) for SO_2, which is 3.0 ppm and the mean, is indicative of a probable increased risk to exposure for occupants at the school, if the school is as assumed in the plume centerline and directly downwind from the source. Figure 5-5 indicates that there's a 72% probability that concentrations at the school would exceed the initial estimate (uncertainty not considered), which marginally exceeds 3 ppm (table 5-14).

In the report [89] of the incident the assessors predicted that there's a 90% probability of concentrations at the school less than 2 ppm and only a 10% probability of concentrations more than 2ppm up to 12 ppm. Drawn from this report the authors estimate a 95% confidence interval of 5ppm for the concentrations at the school. The probabilistic approach used in this thesis results in a 95% confidence of SO_2 concentrations to be below 8.6ppm (table 5 –17), and only a 10% probability of SO_2 concentrations less than

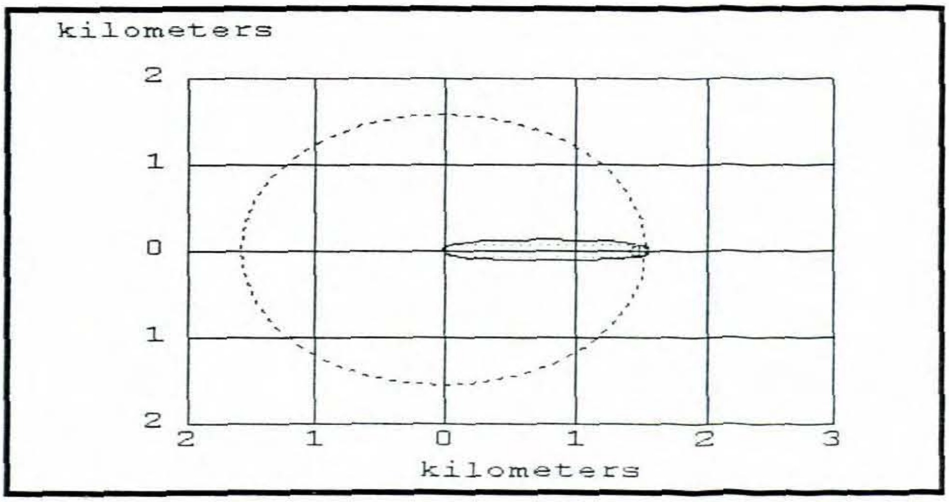
2ppm, which is contrasting to estimates reported in the study by Burger and Sowden [91]. The methodology used by the authors in their assessment however is very unclear.

5.5.2 Cl_2 release

5.5.2.1 Cl_2 concentration at Flix-no uncertainty consideration.

ALOHA has the ability to graphically represent a hazard footprint, indicating the maximum threat zone (width) and distance (length) to which the area will be exposed to concentrations in excess of the user specified Level of Concern. The level of concern selected was the revised IDLH of 10ppm (see table 5-6) for chlorine. Figure 5 –6 represents the hazard footprint for the chlorine release.

Figure 5-6: Hazards Footprint formed due to the accidental Chlorine release, extending over a 1.5 km downwind distance.



The hazards footprint for this run indicates that for downwind distance of **1.6 km** the IDLH (10 ppm) was exceeded. The maximum (highest) outdoor and indoor concentrations possible at the footprint centerline were also determined at a distance 1.5 km downwind from the source. This distance was selected randomly to ensure that the community 1 km downwind is included. ALOHA estimated the maximum outdoors and indoor concentrations to be **9.9 ppm** and **1.64 ppm** respectively.

5.5.2.2 Uncertainty present in input parameters

Three input parameters not commented on in the literature had to be treated as uncertain. In table 5 –18 conclusions regarding input distributions and parameter uncertainty ranges were taken as to what it might have been during the accident.

Table 5-18: Identification of uncertain input parameters, distributions used and its justification for Cl_2 Modeling

Uncertain input parameter	Uncertainty range	Probability Curve	Comments
Chlorine temperature in pipeline (°C)	-41 - -34	Normal (μ=-38;δ=2)	The chlorine in this plant's operation was maintained in a liquid form (this is the norm). The boiling temperature for chlorine is –34 °C. Temperature should have been kept below its boiling temperature and above its freezing temperature of -101°C.
Ground Roughness (m)	50-100	Triangular	The area between the plant and the community seems to be occupied by buildings. The height and density of buildings however are unknown. 50 represent fewer obstacles than 100, which is an indication of an urban establishment with high buildings.
Quantity Released (kg)	5000-6000	Uniform	Articles indicate the tank quantity being released to be between 5000-6000 kg. Any value in this range is possible, with each quantity having equal probability, thus necessitating a uniform distribution.

5.5.2.3 Estimates of Cl_2 concentration at the previously determined locations-uncertainty incorporated

Random number (APPENDIX H2) for inputs was generated from the above probability distributions (table 5 -18). Once again 50 different scenarios will be used to estimate the maximum Cl_2 concentrations 1.5 km downwind.

Distances to Toxic Endpoints.

Distances to the 10 ppm toxic endpoint where determined and is indicated in the graph below (figure 5 –7). A peak is observed in the 1.2 to 1.4 km ranges and Figure 4 –8 indicates that there's a 94% chance that distances were less than 2 km.

Figure 5-7: % Frequency Distribution of Distances to Toxic Endpoint (10ppm) for Cl_2

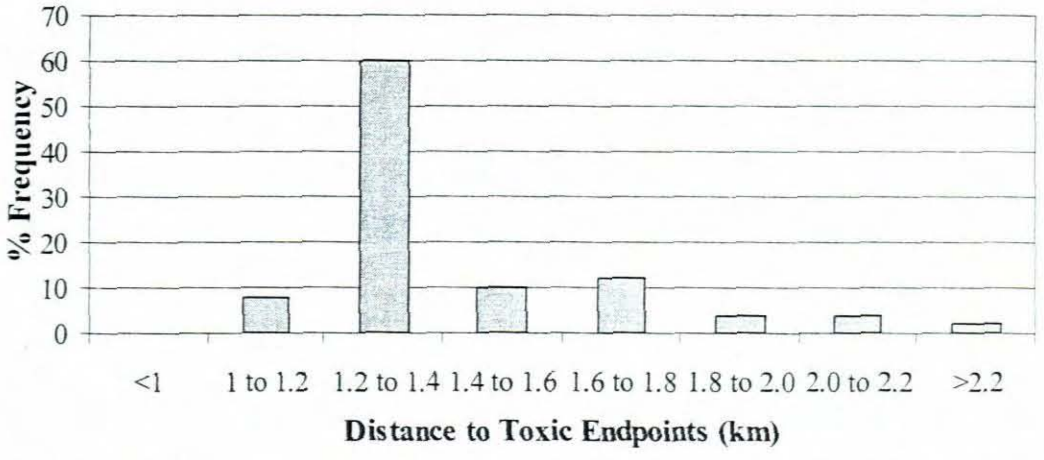
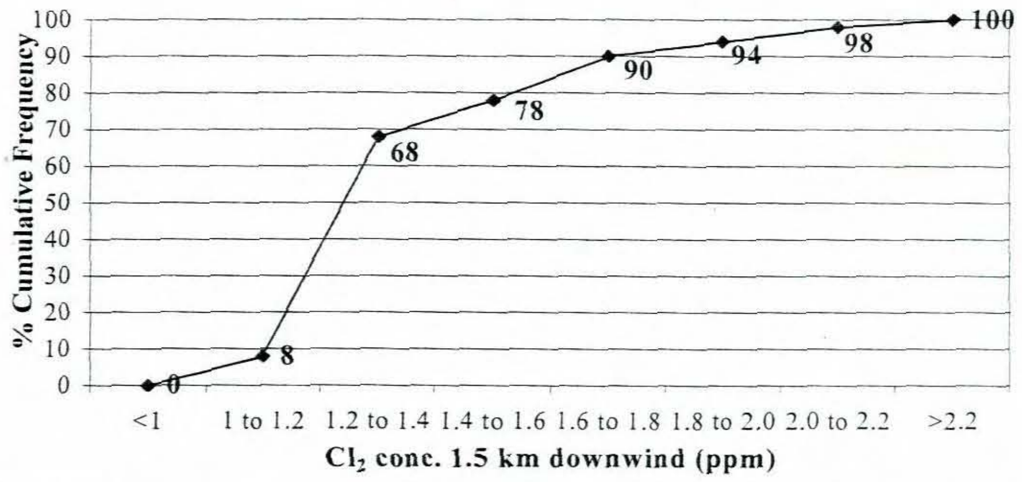
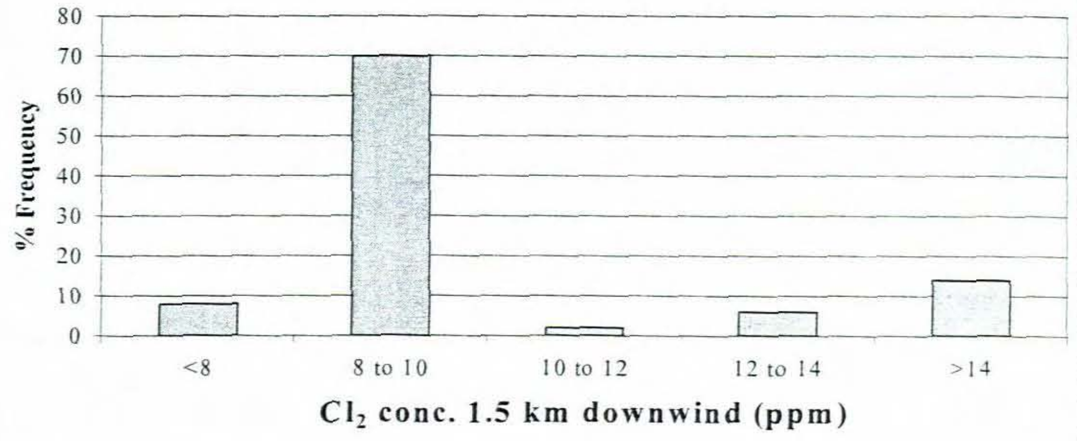


Figure 5-8:% Cumulative Frequency Distribution of Distances to Toxic Endpoints for Cl2



Peak Concentration 1.5 km downwind

Figure 4 - 9: % Frequency Distribution of Cl2 Concentrations 1.5 km Downwind



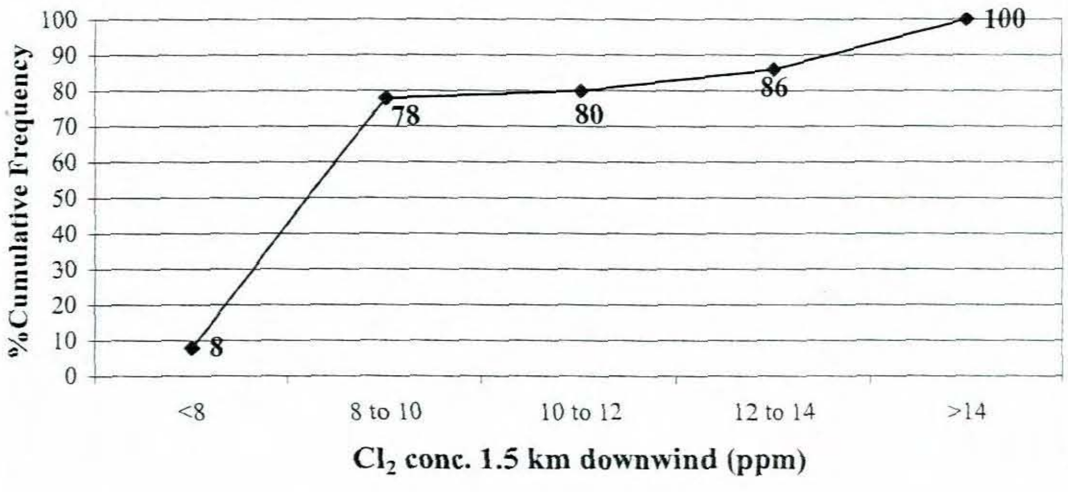


Figure 5 - 10: % Cumulative Frequency Distribution of Cl2 Concentrations 1.5 km Downwind

5.5.2.4 Statistical Analysis

Table 5 - 19: Resultant Statistics for Distances to Toxic Endpoint, which are 10ppm

Statistic	Value
Mean	1.5 km
Median	1.4 km
Mode	1.4 km
Standard Deviation	0.26 km
Variance	0.07 km
95% Confidence Limit	1.58 km
5% Confidence Limit	1.44 km

Statistical Analysis (table 5 – 19) and the % Cumulative Frequency Distribution (figure 5 – 8 reveals distance to the 10ppm toxic endpoint be no more than 2.2 km. The probability however of this distance been reached at the time of the incident is slim. Statistical analysis rather indicates a 95% chance of distances less than 1.58 and a 5% chance of distances less than 1.44 km. Confirmation is given by the mean, which was computed at 1.5 km. Confidence in this estimates should be supported by the fact that the standard deviation, an indication of the dispersion of estimates is very small compared to the mean. This estimates is in agreement with the initial estimation of 1.6 km, which did not incorporate uncertainty.

Table 5 - 20: Resultant Statistics for Concentrations 1.5 km downwind

Statistic	Value
Mean	10.3 ppm
Median	8.8 ppm
Mode	8.8 ppm
Standard Deviation	3.7 ppm
Variance	13.8 ppm
95% Confidence Limit	11.3 ppm
5% Confidence Limit	3.0 ppm

The computed mean value of 10.3 ppm for the maximum outdoors concentrations 1.5km downwind does not deviate much from the initial estimate of 9.9 ppm (see section 5.5.2.1). The certainty about the mean is in question if the confidence limits are assessed. It indicates that there's a 95% confidence that the concentrations would be less than 11.3 ppm and more than 3.0 ppm, this is mainly due to a standard deviation of 3.7, indicating a widespread of estimates within the confidence bounds. However we may argue that the %Frequency Distribution shows a definite peak for the range 8 to 10 ppm, giving us verification that the mean in fact might be a better indication of what the actual concentration 1.5 km downwind must have been. Marco et al (1996) reported Cl_2 concentrations obtained from a monitoring station approximately 1.4km downwind in the direction of the Flix community to be 5.1 ppm from about 30 up to 70 minutes after the release occurred. This concentration value is contrasting to estimates made via probabilistic analysis.

5.5.3 Propane release

For propane and other flammable substances RMP*COMP assumes that the total quantity of the flammable substance forms a vapour cloud within the upper and lower flammability limits and the cloud detonates, which generates a pressure wave that can damage people or structures [96]. The model determines the distance to 1psi overpressure (at 1psi, windows will break), due to the pressure wave resulting from the explosion. Another endpoint which will be determined is the distance at which exposure may cause 2nd degree burns, due to the occurrence of the fires and radiation. The endpoint used by RMP*Comp for this parameter is 5kW/m^2 where after a 40 second period of exposure an individual may sustain 2nd degree burns. The area or distance of interest is that just 78 ft/26m to the north where there's a road.

Mainly due to RMP*COMP's limitations the only input parameter required is the mass of propane released or involved in the explosion. Since propane quantities were reported in units of volume (gallons) a conversion taking its liquid density in consideration was necessary. It was reported that the tank had a capacity of 18,000 gallons and due to the high usage of propane was re-filled on a regular basis. It was also mentioned that at the time of the incident the tank might have contained 10,000 gallons of propane.

5.5.3.1 Conversion of Propane Quantities

Density of Liquid propane [97] = $519.7\ \text{kg/m}^3$

Volume in cubic meters (v) [1] = 10,000 gal = $37.85\ \text{m}^3$
= 18,000 gal = $68.13\ \text{m}^3$

Mass of propane in tank (kg) = $\rho * v$ ....(1)
= $519.7 * 37.85$
= 19,671 kg

Mass of 18,000 gal propane = 35,407 kg

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[1] Conversion Factor multiplies by 0.003785.

5.5.3.2 Distance to 1 psi overpressure -no uncertainty consideration.

The model estimated the maximum distance to 1psi overpressure at 500m from the source.

5.5.3.3 Distance at which exposure may cause 2nd Degree Burns due to radiation-no uncertainty consideration

The model estimated the maximum distance at which exposure may cause 2nd degree burns at 400m from the source.

5.5.3.4 Uncertainty present in input parameters

The mass released is the most uncertain and only input parameter to this model for performing worst case and BLEVE scenario calculations. As previously mentioned the amount of propane present in the storage tank at the time of the incident is questionable. Random numbers were generated for this parameter. Uncertainty as to which distribution to use encouraged the use of a normal distribution. This distribution takes into consideration the initial release of propane prior to the explosion, and that the tank might have been at full capacity. A minimum mass of 1967kg and a maximum of 35,407kg with a mean of 19,671kg and a standard deviation of 9,835kg were utilized.

Distances to 1 psi overpressure

Figure 5 –11 represents the % Frequency distribution of the maximum distance to 1psi overpressure, derived from the modeling outputs obtained after performing 50 iterations, and Figure 5 –12, same applies to Figures 5 –13 and 5 –14, which related to the radiation endpoint.

Figure 5-11: % Frequency Distribution of the Distance to 1 psi Overpressure

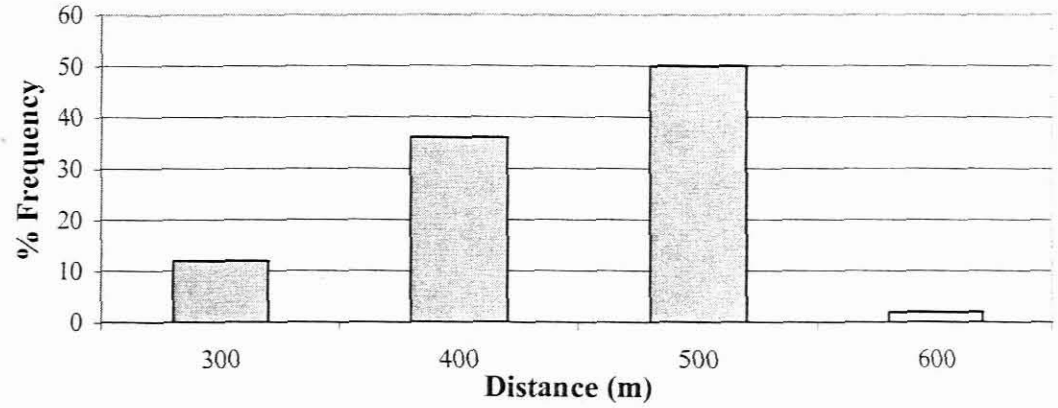
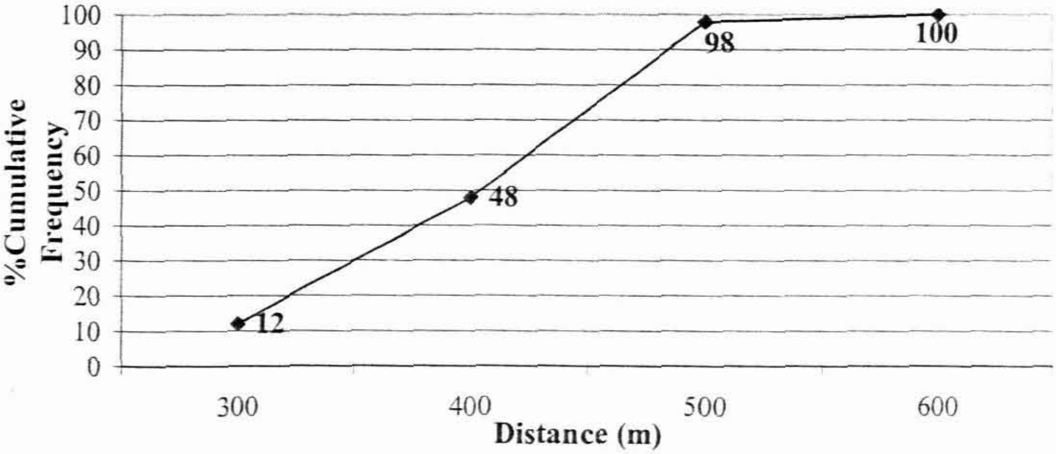


Figure 5-12: % Cumulative Frequency Distribution of the Distance to 1 psi Overpressure



Distances at which exposure may cause 2^{nd} degree burns

Figure 5 - 13: % Frequency Distribution of the Distance at which exposure may cause 2nd degree burns

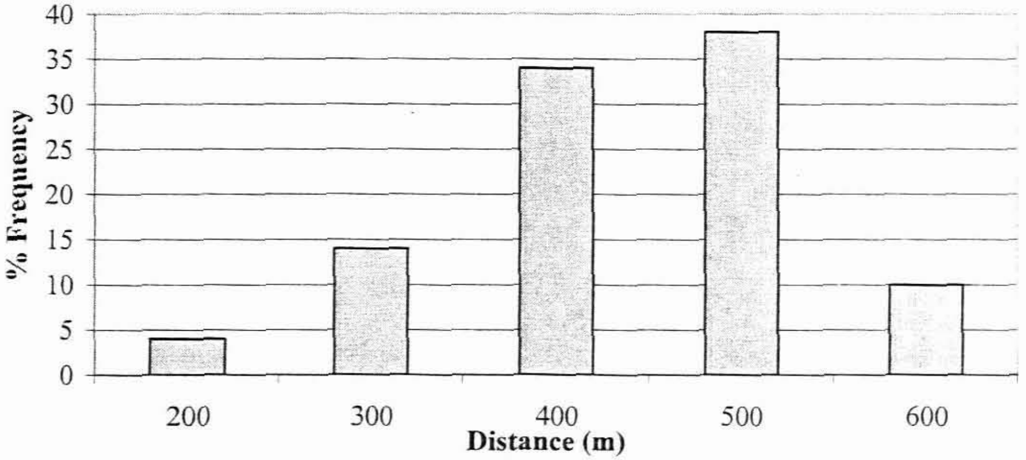
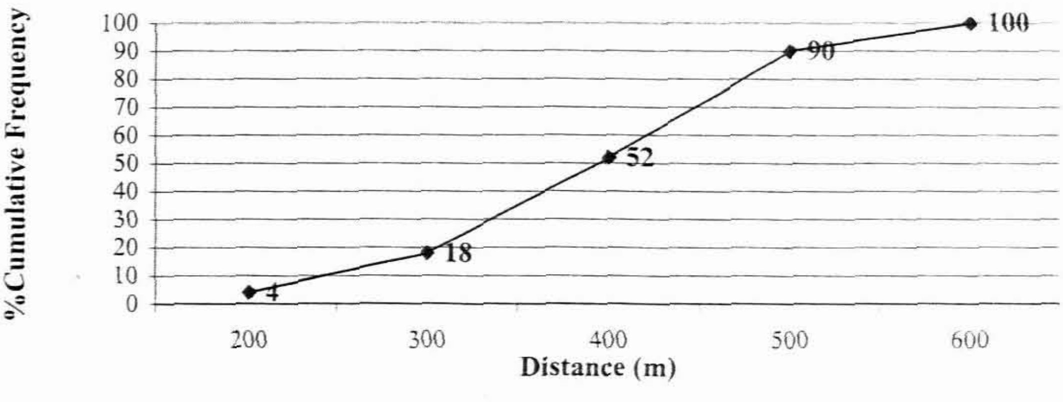


Figure 5 - 14: % Cumulative Frequency Distribution of the Distance at which exposure may cause 2nd degree burns



5.5.3.5 Statistical Analysis

Table 5 -21: Resultant Statistics for Distances to 1psi overpressure

Statistic	Value
Mean	432 m
Median	500 m
Mode	500 m
Standard Deviation	73.8 m
Variance	5445 m
95% Confidence Limit	576.6 m
5% Confidence Limit	287.4 m

Table 5 - 22: Resultant Statistics Distances at which exposure may cause 2nd degree burns

Statistic	Value
Mean	436 m
Median	400 m
Mode	500 m
Standard Deviation	98.5 m
Variance	9698 m
95% Confidence Limit	630 m
5% Confidence Limit	182 m

For both these endpoints the mean distance was determined to be in the vicinity of 435 meters, with a standard deviation relatively small in comparison, indicating estimates to be grouped relatively compact. An estimate of the 5th percentile confirms a 95% probability exceedance of 287 and 182 meters for 1psi overpressure and 2nd degree burns endpoints respectively. These distances extend beyond the road, which are situated 25 meters to the south of the explosion site. Effects to the road were not considered since no casualties were experienced due to the time of the incident (late at night). The results confirm the fatal casualties (two volunteer firefighters) who were 100 feet (33 meters) away were due to the explosion. The report however does not mention effects at any distances beyond 100 feet [93]. Results however indicate endpoints beyond this.

Chapter 6: Discussion

This study looked at traditional air pollution modeling software for determining toxic endpoints. In addition Monte Carlo simulation was utilized as a possible and realistic probabilistic tool to improve confidence in the estimates, whether in terms of concentrations downwind or maximum distances for the appropriate level of concern from the source. Accidents selected were due to accidental releases of hazardous substances from large chemical plants. The probabilistic analysis of impacts due to accidental releases revealed results unlike the initial estimates obtained (results not giving consideration to the possibility of uncertainty). An important finding is that outputs (deterministic and probabilistic) deviated considerably from results reported by previous studies whether in the form of an article or report, especially in the cases of SO_2 and Cl_2 where attempts were made to estimate endpoints. Monte Carlo Simulation was found to be flexible in its approach, and applying this method provides a quantification of uncertainty in modeling estimates.

Results primarily in the form of a % Frequency Distribution (%FD) and % Cumulative Frequency Distribution (% CFD), including an additional statistical analysis with the basic statistics (mean, standard deviation etc.). Plots for the SO_2, the dilute phase modeling appears to give smooth curves (figures 5 -4 and 5 -5) indicate an even spread of concentration estimates, with difficulty in identifying peaks in frequency. The histogram does tail of at the ends with the 2 to 6ppm categories featuring with peaks. For the Cl_2 (heavy gas) a peak in frequency can be observed for both the peak concentration (peak observed in the 8 to 10 ppm category), and distances to toxic endpoints (peak observed in the 1.2 to 1.4 km category) estimates (figures 5 -7 and 5-9). The spread of estimates for the propane release was not that wide for distances computed (figures 5 -11 and 5 -13), this were confirmed by the small standard deviations relative to the means. The reason for this is that RMP*Comp selects worst case distances from a series of look-up tables. These values in the tables are in increments of 100 regardless of the desired output. Peaks were observed in the 400 and 500 m categories only.

The same modeling exercise was practiced for all three cases, where Monte Carlo Simulation has been applied (50 iteration) with the only exception being the difference in models used and in uncertain parameters. Results for all indicated peak frequency and the mean evolving in close proximity of the peaks. Confidence estimates can be considered reliable due to small standard deviation, except for the SO_2 modeling where the standard deviation is big in relation to the mean. These phenomena may be explained by the fact that in the dilute modeling case, modeling output is very sensitive to input especially the wind speed and quantity released which were uncertain and varied.

The probability distribution selection criteria used for uncertain input parameters was a rather crude method. In most of the cases a short comment justifying the probability distribution selected was given. Hoffman *et al* (1999) [30] suggested three methods for obtaining distributions for uncertain inputs. These are 1.) the use of classical statistics, 2.) analyst judgment using all sources of information, and 3.) formal expert elicitation. The absence of large datasets for uncertain inputs crippled the use of classical statistics, which would have been the natural approach for determination of distributions. The 2nd approach was used for distribution selection. The disadvantage of applying this method is that the analyst may have been conservative and/or biased in his/her approach, and may have resulted in estimates being over- or underestimated.

Hertwich *et al.* (2000) suggested that point estimates are normally lower than the computed mean. This statement is generally true as essentially all model inputs are non-negative and have possibilities of high values e.g. follow log-normal distributions. This study is not consistent with their statement, although it is true for 4 out of 5 different endpoints that were computed, a definite pattern could not be observed. In some cases such as the determination of the toxic endpoint distance for the Cl_2 the point estimate is higher than both the mean and the 95th percentile and for the distance to 1 psi overpressure for the propane tank explosion the point estimate is greater than the computed mean. The estimates may therefore, by chance, be higher or lower than the respective mean value.

The SO_2 ERPG (2) of 3 ppm was only marginally exceeded as was indicated by the point estimate (table 5 –14), and according to the probabilistic analysis the mean and median indicates the ambient concentration to be in excess of 4.2 ppm and should have been of some concern to health impacts on the students at the school. It can be said, by means of using this probabilistic method that randomly selecting any point estimate within the population of estimates that the SO_2 guideline, the ERPG (2) is likely to be exceeded with a 90% probability of concentrations at the school more than 0.3ppm and less than 8.6ppm. with a mean of 4.5ppm.

For Cl_2 the pattern is reversed and the respective means are indicative of concentrations and hazardous distances less than the point estimates. The ERPG (2) of 3 ppm are easily exceeded but the results do not suggest that the IDLH will be exceeded, with the mean of 10.3 ppm and a 90% probability of concentrations at 1.5 km downwind more than 3.01 ppm and less than 11.3 ppm.

In the case of the propane explosion no obvious difference between point estimates and probabilistic analysis was observed. This is probably due to the limitations of RMP*Comp. RMP*Comp is a planning tool designed to help you to easily identify high-priority hazards at a facility. It relies on very simplified and generalized calculations, thus having a limited number of input parameters. It excludes parameters such as the meteorological data and terrain roughness, which results in limited flexibility. In this study only one parameter had been varied thus we found limited variation in the output even from the point estimate, which did not consider uncertainty.

Chapter 7: Conclusion and Recommendations

In this thesis a framework was presented for the analysis of uncertainty in exposure assessment methods used for estimating impacts due to accidental releases from large industries. This framework was applied to three forms of analysis of accidental releases of three hazardous substances, with different atmospheric dispersion characteristics into the environment, where immediate receptors (humans, vegetation) might have been in the vicinity. Parameter uncertainty was addressed for all cases except for propane (due to limited input parameter requirements for RMP*Comp), but this study did not cover model- and decision rule uncertainty, which might have been present. The results indicate that uncertainties regarding input parameters can alter the calculation by an order of magnitude, if this form of analysis has not been explored.

Production, usage and accident frequency illustrated and motivated the use of SO_2, Cl_2, and Propane as a basis for the case studies to illustrate the use of Monte Carlo Simulation in conjunction with Air Dispersion Modeling. Each case study presented a unique case of uncertainty. SO_2 for example had a whole list of 4 uncertain input parameters ranging from quantity released up to ground roughness. Propane on the other hand only presented us with one uncertain parameter (quantity released), this is mainly due to the limited input requirements from RMP*Comp. All these parameters were thoroughly investigated and appropriate probability distribution were assigned to them with a brief explanation as to why certain distribution were used or preferred above other. Results for the probabilistic approach did differ from the deterministic approach in all the cases. The magnitude of variation however were much more apparent for the SO_2 and Cl_2 cases, than for propane estimates.

This study concludes that for both SO_2 and Cl_2, there's a probability that the Emergency response guidelines for the respective substances may have been exceeded, and that occupants acutely exposed to this substances may have been at risk. The analysis of the propane incident confirmed the two fatalities, which were experienced at site, but endpoint distances went beyond the road (nest to the incident) otherwise not indicated in the report as being affected.

Failure to fully consider the implication of uncertainties in environmental problems often yields the wrong answer and gives decision-makers an incorrect sense of confidence about numbers. Although quantitative analysis of variability and uncertainties require more critical attention to assumptions and inputs to an analysis, the results are more defensible and meaningful considering the estimates of both the ranges and likelihood of possible outcomes. In this regard, Monte Carlo simulation provides a quantitative basis for acquiring the results of a study, and for simultaneously identifying ways to improve the study in the future.

The USEPA and the US National Academy of Science have recognized Monte Carlo Simulation methods as means of quantifying variability and uncertainty in risk estimates. This was confirmed when the EPA released a "Guiding Principles for Monte Carlo Analysis" [22]. In March 1997. The application of this method for analysis of accidental releases is still in the process of gaining momentum/popularity with the environmentally aware fraternity. This study indicates that probabilistic methods such as Monte Carlo Simulation holds great promise as an analytical tool that can be used for the analysis of accidental releases of hazardous substances in conjunction with dispersion modeling. It also shows that Monte Carlo Simulation can be incorporated into daily routine impact assessments even with limited available computational sophistification.

The choice of probability distributions can be vital to the outcome and ultimately the decisions made based on this outcome. The general recommendation is that many resources need to be geared in the direction of this critical area of any probabilistic study. Often large datasets are necessary to determine the shape of the uncertain input probability distribution. The combination of Bootstrap Simulation with Monte Carlo Simulation may be advantageous in this regard. Bootstrap with its ability to determine the shape of distributions and Monte Carlo to sample randomly from this distributions. This should increase confidence in estimates.

This study was performed manually and this did not make use of graphics available from the @ Risk model. Linking @ Risk with an Air Dispersion Model will enable the user to run literally thousands of different scenarios, eliminating the possibility of too small a sample size, and data transfer errors. Also access to the graphics, which is inclusive of a sensitivity analysis, is excluded from this study. This may also eliminate possible errors related to the manual approach.

APPENDICES

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APPENDIX A: **Occupational Health and Safety Act of South Africa, 1993 General Machinery Regulations, 1988 Schedule A - Notifiable Substances**

(pages 97-98)

Regulation 8

UNO ID No.	Substance	Threshold Quantity (tons)
1001	Acetylene (dissolved)	2
1005	Ammonia (anhydrous, liquefied and solutions containing over 50% ammonia)	20
1010	Butadiene	25
1031	Carbon disulphide	20
1017	Chlorine	10
1154	Diethyl amine	20
1155	Diethyl Ether	20
1033	Dimethyl Ether	20
1032	Dimethylamine (anhydrous)	20
1160	Dimethylamine (solution)	20
1035	Ethane (compressed)	15
1961	Ethane (refrigerated liquid)	15
1962	Ethylene (compressed)	15
1038	Ethylene (refrigerated liquid)	15
1036	Ethylamine	25
1040	Ethylene oxide	5

UNO ID No.	**Substance**	Quantity (tons)
1050	Hydrogen Chloride (anhydrous)	10
1051	Hydrogen Cyanide (anhydrous)	10
1052	Hydrogen Fluoride (anhydrous)	10
1969	ISO-Butane	25
1055	ISO-Butylene (Isobutene)	25
1075	LPG (Liquid Petroleum Gas)	25
1971	Methane (compressed)	15
1011	n-Butane	25
1012	n-Butylene (Butene)	25
1076	Phosgene	2
1978	Propane	25
1077	Propylene	25
1079	Sulphur Dioxide (liquefied)	15
1829	Sulphur Trioxide (liquefied)	15
1083	Trimethylamine (anhydrous)	25
1086	Vinyl Chloride	25

APPENDIX B1: List of regulated toxic substances and its corresponding threshold quantities under the US RMP
(pages 99-101)

Chemical Name	CAS Number	Threshold Quantity (lbs.)
Acrolein (2-Propenal)	107-02-8	5,000
Acrylonitrile (2-Propenenitrile)	107-13-1	20,000
Acrylic chloride (2-Propenoyl chloride)	814-68-6	5,000
Allyl alcohol (2-Propen-1-ol)	107-18-6	15,000
Allylamine (2-Propen-1-amine)	107-11-9	10,000
Ammonia (anhydrous)	7664-41-7	10,000
Ammonia (concentration 20% or greater)	7664-41-7	20,000
Arsenous trichloride	7784-34-1	15,000
Arsine	7784-42-1	1,000
Boron trichloride (Borane, trichloro-)	10294-34-5	5,000
Boron trifluoride (Borane, trifluoro-)	7637-07-2	5,000
Boron trifluoride compound with methyl ether (1:1) (Boron, trifluoro (oxybis (methane)) -, T-4-	353-42-4	15,000
Bromine	7726-95-6	10,000
Carbon disulfide	75-15-0	20,000
Chlorine	7782-50-5	2,500
Chlorine dioxide (Chlorine oxide (ClO2))	10049-04-4	1,000
Chloroform (Methane, trichloro-)	67-66-3	20,000
Chloromethyl ether (Methane, oxybis (chloro-))	542-88-1	1,000
Chloromethyl methyl ether (Methane, chloromethoxy-)	107-30-2	5,000
Crotonaldehyde (2-Butenal)	4170-30-3	20,000
Crotonaldehyde, (E) - (2-Butenal, (E) -)	123-73-9	20,000
Cyanogen chloride	506-77-4	10,000
Cyclohexylamine (Cyclohexanamine)	108-91-8	15,000
Diborane	19287-45-7	2,500
Dimethyldichlorosilane (Silane, dichlorodimethyl -)	75-78-5	5,000
1,1-Dimethylhydrazine (Hydrazine, 1,1-dimethyl -)	57-14-7	15,000
Epichlorohydrin (Oxirane, (chloromethyl) -)	106-89-8	20,000
Ethylenediamine (1,2-Ethanediamine)	107-15-3	20,000

Ethyleneimine (Aziridine)	151-56-4	10,000
Chemical Name	**CAS Number**	**Threshold Quantity (lbs.)**
Ethylene oxide (Oxirane)	75-21-8	10,000
Fluorine	7782-41-4	1,000
Formaldehyde (solution)	50-00-0	15,000
Furan	110-00-9	5,000
Hydrazine	302-01-2	15,000
Hydrochloric acid (concentration 37% or greater)	7647-01-0	15,000
Hydrocyanic acid	74-90-8	2,500
Hydrogen chloride (anhydrous) (Hydrochloric acid)	7647-01-0	5,000
Hydrogen fluoride/Hydrofluoric acid (concentration 50% or greater (Hydrofluoric acid)	7664-39-3	1,000
Hydrogen selenide	2148909	500
Hydrogen sulfide	2148878	10,000
Iron, pentacarbonyl- (Iron carbonyl (Fe (CO) 5), (TB-5-11) -)	13463-40-6	2,500
Isobutyronitrile (Propanenitrile, 2-methyl -)	78-82-0	20,000
Isopropyl chloroformate (Carbonochloridic acid, 1-methylethyl ester)	108-23-6	15,000
Methacrylonitrile (2-Propenenitrile, 2-methyl -)	126-98-7	10,000
Methyl chloride (Methane, chloro -)	74-87-3	10,000
Methyl chloroformate (Carbonochloridic acid, methylester)	79-22-1	5,000
Methyl hydrazine (Hydrazine, methyl -)	60-34-4	15,000
Methyl isocyanate (Methane, isocyanato -)	624-83-9	10,000
Methyl mercaptan (Methanethiol)	75-79-6	10,000
Methyl thiocyanate (Thiocyanic acid, methyl ester)	556-64-9	20,000
Methyltrichlorosilane (Silane, trichloromethyl -)	75-79-6	5,000
Nickel carbonyl	13463-39-3	1,000
Nitric acid (concentration 80% or greater)	7697-37-2	15,000
Nitric oxide (Nitrogen oxide (NO))	10102-43-9	10,000
Oleum (Fuming sulfuric acid) (Sulfuric acid, mixture with sulfur trioxide) 1	8014-95-7	10,000
Peracetic acid (Ethaneperoxoic acid)	79-21-0	10,000
Perchloromethylmercaptan (Methanesulfenyl chloride, trichloro -)	594-42-3	10,000
Phosgene (Carbonic dichloride)	75-44-5	500
Phosphine	7803-51-2	5,000
Phosphorus oxychloride (Phosphoryl chloride)	10025-87-3	5,000
Phosphorus trichloride (Phosphorous trichloride)	2125683	15,000

Piperidine	110-89-4	15,000
Chemical Name	**CAS Number**	**Threshold Quantity (lbs.)**
Propionitrile (Propanenitrile)	107-12-0	10,000
Propyl chloroformate (Carbonochloridic acid, propylester)	109-61-5	15,000
Propyleneimine (Aziridine, 2-methyl -)	75-55-8	10,000
Propylene oxide (Oxirane, methyl -)	75-56-9	10,000
Sulfur dioxide (anhydrous)	7446-09-5	5,000
Sulfur tetrafluoride (Sulfur fluoride (SF4), (T-4) -)	7783-60-0	2,500
Sulfur trioxide	7446-11-9	10,000
Tetramethyllead (Plumbane, tetramethyl -)	75-74-1	10,000
Tetranitromethane (Methane, tetranitro -)	509-14-8	10,000
Titanium tetrachloride (Titanium chloride (TiCl4) (T-4) -)	7550-45-0	2,500
Toluene 2,4-diisocyanate (Benzene, 2,4-diisocyanato-1-methyl -) 1	584-84-9	10,000
Toluene 2,6-diisocyanate (Benzene, 1,3-diisocyanato-2-methyl -) 1	91-08-7	10000.00
Toluene diisocyanate (unspecified isomer) (Benzene, 1,3-diisocyanatomethyl -) 1	26471-62-5	10,000
Trimethylchlorosilane (Silane, chlorotrimethyl -)	75-77-4	10,000
Vinyl acetate monomer (Acetic acid ethenyl ester)	108-05-4	15,000

APPENDIX B2: List of regulated flammable substances all with a threshold quantity of 10,000 pounds under the US RMP (pages 102-103)

Chemical Name	CAS Number
Acetaldehyde	75-07-0
Acetylene (Ethyne)	74-86-2
Bromotrifluorethylene (Ethene, bromotrifluoro -)	598-73-2
1,3 - Butadiene	106-99-0
Butane	106-97-8
1-Butene	106-98-9
2-Butene	107-01-7
Butene	25167-67-3
2-Butene-cis	590-18-1
2-Butene-trans (2-Butene, (E))	624-64-6
Carbon oxysulfide (Carbon oxide sulfide (COS))	463-58-1
Chlorine monoxide (Chlorine oxide)	7791-21-1
2-Chloropropylene (1-Propene, 2-chloro -)	557-98-2
1-Chloropropylene (1-Propene, 1-chloro -)	590-21-6
Cyanogen (Ethanedinitrile)	460-19-5
Cyclopropane	75-19-4
Dichlorosilane (Silane, dichloro -)	4109-96-0
Difluoroethane (Ethane, 1,1-difluoro -)	75-37-6
Dimethylamine (Methanamine, N-methyl -)	124-40-3
2,2-Dimethylpropane (Propane, 2,2-dimethyl -)	463-82-1
Ethane	74-84-0
Ethyl acetylene (1-Butyne)	107-00-6
Ethylamine (Ethanamine)	75-04-7
Ethyl chloride (Ethane, chloro -)	75-00-3
Ethylene (Ethene)	74-85-1
Ethyl ether (Ethane, 1-1'-oxybis -)	60-29-7
Ethyl mercaptan (Ethanethiol)	75-08-1
Ethyl nitrite (Nitrous acid, ethyl ester)	109-95-5
Hydrogen	1333-74-0
Isobutane (Propane, 2-methyl)	75-28-5
Isopentane (Butane, 2-methyl -)	78-78-4
Isoprene (1,3-Butadiene, 2-methyl -)	78-79-5
Isopropylamine (2-Propanamine)	75-31-0
Isopropyl chloride (Propane, 2-chloro -)	75-29-6

Methane	74-82-8
Chemical Name	**CAS Number**
Methylamine (Methanamine)	74-89-5
3-Methyl-1-butene	563-45-1
2-Methyl-1-butene	563-46-2
Methyl ether (Methane, oxybis -)	115-10-6
Methyl formate (Formic acid, methyl ester)	107-31-3
2-Methylpropene (1-Propene, 2-methyl -)	115-11-7
1,3-Pentadiene	504-60-9
Pentane	109-66-0
1-Pentene	109-67-1
2-Pentene, (E) -	646-04-8
2-Pentene, (Z) -	627-20-3
Propadiene (1,2-Propadiene)	463-49-0
Propane	74-98-6
Propylene (1-Propene)	115-07-1
Propyne (1-Propyne)	74-99-7
Silane	7803-62-5
Tetrafluoroethylene (Ethene, tetrafluoro -)	116-14-3
Tetramethylsilane (Silane, tetramethyl -)	75-76-3
Trichlorosilane (Silane, trichloro -)	10025-78-2
Trifluorochloroethylene (Ethene, chlorotrifluoro -)	79-38-9
Trimethlyamine (Methanamine, N,N-dimethyl -)	75-50-3
Vinyl acetylene (1-Buten-3-yne)	689-97-4
Vinyl chloride (Ethene, chloro -)	75-01-4
Vinyl ethyl ether (Ethene, ethoxy -)	109-92-2
Vinyl fluoride (Ethene, fluoro -)	75-02-5
Vinylidene chloride (Ethene, 1,1-dichloro -)	75-35-4
Vinylidene fluoride (Ethene, 1,1-difluoro -)	75-38-7
Vinyl methyl ether (Ethene, methoxy -)	107-25-5

The threshold quantity for accidental release prevention is 10,000 pounds in all cases.

APPENDIX C1: List of regulated substances including corresponding lower and upper threshold quantities as stated in the Seveso II Directive – Part 1

(pages 104 - 106)

Dangerous Substances	Qualifying quantities (tonnes) for the application of	
	Article 6 and 7	Article 9
Ammonium nitrate	350	2500
Ammonium nitrate	1250	5000
Arsenic pentoxide, arsenic (V) acid and/or salts	1	2
Arsenic trioxide, arsenious (III) acid and/or salts	-	0,1
Bromine	20	100
Chlorine	10	25
Nickel compounds in inhalable powder form (nickel monoxide, nickel dioxide, nickel sulphide, trinickel disulphide, dinickel trioxide)	-	1
Ethyleneimine	10	20
Fluorine	10	20
Formaldehyde (concentration (90 %)	5	50
Hydrogen	5	50
Hydrogen chloride (liquefied gas)	25	250
Lead alkyls	5	50
Liquefied extremely flammable gases (including LPG) and natural gas	50	200
Acetylene	5	50
Ethylene oxide	5	50
Propylene oxide	5	50
Methanol	500	5000
4, 4-Methylenebis (2-chloraniline) and/or salts, in	-	0,01

powder form		
Dangerous Substances	**Qualifying quantities (tonnes) for the application of**	
	Article 6 and 7	**Article 9**
Methylisocyanate	-	0,15
Oxygen	200	2000
Toluene diisocyanate	10	100
Carbonyl dichloride (phosgene)	0,3	0,75
Arsenic trihydride (arsine)	0,2	1
Phosphorus trihydride (phosphine)	0,2	1
Sulphur dichloride	1	1
Sulphur trioxide	15	75
Polychlorodibenzofurans and polychlorodibenzodioxins (including TCDD), calculated in TCDD equivalent	-	0,001
The following CARCINOGENS: 4-Aminobiphenyl and/or its salts, Benzidine and/or salts, Bis(chloromethyl) ether, Chloromethyl methyl ether, Dimethylcarbamoyl chloride, Dimethylnitrosamine, Hexamethylphosphoric triamide, 2-Naphtylamine and/or salts, and 1,3 Propanesultone 4-nitrodiphenyl	0,001	0,001
Automotive petrol and other petroleum spirits	5000	50000

Notes:

1. Ammonium nitrate (350 / 2500)
This applies to ammonium nitrate and ammonium nitrate compounds in which the nitrogen content as a result of the ammonium nitrate is more than 28 % by weight (compounds other than those referred to in Note 2) and to aqueous ammonium nitrate solutions in which the concentration of ammonium nitrate is more than 90 % by weight.

2. Ammonium nitrate (1250/5000)
This applies to simple ammonium nitrate based fertilizers, which comply with Directive 80/876/EEC, and to composite fertilizers in which the nitrogen content as a result of the ammonium nitrate is more than 28 % in weight (a composite fertilizer contains ammonium nitrate with phosphate and/or potash).

3. Polychlorodibenzofurans and polychlorodibenzodioxins
The quantities of polychlorodibenzofurans and polychlorodibenzodioxins are calculated using the following factors:

Intentional Toxic Equivalent Factors (ITEF) for the congeners of concern (NATO/CCMS)			
2,3,7,8-TCDD	1	2,3,7,8-TCDF	0,1
1,2,3,7,8-PeCDD	0,5	2,3,4,7,8-PeCDF	0,5
.	.	1,2,3,7,8-PeCDF	0,05
.	.	.	.
1,2,3,4,7,8-HxCDD	0,1	.	.
1,2,3,6,7,8-HxCDD	0,1	1,2,3,4,7,8-HxCDF	0,1
1,2,3,7,8,9-HxCDD	0,1	1,2,3,7,8,9-HxCDF	0,1
.	.	1,2,3,6,7,8-HxCDF	0,1
1,2,3,4,6,7,8-HpCDD	0,01	2,3,4,6,7,8-HxCDF	0,1
.	.	.	.
OCDD	0,001	1,2,3,4,6,7,8-HpCDF	0,01
.	.	1,2,3,4,7,8,9-HpCDF	0,01
.	.	.	.
.	.	OCDF	0,001
(T = tetra, Pe = penta, Hx = hexa, Hp = hepta, O = octa)			

APPENDIX C2: Categories of substances and preparations not specifically named in Part 1 – Part 2 of the Seveso II Directive

Pages 107-110

Categories of dangerous substances	Qualifying quantities (tonnes) for the application of	
	Article 6 and 7	Article 9
1. VERY TOXIC	5	20
2. TOXIC	50	200
3. OXIDIZING	50	200
4. EXPLOSIVE (where the substance or preparation falls within the definition given in Note 2 (a))	50	200
5. EXPLOSIVE (where the substance or preparation falls within the definition given in Note 2 (b))	10	50
6. FLAMMABLE (where the substance or preparation falls within the definition given in Note 3 (a))	5000	50000
7.a. HIGHLY FLAMMABLE (where the substance or preparation falls within the definition given in Note 3 (b) (1))	50	200
7.b. HIGHLY FLAMMABLE liquids (where the substance or preparation falls within the definition given in Note 3 (b) (2))	5000	50000
8. EXTREMELY FLAMMABLE (where the substance or preparation falls within the definition given in Note 3 (c))	10	50
9. DANGEROUS FOR THE ENVIRONMENT in combination with risk phrases:		

(i) R50: 'Very toxic to aquatic organisms'	200	500
Categories of dangerous substances	**Qualifying quantities (tonnes) for the application of**	
	Article 6 and 7	**Article 9**
(ii) R51: 'Toxic to aquatic organisms'; and R53: 'May cause long term adverse effects in the aquatic environment'	500	2000
10. ANY CLASSIFICATION not covered by those given above in combination with risk phrases:		
(i) R14: 'Reacts violently with water' (including R14/15)	100	500
(ii) R29: 'in contact with water, liberates toxic gas'	50	200

Notes:

1. Substances and preparations are classified according to the following Directives (as amended) and their current adaptation to technical progress:

- Council Directive 67/548/EEC of 27 June 1967 on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labeling of dangerous substances (1),
- Council Directive 88/379/EEC of 7 June 1988 on the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labeling of dangerous preparations (2),
- Council Directive 78/631/EEC of 26 June 1978 on the approximation of the laws of the Member States relating to the classification, packaging and labeling of dangerous preparations (pesticides) (3).

In the case of substances and preparations which are not classified as dangerous according to any of the above Directives but which nevertheless are present, or are likely to be present, in an establishment and which possess or are likely to possess, under the conditions found at the establishment, equivalent properties in terms of major-accident potential, the procedures for provisional classification shall be followed according to the relevant Article of the appropriate Directive.
In the case of substances and preparations with properties giving rise to more than one classification, for the purposes of this Directive the lowest thresholds shall apply.
For the purposes of this Directive, a list providing information on substances and preparations shall be established, kept up to date and approved by the procedure set up under Article 22.

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(1) OJ No 196, 16.8.1967, p.1. Directive as fast amended by Directive 93/105/EC (OJ No L 294, 30.11.1993, p.21).

(2) OJ No L 187, 16.7.1988, p.14.

(3) OJ No L 206, 29.7.1978, p.13. Directive as fast amended by Directive 92/32/EEC (OJ No L 154, 5.6.1992, p.1).

2. An 'explosive' means:

1. a substance or preparation which creates the risk of an explosion by shock, friction, fire or other sources of ignition (risk phrase R 2),
2. a pyrotechnic substance is a substance (or mixture of substances) designated to produce heat, light, sound, gas or smoke or a combination of such effects through non-detonating self-sustained exothermic chemical reactions, or
3. an explosive or pyrotechnic substance or preparation contained in objects;

2. a substance or preparation which creates extreme risks of explosion by shock, friction, fire or other sources of ignition (risk phrase R 3).

3. 'Flammable', 'highly flammable', and 'extremely flammable' in categories 6, 7 and 8 mean:

a. flammable liquids:

substances and preparations having a flash point equal to or greater than 21 °C and less than or equal to 55°C (risk phrase R 10), supporting combustion;

b. highly flammable liquids:

1. - substances and preparations which may become hot and finally catch fire in contact with air at ambient temperature without any input of energy (risk phrase R 17),

   - substances, which have a flash point, lower than 55 °C and which remain liquid under pressure, where particular processing conditions, such as high pressure or high temperature, may create major-accident hazards;

2. substances and preparations having a flash point lower than 21 °C and which are not extremely flammable (risk phrase R 11, second indent);

c. extremely flammable gases and liquids:

1. liquid substances and preparations which have a flash point lower than 0 °C and the boiling point (or, in the case of a boiling range, the initial boiling point) of which at normal pressure is less than or equal to 35 °C (risk phrase R 12, first indent), and
2. gaseous substances and preparations which are flammable in contact with air at ambient temperature and pressure (risk phrase R 12, second indent), whether or not kept in the gaseous or liquid state under pressure, excluding liquefied extremely flammable gases (including LPG) and natural gas referred to in Part 1, and
3. liquid substances and preparations maintained at a temperature above their boiling point.

4. The addition of dangerous substances to determine the quantity present at an establishment shall be carried out according to the following rule:

if the sum

$q1 / Q + q2 / Q + q3 / Q + q4 / Q + q5 / Q + q6 / Q + \ldots qx / Q$

where
qx = the quantity of dangerous substances x (or category of dangerous substances) falling within Parts 1 or 2 of this Annex,
Q = the relevant threshold quantity from Parts 1 or 2,

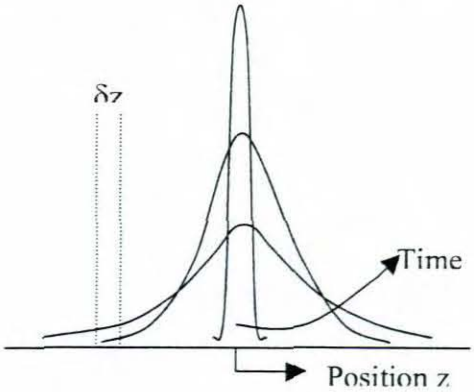
then the establishment is covered by the relevant requirements of this Directive.
This rule will apply for the following circumstances:

a. for substances and preparations appearing in Part 1 at quantities less than their individual qualifying quantity present with substances having the same classification from Part 2, and the addition of substances and preparations with the same classification from Part 2;
b. for the addition of categories 1, 2 and 9 present at an establishment together;
c. for the addition of categories 3, 4, 5, 6, 7a, 7b and 8, present at an establishment together.

APPENDIX D: Derivation of the Gaussian equations obtained from first principles

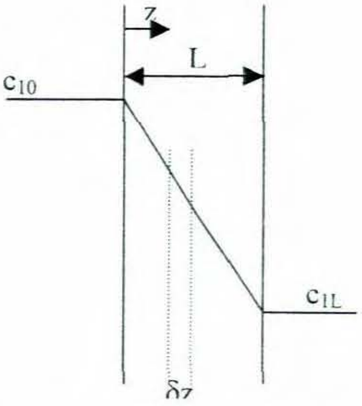
The following derivation is based on that given by Cussler [5] chapter , pages :
Consider the diffusion away from a sharp pulse of solute as shown in the following figure. It is an indication of the diffusion of a pulse. The concentrated solute originally located at z = 0 diffuses as the Gaussian profile shown. This is the third of the three most important cases, along the with the two following cases or figures and brief explanation

FIGURE1



Below we attempt a simple example: steady diffusion across a film. We want to find the diffusion flux and the concentration profile across this film. In other words we want to determine how much solute moves across the film and how the solute concentration changes within the film.

FIGURE 2



On each side of the film is a well-mixed solute solution called species 1. Both these solution are dilute. The solute diffuses from fixed higher concentration located at $z \geq 0$ on the left-hand side of the film, into the fixed, less concentrated solution located at $z \leq L$ on the right-hand side. We want to find the solute concentration profile and the flux across the film. To do this we first need to write a mass balance on a thin layer δz, located at some arbitrary position z within the thin film. The mass balance in this layer is:

$$\begin{pmatrix} solute \\ accumulation \end{pmatrix} = \begin{pmatrix} rate\,of\ diffusion \\ \text{int}\,o\,the\,layer\,at\,z \end{pmatrix} - \begin{pmatrix} rate\,of\ diffusion\,out \\ of\ the\,layer\,at\,z+\delta z \end{pmatrix}$$

Because the process is in steady state, the accumulation is zero. The diffusion rate is the diffusion flux times the film's area A. Thus

$$0 = A\left(j_{1|z} - j_{1|z+\delta z}\right) \qquad \text{...eqn.1}$$

Dividing the equation by the film's volume, $A\delta z$, and rearranging,

$$0 = -\left(\frac{j_{1|z+\delta z} - j_{1|z}}{(z+\delta z)-z}\right) \qquad \text{...eqn.2}$$

When δz becomes very small, this equation becomes the definition of the derivative

$$0 = -\frac{d}{dz}j_1 \qquad \text{...eqn.3}$$

Combining this equation with Fick's law,

$$-j_1 = D\frac{dc_1}{dz} \qquad \text{...eqn.4}$$

we find, for a constant diffusion coefficient D,

$$0 = D\frac{d^2c_1}{dz^2} \qquad \text{...eqn.5}$$

This differential equation is subject to two boundary conditions:

$$z = 0, \quad c_1 = c_{10} \qquad \text{...eqn.6}$$

$$z = L, \quad c_1 = c_{1L} \qquad \text{...eqn.7}$$

Again because the system is steady state, the concentration c_{10} and c_{1L} are independent of time. Physically, this means that the volumes of the adjacent solutions must be much greater than the volume of the film.

Mathematically the concentration profile and flux is easily found. First we integrate eqn. 5 twice to find

$$c_1 = a + bz \qquad \text{...eqn.8}$$

The constants a and b can be found from eqns. 6 and 7, so the concentration profile is

$$c_1 = c_{10} + (c_{1l} - c_{10})\frac{z}{L} \qquad \text{...eqn.9}$$

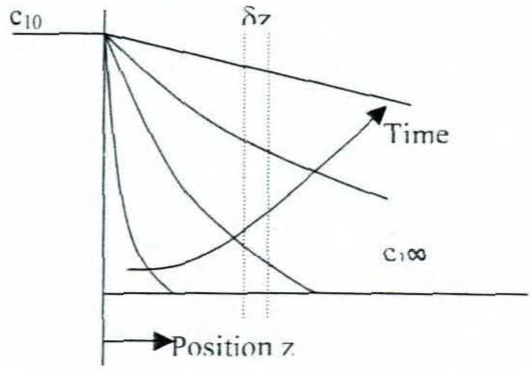
The sketch in figure 2 anticipated this linear variation. The flux is found by differentiating this profile:

$$j_1 = -D\frac{dc_1}{dz} = \frac{D}{L}(c_1 - c_{1L}) \qquad \text{...eqn.10}$$

Because the system is steady state, the flux is constant

Next lets turn to the discussion of diffusion in a semi-infinite slab. We consider a volume of solution that starts at an interface and extends a very long way. Such a solution can be a gas, liquid or solid. We want to find how the concentration varies in this solution as a result of a concentration change at its interface. In mathematical terms, we want to find the concentration and flux as functions of position and time. The diffusion in a semi-infinite slab is schematically sketched in figure 3 below.

FIGURE 3



The slab initially contains a uniform concentration of solute $c_{1\infty}$. At some time, chosen as time zero, the concentration at the interface is suddenly and abruptly increased, although the solute is always present at high dilution. The increase produces the time-dependant concentration profile that develops as solute penetrates into the slab. We want to find the concentration profile and the flux in this situation, and so again we need a mass balance written on the thin layer of volume $A\delta z$:

$$\begin{pmatrix} \text{solute accumulation} \\ \text{in volume } A\delta z \end{pmatrix} = \begin{pmatrix} \text{rate of diffusion} \\ \text{into the layer at } z \end{pmatrix} - \begin{pmatrix} \text{rate of diffusion out} \\ \text{of the layer at } z + \delta z \end{pmatrix}$$

In mathematical terms, this is

$$\frac{\partial}{\partial t}\left(A\delta z c_1\right) = A\left(j_{1|z} - j_{1|z+\delta z}\right) \qquad \text{...eqn.11}$$

Divide by $A\delta z$ to find

$$\frac{\partial c_1}{\partial t} = -\left(\frac{j_{1|z+\delta z} - j_{1|z}}{(z+\delta z) - z}\right) \qquad \text{...eqn.12}$$

Then let δz go to zero and use the definition of the derivative

$$\frac{\partial c_1}{\partial t} = \frac{\partial j_1}{\partial z} \qquad \text{...eqn.13}$$

Combining the equation with Fick's law, and assuming that the diffusion coefficient is independent of concentration, we get

$$\frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial z^2} \qquad \text{...eqn.14}$$

The equation is sometimes called Fick's 2nd law, and it is often referred to as one example of a "diffusion equation". In this case it is subject to the following conditions:

$$t = 0,\ all\ z, \quad c_1 = c_{1\infty} \qquad \text{...eqn.15}$$

$$\begin{aligned} t \geq 0,\ z = 0 \quad & c_1 = c_{10} \\ z = \infty \quad & c_1 = c_{1\infty} \end{aligned} \qquad \text{... eqn.16\&17}$$

Note that both $c_{1\infty}$ and c_{10} are taken as constants. The concentration $c_{1\infty}$ is constant because it so far from the interface as to be affected by events there; the concentration c_{10} is kept constant by adding material at the interface

The mathematical solution of this problem is easiest using the method of "combination of variables."

A new variable is defined

$$\zeta = \frac{z}{\sqrt{4Dt}} \qquad \text{...eqn.18}$$

The differential equation can be written as

$$\frac{dc_1}{d\zeta}\left(\frac{\partial \zeta}{\partial t}\right) = D\frac{d^2 c_1}{d\zeta^2}\left(\frac{\partial \zeta}{\partial z}\right)^2 \qquad \text{...eqn.19}$$

or

$$\frac{d^2 c_1}{d\zeta^2} + 2\zeta \frac{dc_1}{d\zeta} = 0 \qquad \text{...eqn.20}$$

In other words the partial differential equation has been almost magically transformed into an ordinary differential equation. The magic also works for the boundary conditions; from equations 15 to 16

$$\zeta = 0, \qquad c_1 = c_{10} \text{ and} \qquad \ldots\text{eqn.21}$$

$$\zeta = \infty, \qquad c_1 = c_{1\infty} \qquad \ldots\text{eqn.22}$$

With the method of combination of variables, the transformation of the initial and boundary conditions is often more critical than the transformation of the differential equation. The solution is now straightforward. On integration of eqn. 20 gives

$$\frac{dc_1}{d\zeta} = ae^{-\zeta^2} \qquad \ldots\text{eqn.23}$$

where *a* is an integration constant. A second integration and use of the boundary condition gives

$$\frac{c_1 - c_{10}}{c_{1\infty} - c_{10}} = erf\zeta \qquad \ldots\text{eqn.24}$$

where

$$erf\zeta = \frac{2}{\sqrt{\pi}}\int_0^{\zeta} e^{-s^2}\,ds \qquad \ldots\text{eqn.25}$$

which is the error function of ζ. This is the desired concentration profile giving the variation of concentration with position and time. In many practical problems, the flux in the slab is of greater interest than the concentration profile itself. This flux can again be found by combining Fick's law with eqn. 24

$$j_1 = -D\frac{\partial c_1}{\partial z} = \sqrt{D/\pi t}\; e^{-z^2/4Dt}\left(c_{10} - c_{1\infty}\right) \qquad \ldots\text{eqn.26}$$

One particular useful limit is the flux across the interface at $z = 0$:

$$j_{1|z=0} = \sqrt{d/\pi t}\left(c_{10} - c_{1\infty}\right) \qquad \ldots\text{eqn.27}$$

This is the value at a particular time t and not the average over the time

Back to figure 1: The obvious model for a plume like that in Figure 3-3 is that developed earlier for the one-dimensional decay from a pulse. The smoke concentration has roughly a Gaussian shape and has a width of about 1 kilometer when it is 10 kilometers downwind. In this model we assume that x is the wind direction, z the vertical height and y the horizontal direction normal to both the wind and the ground. On this basis we adopt the solution obtained previously (equation 26) to find the following.

$$\bar{c}_1 = \frac{M/A}{\sqrt{4\pi Dt}} e^{-y^2/4Dt} \qquad \text{...eqn.28}$$

where $\overline{c_1}$ is the concentration averaged over time and height z. the quantity M/A was previously the amount of solute per area in the pulse, it now must be closely related to how much comes out of the stack. The distance y must be the amount that the pulse or plume has spread. The time t must be replaced by (x/v^o), the distance the smoke has traveled divided by the wind velocity. Up to this point this model does not predict how much the plume spreads. From arguments it was established that the width of the peak L should be about

$$L = \sqrt{4Dt} \qquad \text{...eqn.29}$$

In gases, diffusion coefficients are about 0,1cm^2/sec, and time is about 10km/(15km/hr), or 40 minutes. On this basis, L should be about 30 centimeters, 3000 times less than the observed width of 1 kilometer. The explanation for the major discrepancy is the wind. In most cases mixing occurred by molecular diffusion caused by Brownian motion. Here, mixing occurs by conventional methods as the wind blows the plume over woods, around hills, and across lakes. The mixing is more rapid than molecular diffusion because of the flow.

We have a good diffusion model in equation 28, that explains most of the qualitative features of the plume, but this model will under predict the effects. To resolve this the plume can be described by,

$$\overline{c_1} \alpha \frac{1}{\sqrt{E_y \left(x/v^o\right)}} e^{-y^2/4E_y t} \qquad \text{...eqn.30}$$

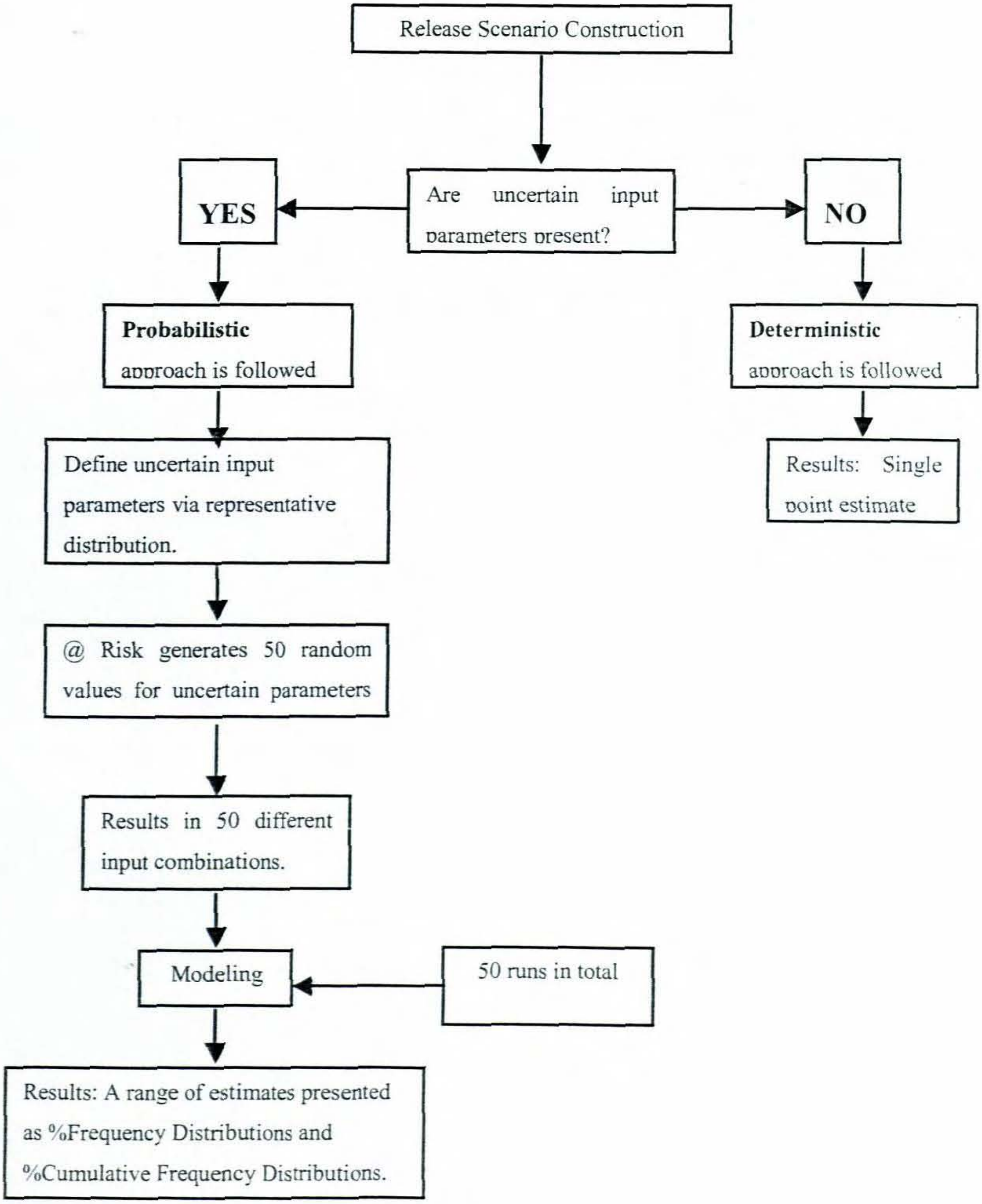
In this equation E_y is a new "dispersion" coefficient, which must be measured experimentally. Like the diffusion coefficient, the dispersion coefficient has dimension (L^2/t). Unlike the diffusion coefficient, the dispersion coefficient is largely independent of chemistry. It will be a strong function of molecular weight or structure, but will have close to the same values for carbon monoxide, styrene and smoke. Unlike the diffusion coefficient, the dispersion coefficient will be a strong function of position. It will have different values in different directions. Thus dispersion may look like diffusion, and it may be described by the same kinds of equations, but it is the result of a different effect.

Using the idea of dispersion coefficients, a variety of concentration can be derived for different boundary conditions, as can be seen in the following table.

Situation	**Basic equation**
Instantaneous point source at $t = 0$, uniform flow v^0 in x direction; source strength S{=}M	$c_1 = \frac{S}{8(\pi t)^{3/2}(E_x E_y E_z)^{1/2}}.\exp\left(-\frac{(x - v^{\circ}t)^2}{4E_x t} - \frac{y^2}{4E_y t} - \frac{z^2}{4E_z t}\right)$ ...eqn. 31
Continuous point source at $x = 0$; uniform flow v^0 in x direction; source strength S{=}M/t	$c_1 = \frac{S}{4\pi v^{\circ}t(E_y E_z)^{1/2}}.\exp\left(-\frac{y^2}{4E_y t} - \frac{z^2}{4E_z t}\right)$ ...eqn. 32
Continuous point source at $x = 0$; uniform flow v^0 in x direction; impermeable boundary at $z = z_o$; source strength S{=}M/t	$c_1 = \frac{S}{4\pi v^{\circ}t(E_y E_z)^{1/2}}.\exp\left(-\frac{y^2}{4E_y t}\right)\left[\exp\left(-\frac{(z - z_0)^2}{4E_z t}\right) + \exp\left(-\frac{(z + z_0)^2}{4E_z t}\right)\right]$ ...eqn. 33
Continuous point source at $x = 0$; uniform flow v^0 in x direction; absorbing boundary at $z = z_o$; source strength S{=}M/t	$c_1 = \frac{S}{4\pi v^{\circ}t(E_y E_z)^{1/2}}.\exp\left(-\frac{y^2}{4E_y t}\right)\left[\exp\left(-\frac{(z - z_0)^2}{4E_z t}\right) - \exp\left(-\frac{(z + z_0)^2}{4E_z t}\right)\right]$ ...eqn. 34

The equations in the table above are similar in form to Equations 3-1 and 3-2 that are used to model the dispersion of atmospheric pollutants.

APPENDIX E: Flowchart showing the steps involved quantifying uncertainty in modeled estimates incorporating Monte Carlo Simulation



APPENDIX F: Method used to quantify uncertainty in modeling estimates: The derivation of % Frequency and % Cumulative Frequency Distributions (CFD)

=1/20 x 100 etc.

=15 + 5

20 Iterations

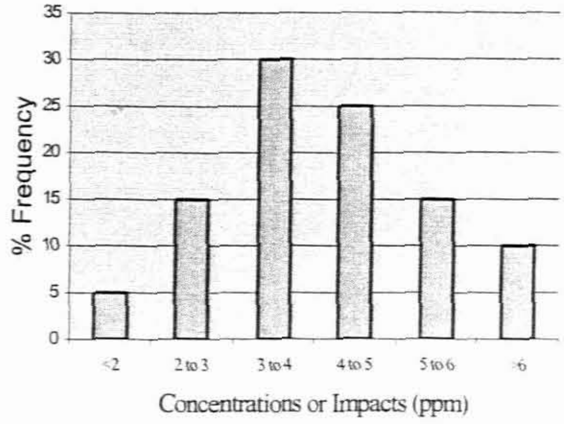
Concentrations or Impacts e.g. units ppm
3.5
4.1
3.7
1.2
7.1
5.9
2.7
4.9
2.1
3.9
3.5
4.6
5.5
6.9
4.4
2.2
4.8
5.1
4.3
3.9

Concentrations or Impact Increments	Frequency	% Frequency	CFD
<2	1	5	5
2 to 3	3	15	20
3 to 4	6	30	50
4 to 5	5	25	75
5 to 6	3	15	90
>6	2	10	100
	20		

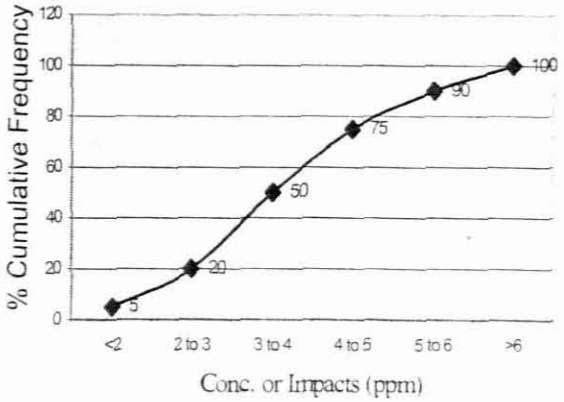
=15 + 75

What are 'impacts'? An impact may be any selected endpoint relevant to the case study, such as ambient concentration (ppm), distance to 1psi overpressure, distance to toxic endpoints, etc…..

% Frequency vs. Conc. or Impacts



% Cumulative Frequency vs Conc or Impacts



APPENDIX G1: **Accidents reported in the RMP*Info per chemical, involved in accidents for the period 1994-1999 in order of descending frequency**

Chemical Name	Number of Accidents
Ammonia	656
Chlorine	518
Hydrogen Fluoride	101
Chlorine dioxide	55
Propane	54
Sulfur dioxide	48
Hydrogen chloride	32
Hydrogen	32
Methane	30
Butane	26
Ethylene oxide	19
Hydrogen sulfide	19
Formaldehyde	17
Isobutane	17
Pentane	17
Titanium tetrachloride	15
Phosgene	12
Nitric Acid	12
Ethane	12
Ethylene	11
Vinyl chloride	11
Methyl chloride	10
Propylene	10
Acrylontrile	8

APPENDIX G2: Annual production figures of chemicals in the US

This list is for the period 1994 and 1995 and is also ranked in order of highest production units per annum. Figures are in units of Billions of kilograms.

Rank		Chemical Name	Billions of kgs.	
1995	1994(a)		1995	1994
1	1	**Sulfuric acid**	43.26	40.66
2	2	**Nitrogen**	30.86	28.99
3	3	**Oxygen**	24.26	22.72
4	4	**Ethylene**	21.31	20.23
5	5	**Lime (b)**	18.70	17.40
6	6	**Ammonia**	16.15	15.65
7	7	**Phosphoric acid**	11.88	11.60
8	8	**Sodium hydroxide**	11.88	11.39
9	10	**Propylene**	11.65	10.86
10	9	**Chlorine**	11.38	11.05
11	11	**Sodium carbonate(c)**	10.11	9.33
12	18	**Methyl *tert-butyl* ether**	7.99	6.17
13	14	**Ethylene dichloride**	7.83	7.60
14	12	**Nitric acid**	7.82	7.81
15	13	***Ammonium nitrate (d)***	7.25	7.72
16	16	**Benzene**	7.24	6.93
17	15	**Urea (e)**	7.07	7.21
18	17	**Vinyl chloride**	6.79	6.28
19	22	**Ethylbenzene**	6.20	4.88
20	21	**Styrene**	5.17	5.12
21	19	**Methanol**	5.12	5.52
22	20	**Carbon dioxide (f)**	4.94	5.35
23	23	**Xylene**	4.25	4.11
24	24	**Formaldehyde (g)**	3.68	3.71
25	25	***Terephthalic acid (h)***	3.61	3.44
26	27	**Ethylene oxide**	3.46	3.28
27	26	**Hydrochloric acid**	3.32	3.39
28	28	**Toluene (i)**	3.05	3.06
29	29	**p-Xylene**	2.88	2.84
30	31	Cumene	2.55	2.37
31	32	**Ammonium sulfate**	2.38	2.35
32	30	**Ethylene glycol**	2.37	2.76
33	33	**Acetic acid**	2.12	1.81
34	34	**Phenol (j)**	1.89	1.78
35	35	**Propylene oxide**	1.81	1.68
36	36	**Butadiene (k)**	1.67	1.53
37	37	**Carbon black**	1.51	1.47
38	39	**Isobutylene**	1.47	1.40
39	38	**Potash (l)**	1.46	1.40
40	41	**Acrylonitrile**	1.46	1.37
41	40	**Vinyl acetate**	1.31	1.38

APPENDIX G3: **Usage Frequency of chemicals in various processes in the US ranked in descending order**

	Number of Processes used	Percentage of Total
Ammonia	8343	32.5
Chlorine	4682	18.3
Flammable Mixture	2830	11
Propane	1707	6.7
Sulfur dioxide	768	3
Ammonia (conc. 20%)	519	2
Butane	482	1.9
Formaldehyde	358	1.4
Isobutane	344	1.3
Hydrogen Fluoride	315	1.2
Pentane	272	1.1
Propylene	251	1
Methane	220	0.9
Hydrogen	205	0.8
Isopentane	201	0.8
All Others	4139	16.1

APPENDIX H1: Random numbers generated for the uncertain parameters-SO_2 modeling

Iteration Number	Wind Speed (m/s)	Release Quantity (kg)	Ground Roughness (cm)
1	1.39	3240	100
2	1.81	3451	50
3	1.69	4327	30
4	1.98	3523	50
5	1.83	4279	100
6	1.79	3694	100
7	2.17	4123	100
8	1.77	3271	30
9	1.64	3347	50
10	1.56	3961	100
11	1.60	3572	50
12	1.32	4348	100
13	2.00	3491	100
14	1.49	4008	50
15	1.68	3853	30
16	1.31	3403	100
17	1.46	4472	30
18	2.09	3219	50
19	1.21	3809	50
20	1.38	3980	50
21	1.91	3751	100
22	1.89	3657	50
23	2.06	3542	30
24	1.27	4411	100
25	1.85	4488	100
26	1.45	4163	100
27	1.62	3284	50
28	1.23	3381	50
29	1.97	4069	30
30	1.50	3895	50
31	2.06	3609	100
32	1.29	3319	30
33	1.40	3464	50
34	1.95	4087	100
35	2.13	3907	100
36	2.15	4142	50
37	1.72	3789	50
38	1.55	4260	100
39	2.11	3640	50
40	2.03	4222	100
41	1.65	4190	50
42	1.44	3410	50
43	1.87	4384	30
44	1.24	3733	100
45	2.20	4300	100
46	1.53	3835	50
47	1.74	4439	100
48	1.73	3674	50
49	1.92	3929	100
50	1.36	4040	30

APPENDIX H2: Random numbers generated for the uncertain parameters-Cl_2 modeling

Iteration Number	Temperature (°C)	Ground Roughness (cm)	Quantity released (kg)
1	-39.9	83.6	5088
2	-39.9	89.3	5155
3	-41.7	63.9	5076
4	-34.9	69.8	5992
5	-37.1	61.7	5542
6	-38.8	66.9	5839
7	-38.5	79.3	5737
8	-38.1	72.1	5081
9	-41.4	70.9	5522
10	-38.4	80.1	5917
11	-38.8	77.3	5875
12	-41.3	75.9	5211
13	-40.5	62.1	5880
14	-37.6	60.0	5925
15	-38.8	98.2	5034
16	-38.1	83.2	5331
17	-38.3	71.9	5518
18	-37.2	58.5	5946
19	-36.8	77.0	5909
20	-41.6	78.6	5698
21	-41.2	89.8	5275
22	-38.0	86.8	5388
23	-37.3	79.8	5075
24	-41.2	76.9	5899
25	-38.5	53.8	5138
26	-40.8	72.9	5443
27	-38.7	74.3	5441
28	-38.1	83.8	5985
29	-35.8	73.0	5314
30	-38.6	65.5	5147
31	-37.6	73.2	5041
32	-36.1	53.9	5181
33	-37.8	70.6	5860
34	-34.7	59.2	5331
35	-34.2	94.3	5943
36	-41.7	87.0	5073
37	-40.8	69.4	5262
38	-37.9	86.1	5486
39	-40.3	78.3	5876
40	-38.3	74.5	5680
41	-35.9	69.3	5814
42	-40.3	95.7	5242
43	-35.1	72.9	5069
44	-40.5	66.4	5348
45	-38.7	58.4	5209
46	-35.2	78.8	5304
47	-35.9	67.4	5546
48	-35.8	89.2	5512
49	-39.1	68.5	5615
50	-35.2	85.9	5770

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